Chapter 9

Chapter 9
Molecular Geometry and Bonding Theories

- Why were these substances selected for the photo?
- What does this have to do with properties of molecules? Which property?

Shapes and Sizes of Molecules

- Chemical basis of odor
- Chemical basis of taste
- Chemical basis of vision: 11-cis-retinal → 11-trans-retinal
- Double-helical structure of DNA
- Explains solubility of substances
- Explains melting and boiling points
- Responsible for molecular interactions

9.1 Molecular Shapes

- CO₂ is linear, SO₂ is bent. Why are they different?
- The shape of a molecule is determined by its bond angles, the angles made by lines connecting the nuclei of the atoms in a molecule.
- The bond angle in CO₂ is 180°; the bond angle in SO₂ is 120°.
- How can we predict the shape of a molecule?
- Examine the shapes of collections of objects with a common center: plastic eggs or rubber balls or acorns. Why do they have these shapes?

Repulsions of Atoms

- Pairs of electrons, being negatively charged, repel one another just like the objects just examined.

9.2 The VSEPR Model

- Valence-Shell Electron-Pair Repulsion
- Electron pairs (or groups of pairs) try to avoid one another because of repulsions between like-charged particles
- Regions where electrons are likely to be found will be called electron domains.
- A double or triple bond comprises a single electron domain.
- Electron domains occur as far apart as possible

VSEPR Theory

- Can predict the angles between electron domains, whether bonding or nonbonding (unshared):
  - 2 domains - linear (180°)
  - 3 domains - trigonal planar (120°)
  - 4 domains - tetrahedral (109.5°)
  - 5 domains - trigonal bipyramidal (90° & 120°)
  - 6 domains - octahedral (90°)
- Examine the shapes of some simple ABₙ molecules
Electron domains can be occupied by atoms (bonding electron pairs) or by a nonbonding pair of electrons, giving various structures.

Water has a tetrahedral arrangement of electron pairs, but a bent arrangement of atoms.

**Electron-Domain Geometry**
This is not the same as molecular geometry!

**Molecular Geometry**
- Molecular geometry describes the shape of only those electron domains that contain bonding electrons.
- Molecular geometry is predicted by writing a Lewis structure, then determining the electron-domain geometry, and finally determining the molecular geometry.

**Molecular Shapes**
- Why do CO₂ and SO₂ have different shapes?
- What are the structures of the following molecules and ions?
  
<table>
<thead>
<tr>
<th>BeF₂(g)</th>
<th>CO₂</th>
<th>HCN</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₂</td>
<td>SO₂</td>
<td>NO₂⁻</td>
<td>SF₂</td>
</tr>
<tr>
<td>BH₃</td>
<td>SO₃</td>
<td>NH₃</td>
<td>ClF₃</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>SiH₄</td>
<td>SF₄</td>
<td>XeF₄</td>
</tr>
<tr>
<td>PF₅</td>
<td>IF₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF₆</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Examine molecular models using Rasmol or Netscape/Rasmol

**Possible Shapes**
- AB linear
- AB₂ linear, bent
- AB₃ trigonal planar, trigonal pyramidal, T-shaped
- AB₄ tetrahedral, see-saw (distorted tetrahedral), square planar
- AB₅ trigonal bipyramidal, square pyramidal
- AB₆ octahedral

**The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles**
- By experiment, the H-X-H bond angle decreases on moving from C to N to O.
- Since electrons in a bond are attracted by two nuclei, they do not repel as much as
lone pairs.
• Therefore, the bond angle decreases as the number of lone pairs increase.
• Similarly, electrons in multiple bonds repel more than electrons in single bonds.

**Molecules with More than One Central Atom**
• In acetic acid, CH₂COOH, there are three central atoms.
• We assign the geometry about each central atom separately.

### 9.3 Polarity of Polyatomic Molecules

• Bonds can be polar if electrons are shared unequally.
• If molecules are polar, they have a separation of positive and negative charge within the molecule, and they exhibit a dipole moment, which is the product of the charge and the distance between centers of positive and negative charge.

