Non degenerate Rayleigh-Schroedinger pert. theory.

$\hat{H}|n\rangle = E_n|n\rangle$ exact Schroedinger eq'n

suppose $\hat{H} = \hat{H}_0 + \hat{V}$ where $\hat{H}_0$ can be solved exactly but $\hat{H}$ cannot and $\hat{V}$ is "small"

$\hat{H}_0|n\rangle_0 = E_n^0|n\rangle_0$ unperturbed Schroedinger equation (exact solution known)

assume $E_n^0 \neq E_m^0$ unless $m=n$ (non degenerate case)

Want to find E_n and $|n\rangle$ as a power series in $\hat{V}$.

$(\hat{H}_0+\hat{V})|n\rangle = (E_n^0+\Delta E_n)|n\rangle$ $\qquad E_n = E_n^0 + \Delta E_n$

$(E_n^0 - \hat{H}_0)|n\rangle = (\hat{V}-\Delta E_n)|n\rangle$

want to somehow "invert" this.

Aside: examine $\frac{1}{E_n^0-\hat{H}_0}$ which is an operator, which can be best expressed in terms of the eigenbasis of $\hat{H}_0$ as

$$\frac{1}{E_n^0-\hat{H}_0}\sum_m |m\rangle_0\,{}_0\langle m|$$

complete set of states $= \mathbb{1}$

but $\hat{H}_0|m\rangle_0 = E_m^0|m\rangle_0$

$$\frac{1}{E_n^0-\hat{H}_0}\sum_m |m\rangle_0\,{}_0\langle m| = \sum_m \frac{1}{E_n^0-E_m^0}|m\rangle_0\,{}_0\langle m|$$

becomes singular when $m=n$

We deal with this by introducing projection operators

Define $\hat{P}_n = |n\rangle_0 \, {}_0\langle n|$ $\quad \hat{Q}_n = \mathbb{1} - \hat{P}_n = \sum_{m \neq n} |m\rangle_0 \, {}_0\langle m|$

properties of projection operators:

$$\hat{P}_n + \hat{Q}_n = \mathbb{1}$$

$\hat{P}_n^2 = \hat{P}_n$ $\quad$ check $\quad \hat{P}_n^2 = |n\rangle_0 \, \underbrace{{}_0\langle n|n\rangle_0}_{1} \, {}_0\langle n| = |n\rangle_0 \, {}_0\langle n| = \hat{P}_n$

so $\hat{P}_n^2 = \hat{P}_n$

also $\hat{Q}_n^2 = (1 - \hat{P}_n)^2 = 1 - \hat{P}_n - \hat{P}_n + \hat{P}_n^2 = 1 - \hat{P}_n - \hat{P}_n + \hat{P}_n = 1 - \hat{P}_n = \hat{Q}_n$

so $\hat{Q}_n^2 = \hat{Q}_n$

$\hat{P}_n \hat{Q}_n = |n\rangle_0 \, {}_0\langle n| \sum_{m \neq n} |m\rangle_0 \, {}_0\langle m|$ $\quad$ but ${}_0\langle n|m\rangle_0 = 0$ if $m \neq n$

$= 0 = \hat{Q}_n \hat{P}_n$

so $[\hat{P}_n, \hat{Q}_n]_- = 0$

How do projection operators act on an arbitrary operator?

$$\hat{O} = \sum_{mm'} O_{mm'} |m\rangle_0 \, {}_0\langle m'|$$

$\hat{P}_n \hat{O} = \sum_{m'} O_{nm'} |n\rangle_0 \, {}_0\langle m'|$ $\quad \hat{P}_n \hat{O} \hat{P}_n = O_{nn} |n\rangle_0 \, {}_0\langle n|$

$\hat{Q}_n \hat{O} = \sum_{m \neq n} \sum_{m'} O_{mm'} |m\rangle_0 \, {}_0\langle m'|$

$\hat{Q}_n \hat{O} \hat{Q}_n = \sum_{m \neq n} \sum_{m' \neq n} O_{mm'} |m\rangle_0 \, {}_0\langle m'|$ $\quad$ and so on

$\hat{Q}_n \hat{O} \hat{P}_n = \sum_{m \neq n} O_{mn} |m\rangle_0 \, {}_0\langle n|$ $\quad$ etc.

