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 $\sim \frac{1}{E_n^{(0)} - E_i^{(0)}}$

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

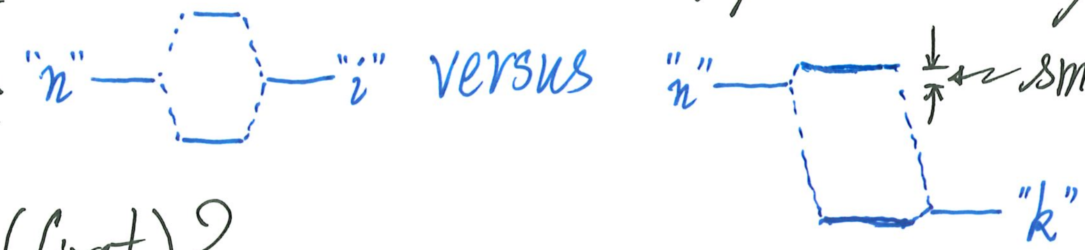
  [Idea: Why not solve it exactly? Then there will be no problem]

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

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

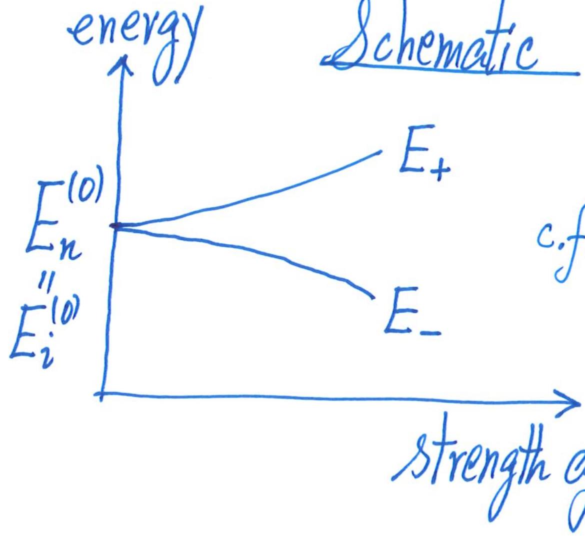
(used $E_i^{(0)} = E_n^{(0)}$)

Solve for E (don't make approximation)

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

- 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))

Schematic



c.f. Eq. (F2)

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

Generalization

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

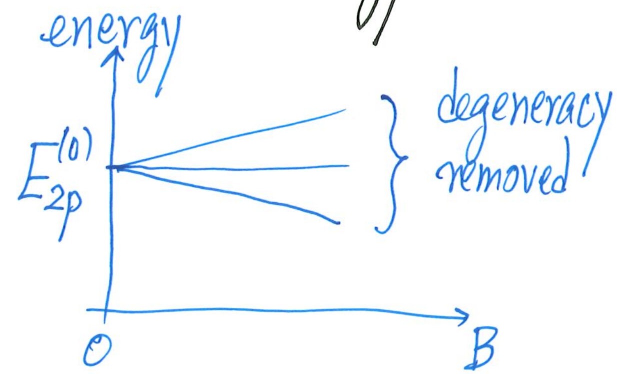
  Treat the "sub-problem" formed by these three states <u>exactly</u>

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. ψ_{210}, ψ_{211}, ψ_{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 2×2 (or 3×3) 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]