**Polar Bonds**
• For diatomic molecules, the bond is more polar (greater dipole moment), the greater the difference in electronegativity between the two atoms.
• \( \delta^+ \delta^- \)
  \( \text{H} : \text{F} \)
  +-----\> Polarity is in the direction of the bond.
• Are molecules polar if they have polar bonds?
• Yes, if they are diatomic.
• Maybe, if they are polyatomic. Bond polarity of two or more bonds can cancel one another.
• \( \delta^- \delta^+ \delta^- \)
  \( \text{Cl} : \text{Be} : \text{Cl} \)
  <-----+ +----->

**Polarity of Molecules**
• Can a molecule be polar if its bonds are all nonpolar?
• What structures will give rise to nonpolarity even when bonds are polar?
• Any completely symmetrical molecule (a symmetrical structure with identical outside atoms) is always nonpolar.
• Many properties of molecules depend on whether they are polar or nonpolar.
• Which of these molecules is polar?
  - H₂O
  - CCl₄
  - CO₂
  - SF₂
  - XeF₂
  - PCl₃
  - CH₄
  - CH₂Cl₂
  - SO₂
  - SF₄
  - SF₆

### 9.4 Covalent Bonding and Orbital Overlap

• Lewis structures and VSEPR give information in the shape of molecules and the distribution of electrons. They don’t explain why a bond forms.
• Valence-bond theory considers both bond formation and molecular shape.
How are electrons donated to be shared in a covalent bond?

- VB theory is based on quantum theory, so it considers the atomic orbitals occupied by the outermost electrons - the valence orbitals.
- Formation of a covalent bond from s + s or s + p orbitals to give a sigma (σ) bond
- A covalent bond is formed by the overlap of two half-filled valence shell orbitals.

Energy Minimization

- The bonded atoms are stable at a bond length that leads to minimization of the potential energy.
- Formation of a covalent bond from p + p orbitals to give a sigma (σ) bond
  \[ F + F \rightarrow F:F \]
- End-to-end overlap of p orbitals gives a sigma bond, with a high probability of finding the electrons between the bonded atoms.

9.5 Hybrid Orbitals

Shortcomings of VB Theory

- Valence-bond theory works well for any diatomic molecule.
- There are some problems for polyatomic molecules:
  - Must unpair electrons in some cases, to form all the bonds.
  - Equivalent bonds are predicted to be different.
  - Measured bond angles are different from predicted bond angles.

Some incorrect predictions

- Wrong bond angles predicted for water and ammonia

Hybridization

- The presence of 2 nuclei changes the behavior of electrons in atoms, so the orbitals in molecules should be expected to be different from those in atoms.
- We make orbitals equivalent in energy and position by combining or mixing the orbitals to make new orbitals, called hybrid orbitals.

sp Hybridization

- We can obtain new orbitals by allowing the 2s and one 2p orbital to mix or form hybrid orbitals (process called hybridization).
- The hybrid orbitals comes from an s and a p orbital and are called sp hybrid orbitals.

sp² Hybridization

- Important: when we mix n atomic orbitals we must get n hybrid orbitals.
- sp² hybrid orbitals are formed with one s and two p orbitals (leaving one unhybridized p orbital).
- The large lobes of sp² hybrids lie in a trigonal plane.
- All molecules with trigonal planar electron pair geometries have sp² orbitals on the central atom.
Hybridization for Boron

- $s + p + p \rightarrow$ three $sp^2$ orbitals, which can overlap with a $p$ orbital on each Cl atom.

$sp^3$ Hybridization

- $sp^3$ Hybrid orbitals are formed from 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 $109.5^\circ$.
- All molecules with tetrahedral electron pair geometries are $sp^3$ hybridized.

