

Chapter 6 – Molecular Structure

Introduction

A method for constructing Lewis structures of simple molecules and ions was presented in Chapter 5. In this chapter, we show how to use Lewis structures to determine the structural and bonding properties of molecules and ions with covalent bonds.

6.1 Molecular Shapes

Introduction

A molecule is a three-dimensional structure, and many of its properties, both chemical and physical, are dictated by that structure. The Lewis structure of a molecule is a two-dimensional representation that can be used to obtain information about its three-dimensional structure. Determining the shape of a molecule from its Lewis structure is the topic of this lesson.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 2.6 Orbital Shapes and Sizes
- 5.6 Determining Lewis Structures (Draw Lewis structures.)

Objectives

- Determine the number of electron regions around an atom.
- Rate the relative strengths of lp-lp, lp-bp, and bp-bp interactions.
- Name the molecular shapes of simple molecules that contain a single central atom.
- Use lines, wedges, and dashes to represent the 3D structure of an atom with four electron regions.
- Distinguish between a ball-and-stick model and a space-filling model.

6.1-1. Electron Regions

One electron group or region can be either a lone pair, a single bond, a double bond, or a triple bond.

Just as a two-dimensional blueprint provides information about a three-dimensional building, the Lewis structure of a molecule provides information about the three-dimensional structure of a molecule. The transition from a two- to a three-dimensional structure is accomplished with the valence-shell electron-pair repulsion (VSEPR) model. VSEPR is based on the premise that the 'electron groups' or 'electron regions' around an atom adopt positions that minimize the repulsions between them.

Each of the following is one electron group or region.

- lone pair
- single bond
- double bond
- triple bond

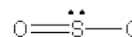
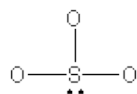
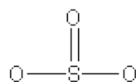
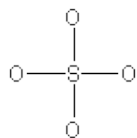
Double and triple bonds each represent a single electron group because the electron pairs in the bonds are all restricted to the region of space between the bound atoms. Thus, the electron pairs in a bonding region cannot move apart, but they can move as a single electron group to minimize their interactions with other electron groups.

Atoms obeying the octet rule can have only two, three, or four electron groups.

6.1-2. Counting Electron Regions Exercise

EXERCISE 6.1:

What is the number of electron regions around the sulfur atom in each of the following?



6.1-3. VSEPR Video

A video or simulation is available online.

6.1-4. VSEPR Summary

In summary, the three possible orientations of electron groups around an atom that obeys the octet rule are the following.

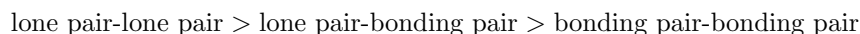
Number of Groups	Angle Between Groups	Image
2	180°	
3	120°	
4	109°	

Table 6.1

6.1-5. Bond Angles

If all of the electron groups around a central atom are not identical, the predicted bond angles are only approximate.

The angles between electron groups shown in Figure 6.1 apply only to situations where all four electron groups are the same, which is not all that common. Thus, the angles between electron groups around an atom that obeys the octet rule will be exactly 180° for two groups, but it will only be close to 120° or 109° for three or four groups unless all of the groups are the same. Deviation from the predicted angles can be caused by differences in the size of the bound atoms as large atoms tend to move apart to avoid ‘bumping’ one another, and from differences between the interactions of lone pairs and bonding pairs as lone pairs are more diffuse than lone pairs, so they are larger and other electron regions tend to move away from them. The following gives the relative strengths of the interactions.



The **bond angle** is the angle formed by the intersection of two bonds. They are generally reduced from the values given in Figure 6.1 by interaction with lone pairs. As a result, the bonding pairs move away from the lone

pairs by moving closer to one another. The deviation from the predicted angles increases with the number of lone pairs. Use the following to predict relative bond angles.

