

## Beyond Lewis Structures

### Exceptions to the Octet Rule Model

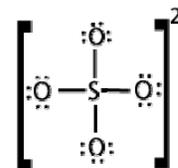
- **Hydrogen** is an exception to the octet rule because it fills its outer energy level with only **2 electrons**.
- The second row elements B and Be often have fewer than eight electrons around them in their compounds. **Beryllium** will only have **4 electrons** and **boron** will only have **6 electrons** in their structural formulas. These electron deficient compounds are very reactive.
- The second-row elements **carbon, nitrogen, oxygen and fluorine always obey the octet rule** and must have 8 electrons in their structural formulas. Second row elements never exceed the octet rule, since their valence orbitals (2s and 2p) can accommodate only 8 electrons.
- **Third row and heavier elements** often satisfy the octet rule but **can exceed the octet rule** by using their empty valence d orbitals. (ex:  $\text{PCl}_5$ ,  $\text{SF}_6$ )
- When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first. **If electrons remain after the octet rule has been satisfied, then place them on the central atom.**

### Paramagnetism & Diamagnetism

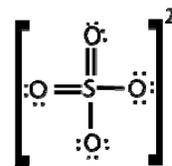
- Most materials have no magnetism until they are placed in a magnetic field. However, in the presence of such a field, magnetism of two types can be induced.
- **Paramagnetism** causes a substance to be **attracted** to the inducing magnetic field due to having **unpaired electrons**.
- **Diamagnetism** causes the substance to be **repelled** from the inducing magnetic field due to having **all paired electrons**.
- To determine whether or not an **element** is paramagnetic or diamagnetic, you need to understand the element's electron configuration and orbital diagram.
  - Example 1: H:  $1s^1$  The s orbital can hold 2 electrons, with only 1 electron it has unpaired electrons and is paramagnetic.  
Orbital diagram:  $\uparrow$
  - Example 2: He:  $1s^2$  The s orbital can hold 2 electrons, with 2 electrons the orbital is full and is diamagnetic.  
Orbital diagram:  $\uparrow\downarrow$
  - Example 3: O:  $1s^2 2s^2 2p^4$  Following the Aufbau and Hund rules, oxygen has a full 1s orbital a full 2s orbital. The 2p orbitals has one full orbital and 2 half filled orbitals so it is paramagnetic.  
Orbital diagram:  $\uparrow\downarrow \uparrow \uparrow$
- A quick way to understand: Elements in group 2, group 12 and group 18 have all paired electrons and are diamagnetic. All other elements are paramagnetic.
- Most molecules have paired electrons and are diamagnetic. NO &  $\text{NO}_2$  have an odd numbers of electrons and are paramagnetic.
- Through experimentation, scientists have discovered that the liquid  $\text{O}_2$  molecule is paramagnetic. This fact violates the octet rule and provides evidence that other models of bonding and structure may work better.

### Formal Charge

- The formal charge of an atom in a molecule is the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule.
- **Formal Charge = valence e<sup>-</sup> on free atom (from periodic table) – dots touching the atom**
- When dealing with bonds, count only the dot (end) next to the atom.
- For example: Calculate the formal charge for each element in the structural formula shown to the right.
  - Oxygen:  $\text{val. e}^- - \text{\#dots}$ 
    - Formal Charge =  $(6) - (7) = -1$
  - Sulfur:
    - Formal Charge =  $(6) - (4) = +2$
- Any negative formal charges are expected to reside on the most electronegative atoms. Oxygen has a higher electronegativity so it makes sense that it has the negative formal charge.

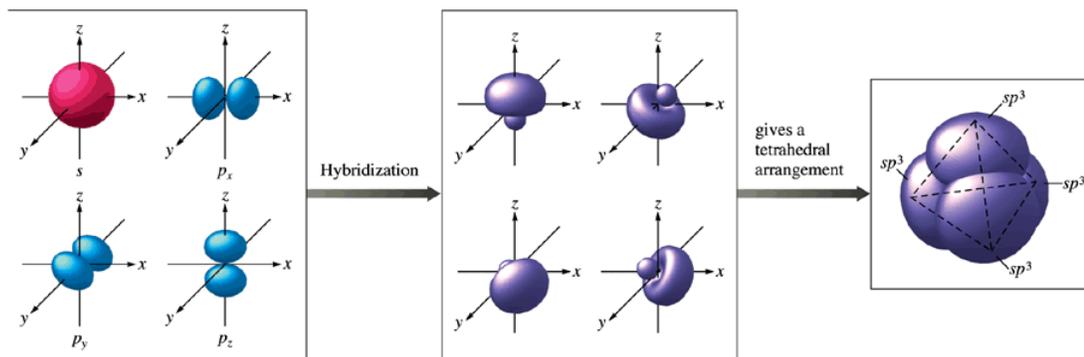


- But, atoms in molecules are best suited when they have formal charges as close to zero as possible.
- Consider an alternative model for sulfate which brings formal charge lower:
- The formal charge for each element in the structural formula shown to the right.
  - Oxygen<sub>(single)</sub>:  $\text{val. } e^- - \text{dots}$ 
    - Formal Charge =  $(6) - (7) = -1$
  - Oxygen<sub>(double)</sub>:
    - Formal Charge =  $(6) - (6) = 0$
  - Sulfur:
    - Formal Charge =  $(6) - (6) = 0$



