

CHEMISTRY

Chapter 8

Advanced Theories of Covalent Bonding



CHAPTER 8: ADVANCED THEORIES OF COVALENT BONDING

- 8.1 Valence Bond Theory
- 8.2 Hybrid Atomic Orbitals
- 8.3 Multiple Bonds
- 8.4 Molecular Orbital Theory

BONDING THEORIES

Lewis Theory and VSEPR

- Dots arrayed about a central atom represent bonds and lone pairs of electrons.
- The arrangement of atoms in three-dimensions and molecular geometry can be predicted.
- Molecular polarity can also be predicted from the molecular structure.

Valence Bond Theory

- Electrons are in orbitals on each atom.
- Orbitals may be hybrids and overlapping orbitals in space form bonds.

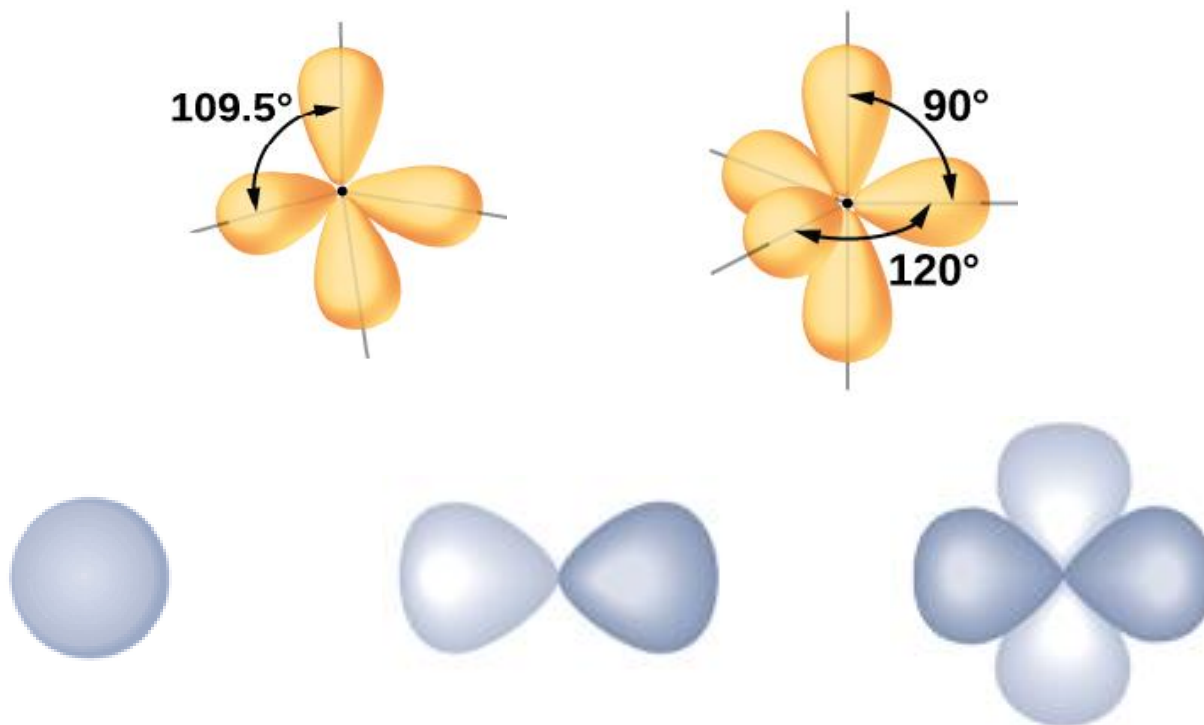
Molecular Orbital Theory

- Electrons are in orbitals spread over the entire molecule rather than attached to specific atoms.
- This model accommodates experimental observations of magnetism not compatible with other, simpler theories.

8.1 VALENCE BOND THEORY

VSEPR Theory Weaknesses

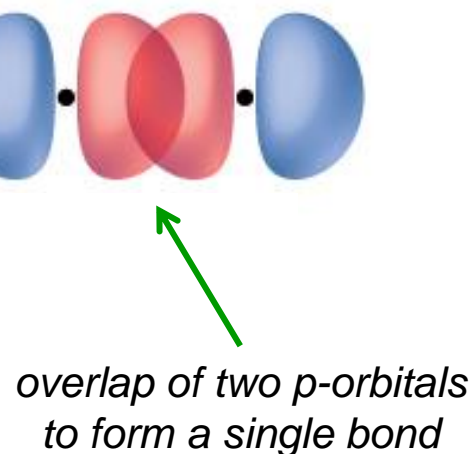
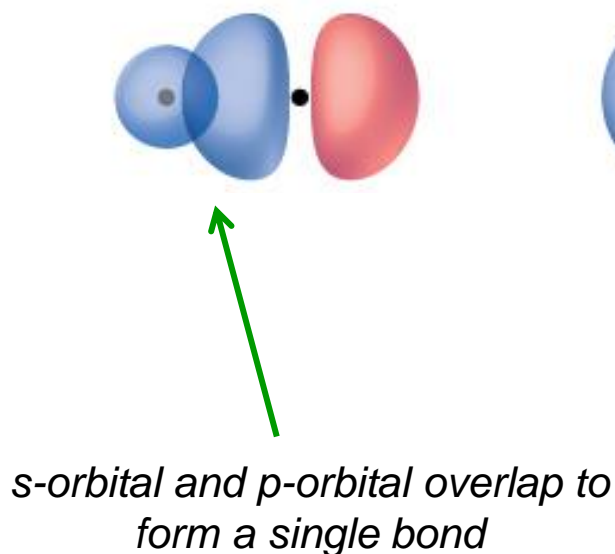
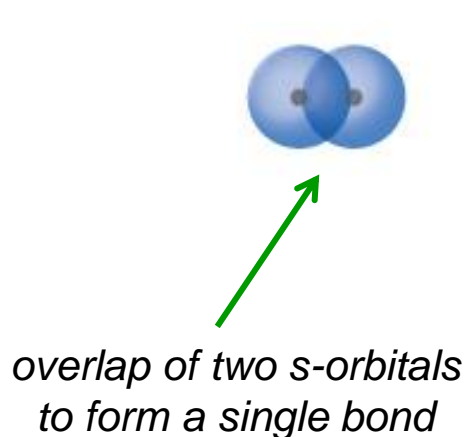
- VSEPR is model that can be used to predict three-dimensional shapes of molecules.
- Bond angles seen in VSEPR models such as 109° and 120° do not agree with the geometries of s , p , and d atomic orbital.



8.1 VALENCE BOND THEORY

Valence Bond Theory

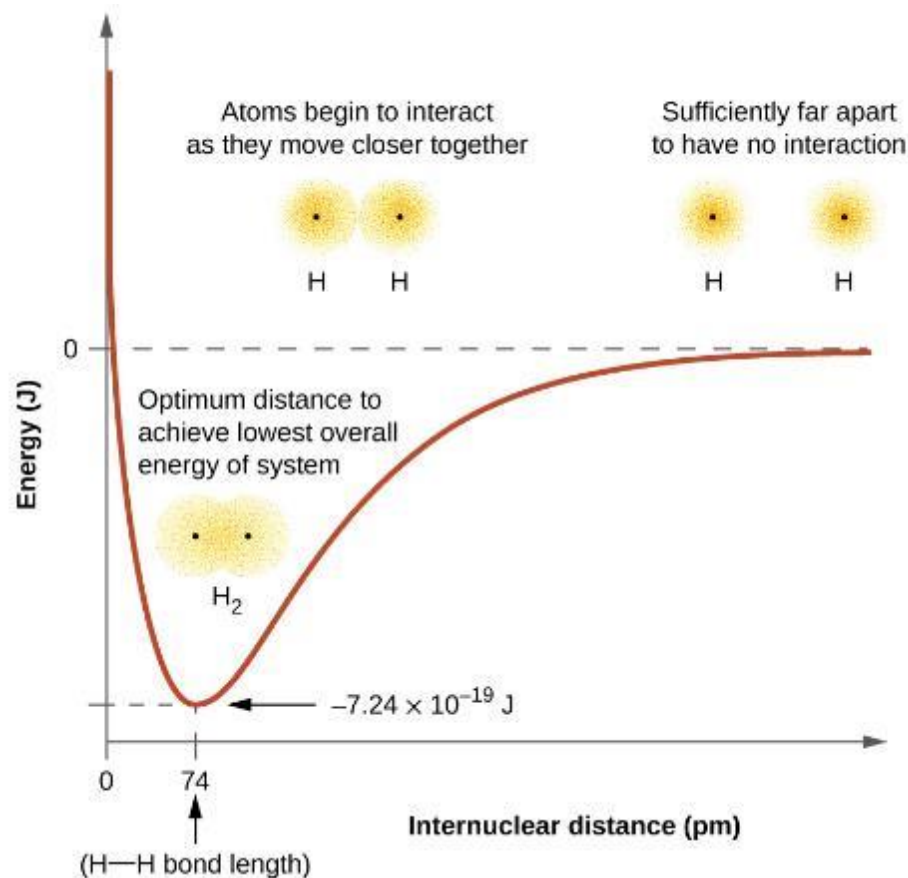
- The covalent overlap of atomic orbitals, each containing a single electron, that yields an electron pair and a bond between two atoms is best described by valence bond theory.
- In valence bond theory, orbitals overlap when a portion of one atomic orbital and a portion of a second atomic orbital occupy the same region of space.



8.1 VALENCE BOND THEORY

Energy and Orbital Overlap

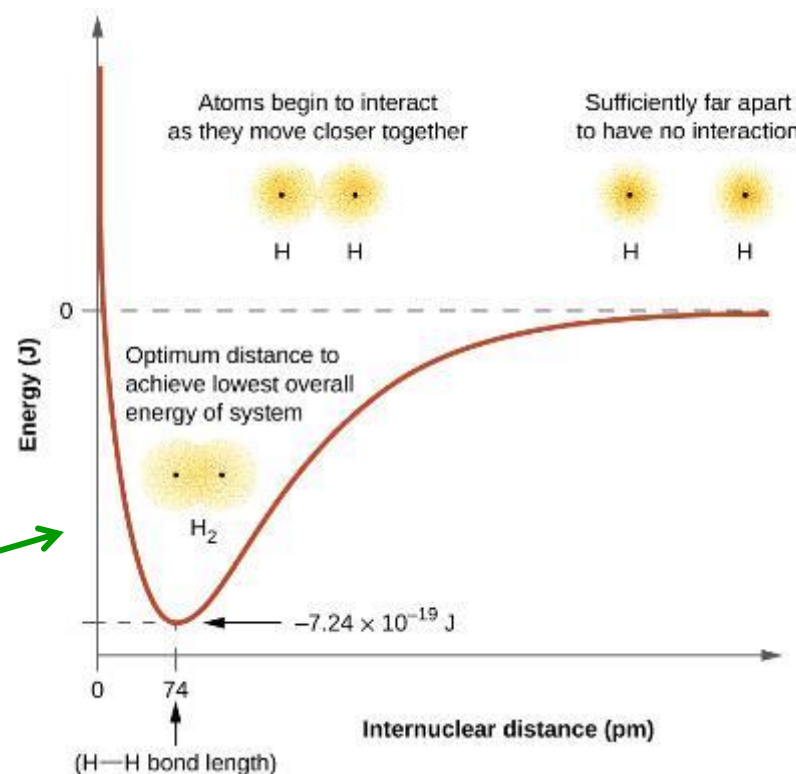
- The energy of a system depends upon orbital overlap.
- No overlap occurs when atoms are far apart and the energy is zero.
- As orbitals approach and begin to overlap, each electron begins to feel the attraction of the nucleus in the other atom.
- Electrons also begin to repel each other, as do the nuclei.
- While separated, attractive forces are greater than repulsive forces, and the energy of the system decreases; a bond begins to form.



8.1 VALENCE BOND THEORY

Energy and Orbital Overlap (*continued*)

- While moving together, overlap increases, and both attractions and repulsions increase.
- At some specific distance between the atoms the energy reaches its lowest value.
- This optimum distance between is where a stable bond between the two atoms form.

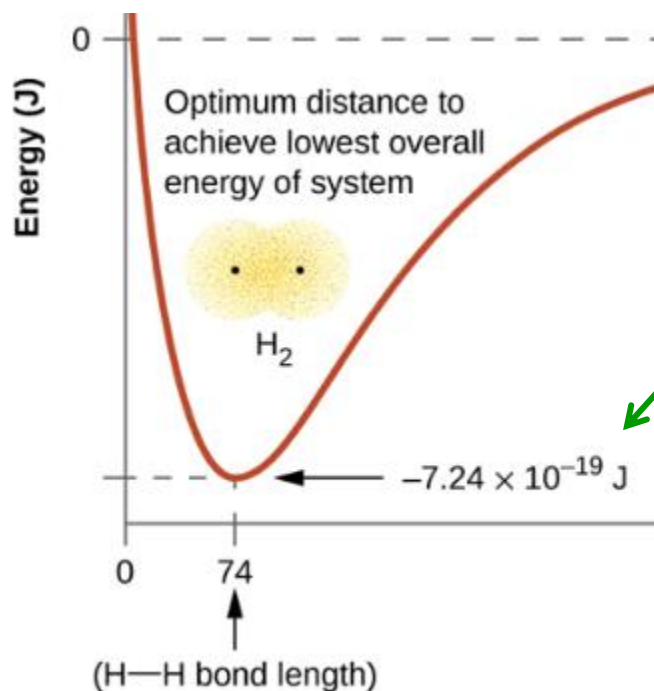


What is happening on the left side of the plot?

8.1 VALENCE BOND THEORY

Bond Energy and Bond Length

- The bond energy is the ΔE between the energy minimum (at the bond length) and the two separated atoms.
- This is the energy required to separate the atoms completely and break the bond.
- This is therefore also the energy released when the bond is formed.



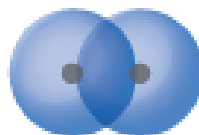
$7.24 \times 10^{-19} \text{ J}$ required to break one H-H bond.

What is the energy required to break one mole of H-H bonds?

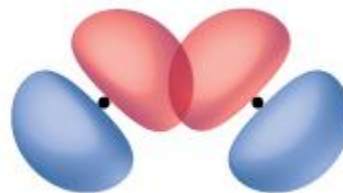
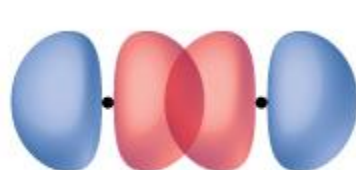
8.1 VALENCE BOND THEORY

Orbital Overlap: Distance and Orientation

- The formation of a bond depends upon the distance between atomic nuclei and the orientation of the orbitals involved.
- Orbitals overlap most effectively when they are oriented on a direct line between two nuclei.
- The overlap between two s-orbitals is simple because they are spherically symmetric.



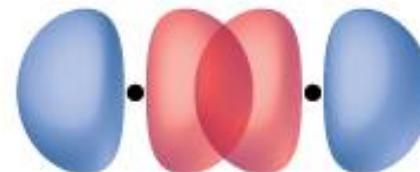
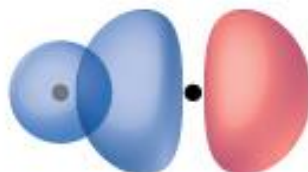
- When two *p*-orbitals interact to form a bond, orientation is important so that overlap is maximized.



