$\boxed{\text{SECOND - ORDER ENERGIES}}$

SECOND - ORDER EQUATION $\quad H^{(0)}\psi_n^{(2)} + H'\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$

$$\boxed{\begin{aligned} \psi_n^{(2)} &= \sum_m a_{nm}^{(2)}\,\psi_m^{(0)} \\ \psi_n^{(1)} &= \sum_m c_{nm}^{(1)}\,\psi_m^{(0)} \end{aligned}}$$

SEE EARLIER

PRE - MULTIPLY BY $\psi_\ell^{(0)*}$ AND INTEGRATE OVER ALL COORDINATES:

TAKE SUM OUT

$$\underbrace{\langle \psi_\ell^{(0)} | H^{(0)} | \sum_m a_{nm}^{(2)}\,\psi_m^{(0)} \rangle}_{E_\ell^{(0)} a_{n\ell}^{(2)}} + \boxed{\langle \psi_\ell^{(0)} | H' | \sum_m c_{nm}^{(1)}\,\psi_m^{(0)} \rangle}$$

$$= \underbrace{E_n^{(0)} \langle \psi_\ell^{(0)} | \sum_m a_{nm}^{(2)}\,\psi_m^{(0)} \rangle}_{E_n^{(0)} a_{n\ell}^{(2)}} + \overbrace{E_n^{(1)} \langle \psi_\ell^{(0)} | \sum_m c_{nm}^{(1)}\,\psi_m^{(0)} \rangle}^{E_n^{(1)} c_{n\ell}^{(1)}}$$

$$+ \underbrace{E_n^{(2)} \langle \psi_\ell^{(0)} | \psi_n^{(0)} \rangle}_{E_n^{(2)} \delta_{n\ell}}$$

GIVES

$$E_\ell^{(0)} a_{n\ell}^{(2)} + \sum_m c_{nm}^{(1)} \langle \psi_\ell^{(0)} | H' | \psi_m^{(0)} \rangle = E_n^{(0)} a_{n\ell}^{(2)} + E_n^{(1)} c_{n\ell}^{(1)} + E_n^{(2)} \delta_{n\ell}$$

$$a_{n\ell}^{(2)} [E_\ell^{(0)} - E_n^{(0)}] + \sum_m c_{nm}^{(1)} \langle \psi_\ell^{(0)} | H' | \psi_m^{(0)} \rangle - E_n^{(1)} c_{n\ell}^{(1)} - E_n^{(2)} \delta_{n\ell} = 0$$

FOR $l = n$:

$$0 + \underbrace{\sum_m}_{\text{m INCLUDES n HERE...}} c_{nm}^{(1)} \langle \psi_n^{(0)} | H' | \psi_m^{(0)} \rangle - \underbrace{E_n^{(1)}}_{\langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle \text{ SEE EARLIER}} c_{nn}^{(1)} = E_n^{(2)}$$

$$E_n^{(2)} = \sum_{m \neq n} \underbrace{c_{nm}^{(1)}}_{\frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \text{ SEE EARLIER}} \langle \psi_n^{(0)} | H' | \psi_m^{(0)} \rangle$$

HERMETIAN

$$\boxed{E_n^{(2)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | H' | \psi_m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_{m \neq n} \frac{| \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle |^2}{E_n^{(0)} - E_m^{(0)}}}$$

- $E_n^{(2)}$ DEPENDS ONLY ON UNPERTURBED WAVE FUNCTIONS AND ENERGIES [NOT ON $a_{nm}^{(2)}$]
- $E_n^{(2)}$ PROPORTIONAL TO SUM OF SQUARES OF MATRIX ELEMENTS CONNECTING $\psi_n^{(0)}$ TO OTHER LEVELS $\psi_m^{(0)}$
- EACH TERM INVERSELY PROPORTIONAL TO ENERGY DIFFERENCE : NEARBY STATES HAVE USUALLY LARGER INFLUENCE THAN FAR AWAY STATES
- IF n IS THE GROUND STATE : $E_n^{(0)} - E_m^{(0)} < 0$, AND $E_n^{(2)}$ IS ALWAYS NEGATIVE FOR ANY PERTURBATION H'

FOR $l \neq n$: CONDITION GIVES $\psi_n^{(2)}$ ... SIMILAR TO BEFORE ...

