Approximate methods

Chapter-4

1. **Variation theorem -** According to this theorem, the wave function which gives the lowest energy of the system is closest to the acc0orate wave function of the system. This method is mainly used for the approximate determination of the lowest energy level (i.e the ground state) of any system the variation theorem is very useful in the treatment of chemical bonding. So, will only discuss this method,

The Schrodinger's wave equation is

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

....................(1)

Rearranging equation (1)we get,

$$\left(-\frac{h^2\nabla^2}{8\pi^2 m} + V\right)\Psi = E\Psi$$

.....................(2)

The term on the left hand side of equation (2) can be considered to be an operator acting on Ψ. Thus , equation (2) may be written as:

$$\widehat{H}\Psi = E\Psi$$

....

(3`

Where $\widehat{H}$ ıs   as Hamiltonian operator . Multiplying both sides of equation (3) by Ψ^* and then integrating over the configuration space, we have

$$\int \Psi^* H\Psi \, d\tau = E \int \Psi \Psi^* d\tau$$

Or $\qquad\qquad E = \frac{\int \Psi^* H\Psi \, d\tau}{\int \Psi\Psi^* d\tau}$ $\qquad$ (4)

Application of variation theorem to hellumatom : The Hamiltonian for helium atom in atomic units is given by

$$\widehat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left(\frac{2}{r_1}+\frac{2}{r_2}\right) + \frac{1}{r_1,r_2}$$

..........(5)

Where r_1 and r_2 are the distances of electrons 1 and 2 respectively from the nucleus. Due to screening effect, each electron 1 and 2 shields the other from the nucleus so that the two electrons do not the same nuclear charge. Here it is necessary to use a wave function with nuclear charge z less

than that 2 i.e. z is a variation parameter which shall be determined from the variational calculation. The Hamiltonian in eq. (5) contains z =2. The variatinlaparameter appear only in the trial wave function.

$$\Psi(r_1,r_2) = \left(\frac{z^3}{\pi}\right)^{1/2} e^{-z\,1.} \left(\frac{z^3}{\pi}\right)^{1/2} e^{-z\,2.} \qquad \ldots\ldots\ldots\ldots(6)$$

$$= \left(\frac{z^3}{\pi}\right) e. \quad [-z(r_1 + r_2)] \qquad \ldots\ldots\ldots(7)$$

$$E = \langle\Psi|\hat{H}| \qquad \ldots\ldots\ldots\ldots(8)$$

Substituting the value of $\hat{H}$ from equation (5) in equation (8), we get

$$E = -\frac{1}{2} \; |\begin{smallmatrix}2\\1\end{smallmatrix}| \; -\frac{1}{2} \; |\begin{smallmatrix}2\\2\end{smallmatrix}| \; -2 \; \left|\frac{1}{r_1}\right| \; -2 \; \left|\frac{1}{r_1}\right| \; +$$

$$\left|\frac{1}{r_12}\right| \quad \ldots(9)$$

The laplacian operator in spherical polar co- ordinate (r,θ,ϕ) is given by ;

$$^2 = \frac{1}{r^2}\cdot\frac{\partial}{\partial}\left(r^2\frac{\partial}{\partial}\right) + \frac{1}{r^2.s\,i}\frac{\partial}{\partial}\left(s\,i\quad\frac{\partial}{\partial}\right) + \frac{1}{r^2.s\,i\;{}^2\theta}\frac{\partial^2}{\partial^2\phi^2}$$

$$\ldots.. \;..(10)$$

Since the equation (6) does not depend upon angle θ and ϕ, the differentiation with respect to $\theta_1, \phi_1, \theta_2,$ and

ϕ_2 disappear so that for the first kinetic energy operator in equation (9), we get

$$-\frac{1}{2} \; |\begin{smallmatrix}2\\1\end{smallmatrix}| \; = \left(\frac{z^3}{\pi}\right)^2 \; e^{-z} \left[\frac{1}{2r_1^2}\cdot\frac{\partial}{\partial}\left(r_1^2\frac{\partial}{\partial r_1}\right)\right]e^{-z}$$

$$x r_1^2 \; s.\; \theta_1\; d\; \theta_1 d\theta_1 d\phi_1, \quad e^{-z\; r_2}\frac{\partial}{\partial}s.\; \theta_2 d\; \theta_2 d\theta_2 d\phi_2,$$

$$\ldots\ldots(11)$$

The functions of r_2 are unaffected by differentiation , if we carry out the integration over all angles. We get.

