Chapter 9. Molecular Geometry and Bonding Theories

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 Cl–C–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 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.

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$_2$O.
    - 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$_2$O).
    - 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 Cl₂CO the O–C–Cl angle is 124.3°, and the Cl–C–Cl bond angle is 111.4°).

We will encounter 11 basic molecular shapes:
- Three atoms (AB₂)  Linear or Bent
- Four atoms (AB₃)  Trigonal planar, Trigonal pyramidal or T-shaped
- Five atoms (AB₄)  Tetrahedral, Square planar or Seesaw
- Six atoms (AB₅)  Trigonal bipyramidal or Square pyramidal
- Seven atoms (AB₆)  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 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 doesn’t matter where the lone pair is placed.
    - The molecular geometry is square pyramidal.
  - If two nonbonding 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, CH₃COOH, there are three interior atoms: two C and one O.
- We assign the molecular (and electron-domain) geometry about each interior (central) 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, \( \mu \), is given by: \( \mu = Qr \)
  - 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 $\delta^+\text{C}–\delta^-\text{O}$ dipole is canceled because the molecule is linear.
  • In H$_2$O, the $\delta^+\text{H}–\delta^-\text{O}^–$ 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 1$s^2$2$s^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 2$s$ orbital on Be to the 2$p$ orbital to get two unpaired electrons for bonding.
  • BUT the geometry is still not explained.
• We can solve the problem by allowing the 2$s$ and one 2$p$ 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 orbitals form shared electron bonds with the two fluorine atoms.

sp² and sp³ Hybrid Orbitals

Important: when we mix n atomic orbitals, we must get n hybrid orbitals.

Three sp² 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 sp² hybrids lie in a trigonal plane.

Molecules with trigonal planar electron-pair geometries have sp² orbitals on the central atom.

Four sp³ 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 sp³ hybridized.

Since there are only three p orbitals, trigonal bipyramidal and octahedral electron-pair geometries must involve d orbitals.

Trigonal bipyramidal electron pair geometries require sp³d hybridization.

Octahedral electron pair geometries require sp³d² 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.

Hybrid Orbital 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, C₂H₄, has a C=C double bond:

- One σ and one π bond.
- Both C atoms sp² hybridized.
- Both C atoms with trigonal planar electron-pair and molecular geometries.

For example: acetylene, C₂H₂, has a C≡C triple bond

- 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., N₂), one π bond is always above and below and the other is in
  front and behind the plane of the nuclei.

Resonance Structures, Delocalization, and π Bonding
• So far all the bonds we have encountered are localized between two nuclei.
• In the case of benzene:
  • There are six localized C–C σ bonds and six localized C–H σ bonds
  • Each C atom is sp² hybridized.
  • There is one unhybridized p orbital on each carbon atom, resulting in six unhybridized carbon p orbitals
    in a ring.
• In benzene the three π bonds are 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.
• σ 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.
  • π bonds in alkenes and alkynes will be discussed in Chapter 24 (section 24.3).
  • Delocalized π bonds in aromatic compounds will be mentioned in Chapter 24 (section 24.3).

9.7 Molecular Orbitals
• Some aspects of bonding are not explained by Lewis structures, VSEPR theory and hybridization.
• For example:
  • Why does O₂ interact with a magnetic field?
  • Why are some molecules colored?
• For these molecules, we use molecular orbital theory.
• Just as electrons in atoms are found in atomic orbitals, electrons in molecules are found in molecular
  orbitals (MO).
• 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 H₂:
  • 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 ($\sigma_{1s}$) and ending when all electrons have been accommodated.
• Note that electrons in MOs have opposite spins.

