**What is variation principle?**

*Other names include variational method, variation theorem*

The variation principle is a quantum mechanical method for approximating the ground state energy and wavefunction of a system when the Schrödinger equation is unsolvable. It states that the expectation value of the Hamiltonian for any normalized trial wavefunction is always greater than or equal to the true ground state energy.

A mathematical statement of the variation principle:

$\phi \rightarrow$ Trial function

$E_\phi \rightarrow$ Approximate energy

$$E_\phi = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau}$$

$E_0$ = Actual ground state energy.

$$E_\phi \geq E_0$$

*According to the variation principle, the minimum value of the variational energy of a trial wavefunction is the best approximation of the true energy of the system.*

**Proof of Linear Variation Theorem**

Let us assume, $\phi = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \dots + c_n\psi_n$

The guess/trial function is expressed as a linear combination of a complete set of normalized and orthogonal eigenfunctions $\Psi_1, \Psi_2, \Psi_3$..........................of the same system. The coefficients refer to some arbitrary parameters, called variational parameters / coefficients.

$$\int \phi^* \hat{H} \phi d\tau = \int \{c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \dots\}^* \hat{H} \{c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \dots\} d\tau$$

$$= \int \{c_0^*\psi_0^* + c_1^*\psi_1^* + c_2^*\psi_2^* + \dots\}\{c_0 E_0\psi_0 + c_1 E_1\psi_1 + c_2 E_2\psi_2 + \dots\} d\tau$$

$$= c_0^* c_0 E_0 \int \psi_0^*\psi_0 d\tau + c_1^* c_1 E_1 \int \psi_1^*\psi_1 d\tau + c_2^* c_2 E_2 \int \psi_2^*\psi_2 d\tau + \dots$$

$$= c_0^* c_0 E_0 + c_1^* c_1 E_1 + c_2^* c_2 E_2 + \dots$$

$$\int d\tau\, \phi^*\phi = \int d\tau \{c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \dots\}^* \{c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \dots\}$$

$$= \int d\tau \{c_0^*\psi_0^* + c_1^*\psi_1^* + c_2^*\psi_2^*\}\{c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \dots\}$$

$$= c_0^* c_0 \int \psi_0^*\psi_0 d\tau + c_1^* c_1 \int \psi_1^*\psi_1 d\tau + \cancel{c_2^* c_2 d} \; c_2^* c_2 \int \psi_2^*\psi_2 d\tau + \dots$$

$$= c_0^* c_0 + c_1^* c_1 + c_2^* c_2 + \dots$$

$$\cancel{E\phi - E_0 =}$$

$$E\phi = \frac{C_0^* C_0 E_0 + C_1^* C_1 E_1 + C_2^* C_2 E_2 + \cdots}{C_0^* C_0 + C_1^* C_1 + C_2^* C_2 + \cdots}$$

$$= \frac{C_0^2 E_0 + C_1^2 E_1 + C_2^2 E_2 + \cdots}{C_0^2 + C_1^2 + C_2^2 + \cdots}$$

$\left.\begin{matrix} C_0 \\ C_1 \\ C_2 \end{matrix}\right\}$ real numbers

$$E\phi - E_0 = \frac{\cancel{C_0^2 E_0} + C_1^2 E_1 + C_2^2 E_2 + \cdots - \cancel{E_0 (C_0^2} + C_1^2 + C_2^2 + \cdots)}{C_0^2 + C_1^2 + C_2^2 + \cdots}$$

$$= \frac{|C_1|^2 (E_1 - E_0) + |C_2|^2 (E_2 - E_0) + \cdots}{C_0^2 + C_1^2 + C_2^2}$$

$\geq 0$

The numerator is a +ve quantity because $E_1, E_2, \cdots E_n$ are upper state energies and larger/greater than $E_0$

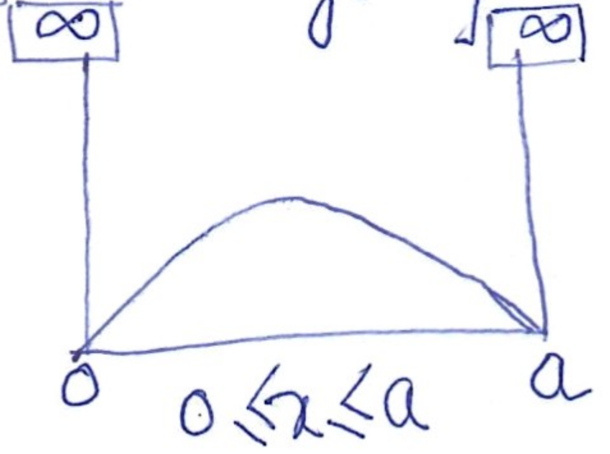
The denominator is a +ve quantity.

