Std-XI science

Unit 2:

STRUCTURE OF ATOM

Vijaykumar N. Nazare

Grade I Teacher in Chemistry (Senior Scale)

vnn001@ chowgules.ac.in

QUANTUM MECHANICAL MODEL OF THE ATOM

- In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms.
- Two important developments which contributed significantly in the formulation of such a model were :

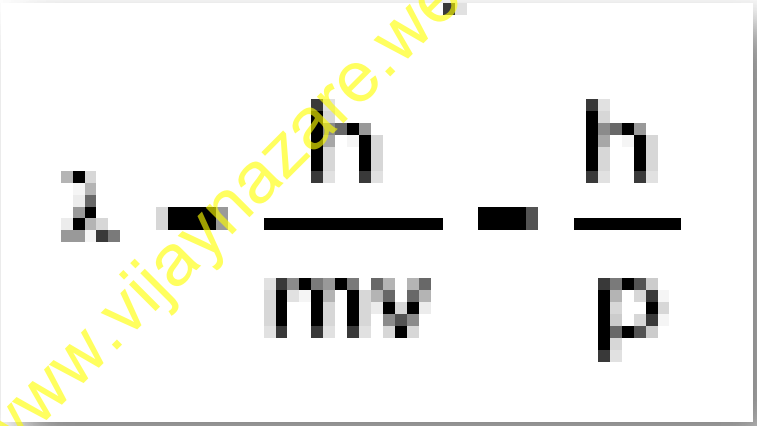
1. Dual behaviour of matter,
2. Heisenberg uncertainty principle.

Dual behaviour of matter

- The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle 
- and wavelike properties. 
- This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie,

Dual behaviour of matter

- from this analogy, gave the following relation between wavelength (l) and momentum (p) of a material particle.



- where m is the mass of the particle, v its velocity and p its momentum.

Problem

- What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

Solution

- According to de Brogile equation

$$\lambda = \frac{h}{mv} = \frac{(6.266 \times 10^{-34}\ Js)}{(0.1\,kg)(10\ m\,s^{-1})}$$

$$= 6.626 \times 10^{-34}\ m\ (J = kg\ m^2\ s^{-2})$$

Problem

- The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Solution

- Since K. E. = ½ mv2

???

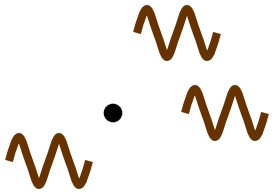
Ans: = 8967×10^{-10} m = 896.7 nm

Heisenberg's Uncertainty Principle

- Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation.
- It states that *it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.*

Heisenberg's uncertainty principle

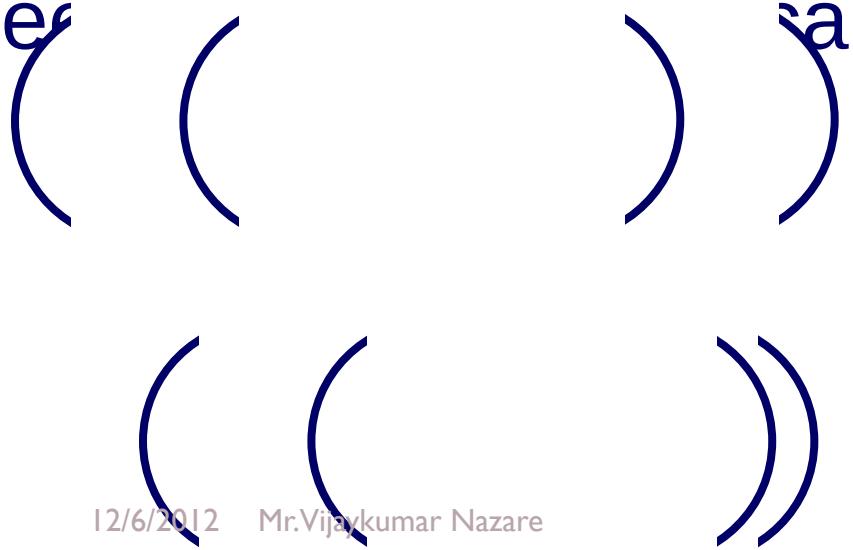
- Electrons are difficult to visualize. As a simplification we will picture them as tiny wave/particles around a nucleus.



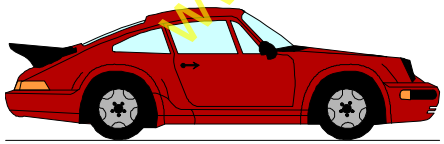
The location of electrons is described by: n, l, m_l

n = size, *l* = shape, m_l = orientation

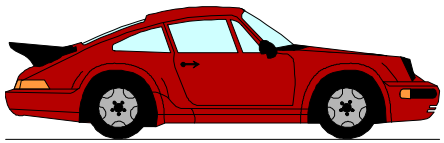
- Heisenberg showed it is impossible to know <u>both</u> the position and velocity of an electron.
- Think of measuring spe ar.



Slo w



Fast



Heisenberg's Uncertainty Principle

- Mathematically, it can be given as in equation

$$\Delta x \times \Delta p_x \geq \frac{h}{4\pi}$$

or $$\Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

or $$\Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$$

where Δ_x is the uncertainty in position and Δp_x (or ΔV_x) is the uncertainty in momentum (or velocity) of the particle.

Reasons for the Failure of the Bohr Model

- In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus.
- The wave character of the electron is not considered in Bohr model.
- Bohr model of the hydrogen atom, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.

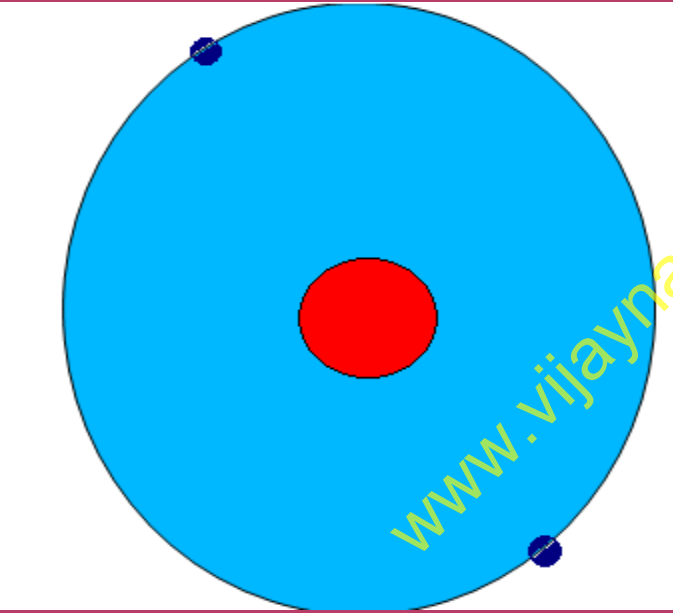
Quantum mechanics

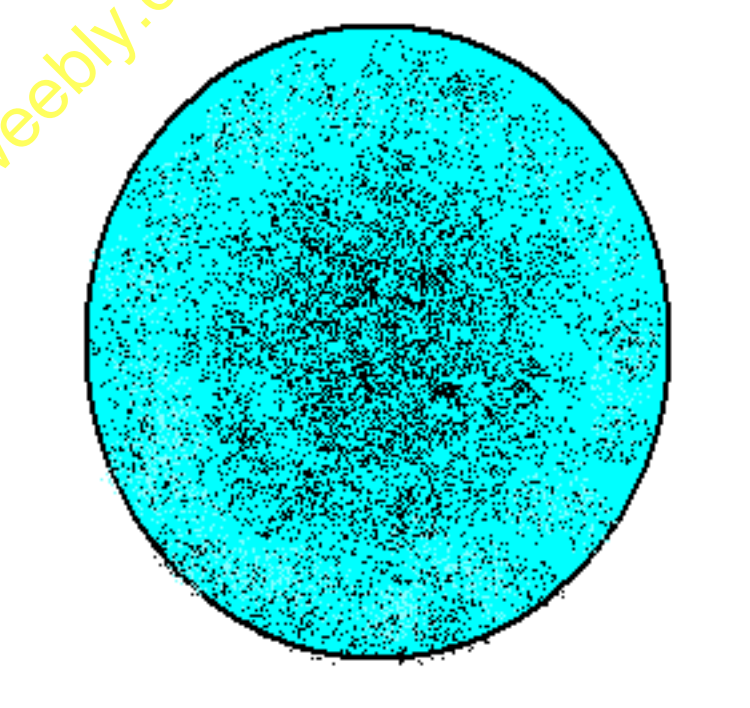
- The branch of science that takes into account this dual behaviour of matter is called quantum mechanics.

- Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties.

Difference Between Orbit & Orbital

Orbit	Orbital





Difference Between Orbit & Orbital

Orbit	Orbital
• Well defined circular path	• It is region of space around the nucleus where the electron is most likely to be found .
• It represents planar motion	• It represents 3D motion of an electron
• Maximum no of electrons in an orbit=$2n^2$. where n= no of Orbit.	• It cannot accommodate more than 2 electrons.
• Non directional.	• Directional.
• Concept of well defined orbit is against Heisenbergs principle	• In agreement with Heisenbergs principle

Orbital's and Quantum Numbers

- A large number of orbitals are possible in an atom.
- Qualitatively these orbitals can be distinguished by their size, shape and orientation.
- Atomic orbitals are precisely distinguished by what are known as quantum numbers.
- Each orbital is designated by three quantum numbers

Quantum numbers

1. **The principal quantum number 'n'**

2. **Azimuthal quantum number. 'l'** 'It is also known as orbital angular momentum or subsidiary quantum number.

3. **Magnetic orbital quantum number. 'm_l'**

4. **spin quantum number (m_s)**

The principal quantum number 'n'

- The principal quantum number determines the size and to large extent the energy of the orbital.

- For hydrogen atom and hydrogen like species (He^{+}, Li^{2+}, ... etc.) energy and size of the orbital depends only on 'n'.

