UNIT 3

The Covalent Bond

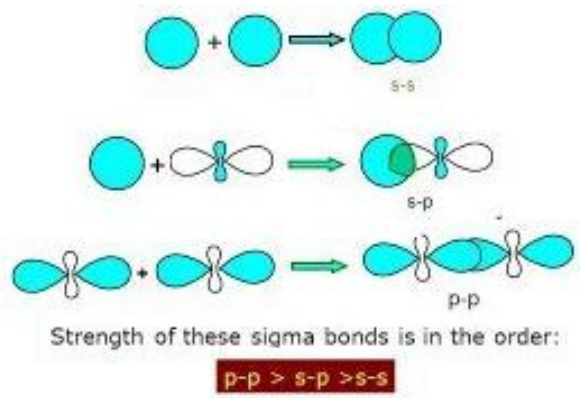
Valence Bond (VB) theory is a quantum mechanical model that describes how the atomic orbitals of atoms within a molecule combine to give individual chemical bonds when the atoms approach each other. The basic idea behind VB theory is that electrons reside in quantum mechanical orbitals localized on individual atoms, but when atoms come close enough to form a bond, their atomic orbitals overlap to form a molecular orbital that encompasses both atoms, leading to a covalent bond. This approach allows us to understand the bonding in molecules in terms of the electronic configuration of the constituent atoms and the spatial orientation of their orbitals.

Key Concepts of Valence Bond Theory

1. Two valence orbitals (half-filled) from two different atoms overlap on each other to form covalent bonds. The electron density in the area between the two bonding atoms increases because of this overlapping, thereby increasing the stability of the resulting molecule.

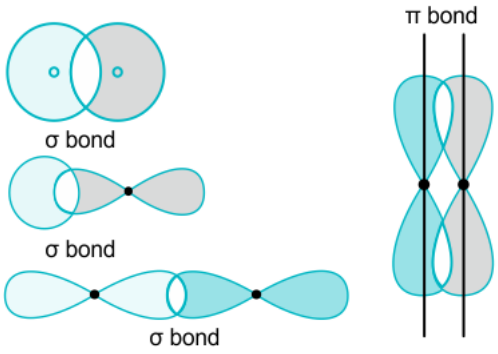
2. Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping.

   Orbital Overlap: The strength of a covalent bond is determined by the extent of overlap between atomic orbitals from each bonding atom. Greater overlap leads to stronger bonds.



   This order suggests that a sigma bond formed by the overlap of two p orbitals (P-P) is stronger than a sigma bond formed by the overlap of an s and a p orbital (S-P), which in turn is stronger than a sigma bond formed by the overlap of two s orbitals (S-S). This ordering is typically due to the extent of overlap that can occur between the different types of orbitals, with greater overlap leading to a stronger bond.

3. **Sigma (σ) and Pi (π) Bonds**: Sigma bonds are formed by the end-to-end overlapping of atomic orbitals, resulting in a bond that is symmetric around the bond axis. Pi bonds are formed by the side-to-side overlap of two p orbitals, with the electron density concentrated above and below the bond axis.



Sigma Bond and Pi Bond

The figure displays the two primary types of covalent bonds: sigma (σ) bonds, formed by the end-on overlap of orbitals, and a pi (π) bond, formed by the side-by-side overlap of two p orbitals. Sigma bonds are illustrated with different orbital interactions (s-s, s-p, p-p), while the pi bond shows two parallel p orbitals. Sigma bonds allow for free rotation around the bond axis, whereas pi bonds restrict this rotation.

4. **Hybridization**: This concept explains the observed bond angles in molecules. Atomic orbitals (s, p, d) can mix to form new hybrid orbitals (sp, sp^2, sp^3, etc.) that are oriented in specific directions to maximize orbital overlap and hence bond strength.

