Exactly Soluble System (II)
(a)

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H – LIKE ATOM – r, θ, ϕ EQUATION

The wave mechanical treatment, which is applied to hydrogen atom, is also used for hydrogen-like or closely related atoms. The schrodinger's wave equation is expressed in the form

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad -(1)$$

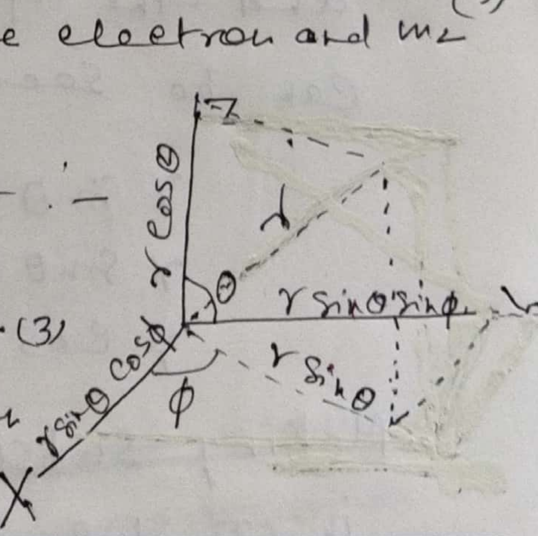
Dividing equation (1) by m, we get

$$\frac{1}{m}\nabla^2 \psi + \frac{8\pi^2}{h^2}(E-V)\psi = 0 \quad -(2)$$

In the hydrogen atom, there are only two Particles, the electron and the nucleus. For such system, it will be convenient to express the equation(2) in the form

$$\frac{1}{m_1}\nabla_1^2 \psi_T + \frac{1}{m_2}\nabla_T^2 + \frac{8\pi^2}{h^2}(E-V)\psi = 0 \quad (3)$$

Where m_1 is the mass of the electron and m_2 mass of the nucleus.



Transformation of coordinate :-

The Total energy, E, in equation (3) has two part (1) the translation motion (#) of the atom as a

Whole, and (ii) the energy of the electron with respect to the proton. x, y, and z which are Cartesian co-ordinates of the centre of mass of hydrogen atom, and the variables, r, θ and ϕ which are the polar coordinates of the electrons with respect to the nucleus. For the hydrogen atom, the Cartesian co-ordinates of the centre of mass will be given by

$$x = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \quad — (4)$$

$$y = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2} \quad — (5)$$

$$z = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2} \quad — (6)$$

and the transformations to spherical co ordinate can be seen from fig to be

$$r \sin\theta \cos\phi = x_2 - x_1 \quad — (7)$$

$$r \sin\theta \sin\phi = y_2 - y_1 \quad — (8)$$

$$r \cos\theta = z_2 - z_1 \quad — (9)$$

Making substitutions of equation (4), (5), (6), (7) (8), (9) in (3) we get

$$\frac{1}{m_1+m_2}\left(\frac{\partial^2 \psi_T}{\partial x^2} + \frac{\partial^2 \psi_T}{\partial y^2} + \frac{\partial^2 \psi_T}{\partial z^2}\right) + \frac{m_1+m_2}{m_1 m_2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi_T}{\partial r}\right)\right.$$

$$\left. + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi_T}{\partial \phi^2} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi_T}{\partial \theta}\right)\right]$$

$$+ \frac{8\pi^2}{h^2}[E - V]\psi_T = 0 \quad —(10)$$

The wave function ψ_T is a function of the variables x, y, z, r, θ and ϕ and energy E possesses translational energy of the atom as well as the energy of the electron with respect to the nucleus in the usual manner, The Total wave function ψ_T is assumed to be expressible as the product of the two wave functions such that

$$\psi_T = F_{xyz}\, \psi_{r\theta\phi} \qquad — (11)$$

For sake of convenience, we will express F and ψ in place of F_{xyz} and $\psi_{r\theta\phi}$, when eq(11) is substituted in equation(10) it is found that the following two equations are obtained

(i) $$\frac{\delta^2 f}{\partial x^2} + \frac{\delta^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} + \frac{8\pi^2(m_1+m_2)}{h^2} E_{Trans}\, f = 0 \qquad -(12)$$

(ii) $$\frac{1}{r^2}\frac{\delta}{\partial r}\left(r^2 \frac{\delta \psi}{\partial r}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\delta^2 \psi}{\partial \phi^2} + \frac{1}{r^2 \sin\theta}\frac{1}{\partial\theta}\left(\sin\theta \frac{\delta\psi}{\delta\theta}\right) + \frac{8\pi^2}{h^2}\mu (E-V)\psi = 0 \qquad -(13)$$

where μ is the reduced mass and is given by

$$\mu = \frac{m_1 m_2}{m_1+m_2}$$

Equation (12) contains only the variables x, y and z but contains no potential energy term.
This is identical to the wave equation for a free particle and therefore represents the translational energy of the atom a a whole. Equation(3), which relates the electron to the proton; we will now consider equation (13) only.