KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)
(Established Under Section 3 of UGC Act 1956)
Coimbatore – 641 021.
(For the candidates admitted from 2018 onwards)

DEPARTMENT OF CHEMISTRY

SUBJECT NAME: INORGANIC CHEMISTRY-I SUBJECT CODE:18CHU102
(Atomic structure and chemical bonding)

SEMESTER: I CLASS: I B.Sc CHEMISTRY

Scope

The course presents the knowledge about the basics of atomic structure and chemical bonding. Quantum mechanical treatment of atomic structure involving quantum numbers and electronic configuration of elements were given. It further presents knowledge about ionic and covalent bonding. The covalent bonding has been explained based on Valence bond theory and molecular orbital theory.

Program Outcome

1. To understand and write the electronic configuration of elements
2. To provide a versatile knowledge of different types of bonding like ionic and covalent bonding.
3. To provide a knowledge about the valence Bond Theory and Molecular Orbital Theory of covalent bonding

Program Learning Outcome

After the completion of the course the student knows how to write the electronic configuration of elements and about ionic and covalent bonding. Also understood about valence Bond Theory and Molecular Orbital Theory of covalent bonding

Atomic Structure:

UNIT I

Review of: Bohr's theory and its limitations, dual behaviour of matter and radiation, de Broglie's relation, Heisenberg Uncertainty principle. Hydrogen atom spectra. Need of a new approach to atomic structure. What is Quantum mechanics? Time independent Schrodinger equation and meaning of various terms in it. Significance of ψ and ψ^2, Schrödinger equation for hydrogen atom. Radial and angular parts of the hydrogenic wave functions (atomic orbitals) and their variations for 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals (Only graphical representation). Radial and angular nodes and their significance. Radial distribution functions and the concept of the most probable distance with special reference to 1*s* and 2*s* atomic orbitals.

UNIT II

Significance of quantum numbers, orbital angular momentum and quantum numbers *ml* and *ms*. Shapes of *s*, *p* and *d* atomic orbitals, nodal planes. Discovery of spin, spin quantum number (*s*) and magnetic spin quantum number (*ms*). Rules for filling electrons in various orbitals, Electronic configurations of the atoms. Stability of half-filled and completely filled orbitals, concept of exchange energy. Relative energies of atomic orbitals, Anomalous electronic configurations.

Chemical Bonding and Molecular Structure

UNIT III

.*Ionic Bonding:* General characteristics of ionic bonding. Energy considerations in ionic bonding, lattice energy and solvation energy and their importance in the context of stability and solubility of ionic compounds. Statement of Born-Landé equation for calculation of lattice energy, Born-Haber cycle and its applications, polarizing power and polarizability. Fajan's rules, ionic character in covalent compounds, bond moment, dipole moment and percentage ionic character

UNIT IV

Covalent bonding: VB Approach: Shapes of some inorganic molecules and ions on the basis of VSEPR and hybridization with suitable examples of linear, trigonal planar, square planar, tetrahedral, trigonal bipyramidal and octahedral arrangements. Concept of resonance and resonating structures in various inorganic and organic compounds.

UNIT V

MO Approach: Rules for the LCAO method, bonding and antibonding MOs and their characteristics for *s-s*, *s-p* and *p-p* combinations of atomic orbitals, nonbonding combination of orbitals, MO treatment of homonuclear diatomic molecules of 1st and 2nd periods (including idea of *s-p* mixing) and heteronuclear diatomic molecules such as CO, NO and NO^+. Comparison of VB and MO approaches.

Suggested Readings:

Text Books:

1. Lee, J.D. (2013). *Concise Inorganic Chemistry*. ELBS.
2. Cotton, F.A., Wilkinson, G. & Gaus, P.L. (2008). *Basic Inorganic Chemistry*. 3rd ed. Hohn Wiley & sons.
3. Madan R.L., (2015) . Chemistry for Degree students B.Sc., First year. S.Chand & Company Private Ltd., New Delhi.

Reference Books:

1. Douglas, B.E., McDaniel, D.H. & Alexander, J.J. (2010).*Concepts and Models in Inorganic Chemistry*. John Wiley & Sons.
2. Huheey, J.E., Keiter, E.A., Keiter, R.L. & Medhi, O.K. (2006). *Inorganic Chemistry: Principles of Structure and Reactivity*. Pearson Education India.
3. Puri B.R., Sharma L.R. and Kalia K.C. (2002). *Principles of Inorganic Chemistry*. Vallabh Publications, Delhi.

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DEPARTMENT OF CHEMISTRY

SUBJECT NAME: INORGANIC CHEMISTRY-III SUBJECT CODE: 18CHU102
(Atomic structure and chemical bonding)

SEMESTER: I CLASS: I B.Sc CHEMISTRY

LECTURE PLAN
DEPARTMENT OF CHEMISTRY

S.No	Lecture Hour	Topics to be Covered	Support Materials/Page Nos
		UNIT I	
1.	1	Bohr's theory and its limitations	T2 - 3-7
2.	1	Dual behaviour of matter and radiation, de Broglie's relation	T2 10-11.
3.	1	Heisenberg Uncertainty principle	T2-15-16
4.	1	Hydrogen atom spectra. Need of a new approach to Atomic structure.	T2-7-9
5.	1	Quantum mechanics definition. Time independent Schrodinger equation and meaning of various terms in it. Significance of ψ and ψ^2.	T2-21-23
6.	1	Schrödinger equation for hydrogen atom.	T2-5-7
7.	1	Radial and angular parts of the hydrogenic wave functions (atomic orbitals) and their variations for 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals (Only graphical representation).	T2-13-16
8.	1	Radial and angular nodes and their significance, Radial distribution functions.	T1-13-16
9.	1	Concept of the most probable distance with special reference to 1*s* and 2*s* atomic orbitals.	T2-17-21
10.	1	Recapitulations and discussion of important questions	
	Total No of Hours Planned For Unit I =10		
		UNIT II	

1.	1	Significance of quantum numbers, orbital angular momentum and quantum numbers *ml* and *ms*.	R2-37-39
2.	1	Shapes of *s*, *p* and *d* atomic orbitals, nodal planes	T2-20-22
3.	1	Discovery of spin, spin quantum number (*s*)	T2-9-11
4.	1	Magnetic spin quantum number (*ms*).	T2-9-11
5.	1	Rules for filling electrons in various orbitals. Electronic configurations of the atoms.	T2-25-32
6.	1	Stability of half-filled and completely filled orbitals.	T2-30-32
7.	1	Concept of exchange energy	T2-30-32
8.	1	Relative energies of atomic orbitals, Anomalous electronic configurations.	T2-167, R2-662
9.	1	Recapitulation and Discussion of important questions	
	Total No of Hours Planned For Unit II =9		
		UNIT III	
1.	1	General characteristics of ionic bonding.	T2-141-142
2.	1	Energy considerations in ionic bonding	T2-148-150
3.	1	Lattice energy and solvation energy	T2-148-150
4.	1	Importance in the context of stability and solubility of ionic compounds	T2-148-150
5.	1	Statement of Born-Landé equation for calculation of lattice energy	T2-150-151
6.	1	Born-Haber cycle and its applications	T2-152-155
7.	1	Polarizing power and polarizability	T2-157
8.	1	Fajan’s rules, ionic character in covalent compounds.	T2-157-159
9.	1	Bond moment, dipole moment and percentage ionic character	T2-159
10.	1	Recapitulations and discussion of important questions	
	Total No of Hours Planned For Unit III =10		
		UNIT IV	
1.	1	*Covalent bonding:* VB Approach	T2-75

2.	1	Shapes of some inorganic molecules and ions on the basis of VSEPR and hybridization with suitable examples of linear, trigonal planar arrangements.	R2-187-188
3.	1	VSEPR and hybridization of square planar arrangements.	R2-188
4.	1	VSEPR and hybridization of tetrahedral arrangements	R2-188-189
5.	1	VSEPR and hybridization of trigonal bipyramidal arrangements	R2-189-190
6.	1	VSEPR and hybridization of octahedral arrangements.	R2-190-191
7.	1	Concept of resonance	T2-79
8.	1	Resonating structures in various inorganic and organic compounds	R1-143-146
9.	1	Recapitulations and discussion of important questions	
	Total No of Hours Planned For Unit IV =9		
		UNIT V	
1.	1	MO Approach: Rules for the LCAO method, Bonding and antibonding MOs	T1-97-98; T1-112
2.	1	Characteristics for *s-s*, *s-p, p-p* combinations of atomic orbitals, Nonbonding combination of orbitals	T1-90-94 T1-96-97
3.	1	MO treatment of homonuclear diatomic molecules of 1st and 2nd periods	T1-98-107
4.	1	MO treatment of homonuclear diatomic molecules of 1st and 2nd periods	T1-98-107
5.	1	Heteronuclear diatomic molecules such as CO, NO and NO^+.	T1-109-112
6.	1	Heteronuclear diatomic molecules such as CO, NO and NO^+.	T1-109-112
7.	1	Comparison of VB and MO approaches	T1-128-129
8.	1	Recapitulations and discussion of important questions	
9.	1	Discussion of Previous year ESE Question Paper	
10.	1	Discussion of Previous year ESE Question Paper	
	Total No of Hours Planned For Unit I =10		

SUPPORTING MATERIALS:

Text books:

T1. Lee, J. D. (2013). *Concise Inorganic Chemistry*. ELBS.
T2. Puri, B. R., Sharma, L. R., & Kalia. K. C., (2017). *Principles of Inorganic Chemistry*. Vishal Publication.
T3. Madan, R. D. (2014). *Modern Inorganic Chemistry*. S.Chand & Company Pvt.Ltd.
T4: Gopalan, M., Ramalingam, R. V. (2008). *Concise of Coordination Chemistry*, Vikas Publications

Reference Books:

1. Malik. U., Tuli. G.D. & Madan. R.D. (2009). *Selected topics in Inorganic Chemistry*. S.Chand & Company Pvt.Ltd.
2. Sathya Prakash, Tuli. G.D., Basu. S.K., & Madan. R.D. (2012). *Advanced Inorganic Chemistry* (Volume II), S.Chand & Company Pvt.Ltd.

UNIT I

SYLLABUS

Review of: Bohr's theory and its limitations, dual behaviour of matter and radiation, de Broglie's relation, Heisenberg Uncertainty principle. Hydrogen atom spectra. Need of a new approach to atomic structure. What is Quantum mechanics? Time independent Schrodinger equation and meaning of various terms in it. Significance of ψ and ψ^2, Schrödinger equation for hydrogen atom. Radial and angular parts of the hydrogenic wave functions (atomic orbitals) and their variations for 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals (Only graphical representation). Radial and angular nodes and their significance. Radial distribution functions and the concept of the most probable distance with special reference to 1*s* and 2*s* atomic orbitals.

Introduction

If you want to have a language, you will need an alphabet, so alphabets are building blocks of language. Similarly atoms join together to create matter. Atoms are the basis of chemistry, rather, for everything that exists in the universe. These atoms create the elements, molecules and the world in large. The word 'atom' has been derived from the Greek word '**atomos'** which means 'uncut-able' or indivisible. The existence of atom was known to Greek and Indian philosophers as early as 400 B.C. They were of the view that continued subdivision of matter would ultimately yield an atom. According to them atoms were the building blocks of matter and could not be further divided. But they could provide no proof to their hypothesis that "all matter is said to be composed of small particles called atoms". This was proposed by John Dalton, a British school teacher in 1805. His theory called 'Daltons Atomic Theory' regarded the atom as the ultimate particle of matter.

At the end of nineteenth century enough experimental evidence (discharge tube experiment by J.J.Thomson, E Goldstein) was accumulated to show that an atom is made up of still smaller particles. These sub atomic particles are called the fundamental particles. Although the number of subatomic particles now known is very large, the three most important among them are **proton, neutron** and **electron**. The Central part of the atom is highly dense and is called NUCLEUS. Protons which are positively charged particles and neutrons which are neutral particles reside in the nucleus. Electrons which are negatively charged particles are present in the orbits around the nucleus. The important properties of these fundamental particles are given in Table 1.

Table 1: Properties of Fundamental Particles

Name	Symbol	Year of Discovery	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx mass/u
Electron	e	1896	-1.6022×10^{-19}	-1	9.10939×10^{-31}	0.00054	0
Proton	p	1886	$+1.6022 \times 10^{-19}$	+1	1.67262×10^{-27}	1.00727	1
Neutron	n	1932	0	0	1.67493×10^{-27}	1.00867	1

The atoms of all known elements contain all the three fundamental particles: electrons, protons and neutrons. The only known exception is hydrogen atom (it contains one electron, one proton but no neutron. The main milestones in the evolution of atomic structures are:

1808 – Dalton’s atomic theory.
1896 – J.J. Thomson’s discovery of electron and proton.
1909 – Rutherford’s nuclear atom.
1913 – Mosley’s determination of atomic number.
1913 – Bohr Atom
1921 – Bohr – Bury scheme of electronic arrangement
1924 – De Broglie’s wave equation
1932 – Chadwick’s discovery of neutron

With the discovery of sub atomic particles, there arose a need to know how these particles are arranged in the atom. Therefore, different atomic models giving different pictures of the structure of atom have been proposed from time to time. Some of the earlier models are discussed here.

Thomson Model of Atom

Thomson, the discoverer of electron in 1898 proposed the **‘raisin pudding’** model of atom. He assumed that an atom consists of a uniform sphere of positive charge with electrons embedded into it in such a way as to give it a stable configuration. In this model, the atom is visualized as a pudding or cake of positive charge with raisins (electrons) embedded into it hence, the name 'raisin pudding' model. Mass of the atom was considered to be evenly spread over the atom.

Thomson proposed that electrons in an atom were not at rest, but were vibrating about their equilibrium position. A vibrating electron would emit electromagnetic radiations (spectral lines) having the same frequency as that of vibrating electrons. Zeeman's effect could also be explained on this basis.

Limitations of Thomson model:

1. Spectral lines obtained even in the simplest case could not be explained by Thomson model. Hydrogen atom is known to have several lines in ultra violet region. However, according to this model only one spectral line is possible.
2. Rutherford's scattering experiments could not be explained by this model.
3. The mass of the electron has been found to be 1/1837 times that of hydrogen atom. This implied that solid spherical atom proposed by Thomson, especially in case of heavier atoms, must contain thousands of electrons, which is not possible.

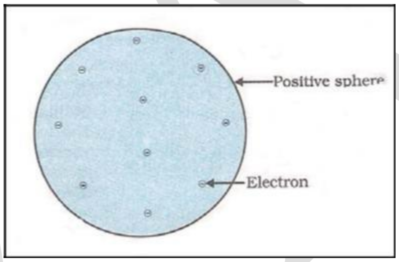


Fig. 1. Picture of atom as viewed by Thomson

Rutherford's Experiment

Lord Rutherford performed an experiment for testing the Thomson model. He bombarded thin foils of gold with high speed α- particles.

A radioactive substance like polonium which can be a source of α- particles carries two units of positive charge (+2 charge) and mass equal to about 4 times that of hydrogen atom. The radioactive substance emits α - particles in all directions. These rays are made to fall on a lead plate with a hole, so that only thin stream of α-particles comes out of the hole, and the remaining particles are absorbed by the lead plate. These α-particles bombard a thin gold foil (thickness 4 x 10^{-5} cm) layer. A movable screen coated with zinc sulphide is placed next to gold foil. When α-particles hit the screen, it produces a flash of light which could be counted. The course of α - particles striking a metallic sheet is represented in Fig 2.

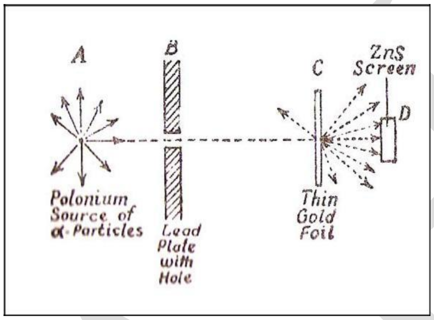


Fig. 2. Rutherford's scattering experiment

Results:

1) Most of the particles (about 99%) passed straight through the foil and struck the screen at the centre.

2) A small fraction of α- particles deflected from their original path through varying angles (Mean scattering was about 0-87^0), small number of α-particles underwent large deflections and approximately one out of 20,000 made a right angle deflection).

3) Hardly one out of 2000 α - particles bounced back. On the basis of these observations Rutherford comes to the following conclusions:

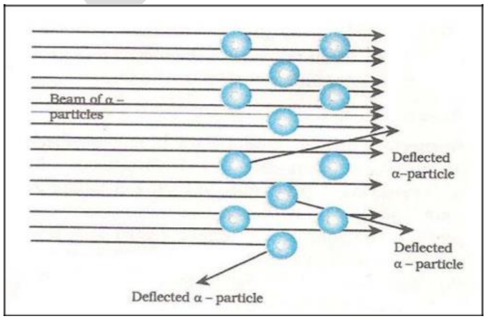


Fig: 3: schematic molecular view of gold foil

1. Atom is extraordinarily hollow i.e. most of the space in the atom is empty as a good number of α- particles passed through the foil.
2. A few positively charged α - particles had deflected. The deflection was attributed to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as suggested by Thomson. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α-particles. This very small portion of the atom was called **nucleus** by Rutherford.

3. Calculations from scattering experiment indicated that nucleus of an atom has a diameter of approximately one to six fermis (1 fermi = 10^{-13} cm) and atoms have diameter about 100000 times the size of the nucleus i.e. of the order of 10^{-8} cm. Due to the rigidness of the nucleus, some α- particles on colliding with it turn back on their original path.

Rutherfod's Model

Rutherford gave his first model in 1912. He suggested that "*an atom consists of a central nucleus of small dimension within which resides the positive charge and most of the mass. Outside this nucleus are electrons to make the atom neutral"*

But Rutherford himself realized that his model could not explain the stability of the atom. If the electrons are assumed to be at rest in the atom, the electrons would be attracted by the nucleus and fall inside it. To remove this limitation, he gave another model which states that "*the atom consists of a central nucleus surrounded by electrons which are not at rest, but revolve round the nucleus in closed paths like the planets revolving round the sun".*

Rutherford called 'electrons' as 'planetary electrons' due to analogy with the planets revolving round the sun. An atom is neutral as the number of electrons equals the number of protons in the nucleus. Later Rutherford concluded that mass number is twice the nuclear charge. He then modified his own model as;

"Atomic nucleus consists of protons and enough electrons to reduce the positive charge to about half the mass number and remaining positive charge on the nucleus was balanced by planetary electrons".

Effective Radius of Nucleus: In the scattering experiment the alpha particles bounce back at a point where the kinetic energy is fully converted into potential energy:

Kinetic energy = $1/2\ mv^2$

Potential energy of ∝ particle = $2kZe^2$

(Charge e unit and distance r from nucleus charge Ze)

where $k = 9 \times 10^9\ Nm^2\ C^{-2}$.

Equating KE. With P.E

$$\frac{1}{2}mv^2 = \frac{2kZe^2}{r}$$

when $r=2\times10^7 m\ s^{-1}$

mass of ∝ particle (2p+2n) = 6.694×10^{-27}kg, Z = 79 for gold atom

r, the effective radius of gold is

$$r = \frac{4kZe^2}{mv^2} = \frac{4 \times 9 \times 10^9 (1.6 \times 10^{-19})^2 \times 79}{6.6\,94\times10^{-27} \times (2 \times 10^7)^2}$$

$r = 2.72 \times 10^{-14}$m.

The radius found is in agreement with that suggested by Rutherford.

Drawbacks: Rutherford had described the atomic model with electrons rapidly revolving around the nucleus as the planets revolve around the sun. When classical mechanics (based on Newtons laws of motion) was applied to the solar system it was found that planets revolve in well defined orbits around the sun. The planetary orbits calculated on the basis of classical mechanics were in agreement with the experimental measurements. Whenever a body is moving in an orbit, it undergoes acceleration. Thus, an electron moving round the nucleus should also undergo acceleration. In accordance with Maxwell’s electromagnetic theory, charged particles when accelerated emit electromagnetic radiations and thus lose energy. In other words the orbiting electrons of the Rutherford’s model, would continuously emit radiation, and in the process would lose energy, and come closer to the nucleus. Ultimately, the electron would fall into the nucleus and destroy the atom. Niels Bohr, a Danish physicist calculated that an atom would collapse in hundred millionth of a second. This was contrary to the fact that atoms are stable. Another limitation of Rutherford’s model was that it was silent about the electronic structure of the atom i.e distribution of electrons around the nucleus and the energies associated with them.

Bohr’s Model of Atom

In 1913, Bohr put forward a theory based on quantization of energy to improve upon the Rutherford’s model of the structure of atom. This theory also satisfactorily explained the line spectrum of hydrogen atom. He postulated that:

1. The electrons move around the nucleus in one of the several fixed circular orbits called energy levels. These energy levels are arranged concentrically around the nucleus, and are characterized by an integer n, the lowest level being given the number 1. The energy level corresponding to n=1, 2, 3, 4… are also known as K, L, M, N … shells.
2. Electrons can move about only in certain orbits which have specific energies. Their movement is possible in only those orbits for which its angular momentum is an integral multiple of $h/2\pi$ or $mvr=nh/2\pi$ where ‘n’ is any integer 1, 2, 3, 4….n.
3. The energy level nearer to the nucleus has low energy, where as that farthest from it has maximum energy. An electron is said to be in ground state, when it moves in energy level having lowest energy. The ground state is the most stable state of the atom. The electron has a definite energy which is characteristic of the orbit in which it is moving. As long as the electron remains in an orbit, it does not lose energy. These orbits are hence called ‘stationary orbits’.

4. Energy is emitted or absorbed when an electron moves from one level to another. Thus by absorbing one particular quantum of energy, the electron will jump from a energy level 1 to 2 or 2 to 3. It is then said to be in excited state. The quantum of energy absorbed in each case is equal to the difference in energies of the two levels. An electron cannot have an energy that would place it in between the two permissible orbits. When an electron moves from a higher energy (E2) orbit to a lower energy (E1) orbit, the energy (ΔE = E2-E1) is emitted in the form of a photon of frequency v such that $\Delta E = E_2 - E_1 = hv$

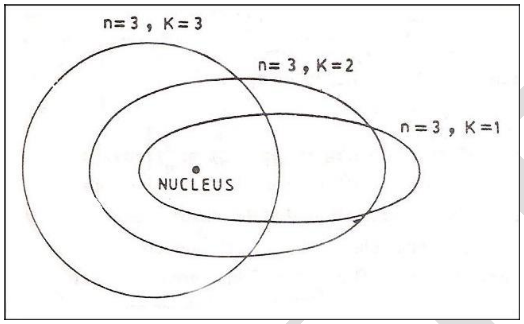
It is also possible to calculate the radius of each circular orbit using the equation rn = 0.529A (n^2) where n = 1,2,3…From the above equation it is clear that with an increase in the value of 'n' the value of 'r' will increase i.e. the distance between the nucleus and election increases. The radius of first orbit r1 is called the BOHR RADIUS, -i.e. n = 1 ;r = 0.529 $\overset{o}{A}$. Bohr's model is also applicable to other hydrogen like atoms, eg, He^+, Li^{+2} which contain only one electron but higher number of protons, i.e. $Z \neq 1$ but may have values 2, 3.The total energy of the electron is the sum of the potential and kinetic energies.

Limitations of Bohr's Model:

1. It could not explain the spectra of atoms containing more than one electron. It could not be applied to even simple helium atom, which has two electrons.
2. It failed to account for splitting of lines into groups of finer lines as observed by means of spectroscopes of high resolving power.
3. It failed to account for splitting of spectral lines in presence of a magnetic field (Zeeman's effect) or an electric field (Stark effect).

Bohr- Sommerfeld Theory

When the spectra were examined with spectrometers of high resolving power, each line was found to consist of a group of several finer lines. To explain this limitation of Bohr's model, Somerfield extended Bohr’s theory. While retaining the first of Bohr’s circular orbit as such, he added one elliptical orbit to Bohr’s second orbit, two elliptical orbits to Bohr’s third orbit and so on. He inferred that like any periodic motion under the influence of central force, it will form an elliptical orbit with the force located at one of the foci.



___ **Fig.4. Sommerfeld orbits in hydrogen atom.**

The angular momentum of an electron moving in an elliptical orbit is supposed to be quantized. Thus, only a definite set of values is permissible. Angular momentum is further assumed to be an integral part of ${}_{2}{}^{h}{}_{\Pi}$ units

∴ angular momentum = $\underline{{}_{2}{}^{kh}{}_{\Pi}}$

where ‘h’ Planck's constant k is azimuthal quantum number

It should be noted here that the quantum number used in Bohr’s theory is principal quantum number (n). The two quantum numbers n and k are related by the expression

n = *<u>lenglh of major axis</u>* *k*

lengh of min *or axis*

When n=k, the orbit will be circular and when k<n, orbit is elliptical.

