(c) Non-degenerate Time-independent Perturbation Theory : Formalism

$$\underbrace{\hat{H}}_{\text{can't solve analytically}} = \underbrace{\hat{H}_0}_{\text{solvable}} + \underbrace{\hat{H}'}_{\text{perturbation}} \quad \text{and know } \hat{H}_0 \underbrace{\psi_n^{(0)}}_{} = \underbrace{E_n^{(0)}}_{} \underbrace{\psi_n^{(0)}}_{} \quad (C6)$$

$\{\psi_n^{(0)}\}$, $\{E_n^{(0)}\}$ knowns
(orthonormal)

- Systematic approach for obtaining correction terms to $E_n^{(0)}$ and $\psi_n^{(0)}$ to 1st order in $\hat{H}'$, 2nd order in $\hat{H}'$, etc.

- Introduce an auxiliary (輔助) parameter λ to book keep the order

Write $$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \quad (C7)$$ ($\lambda = 1$ is our problem)

- $\lambda \hat{H}'$ helps us count (each appearance of $\hat{H}'$ is one order higher)
- $\hat{H} = \lambda^0 \hat{H}_0 + \lambda \hat{H}' = \hat{H}_0 + \lambda \hat{H}'$ (zeroth order $\lambda^0 \Rightarrow$ unperturbed problem)
- $\lambda^0, \lambda^1, \lambda^2, \ldots$ (regarding λ being a small number)
  not small, small, smaller, ...

- λ is auxiliary because it will disappear soon [if you may think as $\lambda = 1$]

<u>Step 1</u>: [Recall $\hat{H} = \hat{H}_0 + \lambda \hat{H}'$] Write down what we want to do

$$E_n = \underbrace{E_n^{(0)}}_{\substack{0^{th}\text{ order} \\ (\hat{H}_0 \text{ problem})}} + \lambda \underbrace{E_n^{(1)}}_{1^{st}\text{ order}} + \lambda^2 \underbrace{E_n^{(2)}}_{2^{nd}\text{ order}} + \underbrace{\cdots}_{\text{higher orders}} \quad (C8)$$

"superscript" labels the order

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots \quad (C9)$$

- Power in λ keeps track of the order of the term
- $\lambda = 1$ is the problem we want to develop perturbation theory
- Eqs. (C7), (C8), (C9) are general starting points of perturbation theory
- Perturbation theory works in classical and quantum physics problems
- [Don't mistaken λ as the variational parameter in Sec. B. No! They are different things. Here, λ is a book-keeping parameter.]

Tasks...

- We want to find formulas for

$E_n^{(1)}$ (already know answer)

$\psi_n^{(1)}$

$E_n^{(2)}$

and get the idea of how to go to higher orders systematically

The only equation we have: $\underbrace{\hat{H}}_{\hat{H}_0 + \lambda \hat{H}'}\psi_n = E_n \psi_n$ (set $\lambda = 1$ later)

Step 2: Write out $\hat{H}\psi_n = E_n\psi_n$

$$\text{LHS} = \hat{H}\psi_n = (\hat{H}_0 + \lambda\hat{H}')(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots)$$

$$= \hat{H}_0\psi_n^{(0)} + \underline{\lambda}(\hat{H}_0\psi_n^{(1)} + \hat{H}'\psi_n^{(0)}) + \underline{\lambda^2}(\hat{H}_0\psi_n^{(2)} + \hat{H}'\psi_n^{(1)}) + \cdots$$

collect $\lambda^0, \lambda^1, \lambda^2, \cdots$ terms

$$\text{RHS} = E_n\psi_n = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots)$$

$$= E_n^{(0)}\psi_n^{(0)} + \underline{\lambda}(E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}) + \underline{\lambda^2}(E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)}) + \cdots$$

But LHS = RHS should hold for arbitrary value of λ

$\therefore$ λ^0 terms on LHS & RHS must be equal
λ^1 terms ... must be equal
λ^2 terms ... must be equal
$\vdots$

