Time-independent Perturbation Theory: Formalism

- Deriving 1^{st} and 2^{nd} order results

Recap: 1^{st} order in energy $\quad E_n \approx E_n^{(0)} + E_n^{(1)} = E_n^{(0)} + \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$

(C4)

$\hat{H}_0 + \hat{H}' \rightsquigarrow \hat{H}\psi = E\psi$ in matrix form with basis $\{\psi_n^{(0)}\}$

$$\begin{pmatrix} H_{11} & H'_{12} & H'_{13} & \cdots \\ H'_{21} & H_{22} & H'_{23} & \cdots \\ H'_{31} & H'_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix}, \quad \text{thus} \quad \underbrace{\begin{vmatrix} H_{11}-E & H'_{12} & H'_{13} & \cdots \\ H'_{21} & H_{22}-E & H'_{23} & \cdots \\ H'_{31} & H'_{32} & H_{33}-E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}}_{\text{gives allowed energies } E} = 0$$

(C5')

Exact

(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 $\hat{H} = \hat{H}_0 + \lambda \hat{H}'$ (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, $\cdots$ (regarding λ being a small number)

  not small, small, smaller, $\cdots$

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

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

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

"superscript" labels the order

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

- 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: $\underbrace{\hat{H}}_{\hat{H}_0 + \lambda \hat{H}'} \psi_n = E_n \psi_n$ (TISE)

(set $\lambda = 1$ later)

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

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

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

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

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

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

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 $\lambda^0, \lambda^1, \lambda^2, \dots$

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, for energy only]
- 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 $\psi_n^{(1)}$ & $E_n^{(1)}$

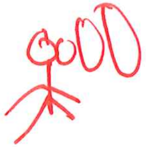
$$\underbrace{\hat{H}_0 \psi_n^{(1)}}_{\psi_n^{(1)}\text{ to solve}} + \hat{H}' \psi_n^{(0)} = \underbrace{E_n^{(1)}}_{\text{to solve}} \psi_n^{(0)} + E_n^{(0)} \underbrace{\psi_n^{(1)}}_{\text{to solve}} \qquad \text{(C10)}$$

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


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

(∵ $\hat{H}_0$ is Hermitian) $$\int \psi_n^{(1)} (\hat{H}_0 \psi_n^{(0)})^* d\tau = \overset{\text{real}}{E_n^{(0)}} \int \psi_n^{*(0)} \overset{\text{not known yet}}{\psi_n^{(1)}} d\tau$$

the same

RHS becomes
$$E_n^{(1)} \underbrace{\int \psi_n^{*(0)} \psi_n^{(0)} d\tau}_{=1} + E_n^{(0)} \int \psi_n^{*(0)} \psi_n^{(1)} d\tau = \underset{\text{stand-alone}}{E_n^{(1)}} + E_n^{(0)} \int \psi_n^{*(0)} \psi_n^{(1)} d\tau$$

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))]

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

  Note condition ($\because$ orthogonal)

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

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

[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]

- Physical Sense / Conceptually thinking...

$$\hat{H}_0 \text{ only} : \psi_n^{(0)} \text{ for } n^{th} \text{ state (no correction term)}$$

$$\hat{H}_0 + \hat{H}' \rightarrow \psi_n = \psi_n^{(0)} + \overbrace{\underbrace{\text{correction term}}_{\hat{H}' \text{ mixes in } \psi_{m\,(m\neq n)}^{(0)} \text{ to give correction term}}}^{\text{due to } \hat{H}'}$$

[question becomes finding correction term to 1st order of $\hat{H}'$ (integrals)]

$$\therefore \text{ Write } \psi_n \approx \psi_n^{(0)} + \psi_n^{(1)} = \psi_n^{(0)} + \sum_{m\neq n} a_{nm}^{(1)} \psi_m^{(0)}$$

i.e. $$\psi_n^{(1)} = \sum_{m \neq n} \underbrace{a_{nm}^{(1)}}_{\uparrow} \psi_m^{(0)}$$

1st order correction of n^{th} state wavefunction

unknowns (find them)

(mixes in $\psi_m^{(0)}$ due to 1st order in H')

we hope/expect $|a_{nm}^{(1)}| \ll 1$

To save notations, we simply write

$$\psi_n^{(1)} = \sum_{m \neq n} \underbrace{a_m}_{\uparrow} \psi_m^{(0)}$$

(we won't do 2nd order correction in wavefunction)

Solve for coefficients a_m $(m \neq n)$ to 1st order in H'

Eq. (C10) does just that!

