Variational Principle

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

1. Solve exactly → Hard
   → Not always possible
2. Perturbation metod: $\hat{H} = \hat{H}_0 + \hat{H}_1$
   where we know $H_0|\psi^{(0)}\rangle = E_n^{(0)}|\psi^{(0)}\rangle$

we need to have solvable H_0 → not always possible :(

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

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

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

Let's observe the following

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

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

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.

$$\langle \psi | \hat{H} | \psi \rangle = \langle \sum_m c_m^* \psi_m | \hat{H} | \sum_n c_n \psi_n \rangle =$$

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

$$= \sum_{n,m} c_m^* c_n E_n \delta_{mn} =$$

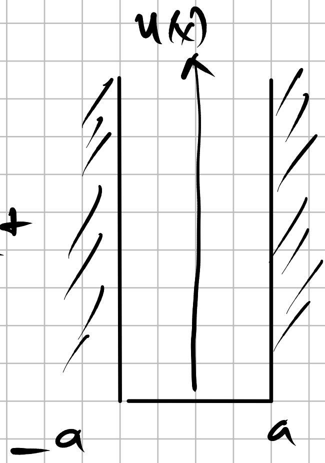
$$= \sum_n E_n |c_n|^2 = \sum_n (E_g + \overbrace{\Delta E_n}^{>0}) |c_n|^2 =$$

$$= E_g \underbrace{\sum_n |c_n|^2}_{1,\text{ since } \langle \psi | \psi \rangle = 1} + \sum_n \Delta E_n |c_n|^2 \geq E_g \quad \therefore$$

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

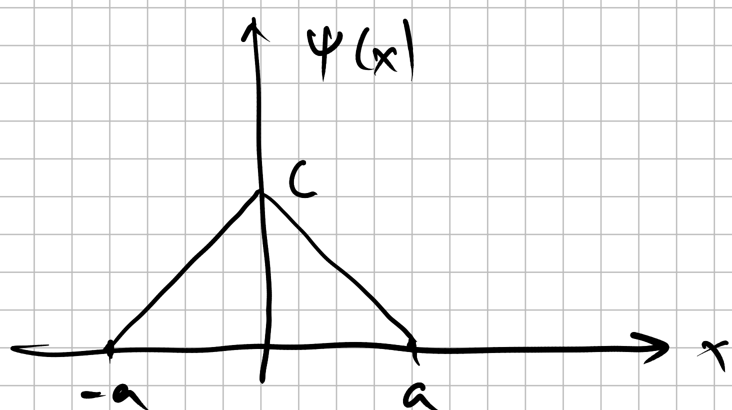
$$U(x) = \begin{cases} 0, & \text{if } |x| < a \\ \infty, & \text{otherwise} \end{cases}$$

Recall that

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

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

We make a guess (anzatz) ψ:

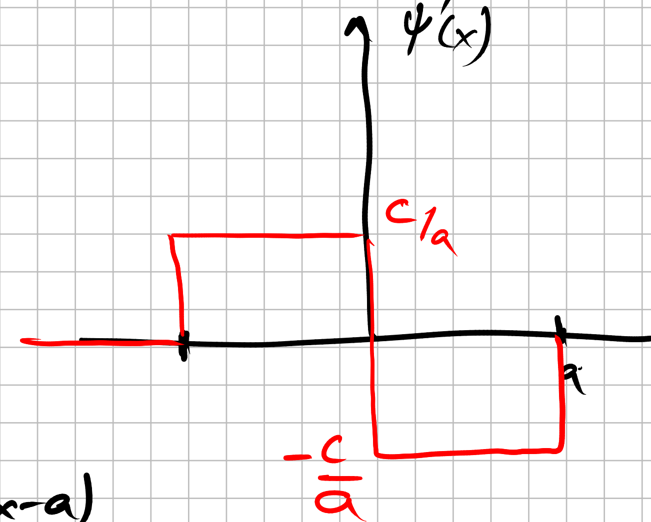


$$\psi(x) = \begin{cases} \frac{C(x+a)}{a}, & -a < x < 0 \\ \frac{C(x-a)}{a}, & 0 < x < a \\ 0, & |x| > a \end{cases}$$

$$\int_{-a}^{a} \psi(x)^2 dx = 2\int_{-a}^{0} \frac{c^2}{a^2}(x+a)^2 dx = \left/ \begin{matrix} x+a=y \\ dx=dy \end{matrix} \right/$$

$$= \frac{2c^2}{3a^2}a^3 \Rightarrow c = \sqrt{\frac{3}{2a}}$$

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



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

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

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

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

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

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

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

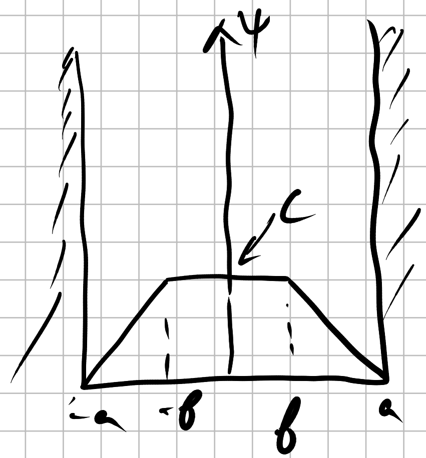
The idea is to make anzatz dependent on some parameter and then vary it to minimize the estimated E_g:

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

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

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

Example: same square well



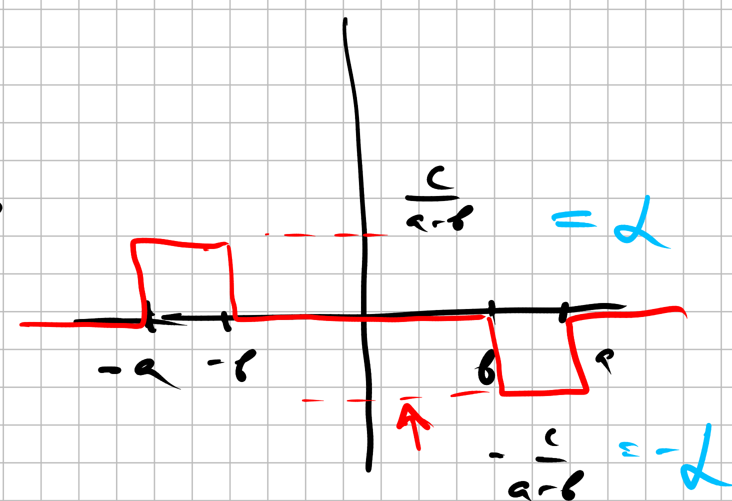
ψ is continuous $= \begin{cases} c\,, & |x|<b \\ c\,\dfrac{(a-|x|)}{a-b}\,, & b<|x|<a \\ 0\,, & \text{elsewhere} \end{cases}$

Normalization

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

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

$\dfrac{d}{dx}\psi = \begin{cases} 0\,, & |x|>a \\ +\dfrac{c}{a-b}\,, & -a<x<-b \\ 0\,, & -b<x<b \\ -\dfrac{c}{a-b}\,, & b<x<a \end{cases}$



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

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

$$= -\frac{\hbar^2}{2m}\alpha\Big[\underbrace{\psi(-a)}_{=0} - \underbrace{\psi(-b)}_{=c} - \underbrace{\psi(b)}_{=c} + \underbrace{\psi(a)}_{=0}\Big]$$

$$= -\frac{\hbar^2}{2m}\alpha\, 2c = \frac{\hbar^2}{m}\frac{c^2}{a-b}$$

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

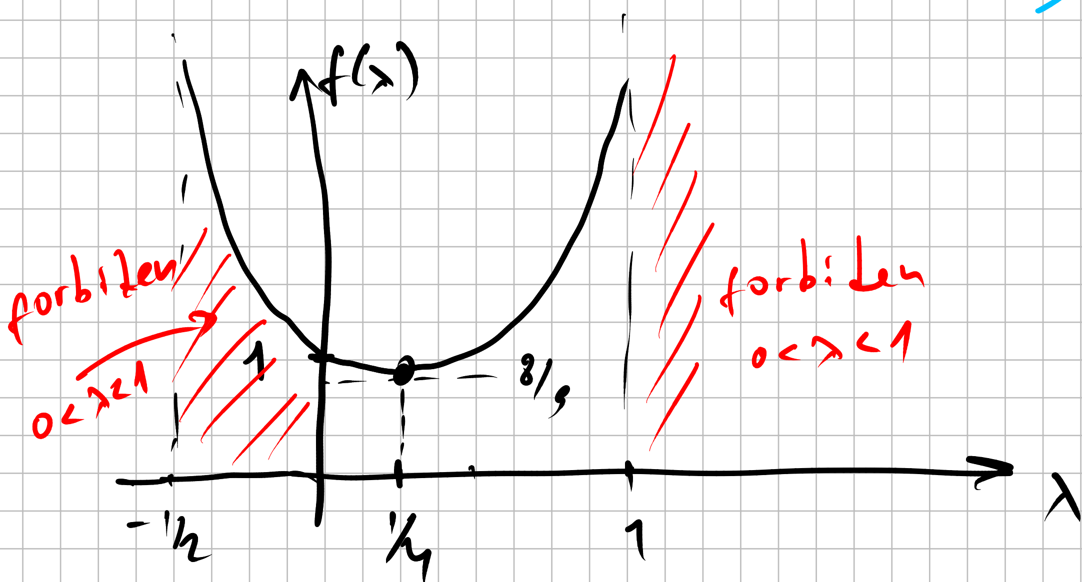
$$= \frac{\hbar^2}{m}\frac{3}{2}\frac{1}{a+2b}\frac{1}{a-b} = \frac{\hbar^2}{m}\frac{3}{2}\frac{1}{a^2}\frac{1}{1+2b/a}\frac{1}{1-b/a}$$

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

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

dimenshionless

$\lambda = 0 - 1$



$$\frac{df}{d\lambda} = \frac{d}{d\lambda}\left(\frac{1}{1+2\lambda}\cdot\frac{1}{1-\lambda}\right) =$$

$$= \frac{-2}{(1+2\lambda)^2}\frac{1}{1-\lambda} + \frac{1}{1+2\lambda}\frac{1}{(1-\lambda)^2}$$

$$= \frac{-2(1-\lambda) + (1+2\lambda)}{(1+2\lambda)^2(1-\lambda)^2} = 0$$

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

$$\boxed{\lambda = 1/4 = b/a}$$

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

$$= \frac{3}{2}\frac{\hbar^2}{ma^2}\frac{8}{9} = \frac{\hbar^2}{ma^2}\frac{4}{3} = E_{min}$$

ground state estimate

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

quite close

True value $E_g = \frac{\hbar^2 \pi^2}{8ma^2} = \frac{\hbar^2}{ma^2} \frac{9.87}{8} = \frac{\hbar^2}{ma^2} \cdot 1.23$

$\psi(x)$ approximation