# Perturbation theory

Rayleigh-Schrödinger perturbⁿ

- A systematic procedure for obtaining approximate solutions to the perturbed problem, by building on the exact solutions to the unperturbed case.

$$H = \underbrace{H^{(0)}}_{\text{unperturbed Hamiltonian}} + \underbrace{H'}_{\text{perturb}^{n}}$$

Exact energy eigenstates $|n^{(0)}\rangle$ & " " eigenvalues $E_n^{(0)}$ are known.

Aim: To find the approximate e.kets and e.values for the full Hamiltonian

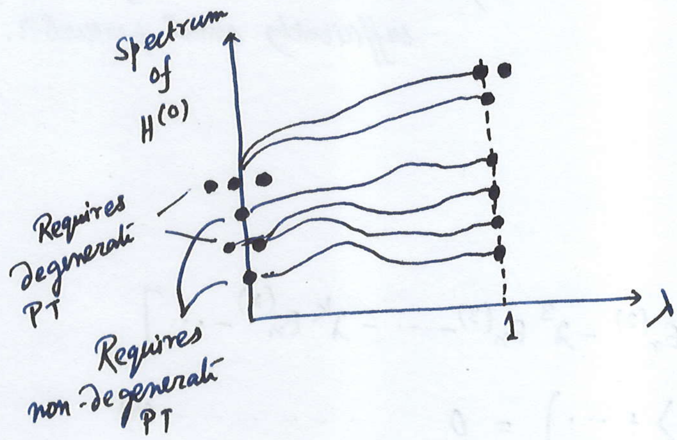
$$\left(H^{(0)} + H'\right)|n\rangle = E_n|n\rangle$$

Introduce a continuous real parameter $\lambda \in [0,1]$

$$\left(H^{(0)} + \lambda H'\right)|n\rangle = E_n|n\rangle \longrightarrow$$

$\lambda = 0 \Rightarrow$ unperturbed $H$ w/ everything known

$\lambda \to 1 \Rightarrow$ perturbed $H$.




$\Rightarrow$ Perturbation in general lifts the degeneracy

Two possibilities $\rightarrow$ (i) non-degenerate PT
(ii) degenerate PT.

## (i) Non-degenerate PT

Unperturbed Hamiltonian $H^{(0)}$ w/ e.states $|n^{(0)}\rangle$

$\langle n^{(0)}|m^{(0)}\rangle = \delta_{nm}$ (orthonormality for Hermitian Hamiltonian)

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

$E_0^{(0)} \leq E_1^{(0)} \leq E_2^{(0)} \leq \dots$ (equality $\Rightarrow$ some states may be degenerate)

If for a fixed $n$, say $|n^{(0)}\rangle$ is a non-degenerate state then

$$\dots \leq E_{n-1}^{(0)} < E_n^{(0)} < E_{n+1}^{(0)} \leq \dots$$

As the perturbation is turned on $(\lambda \neq 0)$

$$\{|n^{(0)}\rangle\} \to \{|n\rangle_\lambda\}$$

$$H^{(0)} \longrightarrow H(\lambda) = H^{(0)} + \lambda H'$$

$$E_n^{(0)} \longrightarrow E_n(\lambda)$$

The governing eqn. $\to$ $H(\lambda)|n\rangle_\lambda = E_n(\lambda)|n\rangle_\lambda$ ---------- (i)

w/ $\left.\begin{aligned} |n\rangle_{\lambda=0} &= |n^{(0)}\rangle \\ E_n(\lambda=0) &= E_n^{(0)} \end{aligned}\right\}$ like initial condiⁿs

Assume the perturbⁿ expanⁿ for $|n\rangle_\lambda$ and $E_n(\lambda)$ as -

$\left.\begin{aligned} |n\rangle_\lambda &= |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots \\ E_n(\lambda) &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \end{aligned}\right\}$ $|n\rangle_\lambda$ may not be normalized but at least normalizable for sufficiently small perturbⁿ.

Now w/ these expanⁿ eqⁿ (i) $\Rightarrow$

$$\left(H^{(0)} + \lambda H' - E_n(\lambda)\right)|n\rangle_\lambda = 0$$

$$\Rightarrow \left[\left(H^{(0)} - E_n^{(0)}\right) - \lambda\left(E_n^{(1)} - H'\right) - \lambda^2 E_n^{(2)} - \lambda^3 E_n^{(3)} - \cdots - \lambda^k E_n^{(k)} - \cdots\right]$$
$$\times \left(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots\right) = 0 \quad \text{-------- (ii)}$$

Collecting co-effⁿ of each power of $\lambda$

$\lambda^0$ : $\left(H^{(0)} - E_n^{(0)}\right)|n^{(0)}\rangle = 0$

$\lambda$ : $\left(H^{(0)} - E_n^{(0)}\right)|n^{(1)}\rangle = \left(E_n^{(1)} - H'\right)|n^{(0)}\rangle$

$\lambda^2$ : $\left(H^{(0)} - E_n^{(0)}\right)|n^{(2)}\rangle = \left(E_n^{(1)} - H'\right)|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle$

