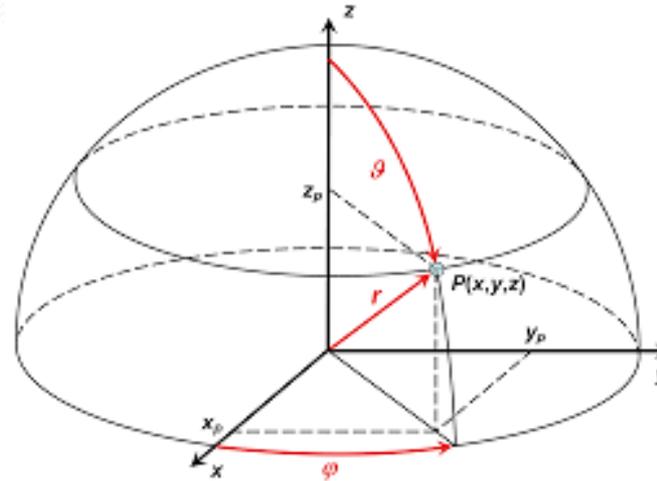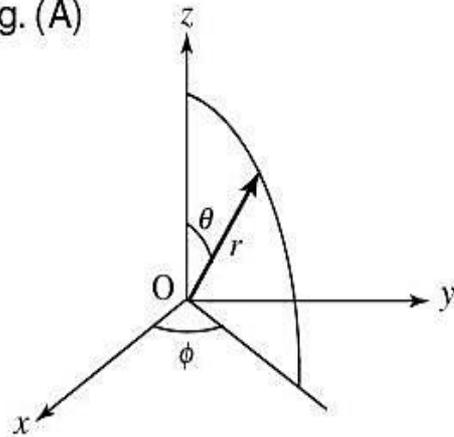# *Atomic Structure*

Lecture by

Dr. Debopam Sinha

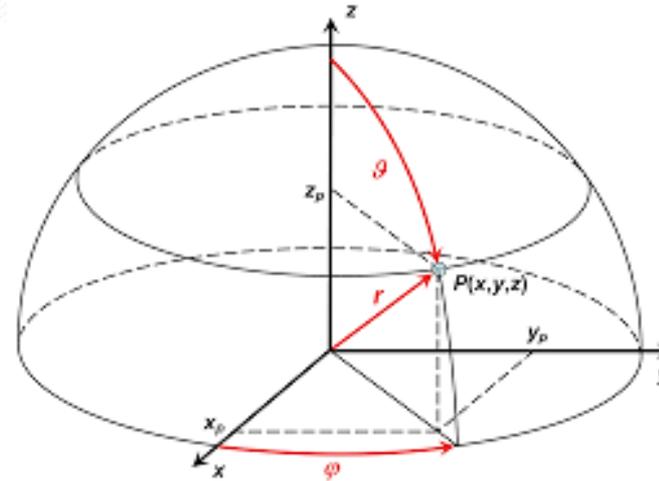**Vijaygarh Jyotish Ray College
Kolkata-700032**

Fig. (A)

We solve the Schroedinger equation (1) represented in the polar coordinate (r, θ, ϕ) setting the boundary condition that the wave function should be smoothly continuous at every point of the coordinate space and should converge to 0 at the infinitely long distance $r = \infty$. Then we have a set of **discrete energy eigenvalues** and the corresponding **eigenstates**. The details of the method to solve it is omitted here. If you want to study them, please refer to some other textbooks of quantum mechanics.

The **wave functions** of the **eigenstates** is expressed as

$$\psi(r, \theta, \phi) = R_{nl}(r)\, Y_{lm}(\theta, \phi). \qquad (2)$$

Here the part $R_{nl}(r)$ is called the **radial wave function** which is specified by a set of integers, n and l. Such numbers (integers) as these n and l are sometimes called **quantum numbers**, which characterize the eigenstates.
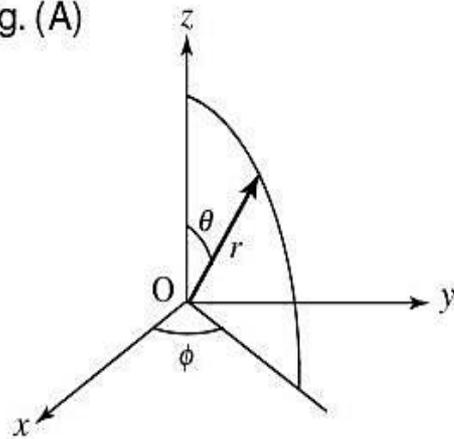
Fig. (A)

