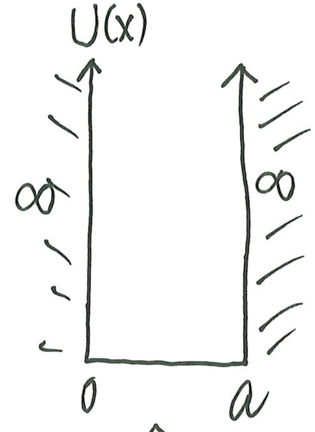
C. Time-independent Perturbation Theories



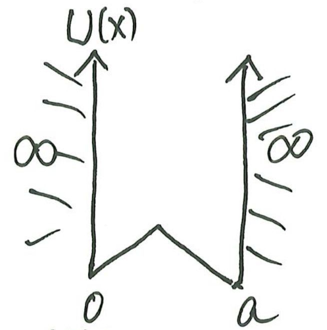
$$E_n^{(0)} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

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

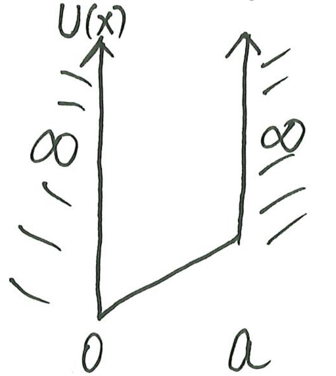
$\hat{H}_0$ (analytically solvable)

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

$\underbrace{E_n^{(0)},\ \psi_n^{(0)}(x)}_{\text{knowns!}}$



$\hat{H}$



$\hat{H}$

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

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

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

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 $\hat{H}$

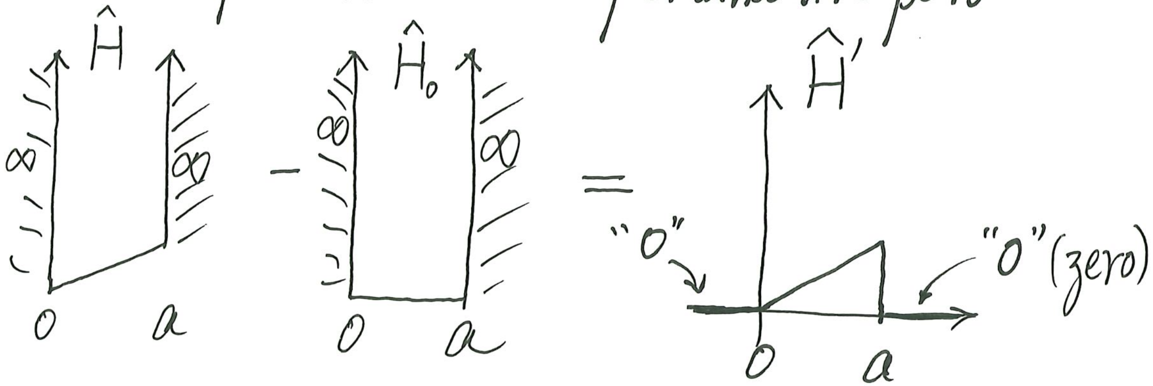
Write: ☹ $\boxed{\hat{H} = \hat{H}_0 + \hat{H}'}$ (C1) ☺

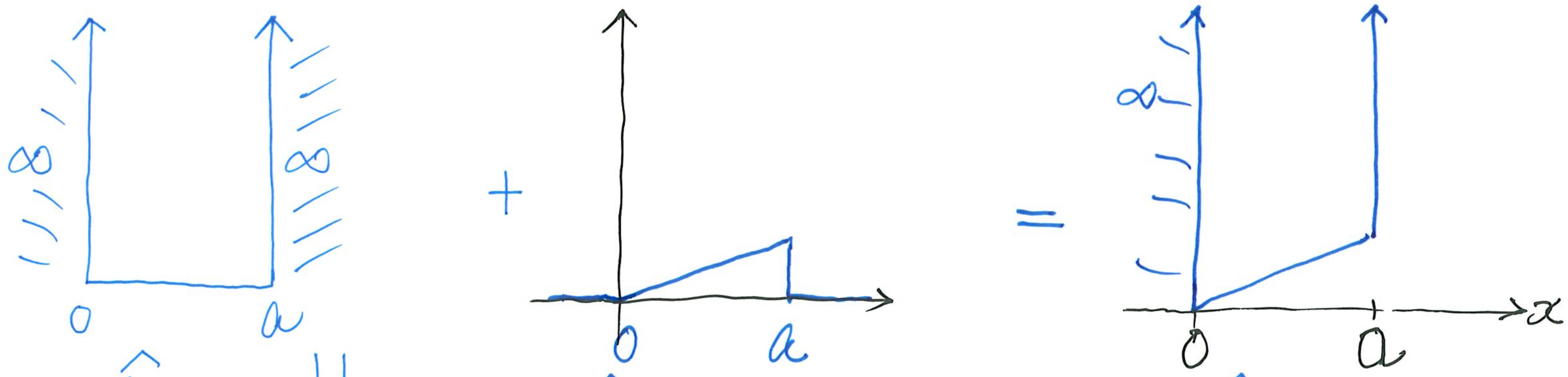
$\hat{H}_0$ should be a big part of the problem defined by $\hat{H}$

