

ATOMIC STRUCTURE

Quantum Numbers:

These are a set of 4 integers necessary to specify the energy, position, shape, size and orientation of orbitals to which electrons belong.

Principal Quantum Number 'n':

It specifies the location and **energy** of an electron. It is a measure of the effective volume or **size** of the electron cloud denoted by 'n' and can have values 1,2,3,4,.....∞

Azimuthal Quantum Number 'l':

l = 0 1 2 3 4
s p d f g

$$\text{Angular Momentum} = \sqrt{l(l+1)} \frac{h}{2\pi}$$

It determines the **shape** of the orbital. It takes integral values from 0 → (n-1) where 'n' is the principal quantum number. When 'l' = 0, 1, 2, the shapes of the orbitals are 's' Spherically symmetrical, 'p' dumbbell, and 'd' double dumbbell.

Magnetic Moment Quantum Number 'm': (2l+1) values

It gives the **orientation** of the orbitals in space. It takes integral values ranging from -l0+l or 's' orbital has got one orientation, 'p' orbital has got 3 orientations, 'd' orbital has got '5' orientations and 'f' orbital has got 7 orientations.

Spin Quantum Number 's':

It indicates the direction in which the electron **spins** on its own axis or the magnetic property that is associated with it. This value is quantised the two values that are permitted are + ½ and - ½ $\mu_s = g \times \sqrt{s(s+1)}$ where g = gyromagnetic constant.

ORBIT	ORBITAL
It is a well defined circular path around the nucleus in which the electron revolves	It is a region in three dimensional space around the nucleus where there is a very high probability of locating the electron
It is circular in shape	's', 'p' and 'd' orbitals are spherical, dumbbell and double dumbbell in shape respectively
It represents the movement of an electron around the nucleus in one plane.	It represents the movement of an electron around the nucleus in a three dimensional space.
It states with certainty the momentum and position of an electron. Violates the Heisenbergs uncertainty principle	It is a consequence of Heisenbergs uncertainty principle. i.e. The position and momentum cannot be known with certainty
The maximum number of electrons in an orbit is 2n ²	The maximum no of electrons in an orbital is 2

The number of orbitals = n²

Schrodinger Wave Equation:

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

'E' is the total energy of the electron in the system and 'V' is the potential energy of the system.

ψ

It is known as an orbital wave function which is a solution the Schrodinger wave equation. It represents the amplitude of the wave and the significant values are Eigen functions.

ψ²

It represents the electron density or the probability of locating electrons of specific energy at different regions in space. It leads to the concept of orbitals.

$$E = -\frac{2\pi^2 m e^4 Z^2}{n^2 h^2}$$

Energy of the electron in the ground state of hydrogen atom:

$$E = -2.17 \times 10^{-18} \text{ J/Atom and } -1.312 \times 10^6 \text{ J/Mole.}$$

Why is the value of the energy of an electron negative?

The value of the energy of an electron in the hydrogen atom is negative because when the electron is far away from the nucleus the Potential Energy is taken as zero. When the electron comes closer to the nucleus work is done by the electron therefore energy is released and the energy of the electron becomes less than zero hence it has a negative value.

The difference in Energy between two energy levels viz. E_2 and E_1 when $E_2 > E_1$:

$$E_2 - E_1 = \Delta E$$

$$\Delta E = 1.312 \times 10^6 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Delta E = h\nu$$

$$\Delta E = \frac{hc}{\lambda}$$

ELECTRONIC CONFIGURATION OF ELEMENTS:

Aufbau Principle:

According to the principle the electrons are filled in the various subshells in the order of their increasing energies.

($n + l$) Rule: The subshell with lower $n+l$ value will possess lower energy and will be filled first.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 4f \dots$$

Pauli's Exclusion Principle:

No two electrons in an atom can have all the 4 quantum numbers alike.

Hund's Rule of Maximum Multiplicity:

Electron pairing will not take place in degenerate orbitals (same energy subshell) until each orbital is first singly filled with electrons having parallel spins.

Why is it that the 4s electrons are lost during the formation of divalent ions in the first transition series e.g. Fe^{2+} & Ni^{2+} ?

The 4s orbital is physically larger than all the orbitals hence present as the outer most electron

The shielding effect of the inner electrons prevents the effective attraction of the 4s electrons by the nucleus.

Exceptional Electronic Configuration:

Cu, Cr, Mo, Ag, W & Au have got exceptional electronic configuration. Explain.

$Z = 29, 24, 42, 47, 74$ & 79 Respectively.

Half Filled 'd' orbital configurations are preferred because

There is extra stability because of the symmetrical distribution of the electrons in the orbitals.

The Exchange energy is High for Cr, Mo & W.

Exchange energy can be calculated using the following equation Where 'n' is the number of electrons having parallel spins.

$$\text{Exchange Energy} = \frac{n!}{n(n-2)!} \text{ where } n \text{ stands for the number of unpaired electrons in the d orbital.}$$

Molecular Orbital Theory

This theory has been proposed by Hund and Mulliken

Basic Concept:

Atomic orbitals of atoms involved in the formation of a molecule get redistributed to give rise to an equivalent number of new molecular orbitals. During the process the identity of the atoms are lost. Linear combination of atomic orbitals leads to the formation of the molecular orbitals.

Bonding Molecular Orbitals ψ_{mo} :

A Constructive Interference leading to Addition Combination of wave fronts.

A bonding molecular orbital is obtained by the addition combination of 2 atomic orbitals with same symmetry.

There is an increased electron density between the two orbitals leading to decreased energy and increased stability

Electrons in this orbital leads to attraction between the atoms.

The energy of the bonding M.O is less than that of the Atomic orbitals.

Antibonding Molecular Orbital ψ_{mo}^* :

A Destructive Interference leading to Subtractive Combination of Wave fronts:

An Antibonding molecular orbital is obtained by the Subtractive combination of 2 atomic orbitals with opposite symmetry.

There is a decreased electron density between the two orbitals leading to decrease in stability

Electrons in this orbital leads to repulsion between the atoms.

The energy of the antibonding molecular orbital is greater than that of the atomic orbitals

Bond Order

It is a measure of the stability of the molecule

It can be calculated by the following relation where N_b stands for the electrons in the bonding molecular orbital and N_a stands for the number of electrons in the antibonding molecular orbital. $B.O = \frac{1}{2}[N_b - N_a]$ We can draw the following

conclusions from the values of the bond order:

A Positive value for the bond order indicates the stability or formation of the molecule.

When the bond order is zero the molecule does not form or exist.

A whole number value for the bond order can also indicate the number of covalent bonds in the molecule

Bond order is directly proportional to Bond Dissociation Energy

Bond order is inversely proportional to Bond Length

When two molecules have the same bond order the molecule with more bonding electrons is more stable.

Examples of molecules showing exceptions in its electronic configuration are B_2, C_2 & N_2 .

Paramagnetic Behaviour of Oxygen can only be explained using M.O. Theory