

Chapter 9. Molecular Geometry and Bonding Theories

Lecture Outline

9.1 Molecular Shapes

- Lewis structures give atomic connectivity: they tell us which atoms are physically connected to which atoms.
- The shape of a molecule is determined by its **bond angles**.
 - The angles made by the lines joining the nuclei of the atoms in a molecule are the bond angles.
- Consider CCl_4 :
 - Experimentally we find all $\text{Cl}-\text{C}-\text{Cl}$ bond angles are 109.5° .
 - Therefore, the molecule cannot be planar.
 - All Cl atoms are located at the vertices of a tetrahedron with the C at its center.
- In order to predict molecular shape, we assume that the valence electrons repel each other.
 - Therefore, the molecule adopts the three-dimensional geometry that minimizes this repulsion.
 - We call this model the **Valence Shell Electron Pair Repulsion (VSEPR)** model.

9.2 The VSEPR Model

- A covalent bond forms between two atoms when a pair of electrons occupies the space between the atoms.
 - This is a **bonding pair** of electrons.
 - Such a region is an **electron domain**.
- A **nonbonding pair** or *lone pair* of electrons defines an electron domain located principally on one atom.
- Example: NH_3 has three bonding pairs and one lone pair.
- VSEPR predicts that the best arrangement of electron domains is the one that minimizes the repulsions among them.
 - The arrangement of electron domains about the central atom of an AB_n molecule is its **electron-domain geometry**.
 - There are five different electron-domain geometries:
 - linear (two electron domains), trigonal planar (three domains), tetrahedral (four domains), trigonal bipyramidal (five domains) and octahedral (six domains).
- The **molecular geometry** is the arrangement of the atoms in space.
 - To determine the shape of a molecule we must distinguish between lone pairs and bonding pairs.
 - We use the electron-domain geometry to help us predict the molecular geometry.
 - Draw the Lewis structure.
 - Count the total number of electron domains around the central atom.
 - Arrange the electron domains in one of the above geometries to minimize electron-electron repulsion.
 - Next, determine the three-dimensional structure of the molecule.
 - We ignore lone pairs in the molecular geometry.
 - Describe the molecular geometry in terms of the angular arrangement of the bonded atoms.
 - Multiple bonds are counted as one electron domain.

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

- We refine VSEPR to predict and explain slight distortions from “ideal” geometries.
- Consider three molecules with tetrahedral electron domain geometries:
 - CH_4 , NH_3 , and H_2O .

- By experiment, the H–X–H bond angle decreases from C (109.5° in CH_4) to N (107° in NH_3) to O (104.5° in H_2O).
- A bonding pair of electrons is attracted by two nuclei. They do not repel as much as lone pairs which are primarily attracted by only one nucleus.
- Electron domains for nonbonding electron pairs thus exert greater repulsive forces on adjacent electron domains.
 - They tend to compress the bond angles.
 - The bond angle decreases as the number of nonbonding pairs increases.
- Similarly, electrons in multiple bonds repel more than electrons in single bonds (e.g., in Cl_2CO the O–C–Cl angle is 124.3° , and the Cl–C–Cl bond angle is 111.4°).
- We will encounter eleven basic molecular shapes:
 - three atoms (AB_2):
 - linear
 - bent
 - four atoms (AB_3):
 - trigonal planar
 - trigonal pyramidal
 - t-shaped
 - five atoms (AB_4):
 - tetrahedral
 - square planar
 - seesaw
 - six atoms (AB_5):
 - trigonal bipyramidal
 - square pyramidal
 - seven atoms (AB_6):
 - octahedral

