

# Chapter 8: Advanced Theories of Covalent Bonding

## 8.1 Valence Bond Theory

### Question 45-1.

Explain how  $\sigma$  and  $\pi$  bonds are similar and how they are different.

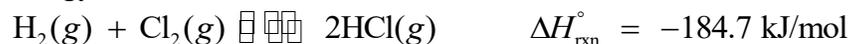
#### Solution

Similarities: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. Differences:  $\sigma$  bonds are stronger and result from end-to-end overlap and all single bonds are  $\sigma$  bonds;  $\pi$  bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more  $\pi$  bonds (in addition to a  $\sigma$  bond).

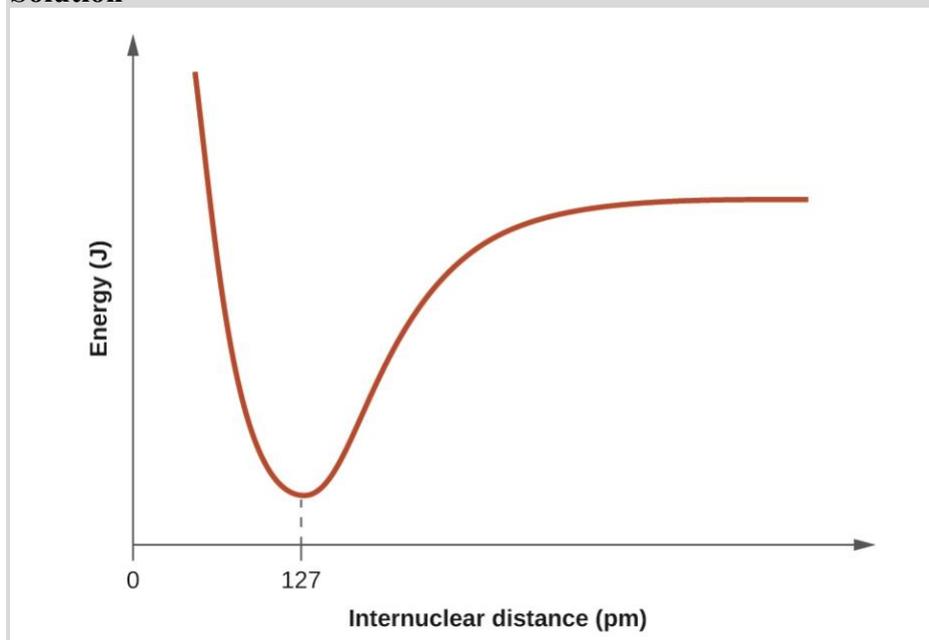
### Question 45-2.

Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.

- Use the bond energy found in Table 8.1 to calculate the energy for one single HCl bond (Hint: How many bonds are in a mole?)
- Use the enthalpy of reaction and the bond energies for  $\text{H}_2$  and  $\text{Cl}_2$  to solve for the energy of one mole of HCl bonds.



#### Solution



When H and Cl are separate (the x axis) the energy is at a particular value. As they approach, it decreases to a minimum at 127 pm (the bond distance), and then it increases sharply as you get closer.

$$(a) \text{H-Cl} \frac{431 \text{ kJ}}{\text{mol}} \times \frac{\text{mol}}{6.022 \times 10^{23} \text{ bonds}} \times \frac{1000 \text{ J}}{\text{kJ}} = 7.16 \times 10^{-19}$$

(b) We know Hess's law related to bond energies:

$$\Delta H^\circ = \sum \Delta H_{\text{BDE}}^\circ (\text{broken}) - \sum \Delta H_{\text{BDE}}^\circ (\text{formed})$$

We are given the enthalpy of reaction

$$-184.7 \text{ kJ/mol} = \left( \Delta H_{\text{BDE}(\text{H-H})}^\circ + \Delta H_{\text{BDE}(\text{Cl-Cl})}^\circ \right) - \left( 2\Delta H_{\text{BDE}(\text{H-Cl})}^\circ \right)$$

H-H is 436 kJ/mol and Cl-Cl is 243

$$-184.7 \text{ kJ/mol} = (436 + 243) - 2x = 679 - 2x$$

$$2x = 863.7 \text{ kJ/mol}$$

$x = 432 \text{ kJ/mol}$ , which is very close to the value we looked up in part (a).

### Question 45-3.

Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.

#### Solution

The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

### Question 45-4.

Use valence bond theory to explain the bonding in  $\text{F}_2$ , HF, and ClBr. Sketch the overlap of the atomic orbitals involved in the bonds.

