Time independent perturbation theory:

→ Non-degenerate Case:

Suppose $H = H_0 + \lambda V$

H_0: unperturbed Hamiltonian.

Assume we know $H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$

Now want to solve: $(H_0 + \lambda V)|n\rangle = E_n |n\rangle$

assume λ is small, Now find E_n, $|n\rangle$ in series of λ.

Ex: 2-level system.

$$H_0 = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix} \quad \text{with} \quad |1^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\lambda V = \begin{pmatrix} 0 & \lambda V_{12} \\ \lambda V_{21} & 0 \end{pmatrix} \quad \text{with} \quad V_{12} = \langle 1^{(0)} | V | 2^{(0)} \rangle, \quad V_{21} = V_{12}$$

For simplicity, $V_{11} = V_{21} = 0$.

$$H = \begin{pmatrix} E_1^{(0)} & \lambda V_{12} \\ \lambda V_{21} & E_2^{(0)} \end{pmatrix}$$

First diagonalize Hamiltonian.

$$(E_1^{(0)}-E)(E_2^{(0)}-E) - \lambda^2|V_{12}|^2 = 0$$

$$E = \frac{E_1^{(0)}+E_2^{(0)}}{2} \pm \sqrt{\left(\frac{E_1^{(0)}-E_2^{(0)}}{2}\right)^2 + \lambda^2|V_{12}|^2}$$

$$= \frac{E_1^{(0)}+E_2^{(1)}}{2} \pm \frac{E_1^{(0)}-E_2^{(0)}}{2}\sqrt{1+\left(\frac{2\lambda V_{12}}{E_1^{(0)}-E_2^{(0)}}\right)^2}$$

Expansion requires $\left(\frac{2\lambda V_{12}}{E_1^{(0)}-E_2^{(0)}}\right)^2 < 1$

$$\cong \frac{E_1^{(0)}+E_2^{(1)}}{2} \pm \frac{E_1^{(0)}-E_2^{(0)}}{2}\left[1 + 2\lambda^2\left|\frac{V_{12}}{E_1^{(0)}-E_2^{(0)}}\right|^2 + \mathcal{O}(\lambda^4)\right]$$

then $E_1 = E_1^{(0)} + \lambda^2 \dfrac{|V_{12}|^2}{E_1^{(0)}-E_2^{(0)}} + \cdots$

$E_2 = E_2^{(0)} + \lambda^2 \dfrac{|V_{12}|^2}{E_1^{(0)}-E_2^{(0)}} + \cdots$

require $\dfrac{2\lambda V_{12}}{E_1^{(0)}-E_2^{(0)}} \ll 1$

so $\lambda V_{12} \ll \dfrac{E_1^{(0)}-E_2^{(0)}}{2}$

Formal Theory of Perturbation Expansion:

$$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$$

suppose $\Delta_n = E_n - E_n^{(0)}$

λ is small parameter.

expect $|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots$

assume $\langle n|n\rangle \neq 1$

but $\langle n|n^{(0)}\rangle = 1$

$$\Delta_n = \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \lambda^3\Delta_n^{(3)} \cdots$$

Formal Development of Perturbation Expansion:

Suppose we know the unperturbed energy eigenket and eigen energy:

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

Here $|n^{(0)}\rangle$ is complete such that $\sum_n |n^{(0)}\rangle\langle n^{(0)}| = 1$.

Assume energy spectrum is non-degenerate:

Now we add perturbation and introduce parameter λ where λ goes from $[0,1]$. We set $\underline{\lambda = 1}$ in the end.

$$(H_0 + \lambda V)|n\rangle = E_n^{(\lambda)} |n\rangle$$

Now define energy shift from unperturbed state as:

$$\boxed{\Delta_n = E_n - E_n^{(0)}}$$

Now we expect $|n\rangle$ to expand in λ:

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots$$

assume $|n\rangle$ is not normalized, $\langle n|n\rangle \neq 1$ but $\langle n|n^{(0)}\rangle = 1$

and

$$\Delta_n = \lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \dots$$

Then we need to solve for

$$(H_0 + \lambda V)|n\rangle_\lambda = E_n^{(\lambda)}|n\rangle_\lambda$$

$$\hookrightarrow (H_0 + \lambda V)|n\rangle_\lambda = (\Delta_n + E_n^{(0)})|n\rangle_\lambda$$

$$\hookrightarrow \boxed{(E_n^{(0)} - H_0)|n\rangle_\lambda = (\lambda V - \Delta_n)|n\rangle_\lambda}$$

Note: we cannot do $|n\rangle_\lambda = \frac{(\lambda V - \Delta_n)}{E_n^{(0)} - H_0}|n\rangle_\lambda$

since it can be non-invertible. since when $|n\rangle$ contains $|n^{(0)}\rangle$ which give $\frac{1}{E_n^{(0)} - E_n^{(0)}}$ = bad.

Now multiply $\langle n^{(0)}|$ on both sides.

$$\underbrace{\langle n^{(0)}| E_n^{(0)} - H_0 |n\rangle_\lambda}_{=0} = \langle n^{(0)}|\lambda V - \Delta_n|n\rangle_\lambda$$

so $\boxed{\langle n^{(0)}|\lambda V - \Delta_n|n\rangle_\lambda = 0}$ *

ϕ_n gets rid of $|n^{(0)}\rangle$ term.

* Now lets introduce: $\phi_n = 1 - |n^{(0)}\rangle\langle n^{(0)}| = \sum_{k \neq n} |k^{(0)}\rangle\langle k^{(0)}|$

it has property $\begin{cases} \phi_n |n^{(0)}\rangle = \langle n^{(0)}|\phi_n = 0 \\ \phi_n^2 = \phi_n \end{cases}$

also note

here we used: $\langle n^{(0)}|\lambda V - \Delta_n|n\rangle_\lambda = 0$

$$\phi_n(\lambda V - \Delta_n)|n\rangle = (1 - |n^{(0)}\rangle\langle n^{(0)}|)(\lambda V - \Delta_n)|n\rangle \overset{!}{=} (\lambda V - \Delta_n)|n\rangle$$

Note that $\frac{1}{E_n^{(0)}-H_0}$ is defined when multiplied to ϕ_n since there is no $|n^{(0)}\rangle\langle n^{(0)}|$ term.

$$\Rightarrow \frac{1}{E_n^{(0)}-H_0}\phi_n = \sum_{k\neq n} \frac{1}{E_n^{(0)}-E_k^{(0)}} |k^{(0)}\rangle\langle k^{(0)}|$$

Now you might be tempted to write

$$(E_n^{(0)}-H_0)|n\rangle = (\lambda V-\Delta_n)|n\rangle \Rightarrow |n\rangle \overset{?}{=} \frac{1}{(E_n^{(0)}-H_0)}\phi_n(\lambda V-\Delta_n)|n\rangle$$

However this cannot be write since we must have $|n\rangle \to |n^{(0)}\rangle$ as $\lambda\to 0$ and $\Delta_n \to 0$. So let's add a homogeneous solution $\underline{C_n(\lambda)|n^{(0)}\rangle}$

↳ $$|n\rangle = \cancel{C_n(\lambda)}|n^{(0)}\rangle + \frac{1}{E_n^{(0)}-H_0}\phi_n(\lambda V-\Delta_n)|n\rangle$$

Where $\lim_{\lambda\to 0} C_n(\lambda) = \lim_{\lambda\to 0}\langle n^{(0)}|n\rangle = 1$

Right we set normalization $\langle n^{(0)}|n\rangle = C_n(\lambda) = 1$.

$$\boxed{\therefore\ |n\rangle = |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)}-H_0}(\lambda V-\Delta_n)|n\rangle}$$

Previously we saw $\langle n^{(0)} | \lambda V - \Delta_n | n \rangle = 0$

rearrange: $\lambda \langle n^{(0)} | V | n \rangle = \underset{\substack{\uparrow \\ \text{some \#}}}{\Delta_n} \underbrace{\langle n^{(0)} | n \rangle}_{=1 \text{ by normalization}}$

So $\Delta_n = \lambda \langle n^{(0)} | V | n \rangle$

now with $|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots$

$$\Delta_n = \lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \lambda^3 \Delta_n^{(3)} + \cdots$$

$\hookrightarrow$ $\Delta_n = \lambda \langle n^{(0)} | V | n \rangle$

$\hookrightarrow$ $\lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \lambda^3 \Delta_n^{(3)} = \lambda \langle n^{(0)} | V \left(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots \right)$

By matching λ terms:

$\mathcal{O}(\lambda^1)$: $\Delta_n^{(1)} = \langle n^{(0)} | V | n^{(0)} \rangle$

$\mathcal{O}(\lambda^2)$: $\Delta_n^{(2)} = \langle n^{(0)} | V | n^{(1)} \rangle$

$\mathcal{O}(\lambda^3)$: $\Delta_n^{(3)} = \langle n^{(0)} | V | n^{(2)} \rangle$

$\vdots$

$\mathcal{O}(\lambda^N)$: $\Delta_n^{(N)} = \langle n^{(0)} | V | n^{(N-1)} \rangle$

Note we need energy correction of previous terms, in order to proceed

but we still need to know terms $|n^{(\neq 0)}\rangle$.

Now lets find $|n^{(\neq 0)}\rangle$ in order to evaluate Δ_n:

we know $$|n\rangle = |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)} - H_0}(\lambda V - \Delta_n)|n\rangle$$

expand $|n\rangle$ and Δ_n in terms of λ:

$$|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \cdots = |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)} - H_0}(\lambda V - \lambda\Delta_n^{(1)} - \lambda^2\Delta_n^{(2)} - \cdots)\left(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \cdots\right)$$

Now collect terms in λ:

Here note that $\phi_n \Delta_n^{(1)}|n^{(0)}\rangle = 0$

$\hookrightarrow \Delta_n^{(1)}(1 - |n^{(0)}\rangle\langle n^{(0)}|)|n^{(0)}\rangle = 0$

$\mathcal{O}(\lambda^0)$: $$|n^{(0)}\rangle = |n^{(0)}\rangle$$

$\mathcal{O}(\lambda)$: $$|n^{(1)}\rangle = \frac{\phi_n}{E_n^{(0)} - H_0}(V - \Delta_n^{(1)})|n^{(0)}\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle$$

then with $$\Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle$$

$$\Rightarrow \boxed{\Delta_n^{(2)} = \langle n^{(0)}|V\frac{\phi_n}{E_n^{(0)} - H_0}V|n^{(0)}\rangle}$$

Now let's rewrite $$\frac{\phi_n}{E_n^{(0)} - H_0} = \sum_{k \neq n} \frac{1}{E_n^{(0)} - E_k^{(0)}}|k\rangle\langle k|$$

then $$|n^{(1)}\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle$$
$$= \sum_{k \neq n} \frac{1}{E_n^{(0)} - E_k^{(0)}}|k^{(0)}\rangle\langle k^{(0)}|V|n^{(0)}\rangle$$

$$\boxed{|n^{(1)}\rangle = \sum_{k \neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}|k^{(0)}\rangle}$$ for $V_{kn} = \langle k^{(0)}|V|n^{(0)}\rangle$

Similarly $\Delta_n^{(2)} = \langle n^{(0)} | V \frac{\phi}{E_n^{(0)} - H_0} V | n^{(0)} \rangle$

$$= \langle n^{(0)} | V \sum_{k \neq n} \frac{|k^{(0)}\rangle\langle k^{(0)}|}{E_n^{(0)} - E_k^{(0)}} V | n^{(0)} \rangle$$

$$\boxed{\Delta_n^{(2)} = \sum_{k \neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}}$$ ← 2nd order energy correction.

Remarks:

→ 1st order energy correction only requires eigenket of the unperturbed state.

→ 2nd order energy correction :

→ suppose $n=0$, ground state, we see $\frac{|V_{k0}|^2}{E_0^{(0)} - E_k^{(0)}}$ always give negative value, so the overall energy goes down.

→ the first excited level, $n=1$, we see $\frac{|V_{k1}|^2}{E_1^{(0)} - E_k^{(0)}}$ give slightly less negative compared to ground level $n=0$, so their overall energy goes in opposite direction, which is the <u>no-level-crossing thm</u>

⇒ Applicability of perturbation theory: $\lambda |V_{kn}|^2 \ll E_n^{(0)} - E_k^{(0)}$

*

<u>Summary</u>: $|n\rangle = |n^{(0)}\rangle + \lambda \sum_{k \neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle$

$$+ \lambda^2 \left(\sum_{k \neq n} \sum_{l \neq n} \frac{|k^{(0)}\rangle V_{kl} V_{ln}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} - \sum_{k \neq n} \frac{|k^{(0)}\rangle V_{nn} V_{kn}}{(E_n^{(0)} - E_k^{(0)})^2} \right) + \cdots$$

$$E_n = E_n^{(0)} + \lambda V_{nn} + \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$+ \lambda^3 \sum_{k \neq n}{}' \sum_{l \neq n}{}' \frac{V_{nl} V_{lk} V_{kn}}{(E_n^{(0)} - E_l^{(0)})(E_n^{(0)} - E_k^{(0)})} - V_{nn} \sum_k{}' \frac{|V_{nk}|^2}{(E_n^{0} - E_k^{0})^2} + \cdots$$

Note that $|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots$
is not normalized.

<u>To normalize:</u>

$${}_N\langle n|n\rangle_N = Z_n \langle n|n\rangle = 1$$

so $$Z_n^{-1} = \langle n|n\rangle$$

$$\stackrel{!}{=} 1 + \lambda^2 \langle n^{(1)}|n^{(1)}\rangle + \mathcal{O}(\lambda^3)$$

$$\stackrel{!}{=} 1 + \lambda^2 \sum_k{}' \frac{(V_{kn})^2}{(E_n^{(0)} - E_k^{(0)})^2}$$

then
$$Z_n = 1 - \lambda^2 \sum_k{}' \frac{|V_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2}$$

let $$|n\rangle_N = \sqrt{Z_N}\,|n\rangle$$

$$\langle n^{(0)}|n\rangle_N = \sqrt{Z_N}\,\underbrace{\langle n^{(0)}|n\rangle}_{=1}$$ by previous definition of $|n\rangle$

$$Z_N = \left|\langle n^{(0)}|n\rangle_N\right|^2$$

$$\boxed{Z_N \stackrel{!}{=} 1 - \lambda^2 \underbrace{\sum_{k\neq n} \frac{|V_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2}}}$$ ← side note: $Z_N = \frac{\partial E_n}{\partial E_n^{(0)}}$

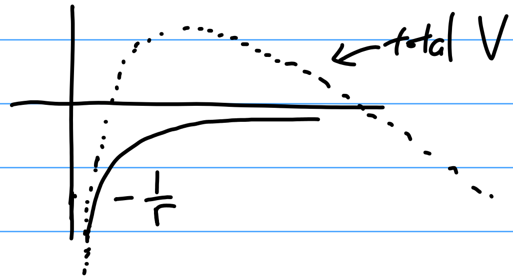
probability for leakage to states other than $|n^{(0)}\rangle$.

