Chapter 5 Approximation Methods

5.1 Time-independent Perturbation theory
Nondegenerate case.

$$H = H_0 + \lambda V$$

assume that
$$H_0 | n^{(0)} \rangle = E_n^{(0)} | n^{(0)} \rangle$$
is solved exactly.

λV : perturbation
$$H | n \rangle = E_n | n \rangle$$
find $| n \rangle$ and E_n such that

$$| n \rangle = | n^{(0)} \rangle + \lambda \square + \cdots$$
$$E_n = E_n^{(0)} + \lambda \square + \cdots$$

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

$$= E_1^{(0)}|1^{(0)}\rangle\langle 1^{(0)}| + E_2^{(0)}|2^{(0)}\rangle\langle 2^{(0)}|$$

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

(λ is real)

$(\lambda V)^\dagger = \lambda V$ Hermiticity. $\Rightarrow V_{12} = V_{21}^*$

$$H_0 = a_0 \mathbb{1} + \vec{\sigma} \cdot \vec{a} = \begin{pmatrix} a_0 + a_3 & a_1 - i a_2 \\ a_1 + i a_2 & a_0 - a_3 \end{pmatrix}$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & \\ & -1 \end{pmatrix}$$

$$\begin{vmatrix} (a_0 + a_3) - E & a_1 - i a_2 \\ a_1 + i a_2 & (a_0 - a_3) - E \end{vmatrix} = 0$$

$$(a_0 - E)^2 - a_3^2 - (a_1^2 + a_2^2) = 0$$

$$E = a_0 \pm \sqrt{a_1^2 + a_2^2 + a_3^2} = a_0 \pm |\vec{a}|$$

H $a_2 = 0$ (real)

$$E = a_0 \pm \sqrt{a_1^2 + a_2^2 + a_3^2}$$

$$\left.\begin{aligned} a_0 + a_3 &= E_1^{(0)} \\ a_0 - a_3 &= E_2^{(0)} \end{aligned}\right\} \quad \begin{aligned} a_0 &= \tfrac{1}{2}(E_1^{(0)} + E_2^{(0)}) \\ a_3 &= \tfrac{1}{2}(E_1^{(0)} - E_2^{(0)}) \end{aligned}$$

$$a_1^2 + a_2^2 = \lambda^2 |V_{12}|^2$$

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

$\Rightarrow$ exactly solved.

We assume $E_1^{(0)} > E_2^{(0)}$

Then

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

Expanding $\sqrt{1+\alpha}$ in powers of $\alpha = \left(\frac{2\lambda |V_{12}|}{E_1^{(0)} - E_2^{(0)}}\right)^2$.

$$\sqrt{1+\alpha} = 1 + \frac{1}{2}\alpha + \frac{1}{2}\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)\alpha^2 + O(\alpha^3)$$

$$= 1 + \frac{\alpha}{2} - \frac{1}{2}\left(\frac{\alpha}{2}\right)^2 + O(\alpha^3)$$

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

$$= \begin{pmatrix} E_1^{(0)} \\ E_2^{(0)} \end{pmatrix} \begin{matrix} + \dfrac{\lambda^2 |V_{12}|^2}{(E_1^{(0)} - E_2^{(0)})^2} \\ - \quad '' \end{matrix}$$

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

$$E_2 = E_2^{(0)} - \frac{\lambda^2 |V_{12}|^2}{(E_1^{(0)} - E_2^{(0)})} > 0 = E_2^{(0)} + \frac{\lambda^2 |V_{12}|^2}{E_2^{(0)} - E_1^{(0)}}.$$

Formal Development of Perturbation Expansion

$$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$$
$$H_0 \to H(\lambda) = H_0 + \lambda V$$
$$|n^{(0)}\rangle \to |n(\lambda)\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots$$
$$E_n^{(0)} \to E_n(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

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

$$\Rightarrow (E_n^{(0)} - H_0)|n(\lambda)\rangle = (\lambda V - \Delta_n)|n(\lambda)\rangle$$

We may try to find

$$(E_n^{(0)} - H_0)^{-1}$$

However, if the operator is applied to $|n^{(0)}\rangle$, $\dfrac{1}{E_n^{(0)} - E_n^{(0)}} = \dfrac{1}{0}$: ill defined!

$$\cancel{(E_n^{(0)} - H_0)|n^{(0)}\rangle \equiv 0 = 1}$$

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

$\Rightarrow (\lambda V - \Delta_n)|n(\lambda)\rangle$ is independent of $|n^{(0)}\rangle$.

We define the projection operator

$$\phi_n \equiv 1 - |n^{(0)}\rangle\langle n^{(0)}| = \sum_{k \neq n} |k^{(0)}\rangle\langle k^{(0)}|.$$

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

$= \sum_{k\neq n} \frac{1}{E_n^{(0)}-E_k^{(0)}}$ is well defined.

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

$$(\lambda V-\Delta_n)|n^{(\lambda)}\rangle = \sum_{k\neq n}|k^{(0)}\rangle\langle k^{(0)}|(\lambda V-\Delta_n)|n^{(\lambda)}\rangle$$

$$= \phi_n(\lambda V-\Delta_n)|n(\lambda)\rangle$$

Therefore $(E_n^{(0)}-H_0)|n(\lambda)\rangle = (\lambda V-\Delta_n)|n(\lambda)\rangle$

$$\downarrow$$

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

$$\downarrow$$

We may try $|n(\lambda)\rangle = \frac{1}{E_n^{(0)}-H_0}\phi_n(\lambda V-\Delta_n)|n(\lambda)\rangle$

However, $\lim_{\lambda\to 0}|n(\lambda)\rangle = |n^{(0)}\rangle$ cannot be reproduced.

