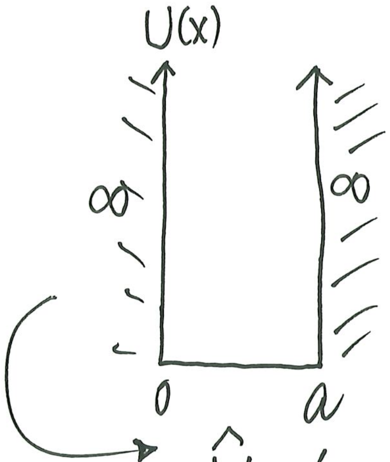
C. Time-independent Perturbation Theories



$$E_n^{(0)} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

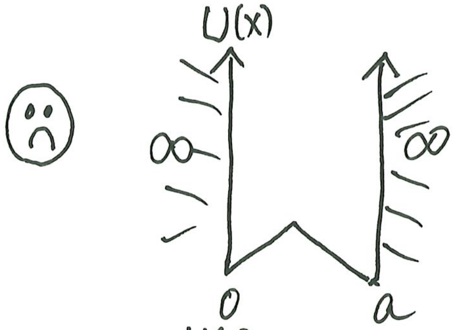
$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi x}{a}\right)$$

$\hat{H}_0$ (analytically solvable)

"(0)" refers to the analytically solvable problem defined by $\hat{H}_0$

$E_n^{(0)}$, $\psi_n^{(0)}(x)$

[called the unperturbed problem]



$\hat{H}$

$\hat{H}$

The Questions are: (take the 7^{th} lowest energy state of the $\hat{H}$ problem, say)

$E_7 = E_7^{(0)}$ + corrections due to change in U(x) ?

$\psi_7 = \psi_7^{(0)}$ + $\underbrace{\text{corrections due to change in } U(x)}$?

can the corrections be expressed systematically in terms of $\{\psi_n^{(0)}\}$ and $\{E_n^{(0)}\}$

(a) $\hat{H} = \hat{H}_0 + \hat{H}'$ and Identifying the perturbation term $\hat{H}'$

$\hat{H}\psi_n = E_n\psi_n$ [Want to solve for $\psi_n \leftrightarrow E_n$; but don't know how]

$\hat{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ [a "nearby" problem, know all solutions, $\psi_n^{(0)} \leftrightarrow E_n^{(0)}$ known]

important idea: $\hat{H}_0$ is not too different from $\hat{H}$

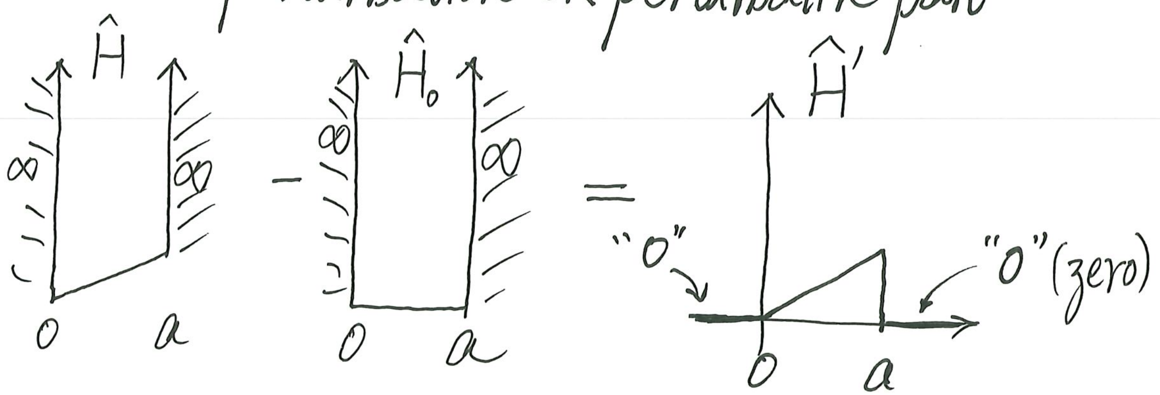
Write: $$\boxed{\hat{H} = \hat{H}_0 + \hat{H}'} \quad \text{(C1)}$$