The principal quantum number 'n'

- The principal quantum number also identifies the shell.
- With the increase in the value of 'n', the number of allowed orbital increases and are given by 'n^2'
- All the orbitals of a given value of 'n' constitute a single shell of atom and are represented by the following letters
  - **n = 1 2 3 4 .....**
  - **Shell = K L M N .....**

Azimuthal quantum number (l)

- It defines the three dimensional shape of the orbital.
- For a given value of n, l can have values ranging from 0 to (n – 1), that is, for a given value of n, the possible value of l are
- l = 0, 1, 2, ...(n–1)

1. For example, when n = 1, value of l is only 0.
2. For n = 2, the possible value of l can be 0 and 1.
3. For n = 3, the possible l values are 0,1 and 2.

- Each shell consists of one or more subshells or sub-levels.

- The number of subshells in a principal shell is equal to the value of n.

- For example in the first shell (n=1) there is only one sub-shell which corresponds to l = 0.

- There are two sub-shells (l = 0, 1) in the second shell (n = 2),
- three (l = 0, 1, 2) in third shell (n = 3) and so on.
- Each sub-shell is assigned an azimuthal quantum number

Sub-shells corresponding to different values of l are represented by the following symbols.

Value for l : 0 1 2 3 4 .....

notation for l : s p d f g h--------

n	l	Subshell notation
1	0	$1s$
2	0	$2s$
2	1	$2p$
3	0	$3s$
3	1	$3p$
3	2	$3d$
4	0	$4s$
4	1	$4p$
4	2	$4d$
4	3	$4f$

Magnetic orbital quantum number. 'm_l'

- Gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis.

- For any sub-shell (defined by 'l' value) 2l+1 values of m_l are possible and these values are given by :

$$m_l = -l, -(l-1), -(l-2) \ldots 0, 1 \ldots (l-2), (l-1), l$$

Thus for l = 0, the only permitted value of m_l = 0, [2(0)+1 = 1, one s orbital].

For l = 1, m_l can be –1, 0 and +1 [2(1)+1 = 3, three p orbitals].

For l = 2, m_l = –2, –1, 0, +1 and +2, [2(2)+1 = 5, five d orbitals].

It should be noted that the values of m_l are derived from l and that the value of l are derived from n.

Each orbital in an atom, therefore, is defined by a set of values for n, l and m_l.

An orbital described by the quantum numbers
n = 2, l = 1, m_l = 0 is an orbital in the p subshell of the second shell.

The following chart gives the relation between the sub-shell and the number of orbitals associated with it.

Value of l	0	1	2	3	4	5
Subshell notation	s	p	d	f	g	h
number of orbitals	1	3	5	7	9	11

Problem

- What is the total number of orbitals associated with the principal quantum number n = 3 ?

Solution

- For n = 3, the possible values of l are 0, 1 and 2. Thus there is one 3s orbital
- (n = 3, l = 0 and ml = 0); there are three 3p orbitals (n = 3, l = 1 and ml = –1, 0, +1); there are five 3d orbitals (n = 3, l = 2 and ml = –2, –1, 0, +1+, +2).
- Therefore, the total number of orbitals is 1+3+5 = 9
- *The same value can also be obtained by using the relation; number of orbitals*
- = n^2, i.e. $3^2 = 9$.

Problem

1. Using s, p, d, f notations, describe the orbital with the following quantum numbers

(a) n = 2, l = 1, (b) n = 4, l = 0, (c) n = 5, l = 3, (d) n = 3, l = 2

Solution

	n	l	orbital
a)	n = 2, l = 1	2p	
b)	n = 4, l = 0	4s	
c)	n = 5, l = 3	5f	
d)	n = 3, l = 2	3d	

s-Shells and Subshells

For $n = 1$, $l = 0$ and $m_l = 0$: $\Psi_{1,0,0}$

There is only one subshell and that subshell has a single orbital

(m_l has a single value ---> 1 orbital)

This subshell is labeled **s** ("ess") and we call this orbital **1s**

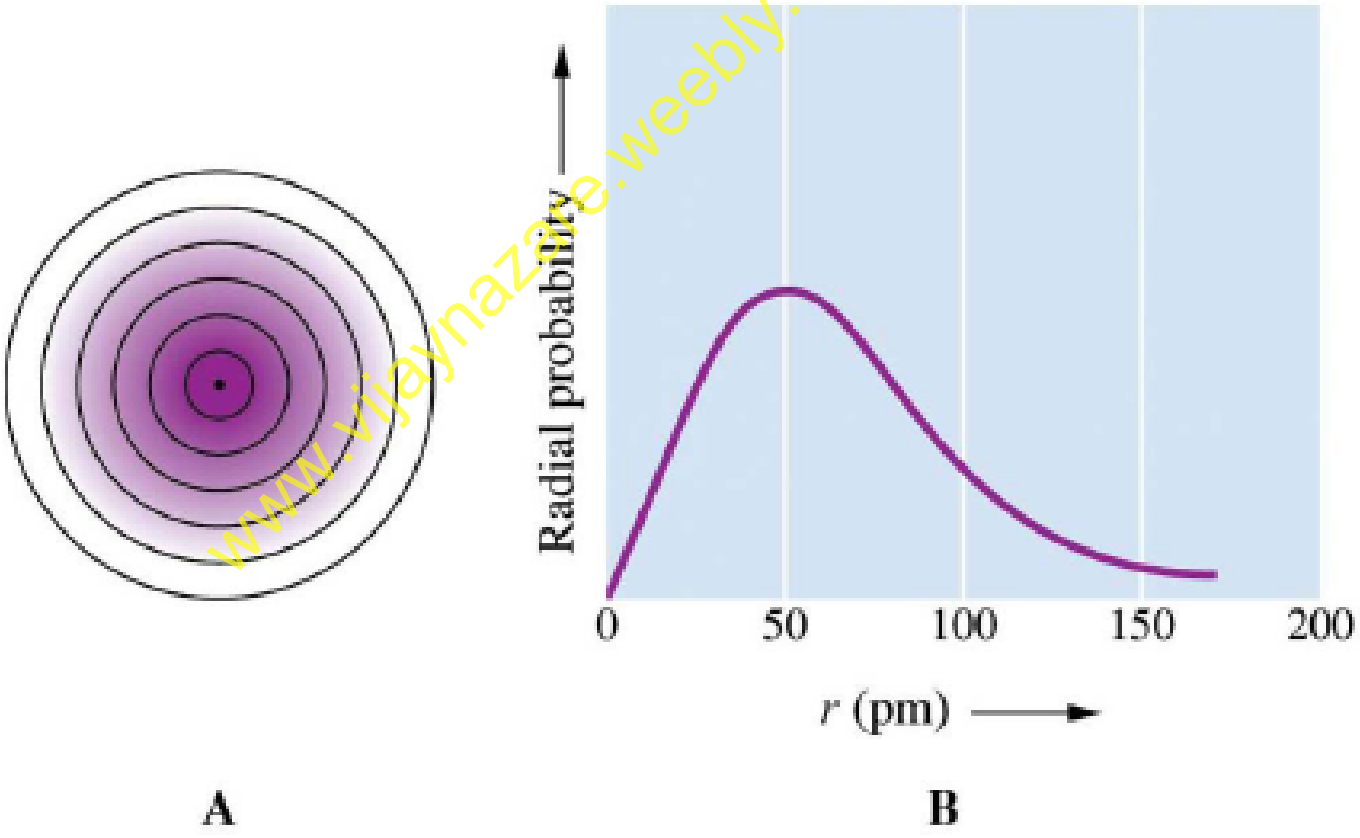
Each shell has 1 orbital labeled s.

It is **SPHERICAL** in shape.

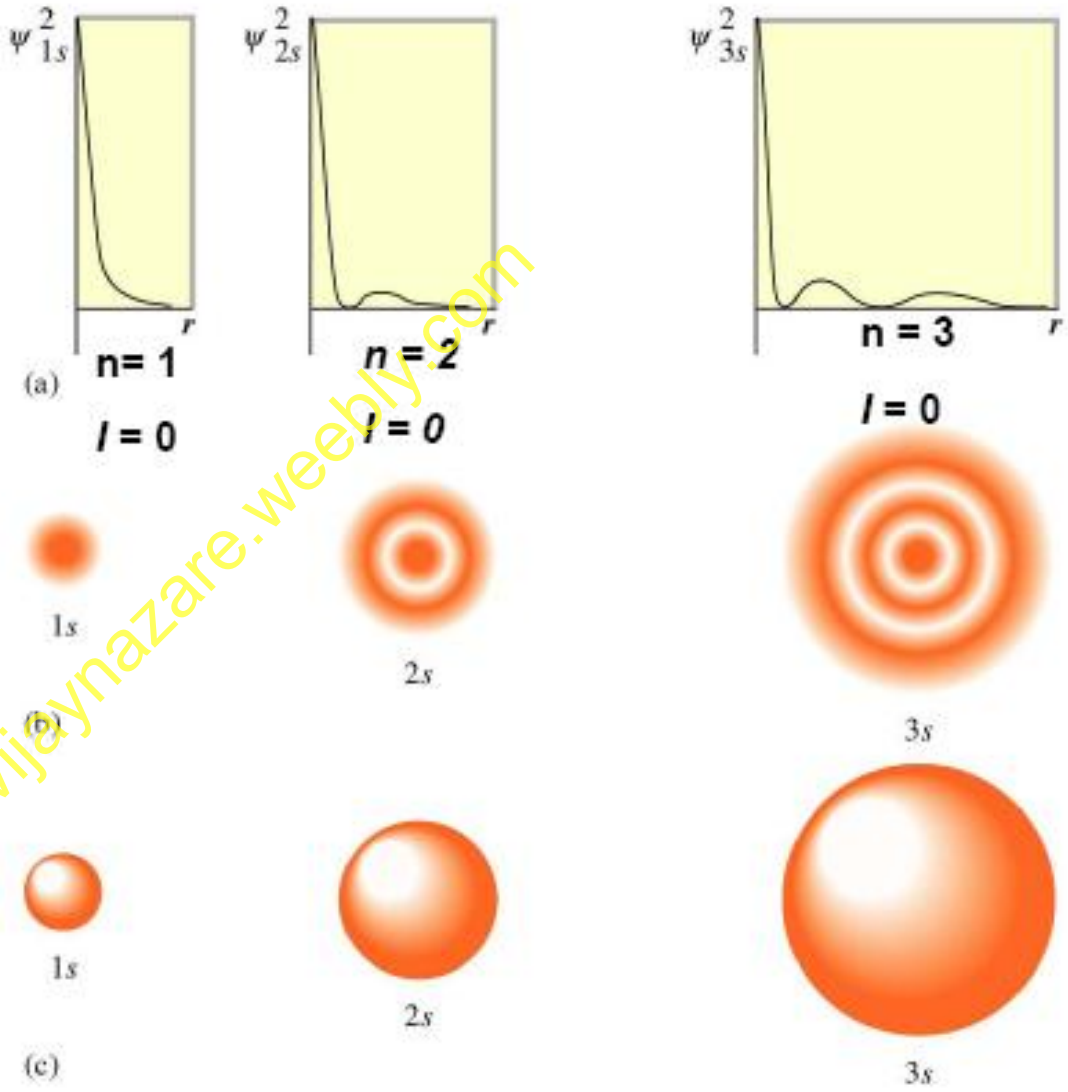
The symbol, **"1s"** is the label of a wave function, Ψ_{1s}. **It means, $n = 1, l = 0, m_l = 0$.**

