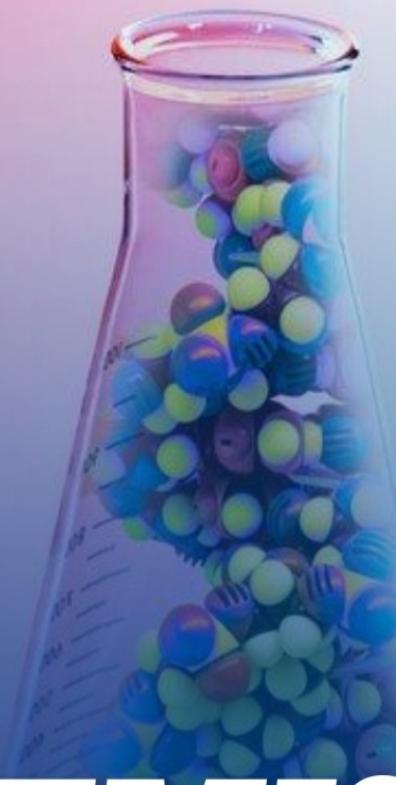


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Dr. Hemant Kulshrestha
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By

Dr. Hemant Kulshrestha

&

Dr. Ajay Taneja

Department of Chemistry

St. Johns College,

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Fax : (0562) 4053330, 4031570

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Section-A
INORGANIC CHEMISTRY

1

ATOMIC STRUCTURE

Some Expressions According to Bohr's Model

- Angular momentum,

$$mv r = n \frac{h}{2\pi}$$

- Number of waves in an orbit

$$\begin{aligned} &= \frac{\text{Circumference of that orbit}}{\text{Wavelength}} \\ &= \frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv} = \frac{2\pi(mvr)}{h} \\ &= \frac{2\pi(nh/2\pi)}{h} \\ &= n \end{aligned}$$

- Radius of orbit in hydrogen and hydrogen like species

$$r_n = \frac{n^2 h^2}{4\pi^2 k m Z e^2}$$

For H-atom $Z = 1$. For the lowest orbit $n = 1$, hence, the radius of the first orbit of H-atom (Bohr radius), on substituting the values in above equation

$$\begin{aligned} r_1 &= 0.529 \text{ \AA} \\ &= 0.529 \times 10^{-10} \text{ m} \end{aligned}$$

Radius of n th orbit of H-atom,

$$r_n = 0.529 \times n^2 \text{ \AA}$$

Radius of 1st orbit in He^+ ion

$$r_n = \frac{n^2}{Z} \times 0.529 \text{ \AA}$$

$$r_{1(\text{He}^+)} = \frac{1^2}{2} \times 0.529 \text{ \AA}$$

$$r_{n(\text{He}^+)} = \frac{r_n(\text{H})}{2}$$

- Velocity of the electron in n th orbit of H-atom and hydrogen like species

$$v_n = \frac{2\pi k Z e^2}{nh}$$

Substituting the values for various constants, we get

$$\begin{aligned} v_n &= \frac{2.18 \times 10^6 \times Z}{n} \text{ ms}^{-1} \\ v_{1(\text{H})} &= 2.18 \times 10^6 \times \frac{1}{1} \text{ ms}^{-1} \\ &= 2.18 \times 10^6 \text{ ms}^{-1} (\because n = 1, Z = 1) \\ v_{1(\text{He}^+)} &= 2.18 \times \frac{2}{1} \text{ ms}^{-1} \\ &= 4.36 \times 10^6 \text{ ms}^{-1} (\because n = 1, Z = 2) \\ v_{n(\text{He}^+)} &= 2 \times v_{n(\text{H})} \text{ and } v_{n(\text{Li}^{2+})} \\ &= 3 \times v_{n(\text{H})} \end{aligned}$$

- Number of revolution per second of an electron in the n th orbit

$$\begin{aligned} &= \frac{\text{Velocity of the electron}}{\text{Circumference of the orbit}} \\ &= \frac{v_n}{2\pi r_n} \end{aligned}$$

- Energy of the electron in n th orbit

$$\begin{aligned} E_n &= -k^2 \frac{2\pi^2 m e^4 Z^2}{n^2 h^2} \\ &= -\frac{1312}{n^2} \text{ kJ mol}^{-1} \end{aligned}$$

For H-like species,

$$E_n = Z^2 E_n$$

In general, $E_n \propto -\frac{1}{n^2}$

$$\text{and } E_n = \frac{E_1}{n^2}$$

4C | Chem.

