VARIATIONAL Method

UNIT IV

MSC 202

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VARIATIONAL METHOD

It is an approximation method to obtain the energy of the particle in the various energy-eigen states of a quantum mechanical system when perturbation is large. Perturbation theory is not applecable when there is a large variation from the exact problem then we use different approximation methods.

In this variational method, trial wave functions are chosen.

Assume a trial wave function in terms of variational parameter which includes all unknown values $\phi(\lambda n)$. The trial wave function is assumed depending on the symmetry, nodes, maxima and behaviour of the system at zero and infinity. There may be some unknown parameter and corresponding to every unknown parameter, a variational parameter is included in the trial wave function $|\phi(\lambda n)\rangle$.

These are the steps followed in variational method to find the eigen- energy values-

Step 1:- Choose a trial wave function.

step 2: Find the expectation value of energy Corresponding to the trial wave function.

$$\boxed{\langle E\rangle = \frac{\langle\phi(\lambda n)|H'|\phi(\lambda n)\rangle}{\langle\phi(\lambda n)|\phi(\lambda n)\rangle}}$$

step 3: Minimize the above expectation value of energy w.r.t to the variational parameter and find the minimum value of energy.

Note: The calculated energy of the particle from this method will be greater than or to the exact energy of the particle.

Ex:- What would be the ground state energy of the hamiltonian $H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x)$. If variational principle is used to calculate it with the trial w.f. $\psi(x) = Ae^{-bx^2}$ with 'b' as a variational parameter.

Sol Here in hamiltonian Dirac delta function is present.
Here α, A and b are Constants.

Step I:- Trial w.f. already given $\psi(x) = Ae^{-bx^2}$

Step II:- $\langle H\rangle = \frac{\int \psi^* H\psi\, dx}{\int \psi^*\psi\, dx}$

$$\langle H\rangle = \frac{|A|^2\int_{-\infty}^{+\infty} e^{-bx^2}\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x)\right]e^{-bx^2}dx}{|A|^2\int_{-\infty}^{+\infty} e^{-2bx^2}dx}$$

$$\langle H\rangle = \frac{b\hbar^2}{2m} - \frac{\alpha(2b)^{1/2}}{\sqrt{\pi}} \quad -(1)$$

Step III:- $\frac{\partial\langle H\rangle}{\partial b} = 0$

$$b = \frac{2\alpha^2m^2}{\pi\hbar^4}$$

Put this value of b in eq (1) we get

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

Ans

Applications

1. Helium Atom

The hamiltonian -

$$H = \frac{-\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

$$r_{12} = |r_1 - r_2|$$

Let us take the wave function as.

$$\psi(\alpha) = \left(\frac{\alpha}{\pi a_0}\right)^3 e^{-\alpha(r_1+r_2)/a_0}$$

with this wave function, the energy.

$$\boxed{E = -77.50 \text{ eV}}$$

we have to derive this.

From hamiltonian, it is clear that the perturbation is the interaction between the two electrons

$$\therefore H' = \frac{e^2}{r_{12}}$$

Here, r_1 and r_2 are the distance of the two electrons from the Helium nucleus of charge Ze and r_{12} is the interelectron distance.

Now w.f. of He-atom can be written as the product of two hydrogenic wave function.

$$\psi(r_1, r_2) = u_1(r_1) \cdot u_2(r_2)$$

where $u_1(r_1)$ and $u_2(r_2)$ are the wave function of particle 1 & particle 2 in a hydrogenic atom with nuclear charge 'Ze'

$$\therefore \psi(r_1, r_2) = \left(\frac{Z^3}{\pi a_0^3}\right) e^{-Zr_1/a_0} \times \left(\frac{Z^3}{\pi a_0^3}\right) e^{-Zr_2/a_0}$$

Now, the unperturbed ground state energy is equal to the sum of the ground state energies of two hydrogenic atoms.

$$E_n = -13.6 Z^2/n^2 \quad (\text{Energy of H-atom})$$

For He atom

$Z = 2$ & $n = 1$ (for Ground state)

$$E = \left(-13.6 \cdot \frac{4}{1}\right) \times 2$$

$$\boxed{E = -13.6 \times 8 = -108.8\,eV}$$

This is the calculated energy value of He-atom. But the experimental value of G.S. (Ground state) of He-atom is 79 eV, so there is a large difference b/w these two values.

