###### Molecular Geometry and Bonding Theories Name: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

*AP Chemistry Lecture Outline*

The properties of a molecule depend on its shape and the nature of its bonds.

In this unit, we will discuss three models.

(1) a model for the geometry of molecules

-- valence-shell electron-pair repulsion (VSEPR) theory

(2) a model about WHY molecules form bonds and WHY they have the shape they do

-- valence-bond theory

(3) a model of chemical bonding that deals with the electronic structure of *molecules*

-- molecular orbital (MO) theory

bond angles: the angles made by the lines joining the nuclei of a molecule’s atoms

**VSEPR**  electron domain: a region in which at least two electrons are found

-- they repel each other because…

bonding domain: 2-to-6 e– that are shared by two atoms; they form a…

nonbonding domain: 2 e– that are located on a single atom; also called a…

For ammonia, there are three bonding

domains and one nonbonding domain.

Domains arrange themselves so as to minimize their repulsions.

The electron-domain geometry is one of five The molecular geometry describes the

basic arrangements of domains. orientation of the atoms in space.

-- it depends only on the total # of e– domains, -- it depends on how many of each kind

NOT the kind of each domain of e– domain

|  |  |  |
| --- | --- | --- |
| **Total # of Domains** | **Electron-Domain Geometry** | **Possible Molecular Geometries** |
| 2 |  |  |
| 3 |  |  |
| 4 |  |  |
| 5 |  |  |
| 6 |  |  |

To find the electron-domain geometry (EDG) and/or molecular geometry (MG), draw the Lewis structure. Multiple bonds count as a single domain.

EX. Predict the EDG and MG of each of the following.

SnCl3–

O3

SeCl2

CO32–

SF4

IF5

ClF3

ICl4–

For molecules with more than one central atom, simply apply the VSEPR model to each part.

EX. Predict the EDG and MG around the three interior atoms of ethanoic (acetic) acid.

Nonbonding domains are attracted to only one nucleus; therefore, they are more spread out than are bonding domains. The effect is that nonbonding domains (i.e., “lone pairs”) compress bond angles. Domains for multiple bonds have a similar effect.

e.g., the ideal bond angle for the tetrahedral EDG is 109.5o

CH4 NH3 H2O COCl2

**Polarity of Molecules**

A molecule’s polarity is determined by its overall dipole, which is the vector sum of the

dipoles of each of the molecule’s bonds. Consider CO2 v. H2S...

CO2 H2S

EX. Classify as polar or nonpolar: PCl3 BCl3

**Valence-Bond Theory**: merges Lewis structures w/the idea of atomic orbitals (2s, 3p, etc.)

Lewis *theory* says… V-B *theory* says…

covalent bonding occurs when covalent bonding occurs when valence

atoms share electrons orbitals of adjacent atoms overlap; then,

two e–s of opposite spin (one from

each atom) combine to form a bond

Consider H2, Cl2, and HCl...

H2 Cl2 HCl

H–H distance

Energy

0

There is always an optimum

distance between two bonded

nuclei. At this optimum distance,

attractive (+/–) and

repulsive (+/+ and –/–) forces balance.

**Hybridized Orbitals** V-B theory can’t explain some observations about molecular

compounds without the concept of hybridized orbitals.

…the central atom …but is ACTUALLY …the result

In… (LS) SHOULD be… hybridized to be… then being…

BeF2

BF3

CH4

H2O

PF5

XeF2

XeF4

**KEY:**

**Multiple Bonds**

 (sigma) bonds are bonds in which the e– density is along the internuclear axis.

-- These are the single bonds we have considered up to this point.

-- e.g., s-s, s-p, or p-p overlap, and also p-sp hybrid overlap

Multiple bonds result from the overlap of two p orbitals

(one from each atom) that are oriented perpendicularly

to the internuclear axis. These are  (pi) bonds.

 bonds are generally weaker than  bonds

because  bonds have less overlap.

