

Lecture note- 5

Physical Chemistry CHE 503

QUANTUM CHEMISTRY

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QUANTUM CHEMISTRY – I

Schrödinger Wave Equation for Hydrogen Atom:

6.1 Introduction:

Hydrogen, being the simplest of all elements, provides a model for the study of elements in general. Moreover, it constitutes one of the basic examples of chemical systems exhibiting rotational motion. The spatial rotation of an electron around the nucleus in the hydrogen atom can be described in terms of electron's two angular variables θ (zenith angle) and ϕ (azimuthal angle) and its radial distance r from the nuclear centre. This system is equivalent to a particle moving in an infinite number of concentric spheres.

6.2 Wave Mechanical Treatment of Hydrogen Atom:

In the study of structure of atoms and molecules, the problem of structure of Hydrogen atom is regarded as very important because it forms the basis for the discussion of more complex atomic systems. The wave mechanics applied to hydrogen atom, is also used for hydrogen-like or closely related atoms.

Positive ions containing only one electron bound to a nucleus of charge Ze (e.g., He^+ , Li^{2+} , B^{3+} etc.) may be treated quantum mechanically like a hydrogen atom and are called hydrogen like atoms.

6.3 Schrödinger Wave Equation for Hydrogen Atom:

Hydrogen atom is a system of one proton (charge $=+e$) and one electron (charge $=-e$).

Assume that proton is stationary and the electron is moving about in its vicinity, common but cannot escape from the positive electronic field of nucleus.

The potential energy of the electron is the amount of work done in bringing the electron from infinity to the distance r is given by

$$\begin{aligned} V &= \int_{\infty}^r \frac{Ze^2}{Ar^2} dr \\ &= \frac{Ze^2}{Ar} \\ &= \frac{Ze^2}{Ar} \quad (\text{as } Z=1 \text{ for hydrogen}) \end{aligned} \quad \dots\dots\dots 6.1$$

Where $\frac{1}{A} = \frac{1}{\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$

ϵ_0 = permittivity of vacuum
 $= 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$

On substituting the value of A in equation 6.1, we get

$$V = \frac{e^2}{4\pi\epsilon_0 r} \quad \dots\dots\dots 6.2$$

Here r is the distance between electron and nucleus.

The schrodinger wave equation for three dimensions is:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

putting the value of potential V from equation (6.2), we get:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = 0 \quad \dots\dots\dots 6.3$$

This is the Schrödinger wave equation for hydrogen atom in terms of Cartesian co-ordinates

It is convenient to solve this equation if we substitute polar co-ordinates r, θ and ϕ in place of Cartesian coordinate x, y and z . The correlation between the two types of coordinates is illustrated in fig 6.1

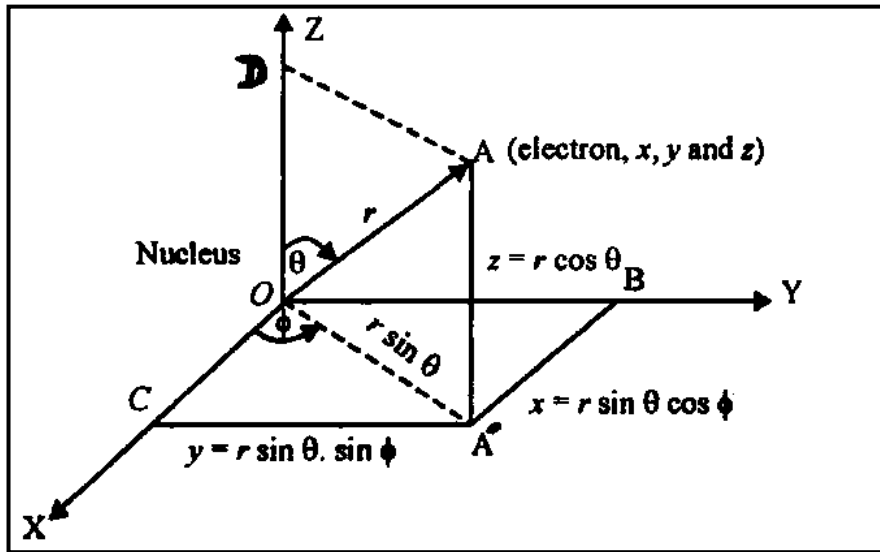


Fig. 6.1 Correlation between Cartesian coordinates (x, y and z) and polar coordinates (r, θ and ϕ).

