



TARGET : JEE (MAIN+ADVANCED)

HANDOUT OF PHYSICAL CHEMISTRY

*Quantum Number &
Electronic Configuration*

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Quantum Number & Electronic Configuration

De-broglie wavelength & Uncertainty principle
De-Broglie Relation (Dual nature of matter and radiation) :

$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

De-Broglie pointed out that the same equation might be applied to material particle by substituting m for the mass of the particle instead of the mass of photon and replacing c , the velocity of the photon, by v , the velocity of the particle.

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(\text{K.E.})}}$$

- From the De-Broglie equation it follows that wavelength of a particle decrease with increase in velocity of the particle. Moreover, lighter particles would have longer wavelengths than heavier particles, provided the velocity is equal.
- If a charged particle Q is accelerated through potential difference V from rest then De-broglie wavelength is

$$\lambda = \frac{h}{\sqrt{2mQV}}$$

- De-Broglie concept is more significant for microscopic or sub-microscopic particles whose wavelength can be measured.
- The circumference of the n th orbit is equal to n times the wavelength of the electron.
 $2\pi r_n = n\lambda$.
- Wavelength of electron is always calculated using De-Broglie calculation.

HEISENBERG'S UNCERTAINTY PRINCIPLE :

It is impossible to measure simultaneously both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainty.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad m \Delta x \cdot \Delta v \geq \frac{h}{4\pi}$$

$$\text{or} \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

where, Δx = uncertainty in position
 Δp = uncertainty in momentum
 h = Planck's constant
 m = mass of the particle
 Δv = uncertainty in velocity

- In terms of uncertainty in energy ΔE , and uncertainty in time Δt , this principle is written as,

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

- Heisenberg replaced the concept of definite orbits by the concept of probability.

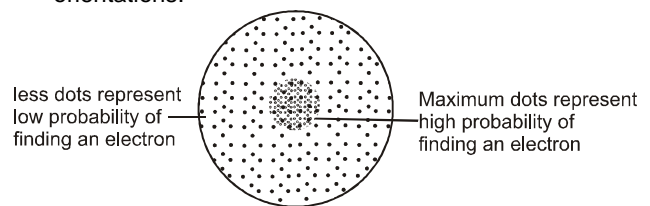
Quantum numbers & electronic configuration

Orbit: Exact path (2D circular) followed by electron rotating around the nucleus, just like earth rotating about the sun. This is how Bohr thought electron is moving around the nucleus. Different orbits have only different sizes given by orbit no. n .

Orbital : Due to uncertainty principle and wave nature of electron, we cannot tell exact path of electron around nucleus.

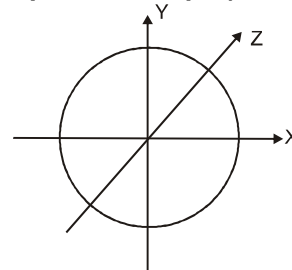
An orbital is 3D region of space around the nucleus in which the probability of finding an electron is 90% to 95%.

Different orbitals may have different size, shape and orientations.



Shapes of different orbitals:

s-orbital : Spherical shape (Not Circular)



s-orbital is non-directional i.e. probability of finding an electron is equal in all directions.

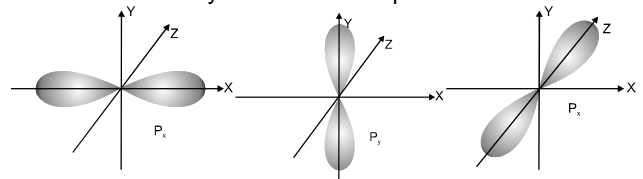
It can penetrate closest to the nucleus among different orbitals of the same shell.

s-subshell can accommodate maximum no. of two electrons.



p-orbitals : Dumb-bell shape

Dumb-bell shape consists of two lobes (like two inflated balloons) which are separated by a plane of zero electron density called as nodal plane.



