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Quantum Mechanics

1. Introduction :

Quantum mechanics (QM; also known as quantum physics, quantum theory, the wave mechanical model, or matrix mechanics). Quantum mechanics is a fundamental theory in physics describing the properties of nature on an atomic scale.

Classical mechanics is the description of physics that existed before the formulation of theory of realitivity and of quantum mechanics. It describes all aspects of nature at macroscopic scale. But extend these discriptions to atomic and subatomic scale. There are few phenomenon which the classical mechanics failed to explain.

1. Stability of an atom
2. Black Body radiation
3. Spectral series of Hydrogen atom.

Max planck in **1900** at a meeting

German physics society read his paper. " On the theory of energy distribution law of the Normal Spectrum". This was the start of revolution of physics i.e. the start of Quantum mechanics. Quantum mechanics is able to explain;

1. Emission of Line Spectra.
2. Compton Effect.
3. Black body radiation
4. Photo Electric effect.

It was outstanding development in modern science was the conception of quantum mechanics in **1925**. This was highly successful in explaining the behavior of atoms, molecules and nuclei.

2. Postulates Of Quantum Mechanics:-

There are four postulates of quantum mechanics;

1. Operator theorm

2. Eigen Value theorm.
3. Expectation Theorm
4. Time dependant Schrodinger wave equation.

1. Operator Theorm:-

To every measurable physical quantity of a system. There corresponds 'n' operators in quantum mechanics. **Operator** is a symbol of certain mathematical procedures which can transform one function into another function.

$$\frac{\partial}{\partial x} x^n = nx^{n-1}$$

$$\frac{\partial}{\partial x} = \text{operator}$$

$$nx^{n-1} = \text{new function.}$$

2. Eigen Value Theorm:-

If result of operations of an operator on function is propotional to original function. This function is known as Eigen function.

$$\frac{\partial}{\partial x} e^{ax} = ae^{ax}$$

Expectation Theorm:-

If so many measurments are made on some system, (function) then some expected value from eign function in terms of eigen values are calculated by mathematical values;

$$\hat{A}\Psi = \lambda\Psi$$

$$\lambda = \frac{\hat{A}\Psi\Psi^*}{\Psi\Psi^*}$$

$$\langle\lambda\rangle = \frac{\hat{A}\int\Psi\Psi^*}{\int\Psi\Psi^*}$$

$\langle\lambda\rangle$ = expectation value.

4- Time dependant Schrodinger wave equation;

In 1926, Schrodinger gives the wave mechanics. He tried to calculate the total energy poccessed by the system. System is represented by Ψ. Ψ gives properties of System Ψ is a complex number.

Schrodinger wave equation in one dimension;

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

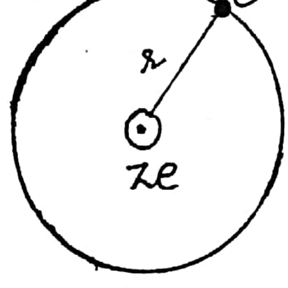
The schrodinger wave equation for a particle in 3-dimension can be written as;

$$\nabla^2 \Psi_{xyz} + \frac{8\pi^2 m}{h^2}(E-V)\Psi_{xyz} = 0.$$

3. Solve Schrodinger wave equation for Hydrogen atom

Concider a single electron revolving around nucleus of Hydrogen atom. Let the charge of Hydrogen electron is **Z.** Whereas of nucleus is **Ze.** The electron is revolving in Spherical Symmetery. The wave function attributed to electron is **$\Psi_{r\theta\phi}$.** The schrodinger wave equation can written as;

$$\hat{H}\Psi = E\Psi \longrightarrow 1$$



and we know that;

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

$\hat{H}$ is Hamiltonion operator and it act on the function the result is equation that is equal to the total energy. ∇^2 is in Cartesian coordinate so we change it into

spherical coordinates;

∇^2 in cartesian coordinate shown as;