} Key idea

Step 3: Write down Equations for $\lambda^0, \lambda^1, \lambda^2, \ldots$

Equating λ^0 terms: $\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ (C0)

- Just the unperturbed $\hat{H}_0$ problem
- True, not surprising

Equating λ^1 terms:

$$\boxed{\hat{H}_0 \psi_n^{(1)} + \hat{H}' \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}} \quad \text{(C10)}$$

- Will use (C10) to obtain $E_n^{(1)}$ and $\psi_n^{(1)}$ [1st order perturbation theory]

Equating λ^2 terms:

$$\boxed{\hat{H}_0 \psi_n^{(2)} + \hat{H}' \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}} \quad \text{(C11)}$$

- Use (C11) to obtain $E_n^{(2)}$ and $\psi_n^{(2)}$ [2nd order perturbation theory]

- Can go on with λ^3 terms, λ^4 terms, ... [but tedious!]
- We will stop at 2nd order [mid-way]
- Must understand symbols in Eq. (C10) and Eq. (C11). They are the key equations.
- See λ drops out of Eqs. (C10) and (C11). Its historical mission is done.

Basically Done! Big Picture...

- (C0) $\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ $\{\psi_n^{(0)} \leftrightarrow E_n^{(0)}\}$ all <u>known</u>
- Need $\{\psi_n^{(0)} \leftrightarrow E_n^{(0)}\}$ in (C10) to get $\psi_n^{(1)}$ & $E_n^{(1)}$

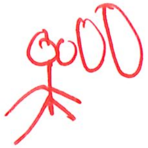
$$\hat{H}_0 \underset{\substack{\uparrow \\ \text{to solve}}}{\psi_n^{(1)}} + \hat{H}' \psi_n^{(0)} = \underset{\substack{\uparrow \\ \text{to solve}}}{E_n^{(1)}} \psi_n^{(0)} + E_n^{(0)} \underset{\substack{\uparrow \\ \text{to solve}}}{\psi_n^{(1)}} \qquad \text{(C10)}$$

- Need $\{\psi_n^{(0)} \leftrightarrow E_n^{(0)}\}$ & $\{\psi_n^{(1)} \leftrightarrow E_n^{(1)}\}$ in (C11) to get $\psi_n^{(2)}$ & $E_n^{(2)}$

$\therefore$ We must work things out order by order!

Step 4: Extract 1st order Results from Eq.(C10)

(C10): $\hat{H}_0 \overset{?}{\psi_n^{(1)}} + \hat{H}'\psi_n^{(0)} = \overset{?}{E_n^{(1)}}\psi_n^{(0)} + E_n^{(0)}\overset{?}{\psi_n^{(1)}}$

 Want $E_n^{(1)}$? How to get stand-alone $E_n^{(1)}$ from "$E_n^{(1)}\psi_n^{(0)}$" term in (C10)?

- Left multiply eq. by $\psi_n^{*(0)}$ and integrate $\int(\cdots)d\tau$ [Recall: $\{\psi_n^{(0)}\}$ orthonormal]

LHS becomes

$$\underbrace{\int \psi_n^{*(0)}\hat{H}_0\psi_n^{(1)}d\tau}_{=\int \psi_n^{(1)}(\hat{H}_0\psi_n^{(0)})^* d\tau \,=\, E_n^{(0)}\int\psi_n^{*(0)}\psi_n^{(1)}d\tau} + \int \psi_n^{*(0)}\hat{H}'\psi_n^{(0)}d\tau = E_n^{(0)}\int\psi_n^{*(0)}\psi_n^{(1)}d\tau + \int\psi_n^{*(0)}\hat{H}'\psi_n^{(0)}d\tau$$

