Chapter 9: Molecular Geometry and Bonding Theories

9.1 Molecular Geometries

-**Bond angles**: angles made by the lines joining the nuclei of the atoms in a molecule
-Bond angles determine overall shape of molecule
-**Valence-shell electron-pair repulsion (VSEPR) model**: model that accounts for the geometric arrangements of shared and unshared electron pairs around a central atom in terms of the repulsions between electron pairs

The Valence-Shell Electron Pair-Repulsion Model

-Electrons repel one another; hence, *the best arrangement of a given number of electron pairs is the one that minimizes the repulsions among them.*

Predicting Molecular Geometries

-Two types of valence-shell electron pairs; bonding pairs and nonbonding pairs.
-**Electron-pair geometry**: 3-D arrangement of electron pairs around an atom according to the VSEPR model
-**Molecular geometry**: the arrangement in space of the atoms of a molecule
-When describing the shapes of molecules, we always give the *molecular* geometry rather than the *electron-pair* geometry. Molecular geometries only include BONDING pairs. For example, NH_3 is a tetrahedral according to electron-pair geometry because it has 3 bonds and an unshared pair of electron. However, according to molecular geometry it is a trigonal pyramidal because it has only 3 bonds.

How to predict molecular geometries using VSEPR model:

1. Sketch the Lewis dot structure of the molecule or ion
2. Count the total number of electron pairs around the central atom and arrange them in the way that minimizes electron-pair repulsions
3. Describe the molecular geometry in terms of the angular arrangement of the *bonding* pairs

Four or Fewer Valence-Shell Electron Pairs

-*A double or triple bond has essentially the same effect on bond angles as a single bond and is therefore counted as one bonding pair (that is, one electron region) when predicting geometry*

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

-Bond angles decrease as the number of nonbonding electron pairs increases. Bonding pairs are attracted by the two nuclei. By contrast, nonbonding electrons move under the attractive influence of only one nucleus and thus spread out more in space.
-*Nonbonding electron pairs exert greater repulsive forces on adjacent electron pairs and thus tend to compress the angles between the bonding pairs*
-*Electrons in multiple bonds, like nonbonding pairs, exert a greater repulsive force on adjacent electron pairs than do single bonds.*

<u>Geometries of Molecules with Expanded Valence Shells</u>

-When the central atom of a molecule or ion is from the third period of the periodic table and beyond (has *d* subshell) that atom may have more than four electron pairs around it
-The most stable electron-pair geometry for five electron pairs is the Trigonal bipyramid.
-Trigonal bipyramid geometries have two distinct types of electron pairs. They are *axial pairs* and *equatorial pairs*. In axial position, an electron pair is situated 90° from the three equatorial pairs. In an equatorial position, an electron pairs is situated 120° from the other two equatorial pairs and 90° from the two axial pairs.
-Because nonbonding pairs exert larger repulsions than bonding pairs, they always occupy the equatorial positions
-The most stable electron-pair geometry for six electron pairs is the *octahedron*.
-In an octahedron, the angles are either 90° or 180°, and all six positions are equivalent

<u>Molecules with No Single Central Atom</u>
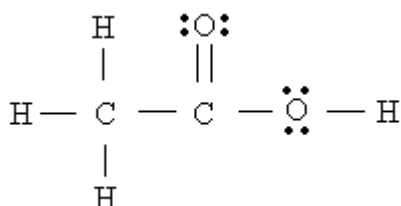
-Consider acetic acid molecule (left)
-Notice that the leftmost C has four bonded pairs around it. Hence, it must be a tetrahedral.
-The central C has 3 bonding pairs around it (counting the double bond as a single pair), hence, it is trigonal planar
-O has two bonding pairs, and two nonbonding ones. Hence, it is bent.