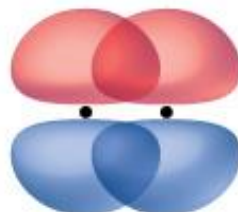
8.1 VALENCE BOND THEORY

Sigma (σ) and Pi (π) Bonds

- Sigma (σ) bonds are produced when overlap occurs between:
 - two s-orbitals
 - one s-orbital and one p-orbital
 - two p-orbitals



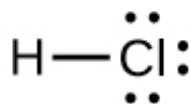
- Pi (π) bonds are produced when two p-orbitals overlap in a side-by-side orientation.



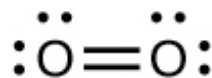
8.1 VALENCE BOND THEORY

Sigma (σ) and Pi (π) Bonds

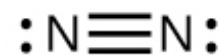
- Single bonds are always σ -bonds.
- Multiple bonds are a combination of σ -bonds and π -bonds.
 - double bond: one σ -bond, one π -bond
 - triple bond: one σ -bond, two π -bond
- Molecules containing these types of bonds are shown below and the bonds will be described in more detail later in the chapter.



One σ bond
No π bonds



One σ bond
One π bond

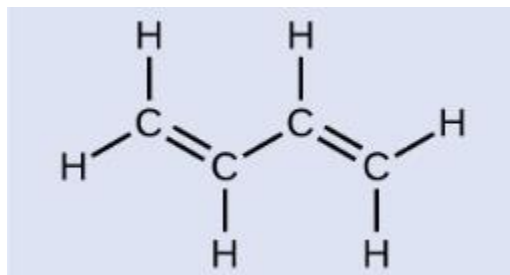


One σ bond
Two π bonds

8.1 VALENCE BOND THEORY

Example 8.1

Butadiene, C_4H_6 , is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.

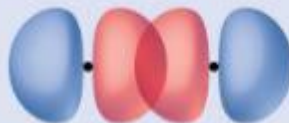


Example 8.1 – Check Your Learning

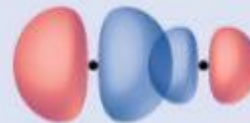
Identify the type of bond depicted in each illustration.



(a)



(b)

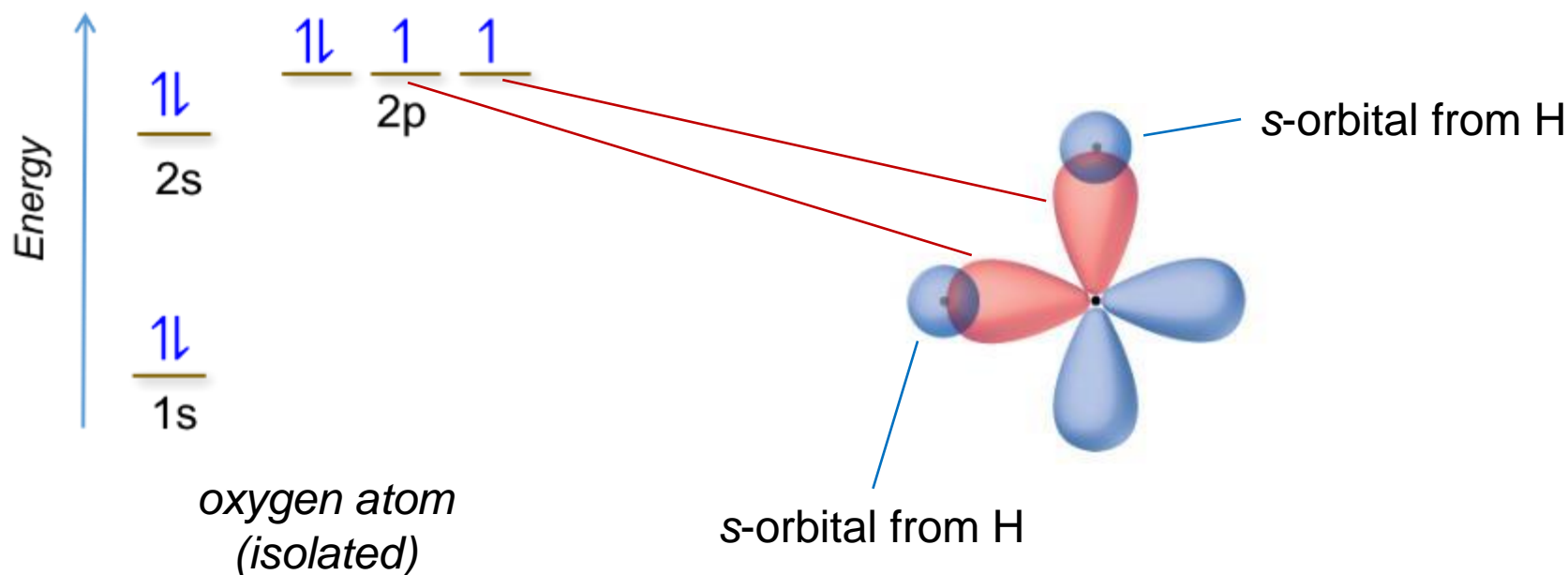


(c)

8.2 HYBRID ATOMIC ORBITALS

Describing Orbital Overlap for Water

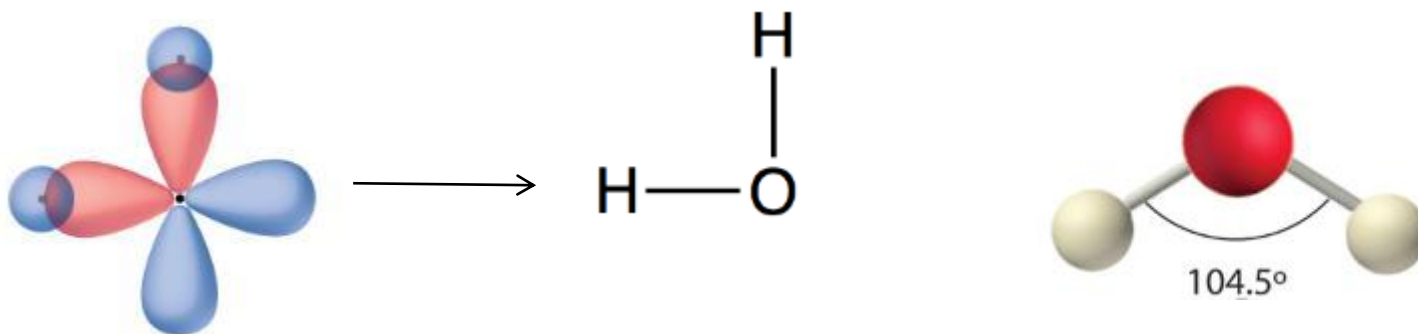
- A water molecule is a central oxygen atom bound to two hydrogen atoms.
- The electron configuration for oxygen is $1s^2 2s^2 2p^4$
- It would make sense to predict that each of the $\frac{1}{2}$ filled p-orbitals would overlap with a spherical s-orbital from a hydrogen atom.



8.2 HYBRID ATOMIC ORBITALS

Describing Orbital Overlap for Water

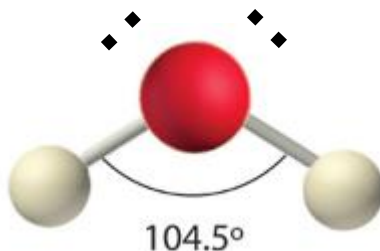
- The problem is that this model gives a molecular structure that is does not match experimental evidence.
- The simple orbital overlap results in a molecule with a 90° bond angle whereas experimental evidence shows that the bond angle for water is 104.9° .



8.2 HYBRID ATOMIC ORBITALS

Describing Orbital Overlap for Water

- Returning to VSEPR theory, there are four regions of electron density around an oxygen atom.
- This means that water is in the tetrahedral group.
- Water has two lone pairs of electrons and therefore has bent molecular geometry.

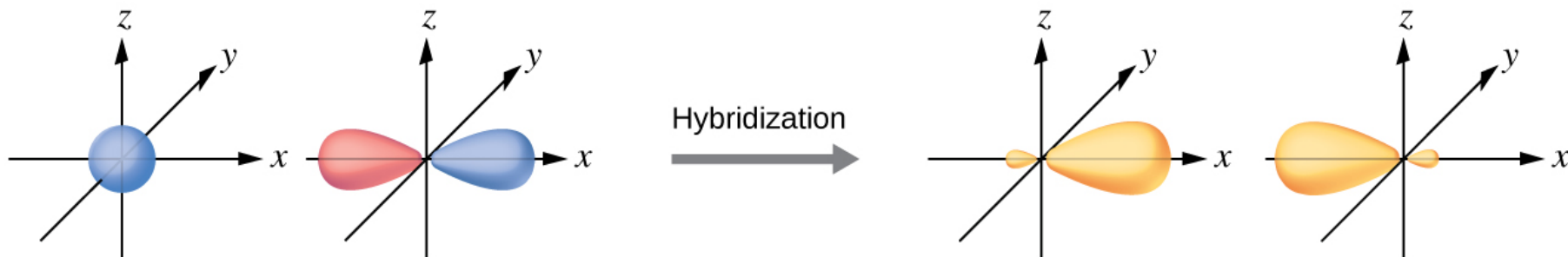


- The bond angles observed experimentally show that valence bond theory must include a hybridization component in order to be an accurate model for bonding.

8.2 HYBRID ATOMIC ORBITALS

Hybrid Orbitals ...

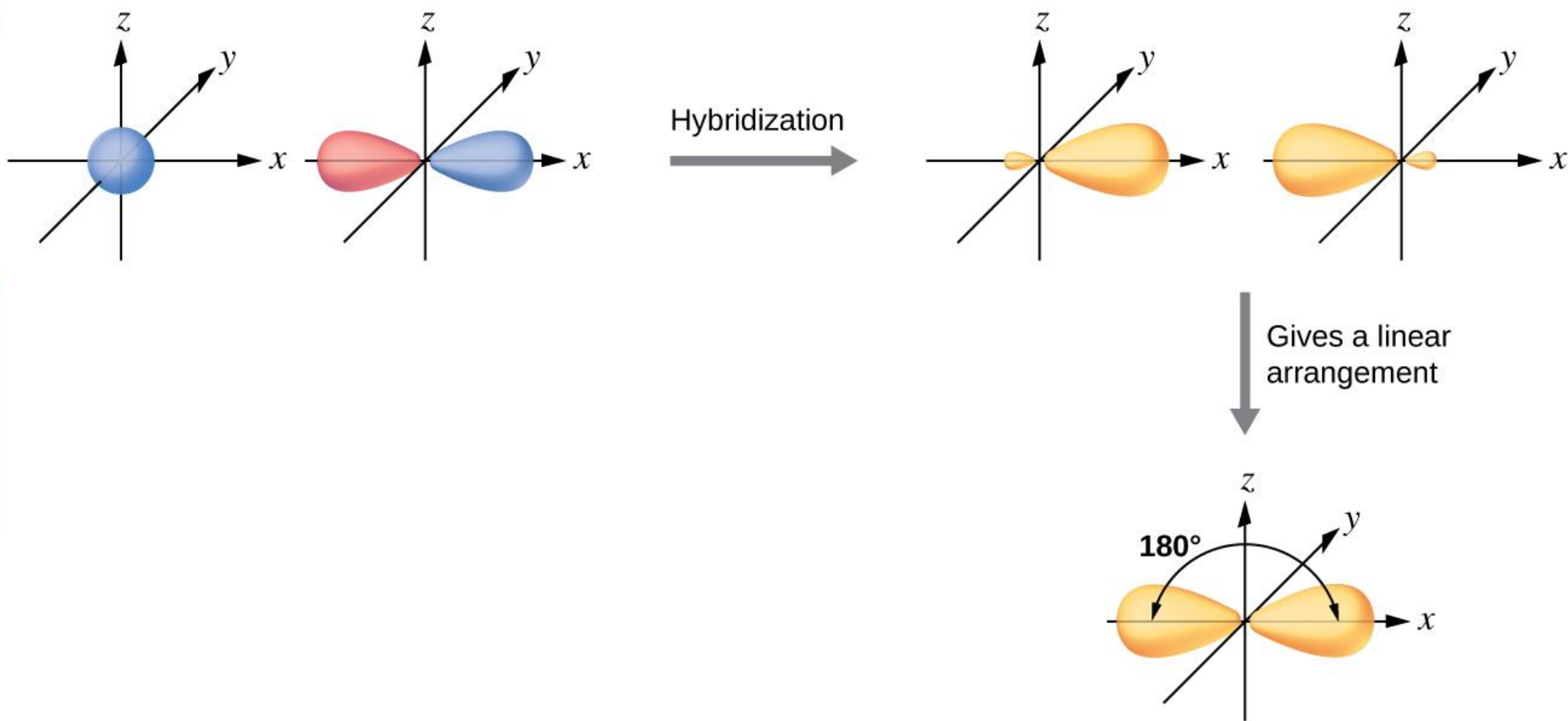
- do not exist in an isolated atom.
- only form when atoms come together to bond.
- have shapes/orientations very different from atomic orbitals.
- are generated by combining a set of atomic orbitals;
 - # of hybrid orbitals created = # of atomic orbitals used.
- in a set are equivalent in shape and energy.
- depend upon electron-pair geometry and VSEPR theory.
- overlap to form σ -bonds; unhybridized orbitals must be used to form π -bonds.



8.2 HYBRID ATOMIC ORBITALS

sp Hybridization

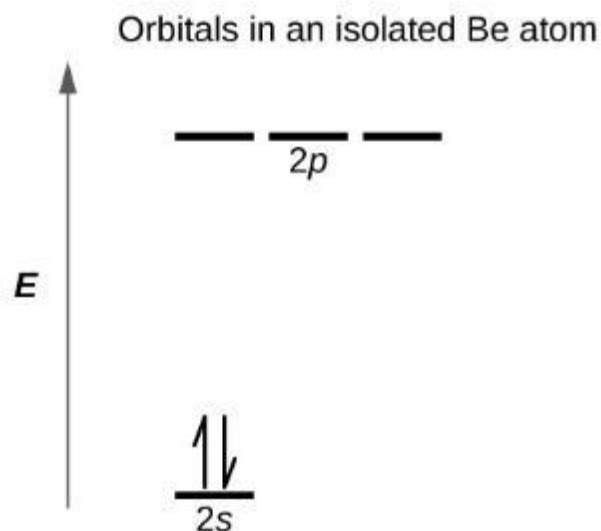
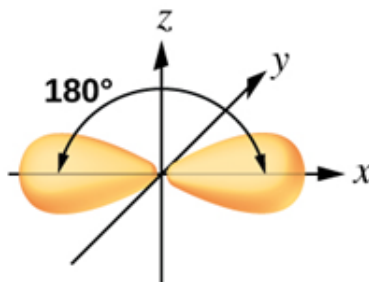
- One valence s-orbital mixes with a valence *p*-orbital to yield two equivalent sp hybrid orbitals.



8.2 HYBRID ATOMIC ORBITALS

***sp* Hybridization**

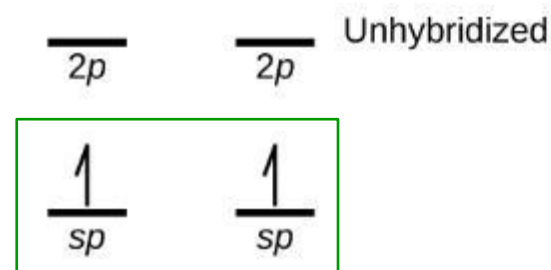
- One valence s-orbital mixes with a valence *p*-orbital to yield two equivalent *sp* hybrid orbitals.