**Bond Order**
• Define bond order $= \frac{1}{2}$ (bonding electrons – antibonding electrons).
  • Bond order = 1 for single bond.
  • Bond order = 2 for double bond.
  • Bond order = 3 for 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:
    \[ \frac{1}{2} \text{ (bonding electrons - antibonding electrons)} = \frac{1}{2} (2 - 0) = 1. \]
  • 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:
    \[ \frac{1}{2} \text{ (bonding electrons - antibonding electrons)} = \frac{1}{2} (2 - 2) = 0. \]
  • 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 Period 2 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., 1$s$ + 1$s$ rather than 1$s$ + 2$s$).
  • 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 1$s$ orbital combines with another 1$s$ orbital to give one $\sigma_{1s}$ and one $\sigma^*_{1s}$ orbital, both of which are occupied (since Li and Be have 1$s^2$ electron configurations).
• Each 2$s$ orbital combines with another 2$s$ orbital to give one $\sigma_{2s}$ and one $\sigma^*_{2s}$ orbital.
• The energies of the 1$s$ and 2$s$ orbitals are sufficiently different so that there is no cross mixing of orbitals (i.e., we do not get 1$s$ + 2$s$).
• Consider the bonding in Li$_2$.
  • There are a total of six electrons in Li$_2$.
    • 2 electrons in $\sigma_{1s}$.
    • 2 electrons in $\sigma^*_{1s}$.
    • 2 electrons in $\sigma_{2s}$.
    • 0 electrons in $\sigma^*_{2s}$.
    • Therefore the bond order is $\frac{1}{2} (4 - 2) = 1$.
• Since the 1$s$ AOs are completely filled, the $\sigma_{1s}$ and $\sigma^*_{1s}$ are filled.
• We generally ignore core electrons in MO diagrams.
• Core electrons usually don’t contribute significantly to bonding in molecule formation.
• Consider bonding in Be$_2$.
  • There are a total of eight electrons in Be$_2$.
    • 2 electrons in $\sigma_{1s}$.
    • 2 electrons in $\sigma^*_{1s}$.
    • 2 electrons in $\sigma_{2s}$.
• 2 electrons in \( \sigma^*_{2s} \).
• Therefore the bond order is \( \frac{1}{2} (4 - 4) = 0 \).
• \( \text{Be}_2 \) 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., \( \sigma \) type orbital).
  • Sideways, so that the resulting MO has electron density above and below the axis between nuclei.
• These are called **pi (\( \pi \)) molecular orbitals**.
• The six \( p \)-orbitals (two sets of three) must give rise to six MOs:
  • \( \sigma_{2p}, \sigma^*_{2p}, \pi_{2p}, \pi^*_{2p}, \pi_{2p} \) and \( \pi^*_{2p} \).
• Therefore, there are a maximum of two \( \pi \) 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:
  • \( 2s \) orbitals are lower in energy than \( 2p \) orbitals so both \( \sigma_{2s} \) orbitals (\( \sigma_{2s} \) and \( \sigma^*_{2s} \)) are lower in energy than the lowest energy MO derived from the \( 2p \) AOs.
  • There is greater overlap between \( 2p \) orbitals.
    • They point directly towards one another, so the \( \sigma_{2p} \) MO is lower in energy than the \( \pi_{2p} \) orbitals.
    • The \( \sigma^*_{2p} \) MO is higher in energy than the \( \pi^*_{2p} \) orbitals.
  • The \( \pi_{2p} \) and \( \pi^*_{2p} \) 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 \( \sigma_{2s} \) MO lowers and the \( \sigma_{2p} \) MO increases in energy.
    • For \( \text{B}_2 \), \( \text{C}_2 \) and \( \text{N}_2 \) the \( \sigma_{2p} \) orbital is higher in energy than the \( \pi_{2p} \).
    • For \( \text{O}_2 \), \( \text{F}_2 \) and \( \text{Ne}_2 \) the \( \sigma_{2p} \) orbital is lower in energy than the \( \pi_{2p} \).
  • 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 and bond energy increases.

**Electron Configurations and Molecular Properties**

• Two types of magnetic behavior:
  • **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, \( \text{O}_2 \) is paramagnetic, has a short bond length (1.21 Å) and high bond dissociation energy (495 kJ/mol).
  • The Lewis structure for \( \text{O}_2 \) shows no unpaired electrons.
  • The MO diagram for \( \text{O}_2 \) shows 2 unpaired electrons in the \( \pi^*_{2p} \) orbital.
  • This suggests a double bond.
  • The MO diagram for \( \text{O}_2 \) predicts both paramagnetism and the double bond (bond order = 2).

**Heteronuclear Diatomic Molecules**

• Heteronuclear diatomic molecules contain 2 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.

Selected Problems: 19, 20, 21, 27, 28, 31, 33, 35, 36, 43, 44, 46, 51, 55, 56, 61, 66, 69, 70, 74, 78, 81, 83.