Type of Hybridisation	Distribution of Hybrid Orbitals in Space
sp	Linear
sp^2	Trigonal planar
sp^3	Tetrahedral
dsp^2	Square planar
sp^3d	Trigonal bipyramidal
sp^3d^2	Octahedral
d^2sp^3	Octahedral

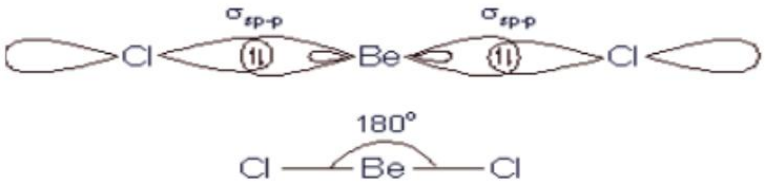
Application of Valence Bond Theory

1. Explains Bond Strength: Valence Bond Theory helps to explain why some bonds between atoms are stronger than others based on how well their outer parts overlap.
2. Predicts Bond Lengths: It can predict why the distances between atoms in a bond (bond lengths) vary from one molecule to another due to the differences in overlap.
3. Describes Molecular Shape: The theory is used to describe the shapes of molecules, as the arrangement of the overlaps determines the molecule's overall shape.
4. Explains Bonding in Different Molecules: Valence Bond Theory can explain how different kinds of molecules form bonds, such as the single bond in a hydrogen molecule (H_2) and the bond between hydrogen and fluorine in HF.

Hybridization Types and Molecular Geometries

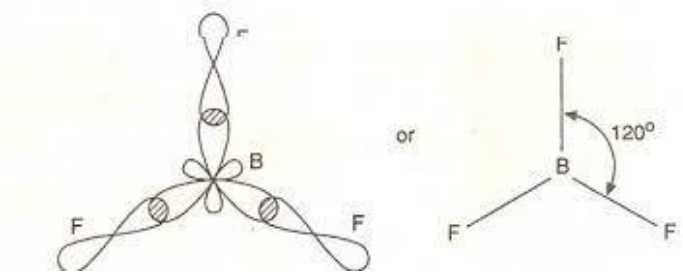
1. **$BeCl_2$ (Beryllium Dichloride)**
   - **Hybridization**: **sp**
   - **Geometry**: Linear
   - **Bond Angle**: 180°

Beryllium (Be) in $BeCl_2$ undergoes sp hybridization, mixing one **s** orbital with one **p** orbital to form two sp hybrid orbitals. These orbitals are oriented 180° apart, resulting in a linear shape for $BeCl_2$. Each sp hybrid orbital overlaps with a **p** orbital from a chlorine atom to form two sigma bonds.



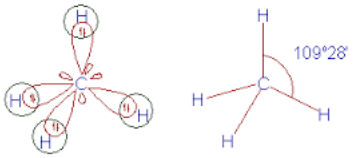
2. **BF3 (Boron Trifluoride)**
   - **Hybridization**: sp^2
   - **Geometry**: Trigonal planar
   - **Bond Angle**: 120°

Boron (B) in BF_3 undergoes sp^2 hybridization, mixing one **s** orbital with two **p** orbitals to form three equivalent sp^2 hybrid orbitals. These orbitals are oriented 120° apart in a plane, leading to a trigonal planar shape. Each sp^2 hybrid orbital overlaps with an orbital from a fluorine atom to form a sigma bond.



3. **CH_4 (Methane)**
   - **Hybridization**: sp^3
   - **Geometry**: Tetrahedral
   - **Bond Angle**: 109.5°

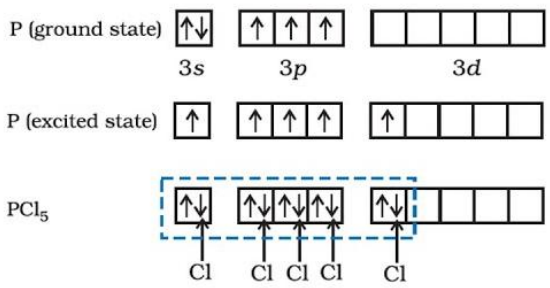
Carbon (C) in CH_4 undergoes sp^3 hybridization, mixing its one **s** orbital with three **p** orbitals to form four equivalent sp3 hybrid orbitals. These orbitals are directed towards the corners of a tetrahedron, resulting in a tetrahedral geometry. Each sp^3 orbital forms a sigma bond with a hydrogen atom.

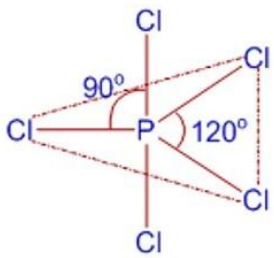


4. PCl_5 (Phosphorus Pentachloride)

- **Hybridization**: sp^3d
- **Geometry**: Trigonal bipyramidal
- **Bond Angle**: 120° between equatorial atoms, 90° between equatorial and axial atoms

Phosphorus (P) in PCl_5 undergoes sp^3d hybridization, mixing one **s** orbital, three **p** orbitals, and one **d** orbital to form five sp^3d hybrid orbitals. These orbitals arrange themselves in a trigonal bipyramidal geometry, with three equatorial positions 120° apart and two axial positions 180° apart. Each hybrid orbital overlaps with a p orbital from a chlorine atom to form a sigma bond.



