# **Chapter 4 - Geometry**

**Organic Chemistry** 

Notes for molecular bonding, geometries, and hybridizations

#### A summary of Electron and Molecular Geometries



# Why is the molecular geometry important?

- What happens to a molecule during a reaction?
  - molecules collide
  - "Old" bonds are broken and "new" bonds are made



 We need to consider the <u>shapes of the molecules</u>, this concept is called <u>sterics</u>. The shape can affect how molecules can effectively collide!

# Part 1 - Bonding Review

#### **Topics to Cover:**

- 1. s orbitals are spherical in shape
- 2. p orbitals have a dumbbell shape



You need a little refresher on what orbitals are and how they work and how all of the things we learned in chem I with regards to bonding ties together!

- 3. a bond is formed when an electron of one atom overlaps with an electron of another atom in atomic orbitals
- 4. when two electrons are shared, it is a covalent bond
- 5. atoms in the second row (C, N, O, F) have one s orbital and three p orbitals in their valence shell
- 6. Orbitals used and valence electrons stem from the electron configurations of each atom

# Review of VSEPR & Electron Config. from Chem

In the 1920s, Quantum Mechanics was established as a theory to explain the wave properties of electrons

The solution to **wave equations** are **wave functions**; The 3D plot of a (wave function)<sup>2</sup> gives an image of an **atomic orbital** 



**Basic Shapes of Orbitals** 



## Atomic Orbitals = Electron Density

- The type of orbital is identified by its shape (s, p, d, f)
- Electron density: term used to refer to probability of finding an electron (the orbital shape is 90-95% of the space where an electron "probably" is)



# "Parts" of Atomic Orbitals (AO)

- Because they are generated mathematically from wavefunctions, orbital regions can also be (–), (+), or ZERO
  - The sign of the wave function has nothing to do with electrical charge.
- In this p-orbital, there is a nodal plane. The sign of the wavefunction will be important when we look at orbital overlapping in bonds.





Note: Ψ is the greek letter PSI pronounced "sigh"

# **Electron filling patterns**

- Electrons are most stable (lowest in energy) if they are in the 1s orbital.
- The 1*s* orbital, like every atomic orbital, can have up to 2 electrons in it. If there are more electrons in the atom they fill up the 2s the 2p orbitals



The 2p orbitals are of equal energy, and thus are "degenerate orbitals"

# Valence Bond Theory

Common elements and their electron configurations







# Valence Bond Theory

• A bond occurs when atomic orbitals overlap. Overlapping orbitals is like overlapping waves



#### Valence Bond Theory

• The bond for a H<sub>2</sub> molecule results from constructive interference







# Molecular Orbital Theory (MO Theory)



- Atomic orbital wavefunctions overlap to form MOs that extend over the entire molecule.
- MOs are a more complete analysis of bonds, because they include both constructive and destructive interference.
- The number of MOs created must be equal to the number of AOs that were used.

#### Molecular Orbitals for H<sub>2</sub>

#### **Molecular Orbital Theory**

• The *antibonding MO* has higher energy because it has *one node*.

Node



 When the AOs over rather than the ant energy state

### **Molecular Orbital Theory**

- The are more than two MOs that exist for CH<sub>3</sub>Br.. But let's focus on only two of them here
  - There are many areas of atomic orbital overlap, and nodes as well
  - Notice how the MOs extend over the entire molecule





# Last bit on Molecular Orbital Theory

- Each MO can hold two electrons. (Think of this as the "line" from our orbital notations)
- In the ground state, electrons occupy lower energy MO's while the higher energy ones remain unoccupied (remember we fill from the bottom-up).



- These two MO's here are the most important ones: The highest Occopied MO (HONO) and in ground state in excited state
- These are the MO's in play when undergoing a chemical rxn

#### Video Review of Part 1



# Part 2 - Hybridization

#### **Topics to Cover:**

- 1. Orbitals mix together to create hybridized or hybrid orbitals (sp<sup>3</sup>, sp<sup>2</sup>, and sp) which have a lower energy than the original p orbital(s) used, but more energy than the s orbital used
- 2. Because the hybrid orbitals have a lower average energy, they are more stable
  - a. if 1 s orbital is mixed with 3 p orbitals, 4 new "sp<sup>3</sup> hybridized orbitals" will be created
  - b. if 1 s orbital is mixed with 2 p orbitals, 3 new "sp<sup>2</sup> hybridized orbitals" will be created, with 1 remaining unhybridized p orbital
  - c. if 1 s orbital is mixed with 1 p orbital, 2 new "sp hybridized orbitals" will be created, with 2 remaining unhybridized p orbitals
- 3. hybridized orbitals can be used to either hold a lone pair of electrons, or overlap to form a sigma (single) bond with another atom
- 4. unhybridized p orbitals can overlap between atoms to form an additional pi bond (double bond) or two pi bonds (triple bond).