The values of k for a given value of n are k = n–1, n-2, n-3 and so on. In other words k will have n possible values (n to 1) for a given value of n.

Although this model successfully explained fine line structure of atomic spectra and introduced the basic concept of stationary states and electronic transitions between them, yet it could not provide a satisfactory picture of the structure of atom.

The structure of atom could only be fully understood by considering the wave mechanical concepts. Two important developments which contributed towards the development of a model free from the limitations of Bohr's model were;

a) Dual behaviour of matter.

b) Heisenberg's uncertainty principle.

Wave Mechanics

The classical 'Mechanical Theory' of matter considers matter to be made up of discrete particles (electrons, protons etc.), where as the 'wave theory interpreted the nature of radiations like x-ray and light. According to the wave theory, radiations such as x-rays and light consisted of continuous collection of waves traveling in space. This theory however could not explain the photoelectric effect i.e. the emission of electrons from metal surfaces by the action of light. In an attempt to explain the same, Planck and Einstein (1905) proposed that energy radiations, including those of heat and light, are emitted as small packets called quanta or photons. This is referred to as 'Wave Mechanical Theory'. It states that light exhibits both a wave and particle nature, under suitable conditions.

The distinction between particles and waves was very hazy. In 1924, Louis de Broglie suggested in his doctoral thesis that dual character – wave and particle – may not be confined to radiations alone but should be extended to matter as well: i.e matter also possessed particle and wave character. In other words electrons and protons, when in motion, bear wave properties having characteristics of waves such as wave amplitude, frequency and wave length. This concept is called the **wave mechanical theory of matter.**

Louis de Broglie was born in an aristocratic family and began to study history at the Sorbonne in Paris, as preparation for a career in diplomacy. But after serving as a radio-operator in the First World War, he followed the lead of his brother Maurice and went into physics. He was awarded Nobel Prize in 1929.

De Broglie's Equation

This gives a relationship between the magnitude of the wave length associated with mass ‘ m’ of a moving body and its velocity.

According to Planck, the photon energy ‘ E’ is given by the equation

$$E = h\nu \ldots\ldots (i)$$

Where h is the Planck’ s constant and ν the frequency of radiation.

According to Einstein’ s mass-energy relationship

$$E = mc^2 \ldots\ldots (ii)$$

Where E is the energy associated with photon of mass ‘ m’ and c is the velocity of radiation, Comparing equations (i) and (ii).

$$mc^2 = h\nu$$

$$Q\ \nu = \frac{c}{\lambda}$$

$$mc^2 = h\frac{c}{\lambda}$$

or $mc = \frac{h}{\lambda}$ ....(iii)....de BROGLIE ' S EQUATION

mass × velocity = momentum (p)

$$\therefore \text{momentum } (p) = \frac{h}{\lambda}$$

The de Broglie’ s equation can be stated as: the momentum of a particle in motion is inversely proportional to its wave length.

The de Brodlie’s equation is true for all particles, but wave characteristic is of significance only for small particles, such as electrons. Large particles in motion do have wavelength, but it is not measurable and hence of no significance.

Applications: de Broglie’s prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon associated with waves. This fact has been applied in making electron microscope which is based on wave- like behaviour of electrons. An electron microscope can magnify objects to about 15 million times.

a) For a body with large mass, the value of λ is found to be too small, to be measured by any instrument.

b) A body with small mass eg. subatomic particle such as electron, has a significant value of λ, which can be measured with a suitable device.

Relationship between de-Broglie's and Bohr's theory

Bohr considered electrons to be moving in circular paths. Since electron has wave characteristic it is assumed that electron wave moves in a circle. The wave motion is considered to be in phase only when two ends of the wave meet to give a regular series of crests and troughs. This condition is possible when the circumference of the circular orbit is equal to the integral multiple of its wavelength.

$$2\pi r = n\lambda \ldots\ldots\ldots\ldots\ldots\ldots \text{(i).}$$

where r is the radius of the orbit, λ is the wavelength of the electron wave.

$$\lambda = \frac{2\Pi}{n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(ii).}$$

From de Broglie equation we know that

$$\lambda = \frac{h}{mv}$$

Thus

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

$$or \quad 2\pi\gamma = \frac{nh}{mv}$$

$$or \quad mvr = \frac{nh}{2\Pi} \qquad (iii).$$

The above equation is same as Bohr's second postulate.

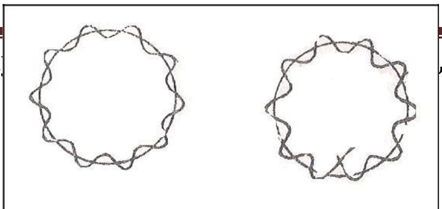


Fig: .5a Fig: .5b

It can be said that electrons can move only in such orbits as have angular momentum an integral multiple of h/2π . If the circumference is bigger than the value obtained by equation (iii), the wave will not be in phase (Fig. 5b). Thus, de Broglie's eqation provides a theoretical basis for Bohr's second postulate.

Three years after de Broglie asserted that particles of matter could possess wavelike properties, the diffraction of electrons from the surface of a solid crystal was experimentally observed by C.J. Davisson and L.H. Germer of the Bell Telephone Laboratory. In 1927 they reported their investigation of the angular distribution of electrons scattered from nickel. They showed that the electron beam was scattered by the surface atoms on the nickel at the exact angles predicted for the diffraction of x-rays according to Bragg's formula, with a wavelength given by the de Broglie equation, $\lambda = h/mv$.

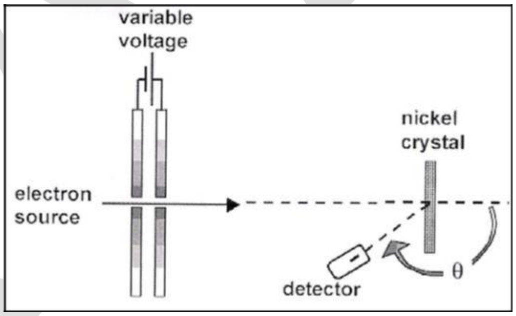


Fig. 6

In 1927, G.P. Thomson, son of J.J. Thomson, reported his experiments, in which a beam of energetic electrons was diffracted by a thin foil. Thomson found patterns that resembled the x-ray patterns made with powdered (polycrystalline) samples. This kind of diffraction, by many randomly oriented crystalline grains, produced rings. When the wavelength of the electrons was changed by altering their incident energy, the diameters of the diffraction rings changed proportionally, as expected from Bragg's equation.

These experiments by Davisson and Germer and by Thomson proved that de Broglie's waves are not simply mathematical conveniences, but have observable physical effects. The 1937 Nobel Prize in Physics was awarded to these scientists for their pioneering work. Just as Compton showed that waves could act like particles, Davisson and Germer showed that particles could act as waves.

Heisenberg's Uncertainty Principle

Werner Heisenberg (1927) a German physicist, 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 velocity of an electron'. This principle is an important feature of wave mechanics and discusses the relationship between a pair of conjugate properties i.e those properties that are interdependent. For example, the position and momentum of a moving particle are interdependent and thus conjugate properties. If the momentum (or velocity) is measured very accurately, the measurement of the position of the particle correspondingly becomes less precise. On the other hand, if the position is determined with accuracy, the measurement of momentum becomes less accurate. Thus, certainty of determination of one property introduces uncertainty in determination of the other.

This principle applies to all bodies but becomes significant when applied to bodies with small masses and is negligible in case of large objects.

The momentum Δp should be along the direction x for the principle to hold good. If the product of uncertainty in position Δx and momentum along the y direction is considered, it will be zero.

i.e $\Delta x \, . \, \Delta py = 0$

The following example illustrates the principle. If one is asked to measure the thickness of a sheet of paper with an unmarked metrestick, the result obtained would obviously be inaccurate and meaningless. In order to obtain accuracy, one would have to use an instrument graduated in units smaller than the thickness of the sheet. A substance can be seen only if it could reflect light or any other radiation from its surface. Since the size of electron is too small, its position may be determined by employing light of very small wavelength such as x-rays or γ rays. A photon of radiation of small wavelength has large energy and also momentum. As one such photon strikes an electron, it immediately changes the momentum of the electron. Now as position of the electron is being determined, the momentum gets changed. Thus it is impossible to determine the exact position of an electron which is moving with a definite velocity.

Experimental verification – A high powered microscope with proper lighting arrangement is set up

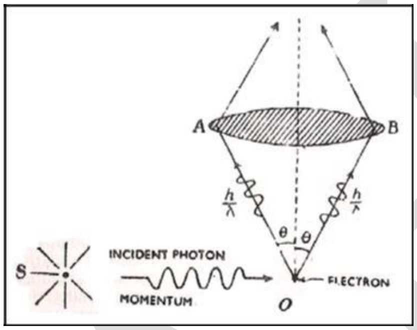


Fig: 7

When photons from sources collide with the electrons, some of the electrons bounce into the microscope and enable the observer to see the flash of light and thus to measure both position and momentum of the electron at a particular instant of time. The position of the electron is determined using the following equation of optics, where the resolving power of microscope.

Δx- is minimum distance between two points which can be distinguished as separate. Radiation of short wavelength (x-rays or gamma ray) is preferred to make Δx value very small. Thus Δx is the error or uncertainty in measurement or the position of electron.

λ - wavelength of photon
θ - semivertical angle of the cone light coming from illuminated electron.

Quantum Mechanical Model of Atom

The motion of all macroscopic objects such as falling stone, planets and their satellites having particle like behaviour is best described by classical mechanics based on Newton’s laws of motion. However, it fails when applied to microscopic objects like atoms, electrons etc. The reason lies in the fact that classical mechanics ignores the dual behaviour of matter and the uncertainty principle.

Quantum mechanics was developed by Werner Heisenberg and Erwin Schrodinger. It is a theoretical science which deals with the study of the motions of the microscopic objects that have both wave and particle like properties. It specifies the laws of motion that these objects obey. When applied to macroscopic objects (for which wave like properties are insignificant), the results are the same as those obtained from classical mechanics.

Schrodinger's Wave Equation

The Schrodinger equation has two 'forms', one in which time explicitly appears, and so describes how the wave function of a particle will evolve in time. In general, the wave function behaves like a wave, and so the equation is often referred to as the time- dependent Schrödinger wave equation. In the other equation time dependence has been 'removed' and it is known as the time- independent Schrödinger wave equation. These are not two separate, independent equations. The time- independent equation can be derived readily from the time- dependent equation.

The time independent equation is written as

$$\hat{H}\Psi = E\Psi$$

Here $\hat{H}$ is the energy operator known as Hamiltonian, Ψ is the wave function of the system and E is the total energy of the system

$$\hat{H}\Psi = \check{T} + V$$

Hamiltonian operator is the sum of kinetic energy operator ($\check{T}$) and potential energy operator (V)

Therefore, Schrodinger equation can be written as

$$(\check{T} + V)\ \Psi = E\Psi$$

By writing the explicit mathematical forms of $\check{T}$ and V the above equation can be solved to get E and Ψ for the system.

For any system, the quantum mechanical study consists of following three steps;

a. Writing Schrödinger equation for the system
b. Solving Schrödinger equation to get meaningful solutions of the wave functions and corresponding energies.
c. Calculation of all the observable properties of the system.

The results obtained by solving the Schrodinger equation for a system are in agreement with the experimental findings.

Some Comments on Schrodinger Equation:

1. The Schrödinger's wave equation is a second degree differential equation. It has several solutions some of which are imaginary and are not valid. If the potential energy term is known, the total energy 'E' and corresponding wave function ψ can be evaluated.
2. ψ is called the probability amplitude and is known as the wave function. It describes the behaviour of a particle as a function of x and t. This concept is known as ' Born interpretation of ψ' and refers to a system in which the probability of finding the particle at any point is independent of time. Such a state is called stationary state.
3. Inspite of ψ being complex, ψ can always be chosen to be real for a 1-D bound state.
4. At infinity the value of ψ is zero. It means that at infinity the electron is not influenced by the attractive force of the nucleus.
5. ψ has only one finite value at any particular point. It means that ψ is single-valued.
6. For any value of potential energy, there will be many solutions (frequently an infinite number) each with a corresponding energy E. But very few solutions describe the known behaviour of electrons. The permitted solutions for ψ are called eigen functions and corresponding values of E are called eigen values.

Physical significance of ψ - The wave function ψ gives the amplitude of the wave. The intensity of wave property is known to be proportional to the square of the amplitude of the wave function. Therefore, the intensity of the electron in the atom is proportional to the square of the amplitude ψ. By intensity of the electron is meant the electron density, i.e if ψ^2 is more near one point than another point in the vicinity of the atom s nucleus, it will be found more often near the point with larger ψ^2 than near the point with less value of ψ^2. Thus it can be said that ψ in itself has no physical significance, and all that can be known about the internal structure of matter is through ψ^2. It helps in locating the relative probability of finding the electron. This uncertainty in finding the electron is in conformity with Heisenberg's uncertainty principle. The exact energy can be found out with the help of equation and hence there would be a great degree of uncertainty in finding the position of the electron.

Important Features of the Quantum Mechanical Model of Atom

The picture of the structure of the atom which emerges from the application of Schrodinger's equation is given by Quantum Mechanical model of atom. Its main features are:

1. The electrons in atoms can have only certain specific values, hence it is said that energy of electrons in atoms is quantized.

2. The existence of quantized electronic energy levels is a direct consequence of the wave like properties of electrons.

3. From Heisenberg's uncertainty priniciple, it is established that both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously. Thus the path of an electron in an atom can never be determined, hence the concept of probability of finding the electron at different points in an atom arises.

4. An atomic orbital is the wave function ψ for an electron in an atom. An electron is said to occupy an orbital, whenever it is described by a wave function. As many such wave functions are possible for an electron, there are many atomic orbitals in an atom. An orbital can contain a maximum of two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For every electron, there is a orbital wave function characteristic of the orbital it occupies. All the information about

the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information from ψ.

5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e ψ^2 at that point. This ψ^2 is the probability density and is always positive.

Difference between Orbit and Orbital

As postulated by Bohr, orbit is a definite circular path around the nucleus in which an electron revolves, whereas an orbital is a three dimensional region in space around the nucleus with in which there is maximum probability of finding an electron having certain energy. An orbit specifies a definite trajectory of an electron in an atom (eg. Bohr suggested that electron of hydrogen atom will always be at a distance of 0.53 ^{0}A from the nucleus) whereas according to wave mechanics, it is impossible to describe the trajectory of an electron in an atom at any time, and only probability or relative chance of finding an electron with a probability velocity can be started. Thus an orbital does not specify a definite trajectory of an electron in an atom as electron may be found at any distance from the nucleus in the orbital. The total probability of finding the electron in a given volume can be calculated by the sum of all the products ψ^2 and the corresponding volume elements. It is thus possible to get the probable distribution of an electron in an orbital. In an orbit, there is certainty about movement of electron which is in violation of Heisenberg's uncertainty principle, where as the orbital follows the uncertainty principle of Heisenberg.

Quantum Mechanical Treatment of the Hydrogen Atom

Hydrogen atom is the simplest chemical system as it consists of one proton and one electron. In a coordinate system, nucleus being stationary is taken as the origin and it is assumed that electron moves at a distance r around the stationary nucleus. Schrodinger equation for the hydrogen atom can be written in terms of the Cartesian coordinates (x,y,z,) or in terms of the spherical polar

coordinates (r, θ, φ) of the electron with respect to the nucleus.

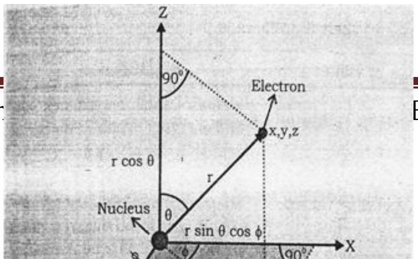


Fig. 8

Since an atom has spherical symmetry it is more convenient to write Schrodinger equation in terms of polar coordinates. The coordinates x, y and z of electron in terms of polar coordinates are given by:

$x = r \sin \theta \cos \varphi$

$y = r \sin \theta \sin \varphi$

$z = r \cos \theta$

$x^2 + y^2 + z^2 = r^2$

For Hydrogen atom, the possible energy states and the corresponding wave function [Ψ (r, θ, φ)] can be obtained on solving Schredinger equation in polar coordinates [Ψ (r, θ, φ)] are known as atomic orbitals The atomic orbital is the product of two factors:

(1) Radial part dependent on r, and
(2) Angular part dependent on θ and φ

The quantized electronic states of the hydrogen atom are given by

$$En = \frac{mee^4}{8\varepsilon 0^2 h^2 n^2}$$

where me is the mass of electron in kg, e its charge in C, h the Planck ‘ s constant, n the principal quantum number and ε0 is the permittivity of free space i.e. the ease with which electromagnetic radiation pass through it.

The quantised energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal ‘n’, azimuthal ‘l’ and magnetic ‘m’) arise as a natural consequence in the solution of Schrodinger equation. The restrictions on the values of three quantum numbers also come naturally from this solution. Thus all aspects of the hydrogen atom spectrum and other phenomena that could not be explained by Bohr model are successfully predicted by quantum mechanical solution of the hydrogen atom.

Shapes of Atomic Orbitals

The quantum-mechanical treatment of electrons in atoms gives a clear picture of the energy levels associated with every atomic orbital which can be defined by a set of four quantum numbers.

The location of an electron can be described in two ways using the quantum-mechanical results. If the electron is visualized as a very small object moving very rapidly, then the space it occupies can be described in terms of the probability of finding the electron at a given point or within a given space at any instant. If the desired probability is set at 99%, or 95%, a physical space occupied by the electron can be calculated on this time-average basis. If on the other hand, the electron is visualized as an electromagnetic wave, then the amplitude of that wave or the wave function will be greater at some locations than at others. The space the electron occupies can be considered to be the space within which the amplitude of its wave function is greater than 1%, or 5%, of its maximum amplitude.

The electron can be described equally well in either way or the three-dimensional spaces defined as "containing" the electron as a wave and as a particle are the same. Chemists find it convenient to describe the location of electrons in atoms and molecules in terms of this type of shape. These representations of orbital shapes are those which are said to contain 99% or 95% of the electron density of the orbital.

s - Orbitals : Orbitals with subshell quantum number l = 0 are called s orbitals. These orbitals are spherical in shape and have spherical symmetry. This means that the wave function will depend only on the distance from the nucleus and not on the direction or on its angular position. The designation 's' refers to the lines in the spectrum as sharp. There can be only one s orbital or sub shell for any specific main energy level and diagrammatically portrayed as a sphere centered at the origin of three mutually perpendicular cartesian axis as depicted in fig 1.8. The figure shows wave function $(\psi)^2$ against radial distance from the nucleus for hydrogen s orbitals. This plot, which represents the relative probability of finding the electron per unit volume, is difficult to visualize physically because there is much less volume close to the nucleus than further out. It is easier to visualize where the electron may be by plotting the radial probability density $4(\pi)r^{2}(\psi)^{2}$, rather than $(\psi)^{2}$, against the distance from the nucleus as shown on the right of the Figure.

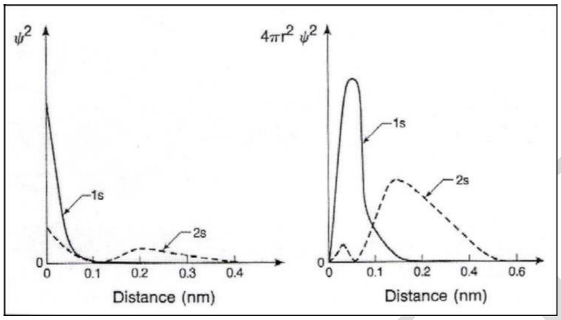


Fig. 9

The size of the s orbital increases as the principal quantum number of the orbital increases but the geometry remains spherical. The electron density also tends to extend further. Other orbitals behave in the same way as the principal quantum number of the orbitals increase.

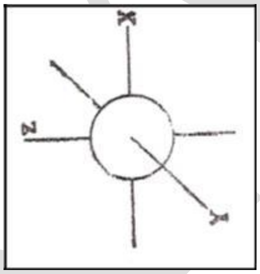


Fig.10. s- orbital

p- Orbitals: Orbitals with subshell quantum number l = 1 are called p orbitals. Since the magnetic quantum number m can be –1, 0 or +1 when the value of the subshell quantum number l is one, the p orbitals come in sets of three. One of these orbitals is aligned along each of the three mutually perpendicular axes of the atom which are traditionally designated x, y, and z. The three 2p orbitals are correspondingly designated 2px , 2py, and 2pz. The p orbitals, either as a set or individually, do not have spherical symmetry and so a simple plot of radial probability density cannot be made for them. If, however, the distance from the nucleus is taken along any one of the three axes and the orbital is along the same axis, then a suitable plot can be made as shown in the Figure 11 below.

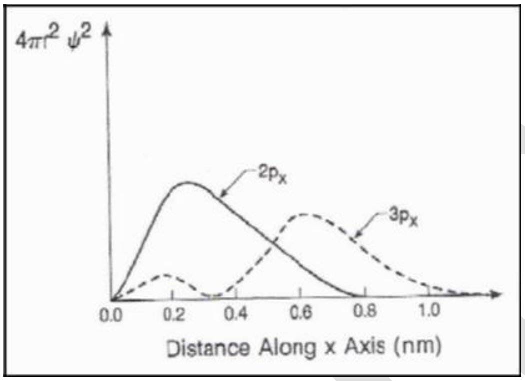
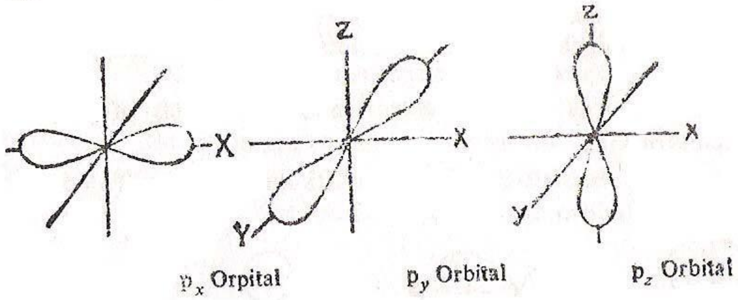


Fig.11

A p orbital has two lobes like a dumb-bell. p refers to designation of spectral lines as 'principal'. The diagrammatic representation of the three separate p orbitals is along the three Cartesian axes X, Y and Z. However, the three individual orbitals collectively considered as superimposed may be totally visualized as concentrically spherical around the origin of the Cartesian axes (fig.12).



d- Orbitals : Orbitals with subshell quantum number l=2 are called d orbitals. Since m can be 2, -1, 0, +1, or +2 when l is two, the d orbitals come in sets of five. These have the same radial function but differ in angular distribution. Four out of five i.e dxy, xyz, dzx and dx2-y2 are similar in shape. These are formed by insertion of two mutually perpendicular planes into spherical pattern dxy lies along the plane XY, dyz lies along the plane YZ and dzx lies along the plane ZX. Their lobes lie in between the axis, making an angle of 45^0 with axes. The orbital dx2 -y2 lies along the plane XY, just as dxy orbital but is related by 45^0 around Z axis, so that the lobes are along X and Y axes and the nodal planes lie midway between the nodal planes of the dxy orbital. The fifth orbital, dz^2 is symmetrical around Z-axis and has two cone shaped nodal surface with the angle between the elements of the cone and Z-axis approximately equal to 45^0.

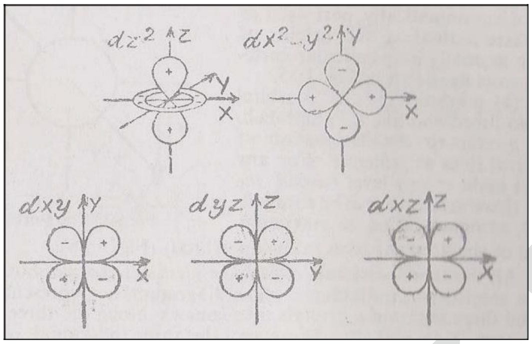


Fig. 13.

f- Orbitals : Orbitals with subshell quantum number l=3 are called f orbitals. Since m can be –3, -2, -1, 0, +1, +2, or +3 when l has the value 3, f orbitals come in sets of seven. Out of the seven orbitals, two f orbitals possess nodal planes separated by 60^0; two others have three mutually perpendicular nodal surfaces and remaining three have two conical and one planar surface each.

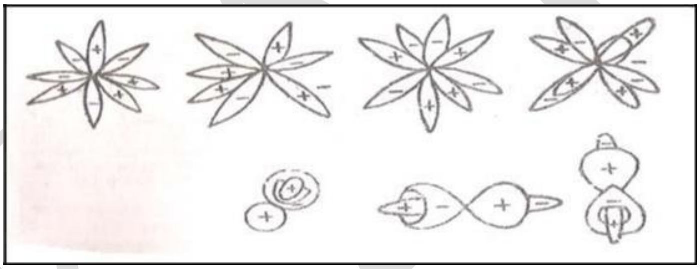


Fig. 14

The f orbitals are rarely of direct chemical interest because they tend to be buried deep within the electronic cloud of an atom, but they do play a role in the spectroscopy of the lanthanides and actinides. These are the most complex orbitals with which most chemists have to deal.