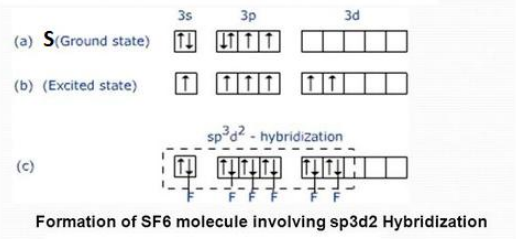


sp^3d hybrid orbitals filled by electron pairs donated by five Cl atoms.

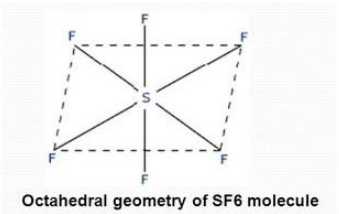
5. SF_6 (Sulfur Hexafluoride)

- **Hybridization**: sp^3d^2
- **Geometry**: Octahedral
- **Bond Angle**: 90° between any two bonds

Sulfur (S) in SF_6 undergoes sp^3d^2 hybridization, mixing one **s** orbital, three **p** orbitals, and two **d** orbitals to form six equivalent sp^3d^2 hybrid orbitals. These orbitals are oriented towards the corners of an octahedron, leading to an octahedral geometry. Each hybrid orbital overlaps with an orbital from a fluorine atom to form a sigma bond.



Formation of SF6 molecule involving sp3d2 Hybridization



Octahedral geometry of SF6 molecule

Valence Shell Electron Pair Repulsion (VSEPR) Theory:

The Valence Shell Electron Pair Repulsion (VSEPR) model is a crucial concept in chemistry for understanding the three-dimensional shapes of molecules. It is based on the principle that electron pairs around a central atom will arrange themselves as far apart as possible to minimize electron pair repulsion. This model helps predict the geometrical structure of molecules, including the effects of both bonding and nonbonding (lone pairs) electron pairs, as well as how electronegativity influences molecular shapes.

Postulates of VSEPR Theory:

1. **Central Atom:** In large molecules, all other atoms attach to the central atom, which is usually located in the center. This atom is known as central atom.
2. **Valence Electrons Dictate Shape:** The number of electron pairs in the outermost shell of the central atom determines the overall shape of the molecule. These pairs are either involved in bonding or are unshared, also known as lone pairs.
3. **Minimising Repulsion:** To keep the molecule stable, electron pairs arrange themselves as far apart as possible. This arrangement reduces repulsive forces and gives the molecule a shape that uses space most efficiently.
4. **Effect of Lone and Bond Pairs:** The presence of lone pairs alters the molecule's shape, making it less symmetrical compared to a molecule with only bonding pairs. Lone pairs exert more repulsive force than bonded pairs, distorting the molecule's shape. The relative repulsions between different electron pairs as follows:

   L.P - L.P > L.P - B.P > B.P - B.P
5. **Stability and Energy:** When electron pairs spread out to minimize repulsion, which lowers the molecule's energy, a molecule is most stable. Conversely, forcing electron pairs closer together increases the molecule's energy and decreases its stability.

Electron Pairs	Lone Pairs (LP)	Bond Pairs (BP)	Molecular Shape	Example
2	0	2	Linear	CO_2
3	0	3	Trigonal Planar	BF_3
3	1	2	Bent or V-shaped	SO_2
4	0	4	Tetrahedral	CH_4
4	1	3	Trigonal Pyramidal	NH_3
4	2	2	Bent or V-shaped	H_2O
5	0	5	Trigonal Bipyramidal	PCl_5
5	1	4	Seesaw	SF_4
5	2	3	T-shaped	ClF_3
5	3	2	Linear	I_3^-
6	0	6	Octahedral	SF_6
6	1	5	Square Pyramidal	BrF_5
6	2	4	Square Planar	XeF_4

Role of Electronegativity in Molecular Geometry:

Differences in electronegativity between atoms can create polar bonds, drawing electrons closer to the more electronegative atom. This affects the geometry of molecules by potentially altering bond angles and lengths, influencing the overall shape and polarity.