<u>Ex:</u> $$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 + \frac{1}{2}\varepsilon m\omega_0^2 x^2$$

Two ways: 1) exact solution and expand in ε.
2) perturbation theory in εV

Quadratic Stark Effect:

$$H = \frac{p^2}{2m} + \underbrace{V_0(r)}_{V_0 \propto \frac{1}{r}} + -e\vec{E}z$$



Imagine spinless electron:

Find shift in ground state.

$$\Delta_k = \Delta_k^{(1)} + \Delta_k^{(2)}$$

$$= \cancel{e|\vec{E}|z_{kk}} + e^2|E|^2 \sum_j{}' \frac{|z_{kj}|^2}{E_k^{(0)} - E_j^{(0)}} = \frac{1}{2}\alpha|\vec{E}|^2$$

but $\langle k^{(0)}|z|k^{(0)}\rangle = 0$ here $|k^{(0)}\rangle$ is nondegenerate so it is a parity eigenket.

$$\underbrace{\langle k^{(0)}|\pi^{-1}}_{\langle k^{(0)}|\varepsilon_k}\underbrace{\pi z \pi^{-1}}_{-z}\underbrace{\pi|k^{(0)}\rangle}_{\varepsilon_k|k^{(0)}\rangle}$$

$\hookrightarrow \langle k^{(0)}|z|k^{(0)}\rangle = -\langle k^{(0)}|z|k^{(0)}\rangle \varepsilon_k^2$ parity - selection rule.

$\to$ never happen, so $\langle k^{(0)}|z|k^{(0)}\rangle = 0$.

$\langle n' \ell' m' | z | n \ell m\rangle = 0$, here $z = T_{q=0}^{k=1}$

unless $|j-k| \le j' \le j+k \Rightarrow j' = \pm 1$, $m' = q+m \to m$.

and parity: $\langle n'\ell' m'|z|n\ell m\rangle \Rightarrow (-1)^{\ell'}(-1)^{\ell} = -1$, then $\ell' - \ell = \underline{\text{odd}}$

Now consider ground state $|1,0,0\rangle$

$$\boxed{\alpha = -2e^2 \sum_{k \neq 0}^{\infty} \frac{|\langle n^{(0)}|z|1,0,0\rangle|^2}{E_0^{(0)} - E_k^{(0)}}}$$

$\vec{p} = \frac{\partial \varepsilon}{\partial \vec{E}} = \alpha \vec{E}$

$\vec{p}$: dipole moment.

$\alpha \sim$ volume of hydrogen

applicability: $|V_{kn}| \ll |E_n^{(0)} - E_k^{(0)}|$

Degenerate Perturbation Theory:

Degenerate Spectrum:

$$H = \begin{pmatrix} \boxed{\begin{matrix} E_1 & & & \\ & E_1 & & \\ & & E_1 & \\ & & & E_1 \end{matrix}} & & 0 \\ & \boxed{\begin{matrix} E_2 & 0 \\ 0 & E_2 \end{matrix}} & \\ 0 & & \ddots \end{pmatrix}$$

Since $|n^{(1)}\rangle \sim \sum_{k \neq n} \frac{V_{nk}}{E_n^{(0)} - E_k^{(0)}}$

→ If $V_{nk} \neq 0$, and $E_n^{(0)} = E_k^{(0)}$, i.e. degenerate, then we have trouble.

✳ Idea: choose zeroth order solution basis such that V has <u>no</u> off diagonal element.

i.e. let $V_{nk} = 0$ for $k \neq n$.

→ Suppose there is a g-fold degeneracy, before perturbation V.

Then there are g- different eigenkets with eigenenergy $E_D^{(0)}$.

→ Let $|m^{(0)}\rangle$, $m = 1, 2, 3 \cdots, g$ to denote those eigenket of degenerate levels.

→ Define

$$\boxed{|l^{(0)}\rangle = \sum_{m \in D} \langle m^{(0)}|l^{(0)}\rangle \, |m^{(0)}\rangle}$$

where $|l^{(0)}\rangle$ diagonalizes $\underline{V}$

with result:

$$\boxed{\begin{aligned} \Delta_l^{(1)} &= \langle l^{(0)}|V|l^{(0)}\rangle = \langle m^{(0)}|V|m^{(0)}\rangle \, |\langle m^{(0)}|l^{(0)}\rangle|^2 \\ \Delta_l^{(2)} &= \sum_{k \notin D} \frac{|V_{kl}|^2}{E_D^{(0)} - E_k^{(0)}} \end{aligned}}$$

$\Rightarrow \det[V - (E - E_D^{(0)})] = 0$, i.e. $\boxed{\Delta_l^{(1)} = \text{eigenvalue of } \langle m^{(0)}|V|m^{(0)}\rangle}$

Linear Stark Effect:

$|n, \underbrace{l, m}_{Y_l^m}\rangle$

hydrogen atom: $a_0 = \frac{\hbar^2}{m_e e^2}$: Bohr radius:

$$E = -\frac{e^2}{a_0}\frac{1}{2n^2}$$

For $|1,0,0\rangle \rightarrow E = -\frac{e^2}{2a_0}$

4 times degenerate. $\left\{ \begin{array}{l} |2,0,0\rangle \rightarrow E = -\frac{e^2}{8a_0} \\ |2,1,\begin{smallmatrix}0\\ \pm 1\end{smallmatrix}\rangle \rightarrow E = -\frac{e^2}{8a_0} \end{array} \right.$

unperturbed state.

$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$, let $V = -ez|\vec{E}|$

$V_0^! \leftarrow$ z has non-vanishing element only between $\underbrace{l=0 \text{ and } l=1}$

since z is odd, we contribution from $\langle\,|\;\,|\,\rangle$ together to be odd. So need $l=0$ and $l=1$

also require m to be the same show

z is $V_0^!$.

$$V = \begin{array}{c} \begin{array}{cccc} 2S & 2p,m=0 & 2p,m=1 & 2p,m=-1 \end{array} \\ \begin{pmatrix} 0 & \langle 2S|V|2p,m=0\rangle & 0 & 0 \\ \langle 2p,m=0|V|2S\rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array}$$

$$\langle 2S|V|2p, m=0\rangle = 3ea_0|\vec{E}|$$

$$V = 3ea_0|\vec{E}| \underbrace{\left(\begin{array}{c|c} \delta^x & 0 \\ \hline 0 & 0 \end{array}\right)}$$

$$\lambda = +1, -1, 0, 0$$

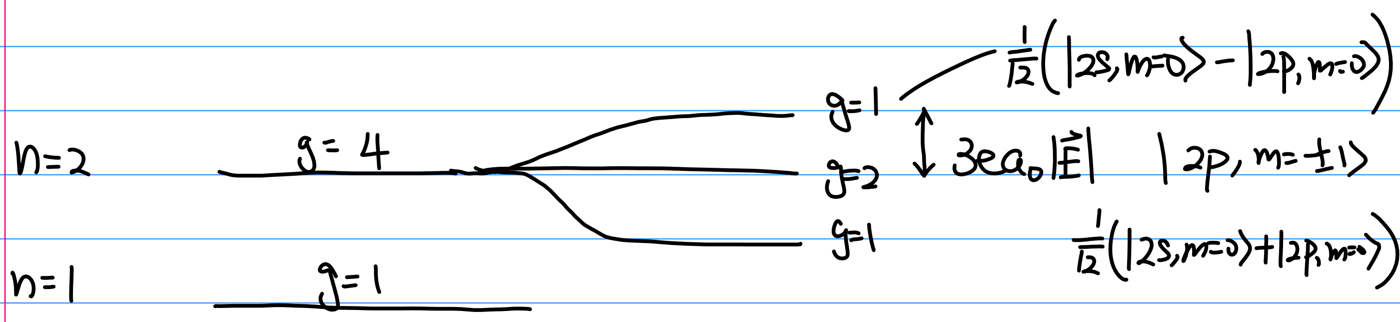
and $\Delta^{(1)} = \langle l^{(0)}|V|l^{(0)}\rangle = \text{eigenvalue}\left\{\langle m^{(0)}|V|m^{(0)}\rangle\right\}$

then

$$\Delta^{(1)}_{\pm} = \pm 3e|\vec{E}|a_0$$ ← linear stark effect.

$$\Delta^{(1)}_{0} = 0$$

with $|\pm\rangle = \frac{1}{\sqrt{2}}\left(|2s, m=0\rangle \pm |2p, m=0\rangle\right)$



Fine Structure of atomic terms, <u>Hydrogen atom</u>:

$$H_0 = \frac{p^2}{2m} + V(r) \quad , \quad \text{let } V(r) = \frac{-Ze^2}{r}$$

$V(r)$ - central potential, rotational symmetry.

$$\left[\frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\partial_r r^2 \partial_r - \frac{l^2}{r^2}\right) + V(r)\right]\psi = E\psi$$

$$\vec{l} = \frac{\vec{L}}{\hbar}$$

and $l^2 = -\left(\frac{1}{\sin\theta}\partial_\theta \sin\theta\partial_\theta + \frac{1}{\sin^2\theta}\partial_\phi^2\right)$

$$\psi = R_{nl}(r)\, Y_l^m(\theta,\phi)$$

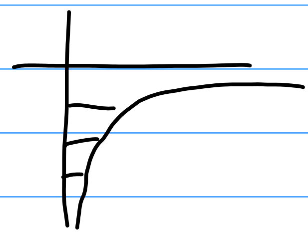
$$\hookrightarrow \left[\frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\partial_r r^2\partial_r - \frac{l(l+1)}{r^2}\right) + V(r)\right] R_{nl}(r) = E_{nl} R_{nl}(r)$$

$V(r) = -\frac{Ze^2}{r}$, Hydrogen atom: $Z = 1$

Typical kinetic energy : $\frac{p^2}{2m} \sim \frac{1}{2m}\left(\frac{\hbar}{r_0}\right)^2$

Typical potential energy: $\sim -\frac{Ze^2}{r_0}$

$\Big\} \; r_0 \sim \frac{\hbar^2}{mZe^2}$



then $E \sim -\frac{1}{2}\frac{me^4}{\hbar^2} Z^2$

then for $Z=1$: $E_{Z=1} = -\frac{1}{2}\frac{me^4}{\hbar^2} \sim -13.5\,\text{eV}$

$$r_0 = \frac{\hbar^2}{me^2} = a_0 \sim 0.529 \times 10^{-8}\,\text{cm}$$

with $Z \neq 1$, $\Rightarrow$ $e \to \sqrt{Z}\, e$ $\quad m \to m' = \frac{mM}{m+M}$

Now rewrite $E = -\frac{Z^2}{2n^2}\frac{me^4}{\hbar^2} = -\frac{Z^2}{2n^2}\frac{\hbar^2}{ma_0^2}$

$$r \to \boxed{\rho = \frac{2Zr}{na_0}}$$

then $\left(\frac{1}{\rho^2}\partial_\rho \rho^2 \partial_\rho - \frac{l(l+1)}{\rho^2} + \frac{n}{\rho}\right) R_{nl}(\rho) = \frac{1}{4} R_{nl}(\rho)$

as $\rho \to \infty$: $\partial_\rho^2 R_{nl} = \frac{1}{4} R_{nl} \Rightarrow R_{nl} \sim e^{-\frac{\rho}{2}}$

Here assume $R_{nl} \sim e^{-\rho}$

as $\rho \to 0$: $R_{nl} \sim \alpha(\alpha+1)\rho^{\alpha-2} - l(l+1)\rho^{\alpha-2} + \cancel{n\rho^{\alpha-1}} = \cancel{\frac{1}{4}\rho^{\alpha}}$

assume $R_{nl} \sim \rho^{\alpha}$ $\quad \hookrightarrow \underline{\alpha = l}, \ \cancel{-l-1}$

as $\rho \to 0$

let $R_{nl} = \rho^{l} e^{-\frac{\rho}{2}} f_{nl}(\rho)$

$\hookrightarrow \left[\rho \partial_\rho^2 + (\underbrace{2l+2}_{\beta} - \rho)\partial_\rho - (\underbrace{l+1-n}_{\alpha})\right] f_{nl} = 0$

then $F(\alpha, \beta; \rho)$ - confluent hypergeometric series.

when n: integer, it doesn't diverge anywhere.
so require n to be integer.

then $\boxed{f_{nl} = L_{n+l}^{2l+1}(\rho) = F(l+1-n, 2l+2, \rho) \quad \text{for } n\text{: integer}, \ n \geq l+1}$

generalized Laguerre Polynomial.

if $n=3$:

$$\left.\begin{array}{lll} l=2 & \to & 5 \\ l=1 & \to & 3 \\ l=0 & \to & 1 \end{array}\right\}$$ so for n, we have n^2 degeneracy.

$$\underbrace{\qquad}_{9}$$

$$L_n^m(\rho) = (-1)^m \frac{n!}{(n-m)!} e^{\rho} \rho^{-m} \partial_\rho^{\,n-m}\left(e^{-\rho}\rho^n\right) \leftarrow \text{generalized Lagurre.}$$

$$L_n^{m=0} = L_n(\rho) = e^{\rho} \partial_\rho^{\,n}\left(e^{-\rho}\rho^n\right) \leftarrow \text{Lagurre Polynomial.}$$

Normalization:

$$\int e^{-\rho}\rho^{2l}\left[L_{n+l}^{2l+1}(\rho)\right]^2 \rho^2 \, d\rho = \frac{2n\left[(n+l)!\right]^3}{(n-l-1)!}$$

then

$*$ $$R_{nl}(\rho) = -\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2} e^{-\frac{\rho}{2}} \rho^{l} L_{n+l}^{2l+1}(\rho)$$

and $\psi_{nlm} = R_{nl}(\rho)\, Y_l^m(\theta,\phi)$ → require $n \geq l+1$ and integer.

