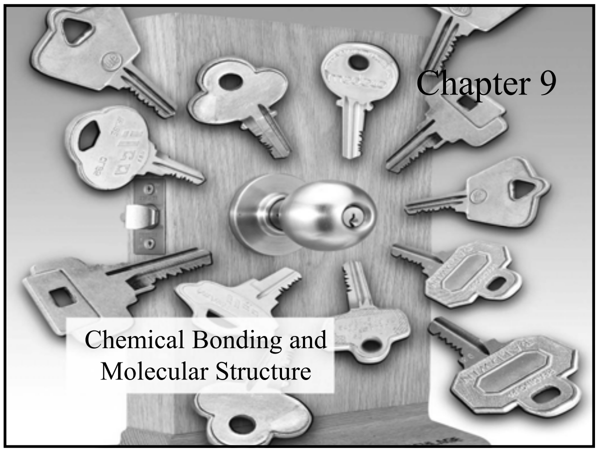
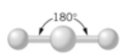
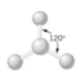
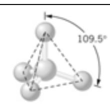


Chapter 9

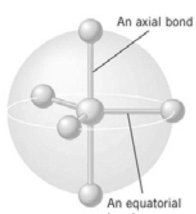
Chemical Bonding and Molecular Structure

9.1 Molecules are 3D

Shape	Angle	
Linear	180˚	
Planar triangular (trigonal planar)	120˚	 
Tetrahedral	109.5˚	 

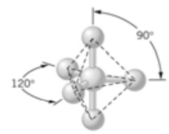
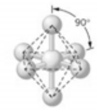
Shapes and Bonds

- Imagine a molecule where the central atom is the Earth.
- Equatorial bonds – bonds located around the “equator”
- Axial bonds – bonds pointing along the north and south axis of the central atom.



3

9.1 Molecular Shapes Continued

Shape	Angle	
Trigonal bipyramidal	120˚ and 90˚	 A trigonal bipyramid  A trigonal bipyramidal molecule
Octahedral	90˚	 An octahedron  An octahedral molecule

4

9.2 Molecular shapes are predicted using the VSEPR model

- You have seen the 5 basic molecular shapes.
- Notice, they assume that the central atom is surrounded only by atoms.
- What if there are electron pairs on the central atom?
- How do they affect the molecular shape?

5

VSEPR Model

- **V**alence **S**hell **E**lectron-**P**air **R**epulsion Model
- Electrons pairs in the outer shell of an atom try to get as far away from each other as possible
- Why? Because like charges repel…they want to be far away from each other.

6

Domains

- Electron domain – a region of space where electrons can be found
  - Bonding domains – electron pairs that are involved in bonds between two atoms, doesn't matter if it is a single, double or triple bond.
  - Nonbonding domains – valence electrons that are associated with a single atom.
- Electron domains keep as far away as possible from each other.

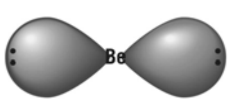
7

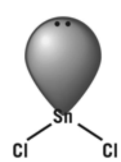
Geometry and Domains

- Let's look at $BeCl_2$ and $SnCl_2$
- What are their Lewis Structures?

- When we draw them, we will tend to draw them linear.
- Does this mean they have linear geometry?
- NO!

8





- $BeCl_2$ is linear.
- $SnCl_2$ is bent.
- We can use what we know about bonding and nonbonding domains to predict the molecular shape.
- If a molecule has nonbonding domains, the shape will deviate from the 5 basic shapes.
- Consider the handout on VSEPR structures.
- Let's look at all the molecules we drew in Chapter 8 and determine their molecular shape.

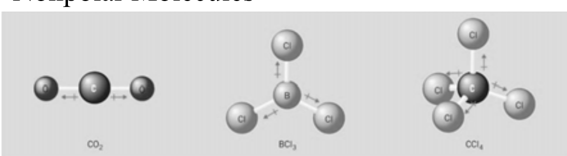
9

9.3 Molecular symmetry affects the polarity of molecules

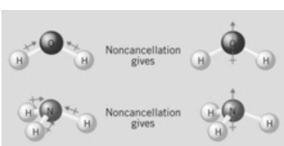
- Remember polar bonds?
- Polar bonds can result in a polar molecule, depending on the geometry of the molecule.
- To determine polarity:
  - Draw Lewis Structure
  - Determine the Molecular Geometry
  - "See if you move" – think of it as a tug-of-war.

