Variational Method:

This method is used to determine an upper bound values for the eigenenergies of a system whose Hamiltonian is known, whereas its eigenvalues and eigenstates are not known. it is mainly usefull for determining the ground state energy.

- how it works ?

first we pick any normalized trial wave function ψ, then we calculate $\langle H \rangle = \langle \psi | H | \psi \rangle$. The claim is that

$$E_{gs} \leq \langle \psi | H | \psi \rangle \quad \text{to be proven}$$

that is the expectation value of H, calculated using the trial wavefunction ψ, is certain to overestimate the ground state energy. of course if the trial wavefunction ψ just happens to be one of the excited states, then $\langle H \rangle$ exceeds E_{gs}

proof: the eigenvalue problem of H reads

$$H \psi_n = E_n \psi_n$$

; but the eigenfunctions ψ_n are unknown. However we know for sure that they form a complete set

then the trial wave function can be expanded in terms of ψ_n

$$\psi = \sum_n a_n \psi_n$$

; where ψ_n are assumed to be orthonormal $\langle \psi_n | \psi_m \rangle = \delta_{mn}$

now since ψ is normalized (or at least can be normalized)

$$1 = \langle \psi | \psi \rangle = \langle \sum_m a_m \psi_m | \sum_n a_n \psi_n \rangle = \sum_m \sum_n a_m^* a_n \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{mn}}$$

$$= \sum_n |a_n|^2$$

Now $\langle H\rangle = \langle\psi|H|\psi\rangle = \langle \sum_m a_m \psi_m | H | \sum_n a_n \psi_n\rangle$

$= \sum_m \sum_n \langle a_m\psi_m | a_n \underbrace{E_n \psi_n}\rangle$, where $H\psi_n = E_n \psi_n$

$= \sum_m \sum_n a_m^* a_n E_n \underbrace{\langle\psi_m|\psi_n\rangle}_{\delta_{mn}} = \sum_n \underset{\geq E_{gs}}{\underline{E_n}} |a_n|^2$

$\geq E_{gs} \underbrace{\sum_n |a_n|^2}_{1} = E_{gs}$

$\therefore \langle H\rangle = \langle\psi|H|\psi\rangle \geq E_{gs}$ Q.E.D

the same method can be applied to find the eigenenergies of the first few excited states.

<u>Example 1</u>: consider 1D harmonic oscillator. use the variational method to estimate the energies of
a) the Ground state b) the first excited state

solution
a) ground state: Trial wave function must satisfy the following; vanish at $x \to \pm\infty$ and finite at zero
A Gaussian function satisfies these requirements

$\psi(x) = A e^{-bx^2}$; b is a constant that determine the width of the function

A: normalization constant

$\langle\psi|\psi\rangle = 1 \Rightarrow |A|^2 \underbrace{\int_{-\infty}^{\infty} e^{-2bx^2} dx}_{\sqrt{\frac{\pi}{2b}}} = 1$

$\Rightarrow |A|^2 \left(\frac{\pi}{2b}\right)^{1/2} = 1$

$\Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}$

$\therefore\ \psi(x) = \left(\frac{2b}{\pi}\right)^{1/4} e^{-bx^2}$, Next we need to find $\langle\psi|H|\psi\rangle$

using $H = \frac{p^2}{2m} + V(x) = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{T} + \underbrace{\frac{1}{2} m\omega^2 x^2}_{V}$

$\Rightarrow \langle H\rangle = \langle T\rangle + \langle V\rangle$

$$\langle T\rangle = -\frac{\hbar^2}{2m}\left(\frac{2b}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-bx^2}\frac{d^2}{dx^2}\left(e^{-bx^2}\right)dx$$

$$= -\frac{\hbar^2}{2m}\left(\frac{2b}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-bx^2}\frac{d}{dx}\left(-2bxe^{-bx^2}\right)dx$$

$$= \cancel{\frac{\hbar^2}{m}\left(\frac{2}{\pi}\right)^{1/2} b^{3/2}}\ \frac{\hbar^2}{m}\left(\frac{2b}{\pi}\right)^{1/2} b\int_{-\infty}^{\infty} e^{-bx^2}\left[e^{-bx^2} - 2bx^2e^{-bx^2}\right]dx$$

