Chapter 9: Molecular Bonding and Bonding Theories
By Nick Keller and Jeff Manzione

(It is suggested that you look at this in PowerPoint Format at:
https://docs.google.com/presentation/d/1-pk8SQRUWulXZkU9_4rilwpjmicPXG0QmzKFYQ2BalU/present#slide=id.p

Molecular Shapes
- The overall shape of the molecule is determined by the number of electron domains that an atom has, and if there are atoms filling those domains ○ One electron domain counts as one lone pair of electrons, so two lone pairs of electrons would be two electron domains

○ **However, multiple bonds only take up one electron domain**
○ Total number of electron domains around the central atom is the number of lone pairs plus the number of bonded atoms

The VSEPR Model
- Molecules adopt their lowest-energy arrangement when bonded together.
- This can be shown by tying balloons together

○ Two balloons naturally adopt a linear arrangement, three balloons naturally adopt a trigonal planar arrangement, four balloons naturally adopt a tetrahedral arrangement, etc.
- It is the same with molecules
- Each combination of filled and unfilled electron domains has it's own specific shape

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles
- Electron domains for nonbonding pairs and multiple bonds push harder on adjacent electron domains, resulting in smaller bond angles.

Predicting Molecular Geometries
1. Sketch the Lewis Structure of the molecule
2. Count the total number of electron domains that the molecule has, keeping track of the number of bonded vs non-bonded domains (NOTE: a double or triple bond is counted as **one** electron domain)
3. Refer to the chart on the previous slides for determining the molecular and electron- domain geometries.

Example problem
1- Determine the electron-domain geometry and the molecular geometry of XeF_4 .
Step 1 First, we determine the Lewis-Structure of the molecule.It should look like this:
Step 2 Determine the total number of electron domains Non-bonded domains : 2 Bonded domains: 4
Total number of electron domains: 6
Step 3 Using the chart, you can see that 6 electron domains is an octahedral electron-domain geometry. Also using the chart, you can see that a molecule with 4 bonding domains and 2 nonbonding domains results in a square planar molecular geometry.

Molecules with More than One Central Atom
The VSEPR Model can easily be expanded to more complex molecules Instead of determining the shape of the whole molecule, just determine the shape of each central molecule For example, when given the acetic acid molecule, just determine the geometries of the two carbon atoms, and the oxygen atom that is not double bonded to carbon

Helpful hints for determining geometries
Non-Organic molecules will generally take the form of AB_n , where n B atoms are bonded around the central atom A. The central atoms of organic molecules will generally be carbons and single-bonded oxygens.

Polarity of Polyatomic Molecules
Bond polarity is a measure of how equally the electrons in a bond are shared between the two atoms of the bond As the difference in electronegativity increases, so does the polarity- If the values are equal, the molecule is nonpolar. Electrons are drawn to atoms with higher electronegativity values

Polarity of Polyatomic Molecules, cont'd
- For molecules that have more than two atoms, the polarity(aka *dipole moment*) depends on the polarities of each bond **and** the geometry of the molecule

○ For that, we consider the **bond dipole** , which is the dipole moment of the two atoms in that bond
- Bond dipoles are represented by this symbol:

-The arrow points to the atom with the higher electronegativity value
- Bond dipoles are vector quantities, the have both a magnitude and a direction

Finding the Polarity of a Molecule
1. Draw the Lewis Structure
2. Draw in all of the dipole moments (there are no dipole moments for lone pairs)
3. Cancel out any dipole moments that are of the same magnitude, and in opposite directions (ex. Two C-F bonds in opposite directions would cancel, but a C-F and a C-H bond would not)
4. If there are any dipole moments left, then the molecule is polar

Example Problem
Is CH_4 a polar or non-polar molecule?
Step 1 Draw the Lewis Structure
Step 2 Draw in all of the dipole moments

Step 3 + Step 4 Cancel out any moments that are equal in magnitude but opposite in direction. All of the dipole moments cancel out in the previous slide, so the molecule is non-polar