9.2 Polarity of Molecules

-**Polar**: in a molecule, if its centers of negative and positive charge don't coincide, aka **dipole**
-If there are no charges on the opposite ends of a molecule, or if the charges have the same sign, the molecule is not a dipole and is therefore nonpolar.
-Any diatomic molecule with a polar bond is a polar molecule
-Polar molecules align themselves with respect to one another. The negative end of a polar molecule is attracted to a positive ion, the positive end is attracted to a negative ion
-**Dipole moment**: measures the degree of polarity of a given molecule. The dipole moment, μ, is the product of the charge at either end of the dipole, Q, times the distance, r, between the charges.

$$\mu = Qr$$

-Therefore, the dipole moment increases as the quantity of charge that is separated increases and as the distance between the positive and negative centers increases.
-Dipole moments are generally reported in debyes (D), a unit equaling 3.33×10^{-30} C-m.

<u>The Polarity of Polyatomic Molecules</u>

-The polarity of a molecule containing more than two atoms depends on both the polarities of the bonds and the geometry of the molecule
-For each polar bond in a molecule, we can consider the *bond dipole,* that is, the dipole moment due only to the two atoms bonded together. We must then ask what the overall dipole moment results from adding up the individual bond dipoles. Let's use CO_2 (linear) as an example
-In CO_2, each C – O bond is polar, and because they are identical, the bond dipoles are equal in magnitude.

-The fact that both C – O bonds are polar doesn't necessarily mean the whole CO_2 molecule is
-Bond dipoles and dipole moments are vector quantities; they have both a magnitude and direction. When calculating the overall dipole moment, both the magnitude and direction of the bond dipoles must be considered in this sum of vectors
-The two bond dipoles in CO_2, although equal in magnitude, are opposite in direction, which makes them cancel each other out. Hence, CO_2 has an overall dipole moment of zero. Even though the oxygen atoms in CO_2 carry a partial negative charge, the geometry of the molecule dictates the overall dipole moment.
-Now, let's consider H_2O. Both of its bonds are identical once again, but the geometry is bent instead of linear. Hence, the bonds do not cancel each other out, and H_2O has a dipole moment
-Molecules in which the central is symmetrically surrounded by identical atoms (BF_3, CCl_4) are nonpolar.
-For AB_n molecules in which ALL of the B atoms are the same, certain symmetrical geometries – linear (AB_2), trigonal planar (AB_3), tetrahedral and square planar (AB_4), trigonal bipyramidal (AB_5), and octahedral (AB_6) – must lead to nonpolar molecules, regardless of how polar the individual bonds are.

9.3 Covalent Bonding and Orbital Overlap

-**Valence bond theory**: model of chemical bonding in which an electron-pair bond is formed between two atoms by the overlap of orbitals on the two atoms
-Covalent bonding occurs when atoms share electrons. This increases the electron density between the two nuclei, and is visualized as occurring when a valence atomic orbital of one atom merges with that of another atom
-As the distance between the atoms decreases, their overlap increases. Because of the resultant increase in electron density between the nuclei, the potential energy of the system decreases, increasing the strength of the bond.
-The observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron-electron and nucleus-nucleus)

9.4 Hybrid Orbitals

sp Hybrid Orbitals

-Use the salt BeF_2 as an example. Its geometry is linear, however it is now hard to determine which orbitals on the Be atom overlap with those of the F atoms. The electron configuration of Be is $1s^2 2s^2$. Hence, Be in its ground state has no unpaired electrons and is unable to form bonds
-Be's only option is to "promote" one of its two electrons in the 2s shell to the 2p shell. It will then have a configuration of $1s^2 2s^1 2p^1$. Since the 2p orbital is at a higher energy level than the 2s orbital, this promotion requires energy
-The Be atom now has two unpaired electrons (2s and 2p) and would be able to form two bonds, which will not be similar. The two new orbitals are identical in shape (two lobes; one much larger than the other) but are oriented in different directions. Two hybrid orbitals have been created
-**Hybrid orbitals**: orbitals that result from the mixing of different kinds of atomic orbitals on the same atom. For example and sp^3 hybrid results from the mixing, or hybridizing, of one *s* orbital and three *p* orbitals

-**Hybridization**: mixing of different types of atomic orbitals to produce a set of equivalent hybrid orbitals
-In this case, we have hybridized one *s* and one *p* orbital, so we call each hybrid an *sp hybrid orbital*. For the Be atom of BeF_2, the orbital diagram is written as follows: $1s^2\ 2sp^2$
-Hybrid orbitals have one large lobe and can therefore be directed at surrounding atoms more effectively, forming stronger bonds. The energy released by such bonds enables the promotion of a 2s electron to the 2p level.