(Go Back to p. C25)

Collecting results up to 1st order

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

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

Results of 1st order Time-independent Non-degenerate Perturbation Theory

- Must understand meaning of symbols
- Only need $\psi_n^{(0)}$ to obtain $E_n^{(1)}$
- Need $\psi_n^{(1)}$ to obtain $E_n^{(2)}$
- Validity?

We have $\psi_n^{(1)} = \sum_{i \neq n} \underbrace{\frac{\int \psi_i^{(0)*} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_i^{(0)}}} \psi_i^{(0)}$

Read Physics out of result

- gives how much $\psi_i^{(0)}$ is mixed into the perturbed problems ψ_n due to $\hat{H}'$
- 1^{st} order because $\langle \psi_i^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$ is involved
- H'_{in} matrix elements matter
- $E_n^{(0)} - E_i^{(0)}$ or $\underbrace{\frac{1}{E_n^{(0)} - E_i^{(0)}}}$ matters

won't work if $E_i^{(0)} \approx E_n^{(0)}$
(non-degenerate perturbation theory)

For the perturbation theory to work (logically consistent), we require

$$\underbrace{\left| \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \right|}_{\text{integral determining how strong } \psi_i^{*(0)} \text{ can affect } \psi_n^{(0)} \text{ due to } \hat{H}' \text{ (mutual influence)}} \ll \underbrace{\left| E_n^{(0)} - E_i^{(0)} \right|}_{\text{zeroth order energy difference (related to } \hat{H}_0 \text{ unperturbed problem)}}$$

Comparing two energies

This is the criteria of Validity

Warning Sign: For states $\psi_i^{(0)}$ [if exist] with $E_i^{(0)} \approx E_n^{(0)}$, then be careful. Effects of these states Cannot be handled by this formula. So state n should be "non-degenerate"

This is why we call the theory "Time-independent Non-degenerate Perturbation Theory"

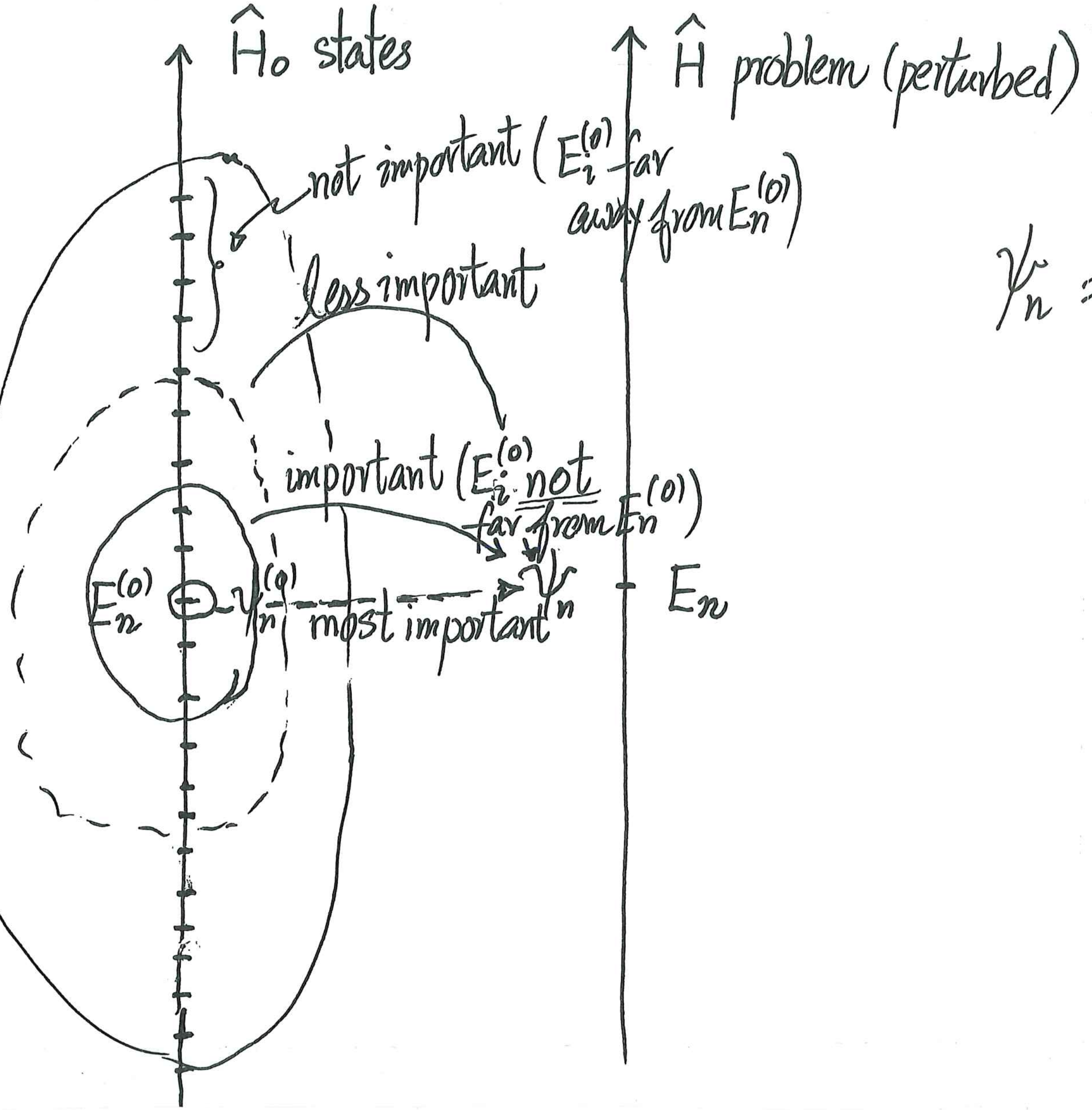
Question:

