Topic: Covalent Bonding

Course: CC1B(CBCS) / CHEM201-I and CHEM202-I(NEP)

Semester II

B.Sc. Chemistry

Department of Chemistry

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Valence Bond Theory:

- Valence orbital theory was first proposed by W. Heitler and F. London.
- This theory was developed by Linus Pauling, who was awarded the Nobel Prize for Chemistry in 1954.
- The theory was very widely used in the period 1940-1960.
- However, it is still much used by organic chemists, and it provides a basis for simple description of small inorganic molecules.

Key points:

1. The model theorizes that a covalent bond forms when two orbitals overlap to produce a new combined orbital containing two electrons of opposite spin.

2. This overlapping results in a decrease in the energy of the atoms forming the bond.

3. The shared electron pair is most likely to be found in the space between the two nuclei of the atoms forming the bonds.

4. The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms.

5. The paired electrons present in the valence shell do not take participate in the formation of chemical bonds as per the valence bond theory.

6. pi bonds are formed from sidewise overlapping whereas the overlapping along the axis containing the nuclei of the two atoms leads to the formation of sigma bonds.

Covalent Bonding

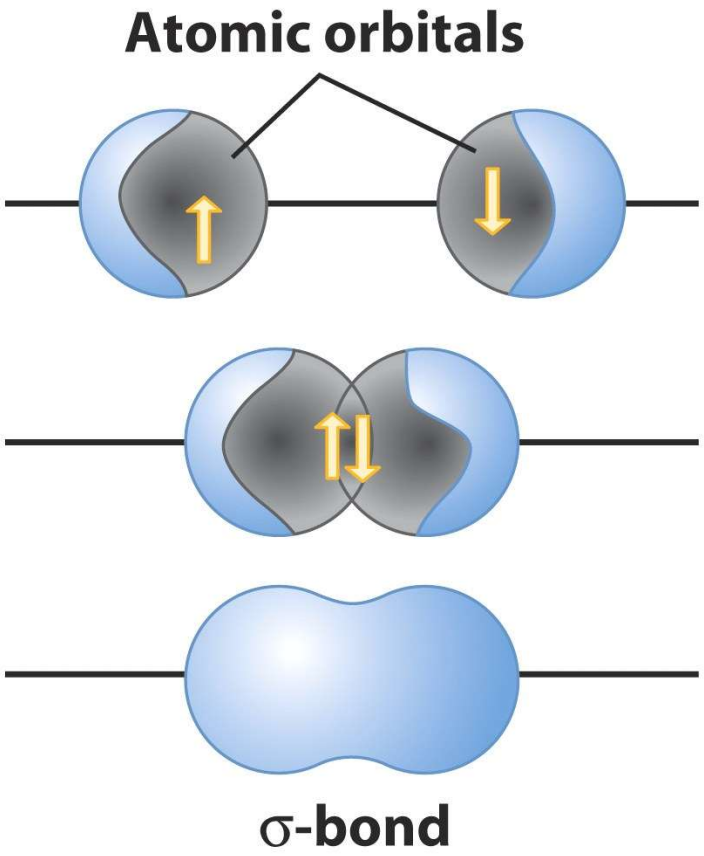
Atomic orbitals: orbitals that are localized on single atoms.

Molecular orbitals: orbitals that span two or more atoms. Constructing molecular orbitals (MOs) by overlapping atomic orbitals (AOs)

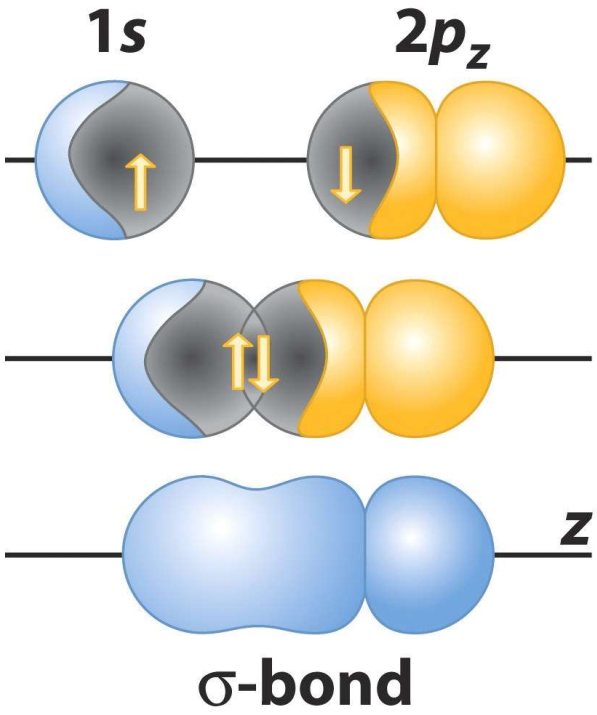
σ bonds: electron density of MO directed along bond axis