10

Nonpolar Molecules



Polar Molecules

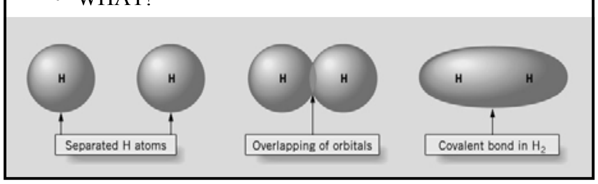


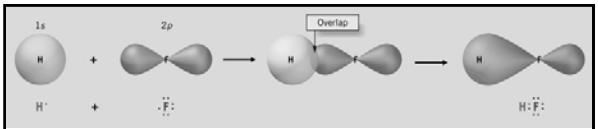
Let's go back to those molecules from Chapter 8 and determine if they are polar or nonpolar.

11

9.4 Valence Bond Theory

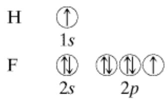
- A bond between two atoms is formed when a **pair of electrons** with their **spins paired** is shared by two **overlapping** atomic orbitals, one orbital from each of the atoms joined by the bond.
- WHAT!





- Atoms tend to position themselves so the maximum amount of orbital overlap occurs
- This yields the minimum potential energy and the strongest bonds.

$$H\cdot + \cdot\ddot{F}: \longrightarrow H—\ddot{F}:$$

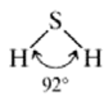


F (in HF)

(Colored arrow is the H electron.)

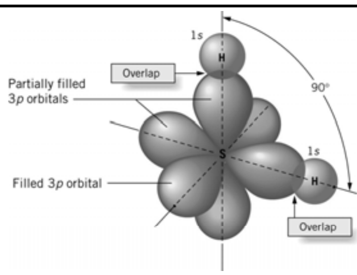
H_2S

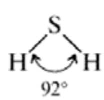
- How does VB balance with bond angles?



- What orbitals in S will overlap with the 1s orbitals of the hydrogen atoms?
- Note: two orbitals from different atoms never overlap simultaneously with opposite ends of the same p-orbital.

14





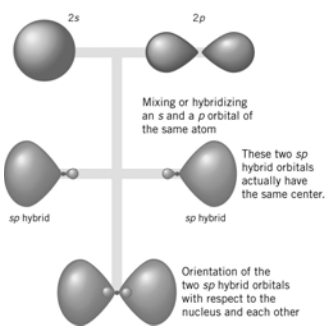
- There is a clear problem!
- The geometry of the p-orbitals dictates an angle of 90˚.
- What was the experimental angle of H_2S?
- How can this be explained?

15

9.5 Hybrid Orbitals

- Think back to sixth grade biology.
- Remember Mendel?
- He made hybrids of pea plants by mixing purebreds.
- We will apply a similar method to atomic orbitals (s, p, d).
- Atomic orbitals can be hybridized to generate a new set of directional orbitals.
- These mixed orbitals match the orbital geometry of the compounds.
- Remember, all electrons around the central atom must be in orbitals --- whether they are nonbonding electrons or bonding electrons.
- What do they look like?

16



Mixing the 2*s* and (one) 2*p* atomic orbital results in a pair of ***sp* hybrid orbitals**. Note that the large lobes of these hybrid orbitals point in opposite directions.