#### Solution

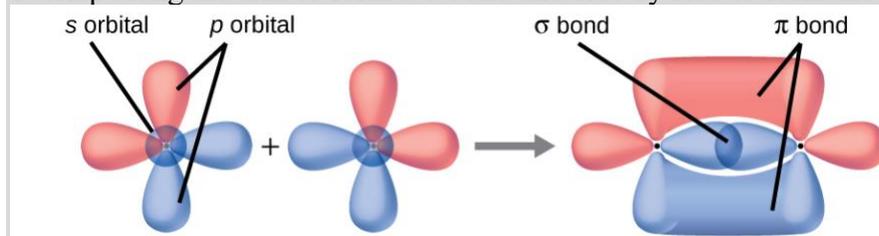
The single bond present in each molecule results from overlap of the relevant orbitals: F  $2p$  orbitals in  $\text{F}_2$ , the H  $1s$  and F  $2p$  orbitals in HF, and the Cl  $3p$  orbital and Br  $4p$  orbital in ClBr.

### Question 45-5.

Use valence bond theory to explain the bonding in  $\text{O}_2$ . Sketch the overlap of the atomic orbitals involved in the bonds in  $\text{O}_2$ .

#### Solution

Bonding: One  $\sigma$  bond and one  $\pi$  bond. The  $s$  orbitals are filled and do not overlap. The  $p$  orbitals overlap along the axis to form a  $\sigma$  bond and side by side to form the  $\pi$  bond.



### Question 45-6.

How many  $\sigma$  and  $\pi$  bonds are present in the molecule HCN?

#### Solution

$\text{H}-\text{C}\equiv\text{N}$  has two  $\sigma$  ( $\text{H}-\text{C}$  and  $\text{C}-\text{N}$ ) and two  $\pi$  (making the  $\text{CN}$  triple bond).

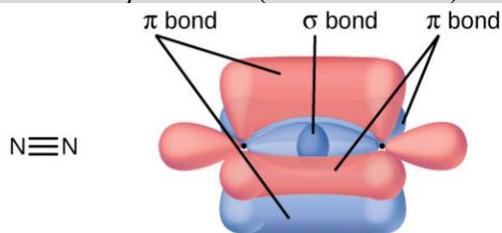


### Question 45-7.

A friend tells you  $\text{N}_2$  has three  $\pi$  bonds due to overlap of the three  $p$ -orbitals on each N atom. Do you agree?

#### Solution

No, two of the  $p$  orbitals (one on each N) will be oriented end to end and will form a  $\sigma$  bond.



### Question 45-8.

Draw the Lewis structures for  $\text{CO}_2$  and  $\text{CO}$ , and predict the number of  $\sigma$  and  $\pi$  bonds for each molecule.

(a)  $\text{CO}_2$

(b)  $\text{CO}$

#### Solution

(a) 2  $\sigma$  2  $\pi$ ;



(b) 1  $\sigma$  2  $\pi$ ;



## 8.2 Hybrid Atomic Orbitals

### Question 46-1.

Why is the concept of hybridization required in valence bond theory?

#### Solution

Hybridization is introduced to explain the geometry of bonding orbitals in valence bond theory.

### Question 46-2.

Give the shape that describes each hybrid orbital set:

(a)  $sp^2$

(b)  $sp^3d$

(c)  $sp$

(d)  $sp^3d^2$

#### Solution

(a) trigonal planar; (b) trigonal bipyramidal; (c) linear; (d) octahedral

### Question 46-3.

Explain why a carbon atom cannot form five bonds using  $sp^3d$  hybrid orbitals.

#### Solution

There are no  $d$  orbitals in the valence shell of carbon.

### Question 46-4.

What is the hybridization of the central atom in each of the following?

- (a)  $\text{BeH}_2$
- (b)  $\text{SF}_6$
- (c)  $\text{PO}_4^{3-}$
- (d)  $\text{PCl}_5$

#### Solution

(a)  $sp$ ; (b)  $sp^3d^2$ ; (c)  $sp^3$ ; (d)  $sp^3d$

### Question 46-5.

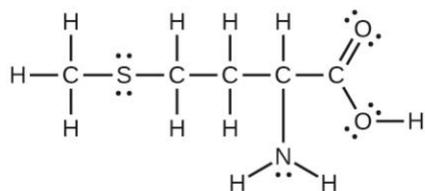
A molecule with the formula  $\text{AB}_3$  could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

#### Solution

trigonal planar,  $sp^2$ , trigonal pyramidal (one lone pair on A)  $sp^3$ , T-shaped (two lone pairs on A)  $sp^3d$ , or (three lone pairs on A)  $sp^3d^2$

### Question 46-6.

Methionine,  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ , is an amino acid found in proteins. Draw a Lewis structure of this compound. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?