Shape of 1s Orbital

Radial Distribution Functions Take Into Account Area of Thin Spherical Shell as You Move Outward from Nucleus



1*s*, 2*s*, 3*s* orbitals



p Orbitals

For n = 2, l = 0 and 1

There are 2 types of orbitals — 2 subshells

For l = 0 m_l = 0 : $\Psi_{2,0,0}$

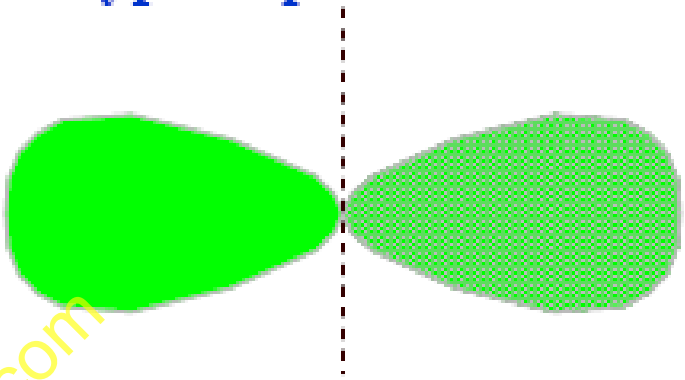
this is a s subshell

For l = 1 m_l = -1, 0, +1

this is a p subshell with 3 orbitals:

$\Psi_{2,1,-1}$, $\Psi_{2,1,0}$, and $\Psi_{2,1,1}$

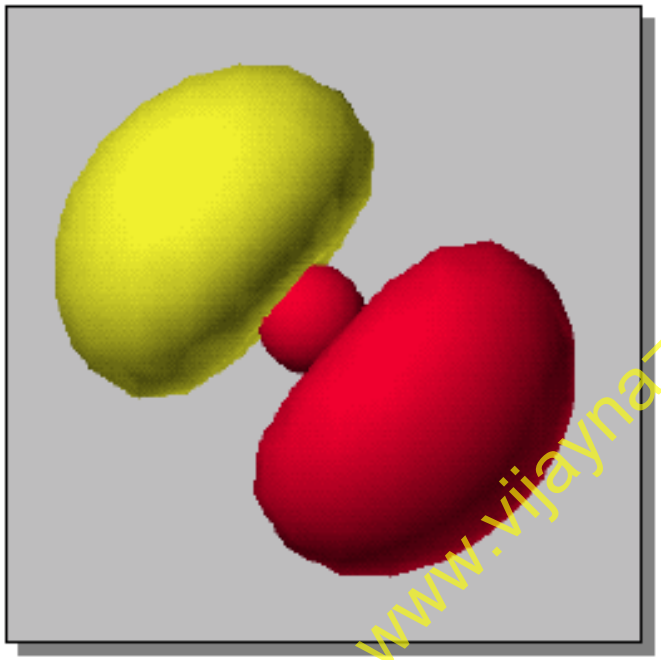
Typical p orbital



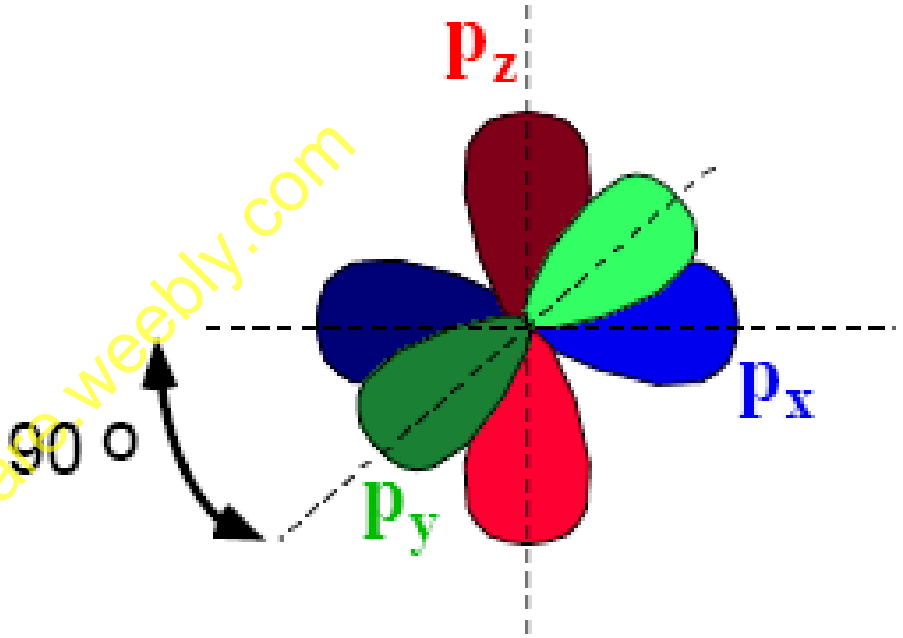
planar node

When l = 1, there is a PLANAR NODE through the nucleus.

How does the electron get from left to right without ever being seen in the node?

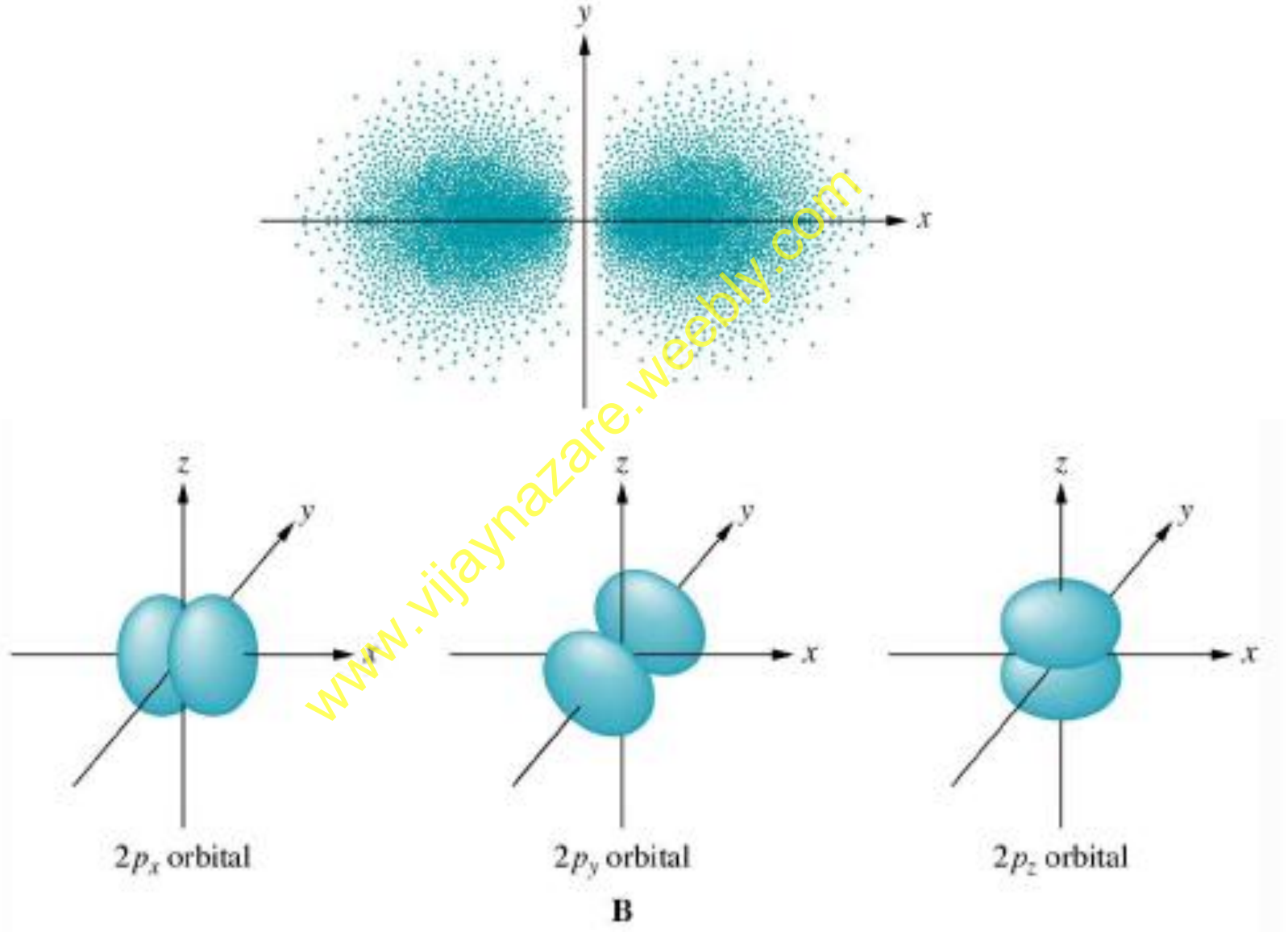


A p orbital



The three p orbitals lie 90° apart in space

Shape of 2p Orbital



B

d Orbitals

For n = 3, what are the values of l?

l = 0, 1, 2

and so there are 3 subshells in the shell.