Radial Probability Distribution

The probability of finding an electron within a small radial space around the nucleus is termed as radial probability distribution. The main feature of radial distribution plots is that they determine the spatial extent of the orbit.

Consider the space around the nucleus to be divided into a large number of uniform concentric shells. In between radii r and r+dr the volume of the spherical shell would be $4\prod r^2 dr$. Thus the probability of finding an electron within this spherical shell would be $4\prod^2 \psi r^2$. This value is the radial probability at a distance r from the nucleus. In the function $4\prod r^2 dr\psi^{\,2}$, the probability factor ψ^2 decreases whereas the volume factor $4\prod r^2 dr$ increases with increase in the value of r. The function $4\prod r^2 dr\ \psi^2$ when plotted against the distance or from the nucleus gives the radial probability distribution of the electron.

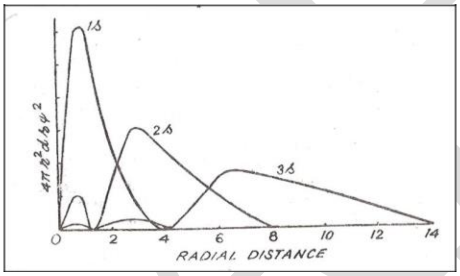


Fig. 15

Fig.15 shows the radial distribution functions for 1s, 2s and 3s states of the hydrogen atom

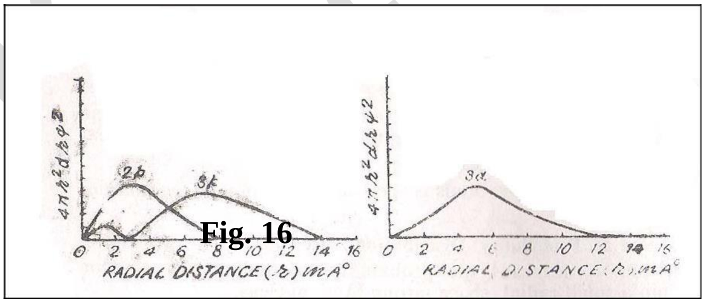


Fig. 16

Fig.16 shows the same for 2p, 3p and 3d states of the hydrogen atom.

1. When r=0, the probability of finding the electron is zero, i.e at nucleus, the probability of finding an electron is zero.

2. For a larger value of principal quantum number n, the electron will be farther from the nucleus.

3. The value r0 = 0.529 $^0 A$ of maximum radial probability in the radial distribution curve from the nucleus has been found to be in close agreement with the Bohr's calculated value for the radius of first circular orbit.

4. Radial distributions overlap, revealing that the outer electrons penetrate the region occupied by inner electrons in an atom.

POSSIBLE QUESTIONS

UNIT-I

PART-A (20 MARKS)

(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. What is the significance of ψ and ψ^2.
2. Write the de Broglie equation.
3. Draw radial probability distribution curves for 2s, 3s orbitals.
4. Define node.
5. What do you understand by the term nodal plane?

PART C (6 MARKS)

6. What do you understand by dual character of matter? Derive the de Broglie relation. How was it verified?

7. Explain Radial and angular nodes and their significance.
8. State the postulates put forth by Bohr to describe the theory of H-atom.How did Bohr derive the expression for the energy and the velocity of an electron moving in a particular orbit of H-atom.
9. Discuss briefly how the radial wave function and angular wave function yield information about the shapes of orbitals.
10. Write a note on Heisenberg uncertainity principle
11. Draw the radial probability distribution curves for 2s and 2p electrons and explain the difference
12. Explain Heisenberg uncertainity principle. Show that this principle is valid only for small particles and not for large objects.
13. Derive the time independent Schrodinger equation.

S.No.	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1.	The wave associated with particles is called	De Broglie wave	electromagnetic wave	radiowaves	infrared wave	De Broglie wave
2.	The wave associated with particles is called	matter wave	electromagnetic wave	radiowaves	infrared wave	matter wave
3.	De Broglie wave is associated with	electron	atom	molecule	particles	particles
4.	Einstein mass energy relationship is	$E = mc/2$	$E = mc2$	$E/2 = mc$	$E = m2c$	$E = mc2$
5.	$E = mc^2$ is called	De Broglie relation	Einstein mass energy relationship	Heisenbergs principle	Hund's rule	Einstein mass energy relationship
6.	$\lambda = h/p$ is called	De Broglie relation	Einstein mass energy relationship	Heisenbergs principle	Hund's rule	De Broglie relation
7.	The wavelength of the wave associated with any material particle was calculated by analogy with photon. This is	De Broglie relation	Einstein mass energy relationship	Heisenbergs principle	Hund's rule	De Broglie relation
8.	$\Delta x.\Delta v = h/4\pi m$ The equation is called	De Broglie relation	Einstein mass energy relationship	Heisenbergs principle	Hund's rule	Heisenbergs principle
9.	Position and velocity of a particle cannot be measured simuntaneously with certainty. This is	De Broglie relation	Einstein mass energy relationship	Heisenbergs principle	Hund's rule	Heisenbergs principle
10.	De Broglie equation has significance only to	microscopic particles	macroscopic particles	rocks	big stones	microscopic particles
11.	De Broglie equation is applicable and siginificant only to microscopic particles because	The wavelength produced by a larger particle is too small to be observed	The wavelength produced by a larger particle is too large to be observed	Planck's constant changes for a bigger particle	momentum is not constant for larger molecules.	The wavelength produced by a larger particle is too small to be observed
12.	In Schrodinger wave equation, the electron motion is considered to be a	superimposed wave	stationary wave	intrifringes	polarised	stationary wave

13.	The number of radial nodes for 3p orbital is ___________	3	4	2	1	1
14.	Among the conditions which one is correct for the wavefunction ψ to satisfy and give meaningful solution	ψ must be single valued	ψ must be discontinuous at all points in space	ψ must become unity at infinity	ψ should not be normalise	ψ must be single valued
15.	Among the conditions which one is correct for the wavefunction ψ to satisfy and give meaningful solution	ψ must be multiple valued	ψ must be continuous at all points in space	ψ must become unity at infinity	ψ should not be normalise	ψ must be continuous at all points in space
16.	Among the conditions which one is correct for the wavefunction ψ to satisfy and give meaningful solution	ψ must not be single valued	ψ must be discontinuous at all points in space	ψ must become zero at infinity	ψ should not be normalise	ψ must become zero at infinity
17.	Among the conditions which one is correct for the wavefunction ψ to satisfy and give meaningful solution	ψ must not be single valued	ψ must be discontinuous at all points in space	ψ must become unity at infinity	ψ should be normalise	ψ should be normalise
18.	The significant values of the wave function ψ are called	Eigen functions	Radial function	angular function	Heisenberg function	Eigen functions
19.	Number of angular nodes for 4d orbital is ___________.	4	3	2	1	2
20.	Orbital angular momentum depends on ___________.	l	n and l	n and m	m and s	1
21.	Photon---------	Value is 4 for N shell	Probability density	Always positive value	Exhibits both momentum and wavelength	Exhibits both momentum and wavelength
22.	Electron------------	Value is 4 for N shell	Probability density	Exhibits both momentum and wavelength	Always positive value	Exhibits both momentum and

						wavelength
23.	There is no difference 2p and a 3p orbital regarding	shape	size	Energy	value of a	shape
24.	Which orbital does not possess angular node	s	p	d	f	s
25.	The number of radial and angular nodes in 3p subshells are ____	1 and 1 respectively	1 and 2 respectively	2 and 1 respectively	1 only	1 and 1 respectively
26.	In the atomic spectrum of hydrogen the series of lines observed in the visible region is	Paschen series	Balmer series	Brackett series	lymann series	Balmer series
27.	The velocity of a photon ----	independent of its wavelength	Depends on its wavelength	Depends on its source	equal to square of its magnitude	independent of its wavelength
28.	Which of the following is not the property of the photons----	velocity	Energy	Momentum	Rest mass	Rest mass
29.	The Planck's constant has a unit of -----	work	energy	Linear momentum	angular momentum	angular momentum
30.	Of the following transitions in hydrogen atom, the one which gives an absorption line of lowest frequency	n=1 to n=2	n=3 to n=8	n=2 to n=1	n=8 to n=3	n=3 to n=8
31.	Transition of electron from n=3 to n=1 level results in ----	emission spectrum	band spectrum	IR spectrum	X-ray spectrum	emission spectrum
32.	The number of spherical nodes in 3p orbitals is -------	1	2	3	zero	1
33.	Which of the following is expressions gives the de Broglie relationship-----	h/mv=p	λ = h/mv	λ = h/mp	λm = v/p	λ = h/mv
34.	In hydrogen atom when electron jumps from 1s to 2s orbital ------	energy is released	energy is absorbed	atom becomes cation	size of the atom decreases	energy is absorbed
35.	For azimuthal quantum number l=3, the maximum number of electrons will be -----	2	14	6	10	14
36.	Transition from n=4,5,6……. to n=3 level in hydrogen spectrum gives ----	Paschen series	Balmer series	Brackett series	lymann series	Paschen series

37.	For which species Bohr's theory does not apply---	H	He+	Li2+	Be	Be
38.	Which represents the correct set of four quantum numbers------	4,3,2,+1/2	4,2,1,0	4,3,-2,+1/2	4,2, 1,+1/2	4,2, 1,+1/2
39.	Which of the following relates to photon both as wave motion and a stream of particles------	interference	E=mc2	diffraction	E=hv	E=hv
40.	Which electronic level will allow the hydrogen atom to absorb photons but not to emit---	1s	2s	2p	3d	1s
41.	De broglie equation describes the relationship of wavelength associated with motion of an electron and	Mass only	mass and velocity	position	distance from the nucleus	mass and velocity
42.	Each subshell of a shell possesses------ in H atom.	same energy level	different energy levelincreasing energy level	decreasing energy level	same energy level	
43.	The energy of electron at infinite distance from the nucleus in Bohr's model is taken as	negative	positive	zero	any value	zero
44.	Energy will be absorbed in separating---	an electron from a proton	an electron from an electron	A proton from a proton	A neutron from a neutron	an electron from a proton
45.	In the Schrodinger wave equation, ψ represents	amplitude function	orbital	wave function	all	all
46.	In hydrogen spectrum least energetic transition are found in -----	Pfund series	Balmer series	Brackett series	lyman series	Pfund series
47.	In hydrogen spectrum most energetic transition are found in -----	Pfund series	Balmer series	Brackett series	lyman series	lyman series
48.	Outer orbits have ----- energy than inner orbits	greater	smaller	same	equal	greater

49.	Bohr model of atom is contradicted by?	pauli's exclusion principle	plancks quantum theory	Heisenberg uncertainity principle	all the three	Heisenberg uncertainity principle
50.	Heisenberg's uncertainity principle is applicable to ------	atoms only	electrons only	nucleus only	any moving object	any moving object
51.	Bohr model of atom explains	zeeman effect	photoelectric effect	stark effect	none of the above	none of the above
52.	Bohr model of atom cannot explains	zeeman effect	stark effect	fine spectrum	all of these	all of these
53.	The de Broglie equation treats an electron to be	a particle	a wave	both a particle and wave	particle,wave not explained	both a particle and wave
54.	The probability of finding the electron in the nucleus is	zero for all objects	zero for some orbitals and finite for others	finite for all orbitals	infinite	zero for all objects
55.	The electronic configuration of H+ is	1s0	1s1	1s2	1s2 2s1	1s1
56.	The electronic density between 1s and 2s orbital is	high	low	zero	two	zero
57.	The uncertainity principle and the concept of wave nature of matter was proposedby --and -- respectively	Heisenberg, de Broglie	de Broglie,Heisenberg	Heisenberg, Planck	Planck,Heisenberg	Heisenberg, de Broglie
58.	The probability of finding an electron residing in a px orbital is zero	in the yz plane	in the xy plane	in the y direction	in the z direction	in the z direction
59.	Bohr's model can explain	spectrum of H only	spectrum of any atom or ion having one electron only	spectrum of hydrogen molecule	solar spectrum	spectrum of any atom or ion having one electron only
60.	The transition of electron from ------- level results in emission spectrum	n=3 to n=1	n=4 to n=1	n=1 to n=4	n=5 to n=1	n=3 to n=1

UNIT II

SYLLABUS

Significance of quantum numbers, orbital angular momentum and quantum numbers *ml* and *ms*. Shapes of *s*, *p* and *d* atomic orbitals, nodal planes. Discovery of spin, spin quantum number (*s*) and magnetic spin quantum number (*ms*). Rules for filling electrons in various orbitals, Electronic configurations of the atoms. Stability of half-filled and completely filled orbitals, concept of exchange energy. Relative energies of atomic orbitals, Anomalous electronic configurations.

Quantum Numbers

The Bohr model was a one-dimensional model that used one quantum number to describe the distribution of electrons in the atom. The only information obtained was the size of the orbit, which was described by principal quantum number ‘n’. This could hardly explain the hydrogen spectrum adequately and the spectra of other elements that are quite complex also remained unexplained by this concept. Many single lines of spectra are found to consist of a number of closely related lines when studied with the help of sophisticated instruments of high resolving power. Spectral lines split up when the source of radiation is placed in a magnetic field (Zeeman effect) or in an electric field (Stark effect). Schrödinger’s model allowed the electron to occupy three dimensional space. It, therefore, required three coordinates or three QUANTUM NUMBERS, to describe the orbitals in which the electrons can be found. The three coordinates that come from Schrödinger’s wave equation are the principal (n), angular (l) and magnetic (m) quantum numbers. In all, there are four identification numbers called quantum numbers which fully describe an electron in an atom. The word quantum is used to signify that all the energy levels which are available to an electron are governed by the laws of quantum mechanics.

1. **Principal Quantum Number:** This quantum number denotes the principal shell to which the electron belongs. This is also referred to as major energy level. This number is designated as ‘n’ and is identical with Bohr’s integers to describe stationary states in an atom. Thus it gives the number of principal shell in which the electron revolves around the nucleus. It designates the average distance of the electron from the nucleus hence specifies the location.

As the value of ‘n’ increases, the energy levels get further away from the nucleus. The value The value of energy of orbit increases with increase in value of ‘ n’ and becomes zero at n=∝. Beyond this, the energy is no longer quantized and the electron is not bound to the nucleus and can have any arbitrary amount of kinetic energy. The spectrum in this region does not contain lines but is continuous and is called continuum. The difference in energy between En-1 and En-∝ is the energy needed to ionize the atom and is called the ionization energy.

The principal quantum number ‘n’ can have non- zero positive integral values from 1 to ∝. The energy levels 1,2,3,4 etc are also designated by letters K, L, M, N, etc. Although the quantum number ‘n’ may theoretically assume any integral value from 1 to ∝, only values from 1 to 7 have so far been established for atoms of known elements in their ground states. As the first energy level is nearest to the nucleus, it binds strongly to the nucleus. The next energy level is farther from the nucleus and hence binds to the nucleus with a lesser force and so on. Therefore, the principal quantum number signifies:

a) The size of the electron orbit i.e distance between the nucleus and the electron.
b) The binding force between the nucleus and the electron.

2. Azimuthal Quantum Number: This quantum number is also known as subsidiary, angular momentum quantum number (l). Each shell is made up of subshells. The number of subshells in a shell is given by its principal quantum number. Thus 1st shell or K has only one sub shell. 2nd shell or L has two sub shells. 3rd shell or M has 3 subshells. These subshells differ from one another in their azimuthal quantum number (l) values, and hence differ in their shapes.

Values of l=0, 1,2,3…… are denoted by the symbols :s, p, d, f which are derived from the names of the spectral lines sharp, principal, diffuse and fundamental respectively. The s subshell is spherical, p the dumb-bell shaped, d and f have complicated shapes. Thus azimutual quantum number determines the shape of the orbital (electron cloud) i.e whether the cloud is spherical, dumb-bell shaped or has some other complicated shape. In a particular energy level the energies of its subshells are in the order

$$s < p < d < f$$

Thus, s electrons will shield p electrons from the attraction of the nucleus and p electrons will shield d electrons from the nucleus. Therefore, the sequence of filling the various subshells is s, p, d, f and so on.

3. Magnetic Quantum Number: This quantum number was introduced to describe the Zeeman's effect i.e splitting of spectral lines under the influence of an applied magnetic field. A shell is made up of one or more subshells and each subshell is made up of one or more orbitals. The number of orbitals in a shell is n^2 where n is the principal quantum number. Each orbital has a characteristic magnetic quantum number and can accommodate up to two electrons.

When an atom is placed in a magnetic field (Zeeman's effect), the orbitals orient themselves relative to the magnetic field. This is due to the presence of negatively charged electrons in it. The orientation in the magnetic field is determined by the magnetic quantum number (m).

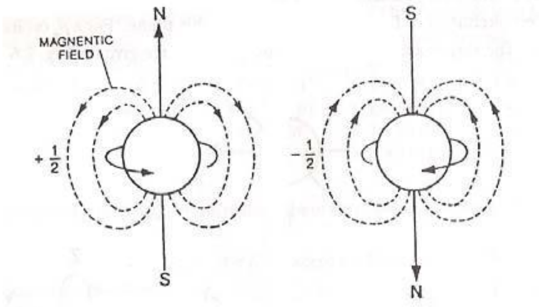
Magnetic quantum number is designated as 'm' and can have values from +l to –l through zero. Every value of m, for a given value of l, corresponds to one orbital in that subshell designated by l. Thus:

1) s will have one orbital as m has only one value, m = 0
2) p will have three orbitals as m has three values +1, 0, -1.
3) d will have five orbitals as m has five values +2, +1, 0, -1, -2).
4) f will have seven orbitals as m has seven values +3, +2, +1, 0, -1, -2,-3.

It means that two orbitals in the same subshell can have identical n & l values but must differ in 'm' values.

Thus p subshell is made up of three identical orbitals. But in a magnetic field, the three orbitals take up different positions with respect to the lines of force of field and thus have slightly different energy levels. Therefore, the three 2p orbitals are designated as 2px, 2py and 2pz. Similarly, in a magnetic field, the 3d orbitals are designated as dx^2-y^2, dz^2, dxz, dyz, dxy.

4. Spin Quantum Number: The fact that an electron in its motion around the nucleus also rotates or spins about its own axis, gives birth to spin quantum number. This quantum number is designated as 's'. It indicates the direction in which the electron is spinning. Spin can be either clockwise or anticlockwise. Clockwise spin is represented by an arrow pointing upwards (↑), while anti-clockwise spin is represented by an arrow pointing downwards (↓). The spin of electron contributes to its overall angular momentum and since it can be either clockwise or anticlockwise relative to the direction of the path of electron, it may cause angular momentum to increase or decrease.



This results in two sub levels of slightly different energy for each value of m, thus corresponding to two possibilities of s. It is assumed that the total energy difference between two sub levels is one quantum i.e. s level will have values $+\frac{1}{2}$ and $-\frac{1}{2}$.

An orbital can accommodate two electrons provided they have opposite spins. Such electrons are known as paired electrons. When an orbital has only one electron, it is known as odd or unpaired electron.

The spin quantum number gives rise to magnetic properties of materials. When the electrons are paired, they have opposite spins and their magnetic moments will be cancelled. Presence of magnetic properties indicates the presence of one or more unpaired electrons.

Pauli’s Exclusion Principle

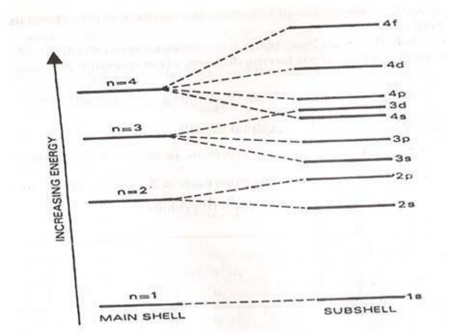
The four quantum numbers ascribed to an electron fully describe its nature, position and energy. Wolfgang Pauli (1925) put forward an ingenious principle which controls the assignment of values of four quantum numbers to an electron. It states that “*No two electrons in a single atom can have all the quantum numbers identical”.*

The above statement implies that even if two electrons have the same values for n, l and m, they must have different values of s. It is clear that electrons having the same value of n, l and m i.e. entering the same orbital should have opposite spin. More so, state of opposite spin gives a lower energy state as compared to that parallel spins. According to the thermodynamics, a system having lower energy has maximum stability. Hence the preferred state is the one with electrons having opposite spins. Pauli’s principle can also be stated as ‘Two electrons can occupy the same orbital only if their spins are opposed’.

Energy Distribution and Orbitals :

a) One electron atom - Hydrogen is the simplest of all atoms as it has only one electron, which in the ground state occupies the first energy level (n=1). On absorbing energy, it may jump to higher energy levels like 2s, 2p, 3s, 3p etc. Then n^2 levels for any value of 'n' in hydrogen atom have the same energy as shown in the energy level scheme for hydrogen atom.

The spectral study of hydrogen has revealed that its spectral lines correspond to the major energy levels only. Thus the energy value of an electron having a particular quantum is fixed, irrespective of the orbital to which it may belong. It implies that energy associated with electrons in s, p, d and f orbitals of a particular principal quantum number is the same, e.g. – the energy level of 3s, 3p and 3d orbitals is equal.



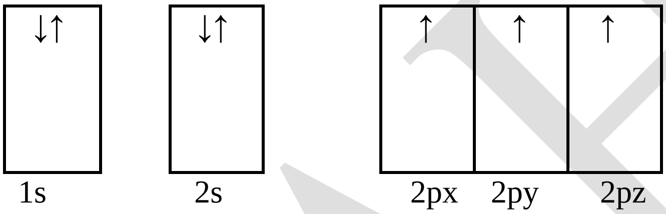
b) **Poly-electron atom** – In a two electron atom, the second electron differs from the first electron in spin only. It is also accommodated in 1s orbital thereby completing the K shell. This completed K shell affects the energy of the electrons occupying subsequent energy levels. For atoms having more than two electrons, the nuclear charge is shielded from the outer electrons by the two K shell electrons. This makes the energy level of any orbital in a principal level 'n' dependent upon the value of orbital quantum number l. The dependence of energy of orbitals of a shell on l (s, l = 0; p, l = 1) is because of the fact that s orbital electrons (l=0), penetrate near the nucleus and are, therefore, less effectively shielded from the nuclear charge. The s electron being less shielded are drawn inwards and possess lesser energy than p-orbital electron (l=1). The same argument can be extended for other values of l. Within each energy level 'n', the various sub levels (different l value orbitals) exhibit slightly different energies. The orbitals at a principal level 'n' get split up and come to possess different energies, which increase in the same order as the values of l. Thus, for a particular principal level, the energy of the sub levels is in the order s < p < d < f. The energy levels of 4s, 4p, 4d and 4f orbitals are different even though they belong to the same shell n = 4. However, the energy of electrons in the same orbital is same. Thus all the 4d orbitals (4dxy, 4dyz, 4dzx, $4dz^2$, $4dx^2$-y^2 or 3p orbitals (3px, 3py and 3pz.) are at the same level of energy, irrespective of their orientation.

Hund's Rule of Maximum Multiplicity

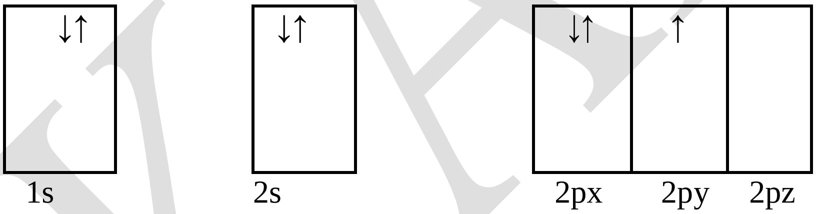
On the basis of magnetic measurements, Hund(1925) put forward an empirical rule known after his name as 'Hund's Rule of Maximum Multiplicity'. This states that 'Electrons are distributed among the orbitals of a sub shell in such a way as to give the maximum number of unpaired electrons and hence the same direction of spin'. It implies that the pairing of electrons in any orbital of a sub shell will occur only when all the available orbitals of it (sub shell) have one electron each.

Examples : The following examples will illustrate the applications of Hund's rule.