Hybridization



Orbitals in the *sp* hybridized Be in BeCl_2

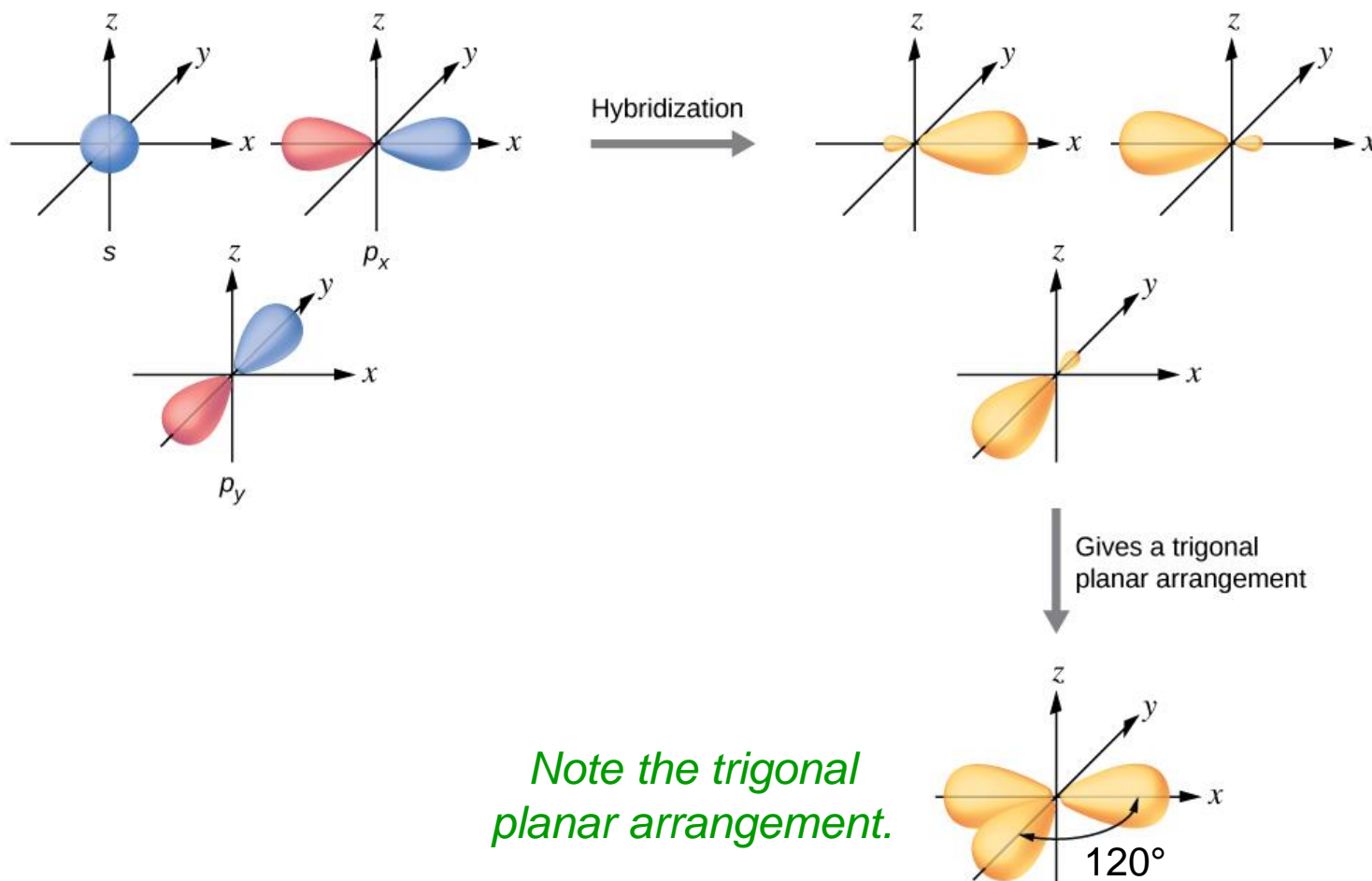


*These hybrid *sp* orbitals on Be overlap with Cl atomic orbitals.*

8.2 HYBRID ATOMIC ORBITALS

sp^2 Hybridization

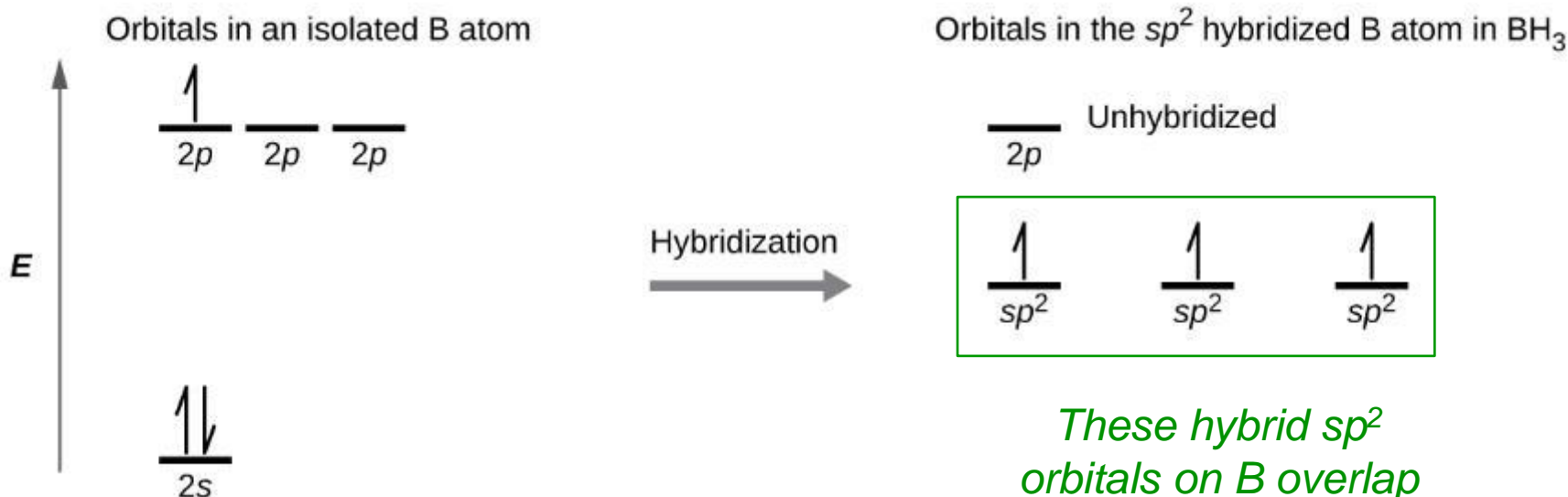
- Any central atom surrounded by three regions of electron density forms a set of three sp^2 hybrid orbitals.



8.2 HYBRID ATOMIC ORBITALS

sp^2 Hybridization

- Any central atom surrounded by three regions of electron density forms a set of three sp^2 hybrid orbitals.

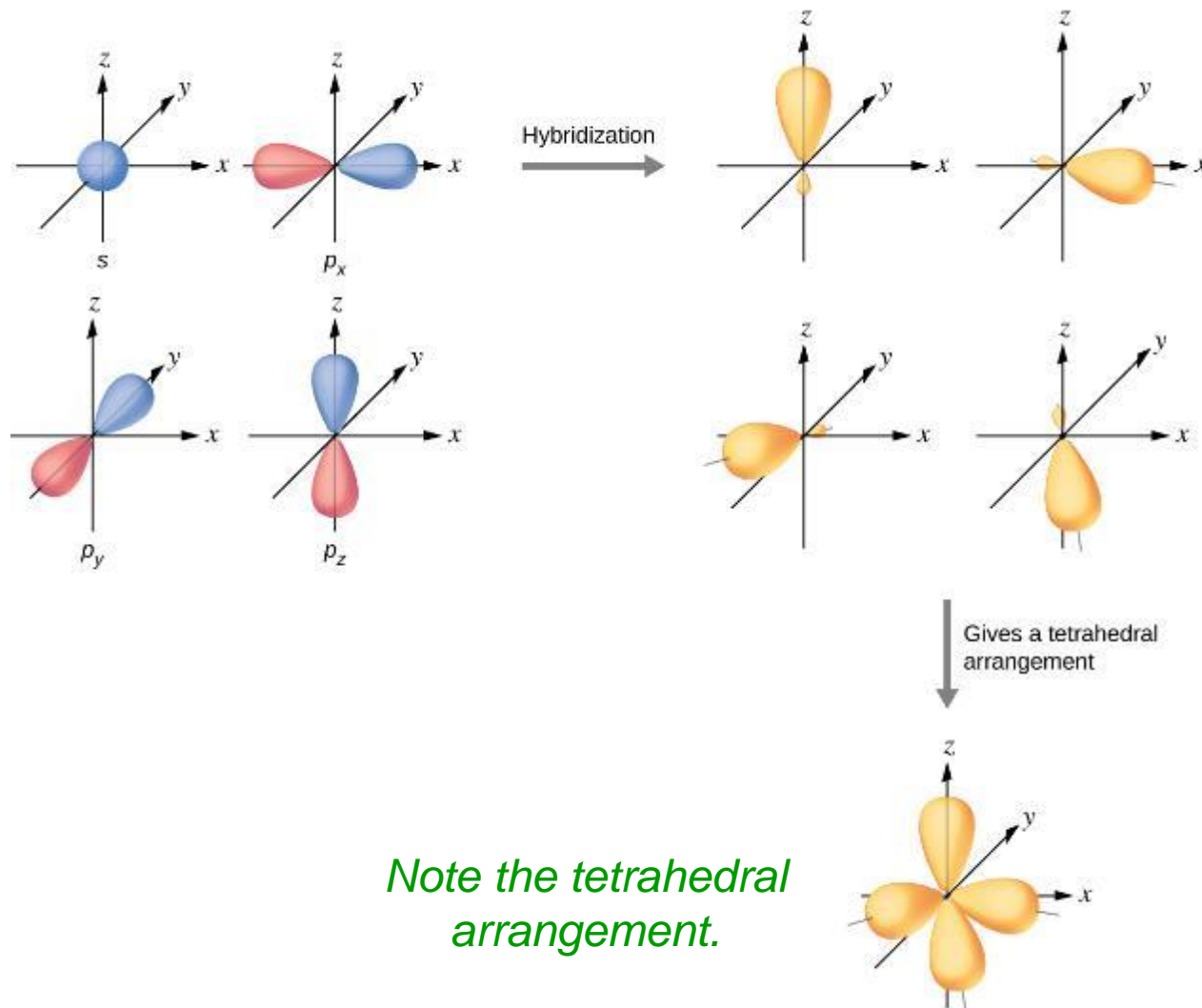


These hybrid sp^2 orbitals on B overlap with H atomic orbitals.

8.2 HYBRID ATOMIC ORBITALS

sp^3 Hybridization

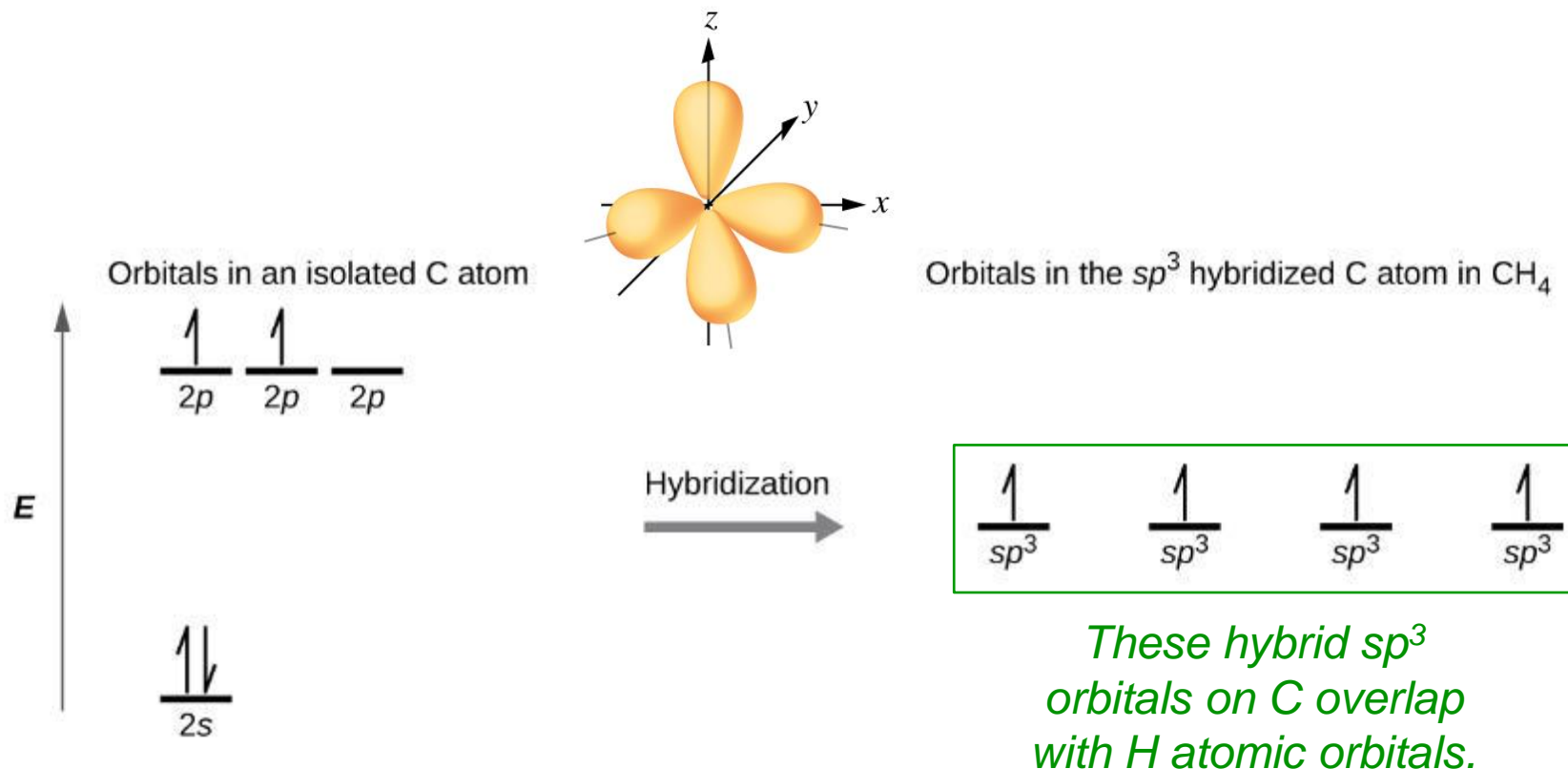
- Any central atom surrounded by four regions of electron density forms a set of four sp^3 hybrid orbitals.