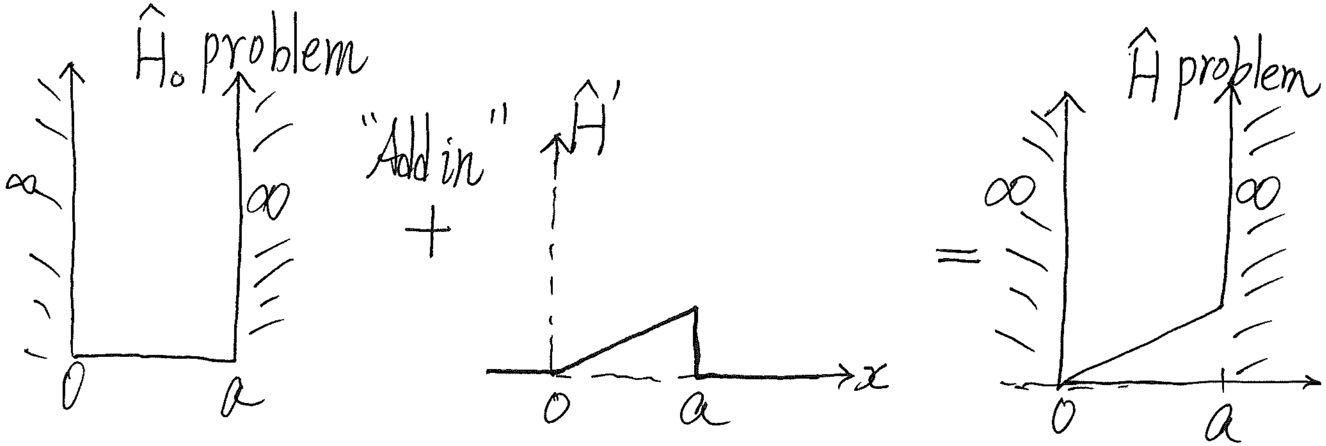
$\hat{H}_0$ should be a big part of the problem defined by $\hat{H}$

perturbation or perturbative part

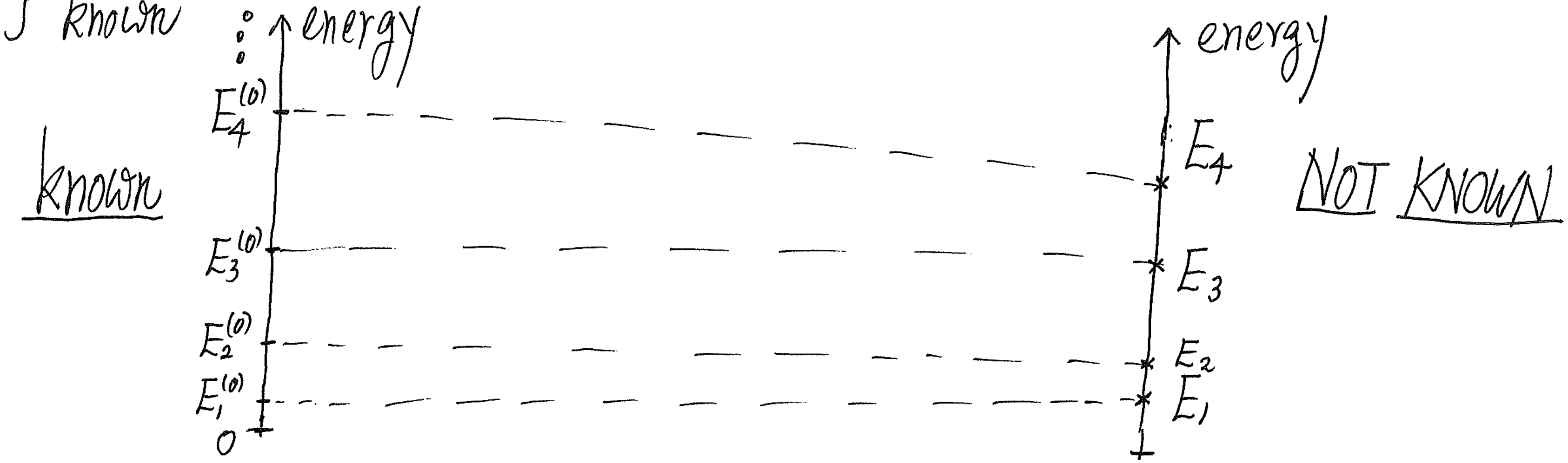
$$\therefore \quad \boxed{\hat{H}' = \hat{H} - \hat{H}_0} \quad \text{(C2)}$$

