

Variational Principle

To solve $\hat{H}|\psi\rangle = E_n|\psi\rangle$ we so far have two methods:

1. Solve exactly \rightarrow Hard
 \rightarrow Not always possible

2. Perturbation method: $\hat{H} = \hat{H}_0 + \hat{H}_1$
where we know $H_0|\psi^{(0)}\rangle = E_n^{(0)}|\psi^{(0)}\rangle$

\swarrow
we need to have solvable H_0

\searrow
complete set of $|\psi_n^{(0)}\rangle$

\rightarrow \hat{H}_1 must be perturbing, i.e. weak

not always possible 😞

In situations of "unsolvable" \hat{H} , we would be happy to have even an approximation to the solution.

Let's observe the following

$$\langle \psi | \hat{H} | \psi \rangle \geq E_{\text{ground}}$$

for any normalized $|\psi\rangle$, $\langle \psi | \psi \rangle = 1$

Proof:

$|\psi\rangle = \sum_n c_n |\psi_n\rangle$, where $|\psi_n\rangle$ are eigen states of \hat{H}
 we do not know them but they should exist.

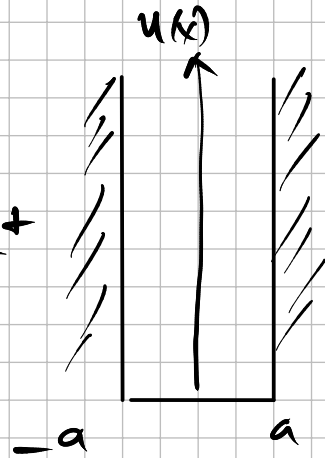
$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= \langle \sum_m c_m^* \psi_m | \hat{H} | \sum_n c_n \psi_n \rangle = \\ &= \langle \sum_m c_m^* \psi_m | E_n c_n \psi_n \rangle = \langle \psi_m | \psi_n \rangle = \delta_{mn} \\ &= \sum_{n,m} c_m^* c_n E_n \delta_{mn} = \\ &= \sum_n E_n |c_n|^2 = \sum_n (E_g + \delta E_n) |c_n|^2 = \\ &= E_g \underbrace{\sum_n |c_n|^2}_1 + \sum_n \delta E_n |c_n|^2 \geq E_g \quad \therefore \end{aligned}$$

1, since $\langle \psi | \psi \rangle = 1$

The above theorem allows us to put the upper limit on E_g .

Example:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x)$$



Square well

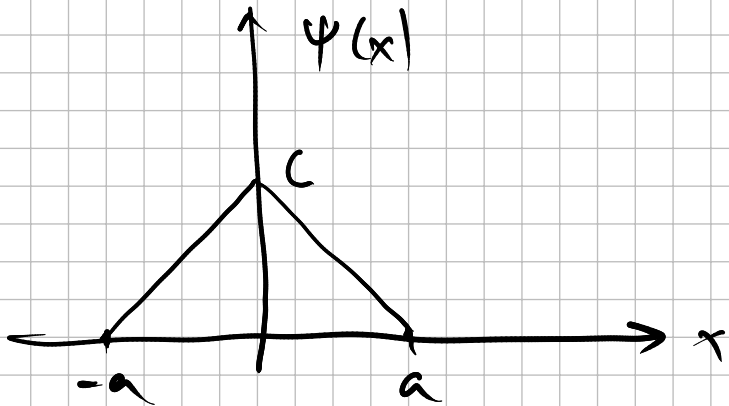
$$U(x) = \begin{cases} 0, & \text{if } |x| < a \\ \infty, & \text{otherwise} \end{cases}$$

