# 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 $(H_{ji} - ES_{ji})$ [exact]

- But $\{\psi_n^{(0)}\}$ are <u>orthonormal</u> [$\because$ 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]

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

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

  $\cancel{\phantom{x}} \to 0$ $(j \neq i)$

  [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 Exact eq. to solve for $E$ and $\begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$ for each solved $E$

(E1)

OR

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

determinant

is the Exact eq. to solve for $E$

(E2)

[ Exact up to here] ...

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

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

  Many "$1\times 1$" problems [one for each $n$]

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

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

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

(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)

Implications

- $2^{nd}$ 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) $2^{nd}$ order corrections in energy

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

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

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

← 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 $2\times2$ 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 "$n$"

# Aside: Street-fighting Matrix Math

$$\begin{pmatrix} \varepsilon_A & \Delta \\ \Delta^* & \varepsilon_B \end{pmatrix} \leftarrow \text{Eigenvalues?} \qquad \begin{vmatrix} \varepsilon_A - E & \Delta \\ \Delta^* & \varepsilon_B - E \end{vmatrix} = 0 \Rightarrow \boxed{E = \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_A - \varepsilon_B)^2 + 4|\Delta|^2}}$$

(Exact)

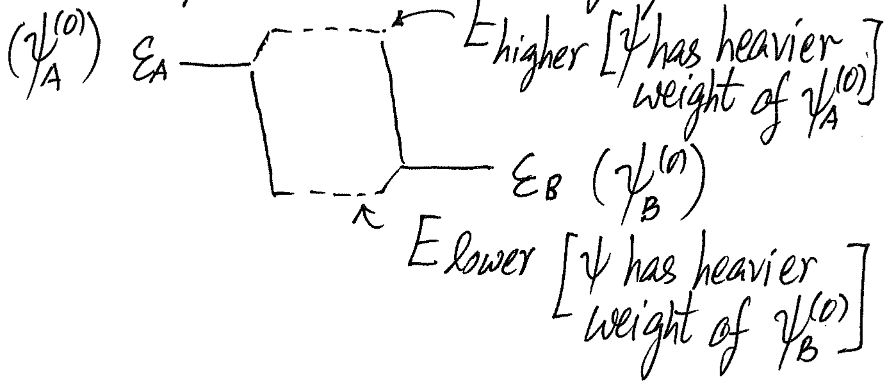
(i) $\varepsilon_A - \varepsilon_B \gg |\Delta|$ (thus $\varepsilon_A \neq \varepsilon_B$) $(\varepsilon_A > \varepsilon_B)$

$\sqrt{1+x} \approx 1 + \frac{1}{2}x$ (small $x$)

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

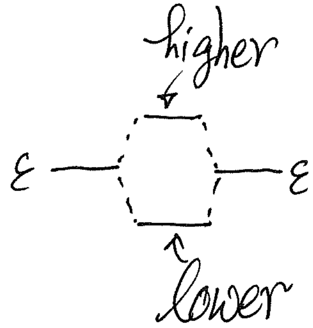
(higher one is pushed higher slightly)

(lower one is pushed lower slightly)




(ii) $\varepsilon_A = \varepsilon_B = \varepsilon$

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



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

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

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

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

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

- 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 $j$) [many 2×2 problems]

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

- Why is it "non-degenerate" theory?

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

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

## Summary

(many 1x1 problems)

- Ignoring all $H'_{ni}$ $(n \neq i)$, 1st order perturbation $E_n \approx E_n^{(0)} + \underbrace{H'_{nn}}_{E_n^{(1)}}$

(many 2x2 problems)

- Consider how a state $i$ affects state $n$ [consider each $i$ separately]

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

## Extensions

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

  [Degenerate Perturbation Theory]

# F. Time-Independent Degenerate Perturbation Theory

- Recall the "mixing in" of state $i$ into $n$ ($2^{nd}$ order in energy and $1^{st}$ order in wavefunction), there is $\sim \dfrac{1}{E_n^{(0)} - E_i^{(0)}}$

  Problematic when $E_n^{(0)} \approx E_i^{(0)}$ OR $E_n^{(0)} = E_i^{(0)}$

  [Troublesome when there are degenerate states when the same energy as $E_n^{(0)}$ in the unperturbed problem!]