($\because \hat{H}_0$ is Hermitian)

the same

RHS becomes

$$E_n^{(1)}\underbrace{\int\psi_n^{*(0)}\psi_n^{(0)}d\tau}_{=1} + E_n^{(0)}\int\psi_n^{*(0)}\psi_n^{(1)}d\tau = E_n^{(1)} + E_n^{(0)}\int\psi_n^{*(0)}\psi_n^{(1)}d\tau$$

stand-alone

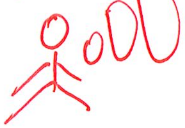
LHS = RHS

LHS = RHS $\Rightarrow$ $\boxed{E_n^{(1)} = \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}$ (C12)

1st order correction in energy = expectation value of $\hat{H}'$ with respect to the unperturbed wavefunction

[This proves our lazy guess is correct! (See Eq. (C4))]

Next,



Want $\psi_n^{(1)}$?

$$\hat{H}_0 \underbrace{\psi_n^{(1)}}_{?} + \hat{H}' \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \underbrace{\psi_n^{(1)}}_{?} \quad \text{(C10)}$$

- Technical thought: Get rid of "$E_n^{(1)} \psi_n^{(0)}$" term

How? Left multiply by $\psi_i^{*(0)}$ with $\underbrace{i \neq n}_{\text{Note condition}}$ and $\int (\cdots) d\tau$

- Left multiply Eq.(C10) by $\psi_i^{*(0)}$ $(i \neq n)$ and $\int(\cdots)d\tau$

$$\int \psi_i^{*(0)} \hat{H}_0 \psi_n^{(1)} d\tau + \underbrace{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}_{\text{can evaluate}} = E_n^{(1)} \cancelto{0\ (i\neq n)}{\int \psi_i^{*(0)} \psi_n^{(0)} d\tau} + E_n^{(0)} \int \psi_i^{*(0)} \psi_n^{(1)} d\tau$$

[to C24 then back]

$$\sum_{m\neq n} a_m \int \psi_i^{*(0)} \overbrace{\hat{H}_0 \psi_m^{(0)}}^{E_m^{(0)} \psi_m^{(0)}} d\tau + \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau = E_n^{(0)} \sum_{m\neq n} a_m \overbrace{\int \psi_i^{*(0)} \psi_m^{(0)} d\tau}^{\delta_{im}}$$

$$\sum_{m\neq n} a_m E_m^{(0)} \delta_{im} + \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau = E_n^{(0)} a_i \qquad (\text{recall: } i \neq n)$$

$$E_i^{(0)} a_i + \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau = E_n^{(0)} a_i$$

$$\therefore \boxed{a_i = \frac{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_i^{(0)}} = \frac{\langle \psi_i^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}}}$$

Done!

- $i \neq n$ means that i refers to a different state from "n" (want $\psi_n^{(1)}$)
- a_i gives the "mixing in" of $\psi_i^{(0)}$ into $\psi_n^{(0)}$ to approximate ψ_n due to $\hat{H}'$ [to C25]

- Conceptual thought $\hat{H}_0$ only $\rightarrow \psi_n^{(0)}$ for n^{th} state

$\hat{H}_0 + \hat{H}' \rightarrow \psi_n \approx \psi_n^{(0)}$ + (something due to $\hat{H}'$)

Formally, $\underset{\text{perturbed } n^{th} \text{ state}}{\psi_n} = \sum_i a_i \psi_i^{(0)}$ [completeness of $\{\psi_i^{(0)}\}$]

$$= a_n \psi_n^{(0)} + \sum_{m \neq n} a_m \psi_m^{(0)}$$

[Formally, should write the 2^{nd} term as $\sum_{m \neq n} a_{nm} \psi_m$]

By perturbation (微擾), we mean $a_n \approx 1$ [$\psi_n \approx \psi_n^{(0)}$ + tiny corrections]

$$\psi_n \approx \psi_n^{(0)} + \sum_{m \neq n} a_m \psi_m^{(0)}$$

If you really want to normalize it, do it at the end. By the spirit of perturbation theory, it is unnecessary.