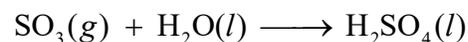
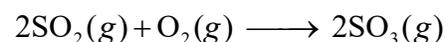
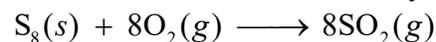


#### Solution

From left to right, the hybridization is C,  $sp^3$ ; S,  $sp^3$ ; C,  $sp^3$ ; C,  $sp^3$ ; C,  $sp^3$ ; C,  $sp^2$ ; N,  $sp^3$ , and O with H is  $sp^3$ .

### Question 46-7.

Sulfuric acid is manufactured by a series of reactions represented by the following equations:

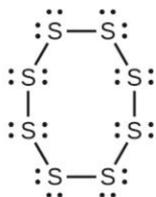


Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

- (a) circular S<sub>8</sub> molecule
- (b) SO<sub>2</sub> molecule
- (c) SO<sub>3</sub> molecule
- (d) H<sub>2</sub>SO<sub>4</sub> molecule (the hydrogen atoms are bonded to oxygen atoms)

**Solution**

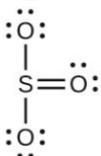
(a) S<sub>8</sub>, each S has a bent (109°) geometry, *sp*<sup>3</sup>



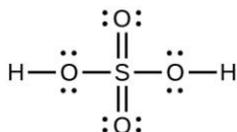
(b) SO<sub>2</sub>, bent (120°), *sp*<sup>2</sup>



(c) SO<sub>3</sub>, trigonal planar, *sp*<sup>2</sup>

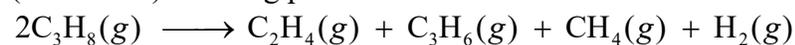


(d) H<sub>2</sub>SO<sub>4</sub>, tetrahedral, *sp*<sup>3</sup>



**Question 46-8.**

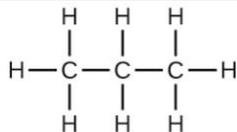
Two important industrial chemicals, ethene, C<sub>2</sub>H<sub>4</sub>, and propene, C<sub>3</sub>H<sub>6</sub>, are produced by the steam (or thermal) cracking process:



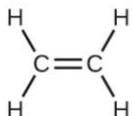
For each of the four carbon compounds, do the following:

- (a) Draw a Lewis structure.
- (b) Predict the geometry about the carbon atom.
- (c) Determine the hybridization of each type of carbon atom.

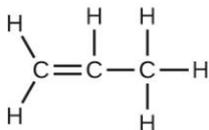
**Solution**



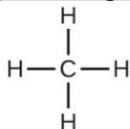
C<sub>3</sub>H<sub>6</sub> Propene, tetrahedral, *sp*<sup>3</sup>



C<sub>2</sub>H<sub>4</sub>, trigonal planar, *sp*<sup>2</sup>



C<sub>3</sub>H<sub>6</sub>, (left to right) C 1 and 2, trigonal planar,  $sp^2$ , C 3 tetrahedral,  $sp^3$



CH<sub>4</sub>, tetrahedral,  $sp^3$

### Question 46-9.

Analysis of a compound indicates that it contains 77.55% Xe and 22.45% F by mass.

- What is the empirical formula of the compound? (*Assume this is also the molecular formula when responding to the remaining parts of this exercise.*)
- Write a Lewis structure for the compound.
- Predict the shape of the molecules of the compound.
- What hybridization is consistent with the shape you predicted?

### Solution

(a) A 100-g sample contains 77.55 g Xe and 22.45 g F. Divide each mass by the atomic weight to find the number of moles. Then, compare the ratio of moles of the two elements.

$$\frac{77.55 \text{ g}}{131.29 \text{ g mol}^{-1}} = 0.5907 \text{ mol}$$

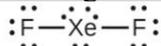
$$\frac{22.45 \text{ g}}{18.998 \text{ g mol}^{-1}} = 1.182 \text{ mol}$$

Find the ratio by dividing by the smaller value.

$$\frac{1.182}{0.5907} = 2.001$$

That is, there are two atoms of F for each atom of Xe. Therefore, the empirical formula is XeF<sub>2</sub>.

