E. Perturbation Results Made Simple by Matrix Point of View

- Using $\{\psi_n^{(0)}\}$ of $\hat{H}_0$ to write TISE $\hat{H}\psi = E\psi$ into matrix eq.

  Elements are $\left(H_{ji} - ES_{ji}\right)$ [exact]

- But $\{\psi_n^{(0)}\}$ are orthonormal [$\because$ they come from $\hat{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$]

  $\therefore\ S_{ii} = 1$ and $S_{ji} = 0$ [Simplification #1]

  $$\Rightarrow \begin{cases} \text{Diagonal elements become } H_{ii} - E & [\text{for every } i] \\ \text{Off-diagonal elements become } H_{ji} & [j \neq i] \end{cases}$$

- But
$$\underset{(j\neq i)}{H_{ji}} = \cancel{\int \psi_j^{(0)*} \underbrace{\hat{H}_0 \psi_i^{(0)}}_{E_i^{(0)}\psi_i^{(0)}} d\tau}^{\to 0} + \int \psi_j^{*(0)} \hat{H}' \psi_i^{(0)} d\tau \equiv H'_{ji}$$

[Simplification #2]

$$\therefore \begin{pmatrix} H_{11}-E & H'_{12} & H'_{13} & \cdots \\ H'_{21} & H_{22}-E & H'_{23} & \cdots \\ H'_{31} & H'_{32} & H_{33}-E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = 0$$

is the <u>Exact</u> eq. to solve for E and $\begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}^{+}$ for each solved E

(E1)

OR

$$\begin{vmatrix} H_{11}-E & H'_{12} & H'_{13} & \cdots \\ H'_{21} & H_{22}-E & H'_{23} & \cdots \\ H'_{31} & H'_{32} & H_{33}-E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0$$

is the <u>Exact</u> eq. to solve for E

(E2)

determinant

[Exact up to here] ...

$^{+}$ Recall $\begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$ means $c_1 \psi_1^{(0)} + c_2 \psi_2^{(0)} + \cdots$, because $\{\psi_n^{(0)}\}$ is the basis set

(a) 1^{st} order approximation to energy

- Ignore all off-diagonal H'_{ij} $(i \neq j)$,

$$\begin{pmatrix} H_{11}-E & 0 & 0 & \cdots \\ 0 & H_{22}-E & 0 & \cdots \\ 0 & 0 & H_{33}-E & \cdots \\ \vdots & \vdots & \text{"}0\text{"} & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = 0$$

Many "1×1" problems [one for each n]

$$\therefore \quad E_n = H_{nn} = \int \psi_n^{*(0)} \hat{H}_0 \psi_n^{(0)} d\tau + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau$$

$$= E_n^{(0)} + \underbrace{\int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}_{E_n^{(1)} \text{ (1st order result)}} = E_n^{(0)} + E_n^{(1)}$$

(see (C4))

1^{st} order approximation in energy in E_n

- Ignore all H'_{ni} $(n \neq i)$ [retain only H'_{nn}] (ignore off-diagonal terms)

<u>Implications</u>

- 2^{nd} order correction in energy? [should retain H'_{nm}] how $\psi_m^{(0)}$ would affect E_n due to H'
- 1^{st} order correction in wavefn? [should retain H'_{nm}]

(b) 2nd order corrections in energy

- How does state $\psi_i^{(0)}$ (of unperturbed $E_i^{(0)}$) affect E_n? $[i \neq n]$

$$\begin{vmatrix} \ddots & & \\ & H_{nn}-E & \\ & & \ddots \end{vmatrix} = 0$$ gives 1st order result

$$\begin{vmatrix} \ddots & & & \\ & H_{nn}-E & H'_{ni} & \\ & H'_{in} & H_{ii}-E & \\ & & & \ddots \end{vmatrix}$$

← focus on how state "i" affects "n"

→ Read out $\begin{vmatrix} H_{nn}-E & H'_{ni} \\ H'_{in} & H_{ii}-E \end{vmatrix} = 0$

↳ meaning: focus on 2×2 problem

$$\begin{pmatrix} H_{nn} & H'_{ni} \\ H'_{in} & H_{ii} \end{pmatrix} \begin{pmatrix} c_n \\ c_i \end{pmatrix} = E \begin{pmatrix} c_n \\ c_i \end{pmatrix}$$ to obtain state "i" effect on state "n"