$\therefore \underset{1^{st} \text{ order correction}}{\psi_n^{(1)}} = \sum_{m \neq n} a_m \psi_m^{(0)}$ with $\underbrace{a_m \text{ (solved) to } 1^{st} \text{ order in } \hat{H}'}_{\text{see page C23}}$

$$\boxed{\begin{aligned} \psi_n &\approx \psi_n^{(0)} + \sum_{i\neq n} \frac{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_i^{(0)}} \psi_i^{(0)} = \psi_n^{(0)} + \sum_{i\neq n} \frac{\langle \psi_i^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} \psi_i^{(0)} \\ E_n &\approx E_n^{(0)} + \int \psi_n^{(0)} \hat{H}' \psi_n^{(0)} d\tau = E_n^{(0)} + \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \end{aligned}} \quad (C13)$$

Results of 1^{st} order perturbation theory

- Important to understand what the symbols mean
- Don't need to know $\psi_n^{(1)}$ to obtain $E_n^{(1)}$ [we obtained $E_n^{(1)}$ before $\psi_n^{(1)}$]
- But need $\psi_n^{(1)}$ to obtain $E_n^{(2)}$ [c.f. only need $\psi_n^{(0)}$ to get $E_n^{(1)}$]
- Inspect Eq. (C13), $\psi_n^{(1)} \sim \sum_{i\neq n} \frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}} \psi_i^{(0)}$ OK if $E_i^{(0)} \neq E_n^{(0)}$ (differ by much)

If $E_i^{(0)} = E_n^{(0)}$ OR $E_i^{(0)} \approx E_n^{(0)}$ [$i \neq n$ but $\psi_i^{(0)}$ and $\psi_n^{(0)}$ are <u>degenerate</u> states],
a_i becomes big $\Rightarrow$ not in line with the idea of "tiny correction"
$\Rightarrow$ Don't use (C13)

Eq. (C13) applies to a state "n" that is <u>Non-degenerate</u>
(OR no other states $\psi_i^{(0)}$ with energies very close)

Theory is called $\boxed{\text{"Time-independent Non-degenerate Perturbation Theory"}}$

- What if there are $\psi_i^{(0)}$ with $\psi_i^{(0)} = \psi_n^{(0)}$ (OR $\psi_i^{(0)} \approx \psi_n^{(0)}$)?
  - Be careful! Go to <u>Degenerate Perturbation Theory</u> (see later)

<u>Making Physical Sense of Eq. (C13)</u>

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

- Mixing in of $\psi_i^{(0)}$ is

$$\frac{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}{(E_n^{(0)} - E_i^{(0)})}$$

1st order

0th order → $(E_n^{(0)} - E_i^{(0)})$

(1st order)

- Depends on $\underbrace{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}_{H'_{in}\text{: May be big/small}}$ <u>AND</u> $\underbrace{\frac{1}{E_n^{(0)} - E_i^{(0)}}}_{\text{state } i \text{ closer to } E_i^{(0)} \text{ is more important (but not too close)}}$

