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Chemical Bonding – Part I

Valence Bond Theory (VB Theory) and its Limitations

Valence bond theory explains the geometry of the complex compound using the concept of hybridization. This theory is a chemical bonding theory that explains the bonding between two **atoms is caused by the overlap of half-filled atomic orbitals**. The two atoms share each other's unpaired electron to form a filled orbital to form a hybrid orbital and bond together. According to this theory, a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron.

A valence bond structure is similar to a Lewis structure, but where a single Lewis structure cannot be written, several valence-bond structures are used. Each of these VB structures represents a specific Lewis structure.

Limitations.

It fails to account for various magnetic, electronic and spectroscopic properties of complexes.

- It describes the bonding in coordination compound qualitatively.
- It does not offer any explanation for the optical absorption spectra of the complexes.
- It offers no possibility of predicting or explaining magnetic behaviour beyond specifying the number of unpaired electrons and correlation of this fact with stereochemistry is often poor and even seriously misleading. For example, it was assumed that all square planar nickel (II) complex formed by dsp^2 hybridization were diamagnetic whereas all tetrahedral nickel (II) complexes formed by sp^3 hybridization are paramagnetic. The recent x-ray diffraction studies reveal that square planar nickel (II) complex can be paramagnetic.

1. The valence bond theory also led to the erroneous conclusion about ionic and covalent structures assigned on the basis of magnetic data.

2. It is unable to amount for or predict even the relative energies of different structures.
3. It does not take into account the splitting of 'd' orbitals.
4. It fails to explain the formation of inner orbital and outer orbital complexes

Directional characteristics of Covalent Bond.

The meaning of covalent bonds being *directional* is that atoms bonded covalently prefer **specific orientations in space relative to one another**. As a result, molecules in which atoms are bonded covalently have definite shapes. The reason for this directionality is that covalent bonds are formed by **sharing electrons between atoms**, or by overlapping the atomic orbitals of participant atoms. And usually only few patterns of overlap are possible, consequently, only few spatial arrangements of atoms are possible. Ionic bonds are different: there is no electron sharing (or atomic orbital overlaps) and the number of anions surrounding a cation is limited by the charges of the ions, their sizes, and the efficiency of the lattice packing.

Hybridization.

Redistribution of the energy of orbitals of individual atoms to give orbitals of equivalent energy happens, when two atomic orbitals combine together to form hybrid orbital in a molecule. This process is called hybridization. The new orbitals thus formed are known as **hybrid orbitals**. The intermixing of atomic orbitals are based on quantum mechanics. The atomic orbitals of the same energy level can only take part in hybridization and both full filled and half-filled orbitals can also take part in this process provided they have equal energy.

Types of Hybridization.

Based on the types of orbitals involved in mixing, the hybridization can be classified as sp , sp^2 , sp^3 , sp^3d , sp^3d^2 , sp^3d^3 . Let us now discuss the various types of hybridization along with their examples.

1. sp Hybridization.

sp hybridization is observed when one s and one p orbital in the same main shell of an atom of equal energy to give a new hybrid orbital known as an sp hybridized orbital. It forms linear molecules with an angle of 180° . sp hybridization is also called **diagonal hybridization**. Each sp hybridized orbital has an equal amount of s and p character, i.e., 50% s and p character.

Examples of sp Hybridization: All compounds of beryllium like BeF_2 , BeH_2 , $BeCl_2$, All compounds of carbon-containing triple Bond like C_2H_2 .

2. sp^2 Hybridization

sp^2 hybridisation is observed when one s and two p orbitals of the same shell of an atom mix to form 3 equivalent orbital. The new orbitals formed are called sp^2 hybrid orbitals. sp^2 hybridization is also called **trigonal hybridization**. A mixture of s and p orbital formed in trigonal symmetry and is maintained at 120° . All the three hybrid orbitals remain in one plane and make an angle of 120° with one another. Each of the hybrid orbitals formed has 33.33% s character and 66.66% 'p' character.