Recall that

$$E_n = \frac{\hbar^2}{8m} \frac{\pi^2 n^2}{a^2} \Rightarrow \boxed{E_g = \frac{\hbar^2 \pi^2}{8m a^2}} \text{ true value}$$

let's pretend that we do not know E_g and $|\psi_n\rangle$

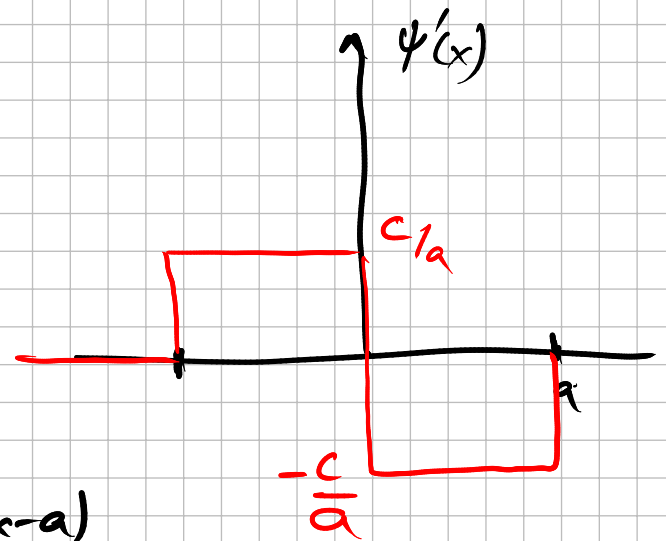
We make a guess (ansatz) ψ :



$$\psi(x) = \begin{cases} \frac{c(x+a)}{a}, & -a < x < 0 \\ -\frac{c(x-a)}{a}, & 0 < x < a \\ 0, & |x| > a \end{cases}$$

$$\int_{-a}^a \psi(x)^2 dx = 2 \int_{-a}^0 \frac{c^2}{a^2} (x+a)^2 dx = \int_{x+a=y}^{dx=dy} = \frac{2c^2}{3a^2} a^3 \Rightarrow c = \sqrt{\frac{3}{2a}}$$

$$\frac{d}{dx} \psi(x) = \begin{cases} \frac{c}{a}, & -a < x < 0 \\ -\frac{c}{a}, & 0 < x < a \\ 0, & |x| > a \end{cases}$$



$$\frac{d^2}{dx^2} \psi(x) = \frac{c}{a} \delta(x+a) - \frac{2c}{a} \delta(x) + \frac{c}{a} \delta(x-a)$$

This example shows that continuous but not smooth guesses are OK.

$$\langle \psi | H | \psi \rangle = \int_{-\infty}^{\infty} \psi(x) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) \right) dx =$$

$$= - \int_{-\infty}^{\infty} \psi(x) \frac{\hbar^2}{2m} \frac{c}{a} (\delta(x+a) - 2\delta(x) + \delta(x-a)) dx =$$

$$= -\frac{\hbar^2}{2m} \frac{c}{a} (0 - 2c + 0) = \frac{\hbar^2}{m} \frac{c^2}{a} = \frac{\hbar^2}{m} \frac{3}{2a^2}$$

$$= \frac{3}{2} \frac{\hbar^2}{ma^2} > \frac{\pi}{8} \frac{\hbar^2}{ma^2}$$

The above guess is not bad. But where is variation?

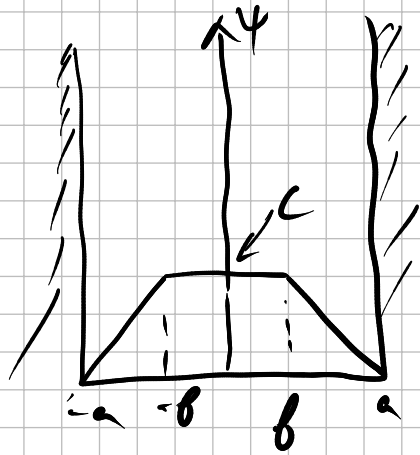
The idea is to make an ansatz dependent on some parameter and then vary it to minimize the estimated E_{ψ} :

$$\psi(\lambda) \rightarrow \langle \psi(\lambda) | H(\lambda) | \psi(\lambda) \rangle = E(\lambda)$$

$$\min(E(\lambda)) \Rightarrow \frac{dE(\lambda)}{d\lambda} = 0 \Rightarrow \text{solve for } \lambda_0 \rightarrow E(\lambda_0) \text{ is the smallest}$$

of course there are bad guesses and good one
so the skill is in choosing the good one.