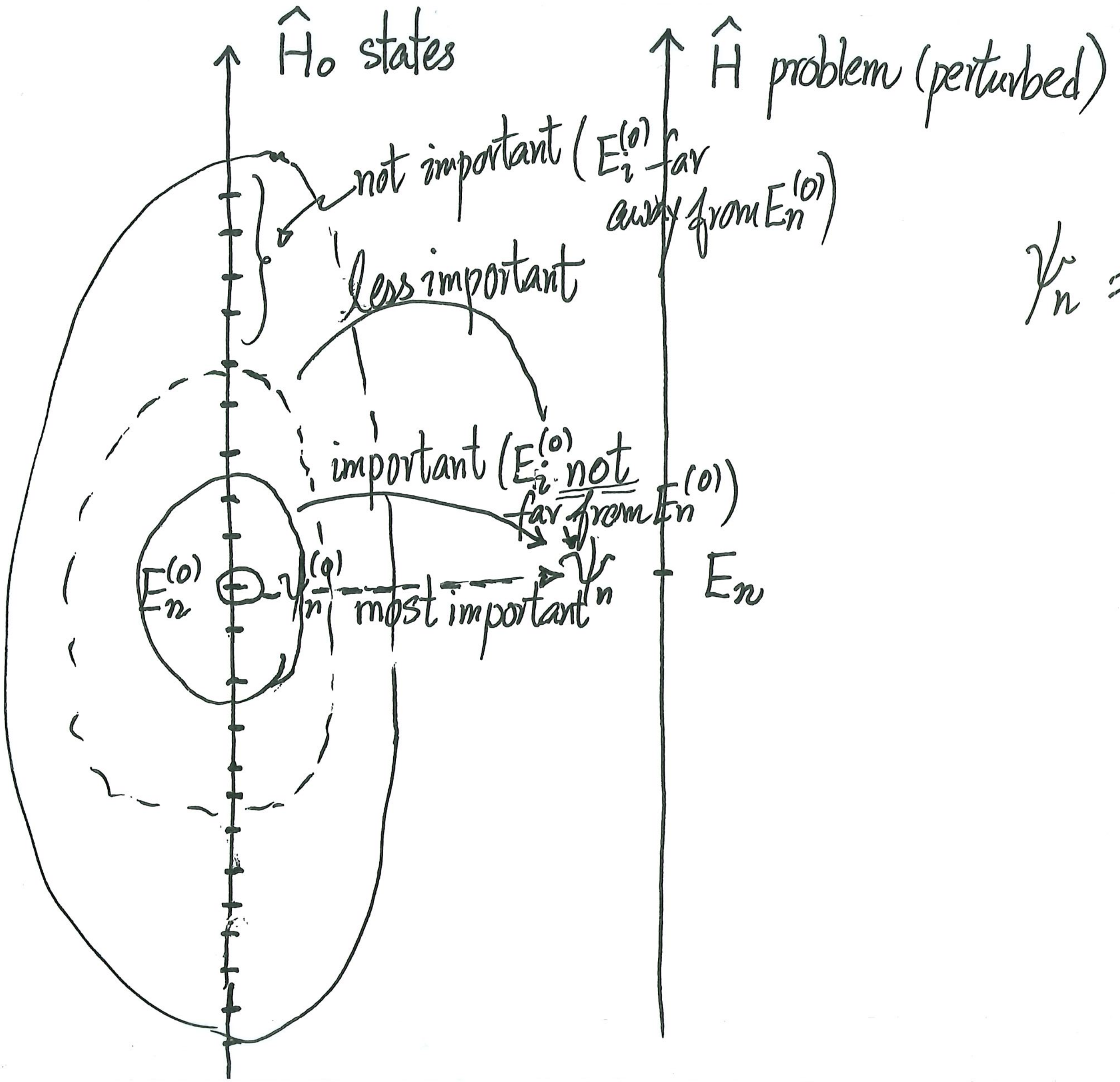
If $\hat{H}' = 0$ (no perturbation), $\psi_n^{(0)}$ & $\psi_i^{(0)}$ have $\underbrace{\text{nothing to do}}_{\text{orthogonal}}$ with each other

$\hat{H}' \neq 0$ serves to "connect" $\psi_n^{(0)}$ & $\psi_i^{(0)}$ via $\underbrace{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}_{\text{mix in } \psi_i^{*(0)} \text{ to describe } \overbrace{\psi_n}^{\text{perturbed}}}$

For states i with $E_i^{(0)}$ very different from $E_n^{(0)}$, i.e.