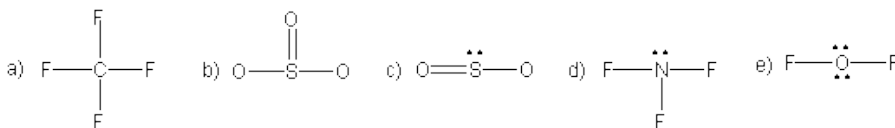
- 1 Determine the number of electron groups around the atom where the angle forms.
- 2 If there are no lone pairs and the atoms are nearly the same size, the angle will be 180° , 120° , or 109° .
- 3 If there are lone pairs, the angles decrease from the values predicted in step 2. The deviation is greater for two lone pairs than for one.

We will indicate that the bond angle deviates from the predicted value with a ‘ \sim ’ in front of the angle. Thus, all bond angles around atoms with lone pairs are preceded by a ‘ \sim ’.

6.1-6. Ordering Bond Angles Exercise

EXERCISE 6.2:

Consider the Lewis structures of CF_4 , SO_3 , SO_2 , NF_3 , and OF_2 , which are given below. Note, only lone pairs around the central atom are shown.



Indicate the molecule with the greater bond angles in each pair.

SO_3 or CF_4
 SO_3
 CF_4

SO_3 or SO_2
 SO_3
 SO_2

NF_3 or OF_2
 NF_3
 OF_2

6.1-7. Molecular Shapes

The locations occupied by the lone pairs are not used when describing the shape of a molecule.

The shapes shown in Table 6.1 show the orientations that can be adopted by the electron groups surrounding a central atom that obeys the octet rule. However, we can determine the positions of only the atoms, not the lone pairs, so a molecular shape describes the shape adopted by only the atoms not the electron groups. The **lone pairs help establish what that shape is, but the name of the shape applies only to that taken by the atoms.** We consider the shapes of some generic molecules in the following sections. Our analysis will follow three steps.

- 1 Determine the number of electron groups around the central atom.
- 2 Determine which of the shapes shown in Table 6.1 applies.
- 3 Name the molecular shape adopted by the **atoms**.

6.1-8. The Common Shapes

Three atoms can be either linear or bent and four atoms can be planar or pyramidal; which geometry is adopted depends upon the presence of lone pairs.

Our discussion concerns molecules with two, three or four atoms (X) attached to one central atom (A), which may have one or more lone pairs (E). Thus, AX_2E indicates that central atom A is bound to two X atoms and has one lone pair. In the molecular representations below, the atoms are shown as spheres, bonds as cylinders, and lone pairs as green balloons. In the table, br = bonding regions and lp = lone pair. The possibilities for molecules in which A obeys the octet rule are the following.

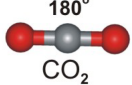
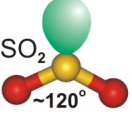
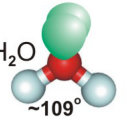
Formula	Groups	Shape	Angle	Example	Comments
AX_2	2 (2br)	linear	180°	 CO_2	Two bonding pairs are always 180° , not $\sim 180^\circ$
AX_2E	3 (2br + lp)	bent	$\sim 120^\circ$	 SO_2	The lone pair forces the angle down slightly from 120°
AX_2E_2	4 (2br + 2lp)	bent	$\sim 109^\circ$	 H_2O	The two lone pairs force the angle down to 104° in water.

Table 6.2

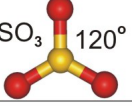
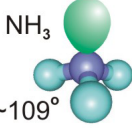
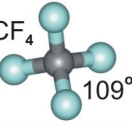
Formula	Groups	Shape	Angle	Example	Comments
AX_3	3 (3br)	planar	120°	 SO_3	The three groups are identical due to resonance
AX_3E	4 (3br + lp)	pyramidal	$\sim 109^\circ$	 NH_3	One lone pair forces the angle down to 107° in ammonia
AX_4	4 (4br)	tetrahedral	109°	 CF_4	All four regions are identical so no \sim is required in bond angles

Table 6.3

6.1-9. Molecular Representations

Ball-and-stick representations are better for showing bond angles, but space-filling representations are closer to how we envision molecules.