For l = 0, m_l = 0

→ s subshell with single orbital

For l = 1, m_l = -1, 0, +1

→ p subshell with 3 orbitals

For l = 2, m_l = -2, -1, 0, +1, +2

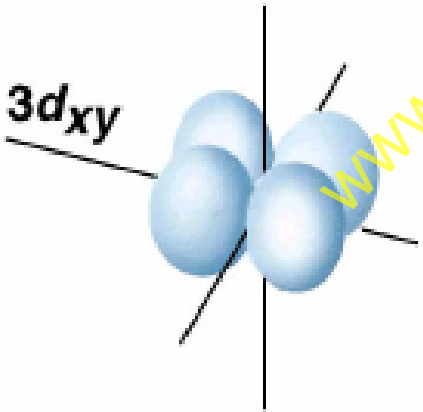
→ d subshell with 5 orbitals

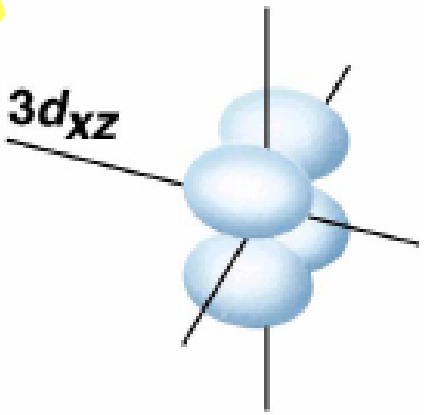
d Orbitals

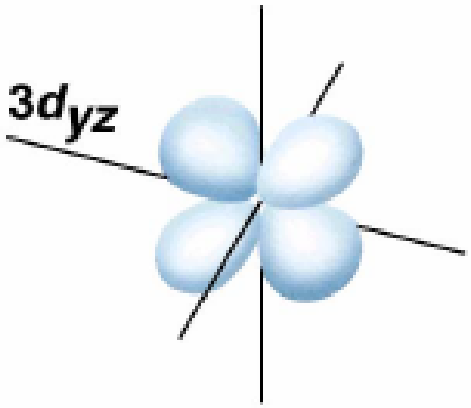
- The *d* orbitals are those for which $l = 2$.

There are five *d* orbitals in each *d* subshell.

Four are "four-leaf clovers", the fifth looks like a *p* orbital with the addition of a ring around the centre





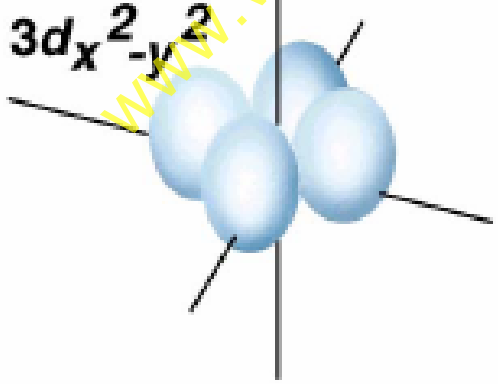


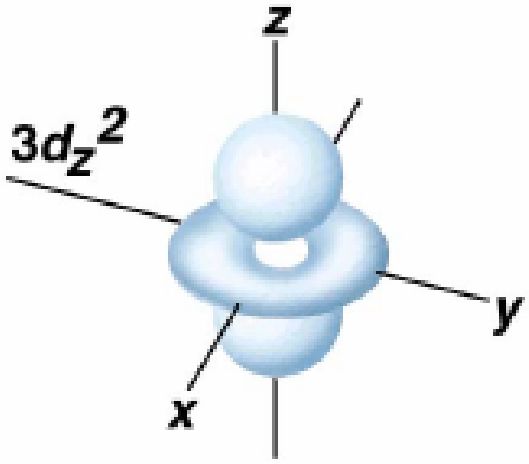
d Orbitals

- The *d* orbitals are those for which $l = 2$.

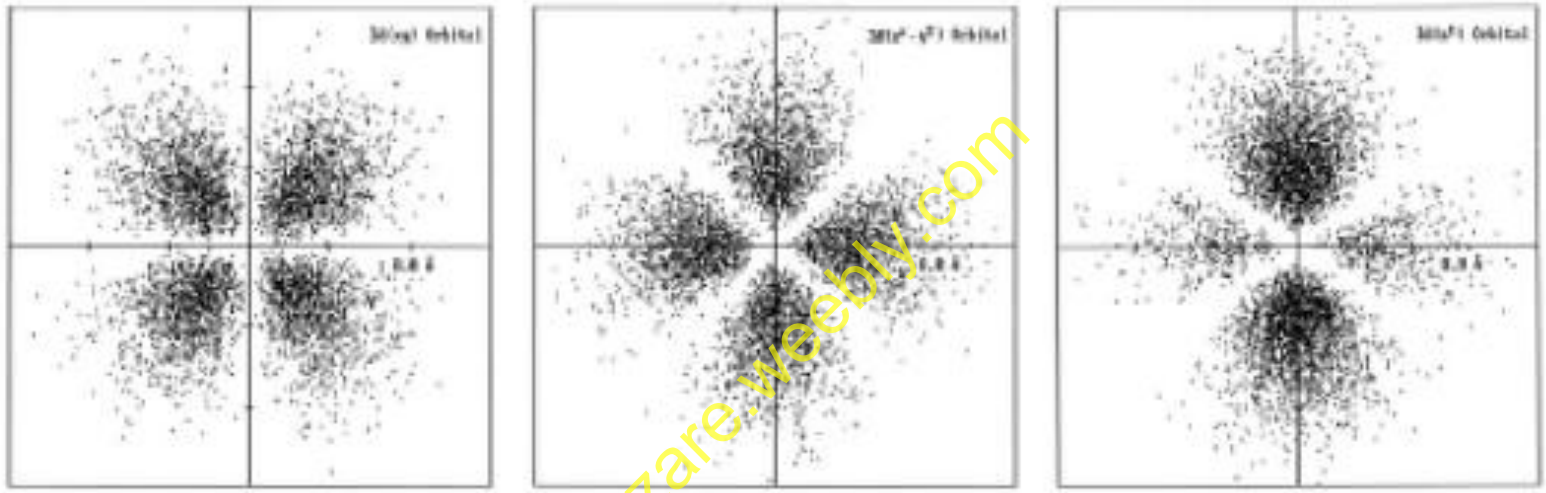
There are five *d* orbitals in each *d* subshell.

Four are "four-leaf clovers", the fifth looks like a *p* orbital with the addition of a ring around the centre

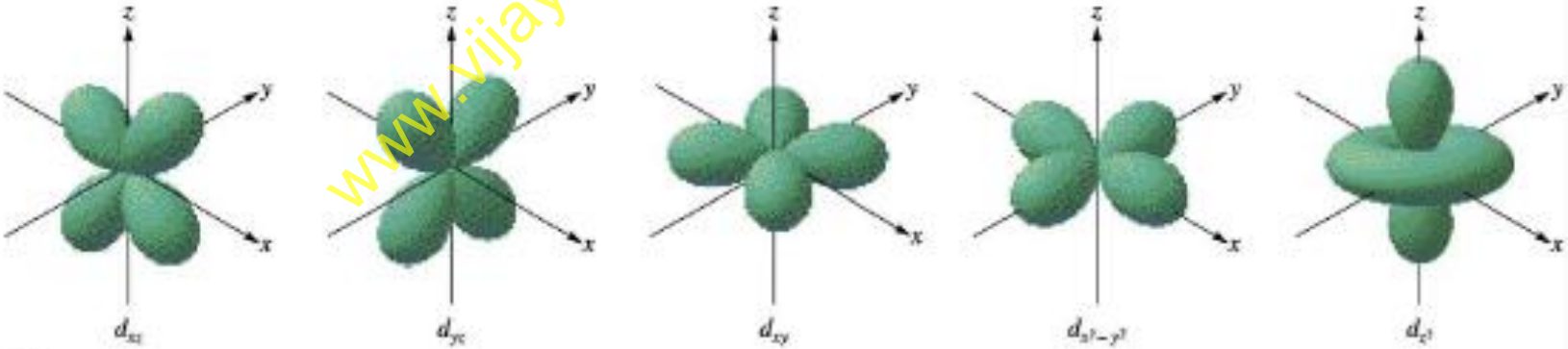




Representation of the 3*d* orbitals

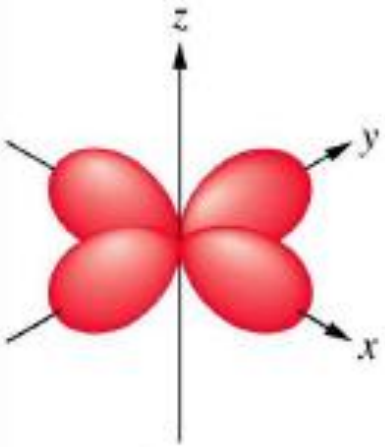


(a)



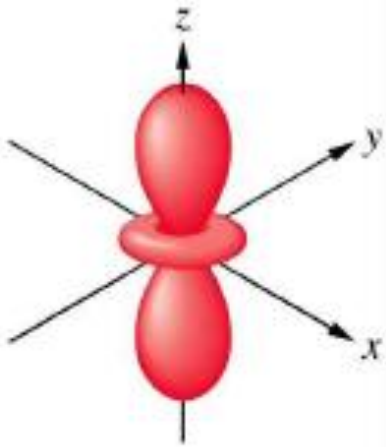
(b)