SUMMARY

USUALLY THAT'S ALL THAT IS NEEDED

FIRST-ORDER THEORY

SECOND-ORDER THEORY

FOR $l=n$: $$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

FOR $l \neq n$: $$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

$$\psi_n^{(2)} = \ldots$$

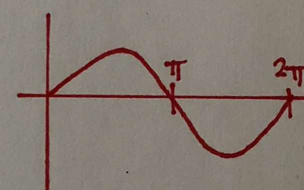
EXAMPLE

CALCULATE SECOND-ORDER CORRECTIONS $E_n^{(2)}$ FOR δ- FUNCTION PERTURBATION AT $x = \frac{a}{2}$ IN INFINITE SQUARE WELL

$$E_n^{(2)} = \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$H'_{mn} \equiv \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle = \frac{2}{a} \alpha \int_{-\infty}^{+\infty} \sin\left(\frac{m\pi}{a} x\right) \delta\left(x - \frac{a}{2}\right) \sin\left(\frac{n\pi}{a} x\right) dx$$

$$= \frac{2}{a} \alpha \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{n\pi}{2}\right)$$



$$= \begin{cases} \pm \frac{2}{a} \alpha & \text{IF } m = \text{ODD } \underline{\text{AND}}\ n = \text{ODD} \\ \emptyset & \text{OTHERWISE} \end{cases}$$

[AGAIN : CORRECTION IS ZERO FOR n=EVEN]

$$E_n^{(2)} = \sum_{\substack{m \neq n \\ n,m \text{ ODD}}} \left(\frac{2\alpha}{a}\right)^2 \frac{1}{E_n^{(0)} - E_m^{(0)}} = \sum_{\substack{m \neq n \\ n,m \text{ ODD}}} \left(\frac{2\alpha}{a}\right)^2 \frac{\frac{2Ma^2}{\pi^2 \hbar^2}}{n^2 - m^2}$$

WE LIKE TO CALCULATE EXPLICITLY SUM OVER m

$$E_n^{(2)} = \begin{cases} \emptyset & \text{IF } n = \text{EVEN} \\ \underbrace{\frac{2Ma^2}{\pi^2\hbar^2} \left(\frac{2\alpha}{a}\right)^2}_{\frac{8M\alpha^2}{\pi^2\hbar^2}} \underbrace{\boxed{\sum_{\substack{m \neq n \\ m \text{ ODD}}} \frac{1}{n^2 - m^2}}}_{\Sigma} & \text{IF } n = \text{ODD} \end{cases}$$

HANDOUT

$\boxed{n=1}$

$$\Sigma = \sum_{m=3,5,7,\ldots} \frac{1}{1^2-m^2} = \sum_{m=3,5,7,\ldots} \frac{1}{2}\left[\frac{1}{1+m} - \frac{1}{m-1}\right]$$

NOT $m=1$!

NOTE: $\frac{1}{n^2-m^2} = \frac{1}{2n}\left[\frac{1}{m+n} - \frac{1}{m-n}\right]$

$$= \frac{1}{2}\left[\frac{1}{4}+\frac{1}{6}+\frac{1}{8}+\ldots-\frac{1}{2}-\frac{1}{4}-\frac{1}{6}-\frac{1}{8}-\ldots\right]$$

$$= \frac{1}{2}\left(-\frac{1}{2}\right) = -\frac{1}{4}$$

$\boxed{n=3}$

$$\Sigma = \sum_{m=1,5,7,\ldots} \frac{1}{3^2-m^2} = \sum_{m=1,5,7,\ldots} \frac{1}{6}\left[\frac{1}{m+3} - \frac{1}{m-3}\right]$$

NOT $m=3$!

$$= \frac{1}{6}\left[\frac{1}{4}+\frac{1}{8}+\frac{1}{10}+\ldots+\frac{1}{2}-\frac{1}{2}-\frac{1}{4}-\frac{1}{6}-\frac{1}{8}-\frac{1}{10}-\ldots\right] = \frac{1}{6}\left(-\frac{1}{6}\right)$$

$$= -\frac{1}{36}$$

$\boxed{n = \text{GENERAL}}$

THERE IS PERFECT CANCELLATION EXCEPT FOR "MISSING" TERM $\frac{1}{2n}$; THUS $\Sigma = -\frac{1}{(2n)^2}$