(b) Assuming the empirical formula is also the molecular formula, the Lewis structure is



(c) The central Xe atom is surrounded by five electron pairs in a trigonal bipyramid geometry. To minimize the greater repulsion between nonbonded electrons, the three lone pairs occupy the trigonal plane of the molecule, with the two bonding pairs above and below the plane, resulting in a linear geometry for XeF<sub>2</sub>.

(d)  $sp^3d$  hybridization is consistent with the linear shape.

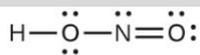
### Question 46-10.

Consider nitrous acid, HNO<sub>2</sub> (HONO).

- Write a Lewis structure.
- What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in the HNO<sub>2</sub> molecule?
- What is the hybridization on the internal oxygen and nitrogen atoms in HNO<sub>2</sub>?

### Solution

(a)

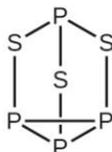


(b) O tetrahedral, N trigonal planar;

(c) O  $sp^3$ , N  $sp^2$

### Question 46-11.

Strike-anywhere matches contain a layer of  $\text{KClO}_3$  and a layer of  $\text{P}_4\text{S}_3$ . The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match.  $\text{KClO}_3$  contains the  $\text{ClO}_3^-$  ion.  $\text{P}_4\text{S}_3$  is an unusual molecule with the skeletal structure.



(a) Write Lewis structures for  $\text{P}_4\text{S}_3$  and the  $\text{ClO}_3^-$  ion.

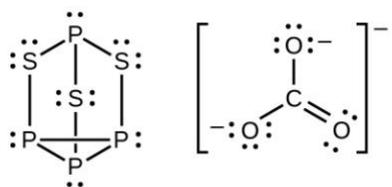
(b) Describe the geometry about the P atoms, the S atom, and the Cl atom in these species.

(c) Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species.

(d) Determine the oxidation states and formal charge of the atoms in  $\text{P}_4\text{S}_3$  and the  $\text{ClO}_3^-$  ion.

### Solution

(a)



(b) P atoms, trigonal pyramidal; S atoms, bent, with two lone pairs; Cl atoms, trigonal pyramidal;

(c) Hybridization about P, S, and Cl is, in all cases,  $sp^3$ ; (d) Oxidation states P +1, S  $-1\frac{1}{3}$ , Cl +5,

O -2. Formal charges: P 0; S 0; Cl +2; O -1

### Question 46-12.

Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.)



### Solution

Left to right:  $sp^3$ ,  $sp^3$ ,  $sp$ ,  $sp$ ,  $sp^2$ ,  $sp^2$

### Question 46-13.

Write Lewis structures for  $\text{NF}_3$  and  $\text{PF}_5$ . On the basis of hybrid orbitals, explain the fact that  $\text{NF}_3$ ,  $\text{PF}_3$ , and  $\text{PF}_5$  are stable molecules, but  $\text{NF}_5$  does not exist.

#### Solution

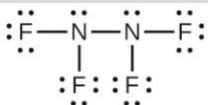


Phosphorus and nitrogen can form  $sp^3$  hybrids to form three bonds and hold one lone pair in  $\text{PF}_3$  and  $\text{NF}_3$ , respectively. However, nitrogen has no valence  $d$  orbitals, so it cannot form a set of  $sp^3d$  hybrid orbitals to bind five fluorine atoms in  $\text{NF}_5$ . Phosphorus has  $d$  orbitals and can bind five fluorine atoms with  $sp^3d$  hybrid orbitals in  $\text{PF}_5$ .

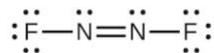
### Question 46-14.

In addition to  $\text{NF}_3$ , two other fluoro derivatives of nitrogen are known:  $\text{N}_2\text{F}_4$  and  $\text{N}_2\text{F}_2$ . What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule?

#### Solution



trigonal pyramidal at each N,  $sp^3$ ;



bent ( $120^\circ$ ) at each N,  $sp^2$ .

## 8.3 Multiple Bonds

### Question 47-1.

The bond energy of a C–C single bond averages  $347 \text{ kJ mol}^{-1}$ ; that of a  $\text{C}\equiv\text{C}$  triple bond averages  $839 \text{ kJ mol}^{-1}$ . Explain why the triple bond is not three times as strong as a single bond.