What if there are $\psi_i^{(0)}$ with $E_i^{(0)} = E_n^{(0)}$ (degenerate states) and/or $\psi_i^{(0)}$ with $E_i^{(0)} \approx E_n^{(0)}$ such that

$$\left| E_n^{(0)} - E_i^{(0)} \right| \lesssim \left| \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau \right| \; ?$$

Answer:

We can readily (easily) develop a Degenerate Perturbation Theory to handle these cases. The theory can be developed easily by the matrix picture of the TISE problem (see later).



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

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.]

Hierarchical Structure of the Theory

Given $\hat{H}'$, Need $E_n^{(0)}$ and $\psi_n^{(0)}$

$\begin{cases} E_n^{(1)} \\ \psi_n^{(1)} \end{cases}$ (zeroth order state sufficient for 1^{st} order energy)

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

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

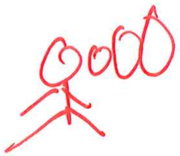
- Now you saw the 1^{st} order perturbation theory
- We we did is the Rayleigh - Schrödinger (non-degenerate) perturbation theory for analyzing the modifications of discrete energy levels and of the corresponding eigenfunctions when a perturbation $\hat{H}'$ is applied to a solvable problem $\hat{H}_0$
- We saw an example of a good (systematic) approach. Moral of the Story:
  - Go head, make approximation, get at a result
  - Result will tell you when it works and it fails!

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.

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

(cancel with 1st term on LHS)

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

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

(almost there)

1st order 1st order (known!)

2nd order

Write result (C14) out in standard form

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

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

$$= \sum_{i \neq n} \frac{H'_{in} \cdot H'_{ni}}{E_n^{(0)} - E_i^{(0)}} \qquad \left(\text{call } H'_{in} = \int \psi_i^{*(0)} \hat{H}' \psi_n^{(0)} d\tau\right)$$

$$= \sum_{i \neq n} \frac{|H'_{in}|^2}{E_n^{(0)} - E_i^{(0)}} \qquad \left(H'_{ni} = H'^{*}_{in} \text{ as } \hat{H}' \text{ is Hermitian}\right)$$

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

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")

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

or how $\psi_i^{(0)}$ can affect $\psi_n^{(0)}$ due to presence of $\hat{H}'$ (as in a_i in (C13))

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

Pictorially:

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

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

H'_{ni} H'_{in}

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

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

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

"What else can it be?"