8.2 HYBRID ATOMIC ORBITALS

sp^3 Hybridization

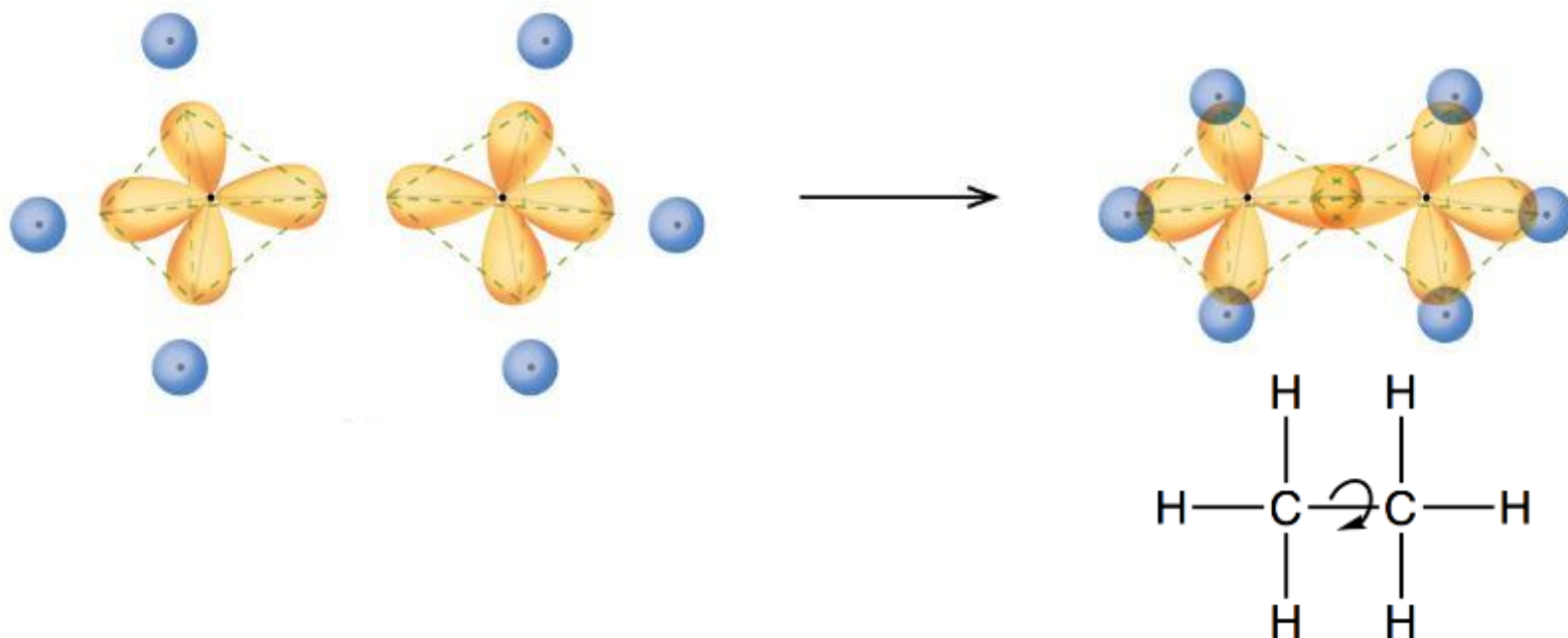
- Any central atom surrounded by four regions of electron density forms a set of four sp^3 hybrid orbitals.



8.2 HYBRID ATOMIC ORBITALS

sp^3 Hybridization

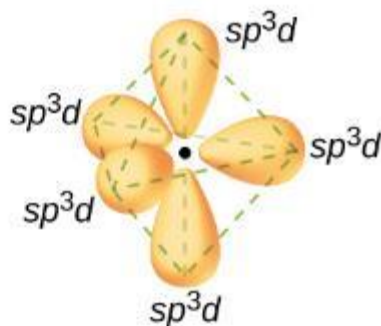
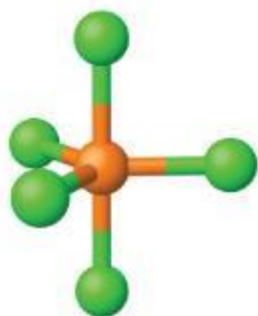
- The structure of ethane, C_2H_6 , is similar to that of methane.
- Each carbon sits at the center of a tetrahedron, and each carbon is sp^3 hybridized.
- Rotation around the σ -bond created between the two carbon atoms occurs readily.



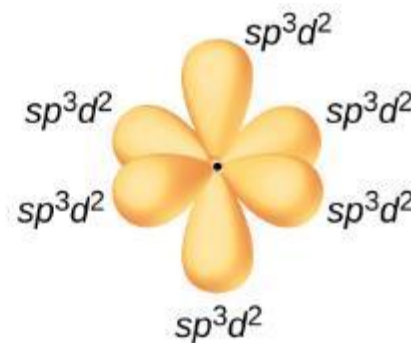
8.2 HYBRID ATOMIC ORBITALS

sp^3d and sp^3d^2 Hybridization

- To describe the five bonding orbitals in a trigonal bipyramidal arrangement, five valence shell atomic orbitals must be used.
 - one s + three p + one d = five sp^3d hybrid orbitals
- For an octahedral arrangement with six bonding orbitals:
 - one s + three p + two d = six sp^3d^2 hybrid orbitals
- These hybrid orbitals are only available for atoms having d -orbitals in the third period and beyond.






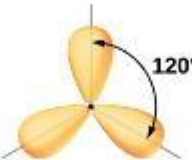
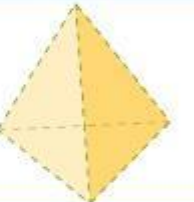
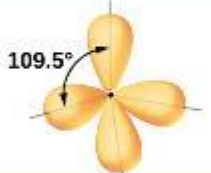

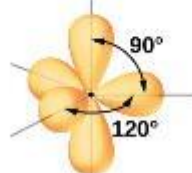

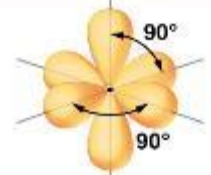
trigonal bipyramidal



octahedral

8.2 HYBRID ATOMIC ORBITALS

Summary of Hybridized Orbitals and Geometries

Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

What is the hybridization for SO_4^{2-} ?

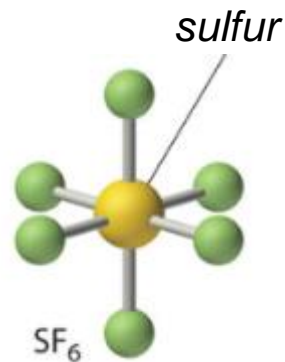
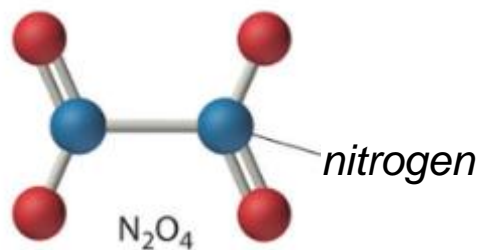
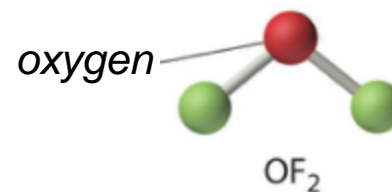
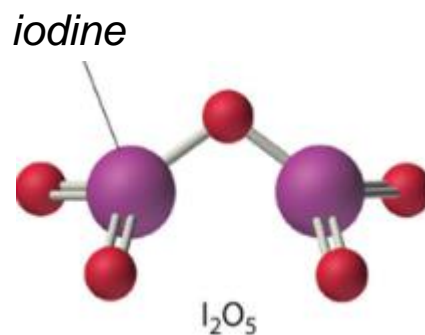
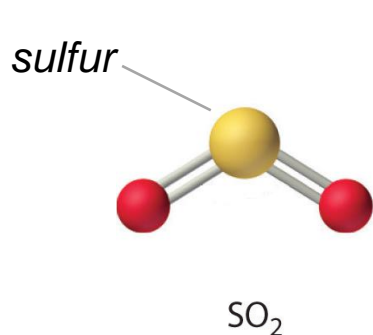
What is the hybridization for SF_4 ?

What is the hybridization for XeF_4 ?

8.2 HYBRID ATOMIC ORBITALS

Examples

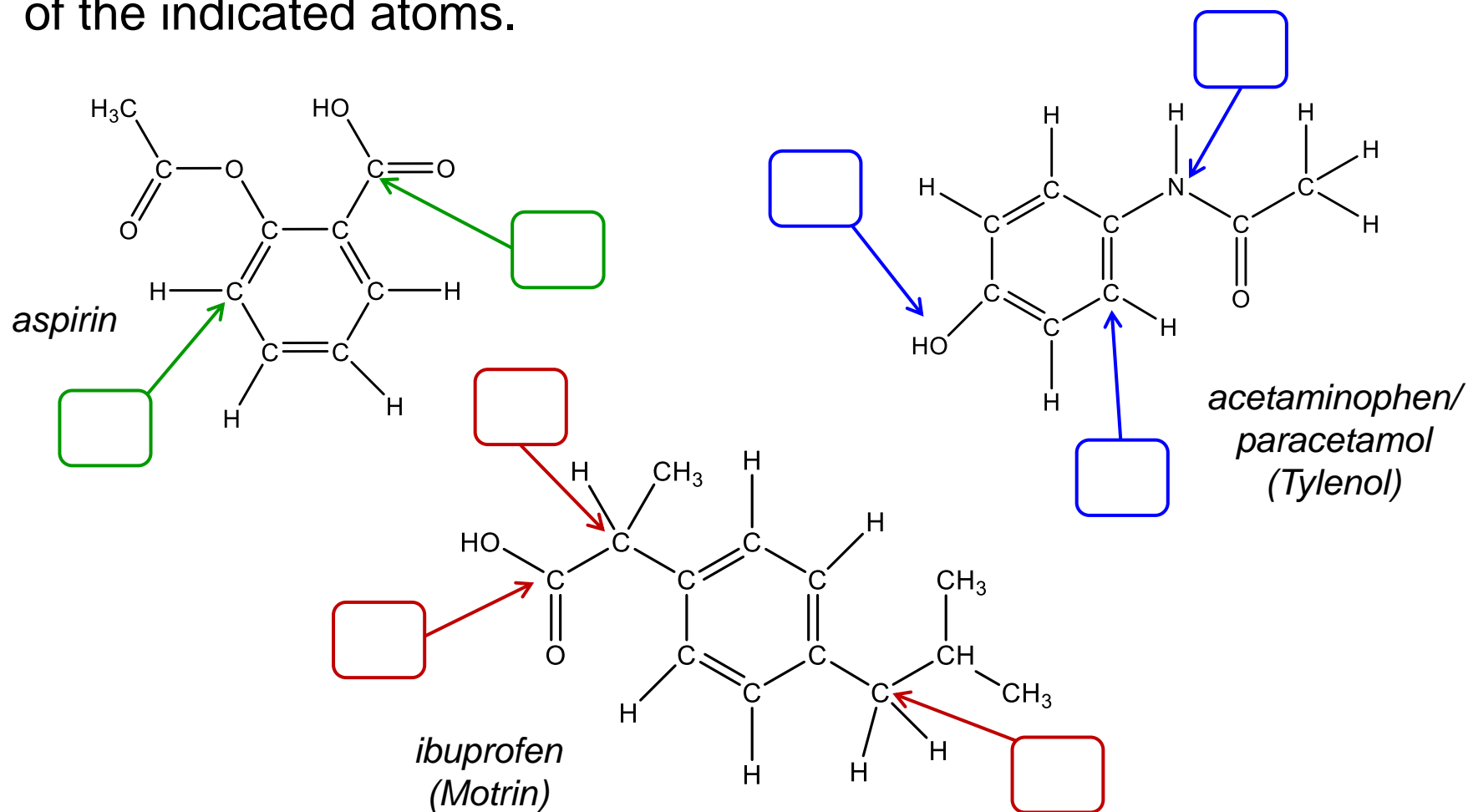
Identify the hybridization of indicated atoms.



8.2 HYBRID ATOMIC ORBITALS

Examples

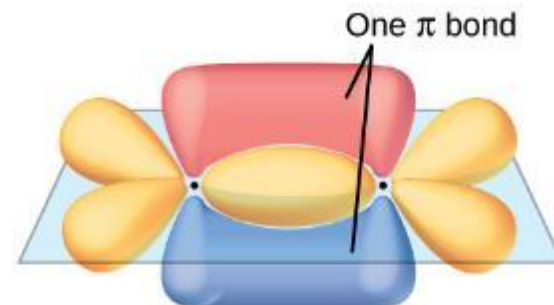
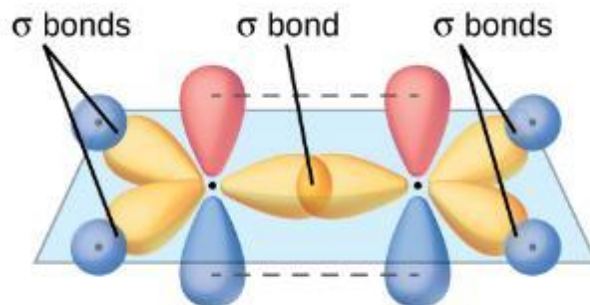
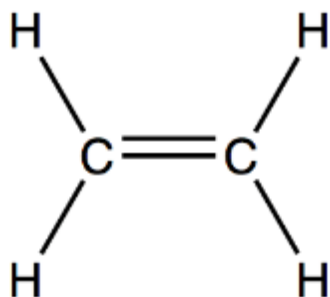
Three different analgesics are shown below. Identify the hybridization of the indicated atoms.



8.3 MULTIPLE BONDS

Sigma (σ) and Pi (π) Bonds in Molecules

- In ethene, C_2H_4 , each carbon atom is surrounded by two hydrogen atoms and another carbon atom.
- The three regions of electron density around each carbon require sp^2 hybrid orbitals.
 - These hybrid orbitals combine to create one σ -bond and one π -bond between the carbon atoms.
 - There are also σ -bonds from each carbon atom to two hydrogen atoms.

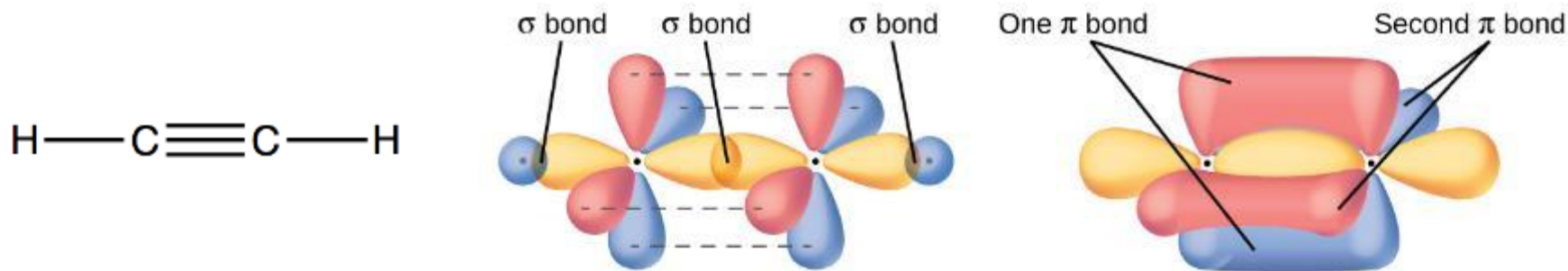


Ethene contains a total of 5 σ -bonds and 1 π -bond.