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In the present case, they are

$$n = 1, 2, 3, \cdots; \quad l = 0, 1, 2, \cdots; \quad l \leq n - 1. \tag{3}$$

The part $Y_{lm}(\theta, \phi)$ denotes the **angular wave function** which is specified by a set of quantum numbers (integers), l and m, and they are given by

$$|m| \leq l \quad \text{i.e.} \quad m = -l, -l+1, \cdots, l-1, l. \tag{4}$$

The angular wave function $Y_{lm}(\theta, \phi)$ describes the revolving state of the electron around the coordinate origin (proton). Namely, the quantum number l expresses the speed of the revolution of the electron, i.e. the magnitude of the **angular momentum** of the electron, and m represents the orientation (direction) of angular momentum vector. The fact that these quantum numbers l and m are **integers** means that both **the magnitude** and **the orientation** of the angular momentum are step-like and discrete.

This result implies that not only energy but also **angular momentum** and its **orientation** are **quantized** in quantum mechanics. This was confirmed by the **Stern-Gerlach experiment** (1922). Needless to say, this also originates from the particle-wave duality of electrons. And this can never understood by the classical theory.

[The Energy Eigenvalues of Hydrogen Atom]

The energy eigenvalues of hydrogen atom are determined only by the quantum number n and they are expressed as

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2} \quad (n = 1, 2, 3, \cdots). \qquad (5)$$

The state with $n = 1$ is the lowest energy state (**the ground state**) and those with $n = 2, 3, \ldots$ are the **excited states**. Thus the ground-state energy is written

$$E_1 = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2} = -13.6 \text{ eV}. \qquad (6)$$

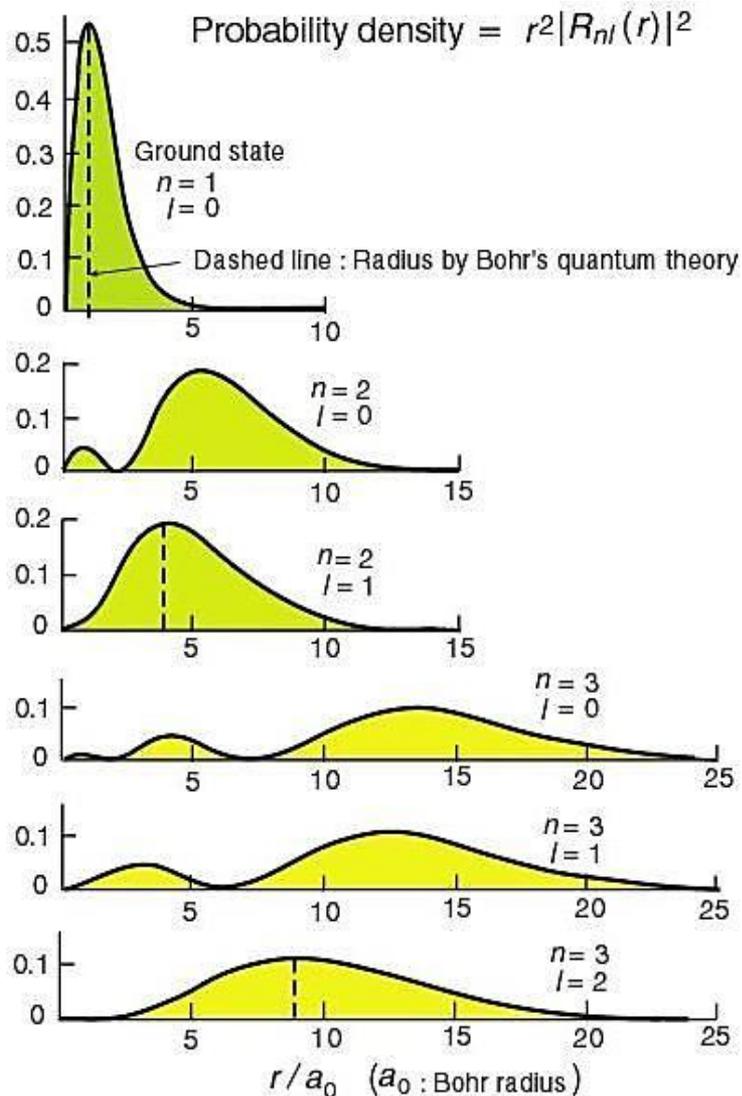## [The Probability that Electron will be Found]

It is very interesting to see how much the probability for a electron to be found at a point in the space is. The probability density

$$r^2 |R_{nl}(r)|^2$$

at a position of the distance r from the center is shown in **Fig. (C)**. Integrating this probability density over the whole space, we have

$$\int_0^\infty r^2 |R_{nl}(r)|^2 dr = 1$$

As shown in this integration, the present wave functions are so normalized that the total probability would be 1 (= 100 %).

