Chapter 2
Molecular Structure and Bonding

Read the section on Lewis dot structures, we will not cover this in class. If you have problems, see me or seek out a general chemistry text. Things of which you should know/be aware

- How to determine the Lewis structure (this only deals with atom connectivity—does NOT tell you the three dimensional shape...you need VSEPR for that)
- Resonance considerations
  - resonance averages bond characteristics (length, strength, order)
  - the energy of a resonance hybrid is lower than that of any single contributing structure
  - molecules or ions do not resonate!
- Formal charge: calculated by

\[ FC = (# \text{ of valence } e^-) - (# \text{ of bonds}) - (# \text{ of } e^- \text{ as lone pairs or radicals}) \]

**Bond lengths**

**Covalent radius:** \((r_{\text{cov}})\) contribution of an atom in a covalent bond. Orbitals must overlap!

**van der Waals radius:** \((r_v)\) size of atoms determined by the distance of nearby atoms in adjacent molecules, but not bonded with that molecule (\(\square\))
**VSEPR theory**

A systematic way of determining the **shape** of a molecule by noting the number of regions of electron density around a central atom.

<table>
<thead>
<tr>
<th>regions of e⁻ density</th>
<th>electronic shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>7</td>
<td>pentagonal bipyramidal</td>
</tr>
<tr>
<td>8</td>
<td>square antiprism</td>
</tr>
</tbody>
</table>

Molecular shapes are based only on the position of atoms.

**EX.** PCl₅  

![Diagram of PCl₅ molecule]

**EX.** SF₄  

![Diagram of SF₄ molecule]
Valence Bond Theory

Considers the interaction of separate atoms brought together as they form a molecule.

EX. Simplest case is H₂

EX. More complex case: O₂

Diamagnetic vs. paramagnetic species

**Diamagnetic**: a material repelled by a magnetic field (why?)

**Paramagnetic**: a material attracted to a magnetic field (why?)

Rationalization of Valence Bond and VSEPR

There are some problems with these theories
1. Bond angles don't match expectation
   EX. H₂O

2. Number of bonds formed doesn't always match prediction
   EX. Carbon
3. Bond strength and length is not always predicted accurately
EX. Carbon (with promotion)

**Molecular Orbital Theory**
- A way of describing the bonding characteristics of a molecule
- Instead of electrons being localized in atomic orbitals, molecular-sized orbitals (orbitals covering the entire molecule) are involved

To have an MO, the interactions between orbitals must have:
- compatible symmetry
- efficient overlap (i.e., be of similar size)
- orbitals relatively close in energy

**Types of Orbitals**
1. **Bonding orbitals** (Ψₜ)
   - positive overlap of atomic orbitals (AO)
   - when filled with electrons, the energy of the molecule is lowered relative to that of the separated atoms

2. **Antibonding orbitals** (Ψₑ)
   - when filled with electrons, the energy of the molecule is raised relative to that of the separated atoms
   - antibonding orbitals are more destabilizing than a bonding orbital is stabilizing

3. **Nonbonding orbitals** (Ψₙ)
   - generally are not involved in bonding and are usually localized on a particular atom
   - often occurs because no atomic orbitals of the correct symmetry can overlap
**Further orbital distinctions**

**σ-orbital**
- formed from head-to-head overlap of orbitals  
- will have cylindrical symmetry

**π-orbital**
- formed **most commonly** from the sideways overlap of p-orbitals (but other overlaps are possible)  
- will have a nodal plane

**δ-orbital**
- formed from the sideways overlap of d-orbitals  
- will have 2 nodal planes

MO diagram for $H_2$

**Bond order:** this is equivalent to a “single”, “double”, “triple”, etc. bond in VB theory.

$$BO = \frac{\text{# of bonding } e^- - \text{# of antibonding } e^-}{2}$$
Rules for diatomic molecules
1. Using \( n \) AO's, you will create \( n \) MO's
2. For period 2 elements there are 4 \( \sigma \) and 4 \( \pi \) orbitals
   - The \( \pi \) orbitals form 1 doubly degenerate pair of bonding orbitals and 1 doubly degenerate pair of antibonding orbitals
3. If the orbital has a center of inversion designate with a \( g \) (gerade, even) or \( u \) (ungerade, odd)
4. To determine the actual energies of the orbitals, experimental evidence must be given (rigorous computation may get you close, but it should be confirmed with photoelectron or electron absorption spectroscopies)