1. Nitrogen has atomic number 7 and hence will have the following configuration. $1\ s^2\ 2s^2\ 2p^3$

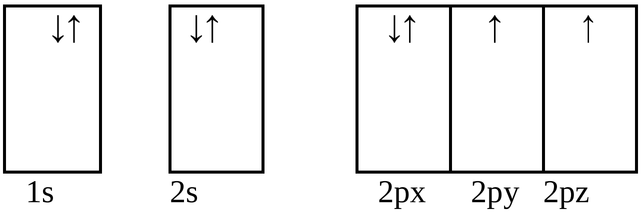


and not



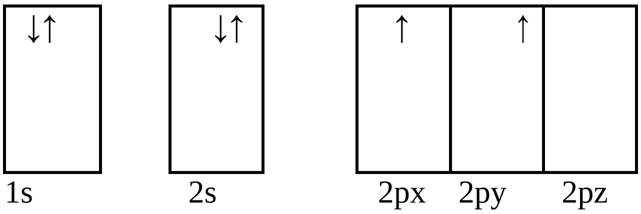
The above configuration also explains the covalency of nitrogen which is three, as three electrons are required for complete pairing of the three electrons present in p-sub shell.

2. Oxygen has atomic number 8 and the following configuration
$1s^2$, $2s^2$, $2p^4$



3. Carbon has atomic number 6

In ground state its electronic configuration is $1s^2\ 2s^2\ 2p^2$



4. In Eu (At no = 63) the electronic configuration is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $4f^7$, $5s^2$, $5p^6$, $6s^2$.

Here seven f orbitals have to accommodate seven electrons. Hence, each f orbital is singly filled i.e there is no pairing.

5) In Tb (At no = 65) the electronic configuration is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$,$4p^6$, $4d^{10}$, $4f^9$, $5s^2$, $5p^6$, $6s^2$.

Here seven f orbitals have to accommodate nine electrons. Hence two of these are doubly filled while the remaining five are singly filled. Thus, in these atoms pairing starts only after all the seven f orbitals have been singly filled first.

In excited state the energies of 2s and 2p come further close and hence the four electrons (all in 2s and 2p) divide themselves between four orbitals. Thus covalency of carbon is four.

6. Iron has atomic number 26. Electronic configuration according to Aufbau principle will be: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^6$

But empty (p^0 d^0), half filled (p^3 d^5) and completely filled (p^6 d^{10}) orbitals of a sub shell provide symmetry and are more stable as compared to other arrangements. Thus, the other stable configuration for iron will be: $1s^2$, $2s^2$, $2p^{-6}$, $3s^2$, $3p^6$, $4s^2$, $3d^5$, $4p^1$

In former case, the valency of iron will be two and in the latter case, it will be three.

Explanation: The three orbitals px, py and pz have equal energy but are concentrated in different regions of space at right angles to each other. Electrons can minimize the repulsive forces between themselves by occupying different orbitals and having parallel spins. This explains their preference to enter different orbitals as long as possible.

Cr (At no = 24) $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4d^5$ $4s^1$

Mn (At no = 25) $1s^2$ $s2^2$ $2p^6$ $3s^2$ $3p^6$ $4d^5$ $4s^2$

The expected electronic configuration of copper (atomic no. 29) is

Cu At no = 29

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^9$ $4s^2$

However it is observed that preferred configuration is

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^1$

The stability of half filled and completely filled orbitals may be explained in terms of lowering of energy due to the exchange energy for a set of two electrons with parallel spins.

According to Hund's rule, electrons avoid entering the same orbital in the given sub shell as far as possible. This reduces coulombic repulsion by enlarging the distance between electrons. Also, the electrons entering the different orbitals of a sub shell have parallel spins. This keeps them further apart and lowers the energy through electron exchange and resonance.

The paramagnetic and diamagnetic character of substances especially transition and rare earth elements can be interpreted with the help of Hund's rule.

Aufbau Principle

This is also known as 'building up principle', (Aufbau is a German word meaning building up or construction). The principle mainly deals with the building up process in which the extra nuclear electrons are added to various available orbitals so as to balance the nuclear charge. It broadly states that in the ground state of an atom, the electrons tend to occupy the available orbitals in the increasing order of energy, the orbitals of lower energy being filled first. The main postulates of this principle are:

(1) Lowest Energy Rule – When an atom in ground or unexcited state, it has minimum energy. The electrons in this state tend to occupy the lowest energy orbitals available. This implies that:

a) The orbitals with lower n-values are filled prior to orbitals with higher n-values.

b) For any given principal quantum number n, the order of filling is s, p, d and f.

(2) Order of Energy Levels – The different orbitals are filled up in the ascending order of energy. The order is

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<5s<4f<5d

The correct order of filling of energy can be obtained by considering the sum of principal and subsidiary quantum number (n+l) for the various possible orbitals. The orbital with lowest (n+1) is filled first e.g. – 1s (n+l = 1) is filled before 2s (n+l = 2). When two orbitals have the same (n+l) value, the one with lower n value is filled first i.e. 3p (n+l = 4) before 4p (n+l = 4)

(3) Degenerate orbitals – The orbitals having equal energy are called degenerate orbitals. So p has three equivalent energy orbitals or three fold degeneracy, d orbital has 5 fold degeneracy and f has seven fold degeneracy. While filling the orbitals, no differentiation is made between three p, five d or seven f level(4) Screening Rule – When the inner shells are completely filled with electrons, the outer electrons are screened against attraction by the nucleus. This effect is known as screening effect. As a result of the screening effect, every ns orbital is filled earlier than the corresponding (n-1) d orbital. Hence 4s is filled before 3d.

Deviations from Aufbau Principle :

In some cases, the electronic configuration predicted by Aufbau Principle is different from actual arrangement of electrons as evidenced by spectroscopic methods. This deviation from regularity involves the placing of one or two ns electrons in an (n-1) d level, the energy difference between s or (n-1) d levels being non-significant.

The deviations from regularity may occur due to one of the following reasons:

a) half filled and completely filled orbitals are more stable than partially filled orbitals,
b) diamagnetic nature of atom,
c) to explain the observed properties of elements like lanthanides and actinides.

Effective Nuclear Charge

A hydrogen like atom is an atom that possesses only one electron. Multi electron atoms are characterized by electron- electron repulsion. Unlike a hydrogen like atom, where analytical solutions of Schrödinger equation are available, this equation cannot be solved analytically for multielectron atom owing to the electron-electron repulsion. Interestingly, it is possible to obtain a crude solution for a multi electron atom by making use of a relatively simple construct employing the “effective” nuclear charge in the equations for a hydrogen like atom. The nuclear charge, Z, is the charge of the nucleus. The effective nuclear charge Z* is the amount of positive charge on the nucleus perceived by an electron. Electrons intervening between the nucleus and an outer electron are said to shield or screen the outer electron from the nucleus so that the outer electron does not experience the full nuclear charge.

The effective nuclear charge Z* which is felt by an electron is not the actual charge of the nucleus (Z). J.C. Slater pointed that the amount of nuclear charge actually experienced by an electron depends on the type of orbital and on the ability of other electrons in more penetrating orbitals to screen the electron in question from the nucleus.

When among the orbitals, the value of principal quantum number is same, s orbital is said to be most stable. An orbital with appreciable electron density between the nucleus and a second orbit is said to penetrate the region of space occupied by the second orbital. Thus, the electron is more stable in the more penetrating orbital. The relative extent to which various orbitals penetrate the electron clouds of other orbitals is s>p>d>f. Thus an electron will experience the highest value of effective nuclear charge in a s orbital than a p orbital and so on for any particular value of n i.e. principal quantum number.

It has been observed that when screening of an electron is poor, the effective nuclear charge is correspondingly high. It implies that electrons occupy degenerate set of orbitals in order to experience maximum effective nuclear charge. The above fact is illustrated by the following example. Boron (at no-5) has electron configuration $1s^2\ 2s^2 2p^1$.

The next element in the periodic table is carbon with atomic no.6 and electronic configuration $1s^2\ 2s^2\ 2p^2$. Here the new electron is added in accordance with Hund's rule, Also each new electron will have a new and different effective nuclear charge. For Boron, if the new electron is housed in px orbital, the new electron for C will be housed in another of 2p orbital, say the py orbital. py orbital is perpendicular to the px orbital and is poorly screened from the nuclear charge by px orbital. Thus the effective nuclear charge for the last electron in Carbon is higher than that for Boron. It is the geometry and orientation of the p-orbital that makes them poor at shielding one another from the nucleus. Next to Carbon in the periodic table is Nitrogen (atomic no7) with electronic configuration $1s^2\ 2s^2\ 2p^3$.

The third p-electron is further poorly screened from the growing nuclear charge because the other two p electrons in px and py orbitals lie at 90°C to this last one. Thus the effective nuclear charge for Carbon is higher than that of Boron and that of Nitrogen is higher than that of Carbon.

Slater's Rules :

In 1930, J. C. Slater devised a simple set of guidelines for shielding or screening constant (S). He proposed that this empirical constant represents the cumulative extent to which the other electrons of an atom shield (or screen) any particular electron from the nuclear charge. Thus:

$$Z^* = Z - S$$

Where Z is the atomic number of the atom and Z* the effective nuclear charge. The value of effective nuclear charge Z* is smaller than Z, since the electron is shielded from Z by an amount equal to S. Thus when screening is small, the effective nuclear charge Z* is large.

The value of S for an electron in a given electronic configuration i.e. in presence of other electrons of the atom is calculated using a set of empirical rules given by Slater known as Slater's rules.

If the electron is housed in s or p orbital then

a) All electrons in principal shells higher than the electron in question contribute zero to S.

b) Each electron in the same principal shell contributes 0.35 to S.
c) Electrons in the (n-1) shell contribute 0.85 to S
d) Electrons in deeper shells each contribute 1.00 to S

If the electron is housed in d or f orbital then,

a) All electrons in principal shells higher than the electron in question contribute zero to S.

b) Each electron in the same principal shell contributes 0.35 to S.

c) All inner shell electrons i.e.(n-1) and lower uniformly contribute 1.0 to S

Thus for 1 s electron S = 0.3

For electrons in an s or p orbital with n >1, the screening constant is given by

S = 1.00 N2 + 0.85 N1 + 0.35 N0

Where N0 is the number of other electrons in the same shell. N1 is the number of electrons in the next smaller shell (n-1) and N2 is the number of electrons in the next smaller shells (n-2 and smaller).

Calculation of effective Nuclear Charge Z* According to Slater's Equation.

n	**Z**	**s**	**Z***
1 (H)	1	0	1.00
(He)	2	0.35	1.65
2(Li)	3	1.70	1.30
(Be)	4	2.05	1.95
(B)	5	2.40	2.60
(C)	6	2.75	3.25
(N)	7	3.10	3.90
(O)	8	3.45	4.55
(F)	9	3.80	5.20
(Ne)	10	4.15	5.85

Trends in Z* become less reliable for heavier elements or in comparisons down a group in periodic table. The Slater rules indicate that electrons in the same shell as the electron of interest reduce the effective nuclear charge by 0.35 even though each electron possesses a full-l charge. Electrons in the next inner shell (n-1) are more effective in shielding the nucleus, reducing Z* by 0.85. Electrons closer to the nucleus are completely effective in screening the nucleus (each electron shields a full –1 charge)

Spin- Orbit Coupling

An electron has spin angular momentum and since moving charges generate magnetic fields. The electron has a magnetic moment that arises from its spin. An electron in an orbital with l>0 is in effect a circulating current and possesses a magnetic moment that arises from its orbital momentum. The interaction of the spin and orbital magnetic moments is called spin-orbit coupling. The strength of the coupling and its effect on the energy levels of the atom depends on relative orientations of the spin and orbital magnetic moments.

The spin-orbit interaction on the relative orientation of the spin and orbital momenta depends on total angular momentum of the electron, the vector sum of its spin and orbital momenta. Thus when spin and orbital angular momenta are parallel, the angular momentum is high. When the two angular momenta are opposed, the total angular momentum is low.

POSSIBLE QUESTIONS

UNIT-I

PART-A (20 MARKS)

(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. What are quantum numbers?
2. What do you understand by anomalous electronic configurations?
3. Give the significance of l and m.
4. What is n+1 rule?
5. What do you understand by the Quantum number?
6. Define spin orbit coupling

PART C (6 MARKS)

1. Explain the terms. Principal quantum number, angular momentum number. Explain the significance of each of these numbers.
2. Write short notes on concept of exchange energy.
3. Explain the terms.magnetic quantum number, spin quantum number. Explain the significance of each of these numbers.
4. Write a note on rules for filling electron and electronic configuration of given atom.
5. How do the d_{x2-y2} and d_{xy} orbitals differ in their orientation in space?
6. Explain why in the filling up of atomic orbitals 4s orbital is filled up before 3d orbital.
7. Write short notes on Azimuthal quantum number and magnetic quantum number.
8. Explain the following giving appropriate reasons:

   i) Half-filled and completely filled orbitals are more stable.

   ii) The valence shell configurationof Cr-atom is $3d^5.4s^1$ and not $3d^4.4s^2$

S.No.	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1.	The quantum number which identifies the shell to which electron belongs	Principal quantum number	Azimuthal quantum number	magnetic quantum number	spin quantum number	Principal quantum number
2.	The quantum number which specifies the subshell to which an electron belongs to	Principal quantum number	Azimuthal quantum number	magnetic quantum number	spin quantum number	Azimuthal quantum number
3.	Quantum number gives the orientiation of orbitals in space	Principal quantum number	Azimuthal quantum number	magnetic quantum number	spin quantum number	magnetic quantum number
4.	The quantum number which gives the spin of an electron	Principal quantum number	Azimuthal quantum number	magnetic quantum number	spin quantum number	spin quantum number
5.	The principal quantum number specifies the	subshell to which an electron belongs to	orientiation of orbitals in space	spin of an electron	The shell to which electron belongs to	The shell to which electron belongs to
6.	The azimuthal quantum number specifies	subshell to which an electron belongs to	orientiation of orbitals in space	spin of an electron	The shell to which electron belongs to	subshell to which an electron belongs to
7.	The magnetic quantum number specifies	subshell to which an electron belongs to	orientiation of orbitals in space	spin of an electron	The shell to which electron belongs to	orientiation of orbitals in space
8.	The spin quantum number specifies	subshell to which an electron belongs to	orientiation of orbitals in space	spin of an electron	The shell to which electron belongs to	spin of an electron
9.	The azimuthal quantum number specifies	The angular momentum of an electron	orientiation of orbitals in space	spin of an electron	The shell to which electron belongs to	The angular momentum of an electron
10.	The principal quantum number 'n' can have values	n= 0,1,2,3……7	n= 1,2,3 ……… infinity	n= 0,1,2,…….infinity	2l+1	n= 1,2,3 ……… infinity

11.	The azimuthal quantum number 'l' can have values	l = 0,1,2,3…(n-1)	l = 1,2,3…(n-1)	l = 0,1,2,3…infinity	l = 1,2,3…infinity	
12.	The magnetic quantum number 'm' can have values	m = -l, …0,….. +l	m = -2l, …0,….. +2l	m = -l, …….. +l	m = -2l, …….. +2l	m = -l, …0,….. +l
13.	The number of possible orientiations of an orbital is given by	2l + 1	2l – 1	l2 + 1	l2 – 1	2l + 1
14.	Principal quantum number represents ---------------	orientation of the orbital	energy and size of orbital	spin of electron	shape of the orbital	orientation of the orbital
15.	Azimuthal quantum number tells------------	orientation of the orbital	energy and size of orbital	spin of electron	shape of the orbital	energy and size of orbital
16.	Magnetic quantum number represents -----------	orientation of the orbital	energy and size of orbital	spin of electron	shape of the orbital	shape of the orbital
17.	Spin quantum number represents -----------	orientation of the orbital	energy and size of orbital	spin of electron	shape of the orbital	spin of electron
18.	The electron has --------- probability of being located at a node.	0	1	2	3	0
19.	If the azimuthal quantum number l = 0, it specifies	s – orbital	P-orbital	d- orbital	f-orbital	s – orbital
20.	If the azimuthal quantum number l = 1, it specifies	s – orbital	P-orbital	d- orbital	f-orbital	P-orbital
21.	If the azimuthal quantum number l = 2, it specifies	s – orbital	P-orbital	d- orbital	f-orbital	d- orbital
22.	If the azimuthal quantum number l = 3, it specifies	s – orbital	P-orbital	d- orbital	f-orbital	f-orbital
23.	For the S- orbital the azimuthal quantum number value is	l = 1	l = 2	l = 0	l = 4	l = 0
24.	For the p- orbital the azimuthal quantum number	l = 1	l = 2	l = 0	l = 4	l = 1

	value is					
25.	For the d- orbital the azimuthal quantum number value is	l = 1	l = 2	l = 0	l = 4	l = 2
26.	For the S- orbital the--------- quantum number value is l=0	azimuthal	principal	magnetic	spin	azimuthal
27.	S – orbital have how many orientations	one	Three	five	seven	one
28.	p – orbital have how many orientations	one	Three	five	seven	Three
29.	d – orbital have how many orientations	one	Three	five	seven	five
30.	f – orbital have how many orientations	one	Three	five	seven	seven
31.	The shape of the s- orbital	Spherical	dumb bell	double dumb bell	square	Spherical
32.	The shape of the p- orbital	Spherical	dumb bell	double dumb bell	square	dumb bell
33.	The shape of the f- orbital	Spherical	dumb bell	double dumb bell	square	double dumb bell
34.	In an atom no two electrons can have the same values for all the quantum numbers proposed by	pauli	hund	aufbau	dalton	pauli
35.	For a given valus for azimuthal quantum number l, the total number of values for m are given by	l+1	2l+1	2l-1	l+2	2l+1
36.	Which shape is associated with orbital designated by n=2, l=1	Spherical	tetrahedral	dumb bell	pyramidal	
37.	The angular momentum of electro in nth orbit is given by	nh	$nh/2\pi$	$n^2h/2\pi$	$h/2\pi n$	$nh/2\pi$
38.	The order of filling of	3d,4s,4p,4d,5s	4s,3d,4p,5s,4d	5s,4p,3d,4d,5s	3d,4p,4s,4d,5s	

	electrons in the orbital of an atom will be					
39.	The number of vacant d-orbitals in completely excited Cl atom is	2	3	1	5	2
40.	The number of unpaired electron present in Cr3+	3	2	5	1	3
41.	How many electrons can be accomadated in a subshell with n=3 and l=1	8	6	18	32	6
42.	The total number of orbitals in a shell with principal quantum number n is	2n	$2n^2$	n^2	n+1	n^2
43.	The quantum number not obtained from the schrodinger's wave equation is	n	l	m	s	s
44.	When 3p orbtals are completely filled then the newely entering electron goes in to	4p	3d	4s	4d	4s
45.	The quantum number which determines the shape of the orbital is	Principal	Azimuthal	magnetic	spin	Azimuthal
46.	The number of spherical nodes in 3p orbitals are	one	three	four	two	one
47.	Electrons are filled in orbitals according to	n+l rule	Hund's rule	Aufbau's principle	Pauli's exclusion principle	Hund's rule
48.	An electron has magnetic quantum number as -3 ,what is its principal quantum	1	2	3	4	4

	number					
49.	The energy of an electron of 2py orbital is	greater than that of 2px orbital	less than that of 2px orbital	equal to that of 2s orbital	same as that of 2pz orbital	same as that of 2pz orbital
50.	The d-orbitals invo;ved in sp3d hybridisation is	dxy	dz2	dx2-y2	dxz	dz2
51.	Degenerate orbitals have	equal energy	equal work function	equal work -function but different energy	equalenergy but different function	equal energy
52.	3p orbitals has	two non spherical lobes	two spherical and one non spherical lobes	two non spherical and one spherical lobe	two spherical lobes	two non spherical lobes
53.	Which orbital notation does not have spherical node	n=2;l=0	n=2;l=1	n=3;l=0	n=4	n=2;l=1
54.	The maximum number of 3d electrons having spin quantum number s=+1/2 are	10	14	5	any number from 1to 10	10
55.	The d orbital with the orientation along X and Y axes is called	dxy	dzy	dyz	dx2-y2	dx2-y2
56.	What is the number of subshells in principal quantum number 3	3	5	9	14	3
57.	The first energy level that can contain d-orbital is	2	3	4	5	3
58.	How many electrons with l=1 will be there in an atom having atomic number	2	3	4	5	3
59.	Dumb-bell shape is associated with orbital designated by	n=2, l=1	n=3, l=1	n=4, l=2	n=5, l=1	n=2, l=1
60.	Which of the following quantum number does not	Principal quantum	Azimuthal quantum	magnetic quantum	spin quantum number,s	spin quantum number,s

	follow from schrodinger wave equation	number,n	number,l	number,m		
61.	The principle which gives a way to fill the electrons in the available energy is	Hund's rule	Aufbau's principle	Pauli's exclusion principle	n+l rule	Aufbau's principle
62.	The orbital with maximum number of possible orientations	s	p	d	f	f

UNIT III

SYLLABUS

Ionic Bonding: General characteristics of ionic bonding. Energy considerations in ionic bonding, lattice energy and solvation energy and their importance in the context of stability and solubility of ionic compounds. Statement of Born-Landé equation for calculation of lattice energy, Born-Haber cycle and its applications, polarizing power and polarizability. Fajan's rules, ionic character in covalent compounds, bond moment, dipole moment and percentage ionic character.

General characteristics of ionic bonding

1. Ionic compounds have ionic bonds which are electrostatic forces of attraction, they can decompose into respective ions.
2. Ionic compounds are ionic in nature and good conductor of electricity.
3. They are usually found in solid state like sodium chloride etc. In ionic compounds, the constituent atoms or ions show strong attractions with other ions.
4. Ionic compoundsgenerally have high melting points, boiling points and found in solid state. Due to presence of ions, ionic compounds are polar in nature and easily soluble in polar solvents like water.

Ionic bonding can result from a redox reaction when atoms of an element (usually metal), whose ionization energy is low, give some of their electrons to achieve a stable electron configuration. In doing so, cations are formed. The atom of another element (usually nonmetal), whose electron affinity is positive, then accepts the electron(s), again to attain a stable electron configuration, and after accepting electron(s) the atom becomes an anion. Typically, the stable electron configuration is one of the noble gases for elements in the s-block and the p-block, and particular stable electron configurations for d-block and f-block elements. The electrostatic attraction between the anions and cations leads to the formation of a solid with a crystallographic lattice in which the ions are stacked in an alternating fashion. In such a lattice, it is usually not possible to distinguish discrete molecular units, so that the compounds formed are not molecular in nature. However, the ions themselves can be complex and form molecular ions like the acetate anion or the ammonium cation.

For example, common table salt is sodium chloride. When sodium (Na) and chlorine (Cl) are combined, the sodium atoms each lose anelectron, forming cations (Na^+), and the chlorine atoms each gain an electron to form anions (Cl^-). These ions are then attracted to each other in a 1:1 ratio to form sodium chloride (NaCl).

$$Na + Cl \rightarrow Na^+ + Cl^- \rightarrow NaCl$$

However, to maintain charge neutrality, strict ratios between anions and cations are observed so that ionic compounds, in general, obey the rules of stoichiometry despite not being molecular compounds. For compounds that are transitional to the alloys and possess mixed ionic and metallic bonding, this may not be the case anymore. Many sulfides, e.g., do form non-stoichiometric compounds.

Many ionic compounds are referred to as **salts** as they can also be formed by the neutralization reaction of an Arrhenius base like NaOH with an Arrhenius acid like HCl

$$NaOH + HCl \rightarrow NaCl + H_2O$$

The salt NaCl is then said to consist of the acid rest Cl^- and the base rest Na^+.

The removal of electrons from the cation is endothermic, raising the system's overall energy. There may also be energy changes associated with breaking of existing bonds or the addition of more than one electron to form anions. However, the action of the anion's accepting the cation's valence electrons and the subsequent attraction of the ions to each other releases (lattice) energy and, thus, lowers the overall energy of the system.

Ionic bonding will occur only if the overall energy change for the reaction is favorable. In general, the reaction is exothermic, but, e.g., the formation of mercuric oxide (HgO) is endothermic. The charge of the resulting ions is a major factor in the strength of ionic bonding, e.g. a salt C^+A^- is held together by electrostatic forces roughly four times weaker than $C^{2+}A^{2-}$ according to Coulombs law, where C and A represent a generic cation and anion respectively.

Statement of Born-Landé equation for calculation of lattice energy:

For a solid crystalline ionic compound the enthalpy change in forming the solid from gaseous ions is termed the lattice energy. The experimental value for the lattice energy can be determined using the Born-Haber cycle. It can also be calculated (predicted) using the Born-Landé equation as the sum of the electrostatic potential energy, calculated by summing interactions between cations and anions, and a short-range repulsive potential energy term. The electrostatic potential can be expressed in terms of the inter-ionic separation and a constant (Madelung constant) that takes account of the geometry of the crystal. The further away from the nucleus the weaker the shield. The Born-Landé equation gives a reasonable fit to the lattice energy of, e.g., sodium chloride, where the calculated (predicted) value is −756 kJ/mol, which compares to −787 kJ/mol using the Born-Haber cycle.

The Born-Lande' equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Lande and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as theCoulomb attractions.

Introduction

Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. To solve for the Born-Landé equation, you must have a basic understanding of lattice energy:

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases.