Probability density = $r^2|R_{nl}(r)|^2$

Ground state
$n = 1$
$l = 0$

Dashed line : Radius by Bohr's quantum theory

$n = 2$
$l = 0$

$n = 2$
$l = 1$

$n = 3$
$l = 0$

$n = 3$
$l = 1$

$n = 3$
$l = 2$

r / a_0 (a_0 : Bohr radius)

The above **Fig. (C)** shows the probability distribution of electron in hydrogen atom. The first figure shows the **ground state**, in which almost all probability concentrated at

$r \approx a_0$ = the Bohr radius.
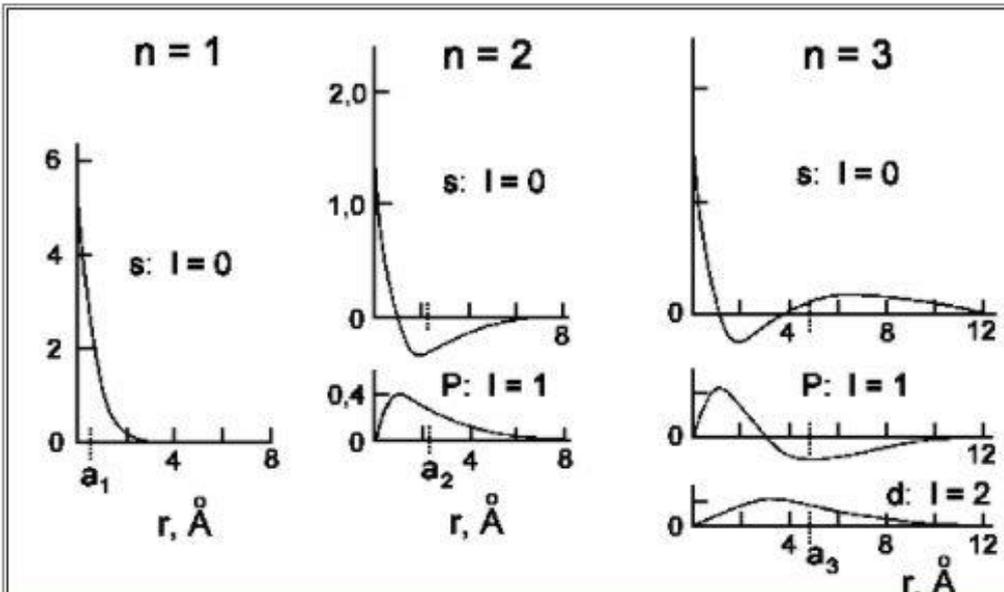
Radial wavefunction of hydrogen atom for n = 1, 2 and 3. The ordinate is always $[R_{n,l}(r)\, m^{-3/2}]\cdot 10^{-8}$.
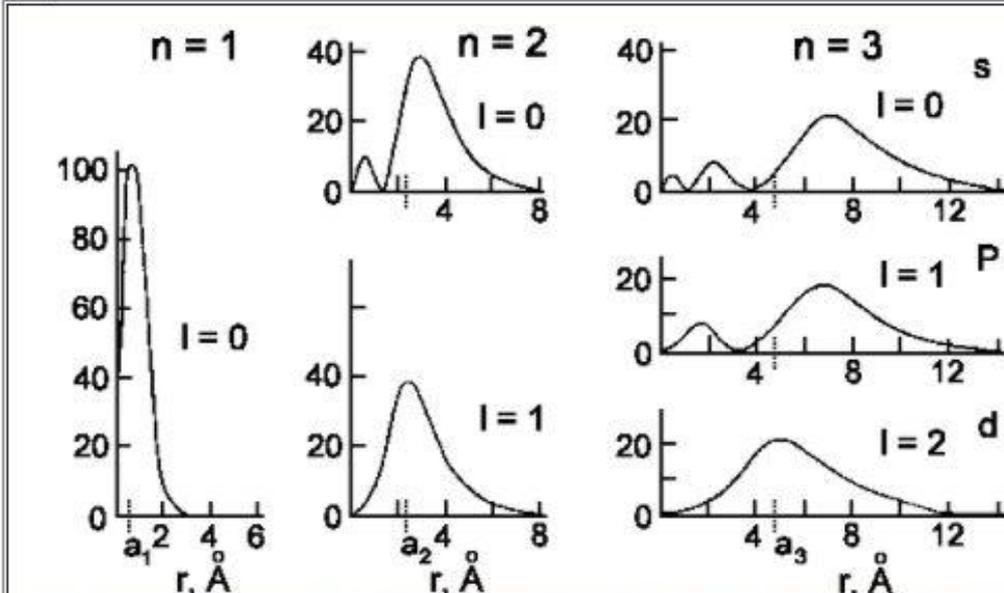
Radial detection probability in the hydrogen atom for n = 1, 2, and 3. The ordinate is always $[e^2\, R_{n,l}^2(r)\cdot 10^{-15}]$.

