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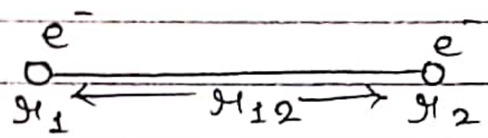
Lecture for M.Sc. Physics II Semester students

Paper – III Quantum Mechanics – II

Unit- I: Variation Method

Affilication of Variation Method for ground state of He-atom :-

The Variation Method is used to Obtain the energy of He-atom in ground state or in the normal state. If two atoms are separated by each other by r_{12} & represented by ;



The He-atom is Consist of nucleus of charge +Ze, then the Hamiltonian can be written as OR Nucleus is said to be in rest condition then, the total Hamiltonian of the particle, can be written as;

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

Where, $\frac{e^2}{r_{12}}$ is the interaction Value of energy & r_{12} are the distances of two electrons. If the interaction energy $\frac{e^2}{r_{12}}$ b/w the two electrons where not present. Then, the ground state eigen function will be the product of two Hydrogen like atom, then the trial func for the He-atom will be given by;

$$\Psi = \frac{\lambda^3}{\pi a_0^3} e^{-\lambda / a_0 (r_1 + r_2)} \quad \text{—} (2)$$

where, λ is Variation parameter.

π is phase difference.

a_0 is Bohr radius (minimum) for particle.

$e^{-\lambda/a_0}$ → the process is Continuous.

We know that;

$$\int \Psi^* \Psi \, d\tau = 1 \quad \text{—} (3)$$

Eq. (3) shows that the wave function is Normalized.

Now; Considering the expectation value of Hamiltonian:

$$\langle H \rangle = \int \Psi^* H \Psi \, d\tau \quad \text{—} (4)$$

Then, the total Energy equation OR the expectation value of Hamiltonian H will be the sum of kinetic Energy, Potential Energy & Interaction Energy of electrons :- & can be written as eq. (5):

$$\langle H \rangle = \langle T \rangle + \langle V \rangle + \left\langle \frac{e^2}{r_{12}} \right\rangle \quad \text{—} (5)$$

Then, by the expectation Value Calculation of Hydrogen like atom. The Value of K.E. & P.E. is given by;

$$\langle T \rangle = \frac{\lambda^2 e^2}{2a_0}$$
$$\langle V \rangle = -\frac{2\lambda e^2}{a_0} \quad \text{(6)}$$

But in the case of He-atom there are two electrons. So, the eq.(6) will be twice of Hydrogen like atom;

$$\langle T \rangle = 2 \times \frac{\lambda^2 e^2}{2a_0} = \frac{\lambda^2 e^2}{a_0}$$
$$\langle V \rangle = 2 \times \frac{-2\lambda e^2}{a_0} = \frac{-4\lambda e^2}{a_0} \quad \text{— (7)}$$

Now putting the values of eq.(7) in eq.(5), To get the expectation value of He-atom, we get;

$$\langle H \rangle = \frac{\lambda^2 e^2}{a_0} - \frac{4\lambda e^2}{a_0} + \left\langle \frac{e^2}{r_{12}} \right\rangle \quad \text{— (8)}$$

Now, since the expectation value of I.E. is to be calculated, then the electron Interaction Energy for He-atom can be given by;

$$\Rightarrow \left\langle \frac{e^2}{r_{12}} \right\rangle = \iint \psi^* \frac{e^2}{r_{12}} \psi \, d\tau \qquad \text{—— (9)}$$

Then, this Interaction can be evaluated by considering the uniform charge distribution of sphere containing each electron & on solving we get, the expectation value of I.E. ;

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{5\lambda e^2}{8a_0} \qquad \text{—— (10)}$$

Then, the expectation value for Hamiltonian can be written as;

$$\langle H \rangle = \frac{\lambda^2 e^2}{a_0} - \frac{4\lambda e^2}{a_0} + \frac{5\lambda e^2}{8a_0}$$

$$= \frac{\lambda e^2}{a_0}\left\{ \lambda - 4 + \frac{5}{8} \right\}$$

$$= \frac{\lambda e^2}{a_0}\left\{ \lambda - \frac{27}{8} \right\}$$

$$= \frac{e^2}{a_0}\left(\lambda^2 - \frac{27}{8}\lambda \right) \qquad \text{—— (11)}$$

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Now for the minimum Value of Hamiltonian H, differentiate eq.(11) w.r.t. "λ", we get;

$$\frac{d\langle H\rangle}{d\lambda} = 0 \quad ; \quad \frac{d}{d\lambda}\left\{\frac{e^2}{a_0}\left(\lambda^2 - \frac{27\lambda}{8}\right)\right\} = 0$$

$$\Rightarrow \frac{e^2}{a_0}\left(2\lambda - \frac{27}{8}\right) + 0 \cdot \left(\lambda^2 - \frac{27\lambda}{8}\right) \Rightarrow \frac{e^2}{a_0}\left(2\lambda - \frac{27}{8}\right) = 0$$

$$\Rightarrow \quad 2\lambda - \frac{27}{8} = 0$$

$$\Rightarrow \boxed{\lambda = \frac{27}{16} = 1.69} \quad \text{—— (12)}$$

Now putting the value of λ, we get ground state energy E_0 in eq.(11);

$$\langle H\rangle = \frac{e^2}{a_0}\left[\left(\frac{27}{16}\right)^2 - \frac{27}{8} \times \frac{27}{16}\right]$$

Then, we get;

$$\boxed{\langle H\rangle = -77.5 \text{ eV}}$$

This is the required ground state energy calculation for He-atom.