$\vdots$

$\lambda^k$ : $\left(H^{(0)} - E_n^{(0)}\right)|n^{(k)}\rangle = \left(E_n^{(1)} - H'\right)|n^{(k-1)}\rangle + E_n^{(2)}|n^{(k-2)}\rangle + \cdots + E_n^{(k)}|n^{(0)}\rangle$

Now w/o loss of generality we can assume that all $|n^{(k)}\rangle$ w/ $k \geq 1$ contain no vector along $|n^{(0)}\rangle$, i.e., $\{|n^{(k)}\rangle\}$ are all orthogonal to $|n^{(0)}\rangle$

$$\langle n^{(0)} | n^{(i)} \rangle = 0 \qquad i \neq 0$$

Consider the general $\mathcal{O}(\lambda^k)$ eqn.

$$\left(H^{(0)} - E_n^{(0)}\right)|n^{(k)}\rangle = \left(E_n^{(1)} - H'\right)|n^{(k-1)}\rangle + E_n^{(2)}|n^{(k-2)}\rangle + \cdots + E_n^{(k)}|n^{(0)}\rangle$$

$$\Rightarrow \langle n^{(0)}|\left(H^{(0)} - E_n^{(0)}\right|n^{(k)}\rangle = \langle n^{(0)}|\left(E_n^{(1)} - H'\right)|n^{(k-1)}\rangle + \langle n^{(0)}|n^{(k-2)}\rangle E_n^{(2)} + \cdots + \langle n^{(0)}|n^{(0)}\rangle E_n^{(k)}$$

$$\Rightarrow \quad 0 = -\langle n^{(0)}|H'|n^{(k-1)}\rangle + E_n^{(k)}$$

$$\Rightarrow \quad E_n^{(k)} = \langle n^{(0)}|H'|n^{(k-1)}\rangle \qquad (k \geq 1)$$

Thus we obtained $E_n^{(1)}, E_n^{(2)}, E_n^{(3)}, \ldots$

To obtain the perturbed eigenstates —

take $\mathcal{O}(\lambda)$ eqn. and multiply by $\langle k^{(0)}|$ $\quad (k \neq n)$

$$\langle k^{(0)}|\left(H^{(0)} - E_n^{(0)}\right)|n^{(1)}\rangle = \langle k^{(0)}|(\underbrace{E_n^{(1)}}_{\Rightarrow 0 \; k \neq n} - H')|n^{(0)}\rangle$$

$$\Rightarrow \left(E_k^{(0)} - E_n^{(0)}\right)\langle k^{(0)}|n^{(1)}\rangle = -\langle k^{(0)}|H'|n^{(0)}\rangle \equiv -\delta H_{kn}$$

$$\Rightarrow \quad \langle k^{(0)}|n^{(1)}\rangle = -\frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}$$

→ the D.r. is safe as long as the ~~up~~ unperturbed spectrum is non-degenerate

$$|n^{(1)}\rangle = \sum_{\text{all } k} |k^{(0)}\rangle\langle k^{(0)}|n^{(1)}\rangle$$

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

$\because$ $k = n$ does not contribute due to orthogonality

$$= -\sum_{k \neq n} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}|k^{(0)}\rangle$$

Now that we have $|n^{(1)}\rangle$, consider $E_n^{(2)}$.

$$E_n^{(2)} = \langle n^{(0)} | H' | n^{(1)} \rangle = -\sum_{k \neq n} \frac{\langle n^{(0)} | H' | k^{(0)} \rangle \, \delta H_{kn}}{E_k^{(0)} - E_n^{(0)}}$$

$$= -\sum_{k \neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}}$$

$(\delta H_{kn})^* = (\langle k^{(0)} | H' | n^{(0)} \rangle)^*$
$= \langle n^{(0)} | H' | k^{(0)} \rangle$
due to hermiticity of $H'$

To summarize,

$$|n\rangle_\lambda = |n^{(0)}\rangle - \lambda \sum_{k \neq n} \frac{\delta H_{kn}}{E_k^{(0)} - E_n^{(0)}} |k^{(0)}\rangle + O(\lambda^2)$$

$$E_n(\lambda) = E_n^{(0)} + \lambda \, \delta H_{nn} - \lambda^2 \sum_{k \neq n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} + O(\lambda^3)$$

* The $O(\lambda)$ ground state energy overestimates the true ground state energy

$$E_0^{(0)} + \lambda E_0^{(1)} = \langle 0^{(0)} | H^{(0)} | 0^{(0)} \rangle + \lambda \langle 0^{(0)} | H' | 0^{(0)} \rangle$$

$$= \langle 0^{(0)} | (H^{(0)} + \lambda H') | 0^{(0)} \rangle$$

$$= \langle 0^{(0)} | H(\lambda) | 0^{(0)} \rangle \geq \underbrace{E_0(\lambda)}_{\text{true ground state energy}}$$

Given this overestimate at first order,
the second order is always -ve. $\rightarrow \underbrace{-\lambda^2 \sum_{k \neq 0} \frac{|\delta H_{k0}|^2}{E_k^{(0)} - E_0^{(0)}}}_{-ve}$