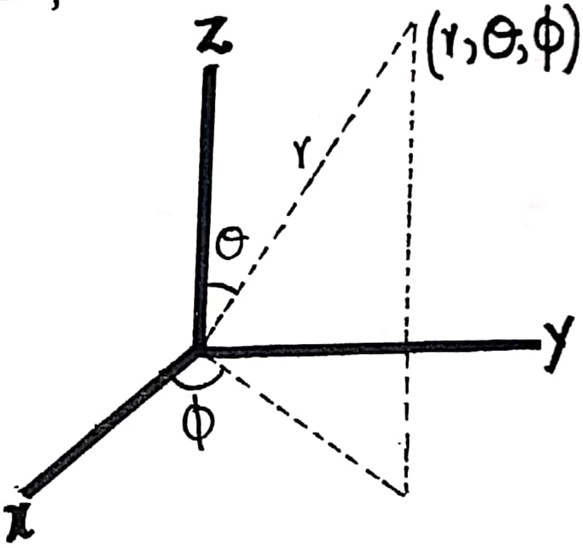
$$\nabla^2_{xyz} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Then we say that x, y and z in Spherical coordinates;

$$x = f(r, \theta, \phi)$$

$$Y = f(r, \theta, \phi)$$

$$z = f(r, \theta, \phi)$$



The values from above become;

$$x = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \longrightarrow \textbf{(a)}$$

$$Y = \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) \longrightarrow \textbf{(b)}$$

$$Z = \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial\phi^2} \longrightarrow \textbf{(c)}$$

By **(a), (b), (c)** the value of $\nabla^2 r\theta\phi$

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

put the values of $\nabla^2 r\theta\phi$ in equation # **(2)**

$$\hat{H} = \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\left[\frac{-h^2}{8\pi^2 m}\right] + V \longrightarrow \textbf{(4)}$$

By putting the value of $\hat{H}$ or value of equation # (4) into equation # (1):

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

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

$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Bigg]\left[\frac{-h^2}{8\pi^2 m}\right]+V = E\Psi r\theta\phi \rightarrow 5$$

Multiply both sides of equation # (5) by $-\frac{8\pi^2 m}{h^2}$

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

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

$$V_r = -\frac{Ze^2}{r}$$

Multiply each term with **$\Psi r\theta\phi$**

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

$$\Psi_{r\theta\phi} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Psi_{r\theta\phi} + \left(-\frac{Ze^2}{r}\right)\Psi_{r\theta\phi}$$
$$\left(-\frac{8\pi^2 m}{h^2}\right) + E\,\Psi_{r\theta\phi}\,\frac{8\pi^2 m}{h^2} = 0$$

Now we take $\left(\frac{8\pi^2 m}{h^2}\right)$ value from E and V.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\Psi_{r\theta\phi} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Psi_{r\theta\phi} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Psi_{r\theta\phi} + \frac{8\pi^2 m}{h^2}$$
$$\Psi_{r\theta\phi}\left(\frac{Ze^2}{r} + E\right) = 0.$$

for derivation of Hydrogen atom;

$$\Psi_{r\theta\phi} = \Psi_{xyz}$$

Wave function of Hydrogen atom consist of three parts;

r, θ, ϕ

radial distance

Azimuthal

4. Seperation of Variables:

$$\Psi_{r\theta\phi} = R_r \Theta_\theta \Phi_\phi$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\Psi_{r\theta\phi}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\Psi_{r\theta\phi}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi^2}\Psi_{r\theta\phi} - \frac{8\pi^2 m}{h^2}\Psi_{r\theta\phi}\left(\frac{Ze^2}{r} + E\right) = 0 \longrightarrow \textbf{(6)}$$

$\Psi_{r\theta\phi} = R_r \Theta_\theta \Phi_\phi$ put this in equation # **6**

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 \frac{\partial}{\partial r}\left(R_r \Theta_\theta \Phi_\phi\right)\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta \frac{\partial}{\partial\theta}\left(R_r \Theta_\theta \Phi_\phi\right)\right] + \left[\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\left(R_r \Theta_\theta \Phi_\phi\right]\right. - \frac{8\pi^2 m}{h^2}\left(R_r \Theta_\theta \Phi_\phi\right)\left(\frac{Ze^2}{r} + E\right) = 0$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\Theta_\theta \Phi_\phi\left[r^2\frac{\partial}{\partial r}R_r\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}R_r\Phi_\phi\left[\sin\theta\frac{\partial}{\partial\theta}\Theta_\theta\right] + R_r\Theta_\theta\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi^2}\left(\Phi_\phi\right) - \frac{8\pi^2 m}{h^2}\left(R_r \Theta_\theta \Phi_\phi\right)\left(\frac{Ze^2}{r} + E\right) = 0$$