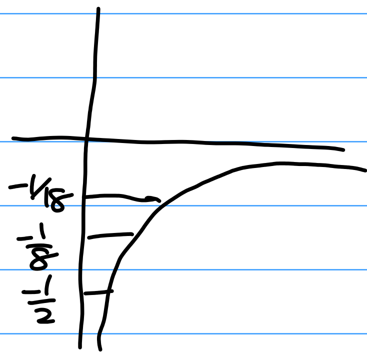
$$E_n = -\frac{1}{2n^2}\frac{Z^2e^2}{a_0} \qquad \rho = \frac{2Z}{na_0} r, \quad a_0 = \frac{\hbar^2}{m_e e^2}$$

Ex:

$$R_{10} = \left(\frac{Z}{a_0}\right)^{3/2} 2 e^{-\frac{Zr}{a_0}}$$

$$R_{20} = \left(\frac{Z}{2a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$$

$$R_{21} = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{\sqrt{3}\,a_0} e^{-\frac{Zr}{2a_0}}$$



n	l	Name	g
1	0	1s	1 ← without spin
2	0	2s	1
	1	2p	3 ← $m = \pm 1, 0$
3	0	3s	1
	1	3p	3
	2	3d	5

2s, 2p: } 4 for energy

3s, 3p, 3d: } 9 for energy

$$\langle r^K \rangle = \int_0^\infty dr\, r^2\, R_{nl}(r)^2\, r^K \quad \underbrace{\int d\Omega\, Y_l^m(\theta,\phi)}_{=1}$$

Sakurai 5.3

$$\left\{ \begin{aligned} \langle r \rangle &= \int_0^\infty dr\, r^2 R_{nl}(r)^2 r = \frac{a_0}{2Z}\left(3n^2 - l(l+1)\right) \\ \langle r^2 \rangle &= \int_0^\infty dr\, r^2 R_{nl}(r)^2 r^2 = \frac{a_0 n^2}{2Z^2}\left[5n^2+1-3l(l+1)\right] \\ \left\langle \frac{1}{r} \right\rangle &= \frac{Z}{n^2 a_0} \\ \left\langle \frac{1}{r^2} \right\rangle &= \frac{Z}{n^3 a_0^2 (l+\frac{1}{2})} \end{aligned} \right.$$

Now consider spin: then we have $2n^2$ degeneracy.

Fine structure corrections:

1) Electron move at $\sim \frac{c}{137}$, need relativistic corrections $\sim Z\alpha^2$ fine structure

2) Radiative Correction: $\sim$ lamb shift $\sim (Z\alpha)^2 \alpha \ln\frac{1}{2}$ small effect

3) external field.

4) Electron Interactions. (hard problem)

5) Nuclear spin → cause magnetic field. → Hyperfine Structure $(Z\alpha)^2 \frac{m_e}{M_{nuc}}$

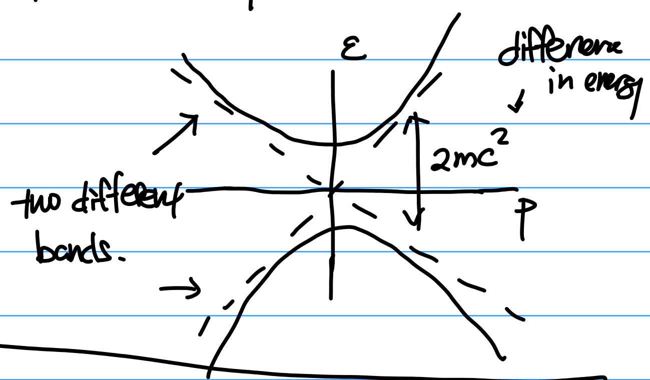
Focus on Relativistic Correction:

$$H_{Dirac} = c\vec{\alpha}\left(\vec{p} - \frac{e}{c}\vec{A}\right) + \beta mc^2 + e\phi$$

$\frac{1}{c}$ expansion [Foldy - Wouthuysen Transformation]

spectrum of H_{dirac}

$$E = \pm\sqrt{(mc^2)^2 + p^2c^2}$$



$$\boxed{\begin{aligned} H = {} & mc^2 + \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 - \frac{p^4}{8m^3c^2} + \theta \\ & + e\phi - \underbrace{\frac{e\hbar}{2mc}\vec{\sigma}\cdot\vec{B}}_{\text{Zeeman term}} - \underbrace{i\frac{e\hbar^2}{8m^2c^2}\vec{\sigma}\cdot(\vec{\nabla}\times\vec{E})}_{\text{ignore.}} - \underbrace{\frac{e\hbar}{4m^2c^2}\vec{\sigma}\cdot(\vec{E}\times\vec{p})}_{\text{spin-orbital interaction}} - \underbrace{\cancel{\frac{e\hbar^2}{8m^3c^2}(\vec{\nabla}\cdot\vec{E})}}_{\text{Darwin Term. (ignore)}} \end{aligned}}$$

Consider spin - orbit interaction:

$$V_{LS} = -\frac{e\hbar}{4m^2c^2}\vec{\sigma}\cdot(\vec{E}\times\vec{p}) = -\frac{e\hbar}{4m^2c^2}\left(-\frac{dV}{dr}\right)\frac{1}{r}\vec{\sigma}\cdot\underbrace{(\vec{r}\times\vec{p})}_{L}$$

$$\vec{E} = -\vec{\nabla}V\frac{1}{e} \stackrel{!}{=} -\frac{dV}{dr}\hat{r}\frac{1}{e} \stackrel{!}{=} -\frac{dV}{dr}\frac{1}{r}\frac{1}{e}\hat{r}$$

$\vec{E} = -\vec{\nabla}\phi$

$\vec{S} = \frac{\hbar}{2}\vec{\sigma}$

$$\boxed{V_{LS} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{L}\cdot\vec{S}}$$

thomas precession.

Spin - Orbit Interaction:

$H = \frac{p^2}{2m} + V(r) \rightarrow |n, l, m_l\rangle$

with spin $\rightarrow |n, l, m_l, s, m_s\rangle$

$[H_{LS}, L^i] \neq 0$

but $[H_{LS}, \underbrace{\vec{L}+\vec{S}}_{J}] = 0$ and $\vec{L}\cdot\vec{S} = \frac{1}{2}[(L+S)^2 - L^2 - S^2] = \frac{1}{2}(J^2 - L^2 - S^2)$

$$= \frac{1}{2}\left(j(j+1) - l(l+1) - s(s+1)\right)$$

where $j = |l-s|, \dots l+s$

then $\vec{L}\cdot\vec{S} = \begin{cases} \frac{\hbar^2}{2}l & j = l+1/2 \\ -\frac{\hbar^2}{2}(l+1) & j = l-1/2 \end{cases}$

So instead of $|n, l, m_l, s, m_s\rangle \rightarrow |n, l, s, j, m\rangle$

Since we're in basis that diagonalizes V_{LS}, we just use first order perturbation theory.

then $E^{(1)} = \langle n, l, s, j, m | V_{LS} | n, l, s, j, m\rangle$

$$\stackrel{|}{=} \langle n, l, s, j, m | \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \vec{L}\cdot\vec{S} | n, l, s, j, m\rangle$$

$$\stackrel{|}{=} \underbrace{\frac{1}{2m^2c^2} \int_0^\infty dr\, r^2 R_{nl}^2 \frac{1}{r} \frac{dV}{dr}}_{\frac{A_{nl}}{\hbar^2}} \underbrace{\langle \vec{L}\cdot\vec{S}\rangle}_{s=\frac{1}{2}}$$

$j = l \pm \frac{1}{2}$

$$= \frac{A_{nl}}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

Lets find the difference in split.

$$E^{(1)}_{nlj} - E^{(1)}_{nl(j-1)} = A_{nl} \frac{1}{2}\left[j(j+1) - (j-1)j\right]$$

$$\boxed{E^{(1)}_{nlj} - E^{(1)}_{nl(j-1)} \stackrel{|}{=} A_{nl}\, j}$$ ← splitting energy.

$$A_{nl} = \left\langle \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \right\rangle \sim \frac{e^2}{a_0^3} \frac{\hbar^3}{m^2c^2}, \quad a_0 = \frac{\hbar^2}{me^2}$$

$$\stackrel{|}{\sim} \frac{e^2}{a_0} \frac{\hbar^2}{ma_0^2} \frac{1}{mc^2} \sim \text{small.}$$

$$A_{nl} \stackrel{|}{\sim} \frac{e^2}{a_0} \underbrace{\frac{e^4}{\hbar^2 c^2}}_{\alpha^2 = \left(\frac{e^2}{\hbar c}\right)^2 \sim \left(\frac{1}{137}\right)^2}$$

Scales:

energy: $E \sim \frac{e^2}{a_0^3} \frac{\hbar^2}{m_e^2 c^2}$ or $\frac{e^2}{a_0} \alpha^2$

Length: $\underbrace{\frac{e^2}{m_e c^2}}_{\text{classical radius of electron}}$ or $\underbrace{\frac{\hbar}{m_e c}}_{\text{compton radius}}$ or $\underbrace{a_0}_{\text{bohr radius}} = \frac{\hbar^2}{m_e c^2} = 1 : \frac{1}{\alpha} : \frac{1}{\alpha^2} = 1 : 137 : 137^2$

estimate $\frac{p^4}{8 m_e^3 c^2} \sim \alpha^2 \frac{e^2}{a_0}$

Zeeman Effect (magnetic field)

→ Consider at uniform magnetic field:

$$\vec{p} \to \vec{p} - \frac{e}{c}\vec{A} \quad , \quad \vec{\nabla}\cdot\vec{A} = \vec{B}$$

Now choose gauge: $\vec{A} = \frac{1}{2}(\vec{B}\times\vec{r})$ ← radial gauge.

$$\Rightarrow \quad H = \frac{p^2}{2m} + V_c(r) - \frac{e}{2m_e c}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + \frac{e^2 A^2}{2m_e c^2}$$

choose $\vec{B} = B_0\hat{z}$ then $\vec{A} = -\frac{1}{2}B(y\hat{x} - x\hat{y})$

generally: $\vec{p}\cdot\vec{A} = \vec{A}\cdot\vec{p} - i\hbar\underbrace{(\vec{\nabla}\cdot\vec{A})}_{\vec{\nabla}\cdot\vec{A}=0 \text{ in the this gauge.}}$

then $\vec{A}\cdot\vec{p} = -\frac{1}{2}B(yP_x - xP_y) = \frac{1}{2}BL_z$

and $A^2 = \frac{1}{4}B^2(x^2+y^2)$

added spin magnetic-moment interaction.

$$\text{Finally: } H = \frac{p^2}{2m} + V_c(r) - \frac{e}{2m_e c}BL_z + \underbrace{\cancel{\frac{e^2}{8m_e c^2}B^2(x^2+y^2)}}_{\propto B^2, \text{ drop}} \underbrace{- \vec{\mu}\cdot\vec{B}}_{\frac{-e}{m_e c}\vec{S}\cdot\vec{B} = \frac{-e}{m_e c}BS_z}$$

<u>After omitting B^2 term:</u>

let $H_0 = \frac{p^2}{2m} + V_c(r)$

$$H_{LS} = \frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{L}\cdot\vec{S} \quad \sim \quad \frac{e^2}{a_0}\left(\frac{1}{137}\right)^2$$

$$H_B = \frac{-eB}{2m_e c}(L_z + 2S_z) \quad \sim \quad \frac{e\hbar B}{2m_e c}$$

In weak Magnetic field limit: if $H_B \ll H_{LS}$ (Lande Limit)
strong Magnetic field limit: if $H_B \gg H_{LS}$ (Paschen-Back)

		Dominant Interaction	Almost good (good for specific case)	No good at all	All case Quantum #'s always good
$\vert j\,l\,s\,m\rangle$	weak B	H_{LS}	J^2 $\vec{L}\cdot\vec{S}$	L_z, S_z	L^2
$\vert l\,s\,m_l\,m_s\rangle$	strong B	H_B	L_z S_z	$J^2, \vec{L}\cdot\vec{S}$	S^2 J_z

↑ Paschen-Back

Consider weak Magnetic limit ($H_B \ll H_{LS}$) (Lande Limit):

Good Quantum #: L^2, S^2, J_z
Almost good: J^2
$\Big\}$ $|j, l, s, m_z\rangle$

$$\Delta E = -\frac{eB}{2m_e c}\langle J_z + S_z\rangle_{j=l\pm\frac{1}{2}} = -\frac{eB}{2m_e c}\left(\hbar m + \langle S_z\rangle_{j=l\pm\frac{1}{2}}\right)$$

$$|j=l\pm 1/2, m\rangle = \pm\underbrace{\sqrt{\frac{l\pm m+\frac{1}{2}}{2l+1}}}_{C_+}\left|m_l=m-\tfrac{1}{2}, m_s=\tfrac{1}{2}\right\rangle + \sqrt{\frac{l\mp m+\frac{1}{2}}{2l+1}}\left|m_l=m+\tfrac{1}{2}, m_s=-\tfrac{1}{2}\right\rangle$$

$$\hookrightarrow \langle S_z\rangle = \frac{\hbar}{2}\left(|C_+|^2-|C_-|^2\right)$$

$$= \frac{\hbar}{2}\frac{1}{2l+1}\left[\left(l\pm m+\tfrac{1}{2}\right)-\left(l\mp m+\tfrac{1}{2}\right)\right] = \pm\frac{m\hbar}{2l+1}$$

$$\boxed{\Delta E_B = \frac{-e\hbar B}{2m_e c}m\left[1\pm\frac{1}{2l+1}\right]}$$ ← energy shift. (Lande formula)

Another Derivation:

assume $\vec{S} = \alpha \vec{J}$

$\hookrightarrow$ constant

then $S_z = \alpha S_z$

then $\underbrace{\vec{S}\cdot\vec{J}}\ = \alpha J^2$

$\hookrightarrow$ same constant

Find $\vec{S}\cdot\vec{J}$:

$$(\vec{J}-\vec{S})^2 = \vec{L}^2 \quad \hookrightarrow -2\vec{J}\cdot\vec{S} + j(j+1) + s(s+1) = l(l+1)$$

$\hookrightarrow -2\vec{J}\cdot\vec{S} + j(j+1) + s(s+1) = l(l+1)$

$$\hookrightarrow \quad \vec{J}\cdot\vec{S} = \frac{j(j+1) - l(l+1) + s(s+1)}{2} = \alpha\, j(j+1)$$

$$\hookrightarrow \quad \alpha = \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$$

so $S_z = \alpha \hbar m$

introduce: Lande factor: $g = 1 + \dfrac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$

if $s = 1/2$, $j = l \pm 1/2 \rightarrow g = 1 \pm \frac{1}{2l+1}$

then

$$\boxed{\Delta E_B = \frac{-e\hbar B}{2m_e c}\left[1 \pm \frac{1}{2l+1}\right]}$$

same answer as before.