perturbation or perturbative part

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

perturbation





$\underbrace{\hat{H}_0 \text{ problem}}$

capture big part of $\hat{H}$ problem and $\{E_n^{(0)}\}$ & $\{\psi_n^{(0)}\}$ are known

$\underbrace{\hat{H}' \text{ problem}}$

small part of $\hat{H}$ problem

give corrections to $E_n^{(0)}$ that give E_n

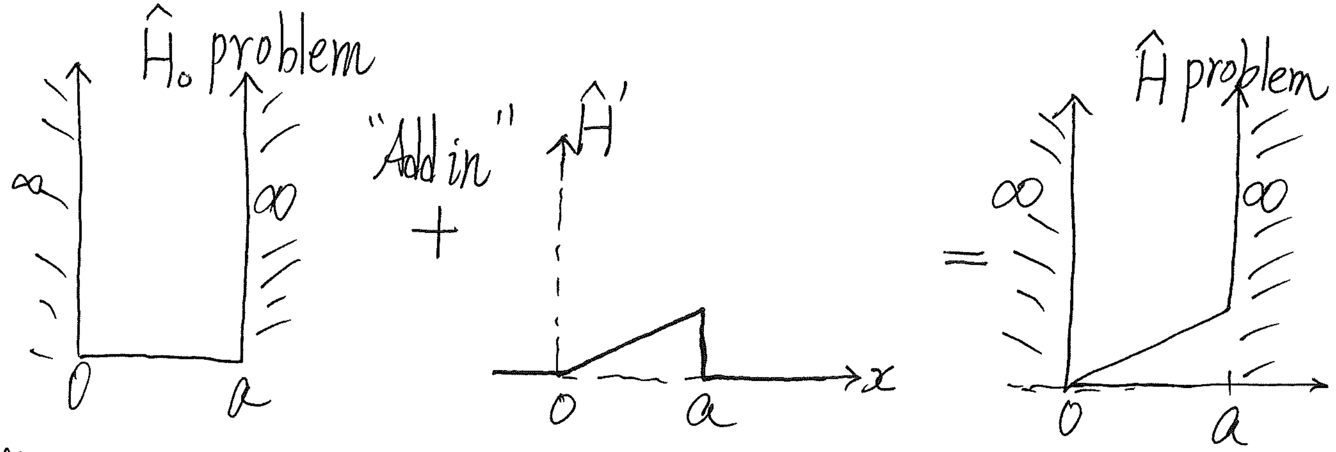
$(\psi_n^{(0)})$ (ψ_n)