8.3 MULTIPLE BONDS

Sigma (σ) and Pi (π) Bonds in Molecules

- In acetylene, C_2H_2 , each carbon atom is surrounded by one hydrogen atom and another carbon atom.
- The two regions of electron density around each carbon require sp hybrid orbitals.
 - These hybrid orbitals combine to create one σ -bond and one π -bond between the carbon atoms.
 - There are also σ -bonds from each carbon atoms to one hydrogen atoms.

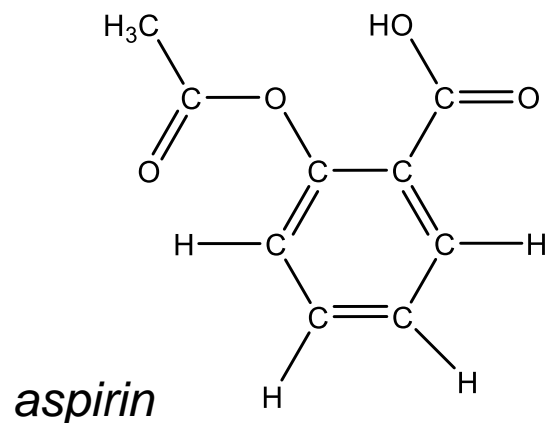


Acetylene contains a total of 3 σ -bonds and 2 π -bonds.

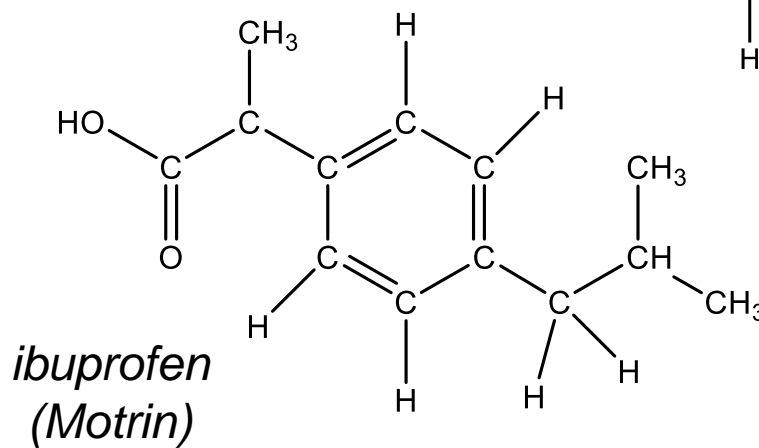
8.3 MULTIPLE BONDS

Examples

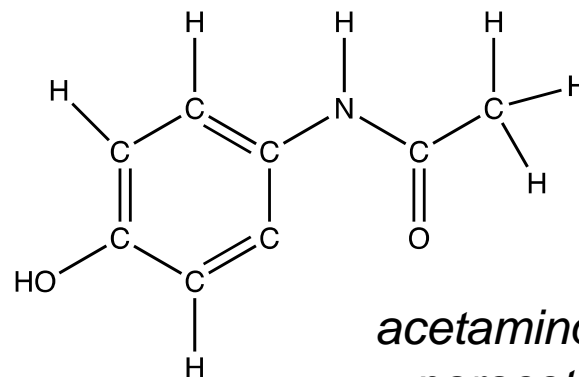
Determine the number of σ -bonds and π -bonds in each of the analgesics shown below.



σ -bonds: _____
 π -bonds: _____



σ -bonds: _____
 π -bonds: _____



σ -bonds: _____
 π -bonds: _____

Practice

What is the geometry and polarity for each molecule?

Molecule	Lewis Structure	Geometry	Hybridization	Polar?
a. BeF_2				
b. BF_3				
c. CF_4				
d. PF_5				
e. SF_6				

Practice

What is the geometry and polarity for each molecule?

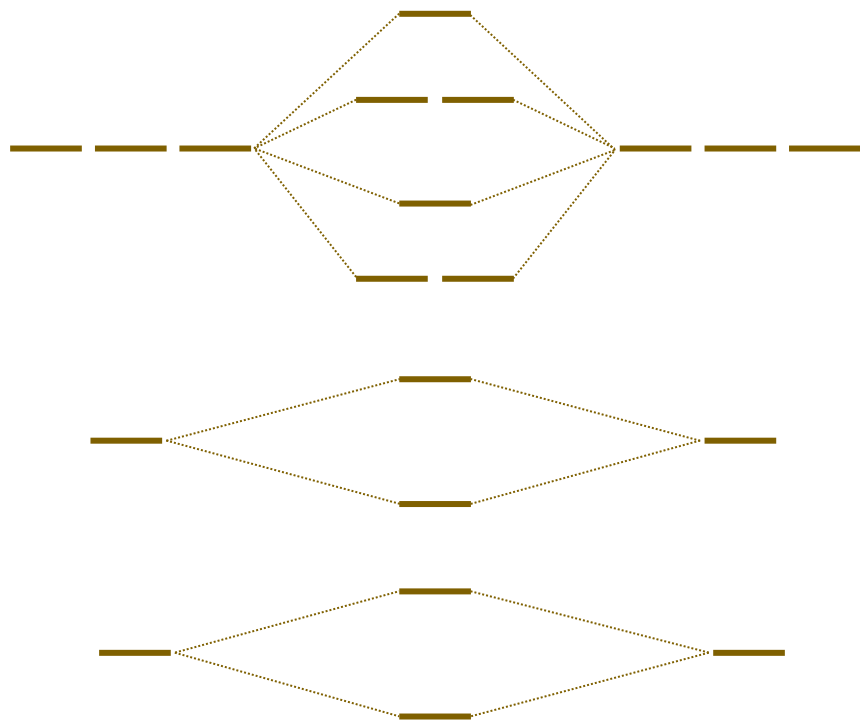
Molecule	Lewis Structure	Geometry	Hybridization	Polar?
f. NH_3				
g. SF_4				
h. ClF_3				
i. XeF_2				
j. ICl_4^-				

Practice

What is the geometry and polarity for each molecule?

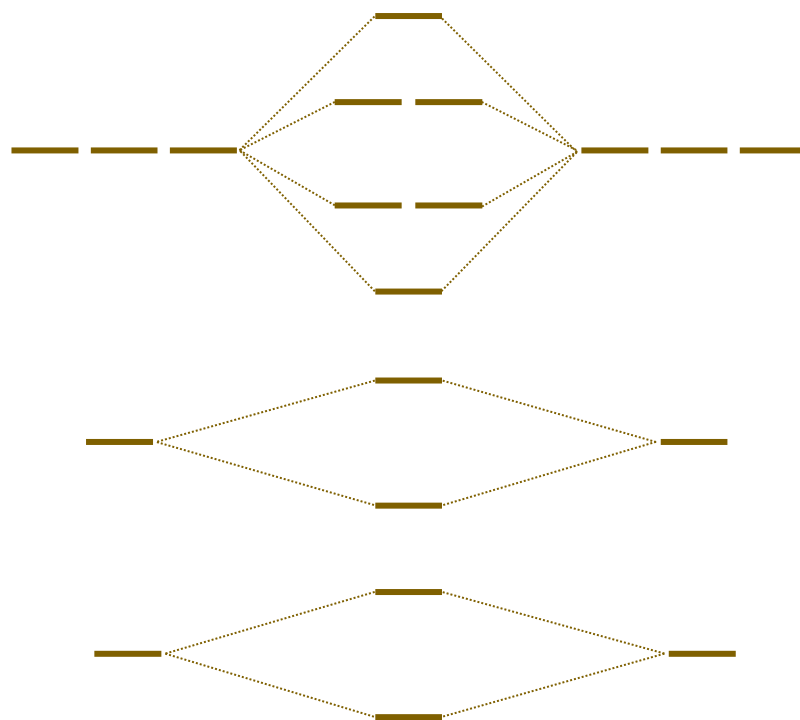
Molecule	Lewis Structure	Geometry	Hybridization	Polar?
k. H_2O				
l. ClF_2^+				
m. BrF_5				
n. XeF_4				
o. XeOF_4				

8.4 MOLECULAR ORBITALS



B_2 , C_2 , N_2

significant s-p mixing

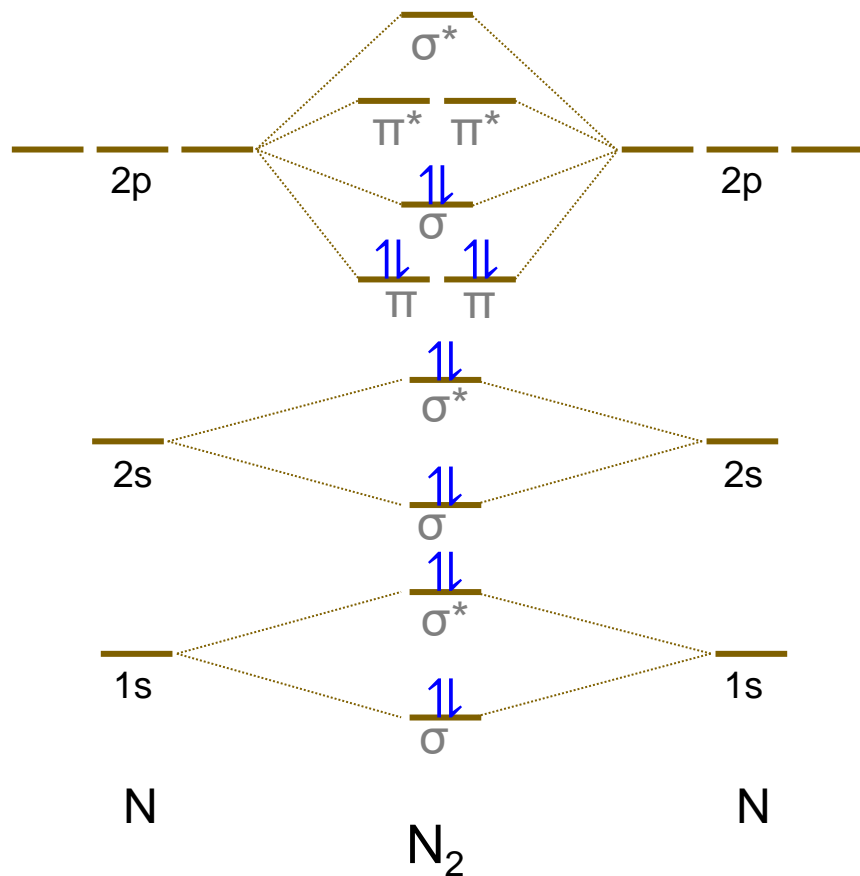


O_2 , F_2 , Ne_2

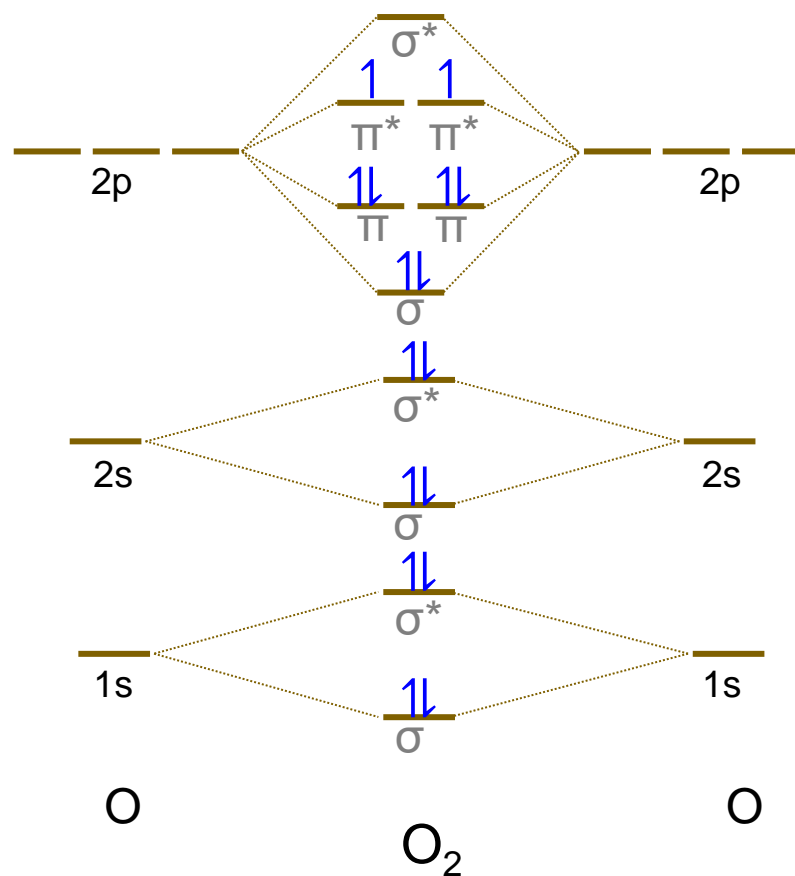
less s-p mixing

8.4 MOLECULAR ORBITALS

diamagnetic

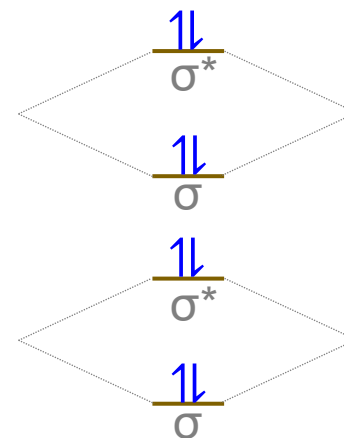
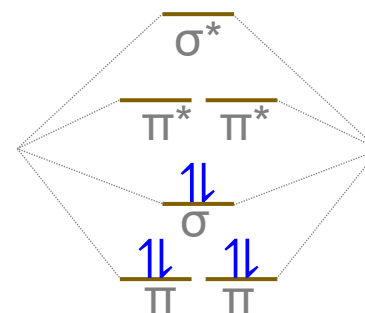
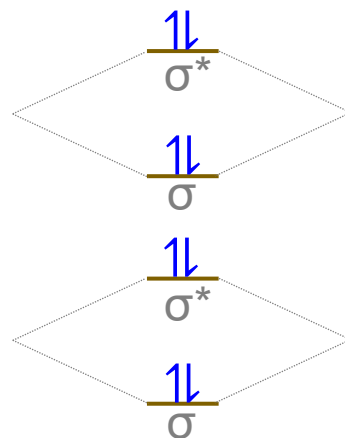
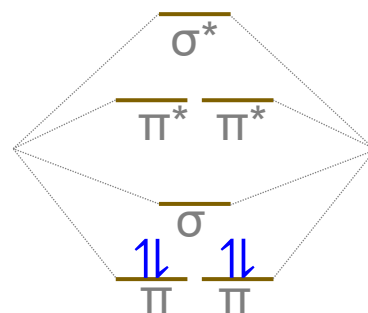
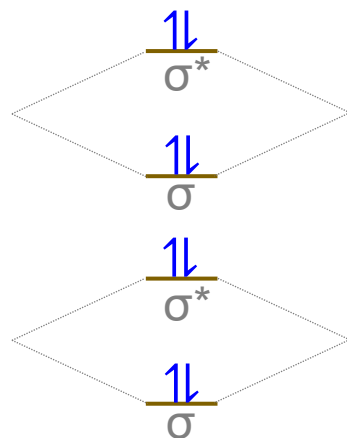
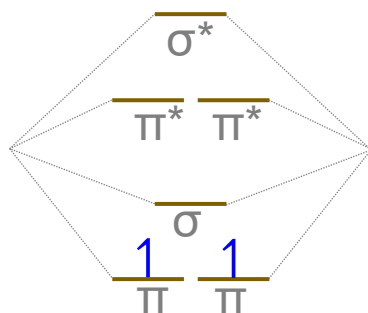
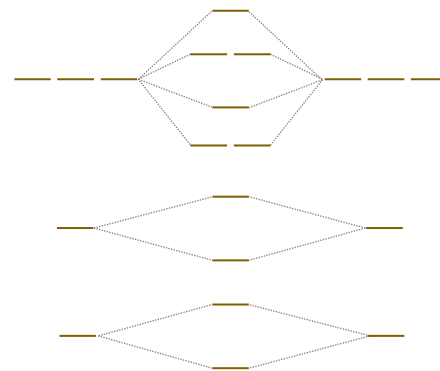