If $Y(\theta,\phi) = 0$, angular nodes result. Angular nodes are planar or conical.
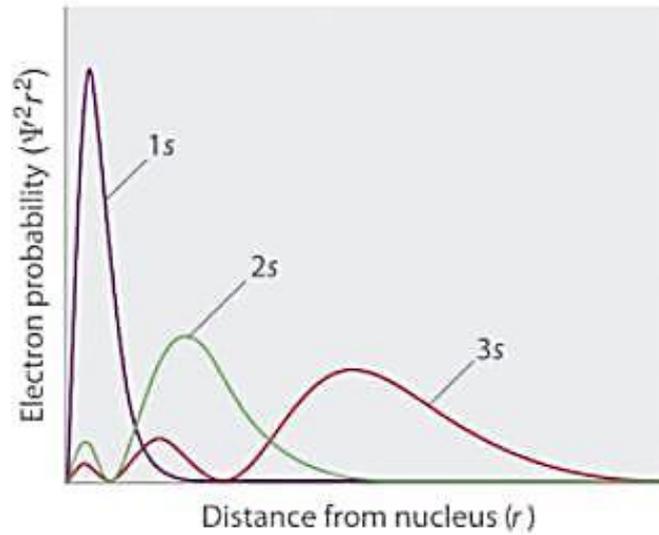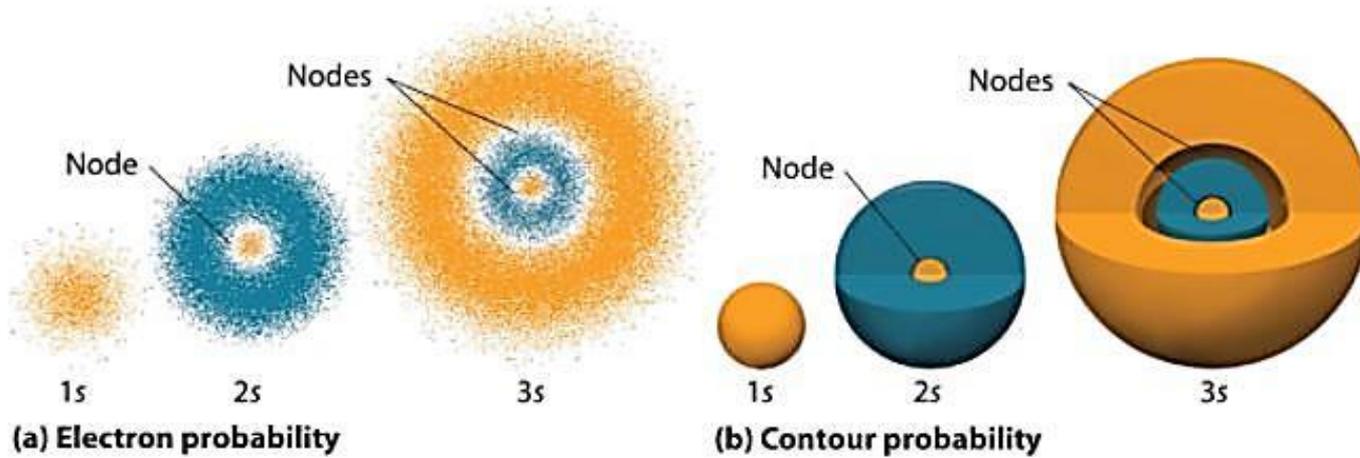
Number of angular nodes = l

