MOLECULAR STRUCTURE

The localized electron bonding model describes and predicts molecular geometry using Lewis diagrams and the VSEPR model.

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 Coulombic 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.
- The combination of Lewis diagrams with the VSEPR model provides a model for predicting structural properties of many covalently bonded molecules and polyatomic ions, including
    - Molecular geometry
    - Bond angles
    - Relative bond energies
    - Presence of a dipole moment.

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 $\mathbf{A_x B_y E_z}$ 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.
- $\mu = \delta \, \mathbf{d}$ 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

- Organic chemists often describe the arrangement of electrons around a central atom in terms of "hybridization" and "hybrid orbitals".
- 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) Bond Angle = 180°.

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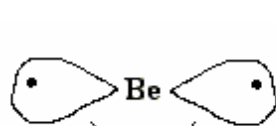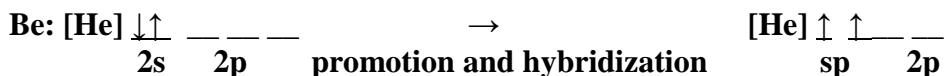
sp hybrid with
1 electron
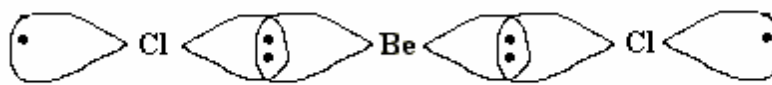
Overlapping of an sp hybrid on Be with a 3p atomic orbital (on Cl)

Summary of hybrid orbitals:

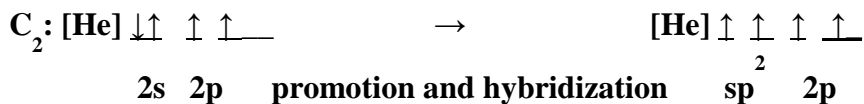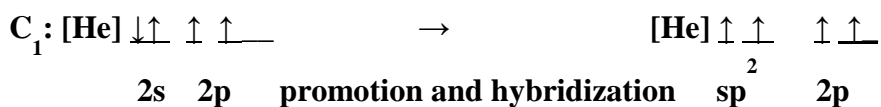| BONDS AROUND CENTRAL ATOM	BOND ANGLE	HYBRIDIZATION	GEOMETRY (SHAPE)
4	109°	sp^3	tetrahedral
3	120°	sp^2	trigonal planar
2	180°	sp	linear

Double Bonds:
Example: C_2H_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] ↓↑ ↑ ↑__   →   **[He]** ↑ ↑ ↑ ↑__
    2s 2p   **promotion and hybridization** sp^2 2p

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 therefore sigma bonds have greater bond energy than pi.
- Double bonds are made up of one sigma and one pi bond.

Triple 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_2N_2).

Geometric Isomerism:
   • The presence of a pi bond prevents the rotation of the bond and leads to structural isomers.
   • 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
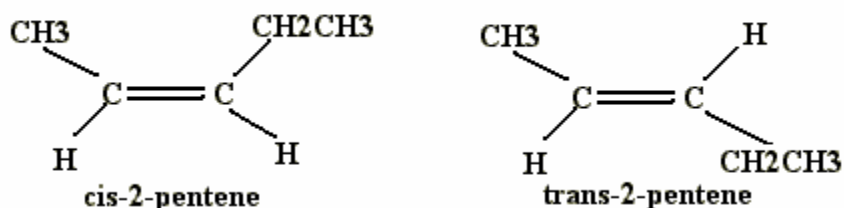
Important Examples: A molecule with the formula $C_2H_2Cl_2$ is found to be nonpolar. Use this information to draw the structural formula.

   • cis-tran isomerism can affect the polarity of the molecule.
   • In systems such as Benzene, where atomic orbitals overlap strongly with more than one other p-orbital, extended pi bonding exists, which is delocalized over more than two nuclei. These descriptions give an alternative description to resonance.
   • Example: In the 1970's, molecular solids were discovered that conduct electricity due to delocalized pi bonding. This overturned the assumption that all molecular solids would be insulators.
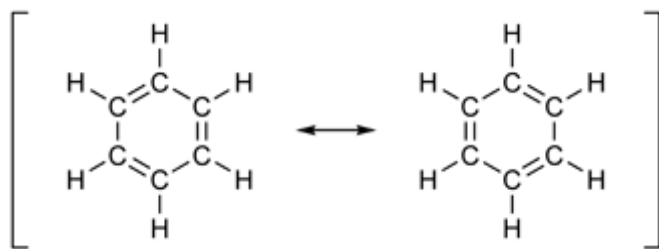
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MOLECULAR ORBITAL THEORY

   • Describes covalent bonding in a way that covers a wider variety of systems than the Lewis or VSEPR models.
   • Assumes electrons in molecules exist in orbitals of a given energy, just like electrons in an atom are assumed to exist according to atomic theory.
   • **Molecular orbitals** can hold 2 electrons of opposite spin.

Example: H_2 molecule

- Assuming that the molecular orbitals can be constructed from the hydrogen $1s$ atomic orbitals, ther are two possible molecular orbitals:

  $MO_1 = 1s_A + 1s_B$

  $MO_2 = 1s_A - 1s_B$

  where $1s_A$ and $1s_B$ represent the 1s orbitals from the 2 separated hydrogen atoms. (Note, these are determined by solving the quantum mechanical equations for the hydrogen molecule).

- **Molecular Orbital Diagrams:** show the correlation between atomic and molecular orbitals and are a useful tool.
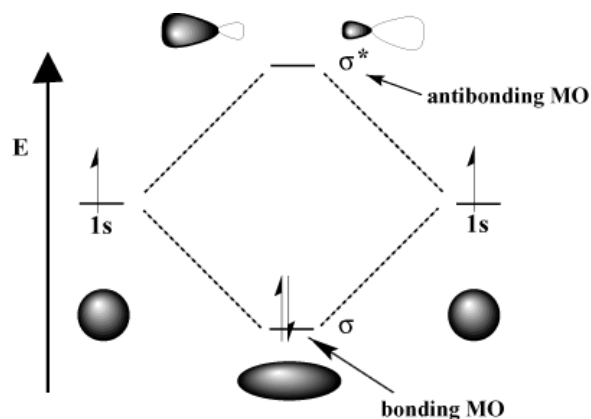
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- The electron probability of both electrons is centered along a line passing through the nuclei. For MO_1 the greatest electron probability is between the nuclei. For MO_2 it is on either side of the nuclei. This type of electron distribution is called sigma (σ).
- In the molecule, the original $1s$ orbitals no longer exist; electrons can only occupy the molecular orbitals.
- MO_1 is lower in energy than the $1s$ orbitals of the free hydrogen atoms (see diagram above), while MO_2 is higher in energy, therefore molecule formation is favorable if the electrons occupy MO_1.
- A **bonding molecular orbital** is one that has lower energy than the atomic orbitals (MO_1)
- An **anti-bonding molecular orbital** has higher energy than the atomic orbitals (MO_2) Anti-bonding orbitals are denoted by an asterisk (see diagram).