- Different spectral lines in the spectrum of hydrogen.

Series	Region	n_1	n_2
Lyman	Ultra-violet	1	2, 3, 4...
Balmer	Visible	2	3, 4, 5...
Paschen	Infra-red	3	4, 5, 6...
Brackett	Infra-red	4	5, 6, 7...
Pfund	Infra-red (far)	5	6, 7, 8...
Humphrey	Infra-red (near)	6	7, 8, 9...

- Wave number of spectral lines in hydrogen atom

$$\begin{aligned}\frac{1}{\lambda} &= \bar{v} \text{ (cm}^{-1}\text{)} \\ &= R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)\end{aligned}$$

R = Rydberg constant = 109678 cm⁻¹

For hydrogen like species

$$\begin{aligned}\frac{1}{\lambda} &= \bar{v} \text{ (cm}^{-1}\text{)} \\ &= R \times Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)\end{aligned}$$

- The number of spectral lines produced when an electron jumps from n th level to the ground level ($n = 1$)

$$= \frac{n(n-1)}{2}$$

de Broglie equation

$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad (p = \text{Momentum})$$

- Particle nature of radiation can account for photoelectric effect, reflection and refraction while wave nature of radiation can account for interference and diffraction.
- Wave character of electron was experimentally verified by Davission and Germer by diffraction experiment.
- Heisenberg uncertainty principle**—It is impossible to measure simultaneously both the position and momentum (velocity) of a microscopic particle (like electron) with absolute accuracy.

$$\Delta_x \cdot \Delta_p \geq \frac{h}{4\pi}$$

$$\Delta_x \propto \frac{1}{\Delta_p}$$

- Schrodinger's wave equation**—Erwin Schrodinger (1926) gave a wave equation which describes the wave motion of an electron-wave propagating in three dimensions (X-, Y- and Z-axes) in space. In this, the discrete energy levels or orbits proposed by Bohr are replaced by mathematical functions, ψ (Psi), which are related with the probability of finding electrons at various places around the nucleus. The equation is written as follows :

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

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

x, y, z = Cartesian coordinates

m = Mass of the electron

n = Planck's constant

E = Total energy of the system

V = Potential energy of the system

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

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

$$\text{where} \quad \nabla^2 = \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right)$$

∇^2 is known as Laplacian mathematical operator. A mathematical operator such as f , $\frac{d}{dx}$, $\sqrt{\dots}$ etc. is always accompanied by a mathematical quantity or mathematical function upon which it operates. In $\nabla^2 \psi$, ∇^2 is a mathematical operator and ψ is a mathematical function on which ∇^2 operates. Thus $\nabla^2 \psi$ should not mean that ∇^2 is multiplied by ψ . The function ψ signifies the amplitude of the electron wave and is called wave function.

Other forms of Schrodinger's wave equation

$$(i) \quad \left[-\frac{h^2}{8\pi^2 m} \nabla^2 + V \right] \psi = E \psi$$

$$(ii) \quad \hat{H} \psi = E \psi$$

where \hat{H} is called Hamiltonian operator and consists of two parts, the kinetic energy part $\left(-\frac{h^2}{8\pi^2 m} \nabla^2 \right)$ and the potential energy part (V).

- **Eigen wave function and eigen value—** Being a differential equation of second order, when we solve Schrodinger wave equation for ψ , we get many values of ψ . Some of these values are imaginary, while other are real values. The imaginary values of ψ can not be accepted. Only those values of ψ which give definite and acceptable value of the total energy (E) of the electron are acceptable. The acceptable values of the wave functions ψ are called **eigen wave functions**. The value of E given by eigen wave function is called **eigen value**. Only that value of ψ is an eigen wave function which has the following characteristics—

- (i) It should not have more than one value at a point in space, i.e., it should be single valued.
- (ii) It should be continuous.
- (iii) The function must be finite.
- (iv) $\frac{\partial^2\psi}{\partial x^2}$, $\frac{\partial^2\psi}{\partial y^2}$ and $\frac{\partial^2\psi}{\partial z^2}$ must be continuous function of x , y and z respectively.
- (v) The function must be normalised, i.e., it should obey the relation $\int_{-\infty}^{+\infty} \psi^2 dr = 1$, where dr is a small volume element and $\psi^2 dr$ represents the probability of finding the electron in small volume element dr .