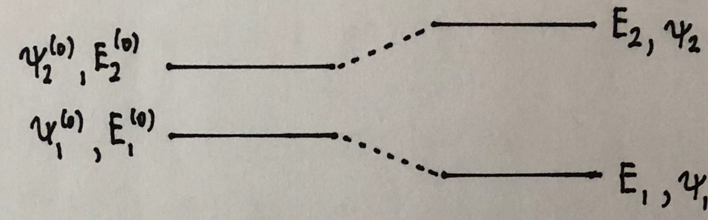
THEREFORE:

$$E_n^{(2)} = \begin{cases} \emptyset & \text{IF } n = \text{EVEN} \\ -\dfrac{2M\alpha^2}{\pi^2\hbar^2}\dfrac{1}{n^2} & \text{IF } n = \text{ODD} \end{cases}$$

DEGENERATE PERTURBATION THEORY

[EXAMPLE : H - ATOM]

UP TO NOW:

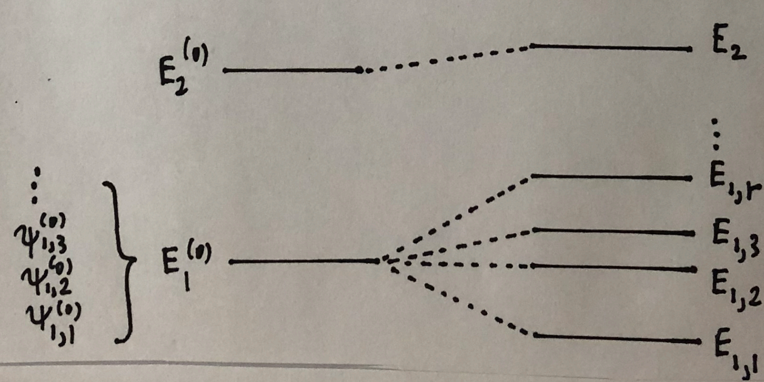


NON-DEGENERATE CASE

$$\psi_n = \psi_n^{(0)} + \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

PERTURBED WAVEFUNCTION APPEARS AS A MIXTURE OF UNPERTURBED STATES

NOW:



DEGENERATE CASE

WE CANNOT EXPAND GIVEN PERTURBED STATE ψ_n IN TERMS OF UNPERTURBED STATES $\psi_m^{(0)}$ BECAUSE ABOVE EXPRESSION DIVERGES FOR $E_n^{(0)} = E_m^{(0)}$ [IF $\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle \neq 0$]

STRATEGY: FIND NEW BASIS FOR DEGENERATE SUBSPACE SUCH THAT

$$\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle = 0$$

GENERAL FEATURE OF QUANTUM SYSTEMS

WHEN PERTURBING HAMILTONIAN HAS A DIFFERENT SYMMETRY THAN ORIGINAL HAMILTONIAN, SOME OF THE DEGENERACY IS BROKEN;

THIS IS BECAUSE THE EIGENSTATES OF THE ORIGINAL HAMILTONIAN WILL BE ACTED UPON DIFFERENTLY BY THE PERTURBING HAMILTONIAN

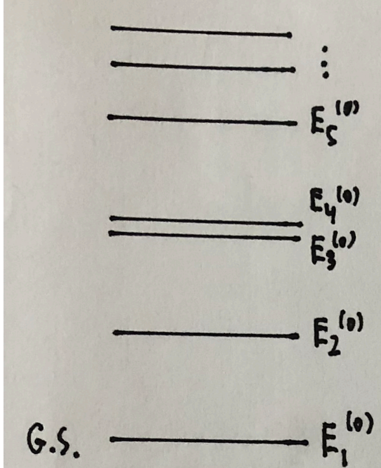
EXAMPLE: STARK EFFECT

[SPLITTING OF ATOMIC OR MOLECULAR SPECTRAL LINES DUE TO PRESENCE OF EXTERNAL ELECTRIC FIELD]

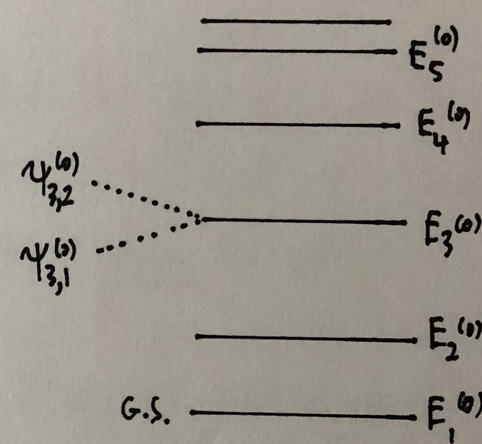
ORIGINAL HAMILTONIAN EXHIBITS SPHERICAL SYMMETRY WHEREAS PERTURBING HAMILTONIAN EXHIBITS PLANAR SYMMETRY. THESE DIFFERENT SYMMETRIES ARE THE REASON WHY THE DEGENERACY IS BROKEN, IN GENERAL