Example: Same square well



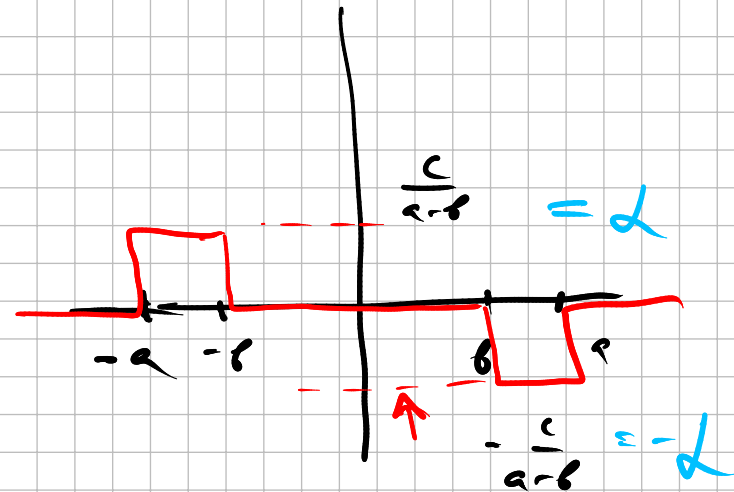
$$\psi \text{ is continuous } = \begin{cases} c, & |x| < b \\ c \frac{(a - |x|)}{a - b}, & b < |x| < a \\ 0, & \text{elsewhere} \end{cases}$$

Normalization

$$\langle \psi | \psi \rangle = 1 = 2 \int_0^b c^2 dx + 2 \int_b^a c^2 \left(\frac{a-x}{a-b} \right)^2 dx = 2c^2 b + \frac{2c^2}{(a-b)^2} \int_0^b x^2 dx$$

$$2c^2 \left(b + \frac{(a-b)^2}{3} \right) = 1$$

$$\frac{1}{\sqrt{2}} \psi = \begin{cases} 0, & |x| > a \\ + \frac{c}{a-b}, & -a < x < -b \\ 0, & -b < x < b \\ - \frac{c}{a-b}, & b < x < a \end{cases}$$



$$\frac{d^2 \psi}{dx^2} = 2\delta(x+a) - 2\delta(x+b) - 2\delta(x-b) + 2\delta(x-a)$$

$$\langle \psi | H | \psi \rangle = \int_{-a}^a \psi(x) \left(-\frac{\hbar^2}{2m} \right) \frac{d^2 \psi}{dx^2} dx =$$

$$= -\frac{\hbar^2}{2m} 2 \left[\underbrace{\psi(-a)}_0 - \underbrace{\psi(-b)}_c - \underbrace{\psi(b)}_c + \underbrace{\psi(a)}_0 \right]$$