MO for \( \text{Li}_2 \) through \( \text{N}_2 \)
Figure 2.9 lists the energy levels of \( \text{Li}_2 \rightarrow \text{F}_2 \). Note the transition between \( \text{N}_2 \) and \( \text{O}_2 \). Note that orbital energies get lower with an increase in electronegativity.

MO of \( \text{N}_2 \) with the corresponding photoelectron (ionization) spectrum.

BO for \( \text{N}_2 \)?
**Aufbau Principle for Molecules**
Follows the same principles as for atoms
- lower energy orbitals fill first
- obey Hund's rule
- obey the Pauli exclusion principle

What is the electron configuration of:
Li₂?

Be₂?

B₂?

F₂?

Important distinctions of orbitals
HOMO: highest occupied molecular orbital

LUMO: lowest unoccupied molecular orbital

SOMO: singly occupied MO

**Electronegativity**
Symbolized with the Greek letter chi, $\chi$
Represents the ability of an atom in a molecule to attract electrons to itself

The most electronegative element?

The least electronegative element? (most electropositive)

Trends in the periodic table?
- Down a group?

- Across a period?
Three scales used:
Pauling ($\chi^p$)
  - Most commonly used
  - Assigned a value of 4.00 for F and scaled others
  - $(\chi_A - \chi_B) = 0.102(\sqrt{\Delta})$
  \[ \Delta = \text{the difference in bond energy between A-B and the arithmetic mean of A-A and B-B bond energies} \]

EX. Calculate the Pauling electronegativity of hydrogen based on the following bond energies
H-H = 436 kJ/mol
F-F = 158 kJ/mol
H-F = 566 kJ/mol

Mulliken ($\chi^M$)
Based on ionization energy and electron affinity
If an element has a high ionization energy AND a high electron affinity, the element will be electronegative.
\[ \chi^M = \frac{\text{IE}_1 + \text{EA}_1}{2} \]

Allred-Rochow ($\chi^{AR}$)
Dependent on the $Z_{\text{eff}}$ and radius
High $Z_{\text{eff}}$ and small size leads to high electronegativity
Constants chosen to give values close to $\chi^p$
\[ \chi^{AR} = \left(3590 \times \frac{Z_{\text{eff}}}{r_{\text{cov}}^2}\right) + 0.744 \]
Dipole Moments

If two atoms have different electronegativities, the bond between them will be polar. Does it follow, then, that any time there is a difference in electronegativity between bonded atoms, that the molecule as a whole will be polar?

Take a look at these structures and determine which are polar: If polar, what is the direction of the net dipole moment?

![Structures](image)

A dipole moment can be calculated by: 
\[ \mu = q \times e \times d \]
where: 
- \( \mu \) = dipole moment in debyes (D)
- \( q \) = charge distribution (no units)
- \( e \) = charge on an electron (coulombs, C)
- \( d \) = distance between charges (m)

1 D (debye unit) = \( 3.336 \times 10^{-30} \) C\( \cdot \)m
1 e = \( 1.60217733 \times 10^{-19} \) C

EX. Determine the charge distribution for HF, given that the bond length is 108 pm (see values in Appendix 6 of your book) and the dipole moment is 1.83 D.

Heteronuclear diatomic molecules

Since 2 different atoms, electronegativities will differ
- The more electronegative atom will “contribute” more to the bonding MO
- The less electronegative atoms will “contribute” more to the antibonding MO

Caveat: this assumption may not always give the correct answer if antibonding orbitals are occupied, particularly for heteronuclear species.
When making an MO diagram, as the energy of two atomic orbitals gets farther apart, there is not as much separation in MO energy levels

**Bonding in HF**
Electron configuration of H?
Electron configuration of F?

EX. Bond order for CO?
Electron configuration of C? of O?