- **Schrodinger's wave equations for hydrogen atom**

In case of H-atom, a single electron having charge equal to $-e$ moves round the nucleus with charge equal to $+e$.

$$\therefore \text{Potential energy of the electron, } V = -\frac{e^2}{r}.$$

Thus, Schrodinger's wave equation in terms of Cartesian coordinates x , y , z takes the form

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

$$\text{or } \nabla^2 \psi + \frac{8\pi^2 m}{h^2} \left(E - \frac{e^2}{r} \right) \psi = 0$$

The transformation from Cartesian coordinates x , y , z into polar coordinates facilitates solution of wave equation. The position variables in polar coordinates are r , θ and ϕ , where r is the radial distance of a point from the origin, θ is the inclination of the radial line to the z -axis and ϕ is the angle made with the x axis by the projection of the radial line

in the xy plane. After this transformation the Schrodinger equation can be factored into two equations one depending only on r and other only on θ and ϕ . The conversion of Cartesian coordinates into polar coordinates is as—

$$\begin{aligned} z &= r \cos \theta \\ y &= r \sin \theta \sin \phi \\ x &= r \sin \theta \cos \phi \end{aligned}$$

- Thus Schrodinger wave equation in terms of polar coordinates is as—

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left(\frac{r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r}}{r^2} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\frac{\sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta}}{\sin \theta} \right) + \frac{1}{h^2 \sin^2 \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} \\ + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{r} \right) \psi(r, \theta, \phi) = 0 \end{aligned}$$

The solution of this equation, evolution of $\psi(r, \theta, \phi)$ is possible only if ψ function can be written in the form

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$

where $R(r)$ is a function which depends on r only (distance of the electron from nucleus but independent of the other two polar coordinates θ and ϕ). $\Theta(\theta)$ is a function dependent on θ and is independent of r and ϕ and $\Phi(\phi)$ is a function dependent on ϕ only but is independent of r and θ .

- The function $R(r)$ is known as the **radial wave function** while the function $\Theta(\theta)$ and $\Phi(\phi)$ are called **angular wave function**.
- The radial wave function $R(r)$ gives the energy and size of the orbitals, i.e., principal (n) and angular quantum numbers (l). It is written as $R_{n,l}(r)$ or $R_{n,l}$.

The angular wave function, which is the product of $\Theta(\theta)$ and $\Phi(\phi)$ gives the shape of orbitals, i.e., magnetic quantum number (m). It is written as $\Theta_{l,m}(\theta)$ or $\Theta_{l,m}$.

- **Significance of ψ and ψ^2** — ψ refers to the amplitude of electron wave. It has got no physical significance. However, the square of ψ , i.e., ψ^2 has a physical significance. Just like light radiations where square of amplitude gives the intensity of light, similarly, in electron wave, ψ^2 gives the intensity of electron of any point, i.e., ψ^2 is helpful in assessing the probability of electron in a particular region. Thus ψ^2 is called **probability density** and ψ is referred to

probability amplitude. In order to avoid imaginary values $\psi\psi^*$ is used for ψ^2 . ψ^* is a complex conjugate of ψ . We expect that if ψ extends over a finite volume in space $dx, dy, dz (= d\tau)$, then the electron would be found in that volume. So $\psi\psi^* d\tau$ gives the probability of finding the electron in the volume $d\tau$. The wave function ψ may be positive, negative or imaginary but the probability density $\psi\psi^*$ will always be positive and real.