Time - Dependent Potential:

Consider Hamiltonian, H such that it can be split into two parts

$$H = H_0 + V(t)$$

part that doesn't contain time variation — part that contains time variation

if only H_0: $|\alpha(t)\rangle = e^{\frac{-iH_0 t}{\hbar}} |\alpha(t=0)\rangle$

Suppose at $t=0$, we have $|\alpha\rangle = \sum_n c_n(0)\,|n\rangle$

We wish to find at later times.

$$|\alpha, t_0=0; t\rangle_S = \sum_n c_n(t) \underbrace{e^{-iE_n t/\hbar}}_{\text{Interaction Picture gets rid of this}} |n\rangle$$

Interaction Picture.

Define

$$\boxed{|\alpha, t_0; t\rangle_I = e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_S = e^{\frac{iH_0 t}{\hbar} - \frac{iHt}{\hbar}} |\alpha, t_0; t\rangle_H}$$

Interaction Picture. — Schrodinger picture — Heinsenberg picture.

For operators (observables):

$$A_I = e^{\frac{iH_0 t}{\hbar}} A_S\, e^{\frac{-iH_0 t}{\hbar}}$$

In particular: $V_I = e^{\frac{iH_0 t}{\hbar}}\, V\, e^{\frac{-iH_0 t}{\hbar}}$

time-dependant potential in schrodinger picture.

Recall Heisenberg: $|\alpha\rangle_H = e^{\frac{iHt}{\hbar}} |\alpha, t_0=0; t\rangle_S$

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

Now let's derive the fundamental differential equation that characterizes time evolution of state ket in interaction picture:

$$i\hbar\partial_t |\alpha, t_0; t\rangle_I = i\hbar\partial_t \left(e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S\right)$$

$$= \cancel{-H_0 e^{\frac{iH_0t}{\hbar}}|\alpha, t_0; t\rangle_S} + e^{\frac{iH_0t}{\hbar}}\underbrace{\partial_t|\alpha, t_0; t\rangle_S}_{\equiv(\cancel{H_0}+V)|\alpha, t_0; t\rangle_S}$$

$$= e^{\frac{iH_0t}{\hbar}} V |\alpha, t_0; t\rangle_S$$

$$\boxed{i\hbar\partial_t |\alpha, t_0; t\rangle_I = e^{\frac{iH_0t}{\hbar}} V e^{\frac{-iH_0t}{\hbar}} |\alpha, t_0; t\rangle_I}$$

$\therefore$ $\boxed{i\hbar\partial_t |\alpha, t_0; t\rangle_I = V_I |\alpha, t_0; t\rangle_I}$

↳ Therefore, $|\alpha, t_0; t\rangle_I$ is constant if $V_I = 0$

We can also show for observable A, (that doesn't contain time explicitly in Schrodinger) that:

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

← Heinsenberg-like, but replaced $H \to H_0$

Table Summary:

	Heinsenberg	Interaction	Schrodinger
State ket	No change	determined by V_I	determined by H
observable	determined by H	determined by H_0	No change.

Let $|\alpha; t_0; t\rangle_I = \sum_n c_n(t)|n\rangle$

then $i\hbar\partial_t \underbrace{\langle n|\alpha, t_0; t\rangle}_{= c_n(t)} = \sum_m \underbrace{\langle n|V_I|m\rangle}_{\langle n|e^{\frac{iH_0t}{\hbar}} V e^{-\frac{iH_0t}{\hbar}}|m\rangle} \underbrace{\langle m|\alpha, t_0; t\rangle_I}_{c_m(t)}$

$\hookrightarrow = V_{nm}(t)\, e^{\frac{i(E_n-E_m)}{\hbar}t}$

System of ODEs to solve

$$** \boxed{\begin{array}{l} \hookrightarrow\ i\hbar \frac{d}{dt} c_n(t) = \sum_m V_{nm} e^{i\omega_{nm}t} c_m(t) \\ \qquad \text{where } \omega_{nm} = \frac{E_n - E_m}{\hbar} \\ \hookrightarrow\ i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & \cdots \\ V_{21}e^{i\omega_{21}t} & V_{22} & \\ \vdots & & V_{33} \\ & & & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \end{array}}$$

Time-Dependent Two-state problem:

Problem with exact solution: sinusoidal oscillating potential.

$$H_0 = E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2| \qquad (E_2 > E_1)$$

$$V(t) = \gamma e^{i\omega t} |1\rangle\langle 2| + \gamma e^{-i\omega t} |2\rangle\langle 1|$$

then $H = \begin{pmatrix} E_1 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & E_2 \end{pmatrix}$ with initial condition $C_1(0) = 1$, $C_2(0) = 0$

then we have:

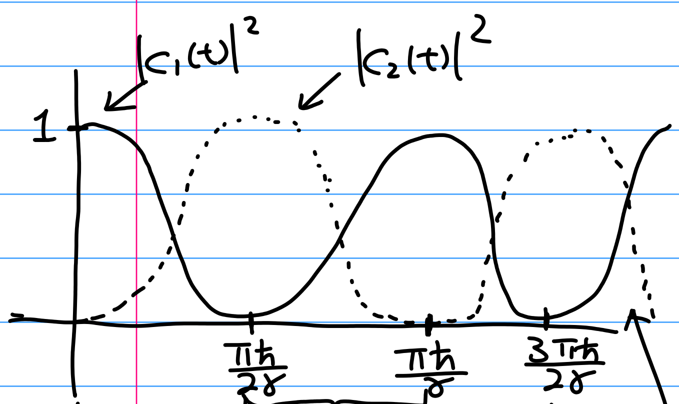
$$i\hbar \begin{pmatrix} \dot{C}_1 \\ \dot{C}_2 \end{pmatrix} = \begin{pmatrix} 0 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & 0 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

This has solution:

probability of finding upper state $\Rightarrow$ $$|C_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega - \omega_{21})^2/4} \sin^2\left\{ \underbrace{\sqrt{\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4}}}_{\equiv \Omega}\, t \right\}$$

resonance when $\omega = \omega_{21}$

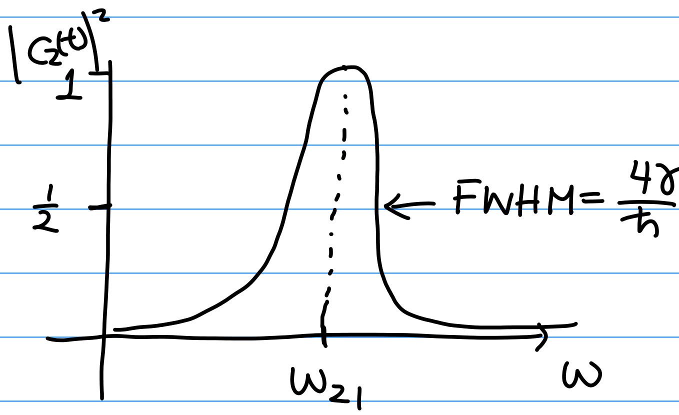
probability of finding lower state $\Rightarrow$ $$|C_1(t)|^2 = 1 - |C_2(t)|^2$$



absorption emission absorption

(higher $|C_2(t)|^2$ so absorb to upper state) (lower $|C_2(t)|^2$ emits photon go to lower state)

when $\omega = \omega_{21}$
otherwise $|C_2(t)|^2_{max} \neq 1$



Time-Dependent Perturbation Theory:

Dyson Series:

previously we derived: $i\hbar \partial_t |\alpha\rangle_I = V_I |\alpha\rangle_I$

where $V_I = e^{\frac{i}{\hbar}H_0 t} V_S e^{-\frac{i}{\hbar}H_0 t}$

$$|\alpha, t\rangle_I = U_I(t, t_0) \, |\alpha, t = t_0\rangle$$

time evolution operator in interaction picture.

then $i\hbar \partial_t U_I(t, t_0) \cancel{|\alpha, t = t_0\rangle} = V_I U_I(t, t_0) \cancel{|\alpha, t = t_0\rangle}$

↳ ① $i\hbar \partial_t U_I(t, t_0) = V_I(t) U_I(t, t_0)$

since $|\alpha, t = t_0\rangle_I = U_I(t = t_0, t_0) \, |\alpha, t = t_0\rangle_I$

↳ ② require $U_I(t, t_0)\Big|_{t=t_0} = 1$ as initial condition.

using ①: $\displaystyle dt' \underbrace{\left[\frac{d}{dt'} U_I(t', t_0)\right]}\Bigg|_{t_0}^{t} = \int_{t_0}^{t} -\frac{i}{\hbar} V_I(t') U_I(t', t_0) \, dt'$

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

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

Dyson series

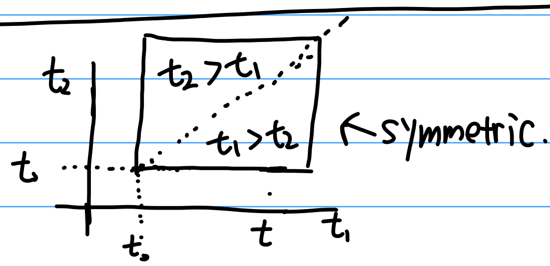
Sole above equation via iteration:

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

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

with requirement : $t > t' > t'' > \cdots > t^{(n-1)} > t^{(n)} > t_0$

Rewriting in a compact form



then $$U_I(t,t_0) = \sum_{n=0}^{\infty} \hat{T}_t \frac{1}{n!}\left(\int_{t_0}^{t} dt_1\, V_I(t_1)\right)^n$$

↳ time ordering operator that orders time into $t > t_1 > t_2 \cdots\cdots$

$$\overset{!}{=} \hat{T}_t \exp\left\{ \int_{t_0}^{t} dt_1\, V_I(t_1)\right\}$$

Transition Probability

Suppose we're given

$$|i, t_0=0; t\rangle_I = U_I(t,0)\,|\underbrace{i, t_0=0; t=t_0}_{\text{initial state}}\rangle$$

$$= \sum_n |n\rangle \underbrace{\langle n| U_I(t,0) |i\rangle}_{C_n(t)}$$

$$\boxed{|i, t_0=0; t\rangle_I = \sum_n C_n(t)\,|n\rangle\,, \quad C_n(t) = \langle n| U_I(t,0) |i\rangle}$$

Now explore connection between $U(t,t_0)$ and $U_I(t,t_0)$

$$|\alpha, t_0; t\rangle_I = e^{\frac{iH_0 t}{\hbar}} |\alpha, t_0; t\rangle_S$$

$$= e^{\frac{iH_0 t}{\hbar}} U(t,t_0)\,|\alpha, t_0; t=t_0\rangle_S$$

$$|\alpha, t_0; t\rangle_I = \underbrace{e^{\frac{iH_0 t}{\hbar}} U_S(t,t_0)\, e^{\frac{-iH_0 t}{\hbar}}}_{U_I(t,t_0)} |\alpha, t_0; t=t_0\rangle_I$$

So $$\boxed{U_I(t,t_0) = e^{\frac{iH_0 t}{\hbar}} U_S(t,t_0)\, e^{\frac{-iH_0 t}{\hbar}}}$$

So $$\langle n| U_I(t,t_0) |i\rangle = \langle n| e^{\frac{iH_0 t}{\hbar}} U_S(t,t_0)\, e^{\frac{-iH_0 t}{\hbar}} |i\rangle$$

$$\boxed{\langle n| U_I(t,t_0) |i\rangle = e^{\frac{i(E_n t - E_i t_0)}{\hbar}} \underbrace{\langle n| U_S(t,t_0) |i\rangle}_{\text{transition amplitude.}}}$$

So we see that $\langle n | U_I(t,t_0) | i \rangle \neq \langle n | U_S(t,t_0) | i \rangle$

However if $|n\rangle$ and $|i\rangle$ are <u>both energy eigenstates</u>:

then $$\left| \langle n | U_I(t,t_0) | i \rangle \right|^2 = \left| \langle n | U_S(t,t_0) | i \rangle \right|^2$$

but if we use $|a'\rangle$ and $|b'\rangle$, which are eigenstates of operator A, B, but $[H, A] \neq 0$ $[H, B] \neq 0$, i.e. not simultaneous eigenket of H, then in general:

$$\left| \langle b' | U_I(t,t_0) | a' \rangle \right|^2 \neq \left| \langle b' | U_S(t,t_0) | a' \rangle \right|^2$$

*Determine $\boxed{\text{Transition Probability: } P(i \to n) \overset{n \neq i}{=\!=} \left| C_n^{(1)}(t) + C_n^{(2)}(t) + \cdots \right|^2}$

Determining: $C_n(t) = \langle n | U_I(t,t_0) | i \rangle$

$$C_n(t) = C_n^{(0)}(t) + C_n^{(1)}(t) + C_n^{(2)}(t) + \cdots\cdots$$

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

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

$$= \langle n | i \rangle - \frac{i}{\hbar} \int_{t_0}^{t} \langle n | V_I(t') | i \rangle \, dt'$$

note: $V_I = e^{\frac{iH_0 t}{\hbar}} V_S e^{\frac{-iH_0 t}{\hbar}}$

$$+ \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \, \langle n | V_I(t') V_I(t'') | i \rangle$$

assume n, i are eigenkets of H

$$C_n(t) = \delta_{ni} - \frac{i}{\hbar} \int_{t_0}^{t} e^{i\omega_{ni} t'} V_{ni}(t') \, dt'$$

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

Ex: Constant Perturbation:

$$V(t) = \begin{cases} 0 & \text{for } t<0 \\ V & \text{for } t \geq 0 \end{cases}$$

assume no time depence, but made up of operators like x p and s.

suppose at $t_0=0$, we're in eigenket $|i\rangle$.