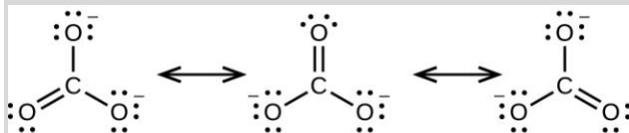
#### Solution

A triple bond consists of one  $\sigma$  bond and two  $\pi$  bonds. A  $\sigma$  bond is stronger than a  $\pi$  bond due to greater overlap.

### Question 47-2.

For the carbonate ion,  $\text{CO}_3^{2-}$ , draw all of the resonance structures. Identify which orbitals overlap to create each bond.

#### Solution



In each structure, the carbon is  $sp^2$  hybridized, and each of the three  $sp^2$  orbitals overlaps with an oxygen orbital to create a  $\sigma$  bond. The unhybridized  $p$  orbital on the carbon atom overlaps with a  $p$  orbital on the oxygen atom to create a  $\pi$  bond. There is only one unhybridized  $p$  orbital on the carbon atom, so only one  $\pi$  bond can be formed, but delocalization can occur over all three C–O bonds.

### Question 47-3.

A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile,  $H_3CCN$ . It is present in paint strippers.

- Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.
- Identify the hybrid orbitals used by the carbon atoms in the molecule to form  $\sigma$  bonds.
- Describe the atomic orbitals that form the  $\pi$  bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

### Solution

(a)



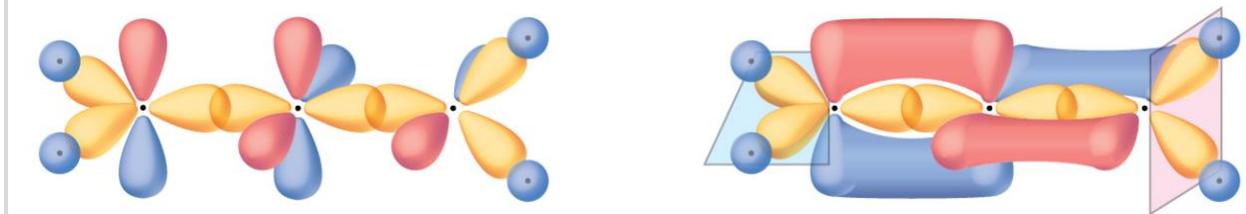
(b) The terminal carbon atom uses  $sp^3$  hybrid orbitals, while the central carbon atom is  $sp$  hybridized. The terminal carbon atom forms four  $\sigma$  bonds (three to the hydrogen atoms and one to the carbon) while the central carbon forms two  $\sigma$  bonds (one to carbon and one to nitrogen). (c) Each of the two  $\pi$  bonds is formed by overlap of a  $2p$  orbital on carbon and a nitrogen  $2p$  orbital.

### Question 47-4.

For the molecule allene,  $H_2C = C = CH_2$ , give the hybridization of each carbon atom. Will the hydrogen atoms be in the same plane or perpendicular planes?

### Solution

$sp^2$ ,  $sp$ ,  $sp^2$ , perpendicular



### Question 47-5.

Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

- $ClNO$  (N is the central atom)
- $CS_2$
- $Cl_2CO$  (C is the central atom)
- $Cl_2SO$  (S is the central atom)
- $SO_2F_2$  (S is the central atom)

(f)  $\text{XeO}_2\text{F}_2$  (Xe is the central atom)

(g)  $\text{ClOF}_2^+$  (Cl is the central atom)

**Solution**

(a)  $sp^2$ ; (b)  $sp$ ; (c)  $sp^2$ ; (d)  $sp^3$ ; (e)  $sp^3$ ; (f)  $sp^3d$ ; (g)  $sp^3$

Question 47-7.

Describe the molecular geometry and hybridization of the N, P, or S atoms in each of the following compounds.

(a)  $\text{H}_3\text{PO}_4$ , phosphoric acid, used in cola soft drinks

(b)  $\text{NH}_4\text{NO}_3$ , ammonium nitrate, a fertilizer and explosive

(c)  $\text{S}_2\text{Cl}_2$ , disulfur dichloride, used in vulcanizing rubber

(d)  $\text{K}_4[\text{O}_3\text{POPO}_3]$ , potassium pyrophosphate, an ingredient in some toothpastes

**Solution**

(a) tetrahedral,  $sp^3$ ; (b)  $\text{NH}_4^+$  tetrahedral,  $sp^3$ ;  $\text{NO}_3^-$  trigonal planar,  $sp^2$ ; (c) bent ( $109^\circ$ ),  $sp^3$ ; (d) tetrahedral,  $sp^3$

Question 47-8.