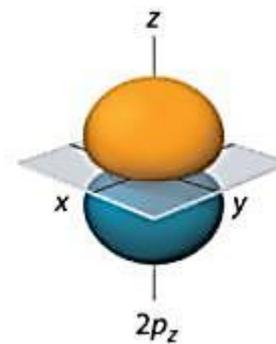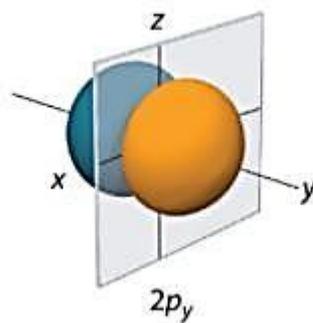| Orbital	No. of angular nodes
s- orbital	0
p-orbital	1
d-orbital	2
f-orbital	3

Total number nodal surface = $n - 1$

If $R(r) = 0$, radial nodes or spherical nodes result.

Number of radial nodes = $n - l - 1$

Orbital	Radial nodes	Orbital	Radial nodes	Orbital	Radial nodes
1s	0	2p	0	3d	0
2s	1	3p	1	4d	1
3s	2	4p	2	5d	2

(a) Electron probability

1s 2s 3s

Node Nodes

(b) Contour probability

1s 2s 3s

Node Nodes

(c) Radial probability

Electron probability ($\Psi^2 r^2$)

Distance from nucleus (r)

1s 2s 3s
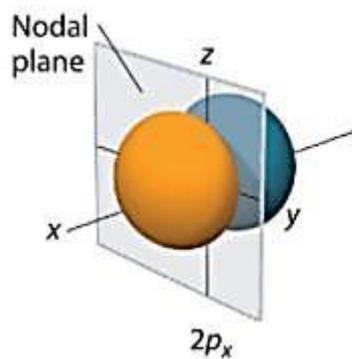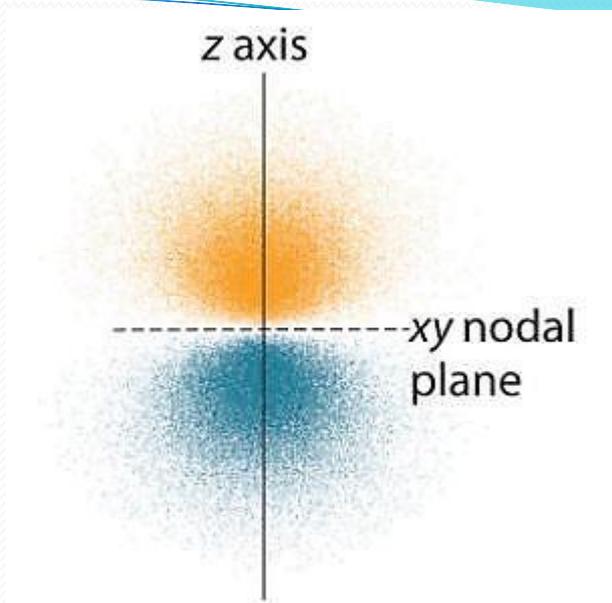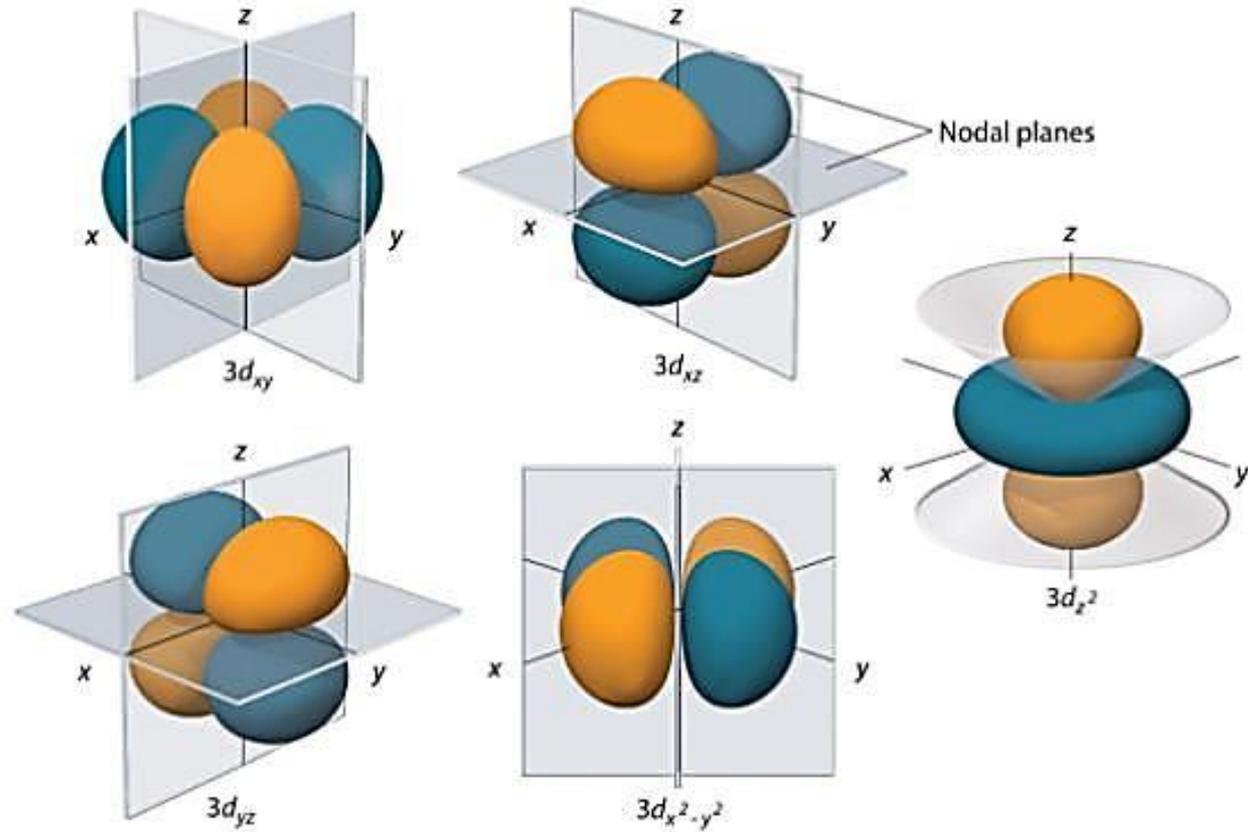
The time-indepdent Schrödinger equation (in spherical coordinates) for a electron around a positively charged nucleus is then