we say $\hat{P}_n$ projects parallel to $|n\rangle_0$

$\hat{Q}_n$ projects perpendicular to $|n\rangle_0$

claim: $(\hat{P}_n, \hat{H}_0)_- = 0$

check: $\hat{P}_n \hat{H}_0 = |n\rangle_0 \, {}_0\langle n| \hat{H}_0 = E_n^0 |n\rangle_0 \, {}_0\langle n|$

$\hat{H}_0 \hat{P}_n = \hat{H}_0 |n\rangle_0 \, {}_0\langle n| = E_n^0 |n\rangle_0 \, {}_0\langle n|$

so $\hat{P}_n \hat{H}_0 - \hat{H}_0 \hat{P}_n = 0$

since $\hat{Q}_n = 1 - \hat{P}_n$ we have $[\hat{Q}_n, \hat{H}_0]_- = [1 - \hat{P}_n, \hat{H}_0]_- = 0$ as well.

Now examine original equation

$$(E_n^0 - \hat{H}_0)|n\rangle = (\hat{V} - \Delta E_n)|n\rangle$$

Then $\hat{Q}_n |n\rangle = \dfrac{\hat{Q}_n}{E_n^0 - \hat{H}_0} (\hat{V} - \Delta E_n)|n\rangle$

check: $\hat{Q}_n |n\rangle = \sum_{m \neq n} |m\rangle_0 \, {}_0\langle m|n\rangle$

$$\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} (\hat{V} - \Delta E_n)|n\rangle = \sum_{m \neq n} |m\rangle_0 \, {}_0\langle m| \frac{\hat{V} - \Delta E_n |n\rangle}{E_n^0 - E_m^0}$$

but $\sum_{m \neq n} |m\rangle_0 \, {}_0\langle m| E_n^0 - \hat{H}_0 |n\rangle = \sum_{m \neq n} |m\rangle_0 \, {}_0\langle m| \hat{V} - \Delta E_n |n\rangle$

but LHS $= \sum_{m \neq n} (E_n^0 - E_m^0) |m\rangle_0 \, {}_0\langle m|n\rangle = \sum_{m \neq n} |m\rangle_0 \, {}_0\langle m| \hat{V} - \Delta E_n |n\rangle$

since each coefficient of $|m\rangle_0$ must be equal and $E_n^0 - E_m^0 \neq 0$ we have

$$\sum_{m \neq n} |m\rangle_0 \, {}_0\langle m|n\rangle = \sum_{m \neq n} |m\rangle_0 \, {}_0\langle m| \frac{\hat{V} - \Delta E_n |n\rangle}{E_n^0 - E_m^0}$$

as claimed.

But $|n\rangle = (\hat{P}_n + \hat{Q}_n)|n\rangle$ $\quad \hat{P}_n |n\rangle = |n\rangle_0 \, {}_0\langle n|n\rangle$

so $|n\rangle = |n\rangle_0 \, {}_0\langle n|n\rangle + \dfrac{\hat{Q}_n}{E_n^0 - \hat{H}_0} (\hat{V} - \Delta E_n)|n\rangle$

$$\left[\mathbb{1} - \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} (\hat{V} - \Delta E_n) \right] |n\rangle = |n\rangle_0 \, {}_0\langle n|n\rangle$$

or we get

$$|n\rangle = {}_0\langle n|n\rangle \left[\mathbb{1} - \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \Delta E_n)\right]^{-1} |n\rangle_0$$

as a convention we choose ${}_0\langle n|n\rangle = 1$ and normalize the true wavefunction $|n\rangle$ only at the end. This simplifies many places in the calculation, but one needs to remember that $\langle n|n\rangle \neq 1$ now.

so
$$\boxed{|n\rangle = \left[\mathbb{1} - \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \Delta E_n)\right]^{-1} |n\rangle_0}$$

by expanding the inverse as a geometric series, we will generate the perturbation theory expansion.

$$|n\rangle = |n\rangle_0 + \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \cancel{\Delta E_n})|n\rangle_0 + \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \Delta E_n)\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \cancel{\Delta E_n})|n\rangle_0$$

$$+ \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \Delta E_n)\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \Delta E_n)\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}(\hat{V} - \cancel{\Delta E_n})|n\rangle_0 + \cdots$$

can always drop the last ΔE_n term since

ΔE_n = number and $\hat{Q}_n \Delta E_n |n\rangle_0 = 0$ always.