6.4 Transformation of Coordinates of Equation 6.3:

The relation between Cartesian system and polar system is shown in Fig.6.1. It can be seen that:

(i) r is radial distance of point A(electron) from the origin O nucleus. The radial distance is given by

$$r = \sqrt{x^2 + y^2 + z^2} \quad \dots\dots\dots 6.4$$

(ii) θ is the angle between two radius vectors, OA and +z - axis (i.e., OZ-axis) which is the axis of sphere. This angle is called zenith angle and is given by $z = r \cos \theta$

Hence $\cos \theta = \frac{z}{r} = \frac{z}{\sqrt{x^2 + y^2 + z^2}} \quad \dots\dots\dots 6.5$

(iii) The perpendicular AA' on the x, y - plane is such that OA' makes an angle ϕ with x - axis, measured in the shown direction. This angle is called azimuthal angle or longitudinal angle and this is given by

$$\tan \phi = \frac{y}{x} \quad \dots\dots\dots 6.6$$

Hence $\phi = \tan^{-1}(y/x)$

A^1B and A^1C are the normal drawn from A^1 OY and OZ - axis, respectively.

(iv) Fig.6.1 also gives the following

$$z = OD = r \cos \theta \quad \dots\dots\dots 6.7$$

$$\text{and } OA^1 = AD = r \cos \theta$$

$$y = OB = CA^1 = r \sin \theta \sin \phi \quad \dots\dots\dots 6.8$$

$$x = A^1B = r \sin \theta \cos \phi \quad \dots\dots\dots 6.9$$

On transforming equation 6.3 with the help of relation (6.7), (6.8) and (6.9), we get

$$\frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi \right] = 0 \quad \dots\dots 6.10$$

Putting the value of V from equation (6.2), we get

$$\frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{4\pi} \epsilon_0 r \right) \psi \right] = 0 \quad \dots\dots 6.11$$

6.4.1 Separation of Variable :

Equation (6.10) or (6.11) is a second order partial differential equation. This contains three variables, r, θ and ϕ . In order to separate these variables it is necessary to suppose that the wave function ψ , may be represented by the product of three wave functions, each having only one of the three variables namely r, θ and ϕ . Therefore,

$$\psi(r, \theta, \phi) = R(r) \cdot T(\theta) \cdot F(\phi) \quad \dots\dots\dots 6.12$$

$$\text{Or we can write } \psi = R(r)T(\theta).F(\phi) \quad \dots\dots\dots 6.13$$

It should be clear that.

- (i) $R(r)$ is a function of r only which means that the function R depends upon r only and is independent of θ and ϕ .
- (ii) $T(\theta)$ is a function of θ only which means that the wave function T depends on θ only and is independent of r , and ϕ .
- (iii) $F(\phi)$ is a function of ϕ only which means that wave function F depends on ϕ only and is independent of r and θ .

Now $\psi(r, \theta, \phi)$ or simply ψ means that the wave function ψ depends on all the three variables r, θ and ϕ .

$$\text{Now } \psi = R(r) T(\theta) F(\phi)$$

$$\text{Hence } \frac{\partial \psi}{\partial r} = T(\theta) F(\phi) \frac{\partial R(r)}{\partial r} \quad \dots\dots\dots 6.14$$

$$\frac{\partial \psi}{\partial \theta} = R(r) F(\phi) \frac{\partial T(\theta)}{\partial \theta} \quad \dots\dots\dots 6.15$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = R(r) T(\theta) \frac{\partial^2 F(\phi)}{\partial \phi^2} \quad \dots\dots\dots 6.16$$

Substituting these values from equations 6.12, 6.15, 6.16 in equation 6.10 and multiplying by $r^2 \sin^2 \theta$ throughout,

We get:

$$\frac{\sin 2\theta}{R(r)} \left[\frac{\partial}{\partial r} (r^2 T(\theta) F(\phi) \frac{\partial R(r)}{\partial r}) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta R(r) F(\phi) \frac{\partial T(\theta)}{\partial \theta}) + \frac{1}{\sin^2 \theta} R(r) T(\theta) \frac{\partial^2 F(\phi)}{\partial \phi^2} \right] + \frac{8\pi^2 m}{h^2} (E - V) r^2 \sin^2 \theta R(r) T(\theta) F(\phi) = 0$$

On dividing by $R(r) T(\theta) F(\phi)$ and simplifying the bracket,

$$\frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} (r^2 \frac{\partial R(r)}{\partial r}) + \frac{\sin \theta}{T(\theta)} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial T(\theta)}{\partial \theta}) + \frac{1}{F(\phi)} \frac{\partial^2 F(\phi)}{\partial \phi^2} + \frac{8\pi^2 m r^2 \sin^2 \theta}{h^2} (E - V) = 0 \quad \dots\dots 6.17$$

$$\text{Or, } \frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} (r^2 \frac{\partial R(r)}{\partial r}) + \frac{\sin \theta}{T(\theta)} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial T(\theta)}{\partial \theta}) + \frac{8\pi^2 m r^2 \sin^2 \theta}{h^2} (E - V) = - \frac{1}{F(\phi)} \frac{\partial^2 F(\phi)}{\partial \phi^2} \quad \dots\dots 6.18$$

