CHEMISTRY

Chapter 8 ADVANCED THEORIES OF COVALENT BONDING

Kevin Kolack, Ph.D.
The Cooper Union
HW problems: 6, 7, 12, 21, 27, 29, 41, 47, 49

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CH. 8 OUTLINE

8.1 Valence Bond Theory

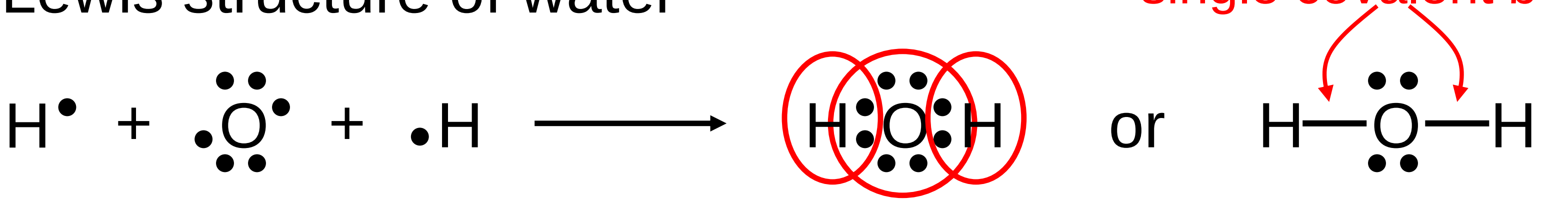
8.2 Hybrid Atomic Orbitals

8.3 Multiple Bonds

8.4 Molecular Orbital Theory

SINGLE, DOUBLE AND TRIPLE BONDS REVISITED

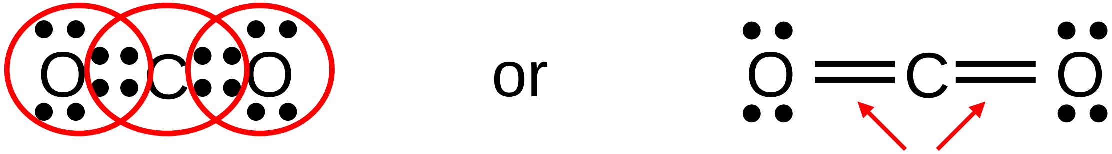
Lewis structure of water



single covalent bonds

$2e^- 8e^- 2e^-$

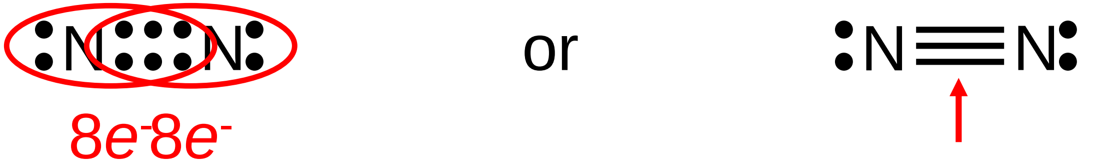
Double bond – two atoms share two pairs of electrons



$8e^- 8e^- 8e^-$

double bonds

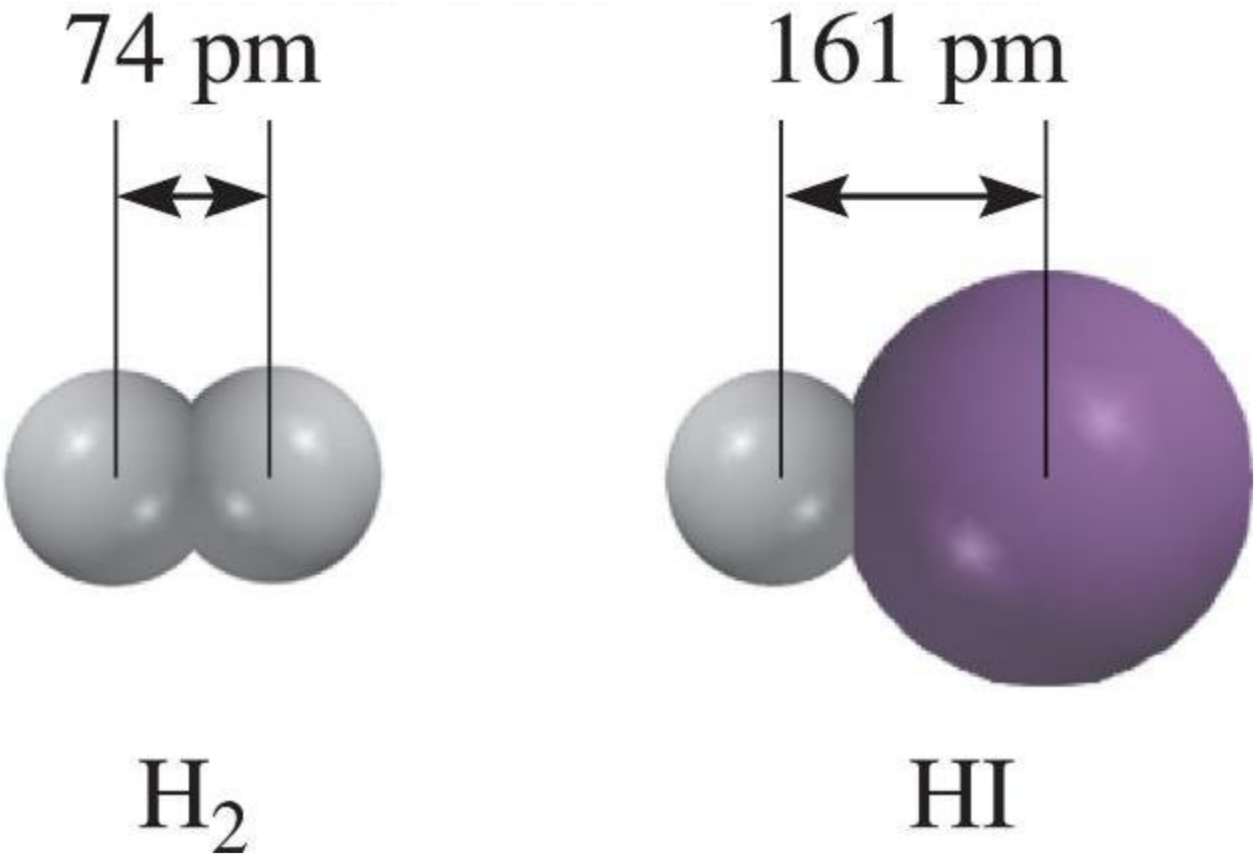
Triple bond – two atoms share three pairs of electrons



$8e^- 8e^-$

triple bond

BOND LENGTH



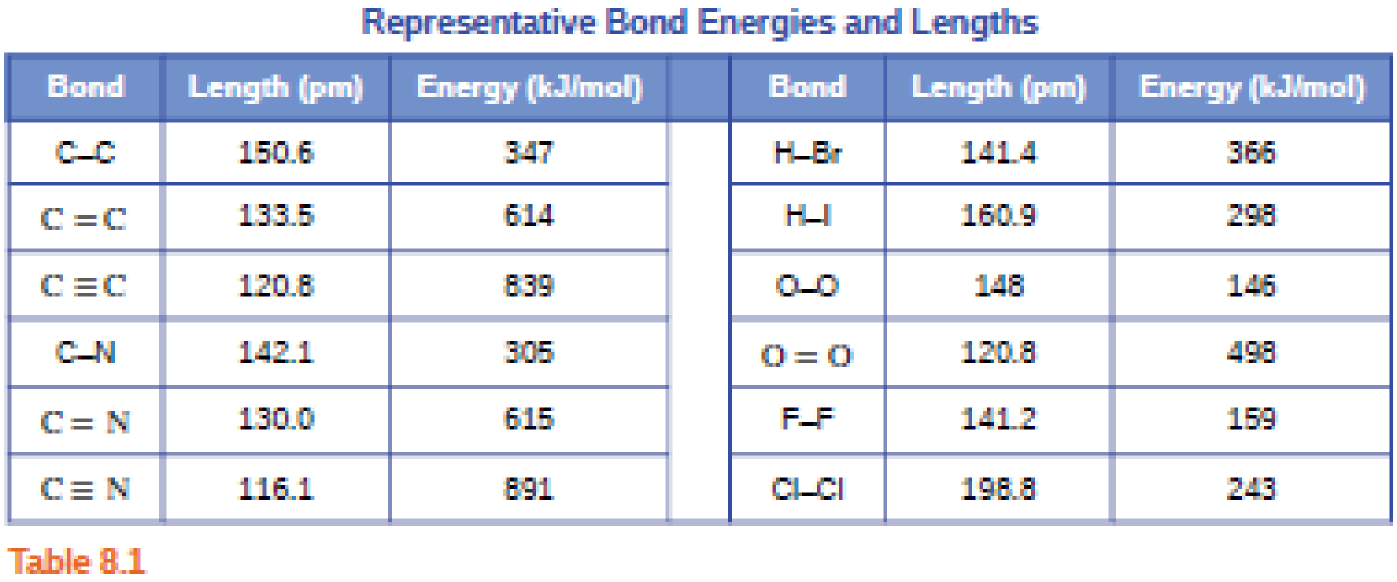
Average Bond Lengths of Some Common Single, Double, and Triple Bonds

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C═O	121
C—C	154
C═C	133
C≡C	120
C—N	143
C═N	138
C≡N	116
N—O	136
N═O	122
O—H	96

Bond Lengths

triple bond < double bond < single bond

BOND STRENGTH



Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)		Bond	Length (pm)	Energy (kJ/mol)
C–C	150.6	347		H–Br	141.4	366
C = C	133.5	614		H–I	160.9	298
C ≡ C	120.8	839		O–O	148	146
C–N	142.1	305		O = O	120.8	498
C = N	130.0	615		F–F	141.2	159
C ≡ N	116.1	891		Cl–Cl	198.8	243

Table 8.1

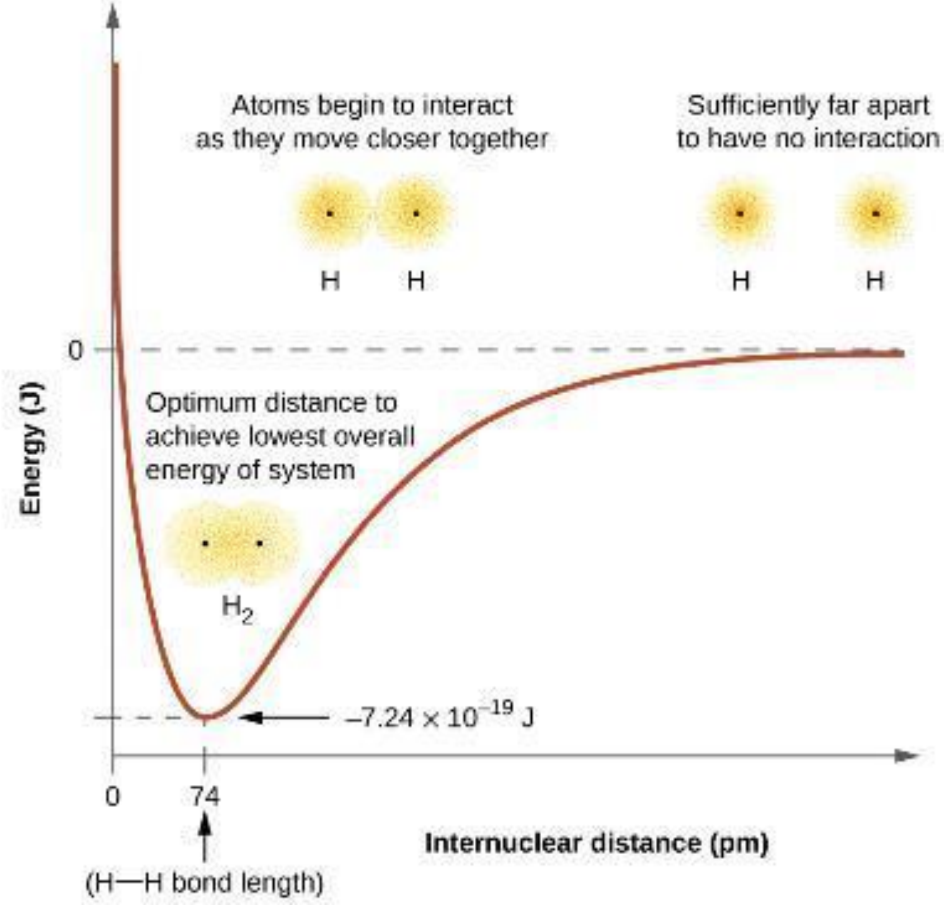
Bond Strengths

triple bond > double bond > single bond

VALENCE BOND THEORY

- **Valence bond theory** describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms.
- We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space.

FIGURE 8.2 (FIG 7.4 REVISITED)

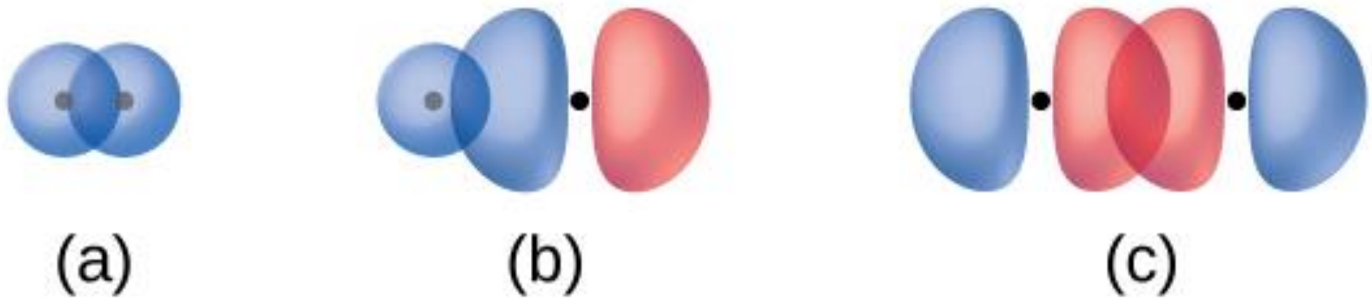


(a) The interaction of two hydrogen atoms changes as a function of distance.

(b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

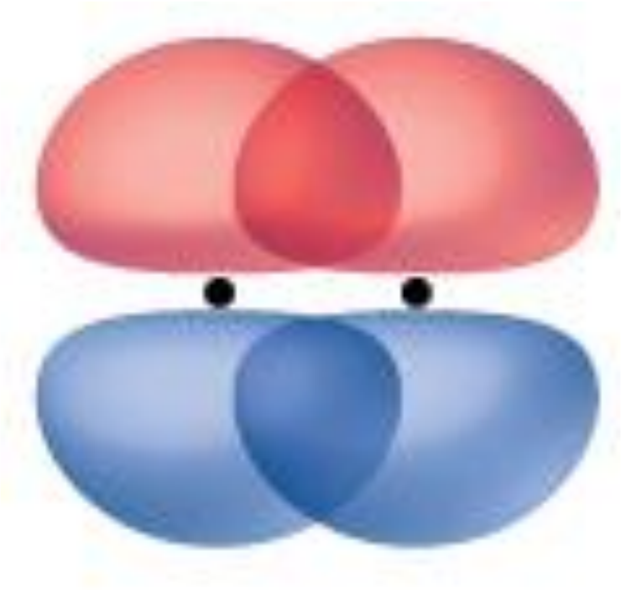
SIGMA BONDING

- A **sigma (σ) bond** is a covalent bond in which the electron density is concentrated in the region along the internuclear axis.
- Single bonds are always σ bonds.
- σ bonds form from the overlap of the following: (a) two *s* orbitals, (b) an *s* orbital and a *p* orbital, or (c) two *p* orbitals.



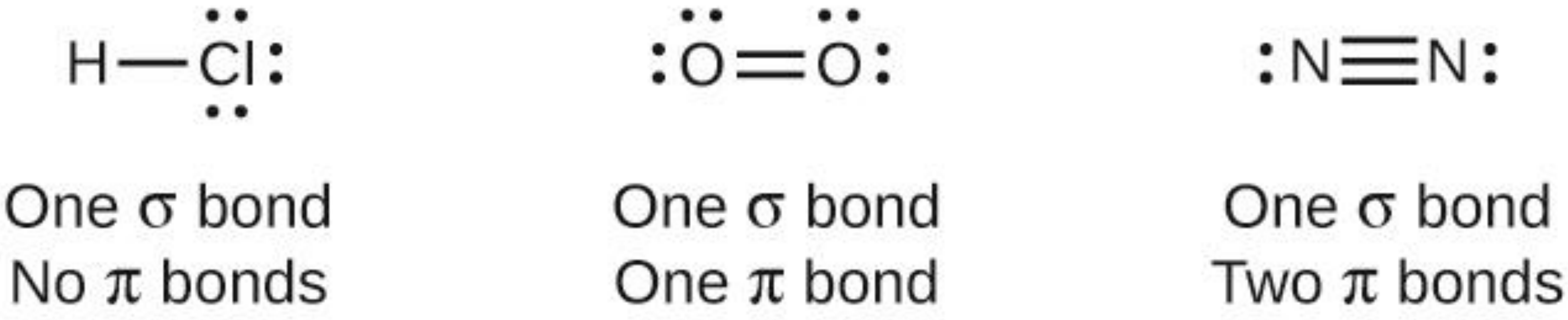
PI BONDING

- A pi (π) bond results from side-to-side overlap of two non-s orbitals. (Your book says p orbitals.)
- In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis.
- Along the axis itself, there is a **node**, that is, a plane with no probability of finding an electron.

