Variational principle

Note Title

In many cases, ground state energy is the most important quantity.

Even if the time-independent Schrödinger Eq. is not solvable, the variational principle provides an upper bound for the ground state energy such that

$$E_{gs} \le \langle \psi | H | \psi \rangle \equiv \langle H \rangle \quad \text{for any}$$

normalized wavefunction ψ.

Proof: any arbitrary normalized wave ftn "ψ" can be written as a linear combination of energy eigen ftns ψ_n:

$$\psi = \sum_n c_n \psi_n, \quad \text{with } H \psi_n = E_n \psi_n$$

Since ψ is normalized,

$$1 = \langle \psi | \psi \rangle = \left\langle \sum_m c_m \psi_m \middle| \sum_n c_n \psi_n \right\rangle$$

$$= \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_m \sum_n c_m^* c_n \delta_{mn}$$

$$= \sum_m |c_m|^2$$

Similarly $\langle H \rangle = \left\langle \sum_m c_m \psi_m \middle| H \sum_n c_n \psi_n \right\rangle$

$$= \sum_m \sum_n c_m^* c_n E_n \langle \psi_m | \psi_n \rangle$$

$$= \sum_n E_n |c_n|^2$$

$$\geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

$$\therefore \quad \underline{\langle H \rangle \ge E_{gs}}$$

If we choose a good trial wave function, we can get very close to the true ground state energy

$\boxed{\text{Ex. 1}}$ 1-D Harmonic oscillator

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

Although this problem can be exactly solved ($E_{gs} = \frac{1}{2}\hbar\omega$), treat this problem as if it is not soluable, and estimate the upperbound of the E_{gs} using

$\psi(x) = A e^{-bx^2}$, the gaussian wave function as the trial wave ftn.

$$1 = \langle\psi|\psi\rangle = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\, dx$$

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

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

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

$$= -\frac{\hbar^2}{2m}|A|^2 \left[\int_{-\infty}^{\infty} e^{-bx^2} \underbrace{\left[\frac{d}{dx}\left(-2bx\, e^{-bx^2}\right)\right]}_{\left[-2b\, e^{-bx^2} + (2b)^2 x^2 e^{-bx^2}\right]} dx \right.$$

$$= -\frac{\hbar^2}{2m}|A|^2 \left[-2b\sqrt{\frac{\pi}{2b}} + (2b)^2 \cdot 2\sqrt{\pi}\,\frac{1}{4}\cdot\frac{1}{(2b)^{\frac{3}{2}}} \right]$$

$$= -\frac{\hbar^2}{2m}\left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \underbrace{\left(-\sqrt{2\pi b} + \frac{\sqrt{\pi}}{2}\sqrt{2b}\right)}_{\substack{\parallel \\ -\frac{\sqrt{2\pi b}}{2}}}$$

$$= \frac{\hbar^2}{2m} \cdot 2b \cdot \frac{1}{2} = \frac{\hbar^2 b}{2m}$$

$$\langle V \rangle = \frac{1}{2} m\omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2 dx = \frac{m\omega^2}{8b}$$

$$\Rightarrow \langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

We have to find "b" that makes $\langle H \rangle$ minimum

$$\Rightarrow \frac{d\langle H \rangle}{db} = 0 = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2}$$

$$\Rightarrow b^2 = \frac{m\omega^2}{8} \cdot \frac{2m}{\hbar^2} = \frac{m^2\omega^2}{4\hbar^2}$$

$$\Rightarrow b = \frac{m\omega}{2\hbar}$$

$$\Rightarrow \langle H \rangle_{min} = \frac{\hbar^2}{2m}\left(\frac{m\omega}{2\hbar}\right) + \frac{m\omega^2}{8}\left(\frac{2\hbar}{m\omega}\right)$$

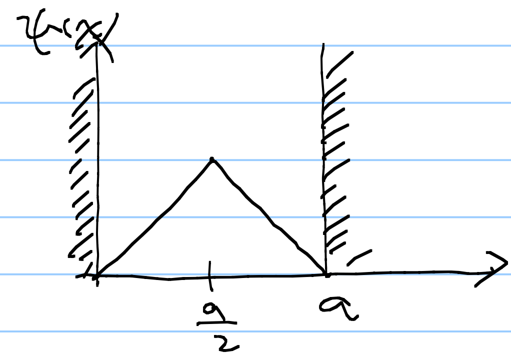
$$= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{1}{2}\hbar\omega$$

$$\therefore \quad E_{gs} \leq \langle H \rangle_{min} = \frac{1}{2}\hbar\omega$$

In this case, we have found the exact ground state because our trial wavefunction was exactly the same shape as the ground state wave function.