π bonds: electron density of MO has a nodal plane that contains the bond axis

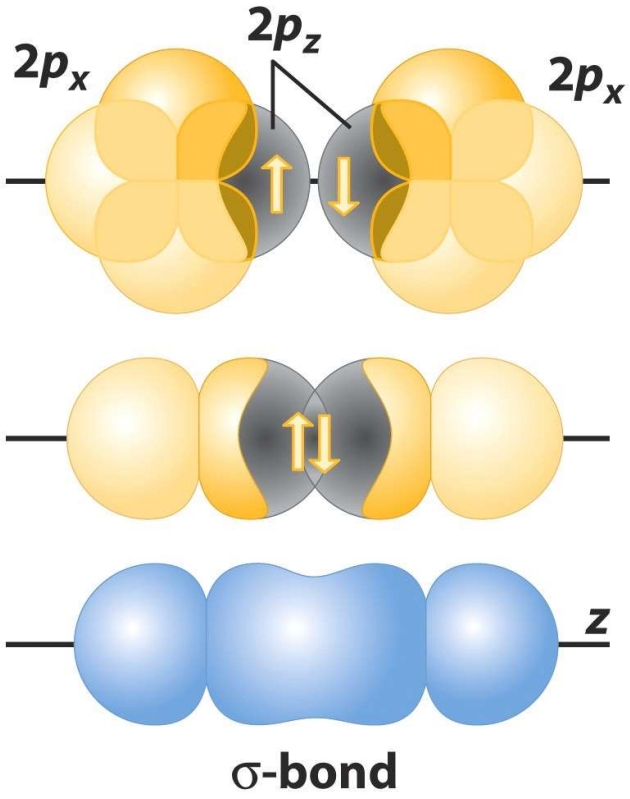
Valence bond: Overlap of two s orbitals to produce a σ bond



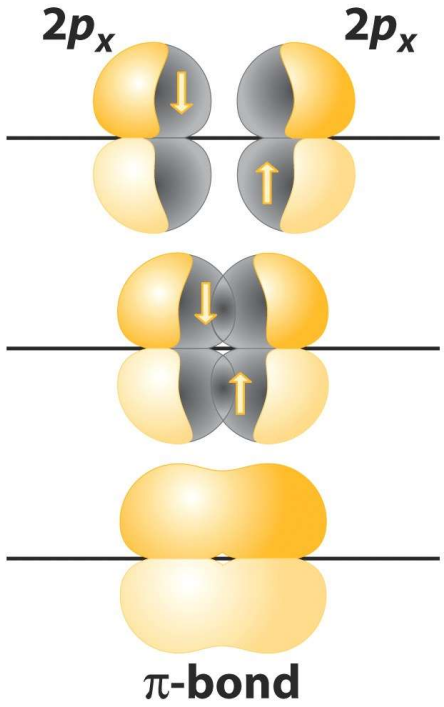
Valence bond: Overlap of an s orbital and a p_z orbital to produce a σ bond