Making drawings that demonstrate the geometry around atoms with only two and three electron regions is easy because they require only one and two dimensions. However, in cases where the central atom has four or more electron regions, you must be able to represent the three-dimensions in a 2D drawing. This is often done by using lines to represent regions in the plane of the paper, solid wedges for regions that extend out from the plane of the paper, and dashed wedges for regions that extend behind the plane of the paper. The use of lines and wedges is demonstrated in the following example of a central atom with four different bonding regions.

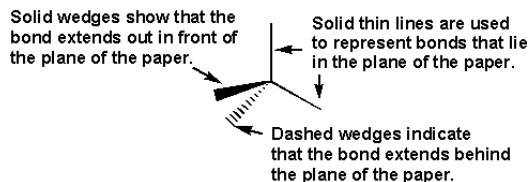


Figure 6.4: Line-Wedge-Dash Representation of a Tetrahedral Geometry

There are two other representations that give a better three dimensional view of molecules, especially larger ones. They are the ball-and-stick and space-filling models. These two models, which will be used frequently to represent molecules, are demonstrated below for an ammonia molecule. Note that **lone pairs are not shown in ball-and-stick or space-filling models**.

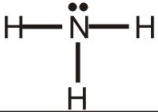
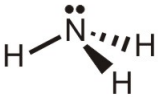

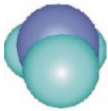
Model Name	Description	Representation
Lewis structure	Bonding pairs are shown as lines. Bonds are usually drawn at right angles.	
line-wedge-dash	A Line-wedge-dash representation attempts to show the three-dimensional structure of the molecule.	
ball andstick	Atoms are represented as spheres and bonds as cylinders. Ball-and-stick models are the better representation for discussing bond angles, but they do not represent the relative sizes of the atoms.	
space filling	Atoms are shown as spheres and bonds as the penetration of two spheres into one another. Space-filling models give a truer picture of the molecule. The relative diameters of the spheres represent the relative sizes of the atoms.	

Table 6.5

6.1-10. Structure Exercise

EXERCISE 6.3:

Draw the Lewis structure to describe the shape and give the approximate bond angles of the following ions.

ClO_2^{1-} shape

linear
bent
planar
pyramidal
tetrahedral

ClO_2^{1-} approximate bond angle

90°
 109°
 120°
 180°

N_3^{1-} shape

linear
bent
planar
pyramidal
tetrahedral

N_3^{1-} approximate bond angle

90°
 109°
 120°
 180°

PO_3^{3-} shape

linear
bent
planar
pyramidal
tetrahedral

PO_3^{3-} approximate bond angle

90°
 109°
 120°
 180°

NO_3^{1-} shape	NO_3^{1-} approximate bond angle
linear	90°
bent	109°
planar	120°
pyramidal	180°
tetrahedral	
BrO_4^{1-} shape	BrO_4^{1-} approximate bond angle
linear	90°
bent	109°
planar	120°
pyramidal	180°
tetrahedral	

6.2 Central Atoms With More Than Four Electron Regions

Introduction

The octet rule applies rigidly only to C, N, O and F, and even nitrogen violates it occasionally because it has an odd number of electrons in some of its molecules. Atoms with more than eight valence electrons are said to have expanded valence shells or expanded octets. Transition metals and the heavier p block elements frequently use expanded octets. In this section, we discuss the shapes of molecules in which the central atom has five and six electron regions.

Objectives

- Name the shapes adopted around atoms with five and six electron regions.

6.2-1. Shapes of Five and Six Electron Regions

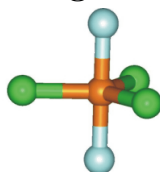


Figure 6.6a: Five Electron Regions

Five groups around a central atom adopt a trigonal bipyramidal structure, which contains two distinctly different types of positions: two positions are axial (blue spheres) and three are equatorial (green spheres). Interactions with other groups are less in the equatorial positions, so lone pairs are always in the equatorial plane.

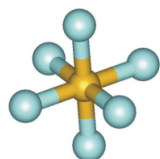


Figure 6.6b: Six Electron Regions

Six groups assume an octahedral structure. All six positions of an octahedron are identical, so lone pairs can be placed in any position. However, two lone pairs are always situated opposite to one another.