By using perturbation let us calculate the I order correction in energy-

$$E_0^{(1)} = \langle \psi^{(0)} | H' | \psi^{(0)} \rangle$$

$$= \iint \psi^{*(0)}(r_1, r_2)\, \hat{H}'\, \psi^{(0)}(r_1, r_2) \cdot d\tau_1 d\tau_2$$

$$E_0^{(1)} = \frac{Z^6}{\pi^2} \iint e^{-2Z(r_1+r_2)} / r_{12} \; d\tau_1 d\tau_2 .$$

where $d\tau = r^2 \sin\theta \cdot dr\, d\theta\, d\phi$

On solving we get.

$$E_0^{(1)} = \left(\frac{5}{8}\right) Z$$

$$E = E_0^{(0)} + E_0^{(1)}$$

$$= -Z^2 + 5/8 Z = -(Z^2 - 5/8 Z)$$

Reincorporating the original units

$$E_0 = -\left(Z^2 - \frac{5}{8} Z\right) \frac{Me^2}{2\hbar^2} \quad \text{(for electron)}$$

$$E_0 = -(Z^2 - 5/8 Z)(27.2\,eV)$$

$$\boxed{E_0 = -74.8\,eV}$$

Here also, the agreement between the theoretical and experimental value is not good.

Now, Applying variational method to find out the G.S. energy of He-atom.

To improve the predictions of the ground state by a variational calculations.

we may write the expectation value of the kinetic energy, of the potential energy and the Coulomb repulsion as functions of the parameter z^* entering the wave function.

The value $z = 2$, ie kept in the hamiltonian

$$\langle \psi^{(0)}(r_1, r_2) | H' | \psi^{(0)}(r_1, r_2) \rangle_{z^*} = -2(z^*)^2 E_H + 4 z z^* E_H - \frac{5}{4} z^* E_H$$

Minimize this w.r.t z^* yields the effective value $z^* = 1.69$ for He.

Put this value of z^*, the final result is -

$$\langle \psi^{(0)}(r_1, r_2) | H' | \psi^{(0)}(r_1, r_2) \rangle_{\text{at } z^* = 1.69} = 5.69 E_H$$

$$\therefore \langle \psi(r_1 r_2) | H' | \psi(r_1, r_2) \rangle = 5.69 \times (-13.6) \text{ eV}$$

$$\boxed{\langle H' \rangle_{G.S.} = -77.384 \text{ eV}}$$

This is even better agreement with the experimental value than the I order perturbation result.

Application 2: The Ground state energy of a one dimension harmonic oscillator of mass 'm'

we know that, hamiltonian of the system

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

Step I:- choose trial wave function

$$\psi(x) = A e^{-\alpha x^2}$$

where α is variable parameter

∴ Normalization condition

$$\int_{-\infty}^{+\infty} \psi^* \psi \, dx = 1$$

$$|A|^2 \int_{-\infty}^{+\infty} e^{-2\alpha x^2} dx = 1$$

$$|A|^2 \sqrt{\pi/2\alpha} = 1$$

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

normalized w.f. $\psi(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} . e^{-\alpha x^2}$

Step II:- $\langle H \rangle = \langle \psi(x) | H | \psi \rangle$

$$\langle H \rangle = \int_{-\infty}^{+\infty} \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}} . e^{-\alpha x^2} . \left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right)\left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\alpha x^2} dx$$

$$\langle H \rangle = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-\alpha x^2}\left(-2\alpha e^{-\alpha x^2} + 4\alpha^2x^2 e^{-\alpha x^2}\right)dx \; (-\hbar^2/2m) + \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}} \int e^{-2\alpha x^2} \cdot \frac{1}{2}m\omega^2x^2 \, dx$$

$$\langle H \rangle = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}} \left[-2\alpha\left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}} + 4\alpha^2 . \frac{1}{2}\left(\frac{\pi}{8\alpha^3}\right)^{\frac{1}{2}}\right] \times \left(\frac{-\hbar^2}{2m}\right) + \text{ '' Two term}$$

$$\langle H \rangle = -\alpha\left(\frac{-\hbar^2}{2m}\right) + \frac{1}{2}m\omega^2\left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} x^2 e^{-2\alpha x^2} dx$$

$$\langle H \rangle = \frac{\hbar^2\alpha}{2m} + \frac{1}{2}m\omega^2\left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}}\left[\frac{1}{2}\left(\frac{\pi}{8\alpha^3}\right)^{1/2}\right]$$

∴ we know $\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} = \frac{1}{2}\sqrt{\pi/\alpha^3}$

$$\langle H \rangle = \frac{\hbar^2\alpha}{2m} + \frac{1}{2}m\omega^2\left[\frac{1}{2}\times\left(\frac{2\alpha\pi}{8\alpha^3\pi}\right)^{\frac{1}{2}}\right]$$

$$\langle H \rangle = \frac{\hbar^2\alpha}{2m} + \frac{1}{2}m\omega^2 \; \frac{1}{2}\times\left(\frac{1}{4\alpha^2}\right)^{\frac{1}{2}}$$

$$\langle H \rangle = \frac{\hbar^2 \alpha}{2m} + \frac{1}{2} m\omega^2 \left(\frac{1}{4\alpha}\right)$$

$$\langle H \rangle = \frac{\hbar^2 \alpha}{2m} + \left(\frac{m\omega^2}{8\alpha}\right) \quad \text{—(1)}$$