Equation

The Born-Landé equation was derived from these two following equations. the first is the electrostatic potential energy:

$\Delta U = -LA|Z+||Z-|e24\pi\mu_o r$

with

- L is Avogadro's constant (6.022×1023)
- A is the Madelung Constant (a constant that varies for different structures)
- e is the charge of an electron (1.6022×10−19 C)
- Z+ is the cation chargeZ− is the anion charge
- μo is the permittivity of free space
- The second equation is the repulsive interaction:

$\Delta U=LBrn$ with

- B is the repulsion coefficient and
- N is the Born Exponent (typically ranges between 5-12) that is used to measure how much a solid compresses

These equations combine to form:

$\Delta U(0K)=LA|Z+||Z-|e24\pi\epsilon oro(1-1n)$with

- r_0 = closest ion distance

Calculate Lattice Energy

Lattice energy, based on the equation from above, is dependent on multiple factors. We see that the charge of ions is proportional to the increase in lattice energy. In addition, as ions come into closer contact, lattice energy also increases.

The Born-Haber cycle

Thermodynamics may be defined as the branch of science which deals with the quantitative relationship between heat and other forms of energies. **Chemical thermodynamics deals with the change in heat during chemical processes. The energy change during the chemical reaction at constant temperature and volume is given by internal energy change.** However chemical reactions are generally involved some change in volume, therefore in order to study the heat changes of chemical reaction at constant temperature and pressure, a new function enthalpy is introduced. Enthalpy is the total energy associated with any system which includes its internal energy and also energy due to environmental factor such as pressure-volume conditions. Mathematically enthalpy can be written as

$$\mathbf{H = U + PV}$$

Where U stands for internal energy and PV is additional energy possesses by the substance. Enthalpy is a state function and an extensive property. It is also known as heat content of the system whose value depends upon amount and chemical nature of substance as well as on pressure and temperature.

Born Haber Cycle Example

Born Haber cycle is a simplified method developed by Max Born and Fritz Haber in 1919 to correlate the lattice energies of ionic solids to other thermodynamic data. Lattice enthalpy or lattice energy is defined as enthalpy change which occurs when one mole of ionic solid is formed by close packing of constituent ions in gaseous state. Or it may be defined as energy released when one mole of ionic solid dissociates into its gaseous state. **For example,** the formation of sodium chloride from sodium and chloride ion involves 788 kj/mol of energy and dissociation of sodium chloride into it constituent ions requires same amount of energy.

$$NaCl(s) \rightarrow Na+(g) + Cl- (g)\ \Delta LH° = 788\ kj/mol$$

$$Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl(s)\ \Delta LH° = -788\ kj/mol$$

When oppositely charged ions interact to form ionic solid, a large amount of energy is released and dissociation of crystal also require a lot of energy which makes melting point and boiling points of crystal very high. Born Haber cycle is used to determine this lattice energy by using other energy values like ionization energy, electron affinity, dissociation energy, sublimation energy and heat of formation.

1.Ionization Energy: It is the energy required to remove an electron from a neutral gaseous atom or an ion.

2. Electron Affinity: It is the energy released when an electron is added to an isolated neutral gaseous atom or an ion

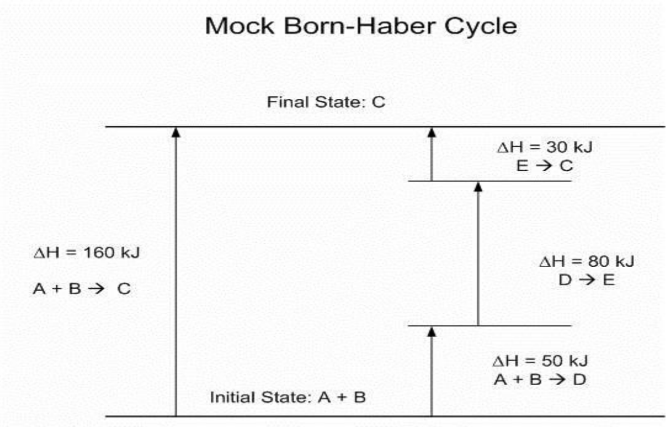
3. Dissociation energy: The energy required to dissociate a compound is called as dissociation energy. Dissociation of a compound is always an endothermic process and requires an input of energy.

4. Sublimation energy: The energy required to change the phase from solid to gas, by passing the liquid phase is called as sublimation energy.

5. Heat of formation: The energy change during the formation of a compound from its elements is known as heat of formation.

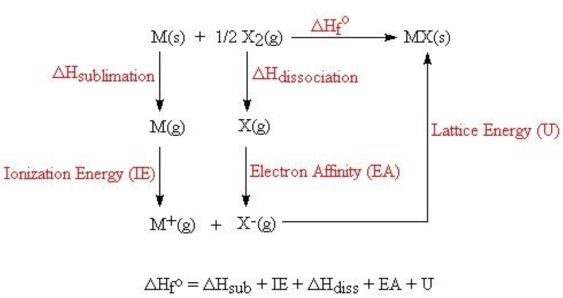
Born Haber cycle is based on Hess law which states that the standard enthalpy change of reactions is the sum of algebraic sum of the standard enthalpies of reactions into which the overall reaction may be splitted or divided.

For example, the formation of C from A and B can take place in two ways. Both ways involve same initial and final states, but one is single step and other one is multi-step reaction which involves intermediates, D and E. Both ways has an enthalpy change of 160 kJ.



The formation of ionic compounds from alkali metals like sodium, potassium with halogen such as chlorine, bromine to form alkali halide can be represent by using Born Haber cycle. Remember the heat of formation of ionic halide is equals to the sum of other energies involves in various steps.

Born - Haber Cycle



Lattice Energy: The Born-Haber cycle

Ionic solids tend to be very stable compounds. The enthalpies of formation of the ionic molecules cannot alone account for this stability. These compounds have an additional stability due to the lattice energy of the solid structure. However, lattice energy cannot be directly measured. The Born-Haber cycle allows us to understand and determine the lattice energies of ionic solids.

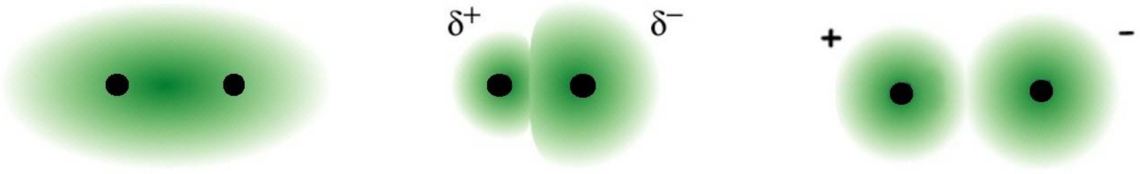
Lattice Energy

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, the lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction. The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Its values are usually expressed with the units kJ/mol. Lattice Energy is used to explain the stability of ionic solids. Some might expect such an ordered structure to be less stable because the entropy of the system would be low. However, the crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points. Some require such high temperatures that they decompose before they can reach a melting and/or boiling point.

Fajans' Rules:

Rules formulated by Kazimierz Fajans in 1923, can be used to predict whether a chemical bond is expected to be predominantly ionic or covalent, and depend on the relative charges and sizes of the cation and anion. *If two oppositely charged ions are brought together, the nature of the bond between them depends upon the effect of one ion on the other.*

non-polar covalent *polar covalent* *ionic*



Although the bond in a compound like **X^+Y^-** may be considered to be 100% ionic, it will always have some degree of covalent character. When two oppositely charged ions (X^+ and Y^-) approach each other, the cation **attracts** electrons in the outermost shell of the anion but **repels** the positively charged nucleus. This results in a distortion, deformation or polarization of the anion. If the degree of polarization is quite small, an ionic bond is formed, while if the degree of polarization is large, a covalent bond results.

The ability of a cation to distort an anion is known as its polarization power **and the tendency of the anion to become polarized by the cation is known as its** polarizability**.**

The polarizing power and polarizability that enhances the formation of covalent bonds is favoured by the following factors:

Small cation: the high polarizing power stems from the greater concentration of positive charge on a small area. This explains why LiBr is more covalent than KBr (Li^+ 90 pm cf. K^+ 152 pm).

Large anion: the high polarizability stems from the larger size where the outer electrons are more loosely held and can be more easily distorted by the cation. This explains why for the common halides, iodides, are the most covalent in nature (I^- 206 pm).

Large charges: as the charge on an ion increases, the electrostatic attractions of the cation for the outer electrons of the anion increases, resulting in the degree of covalent bond formation increasing.

Large cations are to be found on the bottom left of the periodic table and small anions on the top right. The greater the positive charge, the smaller the cation becomes and the ***ionic potential*** is a measure of the charge to radius ratio.

Polarization will be increased by:

High charge and small size of the cation

Ionic potential Å Z+/r+ (= polarizing power)

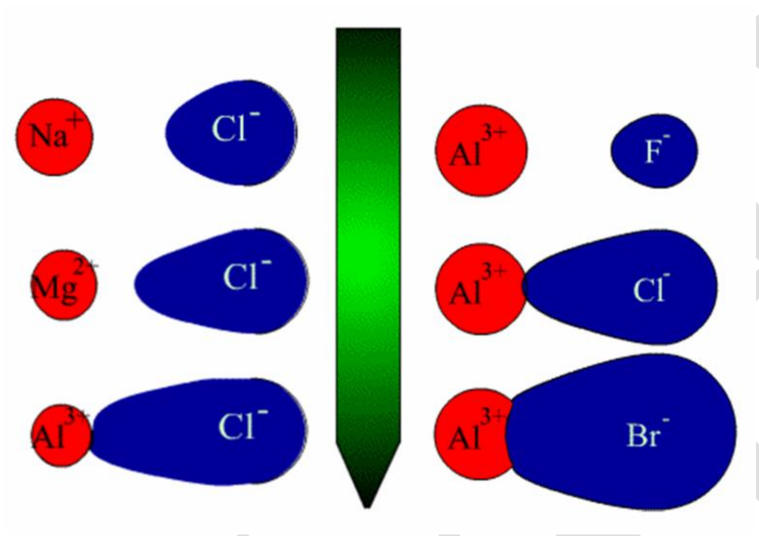
High charge and large size of the anion

The polarizability of an anion is related to the deformability of its electron cloud (i.e. its "softness")

An incomplete valence shell electron configuration

Noble gas configuration of the cation produces better shielding and less polarizing power

e.g. Hg^{2+} (r+ = 102 pm) is more polarizing than Ca^{2+} (r+ = 100 pm)



On the left, the cation charge increases (size decreases) and on the right, the anion size increases, both variations leading to an increase in the covalency.Thus covalency increases in the order:

[Na$^+$ Cl$^-$, NaCl] < [Mg^{2+} 2(Cl)$^-$, MgCl$_2$] < [Al^{3+} 3(Cl)$^-$, AlCl$_3$] and [Al^{3+} 3(F)$^-$, AlF$_3$] < [Al^{3+} 3(Cl)$^-$, AlCl$_3$] < [Al^{3+} 3(Br)$^-$, AlBr$_3$]

Electronic configuration of the cation: for two cations of the same size and charge, the one with a pseudo noble-gas configuration (with 18 electrons in the outer-most shell) will be more polarizing than that with a noble gas configuration (with 8 electrons in the outermost shell). Thus zinc (II) chloride (Zn(II) $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^6\ 3d}^{10}$ and Cl$^-$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) is more covalent than magnesium chloride (Mg(II) $1s^2$ **$2s^2$ $2p^6$**) despite the Zn^{2+} ion (74 pm) and Mg^{2+} ion (72 pm) having similar sizes and charges.

From an MO perspective, the orbital overlap disperses the charge on each ion and so weakens the electrovalent forces throughout the solid, this can be used to explain the trend seen for the melting points of lithium halides.

LiF = 870 °C, LiCl = 613 °C, LiBr = 547 °C, LiI = 446 °C

It is found that the **greater the possibility of polarization, the lower is the melting point and heat of sublimation and the greater is the solubility in non-polar solvents.**

Example: The melting point of KCl is higher than that of AgCl though the crystal radii of Ag^+ and K^+ ions are almost the same.

Solution: When the melting points of two compounds are compared, the one having the lower melting point is assumed to have the smaller degree of ionic character. In this case, both are chlorides, so the anion remains the same. The deciding factor must be the cation. (If the anions were different, then the answer could be affected by the variation of the anion.) Here the significant difference between the cations is in their electronic configurations. K^+= [Ar] and Ag^+ =[Kr] $4d^{10}$. This means a comparison needs to be made between a noble gas core and pseudo noble gas core, which as noted above holds that the pseudo noble gas would be the more polarizing.

Percentage of ionic character and charge distribution

Based on Fajan's rules, it is expected that every ionic compound will have at least some amount of covalent character. The percentage of ionic character in a compound can be estimated from dipole moments.

The bond dipole moment uses the idea of electric dipole moment to measure the polarity of a chemical bond within a molecule. It occurs whenever there is a separation of positive and negative charges. The bond dipole μ is given by:

$\mu = \delta d$

A bond dipole is modeled as +δ - δ- with a distance d between the partial charges. It is a vector, parallel to the bond axis and by convention points from minus to plus . The SI unit for an electric dipole moment is the coulomb-meter, (C m). This is thought to produce values too large to be practical on the molecular scale so bond dipole moments are commonly measured in Debye, represented by the symbol, D.

Historically the Debye was defined in terms of the dipole moment resulting from two equal charges of opposite sign and separated by 1 Ångstrom (10^{-10} m) as 4.801 D. This value arises from $(1.602 \times 10^{-19} * 1 \times 10^{-10}) / 3.336 \times 10^{-30}$

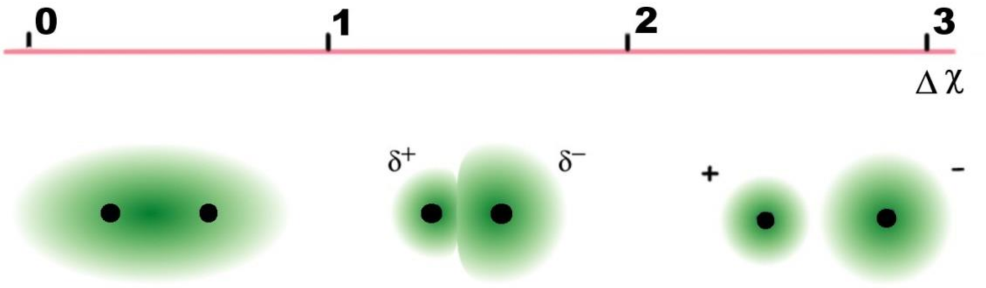
where D = 3.336×10^{-30} C m (or 1 C m = 2.9979×10^{29} D).

Typical dipole moments for simple diatomic molecules are in the range of 0 to 11 D.

The % ionic character = $\mu_{observed} / \mu_{calculated}$ (assuming 100% ionic bond) * 100 %

Bond character based on electronegativity differences

It is possible to predict whether a given bond will be non-polar, polar covalent, or ionic based on the electronegativity difference, since the greater the difference, the more polar the bond.



Electronegativity difference, ΔχP	Bond
$\Delta\chi < 0.4$	covalent
$0.4 < \Delta\chi < 1.7$	polar covalent
$\Delta\chi > 1.7$	$\Delta\chi > 1.7$

Linus Pauling proposed an empirical relationship which relates the percent ionic character in a bond to the electronegativity difference.

percent ionic character= $(1-e^{-(\Delta\chi/2)^{\wedge}2})$* 100

The magnitude of polarization or increased covalent character depends upon a number of factors. These factors are,

(1) Small size of cation:

Smaller size of cation greater is its polarizing power i.e. greater will be the covalent nature of the bond.

(2) Large size of anion:

Larger the size of anion greater is its polarizing power i.e. greater will be the covalent nature of the bond.

(3) Large charge on either of the two ions:

As the charge on the ion increases, the electrostatic attraction of the cation for the outer electrons of the anion also increases with the result its ability for forming the covalent bond increases.

(4) Electronic configuration of the cation:

For the two ions of the same size and charge, one with a pseudo noble gas configuration (i.e.18 electrons in the outermost shell) will be more polarizing than a cation with noble gas configuration (i.e., 8 electron in outer most shell).

Anomalous behaviour of the 2nd row elements: Li, Be, B, C, N, O, F

For the elements in the 2nd row, as the atomic number **increases**, the atomic radius of the elements **decreases**, the electronegativity**increases**, and the ionization energy **increases**. The 2nd row has two metals (lithium and beryllium), making it the least metallic period and it has the most nonmetals, with four. The elements in the 2nd row often have the most extreme properties in their respective groups; for example, fluorine is the most reactive halogen, neon is the most inert noble gas, and lithium is the least reactive alkali metal. These differences in properties with the subsequent rows are a result of:

- the smaller size of the atoms
- an outer shell with a maximum of 8 electrons (2s and 2p) and an underlying shell with just 2 electrons
- no acessible d-orbitals - energy too high for use in bonding

Apart from the 2nd row (ignoring H/He 1st row) the later rows all end with inert gases but these do not have completed quantum levels. The 2nd row elements in general can only use the 2s and 2p electrons for bonding restricting the total number of bonds to 4.

So N is not expected to have more than 4 bonds and 3 is common, while for P 5 and 6 bonded species are quite common.

Reactivity of metals and metalloids

For **Lithium**, compared to other alkali metals

Reaction with water:

Li reacts slowly with water at 25 °C

Na reacts violently and K in flames

$2M(s) + 2H_2O(l) \rightarrow 2M^+(aq) + 2OH^- + H_2(g)$

In general Li, Be, B, C, N, O, F are less reactive towards water than their heavier congeners.

Reaction with oxygen:

In conditions of excess oxygen, only Li forms a simple oxide, Li_2O. Other metals form peroxides and superoxides

Reaction with nitrogen:

Li reacts directly with N_2 to form Li_3N

$6Li(s) + N_2 (g) \rightarrow 2Li_3N(s)$.

No other alkali metal reacts with N_2

Solubility:

LiF, LiOH and Li_2CO_3 are less soluble than the corresponding Na and K compounds

For **Beryllium** compared to the other alkaline earth metals:

With water:

All Group 2 metals except Be, react with water

$M(s) + 2H_2O(l) \rightarrow M^{2+}(aq) + 2OH^{-}(aq) + H_2(g)$

With oxygen (air):

Be only reacts with air above 600 °C if it is finely powdered. The BeO that is formed is amphoteric (other Group 2 oxides are basic).

Of the Group 2 elements only Be reacts with NaOH or KOH to liberate H_2 and form $[Be(OH)_4]^{2-}$.

Li and Be are metals but are less conducting than the higher members of Group 1 and 2 elements due to their high IEs (electrons are close to nucleus).

Ionization of **Boron** to B^{3+} requires a large input of energy and B adopts a covalent polymeric structure with semi-metallic properties.

The other elements of Group 14 become increasingly metallic as the group is descended due to the decrease in ionization energies.

Crystalline Boron is chemically inert - unaffected by boiling HCl and only slowly oxidized by hot concentrated HNO_3 when finely powdered.

Covalent character

Li^+ and Be^{2+} are small and have strong polarizing abilities. Their compounds are more covalent than those of the heavier elements in their groups.

$BeCl_2$ is covalent while MCl_2 (M = Mg-Ba) are ionic. The conductivity of fused beryllium chloride is only 1/1000 that of sodium chloride under similar conditions.

Catenation

Catenation is the linkage of atoms of the same element into longer chains. Catenation occurs most readily in carbon, which forms covalent bonds with other carbon atoms to form longer chains and structures. This is the reason for the presence of the vast number of organic compounds in nature. The ability of an element to catenate is primarily based on the bond energy of the element to itself, which decreases with more diffuse orbitals (those with higher azimuthal quantum number) overlapping to form the bond. Hence, carbon, with the least diffuse valence shell 2p orbital is capable of forming longer p-p sigma bonded chains of atoms than heavier elements which bond via higher valence shell orbitals. Hetero-catenation is quite common in Inorganic Chemistry. Phosphates and silicates with P-O-P-O and Si-O-Si-O linkages are examples of this.

Multiple Bonds

C, N and O are able to form multiple bonds (double and/or triple). In Group 14, C=C double bonds are stable (134 pm) but Si=Si double bonds (227 pm) are uncommon. The diagram below shows how multiple bonds are formed involving π overlap of 2p orbitals. By comparison the 3p orbitals of the corresponding third row elements Si, P, and S are more diffuse and the longer bond distances expected for these larger atoms would result in poor π overlap.

C=C bond length = 134 pm and Si=Si bond length = 227 pm

Oxidizing ability of oxygen and fluorine

Due to the high electron affinities and electronegativities of oxygen and fluorine, they tend to form strong ionic bonds with other elements. They even react with noble gases to form compounds such as XeO_3, XeO_4, XeF_4 and XeF_6. In 1962 Neil Bartlett at the University of

British Columbia reacted platinum hexafluoride and xenon, in an experiment that demonstrated the chemical reactivity of the noble gases. He discovered the mustard yellow compound, xenon hexafluoroplatinate, which is perhaps now best formulated as a mixture of species, $[XeF^+][PtF_5]^-$, $[XeF^+][Pt_2F_{11}]^-$, and $[Xe_2F_3]^+[PtF_6]^-$.

A few hundred compounds of other noble gases have subsequently been discovered: in 1962 for radon, radon difluoride (RnF_2), and in 1963 for krypton, krypton difluoride (KrF_2). The first stable compound of argon was reported in 2000 when argon fluorohydride (HArF) was formed at a temperature of 40 K (-233.2 °C). Neutral compounds in which helium and neon are involved in chemical bonds have still not been formed.

Noble gas compounds have already made an impact on our daily lives. XeF_2 is a strong fluorinating agent and has been used to convert uracil to 5-fluorouracil, one of the first anti-tumor agents.

POSSIBLE QUESTIONS

UNIT-I

PART-A (20 MARKS)

(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. State Fajan's rules.
2. What is an ionic bond?
3. Write the Born-Lande equation.
4. What is dipole moment?
5. What are the applications dipole moments?

PART C (6 MARKS)

1. What is lattice energy? How does the solubility of an ionic solid depend upon its lattice energy?
2. Write a note on polarization and polarizing power
3. Explain why melting point of NaCl is higher than that of $AlCl_3$.
4. The lattice energy of silver halides are almost the same as that of alkali metal halides, yet they are insoluble in water.
5. Explain how Born-Haber cycle is used to calculate the lattice energy of NaCl.
6. Give an account on solvation energy and importance in context of stability and solubility of ionic compounds.
7. What is an ionic bond? List four characteristic properties of ionic compounds.
8. Discuss the Fajan rules.

9. Derive Born –Lande equation for the lattice energy of sodium chloride.
10. What do you understand by the terms polarizing power and polarizability? How do these determine ionic character of a compound?