Street fighting Matrix Math : 2x2 matrices carry much physics

Eigenvalue Problem of $\begin{pmatrix} \varepsilon_A & \Delta \\ \Delta^* & \varepsilon_B \end{pmatrix}$

(i) Exact treatment $\begin{vmatrix} \varepsilon_A - E & \Delta \\ \Delta^* & \varepsilon_B - E \end{vmatrix} = 0$ (quadratic Eq. for E)

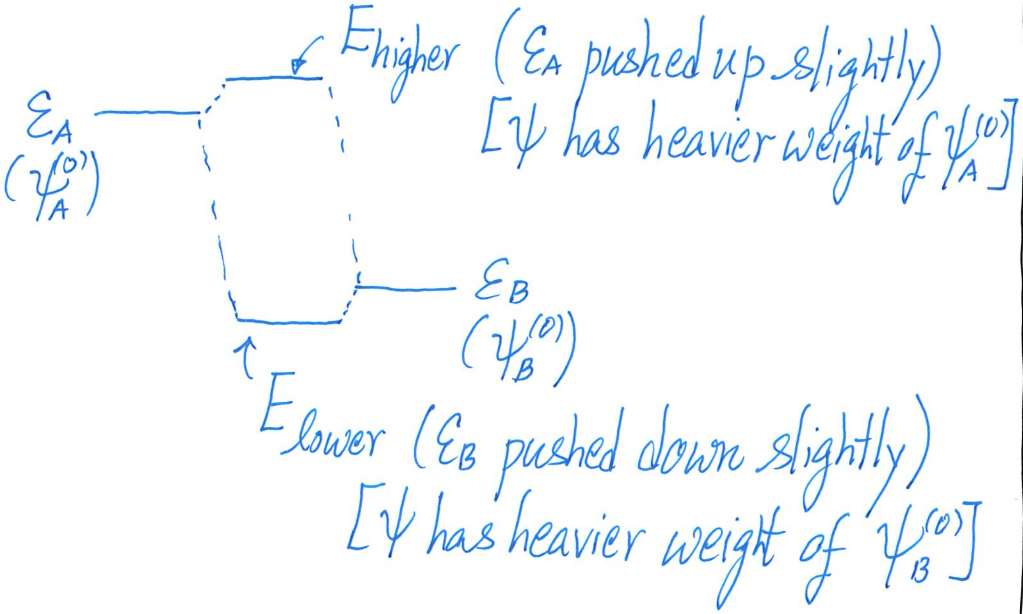
$$\boxed{E = \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_A - \varepsilon_B)^2 + 4|\Delta|^2}}$$ exact!

Applications in physics

- Degenerate perturbation theory (see Sec. F)
- Bonding (general situation)

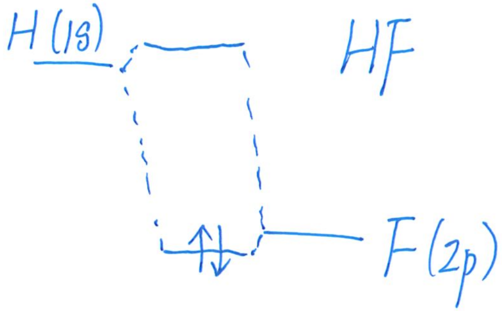
(ii) $\varepsilon_A - \varepsilon_B \gg |\Delta|$ (Using $\sqrt{1+x} \approx 1 + \frac{1}{2}x$)

$$E \approx \begin{cases} \varepsilon_A + \dfrac{|\Delta|^2}{\varepsilon_A - \varepsilon_B} \\[2ex] \varepsilon_B - \dfrac{|\Delta|^2}{\varepsilon_A - \varepsilon_B} \end{cases}$$



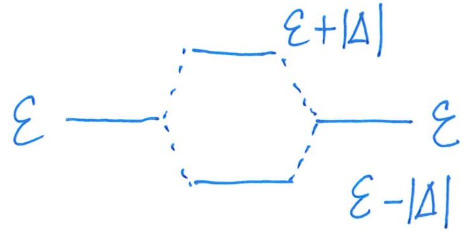
Applications in physics

- 2^{nd} order non-degenerate perturbation theory
- Molecules formed by very different atoms
- 1^{st} order correction in eigenstate



