

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Definition: The Valence-Shell-Electrons-Pair-Repulsion Theory (VSEPR), proposes that the stereochemistry of an atom in a molecule is determined primarily by the repulsive interactions among all the electron pairs in its valence shell.

Postulates of VSEPR Theory : The main postulates of this theory are :

- (1) The shape of the molecule is determined by repulsion between all of the electron pairs present in the valence shell.

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(2) A lone pair of electrons takes up more space round the central atom than a bond pair, since the lone pair is attracted to one nucleus whilst the bond pair is shared by two nuclei. It follows that repulsion between two lone pairs is greater than the repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs. The repulsive interactions decrease in the order :



(3) The magnitude of repulsion between bonding pairs of electrons. depends on the electronegativity difference between the central atom and the other atoms.

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(4) Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond. Repulsive forces decrease sharply with increasing bond angle between the electron pairs.

Example: BF₃ Molecule

In BF₃ the central B atom has the configuration : $1s^2, 2s^2, 2p_x^1$. During the bond formation one 2s-electron is promoted to vacant 2p_y orbital. Thus, excited B (configuration: $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^0$) has three unpaired electrons for bond formation with three fluorine atoms. The three bonds between B and F atoms should be slightly different strengths, because in one, 2s; while in other, two 2p-orbital electrons are involved. But in fact, all the three bonds in BF₃ are of equal strength with bond angle of 120°.

VALENCE BOND THEORY

Introduction: Atoms with unpaired electrons tend to combine with other atoms which also have unpaired electrons. In this way the unpaired electrons are paired up, and the atoms involved all attain a stable electronic arrangement. This is usually a full shell of electrons (i.e., a noble gas configuration). Two electrons shared between two atoms constitute a bond. The number of bonds formed by an atom is usually the same as the number of unpaired electrons in the ground state, i.e., the lowest energy state. However, in some cases the atom may form more bonds than this. This occurs by excitation of the atom (i.e., providing it with energy) when electrons which were paired in the ground state are unpaired and promoted into suitable empty orbitals. This increases the number of unpaired electrons, and hence the number of bonds which can be formed.

VALENCE BOND THEORY

Postulates of Valance Bond Theory :

- (i) A molecule is considered to be made up of atoms.
- (ii) Electrons in atoms occupy atomic orbitals.
- (iii) Orbitals may or may not be hybridized.
- (iv) The atomic orbitals (or the hybrid orbitals) are thought to remain even when the atom is chemically bonded in a molecule.

Example: 1. In HF, H has a singly occupied s-orbital that overlaps with a singly filled 2p orbital on F.

2. In NH_3 , there are three singly occupied p-orbitals on N which overlap with S-orbitals from three H atoms.

VALENCE BOND THEORY

Limitations of valence Bond Theory :

This theory does not explain :

- (i) The directional nature of covalent bond.
- (ii) The formation of co-ordinate bond in which shared pair of electrons is contributed by only one of the combining atoms.
- (iii) The paramagnetic nature of O₂ molecule.
- (iv) The structures of odd electron molecules or ions where no pairing of electrons takes place.

MOLECULAR ORBITAL THEORY

Introduction: The molecular orbital theory given by Hund and Mullikens considers that the valency electrons are associated with all the concerned nuclei, *i.e.*, with the molecule as a whole. Thus, in other words, the atomic orbitals combine together to form molecular orbitals in which the identity of both the atomic orbitals is lost.

Postulates of Molecular Orbital Theory :

(a) During the formation of bond, the two half-filled atomic orbitals with opposite spins combine to form two molecular orbitals (M.O.). One of which is bonding M.O. and other antibonding M.O. The energy of combining atomic orbitals, however, should be of similar magnitude.

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- (b) A bonding M.O. has lower energy than the atomic orbitals from which it is formed; while antibonding M.O. has higher energy than the atomic orbitals from which it is formed.
- (c) Two *s* or *p*-orbitals can overlap end-to-end to form one sigma bonding molecular orbital (σ) and one sigma antibonding molecular orbital (σ^*).
- (d) Two *p*-orbitals can overlap sideways to form one pi (π)-bonding molecular orbital and pi (π^*) anti bonding orbital.
- (e) The energies of σ -bonding orbitals are lower than those of π -bonding orbitals.
- (f) The orbitals of lower energy are filled first. Each orbital may hold up two electrons, provided that they have opposite spins.

MOLECULAR ORBITAL THEORY

- (g) When several orbitals have the same energy, (*i.e.*, they are degenerate), electrons will be arranged so as to give the maximum number of unpaired spins (Hund's rule).
- (h) The order of energy of molecular orbitals has been determined mainly from spectroscopic data. In simple homonuclear diatomic molecules, the order is :

MOLECULAR ORBITAL THEORY

The energies of the σ_{2p} and π_{2p} M.Os. are very close together. The order of M.Os shown above is correct for oxygen and heavier elements, but for the lighter elements boron, carbon and nitrogen the π_{2p_y} and π_{2p_z} are probably lower than σ_{2p_x} . For these atoms the order is :

MOLECULAR ORBITAL THEORY

(g) Molecules or ions having one or more unpaired electrons in the M.O. are paramagnetic in nature; while those with paired electron in the M.O., are diamagnetic in nature.

Bond order : Bond order of a molecule is :

$$= \frac{\left[\begin{array}{l} \text{No. of electrons in the} \\ \text{bonding molecular orbitals} \end{array} \right] - \left[\begin{array}{l} \text{No. of electrons in anti-} \\ \text{bonding molecular orbitals} \end{array} \right]}{2} = \frac{(N_b - N_a)}{2}$$

MOLECULAR ORBITAL THEORY

Significance of Bond order

- (a) A -ve or zero value of bond order indicates that the molecule is unstable and does not exist. A +ve value of bond order indicates that the molecule exists and is stable. Greater the value of bond order, greater is stability of the molecule.
- (b) A bond order of + 1, +2, +3 indicates that the molecule is formed by joining of two atoms by single, double or triple bond respectively.

$$(c) \text{ Bond order} \propto \text{Bond energy} \propto \text{Bond angle} \propto \frac{1}{\text{Bond length}} \propto \text{stability}$$