# Why do we need hybridization?

• the ground state electron configuration for carbon can't explain how carbon makes four bonds





Only two orbitals have unpaired electrons to be shared in the ground

There are 4 unpaired electrons here, but 4 equal bonds cannot be made with two different types of orbitals (s vs p)

If considering the excited state, it still doesn't explain how carbon makes 4 equivalent bonds, like the 4 bonds to H in a methane molecule

#### To create equal energy orbitals!

- The carbon must undergo hybridization to form 4 equal atomic orbitals, with symmetrical geometry
- The atomic orbitals must be equal in energy to form four equal-energy symmetrical C-H bonds



# Mrs. H's Analogy of Hybridization



Everything gets "mixed up" and ends up having characteristics of the combined orbitals, umm berries! The different amounts or proportions will affect the taste... (or shape of orbitals!)



# "Real" Hybridization is similar

- The carbon must undergo hybridization to form 4 equal atomic orbitals, with symmetrical geometry
- The atomic orbitals must be equal in energy to form four equal-energy symmetrical C-H bonds



### Let's analyze the hybridized orbitals



 the shape of an sp<sup>3</sup> orbital results from have 25% s-character, and 75% p-character



# Let's revisit our friend, methane (CH<sub>4</sub>)

• To make CH<sub>4</sub>, the 1s atomic orbitals of four H atoms will overlap with the four  $sp^3$  hybrid atomic orbitals of C



made

#### But it's not always the same number of orbitals

Consider ethene (ethylene).



 Each carbon in ethene must bond to three other atoms, so only three hybridized atomic orbitals are needed



# A closer look at sp<sup>2</sup> hybridization

 An sp<sup>2</sup> hybridized carbon will have three equal-energy sp<sup>2</sup> orbitals and one unhybridized p orbital



 the shape of an sp<sup>2</sup> orbital results from have 33% s-character, and 67% p-character

### How the pi bond is formed (double bond)

• The  $sp^2$  atomic orbitals overlap to form sigma ( $\sigma$ ) bonds



• The *p* orbitals, here, overlap to form a pi bond

# A closer look at the <u>un</u>hybridized p orbitals

 The pi (π) bond is formed by SIDE-BY-SIDE overlap of the p orbitals. The electron density of the pi bond is spread out above and below the plane of the molecule, as shown below



Pi bonds are weaker than sigma bonds.

#### A look back at what MO Theory tells us

• The pi bond is described in a similar way according to MO theory.

Node  $\pi$  Antibonding MO Remember, red and blue regions are all part of the same orbital, but opposite Energy 2p 2p phases  $\pi$  Bonding MO

### But what about triple bonds?

• Consider ethyne (acetylene).

$$H-C\equiv C-H$$

Acetylene

 Each carbon in ethyne must bond to two other atoms, so only two hybridized atomic orbitals are needed



# How the triple bond forms

 The sp atomic orbitals overlap HEAD-ON to form sigma (σ) bonds while the unhybridized p orbitals overlap SIDE-BY-SIDE to form pi bonds



Remember, we made 2 hybridized sp orbitals of equal energy (silver colored) and we had 2 "left over" unhybridized p orbitals (red/blue colored)

#### Let's compare single, double, and triple bonds

Which should be stronger, a pi bond or a sigma bond?

The sigma bond is considered stronger as it requires almost twice the bond energy of a pi bond to break it

 Which should be longer, an sp<sup>3</sup> – sp<sup>3</sup> sigma bond overlap or an sp – sp sigma bond overlap? Realize the more s-character in the orbitals, the shorter they will be

sp<sup>3</sup> bond lengths are the longest, followed by sp<sup>2</sup>, and then sp bonds.