Then $$C_n^{(0)} = \delta_{ni}$$

$$C_n^{(1)} = \frac{-i}{\hbar}\int_{t_0}^{t} e^{i\omega_{ni}t'} V_{ni}(t')\,dt'$$

but $V_{ni}(t') = V_{ni}$

$$= \frac{-i}{\hbar} V_{ni} \int_0^t e^{i\omega_{ni}t'}\,dt'$$

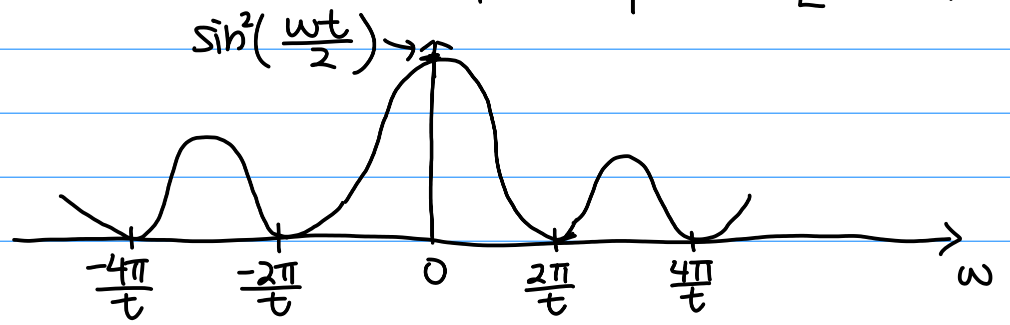
$$= -\frac{V_{ni}}{\hbar\omega_{ni}} e^{i\omega_{ni}t'}\Big|_0^t$$

$$C_n^{(1)} = \frac{V_{ni}}{E_n - E_i}\left(1 - e^{i\omega_{ni}t}\right)$$

Probability to go to other state is:

$$P_{i\to n} \cong |C_n^{(1)}|^2 = \frac{|V_{ni}|^2}{|E_n - E_i|^2}(2 - 2\cos\omega_{ni}t)$$

$$P_{i\to n} = \frac{4|V_{ni}|^2}{|E_n-E_i|^2}\sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right]$$



As $E_n \to E_i$

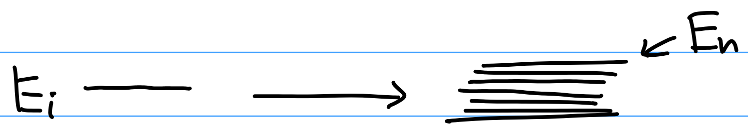
$$P_{i\to n} = \frac{4|V_{ni}|^2}{|E_n - E_i|^2} \sin^2\left(\frac{(E_n-E_i)t}{2\hbar}\right)$$

$$\overset{!}{=} \frac{4|V_{ni}|^2}{(\hbar\omega_{ni})^2} \sin\left(\frac{\omega_{ni} t}{2}\right)$$

take limit $E_n \to E_i$, $\omega_{ni} \to 0$, so $\sin^2\left(\frac{\omega t}{2}\right) \sim \left(\frac{\omega}{2} t\right)^2$

then $P_{i\to n} = |C_n^{(1)}|^2 \approx \frac{1}{\hbar^2} |V_{ni}|^2 t^2$

since $E_n \sim E_i$, the final states form a continuous energy spectrum near E_i:



$\Rightarrow$ If there are many of these states, we want to calculate the total probability, that is, the transition probability summed over final states with $E_n \simeq E_i$.

or $$P_{i\to n, E_n \simeq E_i} = \sum_{n, E_n \simeq E_i} |C_n^{(1)}|^2$$

sum over all states with their energy $\simeq E_i$

Introduce density of final states with energy interval, $(E, E+dE)$:

$$\rightarrow \quad \rho(E)\,dE$$

$$\hookrightarrow \sum_{n, E_n \simeq E_i} |c_n^{(1)}|^2 \Rightarrow \int dE_n\, \rho(E_n)\, |c_n^{(1)}|^2$$

$$\stackrel{!}{=} 4 \int \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right] \frac{|V_{ni}|^2}{|E_n - E_i|^2} \rho(E_n)\, dE_n$$

as $t \to \infty$, using $\lim_{\alpha \to \infty} \frac{1}{\pi} \frac{\sin^2 \alpha x}{\alpha x^2} = \delta(x)$

$$\lim_{t \to \infty} \frac{1}{|E_n - E_i|^2} \sin^2\left(\frac{(E_n - E_i)t}{2\hbar}\right) = \frac{\pi t}{2\hbar} \delta(E_n - E_i)$$

$$\xrightarrow{t \to \infty} 4 \int \rho(E_n) \frac{\pi t}{2\hbar} \delta(E_n - E_i)\, |V_{ni}|^2\, dE_n$$

take average of $|V_{ni}|^2$

$$\lim_{t \to \infty} \sum_{n, E_n \simeq E_i} |c_n^{(1)}|^2 = \frac{2\pi t}{\hbar} \overline{|V_{ni}|^2}\, \rho(E_n)\Big|_{E_n \simeq E_i}$$

Now consider

$$\boxed{\text{Transition rate: } W_{i\to[n]} = \frac{d}{dt} P_{i\to[n]} = \frac{d}{dt}\sum_n |C_n^{(1)}|^2}$$

$[n]$ means a group of states

using $$\lim_{t\to\infty} \sum_{n,\, E_n \simeq E_i} |C_n^{(1)}|^2 = \frac{2\pi t}{\hbar} \overline{|V_{ni}|^2}\, \rho(E_n)\Big|_{E_n \simeq E_i}$$

then $$W_{i\to[n]} = \frac{d}{dt}\sum_n |C_n^{(1)}|^2 = \frac{2\pi}{\hbar} \overline{|V_{ni}|^2}\, \rho(E_n)\Big|_{E_n\simeq E_i}$$

constant rate, instead of oscillating

$$\hookrightarrow \quad W_{i\to n} = \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i)$$ ← Fermi's Golden Rule

switched to a particular state, n.

and note $$W_{i\to[n]} = \int dE_n\, \rho(E_n)\, W_{i\to n}$$

Now consider 2^{nd} order:

$$C_n^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2 \sum_m V_{nm} V_{mi} \int_0^t dt' \, e^{i\omega_{nm}t'} \int_0^{t'} dt'' \, e^{i\omega_{mi}t''}$$

$$\stackrel{!}{=} \frac{i}{\hbar} \sum_m \frac{V_{nm} V_{mi}}{E_m - E_i} \int_0^t \left(e^{i\omega_{ni}t'} - e^{i\omega_{nm}t'}\right) dt'$$

Same as $C_n^{(1)}$ and $\sim t$ as $t \to \infty$

gives rise to rapid oscillation as $t \to \infty$, so it doesn't grow in t, then don't care.

Now with $C_n^{(1)}(t)$ and $C_n^{(2)}(t)$:

$$W_{i \to [n]} = \frac{2\pi}{\hbar} \overline{\left| V_{ni} + \sum_m \frac{V_{nm} V_{mi}}{E_i - E_m} \right|^2} \rho(E_n) \Big|_{E_n \simeq E_i}$$

Harmonic Perturbation:

$$V(t) = V e^{i\omega t} + V^{\dagger} e^{-i\omega t} \qquad t \geq 0$$

Assume 1 eigenstate of H_0 is populated initially, assume perturbation is on at $t=0$.

then

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

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

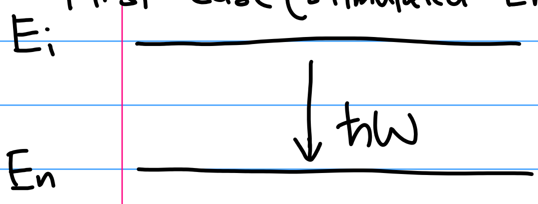
we see as $t \to \infty$: $|C_n^{(1)}|^2$ valid when:

For first term: $\omega_{ni} + \omega \simeq 0$ or $E_n \simeq E_i - \hbar\omega$

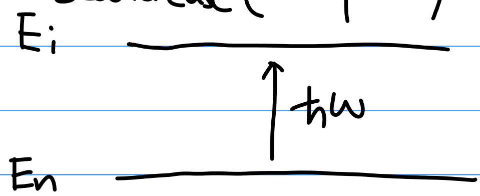
For second term: $\omega_{ni} - \omega \simeq 0$ or $E_n \simeq E_i + \hbar\omega$

when first term is important, second term is not. Vice-Versa.

First case (stimulated Emission)



second case (absorption)



then the transition rates are:

$$w_{i\to[n]} = \frac{2\pi}{\hbar} \overline{|V_{ni}|^2}\, \rho(E_n)\Big|_{E_n \simeq E_i - \hbar\omega}$$ (stimulated Emission) First case.

$$w_{i\to[n]} = \frac{2\pi}{\hbar} \overline{|V_{ni}^{\dagger}|^2}\, \rho(E_n)\Big|_{E_n \simeq E_i + \hbar\omega}$$ (Absorption) second case.

More commonly:

$$W_{i\to n} = \frac{2\pi}{\hbar}\begin{Bmatrix} |V_{ni}|^2 \\ |V_{ni}^{+}|^2 \end{Bmatrix}\delta(E_n - E_i \pm \hbar\omega)$$

Note since $|V_{ni}|^2 = |V_{ni}^{+}|^2$

$$\frac{W_{i\to[n]}}{\rho(E_n)} = \frac{W_{n\to[i]}}{\rho(E_i)}$$ ← detailed balance

Energy Shift and Decay Width:

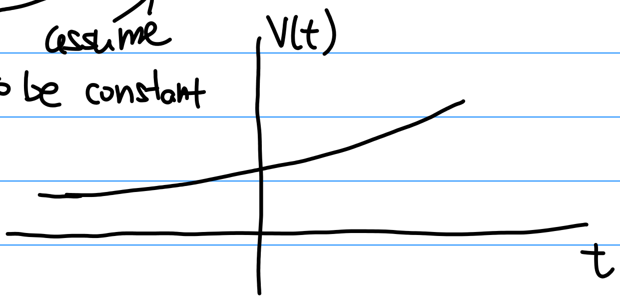
Question: What happens to $C_i(t)$ itself, i.e. $i \to n = i$.

To avoid effect of sudden change in Hamiltonian, let's increase perturbation very slowly.

$$V(t) = e^{\eta t} V, \quad \text{so } V(t) = 0 \text{ as } t = t_0 = -\infty$$

let $\eta \to 0$ in the end to have constant potential.

assume to be constant



let's first calculate $i \to n \neq i$:

$$C_n^{(0)}(t) = 0$$

$$C_n^{(1)}(t) = \frac{-i}{\hbar} V_{ni} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'} e^{i\omega_{ni} t'} dt'$$

$$= \frac{-i}{\hbar} V_{ni} \frac{e^{\eta t + i\omega_{ni} t}}{\eta + i\omega_{ni}}$$

then:

$$\left| C_n^{(1)}(t) \right|^2 \simeq \frac{|V_{ni}|^2}{\hbar^2} \frac{e^{2\eta t}}{\eta^2 + \omega_{ni}^2}$$

then the transition rate:

$$W_{i \to n} = \frac{d}{dt} \left| C_n^{(1)}(t) \right|^2 \simeq \frac{2 |V_{ni}|^2}{\hbar^2} \left(\frac{\eta e^{2\eta t}}{\eta^2 + \omega_{ni}^2} \right)$$

Now let $\eta \to 0^+$,

but note: $\lim_{\eta \to 0^+} \frac{\eta}{\eta^2 + \omega_{ni}^2} = \pi \delta(\omega_{ni}) = \pi \delta\left(\frac{E_n - E_i}{\hbar}\right) = \pi\hbar\, \delta(E_n - E_i)$

then

$$W_{i\to n} \cong \left(\frac{2\pi}{\hbar}\right) |V_{ni}|^2 \delta(E_n - E_i)$$

again, the golden rule.

Now lets consider case $n = i$:

$$C_i^{(0)} = 1$$

$$C_i^{(1)} = \frac{-i}{\hbar} V_{ii} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'} dt' = \frac{-i}{\eta \hbar} V_{ii} e^{\eta t}$$

$$C_i^{(2)} = \left(\frac{-i}{\hbar}\right)^2 \sum_m |V_{mi}|^2 \lim_{t_0 \to -\infty} \int_{t_0}^{t} dt'\, e^{i\omega_{im} t' + \eta t'} \frac{e^{i\omega_{mi} t' + \eta t'}}{i(\omega_{mi} - i\eta)}$$

separate to $m = i$ and $m \neq i$

$$= \left(\frac{-i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} + \left(\frac{-i}{\hbar}\right) \sum_{m \neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta(E_i - E_m + i\hbar\eta)}$$

Now evaluate up to 2^{nd} order:

$$\frac{\dot{C}_i}{C_i} \simeq \frac{\frac{-i}{\hbar} V_{ii} + \left(\frac{-i}{\hbar}\right)^2 \frac{|V_{ii}|^2}{\eta} + \left(\frac{-i}{\hbar}\right) \sum_{m \neq i} \frac{|V_{mi}|^2}{(E_i - E_m + i\hbar\eta)}}{1 - \frac{i}{\hbar} \frac{V_{ii}}{\eta}}$$

$$\simeq \frac{-i}{\hbar} V_{ii} + \left(\frac{-i}{\hbar}\right) \sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta}$$

Now try ansatz: $c_i(t) = e^{\frac{-i}{\hbar}\Delta_i t}$ and $\frac{\dot{c}_i(t)}{c_i(t)} = \frac{-i}{\hbar}\Delta_i$

Now in if in interaction picture:

$$c_i(t)_I = e^{\frac{-i}{\hbar}\Delta_i t}$$

then in schrodinger picture we have:

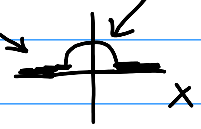
$$c_i(t)_S = e^{\frac{-i}{\hbar}\Delta_i t} e^{\frac{-i}{\hbar}E_i t} = e^{\frac{-i}{\hbar}(E_i + \Delta_i)t}$$ ← we see it's shifting by Δ_i

or $E_i \longrightarrow E_i + \Delta_i$

If we let $\Delta_i = \Delta_i^{(1)} + \Delta_i^{(2)} + \cdots$

then $\Delta_i^{(1)} = V_{ii}$ ← exactly time-independent perturbation theory.