Water (H_2O) showcases the impact of electronegativity and electron pair repulsions on molecular structure. The higher electronegativity of the oxygen atom pulls the shared electrons closer, forming polar bonds. This polarization, along with repulsions between the lone pairs (L.P - L.P) and between the lone and bonding pairs (L.P - B.P), results in a bent geometry. The bond angle is approximately 104.5°, smaller than in a tetrahedral structure, due to these repulsions. These features contribute to water's ability to form hydrogen bonds, underpinning its high boiling point and solvent capabilities.

Isoelectronic Principle and Molecular Geometry:

This principle states that species with the same number of electrons and a similar distribution of those electrons will have similar shapes. It allows for predictions about the structure of unknown molecules by comparing them with known isoelectronic species.

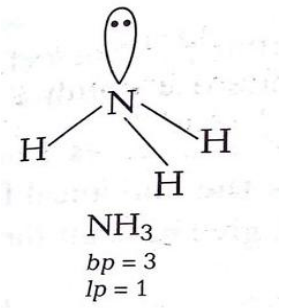
The isoelectronic principle posits that molecules or ions with the same electron count and distribution tend to have similar geometries. For instance, carbon dioxide (CO_2) and nitrous oxide (N_2O) both have linear structures and 22 valence electrons, showcasing this principle. Despite differing atom compositions, their electron similarity results in analogous molecular shapes.

Illustration of structures by VESPR model:

NH_3 (Ammonia):

- **Central Atom:** Nitrogen (N)
- **Electronic Configuration of N:** $1s^2\ 2s^2\ 2p^3$
- **Valence Electrons:** 5

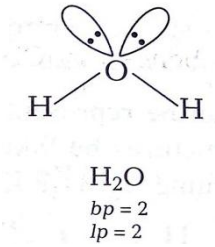
The nitrogen atom is surrounded by three hydrogen atoms and one lone pair of electrons. The ideal electron geometry is tetrahedral due to the four regions of electron density. However, the molecular geometry becomes trigonal pyramidal because the lone pair occupies more space than bonding pairs, pushing the hydrogen atoms closer together and resulting in bond angles slightly less than 109.5°.



H_2O (Water):

- **Central Atom:** Oxygen (O)
- **Electronic Configuration of O:** $1s^2\ 2s^2\ 2p^4$
- **Valence Electrons:** 6

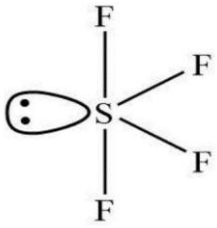
Oxygen is bonded to two hydrogen atoms, with two lone pairs of electrons. The electron geometry is tetrahedral, but the presence of two lone pairs distorts this ideal geometry into a bent shape. The lone pairs exert more repulsion than bonding pairs, decreasing the H-O-H bond angle to approximately 104.5°, less than the tetrahedral angle.



SF_4 (Sulfur Tetrafluoride):

- **Central Atom:** Sulfur (S)
- **Electronic Configuration of S:** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
- **Valence Electrons:** 6 (in the third shell)

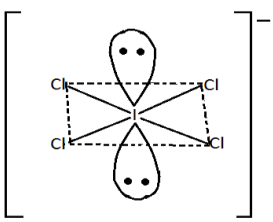
Sulfur forms bonds with four fluorine atoms and has one lone pair. The electron arrangement is trigonal bipyramidal, but the presence of a lone pair in one of the equatorial positions distorts this symmetry, resulting in a see-saw shape. The lone pair repels the bonding pairs more strongly, affecting the molecular geometry.



ICl_4^- (Iodine Tetrachloride Ion):

- **Central Atom:** Iodine (I)
- **Electronic Configuration of I:** $[Kr]\ 4d^{10}\ 5s^2\ 5p^5$
- **Valence Electrons:** 7 (plus one from the negative charge)

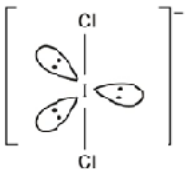
Iodine is surrounded by four chlorine atoms and has two lone pairs, making the electron geometry octahedral. However, the two lone pairs occupy opposite positions, leading to a square planar molecular geometry. The equal repulsion between the lone pairs helps maintain this shape.



