

The variational method can be applied to ground state energy of Helium.

$$E = \int dr_1 dr_2 \psi \hat{H} \psi \quad \text{--- (1)}$$

with  $\hat{H}$  given as

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

$$\text{and } \psi \Rightarrow \psi^{(0)}(r_1, r_2) = \psi_{1s}(r_1) \psi_{1s}(r_2) \quad \text{--- (3)}$$

The resultant of the solution for the equation

$$E = Z^2 - \frac{27}{8} Z \quad \text{--- (4)}$$

On minimizing  $E$  with respect to  $Z$  we find

$$Z_{\min} = \frac{27}{16} \quad \text{--- (5)}$$

$$\text{and } E = -\left(\frac{27}{16}\right)^2 - \left(\frac{27}{8}\right) Z$$

$$\text{or } E = -2.8477 \text{ a.u.} \quad \text{--- (6)}$$

As compared to the first order perturbation theory result of  $-2.7500 \text{ a.u.}$  and the higher order result  $-2.9037 \text{ a.u.}$

The value of  $Z$  that minimizes  $E$  can be interpreted as an effective nuclear charge. The fact that  $Z$  comes out less than 2 reflects the fact that each electron partially screens the nucleus from the other, so that effective nuclear charge is reduced from 2 to  $\frac{27}{16}$ .

There is an agreement between first order perturbation theory result or the variational result and the experimental result may be ~~very~~ close.

The ionization energy of Helium is given as

$$IE = E_{\text{He}^+} - E_{\text{He}} \quad \text{--- (7)}$$

The energy of  $\text{He}^+$  is  $-Z^2/2$  (with  $Z=2$ ) in atomic units. Hence

$$IE = -2 + \frac{11}{4} = 0.750 \text{ au} \quad \text{--- (8)}$$

$$= 20.4 \text{ eV}$$

(According to first order perturbation).

or

$$IE = -2 + \left(\frac{27}{16}\right)^2 = 0.848 \text{ au} = 23.1 \text{ eV} \quad \text{--- (9)}$$

(variational result)

The experimental value of IE is 0.904 eV or 24.6 eV.

This implies that variational result even with 2% discrepancy of experimental value is not satisfactory. This is nearly the order of order chemical bonds  $1.5 \text{ eV} \equiv 145 \text{ kJ.mol}^{-1}$

✓ Thus we need a more trial function rather than equation (3) where

$$\psi^{(0)}(r_1, r_2) = \psi_{1s}(r_1) \psi_{1s}(r_2)$$

Slater (1930) introduced a new set of orbitals called Slater orbitals of the form

$$\psi_{nlm}(r, \theta, \phi) = N_{nlm} r^{n-1} e^{-sr} Y_l^m(\theta, \phi) \quad \text{--- (10)}$$

$N_m$  is a normalization constant and  $Y_l^m$  are the spherical harmonics.

The parameter  $\xi$  is taken to be arbitrary and not similar to hydrogen like orbitals.

$$\Psi = S_{100}(r_1, \theta_1, \phi_1) S_{100}(r_2, \theta_2, \phi_2) \quad \text{--- (11)}$$

On using equation (11) as trial wave function with  $\xi$  as the only variational parameter

$$\xi = 1.6875 = \left(\frac{27}{16}\right)$$

$$\text{and } E = -2.8477 \text{ au.}$$

(The values are obtained from the ground state energy calculations of Helium atom).

The value of IE = 23.1 eV while the experimental value is 24.6 eV.

On keeping another variational parameter  $n$  and hence the trial functions

$$\Psi = S_{n00}(r_1, \theta_1, \phi_1) S_{n00}(r_2, \theta_2, \phi_2) \quad \text{--- (12)}$$

$$\left. \begin{array}{l} n = 0.995 \\ \xi = 1.6116 \\ \text{and } E = -2.8542 \end{array} \right\} \text{The values obtained from solution.}$$

The IE value is 23.2 eV.

On increasing the flexibility of the trial function of the form in which  $\Psi(r_1, r_2)$  is a product of one electron function or orbitals.

$$\boxed{\Psi(r_1, r_2) = \phi(r_1) \phi(r_2)} \quad \text{--- (13)}$$

This is limit of practical and theoretical values.

