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Chapter 9 Chemical Bonding II: Molecular Geometry and Bonding Theories

9.1 Molecular Geometry

• Molecular geometry is the threedimensional shape of a molecule.



Geometry can be predicted using

 Lewis dot structures
 VSEPR model

- Molecules of the type AB_x will be considered
 - A is the central atom
 - B atoms surround the central atom
 - x commonly has integer values from 1 to 6
 - Examples:

All AB₁ molecules are *linear*.





- VSEPR Model: Valence-Shell Electron-Pair Repulsion Model
 - Electron pairs move as far apart as possible to minimize repulsions.
 - Electron domain is a lone pair or a bond (the bond may be single, double, or triple).
 - Strategy to predict geometry:



- Steps to determine Geometry
 - -Step #1: Draw the molecule's Lewis structure.
 - -Step #2: Count the number of electron domains on the central atom.
 - -Step #3: Determine the *electron-domain geometry*.
 - The electron-domain geometry is based on the number of electron domains around the central atom.

Examples

$$H-C=N: \qquad \begin{array}{c} :\ddot{O}: & -\\ \vdots & -\dot{N} = \overleftrightarrow{O}: \end{array} \\ \vdots & -\dot{N} = \overleftrightarrow{O}: \end{array} \qquad \begin{array}{c} :\ddot{F} - \overleftarrow{X}e - \overrightarrow{F}:\\ \vdots & 5 \end{array}$$

• Electron domains and geometry

Number of Electron Domains

2

3

4



Electron-Domain Geometry

Number of Electron Domains

Electron-Domain Geometry

5

6



Trigonal bipyramidal



Octahedral

- Step #4: Determine the *molecular geometry*.

The *electron-domain geometry* and the number of bonded atoms determine the *molecular geometry*.

Example: Ammonia, NH₃







Step #3

molecular geometry = trigonal pyramidal

Note: The common molecular geometries are *all* derived from these 5 electron-domain geometries.



Linear



T-shaped Seesaw Trigonal bipyramidal



Bent Trigonal planar



Bent Trigonal pyramidal Tetrahedral



Linear T-shaped Square planar Square pyramidal Octahedral

Axial and equatorial positions



For SF₄, which geometry is correct?



ea





Exercise: For each of the following species,

- i) draw the Lewis structure.
- determine the number of electron domains on the central atom and its electron-domain geometry.
- iii) predict the molecular geometry.

a) NF₃



ii) 4 electron domains on the central atom.

Electron-domain geometry: tetrahedral

iii) One lone pair on the central atom.

Molecular geometry: trigonal pyramidal



ii) 3 electron domains on the central atom.

Electron-domain geometry: trigonal planar

iii) No lone pairs on the central atom.

Molecular geometry: trigonal planar

- Deviations from ideal bond angles
 - All electron domains repel each other.
 - The repulsion between domains depends on the types of domains involved.





Ione-pair - Ione-pair repulsion is greater than Ione-pair - bonding-pair repulsion is greater than bonding-pair - bonding-pair repulsion

Geometry with more than one central atom



9.2 Molecular Geometry and Polarity

The HF bond is polar and HF has a *dipole moment (\mu)*.



Bond dipoles are vectors and therefore are additive.

- Molecules with more than two atoms
 - Remember bond dipoles are additive since they are *vectors*.



Example: Dichloroethene, $C_2H_2CI_2$, exists as three isomers.







cis-1,2-dichloroethene trans-1,2-dichloroethene 1,1-dichloroethene

polar	nonpolar	polar
μ = 1.90 D	$\mu = 0 D$	μ = 1.34 D
bp = 60.3°C	bp = 47.5°C	bp = 31.7°C

9.3 Valence Bond Theory

- Electrons in molecules occupy *atomic* orbitals.
- Covalent bonding results from the overlap of atomic orbitals.

Representation of singly-occupied and doubly-occupied *s* and *p* atomic orbitals. Singly-occupied orbitals appear light; doubly-occupied orbitals appear darker.



Example: $H(1s^1) + H(1s^1) \rightarrow H_2$



Example: $F(1s^22s^22p^5) + F(1s^22s^22p^5) \rightarrow F_2$



Example: $H(1s^1) + F(1s^22s^22p^5) \rightarrow HF$



9.4 Hybridization of Atomic Orbitals

 Valence bond theory cannot account for many experimental observations.

Beryllium Chloride, BeCl₂





- The atomic orbitals on an atom mix to form **hybrid orbitals**.
 - Orbital shapes (boundary surfaces) are pictorial representations of wave functions.
 - Wave functions are mathematical functions.
 - Mathematical functions can be combined.
- Hybridization of s and p orbitals
 sp hybridization



• The two *sp* orbitals point in opposite directions inline with one another.



 Each Be *sp* orbital overlaps a Cl 3*p* orbital to yield BeCl₂.





 $-sp^2$ hybridization

Example: Boron trifluoride, BF₃



• The three sp^2 orbitals point to the corners of an equilateral triangle.



• Each B sp^2 orbital overlaps a F 2p orbital to yield BF₃.