Therefore, $|n(\lambda)\rangle = c(\lambda)|n^{(0)}\rangle + \frac{1}{E_n^{(0)}-H_0}\phi_n(\lambda V-\Delta_n)|n(\lambda)\rangle$,

where $c(\lambda) = \langle n^{(0)}|n(\lambda)\rangle$.

At the end of the day, we need to renormalize the state because

$\langle n(\lambda)|n(\lambda)\rangle \neq 1$ in general

after perturbation. We ~~use~~ employ the convention that $c(\lambda)=1$

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

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

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

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

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

Therefore, we can define ~~introduce~~ the expression

$$\frac{\phi_n}{E_n^{(0)}-H_0}$$ that is identical to

$$\frac{1}{E_n^{(0)}-H_0}\phi_n = \phi_n\frac{1}{E_n^{(0)}-H_0} = \phi_n\frac{1}{E_n^{(0)}-H_0}\phi_n .$$

In summary,

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

Note that we have chosen the normalization $\langle n^{(0)}|n(\lambda)\rangle = 1$ for convenience.

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

Because $\langle n^{(0)}|n(\lambda)\rangle = 1$,

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

$$1 = 1 + 0.$$

We recall that

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

Because $\langle n^{(0)}|(E_n^{(0)} - H)|n(\lambda)\rangle = 0$.

$$\langle n^{(0)}|\lambda V|n(\lambda)\rangle = \underbrace{\langle n^{(0)}|n(\lambda)\rangle}_{=1} \Delta_n \quad \text{real number}$$

$\therefore$ ~~The first order energy~~

Therefore, the energy shift Δ_n is

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

$$(\quad E_n = E_n^{(0)} + \Delta_n \quad)$$

$$\begin{cases} |n(\lambda)\rangle = |n^{(0)}\rangle + \dfrac{\phi_n}{E_n^{(0)} - H_0}(\lambda V - \Delta_n)|n(\lambda)\rangle \\ \Delta_n = \lambda \langle n^{(0)}|V|n(\lambda)\rangle \end{cases}$$

Now let us substitute

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

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

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

$$\begin{aligned} \Delta_n &= \langle n^{(0)}|\lambda V|n(\lambda)\rangle \\ \therefore \quad &= \langle n^{(0)}|\lambda V\left(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots\right) \\ &= \lambda\langle n^{(0)}|V|n^{(0)}\rangle + \lambda^2\langle n^{(0)}|V|n^{(1)}\rangle \\ &\quad + \lambda^3\langle n^{(0)}|V|n^{(2)}\rangle \\ &\quad + \cdots + \lambda^N\langle n^{(0)}|V|n^{(N-1)}\rangle + \cdots \end{aligned}$$

Therefore, N-th-order energy shift i

$$\lambda^N\langle n^{(0)}|V|n^{(N-1)}\rangle$$

can be computed if we know $|n^{(N-1)}\rangle$.

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

$$\downarrow$$

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

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

~~At order~~ λ

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

at order λ,
$$|n^{(1)}\rangle = \frac{\phi_n}{E_n^{(0)}-H_0}(V - \Delta_n^{(1)})|n^{(0)}\rangle.$$

We recall that $\Delta_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle$

However, $\phi_n \Delta_n^{(1)}|n^{(0)}\rangle = \underbrace{\Delta_n^{(1)}}_{\text{number}}\phi_n|n^{(0)}\rangle = 0$

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

At the second order

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

We know that

$$\begin{cases} \phi_n\Delta_n^{(2)}|n^{(0)}\rangle = \Delta_n^{(2)}\underbrace{\phi_n|n^{(0)}\rangle} = 0. \\ |n^{(1)}\rangle = \dfrac{\phi_n}{E_n^{(0)}-H_0}V|n^{(0)}\rangle. \end{cases}$$

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

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

$$= \frac{\phi_n}{E_n^{(0)}-H_0}\left[V - \langle n^{(0)}|V|n^{(0)}\rangle\right]\frac{\phi_n}{E_n^{(0)}-H_0}V|n^{(0)}\rangle$$

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

The second-order energy shift is

$$\Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle = \langle n^{(0)}|V\frac{\phi_n}{E_n^{(0)}-H_0}V|n^{(0)}\rangle$$

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

$$= \sum_{k\neq n}\frac{|\langle n^{(0)}|V|k^{(0)}\rangle|^2}{E_n^{(0)}-E_k^{(0)}}$$

Combining the results,

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

$$= \lambda \underbrace{\langle n^{(0)}|V|n^{(0)}\rangle}_{V_{nn}} + \lambda^2 \sum_{k\neq n} \frac{|\langle n^{(0)}|V|k^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}} + O(\lambda^3)$$

$$V_{nk} V_{nk}^{*} = |V_{nk}|^2$$

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

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

$$+ \left(\frac{\phi_n}{E_n^{(0)} - H_0} V\right)^2 |n^{(0)}\rangle - \frac{\phi_n}{E_n^{(0)} - H_0} \langle n^{(0)}|V|n^{(0)}\rangle \frac{\phi_n}{E_n^{(0)} - H_0} V|n^{(0)}\rangle.$$