## Hybridization

- **sp<sup>3</sup> Hybridization**
  - Consider methane (CH<sub>4</sub>).
    - The electron configuration of carbon is [He] 2s<sup>2</sup> 2p<sup>2</sup>. The 2p and 2s atomic orbitals of carbon will lead to two different type of C—H bonds: those from the overlap of the carbon 2p orbital with the 1s orbital of hydrogen and those from the overlap of a carbon 2s orbital with the 1s orbital of hydrogen.
    - This is not the case. The methane molecule is tetrahedral with bond angles of 109.5°. Carbon adopts a set of orbitals other than its “native” 2s and 2p orbitals to bond to the hydrogen atoms in forming the methane molecule.
    - The 2s and 2p orbitals present on an isolated carbon atom may not be the best set of orbitals for bonding. It makes sense to assume that the carbon atom has four equivalent atomic orbitals arranged tetrahedrally.
    - Such a set of orbitals can be obtained by combining the carbon 2s and 2p orbitals as shown below.



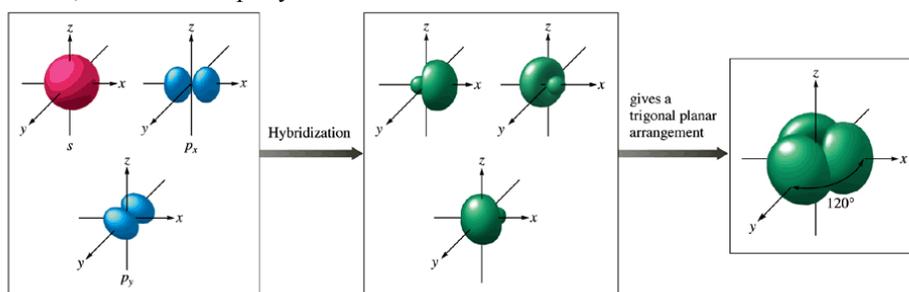
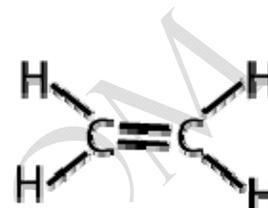
- This mixing of the native atomic orbitals to form special orbitals for bonding is called **hybridization**.
  - The four new orbitals are called sp<sup>3</sup> orbitals because they are formed from one s orbital and three p orbitals (s<sup>1</sup>p<sup>3</sup>).
  - The carbon atom undergoes sp<sup>3</sup> hybridization or is sp<sup>3</sup> hybridized.
- There are 5 types of hybridization; they are listed below. **Hybridization can best be understood by counting the number of effective pair or “bonding sites”.** A bonding site is any bond (single, double and triple bonds are called counted as one bonding site) or unshared pair of electrons on the central atom in a molecule.

- The table below is a guide to determining hybridization of a molecule. Specific details on each type of hybridization will follow.

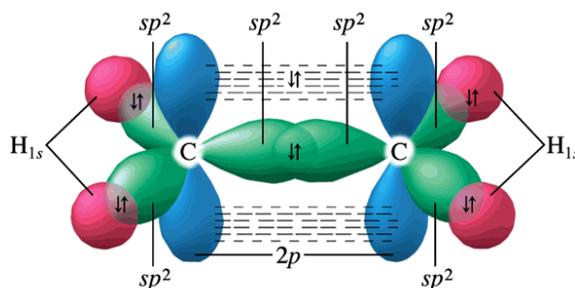
# of Bonding Sites	Hybridization
2	sp
3	sp <sup>2</sup>
4	sp <sup>3</sup>
5	dsp <sup>3</sup>
6	d <sup>2</sup> sp <sup>3</sup>

- sp<sup>2</sup> hybridization**

- Ethylene (C<sub>2</sub>H<sub>4</sub>) has a double bond act as one bonding site, and two single bonds counting as one bonding site each; so each carbon is surrounded by three bonding sites.
- Since one 2s and two 2p orbitals are used to form these hybrid orbitals, this is called sp<sup>2</sup> hybridization.