$$\left| E_n^{(0)} - E_i^{(0)} \right| \gg \left| \int \psi_i^{*(0)} \hat{H} \psi_n^{(0)} d\tau \right|,$$

those states will not get into ψ_n significantly.



$$\psi_n \approx \psi_n^{(0)} + \sum_{\underbrace{i \neq n}} \frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}} \psi_i^{(0)}$$

if you don't want to include all $i (\neq n)$, then include those with $E_i^{(0)}$ closer to $E_n^{(0)}$

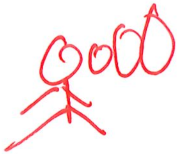
[E.g. Want $\psi_3^{(1)}$? $\psi_2^{(0)}$, $\psi_4^{(0)}$, $\psi_5^{(0)}$ will be important. But $\psi_{238}^{(0)}$ will NOT.]

Step 5: Extracting 2nd order Results from Eq.(C11)

λ^2 Eq.(C11):
$$\hat{H}_0 \underbrace{\psi_n^{(2)}}_{?} + \hat{H}' \psi_n^{(1)} = E_n^{(0)} \underbrace{\psi_n^{(2)}}_{?} + E_n^{(1)} \psi_n^{(1)} + \underbrace{E_n^{(2)}}_{?} \psi_n^{(0)}$$

✓ ≡ known

? ≡ unknown



Want $E_n^{(2)}$? Get stand-alone "$E_n^{(2)}$" from Eq.(C11).

Left multiply (C11) by $\psi_n^{*(0)}$ and $\int(\cdots)d\tau$ will do.

$$\cancel{\underbrace{\int \psi_n^{*(0)} \hat{H}_0 \psi_n^{(2)} d\tau}_{E_n^{(0)} \int \psi_n^{*(0)} \psi_n^{(2)} d\tau \ (\because \text{Hermitian } \hat{H}_0)}} + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(1)} d\tau = \cancel{E_n^{(0)} \int \psi_n^{*(0)} \psi_n^{(2)} d\tau} + \underbrace{E_n^{(1)} \int \psi_n^{*(0)} \psi_n^{(1)} d\tau}_{0} + \overbrace{E_n^{(2)}}^{\text{stand-alone}}$$

$$\left(\because \sim \sum_{i \neq n} a_i \underbrace{\int \psi_n^{*(0)} \psi_i^{(0)} d\tau}_{0\ (i \neq n)}\right)$$

$$\therefore \boxed{E_n^{(2)} = \int \psi_n^{*(0)} \hat{H}' \psi_n^{(1)} d\tau} \quad \text{(C14)}$$

(almost there)

$$\underbrace{\hat{H}' \leftarrow 1^{st} \text{ order} \quad \psi_n^{(1)} \leftarrow 1^{st} \text{ order}}_{2^{nd} \text{ order}}$$

Write result (C14) out in standard form

$$E_n^{(2)} = \int \psi_n^{*(0)} \hat{H}' \psi_n^{(1)} d\tau = \sum_{i \neq n} a_i \int \psi_n^{*(0)} \hat{H}' \psi_i^{(0)} d\tau$$

$$\left(\because \psi_n^{(1)} = \sum_{i \neq n} a_i \psi_i^{(0)} \right)$$

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

$$\left(\because \underbrace{a_i}_{1^{st}\text{ order result}} = \frac{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_i^{(0)}} \right)$$

$$= \sum_{i \neq n} \frac{H'_{in} \cdot H'_{ni}}{E_n^{(0)} - E_i^{(0)}}$$

$$\left(\text{call } H'_{in} = \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \right)$$

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

$$\left(H'_{ni} = H'^{*}_{in} \text{ as } \hat{H}' \text{ is Hermitian} \right)$$

$$= \sum_{i \neq n} \frac{\left| \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \right|^2}{E_n^{(0)} - E_i^{(0)}}$$

Key result!