LET'S CONSIDER AGAIN FOR THE UNPERTURBED SITUATION
THE NON-DEGENERATE AND DEGENERATE SPECTRUM

NON-DEGENERATE



DEGENERATE



EIGENSTATES ARE:

- COMPLETE
- NORMALIZABLE
- ORTHOGONAL

- EIGENSTATES BELONGING TO <u>DIFFERENT</u> $E_n^{(0)}$ ARE COMPLETE, NORMALIZABLE, AND ORTHOGONAL
- EIGENSTATES BELONGING TO <u>SAME</u> $E_n^{(0)}$ ARE <u>NOT NECESSARILY ORTHONORMAL</u>

- BUT WE CAN FORM SUITABLE LINEAR COMBINATIONS THAT ARE ORTHONORMAL FOR SAME $E_n^{(0)}$

- THERE IS AN <u>INFINITE NUMBER</u> OF SUCH LINEAR COMBINATIONS, BECAUSE WITHOUT MEASURING ANOTHER OBSERVABLE, WE DO NOT KNOW THE OCCUPATION PROBABILITIES FOR DEGENERATE EIGENFUNCTIONS

PROPERTIES OF ENERGY EIGENFUNCTIONS WITH DEGENERACY INCLUDED:

(1) WHEN SCHRÖDINGER EQUATION IS SOLVED, THE DEGENERATE EIGENFUNCTIONS OBTAINED FOR A GIVEN EIGENVALUE MAY NOT BE ORTHOGONAL

(2) HOWEVER, IT IS ALWAYS POSSIBLE TO CONSTRUCT FROM LINEAR COMBINATIONS OF DEGENERATE EIGENFUNCTIONS A SET OF ORTHONORMAL EIGENVECTORS FOR GIVEN EIGENVALUE

(3) SUPPOSE WE ALREADY FOUND APPROPRIATE LINEAR COMBINATIONS; THEN

$$\int \psi^*_{E's}(\vec{r})\, \psi_{Er}(\vec{r})\, d\vec{r} = \delta_{EE'}\, \delta_{rs}$$

(4) THERE IS AN INFINITE NUMBER OF POSSIBLE SETS OF ORTHOGONAL EIGENFUNCTIONS [LINEAR COMBINATIONS] BELONGING TO A GIVEN EIGENVALUE

p. 171 POWELL/CRASEMANN

ORTHOGONAL LINEAR COMBINATIONS

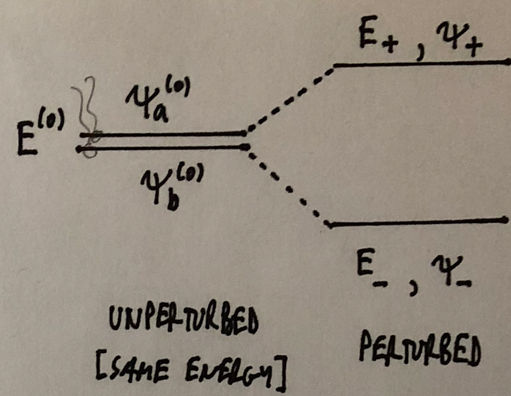
$$\psi_a = c_1\, \psi_i + c_2\, \psi_j$$

$$\psi_b = c_3\, \psi_i + c_4\, \psi_j$$

SOLUTIONS OF SCHRÖDINGER EQUATION [ψ_i AND ψ_j IN GENERAL NOT ORTHOGONAL]

IF YOU CHANGE c_1, c_2, c_3, c_4 CAN BE ADJUSTED TO MAKE ψ_a, ψ_b ORTHOGONAL [W/O MORE INFO, OCCUPATION PROBABILITIES ARE NOT CONSTRAINED]

TWO-FOLD DEGENERACY



ASSUME:

SAME ENERGY [DEGENERATE]

(1)
$$H^{(0)} \psi_a^{(0)} = E^{(0)} \psi_a^{(0)}$$
$$H^{(0)} \psi_b^{(0)} = E^{(0)} \psi_b^{(0)}$$