$$= \frac{\hbar^2}{m}\left(\frac{2b}{\pi}\right)^{1/2} b\underbrace{\int_{-\infty}^{\infty} e^{-2bx^2}dx}_{\sqrt{\frac{\pi}{2b}}} - \frac{\hbar^2}{m}\left(\frac{2b}{\pi}\right)^{1/2} 2b^2\underbrace{\int_{-\infty}^{\infty} e^{-2bx^2}x^2\,dx}_{\sqrt{\frac{\pi}{4(2b)^3}} = \sqrt{\frac{\pi}{32b^3}}}$$

$$= \frac{\hbar^2}{m}b - \frac{\hbar^2}{m}\left(\frac{2b}{\pi}\right)^{1/2} 2b^2\left(\frac{\pi}{32b^3}\right)^{1/2}$$

$$= \frac{\hbar^2 b}{m} - \frac{\hbar^2 b}{2m} = \frac{\hbar^2 b}{2m}$$

Now $\langle V\rangle = \frac{1}{2} m\omega^2\left(\frac{2b}{\pi}\right)^{1/2}\underbrace{\int_{-\infty}^{\infty} x^2 e^{-2bx^2}dx}_{\sqrt{\frac{\pi}{32b^3}}} = \frac{m\omega^2}{8b}$

$\Rightarrow \langle H\rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b} \geq E_{gs}$ for any b

to get the lowest bound $\frac{d}{db}\langle H\rangle = 0$ $\Rightarrow b = \frac{m\omega}{2\hbar}$

$$\frac{d}{db}\left[\frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}\right] = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0$$

$\Rightarrow \langle H\rangle = \frac{\hbar^2}{2m}\left(\frac{m\omega}{2\hbar}\right) + \frac{m\omega^2}{8m\omega}2\hbar = \frac{1}{2}\hbar\omega$ exact value in this case our trial wave function was exact.

- first excited state

try $\psi(x) = A\,x\,e^{-bx^2}$ $\Rightarrow$ normalize $A = \left(\frac{32 b^3}{\pi}\right)^{1/4}$

again calculate $\langle H \rangle = \frac{3\hbar^2}{2m} b + \frac{3m\omega^2}{8b} \geq E_1$ for any b

$\Rightarrow \frac{d}{db}\langle H \rangle = 0 \Rightarrow b = \frac{\hbar\omega}{2\hbar} \Rightarrow E_1 = \frac{3}{2}\hbar\omega$

Example 2: estimate the ground state energy for $V(x) = -\alpha\,\delta(x)$

using the trial function $\psi(x) = \left(\frac{2b}{\pi}\right)^{1/4} e^{-bx^2}$

$\langle H \rangle = \langle T \rangle + \langle V \rangle$

$\langle T \rangle = \frac{\hbar^2 b}{2m}$ as done in example 1

$\langle V \rangle = -\alpha\left(\frac{2b}{\pi}\right)^{1/2} \underbrace{\int_{-\infty}^{\infty} e^{-2bx^2}\,\delta(x)\,dx}_{1 \,=\, e^{-2b(0)} = 1} = -\alpha\left(\frac{2b}{\pi}\right)^{1/2}$

$\Rightarrow \langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha\left(\frac{2b}{\pi}\right)^{1/2} \geq E_{gs}$ $\Rightarrow \frac{d}{db}\langle H \rangle = 0$

for any b

$\frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2b\pi}} = 0 \Rightarrow \frac{\hbar^4}{4m^2} = \frac{\alpha^2}{2b\pi} \Rightarrow b = \frac{2m^2\alpha^2}{\pi\hbar^4}$

$\Rightarrow \langle H \rangle = \frac{\hbar^2}{2m}\left(\frac{2m^2\alpha^2}{\pi\hbar^4}\right) - \alpha\left(\frac{2}{\pi}\,\frac{2m^2\alpha^2}{\pi\hbar^4}\right)^{1/2}$

$= \frac{\alpha^2 m}{\pi\hbar^2} - \frac{\alpha^2 2m}{\pi\hbar^2} = \frac{\alpha^2 m}{\pi\hbar^2} - 2\frac{\alpha^2 m}{\pi\hbar^2} = -\frac{\alpha^2 m}{\pi\hbar^2}$

$\therefore \langle H \rangle = -\frac{m\alpha^2}{\pi\hbar^2} \geq E_{gs}$