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

$$\underbrace{\hat{H}}_{\text{can't solve analytically}} = \underbrace{\hat{H}_0}_{\text{solvable}} + \underbrace{\hat{H}'}_{\text{perturbation}} \quad \text{and know } \hat{H}_0 \underbrace{\psi_n^{(0)}}_{} = \underbrace{E_n^{(0)}}_{} \underbrace{\psi_n^{(0)}}_{} \quad \text{(C0)}$$

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

- Systematic approach for obtaining correction terms to $E_n^{(0)}$ and $\psi_n^{(0)}$ to 1^{st} order in $\hat{H}'$, 2^{nd} order in $\hat{H}'$, etc.
- Introduce an auxiliary (輔助) parameter λ to book keep the order

Write $$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \quad \text{(C7)}$$ ($\lambda = 1$ 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)
- $\lambda^0, \lambda^1, \lambda^2, \cdots$ (regarding λ being a small number)
  not small, small, smaller, $\cdots$

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

Step 1: [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 $\hat{H}\psi_n = E_n\psi_n$

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

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

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

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

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

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:

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

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

Equating λ^2 terms:

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

- 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 $\psi_n^{(1)}$ & $E_n^{(1)}$

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

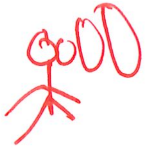
- Need $\{\psi_n^{(0)} \leftrightarrow E_n^{(0)}\}$ & $\{\psi_n^{(1)} \leftrightarrow E_n^{(1)}\}$ in (C11) to get $\psi_n^{(2)}$ & $E_n^{(2)}$

$\therefore$ We must work things out <u>order by order</u>!

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

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

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



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) ; $E_n^{(0)}$ real

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

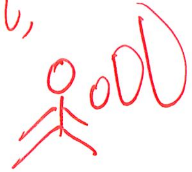
$$LHS = RHS$$

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

1^{st} 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 $\int (\cdots)\, d\tau$

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

[to p. C26 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 p. C27]

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

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

Formally, $\psi_n = \sum_i a_i \psi_i^{(0)}$ [completeness of $\{\psi_i^{(0)}\}$]

perturbed n^{th} state

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

[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.

$$\therefore \psi_n^{(1)} = \sum_{m \neq n} a_m \psi_m^{(0)}$$ with $\underbrace{a_m \text{ (solved) to } 1^{st} \text{ order in } \hat{H}'}_{\text{go back to page C25}}$

1^{st} order correction

meant to be $|a_m| \ll 1$

go back to page C25

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

$$E_n \approx E_n^{(0)} + \int \psi_n^{(0)} \hat{H}' \psi_n^{(0)} d\tau = E_n^{(0)} + \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \quad \text{(C13)}$$

Results of 1st 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 degenerate 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 Non-degenerate
(OR no other states $\psi_i^{(0)}$ with energies very close)

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

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

Making Physical Sense of Eq. (C13)

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

- "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

(1st order)

0th order

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

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

$\hat{H}' \neq 0$ serves to make $\psi_n^{(0)}$ and $\psi_i^{(0)}$ affect each other