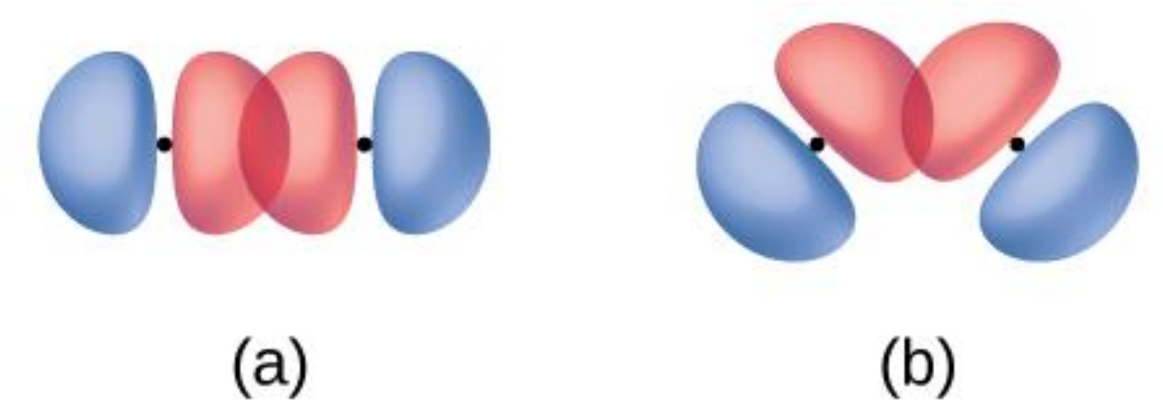


PI BONDING (CONT'D)

- Multiple bonds are composed of one sigma and 1 or 2 pi bonds



MAXIMUM ~~OVERDRIVE~~ OVERLAP

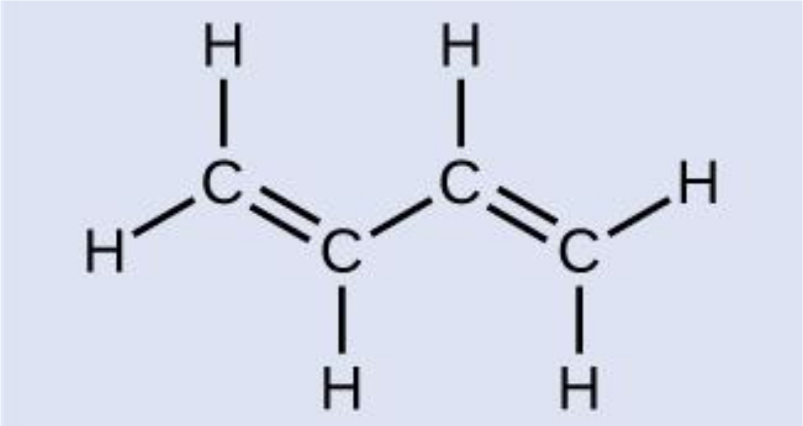


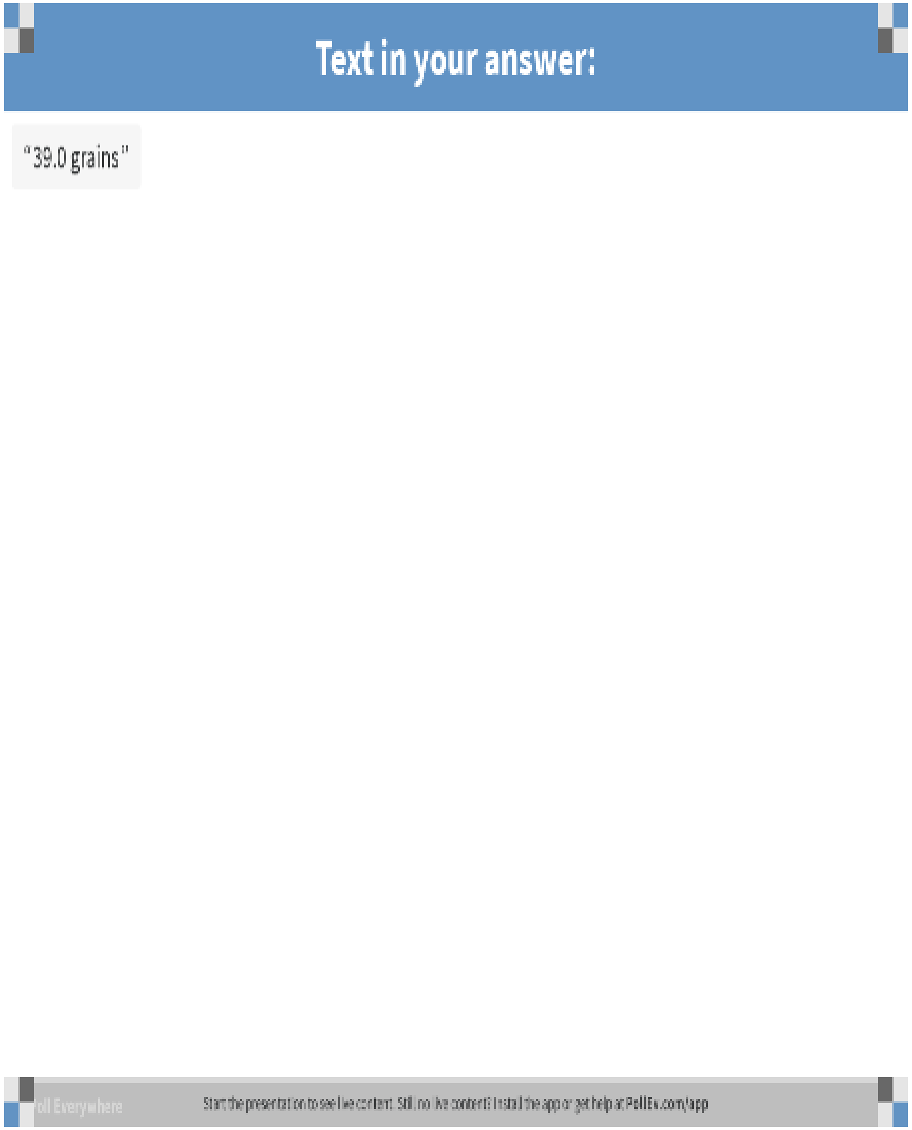
(a) The overlap of two *p* orbitals is greatest when the orbitals are directed end to end.

(b) Any other arrangement results in less overlap.

EXAMPLE 8.1.1

Butadiene, C_4H_6, is used to make synthetic rubber. Identify the number of sigma and pi bonds in this molecule.




Text in your answer:

"39.0 grains"

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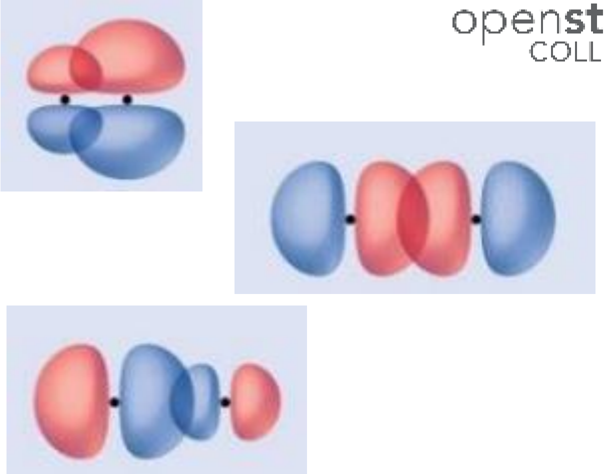
EXAMPLE 8.1.2

Sigma or pi?

1. side-by-side overlap of a 4*p* and a 2*p* orbital
2. end-to-end overlap of a 4*p* and 4*p* orbital
3. end-to-end overlap of a 4*p* and a 2*p* orbital



Sigma or pi?

sigma

pi

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CH. 8 OUTLINE

8.1 Valence Bond Theory

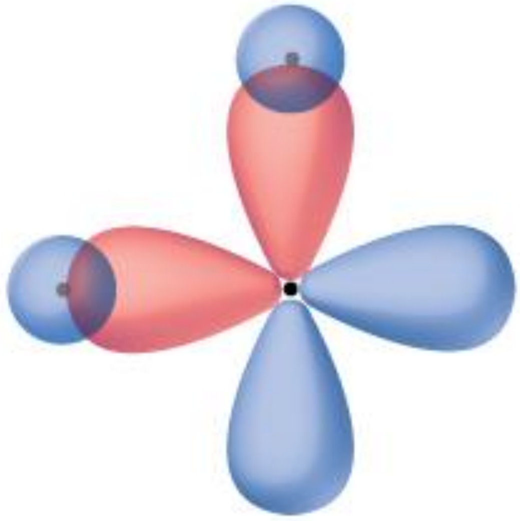
8.2 Hybrid Atomic Orbitals

8.3 Multiple Bonds

8.4 Molecular Orbital Theory

PROBLEM…

- In water, the hypothetical overlap of two of the 2*p* orbitals on an oxygen atom (red) with the 1*s* orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°.
- This is not consistent with experimental evidence.



- What do you do when your theory doesn’t match the experimental evidence?

NEW THEORY - HYBRID ORBITALS

- When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes.
- This process of combining the wave functions for atomic orbitals is called **hybridization** and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later).
- The new orbitals that result are called **hybrid orbitals**.

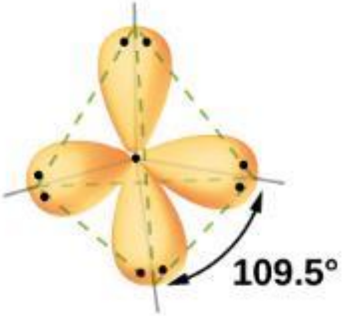
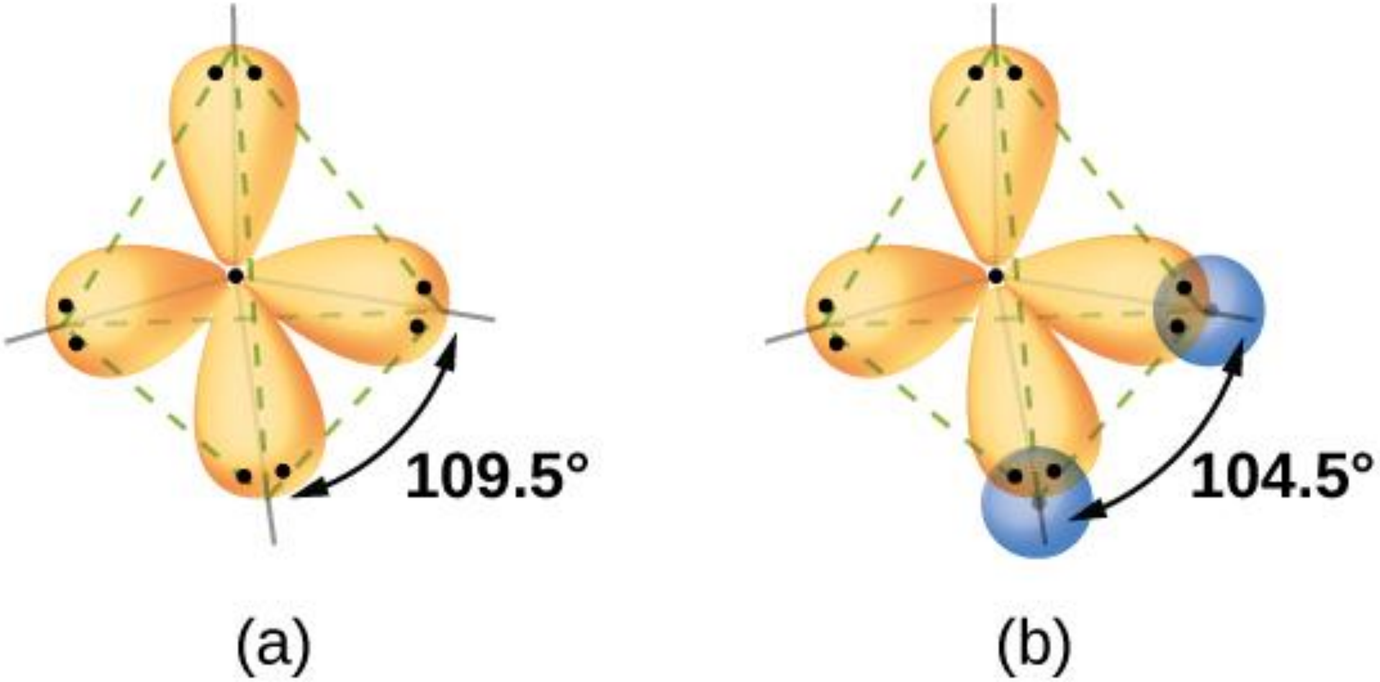


FIGURE 8.7 – VSEPR JUSTIFIED



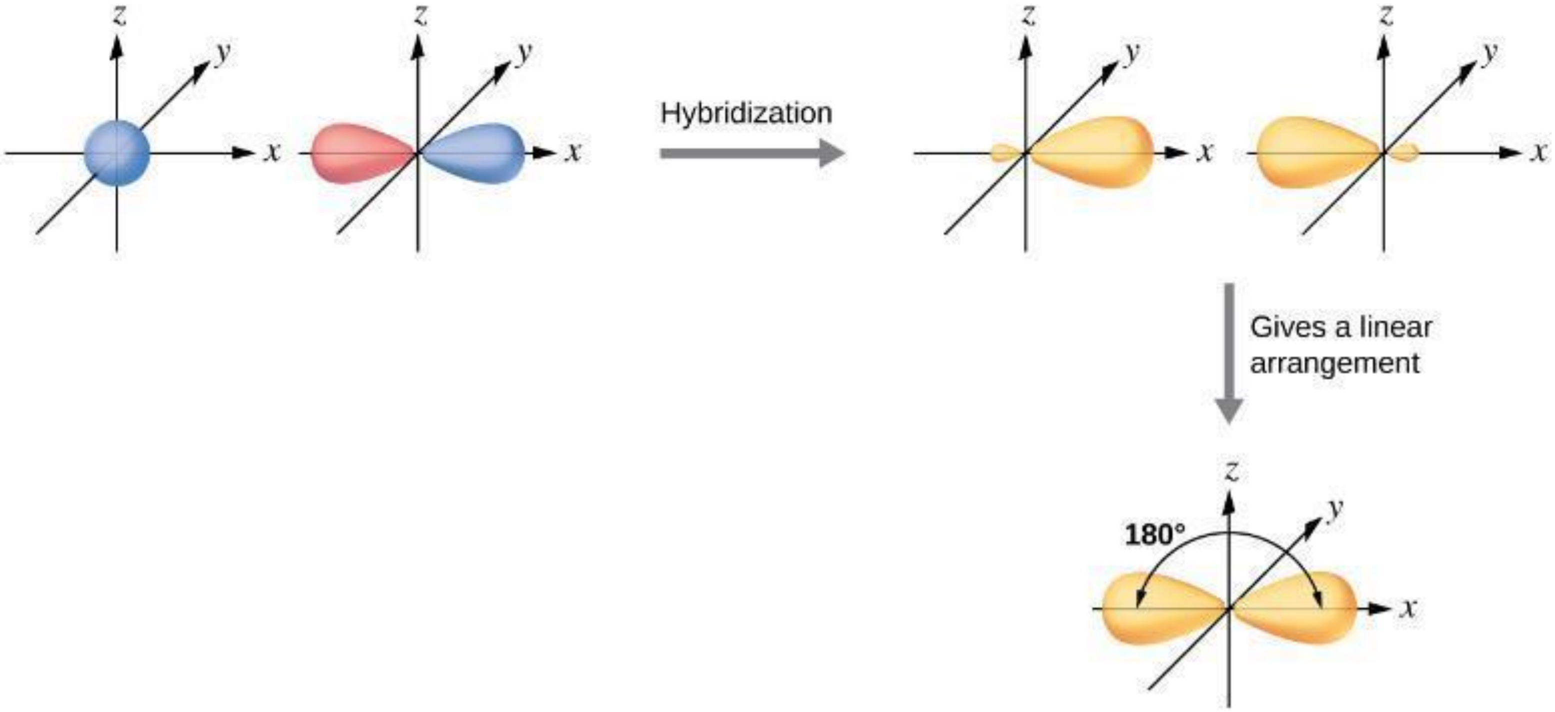
(a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals.

