Chapter 3 - Covalent Bonding

3.0 - Introduction

- Models 360 a great site for exploring molecular structure and molecular orbitals. We will use it extensively in this chapter. (web)

- The cube model for the octet rule. No longer used, but introduced the idea of sharing electrons. Figure 3.1

3.1 Models of Covalent Bonding

- Two main ways of approximating bonding:
  - Valence Bond or Hybridization Theory
  - Molecular Orbital Theory

- Molecular orbital theory will be emphasized. Orbitals over the entire molecule.

- MO is the best theory, but calculations are difficult for larger species.

- Lewis structure of dioxygen O₂ showing all paired electrons and a double bond. Figure 3.2

- Lewis structure of O₂ with a single bond and two unpaired electrons. This agrees with the paramagnetic nature of O₂ Figure 3.3
Molecular orbitals incorporate both the double bond and the paramagnetism of dioxygen.

3.2 - Introduction to Molecular Orbitals

- Linear combination of Atomic Orbitals (LCAO) will be used to form Molecular orbitals.

- Molecular Orbitals are formed by combining atomic orbitals from two or more atoms in a molecule.

- Important ideas concerning molecular orbitals:
  - If the overlapping lobes are of the same sign there is reinforcement of electron density.
  - **Example of a bonding, reinforcing overlap**
  - If the overlapping lobes are of opposite sign there is constructive interference removing electron density.
  - **Example of a antibonding, interfering overlap**
  - Strong bonds are only formed if there is good overlap between orbitals in space.
  - If two atomic orbitals mix a lower energy bonding orbital and a higher energy antibonding orbital will form.
  - If more than two orbitals mix, the result is more complicated, but the number of atomic orbital in = the number of molecular orbitals out.
  - Significant mixing occurs only if the orbitals are of similar energy.
- The Pauli principle holds. Each orbital may hold at most two electrons and their spins must be paired.

- The electron configuration of a molecule fills the orbitals from lower to higher energy in sequence.

- Hund's rule applies for a set of orbitals of the same energy. All orbitals are half filled before the electrons are paired.

- Bond order is one half the number of bonding electrons minus the antibonding electrons.

- *For orbitals to mix they must have the same symmetry. (*Not covered in detail in this class.)

- The most important orbitals for reactivity are the frontier orbitals (HOMO and LUMO).
  - Highest occupied molecular orbital (HOMO) (-) interacts with electrophiles.
  - Lowest unoccupied molecular orbital (LUMO) interacts with nucleophiles.

3.3 - Molecular Orbitals from Period 1 Diatomic Molecules

- Formation of molecular orbitals from two s orbitals Figure 3.4

- Molecular orbital energies as a function of the separation between nuclei. Figure 3.5

- The Orbitron a site that has videos of the formations of molecular orbitals (web)
- Period 1 diatomics use only 1s orbitals as was shown in figure 3.4
- MO diagram of $\text{H}_2^+$ electron configuration is $(\sigma_{1s})^1$ (Text Figure 3.6)
- MO diagram of $\text{H}_2$ electron configuration is $(\sigma_{1s})^2$ (Text Figure 3.7)
- MO diagram of $\text{He}_2^+$ electron configuration is $(\sigma_{1s})^2 (\sigma^*_{1s})^1$ (Text Figure 3.8)
- MO diagram of $\text{He}_2$ electron configuration is $(\sigma_{1s})^2 (\sigma^*_{1s})^2$ (Text Figure 3.9)

<table>
<thead>
<tr>
<th>Species</th>
<th>Bonding Electrons</th>
<th>Antibonding Electrons</th>
<th>Bond Order</th>
<th>Bond Length (pm)</th>
<th>Bond Energies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2^+$</td>
<td>1</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>106</td>
<td>255</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>74</td>
<td>436</td>
</tr>
<tr>
<td>$\text{He}_2^+$</td>
<td>2</td>
<td>1</td>
<td>$\frac{1}{2}$</td>
<td>108</td>
<td>251</td>
</tr>
<tr>
<td>$\text{He}_2$</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.4 - Molecular Orbitals from Period 2 Diatomic Molecules

- For period 2 diatomics we need only consider the 2s and 2p electrons.
- The 1s electrons are core electrons and are buried within the atom and do not interact strongly.

**1s and 2s orbital comparison**

- MO diagram of Li₂ electron configuration is \((\sigma_{2s})^1\) ([Text Figure 3.10](#))

- Be₂ has a bond order of 0 analogous to He₂

- Period 2 introduces p orbitals which can overlap in two geometrically different ways.
  - An end to end overlap produces \(\sigma_{2p}\) and \(\sigma^{*}_{2p}\) orbitals ([Text Figure 3.11](#))
  - \(\sigma\) symmetry means cylindrical symmetry: The orbital has a rotation axis along the bond.
  - An side to side overlap produces \(\pi_{2p}\) and \(\pi^{*}_{2p}\) orbitals ([Text Figure 3.12](#))
  - \(\pi\) symmetry means a nodal plane along the bond. Rotating the orbital 180° along the bond changes the sign from (+) to (-) and *vice versa*.