perturbation





$\{\psi_n^{(0)}\}$ known



e.g. $E_3 \approx E_3^{(0)}$ + corrections due to $\hat{H}'$

Perturbation Theories } $\hat{H}'$ is a small part of the problem defined of $\hat{H}$

- aim to find the "corrections" order-by-order

$\underbrace{1^{st} \text{ order in } \hat{H}'}_{\text{small}}$, $\underbrace{2^{nd} \text{ order in } \hat{H}'}_{\text{smaller}}$, $\underbrace{\ldots}_{\text{even smaller}\ldots}$ and we can stop at 1^{st} or 2^{nd} order

Before exploring effects of $\hat{H}'$, let's appreciate what $\hat{H}_0$ does

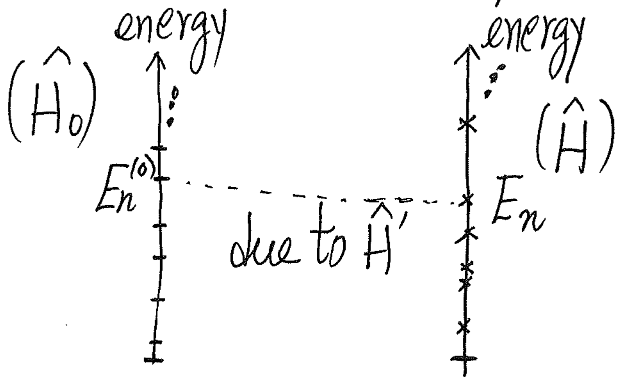
- $\hat{H}_0$ is chosen to be big part of $\hat{H}$
- $\hat{H}_0$ is a solvable TISE problem
- Not many solvable $\hat{H}_0$ problems! [1D, 2D, 3D infinite wells, harmonic oscillators, 2D/3D rotators, $U(r)$, H-atom]
- Don't know solutions $\{E_n^{(0)}\}$ and $\{\psi_n^{(0)}\}$ to $\hat{H}_0$, can't do perturbation!
- Connection to Sec. A: $\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ [known]

  $\{\psi_n^{(0)}\}$ is a complete set (orthonormal) [Hermitian $\hat{H}_0$]

  $\therefore$ $\{\psi_n^{(0)}\}$ can be used as basis function to turn the problem

  $\underbrace{\hat{H}\psi = E\psi}_{\text{no analytic solutions}}$ into a huge matrix problem [exactly]

(b) "Lazy/Clever Approach": Let's guess at the 1^{st} order correction



Pick a state "n" (say) [any, doesn't matter]

- know $E_n^{(0)}$ and $\psi_n^{(0)}$ (two quantities for the chosen "n")
- know $\hat{H}' = \hat{H} - \hat{H}_0$

- Want to guess E_n (estimate E_n) up to 1^{st} order in $\hat{H}'$

Argument: "What else can it be?"