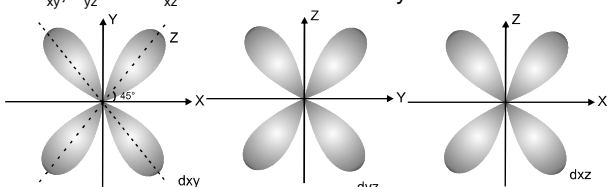
p-orbitals are directional i.e. probability of finding an electron is different in different directions. p-subshell can accommodate maximum no. of six electrons.



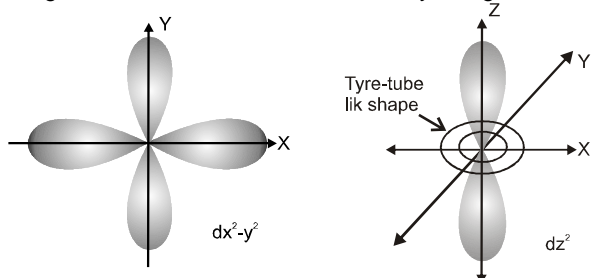


d-Orbital : Double Dumb-bell shape

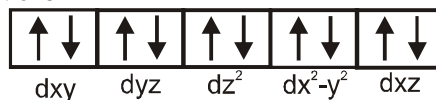
d_{xy} , d_{yz} and d_{xz} have electron density between the axes



Following two d-orbitals have electron density along the axes

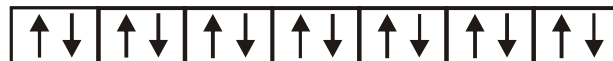


d-orbitals are directional i.e. probability of finding an electron is different in different directions. d-subshell can accommodate maximum no. of 10 electrons.



f-orbital : Complex (leaf like) shape

f-orbitals are directional in nature



f-subshell can accommodate maximum no. of 14 electrons.

Quantum Numbers : The set of four numbers required to completely define an electron in an atom are called quantum numbers. The first three quantum numbers (n , l and m) have been derived from Schrodinger equation

Quantum Numbers			
Symbol	Name & Property	Possible Values	Remark
n shell	Principal Quantum Number describes : 1. Average size of orbital. 2. Energy of orbital completely in single electron system (H, He ⁺ , Li ²⁺ etc.) 3. Energy of orbital to a large extent in multi electron system (He, C, Na, Fe etc.)	Whole numbers 1, 2, 3, 4...etc. Denoted by capital letters K(n=1), L(n=2), M(n=3), N(n=4)...etc.	1. Determines number of subshells. Number of subshells in n^{th} shell = n 2. Total number of orbitals in n^{th} shell = n^2 3. Maximum number of electrons in n^{th} shell = $2n^2$
l subshell	Azimuthal quantum number or Subsidiary Quantum number or Orbital Angular Momentum Quantum Number. Describes : 1. Shape of orbital. 2. Energy of orbital to a small extent in multi electron system (He, C, Na, Fe etc.)	Depends on value of $n : 0 \rightarrow (n - 1)$ Denoted by small letters s ($l = 0$), p ($l = 1$), d ($l = 2$), f ($l = 3$) if $n = 1 \Rightarrow l = 0$ i.e. s-subshell if $n = 2 \Rightarrow l = 0$ i.e. s-subshell & $l = 1$ i.e. p-subshell if $n = 3 \Rightarrow l = 0$ i.e. s-subshell & $l = 1$ i.e. p-subshell & $l = 2$ i.e. d-subshell	1. Determines number of orbitals in a subshell number of orbitals in a subshell = $2l + 1$ 2. Maximum no. of electrons in a subshell = $2(2l+1)$ 3. Orbital angular momentum = l
m or m_l orbital	Magnetic quantum number : Describes orientation of the orbital in 3D-space	Depends on value of l . Integral values from $-l$ to zero to $+l$ Total possible values = $2l + 1$ if $l = 0 \Rightarrow m = 0$ i.e. only one orbital in s-subshell if $l = 1 \Rightarrow m = -1, 0, +1$ i.e. 3 orbitals in p-subshell: p_x, p_y, p_z if $l = 2 \Rightarrow m = -2, -1, 0, +1, +2$ i.e. 5 orbitals in d-subshell : $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$.	1. Each value of m corresponds to a different orbital. For example, in p-subshell three values of m indicate three orbitals orientated in three different directions.



