VARIATIONAL PRINCIPLE

Gr §7

Goal: Find ground state energy E_{gs} of a $\hat{H}$ that cannot be exactly e-solved.

Idea: GUESS the form of ψ_{gs} ... including some adjustable params } ψ_{trial} "wavefunc"

Classic example: Helium ground-state energy → textbook

INGREDIENTS

① know that any $\psi_{trial} = \sum_n c_n \underbrace{\psi_n}$ → $|n\rangle$

e-states of $\hat{H}$, which we can't find

② $E_{gs} \leq E_n^{any}$

→ derive variational theorem:

DERIVATION

Consider expectation value $\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle$

$$\overset{①}{=} \left[\sum_m c_m^* \langle m|\right] \hat{H} \left[\sum_n c_n |n\rangle\right]$$

(unknown) e-states of $\hat{H}$

$$= \sum_m \sum_n c_m^* c_n \langle m | \underbrace{\hat{H} | n \rangle}_{E_n | n\rangle}$$

$$= \sum_m \sum_n c_m^* c_n E_n \underbrace{\langle m | n \rangle}_{\delta_{mn}} = \sum_n |c_n|^2 E_n$$

$\delta_{mn} \rightarrow$ (only m=n survives)

recall: $|c_n|^2$ are probabilities for obtaining E_n if you measure E of trial wavefunction

apply ②: each $E_n \geq E_{gs}$

$$\therefore \langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = \sum_n E_n |c_n|^2$$

$$\underset{②}{\geq} \sum_n E_{gs} |c_n|^2 = E_{gs} \underbrace{\sum_n |c_n|^2}_{\text{Total prob} = 1}$$

OUT

$$\therefore \boxed{E_{gs} \leq \langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}$$

$\langle \hat{H} \rangle_{TRIAL}$ provides an UPPER LIMIT on E_{gs}

Variational Technique to find (approximately) Egs:

MINIMIZE $\langle \hat{H} \rangle_{TRIAL}$ with to the <u>adjustable parameters</u> that you included in ψ_{trial}

TIPS for chosing ψ_{trial}

- must be normalizable!

almost always, $\psi_{trial} = \begin{pmatrix} \text{falling} \\ \text{exponential} \end{pmatrix} \times \begin{pmatrix} \text{simple} \\ \text{function} \end{pmatrix}$

asymptotic behaviour ensures normalizability

1D: $\psi_{trial}(x) \sim \underset{\text{GAUSSIAN}}{e^{-x^2/2\sigma^2}} \cdot \underset{\text{maybe}}{f(x)}$

radial: $\psi_{trial}(r) \sim e^{-r/a} \cdot \underset{\text{maybe}}{f(r)}$

- don't forget: include ADJUSTABLE PARAMs a_i in ψ_{trial}! MINIMIZATION procedure is solving: $\dfrac{\partial \langle H \rangle_{TRIAL}}{\partial a_i} = 0$ for $\{a_i\}^{BEST}$

COROLLARY: finding 1st excited state energy ...

Possible IFF you can find a ψ_{TRIAL} 〈sometimes possible〉

$$\ni \boxed{\langle \psi_{trial} | \psi_{gs} \rangle = 0 \text{ for sure}}$$

i.e. $|\psi_{trial}\rangle$ is ORTHOGONAL to $|\psi_{gs}\rangle$

Most common case: 1D problems where you

<u>know</u> $\psi_{gs}(x) = \text{EVEN}$

then pick $\psi_{trial}(x) = \text{ODD}$

then $\langle \underbrace{\psi_{trial}}_{ODD} | \underbrace{\psi_{gs}}_{EVEN} \rangle$

$$= \int_{-\infty}^{\infty} dx \; \text{even}(x) \cdot \text{odd}(x) = \emptyset$$

Then $\boxed{\langle \hat{H} \rangle_{TRIAL \perp GS} \geq E_{1st\ excited}}$

Proof: $\langle \hat{H} \rangle_{TRIAL} = \sum_n |c_n|^2 E_n$

$$\geq E_{gs} \underbrace{|c_{gs}|^2}_{\text{ZERO when } \psi_{TRIAL} \perp \psi_{gs}} + E_{\substack{1st \\ excited}} \sum_{n \neq gs} |c_n|^2$$

WHEN do we know <u>a priori</u> that ψ_{gs} is EVEN ???

answ: When $V(x)$ is even

reason: Parity $\hat{P}$ is a symmetry of $\hat{H}$
$(x \to -x)$

... which means $[\hat{P}, \hat{H}] = 0$

... which means $\hat{P}$ & $\hat{H}$ share a common set of e-states

... and e-states of $\hat{P} = \begin{cases} \text{even functions} & +1 \\ \text{odd functions} & -1 \end{cases}$ (e-value)

$\therefore$ all energy e-functions are even OR odd

& EVEN will always be ground state

$\because$ has least wiggles $\to$ lowest average slope

$\to$ lowest $\langle p \rangle = \langle i\hbar \frac{\partial}{\partial x} \rangle$

$\to$ lowest $\langle T \rangle$

☆ How close to E_{gs}? $\to$ next time