Lectures of <u>Quantum mechanics of Chemistry</u>

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Lecture No. 9

Electronic structure of Hydrogen atom system

1-Introduction:

Electronic structure of hydrogen atom is considered fundamental system of determination for all other default elements in periodic tables. Mathematic solution of Schrödinger equation at 1926 year gives new sight about clear identification of electronic spectrums and their application.

Q/ What benefits that are achieved from the solution of Schrödinger equation for hydrogen atom?

1. The solution of Schrödinger equation for hydrogen atom can be used for larger electronic systems to estimate their structure such as helium, or lithium atom and so on.
2. Quantum numbers of energies controlling are released mathematically through the differential methods of Schrödinger such as n, l, and m.
3. Solutions are gives information about the electronic levels, different excited states of electronic transitions between these levels
4. Clear idea about the atomic structure and the electronic orientation into the orbitals.
5. All problems of Bohr theory have been solved mathematically and applicably.

Applying the postulates of the Schrödinger atomic model to this equation, we have:

- Electrons behave like standing waves that are distributed in space according to the wave function Ψ.
- Electrons move within the atom in describing orbitals. These are areas where the probability of finding an electron is considerably

higher. The referred probability is proportional to the square of the wave function Ψ^2.

- The electronic configuration of the Schrödinger atomic model explains the periodic properties of atoms and the bonds they form.

However, Schrödinger's atomic model does not take into account the spin of electrons, nor does it take into account variations in the behavior of fast electrons due to relativistic effects.

2-<u>Centre field model:</u>

If supposed that electron and proton of hydrogen atom are masses points, the exchange force according to Coulomb's law. supposing that's, r, is the constant distance between the nuclei(proton) and electron, therefore Coulomb's law determines the exchange potential energy(position energy)as follows:-

$$V \propto \frac{-Z.e^2}{r} \quad \Rightarrow V = \frac{-Z.e^2}{4\pi\epsilon^o r} \ldots\ldots\ldots\ldots (1), \text{ since z=1}$$

$$\epsilon^\circ = permibality\ of\ vaccum$$

Potential energy depends only on the relative coordination's for both masses that is the interpretation of the internal motion for electron and proton around the center of masses for them. Therefore, that can be writing the Schrödinger equation for Hydrogen atom as- HΨ =EΨ

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

$$(-\frac{h^2}{8\pi^2 m}.\nabla^2 - \frac{e^2}{r})\Psi = E\Psi \ldots\ldots(3)$$

Since $\nabla^2 = \left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2$ (Laplacian operator)

By rearrangement Schrödinger, equation becomes

$$-(\nabla^2\Psi + \frac{8\pi^2 m}{h^2} . (E + \frac{e^2}{r}) \Psi = 0 \ldots\ldots\ldots\ldots(4)$$

Now must change the axis dimension into polar spherical dimensions because this system have asymmetry in the central attraction field, therefore can be express the Lap Lucian operator as follows:-

$$\nabla^2 = \{\frac{\partial^2}{\partial r^2} + \frac{2}{r}.\frac{\partial}{\partial r} + \frac{1}{r^2}.\frac{\partial^2}{\partial\theta^2} + \frac{Cos\theta}{r^2.Sin\theta}.\frac{\partial}{\partial\theta} + \frac{1}{r^2 Sin\theta}.\frac{\partial^2}{\partial\emptyset^2}\}\ldots\ldots(5)$$

By substituted eq. (5) into eq. (4) to obtained

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$$\left\{\frac{\partial^2}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial}{\partial r} + \frac{1}{r^2} \cdot \frac{\partial^2}{\partial \theta^2} + \frac{Cos\theta}{r^2.Sin\theta} \cdot \frac{\partial}{\partial \theta} + \frac{1}{r^2 Sin\theta} \cdot \frac{\partial^2}{\partial \emptyset^2}\right\}\Psi + \frac{8\pi^2 m}{h^2} \cdot \left(E + \frac{e^2}{r}\right).\Psi = 0 \dots.(6)$$

This equation gives final formula when wave function inter in the spherical variables.

$$\frac{1}{r^2} \cdot \frac{\partial}{\partial r} \cdot \left(r^2 \cdot \frac{\partial \varphi}{\partial r}\right) + \frac{1}{r^2.Sin\theta} \cdot \frac{\partial}{(Sin\theta.\frac{\partial \varphi}{\partial \theta})} + \frac{1}{r^2.sin^2.\frac{\partial^2 \varphi}{\partial \emptyset^2}} + \frac{8\pi^2 m}{h^2} \cdot \left(E + \frac{e^2}{r}\right).\Psi = 0 \dots (7)$$

Eq. (7) is a second-degree partial differential equation depending on three variables.