Molecules with Expanded Valence Shells

- Atoms that have expanded octets have five electron domains (trigonal bipyramidal) or six electron domains (octahedral) electron-domain geometries.
 - Trigonal bipyramidal structures have a plane containing three electron pairs.
 - The fourth and fifth electron pairs are located above and below this plane.
 - In this structure two trigonal pyramids share a base.
 - For octahedral structures, there is a plane containing four electron pairs.
 - Similarly, the fifth and sixth electron pairs are located above and below this plane.
 - Two square pyramids share a base.
- Consider a trigonal bipyramid.
 - The three electron pairs in the plane are called *equatorial*.
 - The two electron pairs above and below this plane are called *axial*.
 - The axial electron pairs are 180° apart and 90° to the equatorial electrons.
 - The equatorial electron pairs are 120° apart.
 - To minimize electron–electron repulsion, nonbonding pairs are always placed in equatorial positions and bonding pairs are placed in either axial or equatorial positions.
- Consider an octahedron.
 - The four electron pairs in the plane are at 90° to each other.
 - The two axial electron pairs are 180° apart and at 90° to the electrons in the plane.
 - Because of the symmetry of the system, each position is equivalent.
 - If we have five bonding pairs and one lone pair, it does not matter where the lone pair is placed.
 - The molecular geometry is square pyramidal.
 - If two non-bonding pairs are present, the repulsions are minimized by pointing them toward opposite sides of the octahedron.

- The molecular geometry is square planar.

Shapes of Larger Molecules

- In acetic acid, CH_3COOH , there are three interior atoms: two C and one O.
- We assign the molecular (and electron-domain) geometry about each interior atom separately:
 - The geometry around the first C is tetrahedral.
 - The geometry around the second C is trigonal planar.
 - The geometry around the O is bent (tetrahedral).

9.3 Molecular Shape and Molecular Polarity

- Polar molecules interact with electric fields.
- We previously saw that binary compounds are polar if their centers of negative and positive charge do not coincide.
 - If two charges, equal in magnitude and opposite in sign, are separated by a distance d , then a *dipole* is established.
 - The dipole moment, ϵ is given by

$$\epsilon = Qr$$
 - where Q is the magnitude of the charge.
- We can extend this to polyatomic molecules.
 - For each bond in a polyatomic molecule, we can consider the **bond dipole**.
 - The dipole moment due only to the two atoms in the bond is the bond dipole.
 - Because bond dipoles and dipole moments are *vector quantities*, the orientation of these individual dipole moments determines whether the molecule has an overall dipole moment.
 - Examples:
 - In CO_2 each $\oplus\text{C}-\text{O}^\ominus$ dipole is canceled because the molecule is linear.
 - In H_2O , the $\oplus\text{H}-\text{O}^\ominus$ dipoles do not cancel because the molecule is bent.
- It is possible for a molecule with polar bonds to be either polar or nonpolar.
 - Example:
 - For diatomic molecules:
 - polar bonds always result in an overall dipole moment.
 - For triatomic molecules:
 - if the molecular geometry is bent, there is an overall dipole moment.
 - if the molecular geometry is linear and the B atoms are the same, there is no overall dipole moment.
 - if the molecular geometry is linear and the B atoms are different, there is an overall dipole moment.
 - For molecules with four atoms:
 - if the molecular geometry is trigonal pyramidal, there is an overall dipole moment.
 - if the molecular geometry is trigonal planar and the B atoms are identical, there is no overall dipole moment.
 - if the molecular geometry is trigonal planar and the B atoms are different, there is an overall dipole moment.

9.4 Covalent Bonding and Orbital Overlap

- Lewis structures and VSEPR theory give us the shape and location of electrons in a molecule.
- They do not explain why a chemical bond forms.
- How can quantum mechanics be used to account for molecular shape? What are the orbitals that are involved in bonding?
- We use **valence-bond theory**.
 - A covalent bond forms when the orbitals on two atoms **overlap**.
 - The shared region of space between the orbitals is called the orbital overlap.

- There are two electrons (usually one from each atom) of opposite spin in the orbital overlap.
- As two nuclei approach each other their atomic orbitals overlap.
- As the amount of overlap increases, the energy of the interaction decreases.
- At some distance the minimum energy is reached.
 - The minimum energy corresponds to the bonding distance (or bond length).
- As the two atoms get closer, their nuclei begin to repel and the energy increases.
- At the bonding distance, the attractive forces between nuclei and electrons just balance the repulsive forces (nucleus-nucleus, electron-electron).