To find $\Delta_i^{(2)}$, first note: $\lim_{\varepsilon \to 0} \frac{1}{x + i\varepsilon} = \Pr\left\{\frac{1}{x}\right\} - i\pi\delta(x)$



Thus

$$\Delta_i^{(2)} = \underbrace{\Pr\left\{\sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m}\right\}}_{\text{exactly 2nd order time-independent perturbation theory.}} - \underbrace{i\pi \sum_{m \neq i} |V_{mi}|^2 \delta(E_i - E_m)}_{\frac{\hbar}{2\pi}\sum_{m \neq i} W_{i \to m}}$$

Note $\sum_{m \neq i} W_{i \to m} = \frac{2\pi}{\hbar} \sum_{m \neq i} |V_{mi}|^2 \delta(E_i - E_m) = -\frac{2}{\hbar} \operatorname{Im}\left(\Delta_i^{(2)}\right)$

In the end we have:

$$C_i(t) = \underbrace{e^{\frac{-i}{\hbar}\mathrm{Re}(\Delta_i)t}}_{\substack{\text{shift in energy} \\ E_i \to E_i + \mathrm{Re}(\Delta_i)}} \; \underbrace{e^{\frac{-i}{\hbar}\mathrm{Im}(\Delta_i)t}}_{\text{decay.}}$$

if we define $\frac{\Gamma_i}{\hbar} = -\frac{2}{\hbar}\mathrm{Im}(\Delta_i) \leftarrow$ life time.

then $$|C_i(t)|^2 = e^{\frac{2\,\mathrm{Im}(\Delta_i)t}{\hbar}} = e^{\frac{-\Gamma_i t}{\hbar}}$$

define decay width: $\tau_i = \frac{\hbar}{\Gamma_i}$

Also note probability conservation: for small t

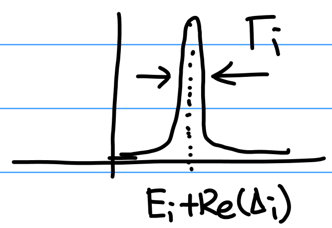
$$|C_i|^2 + \sum_{m\neq i} |C_m|^2 = \left(1 - \frac{\Gamma_i t}{\hbar}\right) + \underbrace{\sum_{m\neq i} W_{i\to m}\, t}_{= \frac{\Gamma_i}{\hbar} t} = 1$$

To see why Γ_i is the width: take Fourier decomposition:

$$\int f(E)\, e^{\frac{-iEt}{\hbar}}\, dE = e^{\frac{-i}{\hbar}(E_i + \mathrm{Re}(\Delta_i))t}\, e^{-\frac{\Gamma_i t}{2\hbar}}$$

then find $f(E)$ by inverse transform:

$$|f(E)|^2 \propto \frac{1}{\{E - [E_i + \mathrm{Re}(\Delta_i)]\}^2 + \frac{\Gamma_i^2}{4}}$$



(semi-classical)
WKB Approximation: $\hbar \to 0$ (Taylor in $\hbar$)

$$-\frac{\hbar^2}{2m}\nabla^2\psi = (E - U(x))\psi$$

smooth in the scale of deBroglie wavelength

assume $\psi(x) = \exp\{\frac{i}{\hbar}\sigma(x)\}$

$$\hookrightarrow -\frac{\hbar^2}{2m}\vec{\nabla}\left(\frac{i}{\hbar}\exp\{\tfrac{i}{\hbar}\sigma(x)\}\vec{\nabla}\sigma(x)\right) = (E-U)\exp\{\tfrac{i}{\hbar}\sigma(x)\}$$

$$\hookrightarrow -\frac{\hbar^2}{2m}\frac{i}{\hbar}\left\{\nabla^2\sigma(x) + \frac{i}{\hbar}\left(\vec{\nabla}\sigma(x)\right)^2\right\} = E-U$$

$$\hookrightarrow \boxed{-i\hbar\nabla^2\sigma(x) + \left(\vec{\nabla}\sigma(x)\right)^2 = 2m(E-U(x))}$$

$\Leftarrow$ Equation to solve

let $\sigma(x) = \sigma^{(0)} + \frac{\hbar}{i}\sigma^{(1)} + \left(\frac{\hbar}{i}\right)\sigma^{(2)} + \cdots$

Now, let's consider 1D:

then we have: $\left(\partial_x\sigma(x)\right)^2 - i\hbar\partial_x^2\sigma(x) = p(x)$

where $p(x) = \sqrt{2m(E-U(x))}$

$\Leftarrow$ Equation that we need to solve for.

First: 0th order solution:

$$\left(\partial_x\sigma^{(0)}(x)\right)^2 - \cancel{i\hbar\partial_x^2\sigma^{(0)}(x)} = p(x)$$

$$\left(\partial_x\sigma^{(0)}(x)\right)^2 = p(x) \Rightarrow \boxed{\sigma^{(0)}(x) = \int^x \pm p(x')dx'}$$

zeroth order solution

$$\boxed{\psi_0(x) = c_1 e^{+\frac{i}{\hbar}\int^x p(x')dx'} + c_2 e^{-\frac{i}{\hbar}\int^x p(x')dx'}}$$

then $\Psi^{(0)}(x,t) = \psi(x)\, e^{-i\frac{E}{\hbar}t}$

$$\Psi^{(0)} \simeq \exp\left\{ \pm \frac{i}{\hbar}\int^{x} p(x')\,dx' - \frac{i}{\hbar}Et \right\}$$

<u>Applicability of WKB:</u>

First require $\quad \hbar\, \partial_x^2 \delta^{(0)}(x) \ll \left(\partial_x \delta^{(0)}(x)\right)^2$

we saw $\quad \delta^{(0)}(x) \sim \pm\int^{x} p(x')\,dx'$

so $\quad \partial_x \delta^{(0)}(x) = p(x)$

then $\quad \partial_x^2 \delta^{(0)}(x) = p'(x)$

Hence condition becomes $\quad \boxed{\hbar\, p'(x) \ll p(x)^2}$

Now since $\quad \hbar k(x) = p(x)$

$\hookrightarrow \quad k'(x) \ll k(x)^2$

using $k(x) = \frac{2\pi}{\lambda}$ $\quad \hookrightarrow \quad \frac{\partial_x k(x)}{k^2} \ll 1$

$\hookrightarrow \quad \left| \frac{d}{dx}\left(\frac{1}{k(x)}\right) \right| \ll 1$

or $\quad * \quad \boxed{\left| \frac{d}{dx} \frac{\lambda}{2\pi} \right| \ll 1}$ $\quad \leftarrow$ change in wavelength is small compare to the wavelength itself.

Another interpretation:

Starting from $\hbar p'(x) \ll p(x)^2$

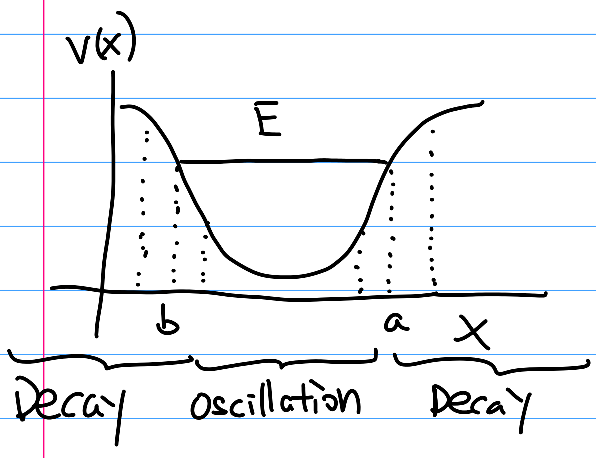
since $p(x) = \sqrt{2m(E - U(x))}$

so $\frac{d}{dx} p(x) = -\frac{m}{p} \frac{dU(x)}{dx} = \frac{mF(x)}{p}$

then $\frac{\hbar m}{p} F(x) \ll p^2$

or $\boxed{\frac{\hbar m}{p^3} F(x) \ll 1}$ ← the overall change of the local momentum must be small compared to the momentum itself

or $\boxed{\lambda F(x) \ll \frac{p^2}{m}}$ ← the potential energy change over a wavelength is much less than local kinetic energy.



At turning point, $E \sim U(x)$, so $P \approx 0$, so $\frac{\hbar m F(x)}{p^3} \ll 1$

is not valid.

Now expand in higher orders:

$$\sigma(x) = \sigma^{(0)} + \left(\frac{\hbar}{i}\right)\sigma^{(1)} + \left(\frac{\hbar}{i}\right)^2 \sigma^{(2)} + \cdots$$

$$\Rightarrow \quad \left(\partial_x \sigma(x)\right)^2 - i\hbar\, \partial_x^2 \sigma(x) = p(x)$$

$$\hookrightarrow \left[\partial_x\left(\sigma^{(0)} + \left(\frac{\hbar}{i}\right)\sigma^{(1)} + \left(\frac{\hbar}{i}\right)^2\sigma^{(2)}\right)\right]^2 - i\hbar\, \partial_x^2\left(\sigma^{(0)} + \frac{\hbar}{i}\sigma^{(1)}\right) = p(x)$$

$$\left(\partial_x \sigma^{(0)}\right)^2 + \frac{2\hbar}{i}\left(\partial_x \sigma^{(0)}\right)\left(\partial_x \sigma^{(1)}\right) + \left(\frac{\hbar}{i}\right)^2\left[\left(\partial_x \sigma^{(1)}\right)^2 + 2\,\partial_x\sigma^{(0)}\partial_x\sigma^{(2)}\right] - i\hbar\,\partial_x^2\left(\sigma^{(0)} + \frac{\hbar}{i}\sigma^{(1)}\right) = p(x)$$

Group by $\hbar$:

$$\hbar^{(0)}: \qquad \left[\partial_x \sigma^{(0)}\right]^2 = p(x) \quad \Rightarrow \quad \boxed{\sigma^{(0)} = \pm\int^x p(x')\,dx'}$$

$$\hookrightarrow \quad \boxed{\psi^{(0)}(x) = C_1 e^{+\int^x p(x')dx'} + C_2 e^{-\int^x p(x')dx'}}$$

$$\hbar^{(1)}: \qquad 2\frac{\hbar}{i}\left[\partial_x \sigma^{(0)}\right]\left[\partial_x\sigma^{(1)}\right] - i\hbar\,\partial_x^2\sigma^{(0)} = 0$$

$$\hookrightarrow \quad \partial_x\sigma^{(0)}\partial_x\sigma^{(1)} + \frac{1}{2}\partial_x^2\sigma^{(0)} = 0$$

know $\partial_x\sigma^{(0)} = p$

$$\hookrightarrow \quad \partial_x \sigma^{(1)} = \frac{\frac{d}{dx}p(x)}{2p(x)}$$

$$\hookrightarrow \quad \boxed{\sigma^{(1)} = -\frac{1}{2}\ln p(x)}$$

then $\psi(x) = \exp\left\{\frac{i}{\hbar}\left(\pm\int^x p(x')dx' - \frac{1}{2}\ln p(x)\right)\right\}$

$$\boxed{\psi^{(0+1)}(x) = \frac{C_1}{\sqrt{p}} e^{\int^x p(x')dx'} + \frac{C_2}{\sqrt{p}} e^{-\int^x p(x')dx'}}$$

$(\hbar)^2$: $\left(\frac{\hbar}{i}\right)^2\left(\left[\partial_x \sigma^{(1)}\right]^2 + 2\,\partial_x\sigma^{(0)}\partial_x\sigma^{(2)}\right) - \hbar^2\partial_x^2\sigma^{(1)} = 0$

$$\hookrightarrow \quad \partial_x\sigma^{(0)}\partial_x\sigma^{(2)} + \frac{1}{2}\left[\partial_x\sigma^{(1)}\right]^2 + \frac{1}{2}\partial_x^2\sigma^{(1)} = 0$$

$$\hookrightarrow \quad \partial_x\sigma^{(2)} = \frac{-\frac{1}{2}\left(\left[\partial_x\sigma^{(1)}\right]^2 + \partial_x^2\sigma^{(1)}\right)}{\partial_x\sigma^{(0)}}$$

$$\overset{!}{=} \frac{-\frac{1}{2}\left[\left(-\frac{1}{2}\frac{p'(x)}{p(x)}\right)^2 + \left(-\frac{1}{2}\right)\frac{p''(x)p(x) - (p'(x))^2}{p(x)^2}\right]}{p(x)}$$

$$\partial_x\sigma^{(2)} \overset{!}{=} \frac{1}{4}\frac{p''(x)}{p(x)^2} - \frac{3}{8}\frac{(p'(x))^2}{p(x)^3}$$

$$\hookrightarrow \quad \sigma^{(2)}(x) = \int dx' \, \frac{p''}{4p} - \frac{3}{8}\frac{(p')^2}{p^3}$$

$$\overset{!}{=} \frac{p'}{4p} + \int \frac{(p')^2}{2p^3} - \frac{3(p')^2}{8p^3}\,dx'$$

using $F = \frac{pp'}{m}$

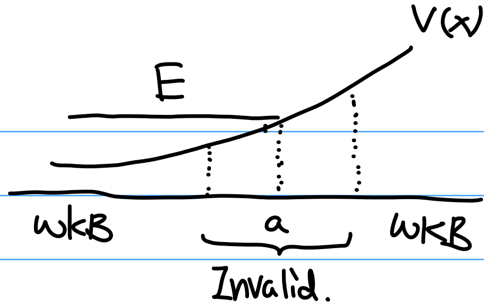
$$\overset{!}{=} \frac{1}{4}\frac{mF}{p^3} + \frac{m^2}{8}\int^x \frac{F^2}{p^5}\,dx'$$

then $\psi^{(0+1+2)}(x) = \exp\left\{\frac{i}{\hbar}\left(\sigma^{(0)} + \frac{\hbar}{i}\sigma^{(1)} + \left(\frac{\hbar}{i}\right)^2\sigma^{(2)}\right)\right\}$

$$\overset{!}{=} \left[\frac{C_1}{\sqrt{p}}e^{\int^x p(x')dx'} + \frac{C_2}{\sqrt{p}}e^{-\int^x p(x')dx'}\right]\left(\exp\left\{\frac{\hbar}{i}\sigma^{(2)}\right\}\right)$$

$$\boxed{\psi^{0+1+2}(x) \overset{!}{\simeq} \left[\frac{C}{\sqrt{p}}e^{\int^x p(x')dx'} + \frac{C_2}{\sqrt{p}}e^{-\int^x p(x')dx'}\right]\left(1 - i\hbar\sigma^{(2)}\right)}$$

Connection Formula:



WKB is invalid about turning point:

Turning point, a and b, when $p(a) = p(b) = 0$

or $E = U(a) = U(b)$

Define $k = \frac{1}{\hbar}\sqrt{2m(E - U(x))}$ when $E > U(x)$

$K = \frac{1}{\hbar}\sqrt{2m(U(x) - E)}$ when $E < U(x)$

then WKB with zeroth and first order tell us:

$$\boxed{\begin{aligned} &\text{(grow/decay)}: \psi_{x \gg a}(x) = \frac{A}{\sqrt{K}} e^{-\int_a^x K(x')dx'} + \frac{B}{\sqrt{K}} e^{\int_a^x K(x')dx'} \\ &\text{oscillation}: \psi_{x \ll a}(x) = \frac{C}{\sqrt{k}} e^{-i\int_a^x k(x')dx'} + \frac{D}{\sqrt{k}} e^{i\int_a^x k(x')dx'} \end{aligned}} \quad *$$

Now the question is how is A, B related with C, D.