Valence bond: Overlap of two p_z orbitals to produce a σ bond



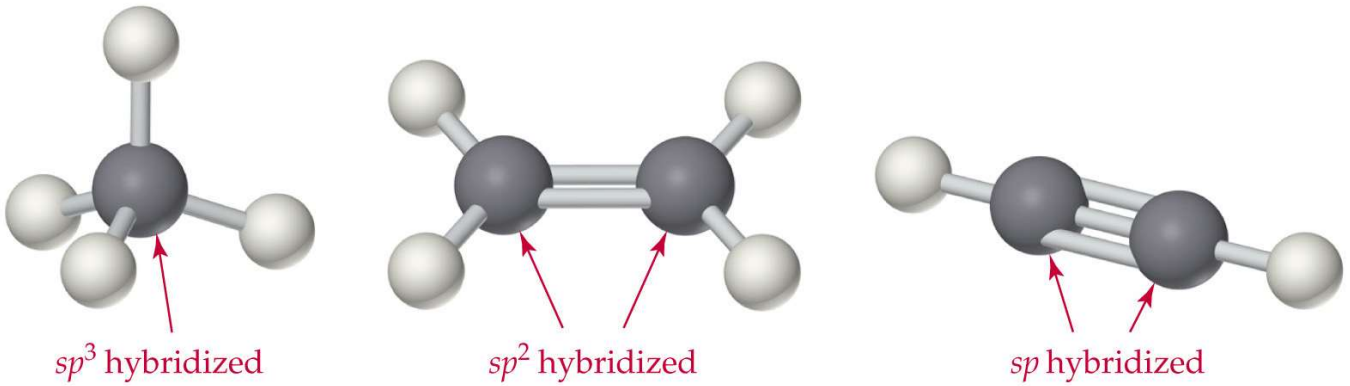
Valence bond: Overlap of two p_x orbitals to produce a π bond



Hybridization

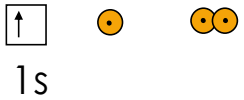
Key points:
If more than two atoms are involved in a molecule, the shapes of the orbitals must match the shape of the bonds that are needed (trigonal, tetrahedral, etc.).

The atomic orbitals do not have these shapes, and must be mixed to achieve the needed shapes.



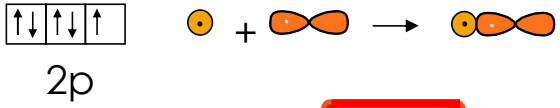
Valence Bond Theory: Overlap of Atomic Orbitals

H-H



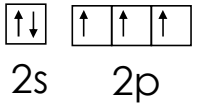
σ bond - overlap of s orbitals

H-F



σ bond - overlap of s orbital and p orbital

N_2



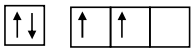
1 σ bond - head/head overlap of p orbitals

2 π bonds - sidewise overlap of p orbitals

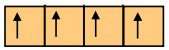
Bonds with hybridization of atomic orbitals:

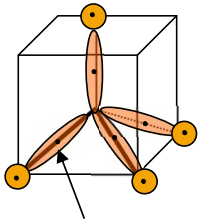
sp^3 hybridization

CH_4 H:  1s

C: 

2s 2p

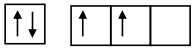




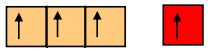
C atom:
4 σ bonds - overlap of H-s orbitals and sp^3 orbitals Of C

A single sp^3 orbital, each with single electron

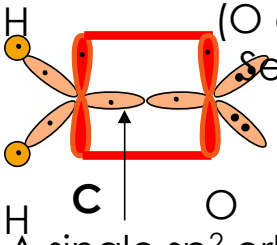
sp^2 hybridization

H_2CO C: 

2s 2p



sp^2 p

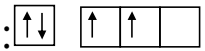


(O also hybridized See next page)

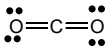
C atom
3 σ bond;
1 π bond

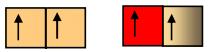
A single sp^2 orbital, each with single electron

sp hybridization

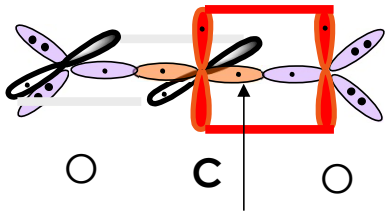
CO_2 C: 

2s 2p





sp p



C atom:
2 σ bonds
2 π bond

A single sp orbital, each with single electron

Valence Bond Theory: Hybridization

TABLE 3.2 Hybridization and Molecular Shape*

Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	2	sp	2
trigonal planar	3	sp^2	3
tetrahedral	4	sp^3	4
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

*Other combinations of *s*-, *p*-, and *d*-orbitals can give rise to the same or different shapes, but these combinations are the most common.

