Molecular Structure

VALENCE-SHELL ELECTRON-PAIR REPULSION THEORY (VSEPR)

- Used to determine molecular geometries.
- Assumes that the valence electrons around the central atom are responsible for the molecular shape.
- The shape of a molecule is determined by the repulsions between electron groups around the central atom; the pairs of valence electrons around the central atom are arranged as far apart from each other as possible.

Predicting Molecular Shapes and Bond Angles:

1. Draw the Lewis structure.
2. Determine the number of bonding pairs and the number of lone pairs around the central atom. **Note:** double and triple bonds are counted as one bonding pair, single electrons are counted as a lone pair.
3. Predict the geometry based on the number of **B**onding **P**airs and **L**one **P**airs.
4. When lone pairs are present, the bond angle is slightly less than expected.
5. Order of repulsion: LP/LP >> LP/BP >> BP/BP.
6. Repulsion is stronger when electron groups are closer together.
7. All plausible Lewis structures for a molecule should have the same geometry.
8. When there is more than one central atom, predict the structure around each central atom individually, then put the molecule together.

Examples: 1) Use VSEPR to predict the molecular geometry of NO_3^- $SiCl_4$, SbF_5, BF^-, N_3^-, XeF_2. 2) Use VSEPR to describe the molecular geometry of nitric acid and dimethyl ether.

Note: The $A_xB_yE_z$ notation is often used to describe molecular geometries. A is the central atom(s), B denotes the terminal atoms, and E denotes the lone pairs of electrons.

Polarity of Molecules:

- Polar molecules have separate areas of positive and negative charge.
- **Dipole moment (μ)** is the significance of the charge separation.
- $\mu = \delta\, d$ δ is the magnitude of the charge   **d** is the distance that separates the positively charged area and the negatively charged area.
- Dipole moments are measured in debyes. **1 debye (D) = 3.34 x 10-30 C m (coulombs x meters)**
- A non-polar molecule will have a zero dipole moment.

Predicting Polarity of Molecules:

1. Predict the molecular geometry using VSEPR theory.
2. Use electronegativity values to give bond polarities.
3. Note: Bond dipoles are vector quantities - they have magnitude and direction.

4. Cancel out bond dipoles. (Bond dipoles that are equal in magnitude and opposite in direction will cancel each other out).
5. Determine if there is a net polarity on the molecule - do the dipoles cancel or do they combine to give an overall dipole moment for the molecule?

An alternative way to look at this:

1. Symmetrical molecules are non-polar.
2. The following are considered symmetrical:
   - Molecules having the same atoms bonded to the central atom without any lone pairs around the central atom.
   - Molecules in which the central atom contains 2 identical BP and 3 LP.
   - Molecules in which the central element contains 4 identical BP and 2 LP.
3. Note that a molecule can have polar bonds and still be non-polar overall.

Examples: 1) Explain whether CCl_4 is polar or non-polar. 2) Explain whether CH_3Cl is polar.

VALENCE BOND THEORY

- Covalent bonds are formed when atomic orbitals on two different atoms overlap and electrons are shared.
- Most of the atoms' electrons remain in the orbitals they occupied in the separated atoms.
- The bonding electrons are **localized** in the region of the orbital overlap.
- When the orbitals have directional lobes, they overlap end to end.
- Molecular geometry depends on the bonding atomic orbitals around the central atom.

Hybridization:

- Experimentally observed geometries can be explained by hybridization.
- Hybridization is a hypothetical model where atomic orbitals are mixed to form a new **hybrid orbital**.
- The number of hybrid orbitals produced in a hybridization scheme is equal to the total number of atomic orbitals combined.
- In forming covalent bonds, hybrid orbitals may overlap with atomic orbitals or other hybrid orbitals.
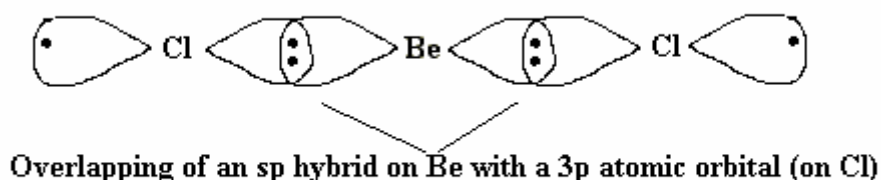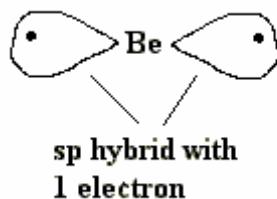- Molecular geometry is determined by the shapes and orientations of the hybrid orbitals.
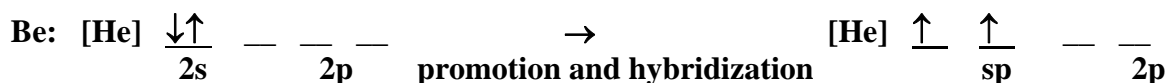
AB_2 Molecules (0 LP): sp hybridization (linear).

Example $BeCl_2$

Electron configuration

Be: [He] ↓↑ __ __ __   **Cl: [Ne]** ↓↑ ↓↑ ↓↑ ↑
            2s   **2p**   **3s**   **3p**
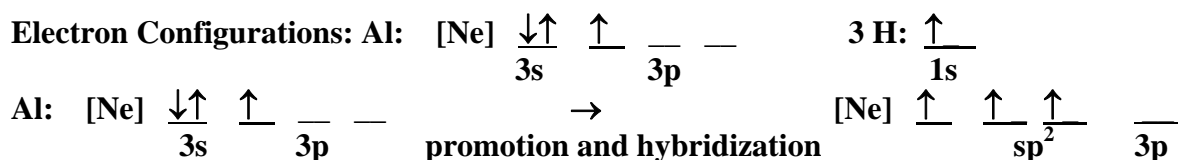
The Be atom has to make two orbitals available, with one electron in each orbital, in order to bond with each Cl (3p) electron. It therefore promotes one 2s electron into one of the 2p orbitals. However, evidence shows that the bonding orbitals on Be are equivalent - they must hybridize to give equivalent orbitals which then bond effectively and equally with the two 3p orbitals of the chlorine electrons.

Be: [He] ↓↑   _ _ _   →   [He] ↑ ↑   _ _
        2s   2p   **promotion and hybridization**   sp   2p

sp hybrid with
1 electron

Overlapping of an sp hybrid on Be with a 3p atomic orbital (on Cl)

AB_3 Molecules (0 LP): sp2 hybridization (trigonal planar)

Example AlH_3

Electron Configurations: Al: [Ne] ↓↑ ↑ _ _   3 H: ↑_
                  3s   3p   1s

Al: [Ne] ↓↑ ↑ _ _   →   [Ne] ↑ ↑ ↑   _
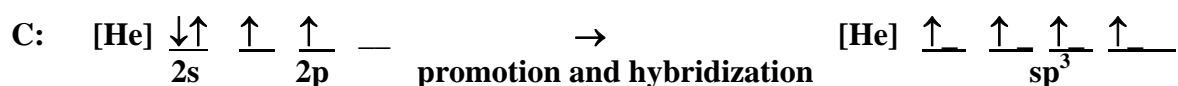   3s   3p   **promotion and hybridization** sp^2 3p

The 3 sp^2 hybrid orbitals on the Al bond with the 1s orbitals of the 3 H's.