Shape of 3d Orbitals

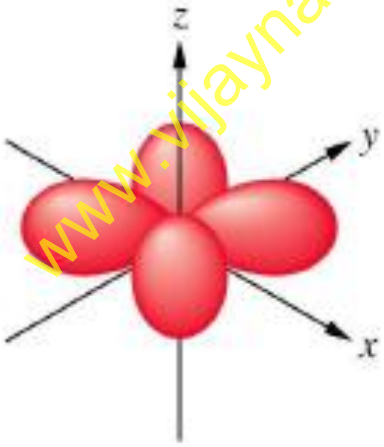


$d_{x^2-y^2}$

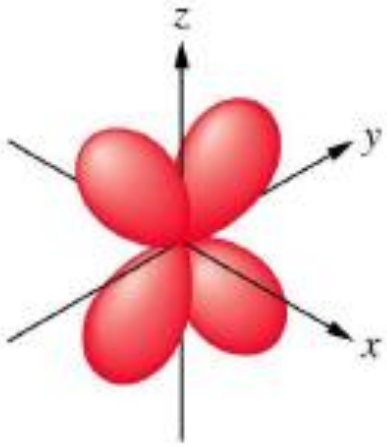
d_{xz}



d_{z^2}



d_{xy}



d_{yz}

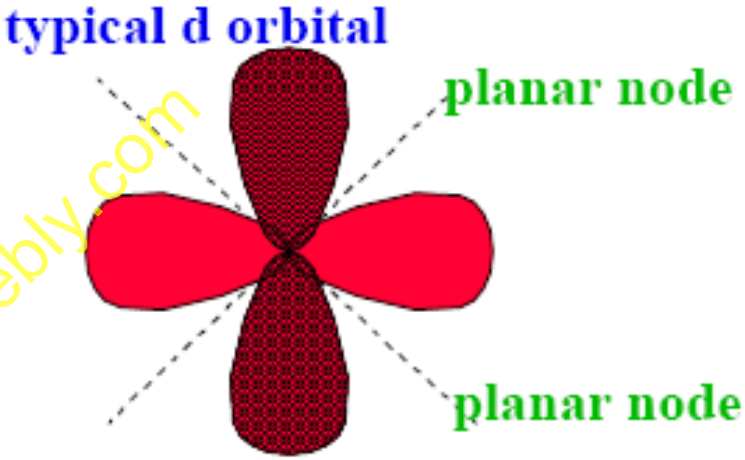
d Orbitals

s orbitals have no planar node (l = 0) and so are spherical.

p orbitals have l = 1, and have 1 planar node,

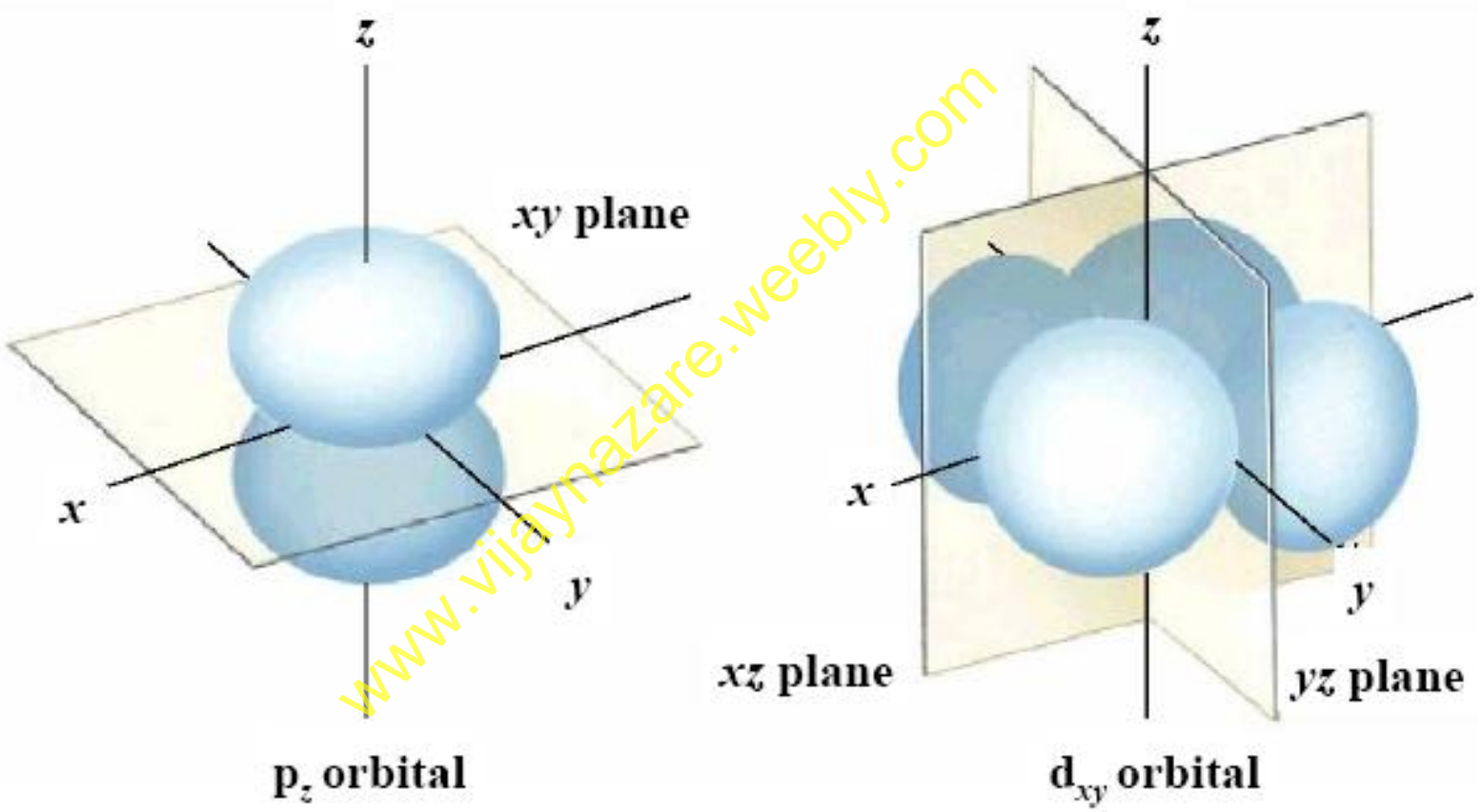
and so are "dumbbell" shaped.

d orbitals (with l = 2) have 2 planar nodes



IN GENERAL the number of NODES = value of angular quantum number (l)

Nodal Planes in Orbitals



Representation of the 4*f* orbitals

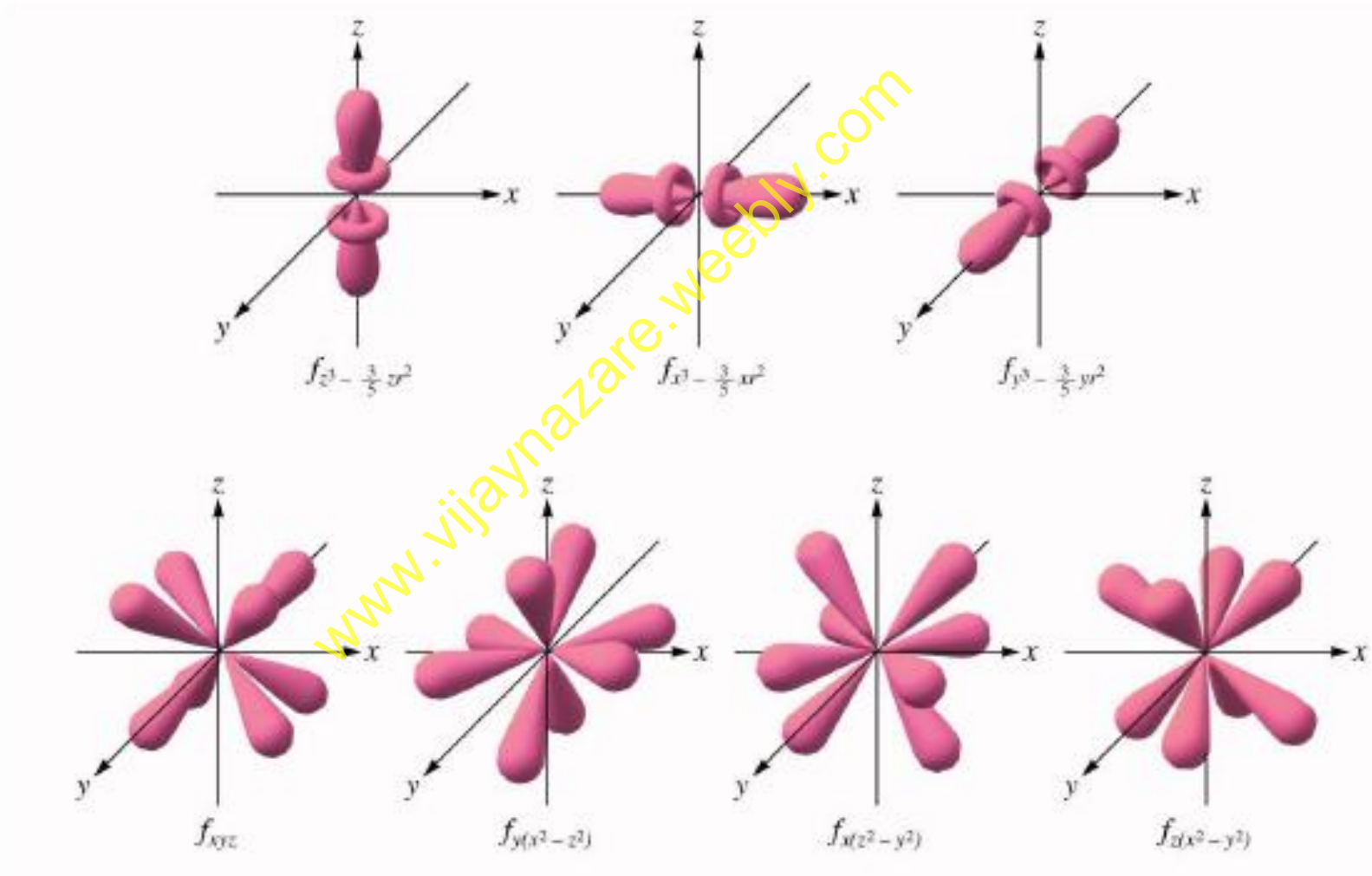


Table 7.1 A Summary of Quantum Numbers & Orbitals

n	*l*	m_l	# & Type of Orbitals
1	0	0	1 - 1*s* orbital
2	0	0	1 - 2*s* orbital
	1	+1, 0, -1	3 - 2*p* orbitals
3	0	0	1 - 3*s* orbital
	1	+1, 0, -1	3 - 3*p* orbitals
	2	+2, +1, 0, -1, -2	5 - 3*d* orbitals
4	0	0	1 - 4*s* orbital
	1	+1, 0, -1	3 - 4*p* orbitals
	2	+2, +1, 0, -1, -2	5 - 4*d* orbitals
	3	+3, +2, +1, 0, -1, -2, -3	7 - 4*f* orbitals

Filling of Orbitals in Atom

- The filling of electrons into the orbitals of different atoms takes place according to the
- aufbau principle which is based on the
- Pauli's exclusion principle,
- the Hund's rule of maximum multiplicity and the
- relative energies of the orbitals.

