Physical chemistry

PAPER- III
Unit - 2

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CLASSMATE

* Schrödinger equation for H-atom and hydrogen-like ions (He^+, Li^{++}, Be^{+++} .....)

The hydrogen atom and hydrogen like ions comprising one electron and a nucleus represent the simplest of atomic systems and secured a unique place in the wave theory of atoms. The Schrodinger equations has been exactly solved only for these simple systems.

I). In Cartesian Co-ordinates :-

This is the Schrodinger equation for the particle of mass m moving in three dimension

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{—— (1)}$$

where, 'ψ' represents a quantity analogous to the amplitude functions in a classical waves.

'V' is the potential energy and E is the total energy of the particles.

The hydrogen atom or hydrogen-like ions consists of a nucleus of $+Ze$ electric charge which exerts a Coulombic force $\left(\frac{Ze^2}{4\pi\varepsilon_0}\right) r^2 \cdot dr$ on a single electron of charge '$-e$' at a distance 'r' from the nucleus. It is given by

$$V = \int_{\infty}^{r} \frac{Ze^2}{(4\pi\varepsilon_0) r^2} dr = \frac{-Ze^2}{(4\pi\varepsilon_0) r}$$

So, Schrödinger equation — (I) for hydrogen atom or hydrogen-like ions may be written as:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)\psi=0$$

or

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 \mu}{h^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)\psi=0$$

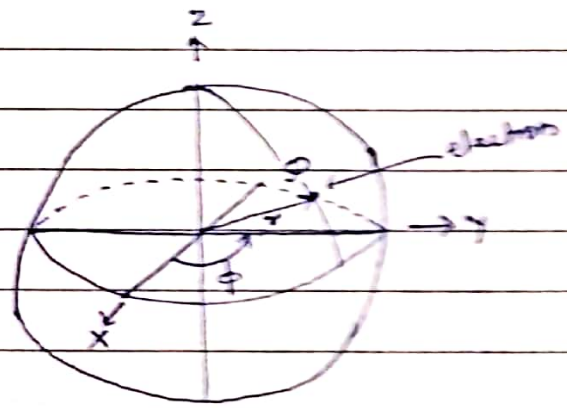
Where, μ = reduced mass $= \frac{m_1 m_2}{m_1+m_2}$

m_1 & m_2 are the mass of electron and nucleus.

II). In spherical polar co-ordinates (r, θ & ϕ) :-

It is more convenient to express schrodinger equation in terms of spherical polar co-ordinate (r, θ & ϕ) where,

'r' is the length of the radius vector,
'θ' is the angle between the axis of sphere and the radius vector and
'ϕ' is the angle between a fixed meridian plane and the meridian plane in which 'r' is measured.



'θ' is called zenith angle (latitude) and 'ϕ' is azimuthal angle (longitude).

On the basis of geometric considerations, we have co-ordinate

$x = r \sin\theta . \cos\phi$;

$y = r \sin\theta . \sin\phi$ &

$z = r \cos\theta$.

Using this relations and applying the theory of partial derivative, the transformation from the Cartision to spherical polar co-ordinates,

Schrödinger Equation may be written as:

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{\sin\theta}.\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \psi}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial \phi^2}\right] + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = 0.$$

This is the partial differential equation for the wave function ψ of the electron in an one-electron atom.

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