

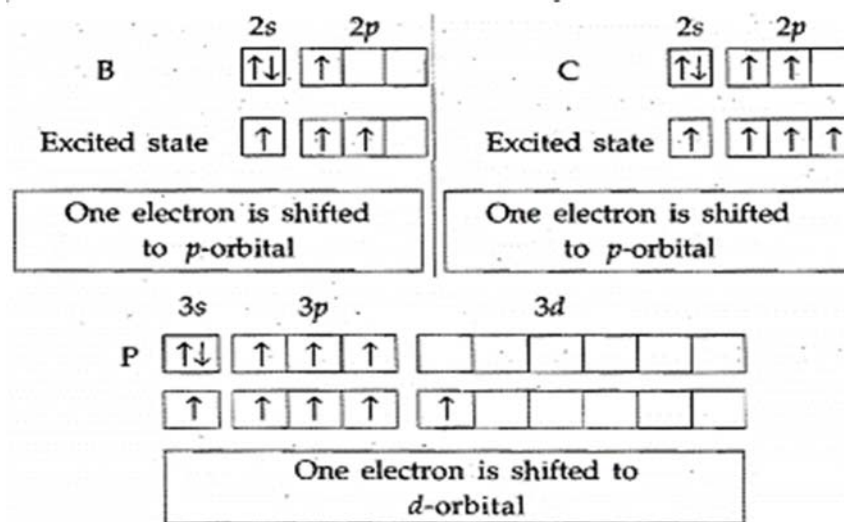
VALENCE BOND THEORY(VBT)

Modern Concept of Covalent Bond

This theory, initially proposed by Hitler and London in 1927 and later expanded upon by Pauling and Slater in 1931, elucidates the formation of a covalent bond.

The main points of the theory are:

- (i) Covalent bonding occurs through the overlap of atomic orbitals in the valence shell of the two involved atoms.
- (ii) Overlapping involves only half-filled atomic orbitals, specifically those singly occupied, resulting in a bond with a pair of electrons featuring opposite spins.
- (iii) Atoms with half-filled orbitals must approach each other closely, aligning their axes appropriately for effective overlapping.
- (iv) Overlapping leads to maximum electron density located between the two atoms, generating a significant portion of the bonding force through electrostatic attraction between the nuclei and the accumulated electron cloud.
- (v) The strength of the chemical bond increases with greater overlapping. The energy released per mole during the overlapping process is termed bond energy, contributing to the stabilization of the system. Consequently, the formed molecule exhibits lower energy and enhanced stability compared to isolated atoms.
- (vi) Paired electrons in the valence shell can participate in bond formation if they are unpaired first and shifted to vacant orbitals of slightly higher energy within the same main energy shell (valence shell). This aspect accounts for the peculiarities observed in elements like boron, the tetravalency of carbon, the Penta valency of phosphorus, the hex valency of sulfur, and the halogens (Cl, Br, I), despite having paired orbitals in the valence shell.



- (vii) Among two orbitals with identical stability (i.e., having the same energy level), the one more directionally concentrated will result in a stronger bond.

For instance, dumbbell-shaped p-orbitals exhibit stronger bonding compared to spherically symmetrical s-orbitals. This bonding is achieved through head-on or axial overlap.

Orbital Overlap Concept,

When examining the formation of a hydrogen molecule in its minimum energy state, it is observed that the two hydrogen atoms approach each other closely enough to enable their atomic orbitals to undergo partial interpenetration. This phenomenon of partial interpenetration of atomic orbitals is termed the "overlapping of atomic orbitals."

The overlapping of atomic orbitals can take on various characteristics, classified as positive, negative, or zero, depending on the specific attributes of the orbitals involved in the overlap. The nature of this overlap is crucial in understanding the molecular bonding and electronic structure of the resulting hydrogen molecule. It reflects the extent to which the electron clouds of the participating atomic orbitals combine, influencing the overall stability and properties of the formed molecular entity.

Positive and Negative Overlap

Positive overlap occurs when the lobes of atomic orbitals with the same signs overlap. This type of overlap results in attractive interactions between the electron clouds of the participating orbitals. In positive overlap, the constructive interference enhances the probability of finding electrons between the nuclei, promoting bonding.

On the other hand, negative overlap involves the overlapping of lobes with opposite signs. This leads to repulsive interactions between the electron clouds of the participating orbitals. Negative overlap, characterized by destructive interference, diminishes the probability of finding electrons between the nuclei, thus discouraging bonding.