Aufbau Principle

- The principle states :

- In the ground state of the atoms, the orbitals are filled in order of their increasing energies.

- In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled.

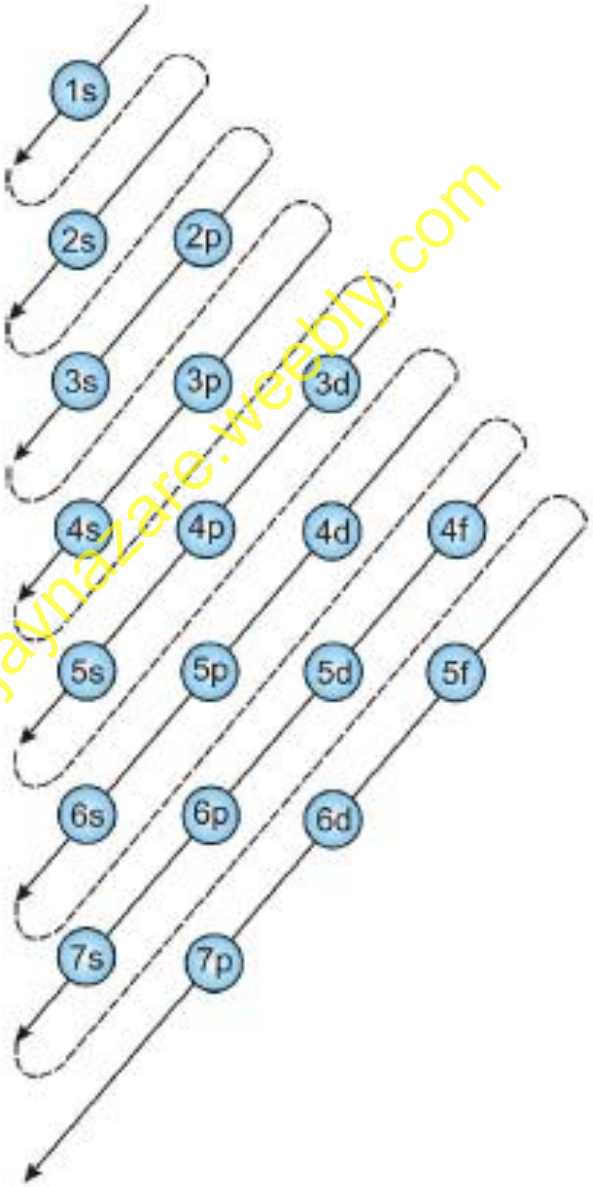
Aufbau Principle

- The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows :

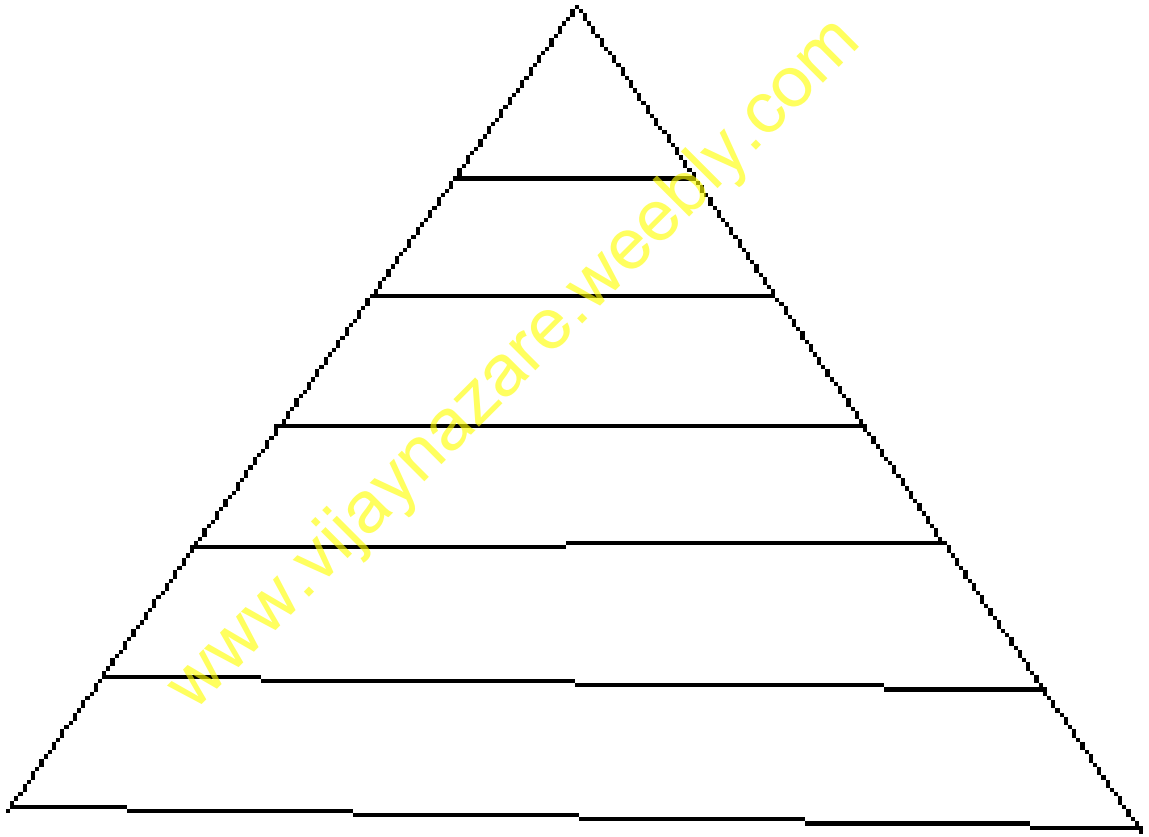
- 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...

c3p12swf

Order of filling of orbitals



Order of filling of orbitals



Pauli Exclusion Principle

- According to this principle :
- *No two electrons in an atom can have the same set of four quantum numbers*.
- Pauli exclusion principle can also be stated as :"*Only two electrons may exist in the same orbital and these electrons must have opposite spin*."

Pauli Exclusion Principle

- Subshell 1s comprises of one orbital and thus the maximum number of electrons present in 1s subshell can be two, in p and d subshells, the maximum number of electrons can be 6 and 10 and so on.

- This can be summed up as :
- the maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.

Hund's Rule of Maximum Multiplicity

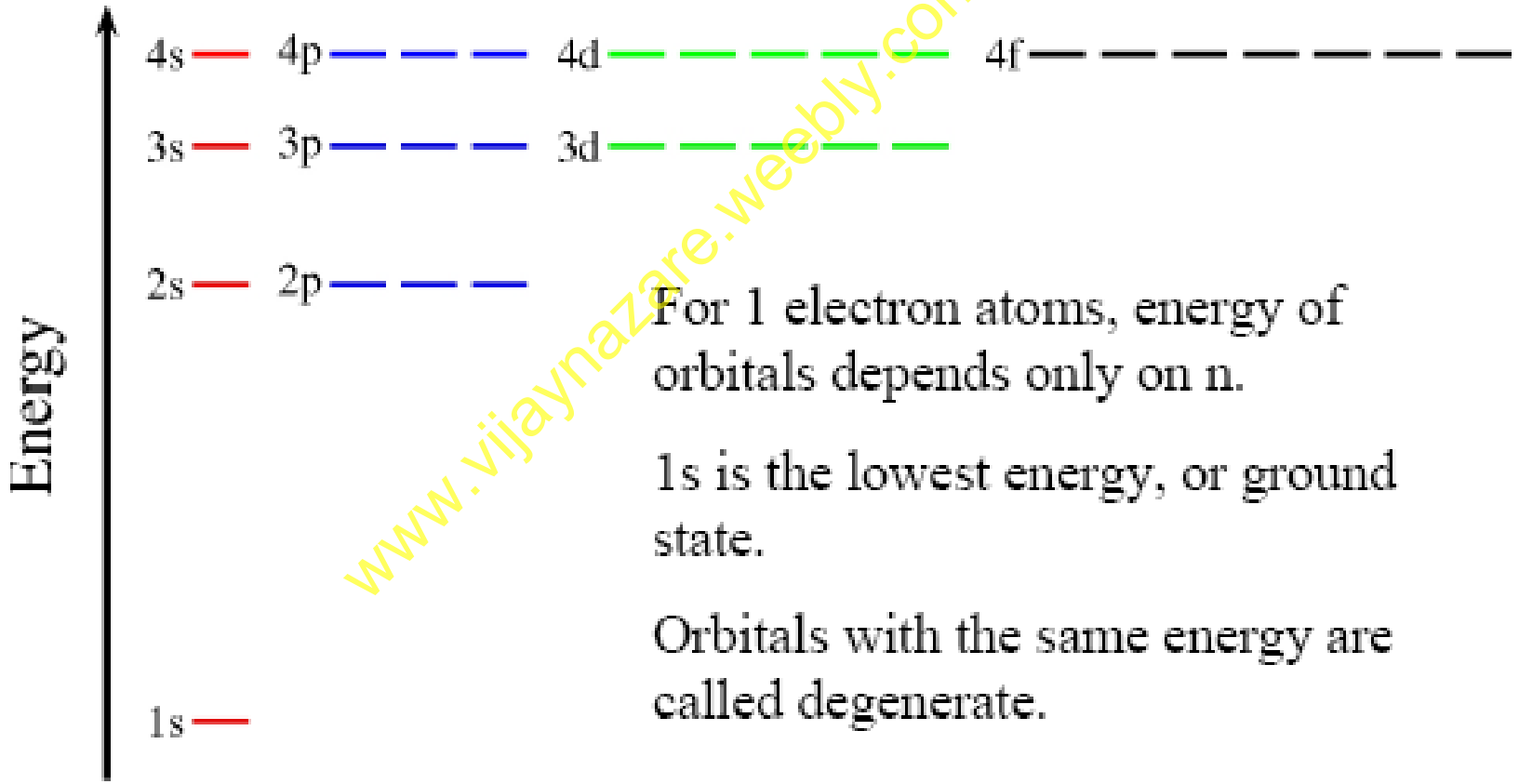
- It states : *pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.*
- Since there are three p, five d and seven f orbitals, therefore, the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron, respectively.

