

Approximate Methods - II

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APPROXIMATE METHOD

Application of first order Perturbation theory to Helium atom:

We shall solve the Schrodinger's wave equation for the ground state of the He atom using first order time independent Perturbation theory. In this case,

$$\hat{H}\psi = E\psi$$

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad - (1)$$

Where \hat{H}_0 is the unperturbed Hamiltonian which is given by

$$\hat{H}_0 = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad - (2)$$

The Perturbed Hamiltonian \hat{H}_1 is given by

$$\hat{H}_1 = \frac{e^2}{4\pi\epsilon_0 r_{1,2}} \quad - (3)$$

Where r_1 and r_2 are the distance of the two electron from the Helium nucleus of charge Ze and $r_{1,2}$ is the distance between the electrons. We shall use atomic units so that-

$$\hat{H}_0 = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \left(\frac{2}{r_1} + \frac{2}{r_2} \right) \quad - (4)$$

$$\hat{H}_1 = \frac{1}{r_{1,2}} \quad - (5)$$

Since $\hat{H}_1 \ll \hat{H}_0$, it is suitable to use Perturbation theory.

The \hat{H}_0 is the sum of two one electron Hamiltonians, the unperturbed wave function $\psi_0(r_1, r_2)$ can be written as

$$\psi_0(r_1, r_2) = \psi_0(r_1) \cdot \psi_0(r_2) \quad (6)$$

When $\psi_0(r_1)$ is the wave function of the i th electron is a hydrogenic atom with nuclear charge $= Ze$ then

$$\psi_0(r_1, r_2) = \left(\frac{Z^3}{\pi a_0^3} \right)^{1/2} e^{-\frac{Zr_1}{a_0}} \left(\frac{Z^3}{\pi a_0^3} \right)^{1/2} e^{-\frac{Zr_2}{a_0}}$$

$$\psi_0(r_1, r_2) = \left(\frac{Z^3}{\pi} \right) e^{-2Z(r_1+r_2)} \quad (7)$$

The unperturbed ground state energy $E_0^{(0)}$ is equal to the sum of the ground state energies of two hydrogenic atoms:

$$E_0^{(0)} = \left(-\frac{Z^2}{2} \right) + \left(-\frac{Z^2}{2} \right) = -Z^2 \quad (8)$$

The first order correction to the ground state energy is

$$E_0^1 = \langle \psi_0 | \hat{H}_1 | \psi_0 \rangle$$

$$E_0^1 = \iint \psi_0(r_1, r_2) \hat{H}_1 \psi_0(r_1, r_2) d\tau_1 d\tau_2 \quad (9)$$

Substituting the value of $\psi_0(r_1, r_2)$ from equation (7) in equation (9) we get

$$E_0^1 = \frac{Z^6}{\pi^2} \iint e^{-2Z(r_1+r_2)} \left(\frac{1}{r_1 r_2} \right) d\tau_1 d\tau_2 \quad (10)$$

Where the volume elements of the two electrons in polar coordinates are:

$$d\tau_1 = r_1^2 \sin\theta_1 dr_1 d\theta_1 d\phi_1$$

$$d\tau_2 = r_2^2 \sin\theta_2 dr_2 d\theta_2 d\phi_2$$

(3)

It is very difficult to solve the equation (10) that it is given by

$$E_0' = \frac{5Z}{8} \quad \text{--- (11)}$$

The repulsion energy between two electrons is always positive.

Adding equation (8) and (10), we get

$$\begin{aligned} E_0 &= E_0^{(0)} + E_0' = -Z^2 + \frac{5Z}{8} \\ &= -\left(Z^2 - \frac{5Z}{8}\right) \text{ (in a.u.)} \end{aligned}$$

By putting the original units we have.

$$E_0 = -\left(Z^2 - \frac{5Z}{8}\right) \frac{me^2}{2h^2} \quad \text{--- (12)}$$

For He-atom we have

$$E_0 = -\left(Z^2 - \frac{5Z}{8}\right) \times 27.2 \text{ eV}$$

$$E_0 = -2.75 \text{ a.u.} = 74.80 \text{ eV} \quad \text{--- (13)}$$

or the experimental value is -2.904 a.u.
or -78.986 eV . Thus, there is difference between the critical and experimental values. If second and higher order contributions are included, the difference decreases.