#1 C

#2 C*

#3



 $2p^3$

- only 2 unpaired electrons
- 2 types of overlap with 2s and 2p

• overlap with *p*-orbitals = 90°



• The *sp*³ hybrid orbitals point to the corners of a tetrahedron.



• Each C $2sp^3$ orbital overlaps a H 1s orbital to yield CH₄.

4H
$$1 + C$$
 $1 + C$ $1 + C$ $1 + C$ H_4







9.5 Hybridization in Molecules Containing Multiple Bonds

 A sigma (o) bond is a bond in which the shared electron density is concentrated directly along the internuclear axis between the two nuclei involved in bonding.

- end-to-end overlap





- Double and triple bonds consist of both sigma (σ) and pi (π) bonds.
- A pi (π) bond forms from the sideways overlap of p orbitals resulting in regions of electron density that are concentrated above and below the plane of the molecule.

sideways overlap



C = C Example: Ethylene, C₂H₄



Remaining p orbitals shown as simplified shape

Н

Double bond = 1σ bond + 1π bond



Triple bond = 1σ bond + 2π bonds

Exercise: How many pi bonds and sigma bonds are in each of the following molecules? Describe the hybridization of each C atom.



- (a) 4 sigma bonds
- (b) 5 sigma bonds, 1 pi bond
- (c) 10 sigma bonds, 3 pi bonds

9.6 Molecular Orbital Theory

- Molecular Orbital Theory (MO)
 - Atomic orbitals combine to form new molecular orbitals which are spread out over the entire molecule. Electrons are in orbitals that belong to the molecule as a whole.
 - Molecular orbitals (wave functions) result from adding and/or subtracting atomic orbitals (wave functions).

- Molecular orbital theory (MO)
 - Atomic orbitals combine to form new, molecular orbitals that are spread out over the entire molecule. Electrons are now in orbitals that belong to the molecule as a whole.



- Pictorial representation.



- Types of molecular orbitals
 - Bonding molecular orbital
 - High electron density between the nuclei



• Lower energy and more stable than the atomic orbitals that were added

- Antibonding molecular orbital
 - Low electron density between the nuclei



• Higher energy and less stable than the atomic orbitals that were subtracted

Bond order



bond order =
$$1/2(2 - 0) = 1$$
 bond order = $1/2(2 - 2) = 0$
single bond no bond

Examples Using Antibonding Orbitals



single bond

no bond

- Pi (π) molecular orbitals
 - Wave functions representing p orbitals combine in two different ways yielding either σ orbitals or π orbitals.
 - End-to-end combination yields sigma (σ) orbitals



– Sideways combination yields pi (π) orbitals



• Energy order of the π_{2p} and σ_{2p} orbitals changes across the period.



Molecular orbital diagram of nitrogen, N₂



Molecular orbital diagram of oxygen, O₂



Magnetism

– Diamagnetic substance

- A substance whose electrons are all paired.
- ↑↓
- Weakly repelled by magnetic fields.
- Paramagnetic substance
 - A substance with one or more unpaired electrons.
 - 1
 - Attracted by magnetic fields.

	Li ₂	B ₂	C_2	N_2	O ₂	F_2	Ne ₂	
$\sigma^*_{2p_x}$							11	$\sigma^*_{2p_x}$
$\pi^*_{2p_y}$, $\pi^*_{2p_z}$					1 1	11 11	11 11	$\pi^*_{2p_y}$, $\pi^*_{2p_z}$
σ_{2p_x}				11	11 11	11 11	11 11	π_{2p_y} , π_{2p_z}
π_{2p_y} , π_{2p_z}		1 1	11 11	11 11	11	11	11	σ_{2p_x}
σ^*_{2s}		11	11	11	11	11	11	σ^*_{2s}
σ_{2s}	11	11	11	11	11	11	11	σ_{2s}
Bond order	1	1	2	3	2	1	0	
Bond length (pm)	267	159	131	110	121	142	_	
Bond enthalpy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9	_	
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	_	

For simplicity the σ_{1s} and σ_{1s}^* orbitals are omitted. These two orbitals hold a total of four electrons. Remember that for O₂ and F₂, σ_{2p_x} is lower in energy than π_{2p_y} , and π_{2p_z} . 9.7 Bonding Theories and Descriptions of Molecules with Delocalized Bonding

- In *localized bonds* the σ and π bonding electrons are associated with only two atoms.
- Resonance requires delocalized bonds when applying valence bond theory.

• In *delocalized bonds* the π bonding electrons are associated with more than two atoms.

Examples:

$$\mathrm{NO_3^{-}},\,\mathrm{CO_3^{2-}},\,\mathrm{C_6H_6}$$
 , $\mathrm{O_3}$

Example: benzene, C_6H_6



Key Points

- Molecular geometry
 VSEPR model
- Molecular geometry and polarity
- Valence bond theory
- Hybridization of atomic orbitals
 - -s and p
 - s, p, and d
- Hybridization involving multiple bonds

Key Points

- Molecular orbital theory
 - Bonding and antibonding orbitals
 - Sigma (σ) molecular orbitals
 - Pi (π) molecular orbitals
 - MO diagrams