- **Normalized wave function**— $\psi\psi^* d\tau$ is proportional (not equal) to the probability of finding the electron in the given volume element $d\tau$. However, if we have a value of ψ such that the integration of $\psi\psi^*$ from $-\infty$ to $+\infty$, that is over the entire space, is not proportional but equal to the total probability of finding the electron, then the probability that the electron is present within the volume element $d\tau$ becomes unity (*i.e.*, 100%), Mathematically

$$\int_{-\infty}^{+\infty} \psi\psi^* d\tau = 1$$

This is the condition of normalization and ψ satisfying this expression is said to be normalized. Sometimes ψ may not be normalized wave function but then it is possible to multiply it by a constant N , so that $N\psi$ is also a solution of the wave equation. Mathematically

$$N^2 \int \psi\psi^* d\tau = 1$$

$$\text{or } \int \psi\psi^* d\tau = N^2$$

where N = Normalizing constant.

- **Orthogonal wave function**—This means that a particular wave function must be different from all other wave functions over the entire space. The condition for orthogonality is that the product of two wave functions, integrated over the entire space must be equal to zero. Two wave functions ψ_1 and ψ_2 are said to be orthogonal if

$$\int \psi_1 \psi_2^* d\tau = 0$$

$$\text{and } \int \psi_1^* \psi_2^* d\tau = 0$$

Here ψ_1^* and ψ_2^* are complex conjugate of ψ_1 and ψ_2 respectively.

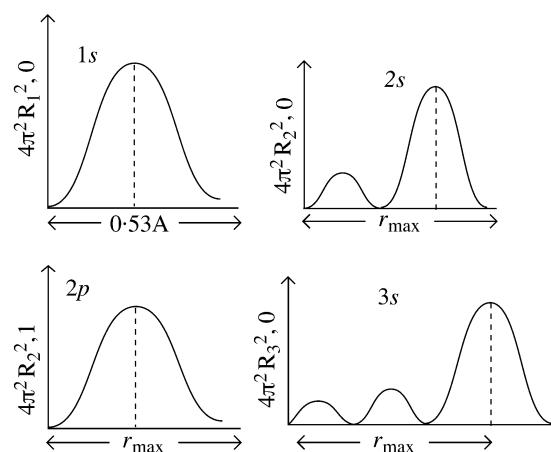
- Wave functions which are both normalized and orthogonal are called orthonormal wave functions.

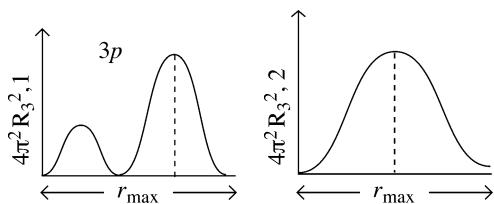
- **Radial probability**—Radial wave function $R_{n,l}$ or $R^2_{n,l}$ can not be directly related with probability of finding an electron at a point, which is at a distant r from the nucleus. The probability of finding electron within small radial shell of thickness dr around the nucleus called radial probability

Radial probability

$$\begin{aligned} &= \text{Probability density} \times \text{Volume of radial shell} \\ &= \psi^2 \cdot 4\pi r^2 dr \\ &= l \cdot 4\pi r^2 dr \end{aligned}$$

- The radial probability distribution curves obtained by plotting radial probability versus distance from the nucleus for $1s, 2s, 2p, 3s, 3p$ and $3d$ orbitals are given below. In case of $1s$ orbital, the probability (ψ^2) of finding $1s$ electron is maximum near the nucleus. However, the volume element $4\pi r^2 dr$ is very small because r is very low near the nucleus. Hence, their product is quite small. As the distance r from the nucleus increases, ψ^2 goes on decreasing whereas volume $4\pi r^2 dr$ goes on increasing. Their product goes on increasing till it reaches a maximum value at a distance of 0.53 \AA and then begins to decrease. An important difference between Bohrs model and wave mechanical model lies in the fact that whereas according to the former the electron revolves at a constant distance of 0.53 \AA from the nucleus, according to the latter the electron is most likely to be found at this distance but there is a probability of finding the electron at distances shorter as well as larger than 0.53 \AA .