ICl_2^- (Iodine Dichloride Ion):

- **Central Atom:** Iodine (I)
- **Electronic Configuration of I:** [Kr] $4d^{10}\ 5s^2\ 5p^5$
- **Valence Electrons:** 7 (plus one from the negative charge)

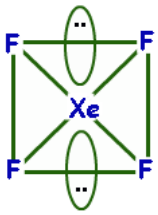
This ion features iodine with two bonding pairs (with chlorine atoms) and three lone pairs. The electron geometry suggests a trigonal bipyramidal arrangement, but the three lone pairs force the bonding pairs into a linear arrangement due to the minimization of repulsion, resulting in a 180° bond angle.



XeF_4 (Xenon Tetrafluoride):

- **Central Atom:** Xenon (Xe)
- **Electronic Configuration of Xe:** [Kr] $4d^{10}\ 5s^2\ 5p^6$
- **Valence Electrons:** 8

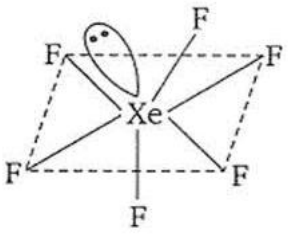
Xenon in XeF_4 forms bonds with four fluorine atoms and has two lone pairs. The electron geometry is octahedral, but the molecular geometry is square planar due to the symmetrical arrangement of the lone pairs opposite each other, minimizing their repulsion on the bonding pairs.



XeF_6 (Xenon Hexafluoride):

- **Central Atom:** Xenon (Xe)
- **Electronic Configuration of Xe:** [Kr] $4d^{10}\ 5s^2\ 5p^6$
- **Valence Electrons:** 8

Xenon hexafluoride has a central xenon atom with six bonding pairs (with fluorine atoms) and one lone pair. The electron geometry is octahedral; however, the presence of a lone pair leads to a distorted octahedral molecular geometry, as the lone pair occupies one position, pushing the bonding pairs slightly, which results in a less symmetric arrangement.



Molecular Orbital Theory - LCAO Method

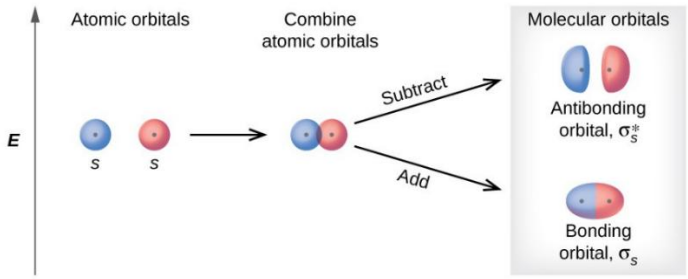
Introduction

Molecular Orbital Theory (MO Theory) provides a way to understand how atoms combine to form molecules. It explains the formation of molecular orbitals through the combination of atomic orbitals. A popular method used in MO Theory is the Linear Combination of Atomic Orbitals (LCAO) method.

LCAO Method:

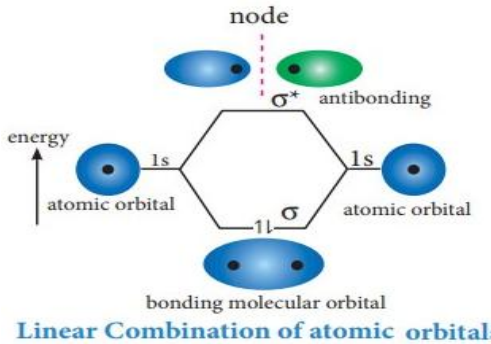
The Linear Combination of Atomic Orbitals (LCAO) method is a fundamental concept in quantum chemistry that explains the formation of molecular orbitals. This image illustrates how two atomic orbitals combine to form molecular orbitals. In this process, the atomic orbitals merge to create new orbitals at the molecular level.

1. **Bonding Orbital (σ_s)**: When the atomic orbitals add constructively (their phases align), a lower-energy bonding molecular orbital is formed. Electrons in this orbital are in a stable configuration, enhancing the bond between the atoms.
2. **Antibonding Orbital (σ^*_s):** On the other hand, when the atomic orbitals combine destructively, a higher-energy antibonding molecular orbital is formed. This orbital is shown as π*_s with a star to show that it is antibonding. Electrons in this orbital can destabilize the bond, as they are in a higher energy state.