- **Properties of 2nd row diatomics. ([Text page 48, Table 3.1](#))**

- Typical bond energies for second row diatomics

  - Single Bonds \(200-300 \text{ kJ/mol}\)
  - Double Bonds \(500-600 \text{ kJ/mol}\)
  - Triple Bonds \(900- \text{ kJ/mol}\)
• For the next three diagrams from the text, the filled \((\sigma_{1s})^2 (\sigma^*_{1s})^2, (\sigma_{2s})^2, \) and \((\sigma^*_{2s})^2\) electrons are not shown.

• MO diagram of \(\text{O}_2\).

(Text Figure 3.13)
Electron configuration is \((\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^2\).
Bond order is \(\frac{1}{2}(8-4) = 2\)

• MO diagram of \(\text{F}_2\)

(Text Figure 3.14)
Electron configuration is \((\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^4\).
Bond order is \(\frac{1}{2}(8-6) = 1\)

• \(\text{F}_2\) at molecules 360 (web) (an example of no s-p mixing)

• For \(\text{O}\) and \(\text{F}\), the \(2s\) and \(2p\) orbitals are widely separated in energy and do not interact.

• s and p mixing
  o For earlier elements in the second row, the \(2s\) and \(2p\) orbitals are close in energy and can interact.
  o For \(\text{Li}_2\), \(\text{Be}_2\), \(\text{B}_2\), \(\text{C}_2\), and \(\text{N}_2\) the s and p orbitals mix when forming molecular orbitals.
  o The \((\sigma_{2s})\) and the \((\sigma_{2p})\) both have the same symmetry so they can mix raising the \(2p\) derived orbital and lowering \(2s\) derived orbital.
  o The \((\sigma^*_{2s})\) and the \((\sigma^*_{2p})\) both have the same symmetry so they can mix raising the \(2p\) derived orbital and lowering \(2s\) derived orbital.
This mixing pushes up the energy of the \((\sigma_{2p})\) orbital until it is higher than the \((\pi_{2p})\) orbital.

- MO diagram of \(N_2\)
  
  \(\text{Electro Configuration is } (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2\)
  Bond order is \(1/2(8-2) = 3\)

- \(N_2\) at molecules 360 (web) (an example of s-p mixing)

3.5 - Molecular Orbitals for Heteronuclear Diatomics

- Diatomic heteronuclear molecular orbital formation must take into account the differing energies of the two atoms.

- The bonding orbitals will have more character of the orbital from the more electronegative atom which has lower energy atomic orbitals.

- The antibonding orbitals will have more character of the less electronegative atom which has higher energy atomic orbitals.

- Molecular orbitals of carbon monoxide, CO. There is s-p mixing. Notice the two orbitals labeled "NB" these are non-bonding, they contribute little to the bonding. \(\text{Figure 3.16}\)

- \(\text{CO at molecules 360 (web)}\)

- Molecular orbital diagram for H-Cl. The H 1s orbital is closest in energy to the Cl 2p orbitals. \(\text{Figure 3.17}\)
• Molecular orbital diagrams for more complicated molecules are beyond the scope of this class. We will use the simpler valence bond approach for more complicated molecules.

3.6 - A Brief Review of Lewis Structures

• Rules for Lewis structures are listed on page 52. I will teach this from my handout.
  o [Handout on Lewis structure, VSEPR, and Polarity. (Note: 5 effective electron pairs should be trigonal bipyramidal]
  o [VSEPR Table]

• Lewis structure for HCl
  [Figure 3.18]

• Lewis structure for CO
  [Figure 3.19]

• Lewis structure for NF₃
  [Figure 3.20]

• An example of a structure that exceeds the octet rule, PF₅
  [Figure 3.21]

3.7 - Partial Bond Order
• Resonance occurs when more than one valid Lewis structure may be drawn that differ only in the arrangement of electrons.

• Resonance delocalizes electrons and lowers the energy.

• Lewis structure for NO$_3^-$
  Figure 3.22

• Resonance structures for NO$_3^-$
  Figure 3.23

• Representation of the partial bond in nitrate. Average bond = (2+1+1)/3 = 1 and 1/3 bond.
  Figure 3.24

3.8 - Formal Charges

• Formal charge is the difference between the number of electrons assigned to an atom and the number of valence electrons.

• All lone pair electrons are assigned to the atom they are on. Bond pair electrons are split between the bonded atoms.

• Resonance structure for dinitrogen oxide, N$_2$O (nitrous oxide). Figure 3.25

• Assignment of formal charge for N$_2$O resonance structures. Structure (c) is unreasonable (too many charges). Structures (a) and (b) have the same number of formal charges, but (b) is best because it puts (-) charge on the more electronegative atom. Figure 3.26
• The partial bond order using the two most reasonable resonance structures Figure 3.27

3.9 - Valence Shell Electron Pair Repulsion Rules

• VSEPR chart

• VSEPR assumes that the electron pairs either lone pairs or any bond type (single, double, or triple) try to minimize electron-electron repulsions.