Zero overlap signifies the inability of any kind of interactions between the atomic orbitals. This lack of overlap results in no net attractive or repulsive forces between the electrons of the interacting orbitals. The various arrangements of s and p orbitals, leading to positive, negative, and zero overlap, are visually represented in the figure below. These depictions illustrate the spatial orientations and interactions of the orbitals, providing insights into the nature of bonding or lack thereof in different molecular configurations.

Types of Overlapping and Nature of Covalent Bond

The process of forming a covalent bond entails the overlap of atomic orbitals that are each partially filled with electrons. Covalent bonds, arising from this orbital overlap, can be categorized into two distinct types based on the specific nature of the overlapping involved.

These categories are:

- (a) Sigma (σ) bonds
- (b) Pi (π) bonds

(a) Sigma (σ) Bond

A bond established through the overlap of singly occupied orbitals along their axes, creating end-to-end overlap, is termed a sigma (σ) bond. This type of bond allows for maximum overlap between electron clouds, resulting in a robust bond. The electron cloud in a sigma bond is symmetrical about the line connecting the two nuclei of the involved atoms.

Therefore, a sigma bond can be described as follows: "A bond orbital that is symmetrical about the line joining the two nuclei is referred to as a sigma bond." This bond is formed through head-on or axial overlap.

Sigma bonds are formed by three types of overlapping:

(i) s-s overlapping (Formation of hydrogen molecule)

Each hydrogen atom possesses a single electron in its 1s orbital, which is spherical. The 1s orbitals of both hydrogen atoms approach each other closely. When they reach the point of maximum attraction between the two nuclei, they overlap, resulting in the formation of a sigma bond.

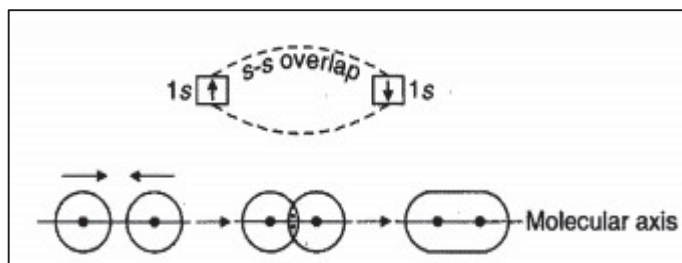


Fig: formation of H_2 molecule by s-s overlapping

The bond comprises two electrons with opposite spins. The likelihood of locating these electrons is highest in the region between the two nuclei along the molecular axis. The electron density of the bond is symmetrically distributed around the molecular axis.

(ii) **s-p overlapping (Formation of HF, H_2O , NH_3 molecules)**

(a) **Formation of HF molecule:** In the formation of HF

In the molecule, the 1s-orbital of hydrogen overlaps with the p-orbital of fluorine containing an unpaired electron.

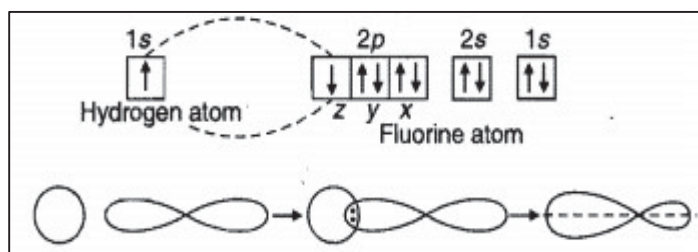


Fig: formation of HF molecule by s-p overlapping

(b) **Formation of a water molecule:** The oxygen atom possesses the valency shell configuration of $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$, indicating that it has two orbitals with single occupancy. These two orbitals overlap with the 1s-orbitals of two hydrogen atoms, resulting in the formation of sigma bonds.

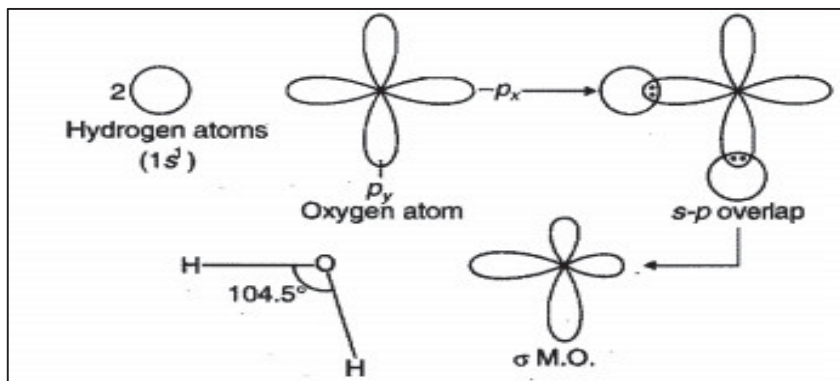


Fig: formation of water molecule by s-p overlapping

Since the two orbitals of oxygen are at right angle to each other an angle of 90° is expected between two sigma bonds but actual bond angle observed is 104.5° .