Hybridization for Carbon

- C $2s^2 \ 2p^1 \ 2p^1 \ 2p^0 \rightarrow$ C $2s^1 \ 2p^1 \ 2p^1 \ 2p^1$ $\rightarrow$ C $(sp^3)^1 \ (sp^3)^1 \ (sp^3)^1 \ (sp^3)^1$
- Now we can form four equivalent bonds at the correct tetrahedral angles.
- C $(sp^3)^1 \ (sp^3)^1 \ (sp^3)^1 \ (sp^3)^1 + 4$ H $1s^1 \rightarrow$ CH$_4$ with four $\sigma$ bonds formed by overlap of $sp^3$ and $1s$ orbitals.

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 $sp^3d$ hybridization.
- Octahedral electron pair geometries require $sp^3d^2$ hybridization.

Geometry and Hybrid Orbitals

- Use hybrid orbitals for the sigma bonding and unshared electrons.
- What orbitals are used in methane, water, and ammonia?
- What bond angles?

9.6 Multiple Bonds

- In the covalent bonds considered so far, the electron density is concentrated symmetrically about the axis between the nuclei.
- $\sigma$-Bonds: electron density lies on the axis between the nuclei.
- All single bonds are $\sigma$-bonds.
- $\pi$-Bonds: electron density lies above and below the plane of the nuclei.
- Formation of a covalent bond by sideways overlap of two p orbitals gives $pi$ ($\pi$) bond, ith a high probability of finding the electrons above and below the bond axis.

Multiple Bonds

- Often, the p-orbitals involved in $\pi$-bonding come from unhybridized orbitals.
- A double bond consists of one $\sigma$-bond and one $\pi$-bond.
- A triple bond has one $\sigma$-bond and two $\pi$-bonds.

How do we form a multiple bond?

- The triple bond in the N$_2$ molecule is formed from one sigma bond and two pi bonds, using overlap of all three p orbitals.
How do we form the double bond in $O_2$?

- $O \ 1s^2 \ 2s^2 \ 2p^4$
- How many unpaired electrons?
- How many bonds will form between 2 $O$ atoms?
- Which orbitals will overlap to form the bonds?
- Double bond: $p + p \rightarrow \sigma$
  and $p + p \rightarrow \pi$
- Which orbitals overlap and what type of bonds are formed?
  
  | H$_2$ | Br$_2$ | HBr | O$_2$ | N$_2$ | NO | HOH | CH$_4$ |

What hybridization for a double bond?

- Use hybrid orbitals only for the sigma bonds, use $p$ orbitals for the pi bond.
- $sp^2 + p$

What hybridization for a triple bond?

- Use hybrid orbitals only for the sigma bond, use $p$ orbitals for the pi bonds.
- $sp + p + p$

Multiple Bonds

- Use hybrid orbitals to form sigma bonds.
- Use $p$ orbitals to form pi bonds.
- Describe the bonding in CO$_2$.

- Describe the bonding in the following molecules:
  
  | HCCH | H$_2$CCH$_2$ | H$_3$CCH$_3$ | HONO | CO | PF$_3$ | CH$_2$Cl$_2$ |

Delocalized $\pi$ Bonding

- How do we explain the bonding in molecules that have delocalized double bonds?
- Structure from sigma framework
- $Pi$ bonds can be used to accommodate the double bonds, representing the two resonance forms
- $Pi$ bonds are delocalized because of continuous overlap of adjacent $p$ orbitals.
Delocalization in Benzene

• Benzene, \( \text{C}_6\text{H}_6 \), has a cyclic structure.
• The Lewis formula can be described as alternating single and double bonds between carbon atoms. What hybridization is used?
• Why does graphite conduct electricity?

Electron Microscope Image of Graphite

• Where are the single bonds and the double bonds?

9.7, 9.8 Molecular Orbital Theory

• Skip these sections
• Molecular orbital theory considers bonding by overlap of atomic orbitals to form molecular orbitals, either bonding or antibonding, with electrons going into the lowest energy orbitals.