$$= -\frac{\hbar^2}{2m} 2 \cdot 2c = \frac{\hbar^2}{m} \frac{e^2}{a-b}$$

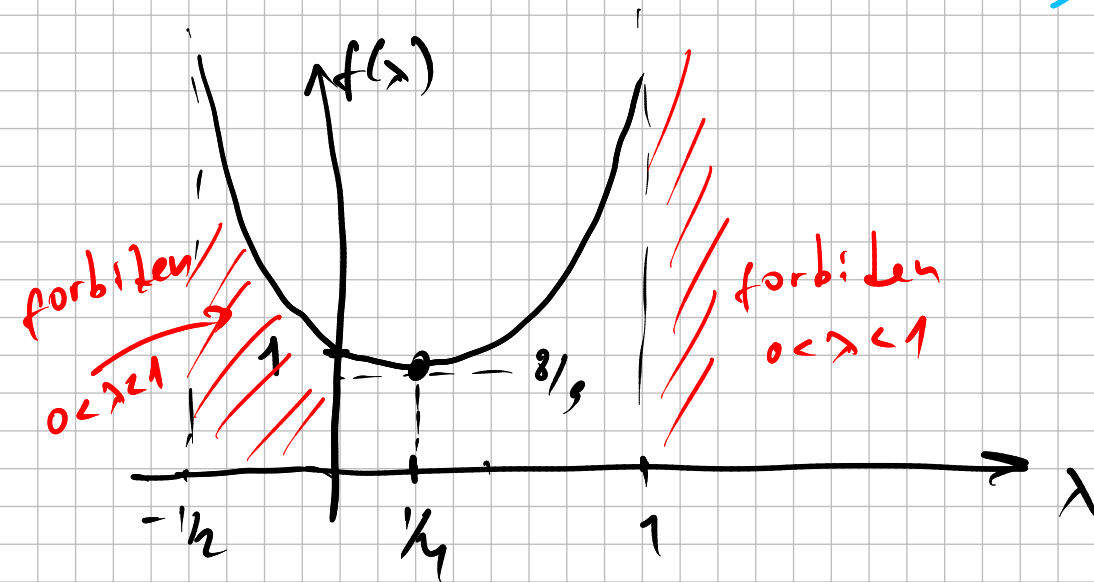
$$= \frac{\hbar^2}{m} \frac{1}{2 \underbrace{b + (a-b)/3}_{a + \frac{2}{3}b}} \frac{1}{a-b} = E(b)$$

$$= \frac{\hbar^2}{m} \frac{3}{2} \frac{1}{a+2b} \frac{1}{a-b} = \frac{\hbar^2}{m} \frac{3}{2} \frac{1}{a^2} \frac{1}{1+2b/a} \frac{1}{1-b/a}$$

minimizing $E(\lambda) \Rightarrow E(\lambda = \frac{b}{a})$

$$E(\lambda) = \frac{1}{2} \frac{\hbar^2}{m} \frac{3}{a^2} \left[\frac{1}{1+2\lambda} \cdot \frac{1}{1-\lambda} \right] = f(\lambda)$$

dimensionless $\lambda = 0-1$



$$\begin{aligned} \frac{d}{d\lambda} f(\lambda) &= \frac{d}{d\lambda} \left(\frac{1}{1+2\lambda} \cdot \frac{1}{1-\lambda} \right) = \\ &= \frac{-2}{(1+2\lambda)^2} \frac{1}{1-\lambda} + \frac{1}{1+2\lambda} \frac{1}{(1-\lambda)^2} \\ &= \frac{-2(1-\lambda) + (1+2\lambda)}{(1+2\lambda)^2 (1-\lambda)^2} = 0 \end{aligned}$$

$$2\lambda - 2 + 1 + 2\lambda = 0$$

$$\lambda = \frac{1}{4} = \frac{b}{a}$$

$$E(\lambda = \frac{1}{4}) = \frac{3}{2} \frac{\hbar^2}{m a^2} \left(\frac{1}{3/2} \cdot \frac{1}{3/4} \right)$$

$$= \frac{3}{2} \frac{\hbar^2}{m a^2} \frac{8}{9} = \frac{\hbar^2}{m a^2} \frac{4}{3} = E_{\text{min ground state estimate}}$$

Estimate $E_j = \frac{\hbar^2}{ma^2} \cdot \frac{4}{3} = \frac{\hbar^2}{ma^2} \cdot 1.33$

↑ quite close

True value

$$E_j = \frac{\hbar^2 \pi^2}{8ma^2} = \frac{\hbar^2}{ma^2} \frac{9.87}{8} = \frac{\hbar^2}{ma^2} \cdot 1.23$$

$\psi(x)$ approximation