## Visuals of bond lengths

Rationalize the bond strengths and lengths below



#### Let's Review!









# Part 3 - Molecular Geometry

#### **Topics to Cover:**

- 1. the type of hybridization occurring can be determined from the sum of lone pairs and the number of bonding regions
  - a. if the sum is 4, then you have 4 sp3 orbitals = tetrahedral geometry, 109.5° BA
  - b. if the sum is 3, then you have 3 sp2 orbitals + 1 p orbital = trigonal planar, 120° BA
  - c. if the sum is 2, then you have 2 sp orbitals + 2 p orbitals = linear, 180° BA
- 2. "Bent" molecules are from lone pairs
- 3. Lone pairs will decrease the actual observed bond length because they "push" in on the bonds more

# **Review of VSEPR Theory**

• Valence shell electron pair repulsion (VSEPR theory)

Valence electrons (shared and lone pairs) repel each other

 To determine molecular geometry, start with the steric number... which gives us a quick prediction



In chem I we called the "steric number" the "number of electron domains"

# **Hybridization & Steric Number**

- The steric number translate to the hybridization of the central atom
  - If the Steric number is 4, then it is sp<sup>3</sup>
  - If the Steric number is 3, then it is *sp*<sup>2</sup>
  - If the Steric number is 2, then it is sp



# For 4 Steric Groups = sp<sup>3</sup> hybridized

 The molecular geometry is described for only the atoms bonded to the central atom; electron group geometry includes lone pairs



In chem I we did not decrease the bond angle as long pairs were added, please note the difference!
# We can simplify things by thinking of sigma bonds as just "attached atoms"

Additional Examples for sp<sup>3</sup>:



#### For 3 Steric Groups = sp<sup>2</sup> hybridized

 The electron pairs in sp<sup>2</sup> hybridized orbitals (either bonded electrons or lone pairs) will form a <u>trigonal planar</u> electron group geometry (steric number = 3 = trigonal planar)



#### For 2 Steric Groups = sp hybridized

 When steric number = 2, the geometry will be linear and the atom will be sp-hybridized



#### **Summary Flowchart of Molecular Geometries**



#### **Additional Molecular Geometries**

(that you will need to answer questions with - but not to memorize!)



#### Practice - Slide 1 What is the molecular geometry (shape) and hybridization of each indicated atom?





#### Practice - Slide 2

Determine the hybridization of the marked atom in the following molecules

don't forget "hidden" lone pairs and hydrogens



#### Explanation videos to check out:









#### **Practice Problem Videos**



#### **Practice Problem**

## VSEPR Theory and Molecular Geometry





# **END OF CHAPTER 3 SLIDES STUDENT VERSION TO FOLLOW**

# **Chapter 4 - Geometry**

Name:

Date: \_\_\_\_\_ Pd: \_\_

#### **Organic Chemistry**

Notes for molecular bonding, geometries, and hybridizations



#### Why is the molecular geometry important?

- What happens to a molecule during a reaction?
  - molecules collide
  - "Old" bonds are broken and "new" bonds are made



 We need to consider the <u>shapes of the molecules</u>, this concept is called <u>sterics</u>. The shape can affect how molecules can effectively collide!

# Part 1 - Bonding Review

#### **Topics to Cover:**

- 1. s orbitals are spherical in shape
- 2. p orbitals have a dumbbell shape



You need a little refresher on what orbitals are and how they work and how all of the things we learned in chem I with regards to bonding ties together!

- 3. a bond is formed when an electron of one atom overlaps with an electron of another atom in atomic orbitals
- 4. when two electrons are shared, it is a covalent bond
- 5. atoms in the second row (C, N, O, F) have one s orbital and three p orbitals in their valence shell
- 6. Orbitals used and valence electrons stem from the electron configurations of each atom

#### Review of VSEPR & Electron Config. from Chem

In the 1920s, Quantum Mechanics was established as a theory to explain the wave properties of electrons

The solution to **wave equations** are **wave functions**; The 3D plot of a (wave function)<sup>2</sup> gives an image of an **atomic orbital** 



**Basic Shapes of Orbitals** 



#### Atomic Orbitals = Electron Density

- The type of orbital is identified by its shape (s, p, d, f)
- Electron density: term used to refer to probability of finding an electron (the orbital shape is 90-95% of the space where an electron "probably" is)



## "Parts" of Atomic Orbitals (AO)

- Because they are generated mathematically from wavefunctions, orbital regions can also be (–), (+), or ZERO
  - The sign of the wave function has nothing to do with electrical charge.
- In this p-orbital, there is a nodal plane. The sign of the wavefunction will be important when we look at orbital overlapping in bonds.