$$\left\{ -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{11.10.3}$$

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 11.10.3 by using a **product wavefunction**. We know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions (Table M4), $Y(\theta,\varphi)$, so a good choice for a product function is

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) \tag{11.10.4}$$

The Spherical Harmonic $Y(\theta,\varphi)$ functions provide information about where the electron is around the proton, and the radial function $R(r)$ describes how far the electron is away from the proton. A solution for both $R(r)$ and $Y(\theta,\varphi)$ with E_n that depends on only one quantum number n, although others are required for the proper description of the wavefunction:

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} \tag{11.10.5}$$

with $n = 1, 2, 3 \ldots \infty$

The hydrogen atom wavefunctions, $\psi(r,\theta,\phi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with n = 1, l l = 0 is called the 1s orbital, and an electron that is described by this function is said to be "in" the ls orbital, i.e. have a 1s orbital state. The constraints on n, l l), and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

The Three Quantum Numbers

Schrödinger's approach requires three quantum numbers (n, l, and m_l) to specify a wavefunction for the electron. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer (NOT zero), only certain values of l and m_l are allowed for a given value of \ (n).

The principal quantum number (n): One of three quantum numbers that tells the average relative distance of an electron from the nucleus. indicates the energy of the electron and the average distance of an electron from the nucleus

$$n = 1,\ 2,\ 3,\ 4,\ \ldots \tag{11.10.6}$$

Asn increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wave functions that have the same value of n are said to constitute a principal shell. All the wave functions that have the same value of n because those electrons have similar average distances from the nucleus. because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number: The second quantum number is often called the azimuthal quantum number (l). One of three quantum numbers that describes the shape of the region of space occupied by an electron.. The value of l describes the shape of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to n − 1:

$$l = 0,\ 1,.,2,\ 3,\ \ldots (n-1) \tag{11.10.7}$$

For example, if n = 1, l can be only 0; if n = 2, l can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both n and l form a subshell. A group of wave functions that have the same values of n and l. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number: The third quantum number is the magnetic quantum number (m_l). One of three quantum numbers that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field.. The value of m_l describes the orientation of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from −l to l in integral steps:

$$m = -l, \ -l+1, \ \ldots .0, \ \ldots .l-1, l \tag{11.10.8}$$

For example, if $l = 0$, ml can be only 0; 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 an allowed combination of n, l, and ml values describes an atomic orbital A wave function with an allowed combination of n, l and ml quantum numbers., a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Postulates of Bohr's Model of an Atom

- In an atom, electrons (negatively charged) revolve around the positively charged nucleus in a definite circular path called orbits or shells.