S.No.	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1.	Which of the following has zero dipole moment	PH_3	CH_4	PH_4	CH_2Cl_2	CH_4
2.	Which of the following is least ionic	AgCl	KCl	$BaCl_2$	$COCl_2$	$COCl_2$
3.	Which of the following compound has least dipole moment	NH_3	NF_3	SO_2	H_2O	NF_3
4.	Which one of the following has least polarity	H-F	H-Cl	H-O	H-S	H-S
5.	Which of the following is most polar	C-O	C-F	O-F	N-F	C-F
6.	According to Fajan's rule,covalent bond is favoured by	large cation and small anion	large cation and large anion	small cation and small anion	small cation and large anion	small cation and large anion
7.	Which contains a co-ordinate and covalent bond	$BaCl_2$	NH_4Cl	HCl	H_2O	NH_4Cl
8.	Which has a net dipole moment	BF_3	CCl_4	BeF_2	SO_2	SO_2
9.	Which of the following compound is non polar	$CHCl_3$	$SiCl_4$	$SnCl_2$	NH_3	$SiCl_4$
10.	The angle between the overlapping of one s-orbital and one p-orbital is	180°	120°	$109_o28'$	120o60'	180°
11.	Which force is strongest	dipole-dipole forces	ion-ion forces	ion -dipole forces	ion-induced dipole forces	ion-ion forces
12.	Greater the bond order,greater is	bond dissociation energy	covalent nature	bond length	paramagnetism	bond dissociation energy
13.	The molecule having largest dipole moment among the following is	CH_4	$CHCl_3$	CCl_4	CHI_3	$CHCl_3$
14.	The molecule which have zero dipole moment	CH_2Cl_2	BF_3	ClO_2	NF_3	BF_3
15.	Which has the lowest bond angle	NH_3	BeF_2	H_{3O+}	CH_4	NH_3

16.	The shape of a molecule which has three bonds and one lone pair is	Octahedral	Pyramidal	Triangular planar	Tetrahedral	Pyramidal
17.	The type of hybridisation in SO2 and SO3 is respectively	sp, sp^2	sp^2, sp^2	sp^2, sp^3	sp, sp^3	sp^2, sp^2
18.	As the s-character of hybridised orbital increases, the bond angle	increases	decreases	does not change	equal	increases
19.	The bond order is maximum in	H_2	H_{2+}	He_2	He2+	H_2
20.	Strongest bond is in	NaCl	CsCl	Both a and b	LiF	CsCl
21.	The weakest among the following is	ionic bond	covalent bond	metallic bond	vanderwaal's forces	vanderwaal's forces
22.	Which has zero dipole moment	ClF	PCl_3	SiF_4	$CFCl_3$	SiF_4
23.	The molecules having dipole moment are	2,2 dimethyl propane	trans-3-hexene	trans-2-pentene	2,2,3,3 tetramethyl butane	trans-2-pentene
24.	Stability of ionic compound is due to	electronegativity	lattice energy	sublimation energy	electron affinity	lattice energy
25.	Ionic compoundsin general possess both	high m.pt and non-directional bonds	high m.pt and low-boiling points	directional bonds and low boiling points	high solubilities in polar and non-polar solvents	high m.pt and non-directional bonds
26.	The magnitude of the lattice energy of a solid increases if	the ions are large	the ions are small	the ions are of equal size	charges on the ions are small	the ions are small
27.	Which of the following bonds has the highest bond dissociation energy	CH_3-H	CH_3-Br	CH_3-Cl	CH_3-F	CH_3-F
28.	Whice of the following forces between atoms or ions or molecules is the strongest	ionc-bond	ion dipole	dipole-dipole	london-dispersive	ionc-bond
29.	The unequal sharing of the bonded pair of electrons between two atoms in a molecule causes	dipole	radical formation	covalent bond	decomposition of molecule	dipole
30.	All chemical bonds are the result of	interaction	interaction of	difference in	interaction of	interaction of the

		of nuclei	electrons	electronegativity	the electrons and nuclei	electrons and nuclei
31.	CCl4 is insoluble in water because	H_2O is polar	CCl4 is non-polar	they do not form intermolecular H-bonding	they do not form intramolecular H-bonding	CCl4 is non-polar
32.	Which has the minimum bond energy	H-Br	H-I	I-I	H-H	I-I
33.	The compound with maximum dipole moment is	p-dichlorobenzene	m-dichlorobenzene	o-dichlorobenzene	CCl_4	o-dichlorobenzene
34.	Dipole-dipole attractive forces are strongest between the molecule of	He	CH_4	CO_2	H_2O	H_2O
35.	Whice of the following molecules does not possess a permanent electric dipole	H_2O	SO_2	SO_3	CS_2	CS_2
36.	The C-H bond distance in the largest in	C_2H_2	C_2H_4	$C_2H_4Br_2$	C_2H_6	$C_2H_4Br_2$
37.	Which is most ionic	P_2O_5	MnO	CrO_3	Mn_2O_7	MnO
38.	The compound which contains both ionic and covalent bond	CH_4	H_2	KCN	KCl	KCN
39.	Which of the following is polar	BF_3	C_2H_5-F	CO_2	CH_4	C_2H_5-F
40.	Which of the following compound has dipole movement zero	CCl_4	$CHCl_3$	HF	NH_3	CCl_4
41.	Which of the following does not conduct electricity	Molten NaOH	Molten KOH	Solid NaCl	Aqueous NaCl	Solid NaCl
42.	Which bond is most polar	Cl-F	Br-F	I-F	F-F	I-F
43.	When sodium and chlorine react, energy is	Released and ionic bond is formed	Released and covalent bond is formed	Absorbed and covalent bond is formed	Absorbed and ionic bond is formed	Released and ionic bond is formed
44.	According to Fajan's rule, ionic character increases when	large cation and small anion	small cation and small anion	large cation and large anion	large cation and small anion	large cation and small anion

45.	AlCl3 is covalent, but AlF3 is ionic.This is justified by	Crystal structure	Valence bond theory	Fajan rule	Lattice energy	Fajan rule
46.	In the case of stable molecule the value of bond order be	negative	positive	zero	all	positive
47.	Which bond has the highest bond energy	sigma bond	covalent bond	multiple bond	polar covalent bond	multiple bond
48.	Both ionic and covalent bonds are present in	CH_4	KCl	SO_2	NaOH	NaOH
49.	Which is least soluble in water	AgCl	AgF	AgI	AgBr	AgI
50.	Greater the dipole moment	Greater is the ionic in nature	lesser is the polarity	smaller the ionic nature	covalent nature	Greater is the ionic in nature
51.	Ionic compounds have -------- melting and boiling points.	high	low	very low	neither high nor low	high
52.	Which of the following has maximum polar character	C-I	C-Br	C-F	C-S	C-F
53.	A substance is soluble in water if	lattice energy> hydration energy	Hydration energy> lattice energy	hydration energy=lattice energy	no relation	Hydration energy> lattice energy
54.	An electrovalent compound is made up of	electrically charged particles	neutral molecules	neutral atoms	only neutral	electrically charged particles
55.	NaCl crystal is made up of	NaCl molecules	Na+ and Cl - ions	Na and Cl atoms	dimers of NaCl	Na+ and Cl - ions
56.	The stability of an ionic solid is measured in terms of its ---------	lattice energy	hydration energy	Haber	Fajan	lattice energy
57.	A salt dissolves in water if hydration energy is -------- than lattice energy	more	low	very low	equal	more
58.	In elecrovalency ---------- of electrons takes place.	transfer	sharing	electrons shared by one atom	no electrons takes place	transfer

				only		
59.	For a given cation ,as the size of the anion increases, the covalent character----and m.pt decreases.	decreases	increases	decreases with increasing	increasing with decreases	decreases
60.	The rule to determine the extent of polarization of an anion by a cation was given by	Pauling	Born	Haber	Fajan	Fajan

UNIT IV

SYLLABUS

Covalent bonding: VB Approach: Shapes of some inorganic molecules and ions on the basis of VSEPR and hybridization with suitable examples of linear, trigonal planar, square planar, tetrahedral, trigonal bipyramidal and octahedral arrangements. Concept of resonance and resonating structures in various inorganic and organic compounds.

Molecular geometry is the three-dimensional arrangement of the atoms that constitute a molecule. It determines several properties of a substance including its reactivity, polarity, phase of matter, color, magnetism, and biological activity. The angles between bonds that an atom forms depend only weakly on the rest of molecule, i.e. they can be understood as approximately local and hence transferable properties.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

In order to predict the geometry of molecules, Nyholm and Gillespie developed a qualitative model known as **Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)**. The basic assumptions of this theory are summarized below.

1) The electron pairs in the valence shell around the central atom of a molecule repel each other and tend to orient in space so as to minimize the repulsions and maximize the distance between them.

2) There are two types of valence shell electron pairs viz., i) Bond pairs and ii) Lone pairs

Bond pairs are shared by two atoms and are attracted by two nuclei. Hence they occupy less space and cause less repulsion.

Lone pairs are not involved in bond formation and are in attraction with only one nucleus. Hence they occupy more space. As a result, the lone pairs cause more repulsion.

The order of repulsion between different types of electron pairs is as follows:

Lone pair - Lone pair > Lone Pair - Bond pair > Bond pair - Bond pair

Note: The bond pairs are usually represented by a solid line, whereas the lone pairs are represented by a lobe with two electrons.

3) In VSEPR theory, the multiple bonds are treated as if they were single bonds. The electron pairs in multiple bonds are treated collectively as a single super pair.

The repulsion caused by bonds increases with increase in the number of bonded pairs between two atoms i.e., a triple bond causes more repulsion than a double bond which in turn causes more repulsion than a single bond.

4) The shape of a molecule can be predicted from the number and type of valence shell electron pairs around the central atom.

When the valence shell of central atom contains only bond pairs, the molecule assumes symmetrical geometry due to even repulsions between them.

However the symmetry is distorted when there are also lone pairs along with bond pairs due to uneven repulsion forces.

5) Primary & Secondary effects on bond angle and shape:

i) The **bond angle** decreases due to the presence of lone pairs, which cause more repulsion on the bond pairs and as a result the bond pairs tend to come closer.

ii) The repulsion between electron pairs increases with increase in electronegativity of central atom and hence the bond angle increases. The bond pairs are closer and thus by shortening the distance between them, which in turn increases the repulsion. Hence the bonds tend to move away from each other.

The bond pairs tend to move away from each other since the distance between them is shortened as they are more localized on more electronegative central atom.

However the bond angle decreases when the electronegativities of ligand atoms are more than that of central atom. There is increase in the distance between bond pairs since they are now closer to ligand atoms. Due to this, they tend to move closer resulting in the decrease in bond angle.

The bond pairs tend to come closer since the distance between them is increased as they are more localized on more electronegative ligand atoms.

iii) The bond angle decreases with increase in the size of central atom.

On smaller central atoms the bond pairs are closer and hence tend to move away from each other so as to minimize repulsion. Hence bond angle will be more.	On bigger central atoms, the bond pairs are more distant from each other and hence there is less repulsion. Hence they tend to move closer and thus by decreasing the bond angle.

However the bond angle increases with increase in the size of ligand atoms, which surround the central atom.

There is less repulsion between smaller ligand atoms and they can move closer to each other and thus decrease the bond angle.	These are more repulsion between bigger ligand atoms and hence they tend to move away from each other. Thus bond angle increases.

iv) The bond angles are also changed when multiple bonds are present. It is due to uneven repulsions.

6) When there are two or more resonance structures, the VSEPR theory is applicable to any of such contributing structure.

Types of molecular structure

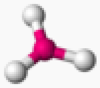
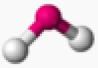
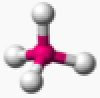
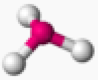
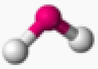
A bond angle is the geometric angle between two adjacent bonds. Some common shapes of simple molecules include:

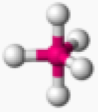
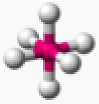
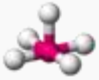
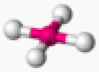
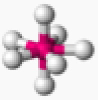
- **Linear:** In a linear model, atoms are connected in a straight line. The bond angles are set at 180°. For example, carbon dioxide and nitric oxide have a linear molecular shape.
- **Trigonal planar:** Molecules with the trigonal planar shape are somewhat triangular and in one plane (flat). Consequently, the bond angles are set at 120°. For example,boron trifluoride.
- **Bent:** Bent or angular molecules have a non-linear shape. For example, water (H_2O), which has an angle of about 105°. A water molecule has two pairs of bonded electrons and two unshared lone pairs.
- **Tetrahedral:** Tetra- signifies four, and -hedral relates to a face of a solid, so "tetrahedral" literally means "having four faces". This shape is found when there are four bonds all on one central atom, with no extra unshared electron pairs. In accordance with the VSEPR (valence-shell electron pair repulsion theory), the bond angles between the electron bonds are $\arccos(-1/3) = 109.47°$. For example, methane (CH_4) is a tetrahedral molecule.
- **Octahedral:** Octa- signifies eight, and -hedral relates to a face of a solid, so "octahedral" means "having eight faces". The bond angle is 90 degrees. For example, sulfur hexafluoride (SF_6) is an octahedral molecule.
- **Trigonal pyramidal:** A trigonal pyramidal molecule has a pyramid-like shape with a triangular base. Unlike the linear and trigonal planar shapes but similar to the tetrahedral

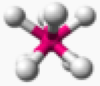
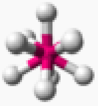
orientation, pyramidal shapes require three dimensions in order to fully separate the electrons. Here, there are only three pairs of bonded electrons, leaving one unshared lone pair. Lone pair – bond pair repulsions change the bond angle from the tetrahedral angle to a slightly lower value. For example, ammonia (NH_3).

VSEPR table

The bond angles in the table below are ideal angles from the simple VSEPR theory, followed by the actual angle for the example given in the following column where this differs. For many cases, such as trigonal pyramidal and bent, the actual angle for the example differs from the ideal angle, but all examples differ by different amounts. For example, the angle in H_2S (92°) differs from the tetrahedral angle by much more than the angle for H_2O (104.48°) does.

Bonding electron pairs	Lone pairs	Electron domains (Steric#)	Shape	Ideal bond angle (example's bond angle)	Example	Image
2	0	2	linear	180°	CO_2	
3	0	3	trigonal planar	120°	BF_3	
2	1	3	bent	120° (119°)	SO_2	
4	0	4	tetrahedral	109.5°	CH_4	
3	1	4	trigonal pyramidal	109.5 (107.8°)	NH_3	
2	2	4	bent	109.5° (104.48°)	H_2O	

Bonding electron pairs	Lone pairs	Electron domains (Steric#)	Shape	Ideal bond angle (example's bond angle)	Example	Image
5	0	5	trigonal bipyramidal	90°, 120°, 180°	PCl_5	
4	1	5	seesaw	ax–ax 180° (173.1°), eq–eq 120° (101.6°), ax–eq 90°	SF_4	
3	2	5	T-shaped	90° (87.5°), 180° < 180°)	ClF_3	
2	3	5	linear	180°	XeF_2	
6	0	6	octahedral	90°, 180°	SF_6	
5	1	6	square pyramidal	90° (84.8°)	BrF_5	
4	2	6	square planar	90°, 180°	XeF_4	
7	0	7	pentagonal bipyramidal	90°, 72°, 180°	IF_7	
6	1	7	pentagonal pyramidal	72°, 90°, 144°	$XeOF_5^-$	
5	2	7	planar pentagonal	72°, 144°	XeF_5^-	

Bonding electron pairs	Lone pairs	Electron domains (Steric#)	Shape	Ideal bond angle (example's bond angle)	Example	Image
8	0	8	square antiprismatic		XeF_8^{2-}	
9	0	9	tricapped trigonal prismatic		ReH_9^{2-}	

RELATION BETWEEN NUMBER & TYPE OF VALENCE ELECTRON PAIRS WITH THE SHAPE OF MOLECULE

* The shape of molecule and also the approximate bond angles can be predicted from the number and type of electron pairs in the valence shell of central atom as tabulated below. In the following table the molecule is represented by "AXE" notation, where

A = Central atom

X = Ligand atom bonded to the central atom either by a single bond or by multiple bond; indicating a bond pair.E = Lone pair

* The sum of number of ligand atoms (**X**) and number of lone pairs (**E**) is also known as **steric number**.

* The bond pairs are shown as green colored thick lines, whereas the lone pairs are shown as point charges using green colored lobes.

Steric number	Number of Bond pairs	Number of Lone pairs	Formula	Shape of molecule	Approximate Bond angles	Examples
1	1	0	AX	Linear	180^o	ClF, BrF, BrCl, HF, O_2
2	2	0	AX_2	Linear	180^o	$BeCl_2$, $HgCl_2$, CO_2
3	3	0	AX_3	Trigonal planar	120^o	BF_3, CO_3^{2-}, NO_3^-, SO_3
	2	1	AX_2E	Angular	120^o	SO_2, $SnCl_2$, O_3, NSF, NO_2^-
4	4	0	AX_4	Tetrahedral	109^{o}28'	CH_4, $SiCl_4$, NH_4^+, PO_4^{3-}, SO_4^{2-}, ClO_4^-
	3	1	AX_3E	Trigonal pyramidal	around 109^{o}28'	NH_3, PCl_3, XeO_3
	2	2	AX_2E_2	Angular	around 109^{o}28'	H_2O, SCl_2, Cl_2O, OF_2
5	5	0	AX_5	Trigonal bipyramidal	120^o & 90^o	PCl_5, SOF_4
	4	1	AX_4E	See saw or distorted tetrahedral	-	SF_4, $TeCl_4$
	3	2	AX_3E_2	T-Shape	90^o	ClF_3, BrF_3, $BrCl_3$
	2	3	AX_2E_3	Linear	180^o	XeF_2, I_3^-
6	6	0	AX_6	Octahedral	90^o	SF_6
	5	1	AX_5E	Square pyramidal	90^o	ClF_5, BrF_5,

						ICl_5
	4	2	AX_4E_2	Square planar	90°	XeF_4
7	7	0	AX_7	Pentagonal bipyramidal	72° & 90°	IF_7
	6	1	AX_6E	Pentagonal pyramidal	around 72° & 90°	$XeOF_5^-$, IOF_5^{2-}

STEPS INVOLVED IN PREDICTING THE SHAPES OF MOLECULES USING VSEPR THEORY

* The first step in determination of shape of a molecule is to write the Lewis dot structure of the molecule.

* Then find out the number of bond pairs and lone pairs in the valence shell of central atom.

While counting the number of bond pairs, treat multiple bonds as if they were single bonds. Thus electron pairs in multiple bonds are to be treated collectively as a single super pair.

* Use the above table to predict the shape of molecule based on steric number and the number of bond pairs and lone pairs.

APPLICATIONS & ILLUSTRATIONS OF VSEPR THEORY

1) Methane (CH_4):

* The Lewis structure of methane molecule is:

* There are 4 bond pairs around the central carbon atom in its valence shell. Hence it has tetrahedral shape with 109°28' of bond angles.

2) Ammonia (NH_3):

* The Lewis structure of ammonia indicates there are three bond pairs and one lone pair around the central nitrogen atom.

* Since the steric number is 4, its structure is based on tetrahedral geometry. However, its shape is pyramidal with a lone pair on nitrogen atom.

* The bond angle is decreased from 109°28' to 107°48' due to repulsion caused by lone pair on the bond pairs.

3) Water (H_2O):

* It is evident from the Lewis structure of water molecule, there are two bond pairs and two lone pairs in the valence shell of oxygen. Hence its structure is based on tetrahedral geometry. However its shape is angular with two lone pairs on oxygen.

* The bond angle is decreased to 104°28' due to repulsions caused by lone pairs on bond pairs. It can be noted that the bond angle decreases with increase in the number of lone pairs on the central atom.

4) Sulfur tetrachloride (SCl_4):

Since there are four bond pairs and one lone pair around sulfur in its valence shell, the structure of SCl_4 is based on trigonal bipyramidal geometry. It has seesaw shape with a lone pair occupying the equatorial position.

The angles between $P\text{-}Cl_{axial}$ and $P\text{-}Cl_{equatorial}$ are less than 90^o due to repulsion exerted by the lone pair. The angle between $P\text{-}Cl_{equatorial}$ bonds also decreases from its usual value, 120^o.

The lone pair occupies the equatorial position to minimize the repulsions.

Usually the lone pairs, bulky groups and less electronegative atoms tend to occupy equatorial position to minimize repulsions. This is because they experience repulsion only from two groups at 90^o, when they occupy the equatorial positions. However the repulsion will be more when they occupy axial positions, since they encounter three groups at 90^o.

5) PF_3Cl_2:

There are only 5 bond pairs on phosphorus atom. Hence it has trigonal bipyramidal shape. The chlorine atoms occupy the equatorial positions to minimize the repulsions since they are not only bulkier and also less electronegative than fluorine atoms.

The bond pair of P-Cl is slightly more closer towards the P atom when compared to the bond pair of P-F, since the chlorine atoms are comparatively less electronegative than fluorine atoms. Hence there is comparatively more negative charge accumulation towards P atom, which makes the P-Cl bonds to experience more repulsion than P-F bonds. Hence they orient in equatorial positions at 120^o to minimize repulsions.

Note that, here we are comparing the polarity of P-Cl bond with P-F bond. But one should keep in mind that the bond pair of P-Cl bond is still closer to Cl, since it is more electronegative than P atom.

6) Formaldehyde (HCHO):

There are three bond pairs around the central carbon atom. The double bond between C and O is considered as a single super pair. Hence the shape of the molecule is trigonal planar and the bond angles are expected to be equal to 120^o.

However, the C=O exerts more repulsion on the C-H bond pairs. Hence the ∠H-C-H bond angle will be less than 120^o and the ∠H-C-O is greater than 120^o.

Resonance

Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. It compares and contrasts two or more possible Lewis structures that can represent a particular molecule. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

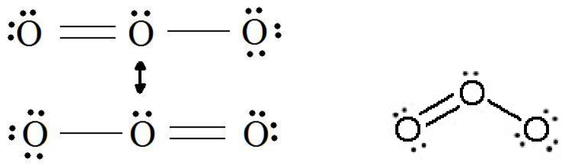
Electrons have no fixed position in atoms, compounds and molecules but have probabilities of being found in certain spaces (orbitals). Resonance forms illustrate areas of higher probabilities (electron densities). This is like holding your hat in either your right hand or your left. The term Resonance is applied when there are two or more possibilities available. Resonance structures do not change the relative positions of the atoms like your arms in the metaphor. The skeleton of the Lewis Structureremains the same, only the electron locations change.

Most arrows in chemistry cannot be used interchangeably and care must be given to selecting the correct arrow for the job.

- ↔: A double headed arrow on both ends of the arrow between Lewis structures is used to show their inter-connectivity
- ⇌: Double harpoons are used to designate equilibria
- ⇀: A single harpoon on one end indicate the movement of **one** electron
- →: A double headed arrow on one end is used to indicate the movement of **two** electrons

Example 1: Ozone

Consider ozone (O_3)



An animation of how one can do a resonance with ozone by moving electrons

Delocalization and Resonance Structures Rules

In resonance structures, the electrons are able to move to help stabilize the molecule. This movement of the electrons is calleddelocalization.

1. Resonance structures should have the same number of electrons, do not add or subtract any electrons. (check the number of electrons by simply counting them).
2. All resonance structures must follow the rules of writing Lewis Structures.
3. The hybridization of the structure must stay the same.
4. The skeleton of the structure can not be changed (only the electrons move).
5. Resonance structures must also have the same amount of lone pairs.

Formal Charge

Even though the structures look the same, the formal charge (FC) may not be. Formal charges are charges that are assigned to a specific atom in a molecule. If computed correctly, the overall formal charge of the molecule should be the same as the oxidation charge of the molecule (the charge when you write out the empirical and molecular formula). We want to choose the resonance structure with the least formal charges that add up to zero or the charge of the overall molecule. The equation for finding Formal Charge is:

Formal Charge = (number of valence electrons in free orbital) - (number of lone-pair electrons) - (12 **number bond pair electrons)**

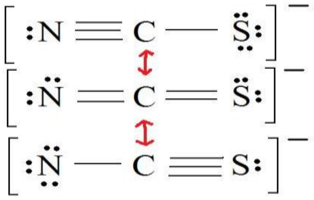
The formal charge has to equal the molecule's overall charge,e.g., the CNS− has an overall charge of -1, so the Lewis structure's formal charge has to equal -1.

Example 2: Thiocyanate Ion

Consider the thiocyanate (CNS−) ion.

1. Find the Lewis Structure of the molecule. (Remember the Lewis Structure rules.)

2. Resonance: All elements want an octet, and we can do that in multiple ways by moving the terminal atom's electrons around (bonds too).

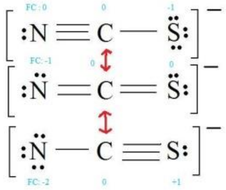


3. Assign Formal Charges

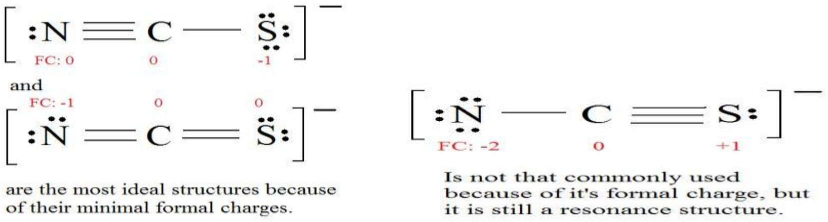
Formal Charge = (number of valence electrons in free orbital) - (number of lone-pair electrons) - (12 number bond pair electrons)

Remember to determine the number of valence electron each atom has before assigning Formal Charges

C = 4 valence e^-, N = 5 valence e^-, S = 6 valence e^-, also add an extra electron for the (-1) charge. The total of valence electrons is 16.

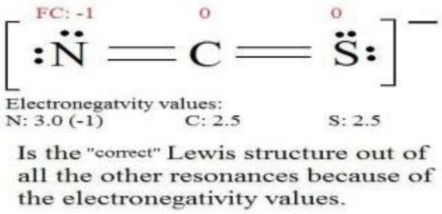


4. Find the most ideal resonance structure. (Note: It is the one with the least formal charges that adds up to zero or to the molecule's overall charge.)



5. Now we have to look at electronegativity for the "Correct" Lewis structure.

The most electronegative atom usually has the negative formal charge, while the least electronegative atom usually has the positive formal charges.



Resonance Hybrids

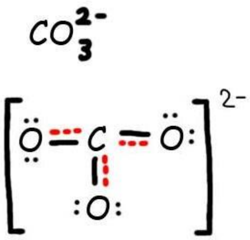
Resonance Structures are a representation of a Resonance Hybrid, which is the combination of all resonance structures. The resonance structure with the Formal Charge closest to zero is the most accepted structure, however, the correct Lewis structure is actually a combination of all the resonance structures and is not solely describe as one.

1. Draw the Lewis Structure & Resonance for the molecule (using solid lines for bonds).
2. Where there **can** be a double or triple bond, draw a dotted line (-----) for a bond.
3. Draw only the lone pairs found in all resonance structures, do not include the lone pairs that are not on all of the resonance structures.