Examples of sp^2 Hybridization: All the compounds of Boron i.e. BF_3 , BH_3 . All the compounds of carbon containing a carbon-carbon double bond, Ethylene (C_2H_4)

3. sp^3 Hybridization

When one 's' orbital and 3 'p' orbitals belonging to the same shell of an atom mix together to form four new equivalent orbital, the type of hybridization is called a **tetrahedral hybridization** or sp^3 . The new orbitals formed are called sp^3 hybrid orbitals. These are directed towards the four corners of a regular tetrahedron and make an angle of $109^\circ 28'$ with one another. The angle between the sp^3 hybrid orbitals is $109^\circ.28'$. Each sp^3 hybrid orbital has 25% s character and 75% p character.

Example of sp^3 hybridization: ethane (C_2H_6), methane.

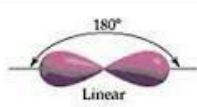

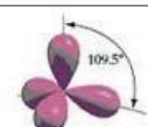
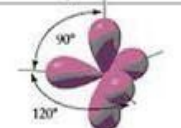
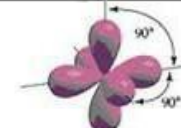
4. sp^3d Hybridization

sp^3d hybridization involves the mixing of 3p orbitals and 1d orbital to form 5 sp^3d hybridized orbitals of equal energy. They have **trigonal bipyramidal geometry**. Three hybrid orbitals lie in the horizontal plane inclined at an angle of 120° to each other known as the equatorial orbitals. The remaining two orbitals lie in the vertical plane at 90° degrees plane of the equatorial orbitals known as axial orbitals.

Example: Hybridization in Phosphorus pentachloride: PCl_5

5. sp^3d^2 Hybridization

sp^3d^2 hybridization has 1s, 3p and 2d orbitals, that undergo intermixing to form 6 identical sp^3d^2 hybrid orbitals. These 6 orbitals are directed towards the corners of an octahedron. They are inclined at an angle of 90° to one another.

Valence electron pair geometry	# of orbitals	Hybrid orbitals	Electron density diagram	Examples
Linear	2	sp		BF_2 $HgCl_2$ CO_2
Trigonal planar	3	sp^2		BF_3 SO_3
Tetrahedral	4	sp^3		CH_4 H_2O NH_4^+
Trigonal bipyramidal	5	sp^3d		PF_5 SF_4 BrF_3
Octahedral	6	sp^3d^2		SF_6 XeF_4 PF_6^-

Key Features of Hybridization

- Atomic orbitals with equal energies undergo hybridization.
- The number of hybrid orbitals formed is equal to the number of atomic orbitals mixing.
- It is not necessary that all the half-filled orbitals must participate in hybridization. Even completely filled orbitals with slightly different energies can also participate.
- Hybridization happens only during the bond formation and not in an isolated gaseous atom.
- The shape of the molecule can be predicted if hybridization of the molecule is known.
- The bigger lobe of the hybrid orbital always has a positive sign while the smaller lobe on the opposite side has a negative sign.

Formula	Shape (Name)	Bond Angles	Hybridization
AX ₂	Linear	180	sp
AX ₃	Trigonal Planar	120	sp ²
AX ₄	Tetrahedral	109.5	sp ³
AX ₅	Triangular Bipyramidal	120, 90	sp ³ d
AX ₆	Octahedral	90	sp ³ d ²
AX ₂ N	Bent	120	sp ²
AX ₂ N ₂	Bent	109.5	sp ³
AX ₃ N	Trigonal Pyramidal	109.5	sp ³