(b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1*s* orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

HYBRIDIZATION

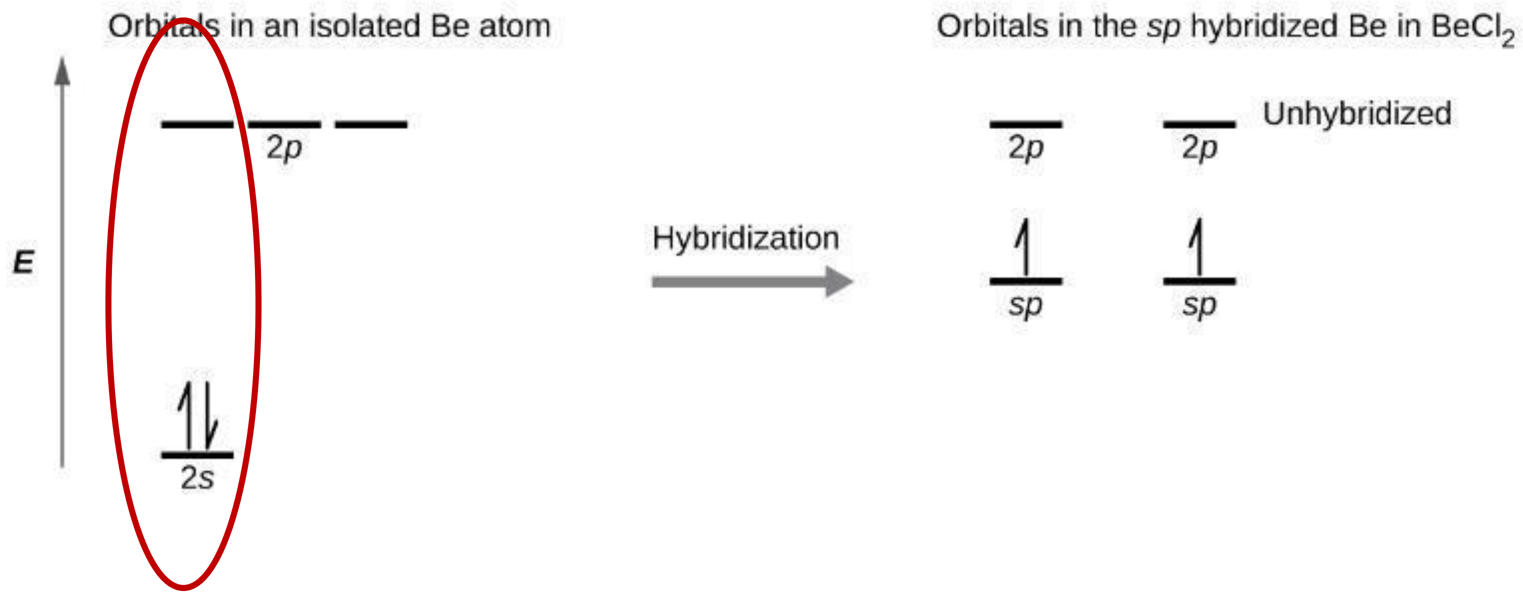
- Mixing of two or more atomic orbitals to form a new set of **hybrid orbitals**.
- **KEY POINT**: The number of hybrids needed = # of electron groups in the Lewis structure
- Mix at least 2 nonequivalent atomic orbitals (e.g., s and p). Hybrid orbitals have very different shape from original atomic orbitals.
- Number of hybrid orbitals is equal to number of pure atomic orbitals used in the hybridization process. (next slides)
- Covalent bonds are formed by:
  - Overlap of hybrid orbitals with atomic orbitals
  - Overlap of hybrid orbitals with other hybrid orbitals

FIGURE 8.8 – sp HYBRIDIZATION



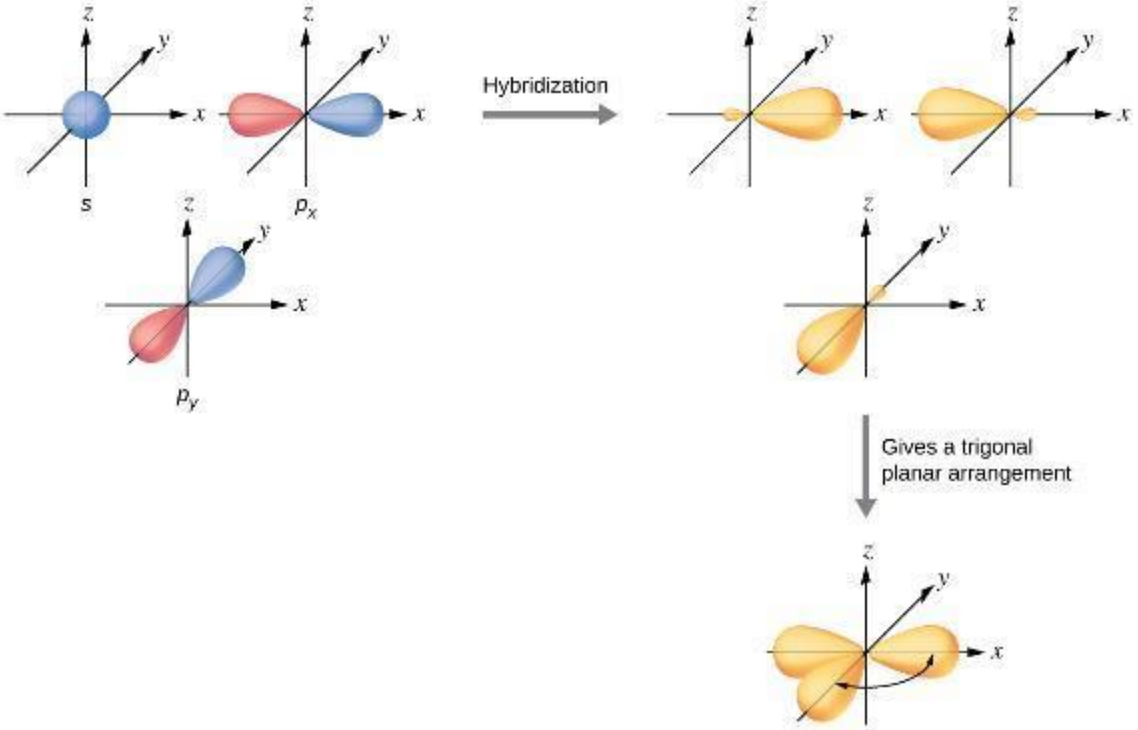
Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (purple). Each hybrid orbital is oriented primarily in just one direction. Note that each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains.

FIGURE 8.9 – sp HYBRIDIZATION



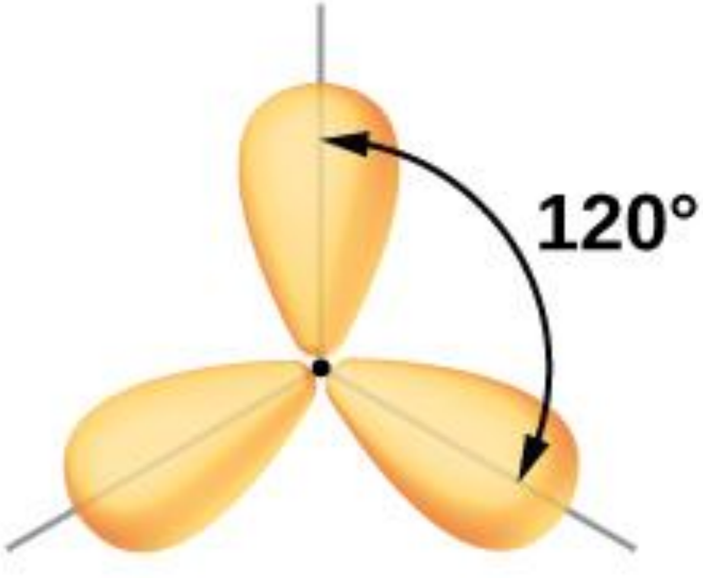
This orbital energy-level diagram shows the *sp* hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two *sp* hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3*p* orbital.

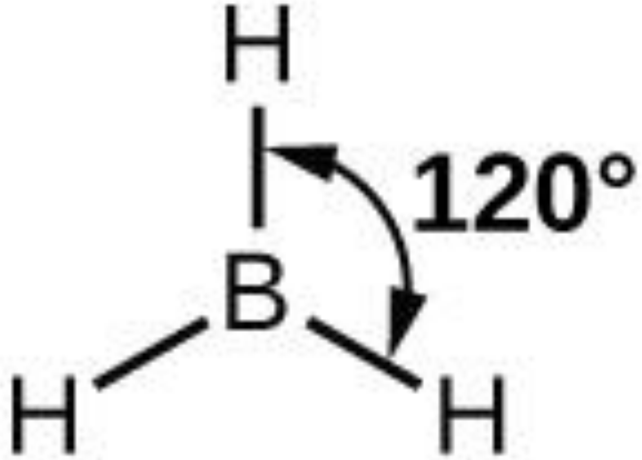
FIGURE 8.10 – sp^2 HYBRIDIZATION



The hybridization of an *s* orbital (blue) and two *p* orbitals (red) produces three equivalent sp^2 hybridized orbitals (purple) oriented at 120° with respect to each other. The remaining unhybridized *p* orbital is not shown here, but is located along the z axis.

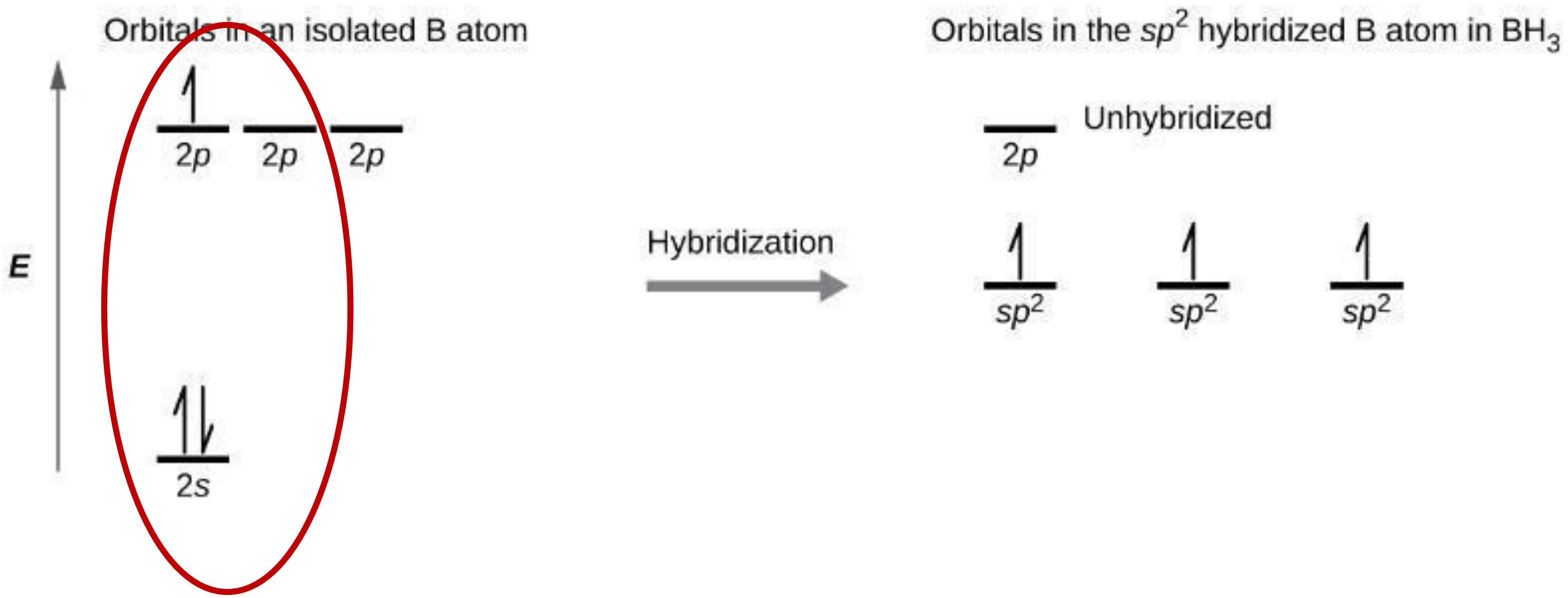
FIGURES 8.11-12 – sp^2 HYBRIDIZATION





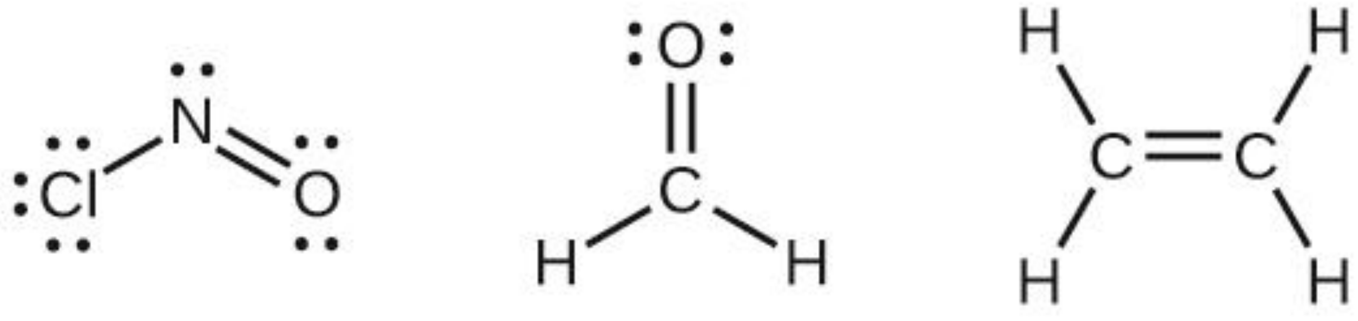
- This alternate way of drawing the trigonal planar *sp*^{2} hybrid orbitals is sometimes used in more crowded figures.
- BH_3 is an electron-deficient molecule with a trigonal planar structure.

FIGURE 8.13 – sp^2 HYBRIDIZATION



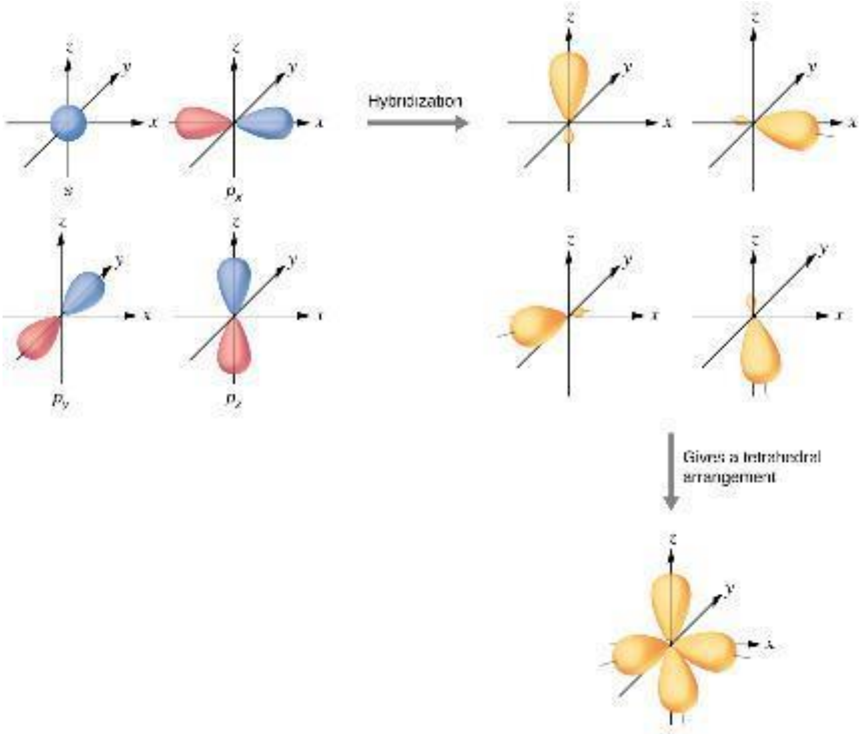
In an isolated B atom, there are one 2*s* and three 2*p* valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three *sp*^{2} orbitals and one unhybridized 2*p* orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

FIGURE 8.14 – sp^2 HYBRIDIZATION EXAMPLES



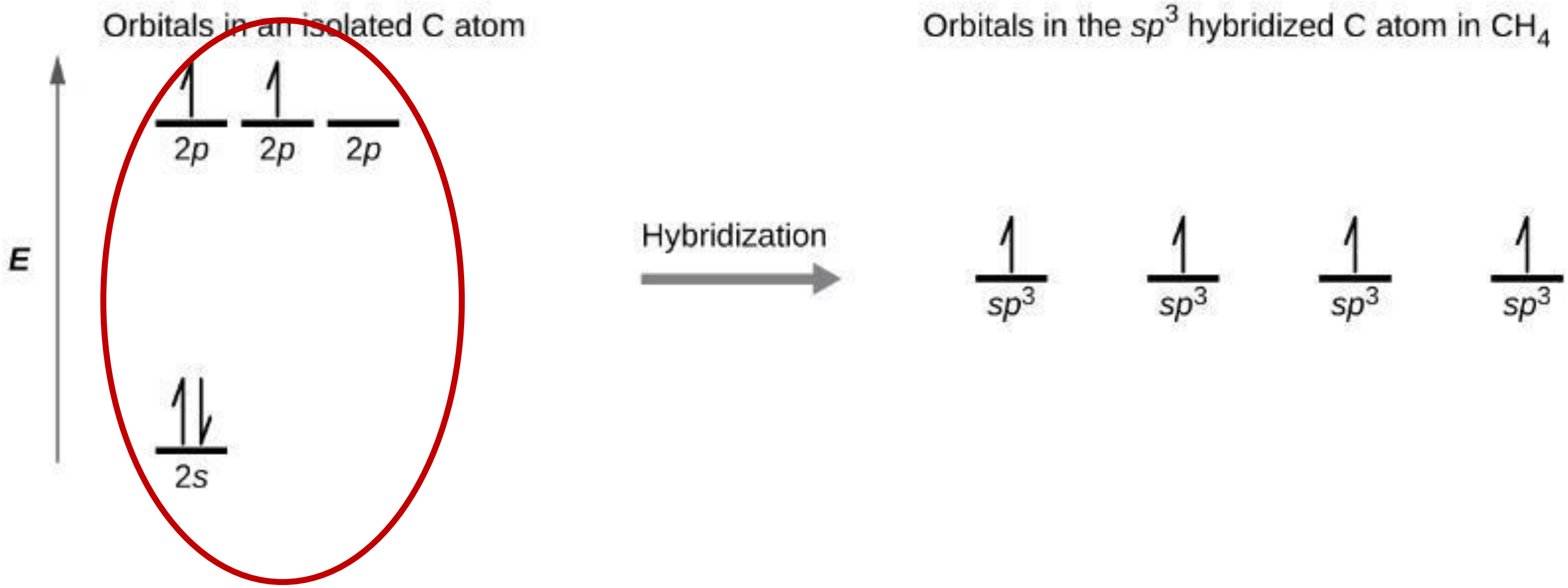
The central atom(s) in each of the structures shown contain three regions of electron density and are *sp*^{2} hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