s or m_s spin	Spin quantum number : Not obtained from Schrodinger equation	$s = +\frac{1}{2}$ or $s = -\frac{1}{2}$ These two values represent quantum mechanical spin states having no classical analogue. We can think one value signifies clockwise spinning and other value signifies anticlockwise spinning. (But which is not actually true).	If n = no. of unpaired electrons in an atom.
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Nodes : Node represents the region where probability of finding an electron is zero

Orbital	Total nodes = $n - 1$	Angular nodes = ℓ	Radial (spherical) nodes = $n - \ell - 1$
1s	$1 - 1 = 0$	0 ($\because \ell = 0$ for s)	$1 - 0 - 1 = 0$
2s	$2 - 1 = 1$	0 ($\because \ell = 0$ for s)	$2 - 0 - 1 = 1$
$2p_x$	$2 - 1 = 1$	1 ($\because \ell = 1$ for p) yz plane is nodal plane	$2 - 1 - 1 = 0$
$3p_y$	$3 - 1 = 2$	1 ($\because \ell = 1$ for p) xz plane is nodal plane	$3 - 1 - 1 = 1$
$3d_{xy}$	$3 - 1 = 2$	2 ($\because \ell = 2$ for d) yz & xz planes are two nodal planes	$3 - 2 - 1 = 0$
$3d_{x^2-y^2}$	$3 - 1 = 2$	2 ($\because \ell = 2$ for d) Both angular nodes are two nodal planes	$3 - 2 - 1 = 0$
$3d_{z^2}$	$3 - 1 = 2$	2 ($\because \ell = 2$ for d) Both angular nodes are two nodal cones	$3 - 2 - 1 = 0$

Note : If angular node is a plane it is called nodal plane
 If angular node looks like a cone it is called nodal cone
 A radial node is the spherical region around nucleus having zero probability of finding electron

Important Formulae :

- No energy shell in the atoms of known elements possesses more than 32 electrons.
- Angular momentum of any orbit (as per Bohr Model) = $nh/2\pi$
- Total number of electrons in n^{th} main energy level

$$= \sum_{\ell=0}^{n-1} 2(2\ell + 1)$$
- Spin angular momentum = $\frac{h}{2\pi} \sqrt{s(s+1)}$
 where, $s = +\frac{1}{2}$

Examples :

- Orbital angular momentum of s orbital electron = 0, since $\ell = 0$.
- Orbital angular momentum of p orbital electron

$$= \sqrt{2} \frac{h}{2\pi}, \text{ since } \ell = 1$$

- Orbital angular momentum of d orbital electron

$$= \sqrt{3} \frac{h}{2\pi}, \text{ since } \ell = 2$$

Degenerate Orbitals

Orbitals belonging to same subshell have same energy and are known as degenerate orbitals. Degeneracy is maintained in absence of magnetic field and destroyed if degenerate orbitals are kept in magnetic field. Thus,

p-subshell :

p_x	p_z	p_y
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(3-fold degenerate)

d-subshell :

d_{xy}	d_{yz}	d_{z^2}	$d_{z^2-y^2}$	d_{xz}
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(5-fold degenerate)

Rules of writing Electronic Configuration

(A) Aufbau principle:

- Aufbau is a German word meaning building up
- An orbital of lowest energy is filled before an orbital of higher energy.
- Electrons in an atom would fill the principal energy levels in order of increasing energy given by $(n+\ell)$ rule.