AB_4 Molecules (0 LP): sp^3 hybridization (tetrahedral)

Example: CH_4

C: [He] ↓↑ ↑ ↑ _   →   [He] ↑_ ↑ ↑ ↑_
   2s   2p   **promotion and hybridization** sp^3
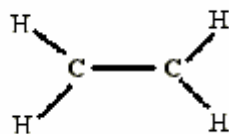
The 4 sp^3 hybrid orbitals on the C bond with the 1s orbitals of the 4 H's

AB$_3$ molecule with one unshared pair of electrons: sp^3 (pyramidal)

Example: NH$_3$

N: [He] ↓↑ ↑ ↑ ↑   →   [He] ↓↑ ↑ ↑ ↑
     2s   2p   **promotion and hybridization**   sp^3
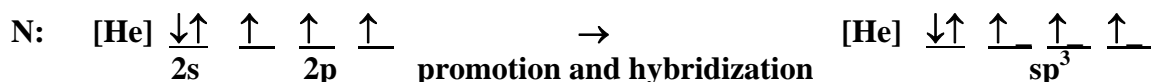
Although 3 orbitals with one electron were already available, hybridization is necessary to explain experimental observations. Note that all valence orbitals on the central atom, whether they contain one or two electrons, must be hybridized. The pair of electrons (the lone pair) is occupying an sp^3 orbital.
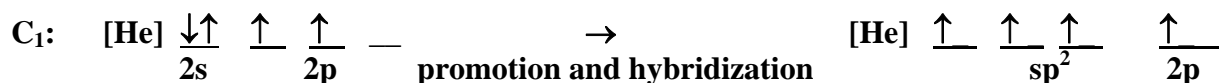
AB$_5$ Molecules (0 LP): dsp3 (trigonal bipyramidal)

Example: PH$_5$

P:[Ne] ↓↑ ↑ ↑ ↑ _ _ _ _ _ _ → [Ne] ↑ ↑ ↑ ↑ ↑ _ _ _ _
    3s   3p   3d   dsp^3 3d
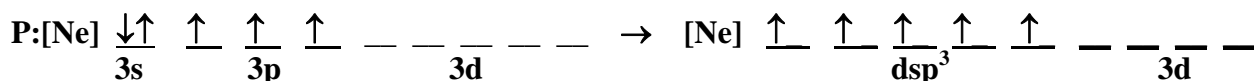
AB$_6$ Molecules (0 LP): d^{2}sp^3 (Octahedral)

Example: SH$_6$

S:[Ne] ↓↑ ↓↑ ↑ ↑ _ _ _ _ _ _ → [Ne] ↑ ↑ ↑ ↑ ↑ ↑ _ _ _ _
    3s   3p   3d   d^{2}sp^3 3d
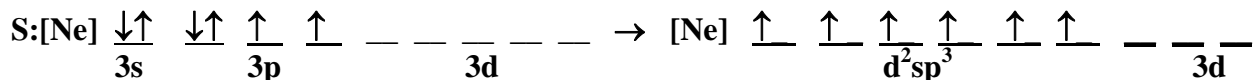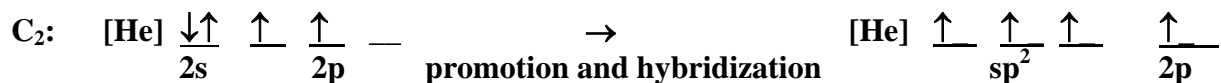
Examples: Describe the hybridization scheme around the central atom and the molecular geometry for IF$_5$, SiCl$_4$, and I$_3^-$.

Double Bonds:

Example: C$_2$H$_4$

(Incomplete structure)

Both carbons need 3 hybrid orbitals each (2 to bond with the hydrogens and 1 to bond with the other carbon)

C$_1$: [He] ↓↑ ↑ ↑ _   →   [He] ↑ ↑ ↑   ↑
     2s   2p   **promotion and hybridization**   sp^2 2p