FIGURE 8.15 – sp^3 HYBRIDIZATION



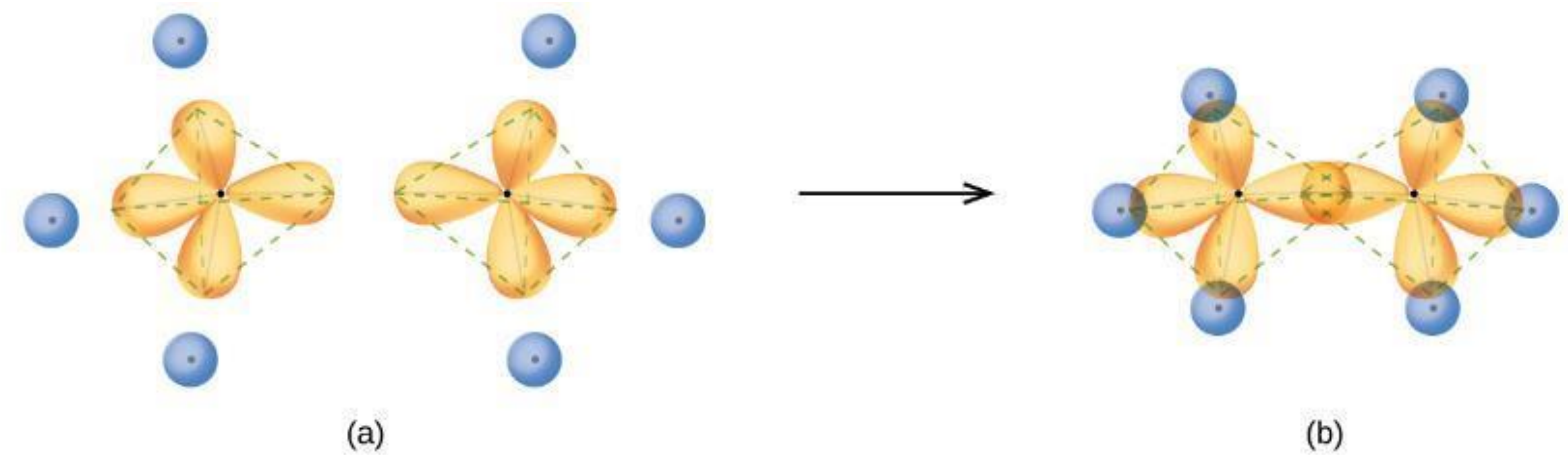
The hybridization of an *s* orbital (blue) and three *p* orbitals (red) produces four equivalent sp^3 hybridized orbitals (purple) oriented at 109.5° with respect to each other.

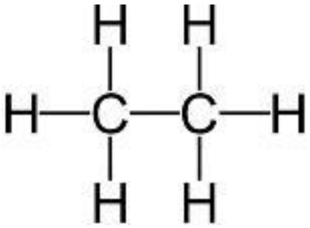
FIGURE 8.16 – sp^3 HYBRIDIZATION



The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

FIGURE 8.17 – sp^3 HYBRIDIZATION EXAMPLE

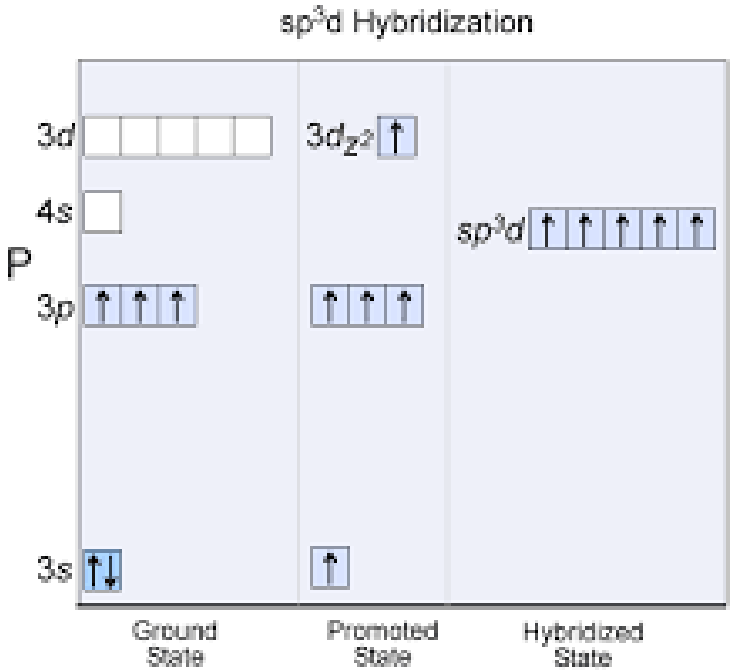


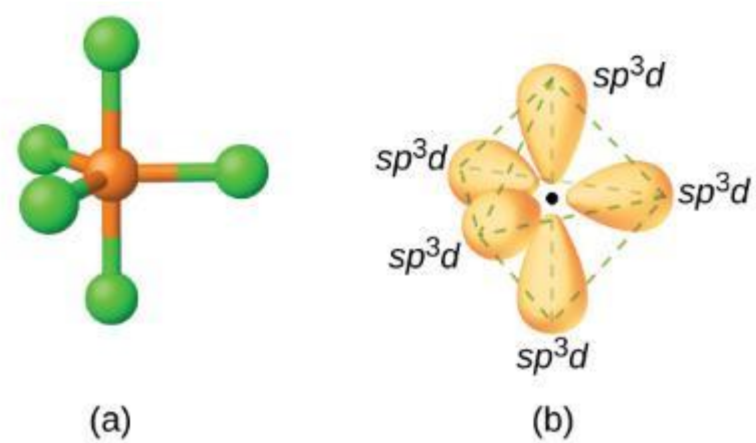


(a) In the ethane molecule, C_2H_6, each carbon has four *sp*^{3} orbitals.

(b) These four orbitals overlap to form seven σ bonds.

FIGURE 8.19 – sp^3d HYBRIDIZATION

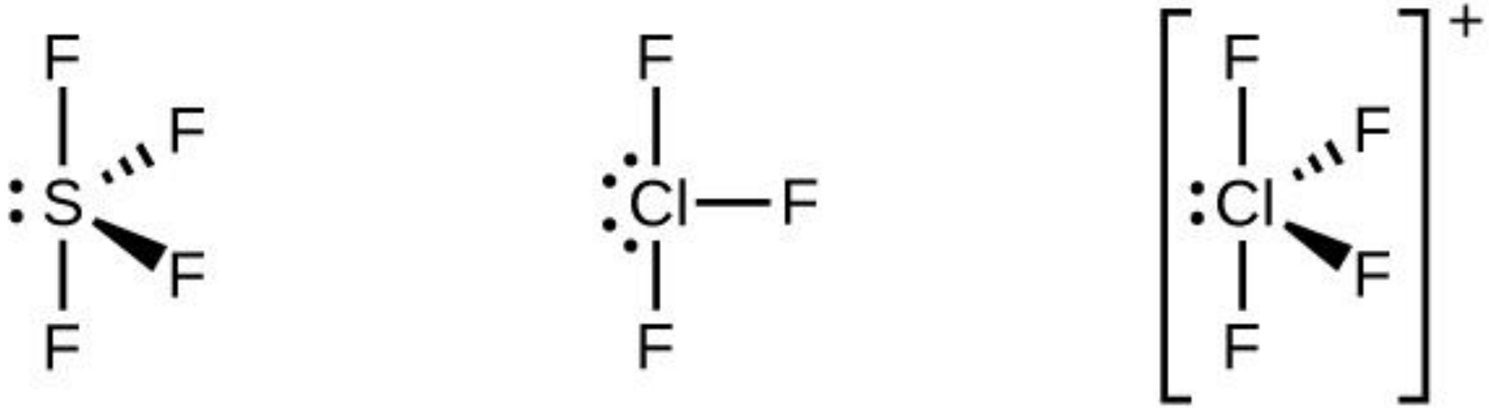




(a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals.

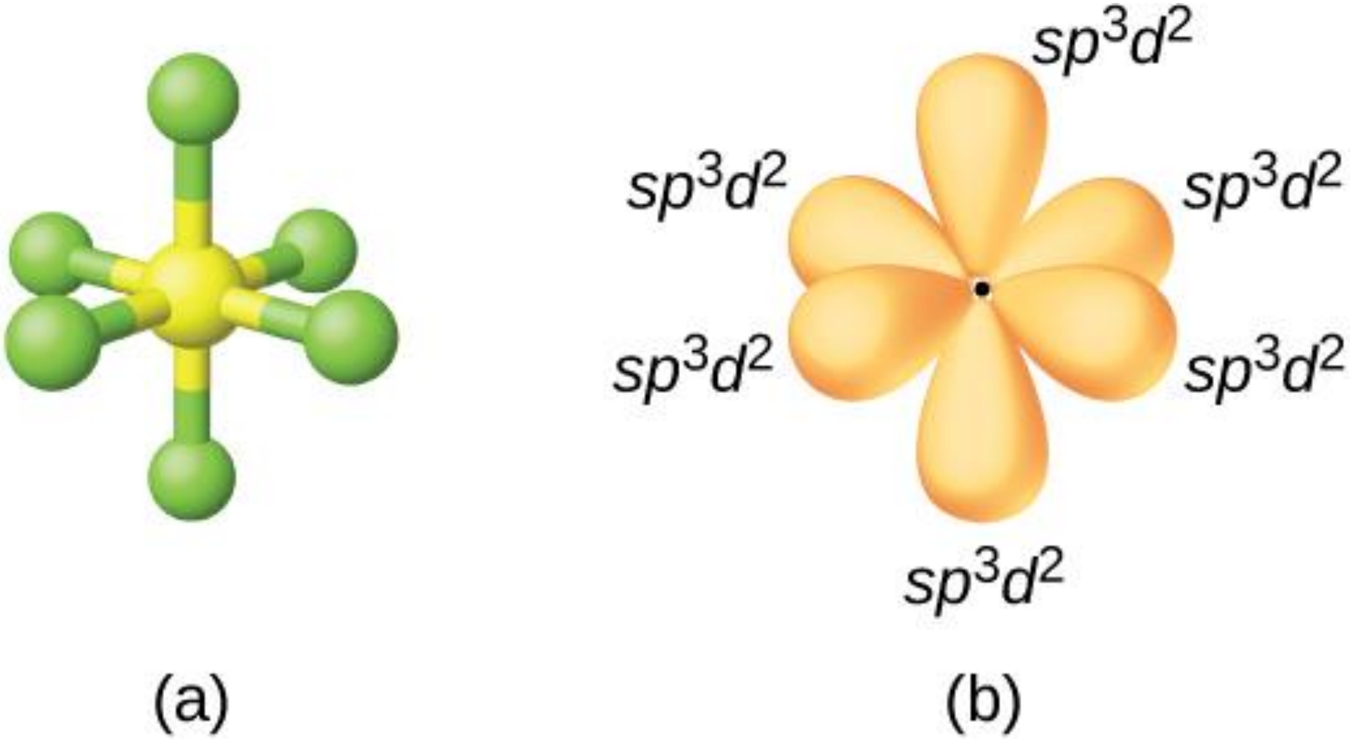
(b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

FIGURE 8.18 – sp^{3}d HYBRIDIZATION EXAMPLES



The three compounds pictured exhibit *sp*^{3}*d* hybridization in the central atom and a **trigonal bipyramidal geometry** of the 5 groups. SF_4 and ClF_4^+ have one lone pair of electrons on the central atom (**seesaw shape**), and ClF_3 has two lone pairs (**T-shape**).

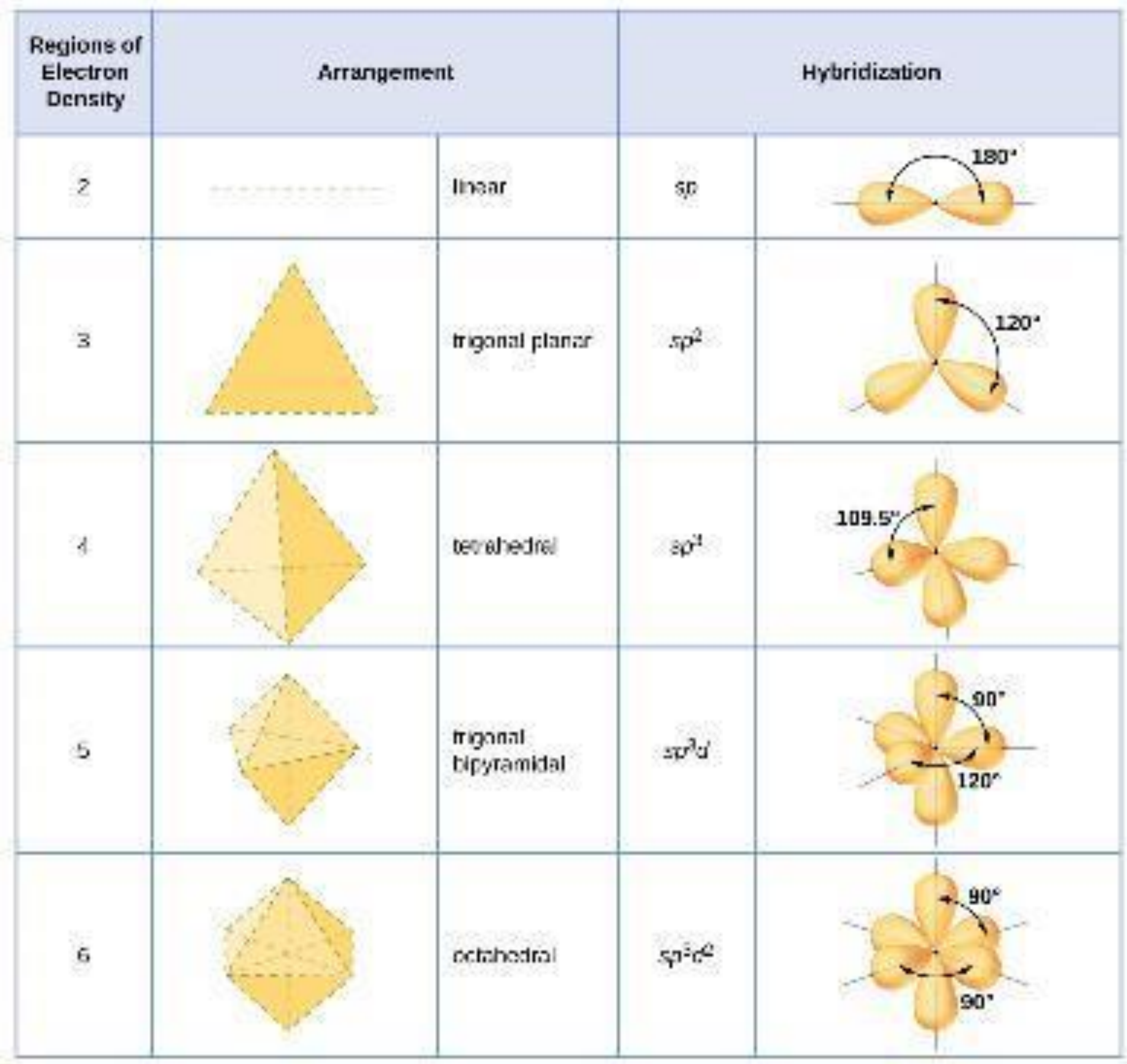
FIGURE 8.20 – sp^3d^2 HYBRIDIZATION



(a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization.

(b) The **six sp^3d^2 orbitals** form an **octahedral geometry** around sulfur and, since there are no lone pairs, an **octahedral-shaped molecule**. Again, the minor lobe of each orbital is not shown for clarity.