Note: Ψ is the greek letter PSI pronounced "sigh"

### **Electron filling patterns**

- Electrons are most stable (lowest in energy) if they are in the 1s orbital.
- The 1*s* orbital, like every atomic orbital, can have up to 2 electrons in it. If there are more electrons in the atom they fill up the 2s the 2p orbitals



The 2p orbitals are of equal energy, and thus are "degenerate orbitals"

### Valence Bond Theory

Common elements and their electron configurations







### Valence Bond Theory

• A bond occurs when atomic orbitals overlap. Overlapping orbitals is like overlapping waves



#### Valence Bond Theory

• The bond for a H<sub>2</sub> molecule results from constructive interference







## Molecular Orbital Theory (MO Theory)



- Atomic orbital wavefunctions overlap to form MOs that extend over the entire molecule.
- MOs are a more complete analysis of bonds, because they include both constructive and destructive interference.
- The number of MOs created must be equal to the number of AOs that were used.

#### Molecular Orbitals for H<sub>2</sub>

#### **Molecular Orbital Theory**

• The *antibonding MO* has higher energy because it has *one node*.

Node



 When the AOs over rather than the ant energy state

#### **Molecular Orbital Theory**

- The are more than two MOs that exist for CH<sub>3</sub>Br.. But let's focus on only two of them here
  - There are many areas of atomic orbital overlap, and nodes as well
  - Notice how the MOs extend over the entire molecule





## Last bit on Molecular Orbital Theory

- Each MO can hold two electrons. (Think of this as the "line" from our orbital notations)
- In the ground state, electrons occupy lower energy MO's while the higher energy ones remain unoccupied (remember we fill from the bottom-up).



- These two MO's here are the most important ones: The highest Occopied MO (HONO) and in ground state in excited state
- These are the MO's in play when undergoing a chemical rxn



# Part 2 - Hybridization

#### **Topics to Cover:**

- 1. Orbitals mix together to create hybridized or hybrid orbitals (sp<sup>3</sup>, sp<sup>2</sup>, and sp) which have a lower energy than the original p orbital(s) used, but more energy than the s orbital used
- 2. Because the hybrid orbitals have a lower average energy, they are more stable
  - a. if 1 s orbital is mixed with 3 p orbitals, 4 new "sp<sup>3</sup> hybridized orbitals" will be created
  - b. if 1 s orbital is mixed with 2 p orbitals, 3 new "sp<sup>2</sup> hybridized orbitals" will be created, with 1 remaining unhybridized p orbital
  - c. if 1 s orbital is mixed with 1 p orbital, 2 new "sp hybridized orbitals" will be created, with 2 remaining unhybridized p orbitals
- 3. hybridized orbitals can be used to either hold a lone pair of electrons, or overlap to form a sigma (single) bond with another atom
- 4. unhybridized p orbitals can overlap between atoms to form an additional pi bond (double bond) or two pi bonds (triple bond).

### Why do we need hybridization?

• the ground state electron configuration for carbon can't explain how carbon makes four bonds





Only two orbitals have unpaired electrons to be shared in the ground

There are 4 unpaired electrons here, but 4 equal bonds cannot be made with two different types of orbitals (s vs p)

If considering the excited state, it still doesn't explain how carbon makes 4 equivalent bonds, like the 4 bonds to H in a methane molecule

#### To create equal energy orbitals!

- The carbon must undergo hybridization to form 4 equal atomic orbitals, with symmetrical geometry
- The atomic orbitals must be equal in energy to form four equal-energy symmetrical C-H bonds



#### Mrs. H's Analogy of Hybridization



Everything gets "mixed up" and ends up having characteristics of the combined orbitals, umm berries! The different amounts or proportions will affect the taste... (or shape of orbitals!)



#### "Real" Hybridization is similar

- The carbon must undergo hybridization to form 4 equal atomic orbitals, with symmetrical geometry
- The atomic orbitals must be equal in energy to form four equal-energy symmetrical C-H bonds



#### Let's analyze the hybridized orbitals



 the shape of an sp<sup>3</sup> orbital results from have 25% s-character, and 75% p-character



#### Let's revisit our friend, methane (CH<sub>4</sub>)

 To make CH<sub>4</sub>, the 1s atomic orbitals of four H atoms will overlap with the four sp<sup>3</sup> hybrid atomic orbitals of C



Remember, we made 4b hybridized sp<sup>3</sup> orbitals of equal energy (all the same, so they are all red colored)

#### But it's not always the same number of orbitals

Consider ethene (ethylene).