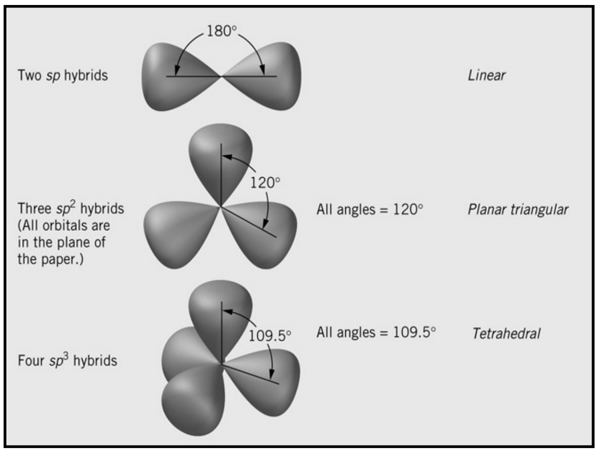
17

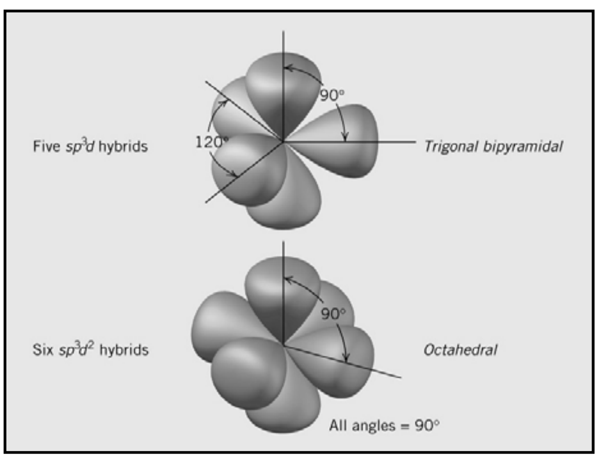
- When an *s* orbital combines with two *p* orbitals, three sp^2 hybrid orbitals are formed.
- When an *s* orbital combines with three *p* orbitals, four sp^3 hybrid orbitals are formed.
- When an *s* orbital combines with three *p* orbitals and a *d* orbital, five sp^3d hybrid orbitals are formed.
- When an *s* orbital combines with three *p* orbitals and two *d* orbitals, six sp^3d^2 hybrid orbitals are formed.
- *The number of orbitals is conserved: the number of hybrid orbitals in a set equals the number of atomic orbitals used to form the set.*

18

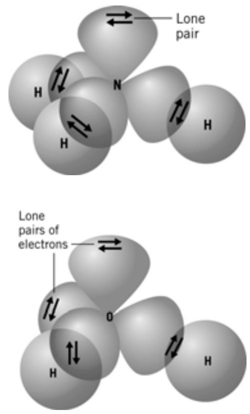
Atomic orbitals that contribute to hybridization	# of hybrid orbitals	Hybrid orbitals formed	Orbitals left over (usually participate in double/triple bonds)
	2		
	3		
	4		none
$s + p_x + p_y + p_z + d$	5	sp^3d	none
$s + p_x + p_y + p_z + d + d$	6	sp^3d^2	none

19





- Molecules with nonbonding domains can also be described with hybrid orbitals
- Lone pairs occupy a bit more volume than bonding electron pairs
- NH_3 is tetrahedral and should have a bond angle of 109.5˚.
- Experimentally, it has a bond angle of 107º.
- This is due to the lone pair electrons.
- Remember the VSEPR Model.
- A similar phenomena is seen in H_2O, but oxygen has two lone pairs of electrons resulting in an angle of 104.5º.
- Let's go back to the molecules from Chapter 8 and determine the hybridization.

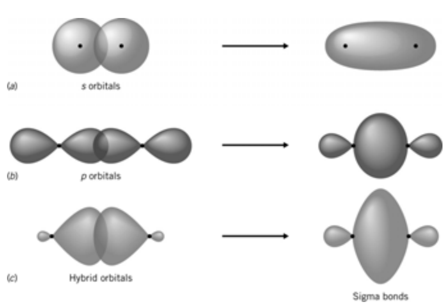


9.6 Hybrid Orbitals and Multiple Bonds

- There are two types of bonds that comprise single, double and triple bonds.
  - **Sigma bond** (σ) – when electron density is between the nuclei of the two atoms
  - **Pi bond** (π) – when electron density is divided between two separate regions.

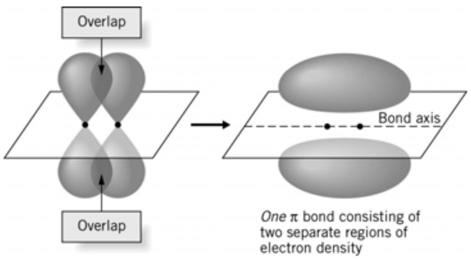
23

σ bonds



24

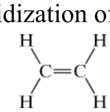
π bonds



25

Multiple Bonds

- Multiple bonds almost always consist of a **single sigma bond** *and* **one or more pi bonds**
- The pi bonds are formed from the p orbitals that are not involved in the hybrid orbitals.
- What is the hybridization of the carbons in ethene?