HYBRIDISATION				
Type of hybridisation	No. of hybrid orbitals obtained	Bond angle	Structure	Examples
sp	2	180°	Linear	BeCl ₂ , CO ₂ , C ₂ H ₂ , HgCl ₂ , CN ⁻ , N ₃
sp ²	3	120°	Plane triangle	SO ₃ , BF ₃ , AlCl ₃ , CO ₃ ²⁻
sp ³	4	109°28'	Tetrahedral	CH ₄ , CCl ₄ , C ₂ H ₆ , SO ₄ ²⁻ , ClO ₄ , [Ni(CO) ₄]
sp ² d	4	90°	Square planar	[Ni(CN) ₄] ²⁻ , [Pd(CN) ₄] ²⁻
sp ³ d	5	90° & 120°	Trigonal bipyramidal	PF ₅ , PCl ₅
sp ³ d ²	6	90°	Octahedral	SF ₆ , [Fe(CN) ₆] ⁴⁻
sp ³ d ³	7	90° & 72°	Pentagonal bipyramidal	IF ₇

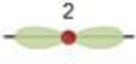













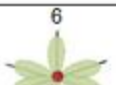





VSEPR THEORY

The two primary founders of the VSEPR (Valence Shell Electron Pair Repulsion) theory are Ronald Nyholm and Ronald Gillespie. This theory is also known as the Gillespie-Nyholm theory to honour these chemists. VSEPR Theory is used to predict the shape of the molecules from the electron pairs that surround the central atoms of the molecule. The theory was first presented

by Sidgwick and Powell in 1940. VSEPR theory is based on the assumption that the molecule will take a shape such that electronic repulsion in the valence shell of that atom is minimized.

The VSEPR theory is based on the premise that there is a repulsion between the pairs of valence electrons in all atoms, and the atoms will always tend to arrange themselves in a manner in which this electron pair repulsion is minimalized. This arrangement of the atom determines the geometry of the resulting molecule.

The different geometries that molecules can assume keeping with VSEPR theory can be seen in the illustration provided below.

Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2 	Linear	 Linear				
3 	Trigonal planar	 Trigonal planar	 Bent			
4 	Tetrahedral	 Tetrahedral	 Trigonal pyramidal	 Bent		
5 	Trigonal bipyramidal	 Trigonal bipyramidal	 Sawhorse	 T-shaped	 Linear	
6 	Octahedral	 Octahedral	 Square pyramidal	 Square planar	 T-shaped	 Linear

Postulates of VSEPR Theory:

According to the VSEPR theory, the repulsion between two electrons is caused by the Pauli exclusion principle that has greater importance than electrostatic repulsion in the determination of molecular geometry.

The postulates of the VSEPR theory are listed below

- In polyatomic molecules (i.e. molecules made up of three or more atoms), one of the constituent atoms is identified as the central atom to which all other atoms belonging to the molecule are linked.
- The total number of valence shell electron pairs decides the shape of the molecule.
- The electron pairs have a tendency to orient themselves in a way that minimizes the electron–electron repulsion between them and maximizes the distance between them.
- The valence shell can be thought of as a sphere wherein the electron pairs are localized on the surface in such a way that the distance between them is maximized.
- Should the central atom of the molecule be surrounded by bond pairs of electrons, then, the asymmetrically shaped molecule can be expected.
- Should the central atom be surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
- The VSEPR theory can be applied to each resonance structure of a molecule.
- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.
- If electron pairs around the central atom are closer to each other, they will repel each other. This results in an increase in the energy of the molecules.
- If the electron pairs lie far from each other, the repulsions between them will be less and eventually, the energy of the molecule will be low.

Limitations of VSEPR Theory.

Some significant limitations of the VSEPR theory include:

- This theory fails to explain isoelectronic species (i.e. elements having the same number of electrons). The species may vary in shapes despite having the same number of electrons.
- The VSEPR theory does not shed any light on the compounds of transition metals. The structure of several such compounds cannot be correctly described by this theory. This is because the VSEPR theory does not take into account the associated sizes of the substituent groups and the lone pairs that are inactive.
- Another limitation of VSEPR theory is that it predicts that halides of group 2 elements will have a linear structure, whereas their actual structure is a bent one.