* 2nd order correction to the energy of the $|n^{(0)}\rangle$ e.state,
i.e. $E_n^{(2)}$ exhibits level repulsion

levels w/ $k > n$ push the state down
& " w/ $k < n$ " " " up

$$-\lambda^2 \sum_{k \neq 0} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} = -\lambda^2 \sum_{k > n} \frac{|\delta H_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} + \lambda^2 \sum_{k < n} \frac{|\delta H_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} \, ;$$

## Validity of perturbⁿ series

- Issues regarding convergence
  - smallness of $\lambda H'$

For illustration consider $H^{(0)} = \text{diag}\left(E_1^{(0)}, E_2^{(0)}\right)$ & $\lambda H' = \lambda \begin{pmatrix} 0 & V \\ V^* & 0 \end{pmatrix}$

$$\Rightarrow H(\lambda) = \begin{pmatrix} E_1^{(0)} & \lambda V \\ \lambda V^* & E_2^{(0)} \end{pmatrix}$$

Clearly, this is a simple example and exact e.vals. of $H(\lambda)$ can be calculated, no need for perturbation theory,

$$E_\pm(\lambda) = \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) + \frac{1}{2}\left(E_1^{(0)} - E_2^{(0)}\right) \underbrace{\left(1 + \frac{4\lambda^2 |V|^2}{\left(E_1^{(0)} - E_2^{(0)}\right)^2}\right)^{1/2}}_{\text{Taylor series expan}^n\text{ of } \lambda \text{ can be done}}$$

$E_\pm(\lambda)$ converges when $|\lambda V| < \frac{1}{2}\left(E_1^{(0)} - E_2^{(0)}\right)$ ⟵ Taylor series expanⁿ of $\lambda$ can be done

** For convergence the perturbation must be small compared to the energy difference in $H^{(0)}$. Only matrix elements of $\lambda H'$ is small compared to $H^{(0)}$ is not enough.

[ * Complex fⁿ. $f(z) = \sqrt{1+z^2} = 1 + z^2/2 - z^4/8 + z^6/16 - \cdots$

$f(z)$ has branch cuts at $z = \pm i$

The expansion of $f(z)$ around $z=0$ has radius of conv. equal to 1.

$\therefore$ The series converges for $|z| < 1$

& diverges for $|z| > 1$. ]

__Example__

A charged particle is performing a SH motion.

$$\therefore \quad H^{(0)} = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

It is subjected to a const. electric field $E$, such that

$$\lambda H' = qEx \qquad (\lambda \equiv qE)$$

Qm. What is the energy shift for the $n$-th level (to 1st and 2nd order in $qE$).

Recall

$$H^{(0)} = \left(a^\dagger a + \frac{1}{2}\right)\hbar\omega$$

$$\left.\begin{aligned} \text{w/} \quad a &= \sqrt{\frac{m\omega}{2\hbar}}\, x + i\frac{p}{\sqrt{2m\omega\hbar}} \\ a^\dagger &= (\ ) - i(\ ) \end{aligned}\right\} \quad x = \sqrt{\frac{\hbar}{2m\omega}}\,(a + a^\dagger)$$

$$|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle \qquad \begin{aligned} a|n\rangle &= \sqrt{n}\,|n-1\rangle \\ a^\dagger|n\rangle &= \sqrt{n+1}\,|n+1\rangle . \end{aligned}$$

$$\mathcal{O}(qE): \quad E_n^{(1)} = qE\langle n^{(0)}|x|n^{(0)}\rangle = qE\sqrt{\frac{\hbar}{2m\omega}}\underbrace{\langle n^{(0)}|(a+a^\dagger)|n^{(0)}\rangle}_{\Downarrow \atop 0} = 0$$

$$\begin{aligned} \mathcal{O}(q^2E^2): \quad E_n^{(2)} &= -q^2E^2\sum_{k\neq n}\frac{|\langle k^{(0)}|x|n^{(0)}\rangle|^2}{E_k^{(0)} - E_n^{(0)}} \\ &= -q^2E^2\left(\sum_{k\neq n}\frac{|\langle k^{(0)}|(a+a^\dagger)|n^{(0)}\rangle|^2}{\hbar\omega(k-n)}\right)\frac{\hbar}{2m\omega} \\ &= -\frac{q^2E^2}{2m\omega^2}\underbrace{\sum_{k\neq n}\frac{|\langle k^{(0)}|(a+a^\dagger)|n^{(0)}\rangle|^2}{k-n}}_{\downarrow} \end{aligned}$$

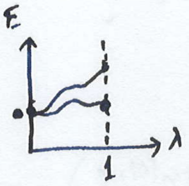
contrib$^{n}$ comes only when $k^{(0)} = n^{(0)} - 1$ & $k^{(0)} = n^{(0)} + 1$

$$= -\frac{q^2E^2}{2m\omega^2}$$

In a different way, the total potential $\frac{1}{2}m\omega^2x^2 + qEx = \frac{1}{2}m\omega^2\left(x + \frac{qE}{m\omega^2}\right)^2 - \frac{q^2E^2}{2m\omega^2}$

i.e. the perturb$^{n}$ shift the centre of the potential by $-\frac{qE}{m\omega^2}$ & lowers the energy by $\frac{q^2E^2}{2m\omega^2}$, agrees w/ the 2nd order result.

