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Lec-01

"Variational Method of Approximation"

⊙ **Overview (What is it ?)**

By variational method of approximation we estimate ground state energy for systems for which we know Hamiltonian but don't have knowledge of wavefunctions. ie →

$\hat{H}$ = known

ψ = Unknown

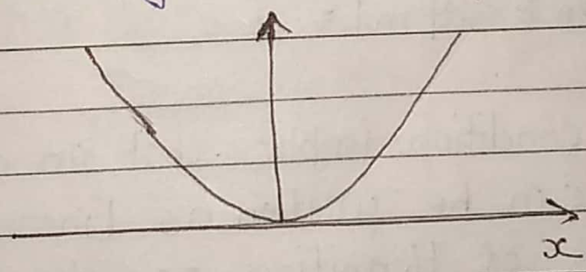
$E_{gs} \simeq$? (approximate ground state E)

Sometimes we can find 1st excited state energy, also second excited state energy and further

⊙ In which situation we can find 1st excited state, 2nd & further

When potential, $V(x)$ is even potential or symmetric about y axis then we can find / estimate energy of excited states by variational method.

eg



$$V(x) = \frac{1}{2} m\omega^2 x^2$$

⊙ Variational method of approximation is based on "Variational principle"

What is variational principle :—

Variational principle gives us an upper bound of ground state energy and according to it ground state energy is less than or equal to expectation value of Hamiltonian in any normalized arbitrary state.

$$\boxed{E_{gs} \leq \langle \hat{H} \rangle}$$

upper bound – can't be more than it (नीचे नीचे होगी ऊपर ज्यादा नहीं

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$$\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle$$

$|\psi\rangle \longrightarrow$ Any arbitrary normalized state

Proof of variational principle :- (Not Important)

$\hat{H}$ = Hamiltonian which is is Quantum mechanical operator ; means it's corresponding to a dynamical variable (energy)
Hence it is Hermition operator

$\Rightarrow$ its eigen values are real

$\Rightarrow$ eigen function are orthogonal and form a complete set

- Orthonormality condition $\rightarrow$

$$\langle \psi_m | \psi_n \rangle = \delta_{m,n} = \begin{cases} 1 & m=n \\ 0 & m \neq n \end{cases}$$

- Completeness condition / closure condition $\rightarrow$

$$\sum_{m=1}^{n} |\psi_m\rangle \langle \psi_m| = \hat{I}$$

Completeness condition implies that an arbitrary wave function can be written as Linear combination of eigen states of Hermition operator.

How ?

$$|\psi\rangle = \hat{I} |\psi\rangle$$

$$|\psi\rangle = \sum_{m=1}^{n} |\psi_m\rangle \langle \psi_m | \psi\rangle$$

$|\psi_m\rangle$ — eigen states of $\hat{H}$ operator

Let $\hat{H}$ have three eigen states

$E_1 = gs$ $\quad \hat{H} |\psi_1\rangle = E_1 |\psi_1\rangle$ $\quad |\psi\rangle \longrightarrow$ unknow but exists

E_2 = 1st exc. state $\quad \hat{H} |\psi_2\rangle = E_2 |\psi_2\rangle$

E_3 = 2nd ex. state $\quad \hat{H} |\psi_3\rangle = E_3 |\psi_3\rangle$

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$$|\psi\rangle = |\psi_1\rangle\langle\psi_1|\psi\rangle + |\psi_2\rangle\langle\psi_2|\psi\rangle + |\psi_3\rangle\langle\psi_3|\psi\rangle$$

Complex No / scalar quantity ⇒ Let a_1

$$|\psi\rangle = a_1|\psi_1\rangle + a_2|\psi_2\rangle + a_3|\psi_3\rangle$$

↑ An arbitrary state $|\psi\rangle$ can be written as Linear combination of eigen states of eigen function of Hamiltonian operator

$$\langle\hat{H}\rangle = \langle\psi|\hat{H}|\psi\rangle$$

$$\langle\hat{H}\rangle = (a_1^*\langle\psi_1| + a_2^*\langle\psi_2| + a_3^*\langle\psi_3|) \times \hat{H}\{a_1|\psi_1\rangle + a_2|\psi_2\rangle + a_3|\psi_3\rangle\}$$

$$\langle\hat{H}\rangle = \{a_1^*\langle\psi_1| + a_2^*\langle\psi_2| + a_3\langle\psi_3|\} \times \{a_1E_1|\psi_1\rangle + a_2E_2|\psi_2\rangle + a_3E_3|\psi_3\rangle\}$$