Valence shell electron repulsion theory (VSEPR)

The two primary founders of the VSEPR theory are Ronald Nyholm and Ronald Gillespie. This theory is also known as the Gillespie-Nyholm theory

Key points:

1. The total number of valence shell electron pairs decides the shape of the molecule.
2. The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom.
3. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible.
4. Should the central atom be surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
5. The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.
6. l.p>b.p.>b.p. repulsion

Valence shell electron repulsion theory (VSEPR)

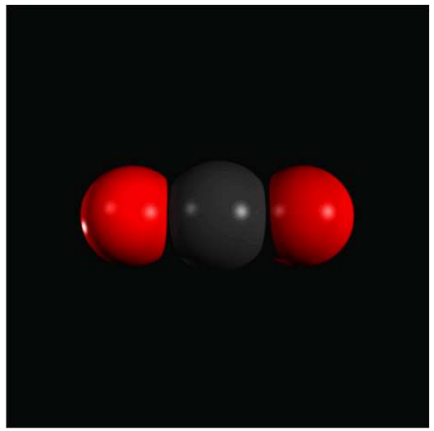
Method to apply VSEPR:

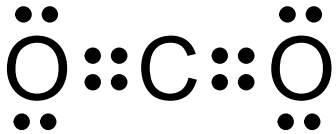
1. Draw the correct Lewis structure
2. Determine count of electron pairs around the central element
3. Determine how those electron pairs orient around the central element
4. Attach terminal atoms to the central element
5. The orientation of the atoms in space determine the molecular geometry

Valence shell electron repulsion theory (VSEPR)

Molecular Geometries

- VSEPR Formula: AX_2
- Geometry: Linear
- Bond Angle: 180°
- Example: CO_2

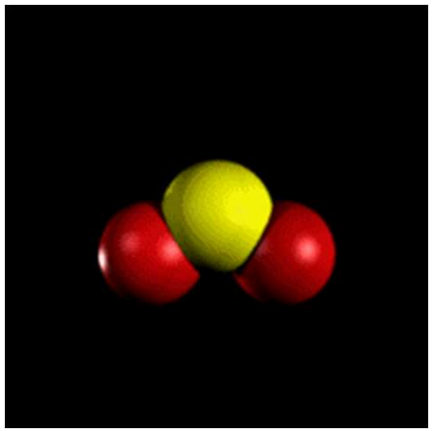


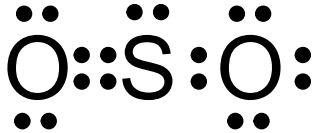


Valence shell electron repulsion theory (VSEPR)

Molecular Geometries

- VSEPR Formula: AX_2E
- Geometry: Bent (Angular)
- Bond Angle: Less than 120°
- Example: SO_2

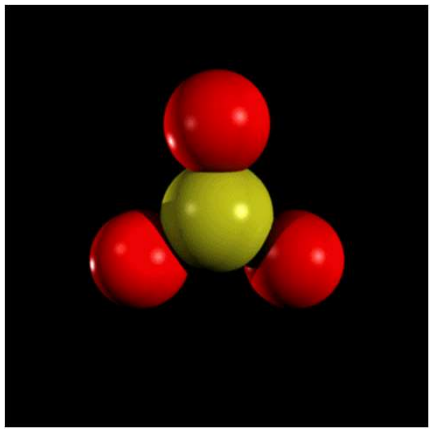


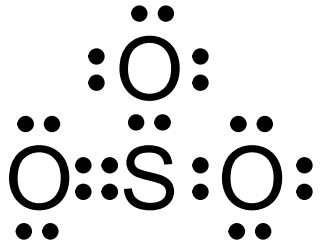


Valence shell electron repulsion theory (VSEPR)

Molecular Geometries

- VSEPR Formula: AX_3
- Geometry: Trigonal Planar
- Bond Angle: 120°
- Example: SO_3

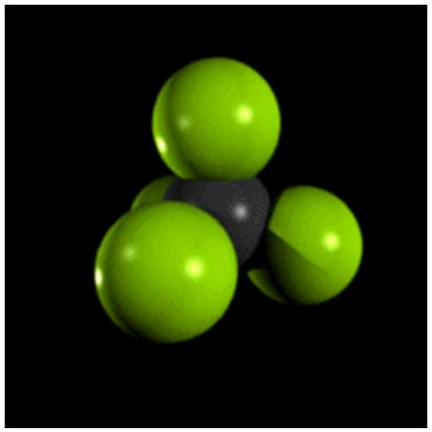


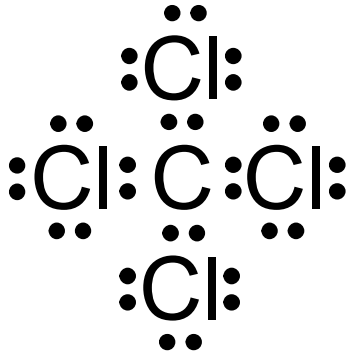


Valence shell electron repulsion theory (VSEPR)