3-Wave function and bound states of hydrogen atom:

The mathematical way for a solution is a separate variable, The wave function is Ψ(r,**θ**,**ϕ**) function for three variables, therefore must be separate function into three supposed functions, each one represented by a simple equation so that

$$\Psi(r, \boldsymbol{\theta}, \boldsymbol{\phi}) = R_r \cdot \boldsymbol{\Theta_\theta} \cdot \boldsymbol{\Phi_\phi} \dots\dots\dots\dots\dots (8)$$

By taking the second derivative for one function at constant, other two functions and repeating this process for each rest function respectively.

The results are substitute in equation (7) with rearrangement of the resultant equation to obtain.

$$\frac{Sin^2\theta}{R} \cdot \frac{\partial}{\partial r(r^2\frac{\partial R}{\partial r})} + \frac{1}{\Phi} \cdot \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{sin\theta}{\Theta} \cdot \left(Sin\theta. \frac{\partial \Theta}{\partial \theta}\right) + \frac{8\pi^2 m}{h^2} \cdot \left(E + \frac{e^2}{r}\right).r^2.Sin^2\theta = 0 ..(9)$$

Every function will treat in a lonely state, due to the presence of separate variables. Equation (9) have mathematical unsymmetrical, therefore the term of **Φ** function must be equal to a constant value (supposed $-m^2$). That is mean:-

$$\frac{1}{\Phi} \cdot \frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \dots\dots\dots\dots.. (10)$$

$$\Phi_\phi = \frac{1}{\sqrt{2\pi}} \cdot e^{\pm im\emptyset} \dots\dots\dots\dots\dots (11)$$

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By substituting the constant value (-m^2) instead of the term in the equation (9), and the resultant equation divided on (Sin$^2\boldsymbol{\theta}$) to obtain the following: -

$$\frac{1}{R} \cdot \frac{\partial}{\partial r (r^2 \frac{\partial R}{dr})} - \frac{m^2}{\partial Sin^2\theta} + \frac{1}{\Theta.sin\theta} \cdot \frac{\partial\left(Sin\theta.\frac{\partial\Theta}{\partial\theta}\right)}{\partial\theta} + \frac{8\pi^2 m.r^2}{h^2} \cdot (E + \frac{e^2}{r}) = 0 \dots (12)$$

Eq.12, can be separated into two parts both of them equal to the same constant -β, so that:

$$\frac{1}{\Theta.sin\theta} \cdot \frac{\partial\left(Sin\theta.\frac{\partial\Theta}{\partial\theta}\right)}{\partial\theta} - \frac{m^2}{Sin^2\theta} = -\beta \quad \dots\dots(13)$$

By multiplying with $\boldsymbol{\theta}$ and rearrangements:

$$\frac{\partial^2\Theta}{\partial\theta^2} + \frac{Cos\theta}{Sin\theta} \cdot \frac{\partial\Theta}{\partial\theta} + \left(\frac{\beta - m^2}{Sin^2\theta}\right) \cdot \Theta = 0 \dots(14)$$

Equation (14) like the rigid rotator equation:

$$\frac{\partial^2 T}{\partial\theta^2} + \frac{Cos\theta}{Sin\theta} \cdot \frac{\partial T}{\partial\theta} + \left(\frac{8\pi^2 IE}{h^2} - \frac{m^2}{Sin^2\theta}\right) \cdot T_\theta = 0 \dots 24$$

Both of them represent the stander form of a mathematical equation, since the final solution of this equation are represented by the associated Legendre polynomial ($P_l^{ImI}.x$), and the initial solution of equation (14) is represented by the serious of

$$\boldsymbol{\theta} = Sin\boldsymbol{\theta}|m|\Sigma_0^\infty a_j(Cos\boldsymbol{\theta})^i \dots\dots\dots\dots(15)$$

By differential eq. (15), multiple by Sin$\boldsymbol{\theta}$, differential, multiple by (1/Sin$\boldsymbol{\theta}$) , the addition [β-m^2/Sin$^2\boldsymbol{\theta}$],at last equalization the products to the zero to obtained the recursion formula as follows:-

$$a_{j+2} = l(l + 1) - \frac{\beta}{(j+1)(j+2)} \cdot a_j \quad \dots\dots (16)$$

Since:- $l = (j + ImI)$, l , equal to the higher value of j and both of l, m can be defined by l=0,1, 2, 3, 4….. m=0, ±1, ±2, ±3, ±4…..