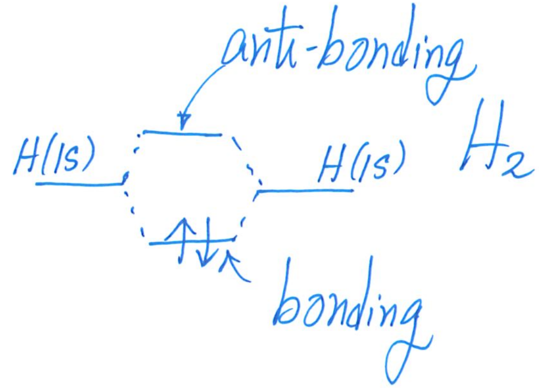
(iii) $\varepsilon_A = \varepsilon_B = \varepsilon$ (or $\varepsilon_A \approx \varepsilon_B$)

$$E = \begin{cases} \varepsilon + |\Delta| \\ \varepsilon - |\Delta| \end{cases}$$



Applications in physics

- Molecules formed by identical atoms
- Band Gap in Solids



$$\begin{vmatrix} H_{nn}-E & H'_{ni} \\ H'_{in} & H_{ii}-E \end{vmatrix} = 0$$

For the root closer to H_{nn}, it is

$$E_n \approx \underbrace{H_{nn}}_{0^{th}+1^{st}\text{ order}} + \frac{|H'_{ni}|^2}{\underbrace{H_{nn}-H_{ii}}_{\text{must relate to }2^{nd}\text{ order}}} \quad (\text{due to state "}i\text{"})$$

Denominator $= H_{nn}-H_{ii} = \underbrace{(E_n^{(0)}-E_i^{(0)})}_{0^{th}\text{ order}} + \underbrace{(H'_{nn}-H'_{ii})}_{1^{st}\text{ order } (\because H')}$

Numerator $= |H'_{ni}|^2$ (already 2^{nd} order) $\Rightarrow$ keep Denominator zeroth order is sufficient

$$\therefore E_n \approx \overbrace{(E_n^{(0)}+H'_{nn})}^{H_{nn}} + \underbrace{\frac{|H'_{ni}|^2}{E_n^{(0)}-E_i^{(0)}}}_{\text{this is the same as }2^{nd}\text{ order result}}$$

(considered only effect of state "i" on "n")

- Repeat argument for another state "j"'s effect on state "n"

$$\begin{vmatrix} H_{nn}-E & H'_{nj} \\ H'_{jn} & H_{jj}-E \end{vmatrix} = 0 \Rightarrow \text{correction term } \frac{|H'_{nj}|^2}{E_n^{(0)}-E_j^{(0)}}$$

- Consider all states i (effects on n) [repeating 2x2 arguments]

$$\text{correction terms} = E_n^{(2)} = \sum_{i\neq n} \frac{|H'_{nj}|^2}{E_n^{(0)}-E_i^{(0)}} = \underbrace{\sum_{i\neq n} \frac{\left|\int \psi_n^{*(0)} \hat{H}' \psi_j^{(0)} d\tau\right|^2}{E_n^{(0)}-E_i^{(0)}}}_{\text{same as } 2^{nd} \text{ order perturbation}}$$

- <u>Why is it "non-degenerate" theory?</u>

Clear! We used $|E_n^{(0)}-E_i^{(0)}| \gg |\Delta|$ in the approximation

quite different (non-degenerate) [compared with $|\Delta|$]

Summary

- Ignoring all H'_{ni} $(n \neq i)$, 1^{st} order perturbation (many 1x1 problems) $E_n \approx E_n^{(0)} + \underbrace{H'_{nn}}_{E_n^{(1)}}$
- Consider how a state i affects state n [consider each i separately] (many 2x2 problems)

  2^{nd} order perturbation $E_n^{(2)} = \sum_{i \neq n} \frac{|H'_{ni}|^2}{E_n^{(0)} - E_i^{(0)}}$

Extensions

- How about 1^{st} order correction to ψ_n?
- What if we want to develop "3^{rd} order" corrections? [many 3x3 problems?]
- What if $E_n^{(0)} \approx E_i^{(0)}$ for some i?

  [Degenerate Perturbation Theory]