paramagnetic



8.4 MOLECULAR ORBITALS

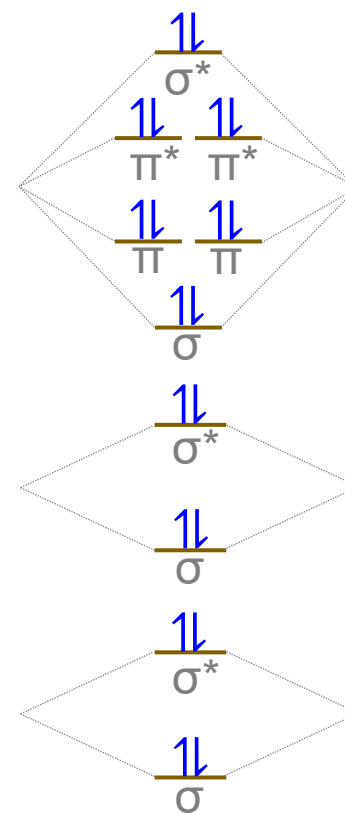
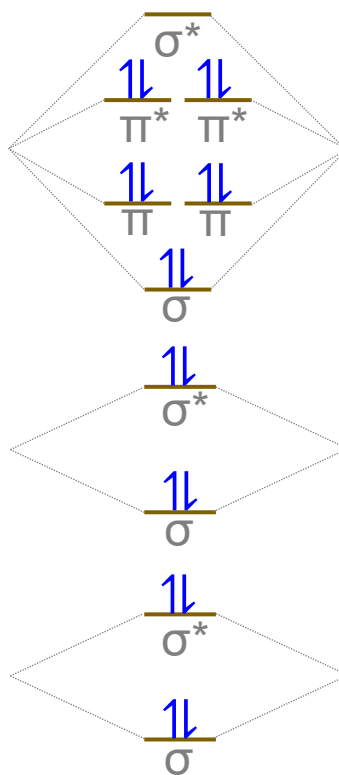
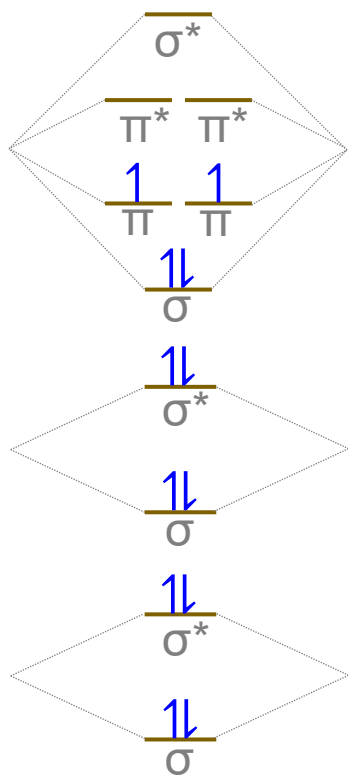
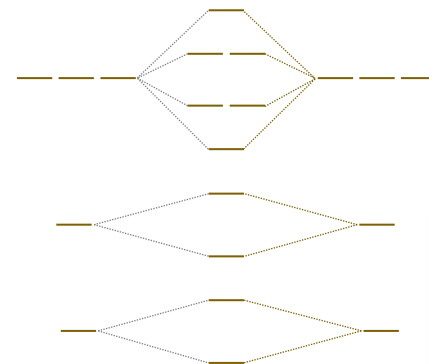
B_2 , C_2 , N_2 *significant s-p mixing*



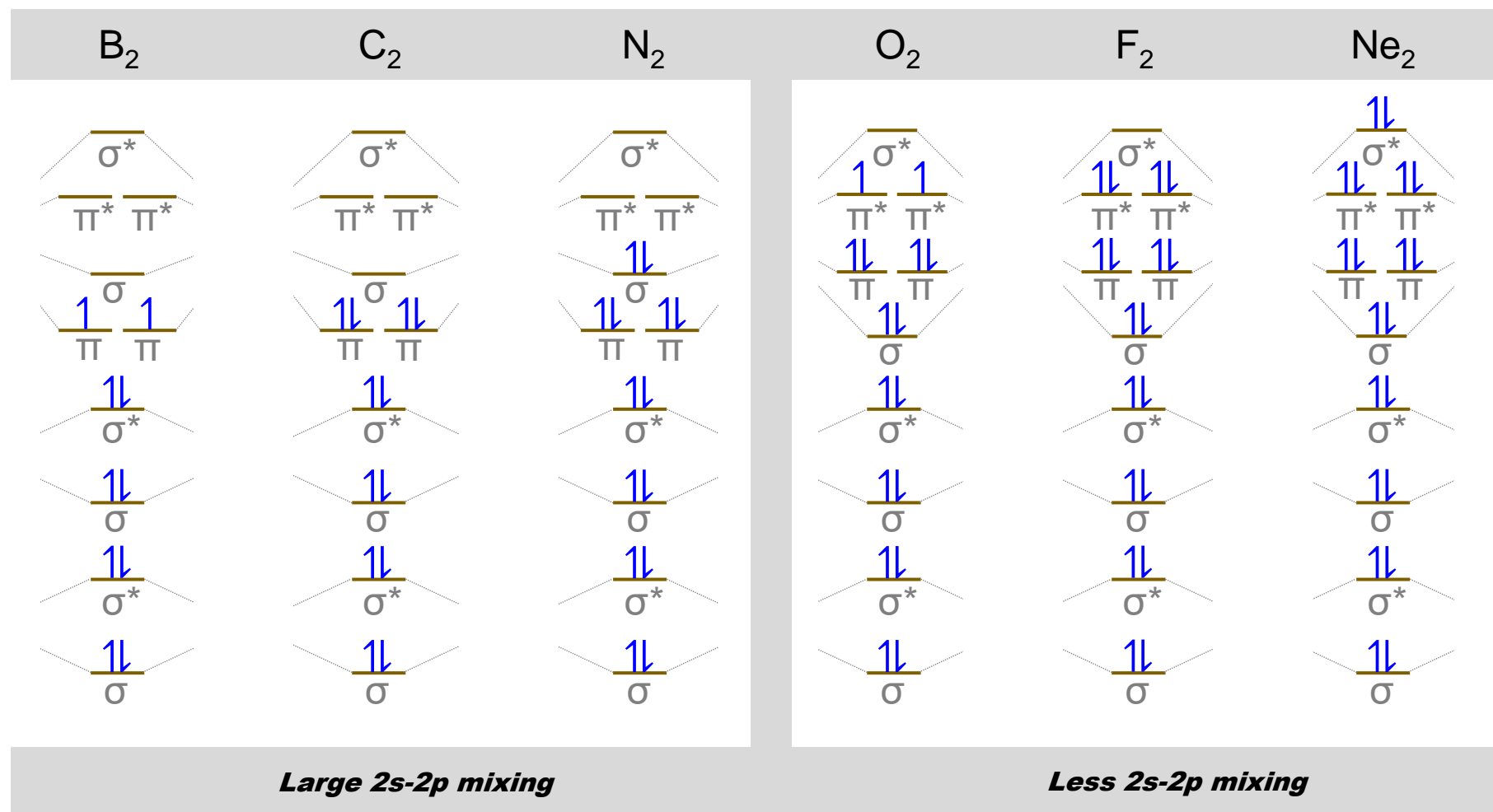
8.4 MOLECULAR ORBITALS

O_2 , F_2 , Ne_2

less s-p mixing



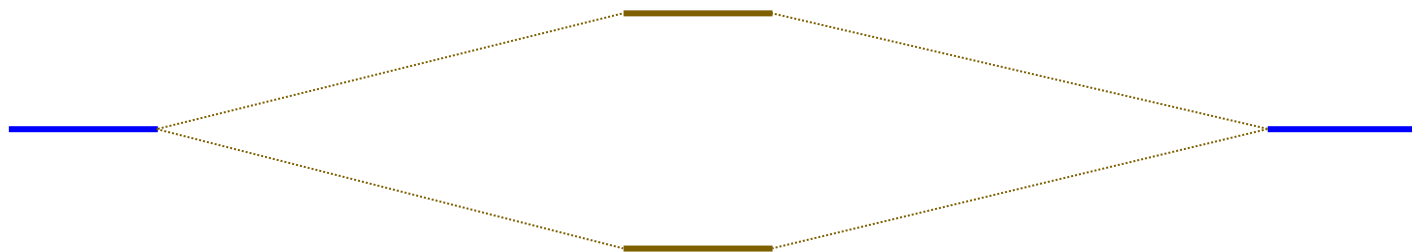
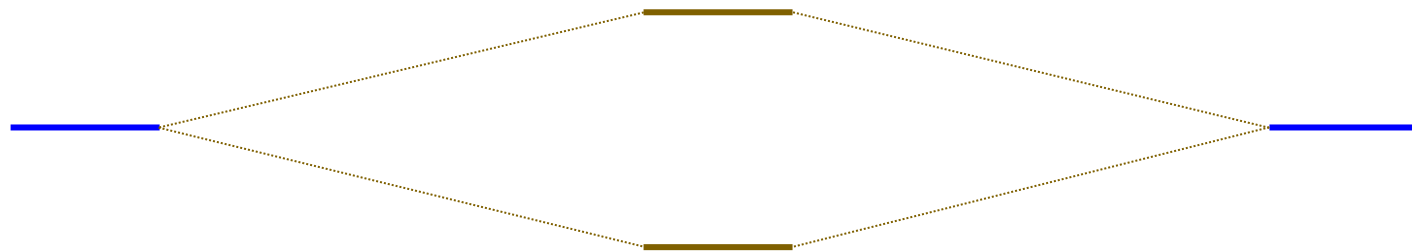
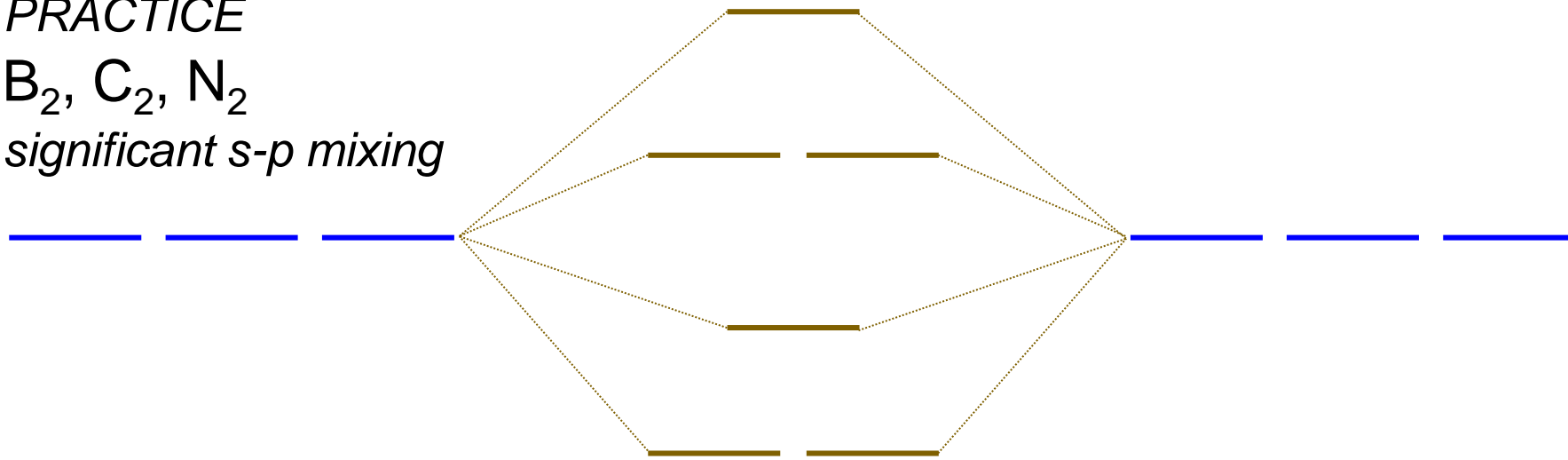
8.4 MOLECULAR ORBITALS



PRACTICE

B_2 , C_2 , N_2

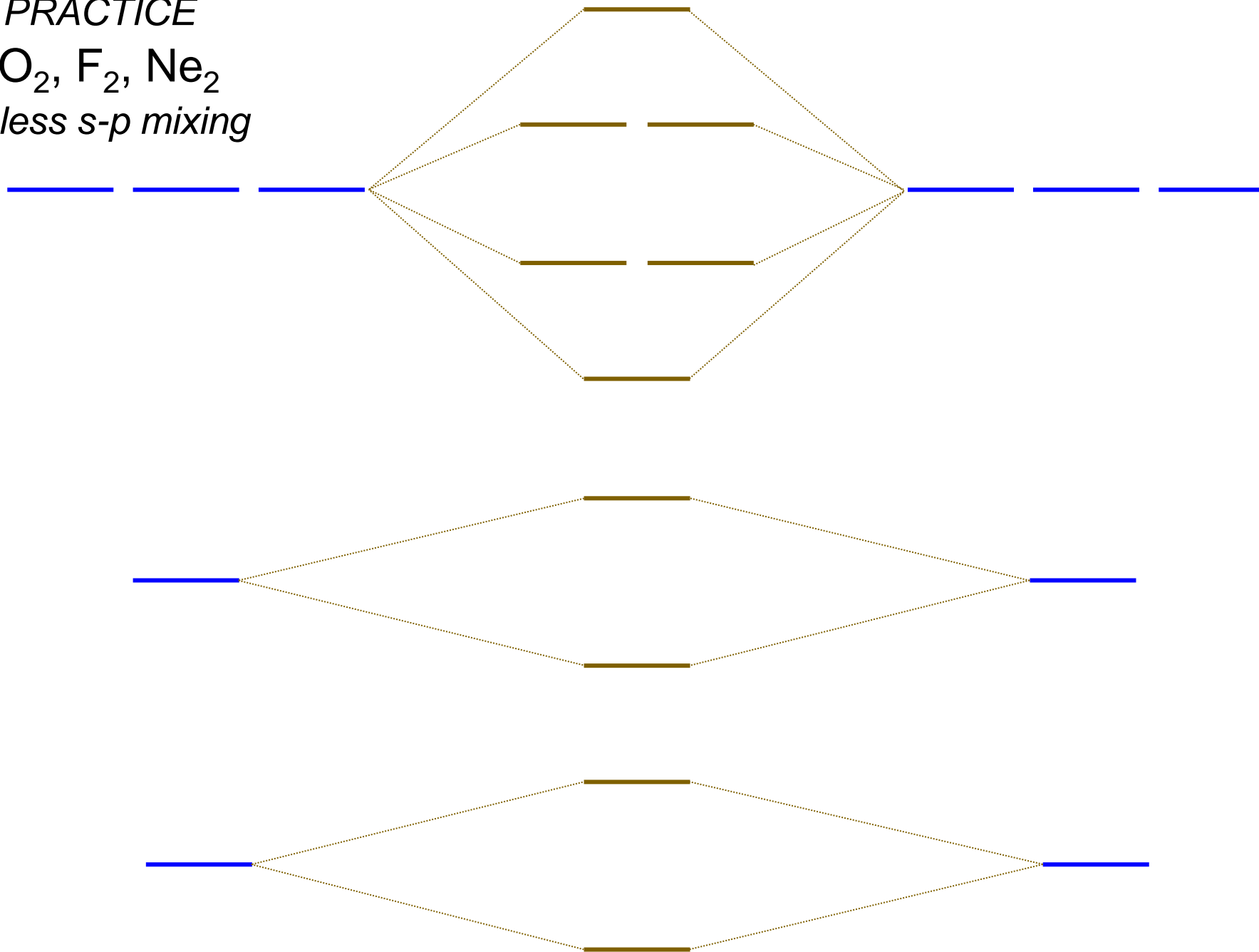
significant s-p mixing



PRACTICE

O_2 , F_2 , Ne_2

less s-p mixing



PARAMAGNETIC O₂!