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$$\frac{1}{2} \; |\begin{smallmatrix}2\\1\end{smallmatrix}| \quad =$$

$$\left(\frac{z^3}{\pi}\right)^2 (4r)^2 \;\; {}_0\!\int^\infty e^{-z} \left[-\frac{1}{2r_1^2}\cdot\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1,}^{-z}\right)\right] r_1^2 d\; {}_1 x \;\; {}_0\!\int^\infty e^{-z\;r_2}.r_2^2 d\; {}_2$$

$$\ldots\ldots(12)$$

The second integral, calculated using the slandered integer , is equal to $\frac{2!}{(2z)^3}$ so that equation (12) becomes

$$(4z^3)^2 \left(-\frac{1}{2}\right)\frac{2!}{(2z)^3}\int_0^\infty e^{-z}\left[\frac{\partial}{\partial r_1}(-zr_1^2 e^{-z}\,)\right]d\;{}_1$$

$$= (-2z^3) \;\; {}_0\!\int^\infty e^{-z} \; (-2zr_1 + z^2 r_1^2)e^{-z}\; d\;{}_1$$

$$= (-2z^3)\left[\int_0^\infty e^{-z\ r_1}e^{-z\ r_1}d\ _1 + z^2\int_0^\infty r_1^2 e^{-z\ r_1}d\ _1\right]$$

$$= (-2z^3)\left[-\frac{2z}{(2z)^2} + \frac{z^2 2!}{(2z)^3}\right] = \frac{z^2}{2} \qquad \ldots\ldots\ldots(13)$$

Similarly, the second kinetic energy operator in equation (9) gives $Z^2/2$. the third and the fourth electron nuclear attraction energy terms can be handled easily. For example the third terms amplifies to

$$\left(\frac{Z^2}{\pi}\right)^2\int e^{-z}\ e^{-z\ r_2}\left[-\frac{2}{r_2}\right]e^{-z}.e^{-z\ r_2}r_1^2 s_1\ \theta_1 d\ _1 d\theta_1 d\ _1 x\ r_2^2 s_2\ d_2$$

$$= (4z^3)^2(-2)\int_0^\infty r_1^2 e^{-z\ r_1}d\ _1\int_0^\infty r_2^2 e^{-z\ r_2}d\ _2$$

$$= 32Z^6.\frac{2}{(2x)^2}.\frac{2!}{(2z)^3} = 2z \qquad \ldots\ldots (14)$$

Similarly, the fourth terms in equation (9) gives -2z. The fifth terms is somewhat more difficult. It is given by 5z/8. Combining all these contributions, equation (9) becomes .

$$E = 2\left(\frac{z^2}{2}\right) + 29 - 2z) + \frac{5}{8}z$$

Or $\qquad E = z^2 - \frac{2}{8}z \qquad \ldots\ldots\ldots\ldots\ldots(15)$

Using the variation method, minimize the energy with respect to the z and get

$$\frac{\partial}{\partial} = 2z - \frac{2}{8} = 0\ \text{when}\ z = \frac{2}{8} = 1.69$$

Substituting he value of z in equation (15), we get the lowest energy level of the atom i. e.

$$E_0 = \left(\frac{27}{16}\right)^2 - \left(\frac{27}{16}\right)\left(\frac{27}{16}\right) = 2.8476.\,a.\,u$$

$$= -(2.8476)(27.21.\text{eV})$$

Or $\qquad\qquad\qquad E_0 = 77.48e$

Perturbation Theory: The perturbation theory is another way for approximate solution of the problem. This method is based on the fact the actual problem can be treated as a slight modification or perturbation of another problem capable of exact solution.

If $\hat{H}\psi = E\psi$ represents the actual Schrödinger's wave equation to be solved then it is assumed that an exact solutio9n is available for $\hat{H}_0\psi_0 = E_0\psi_0$ where $\hat{H}_0$ differs slightly from Hamiltonian for the actual problem .

This method may be illustrated by taking the state of any system (say that of H – atom) characterized by the wave function ψ .

Where acted on by external electrical filed ,it s electronic state will be change . Let the wave function of the perturbed state is($\psi + \psi$).