6.2-2. Determining Structures of Expanded Octets with Lone Pairs

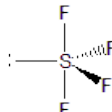
The number of lone pairs around a central atom (LP) can be determined from its group number and its oxidation state as follows.

$$LP = \frac{1}{2}(\text{group number} - \text{oxidation state}) \quad (6.1)$$

Atoms with expanded valence shells can be identified because the predicted number of shared pairs is always too small to accommodate all of the bonds. See the following example.

EXAMPLE:

We determine for SF₄: ER = 5(8) = 40 electrons; VE = 6 + 4(7) = 34 electrons; SP = 1/2(40 - 34) = 3 shared pairs. However, a minimum of 4 shared pairs is required for the four S-F bonds, so the three shared pairs cannot be correct and the octet rule cannot be obeyed. The group number of sulfur is 6 and its oxidation state in SF₄ is +4, so the number of lone pairs around the sulfur atom is LP = 1/2(6 - 4) = 1 lone pair. Thus, there are five electron groups around the sulfur: four S-F bonds and one lone pair. As shown below, the five groups adopt the trigonal bipyramidal structure with the lone pair in the equatorial plane.



6.2-3. Expanded Octet Structure Exercise

EXERCISE 6.4:

Determine the number of lone pairs on the central atom in and the structures of XeF₂ and BrF₄¹⁻.

XeF₂

group number _____

oxidation state _____

lone pairs _____

number of electron regions _____

Are the three atoms linear or bent?

linear

bent

BrF₄¹⁻

group number _____

oxidation state _____

lone pairs _____

number of electron regions _____

Do the five atoms lie in a plane?

Yes

No

6.3 Larger Molecules

Introduction

Groups connected by single bonds can rotate relative to one another about the bond, so VSEPR cannot be used to predict the exact structure of complicated molecules, but it can be used to look at the geometry around individual atoms. In this section, we examine the structure of three common molecules: acetic acid (the active ingredient in vinegar), benzene, and aspirin.

Objective

- Predict bond angles in larger molecules.

6.3-1. Acetic acid

We deduce the following bond angles in acetic acid from its Lewis structure.

- 1 $\alpha \sim 109^\circ$ because there are four electron regions around the carbon 1.
- 2 $\beta \sim 120^\circ$ because the C at 2 is surrounded by three electron regions.
- 3 $\gamma \sim 109^\circ$ because there are four electron regions around the oxygen atom at 3.

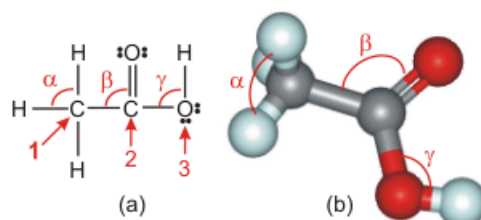


Figure 6.7: Acetic Acid

6.3-2. Benzene

Benzene has the formula C₆H₆ and is a six-membered ring (the six carbon atoms bond so as to form a hexagon). The Lewis structures of its two resonance forms that are shown in Figure 6.8a. We conclude the following based on these Lewis structures.

- 1 Each carbon has three regions, so each is trigonal planar and all bond angles are 120° .
- 2 The double bonds require that the molecule is planar.
- 3 As a result of resonance, all of the carbon atoms are identical as are all six of the bonds between them. The measured C-C bond lengths are all 1.4 Å. Thus, the bond lengths all lie between the 1.5 Å of a single C-C bond and the 1.3 Å of a C=C double bond, which is consistent with a bond order of 1.5. The three double bonds are therefore shared equally between the six bonding regions in the ring. Indeed, the double bonds are frequently represented as a circle rather than three lines (Figure 6.8b) to emphasize the equivalence of the carbon-carbon bonds. We will revisit this important bonding characteristic of benzene in our discussion of molecular orbital theory at the end of the chapter.