$\underbrace{\hat{H} \text{ problem}}$

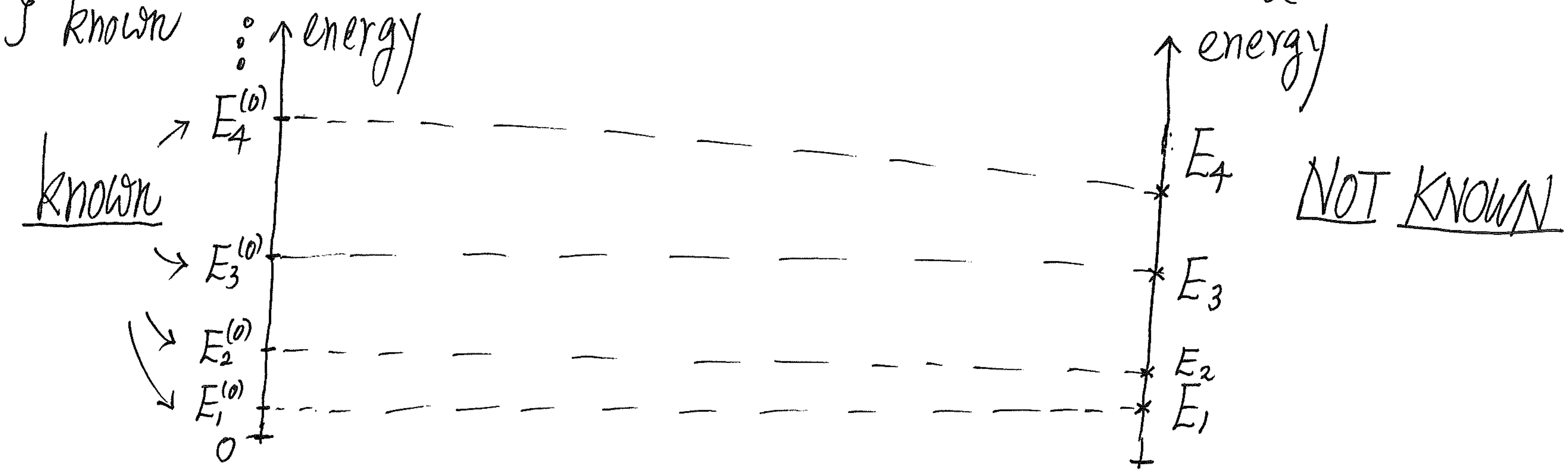
problem can't solve exactly

Q: $\{E_n\}$ & $\{\psi_n\}$?

This is what we want to do!



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



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

Perturbation Theories

- $\hat{H}'$ is a small part of the problem defined of $\hat{H}$
- aim to find the "corrections" order-by-order

$$\underbrace{1^{st} \text{ order in } \hat{H}'}_{\text{small}}, \quad \underbrace{2^{nd} \text{ order in } \hat{H}'}_{\text{smaller}}, \quad \underbrace{\ldots}_{\text{even smaller}\ldots}$$

and we can stop at 1^{st} OR 2^{nd} order

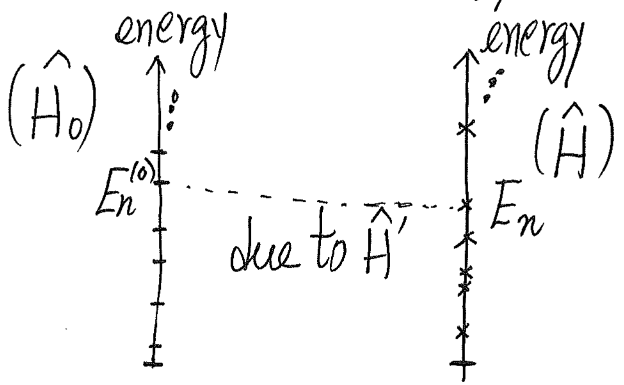
Before exploring effects of $\hat{H}'$, let's appreciate what $\hat{H}_0$ does

- $\hat{H}_0$ 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 functions 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 1st 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 1st order in $\hat{H}'$

Argument: "What else can it be?"

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

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

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

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

"What else can it be?" [First order perturbation (time-independent)]

$$E_n \approx \int \psi_n^{*(0)} \hat{H} \psi_n^{(0)} d\tau \qquad (C3)$$

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

$(\because \hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)})$

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

Key Result

1st order time-independent perturbation theory ⇒

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

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

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

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

$$\underbrace{\int \psi_n^{(0)} \hat{H}' \psi_n^{(0)} d\tau}$$

$\psi_n^{(0)}$: (no $\hat{H}'$ effect)

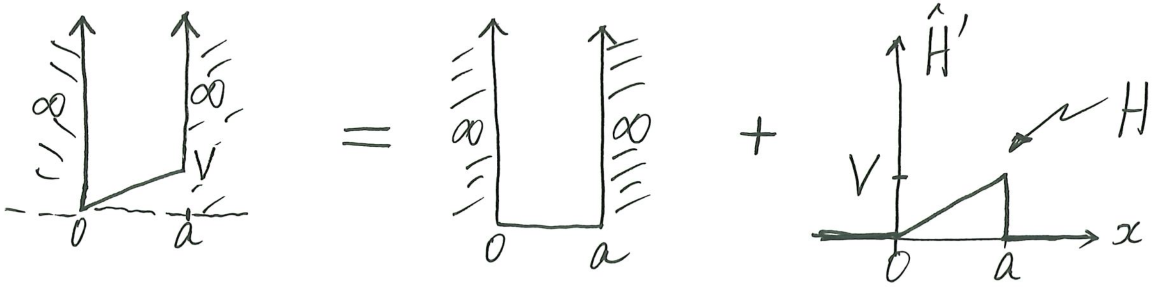
$\hat{H}'$: one factor of $\hat{H}'$

Eq. (C4) in words: $E_n^{(1)} = \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau$