• The number of positions around the central atom go by several names:
  o Effective electron pairs
  o Steric number
  o Bonding directions
  o Coordination number

• The most common structures have between 2 and 6 bonding directions.
  o Linear (2)
    • Shape of BeCl₂ Figure 3.28

• Shape of CO₂ Figure 3.29

  o Trigonal Planar (3)
    • Shape of BCl₃ Figure 3.30
    • Shape of NO₂⁻ Figure 3.31
- Comparison of bond angles for NO$_2^+$, NO$_2$, and NO$_2^-$ **Figure 3.32**

- Molecules with trigonal planar arrangement of lone pairs and bonds **Table 3.2**
  - Tetrahedral (4)
    - Shape of CH$_4$ **Figure 3.33**
    - Shape of NH$_3$ **Figure 3.34**
    - Shape of H$_2$O **Figure 3.35**
    - Molecules with tetrahedral arrangement of lone pairs and bonds **Table 3.3**
  - Trigonal Bipyramidal (5)
    - Shape of PF$_5$ **Figure 3.36**
    - Possible geometries for SF$_4$ **Figure 3.37**
    - Actual structure SF$_4$ **Figure 3.38**
    - Shape of BF$_3$ **Figure 3.39**
    - Shape of XeF$_2$ **Figure 3.40**
    - Molecules with trigonal bipyramidal arrangement of lone pairs and bonds **Table 3.4**
  - Octahedral (6)
    - Shape of SF$_6$ **Figure 3.41**
    - Shape of IF$_5$ **Figure 3.42**
    - Shape of XeF$_4$ **Figure 3.43**
    - Molecules with octahedral arrangement of lone pairs and bonds **Table 3.5**
  - Greater than six bonding directions
    - Some examples with more than six bonding directions.
    - Geometry of UF$_7^2-$, NbF$_7^2-$, and XeF$_6$ **Figure 3.44**
3.10 - Valence Bond Concept

- Valence Bond principles
  - Bonds are formed by pairing of electrons from neighboring atoms.
  - Spins of the two atoms in the bond are antiparallel.
  - Excitation of electrons may be necessary to provide unpaired electrons = hybridization.
  - Shapes are determined by the geometry of the hybrids on the central atom.

- Example of a hybrid orbital Figure 3.45

- Table of hybrid orbitals Table 3.6

- sp\(^2\) hybrid formation in BF\(_3\) Figure 3.46

- sp hybrid formation in CO Figure 3.47

3.11 - Network Covalent Substances

- Examples of several network covalent structures
  - Structure of diamond (tetrahedral carbons) Figure 3.48
  - Diamond and graphite (trigonal planar carbons) crystal structures (from farm4.static.flickr.com)
  - Diamond structure at Models 360 (click the menu Crystal structures of the elements)
Graphite structure at Models 360 (click the menu Crystal structures of the elements)

Quartz crystal structure (tetrahedral SiO$_4$ units)

Boron crystal structure

3.12 - Intermolecular Forces

- Types of intermolecular forces
  - Non polar molecules - London dispersion or van der Waals forces
    - Instantaneous dipole formation Figure 3.49
    - The London dispersion forces. Figure 3.50
    - For structures of a similar type, London dispersion forces increase with the number of electrons.
    - Shape can also affect London forces.
      - SF$_6$ - 70 electrons, nearly spherical - Boiling Point -51°C
      - $n$-decane, CH$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ - 72 electrons, long thin shape - Boiling Point -30°C
      - boiling point of noble gases
      - Halogen diatomic boiling and melting points
      - Boiling points of group 14 hydrides Figure 3.51

- Polar molecules - dipole dipole interactions
  - Electronegativity scale Figure 3.52
• Reminder: trend in electronegativity Trend in Electronegativity

• Polar molecule showing the dipole, HCl Figure 3.53
• Nonpolar molecule showing how bond vector cancel, CO₂ Figure 3.54
• Boiling points of Group 17 hydrides. HF has hydrogen bonding Figure 3.55
• Sometimes there is a balance of dipole-dipole forces and dispersion forces to consider: HCl versus HBr (higher boiling point?) Table 3.7

  o Polar molecules with F-H, N-H, O-H, and sometimes other bonds - Hydrogen bonding
    ▪ Hydrogen bonds are of the form D-H------A (D is hydrogen bond donor, and A is the hydrogen bond acceptor.
    ▪ boiling point of hydrides

3.13 - Molecular Symmetry

  • SKIP THIS SECTION (Take Advanced Inorganic Chemistry to learn about symmetry)

3.14 - Symmetry and Vibrational Spectroscopy

  • SKIP THIS SECTION

3.15- Covalent bonding and the Periodic Table
- This chapter emphasized covalent compounds of non-metals
- Other types of bonding - ionic or metallic
- Some metals use covalent bonding $\text{MnO}_4^-$