Multiply the equation with $\dfrac{r^2\sin^2\theta}{R_r\,\Theta_\theta\,\Phi_\phi}$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\Theta_\theta\Phi_\phi\left[r^2\frac{\partial}{\partial r}R_r\right]\times\frac{r^2\sin^2\theta}{R_r\Theta_\theta\Phi_\phi}+\frac{1}{r^2\sin\theta}$$
$$\frac{\partial}{\partial\theta}R_r\Phi_\phi\left[\sin\theta\frac{\partial}{\partial\theta}\Theta_\theta\right]\times\frac{r^2\sin^2\theta}{R_r\Theta_\theta\Phi_\phi}+$$
$$R_r\Theta_\theta\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi^2}\Phi_\phi\times\frac{r^2\sin^2\theta}{R_r\Theta_\theta\Phi_\phi}-\frac{8\pi^2 m}{h^2}$$
$$(R_r\Theta_\theta\Phi_\phi\times\frac{r^2\sin^2\theta}{R_r\Theta_\theta\Phi_\phi}\left(\frac{Ze^2}{r}-E\right)=0$$

$$\frac{\sin^2\theta}{R_r}\frac{\partial}{\partial r}\left(r^2.\frac{\partial R_r}{\partial r}\right)+\frac{\sin\theta}{\Theta_\theta}.\frac{\partial}{\partial\theta}\sin\theta.$$
$$\frac{\partial\Theta_\theta}{\partial\theta}+\frac{1}{\Phi_\phi}\frac{\partial}{\partial\phi^2}\Phi_\phi+r^2\sin^2\theta\frac{8\pi^2 m}{h^2}$$
$$\left(\frac{Ze^2}{r}+E\right)=0$$

$$\frac{\sin^2\theta}{R_r}\frac{\partial}{\partial r}r^2\left[\frac{\partial}{\partial r}R_r\right]=\beta$$
$$\frac{\sin\theta}{\Theta_\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta_\theta}{\partial\theta}=\beta$$

Third term depends on ϕ and it is independant of Θ_θ and R_r.

$$-\frac{1}{\Phi_\phi}\frac{\partial \Phi_\phi^2}{\partial \phi^2} = +m^2$$

$$\frac{1}{\Phi_\phi}\frac{\partial \Phi_\phi}{\partial \phi^2} = -m^2$$

$$\frac{\partial^2 \phi}{\partial \phi^2} + m^2 \phi = 0 \longrightarrow \textbf{(8)}$$

$$\frac{\sin^2\theta}{R_r}\frac{\partial}{\partial r}\left(r^2\frac{\partial R_r}{\partial r}\right) + \frac{\sin\theta}{\Theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \Theta_\theta}{\partial \theta}\right) - m^2 + \frac{8\pi^2 m}{h^2} r^2\sin^2\theta\left(\frac{ze^2}{r}+E\right) = 0.$$

1st term $\frac{\sin^2\theta}{R_r}\frac{\partial}{\partial r}\left(r^2\frac{\partial R_r}{\partial r}\right)$

2nd term $\frac{\sin\theta}{\Theta_\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \Theta_\theta}{\partial \theta}\right)$

3rd term m^2

4th term $\frac{8\pi^2 m}{h^2} r^2\sin^2\theta\left(\frac{ze^2}{r}+E\right)$

By this method we have to seperate the r and θ.

Now from this equation;

$$\frac{\sin^2\theta}{R_r}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R_r\right)+\frac{\sin\theta}{\Theta_\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_\theta}{\partial\theta}\right)-m^2+\frac{8\pi^2 m}{h^2}r^2\sin^2\theta\left(\frac{Ze^2}{r^2}+E=0\right)$$

Now We have to seperate R from this equation;

By dividing the equation with $\sin^2\theta$.

$$\frac{1}{\sin^2\theta}\times\frac{\sin^2\theta}{R_r}\frac{\partial}{\partial r}\left(r^2\frac{\partial R_r}{\partial r}\right)+\frac{1}{\sin^2\theta}\frac{\sin\theta}{\Theta_\theta}\frac{\partial}{\partial\theta}\left(\sin\frac{\partial\Theta_\theta}{r\theta}\right)-\frac{m^2}{\sin^2\theta}+\frac{1}{\sin^2\theta}\left(\frac{8\pi^2 m}{h^2}\right.$$
$$\left.r^2\sin^2\theta\right.\left(\frac{Ze^2}{r^2}+E\right)=0\longrightarrow(9)$$