write

$$|n\rangle = \sum_{m=0}^{\infty} |n\rangle^{(m)} \qquad |n\rangle^{(0)} = |n\rangle_0$$ Index denotes powers of $\hat{V}$

$$E_n = \sum_{m=0}^{\infty} E_n^{(m)} \qquad E_n^{(0)} = E_n^0$$

$$\Delta E_n = \sum_{m=1}^{\infty} E_n^{(m)}$$

need to know up to $E_n^{(m)}$ to find $|n\rangle^{(m+1)}$

$$|n\rangle^{(0)} = |n\rangle_0$$

$$|n\rangle^{(1)} = \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} \hat{V} |n\rangle_0 \qquad |n\rangle^{(2)} = \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} (\hat{V} - E_n^{(1)}) \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} \hat{V} |n\rangle_0$$

$$|n\rangle^{(3)} = \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} (-E_n^{(2)}) \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} \hat{V} |n\rangle_0 + \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} (\hat{V} - E_n^{(1)}) \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} (\hat{V} - E_n^{(1)})$$

$$* \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0} \hat{V} |n\rangle_0$$

and so on

How do we find $E_n^{(m)}$?

$$(E_n^0 - \hat{H}_0) |n\rangle = (\hat{V} - \Delta E_n) |n\rangle$$ multiply by ${}_0\langle n|$

$${}_0\langle n| E_n^0 - \hat{H}_0 |n\rangle = {}_0\langle n| \hat{V} - \Delta E_n |n\rangle$$

$$\overset{\shortparallel}{0}$$

$$\Delta E_n = \frac{{}_0\langle n| \hat{V} |n\rangle}{{}_0\langle n|n\rangle} = {}_0\langle n| \hat{V} |n\rangle$$ since ${}_0\langle n|n\rangle = 1$

so $$\sum_{m=1}^{\infty} E_n^{(m)} = \sum_{m=0}^{\infty} {}_0\langle n|\hat{V}|n\rangle^{(m)}$$ by matching powers of $\hat{V}$ we get

$$\boxed{E_n^{(m)} = {}_0\langle n|\hat{V}|n\rangle^{(m-1)}}$$

so

$$E_n^{(1)} = {}_0\langle n|\hat{V}|n\rangle_0 = \boxed{V_{nn}}$$

$$|n\rangle^{(1)} = \frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\hat{V}|n\rangle_0 = \sum_{m\neq n}\frac{V_{mn}}{E_n^0 - E_m^0}|m\rangle_0$$

so $$E_n^{(2)} = \sum_{m\neq n}\frac{V_{nm}V_{mn}}{E_n^0 - E_m^0} = \sum_{m\neq n}\frac{|V_{nm}|^2}{E_n^0 - E_m^0} = \boxed{\sum_m{}'\frac{|V_{nm}|^2}{E_n^0 - E_m^0}}$$

prime $\Rightarrow$ $m\neq n$

$$|n\rangle^{(2)} = \frac{\hat{Q}_n(\hat{V} - E_n^{(1)})}{E_n^0 - \hat{H}_0}\frac{\hat{Q}_n}{E_n^0 - \hat{H}_0}\hat{V}|n\rangle_0$$

$$= \sum_{m\neq n}\sum_{m'\neq n}|m'\rangle_0\frac{(V_{m'm} - E_n^{(1)}\delta_{mm'})}{E_n^0 - E_{m'}^0}\frac{V_{mn}}{E_n^0 - E_m^0}$$ $E_n^{(1)} = V_{nn}$

an $$E_n^{(3)} = \sum_{m\neq n}\sum_{m'\neq n}\frac{V_{nm'}V_{m'm}V_{mn}}{(E_n^0 - E_{m'}^0)(E_n^0 - E_m^0)} - V_{nn}\sum_{m\neq n}\frac{|V_{nm}|^2}{(E_n^0 - E_m^0)^2}$$

$$= \boxed{\sum_m{}'\sum_{m'}{}''\frac{V_{nm'}V_{m'm}V_{mn}}{(E_n^0 - E_{m'}^0)(E_n^0 - E_m^0)} - V_{nn}\sum_m{}'\frac{|V_{nm}|^2}{(E_n^0 - E_m^0)^2}}$$

this process can be continued to arbitrary order

(on the HW you will examine through 4th order.)