Single bonds Double bonds consist of Triple bonds consist of

are  bonds. one  and one . one  and two .

Experiments indicate that all of C2H4’s atoms lie in the same plane.

This suggests that  bonds introduce rigidity (i.e., a reluctance to rotate) into molecules.

--  bonding does NOT occur with *sp3* hybridization, only *sp* and *sp2*

--  bonding is more prevalent with small molecules (e.g., C, N, O)

**Delocalized  Bonding**

Localized  bonds are between…

-- e.g.,

Delocalized  bonds are “smeared out” and shared among…

-- these are common for molecules with…

-- The electrons involved in these bonds are delocalized electrons.

Consider benzene, C6H6.

-- Each carbon atom is \_\_\_\_\_ hybridized.

-- This leaves...

EX. Which of the following exhibit delocalized bonding?

O

H3C–C–CH3 SO2 SO42–

**Molecular Orbitals**

-- The VSEPR and valence-bond theories don’t explain the excited states of molecules,

which come into play when molecules absorb and emit light.

-- This is one thing that the molecular orbital (MO) theory attempts to explain.

molecular orbitals: wave functions that describe the locations of electrons in molecules

-- these are analogous to atomic orbitals in atoms (e.g., 2s, 2p, 3s, 3d, etc.), but

MOs are possible locations of electrons in *molecules* (not atoms)

-- MOs, like atomic orbitals, can hold a maximum of two e– with opposite spins

-- but MOs are for entire molecules

*Hydrogen (H2)*

The overlap of two atomic

orbitals produces two MOs.

-- The lower-energy bonding molecular orbital concentrates e– density between nuclei.

-- For the higher-energy antibonding molecular orbital, the e– density is concentrated outside the nuclei.

-- Both of these are  molecular orbitals.

**Energy-level diagram**

**(molecular orbital diagram)**

Consider the energy-level diagram

for the hypothetical He2 molecule...

bond order = ½ (# of bonding e– – # of antibonding e–)

-- the higher the bond order, the greater the bond stability

-- a bond order of... 0 = 1 = 2 = 3 =

-- MO theory allows for fractional bond orders as well.

EX. What is the bond order of H2+?

**Second-Row Diatomic Molecules**

1. # of MOs = # of combined atomic orbitals

2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy.

3. As atomic orbital overlap increases, bonding MO is lowered in energy, and the antibonding MO is raised in energy.

4. Both the Pauli exclusion principle and Hund’s rule apply to MOs.

Use MO theory to predict whether Li2 and/or Be2 could possibly form.

2s

2s

\*2s

2s

2s

1s

1s

2s

\*2s

2s

1s

\*1s

**Li**

**Li**

**Li2**

**Be2**

**Be**

**Be**

**Molecular Orbitals from 2p Atomic Orbitals**

The 2pz orbitals overlap in head-to-head fashion, so these bonds are...

-- the corresponding MOs are:

The other 2p orbitals (i.e., 2px and 2py) overlap in sideways fashion, so the bonds are...

-- the corresponding MOs are:

Rule 3 above suggests that, from low energy to high, the 2p MOs SHOULD follow the order:

General energy-level diagrams for MOs of second-row homonuclear diatomic molecules...

*For B2, C2, and N2... For O2, F2, and “Ne2”...*

2s

\*2s

\*2p

2p

2p

\*2p

\*2s

2s

2p

2p

\*2p

\*2p

Here, the interaction between the 2s of Here, the interaction is weak. The

one atom and the 2p of the other is strong. energy distribution is as expected.

The orbital energy distribution is altered.

paramagnetism: describes the attraction of molecules with unpaired e– to a magnetic field

diamagnetism: describes substances with no unpaired e–

-- such substances are VERY weakly (almost unnoticeably) repelled by a magnetic field

Use the energy diagrams above to tell if diatomic species are paramagnetic or diamagnetic.

EX. Paramagnetic or diamagnetic?

B2 C2 N2 O2 F2 O2+ O22– C22–