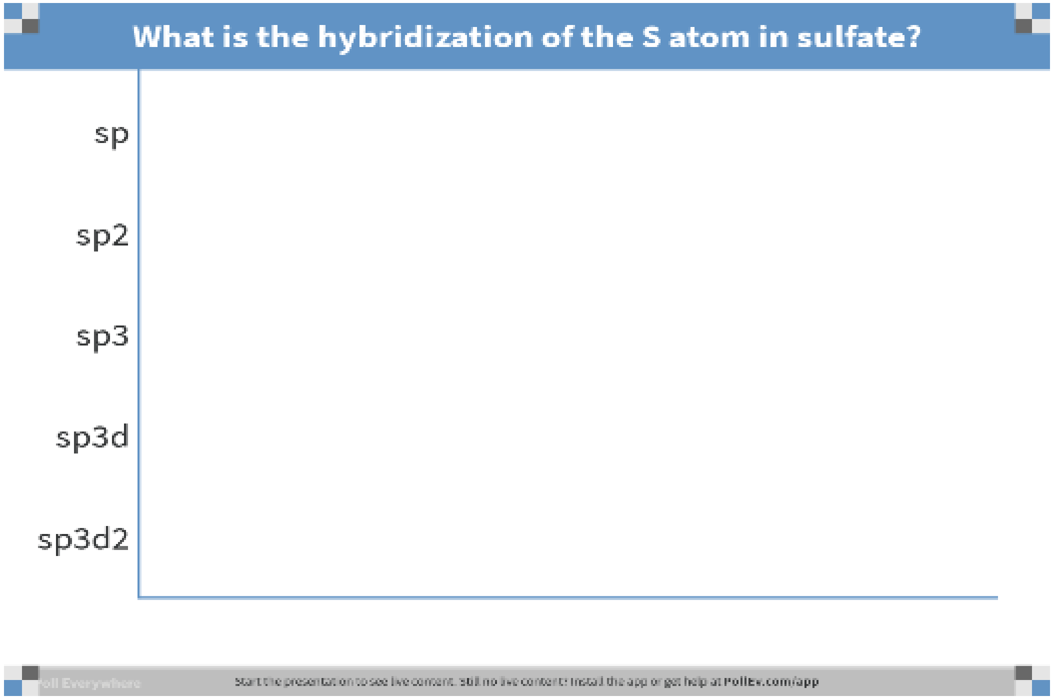
FIGURE 8.21 – HYBRIDIZATION SUMMARY



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	

EXAMPLE 8.2.1

What is the hybridization of the S atom in sulfate (SO_4^{2-})?



What is the hybridization of the S atom in sulfate?

- sp
- sp2
- sp3
- sp3d
- sp3d2

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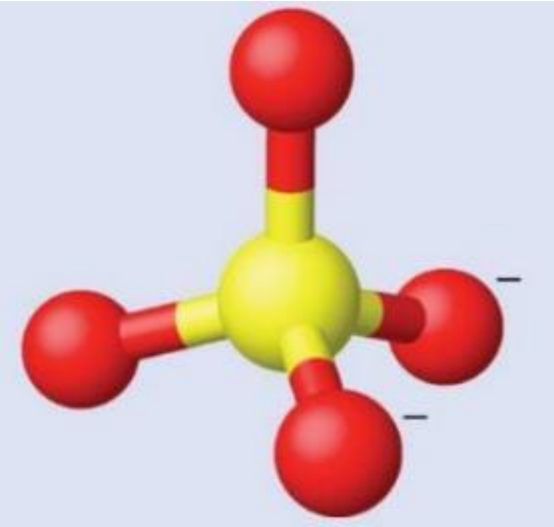
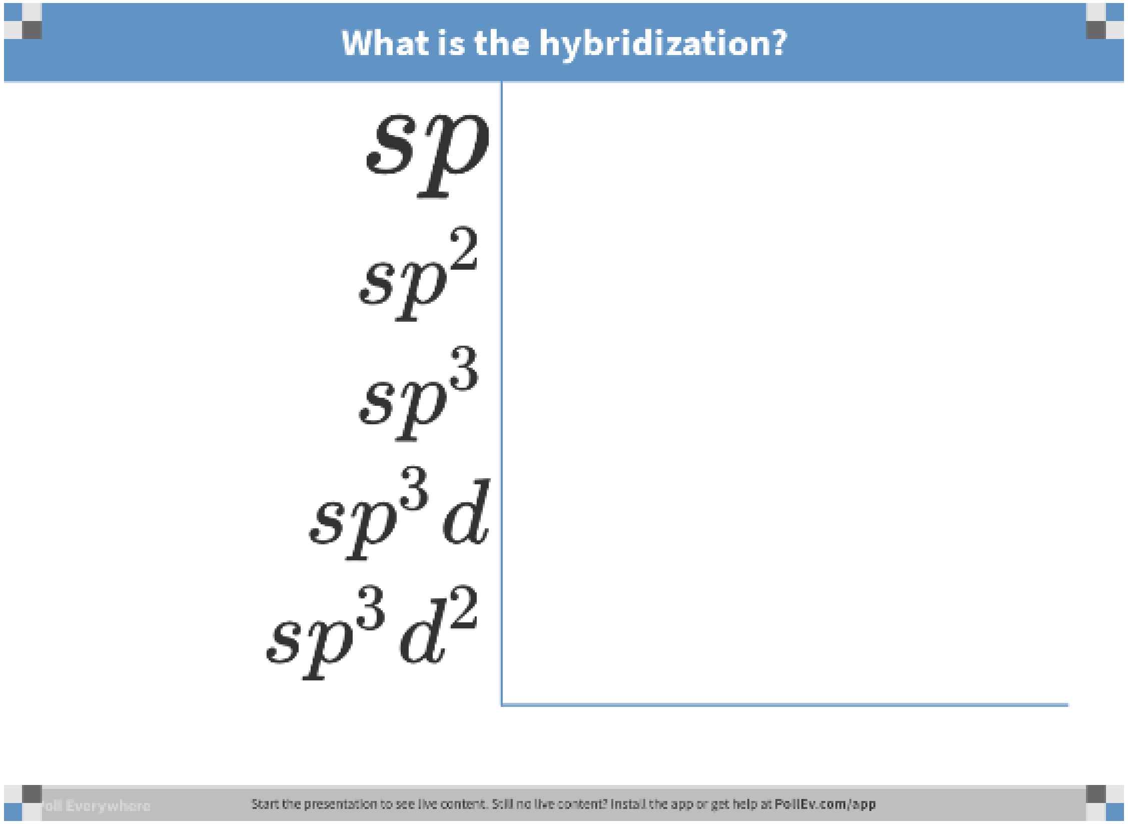


EXAMPLE 8.2.2

What is the hybridization of the Se atom in selenium tetrafluoride?



What is the hybridization?

- sp
- sp^2
- sp^3
- sp^3d
- sp^3d^2

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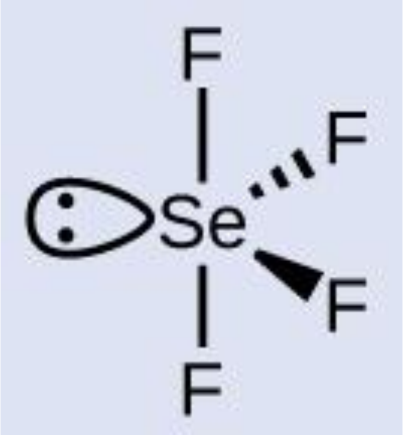
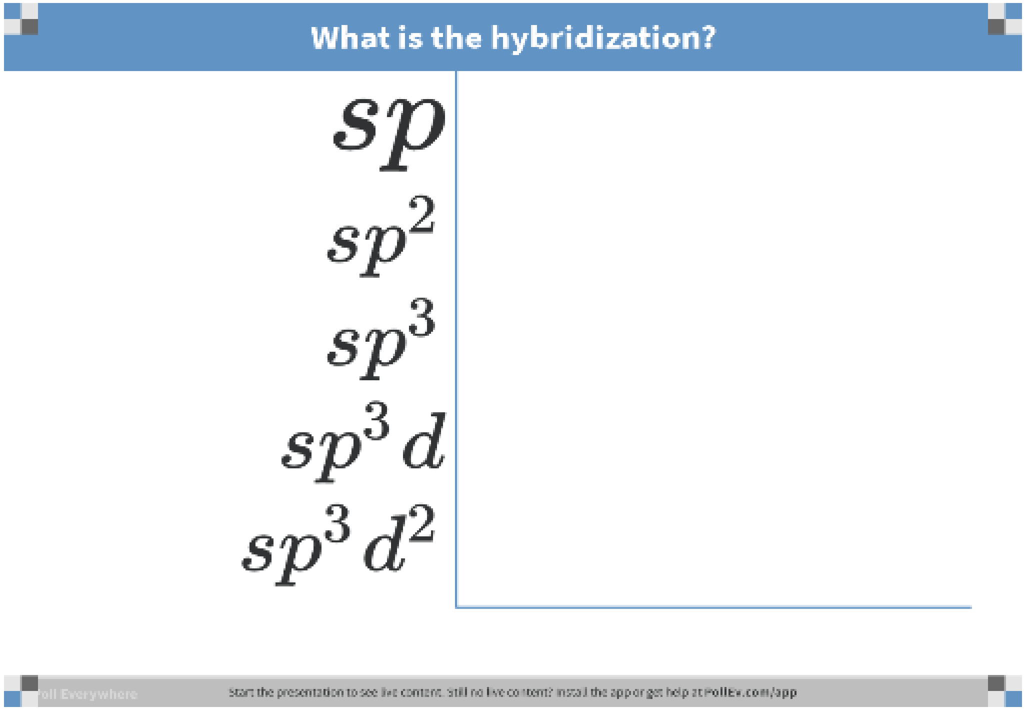


EXAMPLE 8.3.1

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen, carbon, and oxygen atom in urea?



What is the hybridization?

sp

sp^2

sp^3

sp^3d

sp^3d^2

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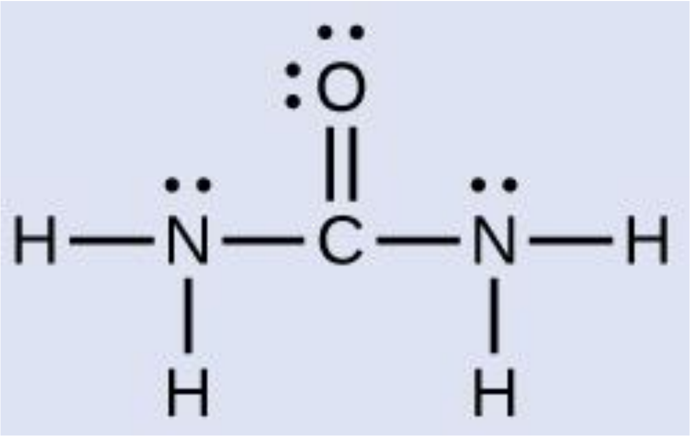
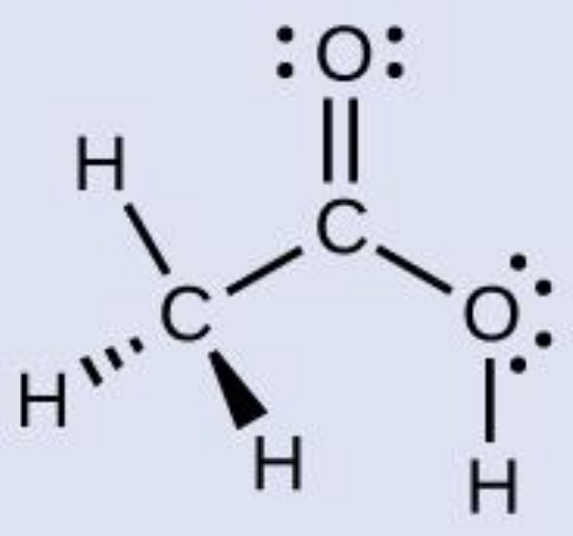
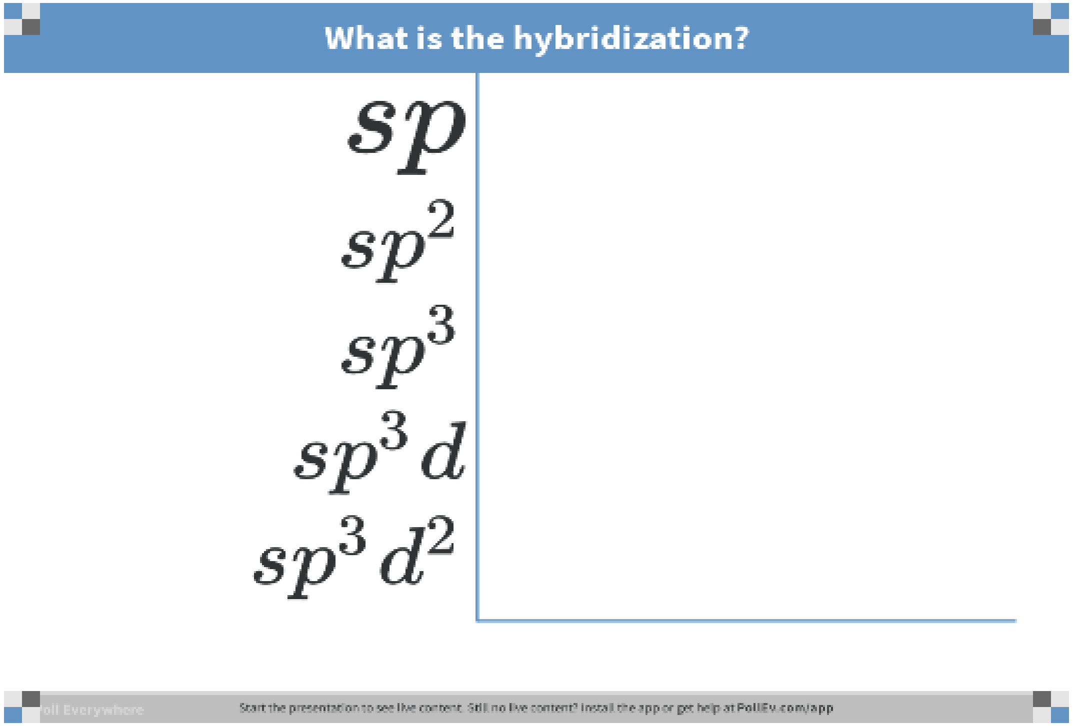


EXAMPLE 8.3.2

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste at ~5% concentration. What is the hybridization of the carbon and oxygen atoms in acetic acid?





What is the hybridization?

- sp
- sp^2
- sp^3
- sp^3d
- sp^3d^2

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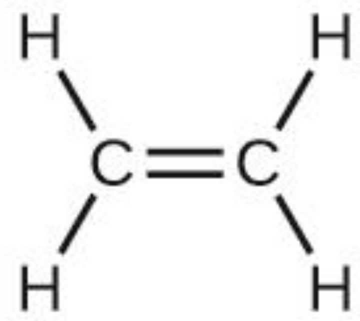
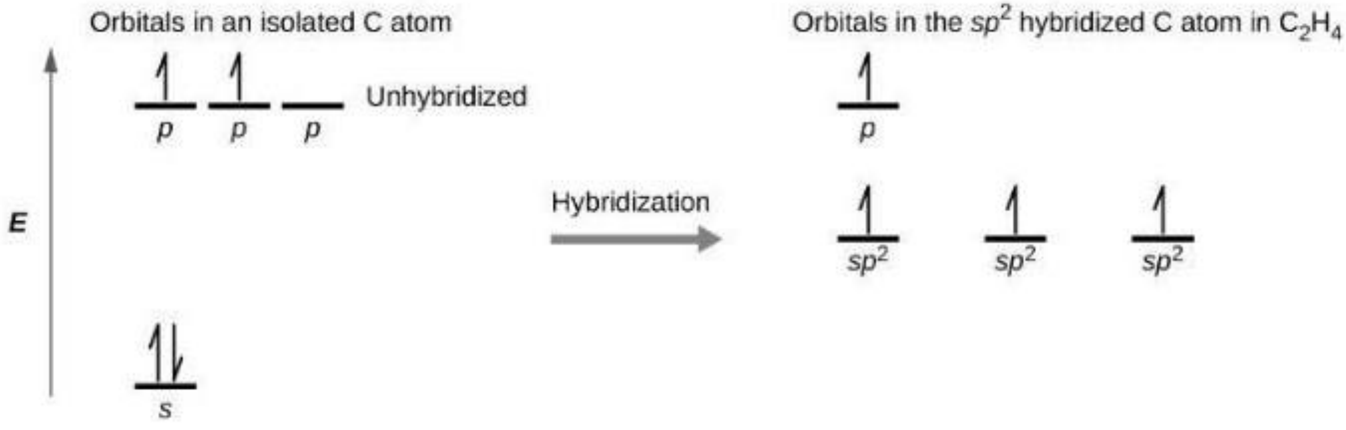
8.2 Hybrid Atomic Orbitals

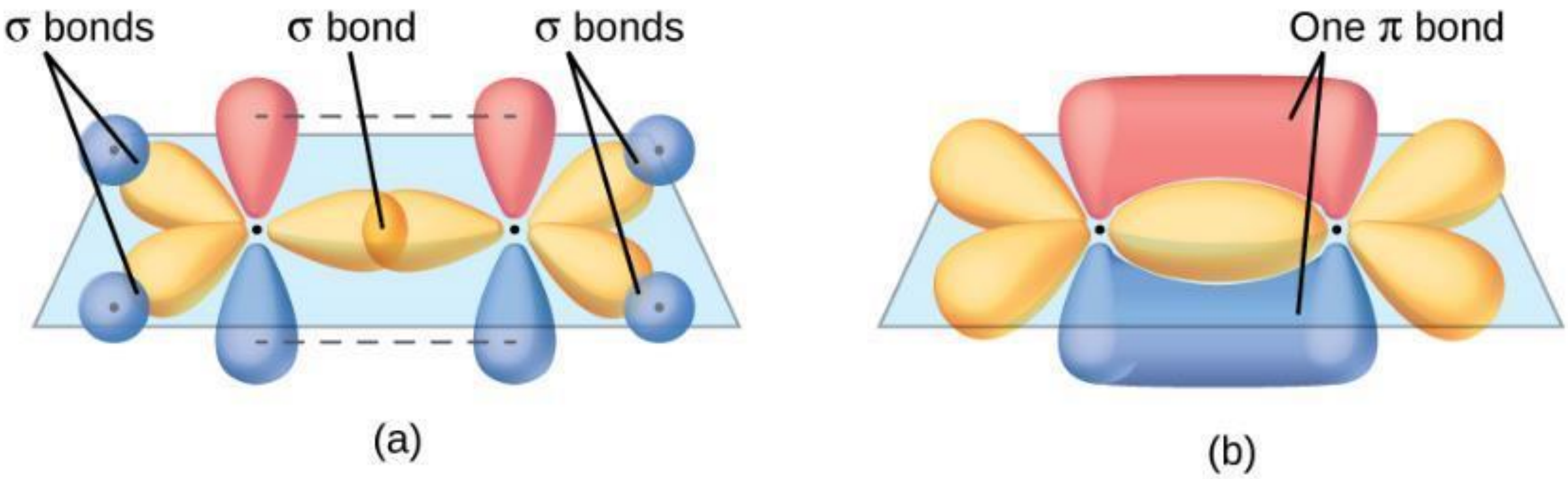
8.3 Multiple Bonds

8.4 Molecular Orbital Theory

ETHYLENE


H
H
C
C
H
H


Orbitals in an isolated C atom
E
p
p
p
Unhybridized
s
Hybridization
Orbitals in the sp² hybridized C atom in C₂H₄
p
sp²
sp²
sp²