- Want an energy
- know $\psi_n^{(0)}$
- know $\hat{H} = \hat{H}_0 + \hat{H}'$

How about the expectation value of $\hat{H}$ w.r.t. $\psi_n^{(0)}$?

give an energy knowing $\psi_n^{(0)}$ and $\hat{H}$

$$E_n \approx \int \underbrace{\psi_n^{*(0)}}_{0^{th}\text{ order}} \underbrace{\hat{H}}_{\substack{\text{up to } 1^{st}\text{ order} \\ (\hat{H}_0 + \hat{H}')}} \underbrace{\psi_n^{(0)}}_{0^{th}\text{ order}} \, d\tau \qquad (C3)$$

Let's see... $E_n \approx \int \psi_n^{*(0)} \hat{H} \psi_n^{(0)} d\tau = \int \psi_n^{*(0)} \underbrace{\hat{H}_0 \psi_n^{(0)}}_{E_n^{(0)} \psi_n^{(0)}} d\tau + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau$

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

Key Result[†]

first-order time-independent perturbation theory

$\therefore$

$$\boxed{\begin{aligned} E_n &\approx E_n^{(0)} + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \\ &= E_n^{(0)} + E_n^{(1)} \end{aligned}}$$

OR $E_n \approx E_n^{(0)} + \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$ (C4)

$E_n^{(0)}$: 0th order (no $\hat{H}'$ effect)

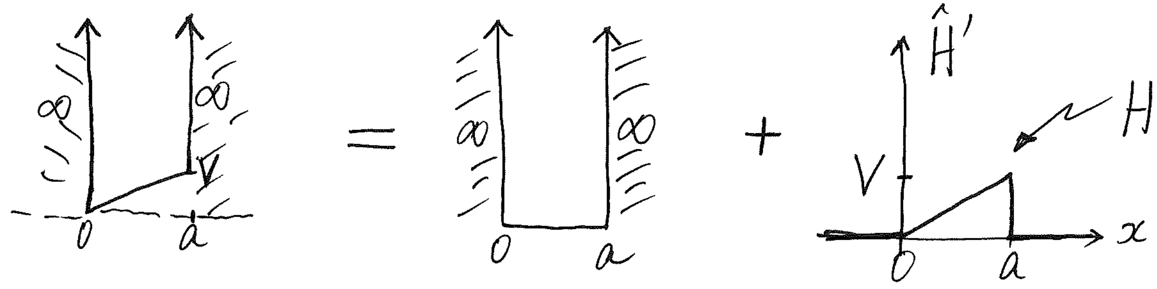
$E_n^{(1)}$: 1st order correction due to $\hat{H}'$

In words, the 1st order correction to energy $E_n^{(1)}$ is the expectation value of the perturbation $\hat{H}'$ w.r.t. the unperturbed state $\psi_n^{(0)}$.

- A very important result in applying QM
- More important to know what (C4) means and how to apply it than deriving it

† Derivation will be given later

Example



$H' = \frac{x}{a}V \quad (0<x<a)$

Ground state energy of tilted well

$$E_1 \approx E_1^{(0)} + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} dx = E_1^{(0)} + \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\underbrace{\left(\frac{x}{a}V\right)}_{\hat{H}'}\sin\left(\frac{\pi x}{a}\right) dx$$

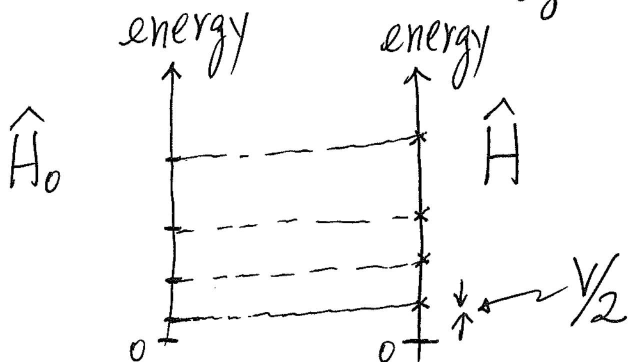
$$= E_1^{(0)} + \frac{2V}{a^2}\int_0^a x \sin^2\left(\frac{\pi x}{a}\right)dx = E_1^{(0)} + \frac{2V}{a^2}\left(\frac{a}{\pi}\right)^2\int_0^\pi y \sin^2 y\, dy$$