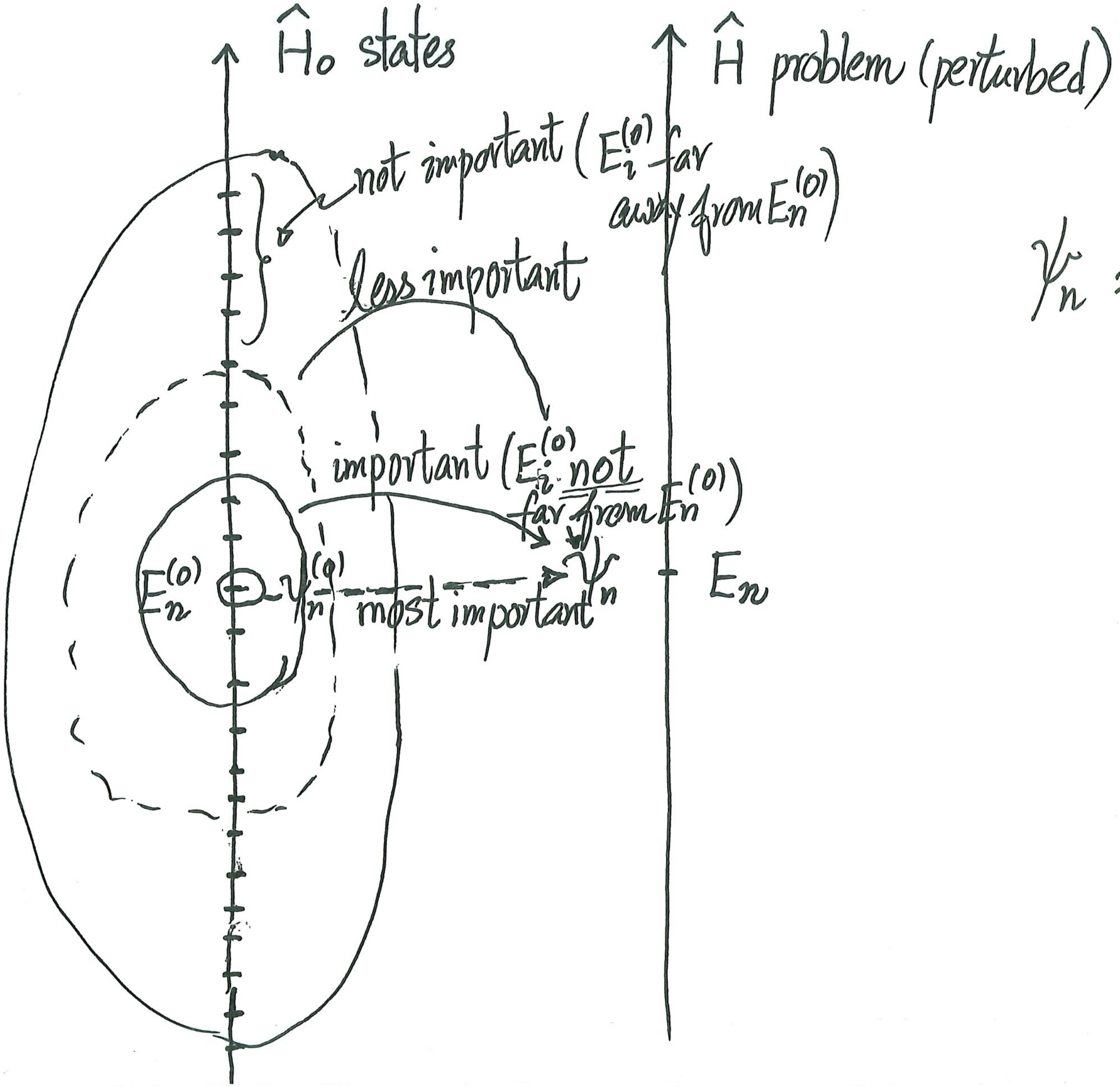
How strong $\psi_i^{(0)}$ can affect ψ_n due to $\hat{H}'$ is determined by

$$\underbrace{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}_{\text{mixing } \psi_i^{*(0)} \text{ into description of } \psi_n} = H'_{in} \quad \text{(unit of energy)}$$

This is the same as $H_{in} \equiv \int \psi_i^{*(0)} (\hat{H}_0 + \hat{H}') \psi_n^{(0)} d\tau = \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau$

For perturbation theory to hold, requires

$$\underbrace{\left| E_n^{(0)} - E_i^{(0)} \right|}_{0^{th}\text{ order energy difference}} \gg \underbrace{\left| \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \right|}_{\text{integral determining mutual influence}} \quad \text{(comparison of two energies)}$$



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

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.]

Hierarchical Structure of the Theory

Need $E_n^{(0)}$ and $\psi_n^{(0)}$

$E_n^{(1)}$ (zeroth order state sufficient for 1st order energy)

$\psi_n^{(1)}$

$E_n^{(2)}$ (need $\psi_i^{(1)}$ for getting 2nd order energy)

$\psi_n^{(2)}$

These can be used to get 3rd order energy
[if we don't need that, stop at $E_n^{(2)}$]