For stopped the serious from to infinity must be inserted β value according to the following relation:-

$$\beta = \boldsymbol{l}(\boldsymbol{l}+1)\dots\dots.(17)$$

Therefore the solution of eq. 14, at the same style for associated Legendre polynomial as follows:-

$$P_l^{ImI}.Cos\theta = \frac{1}{2^l.l!}.\frac{\partial^{m+1}}{\partial(Cos\theta)^{m+1}}.(Cos\theta^2 - 1)^l...(18)$$

The final solution is equal to

$$\Theta_l^{ImI} = \left[(2l + 1).\frac{(l-ImI)!}{(l+ImI)!}\right]^{0.5} Sin\theta.P_l^{ImI}.Cos\theta \ ....\ (19)$$

To find the solutions of R function depending on the equation of

$$\frac{1}{R}.\frac{d}{dr(r^2\frac{dR}{dr})} - \frac{m^2}{dSin^2\theta} + \frac{1}{\Theta.sin\theta}.\frac{\partial\left(Sin\theta.\frac{d\Theta}{d\theta}\right)}{\partial\theta} + \frac{8\pi^2m.r^2}{h^2}.(E + \frac{e^2}{r}) = 0...(12)$$

By rearrangement into two side

$$\frac{1}{R}.\frac{d}{\partial r(r^2\frac{dR}{dr})} + \frac{8\pi^2m.r^2}{h^2}.(E + \frac{e^2}{r}) = \frac{m^2}{Sin^2\theta} - \frac{1}{\Theta.sin\theta}.\frac{\partial\left(Sin\theta.\frac{\partial\Theta}{\partial\theta}\right)}{\partial\theta} \ ....\ (20)$$

Since write side equal β =$l(l$+1)the resultant equation multiple by R/r^2 and rearrangement to produced:-

$$\frac{1}{r^2}.\frac{d}{\partial r(r^2.\frac{\partial R}{\partial r})} + [\frac{l(l+1)}{r^2} + \frac{8\pi^2m.}{h^2}.(E + \frac{e^2}{r})]R = 0$$

By more rearrangements

$$\frac{1}{r^2}.\frac{2r\partial R}{\partial r} + r^2.\left(\frac{\partial^2R}{\partial r^2}\right) + [-\frac{l(l+1)}{r^2} + \frac{8\pi^2mE.}{h^2} + \frac{8\pi^2me^2}{rh^2})]R = 0......\ (21)$$

The final result is consist from S_p =f(ρ) e$^{-ρ/2}$ ....(22)

According to the serious expansion, methods can determine the recursion formula of the variable for the series terms into the following equation:-

$$f_\rho = \rho^l \Sigma_0^\infty a_j\rho^j \ ....(23)$$

Can find the value of variables in form of associated Laquerre polynomial, that is symbolized as L_{n+1}^{2l+1} , and can be defined mathematically as follows:-

$$L_{n+l}^{2l+1} = \frac{\partial^{2l+1}}{\partial\rho^{2l+1}}.\left[e^\rho.\frac{\partial^{2l+1}}{\partial\rho^{2l+1}(\rho^{n+1}.e^{-\rho})}\right] \ .....\ (24)$$

the condition is $\lambda = l + j + 1$…….. (25)

The general solution for R function becomes as follows:-

$$R_{(r)} = -N \left(\frac{\rho}{n}\right)^l . e^{\frac{-\rho}{2n}} . L_{n+l}^{2l+1} . \frac{\rho}{n} \text{ ………..}(26)$$

Equation 26 can be derivative by atomic Bohr's radius

Since $\quad a_\circ = \frac{h^2}{4\pi^2 m e^2} \quad$ and $\rho = \frac{2r}{a_\circ}$ …..(27)

Therefore can be writing eq.26 in the form of Bohr's radius as in

$$R_{n,l} = -N . \left(\frac{2r}{na_\circ}\right)^r . e^{\frac{r}{na_\circ}} . L_{n+l}^{2l+1} \left(\frac{2r}{na_\circ}\right) \text{ …… (28)}$$

N is the normalization constant that's equal to $N = \sqrt{\left(\frac{2Z}{na_\circ}\right)^3 . \frac{(n-l-1)!}{2n\left((n+l)!\right)^3}}$

For Hydrogen atom (z=1) final solution of R function as

$$R_{n,l} = -\sqrt{\left(\frac{2Z}{na_\circ}\right)^3 . \frac{(n-l-1)!}{2n\left((n+l)!\right)^3}} . \left\{\left(\frac{2r}{na_\circ}\right)^r . e^{\frac{r}{na_\circ}} . L_{n+l}^{2l+1} \left(\frac{2r}{na_\circ}\right)\right\} ..(29)$$