sp^2 and sp^3 Hybrid Orbitals

-Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each of these hybrid orbitals is equivalent to the others but points in a different direction.
-Consider BF_3. B has an electron configuration of $2s^2\ 2p^1$. It promotes one of its 2s electron to the 2p orbital to have a configuration of $2s^1\ 2p^2$. Then, it hybridizes into 3 sp^2 hybrid orbitals
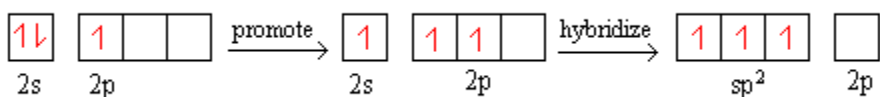
-The same process can apply to the creation of sp^3 hybrid orbitals

Hybridization Involving *d* Orbitals

-Same process as sp^2 orbitals. For example, mixing one *s* orbital, three *p* orbitals, and two *d* orbitals gives six sp^3d^2 hybrid orbitals, which are directed at the vertices of an octahedron

Summary

-The molecular geometry needs to be known first in order to use the concept of hybridization, then we can use the following rules:

1. Draw the Lewis structure for the molecule or ion
2. Determine the electron-pair geometry using the VSEPR model
3. Specify the hybrid orbitals needed to accommodate the electron pairs based on their geometrical arrangement

9.5 Multiple Bonds

-In each covalent bond we have considered so far, the electron density is concentrated symmetrically about the line that connects the two nuclei (*internuclear axis*). This axis passes through the middle of the overlap region
-**Sigma (σ) bond**: covalent bond in which electron density is concentrated along the internuclear axis
-**Pi (π) bond**: covalent bond in which electron density is concentrated above and below the internuclear axis
-Pi bonds are generally weaker than sigma bonds (less overlap)
-Usually, single bonds are σ bonds. A double bond has one σ bond and one π bond. A triple bond has one σ bond and two π bonds.

-Consider C_2H_4 as an example. After hybridization, C has 3 sp^2 hybrid orbitals and one electron in the remaining unhybridized 2p orbital. The unhybridized 2p electron is directly perpendicular to the plane that contains the three sp^2 hybrid orbitals
-The C – H σ bond is formed by the overlap of a sp^2 hybrid orbital with the 1s orbital of hydrogen. Hence, the bond uses two electrons
-The C – C σ bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. Overall, C_2H_4 has 12 valence electrons, 10 of which are used in the formation of the bonds
-The remaining two valence electrons reside in the unhybridized 2p orbitals, one electron on each of the atoms
-The 2p orbitals can overlap with one another in a sideways fashion. This will lead to the electron density being concentrated above and below the C – C bond axis, hence being a π bond
-Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules (strongly affects the properties of substances)
-Although π bonds can be formed from *d* orbitals, we will only consider those formed by *p* orbitals. They can only form if unhybridized *p* orbitals are present on the bonded atoms. Only atoms having *sp* or *sp^2* hybridization can be involved in π bonding
-Double and triple bonds are more common in molecules with small atoms

Delocalized Bonding

-σ and π electrons are *localized* when they are associated totally with two atoms forming the bond.
-In some molecules, particularly those with more than one resonance form, we cannot accurately describe the bonding as localized. In order to deal with this, we "smear out" the bonds (*delocalize* them) so that it fits both resonance structures as best as possible
-**Delocalized electrons**: electrons that are spread over a number of atoms in a molecule rather than localized between a pair of atoms

General Conclusions

1. Every pair of bonded atoms shares one or more pairs of electrons. In every bond, at least one pair of electrons is localized in the space between the atoms, in a σ bond. The appropriate set of hybrid orbitals used to form the σ bonds between an atom and its neighbors is determined by the observed geometry of the molecule
2. The electrons in σ bonds are localized in the region between two bonded atoms and do not make a significant contributions to the bonding between any other two atoms
3. When atoms share more than one pair of electrons, the additional pairs are in π bonds. The centers of chare density in a π bond lie above an below the bond axis.
4. Molecules with two or more resonance forms can have π bonds that extend over more than two bonded atoms. Electrons in π bonds that extend over more than two bonded atoms are said to be delocalized