**(n + ℓ) Rule :**

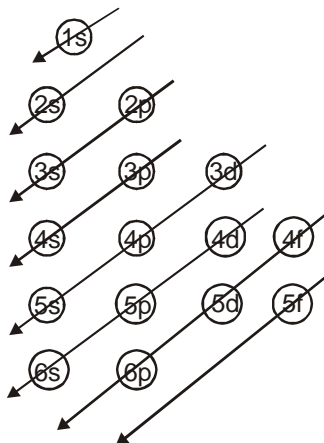
- (i) The sub-shell with lower value of $(n + \ell)$ has lower energy and it should be filled first.

eg. 3d: $(n + \ell) = 3 + 2 = 5$; 4s: $(n + \ell) = 4 + 0 = 4$
 $(n + \ell)$ value of 3d is more than 4s. Thus, 4s will be filled before 3d.

- (ii) If two sub-shell has same value of $(n + \ell)$ then the subshell with lower value of n has lower energy and it should be filled first.

eg. 3d: $(n + \ell) = 3 + 2 = 5$; 4p: $(n + \ell) = 4 + 1 = 5$.
 Both have same value of $(n + \ell)$. But 3d has lower value of n than 4p. Thus, 3d is filled before 4p.
 The sequence of orbitals in order of their increasing energy is
 $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s \dots$

This order can be easily remembered by using Memory Map as shown below. Just follow the arrows, one by one, from top to bottom

MEMORY MAP:**(B) Pauli's exclusion principle :**

No two electrons in an atom can have the same set of all the four quantum numbers, i.e. an orbital cannot occupy more than 2 electrons

The first three quantum nos. (n , l , and m) may be similar but the 4th quantum number (s) must be different.

If first three quantum numbers are $n = 1$, $\ell = 0$ and $m = 0$ then only 2 electrons can correspond to these set, which would be either $s = -1/2$ or $s = +1/2$.

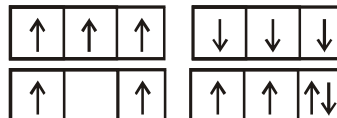
Not allowed by Pauli's Principle: $\uparrow\uparrow$ $\uparrow\uparrow\downarrow$

(C) Hund's rule of Maximum Multiplicity :

No electron pairing takes place in the orbitals of a sub-shell until each orbital is occupied by one electron with parallel spins.

Thus, the first three electrons will occupy each p-orbital of a p-subshell singly (either all with

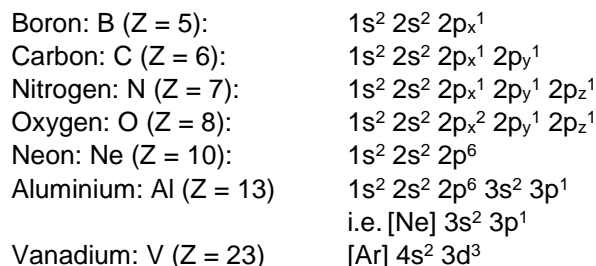
clockwise spin or all with anticlockwise spin) and the 4th electron will undergo pairing with any of the three single electrons.

Allowed by Hund's Rule :**Not allowed by Hund's Rule :**

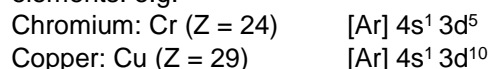
Note: Exactly half filled and fully filled orbitals are more stable, i.e. s^1 , s^2 , p^3 , p^6 , d^5 , d^{10} , f^7 and f^{14} configuration are most stable.

Electronic configuration of atoms:

- Total number of electrons to be filled is the atomic number Z .
- Write the subshells in increasing order of energy and go on filling one electron at a time keeping in mind above rules.



Important Exceptions: Aufbau principle is not followed all the times, there are some exceptions that occur the transition metals and heavier elements. e.g.



These exceptions can be explained by extra stability of half filled and fully filled subshells on account of greater exchange energy and symmetry.

Electronic Configuration of Ions:

- First write configuration of neutral atom
- Remove or add appropriate number of electrons
- While removing electrons to form cations electrons must be removed first from the highest shell (i.e. highest n value). e.g.



i.e. remove 2 electrons from 4s and not from 3d



i.e. first remove 1 electron from 4s and then remove 1 electron from 3d.