C$_2$:   [He] $\underset{\text{2s}}{\downarrow\uparrow}$ $\underset{\text{2p}}{\uparrow \quad \uparrow \quad \_\_}$ $\rightarrow$ **promotion and hybridization**   [He] $\underset{\text{sp}^2}{\uparrow \quad \uparrow \quad \uparrow}$ $\underset{\text{2p}}{\uparrow \_\_}$
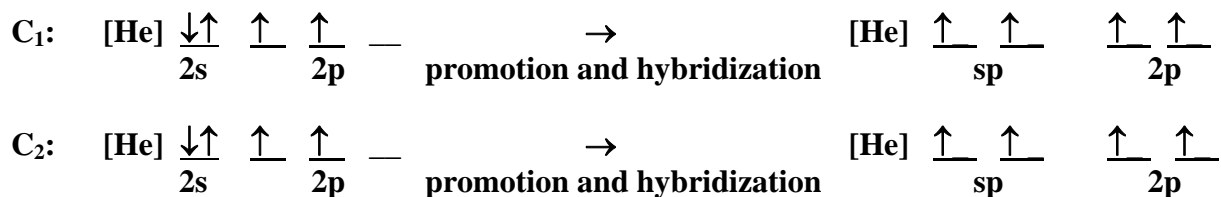
The 2 unhybridized 2p orbitals (one from each carbon) bond by overlapping sideways; this is called a pi-bond.

- **Sigma (σ) bonds** are formed from the head-on overlap of atomic orbitals (Ex: the C-H bond and the C-C bond formed by the overlap of the two sp^2 orbitals).
- **Pi (π) bonds** result from the side-on overlap of atomic orbitals.
- The pi-bond is perpendicular to the sigma bond.
- Pi bonds are weaker than sigma bonds.
- Double bonds are made up of one sigma and one pi bond.

Triple Bonds:

Example C$_2$H$_2$

Each C needs 2 hybrid orbitals (1 to bond with the H and 1 to bond with the other C)

C$_1$:   [He] $\underset{\text{2s}}{\downarrow\uparrow}$ $\underset{\text{2p}}{\uparrow \quad \uparrow \quad \_\_}$ $\rightarrow$ **promotion and hybridization**   [He] $\underset{\text{sp}}{\uparrow \quad \uparrow}$ $\underset{\text{2p}}{\uparrow \quad \uparrow}$

C$_2$:   [He] $\underset{\text{2s}}{\downarrow\uparrow}$ $\underset{\text{2p}}{\uparrow \quad \uparrow \quad \_\_}$ $\rightarrow$ **promotion and hybridization**   [He] $\underset{\text{sp}}{\uparrow \quad \uparrow}$ $\underset{\text{2p}}{\uparrow \quad \uparrow}$

2 unhybridized p orbitals (one from each C) form a pi-bond. The other 2 unhybridized p orbitals form another pi-bond. The sp orbitals form sigma-bonds.

- A triple bond has 2 pi-bonds and 1 sigma-bond.
- Bond strength: triple > double > single.

Examples: Give a plausible molecular geometry and hybridization scheme for formic acid (HCOOH), methanol, and cyanogen (C$_2$N$_2$).

Organic Molecules:

Hybridization on Carbon:

BP AROUND CARBON	HYBRIDIZATION	GEOMETRY (SHAPE)
4	sp^3	tetrahedral
3	sp^2	trigonal planar
2	sp	linear

Geometric Isomerism:

- Where there is a double bond between carbons, the CH_2 group is prevented from rotating around the bond.
- Two geometric isomers are produced which are distinctly different compounds.
- The **cis** isomer has both groups on the same side of the molecule with respect to the double bond.
- The **trans** isomer has both groups on opposite sides of the molecule.
- If either carbon in the double bond has 2 identical groups or atoms bonded to it, cis-trans isomerization is not possible.

cis-2-pentene   trans-2-pentene
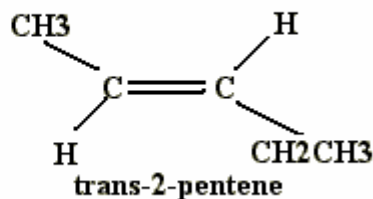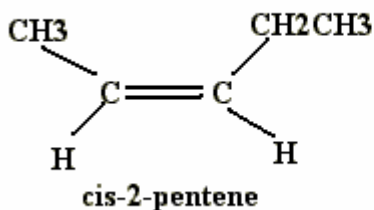
Important Example: A molecule with the formula $C_2H_2Cl_2$ is found to be nonpolar. Use this information to draw the structural formula.

- cis-trans isomerism can affect the polarity of the molecule.