(2) $\psi_a^{(0)}$ AND $\psi_b^{(0)}$ ARE LINEAR COMBINATIONS OF DEGENERATE UNPERTURBED EIGENFUNCTIONS;

THEY ARE ALREADY ORTHOGONAL : $\langle \psi_a^{(0)} | \psi_b^{(0)} \rangle = 0$;

THERE IS AN INFINITE NUMBER OF POSSIBLE SETS OF SUCH ORTHONORMAL FUNCTIONS

WE WOULD LIKE TO SOLVE:

$$H \psi_\pm = E_\pm \psi_\pm$$

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

$$E_\pm = E^{(0)} + \lambda E_\pm^{(1)} + \mathcal{O}(\lambda^2)$$

$$\psi_\pm = \psi_\pm^{(0)} + \lambda \psi_\pm^{(1)} + \mathcal{O}(\lambda^2)$$

NOT, IN GENERAL, $\psi_a^{(0)}$ OR $\psi_b^{(0)}$

[NOT ANY, BUT ONLY ONE COMBINATION]

FOR TWO-FOLD DEGENERACY : $\psi_a^{(0)}$, $\psi_b^{(0)}$, $E^{(0)}$

UNPERTURBED

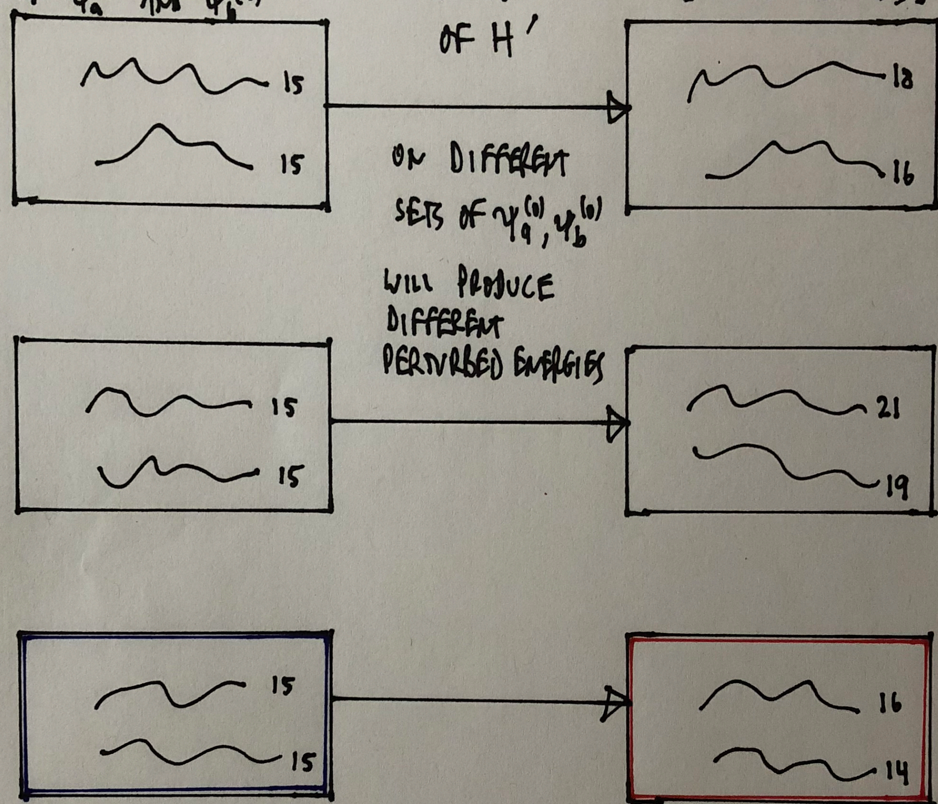
INFINITE # OF ORTHONORMAL SETS OF $\psi_a^{(0)}$ AND $\psi_b^{(0)}$

PERTURBED

[SMALL CHANGES]

ACTION OF H'

ON DIFFERENT SETS OF $\psi_a^{(0)}, \psi_b^{(0)}$ WILL PRODUCE DIFFERENT PERTURBED ENERGIES



"ADAPTED EIGENFUNCTIONS"

ONLY A SINGLE PERTURBED SET CORRESPONDS TO THE MEASURED DIFFERING ENERGIES

[EACH H' WILL CORRESPOND TO A DIFFERENT SET OF ADAPTED EIGENFUNCTIONS]