(c) **Formation of ammonia molecule:** The nitrogen atom exhibits the valency shell configuration of $2s^2 2p_x^1 2p_y^1 2p_z^1$, indicating the presence of three singly occupied orbitals. These orbitals overlap with the 1s-orbitals of three hydrogen atoms, resulting in the formation of three sigma bonds.

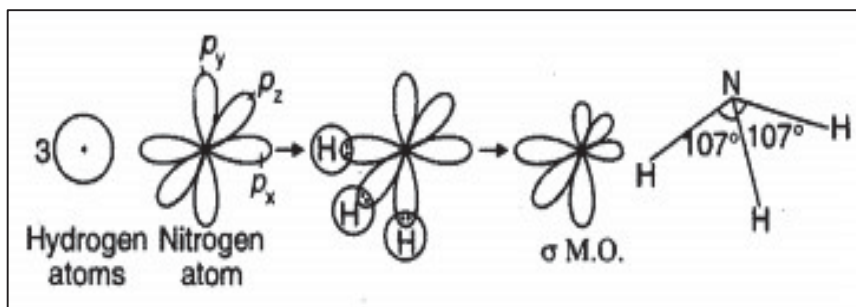


Fig: formation of NH_3 molecule by **s-p** overlapping

Since the three orbitals of nitrogen are at right angle to each other, the expected angle between two sigma bonds should be 90° but actual bond angle observed is 107° .

(iii) p-p overlapping (Formation of fluorine molecule)

This concept is exemplified through the creation of a fluorine molecule. The electronic configuration of a fluorine atom is $1s^2 2s^2 2p^5$, indicating one singly occupied orbital. As p-orbitals from two fluorine atoms draw near, aligning their heads directly toward each other, they undergo an overlap, leading to the establishment of a sigma (σ) bond.



Distinguishing Characteristics of Sigma (σ) Bonds

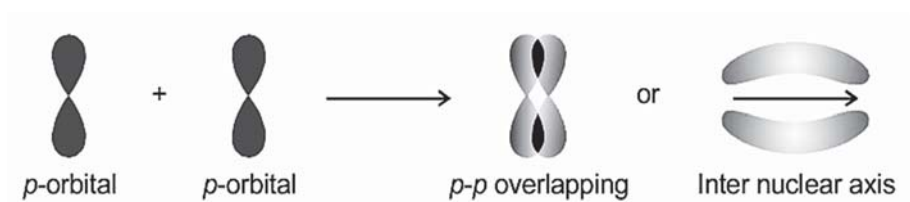
1. A σ -bond is established through the axial overlapping of atomic orbitals.
2. σ -bond formation involves the overlapping of s-s, s-p, and p-p orbitals.
3. σ -bonds are stronger due to a larger extent of overlapping.
4. The molecular orbital resulting from a σ -bond is symmetrical about the internuclear axis, with the electron cloud present on this axis.
5. Free rotation is allowed around a σ -bond.
6. A sigma bond may exist either alone or in conjunction with π -bonds.
7. Hybridized or unhybridized orbitals are involved in the formation of σ -bonds.

(b) Pi (π) bonds

The pi (π) bond, a specific class of covalent bond, emerges from the overlapping of atomic orbitals in a distinctive manner. In the formation of a pi bond, atomic orbitals align in a manner where their axes are parallel to each other and perpendicular to the internuclear axis. This unique spatial arrangement distinguishes pi bonds from other types of covalent bonds.

The resulting orbitals, generated through this sidewise overlapping, exhibit a characteristic structure. They manifest as two saucer-shaped charged clouds positioned both above and below the plane defined by the atoms participating in the bond. This specific geometry contributes to the distinctive properties associated with molecules containing pi bonds.

The electrons actively participating in the formation of pi bonds are termed pi-electrons. These electrons play a crucial role in the bonding process, influencing the overall electronic structure and behavior of the molecules involved. Understanding the nature of pi bonds enhances our comprehension of molecular characteristics, such as geometry and reactivity, offering valuable insights into the complexities of chemical bonding.



Distinguishing Characteristics of Pi (π) Bonds

1. A π -bond is established through the sideways overlapping of orbitals.
2. The formation of a π -bond involves the overlapping of p-p orbitals.
3. π -bonds are relatively weaker due to a smaller extent of overlapping.
4. The molecular orbital resulting from a π -bond is discontinuous, comprising two electron clouds situated below and above the internuclear axis.
5. Free rotation is not permissible around π -bonds.
6. A π -bond is consistently present along with a sigma (σ)-bond.
7. Hybridized orbitals are never engaged in the formation of π -bonds.