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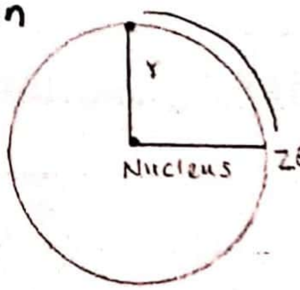
Solve schrodinger's wave equation for Hydrogen atom.

The hydrogen atom, consisting of an electron and a proton, is a two particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass.

→ consider an electron of a charge 'e' revolving around nucleous of hydrogen atom of charge 'ze' The P.E of electron can be defined as :-

The workdone in bringing the electron from infinity to r distance to the nucleus.



$$P\cdot E = \int_{\infty}^{r} w$$

$$= \int_{\infty}^{r} F\cdot dr$$

$$= \int_{\infty}^{r} \frac{ze^2}{r^2}\, dr$$

$$P\cdot E = \frac{-ze^2}{r}$$

$$P.E = V = \frac{-ze^2}{r}$$

Wave Character :-

Wave character of the electron can be represented by equation.

$$H\Psi = E\Psi \qquad \hat{H} = -\frac{h^2}{8\pi m}\nabla^2 + V$$

$$\Psi\left[\frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{ze^2}{r}\right] = E\Psi \quad \text{— (i)}$$

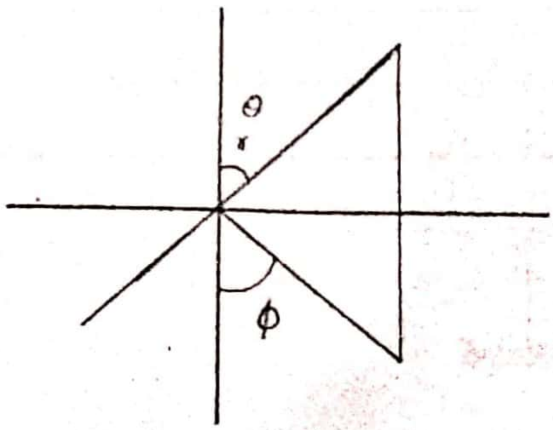
Due to spherical symmetry we will into polar coordinates (r, θ, ϕ)

Hence ∇^2 in spherical co-ordinate can be written as

$$\nabla^2 = \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \cdot \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 \sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}$$

Substituting the value of ∇^2 in eavution (i)



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$$-\frac{h^2}{8\pi^2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}\psi\right)+\frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2}\right]+$$

$$-\frac{ze^2}{r}\psi = E\psi$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}\psi_{r\theta\phi}\right)+\frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_{r\theta\phi}}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\cdot$$

$$\frac{\partial^2\psi_{r\theta\phi}}{\partial\phi^2}+\frac{8\pi^2 m}{h^2}\cdot\frac{ze^2}{r}\psi_{r\theta\phi}+\frac{8\pi^2}{h}$$

This equation can be solved by the method of separation.

Separation of variables

The wave function consist of three parts.

$$\psi_{r\theta\phi} = R_r\,\Theta_\theta\,\Phi_\phi \quad \text{---} \ (3)$$

substituting the value of wave function equation

$$\Theta_\theta\Phi_\phi\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial R_r}{\partial r}\right)+\frac{R_r\Phi_\phi}{r^2\sin^2\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\Theta_\theta}{\partial\theta}\right)+$$

$$\frac{R_r\Theta_\theta}{r^2\sin^2\theta}\cdot\frac{\partial^2\Phi_\phi}{\partial\phi^2}$$

On multiplying by

$$\frac{r^2\sin^2\theta}{R_r\Theta_\theta\Phi_\phi}$$

we get.

We get.

$$\underbrace{\frac{\sin^2\theta}{R_r}\cdot\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial R_r}{\partial r}\right)}_{\text{1st term}}+\underbrace{\frac{\sin\theta}{\Theta_\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\Theta_\theta}{\partial\theta}\right)}_{\text{2nd term}}+\underbrace{\frac{1}{\Phi_\phi}\cdot\frac{\partial^2\Phi_\phi}{\partial\phi}}_{\text{3rd Term}}$$

Solution of Φ Equation :-

Φ equation can be derived from the Schrodinger wave equation which is written as.

$$\frac{d^2\Phi}{d\phi^2}+m^2\Phi=0$$

This is 2nd order differential equation changing the general solution as.

$$\Phi = A\sin m\Phi$$

In the exponential form it is written as.

$$\Phi_\phi = A e^{\pm im\phi}$$

It is an acceptable solution only if 'm' in the form of integar. For wavefunction to single valued.

$$\phi = (\phi+2\pi)$$

$$\Phi_\phi = A e^{\pm im(\phi+2\pi)}$$

Putting the value of ϕ in equation

$$Ae^{\pm im\phi} = Ae^{\pm im(\phi + 2\pi)}$$

$$\therefore im\phi \mp im2\pi$$

Angular wave equation

Angular wave equation may be written in the form

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = -l(l+1)Y(\theta,\phi)$$

Normalized solutions are spherical harmonics

$$Y_{lm}(\theta,\phi) = (-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}\, e^{im\phi}\, P_l^m(\cos\theta)$$

("degree" of harmonic function) $l = 0, 1, 2, 3, \ldots$

("order" of harmonic function) $m = 0, 1, 2, \ldots, l$

$$Y_{l,-m}(\theta,\phi) = (-1)^m Y^*_{lm}(\theta,\phi)$$

The three Quantum numbers

Schodinger's approch requires three quantum numbers (n, l, m) to specify a wavefunction for the electron. The quantum number provide information about the special distribution of electron. Although 'n' cab be positive integar (not zero), Only certain values of l and m_l are allowed for a given value of (n).

principle quantum no : One of three quantum number that tells the average relative distance of an electron from the nucleus. Indicate energy of the electron and the average distance of an electron from the nucleus

$$n = 1, 2, 3, 4, \ldots$$

2nd quantum number is often called the azimuthal quntum number (1). The allowed values of 1 depend on the value of 'n' and can range from 0 to n - 1 :

$$l = 0, 1, ., 2, 3, \ldots (n-1)$$

For example, if n = 1, 1 can be only 0; If m = 2, 1 can be zero or 1 and so forth.