In this equation

$$E = -2.8617 \text{ au}$$

$$\text{and } IE = 0.8617 \text{ au or } 23.4 \text{ eV}$$

The variational result is  $2.9037 \text{ au}$  and  $0.9037 \text{ au}$  respectively for  $E$  and  $IE$

The limiting value is the best value of energy that can be obtained using a trial function of the form of a product of  $n$  electron wave functions. The limit is called Hartree - Fock Limit and the concept of electron orbital preservation is known as Hartree Fock approximation.

### Hartree - Fock equations (Self Consistent Field Method)

The starting of HF procedure for He is the setting of two-electron wave function as a product of orbitals

$$\psi(r_1, r_2) = \phi(r_1) \phi(r_2) \text{ --- (1)}$$

According to eq (1), the probability distribution function of electron (2) is  $\phi^*(r_2) \phi(r_2) dr_2$ .

The probability distribution can be interpreted as classical charge density and potential energy that electron 1 experiences at point  $r_1$  due to electron 2 is

$$U_1^{\text{eff}}(r_1) = \int dr_2 \phi^*(r_2) \frac{1}{r_{12}} \phi(r_2) \text{ --- (2)}$$

where  $U_1^{\text{eff}}(r_1)$  is effective/average potential

Effec. One - electron Hamiltonian operator can be defined as

$$\hat{H}_1^{\text{eff}}(r_1) = -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} + U_1^{\text{eff}}(r_1) \quad \text{--- (3)}$$

The Schrodinger equation corresponding to this effective Hamiltonian is

$$\hat{H}_1^{\text{eff}}(r_1) \phi(r_1) = \epsilon_1 \phi(r_1) \quad \text{--- (4)}$$

This is the Hartree Fock equation equation for Helium atom.

The solution eq. (4) gives orbital wave function for Helium atom.

Applying variational principle to the energy of a Helium atom

$$E = \iint dr_1 dr_2 \phi^*(r_1) \phi^*(r_2) \hat{H} \phi(r_1) \phi(r_2) \quad \text{--- (5)}$$

Here  $\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$  as

solved,

using  $\hat{H}$  in equation (5) and solving

$$E = I_1 + I_2 + J_{12} \quad \text{--- (6)}$$

where  $I_j = \int dr_j \phi(r_j) \left[ -\frac{1}{2} \nabla_j^2 - \frac{Z}{r_j} \right] \phi(r_j) \quad \text{--- (7)}$

and  $J_{12} = \iint dr_1 dr_2 \phi^*(r_1) \phi(r_2) \frac{1}{r_{12}} \phi(r_1) \phi(r_2) \quad \text{--- (8)}$

Also  $J_{12}$  is called Coulomb Integral.

On minimizing  $E$  with respect to  $\phi$ . we get eq. (4) and  $\hat{H}_1^{\text{eff}}$  in this equation is spherically symmetrical we get

$$\phi(r) = R(r) Y_l^m(\theta, \phi) \quad \text{--- (9)}$$

$R(r)$  is radial function to be determined and  $Y_l^m(\theta, \phi)$  is spherical harmonic.

Using eq. (9) in eq. (4) we get

$$\left[ -\frac{1}{2r_1^2} \frac{d}{dr_1} \left( r_1^2 \frac{d}{dr_1} \right) - \frac{Z}{r_1} + \frac{l(l+1)}{2r_1^2} + U_1^{\text{eff}}(r_1) \right] R(r_1) = ER(r_1) \quad \text{--- (10)}$$

As  $U_1^{\text{eff}}(r_1)$  depends on  $\phi(r_2)$  or  $R(r_2)$  according to equation (2)

The self consistent method involves following assumptions:-

- i) guess the form of  $\phi(r)$ .
- ii) Use  $\phi(r)$  to evaluate  $U_1^{\text{eff}}(r)$  in such a way the  $\phi(r_1)$  as input and  $\phi(r_2)$  are different than the output.
- iii) Continue to cyclic process until  $\phi(r)$  input and  $\phi(r)$  output are sufficiently close to each other. In other ~~words~~ words their value is self consistent.

The orbitals obtained by this method is known as Hartree-Fock orbitals.

The linear combinations of Slater orbitals are performed for  $\phi(r)$  varying the parameter in each Slater orbitals and number of Slater orbitals used until convergence is obtained.