1st order correction to energy ($E_n^{(1)}$) is the expectation value of the perturbation $\hat{H}'$ with respect to the unperturbed state (of $\hat{H}_0$) $\psi_n^{(0)}$ (C4')

- A very (the most perhaps) important result in applications of QM
- Simple but powerful!
- Knowing what (C4) means is more important than deriving it
- Derivation will come later (then will see condition of validity)

Example



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

Ground state energy of tilted well

$$E_1 \approx E_1^{(0)} + \int \psi_1^{*(0)} \hat{H}' \psi_1^{(0)} dx = E_1^{(0)} + \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\underbrace{\left(\frac{x}{a}V\right)}_{\hat{H}'}\sin\left(\frac{\pi x}{a}\right)dx$$

$$\boxed{\psi_1^{(0)}(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)}$$

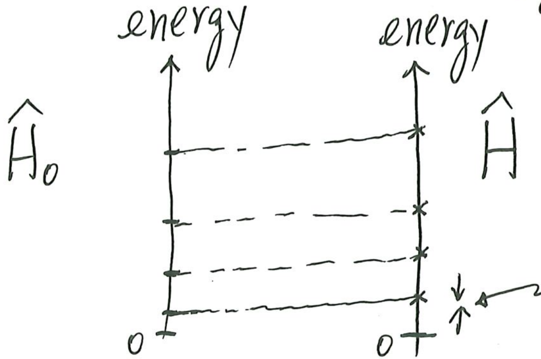
$$= E_1^{(0)} + \frac{2V}{a^2}\int_0^a x\sin^2\left(\frac{\pi x}{a}\right)dx = E_1^{(0)} + \frac{2V}{a^2}\left(\frac{a}{\pi}\right)^2\int_0^\pi y\sin^2 y\, dy$$

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

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

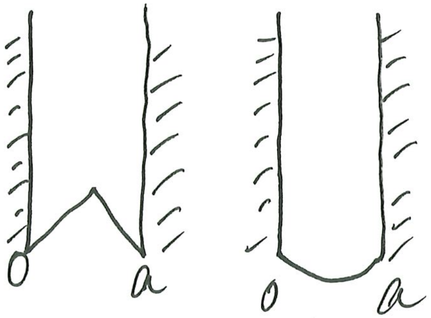
Exercise: Show

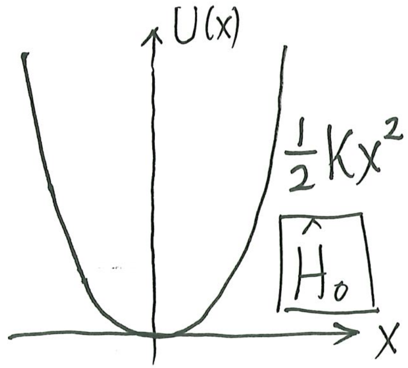
$$E_n \approx E_n^{(0)} + \frac{2V}{a^2}\int_0^a x\sin^2\left(\frac{n\pi x}{a}\right)dx = E_n^{(0)} + \frac{V}{2} \quad \left(\text{all energies shifted by } \frac{V}{2}\right)$$

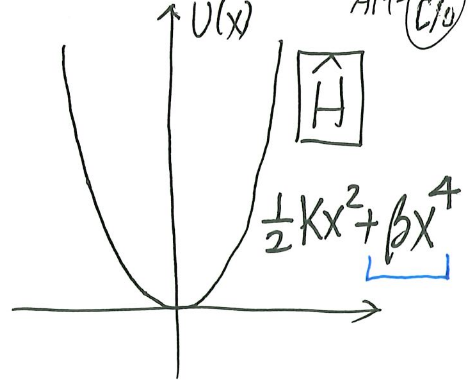


$V/2$ (1st order) (an approximated value)

Ex. Try







We are <u>free</u> (from analytically solvable problems) <u>at last</u>!