For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:

(a) ozone ( $\text{O}_3$ ) central O hybridization

(b) carbon dioxide ( $\text{CO}_2$ ) central C hybridization

(c) nitrogen dioxide ( $\text{NO}_2$ ) central N hybridization

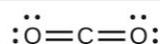
(d) phosphate ion ( $\text{PO}_4^{3-}$ ) central P hybridization

**Solution**

(a)  $sp^2$ , delocalized



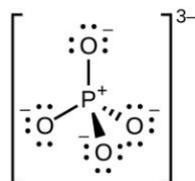
(b)  $sp$ , localized



(c)  $sp^2$ , delocalized



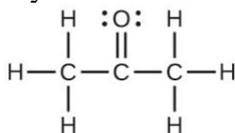
(d)  $sp^3$ , delocalized



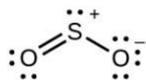
Question 47-9.

For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:

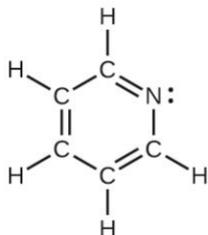
(a) Hybridization of each carbon



(b) Hybridization of sulfur



(c) All atoms



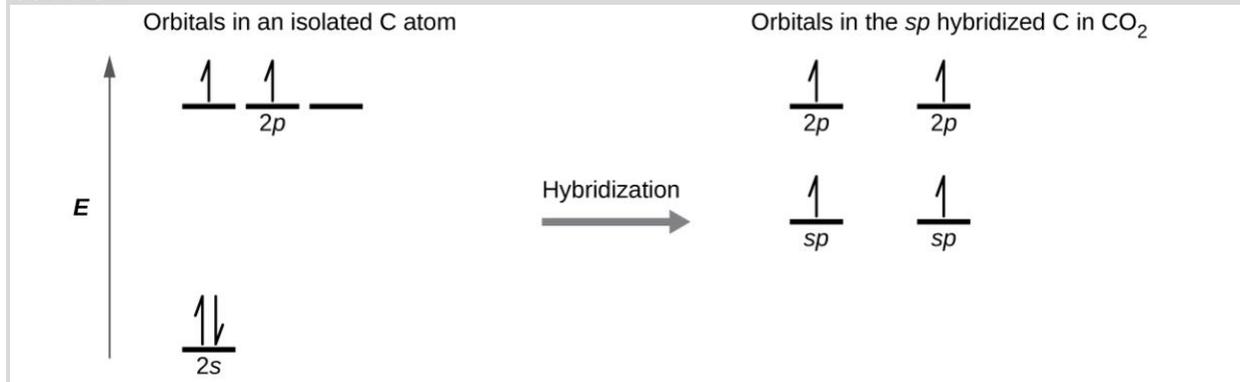
### Solution

(a)  $sp^3$ ,  $sp^2$   $sp^3$  not delocalized, (b)  $sp^2$  delocalized, (c) hydrogens are  $s$ , carbons and nitrogens  $sp^2$ , delocalized

### Question 47-10.

Draw the orbital diagram for carbon in  $CO_2$  showing how many carbon atom electrons are in each orbital.

### Solution



Each of the four electrons is in a separate orbital and overlaps with an electron on an oxygen atom.

## 8.4 Molecular Orbital Theory

### Question 48-1.

Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two  $s$  orbitals and from two  $p$  orbitals.

### Solution

See Figure 8.29 and Figure 8.30 for details.

#### Question 48-2.

How are the following similar, and how do they differ?

- (a)  $\sigma$  molecular orbitals and  $\pi$  molecular orbitals
- (b)  $\psi$  for an atomic orbital and  $\psi$  for a molecular orbital
- (c) bonding orbitals and antibonding orbitals

#### **Solution**

(a) Similarities: Both are bonding orbitals that can contain a maximum of two electrons.

Differences:  $\sigma$  orbitals are end-to-end combinations of atomic orbitals, whereas  $\pi$  orbitals are formed by side-by-side overlap of orbitals.

(b) Similarities: Both are quantum-mechanical constructs that represent the probability of finding the electron about the atom or the molecule.

Differences:  $\psi$  for an atomic orbital describes the behavior of only one electron at a time based on the atom. For a molecule,  $\psi$  represents either a mathematical combination of atomic orbitals.

