Chapter 9. Molecular Geometry and Bonding Theories

PART I

Molecular Shapes
- <mark>Lewis structures give atomic connectivity</mark>: they tell us which atoms are physically connected to which atoms.
- The <mark>shape of a molecule is determined by its **bond angles**</mark>.
  - The angles made by the lines joining the nuclei of the atoms in a molecule are the bond angles.
- Consider SO4 2-

The VSEPR Model
- A covalent bond forms between two atoms <mark>when a pair of electrons occupies the space</mark> 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.

- <mark>VSEPR predicts that the best arrangement of electron domains is the one that minimizes the repulsions among them.</mark>
  - 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)
    octahedral (six domains).

SEE SLIDES

- 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.

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 11 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

Shapes of Larger Molecules

- In methanol, CH_3CH_2OH, 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 tetrahedral.
  - The geometry around the O is bent (tetrahedral).

PART II

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?

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 - An incomplete, but useful story!
- 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 predict 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 orbitals 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.

Examples

H_2O, SF_6

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:

CO_2, Carbonate – talk about resonance

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.

PART III

Molecular Orbitals   - the real story.   This is why we use SPARTAN

- Some aspects of bonding are not explained by Lewis structures, VSEPR theory, and hybridization.

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, O_2 is paramagnetic.
  - The Lewis structure for O_2 shows no unpaired electrons.
  - The MO diagram for O_2 shows 2 unpaired electrons in the π^*_{2p} 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.
  - For example:
    - Why does O_2 interact with a magnetic field?

<mark>**DEMO** Oxygen Demo</mark>

- 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) MO**s 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
- Define **bond order** = ½ (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:
    - ½ (bonding electrons - antibonding electrons) = ½ (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:
    - ½ (bonding electrons - antibonding electrons) = ½ (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!

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 Li₂ and Be₂
- Each $1s$ orbital combines with another $1s$ orbital to give one σ_{1s} and one σ^*_{1s} orbital, both of which are occupied (since Li and Be have $1s^2$ electron configurations).
- Each $2s$ orbital combines with another $2s$ orbital two give one σ_{2s} and one σ^*_{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.
    - 2 electrons in σ_{1s}.
    - 2 electrons in σ^*_{1s}.
    - 2 electrons in σ_{2s}.
    - 0 electrons in σ^*_{2s}.

- Therefore the bond order is $\frac{1}{2}(4-2) = 1$.
- Since the $1s$ AOs are completely filled, the σ_{1s} *and* σ^*_{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 σ_{1s}.
    - 2 electrons in σ^*_{1s}.
    - 2 electrons in σ_{2s}.
    - 2 electrons in σ^*_{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., σ type orbital).
  - Sideways, so that the resulting MO has electron density above and below the axis between nuclei.
    - These are called **pi (π) molecular orbitals**.
- The six p-orbitals (two sets of three) must give rise to six MOs:
  - σ_{2p}, σ_{2p}^*, π_{2p}, π_{2p}^*, π_{2p} and π_{2p}^*.
  - Therefore there are a maximum of two π bonds which can come from p orbitals.
  - The relative energies of these six orbitals can change.

Electron Configurations for B₂ through Ne₂

- Features of the energy-level diagrams for these elements:
  - $2s$ Orbitals are lower in energy than $2p$ orbitals so both σ_{2s} orbitals (σ_{2s} and σ^*_{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 σ_{2p} MO is lower in energy than the π_{2p} orbitals.
    - The σ^*_{2p} MO is higher in energy than the π^*_{2p} orbitals.
  - The π_{2p} and π^*_{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} MO lowers in energy and the σ_{2p} orbital increases in energy.
    - For B_2, C_2 and N_2 the σ_{2p} orbital is higher in energy than the π_{2p}.
    - For O_2, F_2 and Ne_2 the σ_{2p} orbital is lower in energy than the π_{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.
  - bond energy increases.

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.
    - Paramagnetism will be revisited in Ch. 23 (section 23.8) for materials containing transition