The final solution of the wave function for Hydrogen atom system $\Psi(r,\boldsymbol{\theta},\boldsymbol{\phi})$ as represented in eq(8), by all sub-wave functions as follows:-

$$\Psi(r, \boldsymbol{\theta}, \boldsymbol{\phi}) = -\left\{\left(\frac{2Z}{na_\circ}\right)^3 . \frac{(n-l-1)!}{2n\left((n+l)!\right)^3}\right\}^{0.5} . \left\{\left(\frac{2r}{na_\circ}\right)^r . e^{\frac{r}{na_\circ}} . L_{n+l}^{2l+1} \left(\frac{2r}{na_\circ}\right)\right\} .$$

$$\left[(2l + 1) . \frac{(l-ImI)!}{(l+ImI)!}\right]^{0.5} Sin\theta . P_l^{ImI} . Cos\theta . \frac{1}{\sqrt{2\pi}} . e^{\pm im\phi} \text{…………..}(30)$$

The Eigen values can be calculated for the wave function according to $n = \lambda = \pm \frac{2\pi e^2 im}{h^2(2E)} \qquad$ so that $\qquad E_n = \frac{4\pi e^2 m}{n^2 h^2}$ …….(31)

The energy of hydrogen atom according to eq. (31) is a very agreement with the energy of the hydrogen atom according to Bohr's theory.

The wave functions can be calculated some of for some values of variables for hydrogen function, a symbol of $\Psi(r, \boldsymbol{\theta}, \boldsymbol{\phi})$ or $\Psi_{(n, l, m)}$. The wave function for the first energetic level expressed by Ψ_{1s} that is mean, n=1, l=0, m=0 and so on for other levels.

$$\Psi_{(1, 0, 0)} = \frac{1}{\sqrt{\pi}} \cdot \left(\frac{Z}{a_\circ}\right)^{3/2} \cdot e^{-Zr/a_\circ} \quad \ldots\ldots (32)$$

$$\Psi_{(2, 0, 0)} = \frac{1}{4}\frac{1}{\sqrt{\pi}} \cdot \left(\frac{Z}{a_\circ}\right)^{3/2} \cdot \left(2 - \frac{Zr}{2a_\circ}\right) \cdot e^{-Zr/2a_\circ} \ldots\ldots (33)$$

$$\Psi_{(2, 1, 0)} = \frac{1}{4}\frac{1}{\sqrt{\pi}} \cdot \left(\frac{Z}{a^\circ}\right)^{3/2} \cdot \left(\frac{Zr}{2a}\circ\right) \cdot e^{-Zr/2a^\circ} \cdot Cos\theta \ldots (34)$$

5-Applications:-

Example/1 //Calculate the relative probability of electron foundation in a hydrogen atom (H) at energy levels (2s) for 0.3 nm and 0.053 nm distance, what the two results represented the true distance of the electron from the nuclei in these levels?

Solution:- $\Psi_{(2s)} = \Psi_{(2,0,0)} = \frac{1}{4}\frac{1}{\sqrt{\pi}} \cdot \left(\frac{Z}{a_\circ}\right)^{3/2} \cdot \left(2 - \frac{Zr}{2a_\circ}\right) \cdot e^{-Zr/2a_\circ}$

The relative probability is $\Psi^2 \cdot r^2$

$\Psi_{(2s)}^2 \cdot r^2 = (0.3)^2 \cdot {}^1/_{32\boldsymbol{\pi}} \cdot (1/0.059)^3 \cdot (2 - {}^{0.3}/_{0.059})^2 e^{(-0.6/2*0.059)}$

$\Psi_{(2s)}^2 \cdot r^2 = 0.281$ when r=0.3 nm , $\Psi_{(2s)}^2 \cdot r^2 = 2,71*10^{-5}$ when r=0.053nm

As they see from two results that first result has larger relative probability than the second result by 28100/2.71=103691 times ,that mean the 0.3 nm distance is the true distance of electron from the nuclei in 2s orbital for hydrogen atom.

Example/2/ If an electron has 0.64 nm distance from nuclei of a hydrogen atom, can you respect that electron around in 1s orbital or 3s orbital?

Solution:- $\Psi_{(1s)} = \Psi_{(1, 0, 0)} = \frac{1}{\sqrt{\pi}} \cdot \left(\frac{Z}{a^\circ}\right)^{3/2} \cdot e^{-Zr/a^\circ}$

$\Psi_{(3s)} = \Psi_{(3,0,0)} = {}^1/81\sqrt{3\pi} \left({}^z/a_\circ\right)^{3/2} \cdot (27-18r/a_\circ + r^2/a_\circ) e^{-zr/3}a_\circ$

The relative probability is $\Psi^2 \cdot r^2$: $\Psi_{(1s)}^2 \cdot r^2 = 2,74*10^{-8}$, $\Psi_{(3s)}^2 \cdot r^2 = 0.48$

Relative probabilities for 3s-orbital is larger than by175182 times at 0.64 nm, therefore distance of 3s is true for electron moving.