Experiments show that O₂ is attracted to a magnet while N₂ is not ([video](#)).



Draw the Lewis structures of N₂ and O₂.

Explain why the structures conflict with the experimental results shown in the picture and seen in the video.

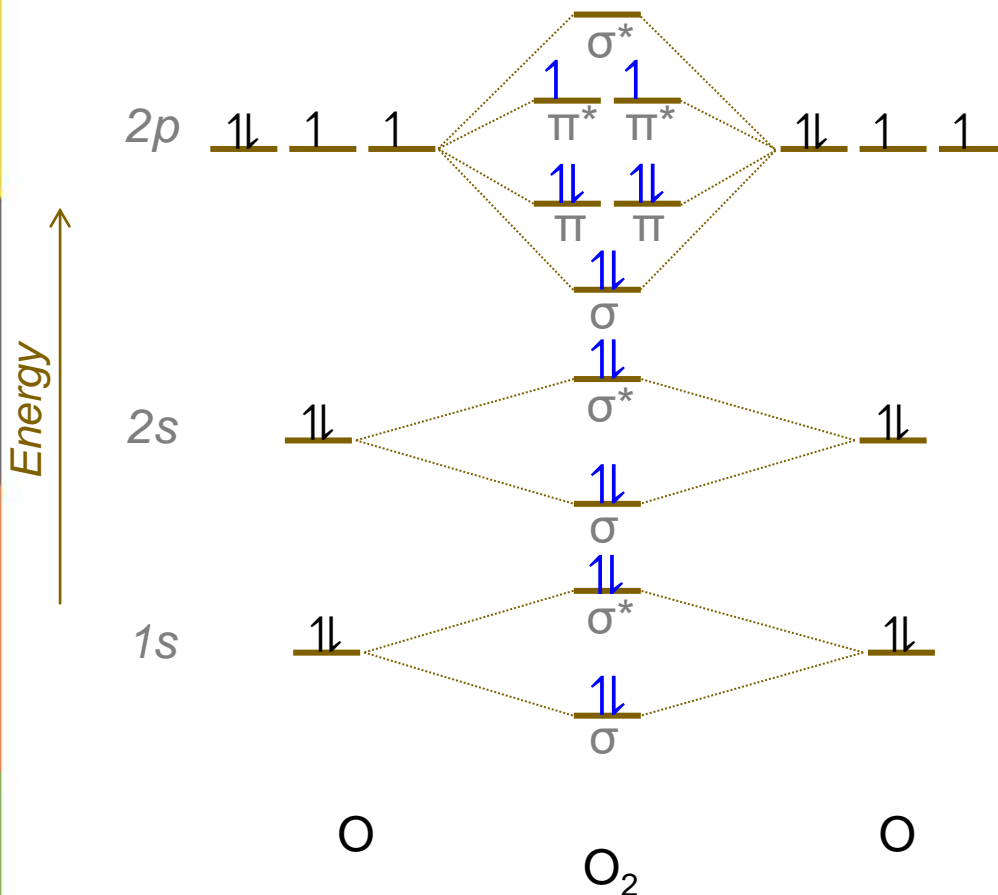
8.4 MOLECULAR ORBITALS



Molecular Orbital Diagram

Lewis Dot Structure

Bond Order



There are two bonding interactions.
One σ and one π .

Note: It is still a π bond even if the electrons are unpaired in those orbitals. Electron pairing is nice to have and stable, but it is not required.

The two π orbital unpaired electrons show that this molecule is paramagnetic.

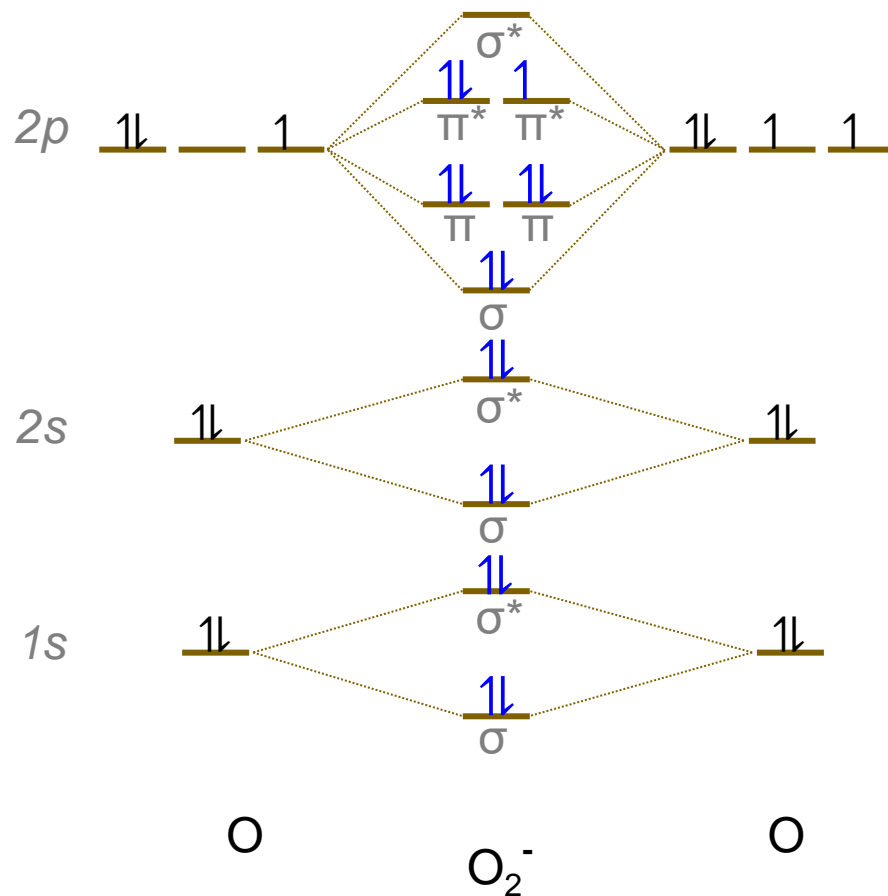
8.4 MOLECULAR ORBITALS

O_2 vs. O_2^- vs. O_2^{2-}

Molecular Orbital Diagram

Lewis Dot Structure

Bond Order



There are two bonding interactions, but there are now three antibonding electrons. The overall bond order is 1.5 making the bond longer than O_2 but shorter than O_2^{2-} .

The molecule is paramagnetic.

8.4 MOLECULAR ORBITALS

O_2 vs. O_2^- vs. O_2^{2-}

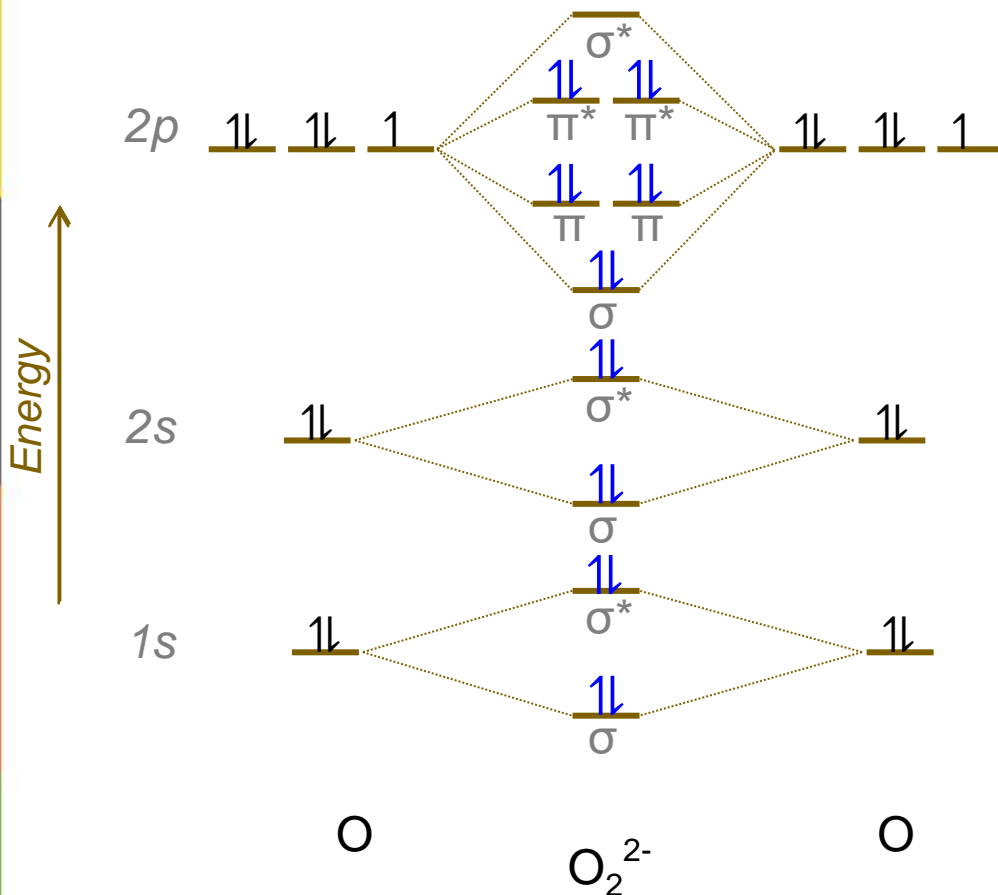
Molecular Orbital Diagram

Lewis Dot Structure

Bond Order

There is one σ bond and the overall bond order is 1. The bond is longer than both O_2 but and O_2^- .

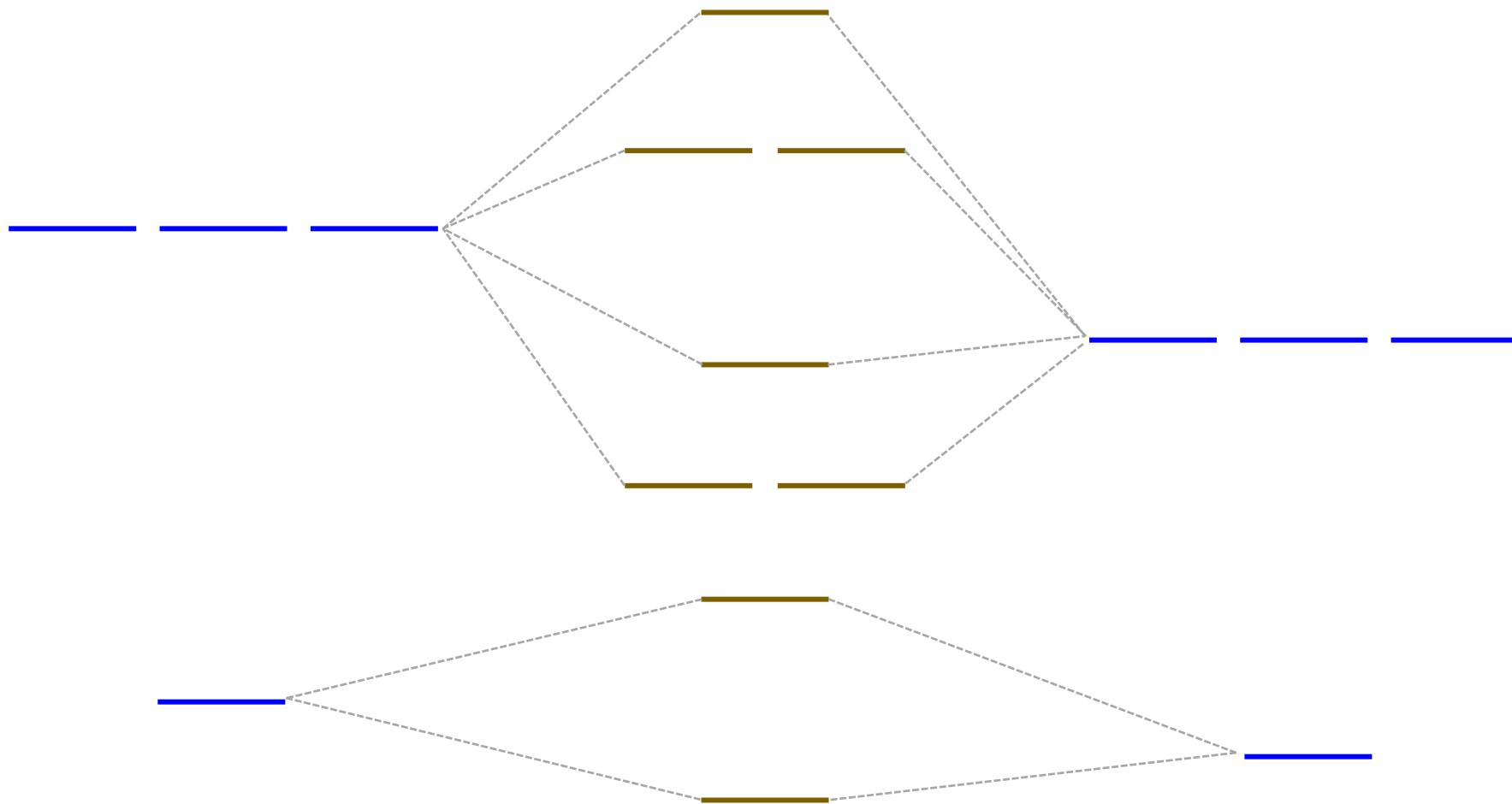
The molecule is diamagnetic.