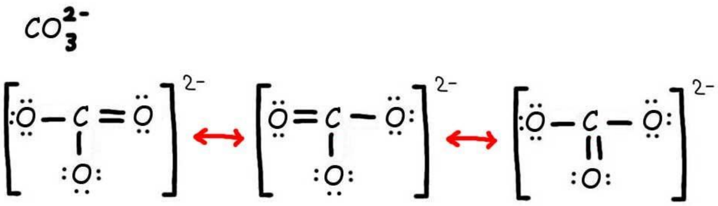
The correct Lewis structure is actually a combination of all the resonance structures and hence is not solely described as one.

Example 3: Carbonate Ion

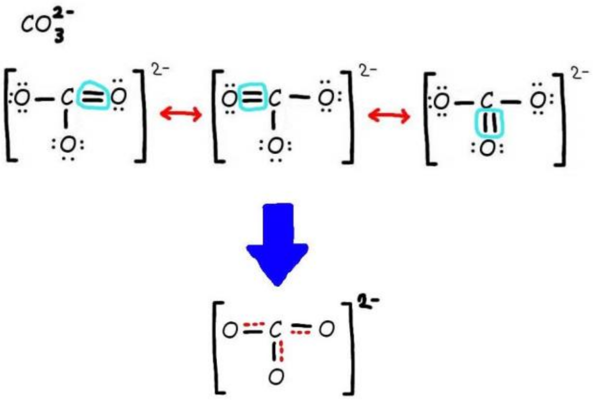
Consider the carbonate ion: CO_3^{2-}



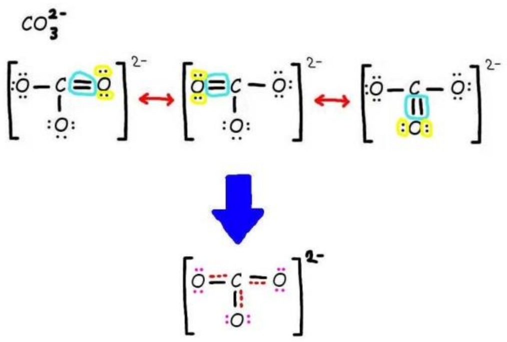
Step 1: Draw the Lewis Structure & Resonance.



Step 2: Combine the resonance structures by adding (dotted) bonds where other resonance bonds can be formed.



Step 3: Add only the lone pairs found on **ALL** resonance structures.



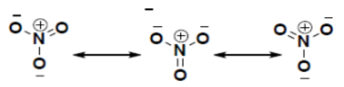
The bottom is the finished resonance hybrid for **CO_3^{2-}**.

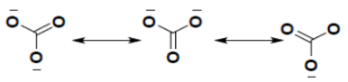
Rules for estimating stability of resonance structures

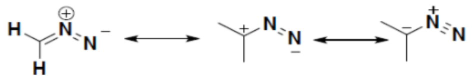
1. The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
2. The structure with the **least number of formal charges** is more stable
3. The structure with the **least separation of formal charge** is more stable
4. A structure with a **negative charge on the more electronegative atom** will be more stable
5. **Positive charges on the least electronegative atom** (most electropositive) is more stable
6. Resonance forms that are equivalent have no difference in stability and contribute equally (eg. benzene)

Example 4: Multiple Resonance of other Molecules

Molecules with multiple resonance forms

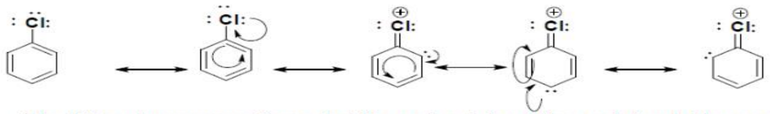






Some structural resonance conformations are the major contributor or the dominant forms that the molecule exists. For example, if we look at the above rules for estimating the stability of a molecule, we see that for the third molecule the first and second forms are the major contributors for the overall stability of the molecule. The nitrogen is more electronegative than carbon so, it can handle the negative charge more than carbon. A carbon with a negative charge is the least favorable conformation for the molecule to exist, so the last resonance form contributes very little for the stability of the Ion.

Hybrid Resonance



The different resonance forms that the molecule has helps and directs the reactivity to specific sites

The Hybrid Resonance forms show the different Lewis structures with the electron been delocalized. This is very important for the reactivity of chlorobenzene because in the presence of an electrophile it will react and the formation of another bond will be directed and determine by resonance. The long pair of electrons delocalized in the aromatic substituted ring is where it can potentially form a new bond with an electrophile, as it is shown there are three possible places that reactivity can take place, the first to react will take place at the para position with respect to the chloro substituent and then to either ortho position.

POSSIBLE QUESTIONS

UNIT-I

PART-A (20 MARKS)

(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. What do you understand by resonance.
2. What shapes are associated with the following hybrid orbitals sp^2, sp^3, sp^3d,sp^3d^2
3. On the basis of hybridization, discuss the geometry of the following molecules

   SF_6, IF_7, H_2O, NH_3.
4. What is meant by hybridization.
5. What is sigma and pi bonds.

PART C (6 MARKS)

1. What is valence bond theory of bonding? How does valence bond theory account for bonding in a hydrogen molecule.
2. Account for the following:

   i) All the bond lengths in SF_6 are equal but these are not equal in IF_5 molecule.

   ii)The geometries of H_2O and H_2S are same, but their bond angles are $H_2O>H_2S$.

   iii)BH_3 is trigonal planar while NH_3 is pyramidal.
3. Give examples and explain the concept of hybridisation with reference to : i)sp^3 ii)sp^3d
4. What do you understand by the term resonance energy? What are the essential rules for writing resonating structure.
5. With suitable examples explain the hybridization and geometry of molecules in octahedral complexes.

6. What is resonance? What are the rules which have restricted our choice of resonating structures?
7. Explain the hybridization and geometry of molecules in tetrahedral complexes by giving suitable examples.
8. What do you mean by resonance? Write the resonance structure of CO and cause of its low dipole moment.
9. i) What are the essential conditions for writing resonating structures?

   ii) Draw all the resonating structures of nitrous oxide.
10. State the geometrical arrangements possible in sp^3d and sp^3d^2hybridisations.Name the d-orbitals involved in these.

S.No.	**Questions**	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
1.	In ------- the atoms retain their individuality in the molecule.	Valence bond theory	Molecular orbital theory	Crystal field theory	coordinate compounds	Valence bond theory
2.	Resonance energy is equal to actual bond energy minus energy of the pure -------	ionic bond	Covalent bond	Coordinate bond	isomorphous compound	Covalent bond
3.	Carbon dioxide has dipole moment equal to ------	one	two	zero	three	zero
4.	Bond order in a molecule of NO is -----	1	2.5	3	3.5	2.5
5.	Which one of the following compound is covalent	H_2	CaO	KCl	Na_2S	H_2
6.	BF3 involves ------- hybridisation and the shape of the molecule is triangular planar.	sp	sp^2	sp^3	d^2sp^3	sp^2
7.	The shape of the sulphate ion is	tetrahedral	square planar	trigonal bipyramidal	hexagonal	tetrahedral
8.	In a double bond connecting two atoms , there is a sharing of	two electrons	four electrons	one electrons	all electrons	four electrons
9.	Which of the following compound has not sp3 hybridisation.	H_2O	NH_3	CH_4	SF_4	SF_4
10.	The shape of SiCl4	planar triangle	octahedral	tetrahedral	square planar	tetrahedral
11.	BF3 involves sp2 hybridisation and the shape of the molecule is---------	tetrahedral	square planar	triangular planar	linear	triangular planar
12.	Which of the following be octahedral	SF_6	BF4-	PCl_5	H_2	SF_6
13.	When the hybridisation state of carbon atom changes from sp3 to sp2 to sp ,the angle between the hybridised orbitals	decreases gradually	increases gradually	decreases with increasing	decreases considerably	increases gradually
14.	According to VSEPR theory the shape of water molecule is	octahedral	distorted tetrahedral	planar triangle	linear	distorted tetrahedral
15.	Directed bond in water form an angle of --------	90◦C	120◦C	105◦C	60◦C	105◦C
16.	Which of the following involves sp2	CO_2	SO_2	N_2O	CO	SO_2

	hybridisation					
17.	The structure of ICl2- is	trigonal	trigonal bipyramidal	octahedral	square planar	trigonal bipyramidal
18.	A sp3 hybrid orbital contains	1/4 s-character	1/2 s-character	2/3 rd s-character	3/4 s-character	1/4 s-character
19.	In which of the following the angle between the covalent bonds is maximum	SO_2	CH_4	NH_3	H_2O	CO_2
20.	Compounds formed by sp3d hybridisation will have structure	planar triangle	pyramidal	angular	trigonal bipyramidal	trigonal bipyramidal
21.	Which one of the following is most polar	CCl_4	$CHCl_3$	CH_3Cl	CH_3OH	CH_3OH
22.	Which of the following possess strong covalent bond	H-Cl	Cl-Cl	C-Cl	B-Cl	H-Cl
23.	Which one of the following is strongest bond	Cl-F	F-F	Br-F	Br-Cl	Br-F
24.	Decreasing order of size of various hybrid orbitals is	sp>sp2>sp3	sp3>sp2>sp	sp2>sp>sp3	sp>sp3>sp2	sp3>sp2>sp
25.	Bonded electron pairs present in octahedral SF6 molecule	3	4	6	8	6
26.	In PCl5 molecule, P is	sp3 hybridised	dsp2 hybridised	ds3p hybridised	sp3d hybridised	sp3d hybridised
27.	The equilateral triangle shape has	sp hybridisation	sp2 hybridisation	sp3 hybridisation	sp3d hybridisation	sp2 hybridisation
28.	Which hybrid orbitals are used for bonding in a square planar molecule or ion	sp3	dsp2	sp	sp3d	dsp2
29.	The molecule which has pyramidal shape	PCl_3	SO_3	SF_6	NO3-	PCl_3
30.	Which molecule is not linear	CO_2	SO_3	C_2H_2	$MgCl_2$	SO_3
31.	Which of the following molecule does not have a linear arrangement of molecules	C_2H_2	H_2S	$BeCl_2$	CS_2	H_2S
32.	Which hybridisation results in non-planar orbitals	sp	sp2	sp3	dsp2	sp3
33.	How many bonded electron pairs are present in IF7 molecule	6	7	8	5	7

34.	In compound X all the bond angles are exactly 109◦28' . The X is	chloromethane	iodoform	Carbon tetrachloride	Chloroform	Carbon tetrachloride
35.	Which is expected to have linear structure	SO_2	CO_2	CO_3^{2-}	SO_4^{2-}	CO_2
36.	Which is not linear	CO_2	HCN	C_2H_2	H_2O	H_2O
37.	Which compound does not contain double or triple bond	C_2H_4	H_2O	N_2	HCN	H_2O
38.	H2O is not ----------molecule	linear	pyramidal	angular	octahedral	linear
39.	Thehybridisationof Ag in the linear complex [Ag(NH3)2]+ is	sp3	sp2	sp	dsp2	sp
40.	The octet rule is not valid for the molecule	CO_2	H_2O	O_2	CO	H_2O
41.	Which of the following molecule /ion has triangular pyramidal shape	BF_3	NO^{3-}	H3O+	CO_3^{2-}	H3O+
42.	Which of the following does not have a covalent bond	O_3	H3O+	PCl5	HNO_3	PCl5
43.	The unequal sharing of the bonded pair of electrons between two atoms in a molecule gives rise to	ionic bond	polar covalent bond	non-polar covalent bond	co-ordinate bond	polar covalent bond
44.	Which of the following is not tetrahedral	BF^{4-}	NH4+	CO_3^{2-}	SO_4^{2-}	CO_3^{2-}
45.	The shape of SO42- ion is	tetrahedral	square planar	trigonal	trigonal planar	tetrahedral
46.	A molecule with four bonded electron pairs on the central atom and no lone pair is likely to be	linear	tetrahedral	octahedral	trigonal planar	tetrahedral
47.	The shape of ClO4- ion is	square planar	square pyramidal	tetrahedral	trigonal bipyramidal	tetrahedral
48.	The bond angle in NH3 molecule is	109◦28'	90◦	107◦	105◦	107◦
49.	Shape of molecules is decided by	sigma bonds	Pi bonds	both sigma and pi bonds	neither sigma nor pi bonds	sigma bonds
50.	Which one of the following is not tetrahedral	H_2O	C_2Cl_6	CH_4	diamond	H_2O
51.	Metallic sodium is -----	insulator	semiconductor	conductor of electricity	conductor only in molten state	conductor of electricity
52.	For which of the following hybridisation the	sp	sp2	sp3	dsp2	sp

	bond angle is maximum					
53.	Aqueous solution contains	H+	OH+	H_3O+	H2	H_3O+
54.	Which of the following has square planar geometry	HgCl2	CO_3^{2-}	NH4+	$Ni(CN)_4^{2-}$	$Ni(CN)_4^{2-}$
55.	Phosphorous tri fluoride molecule is	square planar	trigonal bipyramidal	tetrahedral	trigonal pyramidal	trigonal pyramidal
56.	Which is the highest melting halide	NaCl	NaBr	NaF	NaI	NaF
57.	The hybridisation in SiCl4	sp3	sp2	sp	dsp2	sp3
58.	The greater the number of ------ in a contributing structure ,greater is the importance of that structure	covalent bonds	ionic bond	metallic bond	co-ordinate bond	covalent bonds
59.	The resonance energy of carbon dioxide molecule is --------	142	138.2	156.5	162.2	138.2
60.	The resonating structure fail to explain the paramagnetic character of -----	oxygen molecule	nitric oxide molecule	carbon dioxide molecule	nitrate ion	oxygen molecule

Comparison of VB and MO approaches

The molecular orbital (MO) theory is a powerful and extensive approach which describes electrons as delocalized moieties over adjacent atoms. The applications of the MO theory extend beyond the limitations of the Valence Shell Electron Pair Repulsion (VSEPR) model and the Valence Bond theory. These previous theories provide substantial information on predicting the structure and bonding properties of a molecule by portraying electrons as localized "balloons" of high density.

Introduction

Although VSEPR and the Valence Bond theory accurately predict bond properties, they fail to fully explain some molecules. The MO theory incorporates the wave character of electrons in developing MO diagrams. MO diagrams predict physical and chemical properties of a molecule such as shape, bond energy, bond length and bond angle. They also provide information in predicting a molecule's electronic spectra and paramagnetism. The objective of this wiki is to provide readers with the fundamental steps in constructing simple homonuclear and heteronuclear diatomic molecular orbital diagrams. These steps may then be extrapolated to construct more difficult polyatomic diagrams.

Molecular Orbitals

The region an electron is most likely to be found in a molecule. A MO is defined as the combination of atomic orbitals.

Homonuclear Diatomics

Molecules consisting of two identical atoms are said to be homonuclear diatomic, such as: H_2, N_2, O_2, and F_2.

Heteronuclear Diatomics

Molecules consisting of two non-identical atoms are said to be heteronuclear diatomic, such as: CO, NO, HF, and LiF.

Bonding and Antibonding Orbitals

Orbitals that are out-of-phase with one of another are "antibonding" orbitals because regions with dense electron probabilities do not merge which destabilizes the molecule. "Bonding" orbitals are less energetic than antibonding atomic orbitals and are in-phase, as depicted in the figure below. Note how the bonding orbitals come together constructively, while the antibonding orbitals do not.

According to Valence bond theory:

- A covalent bond is formed by the overlapping of partially filled orbitals of two atoms.
- Overlapping orbitals must have electrons with opposite spin.
- Atoms involved in bond formation should have unpaired electrons.
- The number of covalent bonds formed by an atom would be equal to the number of half filled orbital.
- **Molecular Orbital Theory :**

  Resulting molecular orbital is obtained by the combination of the two wave functions (AOs) of two unpaired electrons.

- Atoms which are involved in bond formation maintain their identity.

Sigma bond:

1.Sigma bond is formed by the linear or head to head or end on overlapping of orbitals.
2. Sigma bonds are the strong bonds due to maximum overlapping of orbitals.
3. Electron density is maximum around the bond axis.
4. Compounds having sigma bonds are stable and hence less reactive.
5. First bond formed between two atoms is always a sigma bond.
6. s-s overlap, s-p overlap and p-p overlap give rise to sigma bond.

The relative strength of a sigma bond is related to the extent of overlap of the atomic orbitals. This is known as the '**principle of maximum overlap**'

Due to spherical charge distribution in s-orbital, generally s-s overlapping is not so effective as s-p and p-p overlapping.

P-orbitals have directional charge distribution and longer lobes which cause more effective overlapping. Thus s-s sigma bond is relatively weak.

Order of the strength of sigma bonds is as follows:

nature of sigma bond	**s-s**	**s-p**	**p-p**
bond strength	**1.0**	**1.73**	**3.0**

:

Pi bond

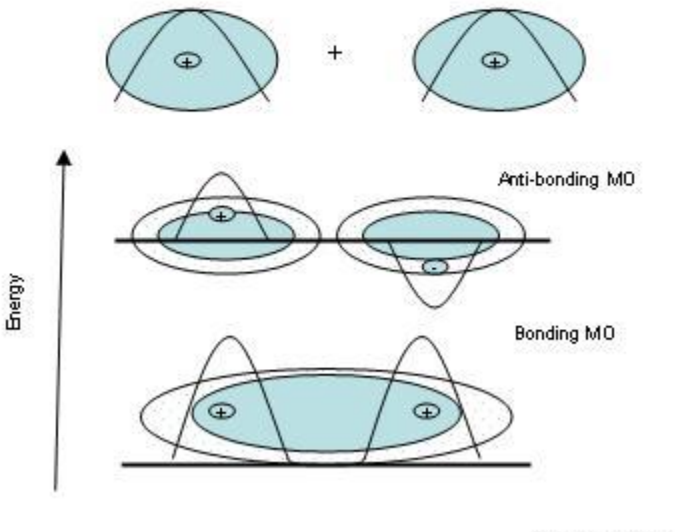
A Pi bond is formed by the lateral or side ways or parallel overlapping of P-orbital of the atoms which are already bonded by a sigma bond and their axes are coplanar. This type of overlap generates two types of molecular orbitals:

(a) Pi-bonding molecular orbital (□-orbital)

(b) Pi-antibonding molecular orbital (□*-orbital)

A pi-bonding orbital has two regions of electron density below and above the nodal plane.The electron contained in it are called pi-bonding electrons which form the pi bond. It is not linearly symmetrical with respect to the bond axis, rather it has a nodal plane. Pi-bonds are weaker than sigma bonds.

(b) In Pi-bonds, electron density lies in the regions above and below the nuclei. Compounds having pi bonds are more reactive. Pi bond is formed when two atoms already bonded by a sigma bond.



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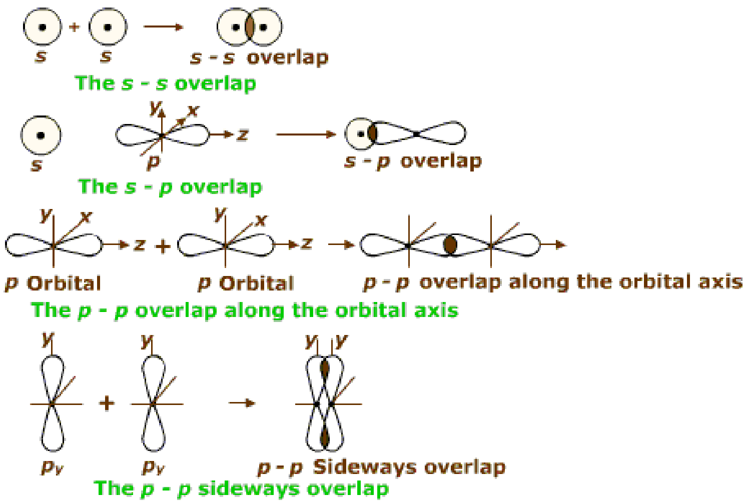
Phases and nodes

Phases are designated either (+) or (-) relative to their wave "up" or wave "down" displacements. A node occurs if the phase signs change from (+) to (-) or vice versa. It is important to notice that the phase signs do NOT symbolize charges. Nodes are regions where the probability of finding an electron is ZERO.

Sigma and Pi Bonds

A sigma-bond is an "end-to-end" bond formed from symmetric atomic orbitals. A pi-bond is formed from a "sideways" overlap.

Valence bond theory



Molecular Orbital Diagrams

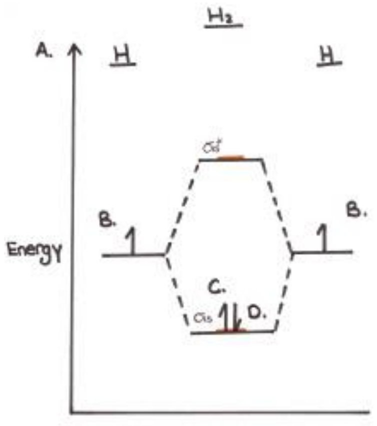


Figure 1: MO Diagram of H_2

1. The Y-axis of a MO diagram represents the total energy (not potential nor Gibbs Energy) of the orbitals.
2. Individual atomic orbitals (AO) are arranged on the far left and far right of the diagram.
3. Overlapping atomic orbitals produce molecular orbitals located in the middle of the diagram. These MO overlap with either a sigma or pi bond and are designated in bonding, nonbonding, or antibonding orbitals with respect to their phases.
4. Electrons from the atomic orbitals are assigned molecular orbitals in accordance with the Pauli Exclusion Principle. Lower energy MOs are filled first, followed by consecutively increasing orbitals.

FUNDAMENTAL STEPS IN DERIVING MO DIAGRAMS

There are several steps common in all MO diagrams. Understanding these basic steps to derive simple homonuclear and heteronuclear MOs will enable us to construct more complicated, polyatomic diagrams.

STEP 1

Find the valence electron configuration of each atom in the molecule. The valence electrons will be placed on the atomic orbital for that atom. Do this for **each** atom. Ex) Boron (B) = (He)$2s^2$ $2p^1$ = 3 valence electrons

STEP 2

Decide if the molecule is homonuclear of heteronuclear. If the molecule is homonuclear, the AOs will be symmetric. Heteronuclear AOs will be slightly different because the more electronegative atom will be placed lower on the diagram. This is due to lone pairs of electrons being more stable on more electronegative elements leading them to be lower in energy. Ex) HF = “F” will be placed lower in the diagram than “H”.

STEP 3

Fill molecular orbitals using energy and bonding properties of the overlapping atomic orbitals. Keep in mind the energy of the atomic orbitals and molecular orbitals! The following factors contribute to the position of one MO with respect to other MOs.

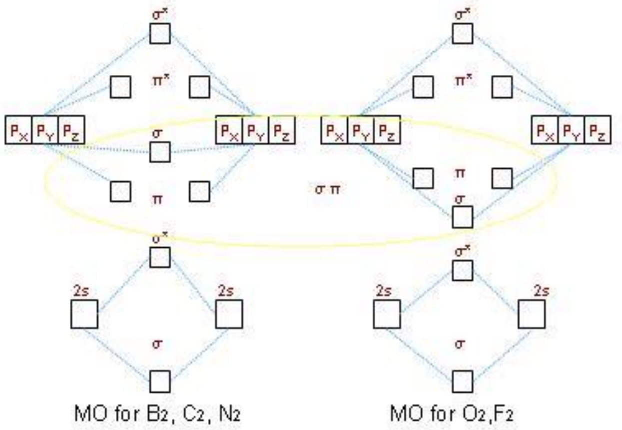
- More nodes = more energetic = higher MOs
- Sigma orbitals are stronger than pi bonds
- Antibonding MOs are higher in energy than bonding MOs
- Constructive overlap = fewer nodes = more stable (less energetic)
- Destructive overlap = more nodes = less stable (more energetic)

STEP 4

Use the diagram to predict properties of the molecule. Remember: the number of individual atomic orbitals should equal the number of MOs! Ex) Bond order, bond angle, paramagnetism, etc.

Building Molecular Orbital Diagrams for Homonuclear and Heteronuclear Diatomic Molecules

Due to symmetry of the molecule, homonuclear MO's are less difficult to derive than heteronuclear molecules and polyatomic molecules. (Such as H_2O, NH_3, and CH_4.) However, **notice** the difference between orbitals of homonuclear diatomics for elements with an atomic number less than or equal to 7 versus more than 7. In general, B_2, C_2, and N_2 have the MO diagram depicted on the left. O_2 and F_2 have the MO on the right. Why does this difference exist?



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Constructing MO diagrams for heteronuclear molecules require the same 4 steps as above. However, recall that the more electronegative atom will be lower on the diagram. The best way to learn how to draw MO diagrams is to work on practice problems. Try the following MO's on your own, and then check with the answers provided

MO diagram for N2:

STEP 1: N_2 = (He) $2s^2$ $2p^3$ (5 valence electrons for each atom)

STEP 2: Homonuclear molecule; each "N" AO will be equivalent in energy.