- Recall: $\dfrac{|H'_{ni}|^2}{E_n^{(0)} - E_i^{(0)}}$ appears when we make an approximation in solving the 2x2 problem

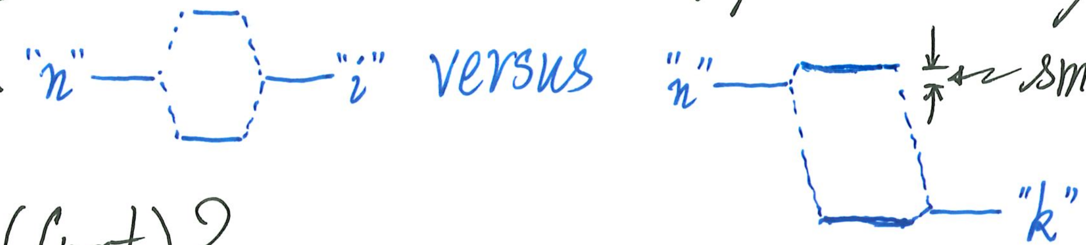
  [Idea: Why not solve it exactly? Then there will be no problem]

# Degenerate Perturbation Theory

- Let's say (for simplicity) there is only one other state $i$ ($E_n^{(0)} = E_i^{(0)}$) that is degenerate with state $n$

  $\Rightarrow$ $\psi_n^{(0)}$ will be coupled most strongly with $\psi_i^{(0)}$ by $\hat{H}'$

strong influence from state "i"




smaller influence from state "k"

- What to do (first)?
  - Work on the more important effect accurately! [common sense!]

Read out

$$\begin{vmatrix} H_{nn} - E & H'_{ni} \\ H'_{in} & H_{ii} - E \end{vmatrix} = 0 \Rightarrow \begin{vmatrix} E_n^{(0)} + H'_{nn} - E & H'_{ni} \\ H'_{in} & E_n^{(0)} + \underbrace{H'_{ii}}_{E_i^{(1)}} - E \end{vmatrix} = 0 \quad (F1)$$

(used $E_i^{(0)} = E_n^{(0)}$)

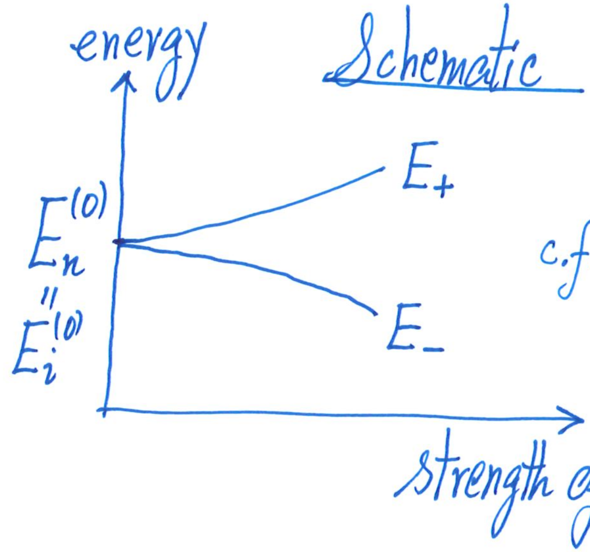
## Solve for E (don't make approximation)

$$\boxed{E_{\pm} = E_n^{(0)} + \frac{E_n^{(1)} + E_i^{(1)}}{2} \pm \frac{1}{2}\sqrt{\left(E_n^{(1)} - E_i^{(1)}\right)^2 + 4\,|H'_{ni}|^2}} \qquad (F2)$$