So, $\boxed{E\phi - E_0 \geq 0}$ also, $\boxed{E\phi \geq E_0}$

Apply variation theorem for guessing the energy of a particle in a box.

use trial fn $\phi = x(a-x)$

use Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$




$\phi = x(a-x)$

$\phi^* = x(a-x)$

$$\boxed{E_\phi = \frac{\int_0^a dx\, \phi^* \hat{H} \phi}{\int_0^a dx\, \phi^* \phi}}$$

$$\int_0^a dx\, \phi^* \hat{H} \phi$$

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

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

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

$$= +\frac{\hbar^2}{m}\left[\frac{ax^2}{2} - \frac{x^3}{3}\right]_0^a$$

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

$$\int_0^a dx\, \phi^* \phi$$

$$= \int_0^a dx\, x^2(a-x)^2$$

$$= \int_0^a dx\{x^2(a^2 - 2ax + x^2)\}$$

$$= \int_0^a dx\{x^2a^2 - 2ax^3 + x^4\}$$

$$= \left[\frac{a^2x^3}{3} - \frac{2a^5}{4} + \frac{a^5}{5}\right]_0^a$$

$$= \frac{1}{30}a^5$$

$$E_\phi = \frac{\frac{\hbar^2}{m}\frac{a^3}{6}}{\frac{1}{30}a^5}$$

$$= \frac{5\hbar^2}{ma^2}$$

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

Actual energy for particle in 1D box

$$\frac{\pi^2\hbar^2}{2ma^2}$$

Accuracy $\simeq 86\%$

Hydrogen Atom Ground state energy

Using Variation theorem

$$\hat{H} = \left[-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{e^2}{4\pi\varepsilon r}\right]$$

Let us take a trial function, $\phi = e^{-\alpha r}$

$\alpha \to$ variational parameter

$$\hat{H}\phi \left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}e^{-\alpha r}\right) - \frac{e^2}{4\pi\varepsilon r}e^{-\alpha r}\right]$$

$$= -\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2(-\alpha)e^{-\alpha r}\right) - \frac{e^2}{4\pi\varepsilon r}e^{-\alpha r}$$

$$= \frac{\alpha\hbar^2}{2mr^2}\left(2r - \alpha r^2\right)e^{-\alpha r} - \frac{e^2}{4\pi\varepsilon r}e^{-\alpha r}$$

$$E_\phi = \frac{\int \phi^* \hat{H}\phi \, d\tau}{\int \phi^*\phi \, d\tau}$$

$$\int \phi^* \hat{H}\phi \, 4\pi r^2 dr = 4\pi \int \phi^* \hat{H}\phi \, r^2 dr$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$= 4\pi \int e^{-\alpha r}\left[\frac{\alpha\hbar^2}{2mr^2}\left(2r - \alpha r^2\right)e^{-\alpha r} - \frac{e^2}{4\pi\varepsilon r}e^{-\alpha r}\right] r^2 dr$$

$$= \frac{2\cancel{4}\pi\alpha\hbar^2}{\cancel{\alpha}\,\cancel{2}m\cancel{r^2}} \cdot \cancel{r^2}\int_0^\infty \left(2r - \alpha r^2\right)e^{-2\alpha r} dr - \frac{e^2}{\varepsilon_0}\int_0^\infty e^{-2\alpha r} r \, dr$$

$$= \frac{2\pi\alpha\hbar^2}{m}\left[\frac{2}{(2\alpha)^2} - \frac{2\alpha}{(2\alpha)^3}\right] - \frac{e^2}{\varepsilon_0}\left[\frac{1}{(2\alpha)^2}\right]$$

$$= \frac{2\pi\alpha\hbar^2}{m}\left[\frac{2\cdot 2\alpha - 2\alpha}{(2\alpha)^3}\right] - \frac{e^2}{4\varepsilon_0\alpha^2} = \frac{\pi\hbar^2}{2m\alpha} - \frac{e^2}{4\varepsilon_0\alpha^2}$$

$$\int \phi^* \phi \, d\tau = 4\pi \int e^{-2\alpha r} r^2 \, dr$$

$$= 4\pi \left[ \frac{2}{(2\alpha)^3} \right] = \frac{\pi}{\alpha^3}$$

$$E_\phi = \frac{\left[ \frac{\pi \hbar^2}{2m\alpha} - \frac{e^2}{4\pi\varepsilon_0 \alpha^2} \right]}{\frac{\pi}{\alpha^3}} = \frac{\hbar^2 \alpha^2}{2m} - \frac{e^2 \alpha}{4\pi\varepsilon_0}$$

At minima, $\frac{dE}{d\alpha} = 0$, $\quad \frac{\hbar^2}{2m} \cdot 2\alpha - \frac{e^2}{4\pi\varepsilon_0} = 0$

$$\boxed{\alpha = \frac{m e^2}{4\pi\varepsilon_0 \hbar^2}}$$

$$E_\phi = \frac{\cancel{\hbar^2}}{2\cancel{m}} \left[ \frac{m^{\cancel{2}} e^4}{16\pi^2 \varepsilon_0^2 \cancel{\hbar^4}_{\hbar^2}} \right] - \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{m e^2}{4\pi\varepsilon_0 \hbar^2}$$

$$\boxed{E_\phi = -\frac{1}{2} \frac{m e^4}{16\pi^2 \varepsilon_0^2 \hbar^2}} =$$

$$\boxed{E_n = -\frac{1}{n^2} \frac{m e^4}{8\varepsilon_0^2 h^2}}$$

(Actual energy ground state)