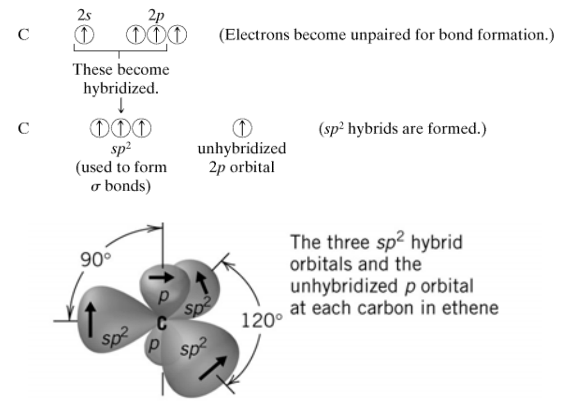
ethene

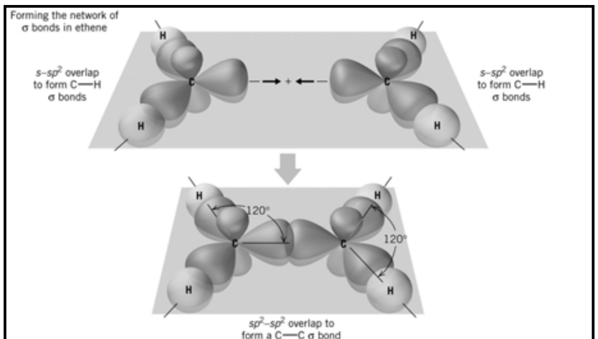
26

Ethene Hybridization

- The carbons have 3 bonding domains.
- Therefore, they are each sp^2 hybridized.
- To make the sp^2 hybrid orbitals, one s orbital and two p orbitals were mixed.
- What is left over?

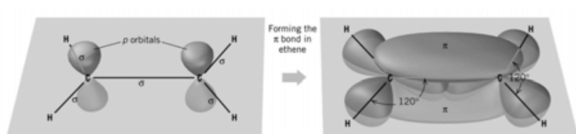
27





- The sp^2 hybrid orbitals overlap to form a sigma bond.
- Where does the double bond come from?

29

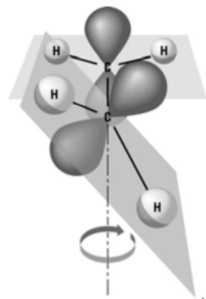


- The p-orbitals on each carbon that is left over (after hybridization) will form a π overlap.
- A double bond consists of a sigma and a pi overlap (σ + π)

30

Bonds and Rotation

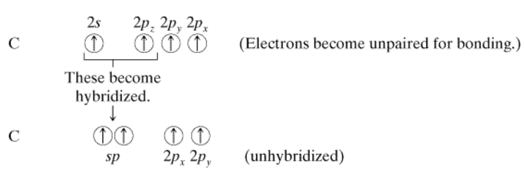
- Groups connected by single bonds can freely rotate
- Rotation is restricted around double bonds.
- The overlap for the pi bond would be lost.



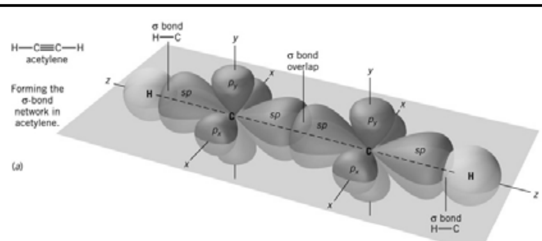
31

Triple Bonds

- Let's examine acetylene (H-C≡C-H)
- What is the hybridization of the carbons?

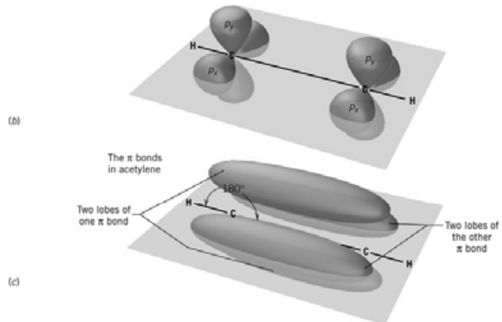


32



- The sp hybrid orbital is formed from one s and one p orbital.
- There are still two p orbitals left.

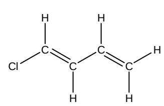
33

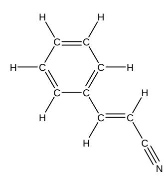


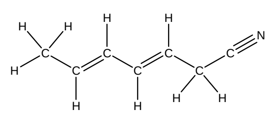
- A triple bonds results from a sigma bond and two pi bonds ($\sigma + \pi + \pi$).

34

How many sigma and pi bonds in the following molecules?







35

VB Theory Summary

1. The basic framework of the molecule is determined by the arrangement of its sigma-bonds
2. Hybrid orbitals are used by an atom to form its sigma-bonds and to hold the lone pairs of electrons.
3. The number of hybrid orbitals needed by an atom in a structure equals the number of atoms to which it is bonded plus the number of lone pairs of electrons in its valence shell.
4. When there is a **double bond** in a molecule, it consists of **one sigma** and one **pi bond**
5. When there is a **triple bond**, it consists of **one sigma** and **two pi bonds**

36