- Each orbit or shell has a fixed energy and these circular orbits are known as orbital shells.

- The energy levels are represented by an integer (n=1, 2, 3...) known as the quantum number. This range of quantum number starts from nucleus side with n=1 having the lowest energy level. The orbits n=1, 2, 3, 4... are assigned as K, L, M, N.... shells and when an electron attains the lowest energy level, it is said to be in the ground state.

- The electrons in an atom move from a lower energy level to a higher energy level by gaining the required energy and an electron moves from a higher energy level to lower energy level by losing energy.

n = 3

n = 2

n=1

Increasing enrgy of orbits

A photon is emitted with energy **E = hf**
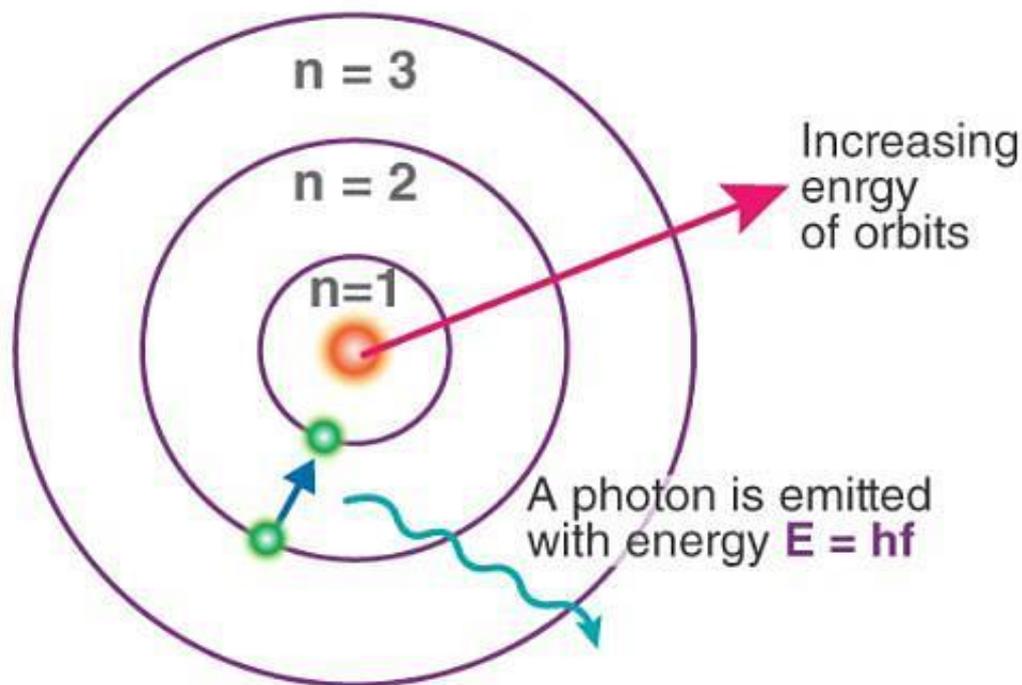
Bohr's three postulates

1. Quantised orbits. The classical equations of motion are valid for electrons in atoms. However, only certain discrete orbits with the energy E_n are allowed. These are the energy levels of the atom.

2. The motion of the electron in these quantised orbits is radiationless. An electron can be transferred from an orbit to another orbit. Emission: transferring from an orbit with lower binding energy E_n to an orbit with higher binding energy $E_{n'}$; absorption: higher to lower binding energy levels.

3. Corresponding principle. The orbital frequency is comparison with the frequency of emission or absorption. For large n, one can calculate the Rydberg constant R_H from atomic quantities.

Limitations of Bohr's Model of an Atom

- Bohr's model of an atom failed to explain the Zeeman Effect (effect of magnetic field on the spectra of atoms).

- It also failed to explain the Stark effect (effect of electric field on the spectra of atoms).

- It violates the Heisenberg Uncertainty Principle.