FOR DEGENERATE LEVELS, THERE IS AN INFINITE NUMBER OF SETS OF DIFFERENT LINEAR COMBINATIONS THAT ARE ORTHOGONAL, BUT PERTURBED LEVELS WILL TRANSITION INTO ONE SPECIFIC SET FOR $\lambda \to 0$

[WHAT YOUR TEXTBOOK CALLS THE "GOOD" UNPERTURBED STATES], AND OTHER TEXTBOOKS CALL "ADAPTED" EIGENFUNCTIONS

SEE DISCUSSION ON p. 171/172 IN K. ZIOCK, BASIC QUANTUM MECHANICS (WILEY, 1969)

[OF DEGENERATE EIGENSTATES ONLY]

TO FIND "GOOD" UNPERTURBED STATES, WE ALLOW FOR LINEAR COMBINATION WITH COEFFICIENTS TO BE DETERMINED

"GOOD" UNPERTURBED STATES

$$\psi_{\pm}^{(0)} = \alpha_{\pm}\,\psi_a^{(0)} + \beta_{\pm}\,\psi_b^{(0)}$$

ORTHOGONAL EIGENFUNCTIONS

$$H^{(0)}\,\psi_{\pm}^{(0)} = E^{(0)}\,\psi_{\pm}^{(0)}$$

WE WOULD LIKE TO SOLVE:

$$H\,\psi_{\pm} = E_{\pm}\,\psi_{\pm}$$

DROP SUBSCRIPTS $\pm$; SUBSTITUTE SERIES FOR E, ψ; COLLECT POWERS OF λ AS BEFORE; FIND FIRST-ORDER EQUATION:

$$[H^{(0)} + \lambda H'][\psi^{(0)} + \lambda\psi^{(1)}] = [E^{(0)} + \lambda E^{(1)}][\psi^{(0)} + \lambda\psi^{(1)}]$$

$$H^{(0)}\psi^{(1)} + H'\psi^{(0)} = E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)}$$

ONLY TERMS THAT DEPEND ON λ^1

[SAME EQUATION AS IN NON-DEGENERATE PERTURBATION THEORY]

PRE-MULTIPLY BY $\psi_a^{(0)}$ AND INTEGRATE:

$$\underbrace{\langle \psi_a^{(0)} | H^{(0)} | \psi^{(1)} \rangle}_{} + \langle \psi_a^{(0)} | H' | \psi^{(0)} \rangle = E^{(0)} \langle \psi_a^{(0)} | \psi^{(1)} \rangle + E^{(1)} \langle \psi_a^{(0)} | \psi^{(0)} \rangle$$

$$= \langle H^{(0)} \psi_a^{(0)} | \psi^{(1)} \rangle$$ HERMETIAN

$$= E^{(0)} \langle \psi_a^{(0)} | \psi^{(1)} \rangle$$

SUBSTITUTE: $\psi^{(0)} = \alpha \psi_a^{(0)} + \beta \psi_b^{(0)}$ SIMILAR TO WHAT WE DID BEFORE IN THE NON-DEG CASE

$$\langle \psi_a^{(0)} | H' | \alpha \psi_a^{(0)} \rangle + \langle \psi_a^{(0)} | H' | \beta \psi_b^{(0)} \rangle = E^{(1)} \langle \psi_a^{(0)} | \alpha \psi_a^{(0)} \rangle + \emptyset$$

$$\Rightarrow \boxed{\alpha \underbrace{\langle \psi_a^{(0)} | H' | \psi_a^{(0)} \rangle}_{\equiv W_{aa}} + \beta \underbrace{\langle \psi_a^{(0)} | H' | \psi_b^{(0)} \rangle}_{\equiv W_{ab}} = \alpha E^{(1)}}$$