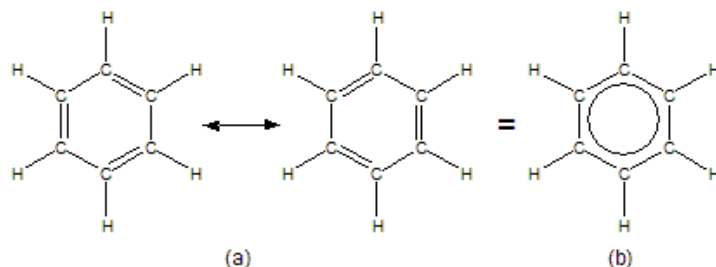


Figure 6.8: Benzene

6.3-3. Aspirin

- 1 Carbon atoms at positions 1, 2, and 5 all have three regions, so their bond angles are $\sim 120^\circ$.
- 2 The carbon at position 6 has four regions, so the bond angles there are $\sim 109^\circ$.
- 3 Oxygen obeys the octet rule, but only four electrons (two bonding pairs) are shown in the Lewis structure. Consequently, two lone pairs must be added to each to produce four regions, which requires bond angles of $\sim 109^\circ$.
- 4 Aspirin contains the same structural features that are found in acetic acid and benzene.

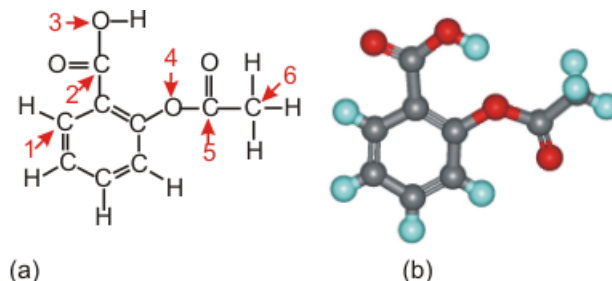
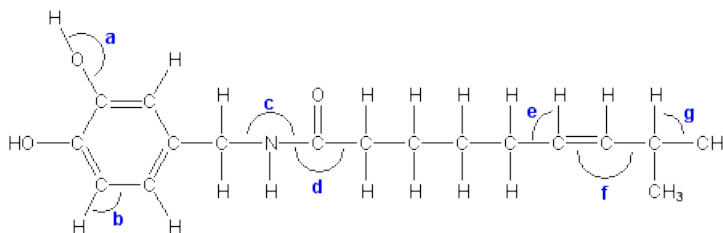


Figure 6.9: Aspirin

6.3-4. Predicting Bond Angles Exercise

EXERCISE 6.5:

The structure below is that of capsaicin, the molecule responsible for the heat in chili peppers. Estimate each of the labeled bond angles. Note that lone pairs are not drawn, but C and O both obey the octet rule. Enter only the number, not the degree sign ($^\circ$).



a _____ $^\circ$ b _____ $^\circ$ c _____ $^\circ$
d _____ $^\circ$ e _____ $^\circ$ f _____ $^\circ$
g _____ $^\circ$

6.4 Valence Bond Theory and Hybridization

Introduction

In valence bond theory, each bond results from the overlap of two atomic orbitals on adjacent atoms. The bonding electrons in such bonds are localized in the region between the two atoms. A single bond is composed of two bonding electrons, so the total number of electrons in the two overlapping atomic orbitals used to produce a bond cannot exceed two. In most cases, each orbital contains one electron, and the two electrons pair when the orbitals overlap. However, both electrons can reside in one of the atomic orbitals (a lone pair), but, in this case, the other orbital must be empty. A bond in which a lone pair is converted into a covalent bond is called a coordinate covalent bond. Coordinate covalent bonds are produced in Lewis acid-base reactions, which are discussed in Chapter 12. We limit our discussion here to cases where each overlapping orbital has one electron.

Objective

- Define the term *hybridization* and name the types of hybrid orbitals used by atoms that obey the octet rule.

6.4-1. Sigma Bonds

The bonding in diatomic molecules can be explained with the overlap of the atomic orbitals that contain unpaired electrons. Bonds formed from the end-on overlap of orbitals place electron density on the internuclear axis (shown as the dotted line in the figures) and are called sigma (σ) bonds. As examples of σ bond formation, we consider the cases of H_2 , F_2 , and HF . Note that the electrons are shown as arrows and the overlap region is shown in yellow in the figures.