- Radial nodes**—The number of minima appearing in a particular curve gives the number of radial nodes or nodal points for the orbital. The number of radial nodes is equal to $(n - l - 1)$. Thus for $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ electrons, the number of nodal points is equal to 0, 1, 0, 2, 1 and 0 respectively. Radial node in that point at which the probability density of electronic charge is zero. Due to greater number of radial nodes for $3s$ orbital ($= 2$) than that of $1s$ ($= 0$) and $2s$ ($= 1$), $3s$ orbital is bigger in size and more diffused.
- Angular probability**—The angular part of the wave function determines the shape of the electron cloud and varies depending upon the type of orbital involved (s , p , d or f) and its orientation in space. Thus, the use of $\psi_\theta^2 \psi_\phi^2$ represent the probability in terms of θ and ϕ . The angular wave function is independent of the principal quantum number. Some typical angular functions are—

$$l = 0, m_l = 0, \Theta\Phi = \left(\frac{1}{4\pi}\right)^{1/2} \quad s\text{-orbital}$$

$$l = 1, m_l = 0, \Theta\Phi = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \quad p_z\text{-orbital}$$

$$l = 1, m_l = 1, \Theta\Phi = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \cos\phi \quad p_x\text{-orbital}$$

$$l = 2, m_l = 0, \Theta\Phi = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \quad dz^2 \text{ orbital}$$

For an s -orbital angular wave function is independent of angle and is of constant value. Hence, its graph is circular or in three dimensions spherical. For p_z orbital we obtain two tangent spheres. The p_x and p_y orbitals are identical in shape but are oriented along the x - and y -axes.

- The number of angular nodes in just equal to l .
- A complete representation of electron distribution probability includes both radial

and angular probabilities and requires a three dimensional model.

- Total number of nodes in a shell = $(n - 1)$
Angular nodes = l
Radial/spherical nodes = $n - l - 1$
- There are l nodal surfaces in the angular distributional functions of all orbitals.
- Quantum numbers**—The solution of the Schrodinger wave equation for hydrogen atom yields three quantum numbers viz., principal, angular and magnetic. The fourth one viz., spin quantum number does not follow from the wave mechanical treatment.

■ **Principal quantum number (n)**—It arises from the solution of radial part of wave function. It is required to explain the main lines of a spectrum. It tells about the

- Main shell in which the electron resides.
- Approximate distance of the electron from the nucleus.
- Energy of the shell, the energy increases with increasing n .
- Maximum number of electrons present in the shell ($2n^2$).

Values of $n = 1, 2, 3, 4, 5 \dots \infty$
K, L, M, N, O ...

As the value of n increases, the electron gets farther away from the nucleus and its energy increases.

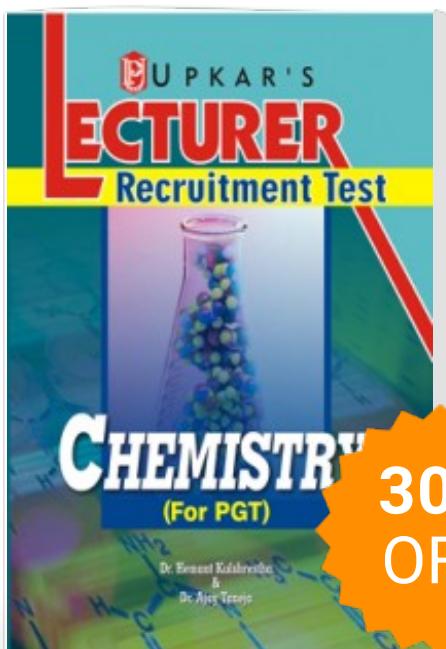
■ **Azimuthal or subsidiary quantum number (l)**—It also arises from the radial part of wave function. It is required to explain the fine structure of the line spectrum. It tells about the

- number of sub-shells present in any main shell.
- relative energies of the sub-shells.
- shapes of orbitals.

Its values for a particular value of n are, $l = 0$ to $n - 1$, i.e., when $n = 1$, $l = 0$ (one sub-shell), $n = 2$, $l = 0, 1$ (two sub-shells) $n = 3$, $l = 0, 1, 2$ (three sub-shell), $n = 4$, $l = 0, 1, 2, 3$ (four sub-shells)

Quantum No. $l = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ \dots$
Sub-shell notation $s \ p \ d \ f \ g \ h \ \dots$

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Author : Dr. Hemanth
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