Ex. 2 Find an upper bound on the ground state energy of the 1-D infinite square well, using the triangular trial wave function

$$\psi(x) = \begin{cases} Ax & , \text{ if } 0 \le x \le \frac{a}{2} \\ A(a-x) & , \text{ if } \frac{a}{2} \le x \le a \\ 0 & \text{otherwise} \end{cases}$$



$$1 = |A|^2 \left[\int_0^{\frac{a}{2}} x^2 dx + \int_{\frac{a}{2}}^{a} (a-x)^2 dx \right]$$

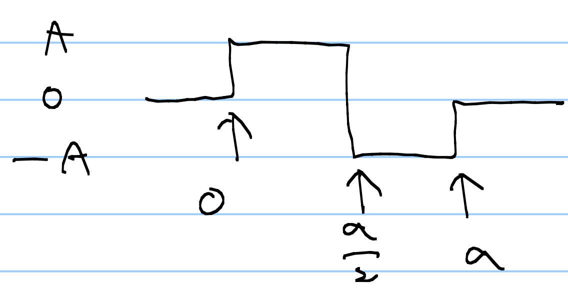
$$= |A|^2 \frac{1}{3} \cdot \left(\frac{a}{2}\right)^3 \cdot 2 = |A|^2 \cdot \frac{a^3}{12}$$

$$\Rightarrow A = \left[\frac{12}{a^3}\right]^{\frac{1}{2}}$$

$$\frac{d\psi}{dx} = \begin{cases} A & , \text{ for } 0 < x < \frac{a}{2} \\ -A & , \text{ for } \frac{a}{2} < x < a \\ 0 & , \text{ else} \end{cases}$$

Using the step functions,

$$\frac{d\psi}{dx} = A\theta(x) - 2A\theta\left(x - \frac{a}{2}\right) + A\theta(x-a)$$



Since $\frac{d\theta(x-a)}{dx} = \delta(x-a)$,

$$\frac{d^2\psi}{dx^2} = A\left[\delta(x) - 2\delta(x-\tfrac{a}{2}) + \delta(x-a)\right]$$

Thus

$$\langle H\rangle = \langle T\rangle + \cancel{\langle V\rangle}^{\,0}$$

$$= -\frac{\hbar^2}{2m}\int \psi(x)\frac{d^2}{dx^2}\psi(x)\,dx$$

$$= -\frac{\hbar^2}{2m}A\int \psi(x)\left[\delta(x) - 2\delta(x-\tfrac{a}{2}) + \delta(x-a)\right]dx$$

$$= -\frac{\hbar^2}{2m}A\left[\cancel{\psi(0)}^{\,0} - 2\psi(a/2) + \cancel{\psi(a)}^{\,0}\right]$$

$$= \frac{\hbar^2}{m}A^2\cdot\frac{a}{2} = \frac{\hbar^2}{m}\cdot\frac{a}{2}\cdot\frac{12}{a^3}$$

$$= \frac{12\hbar^2}{2ma^2}$$

Compare this with the exact result

$$E_{gs} = \frac{\pi^2\hbar^2}{2ma^2}$$

$$\pi^2 < 12$$

So the theorem works.

$\boxed{\text{Ex. 3}}$ This time in the infinite square well problem, use another trial wave function

$$\psi(x) = \begin{cases} -A\left((x-\frac{a}{2})^2 - \frac{a^2}{4}\right), & 0<x<a \\ 0, & \text{else} \end{cases}$$

$$1 = \langle \psi | \psi \rangle = A^2 \int_0^a \left(\left(x - \frac{a}{2}\right)^2 - \frac{a^2}{4} \right)^2 dx$$

$$= A^2 \int_0^a \left[x^2 - ax \right]^2 dx$$

$$= A^2 \int_0^a \left[x^4 - 2ax^3 + a^2 x^2 \right] dx$$

$$= A^2 \left[\frac{a^5}{5} - \cancel{2}a \frac{a^4}{\cancel{4}_{2}} + a^2 \frac{a^3}{3} \right]$$

$$= A^2 \frac{6 - 15 + 10}{30} a^5 = \frac{a^5}{30} \cdot A^2$$

$$\Rightarrow A = \left(\frac{30}{a^5} \right)^{\frac{1}{2}}$$

$$\langle H \rangle = \langle T \rangle + \cancel{\langle V \rangle}^{\to 0}$$

$$= -\frac{\hbar^2}{2m} A^2 \int_0^a (x^2 - ax) \frac{d^2}{dx^2} (x^2 - ax)\, dx$$

$$= -\frac{\hbar^2}{m} A^2 \int_0^a (x^2 - ax)\, dx$$

$$= -\frac{\hbar^2}{m} A^2 \cdot \left[\frac{a^3}{3} - a \frac{a^2}{2} \right]$$

$$= \frac{\hbar^2}{m} \cdot \frac{a^3}{6} A^2 = \frac{\hbar^2}{m} \cdot \frac{a^3}{6} \cdot \frac{30}{a^5}$$

$$= \frac{10 \hbar^2}{2ma^2}$$

Comparing with what we obtained above

$$E_{gs}(\text{exact}) < \langle H \rangle_{Ex,3} < \langle H \rangle_{Ex,2}$$

$$\frac{\pi^2 \hbar^2}{2ma^2} \qquad \frac{10\, \hbar^2}{2ma^2} \qquad \frac{12\, \hbar^2}{2ma^2}$$

So the better the trial wave fcn, the closer $\langle H \rangle$ is to the true ground state energy.