(ii) ~~Non~~ Degenerate PT



In case of degeneracy the expansion we did earlier breaks down as $\delta H_{kn}/(E_k^{(0)} - E_n^{(0)})$ may become singular if $\delta H_{kn} \neq 0$ & $E_k^{(0)} = E_n^{(0)}$.

$$H(\lambda) = \underbrace{H^{(0)}}_{} + \lambda H'$$

↳ contains a degenerate subspace of e. states of dim $N > 1$, i.e. a space w/ lin. indep. e. states of the same energy

In the basis where $H^{(0)}$ is diagonal –

$$H^{(0)} = \mathrm{diag}\Big(E_1^{(0)}, E_2^{(0)}, \dots, \underbrace{E_n^{(0)}, E_n^{(0)}, \dots, E_n^{(0)}}_{N}, \dots\Big)$$

In the degenerate subspace choose a collection of $N$ orthonormal eigenstates –

$$|n^{(0)};1\rangle, |n^{(0)};2\rangle, \dots, |n^{(0)};N\rangle$$

$$\langle n^{(0)};i|n^{(0)};j\rangle = \delta_{ij}$$

$$\& \quad H^{(0)}|n^{(0)};j\rangle = E_n^{(0)}|n^{(0)};j\rangle \quad \forall\ j = 1,2,\dots,N.$$

Define $\mathbb{V}_N = \mathrm{span}\{|n^{(0)};j\rangle, j = 1,2,\dots,N\}$

Total space $\mathcal{H} = \mathbb{V}_N \oplus \underbrace{\mathbb{V}}_{}$

↓ span of all other states $\{|p^{(0)}\rangle\}$ (this basis may include both degenerate and non-degenerate states)

$$\mathbb{V}_N \perp \mathbb{V}$$

Also $\langle p^{(0)}|q^{(0)}\rangle = \delta_{pq}$

$$\langle p^{(0)}|n^{(0)};j\rangle = 0$$

We now assume the $\lambda$-expan$^n$

$$k = 1,2,\dots,N \begin{cases} |n^{(0)};k\rangle \to |n;k\rangle_\lambda = |n^{(0)};k\rangle + \lambda|n^{(1)};k\rangle + \lambda^2|n^{(2)};k\rangle + \mathcal{O}(\lambda^3) \\ E_n^{(0)} \to E_{n,k}(\lambda) = E_n^{(0)} + \lambda \underbrace{E_{n,k}^{(1)}}_{} + \lambda^2 E_{n,k}^{(2)} + \mathcal{O}(\lambda^3) \end{cases}$$

↓ for each value of $k$, there might be different amount of correction, that is why two indices on $E$.

Aim: • find the correction in states $|n^{(p)};k\rangle$

" " " " " energy $E^{(p)}_{n,k}$ $\quad \forall\, p \geq 1$ & $\forall\, k$

As before, demand $\langle n^{(0)};k\,|\,n^{(p)};k\rangle = 0 \quad \forall\, p \geq 1$

but $|n^{(p)};k\rangle$ may have components along $|n^{(0)};l\rangle$ w/ $l \neq k$

So, $|n^{(0)};k\rangle$ may and in fact will have a component in $\mathbb{V}_N$

Now, $H(\lambda)|n;k\rangle_\lambda = E_{n,k}(\lambda)|n;k\rangle_\lambda$

Substituting and collecting order by order $\lambda$-terms

$$\left.\begin{aligned}
\mathcal{O}(\lambda^0) &: \ (H^{(0)} - E_n^{(0)})|n^{(0)};k\rangle = 0 \\
\mathcal{O}(\lambda) &: \ (H^{(0)} - E_n^{(0)})|n^{(1)};k\rangle = (E^{(1)}_{n,k} - H')|n^{(0)};k\rangle \\
\mathcal{O}(\lambda^2) &: \ (H^{(0)} - E_n^{(0)})|n^{(2)};k\rangle = (E^{(1)}_{n,k} - H')|n^{(1)};k\rangle + E^{(2)}_{n,k}|n^{(0)};k\rangle \\
&\ \ \vdots \qquad\qquad \vdots \qquad\qquad\qquad \vdots
\end{aligned}\right\} k = 1, 2, \ldots, N$$

Case-I

Degeneracy in $\mathbb{V}_N$ is completely broken to 1st order in PT → 1st order correc^ns to the energies split the N states completely.

Case-II

Degeneracy is completely unbroken to first order, i.e., the first order correc^n is the same, and equal for all the degenerate states. The degeneracy is completely broken at 2nd order

Case-I

Three steps to follow here – (i) multiply $O(\lambda)$ w/ $\langle n^{(0)}; l|$ to learn that $H'$ must be diagonal in the chosen basis for $\mathbb{V}_N$ & to determine the 1st order energy shifts.

(ii) Use $O(\lambda)$ eqn. to calculate the components of $|n^{(1)}; k\rangle$ in $\mathbb{V}$

(iii) multiply $O(\lambda^2)$ eqn. w/ $\langle n^{(0)}; l|$ to determine $E^{(2)}_{n,k}$ and the components $|n^{(1)}; k\rangle$ in $\mathbb{V}_N$.