Molecular Geometries

- VSEPR Formula: AX_4
- Geometry: Tetrahedral
- Bond Angle: 109.5°
- Example: CCl_4

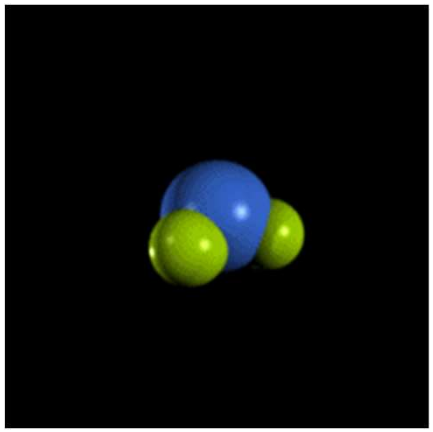


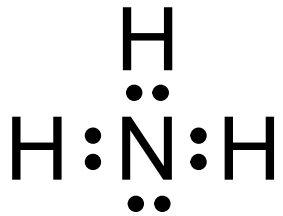


Valence shell electron repulsion theory (VSEPR)

Molecular Geometries

- VSEPR Formula: AX_3E
- Geometry: Trigonal Pyramidal
- Bond Angle: Less than 109.5°
- Example: NH_3

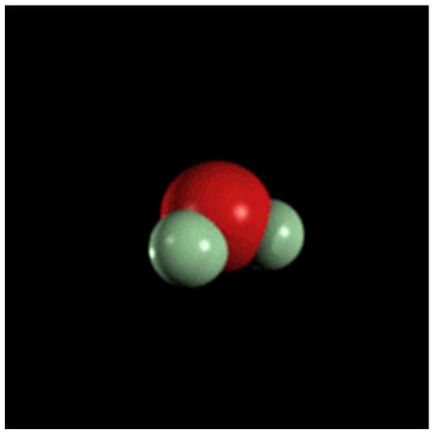


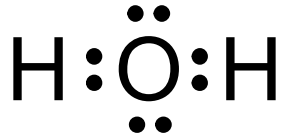


Valence shell electron repulsion theory (VSEPR)

Molecular Geometries

- VSEPR Formula: AX_2E_2
- Geometry: Bent (Angular)
- Bond Angle: Less than 109.5°
- Example: H_2O





Valence shell electron repulsion theory (VSEPR)

State the number of electron groups, lone pairs, and bonded atoms, and use VSEPR theory to determine the shape of the following molecules:

PF_3, H_2S, CCl_4, PO_4^{3-}

Valence shell electron repulsion theory (VSEPR)

State the number of electron groups, lone pairs, and bonded atoms, and use VSEPR theory to determine the shape of the following molecules:

PF_3 4 electron groups, 3 bonded atoms, 1 lone pair, trigonal pyramidal

H_2S 4 electron groups, 2 bonded atoms, 2 lone pairs, bent

CCl_4 4 electron groups,4 bonded atoms, 0 lone pairs, tetrahedral

PO_4^{3-} 4 electron groups, 4 bonded atoms, 0 lone pairs, tetrahedral

Valence shell electron repulsion theory (VSEPR)