(C15) 2nd order correction to energy
[non-degenerate perturbation theory]

Physical Sense: Read the physics behind $E_n^{(2)} = \sum_{i \neq n} \frac{\left| \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \right|^2}{E_n^{(0)} - E_i^{(0)}}$

- $|H'_{in}|^2 > 0$ always
- for unperturbed states i with $E_i^{(0)} < E_n^{(0)}$ [those lower than $E_n^{(0)}$], they tend to "push" E_n up in energy ($\because E_n^{(0)} - E_i^{(0)} > 0$)
- for unperturbed states i with $E_i^{(0)} > E_n^{(0)}$ [those higher than $E_n^{(0)}$], they tend to "push" E_n down in energy ($\because E_n^{(0)} - E_i^{(0)} < 0$)
- Net effect depends on "pushing" by all states i (see $\sum_{i \neq n}(\cdots)$)
- But states with $E_i^{(0)}$ far apart from $E_n^{(0)}$ cannot push E_n by much ($\because \propto \frac{1}{E_n^{(0)} - E_i^{(0)}}$)

[e.g. Consider $E_{18}^{(2)}$, $\psi_{16}^{(0)}, \psi_{17}^{(0)}, \psi_{19}^{(0)}, \psi_{20}^{(0)}$ are more important; but $\psi_1^{(0)}$ and $\psi_{88}^{(0)}$ are not.]

- On $\underbrace{H'_{ni}}$ or H'_{in} ("matrix elements") [optional]

$$\int \psi_n^{*(0)} \hat{H}' \psi_i^{(0)} d\tau$$ [gives how strong $\hat{H}'$ can "connect" states $\psi_n^{(0)}$ & $\psi_i^{(0)}$]

$$\frac{H^*_{ni} H_{in}}{E_n^{(0)} - E_i^{(0)}} =$$ 2^{nd} order shift in energy of n^{th} state due to i^{th} state

Pictorially:

- $E_i^{(0)} [\psi_i^{(0)}]$ — i

$\uparrow H'_{ni}$ $\downarrow H'_{in}$

- $E_n^{(0)} [\psi_n^{(0)}]$ — n

$H'_{ni} H'_{in} = |H'_{ni}|^2$ expresses how $\hat{H}'$ connects <u>n to some i</u> and <u>then back to n</u>

$|H'_{ni}|^2$ has unit of (energy)^2

Shift in energy $\sim \dfrac{|H'_{ni}|^2}{\text{some energy}}$ $\leftarrow (E_n^{(0)} - E_i^{(0)})$

"What else can it be?"

Summary: $\hat{H} = \hat{H}_0 + \hat{H}'$ with $\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$

$$E_n \approx E_n^{(0)} + E_n^{(1)} + E_n^{(2)} \quad \text{(to 2nd order)}$$

$$= E_n^{(0)} + \int \psi_n^{*(0)} \hat{H}' \psi_n \, d\tau + \sum_{i \neq n} \frac{\left| \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \right|^2}{E_n^{(0)} - E_i^{(0)}}$$

$$\psi_n \approx \psi_n^{(0)} + \psi_n^{(1)} \quad \text{(to 1st order)} \qquad \text{(C16)}$$

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

Non-degenerate time-independent Perturbation Theory

- We won't work out $\psi_n^{(2)}$, because we won't do $E_n^{(3)}$.

More important to understand the meaning, symbols, and to apply Eqs. (C16).

Picture of the results in Eqs. (C16) [Perturbation Theory]

$\hat{H}_0$ only

Add in $\hat{H}'$

1st order

2nd order

Eigenstates are independent of each other

pushing my energy down (2nd order effect)

(1st order)

$E_n^{(0)}$ — shifted by $\int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$ — where am I?

[Net effect of being pushed up by lower states & pushed down by higher states]

pushing my energy up (2nd order effect)

$E_2^{(0)}$

$E_1^{(0)}$

$$E_n \approx E_n^{0} + E_n^{(1)} + E_n^{(2)}$$