Left hand side of the equation (6.18) has two variables r and θ , where as the right hand side of the equation has only one variable ϕ . If we put right hand side equal to $-m_l^2$, then equation 6.18 becomes

$$\frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} (r^2 \frac{\partial R(r)}{\partial r}) + \frac{\sin \theta}{T(\theta)} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial T(\theta)}{\partial \theta}) + \frac{8\pi^2 m r^2 \sin^2 \theta}{h^2} (E - V) = -m_l^2 \quad \dots\dots 6.19$$

$$\text{And } \frac{1}{F(\phi)} \frac{\partial^2 F(\phi)}{\partial \phi^2} = -m_l^2$$

$$\text{Or, } \frac{1}{F(\phi)} \frac{\partial^2 F(\phi)}{\partial \phi^2} + m_l^2 = 0 \quad \dots\dots\dots (6.20)$$

Equation (6.20) is called $F(\phi)$ equation and contains only one variable ϕ .

Equation 6.19 contains two variables r and θ . For the separation of the remaining two variables r and θ , we divide the equation (6.19) by $\sin^2 \theta$ we get

$$\frac{1}{R(r)} \frac{\partial}{\partial r} (r^2 \frac{\partial R(r)}{\partial r}) + \frac{1}{T(\theta) \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial T(\theta)}{\partial \theta}) + \frac{8\pi^2 m r^2}{h^2} (E - V) - \frac{m_l^2}{\sin^2 \theta} = 0 \quad \dots\dots 6.21$$

Rearrangement of equation (6.21) gives

$$\frac{1}{R(r)} \frac{\partial}{\partial r} (r^2 \frac{\partial R(r)}{\partial r}) + \frac{8\pi^2 m r^2}{h^2} (E - V) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{T(\theta) \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial T(\theta)}{\partial \theta}) \quad \dots\dots 6.22$$

A close inspection of equation (6.22) shows that each side of the equation contains only one variable. Left hand side contains r only and the right hand side contains only θ . If we put right hand side equal to β , then equation 6.22 becomes.

$$\frac{1}{R(r)} \frac{\partial}{\partial r} (r^2 \frac{\partial R(r)}{\partial r}) + \frac{8\pi^2 m r^2}{h^2} (E - V) = \beta \quad \dots\dots\dots (6.23)$$

$$\text{Hence } \frac{m_l^2}{\sin^2 \theta} - \frac{1}{T(\theta) \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial T(\theta)}{\partial \theta}) = \beta \quad \dots\dots\dots (6.24)$$

Multiplying equation (6.24) by $T(\theta)$, we get,

$$\frac{m_l^2 T(\theta)}{\sin^2 \theta} - \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial T(\theta)}{\partial \theta}) - \beta T(\theta) = 0 \quad \dots\dots\dots (6.25)$$

This is a desired equation which is in terms of θ only

On combining equation (6.21) with equation (6.24) we get,

$$\frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) - \beta + \frac{8\pi^2 m r^2}{h^2} (E-V) = 0 \quad \dots\dots\dots(6.26)$$

Multiplying both sides of equation (6.26) by $\frac{R(r)}{r^2}$, we get,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) - \beta \frac{R(r)}{r^2} + \frac{8\pi^2 m}{h^2} (E-V) R(r) = 0 \quad \dots\dots\dots(6.27)$$

It is the $R(r)$ equation and contains only one variable r .

Thus the three variables (r, θ and ϕ) has been successfully separated, resulting into three independent differential equations. Therefore, the solution of the Schrödinger wave equation for hydrogen atom in terms of spherical coordinates are given by equations (6.20),(6.25) and (6.27). These equations are given below-

$$(i) \quad \frac{\partial^2 F(\phi)}{\partial \phi^2} + m_l^2 F(\phi) = 0 \quad \dots\dots\dots 6.28$$

$$(ii) \quad \frac{m_l^2 T(\theta)}{\sin^2 \theta} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T(\theta)}{\partial \theta} \right) - \beta T(\theta) = 0 \quad \dots\dots\dots 6.29$$

$$(iii) \quad \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) - \beta \frac{R(r)}{r^2} + \frac{8\pi^2 m}{h^2} (E-V) R(r) = 0 \quad \dots\dots\dots 6.30$$