Hund's Rule of Maximum Multiplicity

- It has been observed that half filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry

n+l Rule

Energies of orbitals in one electron atoms

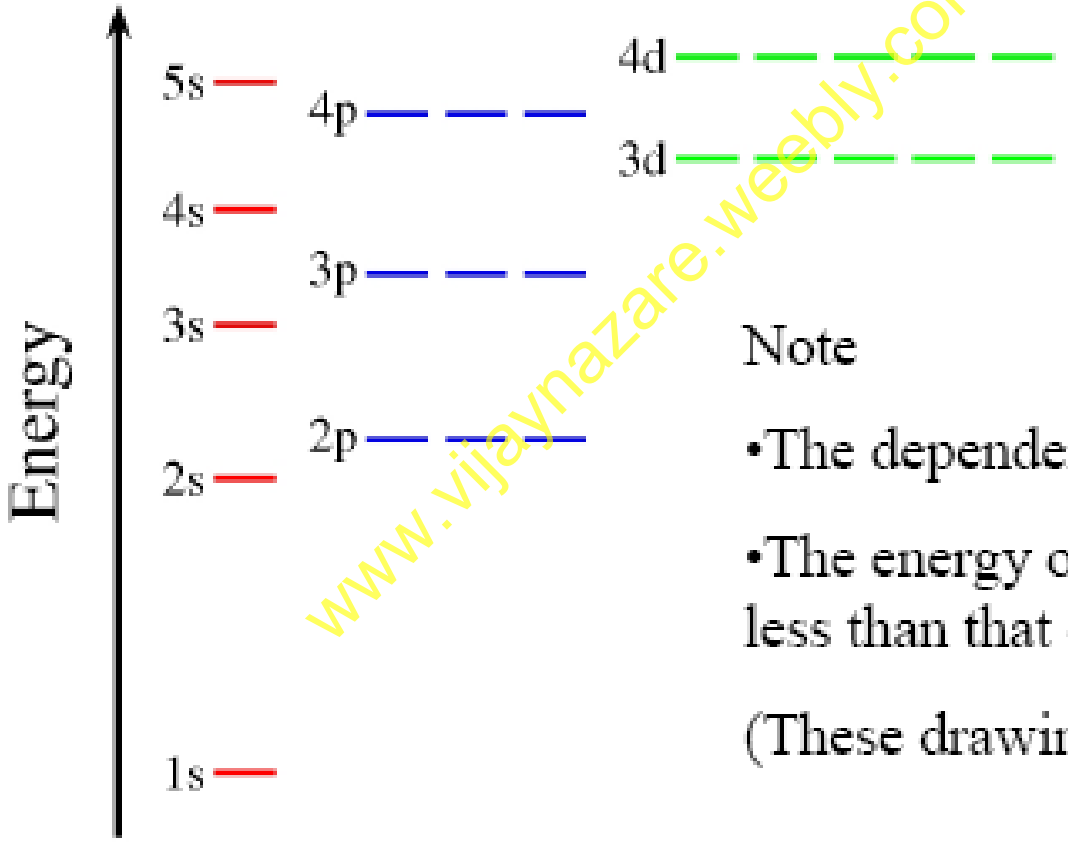


For 1 electron atoms, energy of orbitals depends only on n.

1s is the lowest energy, or ground state.

Orbitals with the same energy are called degenerate.

Energies of orbitals in many electron atoms



Note

- The dependence on *l*.
- The energy of the 4s orbital is less than that of the 3d

(These drawings are not to scale)

Electronic Configuration of Atoms

Electronic Configuration of Atoms

Element	Atomic No	Electronic Configuration
H	1	
He	2	
Li	3	
Be	4	
B	5	
C	6	
N	7	

Electronic Configuration of Atoms

Element	Atomic No	Electronic Configuration
H	1	$1s^1$
He	2	$1s^2$
Li	3	$1s^2\ 2s^1$
Be	4	$1s^2\ 2s^2$
B	5	$1s^2\ 2s^2 2p^1$
C	6	$1s^2\ 2s^2 2p^2$
N	7	$1s^2\ 2s^2 2p^3$

Electronic Configuration of Atoms

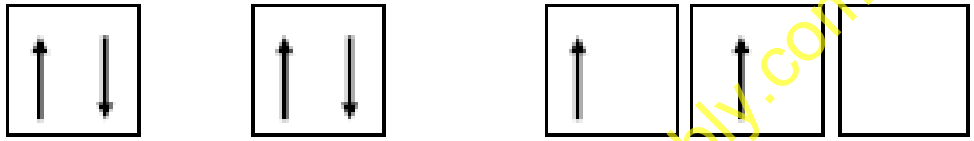
Element	Atomic No	Electronic Configuration
O	8	
F	9	
Ne	10	
Na	11	
Mg	12	
Al	13	
Si	14	

Electronic Configuration of Atoms

Element	Atomic No	Electronic Configuration
O	8	$1s^2\ 2s^2 2p^4$
F	9	$1s^2\ 2s^2 2p^5$
Ne	10	$1s^2\ 2s^2 2p^6$
Na	11	$1s^2\ 2s^2 2p^6 3s^1$ Or [Ne] $3s^1$
Mg	12	$1s^2\ 2s^2 2p^6 3s^2$ Or [Ne] $3s^2$
Al	13	$1s^2\ 2s^2 2p^6 3s^2 3p^1$
Si	14	$1s^2\ 2s^2 2p^6 3s^2 3p^2$

The Aufbau Principle (C and N)

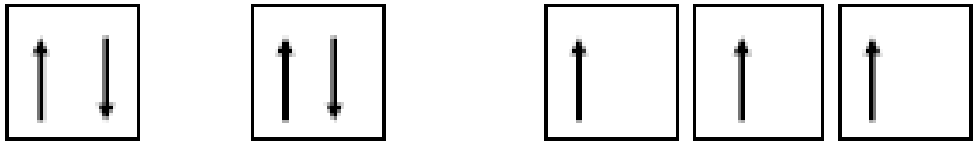
- Carbon (Z = 6)



$1s^2 2s^2 2p^2$

Hund's Rule: Lowest energy configuration is the one in which the maximum number of unpaired electrons are distributed among a set of degenerate orbitals.

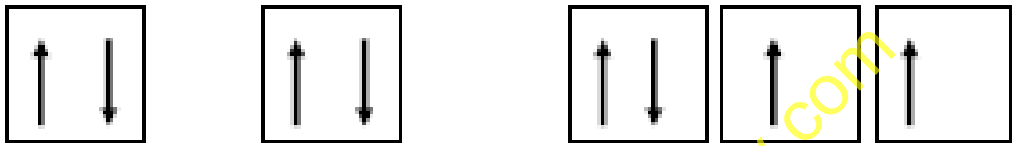
- Nitrogen (Z = 7)



$1s^2 2s^2 2p^3$

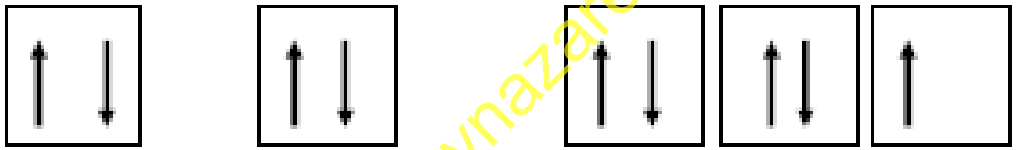
The Aufbau Principle (O, F and Ne)

- Oxygen (Z = 8)



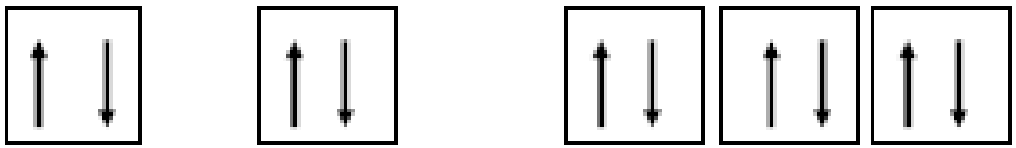
$1s^2 2s^2 2p^4$

- Fluorine (Z = 9)



$1s^2 2s^2 2p^5$

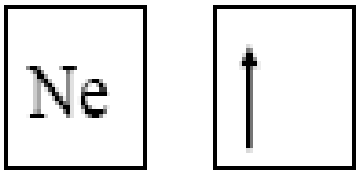
- Neon (Z = 10)



$1s^2 2s^2 2p^6$

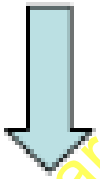
full

- Sodium (Z = 11)