σ bonds
σ bond
σ bonds
One π bond

(a)

(b)

FIGURE 8.24 – sp HYBRIDIZED CARBON

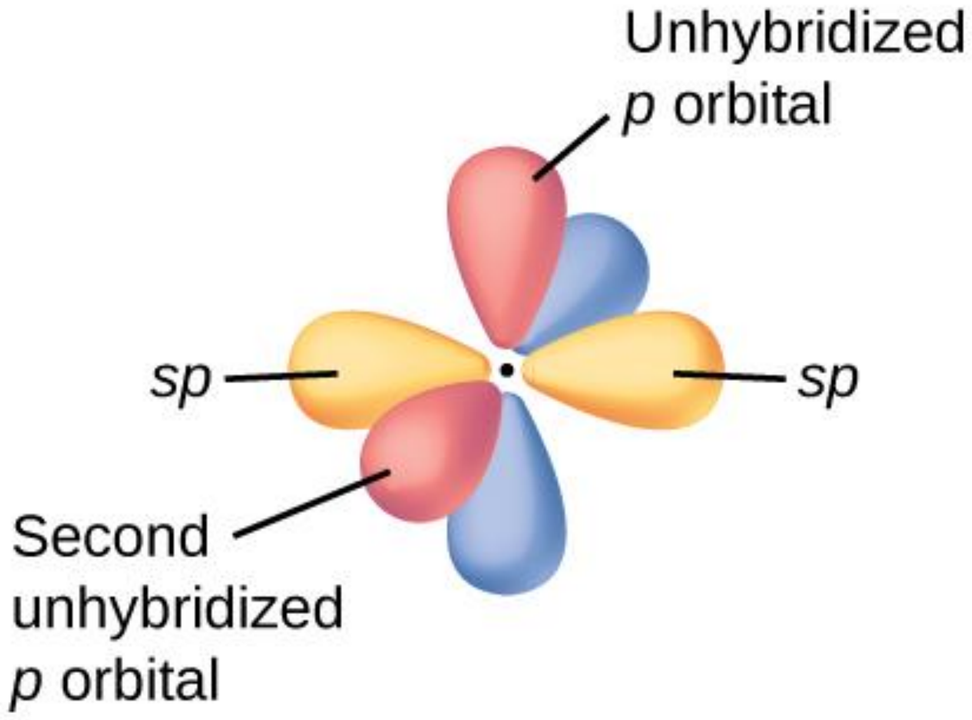
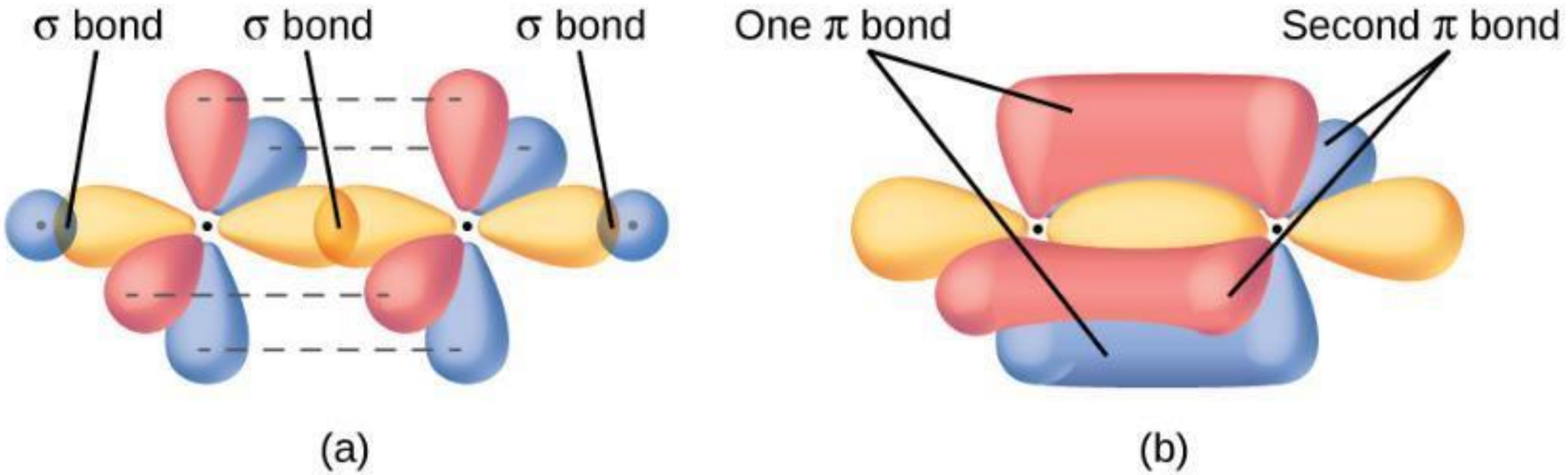


Diagram of the two linear *sp* hybrid orbitals of a carbon atom, which lie in a straight line, and the two **unhybridized** *p* orbitals at perpendicular angles.

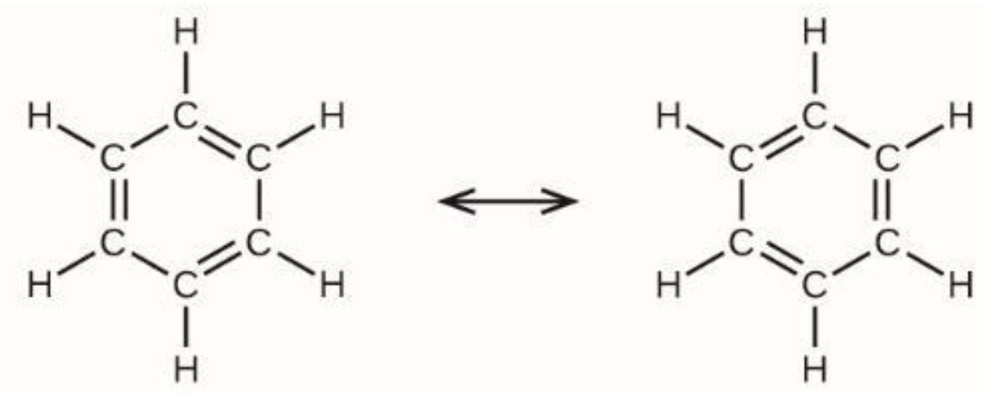
FIGURE 8.25 - ACETYLENE



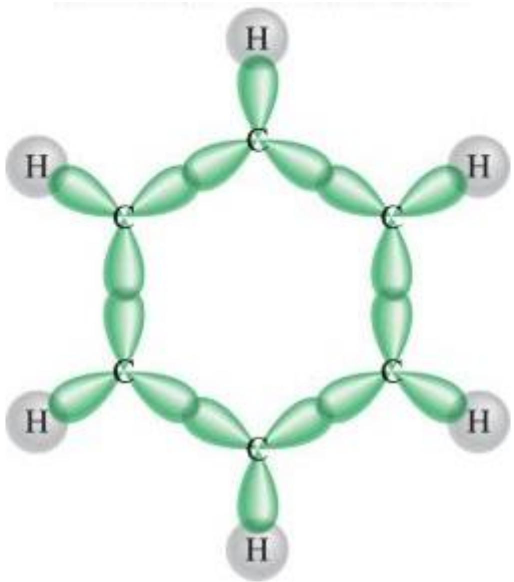
(a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a C ≡ C triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized *p* orbitals.

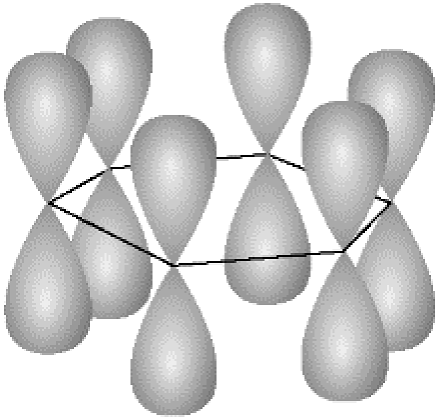
(b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

FIGURE 8.26 - BENZENE



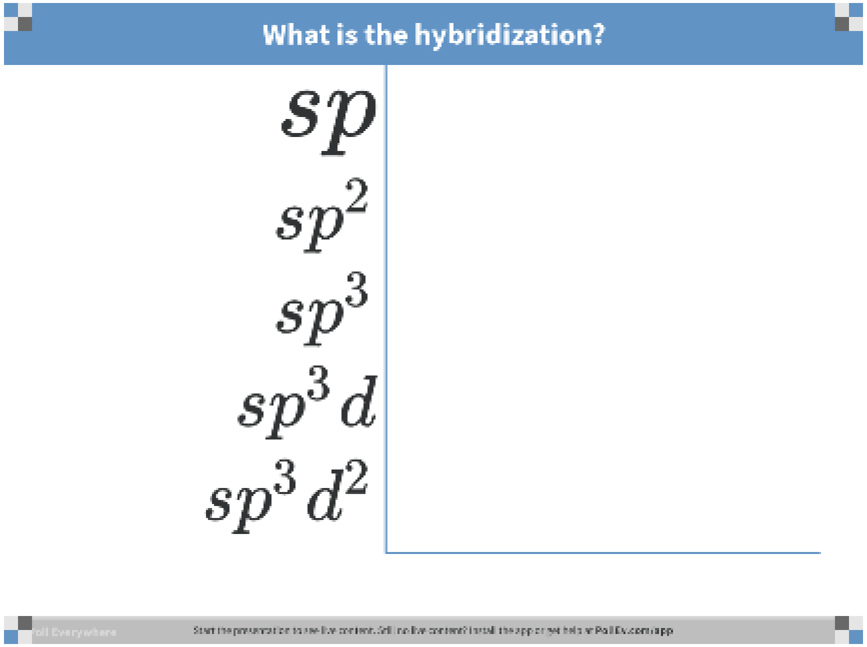
Each carbon atom in benzene, C_6H_6, is *sp*^{2} hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of *p* orbitals or the other, but rather delocalized throughout the molecule.





EXAMPLE 8.4

What is the hybridization of S in SO_2?



What is the hybridization?

sp

sp^2

sp^3

sp^3d

sp^3d^2

The N in NO_2?

CH. 8 OUTLINE

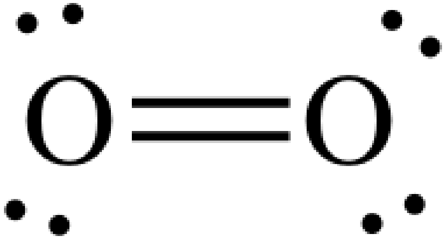
8.1 Valence Bond Theory

8.2 Hybrid Atomic Orbitals

8.3 Multiple Bonds

8.4 Molecular Orbital Theory

THE OXYGEN CONUNDRUM



…..What do you do when your theory fails?

MAGNETISM

- **Diamagnetic** – all electrons paired
- **Paramagnetic** – has unpaired electrons
- (**Ferromagnetic** – bulk material magnetism)

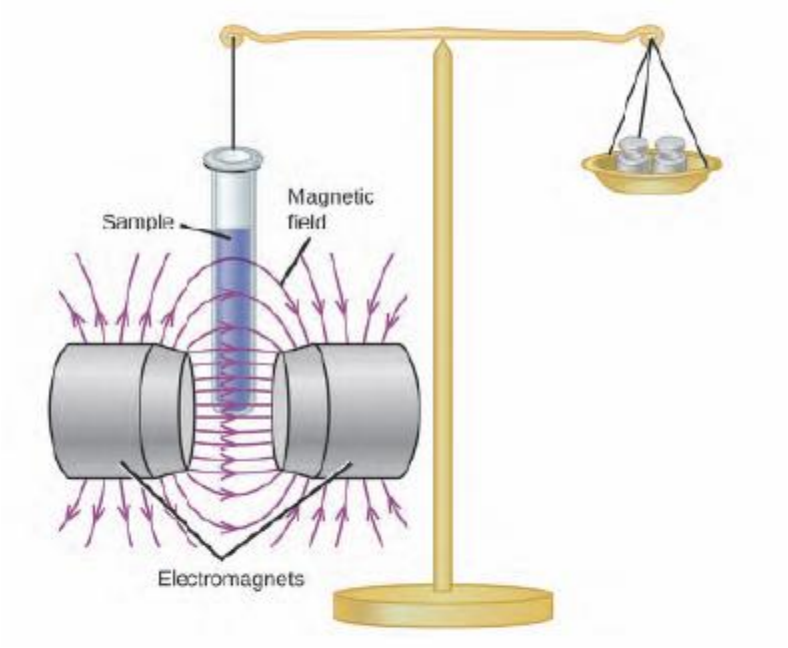
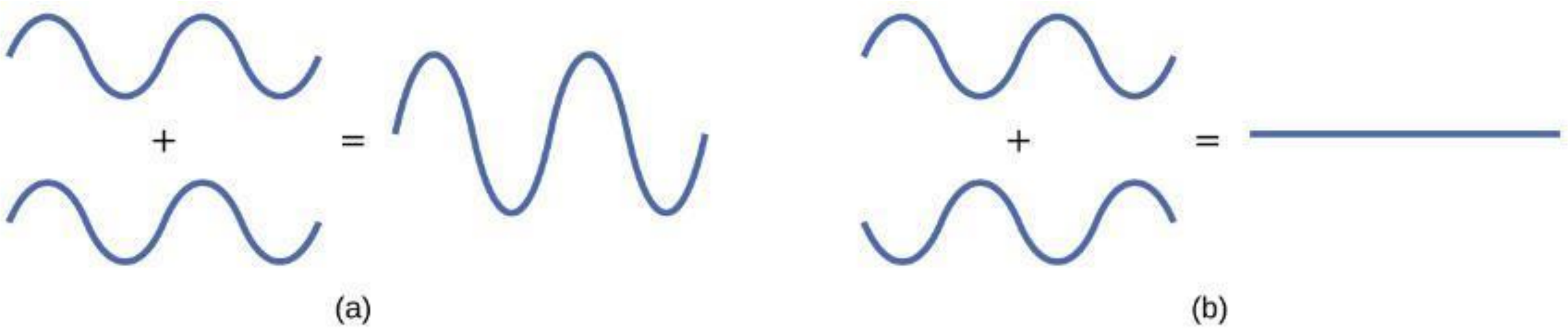


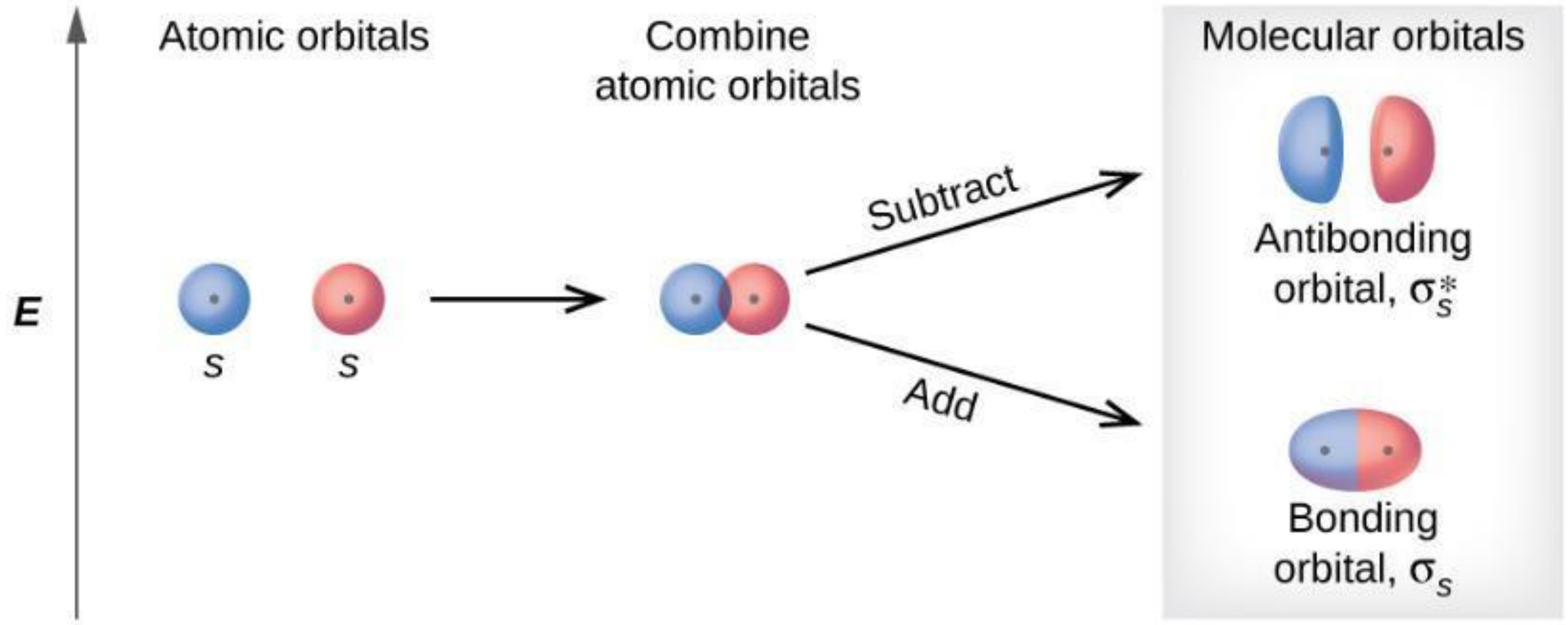
FIGURE 8.28 – LCAO IN THEORY



(a) When in-phase waves combine, constructive interference produces a wave with greater amplitude.