It is clear from equation 6.28 that it is same wave equation for particle in one dimensional box. In term of sine and cosine functions, the solution of 6.28 is written as,

$$F\phi = A \sin(m_\ell \phi) + B \cos(m_\ell \phi)$$

For a solution to be acceptable, the wave function should be single valued, continuous and finite. In order to meet the first condition (single valued), the function $F\phi$ should have the same value for $\phi = 0$, as it has $\phi = 2\pi$. Thus,

case I: when $\phi = 0$ then,

$$F(0) = A \sin(m_\ell \times 0) + B \cos(m_\ell \times 0) = B$$

Case II: when $\phi = 2\pi$, then

$$F(2\pi) = A \sin(m_\ell \times 2\pi) + B \cos(m_\ell \times 2\pi)$$

Under the above restrictions (single valued),

$$F(0) = F(2\pi)$$

$$B = A \sin(m_\ell \times 2\pi) + B \cos(m_\ell \times 2\pi) \quad \dots\dots\dots 6.31$$

Equation (6.31) is true only if $m_\ell = 0$, $m_\ell =$ positive integer or $m_\ell =$ negative integer. Such a characteristics are those that would be expected of a quantum number and the particular restrictions on m_ℓ indicate that it is similar to magnetic quantum number of Bohr's -Sommerfield atomic model.

In the normal practice, equation 6.28 is expressed in the exponential way, i.e.,

$$F(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i m_\ell \phi}$$

where $m_\ell = 0, \pm 1, \pm 2, \dots$

In order $F(\phi)$ must be single valued, $F(\phi)$ must have the same value after any number of whole revolutions, so,

$$\begin{aligned} e^{im_\ell\phi} &= e^{im_\ell(\phi+2\pi n)} \\ &= e^{i(m_\ell\phi+2\pi nm_\ell)} \end{aligned}$$

Where n is a whole number and, therefore, the product nm must be a whole number, hence m must be a whole number. Possible values of m_ℓ are $0, \pm 1, \pm 2, \pm 3, \dots$

Thus m_ℓ is known as magnetic quantum number. This quantum number controls the direction of the angular momentum. That is magnetic quantum number describes the behavior of electron in the atom when it is placed in a magnetic field. In the same manner azimuthal quantum number can be described from Legendre polynomial.

Evaluation of Total Energy of Hydrogen Atom:

As we know that:

$$\alpha^2 = \frac{-8\pi^2 mE}{h^2} \dots\dots\dots(6.32)$$

$$\text{And } \lambda = \frac{4\pi^2 mze^2}{h^2 \alpha} \dots\dots\dots(6.33)$$

Squaring both sides of equation (6.33),

$$\text{We get } \lambda^2 = \frac{16\pi^4 m^2 z^2 e^4}{h^4 \alpha^2}$$

$$\text{Hence } \alpha^2 = \frac{16\pi^4 m^2 z^2 e^4}{h^4 \lambda^2} \dots\dots\dots(6.34)$$

Comparing equation (6.32) and (6.34), we get,

$$\begin{aligned} \frac{-8\pi^2 mE}{h^2} &= \frac{16\pi^4 m^2 z^2 e^4}{h^4 \lambda^2} \\ \text{Or, } E &= -\frac{2\pi^2 m z^2 e^4}{h^2 \alpha^2} \dots\dots\dots(6.35) \end{aligned}$$

Putting n for λ , we get,

$$E = -\frac{2\pi^2 m z^2 e^4}{n^2 h^2}$$

For hydrogen atom $z = 1$

$$E = -\frac{2\pi^2 m e^4}{n^2 h^2}$$

This is the same result as is obtained from Bohr's theory.

The Quantum Mechanical Model:

Quantum mechanics provides a new model for representing the structure of hydrogen atom and hence of other atoms, with sound theoretical basis. The electron rotates round the nucleus but not in a well defined orbit, the rotation is three dimension and motion is described by a

wave equation- the Schrödinger equation. Rather than locating the electron in any instant exactly, this model provides the position of the electron in terms of a probability function, there being a finite, even through small, probability of its being found at all points in the infinite space outside the nucleus. The probability is maximum at a certain distance from the nucleus, interestingly in the ground state of H atom, this distance is the same as the radius (a_0) of the Bohr's orbit which is:

$$\frac{h^2}{4\pi^2 m e^2}, \quad \text{i.e., } 0.529 \text{Å}^0$$

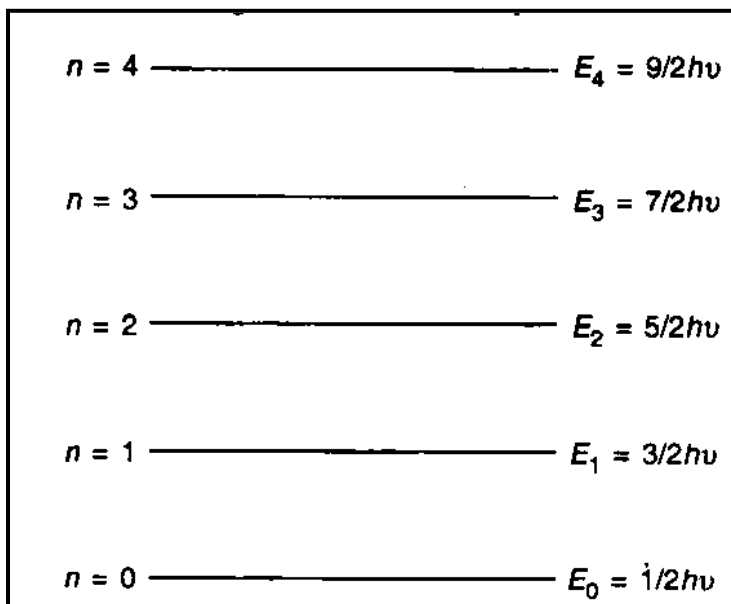
The maximum probability is uniformly distributed in all direction at a distance of a_0 from the nucleus (i.e., it is spherically symmetrical). In excited states with non zero angular momentum of the electron ($l \neq 0$), the maximum lies in certain referred directions.

In each state one can visualize a three dimension surface encompassing the nucleus that encloses a large fraction ($\sim 90\%$) of the total probability; in other words, the electron may be supposed to spend 90% of its time inside this surface. This entire region within this surface is quantum mechanical analogue of classical orbit and is the physical representation of orbital.

There is an equivalent way of representing the probability distribution by considering the electron as a cloud of negative charge. The density of the electron cloud (probability density) in the ground state of the H atom is maximum at the nucleus and 90% of the charge of the cloud is contained within the surface of the orbital. Although the electron is most likely to be found at a distance a_0 from the nucleus, its average distance is $1.5a_0$.

As in the old planetary model, the stability of the atom, qualitatively, attributed to (i) a force tending to bring the nucleus and the electron together and (ii) an opposing force tending to keep the electron away from the nucleus. The former is electrostatic in nature ($F = \frac{ze^2}{r^2}$); for the latter quantum mechanics provides a more constant picture. We visualize the electron as diffuse cloud of matter and charge around nucleus. The former tends to make the electron cloud smaller and smaller. This makes the wavelength of the electron shorter and shorter and hence the energy greater. Rubinstein prefers to call it the "energy of confinement" (E_{conf}). Below the optimum distance (a_0) the confinement energy is sufficiently great for the nucleus to pull the electron cloud further toward itself. An equilibrium is ultimately established at the optimum distance for the atom to be stable when the two forces balance.

The energy is shown in fig. 6.2. The levels are horizontal



Discussion:

quantization of shown in fig. allowed energy shown as lines.

Fig 6.2 Quantization of energy

That these lines are straight emphasizes the fact that energy (E) is the same irrespective of the position (x) of the particle. Since for a particular value of n , the energy E does not change with x , the latter is often termed as “constant motion.” Further, since \hat{H} or E is independent of time (t) the system under consideration is a good and simple example of “conservative system”.

Conclusion:

The most important application of quantum mechanics to chemistry has been its explanation of the nature of covalent bond. G.N. Lewis, declared that this bond consists of a shared pair of electron. In 1927 Heitler and F. London applied quantum mechanism to give the first quantitative theory of the bond.

If two H atoms are brought together, the system consists of two protons and two electrons. If the atoms are far apart, their mutual interaction is effectively nil. In other words, the energy of interaction $U \longrightarrow 0$ as the inter-nuclear distance $R \longrightarrow \infty$. At the other extreme if two atoms are forced closely together, there is a large repulsive force between the positive nuclei, so that $R \longrightarrow 0$ $U \longrightarrow \infty$. Experimentally we know that two hydrogen atoms can unite to form a stable hydrogen molecule, whose dissociation energy is $458.1 \text{ kJ.mol}^{-1}$. The equilibrium inter nuclear separation in the molecule is 0.0740 nm .

To sum up, the solution of the radial equation 6.30 gives the quantum numbers n and l . The solution of $T(\theta)$ equation (6.29) gives the quantum numbers n , l and m and the solution of $F(\phi)$ equation (6.28) gives the quantum number m . In other words the quantum numbers n , l and m follow directly from the wave mechanical treatment.

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