- This is degenerate perturbation theory when $n$ and $i$ are degenerate
- Idea is to treat degenerate states on the same footing [not one "perturbing" another] and treat that part of the matrix problem exactly
- $\hat{H}'$ removes (or lifts) the degeneracy (see (F2))

[will see this in solid state physics for "opening" a gap between two bands]

Schematic




c.f. Eq. (F2)

## Generalization

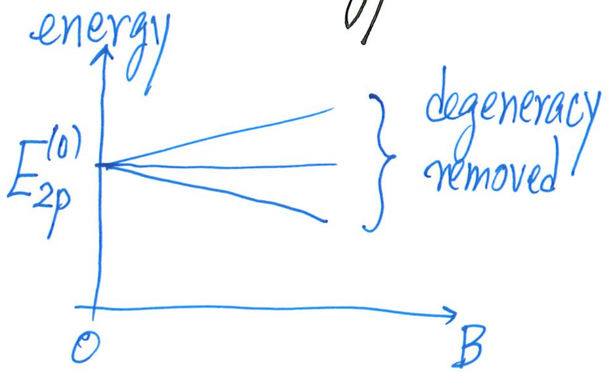
- What if $E_i^{(0)} = E_j^{(0)} = E_k^{(0)}$ (three degenerate states)?

  Treat the "sub-problem" formed by these three states <u>exactly</u>

Read out
$$\begin{vmatrix} E_i^{(0)} + H'_{ii} - E & H'_{ij} & H'_{ik} \\ H'_{ji} & E_i^{(0)} + H'_{jj} - E & H'_{jk} \\ H'_{ki} & H'_{kj} & E_i^{(0)} + H'_{kk} - E \end{vmatrix} = 0$$

E.g. $\psi_{210}$, $\psi_{211}$, $\psi_{21-1}$ (2p states) [same energy]

$$\hat{H} = \underbrace{\left[ -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \right]}_{\hat{H}_0 \text{ (hydrogen atom)}} + \overbrace{\gamma \underbrace{\vec{L}\cdot\vec{B}}_{\text{external magnetic field on angular momentum}}}^{\hat{H}'}$$



## Remarks [Optional] (Deeper)

- Focused on $i$ & $j$ (or $i$ & $j$ & $k$) and do it exactly (alright)
- But how about the effects of the other states (recall huge matrix)?
  - Treat 2x2 (or 3x3) exactly $\Leftrightarrow$ changing basis from $\psi_i^{(0)}$ and $\psi_j^{(0)}$ to $\underbrace{\tilde{\psi}_i \text{ and } \tilde{\psi}_j}_{\text{new basis}}$.
  - Huge matrix is still there
    $$\{\underbrace{\psi_1^{(0)}, \psi_2^{(0)}, \ldots}_{\text{old}}; \underbrace{\tilde{\psi}_i, \tilde{\psi}_j}_{\text{new}}, \underbrace{\ldots \psi_n^{(0)} \ldots}_{\text{old}}\}$$
  - then apply $\underbrace{\text{non-degenerate}}_{\text{degeneracy removed by doing 2x2 exactly}}$ perturbation theory [$2^{nd}$ order effect]

# Let's take stock : Summary

- TISE → Huge Matrix [Exact] (useful in Variational Method/Perturbation)
- Variational Method
  - Theorem, How it works, $\phi_{trial} = c_1\phi_1 + c_2\phi_2$
- Time-independent Perturbation Theory

$$E_n \approx E_n^{(0)} + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau + \sum_{i \neq n} \frac{|H'_{in}|^2}{E_n^{(0)} - E_i^{(0)}}$$

$$\psi_n \approx \psi_n^{(0)} + \sum_{i \neq n} \frac{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_i^{(0)}} \psi_i^{(0)}$$

Non-degenerate Perturbation Theory

- Matrix interpretation of results
- Degenerate Perturbation Theory [Treat 2x2 (OR 3x3) exactly]

We will apply these methods to understand the

- physics of atoms and molecules