Find out the approximate solution of Schrodinger equation for helium atom using variation method.

Ans. The hamiltonian for helium atom in atomic units is

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left(\frac{2}{r_1} + \frac{2}{r_2}\right) + \frac{1}{r_{12}} \quad \ldots (1)$$

Where

∇_1^2 = Laplacian operator for electron 1

$\nabla_2^2 =$,, ,, ,, ,, 2

r_1 = distance of electron 1 from the nucleus

r_2 = ,, ,, 2 ,, ,,

r_{12} = distance between electron 1 and electron 2

$2 = Z$ = nuclear charge of *He* atom .

As a result of screening, each electron (1 and 2) shields the other from the nucleus so that the two electrons do not experience the same nuclear charge. So, it is obvious to use a wave function with nuclear charge Z, less than 2. Thus, Z is a variation parameter which is determined from the variational calculation. Let the trial wave function for the *He* atom be

$$\psi(r_1, r_2) = \left(\frac{z^3}{\pi}\right)^{1/2} e^{-zr_1} \times \left(\frac{z^3}{\pi}\right)^{1/2} e^{-zr_2}$$

$$= \left(\frac{z^3}{\pi}\right) e^{-z(r_1 + r_2)} \qquad \dots (2)$$

Now, $\quad E = < \psi \,|\, \hat{H} \,|\, \psi > \qquad \dots (3)$

Putting the value of $\hat{H}$ from equation (1) in equation (3); we get

$$E = -\frac{1}{2} < \psi \,|\, \nabla_1^2 \,|\, \psi > -\frac{1}{2} < \psi \,|\, \nabla_2^2 \,|\, \psi >$$

$$-2\,\psi < \left| \frac{1}{r_1} \right| \psi > -2\,\psi < \left| \frac{1}{r_2} \right| \psi > + \psi < \left| \frac{1}{r_{12}} \right| \psi > \qquad \dots (4)$$

The Laplacian operator in spherical polar co-odinates (r, θ, ϕ) is given by

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta . \frac{\partial}{\partial \theta}\right)$$

$$+ \frac{1}{r^2 \sin^2\theta} \cdot \frac{\partial^2}{\partial \phi^2} \qquad \dots (5)$$

Since the trial wave function does not depend upon the angles θ and ϕ, differentiations with respect to θ_1; θ_2, ϕ_1 and ϕ_2 vanish so that for the first kinetic energy operator in equation (4), we get

$$-\frac{1}{2} < \psi |\nabla_1^2| \psi > = \left(\frac{z^3}{\pi}\right)^2 \int e^{-zr_1}\left[-\frac{1}{2r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right)\right]$$

$$\times e^{-zr_1}\, r_1^2 \sin\theta_1\, dr_1\, d\theta_1\, d\phi_1 \int e^{-2zr_2} \times r_2^2 \sin\theta_2\, dr_2\, d\theta_2\, d\phi_2 \quad \ldots (6)$$

The functions of r_2 are not affected by differentiation carrying out integrations over all angles, we obtain

$$-\frac{1}{2} < \psi |\nabla_1^2| \psi > = \left(\frac{z^3}{\pi}\right)^2 (4\pi^2) \int_0^\infty e^{-zr_1}\left[-\frac{1}{2r_1^2}\cdot\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial e^{-zr_1}}{\partial r_1}\right)\right]$$

$$\times r_1^2\, dr_1 \times \int_0^\infty e^{-2zr_2}\, r_2^2\, dr_2 \quad \ldots (7)$$

The second integral in equation (7), evaluated using the standard integral, is equal to $\frac{2!}{(2z)^3}$ so that equation (7) becomes

$$(4z^3)^2\left(-\frac{1}{2}\right)\frac{2!}{(2z)^3}\int_0^\infty e^{-zr_1}\left[\frac{\partial}{\partial r_1}(-zr_1^2\, e^{-zr_1})\right] dr_1$$

$$= -(2z^3)\int_0^\infty e^{-zr_1}(-2zr_1 + z^2r_1^2)\, e^{-zr_1}\, dr_1$$

$$= -(2z^3)\left[-2z\int_0^\infty r_1\, e^{-zr_1}\, dr_1 + z^2\int_0^\infty r_1^2\, e^{-zr_1}\, dr_1\right]$$

$$= -(2z^3)\left[-\frac{2z}{(2z)^2} + \frac{z^2 2!}{(2z)^3}\right] = \frac{z^2}{2} \quad \ldots (8)$$

Similarly, the second kinetic energy operator term in equation (4) gives $z^2/2$. The third electron-nuclear attraction energy terms simplifies to

$$\left(\frac{z^3}{\pi}\right)^2 \int e^{-zr_1} e^{-zr_2}\left[-\frac{2}{r_1}\right] e^{-zr_1} e^{-zr_2}\, r_1^2 \sin\theta_1$$

$$\times dr_1 d\theta_1 d\phi_1 \times r_2^2 \sin\theta_2 . dr_2 d\theta_2\, d\phi_2 .$$

$$= (4z^3)^2 (-2) \int_0^{\infty} r_1 e^{-2zr_1} dr_1 \int_0^{\infty} r_2^2 e^{-2zr_2} dr_2$$

$$= -32 z^6 \times \frac{1}{(2z)^2} \times \frac{2!}{(2z)^3} = -2z$$

Similarly the fourth term in equation (4) gives $-2z$. The fifth term, the interelectronic repulsion energy integral, is some what more tedious. It evaluates to 5/8 z. Combining all these contributions, equation (4) becomes

$$E = 2 . \frac{z^2}{2} + 2(-2z) + \frac{5}{8} z$$

$$= z^2 - \frac{27}{8} z \qquad \dots (9)$$

Now, the energy is minimised with respect to z, obtaining

$$\frac{\partial E}{\partial z} = 2z - \frac{27}{8} = 0$$

or, $$z = \frac{27}{16} = 1.69$$

Putting the value of z in equation (9), we get the ground state energy of He atom as

$$E_0 = \left(\frac{27}{16}\right)^2 - \frac{27}{8} \times \frac{27}{16}$$

$$= -2.8476 \text{ a.u.}$$

$$= -2.8476 \times 27.21 \text{ eV } (1 \text{ a.u.} = 27.21 \text{ eV})$$

$$= -77.48 \text{ eV}.$$

The experimental value of ground state energy of He atom is –78.986 eV.