

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 AB_n 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?

BeF ₂ (g)	CO ₂	HCN	H ₂ O
XeF ₂	SO ₂	NO ₂ ⁻	SF ₂
BH ₃	SO ₃	NH ₃	ClF ₃
NO ₃ ⁻			
SiH ₄	SF ₄	XeF ₄	SO ₄ ²⁻
PF ₅	IF ₅		
SF ₆			

- 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

- Group Work: What are the structures of the following molecules and ions?

HCN	XeF ₂
NO ₂ ⁻	SF ₂
NH ₃	ClF ₃
NO ₃ ⁻	SF ₄
XeF ₄	SO ₄ ²⁻

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, CH₃COOH, there are three central atoms.
- We assign the geometry about each central atom separately.

9.3 Polarity of Polyatomic Molecules

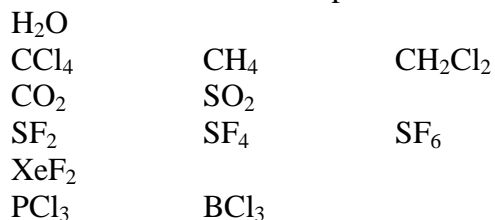
- Bonds can be polar if electrons are shared unequally
- If molecules are polar, they have a separation of positive and negative charge within the molecule, and they exhibit a dipole moment, which is the product of the charge and the distance between centers of positive and negative charge

Polar Bonds

- For diatomic molecules, the bond is more polar (greater dipole moment), the greater the difference in electronegativity between the two atoms.
- $\delta^+ \quad \delta^-$
H : 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.
- $\delta^- \quad \delta^+ \quad \delta^+ \quad \delta^-$
Cl : Be : 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?



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
$$\text{F} \cdot + \cdot \text{F} \rightarrow \text{F}:\text{F}$$
- 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°
- 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 σ 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.
- σ -Bonds: electron density lies on the axis between the nuclei.
- All single bonds are σ -bonds.
- π -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 (π) bond, with a high probability of finding the electrons above and below the bond axis.

Multiple Bonds

- Often, the p-orbitals involved in π -bonding come from unhybridized orbitals.
- A double bond consists of one σ -bond and one π -bond.
- A triple bond has one σ -bond and two π -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 O₂?

- O 1s² 2s² 2p⁴
 - 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 → sigma
and p + p → pi
 - Which orbitals overlap and what type of bonds are formed?
- H₂
Br₂
HBr
O₂
N₂
NO
HOH
CH₄

What hybridization for a double bond?

- Use hybrid orbitals only for the sigma bonds, use p orbitals for the pi bond.
- sp² + 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 CO₂.
- Describe the bonding in the following molecules:
HCCH
H₂CCH₂
H₃CCH₃
HONO
CO
PF₃
CH₂Cl₂

Delocalized π 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, C₆H₆, 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.