In details –

(i) $O(\lambda^0)$ : $(H^{(0)} - E_n^{(0)})|n^{(0)}; k\rangle = 0$ ------- ①

$O(\lambda)$ : $(H^{(0)} - E_n^{(0)})|n^{(1)}; k\rangle = (E^{(1)}_{n,k} - H')|n^{(0)}; k\rangle$

$\Rightarrow \langle n^{(0)}; l|(H^{(0)} - E_n^{(0)})|n^{(1)}; k\rangle = \langle n^{(0)}; l|(E^{(1)}_{n,k} - H')|n^{(0)}; k\rangle$

$\Rightarrow \langle n^{(0)}; l|(E^{(1)}_{n,k} - H')|n^{(0)}; k\rangle = 0$ (using eq. ① in LHS)

$\Rightarrow \langle n^{(0)}; l|H'|n^{(0)}; k\rangle = E^{(1)}_{n,k}\delta_{lk}$ $(\forall\ l, k = 1, 2, \dots, N)$

** The basis $|n^{(0)}; k\rangle$ must be chosen to make the matrix $H'$ diagonal in the subspace $\mathbb{V}_N$.

$\Rightarrow E^{(1)}_{n,k} = \langle n^{(0)}; k|H'|n^{(0)}; k\rangle \equiv \delta H_{nk,nk}$

$\therefore$ To 1st order $E_{n,k}(\lambda) = E_n^{(0)} + \lambda\,\delta H_{nk,nk}$.

Ⓐ This result is true irrespective of whether the degeneracy lifted or not.

Degeneracy is lifted when

$$E^{(1)}_{n,k} \neq E^{(1)}_{n,l} \quad \forall\ k \neq l \quad \text{w/}\ k, l = 1, 2, \dots, N$$

"Good states" :- If the degeneracy is lifted, the basis states $|n^{(0)}; k\rangle$ that make $H'$ diagonal in $\mathbb{V}_N$ are the "good states".

– They are the basis states in $\mathbb{V}_N$ that get deformed continuously as $\lambda \to$ non-zero

• If the degeneracy is not lifted to the first order, search for "good states" to be continued to 2nd order.

(B) $H'$ is diagonalized in the subspace $\mathbb{V}_N$ & not in whole $\mathcal{H}$

$$H'|n^{(0)};l\rangle = \sum_j |n^{(0)};j\rangle\langle n^{(0)};j|H'|n^{(0)};l\rangle$$
$$+ \sum_i |i^{(0)}\rangle\langle i^{(0)}|H'|n^{(0)};l\rangle$$
$$= \sum_j E_{n,l}^{(1)}\delta_{lj}|n^{(0)};j\rangle + \sum_i |i^{(0)}\rangle\langle i^{(0)}|H'|n^{(0)};l\rangle$$

$$\Rightarrow \quad H'|n^{(0)};l\rangle = \underbrace{E_{n,l}^{(1)}|n^{(0)};l\rangle}_{\text{almost an eigenstate}} + \sum_i \underbrace{|i^{(0)}\rangle\langle i^{(0)}|H'|n^{(0)};l\rangle}_{\text{extra state along } \mathbb{V}} \quad \text{------ (B)}$$

(C) Sometimes we can guess that a certain basis in $\mathbb{V}_N$ makes $H'$ diagonal.

$H'$ is diagonal for a choice of basis in $\mathbb{V}_N$

if $\exists$ a hermitian $\hat{op}$ $K$, s.t. $[H', K] = 0$

and for which the chosen basis states are eigenstates of

$K$ of different eigenvalues.

Consider two different basis states: $|n^{(0)};p\rangle$ and $|n^{(0)};q\rangle$
$(p \neq q)$

$$\because \; [H', K] = 0$$
$$\Rightarrow \langle n^{(0)};p|[H',K]|n^{(0)};q\rangle = 0$$
$$\Rightarrow (\lambda_q - \lambda_p)\langle n^{(0)};p|H'|n^{(0)};q\rangle = 0$$
$$\because \; \lambda_p \neq \lambda_q \Rightarrow \langle n^{(0)};p|H'|n^{(0)};q\rangle = 0 .$$
$\Downarrow$

non-diagonal elements of $H'$ vanish.

(ii) $\mathcal{O}(\lambda)$ eqn. i.e., $(H^{(0)} - E_n^{(0)})|n^{(1)};k\rangle = (E_{n,k}^{(1)} - H')|n^{(0)};k\rangle$ can not determine the component of $|n^{(1)};k\rangle$ along $\mathbb{V}_N$

$\longrightarrow$ to be determined from $\mathcal{O}(\lambda^2)$ eqn.