$$= E_1^{(0)} + \frac{V}{2} = \frac{\pi^2\hbar^2}{2ma^2} + \frac{V}{2}$$

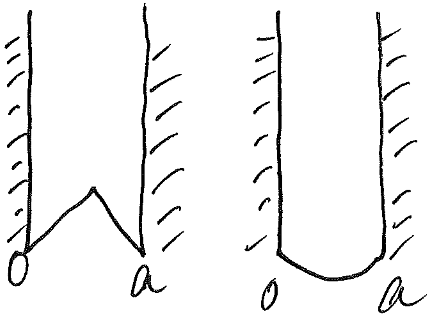
$\underbrace{\text{(shifted up by } \tfrac{V}{2}}_{\text{makes sense (?)}}\text{, 1st order result)}$

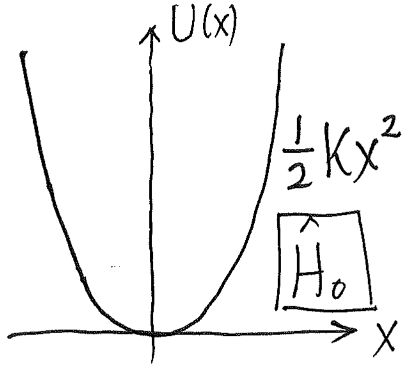
Exercise: Show

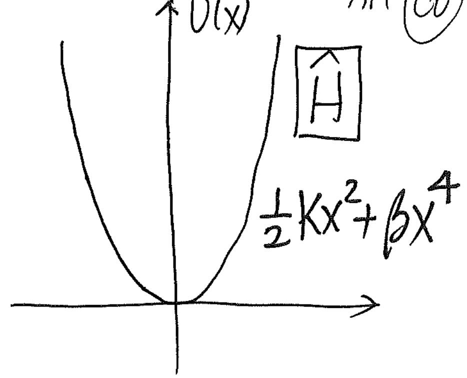
$$E_n \approx E_n^{(0)} + \frac{2V}{a^2}\int_0^a x \sin^2\left(\frac{n\pi x}{a}\right)dx = E_n^{(0)} + \frac{V}{2} \quad \left(\text{all energies shifted by } \frac{V}{2}\right)$$



Ex. Try







We are *free* (from analytically solvable problems) at last!

- Suddenly, $E_n \approx E_n^{(0)} + \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$ allows us to study a large number of QM problems
- But don't be carried away ...
  - Check point: Meaning of E_n, $E_n^{(0)}$, $\hat{H}'$, $\psi_n^{(0)}$ in the formula?
  - Derivation?
  - How about 2^{nd} order correction $E_n^{(2)}$?
  - How about 1^{st} order correction to the n^{th} state's wavefunction?
  - Any limit on its validity?

What is 1st order approximation in the Huge Matrix Picture?

$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ (known) $\quad \{\psi_n^{(0)}\}$ is a natural choice of basis functions

Write $\hat{H}\psi = E\psi$ into a matrix

- Formally, matrix elements are $H_{ji} - ES_{ji}$

But $\{\psi_n^{(0)}\}$ are orthonormal $\Rightarrow S_{ii} = 1, \; S_{ij} = 0$

$$\therefore \begin{vmatrix} H_{11}-E & H_{12} & H_{13} & \cdots & H_{1n} & \cdots \\ H_{21} & H_{22}-E & H_{23} & \cdots & H_{2n} & \cdots \\ H_{31} & H_{32} & H_{33}-E & \cdots & H_{3n} & \cdots \\ \vdots & \vdots & \vdots & \ddots & \vdots & \\ H_{n1} & H_{n2} & H_{n3} & \cdots & H_{nn}-E & \cdots \\ \vdots & \vdots & \vdots & & \vdots & \end{vmatrix} = 0$$

equation to solve for E

(Exact!)