The Hamiltonian will also change due to the change in potential energy. Let $\hat{H}$ be the Hamiltonian in the unperturbed state and $(\hat{H} + \hat{H}_1)$ that of the perturbed state. $\hat{H}_1$ is called the amount of perturbation. Suppose $\psi_0, \psi_1 \ldots\ldots$ are the solution of the equation in unperturbed state . since these are solutions of the Schrödinger's wave equation, they must from an orthogonal set. Thus, ψ must be represented as:

$$\psi = c_1\psi_1 + c_2\psi_2 + \ldots\ldots\ldots..(1)$$

where c_1, c_2 and ψ_1, ψ_2 are very small quantities.

Let a perturbed state of the system is ψ . the wave function in the perturbed states is given by $\psi_2 +\psi$ i.e

$$\psi = \psi_2 + c_1\psi_1 + c_3\psi_3 \qquad\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Since $c_2\psi_2$ makes no contributio0n hence it does not appear in the perturbed state of ψ_2. from Schrodinger's wave equation. $\hat{H}\psi = E\psi$ .in the present case $(\hat{H} + \hat{H}_1)\psi = E\psi$ where E is energy in the perturbed state.

$$\left(\hat{H} + \hat{H}_1\right)(\psi_2 + c_1\psi_1 + c_3\psi_3) = E(\psi_2 + c_1\psi_1 + c_3\psi_3)$$

Or $\qquad \hat{H}\psi_2 + c_1\hat{H}_1\psi_1 + c_3\hat{H}\psi_3 + +\hat{H}_1\psi_2 + + c_1\hat{H}_1\psi_1 + c_3\hat{H}_1\psi_3 = E\psi_3 + Ec_3\psi_1 + Ec_3\psi_3 \qquad\ldots\ldots\ldots\ldots\ldots\ldots(3)$

Since c_1, c_3 and $\hat{H}_1$ are small quantities, the terms $c_1\hat{H}_1\psi_1$ and $\hat{H}_1 c_3\psi_3$ can be neglected form equation (3). Thus we get

$E\psi_2 - \hat{H}\psi_2 + Ec_1\psi_1 - c_1\hat{H}_1\psi_1 + Ec_3\psi_3 - c_3\hat{H}\psi_3 = \hat{H}_1\psi$

......(4)

Multiplying equation (4) by ψ_2 and then integrating over the entire configuration space, we get

$$\int\psi_2(E-H)\psi_2 d\tau + c_1\int\psi_2(E-H)\psi_2 d\tau + c_3\int\psi_2(E-H)\psi_3 d\tau = \int\psi_2\hat{H}_1\psi_2 d\tau \quad \dots$$

...........(5)

or

$$\int\psi_2 E\psi_2 d\tau - \int\psi_2\hat{H}\psi_2 d\tau = \int\psi_2\hat{H}_1\psi_2 d\tau$$

..............(6)

or

$$\int\psi_2 E\psi_2 d\tau = \int\psi_2\hat{H}\psi_2 d\tau + \int\psi_2\hat{H}_1\psi_2 d\tau$$

or

$$E = E_o + \int\psi_2\hat{H}_1\psi_2 d\tau$$

...................(7)

Where E_o = Energy of unperturbed state

The value of $\hat{H}_1$ is given by $\hat{H}_1 = eEx$ where is the electric charge, e is strength of electric filed and X is the co- ordinate of the system in the direction of field. Thus,

$$E = E_o + E\int\psi_2 X\psi_2 d\tau$$

Since all the terms of the right hand side of the above equation can be known and hence E can be found out. The wave function of the perturbed state is given by

$$(E\text{-}\hat{H})\psi_2 + c_1(E-\hat{H})\psi_1 + c_3(E-\hat{H})\psi_3 = \hat{H}_1\psi_2$$

Or $\int\psi_1(E-\hat{H})\psi_2 d\tau + c_1\int\psi_1(E-\hat{H})\psi_1 d\tau + c_3\int\psi_1(E-\hat{H})\psi_3 d\tau = \int\psi_1\hat{H}_1\psi_2 d\tau$

Or $c_1\int\psi_1 E\psi_1 d\tau + c_1\int\psi_1\hat{H}\psi_1 d\tau = \int\psi_1\hat{H}_1\psi_2 d\tau$

Or $c_1 E + c_1\int\psi_1\hat{H}\psi_1 d\tau = \int\psi_1\hat{H}_1\psi_2 d\tau$

Since all the terms are known, we can calculate c_1.