H' HERMETIAN:

$$W_{ab} = W_{ba}^*$$

PRE-MULTIPLICATION WITH $\psi_b^{(0)}$ SIMILARLY GIVES:

$$\Rightarrow \boxed{\alpha W_{ba} + \beta W_{bb} = \beta E^{(1)}}$$

TASK: FIND EIGENVALUES FROM THESE EQUATIONS

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^{(1)}$$

$$\alpha W_{ba} W_{ab} + \beta W_{bb} W_{ab} = \beta E^{(1)} W_{ab}$$

MULTIPLY 2. EQUATION BY W_{ab}

$$\alpha W_{ba} W_{ab} + \beta W_{ab} [W_{bb} - E^{(1)}] = 0$$

$$\alpha W_{aa} - \alpha E^{(1)} + \left[- \frac{\alpha W_{ba} W_{ab}}{W_{bb} - E^{(1)}} \right] = 0$$

$$\Rightarrow \quad \alpha W_{aa} W_{bb} - \alpha W_{aa} E^{(1)} - \alpha E^{(1)} W_{bb} + \alpha [E^{(1)}]^2 - \alpha W_{ba} W_{ab} = 0$$

$$\alpha \left[[E^{(1)}]^2 - E^{(1)} (W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} \underbrace{W_{ba}}_{W_{ab}^*}) \right] = 0 \quad *$$

YIELDS FOR $\alpha \neq 0$:

$$\left[E^{(1)} - \frac{W_{aa} + W_{bb}}{2} \right]^2 = -\frac{4}{4} [W_{aa} W_{bb} - |W_{ab}|^2] + \frac{1}{4} [W_{aa} + W_{bb}]^2$$

$$\boxed{E_{\pm}^{(1)} = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4 |W_{ab}|^2} \right]}$$

- PERTURBATION REMOVES DEGENERACY [DEGENERATE LEVEL SPLITS INTO TWO]
- PERTURBED 1. ORDER ENERGIES DO NOT DEPEND ON "GOOD" EIGENFUNCTIONS [α, β]
- SOLUTIONS $E_{\pm}^{(1)}$ COULD BE SUBSTITUTED INTO ⇨ EQUATIONS TO FIND COEFFICIENTS OF UNPERTURBED "GOOD" EIGENVECTORS

$$\psi_{\pm}^{(0)} = \alpha_{\pm} \psi_a^{(0)} + \beta_{\pm} \psi_b^{(0)}$$

BUT WHAT IF $\alpha = 0$?

- $\beta = 1$ IN $\psi^{(0)} = \alpha \psi_a^{(0)} + \beta \psi_b^{(0)} = \psi_b^{(0)}$
- EQS. ⇨ GIVE $W_{ab} = 0$ AND $E_{\ominus}^{(1)} = W_{bb} = \langle \psi_b^{(0)} | H' | \psi_b^{(0)} \rangle$

MINUS SOLUTION

SIMILARLY, WHAT IF $\beta = 0$?

- $\alpha = 1$ IN $\psi^{(0)} = \alpha \psi_a^{(0)} + \beta \psi_b^{(0)} = \psi_a^{(0)}$
- EQS. ⇨ GIVE $W_{ba} = 0$ AND $E_{\oplus}^{(1)} = W_{aa} = \langle \psi_a^{(0)} | H' | \psi_a^{(0)} \rangle$

PLUS SOLUTION

- THESE ARE THE RESULTS OF NON-DEGENERATE PERTURBATION THEORY
- IN THIS CASE, $\psi_a^{(0)}$ AND $\psi_b^{(0)}$ ARE ALREADY THE "GOOD" SOLUTIONS
- IF ONE CAN GUESS THE "GOOD" SOLUTIONS [LINEAR COMBINATIONS] FROM THE START, DEGENERATE PERTURBATION THEORY TRANSITIONS INTO NON-DEGENERATE PERTURBATION THEORY

OFTEN, IT IS POSSIBLE TO GUESS "GOOD" SOLUTIONS [SEE LATER: FINE STRUCTURE OF HYDROGEN], BY USING THEOREM :

> IF A IS AN HERMETIAN OPERATOR COMMUTING WITH $H^{(0)}$ AND H', AND IF $\psi_a^{(0)}$ AND $\psi_b^{(0)}$, THE DEGENERATE EIGENFUNCTIONS OF $H^{(0)}$, ARE ALSO EIGENFUNCTIONS OF A, WITH DISTINCT EIGENVALUES :
>
> $$A\psi_a^{(0)} = \mu\,\psi_a^{(0)} \quad , \quad A\psi_b^{(0)} = \nu\,\psi_b^{(0)} \quad , \quad \mu \neq \nu$$
>
> THEN $W_{ab} = 0$ AND THUS $\psi_a^{(0)}$ AND $\psi_b^{(0)}$ ARE THE "GOOD" SOLUTIONS TO USE IN <u>NON</u>-DEGENERATE PERTURBATION THEORY

[FOR PROOF : SEE p. 260 IN GRIFFITHS]