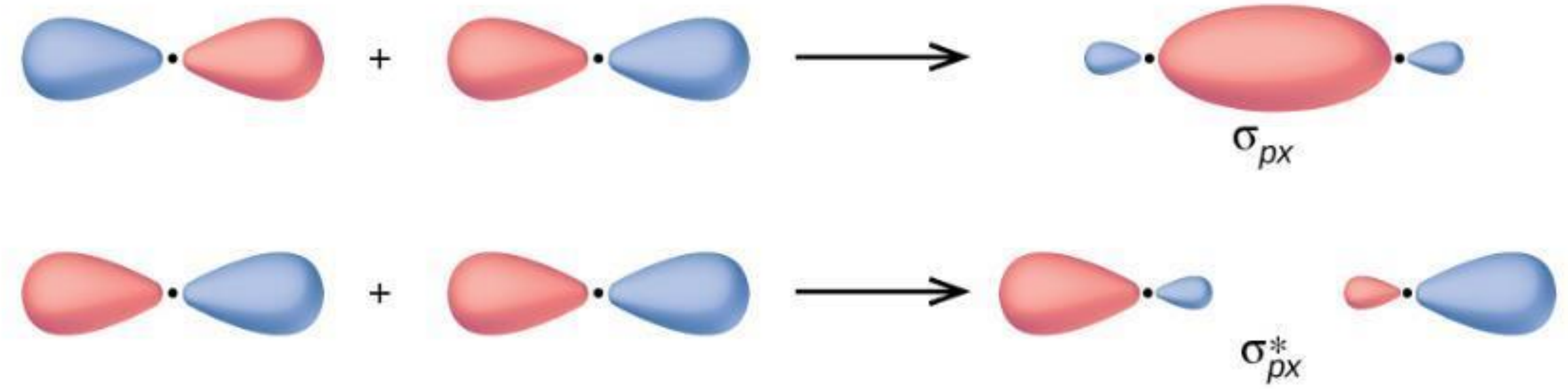
(b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

FIGURE 8.29 – LCAO FOR REAL



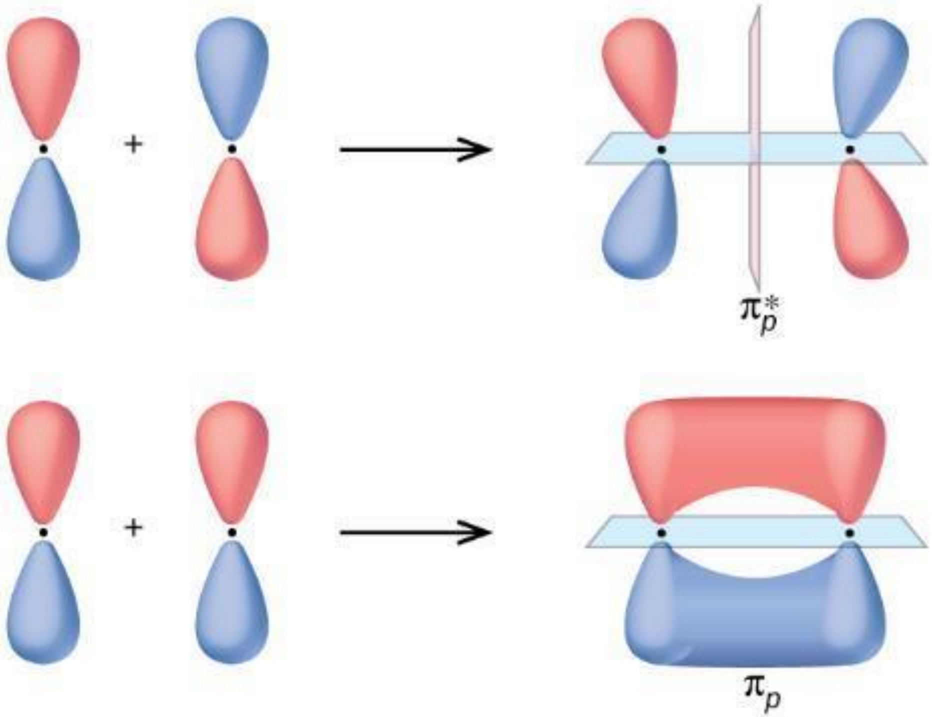
Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two *s* atomic orbitals.

FIGURE 8.30 – LCAO OF p ORBITALS – σ BONDING



Combining wave functions of two *p* atomic orbitals along the internuclear axis produces two molecular orbitals, σ_p and σ^*_p .

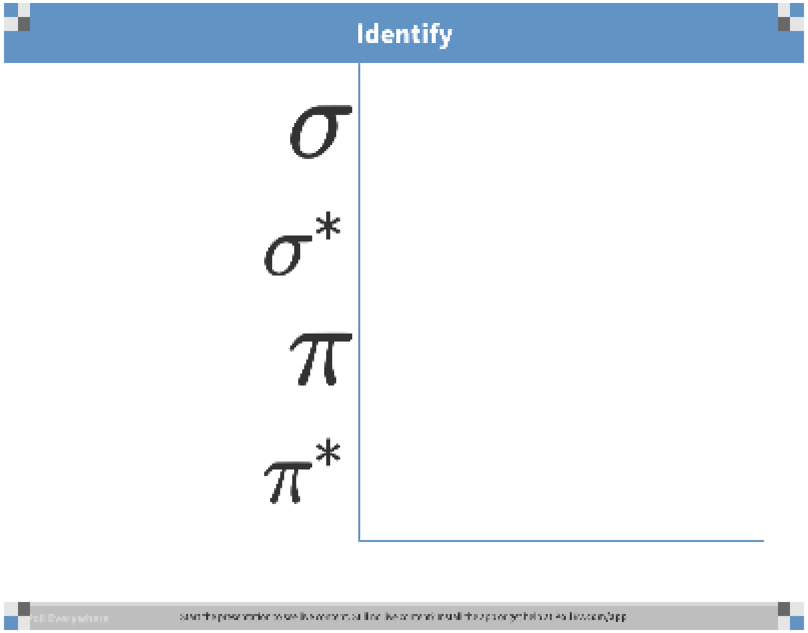
FIGURE 8.31 – LCAO OF P ORBITALS – π BONDING



- Side-by-side overlap of each two *p* orbitals results in the formation of two π molecular orbitals, one bonding and one antibonding.
- Combining the in-phase orbitals results in a bonding orbital. There is a nodal plane (blue) directly along the internuclear axis, but the orbital is located between the nuclei above and below this nodal plane.
- Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodal planes. One contains the axis, and one contains the perpendicular.

EXAMPLE 8.5.2

Identify the molecular orbital shown as *σ* or π, bonding or antibonding, and indicate where the node occurs.



Identify

σ

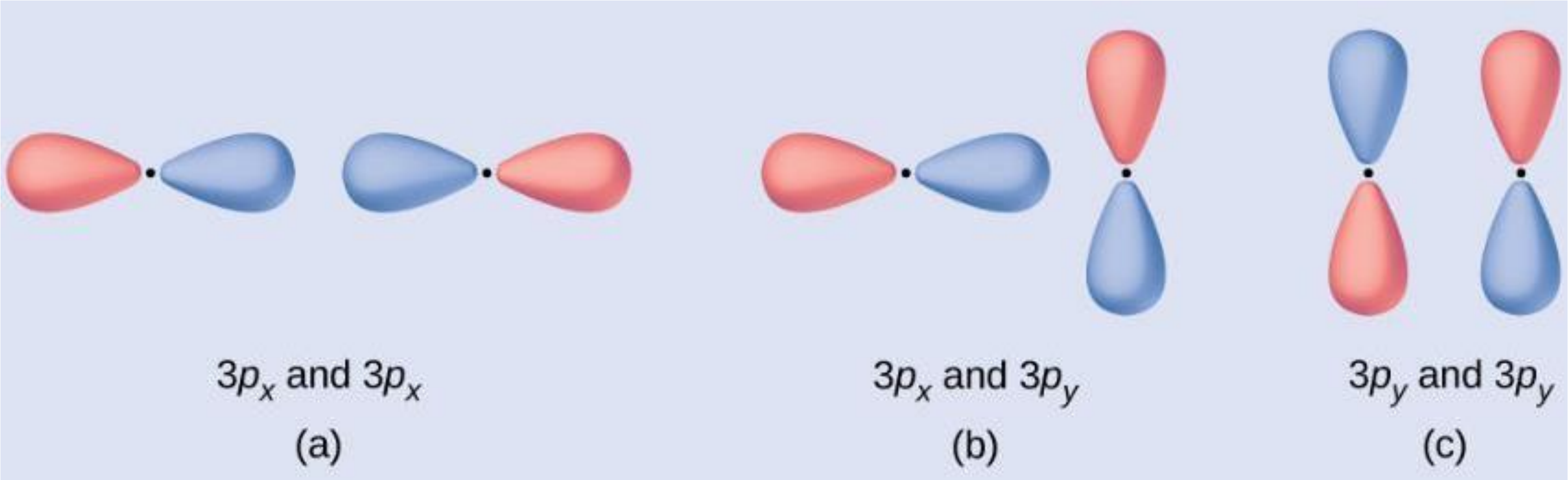
σ^*

π

π^*

EXAMPLE 8.5.1

Predict what type (if any) of molecular orbital (σ or π, binding or antibonding) would result from adding the wave functions so each pair of orbitals shown overlap.



$3p_x$ and $3p_x$
(a)

$3p_x$ and $3p_y$
(b)

$3p_y$ and $3p_y$
(c)

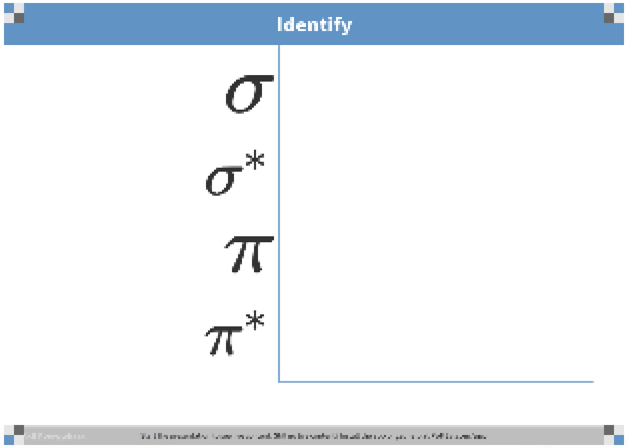
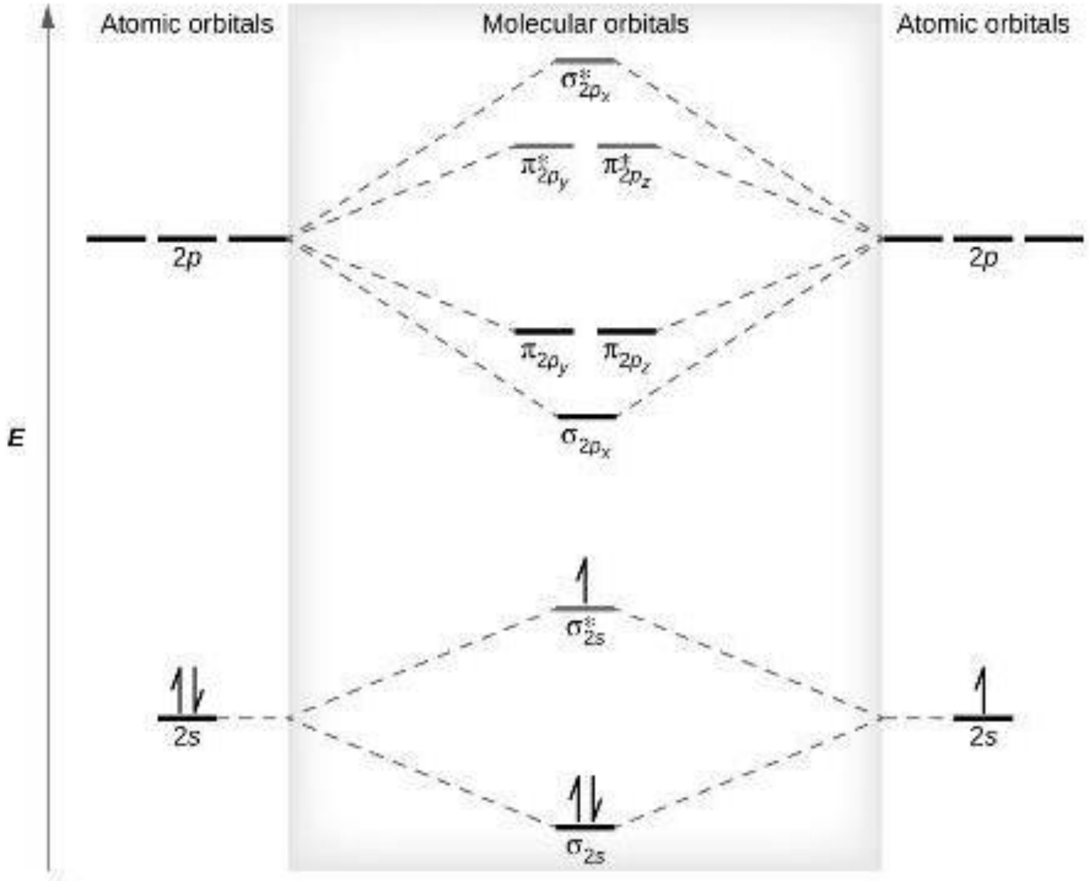


FIGURE 8.34 – MO DIAGRAM OF Be_2^+

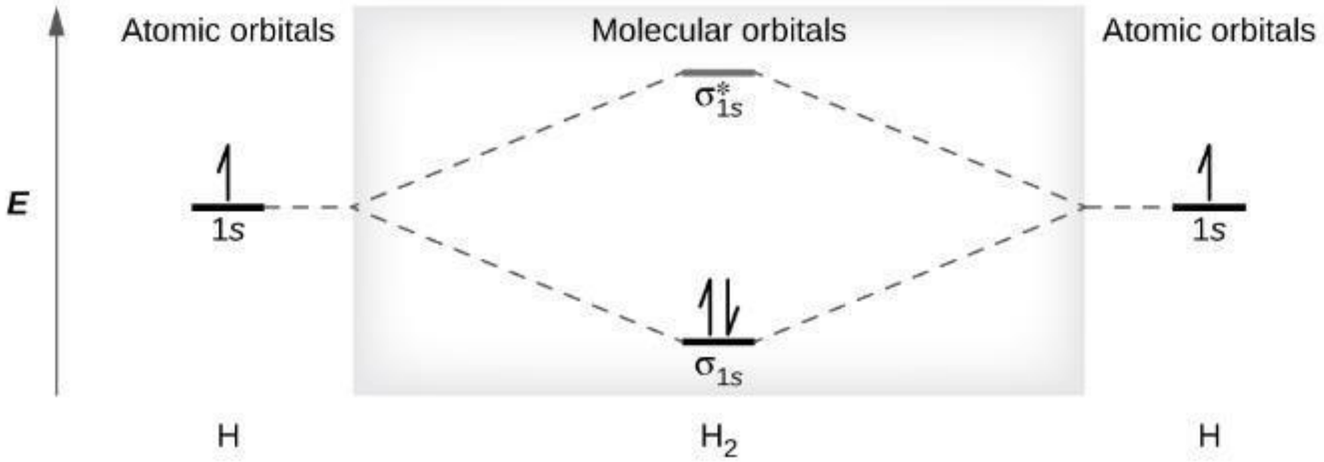


This is the molecular orbital diagram for the homonuclear diatomic $Be_2{}^+$, showing the molecular orbitals of the **valence shell only**. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund’s rule.