9.6 Molecular Orbitals

-**Molecular orbital theory**: theory that predicts that electrons in molecules exist in allowed energy states.
-**Molecular orbitals**: allowed state for an electron in a molecule

-Molecular orbitals are very similar to atomic orbitals. Both hold a maximum of two electrons (with opposite spins), have definite energies, and their electron-density distribution can be visualized by using contour representations. However, molecular orbitals are associated with the *entire* molecule

The Hydrogen Molecule

-Consider H_2 as an example. Whenever two atomic orbitals overlap, two molecular orbitals form. Thus, the overlap of the 1s orbitals of two hydrogen atoms to form H_2 produces two molecular orbitals.
-**Bonding molecular orbital**: molecular orbital in which the electron density is concentrated in the internuclear region. The energy of a bonding molecular orbital is lower than the energy of the separate atomic orbitals from which it forms.
-The bonding molecular orbital results from summing the two atomic orbitals so that the atomic orbital wave functions enhance each other in the bond region. Because an electron in this molecular orbital is strongly attracted to both nuclei, the electron is more stable (lower energy) than it is in the 1s orbital of hydrogen. Because it concentrates electron density between both nuclei, the bonding molecular orbital holds the atoms together in a covalent bond.
-**Antibonding molecular orbital**: molecular orbital in which electron density is concentrated outside the region between the two nuclei of bonded atoms. Such orbitals, designated as σ* or π*, are less stable (of higher energy) than bonding molecular orbitals
-An electron in the antibonding molecular orbital is repelled from the bonding region and is therefore less stable (higher energy) than it is in the 1s orbital of the hydrogen atom
-**Sigma (σ) molecular orbital**: molecular orbital that centers the electron density about an imaginary line passing through two nuclei
-**Energy level diagram**: aka **Molecular orbital diagram**; diagram that shows the energies of molecular orbitals relative to the atomic orbitals from which they are derived
-Electrons occupying a bonding molecular orbital are called *bonding* electrons

Bond Order

-**Bond order**: related to the stability of a covalent bond.

Bond order = ½ (number of bonding electrons – number of antibonding electrons)

-*A bond order of 1 represents a single bond, a bond order of 2 represents a double bond, and a bond order of 3 represents a triple bond. A bond order of 0 means that no bonds exist*


9.7 Second-Period Diatomic Molecules

-Material here applies to *homonuclear* diatomic molecules (those composed of identical atoms)
1. The number of atomic orbitals formed equals the number of atomic orbitals combined
2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy
3. The effectiveness with which two atomic orbitals combine is proportional to their overlap with one another; that is, as the overlap increases, the bonding orbital is lowered in energy, and the antibonding orbital is raised in energy
4. Each molecular orbital can accommodate at most two electrons, with their spins paired (Pauli exclusion principle)

5. When molecular orbitals have the same energy, one electron enters each orbital (with parallel spins) before spin pairing occurs (Hund's rule)

Molecular Orbitals for Li_2 and Be_2
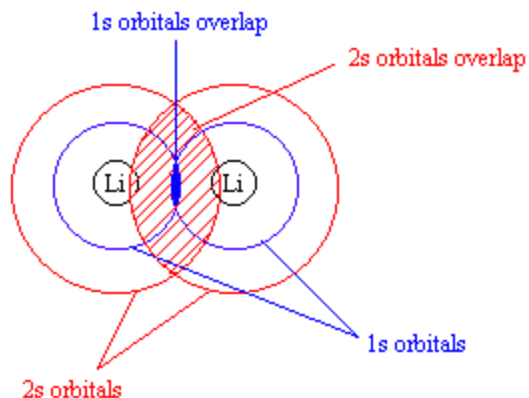
-Lithium has 1s and 2s orbitals, but both are extremely different. According to the Lewis structure of Li_2, there is a single Li – Li bond.
-Because the 1s and 2s orbitals are so different in energy, it is likely that the 1s orbitals interact with each other. (See rule 2)
-This would create a much larger overlap between the 2s orbitals (see figure)
-As a result, the energy seperation between the σ_{2s} and σ^*_{2s} is greater than that for the 1s-based orbitals.