(see Sec. A)

(C5)

- Let's make the simplest possible approximation

$$\boxed{\underline{\text{Ignore}} \text{ all } H_{ij} \text{ with } i \neq j \text{ (ignore all off-diagonal elements)!}}$$

Eq.(C5) becomes

$$\begin{vmatrix} H_{11}-E & & & \text{all zeros} \\ & H_{22}-E & & \\ & & H_{33}-E & \\ \text{all zeros} & & & \ddots \end{vmatrix} = 0 \qquad \text{(C6)}$$

Simplest Approximation!

Many "1×1" problems

$$E_n \approx H_{nn} \quad \text{(every } n\text{)}.$$

$$\Rightarrow \boxed{E_n = \int \psi_n^{*(0)} \hat{H} \psi_n^{(0)} d\tau = E_n^{(0)} + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}$$

which is the 1st order formula (C4)

- 1st order approximation amounts to ignoring off-diagonal terms
- Also imply that we should consider H_{ij} $(i \neq j)$ in higher-order corrections

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

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

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

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

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

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

- 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.]

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

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

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

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

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

But LHS = RHS should hold for arbitrary value of λ

$$\therefore \left.\begin{array}{l} \lambda^0 \text{ terms on LHS \& RHS must be equal} \\ \lambda^1 \text{ terms} \quad \cdots \quad \text{must be equal} \\ \lambda^2 \text{ terms} \quad \cdots \quad \text{must be equal} \\ \vdots \end{array}\right\} \text{Key idea}$$

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.

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

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

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

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))]

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 $i \neq n$ and $\int (\cdots) d\tau$

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

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

[Formally, should write the 2nd 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.

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

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

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

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

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

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

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

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

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

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 <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

$$\frac{\int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \leftarrow \text{1st order}}{\text{0th order} \rightarrow (E_n^{(0)} - E_i^{(0)})} \quad \text{(1st order)}$$

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

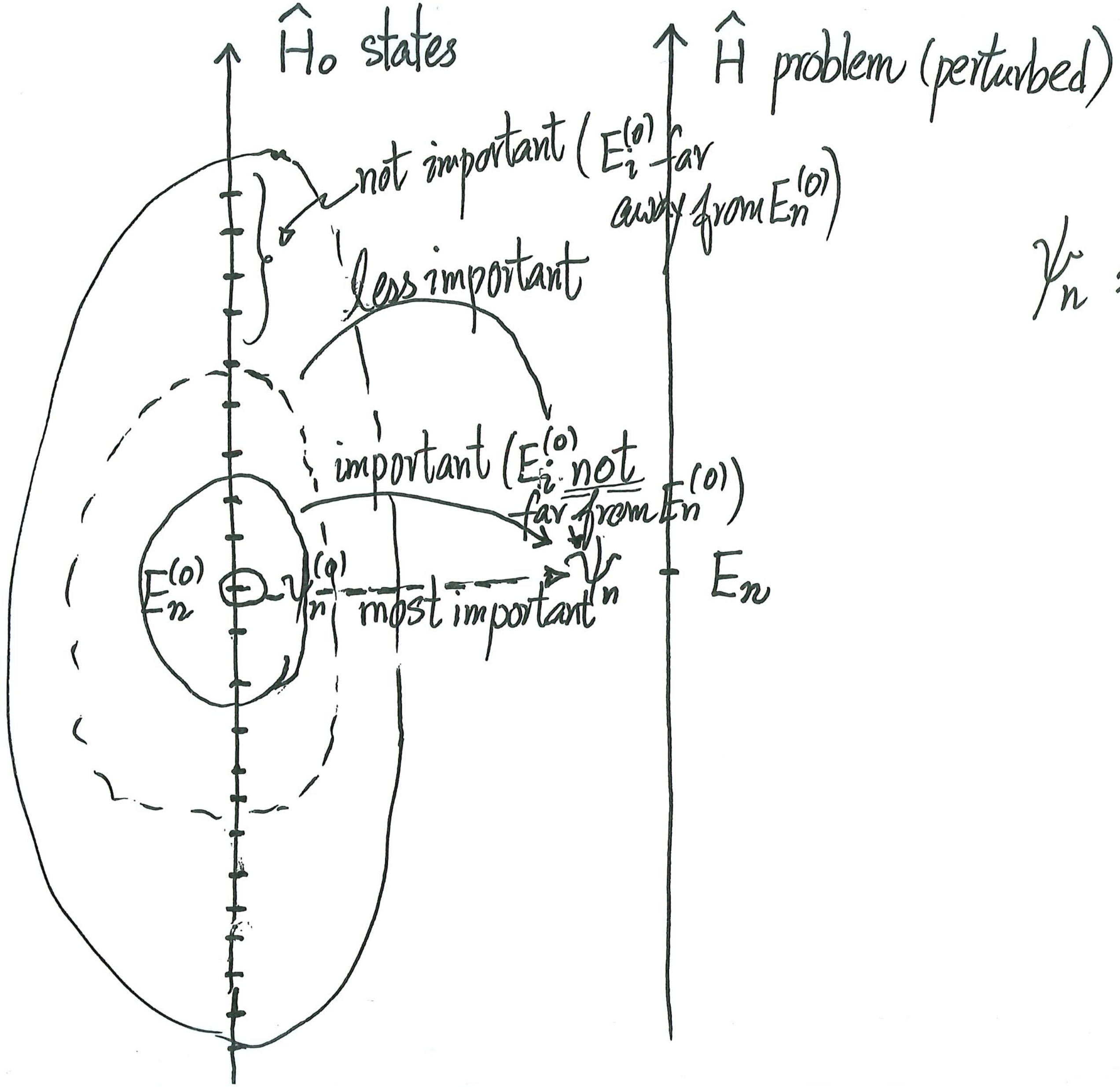
If $\hat{H}' = 0$ (no perturbation), $\psi_n^{(0)}$ & $\psi_i^{(0)}$ have $\underbrace{\text{nothing to do}}_{\text{orthogonal}}$ with each other