BOND ORDER

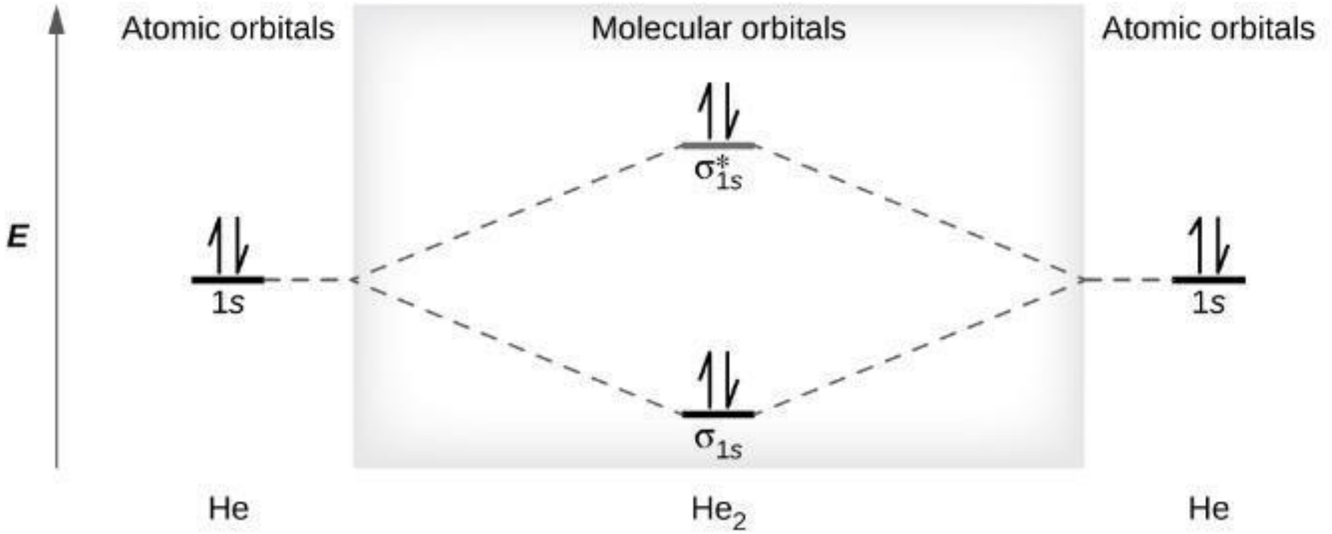
- The net contribution of the electrons to the bond strength of a molecule is identified by determining the **bond order** that results from filling molecular orbitals with electrons.
- When using Lewis structures to describe the distribution of electrons in molecules, bond order is defined as the number of bonding pairs of electrons between two atoms.
  - Thus, a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3.
- We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same.
- Bond order = (#bonding e^- – #antibonding e^-)/2
- The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

FIGURE 8.35 – MO DIAGRAM OF H_2



- The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.
- Bond order = 1.

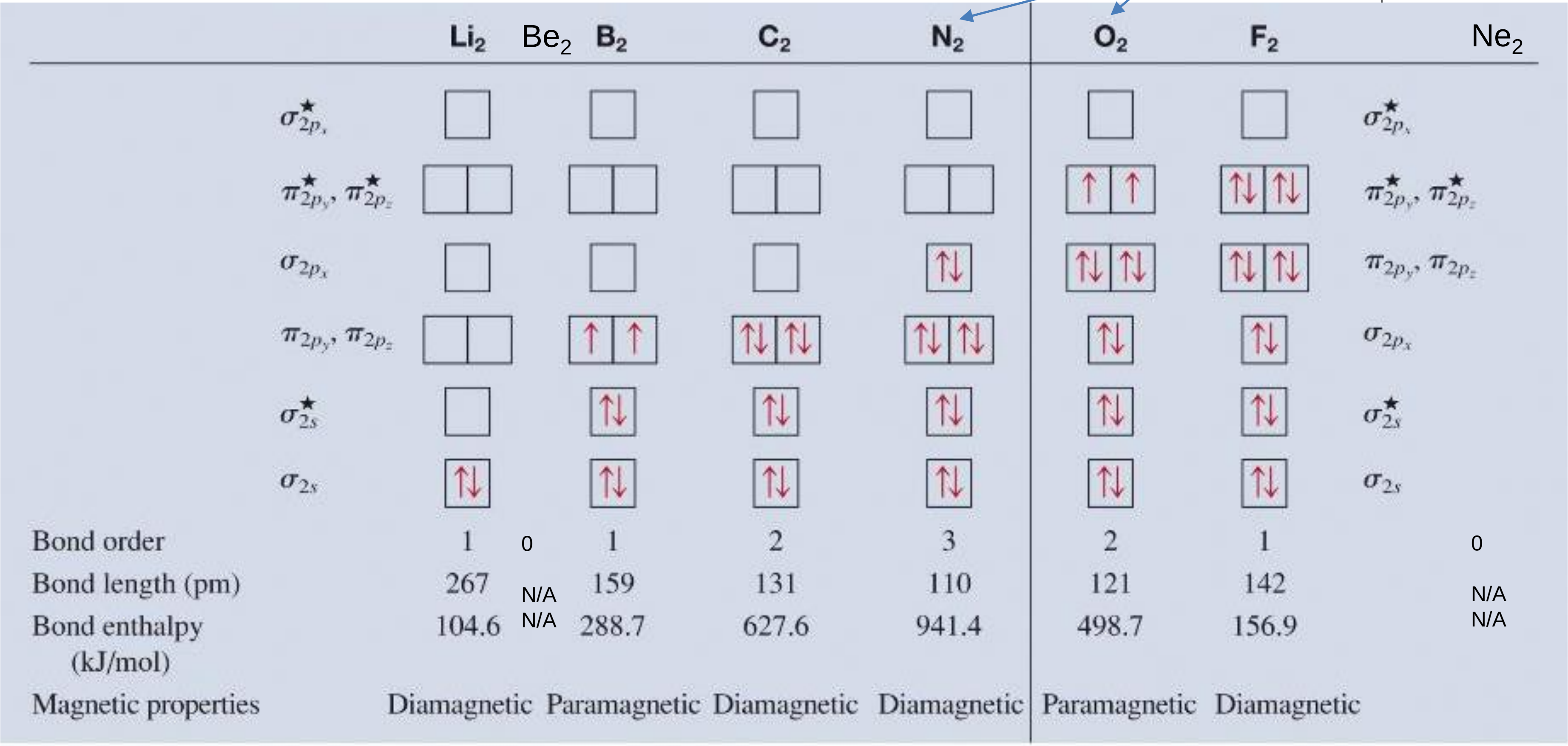
FIGURE 8.36 – He_2



- The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.
- Bond order = 0.

FIGURE 8.37 WITH ELECTRONS

Ex. 8.6

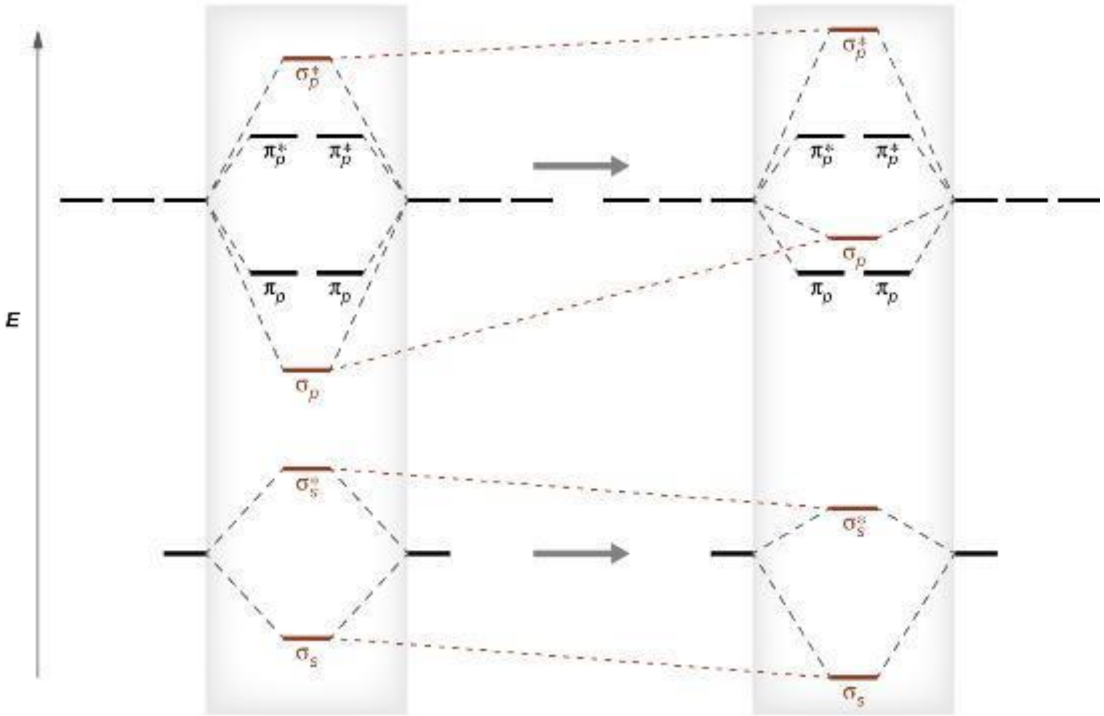


	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2	
$\sigma^{\star}_{2p_x}$	☐		☐	☐	☐	☐	☐		$\sigma^{\star}_{2p_x}$
$\pi^{\star}_{2p_y}, \pi^{\star}_{2p_z}$	☐☐		☐☐	☐☐	☐☐	↑ ↑	↑↓ ↑↓		$\pi^{\star}_{2p_y}, \pi^{\star}_{2p_z}$
σ_{2p_x}	☐		☐	☐	↑↓	↑↓ ↑↓	↑↓ ↑↓		π_{2p_y}, π_{2p_z}
π_{2p_y}, π_{2p_z}	☐☐		↑ ↑	↑↓ ↑↓	↑↓ ↑↓	↑↓	↑↓		σ_{2p_x}
$\sigma^{\star}_{2s}$	☐		↑↓	↑↓	↑↓	↑↓	↑↓		$\sigma^{\star}_{2s}$
σ_{2s}	↑↓		↑↓	↑↓	↑↓	↑↓	↑↓		σ_{2s}
Bond order	1	0	1	2	3	2	1	0	
Bond length (pm)	267	N/A	159	131	110	121	142	N/A	
Bond enthalpy (kJ/mol)	104.6	N/A	288.7	627.6	941.4	498.7	156.9	N/A	
Magnetic properties	Diamagnetic		Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic		

*For simplicity the σ_{1s} and $\sigma^{\star}_{1s}$ orbitals are omitted. These two orbitals hold a total of four electrons. Remember that for O_2 and F_2, σ_{2p_x} is lower in energy than π_{2p_y} and π_{2p_z}.

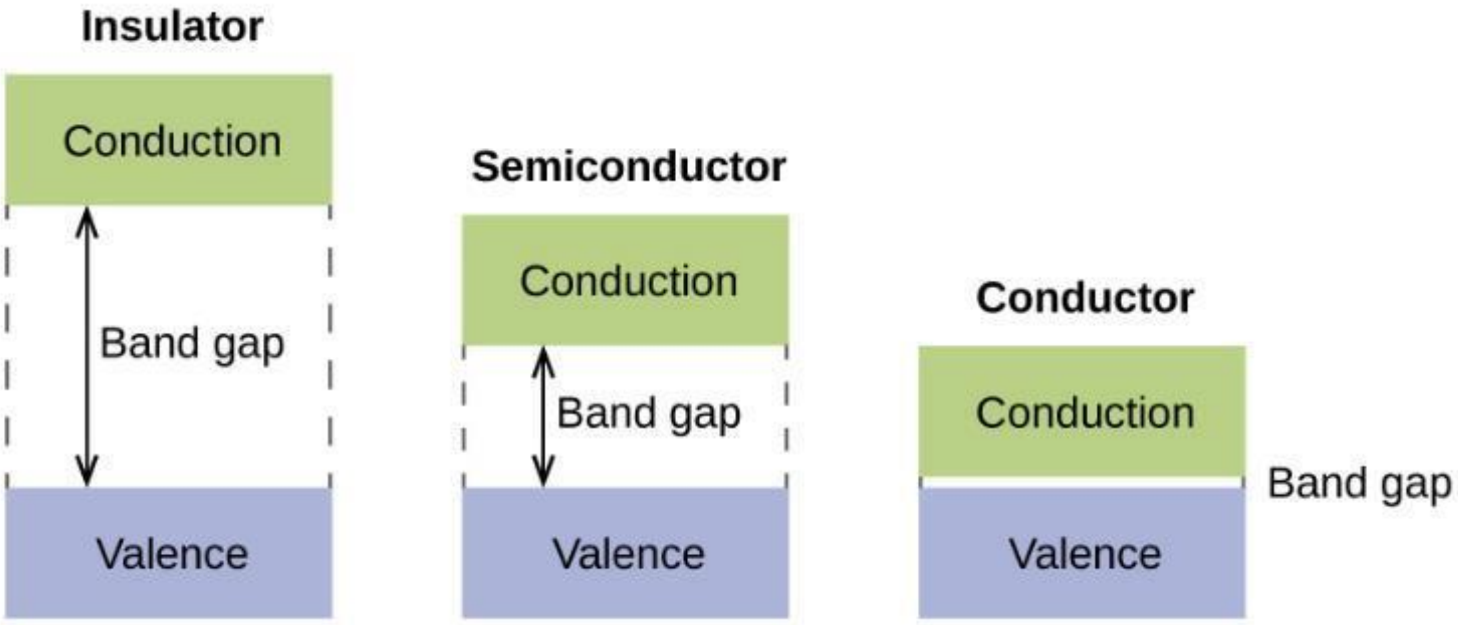
- MO diagrams for each homonuclear diatomic molecule of the second period.
- The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases.
- Between N_2 and O_2, the order of the orbitals changes due to lack of s-p mixing for O_2, F_2, and Ne_2 (p. 438).

FIGURE 8.38 – sp MIXING (MINOR POINT)



- Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.
- The energy difference between 2*s* and 2*p* orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne_2 exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the “normal pattern” of $\sigma < \pi$.

FIGURE 8.39 – BAND THEORY



Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valance band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

EXAMPLE 8.7

Give the molecular orbital configuration for the valence electrons in C_2^{2-}. Will this ion be stable, yes or no?

$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py}, \pi_{2pz})^4(\sigma_{2px})^2$

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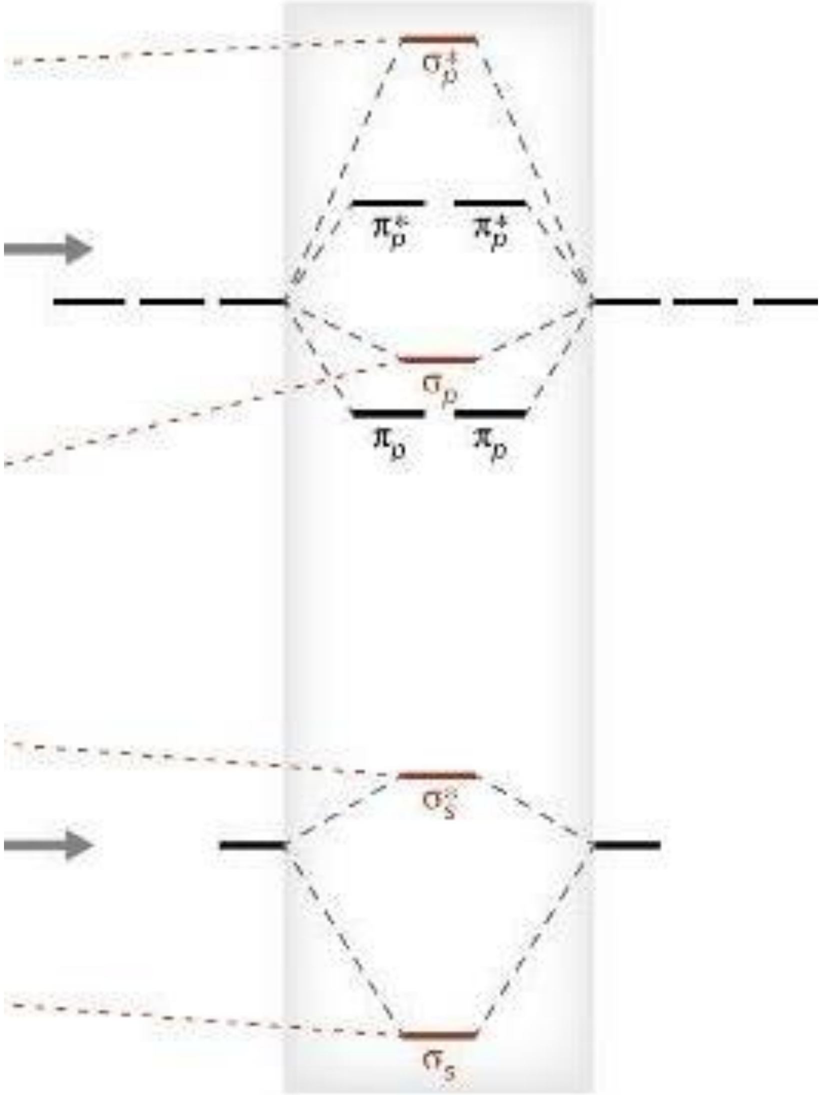

BIGGER MOLECULES

- Creating molecular orbital diagrams for molecules with more than two atoms relies on the same basic ideas as the diatomic examples presented here. However, with more atoms, computers are required to calculate how the atomic orbitals combine.
- See (http://openstaxcollege.org/l/16orbitaldiag) has three-dimensional drawings of the 66 lowest-energy molecular orbitals for C_6H_6.
- Semiconductor (and other) research often examines the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

Chapter 8 Advanced Theories of Covalent Bonding

HW problems:

6, 7, 12, 21, 27, 29, 41, 47, 49