- It could not explain the spectra obtained from larger atoms.

The Hund rule of maximum multiplicity states:

1. When two or more orbitals of equal energy (or very close energy) are available, electrons will fill the orbitals singly before filling doubly.
2. All the electrons in the orbitals will have the same spin to maximize the multiplicity.

In simple words, the rule says the lowest-energy electronic configuration is attained with the maximum number of parallel electron spins.
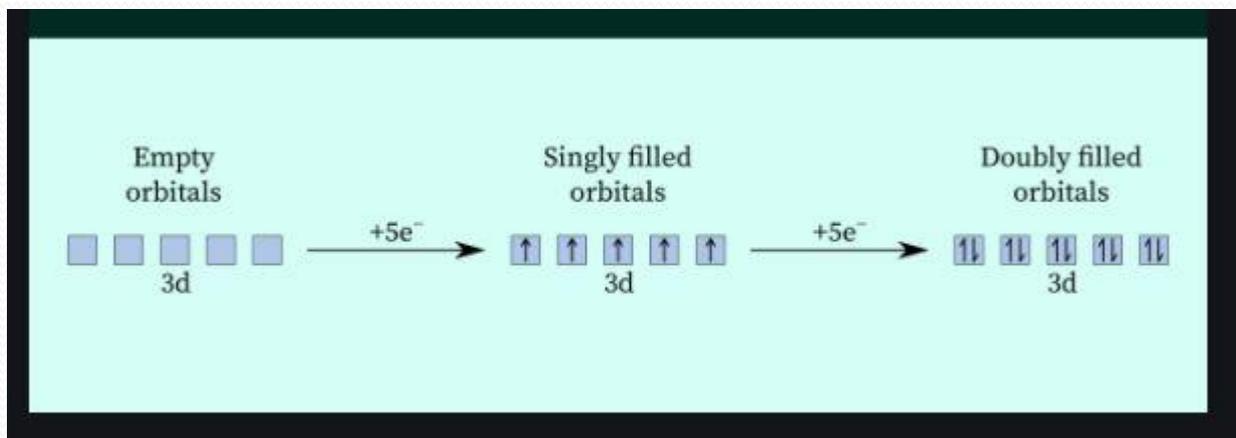
The Pauli Exclusion Principle states that, in an atom or molecule, no two electrons can have the **same** four electronic quantum numbers. As an orbital can contain a maximum of only two electrons, the two electrons must have opposing spins. This means if one is assigned an up-spin (+1/2), the other must be down-spin (-1/2).

Electrons in the same orbital have the same first three quantum numbers, e.g., $n = 1$, $l = 0$, $m_l = 0$ for the $1s$ subshell. Only two electrons can have these numbers, so that their spin moments must be either $m_s = -1/2$ or $m_s = +1/2$. If the $1s$ orbital contains only one electron, we have one m_s value and the electron configuration is written as $1s^1$ (corresponding to hydrogen). If it is fully occupied, we have two m_s values, and the electron configuration is $1s^2$ (corresponding to helium). Visually these two cases can be represented as
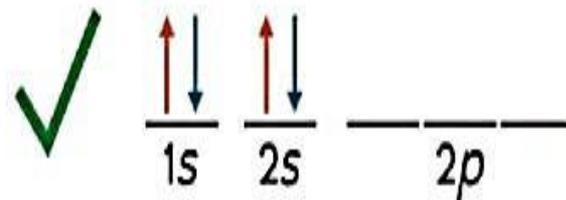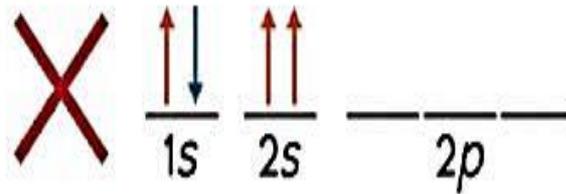
What is the Aufbau Principle?

The Aufbau principle dictates the manner in which electrons are filled in the atomic orbitals of an atom in its ground state. It states that electrons are filled into atomic orbitals in the increasing order of orbital energy level. According to the Aufbau principle, the available atomic orbitals with the lowest energy levels are occupied before those with higher energy levels.

The word 'Aufbau' has German roots and can be roughly translated as 'construct' or 'build up'. A diagram illustrating the order in which atomic orbitals are filled is provided below. Here, 'n' refers to the principal quantum number and 'l' is the azimuthal quantum number.