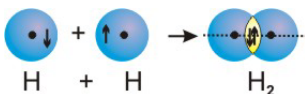


Figure 6.10a: Bond from Overlap of Atomic Orbitals

The H-H bond discussed in Section 5.1 is produced when the distance between the two H atoms is so small that their 1s orbitals overlap to form the H-H covalent bond.

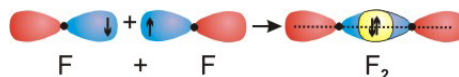


Figure 6.10b: Bond from Overlap of Atomic Orbitals

The valence electron configuration of a fluorine atom is $2s^2 2p^5$, so an unpaired electron resides in one of the 2p orbitals. An F-F bond is then viewed as resulting from the overlap of two p orbitals as shown in the Figure 6.10b. Note that this bond results from the end-on interaction of two p orbitals.

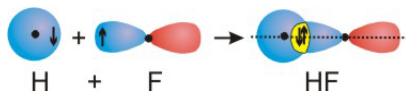


Figure 6.10c: Bond from Overlap of Atomic Orbitals

In the two previous examples, the bonding atoms were the same, so the overlapping orbitals were the same type (both s or both p orbitals). However, the overlapping orbitals do not have to be the same type. The H-F bond is the result of overlap between the 1s orbital of H and the 2p orbital of F. The lone pairs on fluorine would then reside in its s and remaining p orbitals.

In all of the examples shown in Figures 6.10a, 6.10b, and 6.10c, the overlap region lies on the line between the two atoms, which is called the *internuclear axis*. **Bonds in which the bonding electron density falls on the internuclear axis are called *sigma* (σ) bonds.** Thus, the H-H, F-F, and H-F bonds are all sigma bonds. Indeed, all single bonds are sigma bonds.

6.4-2. Pi Bonds

A video or simulation is available online.

The sigma bonds in F_2 are formed when p orbitals overlap end-on. However, p orbitals can also overlap in a side-on fashion to form pi bonds as shown in Figure 6.11. The electron density in a pi bond lies above and below the internuclear axis, not on it. Thus, σ bonds result from end-on overlap of s or p orbitals and place electron density on the internuclear axis, while *pi* (π) bonds are produced from side-on overlap of p and/or d orbitals, which places the internuclear axis on a nodal plane.

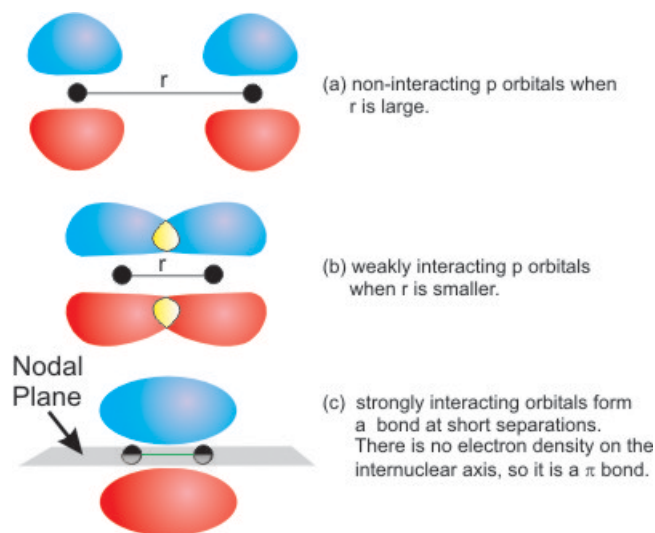


Figure 6.11: Pi Bond

6.4-3. Valence Bond Description of O₂ Bonding

O₂ is a diatomic molecule that contains both σ and π bonds. The valence electron configuration of an oxygen atom is $2s^2 2p^4$, so there are paired electrons in the 2s and one of the 2p orbitals. The unpaired electrons in an oxygen atom lie in the other two p orbitals. In Figure 6.12, the unpaired electrons are assumed to be in the p_z and p_y orbitals. As the atoms approach along the z -axis, the p_z orbitals of the two oxygen atoms overlap in an end-on fashion (orange line) to produce an σ bond, while the p_y orbitals overlap side-on (both violet lines) to produce a π bond. Thus, the O=O double bond consists of one σ and one π bond. All bonds contain one and only one σ bond. Double bonds contain one σ and one π bond, and triple bonds contain one σ and two π bonds. The bond order of a bond is simply the sum of the number of σ and π bonds that it contains.