STEP 3: Fill the MOs with electrons:

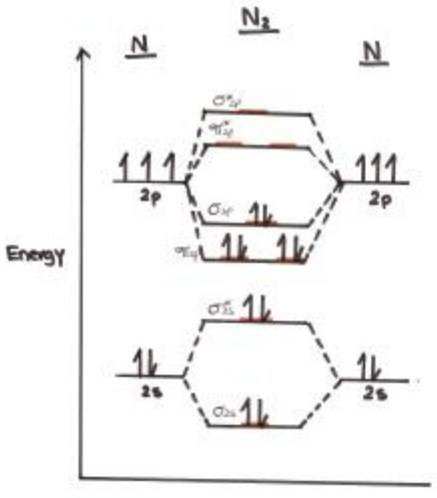


Figure 2: M.O. Diagram of N_2

STEP 4

BOND ORDER: 1/2 (Number of Bonding orbitals – Number of Antibonding orbitals)

=1/2(8-2) =3.

MO for O_2:

STEP 1: O_2 = (He) $2s^2$ $2p^4$ (6 valence electrons for each atom)

STEP 2: Homonuclear molecule; each "O" AO will be equivalent in energy.

STEP 3: Fill the MOs with electrons:

STEP 4: Check. Do the number of AO's = number of MO's? If so, calculate the bond order.

BOND ORDER: 1/2 (#Bonding orbitals - #Antibonding orbitals)

=1/2(8-4) =2. Consistent with Oxygen's double bond.

MO diagram for HF

STEP 1: H = $1s^1$ (1 valence electron) F= (He) $2s^2$ $2p^5$ (7 valence electrons)

STEP 2: Heteronuclear molecule; "F" will be lower on the diagram.

STEP 3: Fill the MOs with electrons:

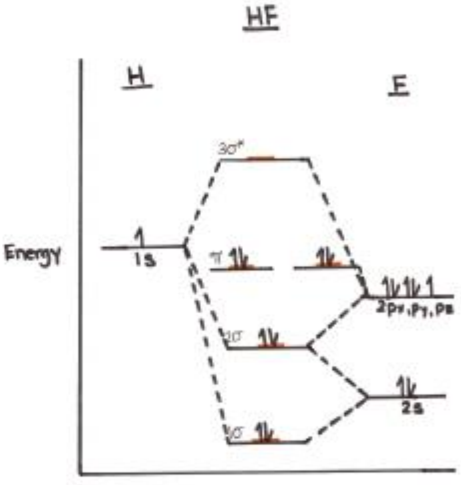


Figure 4: M.O. Diagram of HF

Bonding and antibonding orbitals

Molecular orbital theory is concerned with the combination of atomic orbitals to form new molecular orbitals. These new orbitals arise from the linear combination of atomic orbitals to form bonding and antibonding orbitals. The bonding orbitals are at a lower energy than the antibonding orbitals, so they are the first to fill up. By figuring out the molecular orbitals, it is easy to calculate bond order.

Introduction

The valence bond theory is an extension of the Lewis Structures that considers the overlapping of orbitals to create bonds. The valence bond theory is only limited in its use because it does not explain the molecular geometry of molecules very well. This is where hybridization and the molecular orbital theory comes into place.

Hybridization

Hybridization is a simple model that deals with mixing orbitals to from new, hybridized, orbitals. This is part of the valence bond theory and helps explain bonds formed, the length of bonds, and bond energies; however, this does not explain molecular geometry very well.

sp :

An example of this is acetylene (C_2H_2). This combines one s orbital with one p orbital. This means that the s and p characteristics are equal.

sp^2

An example of this is ethylene (C_2H_4). This is the combination of one s orbital and two p orbitals.

sp^3

An example of this is methane (CH_4). This is the combination of one s orbital and three p orbitals.

If you add the exponents of the hybridized orbitals, you get the amount of sigma bonds associated with that bond. The sp^2 hybridized orbital has one p orbitals that is not hybridized and so it can form a pi bond. This means that sp^2 orbitals allow for the formation of a double bond. Also, sp hybridized orbitals form a triple bond.

Antibonding vs. Bonding Orbitals

Electrons that spend most of their time between the nuclei of two atoms are placed into the bonding orbitals, and electrons that spend most of their time outside the nuclei of two atoms are placed into antibonding orbitals. This is because there is an increasing in electron density between the nuclei in bonding orbitals, and a decreasing in electron density in antibonding orbitals (Chang 459). Placing an electron in the bonding orbital stabilizes the molecule because it is in between the two nuclei. Conversely, placing electrons into the antibonding orbitals will decrease the stability of the molecule. Electrons will fill according to the energy levels of the orbitals. They will first fill the lower energy orbitals, and then they will fill the higher energy orbitals. If a bond order of zero is obtained, that means that the molecule is too unstable and so it will not exist.

Below are a few examples of bonding and antibonding orbitals drawn out:

- Hydrogen Example (homonuclear):
- Oxygen Example (homonuclear):
- Hydrogen Flouride Example (heteronuclear)

Bond Order

Bond order is the amount of bonds formed between two atoms. For example, two bonds are formed between oxygen atoms, so the bond order is 2. The following is the equation to find bond order.

1/2(electrons in bonding molecular orbitals - electrons in antibonding molecular orbitals)

Bond order gives information about bond length and strength. Generally, higher bond order correlates to a shorter bond length. This is due to the greater number of bonds between the atoms. In addition, because of the greater number of bonds between the atoms, the strength should also be greater as bond order increases.

Molecular orbital

Molecular orbital theory and Molecular orbital diagram

Complete acetylene (H–C≡C–H) molecular orbital set. The left column shows MO's which are occupied in the ground state, with the lowest-energy orbital at the top. The white and grey line visible in some MO's is the molecular axis passing through the nuclei. The orbital wave functions are positive in the red regions and negative in the blue. The right column shows virtual MO's which are empty in the ground state, but may be occupied in excited states.

In chemistry, a **molecular orbital** (**MO**) is a mathematical function describing the wave-like behavior of an electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region. The term orbital was introduced by Robert S. Mulliken in 1932 as an abbreviation for one-electron orbital wave function.[1] At an elementary level, it is used to describe the region of space in which the function has a significant amplitude. Molecular orbitals are usually constructed by combining atomic orbitals or hybrid orbitals from each atom of the molecule, or other molecular orbitals from groups of atoms. They can be quantitatively calculated using the Hartree–Fock or self-consistent field (SCF) methods.

A molecular orbital (MO) can be used to represent the regions in a molecule where an electron occupying that orbital is likely to be found. Molecular orbitals are obtained from the combination of atomic orbitals, which predict the location of an electron in an atom. A molecular orbital can specify the electron configuration of a molecule: the spatial distribution and energy of one (or one pair of) electron(s). Most commonly an MO is represented as a linear combination of atomic orbitals (the LCAO-MO method), especially in qualitative or very approximate usage. They are invaluable in providing a simple model of bonding in molecules, understood through molecular orbital theory. Most present-day methods incomputational chemistry begin by calculating the MOs of the system. A molecular orbital describes the behavior of one electron in the electric field generated by the nuclei and some average distribution of the other electrons. In the case of two electrons occupying the same orbital, the Pauli principle demands that they have opposite spin. Necessarily this is an approximation, and highly accurate descriptions of the molecular electronic wave function do not have orbitals (see configuration interaction).

Formation of molecular orbitals

Molecular orbitals arise from allowed interactions between atomic orbitals, which are allowed if the symmetries (determined from group theory) of the atomic orbitals are compatible with each other. Efficiency of atomic orbital interactions is determined from the overlap (a measure of how well two orbitals constructively interact with one another) between two atomic orbitals, which is significant if the atomic orbitals are close in energy. Finally, the number of molecular orbitals that form must equal the number of atomic orbitals in the atoms being combined to form the molecule.

In the molecular structure, the molecular orbitals can be obtained from the "Linear combination of atomic orbitals molecular orbital method" ansatz. Here, the molecular orbitals are expressed as linear combinations of atomic orbitals.

Linear combinations of atomic orbitals (LCAO)

Molecular orbitals were first introduced by Friedrich Hund and Robert S. Mulliken in 1927 and 1928. The linear combination of atomic orbitals or "LCAO" approximation for molecular orbitals was introduced in 1929 by Sir John Lennard-Jones. His ground-breaking paper showed how to derive the electronic structure of thefluorine and oxygen molecules from quantum principles. This qualitative approach to molecular orbital theory is part of the start of modern quantum chemistry. Linear combinations of atomic orbitals (LCAO) can be used to estimate the molecular orbitals that are formed upon bonding between the molecule's constituent atoms. Similar to an atomic orbital, a Schrödinger equation, which describes the behavior of an electron, can be constructed for a molecular orbital as well. Linear combinations of atomic orbitals, or the sums and differences of the atomic wavefunctions, provide approximate solutions to the Hartree–Fock equations which correspond to the independent-particle approximation of the molecular Schrödinger equation. For simple diatomic molecules, the wavefunctions obtained are represented mathematically by the equations

$$\Psi = c_a \psi_a + c_b \psi_b$$

$$\Psi^* = c_a\psi_a - c_b\psi_b$$

where Ψ and Ψ^* are the molecular wavefunctions for the bonding and antibonding molecular orbitals, respectively, ψ_a and ψ_b are the atomic wavefunctions from atoms a and b, respectively, and c_a and c_b are adjustable coefficients. These coefficients can be positive or negative, depending on the energies and symmetries of the individual atomic orbitals. As the two atoms become closer together, their atomic orbitals overlap to produce areas of high electron density, and, as a consequence, molecular orbitals are formed between the two atoms. The atoms are held together by the electrostatic attraction between the positively charged nuclei and the negatively charged electrons occupying bonding molecular orbitals.

Bonding, antibonding, and nonbonding MOs

When atomic orbitals interact, the resulting molecular orbital can be of three types: bonding, antibonding, or nonbonding.

Bonding MOs:

- Bonding interactions between atomic orbitals are constructive (in-phase) interactions.
- Bonding MOs are lower in energy than the atomic orbitals that combine to produce them.

Antibonding MOs:

- Antibonding interactions between atomic orbitals are destructive (out-of-phase) interactions, with a nodal plane where the wavefunction of the antibonding orbital is zero between the two interacting atoms
- Antibonding MOs are higher in energy than the atomic orbitals that combine to produce them.

Nonbonding MOs:

- Nonbonding MOs are the result of no interaction between atomic orbitals because of lack of compatible symmetries.
- Nonbonding MOs will have the same energy as the atomic orbitals of one of the atoms in the molecule.

Sigma and pi labels for MOs

The type of interaction between atomic orbitals can be further categorized by the molecular-orbital symmetry labels σ (sigma), π (pi), δ (delta), φ (phi), γ (gamma) etc. paralleling the symmetry of the atomic orbitals s, p, d, f and g. The number of nodal planes containing the internuclear axis between the atoms concerned is zero for σ MOs, one for π, two for δ, etc.

σ symmetry

A MO with σ symmetry results from the interaction of either two atomic s-orbitals or two atomic p_z-orbitals. An MO will have σ-symmetry if the orbital is symmetric with respect to the axis joining the two nuclear centers, the internuclear axis. This means that rotation of the MO about the internuclear axis does not result in a phase change. A σ* orbital, sigma antibonding orbital, also maintains the same phase when rotated about the internuclear axis. The σ* orbital has a nodal plane that is between the nuclei and perpendicular to the internuclear axis.

π symmetry

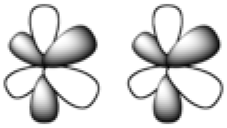
A MO with π symmetry results from the interaction of either two atomic p_x orbitals or p_y orbitals. An MO will have π symmetry if the orbital is asymmetric with respect to rotation about the internuclear axis. This means that rotation of the MO about the internuclear axis will result in a phase change. There is one nodal plane containing the internuclear axis, if real orbitals are considered.

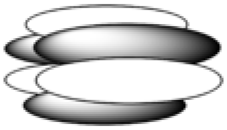
A π* orbital, pi antibonding orbital, will also produce a phase change when rotated about the internuclear axis. The π* orbital also has a second nodal plane between the nuclei.[11

δ symmetry

A MO with δ symmetry results from the interaction of two atomic d_{xy} or $d_{x^2-y^2}$ orbitals. Because these molecular orbitals involve low-energy d atomic orbitals, they are seen in transition-metal complexes. A δ bonding orbital has two nodal planes containing the internuclear axis, and a δ* antibonding orbital also has a third nodal plane between the nuclei.

φ symmetry





Suitably aligned f atomic orbitals overlap to form phi molecular orbital (a phi bond)

Theoretical chemists have conjectured that higher-order bonds, such as phi bonds corresponding to overlap of f atomic orbitals, are possible. There is as of 2005 only one known example of a molecule purported to contain a phi bond (a U−U bond, in the moleculeU_2).

Gerade and ungerade symmetry]

For molecules that possess a center of inversion (centrosymmetric molecules) there are additional labels of symmetry that can be applied to molecular orbitals. Centrosymmetric molecules include:

- Homonuclear diatomics, X_2
- Octahedral, EX_6
- Square planar, EX_4.

Non-centrosymmetric molecules include:

- Heteronuclear diatomics, XY
- Tetrahedral, EX_4.

If inversion through the center of symmetry in a molecule results in the same phases for the molecular orbital, then the MO is said to have gerade (g) symmetry, from the German word for even. If inversion through the center of symmetry in a molecule results in a phase change for the molecular orbital, then the MO is said to have ungerade (u) symmetry, from the German word for odd. For a bonding MO with σ-symmetry, the orbital is σ_g (s' + s'' is symmetric), while an antibonding MO with σ-symmetry the orbital is σ_u, because inversion of s' – s'' is antisymmetric. For a bonding MO with π-symmetry the orbital is π_u because inversion through the center of symmetry for would produce a sign change (the two p atomic orbitals are in phase with each other but the two lobes have opposite signs), while an antibonding MO with π-symmetry is π_g because inversion through the center of symmetry for would not produce a sign change (the two p orbitals are antisymmetric by phase).[16]

Bonding in molecular orbitals

Orbital degeneracy

Molecular orbitals are said to be degenerate if they have the same energy. For example, in the homonuclear diatomic molecules of the first ten elements, the molecular orbitals derived from the p_x and the p_y atomic orbitals result in two degenerate bonding orbitals (of low energy) and two degenerate antibonding orbitals (of high energy).

Ionic bonds

When the energy difference between the atomic orbitals of two atoms is quite large, one atom's orbitals contribute almost entirely to the bonding orbitals, and the others atom's orbitals contribute almost entirely to the antibonding orbitals. Thus, the situation is effectively that some electrons have been transferred from one atom to the other. This is called an (mostly) ionic bond.

Bond order

The bond order, or number of bonds, of a molecule can be determined by combining the number of electrons in bonding and antibonding molecular orbitals. A pair of electrons in a bonding orbital creates a bond, whereas a pair of electrons in an antibonding orbital negates a bond. For example, N_2, with eight electrons in bonding orbitals and two electrons in antibonding orbitals, has a bond order of three, which constitutes a triple bond.

Bond strength is proportional to bond order—a greater amount of bonding produces a more stable bond—and bond length is inversely proportional to it—a stronger bond is shorter.

There are rare exceptions to the requirement of molecule having a positive bond order. Although Be_2 has a bond order of 0 according to MO analysis, there is experimental evidence of a highly unstable Be_2 molecule having a bond length of 245 pm and bond energy of 10 kJ/mol.

POSSIBLE QUESTIONS

UNIT-I

PART-A (20 MARKS)

(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. What is LCAO molecular orbital approach
2. What is bond order?
3. What is meant by bonding molecular orbital.
4. What is meant by non bonding molecular orbital
5. What is the bond order of N_2 and O_2 molecule.

PART C (each question carries six marks)

1. What are the main postulates of VSEPR theory.
2. Distinguish between molecular orbital theory and valence bond theory.
3. Distinguish two aspects of the following:

   i)atomic and molecular orbitals

   ii)bonding and antibonding orbitals
4. Draw MO diagram of CO and calculate its bond order.
5. What is the meaning of overlap of atomic orbitals? Explain s-s,s-p and p-p overlap with examples.

6. With the help of M.O. diagrams explain why
    i) the bond order in N_2^+ ion is less than that in N_2 molecule whereas the bond order in O_2^+ is greater than that in O_2 molecule.

    sthe bond energy of NO^+ is higher than that of NO.
7. Explain how the atomic orbitals combine to form bonding and antibonding M.O. What are the limitations to such combination.
8. Draw the molecular orbital diagram of CO molecule and explain.
9. Sketch the shapes of Mo obtained by the overlap of

    i)two s-orbitals ii)end on overlap of two p-orbitals iii)sidewise overlap of two p-orbitals
10. Write the electronic configuration of NO molecule.
    ii) What is meant by bond order
    iii) Will the bond length be shorter or longer than in NO^+
11. How many unpaired electrons will be present.

S.No.	**Questions**	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
1.	The molecule having bond order 3 is	H_2	N_2	O_2	He2+	N_2
2.	The number of antibonding electron pairs in O22- molecular ion on the basis of MOT is (Atomic number of O=8)	4	3	2	5	4
3.	O2 molecule is	paramagnetic	diamagnetic	ferromagnetic	ferrimagnetic	paramagnetic
4.	Which of the following is paramagnetic	O_2	CN-	CO	NO+	O_2
5.	The bond order of O2+ is	2	2.5	1.5	3	
6.	Which one of the following molecule is paramagnetic	CO_2	SO_2	NO	H_2O	NO
7.	Which of the following is not paramagnetic	NO	S^{2-}	O^{2-}	N^{2-}	S^{2-}
8.	The molecular species having highest bond order is---	O_2	O^{2-}	O^{2+}	H2+	O^{2+}
9.	Which species is paramagnetic	O^{2-}	CH^{3-}	CO	NO3-	O^{2-}
10.	The linear combination of two hybridised orbitals each having one electron and belonging two different atoms leads to a	sigma bond	Pi bonds	double bond	coordinate bond	sigma bond
11.	Strongest bond is formed by the overlapping of	2s and 2p orbitals	2p and 2p orbitals	2s and 2s orbitals	is orbital	2s and 2p orbitals
12.	The bond order of CO molecule on the basis of M.O. theory is	0	2	3	1	3
13.	Which can not exist on the basis of MO theory	O_2	He2+	NO3-	He2	He2
14.	When two atomic orbitals combine they form	one molecular orbital	two molecular orbitals	two bonding molecular orbital	two antibonding molecular orbitals	two molecular orbitals
15.	Which has the largest bond angle	H2O2	NH_3	H_2S	H_2O	NH_3
16.	Which of the following species has the longest bond length	NO+	O^{2-}	O2+	N2+	O2+
17.	HCl involves	s-s overlapping	sp-overlapping	p-p overlapping	Pπ-Pπ overlapping	sp-overlappi

						ng
18.	Which shows non directional bonding	BCl3	CsCl	NCl3	BeCl3	NCl3
19.	Which species has lone pair of electrons on central atom	CCl4	CH4	NH4+	H_2O	H_2O
20.	Which atomic orbital is always involved in sigma bonding only	s	p	d	f	s
21.	Lateral overlapping is expected in	sigma bonds	pi bonds	metallic bonds	coordinate bonds	pi bonds
22.	The energy of antibonding molecular orbital is	greater than the bonding M.O	smaller than the bonding M.O	equal to that of bonding orbital	very low	greater than the bonding M.O
23.	Pi bond	increases bond length	decrease s bond length	Distorts the geometry of molecule	makes homoatomic molecules more reactive	decrease s bond length
24.	The example of the p-p orbital overlapping is the formation of	H2 molecule	Cl2 molecule	Hydrogen chloride	Hydrogen bromide molecule	Cl2 molecule
25.	Maximum covalency of an atom of an element is equal to	No. of unpaired lectrons in the s and p-orbitals	No.of unpaired electrons in the p-orbitals	total number of s and p- electrons in the outermost shell	total number of electrons in the p-orbitals	total number of s and p-electrons in the outermost shell
26.	A pi bond is formed by sideway overlapping of	s-s orbitals	p-p orbitals	s-p orbitals	s-p-s orbitals	p-p orbitals
27.	Sigma bond is formed by	orbitals	p-p orbitals	end to end overlapping of orbitals	shortens the internuclear distance	end to end overlappi

						ng of orbitals
28.	Fluorine molecule is formed by the overlap of	s-p orbitals	s-s	p-p orbitals by end to end manner	p-p orbitals by side to side manner	p-p orbitals by end to end manner
29.	Linear combination of two hybridised orbitals , belonging to two atoms and each having one elctron leads to	sigma bond	double bond	co-ordinate covalent bond	pi bond	sigma bond
30.	Which is not characteristic of pi bond	pi bond is formed when asigma bond already exists	Pi bonds are formed from hybrid orbitals	pi bond may be formed by the overlapping of p and or d orbitals	pi bond results from lateral overlap of atomic orbitals	pi bonds are formed from hybrid orbitals
31.	Which of the following has maximum bond energy	O_2	O2+	O_2^{2-}	O^{2-}	
32.	Hybridisation involves	addition of an electron pair	mixing up of atomic orbitals	separation of orbitals	removal of electron pair	mixing up of atomic orbitals
33.	The bond strength increases	with increasing bond order	with increasing extent of overlapping of orbitals	with decreasing diference between energies of overlapping orbitals	with decreasing order	with increasing bond order
34.	The HCN molecule contains	3 sigma and 2 pi bonds	2 sigma and 2 pi bonds	3 sigma and 3 pi bonds	2 sigma one pi bond	2 sigma and 2 pi bonds
35.	The formation of N2+ from N2 , the electron is	a σ orbital	π orbital	σ* orbital	π* orbital	a σ orbital

	removed from					
36.	MOT put forwarded by	Hund and Mullikan	Heisenberg	debroglie	Aufbau	Hund and Mullikan
37.	The valence shell configuration of O-atom has --------- unpaired electrons	1	2	4	3	2
38.	Hydrogen molecule is formed by -----------------	s-s overlap	s-p overlap	p-p head to head overlap	p-p side to side overlap	s-s overlap
39.	Hydrogen fluoride is formed by -----------------	s-s overlap	s-p overlap	p-p head to head overlap	p-p side to side overlap	s-p overlap
40.	The example of ammonia molecule belongs to	s-p overlap	p-p head to head overlap	p-p side to side overlap	s-s overlap	s-p overlap
41.	Oxygen molecule is formed by the overlap of	s-p overlap	s-s overlap	p-p head to head overlap	p-p overlap	p-p head to head overlap
42.	p-p head to head overlap is otherwise called as	end to end overlap	sideway overlap	lateral overlap	sidewise	end to end
43.	Nitrogen molecule is an example for	p-p head to head overlap	s-p overlap	s-s overlap	p-p overlap	p-p head to head overlap
44.	p-p side to side overlap is otherwise called as-----	lateral overlap	end to end overlap	head on overlap	linear overlap	lateral overlap
45.	Two s-orbitals on two different atom is --------	s-s overlap	s-p overlap	p-p head to head overlap	p-p side to side overlap	s-s overlap
46.	The electron density in this bond is distributed -----------about the nuclear axis	symmetrical	unsymmetrical	parallel	perpendicular	symmetrical
47.	Atomic orbitals are -----------	polycenteric	monocentric	bicentric	zero	monocentric
48.	Bonding MO is formed by the combination of electron waves of the ---------sign	same	opposite	positive and negative	negative and positive	same
49.	Molecular orbitals are ----	polycenteric	monocentric	bicentric	zero	polycenteric

50.	Antibonding MO possesses ----------energy than the atomic orbitals from which it is formed	lesser	higher	very less	low and high	higher
51.	In antiboding MO the electron density in between the nuclei is ------ and hence the repulsion between the nuclei high	low	high	very low	very low	low
52.	Bonding MO possesses ----------energy than the atomic orbitals from which it is formed	higher	lower	very high		lower
53.	The degenerate molecular orbitals obeyed by ----------	Hund's rule	Heisenberg	debroglie	Aufbau	Hund's rule
54.	The maximum number of electrons that a MO can contain two.These two electrons must have opposite spin is called	pauli exclusion principle	Heisenberg	Hund's rule	Aufbau	pauli exclusion principle
55.	Resonance plays an important role in ---------	VBT	MOT	CFT	Metallic	VBT
56.	The -----starts with the nuclei of the constituent atoms	VBT	MOT	CFT	Metallic	MOT
57.	Bond order of Boron molecule is equal to	1	2	3	4	1
58.	The neon molecule has the bond order of	0	1	2	3	0
59.	The NO molecule is ---------	paramagnetic	diamagnetic	ferromagnetic	ferrimagnetic	paramagnetic
60.	In Nitrosyl ion (No+) it has --------in character.	paramagnetic	diamagnetic	ferromagnetic	ferrimagnetic	diamagnetic