Key Concepts

1. **Orbital Formation:** Atomic orbitals combine when they have the same or similar energy levels, facilitating the formation of molecular orbitals. These are the new regions where electrons can be found, associated with the molecule rather than individual atoms.
2. **Bonding and Antibonding Orbitals**: The combination of atomic orbitals leads to the formation of two types of molecular orbitals:



Linear Combination of atomic orbitals

Bonding Orbitals: Lower energy orbitals that stabilize the molecule by holding atoms together. **HOMO** (Highest Occupied Molecular Orbital) usually aligns with a bonding molecular orbital, filled with electrons that help stabilize the molecule.

Antibonding Orbitals: Higher-energy orbitals that can destabilize the molecule if occupied by electrons. **LUMO** (Lowest Unoccupied Molecular Orbital) often corresponds to an antibonding molecular orbital that is empty in the ground state. Transitions of electrons from HOMO to LUMO can lead to increased reactivity or destabilization of the molecule.

3. **Filling Up Orbitals with Electrons**: Electrons fill molecular orbitals starting with the lowest energy ones. The specific sequence of filling these orbitals follows principles that aim to maximize the stability of the molecule.

$$\sigma_{1s}<\sigma^*_{1s}<\sigma_{2s}<\sigma^*_{2s}<\sigma_2p_z<\pi_2p_x=\pi_2p_y<\pi^*_2p_x=\pi^*_2p_y<\sigma_2p_z$$

4. **The Importance of Bond Order**: Bond order is a concept that indicates the strength of the bond between atoms. It is calculated based on the difference in the number of electrons in bonding versus antibonding orbitals. A higher bond order implies a stronger bond.

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

Here, N_b = No. of electron present in bonding molecular orbital

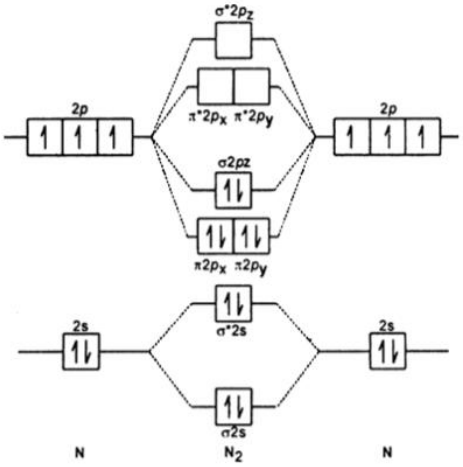
N_a = No. of electron present in antibonding molecular orbital

5. **Molecular Stability**: A molecule is considered stable when it has more electrons in bonding orbitals compared to antibonding orbitals. This configuration leads to a net energy gain, making the molecule energetically favorable.
6. **Delocalization**: Certain molecules exhibit electron delocalization, where electrons are not confined between two atoms but are shared among several atoms. This contributes to the stability and unique properties of molecules like benzene.

construction of M.O. diagrams:

Homonuclear Diatomic Molecules

N_2 (Nitrogen):

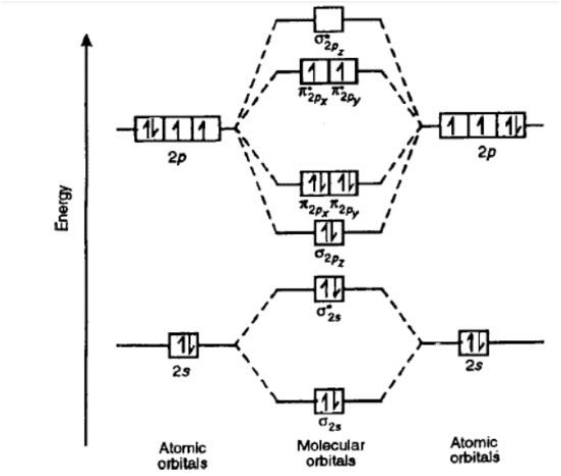


1. Atomic Orbitals: Both nitrogen atoms contribute 1s, 2s, and three 2p orbitals.
2. MO Formation: The 1s and 2s orbitals combine to form σ(1s), σ*(1s), σ(2s), and σ*(2s) orbitals. The 2p orbitals form one σ(2p) orbital along the internuclear axis and two π(2p) orbitals perpendicular to the axis, along with their corresponding antibonding orbitals (σ*(2p) and π*(2p)).
3. Electron Filling: N_2 has a total of 10 valence electrons. Filling the MOs from lowest to highest energy, all bonding orbitals (σ and π) are filled, with no electrons in antibonding orbitals.

$$\sigma(2s)^2,\sigma*(2s)^2,\ \pi(2p)_x^2,\pi(2p)_y^2,\sigma(2p)_z^2$$

4. Bond Order: Calculated as half the difference between bonding and antibonding electrons. For N_2, the bond order is 3, indicating a strong triple bond.
5. Magnetic Properties: N_2 has no unpaired electrons and is diamagnetic.