- In forming the sp<sup>2</sup> orbitals, one 2p orbital on carbon has not been used. This remaining p orbital (p<sub>z</sub>) is oriented perpendicular to the plane of the sp<sup>2</sup> orbitals.
- The three sp<sup>2</sup> orbitals on each carbon can be used to share electrons, as shown below.

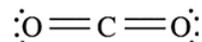


- In each of these bonds, the electron pair is shared in an area centered on a line running between the atoms. This type of covalent bond is called a **sigma(σ) bond**. In the ethylene molecule, the σ bonds are formed using sp<sup>2</sup> orbitals on each carbon atom and the 1s orbital on each hydrogen atom.
- The second bond must therefore result from sharing an electron pair in the space above and below the σ bond.
- The parallel p orbitals can share an electron pair, to form a **pi(π) bond**.
- σ bonds are formed from orbitals whose lobes point toward each other, but π bonds result from parallel orbitals. A double bond always consists of one σ bond where the electrons are located between the atoms and one π bond which occupies the space above and below the σ bond.

Type of bond	# of sigma(σ) bond	# of pi(π) bonds
single bond	1	0
double bond	1	1
triple bond	1	2

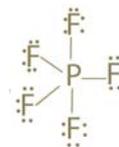
- **sp hybridization**

- In the CO<sub>2</sub> molecule the carbon has **two bonding sites** (each double bond is one bonding site.).
- Two bonding sites around an atom will always require sp hybridization of that atom.



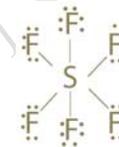
- **dsp<sup>3</sup> hybridization\***

- Since **five bonding sites** are needed for atoms such as phosphorus in PF<sub>5</sub>, a dsp<sup>3</sup> hybridization is necessary.
- The dsp<sup>3</sup> hybridized phosphorus atom in PF<sub>5</sub> molecule uses its 5 dsp<sup>3</sup> orbitals to share electrons with five chlorine atoms.



- **d<sup>2</sup>sp<sup>3</sup> hybridization\***

- Since **six bonding sites** are needed for atoms such as sulfur in SF<sub>6</sub>, a d<sup>2</sup>sp<sup>3</sup> hybridization is necessary.
- A set of six effective pairs around a given atom always requires an octahedral arrangement which in turn requires d<sup>2</sup>sp<sup>3</sup> hybridization of that atom.



**\* Current evidence suggests that hybridization involving d orbitals does not exist, and there is controversy about the need to teach any hybridization. Until this controversy is settled hybridization is a model that will be used to better understand molecular geometry.**

**Homework:**

1. Name four elements that follow the octet rule.
2. Name two elements that have fewer than eight electrons around them in their compounds.
3. Why can elements in the third row and greater can exceed their octet?
4. When writing Lewis structures and the octet must be exceeded, where should the additional electrons be placed?
5. What term is used to describe substances in which all the electrons are paired?
6. What effect does an external magnet have on a diamagnetic substance?
7. What term is used to describe substances in which not all the electrons are paired?
8. What effect does an external magnet have on a paramagnetic substance?
9. Identify each of the following elements as being either paramagnetic or diamagnetic.
 

a. Magnesium -	b. Argon -
c. Cobalt -	d. Phosphorus -
e. Mercury -	f. Potassium -

10. Experimental evidence has shown that oxygen molecules are paramagnetic. With this in mind, draw the irregular Lewis structure for the oxygen ( $O_2$ ) molecule.

11. **Draw structural formulas** for the following covalent compounds that do not follow the octet rule and write how they do not follow the octet rule. **Determine the formal charge** for each element in the molecule.



12. Nitrogen monoxide (NO) and nitrogen dioxide ( $NO_2$ ) have an odd number of total electrons. Use your knowledge of formal charge to determine the correct Lewis structures for each of the molecules. You must show a formal charge calculation for each atom in each possible Lewis structure.

Name	Formula	Lewis Structure	Hybridization of central element	# sigma bonds	# pi bonds
phosphate ion					
boron trifluoride					
phosphorus pentachloride					
carbon dioxide					
ammonia					
methane					
diatomic nitrogen					
sulfur dioxide					

Name	Formula	Lewis Structure	Hybridization of central element	# sigma bond	# pi bonds
chlorine trifluoride					
nitrate ion					
carbonate ion					
hydrocyanic acid	HCN				
dihydrogen monoxide					
silicon tetrafluoride					
beryllium dichloride					

At the completion of this assignment you will be prepared to take the following Chapter 5 on-line quizzes:

- diamagnetic or paramagnetic quiz
- elemental diamagnetic or paramagnetic quiz
- formal charge quiz 1
- hybridization quiz 1
- hybridization quiz 2
- sigma and pi bonds quiz 1
- sigma and pi bonds quiz 2
- sigma and pi bonds quiz 3
- sigma and pi bonds quiz 4
- sigma and pi bonds quiz 5