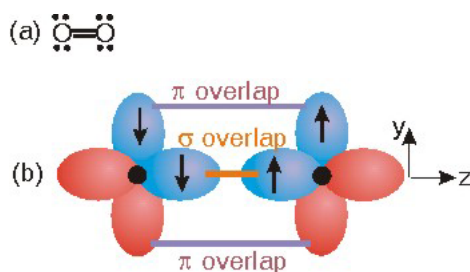


Figure 6.12: Valence Bond Picture of O₂ Bonding

6.4-4. Hybrid Orbitals

The simple overlap of atomic orbitals used for diatomic molecules cannot be used for larger ones. Consider the molecule formed between a carbon atom and hydrogen atoms. Carbon has a valence electron configuration of $2s^2 2p^2$, so it has two unpaired electrons in its p orbitals. If carbon used only atomic orbitals with one electron, its compound with hydrogen would be CH₂, and the H-C-H bond angle would be 90° (the angle between two p orbitals). However, the simplest compound involving carbon and hydrogen is CH₄, which has the 109° bond angles predicted from VSEPR.

In order to account for molecular geometries in the valence bond model, orbitals on a central atom must be combined to produce new orbitals before they overlap with the orbitals of another atom. By choosing the appropriate combination of the atomic orbitals, we can create orbitals that have the geometries required by VSEPR. Orbitals produced by combining two or more atomic orbitals on the same atom are called **hybrid orbitals**, and the process by which they are formed is called **hybridization**. However, before we can understand hybridization, we must examine how orbitals combine.

6.4-5. Orbital Phase

To understand the process of combining orbitals, we must first review the nature of atomic orbitals. Recall from Chapter 2 that atomic orbitals describe algebraic functions that are solutions to an atom's wave equation, and that the phase or algebraic sign of an orbital in a particular region is frequently indicated with shading (Section 2.6). In Figure 6.13, we adopt the convention of using blue to indicate regions where the function is positive and red for regions where it is negative.









<p>s orbitals are positive everywhere, so they are shown in blue and their negative in red.</p>		
	s	-s
<p>p orbitals have one positive lobe that is shown in blue and one negative lobe that is shown in red. Multiplication by -1 simply reverses the phase (color) of the lobes.</p>		
	p_z	$-p_z$
		
	p_x	$-p_x$
		
	p_y	$-p_y$

Table 6.13

6.4-6. An Example of Mixing Two Functions

Mixing orbitals is the mathematical combination of these functions by addition and/or subtraction. Consider the two combinations of the functions P and Q shown in the Figure 6.14. Regions where the functions are positive are shaded in blue, while negative regions are shown in red. This is consistent with our use of these colors to describe the sign of orbital functions. In Figure 6.14a, the two functions are added to produce function $R = P + Q$. R is amplified on the ends because both P and Q have the same phase (sign) there, but it is reduced dramatically in the center because the phases of P and Q are opposite there. We conclude the following.

Adding regions of the same phase (blue + blue) is constructive and produces a region of increased amplitude, while adding regions of opposite phase (blue + red) is destructive and produces a region of decreased or even annihilated amplitude.

To obtain the difference $S = P - Q$ in the Figure 6.15b, the phase of Q is reversed (its sign is changed) to produce $-Q$ and then the two waves are added to produce S . The ends of P and $-Q$ have different phases, so they add destructively to nearly annihilate one another, while the regions in the middle have the same phase and add constructively to produce an amplified region in S .