<u>Summary</u>- $\hat{H} = \hat{H}_0 + \hat{H}'$ with $\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$

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

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

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

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

Non-degenerate time-independent Perturbation Theory

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

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

In the Dirac Notation,

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

$$= E_n^{(0)} + \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle + \sum_{i \neq n} \frac{|\langle \psi_i^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_i^{(0)}}$$

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

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

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)

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

<u>Remark</u> (see also Problem Set):

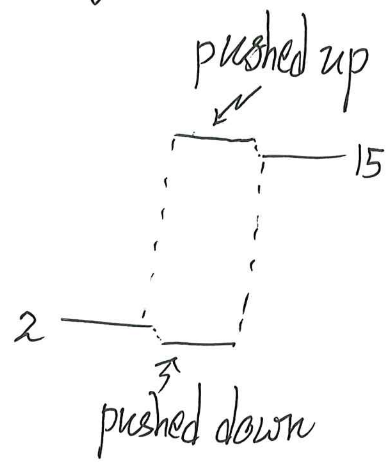
The 2^{nd} order result reminded us of some matrix math

E.g. $\begin{pmatrix} 2 & 1 \\ 1 & 15 \end{pmatrix}$ can find exact eigenvalues easily

but

$$E_1 \approx 2 + \frac{1^2}{2-15} = 2 - \frac{1}{13}$$
(close to 2)

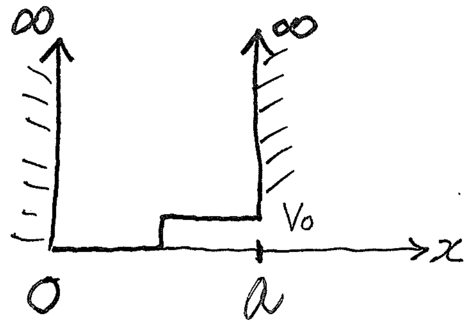
$$E_2 \approx 15 + \frac{1^2}{15-2} = 15 + \frac{1}{13}$$
(close to 15)

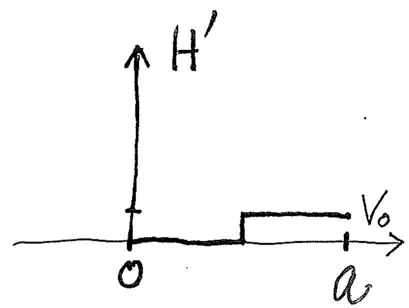


Perturbation results must be related to approximating the exact big matrix of a QM problem, written in the basis of the "unperturbed" (known) eigenfunctions of $\hat{H}_0$.

D. Example

A step in 1D infinite well





Unperturbed system: $E_n^{(0)} = \dfrac{n^2\pi^2\hbar^2}{2ma^2}$; $\psi_n^{(0)} = \sqrt{\dfrac{2}{a}}\sin\left(\dfrac{n\pi x}{a}\right)$, $n=1,2,3,\ldots$

Q: Shift in energy for ground state by perturbation theory?

[1st order] $\underset{\text{G.S.}}{E_1^{(1)}} \leftarrow$ 1st order shift

$$E_1^{(1)} = \int_0^a \psi_1^{*(0)}\hat{H}'\psi_1^{(0)}dx = \frac{2}{a}\int_{a/2}^{a} V_0 \sin^2\left(\frac{\pi x}{a}\right)dx = \frac{V_0}{2} \quad \text{(Ex.)}$$

[2nd order] Need

$$\int_0^L \psi_{m\,(m\neq 1)}^{*(0)}\hat{H}'\psi_1^{(0)}dx = \frac{2}{a}V_0\int_{a/2}^{a}\sin\left(\frac{m\pi x}{a}\right)\cdot\sin\left(\frac{\pi x}{a}\right)dx$$

$$= \frac{2V_0}{\pi}\int_{\pi/2}^{\pi}\sin(my)\sin y\,dy = \frac{2V_0}{\pi}\,\frac{m\cos\left(\frac{m\pi}{2}\right)}{m^2-1} \quad \text{(Ex.)}$$

$$= \begin{cases} \dfrac{2V_0}{\pi}\,\dfrac{m\cos\left(\frac{m\pi}{2}\right)}{m^2-1} & \text{for } m=2,4,6,\ldots \\ 0 & \text{for } m=3,5,7,\ldots \quad \text{[Why so?]} \end{cases}$$

$$\therefore E_1 \approx E_1^{(0)} + E_1^{(1)} + E_1^{(2)} \approx \underbrace{\frac{\pi^2\hbar^2}{2ma^2}}_{0^{th}\text{ order}} + \underbrace{\frac{V_0}{2}}_{\substack{1^{st}\text{ order}\\ \text{(shift up)}}} + \underbrace{\sum_{m=2,4,\ldots} \frac{4V_0^2}{\pi^2} \frac{m^2\cos^2\left(\frac{m\pi}{2}\right)}{(m^2-1)^2} \frac{1}{\left(\frac{\pi^2\hbar^2}{2ma^2}\right)\underbrace{(1-m^2)}}}$$