Helpful Hints for Determining Polarity

- A cheat for polarity is to "cut" the molecule in half after writing in all of the dipole moments. If you can "cut" the molecule in half in a way where the number of dipole moments would be asymmetrical, the molecule is polar
- Normally, if the dipole moments are all pointing in towards the central atom, or all away from it, and there are no lone pairs, and all of the surrounding atoms are the same, then the molecule is non-polar
- If a molecule follows the AB format, and there are no lone pairs, it is non-polar
- Molecules with a bent geometry will usually be polar
- Molecules with an AB n format with another extraneous atom (ex: CH 3 Cl) will be polar, because the extraneous atom will have a different pull

Covalent Bonding and Orbital Overlap

The VSEPR Model is a means for predicting the shapes of molecules, but it does not explain why bonds exist Valence-Bond Theory- A theory that states that orbitals overlap in a bond, allowing two electrons of opposite spin to share space, forming a covalent bond

9.5 Hybrid Orbitals

- Rationalizes the observed geometries of molecules. In order for atoms to bond with more

sp Hybrid Orbitals

With no half-filled orbitals, **Be** would not be able to bond with other elements. If the **s** and **p** orbitals are hybridized to become **sp** , Beryllium can form bonds with other elements.

Helpful Hint for determining Hybridized Orbitals (**BF_3**)

1. Count the atoms around the central atom. (3) This will be the number of hybridized orbitals.
2. Count the number of valence electrons. (3) This will be the number of electrons in the orbitals.
3. Fill in the orbitals.

sp_x and spd3x

In the same way as sp hybridized orbitals are created, so are all other types of hybridized orbitals. The type of hybridized orbital depends solely on the **number of bonding orbitals** on the central atom. Atoms can also have expanded octets which allow them to have more than four bonding regions as seen with SF_6 .

9.6 Multiple Bonds

Single bonds between two elements in a lewis dot diagram are called **sigma (σ) bonds.** Additional bonds (double or triple) are created by the overlap between two p orbitals oriented perpendicularly to the *internuclear axis* . This sideways overlap of p orbitals produces a **pi (π) bond** .

Delocalized π Bonding

Localized π bonds are only between two specific atoms. *Delocalized* π bonds are cannot be described with localized π bonds. They are usually associated with resonance structures and spread between all resonance regions in the molecules.

9.7 Molecular Orbitals Molecular orbital (MO) theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. Electrons move by specific wave functions called **molecular orbitals** . When two electron orbitals overlap, two molecular orbitals form. One orbital is lower energy (**bonding molecular orbital**) and concentrates electron density between the two nuclei. The other orbital is higher energy (**antibonding molecular orbital**) and has very little electron density between the nuclei. The electron density in both molecular orbitals is concentrated along the internuclear axis and are called sigma (σ) molecular orbitals. The interaction between two 1s orbitals to form σ_{1s} (bonding) and σ* 1s (antibonding) molecular orbitals can be represented by an **energy-level diagram (molecular orbital diagram)** .

Bond Order

In molecular orbital theory, the stability of a covalent bond is related to its bond order, defined as follows: Bond order = ½(# bonding electrons - # antibonding electrons)

Bond order 1 = single bond
Bond order 2 = double bond
Bond order 3 = triple bond

Example: Bond Order

What is the bond order of the He_2^+ ion? The He2+ ion has three electrons. Two are placed in the bonding orbital, the third in the antibonding orbital. Bonding Order = ½(2-1) = ½

9.8 Second Row Diatomic Molecules

Pi (π) molecular orbitals are orbitals that overlap in a sideways fashion and thus concentrate electron density on opposite sides of the line through the nuclei.

Paramagnetism is the magnetic behavior where unpaired electrons are attracted to a magnetic field. The greater the number of unpaired electrons, the greater the attraction.

Diamagnetism is the weak repelling force from a magnetic field observed by substances with no unpaired electrons.