Now step III:- $\frac{d}{d\alpha}\langle H \rangle = 0$

$$\frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0$$

$$\frac{\hbar^2}{2m} = \frac{m\omega^2}{8\alpha^2}$$

$$8\alpha^2 \hbar^2 = 2m^2\omega^2$$

$$\alpha^2 = \frac{m^2\omega^2}{4\hbar^2}$$

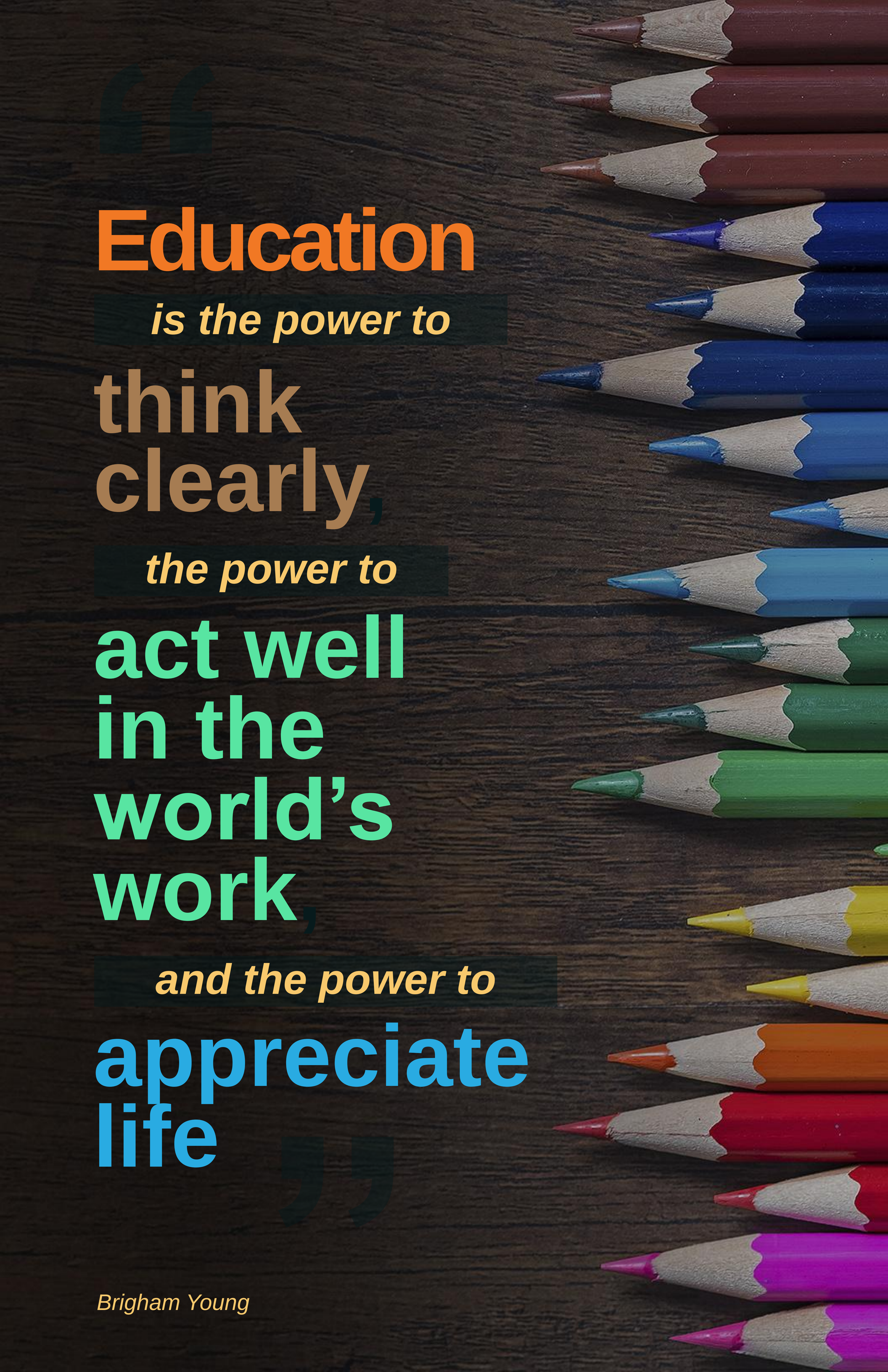
$$\boxed{\alpha = \frac{m\omega}{2\hbar}}$$

Put the value of 'α' in eq (1)

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

$$\langle H \rangle = \cancel{2}\hbar\omega/\cancel{4}_2$$

$$\boxed{\langle H \rangle_{min} = \hbar\omega/2}$$


“
Education
is the power to
think clearly,
the power to
act well in the world’s work,
and the power to
appreciate life
”
Brigham Young