To connect, we need to solve Schrodinger more accurately near turning points. by approximating the potential as a linear potential near turning point.

Suppose we want to solve a specific case:

at $x \approx a$ (turning point):

linear potential: $U(x) - E = g(x-a)$ where $g > 0$

then we have $-\frac{\hbar^2}{2m} \partial_x^2 \psi + g(x-a)\psi = 0$

lets convert $x \to z = \left(\frac{2mg}{\hbar^2}\right)^{1/3}(x-a)$

$$\Rightarrow \quad \frac{d^2\psi}{dz^2} - z\psi = 0$$

since $k^2 = \frac{2m}{\hbar^2}(E - U(x))$

$\qquad = -\frac{2mg}{\hbar^2}(x-a)$ $\qquad E - U(x) = -g(x-a)$

$k^2 = -\left(\frac{2mg}{\hbar^2}\right)^{2/3} z$

using applicability condition:

$$\left|\frac{d}{dx}k(x)\right| \ll k(x)^2 \quad \text{or} \quad \left|\frac{d}{dx}\left(\frac{1}{k}\right)\right| \ll 1$$

$$\hookrightarrow \quad \frac{d}{dz}\left(\frac{2mg}{\hbar^2}\right)^{1/3}(-)\left(\frac{2mg}{\hbar^2}\right)^{-1/3} z^{-\frac{1}{2}} \ll 1$$

$$\hookrightarrow \quad \frac{1}{2} z^{-3/2} \ll 1$$

or $\boxed{|z|^{3/2} \gg 1/2}$ $\leftarrow$ For WKB-Applicability.

The exact solution to

$$\frac{d^2}{dz^2}\psi - z\psi = 0$$

are Airy Functions: $A_i(z)$ and $B_i(z)$

Since WKB condition is $|z|^{3/2} \gg \frac{1}{2}$

this means we can use WKB for Airy Functions for very large z in both positive and negative.

In general:

$$A_i(z) = \frac{1}{\pi}\int_0^\infty \cos\left(\frac{s^3}{3} + sz\right) ds$$

$$B_i(z) = \frac{1}{\pi}\int_0^\infty \left(\exp\left\{-\frac{s^3}{3} + sz\right\} + \sin\left(\frac{s^3}{3} + sz\right)\right) ds$$

For $z \to +\infty$:

$$A_i(z) \simeq \frac{1}{2\sqrt{\pi}} z^{-1/4} e^{-\frac{2}{3}|z|^{3/2}}$$

$$B_i(z) \simeq \frac{1}{\sqrt{\pi}} z^{-1/4} e^{\frac{2}{3}|z|^{3/2}}$$

For $z \to -\infty$:

$$A_i(z) \simeq \frac{1}{\sqrt{\pi}} |z|^{-1/4} \cos\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right)$$

$$B_i(z) \simeq -\frac{1}{\sqrt{\pi}} |z|^{-1/4} \sin\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right)$$

Now recognize for linear potential case:

$$\int_x^a k(x)dx = \frac{2}{3}\left(\frac{2mg}{\hbar^2}\right)^{1/2}(a-x)^{3/2} = \frac{2}{3}|z|^{3/2} \quad \text{for } z<0$$

$$\int_x^a k(x)dx = \frac{2}{3}\left(\frac{2mg}{\hbar^2}\right)^{1/2}(x-a)^{3/2} = \frac{2}{3}|z|^{3/2} \quad \text{for } z>0$$

we see that the asymptotic solution of the exact solution are the same as WKB-solutions.

Therefore: we use the fact of asymptotic solution and write:

$$\boxed{\begin{aligned} &\frac{2A}{\sqrt{k(x)}}\cos\left(\int_x^a k(x)dx - \frac{\pi}{4}\right) - \frac{B}{\sqrt{k(x)}}\sin\left(\int_x^a k(x)dx - \frac{\pi}{4}\right) && x \ll a \text{ (rising slope)} \\ &= \frac{A}{\sqrt{k(x)}}\exp\left(-\int_a^x k(x)dx\right) + \frac{B}{\sqrt{k(x)}}\exp\left(\int_a^x k(x)dx\right) && x \gg a \end{aligned}}$$

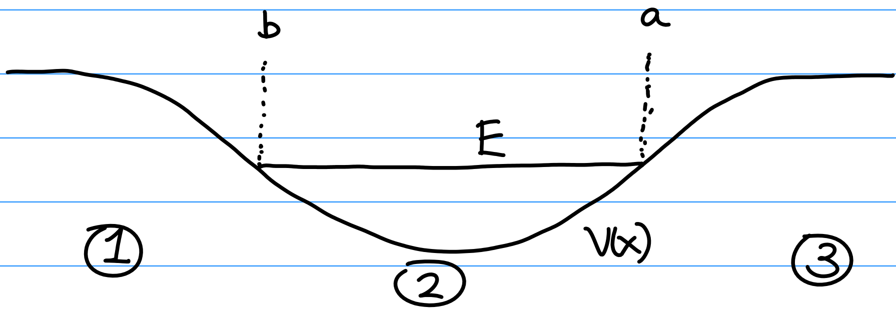
Connection Formula

Similarly:

$$\boxed{\begin{aligned} &\frac{A}{\sqrt{k(x)}}\exp\left(-\int_x^b k(x)dx\right) + \frac{B}{\sqrt{k(x)}}\exp\left(\int_x^b k(x)dx\right) && x \ll b \text{ (lowering slope)} \\ &= \frac{2A}{\sqrt{k(x)}}\cos\left(\int_b^x k(x)dx - \frac{\pi}{4}\right) - \frac{B}{\sqrt{k(x)}}\sin\left(\int_b^x k(x)dx - \frac{\pi}{4}\right) && x \gg b \end{aligned}}$$

Remarks:
1) If turning points are too close, then cannot use WKB, invalid region spans entirely.
2) If $V(x)$ is singular then $k(x)$ also becomes singular.

Example: Bound State: (1D potential well)



In region 1: since wave function must decay as $x \to -\infty$,

$$\psi(x) \cong \frac{1}{\sqrt{K}} \exp\left\{-\int_x^b K(x)\,dx\right\} \quad \text{for} \quad x < b$$

Since for $x<b$, we have no growing term, then $\underline{B=0}$
we also observe $A=1$ by matching.

so in region 2:

$$\psi(x) = \frac{2}{\sqrt{K}} \cos\left(\int_b^x k(x)\,dx - \frac{\pi}{4}\right) \quad \text{for} \quad b > x > a$$

$$\stackrel{!}{=} \frac{2}{\sqrt{K}} \cos\left(\int_b^a k(x)\,dx - \int_x^a k(x)\,dx - \frac{\pi}{4}\right)$$

with Trig addition formula

$$\stackrel{!}{=} -\frac{2}{\sqrt{K}} \cos\left(\int_b^a k(x)\,dx\right) \sin\left(\int_x^a k(x)\,dx - \frac{\pi}{4}\right)$$

$$+ \frac{2}{\sqrt{K}} \sin\left(\int_b^a k(x)\,dx\right) \cos\left(\int_x^a k(x)\,dx - \frac{\pi}{4}\right)$$

using connection formula we see

$$B = \frac{2}{\sqrt{K}} \cos\left(\int_b^a k(x)\,dx\right) \quad \text{and} \quad A = \frac{1}{\sqrt{K}} \sin\left(\int_b^a k(x)\,dx\right)$$

Then in region (3):

$$\psi(x) = \underbrace{\frac{1}{\sqrt{k}}\sin\left(\int_b^a k(x)dx\right)}_{A} \frac{1}{\sqrt{K}} \exp\left(-\int_a^x K(x)dx\right)$$

$$+ \underbrace{\frac{2}{\sqrt{k}}\cos\left(\int_b^a k(x)dx\right)}_{B} \frac{1}{\sqrt{K}} \exp\left(\int_a^x K(x)dx\right)$$

However, we don't want growing terms in (3):
so choose $B=0$

or $\cos\left(\int_b^a k(x)dx\right) = 0$

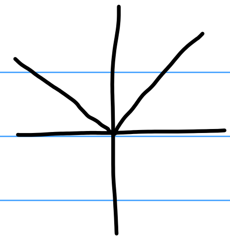
this means $\boxed{\int_b^a k(x)dx = \left(n+\frac{1}{2}\right)\pi \quad \text{for } n=0,1,2\cdots}$ Bohr-Sommerfeld Formula.

then $\psi(x) = \frac{2}{\sqrt{k}}\sin\left(\int_b^a k(x)dx\right)\cos\left(\int_x^a k(x)dx - \frac{\pi}{4}\right)$ for $b > x > a$

and $\psi(x) = \frac{1}{\sqrt{k}}\sin\left(\int_b^a k(x)dx\right)\frac{1}{\sqrt{K}} \exp\left\{-\int_a^x K(x)dx\right\}$ for $x > a$

or $\boxed{\oint p\,dx = 2\pi\hbar\left(n+\frac{1}{2}\right)}$

example: $-\frac{\hbar^2}{2m}\partial_x^2\psi + g|x|\psi = E\psi$

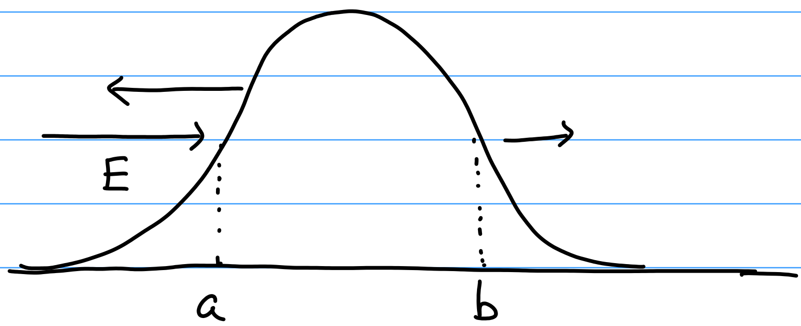


$$2\int_0^{E/g}\sqrt{\frac{2m}{\hbar^2}(E-gx)} = \left(n+\frac{1}{2}\right)\pi$$

$$E_{WKB}^3 = \frac{9}{32}\pi^2\left(n+\frac{1}{2}\right)^2\frac{g^2\hbar^2}{m}$$

$$E_{WKB} \approx \left(n+\frac{1}{2}\right)^{2/3}$$

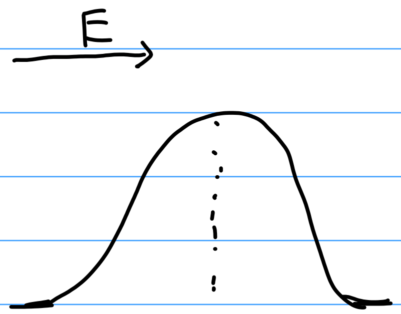
Transmission through a barrier:



find $\boxed{T = |t|^2 \cong e^{-2\int_a^b \kappa(x)dx}}$ when WKB is valid

$$t \sim e^{\frac{i}{\hbar}\int_a^b p\,dx} \sim e^{\frac{i}{\hbar}\int_a^b i\hbar\kappa\,dx} \sim e^{-\int_a^b \kappa\,dx}$$

Reflection about Barrier:



if classical, particle slows down as it goes through potential, but all goes through.

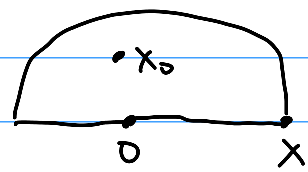
$$\psi = \frac{1}{\sqrt{k(x)}} e^{i\int_0^x k(x)dx}$$

Find turning points: $V(x) = E$

but in case $E > V(x)$, we get complex turning points.

Ex: $V(x) = -\frac{1}{2}ax^2 = E \rightarrow x = \pm i\sqrt{\frac{2E}{a}}$

Now solve



then

$$R = e^{-4\,\mathrm{Im}\int_0^{x_0} k(x)dx}$$

$$\overset{\downarrow}{=} e^{-2\pi\varepsilon} \quad \text{vs exact} \quad \frac{1}{1+e^{2\pi\varepsilon}}$$

where $\varepsilon = \frac{E}{\hbar}\sqrt{\frac{m}{a}}$

Adiabatic Approximation (Born-Oppenheimer)

Hamiltonian changing slowly:

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

assume $\quad H(\lambda(t))\, \psi_n = E_n(t)\, \psi_n$

↖ instantaneous eigenstate.

then $\quad i\hbar\, \partial_t \psi_n = E_n(t)\, \psi_n$

$$\psi_n = \boxed{\underbrace{e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'}}_{\text{Dynamical phase, } i\theta_n(t)}}\, \psi_n(t=0)$$

↖ but we're not solving for time-dependent Schrodinger.

But we can do better:

$$\psi(t) = \sum_m c_m(t)\, \psi_n(t)\, e^{i\theta_n(t)} \qquad \text{and} \qquad \langle \psi_n | \psi_m \rangle = \delta_{nm}$$

↳ plug into $\quad i\hbar\, \partial_t \psi = H\psi$

$$\Rightarrow \quad \dot{c}_m(t) = -\sum_n c_n \langle \psi_m | \dot{\psi}_n \rangle\, e^{i(\theta_n - \theta_m)}$$

then $\quad \langle \psi_m | \dot{H} | \psi_n \rangle_{m \neq n} = (E_n - E_m) \langle \psi_m | \dot{\psi}_n \rangle$

$$\dot{c}_m(t) = \underbrace{-c_m \langle \psi_m | \dot{\psi}_m \rangle}_{\text{when } n=m} - \sum_{m \neq n} c_m \frac{\langle \psi_n | \dot{H} | \psi_m \rangle}{E_n - E_m}\, e^{\frac{i}{\hbar}\int_0^t [E_n(t') - E_m(t')]dt'}$$

If H changes slowly, i.e. $\dot{H} \ll 1$, and energy do not cross, i.e. $E_n \neq E_m$

then

$$\dot{c}_m(t) = \underbrace{-c_m \langle \psi_m | \dot{\psi}_m \rangle}_{\text{when } n=m}$$

so $$c_m(t) = c_m(0) e^{i\gamma_m(t)}$$

$$\boxed{\gamma_m(t) = i\int_0^t \langle \psi_m(t') | \frac{\partial}{\partial t'} \psi_m(t') \rangle \, dt'}$$

Berry's phase.

then $$\boxed{\psi_n(t) = e^{i\theta_n(t)} e^{i\gamma_m(t)} \psi_n(0)}$$

If $H(t) \to H(\lambda(t))$

then $$\gamma_m(t) = i\int_0^t \langle \psi_m | \nabla_\lambda \psi_m \rangle \frac{d\lambda}{dt} \, dt$$

$$\overset{!}{=} i\int_C d\lambda \, \langle \psi_m | \nabla_\lambda \psi_m \rangle$$

geometric phase.
or Berry phase.