- 2^{nd} order [pushed down by $m=2,4,\ldots$ states]
- Most important term is $m=2$, effect drops as m increases

By-product:

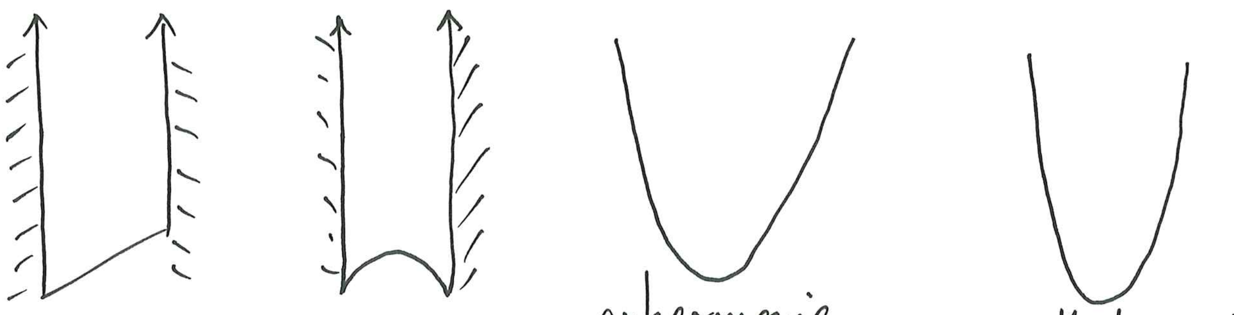
$$\underbrace{\psi_1}_{\text{up to }1^{st}\text{ order}} \approx \psi_1^{(0)} + \psi_1^{(1)} \approx \psi_1^{(0)} + \underbrace{\sum_{m=2,4,\ldots} \frac{2V_0}{\pi} \frac{m\cos\left(\frac{m\pi}{2}\right)}{m^2-1} \cdot \frac{1}{\left(\frac{\pi^2\hbar^2}{2ma^2}\right)(1-m^2)} \cdot \psi_m^{(0)}}$$

- mix in $\psi_2^{(0)}, \psi_4^{(0)}, \ldots$ to $\psi_1^{(0)}$
- most important mixing from $\psi_2^{(0)}$, other drops as m increases
- Practically, OK to keep only a few terms

Extensions

- Relate results here to variational approach using $\phi_{trial} = c_1\psi_1^{(0)} + c_2\psi_2^{(0)}$
- Think: What perturbation theory tells us what variational method doesn't?

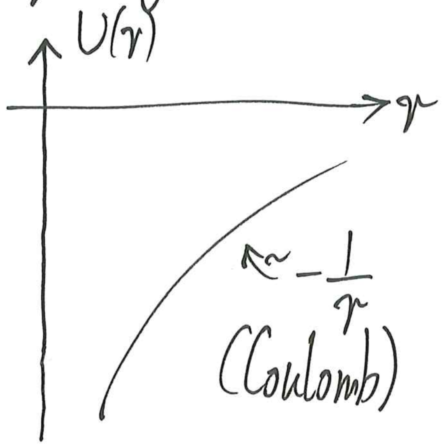
- Try



anharmonic oscillator

oscillator with quartic term

Hydrogen Atom + (something)



$$+ \begin{cases} \text{electric field (atomic polarizability)} \\ \text{magnetic field (Zeeman effects)} \\ \text{spin-orbit coupling (total angular momentum)} \\ \text{relativistic correction} \\ \vdots \end{cases}$$

Helium Atom

$$\hat{H}_{Helium} = \left(\frac{-\hbar^2}{2m} \nabla^2_{\vec{r}_1} - \frac{2e^2}{4\pi\varepsilon_0 r_1} \right) + \left(\frac{-\hbar^2}{2m} \nabla^2_{\vec{r}_2} - \frac{2e^2}{4\pi\varepsilon_0 r_2} \right) + \overbrace{\frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}}^{\hat{H}'}$$

(a real problem)