Similarly, multiplying equation $\hat{H}\psi = E b_3$, we can calculate

c_3.

Thus, $\psi = \psi_2 + c_1\psi_1 + c_3\psi_3$ can be known since.

$\psi_1, \psi_2,$ and ψ_3 can be easily known.

Application of fi8rst order perturbation theory to hellumatom : 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,

$$\hat{H} \psi = E \psi \qquad \ldots\ldots\ldots\ldots\ldots(8)$$

$$\hat{H} = \hat{H}_o + \hat{H}_1$$

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

$$\hat{H}_o = -\frac{h^2}{2\mu}(\nabla_1^2 + \nabla_2^2) - \frac{z\,e^2}{4\pi}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad \ldots\ldots\ldots\ldots(9)$$

The perturbed Hamiltonian $\hat{H}_1$ is given by,

$$\hat{H}_1 = \frac{z\,e^2}{4\pi}\,\frac{1}{r_{1,2}}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

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

$$\hat{H}_o = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left(\frac{2}{r_1} + \frac{2}{r_2}\right) \qquad \ldots\ldots\ldots\ldots..(11)$$

And $\hat{H}_1 = \frac{1}{r_{1,2}}$ $\qquad$ $\ldots\ldots\ldots\ldots.(12)$

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

The $\hat{H}_o$ is the sum of two one electron Hamiltonians, the unperturbed wave function $\psi_o(r_{1,2})$ can be written as

$$\psi_o(r_{1,2}) = \psi_o(r_1). \psi_o(r_2) \qquad \ldots\ldots\ldots\ldots..(13)$$

When $\psi_o(r_1)$ is the wave function of the ith electron in a hydrogenic atom with nuclear charge = ze then

$$\psi_o(r_1 r_2) = \left(\frac{z^2}{\pi\,a_0^3}\right)^{1/2} e^{-zr_1/a} \left(\frac{z^3}{\pi\,a_0^3}\right) e^{-zr_2/a}$$

Or $\quad \psi_o(r_1 r_2) = \left(\frac{z^3}{\pi}\right) e^{-z(r_1+r_2)} \qquad \ldots\ldots\ldots.. (14)$

The unperturbed ground state energy $E_0^{(0)}$ is equal to the sum of the round state energies of two hydrogenise atoms. i.e.

$$E_0^{(0)} = -\left(\frac{z^3}{\pi}\right) + \left(-\frac{z^3}{\pi}\right) = -z^3$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(15)$$

The first order correction to the ground state energy is

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

Or $E_0^1 = \int_{(r_1+r_2)} \hat{H}_1 \int_{(r_1+r_2)} d_1 d_2$

..........(16)

Substituting the value of (r_1+r_2) from equation (4) in equation (16) we get,

$$E_0^1 = \frac{z^6}{\pi^2} \int e^{-2z(r_1+r_2)(\frac{1}{r_1}+2)} d_1 d_2 \qquad ....(17)$$

Where the volume elements of the two electron in polar co-ordinate are :

$$d_1 = r_1^2 \, s\, \theta_1 \, d_1 d_1 d_1$$

And $d_2 = r_2^2 \, s\, \theta_2 \, d_2 d_2 d_2$

It is very difficult to solve the equation (17) .it can be shown that it is given by

$$E_0^1 = \frac{5z}{8}$$

.....................(18)

It is positive quantity as was expected (the repulsion energy between two electrons is always positive).

Adding equation (15) and (18), we get

$$E_0 = E_0^{(0)} + E_0 = -z^2 + \frac{5z}{8}$$

$$= -\left(z^2 - \frac{5z}{8}\right) \text{ (in a.u)}$$

By putting the original units we have,

$$E_0 = -\left(z^2 - \frac{5z}{8}\right)\frac{\mu^2}{2h^2} \qquad ....(19)$$

For He atom we have,

$$E_0 = -\left(z^2 - \frac{5z}{8}\right) \times 27.2 \, e$$

or $E_0 = -2.75$ a.u $= 74.80$. eV

...................(20)

The experimental value is -2.904 a.u or-78.986 eV. Thus. There is difference between theoretical and experimental value, if second and higher orde3r contributions are included, the difference decreases.