Ex: $i\hbar\partial_t\psi = -\mu\vec{B}(t)\vec{\sigma}\psi$

$\hookrightarrow$ slow

$H = -\mu\vec{B}\cdot\vec{\sigma} \quad \rightarrow \quad E = \pm\mu|\vec{B}|$

$$\chi_- \begin{cases} \sin\frac{\theta}{2}\, e^{-i\varphi} \\ -\cos\frac{\theta}{2} \end{cases}$$

$\vec{B} = B(t)\left[\sin\theta\cos\phi\,\hat{x},\ \sin\theta\sin\phi\,\hat{y},\ \cos\theta\,\hat{z}\right]$

Find $\gamma_- = \frac{1}{2}\oint_{\vec{n}_1}^{\vec{n}_2} d\phi\,(1-\cos\theta)$

$\hookrightarrow$ initial direction of magnetic field

Identical Particles

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V_{pair}(|x_1 - x_2|) + V_{ext}(x_1) + V_{ext}(x_2)$$

classically: due to symmetry:

$$\begin{matrix} x_1(t) \\ x_2(t) \end{matrix} \Rightarrow \begin{matrix} x_2(t) \\ x_1(t) \end{matrix}$$

In QM:

we have permutation symmetry.

$V \otimes V$:

$$|k'\rangle \otimes |k''\rangle \overset{\text{permutation.}}{\Longleftrightarrow} |k''\rangle \otimes |k'\rangle$$

or $\quad V \otimes V \longleftrightarrow V \otimes V$

Define permutation operator: P_{12} :

$$P_{12} |k'\rangle \otimes |k''\rangle = |k''\rangle \otimes |k'\rangle$$

so $\quad P_{12} = P_{21} \qquad$ so $\quad P_{12}^2 = 1$

or $\boxed{P_{12} = \pm 1}$ ← eigenvalue.

$$P_{12} A_1 P_{12}^{-1} = A_2$$

$$P_{12} H P_{12}^{-1} = H$$ $\Leftarrow$ if Hamiltonian is permutation invariant.

then $[H, P_{12}] = 0$ then P_{12} is constant of motion.

let $$|k', k''\rangle_\pm = \frac{1}{\sqrt{2}}\left(|k', k''\rangle \pm |k'', k'\rangle\right)$$

$$P_{12} |k', k''\rangle_\pm = \pm |k', k''\rangle_\pm$$

introduce P_{ij}, exchange particle i and particle j.

Show $P_{ij}^2 = 1$ and $[P_{ij}, P_{kl}] = 0$ if $(i,j) \cap (k,l) = \emptyset$

and $$P_{12} P_{23} P_{12} = P_{23} P_{12} P_{23}$$

P_{ij} : $\sigma_{ij} = \pm 1$

$$\sigma_{23} = \sigma_{12}$$

Symmetry Postulate:

There are two kinds:

1) $P_{ij} | N \text{ identical bosons} \rangle = + | N \rangle$

and $S =$ integer then its boson.

2) $P_{ij} | N \text{ identical Fermion} \rangle = - | N \rangle$

$S =$ half-integer then its fermion

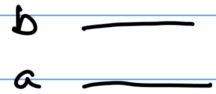
Now what about composite system:

boson + boson = boson

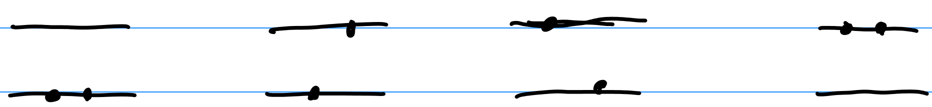
fermion + boson = fermion

fermion + fermion = boson

Suppose we have one-particle spectrum:

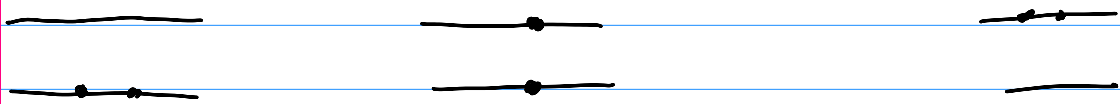


Now suppose two particle, that are close but distinguishable.



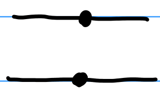
$|a\rangle|a\rangle$ $\quad$ $|a\rangle|b\rangle$ $\quad$ $|b\rangle|a\rangle$ $\quad$ $|b\rangle|b\rangle$ $\Big\}$ Distinguishable

Now indistinguishable: bosons



$|a\rangle|a\rangle$ $\quad$ $\frac{1}{\sqrt{2}}\left(|a\rangle|b\rangle + |b\rangle|a\rangle\right)$ $\quad$ $|b\rangle|b\rangle$

indistinguishable : fermion



$$\frac{1}{\sqrt{2}}\left(|a\rangle|b\rangle - |a\rangle|b\rangle\right)$$

Two electron system with spin:

$\psi(x_1, \sigma_1 ; x_2, \sigma_2)$ $\qquad$ $\sigma_1 = \pm 1$ spin $\uparrow$ or $\downarrow$

For 1 electron.

$$\psi(x, \sigma_1) = \begin{pmatrix} \psi(x, +1) \\ \psi(x, -1) \end{pmatrix}$$

$$= \underbrace{\psi_\uparrow(x)}_{\text{orbital wave-func}} \underset{\substack{\begin{pmatrix}1\\0\end{pmatrix} \\ \text{spin-wavefunc.}}}{|\uparrow\rangle} + \psi_\downarrow(x) \underset{\begin{pmatrix}0\\1\end{pmatrix}}{|\downarrow\rangle}$$

With 2 electrons:

$$\psi(x_1, \sigma_1 ; x_2, \sigma_2) = \psi_{\uparrow\uparrow}(x_1, x_2)|\uparrow\uparrow\rangle + \psi_{\uparrow\downarrow}(x_1, x_2)|\uparrow\downarrow\rangle$$
$$+ \psi_{\downarrow\uparrow}(x_1, x_2)|\downarrow\uparrow\rangle + \psi_{\downarrow\downarrow}(x_1, x_2)|\downarrow\downarrow\rangle$$

$$S_{1+2} = \vec{S}_1 + \vec{S}_2$$
$$= S_1 \otimes 1 + 1 \otimes S$$

$S^2 =$ $s = 0 \rightarrow 0$ $\qquad$ singlet — $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$

$\quad s = 1 \rightarrow 2\hbar^2$ $\qquad$ triplet. — $|\uparrow\uparrow\rangle$, $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$, $|\downarrow\downarrow\rangle$

$$P_{12}\, \psi_{orb}(x_1, x_2)\, \chi(s_1, s_2) = \psi_{orb}(x_2, x_1)\, \chi(s_2, s_1)$$

$$P_{12} = P_{12}^{orb} P_{12}^{spin} = -1$$

$$\begin{cases} P_{12}^{spin} |\text{triplet}\rangle = +1\, |\text{triplet}\rangle \\ P_{12}^{orb} = -1 \end{cases}$$

or $\psi^{orb}(x_1, x_2) = -\psi_{orb}(x_2, x_1)$

$$\begin{cases} P_{12}^{spin} |\text{singlet}\rangle = -\, |\text{singlet}\rangle \\ P_{12}^{orb} = +1 \end{cases}$$

or $\psi^{orb}(x_1, x_2) = \psi^{orb}(x_1; x_2)$

Consider $P_{12}^{spin} = \dfrac{1 + \sigma_1 \cdot \sigma_2}{2}$

$$\vec{S}_1 \cdot \vec{S}_2 = \begin{cases} \hbar^2/4 & \text{triplet} \quad \sigma_1 \cdot \sigma_2 = 1 \quad P_{12}^{spin} = +1 \\ -\frac{3}{4}\hbar^2 & \text{singlet} \quad \sigma_1 \cdot \sigma_2 = -3 \quad P_{12}^{spin} = -1 \end{cases}$$

Consider two orbital states A, B:

1 electron: $w_A(x)\left|\begin{matrix}\uparrow\\\downarrow\end{matrix}\right\rangle$ or $w_B(x)\left|\begin{matrix}\uparrow\\\downarrow\end{matrix}\right\rangle$

2 electrons: $w_A(x_1)\,w_B(x_2)\;\chi(\sigma_1,\sigma_2)$

$$\phi^{orb}(x_1,x_2)=\frac{1}{\sqrt{2}}\left(w_A(x_1)\,w_B(x_2)\pm w_A(x_2)\,w_B(x_1)\right)$$

$$|\phi(x_1,x_2)|^2 d^3x_1 d^3x_2 = d^3x_1 d^3x_2\,\frac{1}{2}\Big\{|w_A(x_1)|^2|w_B(x_2)|^2+|w_B(x_1)|^2|w_A(x_2)|^2$$

$$\underbrace{\pm 2\left[w_A^*(x_1)\,w_B^*(x_2)\,w_A(x_2)\,w_B(x_1)\right]}_{\text{exchange density.}}\Big\}$$

if $x_1=x_2=x$

$\rightarrow$

$$|\phi(x,x)|^2=|w_A(x)|^2|w_B(x)|^2\pm|w_A(x)|^2|w_B(x)|^2$$

$$=\begin{cases}0 & \text{if triplet}\\ \text{double} & \text{if singlet.}\end{cases}$$

→ Born approximation. (scattering theory)

→ Time-dependent

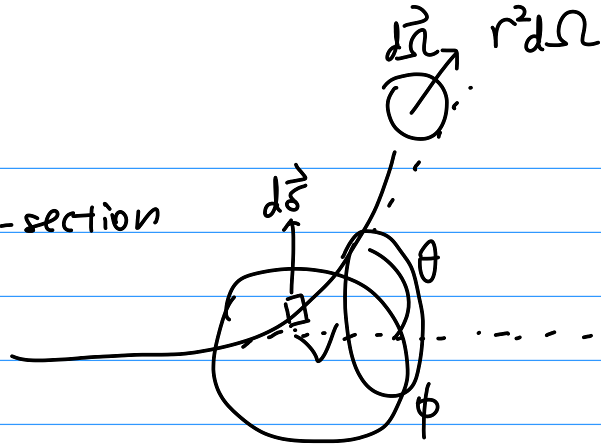
→ WKB.

Scattering theory :

cross-section

$\vec{J}_{incident} \cdot d\vec{\sigma}$

incident flux



$$dN = r^2 \vec{J}_{scatter}\, d\vec{\Omega}$$

$$\hookrightarrow \vec{J}_{incident}\, d\vec{\sigma} = r^2 \vec{J}_{scattered}\, d\vec{\Omega}$$

$$d\vec{\sigma} = \frac{J_{scatter}}{J_{incident}} r^2 d\vec{\Omega}$$

$$\boxed{\frac{d\vec{\sigma}}{d\vec{\Omega}} = \frac{J_{scatter}}{J_{incident}} r^2 \qquad (\theta, \cancel{\phi})}$$

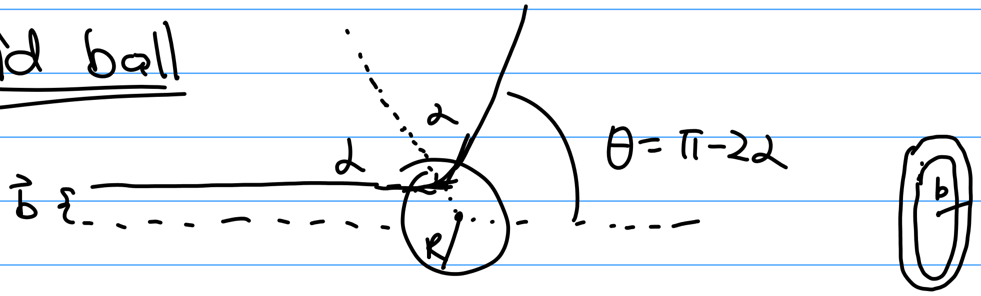
↳ assume azimuthal symmetry.

then

$$\sigma = \int \frac{d\sigma}{d\Omega} \underbrace{d\Omega}_{\sin\theta d\theta d\phi}$$

total cross-section.

ex: <u>solid ball</u>



$$b = R\sin\alpha = R\sin\left(\frac{\pi-\theta}{2}\right) = R\cos\frac{\theta}{2}$$

$$d\sigma = 2\pi b\, db = \frac{d\sigma}{d\Omega}\, 2\pi \underbrace{\sin\theta\, d\theta}_{d\phi}$$

$$= 2\pi R\cos\frac{\theta}{2}\, dR\, \cos\frac{\theta}{2}$$

$$= 2\pi R^2 \underbrace{\cos\frac{\theta}{2}\sin\frac{\theta}{2}\frac{1}{2}}_{\frac{1}{4}\sin\theta} d\theta$$

compare with

$$\frac{d\sigma}{d\Omega}\, 2\pi\sin\theta\, d\theta$$

then find $\boxed{\frac{d\sigma}{d\Omega} = \frac{R^2}{4}}$ using classical mechanics. using solid ball

ex 2:

For $V = \frac{Ze^2}{r}$, we find

$$\frac{d\sigma}{d\Omega} = \frac{Ze^2}{E}\,\frac{1}{16\sin^4\frac{\theta}{2}}$$

In quantum mechanics:

e^{ikx} with $E = \frac{\hbar^2 k^2}{2m}$

$$\frac{e^{i\vec{k}\cdot\vec{r}}}{r} f(\theta, \phi)$$

$\phi_{incident} \sim e^{ikx}$ ← cartesian

$\phi_{scatter} \sim \frac{e^{ikr}}{r} f(\theta, \phi)$ → spherical cordinate

so $|\phi_{scatter}|^2 \sim J_{scattered}$

so $d\sigma = |f(\theta, \phi)|^2 \, d\Omega$

↑ determine this for scattering wave func
solve perturbatively using Bohr-Approximation