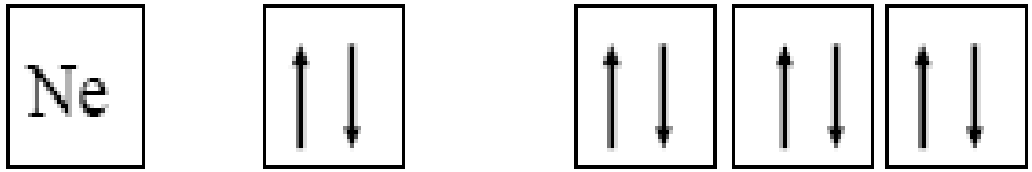


3s

$1s^2 2s^2 2p^6 3s^1$ → $[Ne]3s^1$



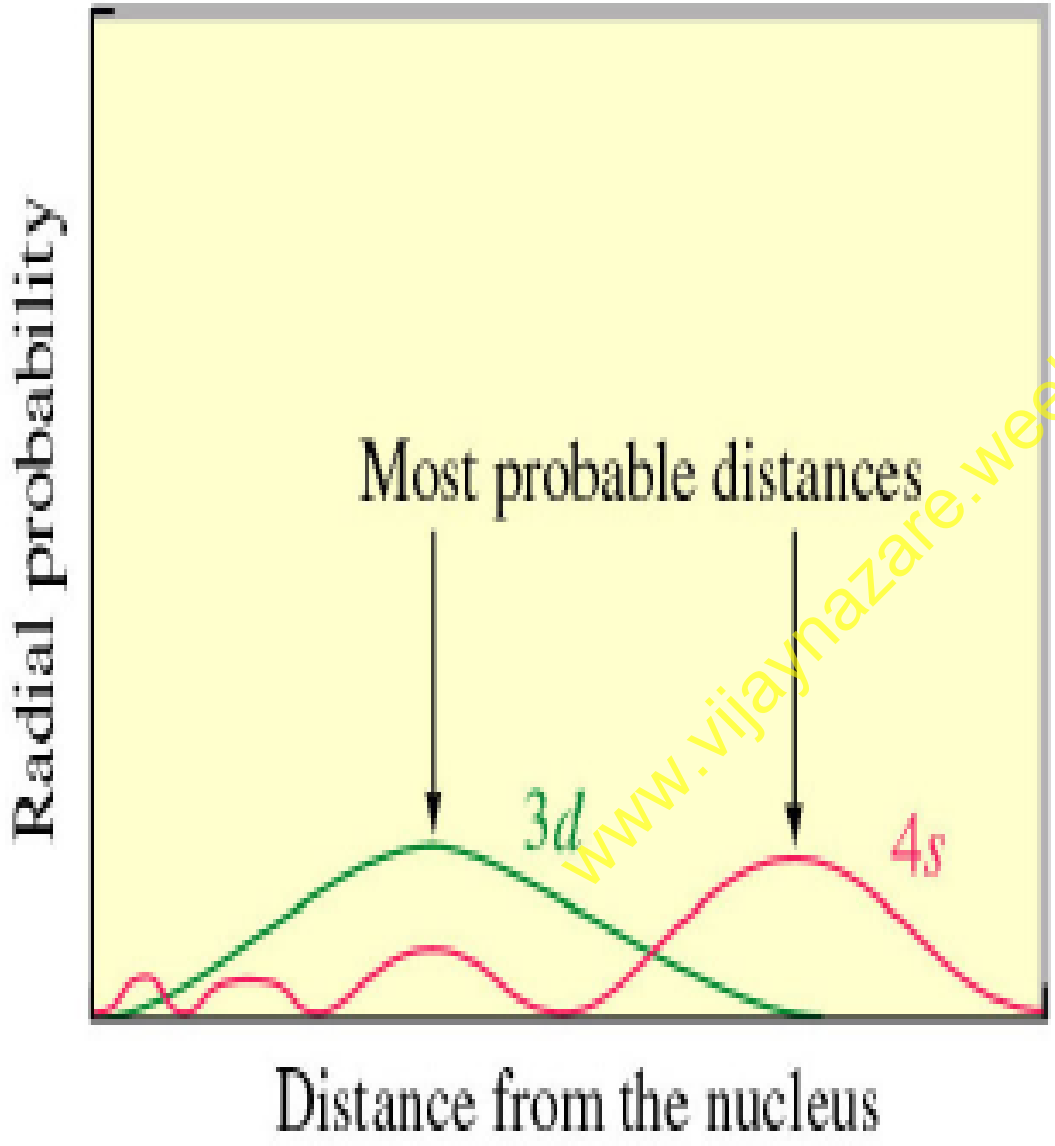
- Argon (Z = 18)



3s 3p

$[Ne]\ 3s^2 3p^6$

- Why not 3d before 4s?



- 3d is closer to the nucleus
- 4s allows for closer approach; therefore, is energetically preferred.

- Elements Z=19 and Z= 20:

Z = 19, Potassium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 = [Ar]4s^1$

Z = 20, Calcuim: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 = [Ar]4s^2$

- Elements Z=21 to Z=30 have occupied d orbitals:

Z= 21, Scandium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1 = [Ar]\ 4s^2 3d^1$

Z = 24, Chromium: $[Ar]\ 4s^1 3d^5$ exception

Z = 30, Zinc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} = [Ar]\ 4s^2 3d^{10}$

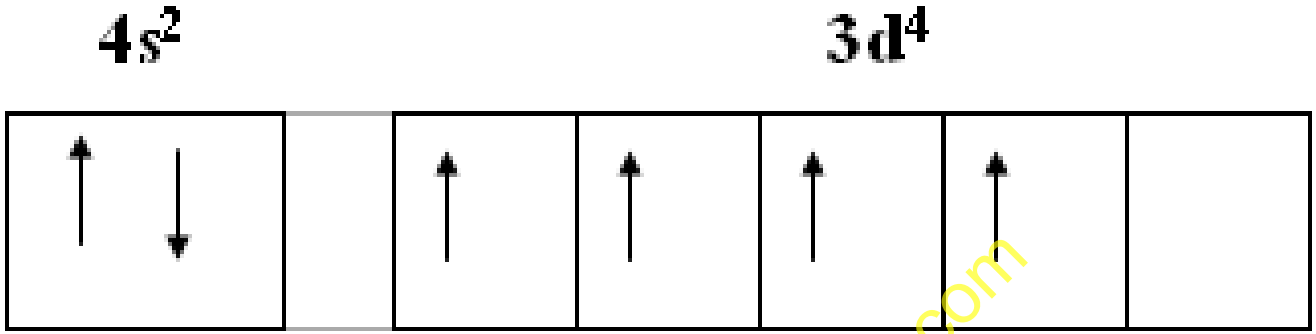
- Elements Z=21 to Z=30 have occupied d orbitals:

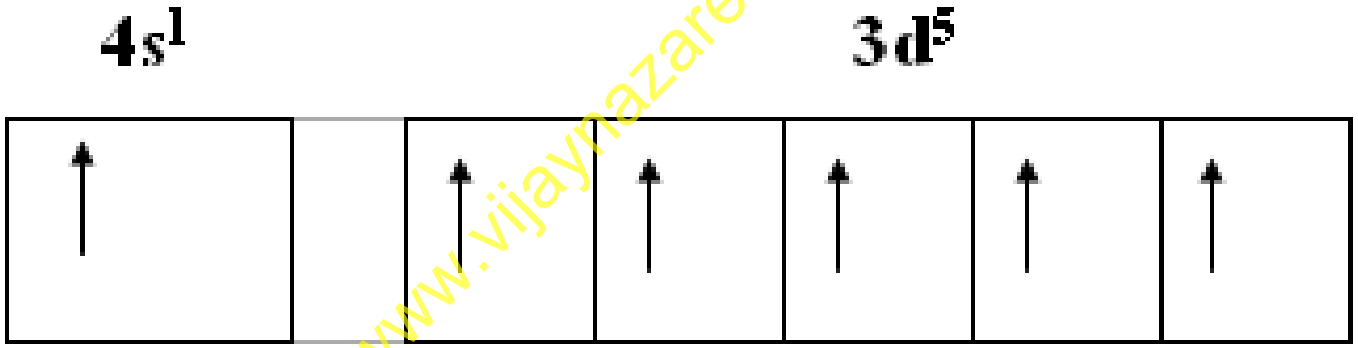
Z= 21, Scandium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1 = [Ar]\ 4s^2 3d^1$

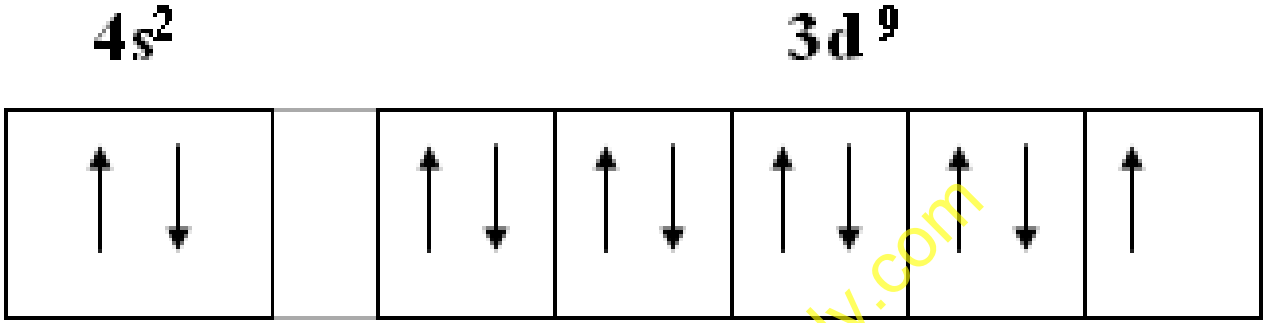
Z = 24, Chromium: $[Ar]\ 4s^1 3d^5$ exception

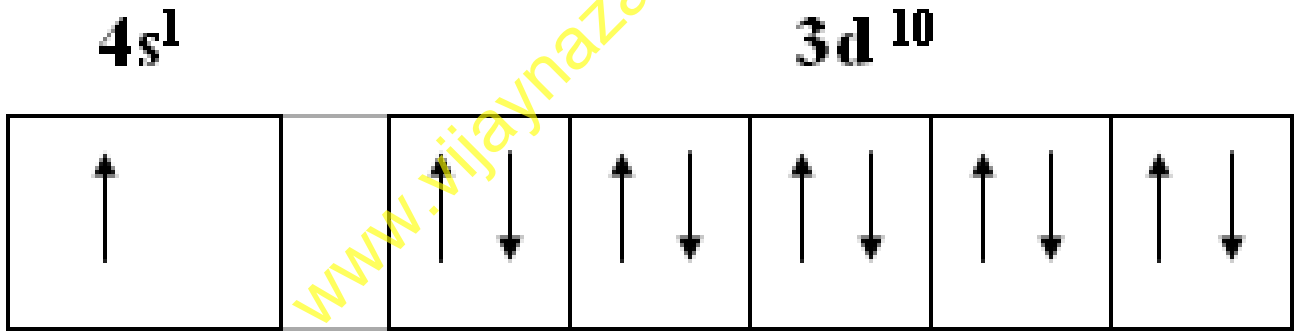
Z = 29, Copper: $[Ar]\ 4s^1 3d^{10}$ exception

Z = 30, Zinc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} = [Ar]\ 4s^2 3d^{10}$









Thank you

- Vijaykumar N. Nazare.
- Grade I Teacher Senior Scale
- vnn001@ chowgules.ac.in