By joining part # 1 and 4 together and that is equal to β.

term 1 + term 4 = β

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$$\frac{1}{R_r}\frac{\partial}{\partial r}\left(r^2 \cdot \frac{\partial R_r}{\partial r}\right) + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r^2}\right)r^2$$
$$= \beta \longrightarrow (10)$$

Multiply equation # (10) by $\frac{R}{r^2}$ we get;

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \cdot \frac{\partial R_r}{\partial r}\right) + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)R$$
$$= \beta \frac{R}{r^2}$$

Or

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \cdot \frac{\partial R_r}{\partial r}\right) + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)R -$$
$$\beta \frac{R}{r^2} = 0 \longrightarrow (11)$$

Equation no. 11 is called as **R- equation.**

$$\frac{1}{\Theta \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \Theta_\theta}{\partial \theta}\right) - \frac{m^2}{\sin^2\theta} =$$
$$-\beta \longrightarrow (12)$$

This is 2nd and third term of equation that is equal to

$-\beta$

Multiply above equation by θ we get;

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)=0$$

Now we have three equations;

1- ϕ - Equation
2- R - Equation
3- θ - Equation

4.1 Solution of ϕ Equation

As we know ϕ equation is;

$$\frac{\partial^2\phi}{\partial\phi^2}+m^2\phi_\phi=0.$$

This equation is Second ordered differential equation;
This equation has two forms first is general form and

Other is exponential form.

The general form of equation is;

$$\phi = A \sin m\phi \longrightarrow (a)$$

In exponential form it is written as;

$$\phi_\phi = Ae^{\pm im\phi} \longrightarrow (b)$$

equation (b) is acceptable only if m is in the form of integar.

$$\phi = \phi + 2\pi$$

now, by putting the value of ϕ in equation # (b)

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

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

By comparing equation (b) and equation (c);

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

$$e^{\cancel{\pm im\phi}} = \cancel{e^{\pm im\phi}} \cdot e^{\pm im2\pi}$$

$$1 = e^{\pm lm2\pi}$$

$$1 = e^{\pm im2\pi} \longrightarrow (d)$$

$\therefore e^{i\theta} = (\cos\theta + \sin\theta)$
So equation (d) can be written as;

$$1 = \cos m 2\pi + i \sin m 2\pi.$$

This is only possible if $m = 0, \pm 1, \pm 2, \pm 3 \ldots\ldots$) These are called as megnatic quantum number.

Megnatic quantum number;

megnatic quantum number describes the orientation of region of space that is occupied by electron.
The values of m_l depend upon the l: m_l. That range from $-l$ to l in integral steps;

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

for example; $l = 0$ then m_l can be only zero; If $l = 1$, m_l can be $-1, 0$, or $+1$. and If $l = 2$, m_l can be $-2, -1, 0, +1$, or $+2$.

Each wave function with allowed combination of n, l and ml values describes the atomic orbital and particular spectral distribution of an electron. Each principle shell has fixed number of subshells and each subshell has fixed number of orbitals.

4.2 Solution of R equation;

Solution of R equation provides the eigen values which are characterized to be principal quantum number (n) and azimuthal quantum number.

Principal Quantum number (n):

It tells average relative distance of an electron from nucleus. Indicate the energy of electron and the average distance of (nucleus) an electron from nucleus.

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

The electron that have higher values of n are easier to remove from an atom. All wave functions that have same value of n are said to constitute a principal shell. same value of n because electrons have similar average distance from the nucleus.

Azimuthal Quantum Number:-

It describes the shape of region of space occupied by electron. Value of l depend upon value of n that can range from 0 to n-1.

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

A group of wave function that have similar value of n and l The region of space occupied by electrons in same subshell usually have same shape, but oriented different in space.

4.3 Solution of Θ Equation:-
(m, l)

Solution of θ equation provides the eigen values which are character_ized to be megnatic quantum number (m) and azimuthal quantum number (l).