We can, however, determine the comp. of $|n^{(1)};k\rangle$ along $\mathbb{V}$ (in $\mathcal{O}(\lambda)$)

$$\langle p^{(0)}|(H^{(0)} - E_n^{(0)})|n^{(1)};k\rangle = \langle p^{(0)}|(\underbrace{E_{n,k}^{(1)}}_{\to 0 \ \because\ |p^{(0)}\rangle \perp \mathbb{V}_N} - H')|n^{(0)};k\rangle$$

$$\Rightarrow (E_p^{(0)} - E_n^{(0)})\langle p^{(0)}|n^{(1)};k\rangle = \langle p^{(0)}|H'|n^{(0)};k\rangle$$

$$\equiv -\delta H_{p,nk}$$

$$\therefore\ |n^{(1)};k\rangle = -\sum_p \frac{\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}|p^{(0)}\rangle + \underbrace{|n^{(1)};k\rangle\big|_{\mathbb{V}_N}}_{\text{yet to be determined}}$$

(iii) $\mathcal{O}(\lambda^2)$ eqn. $\Rightarrow$

$$0 = \langle n^{(0)};l|(E_{n,k}^{(1)} - H')\left(-\sum_p \frac{\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}|p^{(0)}\rangle + |n^{(1)};k\rangle\big|_{\mathbb{V}_N}\right)$$

$$+ E_{n,k}^{(2)}\delta_{kl}$$

$$= -\langle n^{(0)};l|(\underbrace{\cancel{E_{n,k}^{(1)}}}_{0\ \Rightarrow\ |p^{(0)}\rangle \perp \mathbb{V}_N} - H')\sum_p \frac{\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}|p^{(0)}\rangle$$

$$+ \langle n^{(0)};l|(E_{n,k}^{(1)} - H')|n^{(1)};k\rangle\big|_{\mathbb{V}_N} + E_{n,k}^{(2)}\delta_{kl}$$

$$\Rightarrow \langle n^{(0)};l|H'\sum_p \frac{\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}|p^{(0)}\rangle + \langle n^{(0)};l|E_{n,k}^{(1)}|n^{(1)};k\rangle\big|_{\mathbb{V}_N}$$

$$- \langle n^{(0)};l|H'|n^{(1)};k\rangle\big|_{\mathbb{V}_N} + E_{n,k}^{(2)}\delta_{kl} = 0 \qquad \text{---- } ①$$

From eqn. Ⓑ in p. 10

$$\langle n^{(0)};l|H' = \langle n^{(0)};l|E_{n,l}^{(1)} + \sum_p \langle n^{(0)};l|H'|p^{(0)}\rangle\langle p^{(0)}|$$

$|p^{(0)}\rangle \perp \mathbb{V}_N$

$$\Rightarrow \langle n^{(0)};l|H'|n^{(1)};k\rangle\big|_{\mathbb{V}_N} = \langle n^{(0)};l|E_{n,l}^{(1)}|n^{(1)};k\rangle\big|_{\mathbb{V}_N} + 0$$

$$\Rightarrow \langle n^{(0)};l|H'|n^{(1)};k\rangle\big|_{\mathbb{V}_N} = E_{n,l}^{(1)}\langle n^{(0)};l|n^{(1)};k\rangle\big|_{\mathbb{V}_N} \qquad \text{---- } ②$$

Substituting ② in ① ⇒

$$\sum_p \frac{\delta H_{nl,p}\,\delta_{p,nk}}{E_p^{(0)} - E_n^{(0)}} + \left(E_{n,k}^{(1)} - E_{n,l}^{(1)}\right) \langle n^{(0)}; l \,|\, n^{(1)}; k \rangle \Big|_{V_N} + E_{n,k}^{(2)} \delta_{kl} = 0 \quad \text{---} ①$$

Setting $k = l$ ⇒ second correction to the energies →

$$\Rightarrow \quad E_{n,l}^{(2)} = -\sum_p \frac{|\delta H_{p,nk}|^2}{E_p^{(0)} - E_n^{(0)}}$$

Also for $k \neq l$ case eq. ① ⇒

$$|n^{(1)}; k\rangle \Big|_{V_N} = -\sum_{l \neq k} |n^{(0)}; l\rangle \frac{1}{E_{n,k}^{(1)} - E_{n,l}^{(1)}} \sum_p \frac{\delta H_{nl,p}\,\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} \quad \text{----} ②$$

∴ To summarise,

for degenerate PT w/ degeneracies lifted at $\mathcal{O}(\lambda)$ is —

$$|n; k\rangle_\lambda = |n^{(0)}; k\rangle - \lambda \sum_p \left( \frac{\delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}} |p^{(0)}\rangle + \sum_{l \neq k} \frac{\delta H_{nl,p}\,\delta H_{p,nk}}{\left(E_{n,k}^{(1)} - E_{n,l}^{(1)}\right)\left(E_p^{(0)} - E_n^{(0)}\right)} |n^{(0)}; l\rangle \right)$$

$$+ \mathcal{O}(\lambda^2).$$

## Case - II

(Degeneracy lifted at second order)

The degeneracy of $H^{(0)}$ is not broken to first order in the perturbation $H'$

$\Rightarrow$ On $\mathbb{V}_N$ basis $|n^{(0)}; k\rangle$ w/ $k = 1, 2, \ldots, N$ we now have

$$\langle n^{(0)}; l | H' | n^{(0)}; k\rangle = E_n^{(1)} \delta_{lk}$$

Recall in case-I it was $E_{n,k}^{(1)} \delta_{lk}$

$\Rightarrow$ The 1st order energy correcⁿ is the same, and equal to $E_n^{(1)}$ $\forall$ basis states $\mathbb{V}_N$.