O_2 (Oxygen):



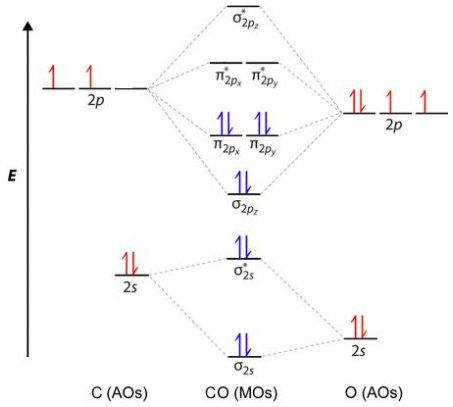
1. Atomic Orbitals: Each oxygen atom contributes 1s, 2s, and three 2p orbitals.
2. MO Formation: Like N_2, but with a key difference in the energy ordering of the 2p-derived orbitals. The π(2p) orbitals are lower in energy than the σ(2p) orbital due to electron repulsion effects.
3. Electron Filling: O_2 has 12 valence electrons. The σ(2p) orbital is higher in energy and gets filled after the π(2p) orbitals.

$$\sigma(2s)^2,\sigma*(2s)^2,\sigma(2p)_z^2,\pi(2p)_x^2,\pi(2p)_y^2,\pi*(2p)_x^1,\pi*(2p)_y^1$$

4. Bond Order: For O_2, the bond order is 2, indicating a double bond.
5. Magnetic Properties: O_2 has two unpaired electrons in the π*(2p) orbitals, making it paramagnetic.

Heteronuclear Diatomic Molecules:

CO (Carbon Monoxide):

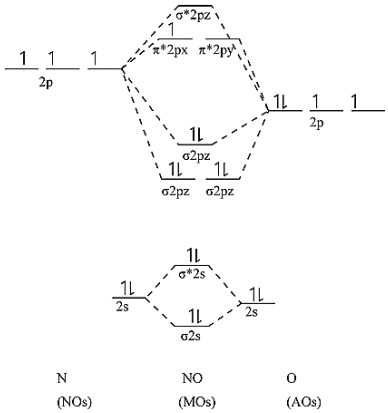


1. Atomic Orbitals: Carbon and oxygen contribute 1s, 2s, and 2p orbitals, but the difference in their electronegativities affects the energy levels of the MOs.
2. MO Formation: The MO diagram for CO shows a greater contribution of oxygen 2p orbitals to the bonding MOs due to oxygen's higher electronegativity. The σ(2p) MO is mainly oxygen in character.
3. Electron Filling: CO has 10 valence electrons. The electrons fill the MOs, emphasizing the contribution of the more electronegative oxygen to the bonding orbitals.

$$\sigma(2s)^2,\sigma*(2s)^2,\sigma(2p)_z^2,\pi(2p)_x^2,\ \pi(2p)_y^2$$

4. Bond Order: The bond order in CO is 3, indicating a triple bond character.
5. Magnetic Properties: CO is diamagnetic with no unpaired electrons.

NO (Nitric Oxide):



1. Atomic Orbitals: Nitrogen and oxygen contribute their 1s, 2s, and 2p orbitals, with the energy levels influenced by the electronegativity difference.
2. MO Formation: Like CO, the MO diagram for NO shows a significant influence of oxygen's electronegativity, especially in the bonding MOs derived from 2p orbitals.
3. Electron Filling: NO has 11 valence electrons, leading to one unpaired electron in the highest occupied molecular orbital (HOMO).

$$\sigma(2s)^2,\sigma*(2s)^2,\sigma(2p)_z^2,\pi(2p)_x^2,\ \pi(2p)_y^2,\ \pi*(2p)_x^1$$

4. Bond Order: The bond order in NO is 2.5, indicating a bond strength between a double and a triple bond.
5. Magnetic Properties: NO has one unpaired electron, making it paramagnetic.