- 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} <u>state's</u> <u>wavefunction</u>?
  - 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) $\{\psi_n^{(0)}\}$ is a natural choice of basis functions

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

- Formally, matrix elements are $H_{ji} - ES_{ji}$ $\quad H_{ji} \equiv \int \psi_j^{(0)*} \hat{H} \psi_i^{(0)} d\tau$

But $\{\psi_n^{(0)}\}$ are orthonormal $\Rightarrow S_{ii} = 1,\ S_{ij} = 0$ ($\because$ eigenstates of $\hat{H}_0$)

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

equation to solve for E

(Exact!)

(see Sec. A)

(C5)

- Let's make the simplest possible approximation

pretend that they are zero

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

Eq.(C5) becomes

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

Simplest Approximation!

Many "1×1" problems

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

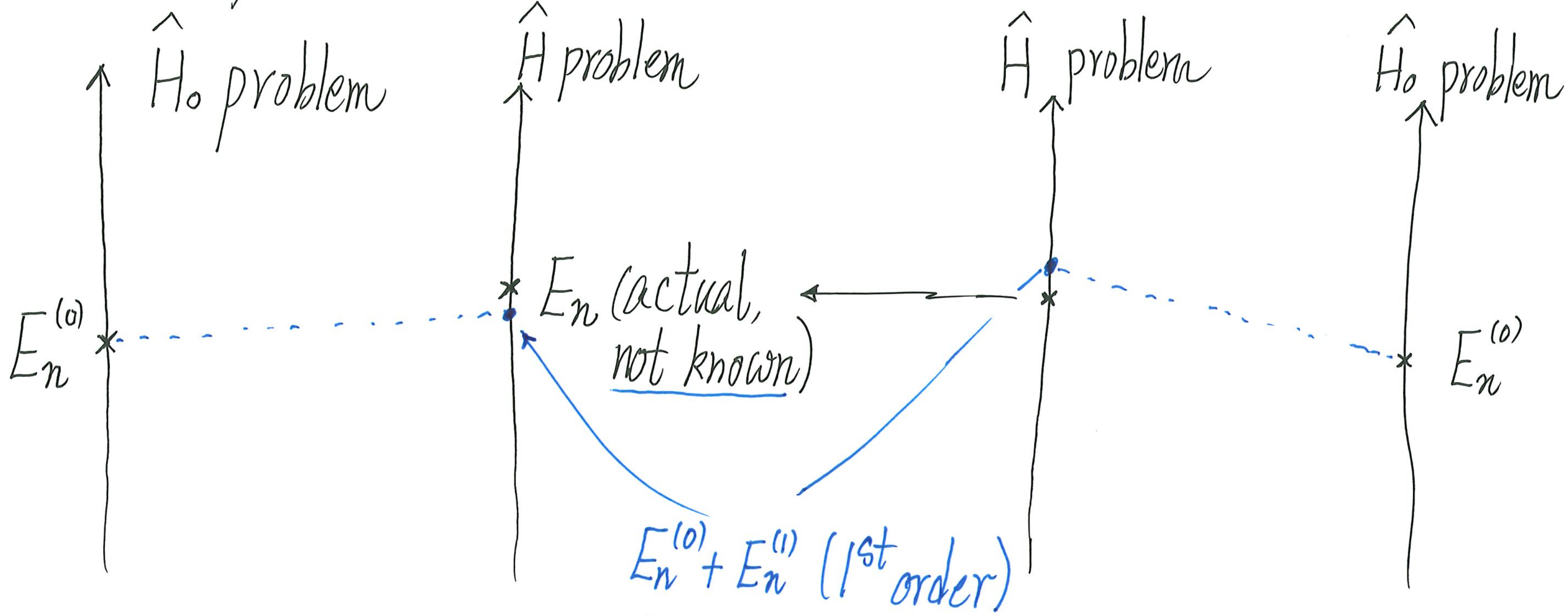
$$\Rightarrow \boxed{E_n = \int \psi_n^{*(0)} \hat{H} \psi_n^{(0)} d\tau = E_n^{(0)} + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}$$

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 (logic)

Schematically

Could be...



$\therefore$ Need 2nd order (higher order) term(s) to get closer to E_n (actual value)

Summary

- Eq. (C4) is the key result $E_n \approx E_n^{(0)} + \int \psi_n^{*(0)} \hat{H}' \psi_n^{(0)} d\tau = E_n^{(0)} + E_n^{(1)}$
- 1st order change in energy eigenstate? $\psi_n \approx \psi_n^{(0)} + \underbrace{\psi_n^{(1)}}_{\text{What is it?}}$
- 2nd order corrections?
- Derivations come next