8.4 MOLECULAR ORBITALS

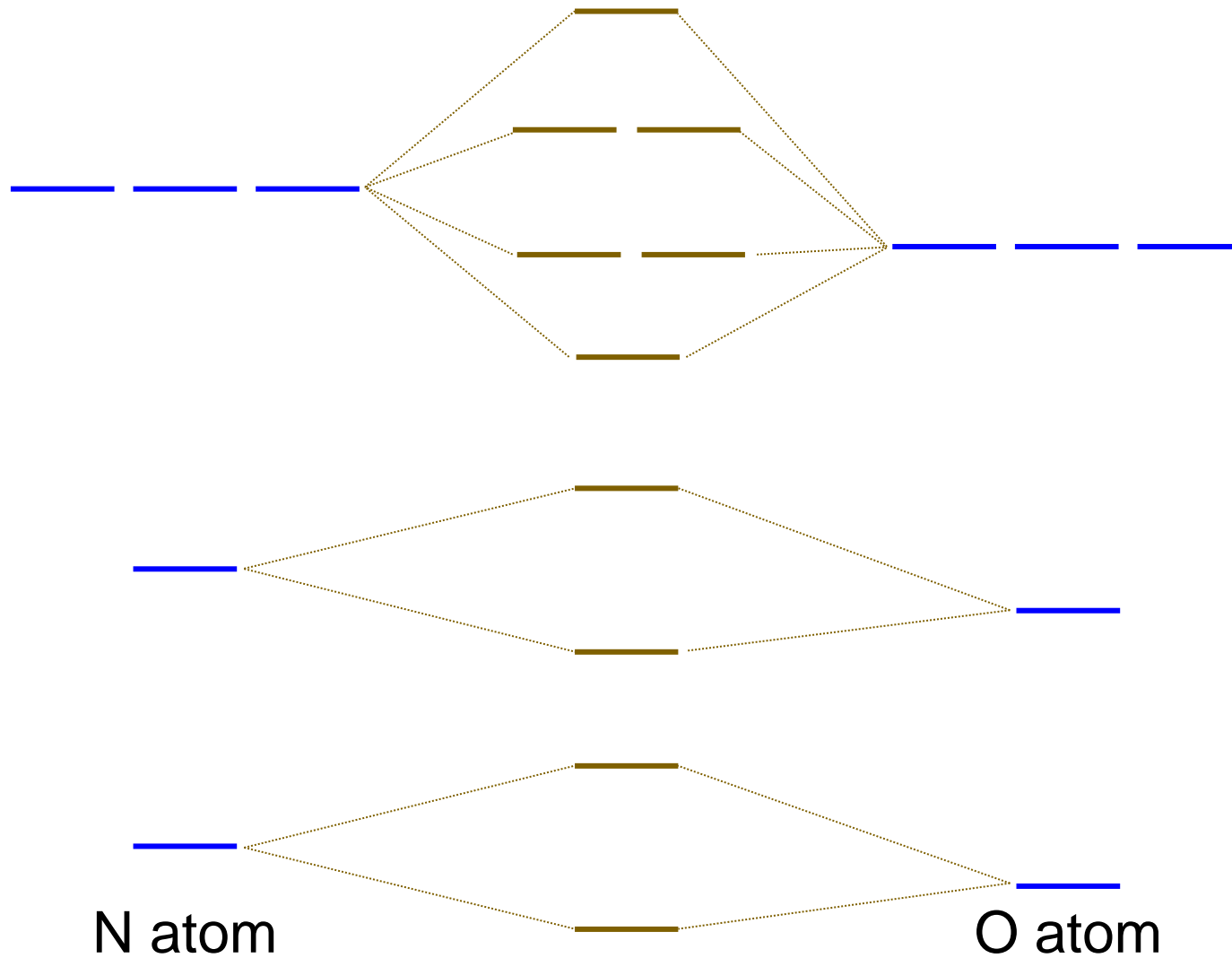
Heteronuclear Diatomic Molecules

Energy levels differ for
the atomic orbitals.



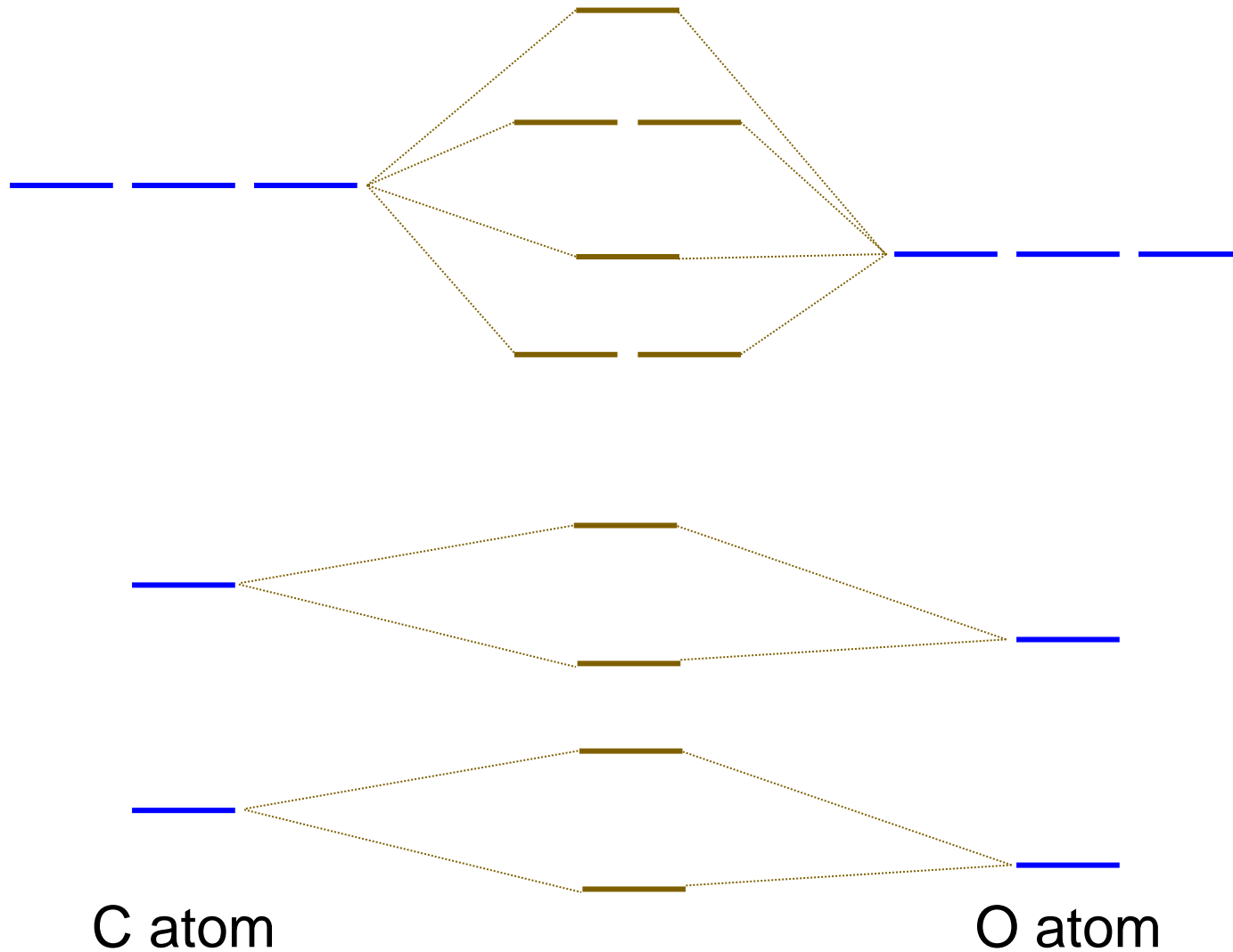
8.4 MOLECULAR ORBITALS

Nitric Oxide



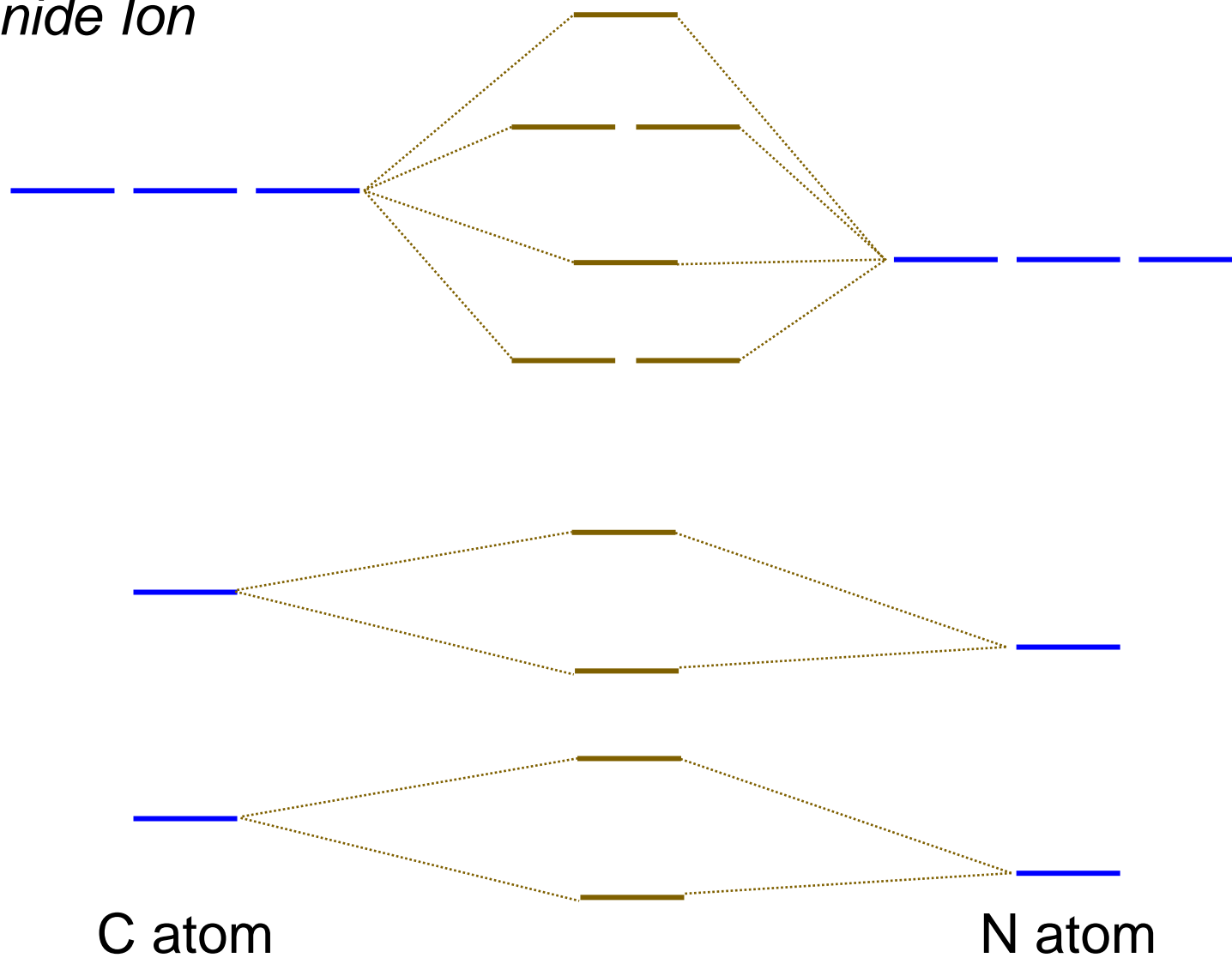
8.4 MOLECULAR ORBITALS

Carbon Monoxide



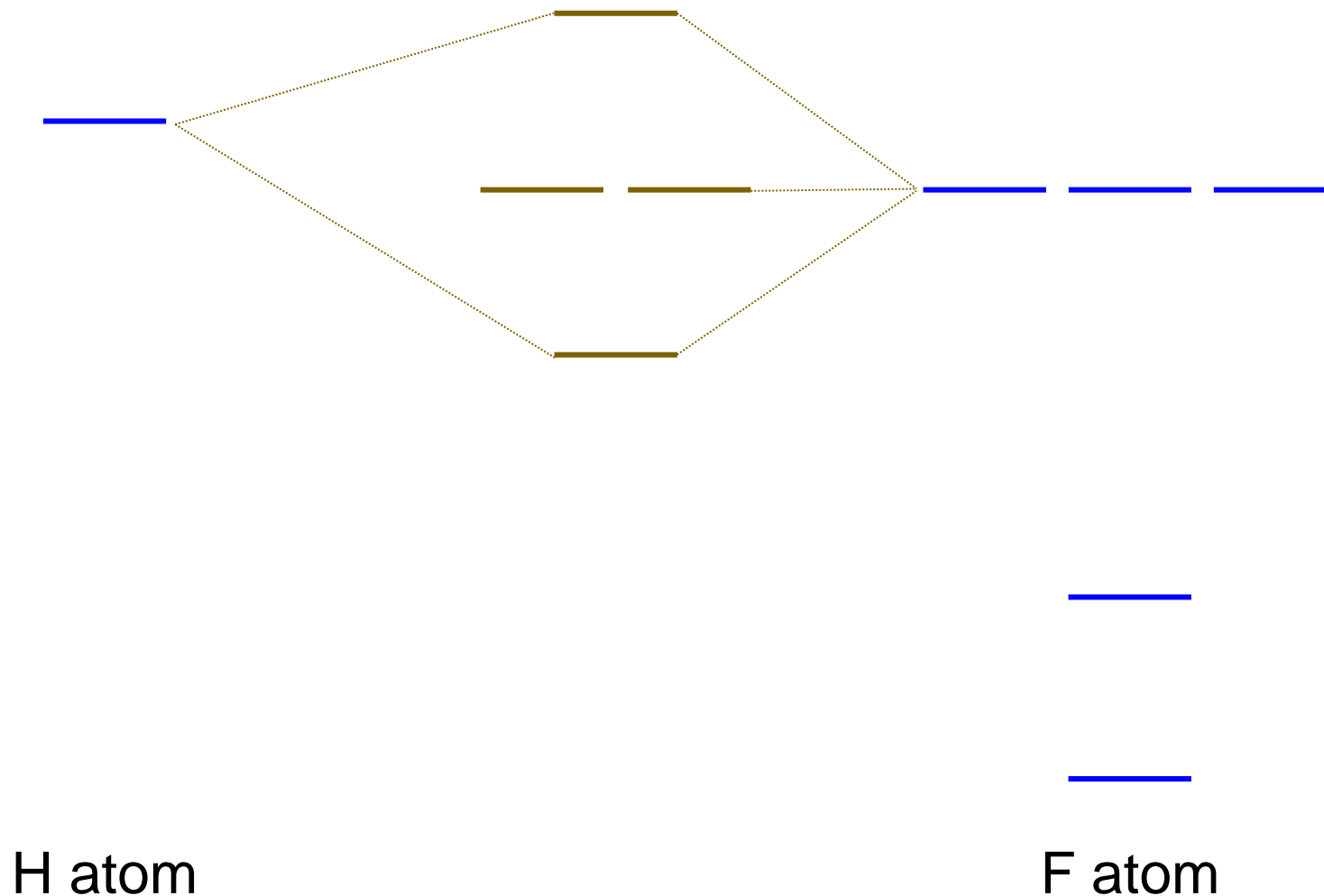
8.4 MOLECULAR ORBITALS

Cyanide Ion



8.4 MOLECULAR ORBITALS

Hydrofluoric Acid



END OF CHAPTER PROBLEMS – CHAPTER 8

Valence Bond Theory: #13, 15, 19

Multiple Bonds: #25, 27

Molecular Orbital Theory: #41a-c

For detailed solutions to these problems, go to the OpenStax Chemistry website and download the [Student Solution Guide](#).

VIDEOS – CHAPTER 8

Paramagnetism of Liquid Oxygen
(Harvard Natural Sciences Lecture Demonstration)

<https://www.youtube.com/watch?v=Lt4P6ctf06Q>

**All videos were created by MC Chemistry faculty unless otherwise indicated.*