$\hat{H}' \neq 0$ 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.



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

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

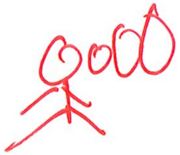
Step 5: Extracting 2nd order Results from Eq. (C11)

λ^2 Eq. (C11)

$$\overset{\checkmark}{\hat{H}_0}\underbrace{\psi_n^{(2)}}_{?} + \overset{\checkmark}{\hat{H}'}\overset{\checkmark}{\psi_n^{(1)}} = \overset{\checkmark}{E_n^{(0)}}\underbrace{\psi_n^{(2)}}_{?} + \overset{\checkmark}{E_n^{(1)}}\overset{\checkmark}{\psi_n^{(1)}} + \underbrace{E_n^{(2)}}_{?}\overset{\checkmark}{\psi_n^{(0)}}$$

$\checkmark \equiv$ known

$? \equiv$ 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.

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

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

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

(almost there)

$\hat{H}'$: 1st order, $\psi_n^{(1)}$: 1st order $\Rightarrow$ 2nd order

Write result (C14) out in standard form

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

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

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

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

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

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

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

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

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

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.]

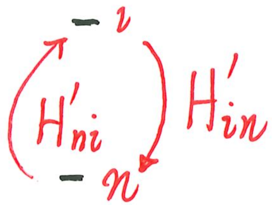
- On $\underbrace{H'_{ni}}$ or H'_{in} ("matrix elements") [optional]

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

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

Pictorially: $- E_i^{(0)} [\psi_i^{(0)}]$

$- E_n^{(0)} [\psi_n^{(0)}]$



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

$|H'_{ni}|^2$ 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?"

<u>Summary</u>- $\hat{H} = \hat{H}_0 + \hat{H}'$ 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

$E_n^{(0)}$

$E_2^{(0)}$

$E_1^{(0)}$

pushing my energy down (2nd order effect)

(1st order)

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)