9.5 Hybrid Orbitals

- We can apply the idea of orbital overlap and valence-bond theory to polyatomic molecules.

sp Hybrid Orbitals

- Consider the BeF_2 molecule.
 - Be has a $1s^2 2s^2$ electron configuration.
 - There is no unpaired electron available for bonding.
 - We conclude that the atomic orbitals are not adequate to describe orbitals in molecules.
- We know that the F–Be–F bond angle is 180° (VSEPR theory).
- We also know that one electron from Be is shared with each one of the unpaired electrons from F.
- We assume that the Be orbitals in the Be–F bond are 180° apart.
- We could promote an electron from the $2s$ orbital on Be to the $2p$ orbital to get two unpaired electrons for bonding.
 - BUT the geometry is still not explained.
- We can solve the problem by allowing the $2s$ and one $2p$ orbital on Be to mix or form two new **hybrid orbitals** (a process called **hybridization**).
 - The two equivalent hybrid orbitals that result from mixing an s and a p orbital and are called *sp* hybrid orbitals.
 - The two lobes of an *sp* hybrid orbital are 180° apart.
 - According to the valence-bond model, a linear arrangement of electron domains implies *sp* hybridization.
 - Since only one of $2p$ orbitals of Be has been used in hybridization, there are two unhybridized p orbitals remaining on Be.
 - The electrons in the *sp* hybrid orbital form shared electron bonds with the two fluorine atoms.

*sp*² and *sp*³ Hybrid Orbitals

- Important: when we mix n atomic orbitals we must get n hybrid orbitals.
- Three *sp*² hybrid orbitals are formed from hybridization of one s and two p orbitals.
 - Thus, there is one unhybridized p orbital remaining.
 - The large lobes of the *sp*² hybrids lie in a trigonal plane.
 - Molecules with trigonal planar electron-pair geometries have *sp*² orbitals on the central atom.
- Four *sp*³ hybrid orbitals are formed from hybridization of one s and three p orbitals.
 - Therefore, there are four large lobes.
 - Each lobe points towards the vertex of a tetrahedron.
 - The angle between the large lobes is 109.5° .
 - Molecules with tetrahedral electron pair geometries are *sp*³ hybridized.

Hybridization Involving d Orbitals

- Since there are only three p orbitals, trigonal bipyramidal and octahedral electron-pair geometries must involve d orbitals.
- Trigonal bipyramidal electron pair geometries require *sp*³ d hybridization.
- Octahedral electron pair geometries require *sp*³ d^2 hybridization.
- Note that the electron pair VSEPR geometry corresponds well with the hybridization.

- Use of d orbitals in making hybrid orbitals corresponds well with the idea of an expanded octet.

Summary

- We need to know the electron-domain geometry before we can assign hybridization.
- To assign hybridization:
 - Draw a Lewis structure.
 - Assign the electron-domain geometry using VSEPR theory.
 - Specify the hybridization required to accommodate the electron pairs based on their geometric arrangement.
 - Name the geometry by the positions of the atoms.

9.6 Multiple Bonds

- In the covalent bonds we have seen so far the electron density has been concentrated symmetrically about the *internuclear axis*.
- **Sigma (σ) bonds:** electron density lies on the axis between the nuclei.
 - All single bonds are σ bonds.
- What about overlap in multiple bonds?
 - **Pi (π) bonds:** electron density lies above and below the plane of the nuclei.
 - A double bond consists of one σ bond and one π bond.
 - A triple bond has one σ bond and two π bonds.
- Often, the p orbitals involved in π bonding come from unhybridized orbitals.
- For example: ethylene, C_2H_4 , has:
 - One σ and one π bond.
 - Both C atoms are sp^2 hybridized.
 - Both C atoms have trigonal planar electron-pair and molecular geometries.
- For example: acetylene, C_2H_2 :
 - The electron-domain geometry of each C is linear.
 - Therefore, the C atoms are sp hybridized.
 - The sp hybrid orbitals form the C–C and C–H σ bonds.
 - There are *two* unhybridized p orbitals on each C atom.
 - *Both* unhybridized p orbitals form the *two* π bonds;
 - One π bond is above and below the plane of the nuclei;
 - One π bond is in front and behind the plane of the nuclei.
- When triple bonds form (e.g., N_2), one π bond is always above and below and the other is in front and behind the plane of the nuclei.