 Each carbon in ethene must bond to three other atoms, so only three hybridized atomic orbitals are needed



#### A closer look at sp<sup>2</sup> hybridization

 An sp<sup>2</sup> hybridized carbon will have three equal-energy sp<sup>2</sup> orbitals and one unhybridized p orbital



 the shape of an sp<sup>2</sup> orbital results from have 33% s-character, and 67% p-character

#### How the pi bond is formed (double bond)

• The  $sp^2$  atomic orbitals overlap to form sigma ( $\sigma$ ) bonds



• The *p* orbitals, here, overlap to form a pi bond

#### A closer look at the <u>un</u>hybridized p orbitals

 The pi (π) bond is formed by SIDE-BY-SIDE overlap of the p orbitals. The electron density of the pi bond is spread out above and below the plane of the molecule, as shown below



Pi bonds are weaker than sigma bonds.

#### A look back at what MO Theory tells us

• The pi bond is described in a similar way according to MO theory.

Node  $\pi$  Antibonding MO Remember, red and blue regions are all part of the same orbital, but opposite Energy 2p 2p phases  $\pi$  Bonding MO
#### But what about triple bonds?

• Consider ethyne (acetylene).

$$H-C\equiv C-H$$

Acetylene

 Each carbon in ethyne must bond to two other atoms, so only two hybridized atomic orbitals are needed



#### How the triple bond forms

 The sp atomic orbitals overlap HEAD-ON to form sigma (σ) bonds while the unhybridized p orbitals overlap SIDE-BY-SIDE to form pi bonds



Remember, we made 2 hybridized sp orbitals of equal energy (silver colored) and we had 2 "left over" unhybridized p orbitals (red/blue colored)

#### Let's compare single, double, and triple bonds

Which should be stronger, a pi bond or a sigma bond?

The sigma bond is considered stronger as it requires almost twice the bond energy of a pi bond to break it

 Which should be longer, an sp<sup>3</sup> – sp<sup>3</sup> sigma bond overlap or an sp – sp sigma bond overlap? Realize the more s-character in the orbitals, the shorter they will be

sp<sup>3</sup> bond lengths are the longest, followed by sp<sup>2</sup>, and then sp bonds.

### Visuals of bond lengths

Rationalize the bond strengths and lengths below



Write down a few points from the video in the space below:



## Part 3 - Molecular Geometry

#### **Topics to Cover:**

- 1. the type of hybridization occurring can be determined from the sum of lone pairs and the number of bonding regions
  - a. if the sum is 4, then you have 4 sp3 orbitals = tetrahedral geometry, 109.5° BA
  - b. if the sum is 3, then you have 3 sp2 orbitals + 1 p orbital = trigonal planar, 120° BA
  - c. if the sum is 2, then you have 2 sp orbitals + 2 p orbitals = linear, 180° BA
- 2. "Bent" molecules are from lone pairs
- 3. Lone pairs will decrease the actual observed bond length because they "push" in on the bonds more

### **Review of VSEPR Theory**

• Valence shell electron pair repulsion (VSEPR theory)

Valence electrons (shared and lone pairs) repel each other

 To determine molecular geometry, start with the steric number... which gives us a quick prediction



In chem I we called the "steric number" the "number of electron domains"

### **Hybridization & Steric Number**

- The steric number translate to the hybridization of the central atom
  - If the Steric number is 4, then it is sp<sup>3</sup>
  - If the Steric number is 3, then it is *sp*<sup>2</sup>
  - If the Steric number is 2, then it is sp



#### For 4 Steric Groups = sp<sup>3</sup> hybridized

 The molecular geometry is described for only the atoms bonded to the central atom; electron group geometry includes lone pairs



In chem I we did not decrease the bond angle as long pairs were added, please note the difference!

# We can simplify things by thinking of sigma bonds as just "attached atoms"

Additional Examples for sp<sup>3</sup>:



#### For 3 Steric Groups = sp<sup>2</sup> hybridized

 The electron pairs in sp<sup>2</sup> hybridized orbitals (either bonded electrons or lone pairs) will form a <u>trigonal planar</u> electron group geometry (steric number = 3 = trigonal planar)



#### For 2 Steric Groups = sp hybridized

 When steric number = 2, the geometry will be linear and the atom will be sp-hybridized



#### **Summary Flowchart of Molecular Geometries**



#### **Additional Molecular Geometries**

(that you will need to answer questions with - but not to memorize!)



#### Practice - Slide 1 What is the molecular geometry (shape) and hybridization of each indicated atom?



#### Practice - Slide 2

Determine the hybridization of the marked atom in the following molecules

don't forget "hidden" lone pairs and hydrogens