$\langle\psi_1|\psi_1\rangle = 1$
$\langle\psi_1|\psi_2\rangle = 0$
$\langle\psi|\psi_3\rangle = 0$

$$\langle\hat{H}\rangle = |a_1|^2E_1 + |a_2|^2E_2 + |a_3|^2E_3 \qquad (1)$$

Since $|\psi\rangle$ is normalized. $\langle\psi|\psi\rangle = 1$

$$\Rightarrow |a_1|^2 + |a_2|^2 + |a_3|^2 = 1 \qquad (2)$$

By eqn (1) & (2) We can conclude that —

$$E_1 \le \langle\hat{H}\rangle$$

$$\boxed{E_{gs} \le \langle\hat{H}\rangle}$$

E_1 = ground state.

* $\hat{H}|\psi_1\rangle = E_1|\psi_1\rangle$

$\hat{H}|\psi_2\rangle = E_2|\psi_2\rangle$

$\hat{H} = |a_1|^2E_1 + |a_2|^2E_2$

$|\psi\rangle = a_1|\psi_1\rangle + a_2|\psi_2\rangle$

$|a_1|^2 + |a_2|^2 = 1$

Let $a_1 = \sqrt{3/4}$, $a_2 = \sqrt{1/4}$

$3/4 + 1/4 = 1$

$$\Rightarrow \hat{H} = \frac{3}{4}E_1 + \frac{1}{4}E_2$$

$E_1 = gs = 5$
$E_2 = 1^{st}$ ex.

$E_2 > E_1$
($E_2 = 10$ $E_1 = 5$)

$$\langle\hat{H}\rangle = 3/4 \times 5 + 1/4 \times 10$$

$$\langle H\rangle = 15/4 + 10/4 = 25/4 = 6.25$$

$E_1 = 5$ $\langle H\rangle = 6.25$

$\boxed{E_1 < \langle H\rangle}$ Satisfied

When $a_1 = 1$ $a_2 = 0$
$\langle H\rangle = E_1$
$E_1 = \langle\hat{H}\rangle$

Variational method of Approximation →

By this we estimate ground state energy for systems for which $\hat{H}$ is known but wave function are unknown.

$$\boxed{E_{gs} \simeq \langle H_{min} \rangle}$$

$\left\{ E_g \le \langle H \rangle \right.$
↳ Principle

Here

$\langle H \rangle = \langle \psi | \hat{H} | \psi \rangle$

$|\psi\rangle$ = Normalized trial wave function

- $|\psi\rangle$ trial wave function should be acceptable quantum mechanically.
  Means $|\psi\rangle$ & its first order derivative should be finite, continious and differentiable everywhere
- $|\psi\rangle$ should be square integrable and it should vanish as $x \to \pm\infty$
- In trial wave function there is a parameter (adjustable parameter)

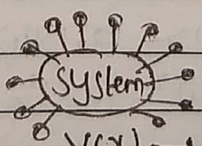
$\psi(x) = A e^{-bx^2}$ ⟶ trial wave function → Not exact.

A = Normalization constant

b = Adjustable parameter

→ The best value of adjustable parameter will give an approximate ground state wave function.

Story :) behind —



$V(x)$ → given

$\hat{H} = \hat{T} + \hat{V}$ → known

$E_{gs} = ?$ ⟶ SE solve XXXXX

Best way —

✓ $E_{gs} \simeq \langle \psi | \hat{H} | \psi \rangle$ min

$|\psi\rangle$ → arbitrary → make it exact

$\boxed{|\psi\rangle = A e^{-bx^2}}$ ⇒ b = adjustable par.
↳ Best value.