The third quantum number is the magnetic quantum number (m_l). One of three quantum number the describes the orientation of the region of Space Occupied by an electron with respect to an applied magnetic field.

$$m = -l, -l+1, \ldots 0, \ldots l-1, l$$

The Time - Independent Schrodinger Eeauation :-

The time - independent Schrodinger eauation can be expressed in highly compressed as.

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

$\hat{H}\Psi$ = Hamiltonian operator (energy operator)
$E\psi$ - Eenergy eignvalue.

The equation says :

• The sum of the wave function's kinetic energy and potential energy is eaual the wave function's total energy.

The time-indpendent eauation can be written in any suitable coordinates (x, y, z).

Hence,

$$\frac{h^2}{2m} \nabla^2 \psi(r) + V(r)\, \Psi(r) = E\, \Psi(r)$$

Kinetic energy + Potential energy = Total energy

h is the reduced plank constant
m is the electron mass
∇ is the Lapcian operator
ψ is the wave function
E is the energy eigenvalue
(r) denotes the quantities are functions of Spherical polar coordinates (r, θ, ϕ)

Second derivatie with respet to z   Schrodinge wave function

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

Position   Energy   Potential energy

The schrodinger's equation is a linear partial differential equation that describes the wave function or state function of quantum - mechanical system.

Expectation Value of Momentum :-

We can make use of Schrodinger's equation obtain an alternative expression for the expectation value of momentum given.

$$(P) = m(v(t)) = m\int_{-\infty}^{+\infty} x\left[\frac{\partial \psi^*(x,t)}{\partial t}\psi(x,t) + \psi^*(x,t)\frac{\partial \psi(x,t)}{\partial t}\right]dx$$

We can substitute for these time derivatives to give

$$i\hbar(P) = m\int_{-\infty}^{+\infty} x\left[\left\{\frac{h^2}{2m}\frac{\partial^2 \psi^*(x,t)}{\partial x^2} - V(x)\psi^*(x,t)\right\}\psi(x,t) +\right.$$

$$\left.\psi^*(x,t)\left\{-\frac{h^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t)\right\}\right]dx,$$

The term involving potential cancel. The common factor $h^2/2m$ can be moved outside the integral

$$(P) = -\frac{1}{2}i\hbar\int_{-\infty}^{+\infty} x\left[\frac{\partial^2 \psi^*(x,t)}{\partial x^2}\psi(x,t) - \psi^*(x,t)\frac{\partial^2 \psi(x,t)}{\partial x^2}\right]dx$$

Integrating both terms in the integered by parts then gives

$$(P) = \frac{1}{2} i\hbar \int_{-\infty}^{+\infty} \left[\frac{\partial \psi^*(x,t)}{\partial x} \frac{\partial x \psi(x,t)}{\partial x} - \frac{\partial x \psi^*(x,t)}{\partial x} \frac{\partial \psi(x,t)}{\partial x} \right] dx +$$

$$\frac{1}{2} i\hbar \left[\frac{\partial \psi^*(x,t)}{\partial x} \psi(x,t) - \psi^*(x,t) \frac{\partial \psi(x,t)}{\partial x} \right]^{+\infty}$$

Integrating the first term by parts once

$$(P) = -i\hbar \int_{-\infty}^{+\infty} \psi^*(x,t) \frac{\partial \psi(x,t)}{\partial x} dx + \frac{1}{2} i\hbar \psi^*(x,t)\, \psi(x,t) \Big]_{-\infty}^{+\infty}$$

The last term vanish as the wave function itself vanishes for $x \longrightarrow \pm\infty$

$$(P) = -i\hbar \int_{-\infty}^{+\infty} \psi^*(x,t) \frac{\partial \psi(x,t)}{\partial x} dx$$

$$p \rightarrow -i\hbar \frac{\partial}{\partial x}$$

which further suggests that we can make the replacement.

$$p^n \longrightarrow \left(-i\hbar \frac{\partial}{\partial x}\right)^n$$

$$(P^2) = -\hbar^2 \int_{-\infty}^{+\infty} \psi^*(x,t) \frac{\partial^2 \psi(x,t)}{\partial x^2} dx$$

hence,

$$K = \frac{P^2}{2m} = -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \psi^*(x,t) \frac{\partial^2 \psi(x,t)}{\partial x^2} dx$$

$$\frac{p^2}{2m} + V(x) = E$$

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If we multiply this equation by $\psi(x,t) = \psi(x) \exp(-iEt$

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$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)$$

For instance, the observeable k, the Kinetic energy, is represented by differential operator

$$K \longrightarrow \hat{K} = \hbar^2 \frac{\partial^2}{\partial x^2}$$

while opretor associated with position of the partic $\hat{x}$ with

$$x \longrightarrow \hat{x} = x$$

Schrodinger's Eauation :

$$i\hbar \frac{\partial}{\partial t}\psi(r,t) = -\frac{\hbar^2}{2m}\nabla^2\psi(r,t) + V(r,t)\,\psi(r,t)$$

i is the imaginary number, $\sqrt{-1}$

$\hbar$ is plank's constant divided by 2π

$\psi(r,t)$ is the wave function

m is the mass of the particle

∇^2 is the Laplacin operator $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$V(r,t)$ is the potential energy