Delocalized π Bonding

- So far all the bonds we have encountered are localized between two nuclei.
- In the case of benzene:
 - There are six C–C σ bonds and six C–H σ bonds.
 - Each C atom is sp^2 hybridized.
 - There is one unhybridized p orbital on each carbon atom, resulting in six unhybridized carbon p orbitals in a ring.
- In benzene there are two options for the three π bonds:
 - localized between carbon atoms or
 - **delocalized** over the entire ring (i.e., the π electrons are shared by all six carbon atoms).
- Experimentally, all C–C bonds are the same length in benzene.
 - Therefore, all C–C bonds are of the same type (recall single bonds are longer than double bonds).

General Conclusions

- Every pair of bonded atoms shares one or more pairs of electrons.
- Two electrons shared between atoms on the same axis as the nuclei are σ bonds.

- π bonds are always localized in the region between two bonded atoms.
- If two atoms share more than one pair of electrons, the additional pairs form π bonds.
- When resonance structures are possible, delocalization is also possible.

9.7 Molecular Orbitals

- Some aspects of bonding are not explained by Lewis structures, VSEPR theory, and hybridization.
 - For example:
 - Why does O_2 interact with a magnetic field?
 - Why are some molecules colored?
- For these molecules, we use **molecular orbital (MO) theory**.
- Just as electrons in atoms are found in atomic orbitals, electrons in molecules are found in **molecular orbitals**.
- Molecular orbitals:
 - Some characteristics are similar to those of atomic orbitals.
 - Each contains a maximum of two electrons with opposite spins.
 - Each has a definite energy.
 - Electron density distribution can be visualized with contour diagrams.
 - However, unlike atomic orbitals, molecular orbitals are associated with an *entire molecule*.

The Hydrogen Molecule

- When two AOs overlap, two MOs form.
- Therefore, $1s(H) + 1s(H)$ must result in two MOs for H_2 .
 - One has electron density between the nuclei (**bonding MO**).
 - One has little electron density between the nuclei (**antibonding MO**).
- **Sigma (σ) MOs** have electron density in both molecular orbitals centered about the internuclear axis.
- The σ bonding MO is lower in energy than the σ^* (antibonding) MO.
- **The energy level diagram, or MO diagram**, shows the energies of the orbitals in a molecule.
 - The total number of electrons in all atoms are placed in the MOs starting from lowest energy (σ_{1s}) and ending when all electrons have been accommodated.
 - Note that electrons in MOs have opposite spins.

Bond Order

- **Bond order** = $\frac{1}{2}$ (bonding electrons – antibonding electrons).
 - Bond order = 1 for a single bond.
 - Bond order = 2 for a double bond.
 - Bond order = 3 for a triple bond.
 - Fractional bond orders are possible.
- For example, consider the molecule H_2 .
 - H_2 has two bonding electrons.
 - Bond order for H_2 is:

$$\frac{1}{2} (\text{bonding electrons} - \text{antibonding electrons}) = \frac{1}{2} (2 - 0) = 1$$
 - Therefore, H_2 has a single bond.
- For example, consider the species He_2 .
 - He_2 has two bonding electrons and two antibonding electrons.
 - Bond order for He_2 is:

$$\frac{1}{2} (\text{bonding electrons} - \text{antibonding electrons}) = \frac{1}{2} (2 - 2) = 0.$$
 - Therefore, He_2 is *not* a stable molecule.
- MO theory correctly predicts that hydrogen forms a diatomic molecule but that helium does not!

9.8 Second-Row Diatomic Molecules

- We look at homonuclear diatomic molecules (e.g., Li_2 , Be_2 , B_2 etc.).
- AOs combine according to the following rules:

- The number of MOs = number of AOs.
- AOs of similar energy combine (e.g., $1s + 1s$ rather than $1s + 2s$).
- As overlap increases, the energy of the bonding MO decreases and the energy of the antibonding MO increases.
- Pauli: each MO has at most two electrons, with spins paired.
- Hund: for degenerate orbitals, each MO is first occupied singly before spin pairing occurs.