-Each Li atom has 3 electrons; so six electrons must be placed in the molecular orbitals of Li_2
-The electrons occupy the σ_{1s}, σ^*_{1s}, and σ_{2s} orbitals (not the σ^*_{2s} orbital). There are 4 bonding orbitals and 2 nonbonding ones, so the bond order equals ½ (4 – 2) = 1. The molecule has a single bond, in accord with its Lewis structure.
-Filled atomic subshells usually do not contribute significantly to bonding in molecule formation
-In Be_2, each Be has 4 electrons, for a total of eight. When we place them in molecular orbitals, we fill the σ_{1s}, σ^*_{1s}, σ_{2s}, and σ^*_{2s} orbitals. There is an equal number of bonding and antibonding electrons, so the bond order is 0. Thus, Be_2 doesn't exist.

Molecular Orbitals from *2p* Atomic Orbitals

-*z* axis is internuclear axis (in this example). $2p_z$ orbitals face each other in a "head-to-head" fashion along the *z*-axis. They combine like the *s* orbitals, with one combination concentrating electron density between both nuclei, and the other excluding the electron density from the bonding region. In each of these combinations, the electron density lies along the internuclear axis. Hence, they are σ molecular orbitals: σ_{2p} and σ^*_{2p}
-The other 2p orbitals overlap in a sideways fashion and thus concentrate electron density on opposite sides of the internuclear axis. Molecular orbitals of this type are called **pi molecular orbitals**. We get two π_{2p} molecular orbitals by combining $2p_x$ and $2p_y$ molecular orbitals. The resulting π_{2p} molecular orbitals are degenerate (same energy). Likewise, two degenerate π^*_{2p} antibonding molecular orbitals are formed.
-The $2p_z$ orbitals on two atoms point directly at one another, hence, having a greater overlap than the $2p_x$ and $2p_y$ orbitals. From rule 3, we can expect the σ_{2p} molecular orbital to be lower in energy (more stable) than the π_{2p} molecular orbitals.

Electron Configurations for B_2 Through F_2

-The elements Boron through Fluorine all have 2s and 2p valence electrons
-In the energy diagram, the σ_{2p} molecular orbital is at higher energy than the π_{2p} molecular orbitals, contrary to what we would expect from rule 3.
-This is because of interaction between the σ_{2s} and σ_{2p} molecular orbitals. It results in the σ_{2p} molecular orbital being pushed upward in energy to the point where it is above the π_{2p} orbitals,

and the σ_{2s} molecular orbital is pushed down in energy. (The interaction between σ_{2p} and σ_{2s} molecular orbitals decreases as we move from left to right in the second period. As a result, the σ_{2p} is higher in energy than the π_{2p} orbitals for B_2, C_2, and N_2. For O_2, F_2, and Ne_2, the σ_{2p} orbital is lower in energy than the π_{2p} orbitals)

-Boron has 3 valence electrons. Thus, for B_2, we must place 6 electrons in molecular orbitals. Four of these occupy the σ_{2s} and σ^*_{2s} molecular orbitals, leading to no net bonding. The last two electrons are put in the π_{2p} bonding molecular orbitals; one electron is put in each π_{2p} molecular orbital with the same spin (rule 5). Therefore, B_2 has a bond order of 1.

Electron Configurations and Molecular Properties

-Molecules with one or more unpaired electrons are attracted into a magnetic field. The more unpaired electrons, the stronger the force of the attraction
-**Paramagnetism**: property that a substance possesses if it contains one or more unpaired electrons. A paramagnetic substance is drawn into a magnetic field
-**Diamagnetism**: type of magnetism that causes a substance with no unpaired electrons to be weakly repelled from a magnetic field.
-Diamagnetism is a much weaker effect than paramagnetism
-As bond orders increase, bond distances decrease and bond-dissociation energies increase.
-Molecules with the same bond order do not have the same bond distances and bond-dissociation energies. There are other factors involved, such as nuclear charges and the extend of orbital overlap.