$\because$ the degeneracy is not broken to 1st order, at this point, the "good basis" in $\mathbb{V}_N$ is not known.

Here we are going to consider that the degeneracy is completely lifted to 2nd order.

* Dump the ignorance about "good states" by defining -

$$\left\{ |\psi^{(0)}\rangle = \sum_{k=1}^{N} \underbrace{a_k^{(0)}}_{\text{consts.}} |n^{(0)}; k\rangle \right.$$

This is just one state, but we need $N$ of such states

So, $$|\psi_I^{(0)}\rangle = \sum_{k=1}^{N} a_{Ik}^{(0)} |n^{(0)}; k\rangle \qquad I = 1, 2, \ldots, N$$

$I$ : index that labels the different "good states" & their different vector repⁿ $a_I^{(0)}$.

First we need to find the $a_I^{(0)}$ and thus the "good basis".

$|\psi_I^{(0)}\rangle$ form an ON basis in $\mathbb{V}_N$ if

$$\langle \psi_I^{(0)} | \psi_J^{(0)} \rangle = \delta_{IJ} \Rightarrow \sum_k \left(a_{Jk}^{(0)}\right)^* a_{Ik}^{(0)} = \delta_{IJ}$$

Now we write the perturbation expansion as -

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

$$E_{nI}(\lambda) = \underbrace{E_n^{(0)} + \lambda E_n^{(1)}}_{\text{(Degeneracy to 0-th and 1st order)}} + \lambda^2 E_{nI}^{(2)} + \lambda^3 E_{nI}^{(3)} + \cdots$$

$$H(\lambda)|\psi_I\rangle_\lambda = E_{nI}(\lambda)|\psi_I\rangle_\lambda$$

$\therefore$ Order-wise eqns $\rightarrow$

$$\mathcal{O}(\lambda^0) : \quad (H^{(0)} - E_n^{(0)})|\psi_I^{(0)}\rangle = 0$$

$$\mathcal{O}(\lambda) : \quad (H^{(0)} - E_n^{(0)})|\psi_I^{(1)}\rangle = (E_n^{(1)} - H')|\psi_I^{(0)}\rangle$$

$$\mathcal{O}(\lambda^2) : (H^{(0)} - E_n^{(0)})|\psi_I^{(2)}\rangle = (E_n^{(1)} - H')|\psi_I^{(1)}\rangle + E_{nI}^{(2)}|\psi_I^{(0)}\rangle$$

$$\mathcal{O}(\lambda^3) : (H^{(0)} - E_n^{(0)})|\psi_I^{(3)}\rangle = (E_n^{(1)} - H')|\psi_I^{(2)}\rangle + E_{nI}^{(2)}|\psi_I^{(1)}\rangle + E_{nI}^{(3)}|\psi_I^{(0)}\rangle$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

- zeroth order $\mathcal{O}(\lambda^0)$ is trivially satisfied
- 1st " $\mathcal{O}(\lambda) \rightarrow$

$$0 = \langle n^{(0)}; l|E_n^{(1)} - H'|\psi_I^{(0)}\rangle$$

Recall
$$H'|n^{(0)};l\rangle = E_{n,l}^{(1)}|n^{(0)};l\rangle + \sum_p |p^{(0)}\rangle\langle p^{(0)}|H'|n^{(0)};l\rangle$$

(no new info. by multiplying $\langle n^{(0)}; l|$)

But multiplying by $\langle p^{(0)}| \rightarrow$ new info.

$$(E_p^{(0)} - E_n^{(0)})\langle p^{(0)}|\psi_I^{(1)}\rangle = \langle p^{(0)}|(E_n^{(1)} - H')|\psi_I^{(0)}\rangle$$

$$= -\langle p^{(0)}|H'|\psi_I^{(0)}\rangle \quad \text{(using } \mathbb{V} \perp \mathbb{V}_N \text{ etc.)}$$

$$\Rightarrow \langle p^{(0)}|\psi_I^{(1)}\rangle = -\frac{\delta H_{pI}}{E_p^{(0)} - E_n^{(0)}} \quad \text{------} \quad (1)$$

$$\delta H_{pI} = \sum_{k=1}^{N}\langle p^{(0)}|H'|n^{(0)};k\rangle \times a_{Ik}^{(0)} = \sum_{k=1}^{N}\delta H_{p,nk}\, a_{Ik}^{(0)}$$

$$= -\frac{1}{E_p^{(0)} - E_n^{(0)}}\sum_{k=1}^{N}\delta H_{p,nk}\, a_{Ik}^{(0)}$$

$\downarrow$

(Part of $|\psi_I^{(1)}\rangle$ in $\mathbb{V}$ in terms of the unknown zeroth order eigenstates)

(All info from $\mathcal{O}(\lambda)$ are already obtained) $\quad |\psi_I^{(0)}\rangle$ is yet undetermined

$O(\lambda^2)$ : This will give us second order correction to energies, that will help us determine the zeroth order "good states".