Molecular Orbitals for Li_2 and Be_2

- Each $1s$ orbital combines with another $1s$ orbital to give one TM_{1s} and one TM_{1s}^* orbital, both of which are occupied (since Li and Be have $1s^2$ electron configurations).
- Each $2s$ orbital combines with another $2s$ orbital give one TM_{2s} and one TM_{2s}^* orbital.
- The energies of the $1s$ and $2s$ orbitals are sufficiently different so that there is no cross mixing of orbitals (i.e., we do not get $1s + 2s$).
- Consider the bonding in Li_2 .
 - There are a total of six electrons in Li_2 .
 - two electrons in TM_{1s} .
 - two electrons in TM_{1s}^* .
 - two electrons in TM_{2s} .
 - zero electrons in TM_{2s}^* .
 - Therefore the bond order is $\frac{1}{2}(4 - 2) = 1$.
- Since the $1s$ AOs are completely filled, the TM_{1s} and TM_{1s}^* are filled.
 - We generally ignore core electrons in MO diagrams.
 - Core electrons usually do not contribute significantly to bonding in molecule formation.
- Consider bonding in Be_2 .
 - There are a total of eight electrons in Be_2 .
 - two electrons in TM_{1s} .
 - two electrons in TM_{1s}^* .
 - two electrons in TM_{2s} .
 - two electrons in TM_{2s}^* .
 - Therefore the bond order is $\frac{1}{2}(4 - 4) = 0$.
 - Be_2 does not exist.

Molecular Orbitals from $2p$ Atomic Orbitals

- There are two ways in which two p orbitals can overlap:
 - end on so that the resulting MO has electron density on the axis between nuclei (i.e., TM type orbital).
 - Sideways, so that the resulting MO has electron density above and below the axis between nuclei.
 - These are called **π (∇) molecular orbitals**.
- The six p -orbitals (two sets of three) must give rise to six MOs:
 - TM , TM^* , ∇ , ∇^* , ∇ and ∇^* .
 - Therefore, there are a maximum of two ∇ bonds which can come from p orbitals.
 - The relative energies of these six orbitals can change.

Electron Configurations for B_2 Through Ne_2

- Features of the energy-level diagrams for these elements are:
 - $2s$ orbitals are lower in energy than $2p$ orbitals so both TM_{2s} orbitals (TM_{2s} and TM_{2s}^*) are lower in energy than the lowest energy MO derived from the $2p$ AOs.
 - There is greater overlap between $2p_z$ orbitals.
 - They point directly towards one another, so the TM_{2p} MO is lower in energy than the ∇_{2p} orbitals.
 - The TM_{2p}^* MO is higher in energy than the ∇_{2p}^* orbitals.
 - The ∇_{2p} and ∇_{2p}^* orbitals are doubly degenerate.

- As the atomic number decreases, it becomes more likely that a $2s$ orbital on one atom can interact with the $2p$ orbital on the other.
- As the $2s-2p$ interaction increases, the σ_{2s}^{TM} MO lowers in energy and the σ_{2p}^{TM} orbital increases in energy.
 - For B_2 , C_2 , and N_2 the σ_{2p}^{TM} orbital is higher in energy than the σ_{2p}^{V} .
 - For O_2 , F_2 , and Ne_2 the σ_{2p}^{TM} orbital is lower in energy than the σ_{2p}^{V} .
- Once we know the relative orbital energies, we add the required number of electrons to the MOs, taking into account Pauli's exclusion principle and Hund's rule.
- As bond order increases,
 - bond length decreases.
 - bond energy increases.

Electron Configurations and Molecular Properties

- Two types of magnetic behavior are:
 - **paramagnetism** (unpaired electrons in molecule)
 - strong attraction between magnetic field and molecule
 - **diamagnetism** (no unpaired electrons in molecule)
 - weak repulsion between magnetic field and molecule
- Magnetic behavior is detected by determining the mass of a sample in the presence and absence of a magnetic field.
 - A large increase in mass indicates paramagnetism.
 - A small decrease in mass indicates diamagnetism.
- Experimentally, O_2 is paramagnetic.
 - The Lewis structure for O_2 shows no unpaired electrons.
 - The MO diagram for O_2 shows two unpaired electrons in the $\sigma_{2p}^{\text{V}*}$ orbital.
 - Experimentally, O_2 has a short bond length (1.21 Å) and high bond dissociation energy (495 kJ/mol).
 - This suggests a double bond.
 - The MO diagram for O_2 predicts both paramagnetism and the double bond (bond order = 2).

Heteronuclear Diatomic Molecules

- Heteronuclear diatomic molecules contain two different elements.
- If both atoms do not differ greatly in electronegativity, the description of their MOs will be similar to those for homonuclear diatomic molecules.