(c) Similarities: Both are orbitals that can contain two electrons. Differences: Bonding orbitals result in holding two or more atoms together. Antibonding orbitals have the effect of destabilizing any bonding that has occurred.

#### Question 48-3.

If molecular orbitals are created by combining five atomic orbitals from atom A and five atomic orbitals from atom B combine, how many molecular orbitals will result?

#### **Solution**

10

#### Question 48-4.

Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

#### **Solution**

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

#### Question 48-5.

Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

#### **Solution**

An even number of electrons can contain unpaired electrons if there are half-filled degenerate orbitals. This is the case for  $O_2$ .

#### Question 48-6.

Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

#### **Solution**

Bonding orbitals have electron density in close proximity to more than one nucleus. The interaction between the bonding positively charged nuclei and negatively charged electrons stabilizes the system.

#### Question 48-7.

Calculate the bond order for an ion with this configuration:

$$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}, \pi_{2pz})^4 (\pi_{2py}^*, \pi_{2pz}^*)^3$$

**Solution**

$$\frac{(8 - 5)}{2} = 1.5$$

Question 48-8.

Explain why an electron in the bonding molecular orbital in the H<sub>2</sub> molecule has a lower energy than an electron in the 1s atomic orbital of either of the separated hydrogen atoms.

**Solution**

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

Question 48-9.

Predict the valence electron molecular orbital configurations for the following, and state whether they will be stable or unstable ions.

- (a) Na<sub>2</sub><sup>2+</sup>
- (b) Mg<sub>2</sub><sup>2+</sup>
- (c) Al<sub>2</sub><sup>2+</sup>
- (d) Si<sub>2</sub><sup>2+</sup>
- (e) P<sub>2</sub><sup>2+</sup>
- (f) S<sub>2</sub><sup>2+</sup>
- (g) F<sub>2</sub><sup>2+</sup>
- (h) Ar<sub>2</sub><sup>2+</sup>

**Solution**

(a) Na<sub>2</sub><sup>2+</sup> (σ<sub>3s</sub>)<sup>0</sup>, unstable; (b) Mg<sub>2</sub><sup>2+</sup> (σ<sub>3s</sub>)<sup>2</sup>, stable; (c) Al<sub>2</sub><sup>2+</sup> (σ<sub>3s</sub>)<sup>2</sup> (σ<sub>3s</sub><sup>\*</sup>)<sup>2</sup>, unstable; (d) Si<sub>2</sub><sup>2+</sup> (σ<sub>3s</sub>)<sup>2</sup> (σ<sub>3s</sub><sup>\*</sup>)<sup>2</sup> (π<sub>3py</sub>, π<sub>3pz</sub>)<sup>2</sup>, stable; (e) P<sub>2</sub><sup>2+</sup> (σ<sub>3s</sub>)<sup>2</sup> (σ<sub>3s</sub><sup>\*</sup>)<sup>2</sup> (σ<sub>3px</sub>)<sup>2</sup> (π<sub>3py</sub>, π<sub>3pz</sub>)<sup>2</sup>, stable; (f) S<sub>2</sub><sup>2+</sup> (σ<sub>3s</sub>)<sup>2</sup> (σ<sub>3s</sub><sup>\*</sup>)<sup>2</sup> (σ<sub>3px</sub>)<sup>2</sup> (π<sub>3py</sub>, π<sub>3pz</sub>)<sup>4</sup>, stable; (g) F<sub>2</sub><sup>2+</sup> (σ<sub>3s</sub>)<sup>2</sup> (σ<sub>3s</sub><sup>\*</sup>)<sup>2</sup> (σ<sub>3px</sub>)<sup>2</sup> (π<sub>3py</sub>, π<sub>3pz</sub>)<sup>4</sup> (π<sub>3py</sub><sup>\*</sup>, π<sub>3pz</sub><sup>\*</sup>)<sup>2</sup>, stable; (h) Ar<sub>2</sub><sup>2+</sup> (σ<sub>3s</sub>)<sup>2</sup> (σ<sub>3s</sub><sup>\*</sup>)<sup>2</sup> (σ<sub>3px</sub>)<sup>2</sup> (π<sub>3py</sub>, π<sub>3pz</sub>)<sup>4</sup> (π<sub>3py</sub><sup>\*</sup>, π<sub>3pz</sub><sup>\*</sup>)<sup>4</sup>, stable

Question 48-10.

Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

- (a) H<sub>2</sub>, H<sub>2</sub><sup>+</sup>, H<sub>2</sub><sup>-</sup>
- (b) O<sub>2</sub>, O<sub>2</sub><sup>2+</sup>, O<sub>2</sub><sup>2-</sup>
- (c) Li<sub>2</sub>, Be<sub>2</sub><sup>+</sup>, Be<sub>2</sub>
- (d) F<sub>2</sub>, F<sub>2</sub><sup>+</sup>, F<sub>2</sub><sup>-</sup>
- (e) N<sub>2</sub>, N<sub>2</sub><sup>+</sup>, N<sub>2</sub><sup>-</sup>

**Solution**

The bond order is equal to half the difference between the number of bonding electrons and the number of antibonding electrons. The bond with the greatest bond order is predicted to be the strongest. (a)  $\text{H}_2$  bond order = 1,  $\text{H}_2^+$  bond order = 0.5,  $\text{H}_2^-$  bond order = 0.5, strongest bond is  $\text{H}_2$ ; (b)  $\text{O}_2$  bond order = 2,  $\text{O}_2^{2+}$  bond order = 3;  $\text{O}_2^{2-}$  bond order = 1, strongest bond is  $\text{O}_2^{2+}$ ; (c)  $\text{Li}_2$  bond order = 1,  $\text{Be}_2^+$  bond order = 0.5,  $\text{Be}_2$  bond order = 0, strongest bond is  $\text{Li}_2$ ; (d)  $\text{F}_2$  bond order = 1,  $\text{F}_2^+$  bond order = 1.5,  $\text{F}_2^-$  bond order = 0.5, strongest bond is  $\text{F}_2^+$ ; (e)  $\text{N}_2$  bond order = 3,  $\text{N}_2^+$  bond order = 2.5,  $\text{N}_2^-$  bond order = 2.5, strongest bond is  $\text{N}_2$ .

**Question 48-11.**

For the first ionization energy for an  $\text{N}_2$  molecule, what molecular orbital is the electron removed from?

**Solution**

$\sigma_p$

**Question 48-12.**

Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

- (a) H and  $\text{H}_2$
- (b) N and  $\text{N}_2$
- (c) O and  $\text{O}_2$
- (d) C and  $\text{C}_2$
- (e) B and  $\text{B}_2$

**Solution**

(a)  $\text{H}_2$ ; (b)  $\text{N}_2$ ; (c) O; (d)  $\text{C}_2$ ; (e)  $\text{B}_2$

**Question 48-13.**

Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

**Solution**

$\text{B}_2$  and  $\text{O}_2$

**Question 48-14.**

A friend tells you that the  $2s$  orbital for fluorine starts off at a much lower energy than the  $2s$  orbital for lithium, so the resulting  $\sigma_{2s}$  molecular orbital in  $\text{F}_2$  is more stable than in  $\text{Li}_2$ . Do you agree?

**Solution**

Yes, fluorine is a smaller atom than Li, so atoms in the  $2s$  orbital are closer to the nucleus and more stable.

Question 48-15.

True or false: Boron contains  $2s^2 2p^1$  valence electrons, so only one  $p$  orbital is needed to form molecular orbitals.

**Solution**

False. All valence orbitals combine to form molecular orbitals, regardless of whether they are full or empty.

Question 48-16.

What charge would be needed on  $F_2$  to generate an ion with a bond order of 2?

**Solution**

$2+$

Question 48-17.

Predict whether the MO diagram for  $S_2$  would show s-p mixing or not.

**Solution**

No, any atom with four or more  $p$  electrons has paired electrons in the  $p$  orbitals so it does not mix, just like  $O_2$ .

Question 48-18.

Explain why  $N_2^{2+}$  is diamagnetic, while  $O_2^{4+}$ , which has the same number of valence electrons, is paramagnetic.

**Solution**

$N_2$  has s-p mixing, so the  $\pi$  orbitals are the last filled in  $N_2^{2+}$ .  $O_2$  does not have s-p mixing, so the  $\sigma_p$  orbital fills before the  $\pi$  orbitals.

Question 48-19.

Using the MO diagrams, predict the bond order for the stronger bond in each pair:

- (a)  $B_2$  or  $B_2^+$
- (b)  $F_2$  or  $F_2^+$
- (c)  $O_2$  or  $O_2^{2+}$
- (d)  $C_2^+$  or  $C_2^-$

**Solution**

(a)  $B_2$ , bond order 1; (b)  $F_2^+$ , bond order 1.5; (c)  $O_2^{2+}$ , bond order 3; (d)  $C_2^{2-}$ , bond order 3