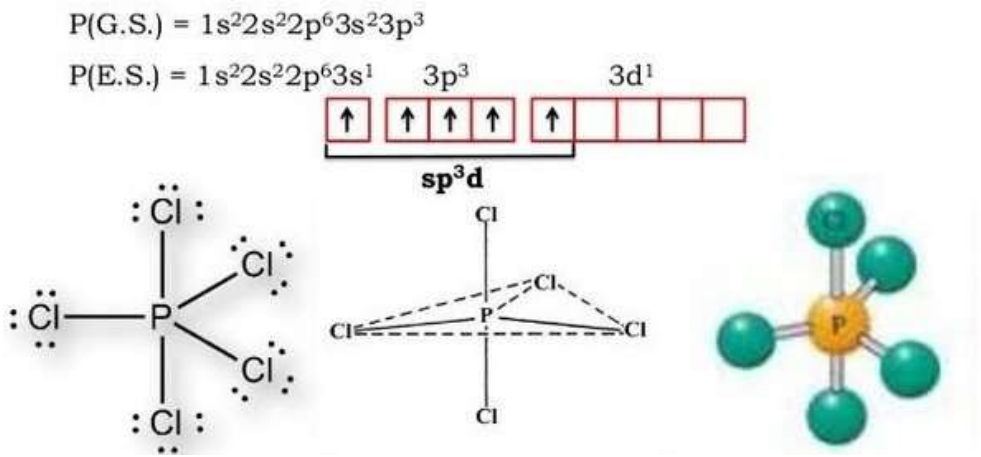
PCl_5

According to the VSEPR theory,

three bonds are arranged in an equatorial configuration

two bonds arranged axially perpendicular to the equatorial bonds.

Geometry will be has a trigonal bipyramidal shape.



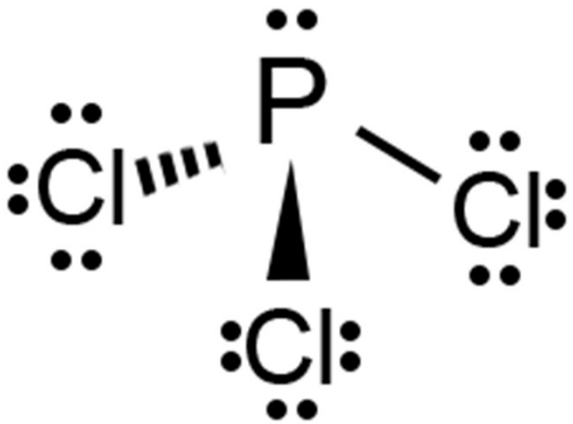
Valence shell electron repulsion theory (VSEPR)

PCl_3

According to the VSEPR theory,

Three bonds pair around P and one lone pair.

the shape and hybridization of the molecule are trigonal pyramidal and sp3 respectively.



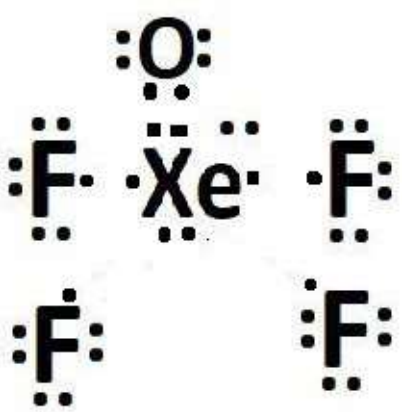
Valence shell electron repulsion theory (VSEPR)

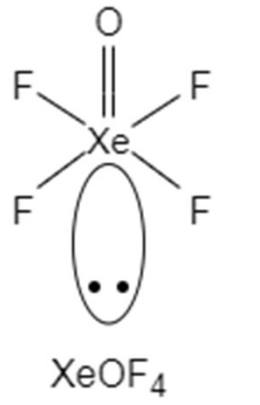
$XeOF_4$

According to the VSEPR theory,

The xenon contains eight electrons in their valence shell.

Therefore, Xenon oxyfluoride molecular geometry is square pyramidal sp^3d^2





$XeOF_4$

Square pyramidal

Linear combination of atomic orbitals

1. Atomic orbitals must be roughly of the same energy.
2. The orbital must overlap one another as much as possible- atoms must be close enough for effective overlap.
3. In order to produce bonding and antibonding MOs, either the symmetry of two atomic orbital must remain unchanged when rotated about the internuclear line or both atomic orbitals must change symmetry in identical manner.

Features of MO:

✓ When two AOs mix, two MOs will be produced

✓ Each orbital can have a total of two electrons (Pauli principle)

✓ Lowest energy orbitals are filled first (Aufbau principle)

✓ Unpaired electrons have parallel spin (Hund's rule)

✓ Bond order = ½ (bonding electrons – antibonding electrons)

Things to remember:

- Electrons go into the lowest energy orbital available to form lowest potential energy for the molecule.
- The maximum number of electrons in each molecular orbital is two. (Pauli exclusion principle)
- One electron goes into orbitals of equal energy, with parallel spin, before they begin to pair up. (Hund's Rule.)