Take the $O(\lambda^2)$ eqn. and multiply by $\langle n^{(0)}; l|$

$$\Rightarrow \quad 0 = \langle n^{(0)}; l|(\underbrace{E_n^{(1)}}_{0\ \forall_N \perp \forall} - H')|\psi_I^{(1)}\rangle\Big|_{\forall} + \underbrace{\langle n^{(0)}; l|(E_n^{(1)} - H')|\psi_I^{(1)}\rangle\Big|_{\forall_N}}_{0} + \underbrace{E_{nI}^{(2)}\langle n^{(0)}; l|\psi_I^{(0)}\rangle}_{E_{nI}^{(2)} a_{Il}^{(0)}}$$

(use $\langle n^{(0)}; l|H'$ expression)

$$\Rightarrow \quad E_{nI}^{(2)} a_{Il}^{(0)} = \langle n^{(0)}; l|H'|\psi_I^{(1)}\rangle\Big|_{\forall}$$

$$= \sum_p \langle n^{(0)}; l|H'|p^{(0)}\rangle\langle p^{(0)}|\psi_I^{(1)}\rangle$$

( $|_{\forall}$ no longer needed as $\forall_N \perp \forall$ so other states won't contribute)

$$\Rightarrow \sum_{k=1}^{N} E_{nI}^{(2)} \delta_{lk} a_{Ik}^{(0)} = \sum_p \langle n^{(0)}; l|H'|p^{(0)}\rangle \times \left(-\frac{1}{E_p^{(0)} - E_n^{(0)}} \sum_{k=1}^{N} \delta H_{p,nk}\, a_{Ik}^{(0)}\right)$$

$$\Rightarrow \sum_{k=1}^{N} \left(E_{nI}^{(2)} \delta_{lk} + \sum_p \frac{\delta H_{nl,p}\, \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}\right) a_{Ik}^{(0)} = 0$$

$$\Rightarrow \sum_{k=1}^{N} \left(E_{nI}^{(2)} \delta_{lk} - M_{l,k}^{(2)}\right) a_{Ik}^{(0)} = 0$$

$$M_{l,k}^{(2)} = -\sum_p \frac{\delta H_{nl,p}\, \delta H_{p,nk}}{E_p^{(0)} - E_n^{(0)}}$$

$N \times N$ Hermitian matrix

$$\xrightarrow[\text{matrix form}]{\text{In the}} \quad \left(E_{nI}^{(2)} \mathbb{1} - M^{(2)}\right) a_I^{(0)} = 0$$

$\therefore$ Energy corrections $E_{nI}^{(2)}$ are eigenvalues of $M^{(2)}$ & the vectors $a_I^{(0)}$ are the associated normalized eigenvectors

$\rightarrow$ This determine, via $|\psi^{(0)}\rangle = \sum_{k=1}^{N} a_k^{(0)} |n^{(0)}; k\rangle$, the orthonormal basis of zeroth order "good states".

If $H'$ is known, $M^{(2)}$ is computable and Hermitian and thus diagonalizable

* The computation of $|\psi_I^{(1)}\rangle$ on the degenerate subspace can be done if the degeneracy is completely broken at 2nd order (i.e., the e. vals of $M^{(2)}$ are all different). For that one has to use $\mathcal{O}(\lambda^3)$ eqns.

Final result

$$|\psi_I\rangle_\lambda = |\psi_I^{(0)}\rangle + \lambda\left(\sum_p |p^{(0)}\rangle \frac{\delta H_{pI}}{E_n^{(0)} - E_p^{(0)}} + \sum_{J\neq I} |\psi_J^{(0)}\rangle\, a_{JI}^{(1)}\right) + \mathcal{O}(\lambda^2)$$

$$E_{In}(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_{In}^{(2)} + \lambda^3 E_{In}^{(3)} + \cdots$$

w/ $$a_{JI}^{(1)} = \frac{1}{E_{nI}^{(2)} - E_{nJ}^{(2)}}\left(\sum_{p,q} \frac{\delta H_{Jp}\,\delta H_{pq}\,\delta H_{qI}}{(E_p^{(0)} - E_n^{(0)})(E_q^{(0)} - E_n^{(0)})} - E_n^{(1)} \sum_p \frac{\delta H_{Jp}\,\delta H_{pI}}{(E_p^{(0)} - E_n^{(0)})^2}\right)$$

also, $$E_{In}^{(3)} = \sum_{p,q} \frac{\delta H_{Ip}\,\delta H_{pq}\,\delta H_{qI}}{(E_p^{(0)} - E_n^{(0)})(E_q^{(0)} - E_n^{(0)})} - E_n^{(1)} \sum_p \frac{|\delta H_{pI}|^2}{(E_p^{(0)} - E_n^{(0)})^2}.$$ //

* Applications

For example in hydrogen atom $H^{(0)}$ : hamiltonian for the electron

corrections/ perturbns
- Relativistic effects, spin of $e^-$ )- breaks much of the degeneracy present otherwise
- Application of external fields

external electric field → Stark effect

" magnetic " → Zeeman effect.