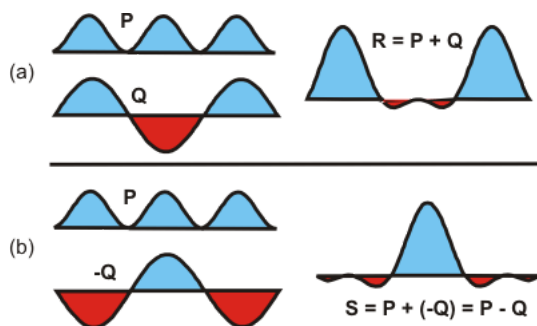


Figure 6.14: Mixing Two Functions

6.4-7. Rules for Mixing

Use the following rules when mixing orbitals.

- 1 The number of orbitals produced must always equal the number of atomic orbitals used to construct them.
- 2 Regions in which the atomic orbitals have the same sign (shading) add constructively, which makes the produced orbital larger in that region, but regions where the orbitals have opposite phases add destructively, which makes the combined orbital smaller in that region.

6.4-8. Hybridizing an s and a p Orbital

A video or simulation is available online.

The orbitals constructed from the addition and subtraction of one s and one p orbital are called sp hybrid orbitals. The sp hybrid orbitals are formed from $s + p$ and $s - p$.

In (a) in Figure 6.15, the s and p orbitals are added to produce $s + p$, one sp hybrid orbital. Both atomic orbitals are positive (blue) to the right, but they have opposite phases to the left. Thus, they add constructively to the right to produce a large lobe, but they add destructively to the left to produce a small negative lobe. The other hybrid is produced by taking the difference between the atomic orbitals in (b). To obtain $s - p$, we change the phase of the p orbital and then add it to the s orbital. Now, the regions to the left have the same phase and add constructively and those on the right add destructively. The two sp hybrid orbitals are centered on the same atom, so they would look like (c). However, the small negative lobes are not used in bonding and are usually omitted. Thus, the two sp hybrid orbitals are normally represented as in (d). Note that forming the two sp hybrid orbitals required the use of only one p orbital, so an sp hybridized atom would have two p orbitals available to form bonds.

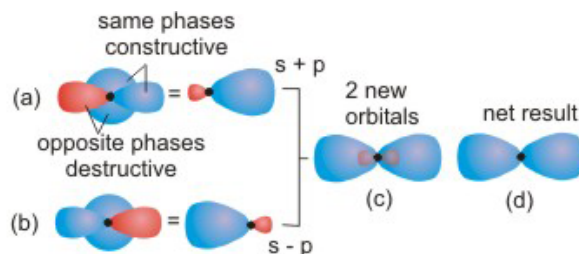


Figure 6.15: Mixing an s and a p Orbital on the Same Atom

6.4-9. Hybrid Orbital Descriptions

The number of hybrid orbitals used by an atom equals the number of electron groups around the atom.

Two sp hybrid orbitals are produced by combining one s and one p orbital as shown in the previous video. They are oriented 180° from one another. Only one p orbital is used to construct the hybrid orbitals, so two p orbitals are available to form π bonds. Thus, sp hybridized atoms form two π bonds (one triple bond or two double bonds) and have bond angles of 180° . Note that the sp hybrid orbitals lie along the axis of the p orbital used to construct them, so if the σ bonds are directed along the z-axis, then the s and the p_z orbitals would be used to make the hybrid orbitals, and the p_x and p_y orbitals would be used to form π bonds.

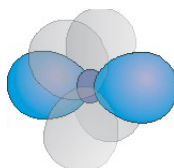


Figure 6.16a: A Hybridization Used by Atoms Obeying the Octet Rule

Three sp^2 (spoken “sp two”) hybrid orbitals are produced by combining one s and two p orbitals. The three hybrid orbitals lie in the plane defined by the two p orbitals used to construct them and are oriented 120° from one another. Two p orbitals are used in the hybridization, so only one p orbital remains to form a π bond. Thus, sp^2

hybridized atoms have one double bond and 120° bond angles. If the hybrids lie in the xy -plane, then the p_x and p_y orbitals must be used to construct them, which leaves the p_z orbital available for π bonding.

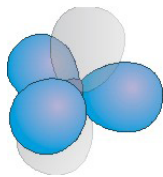


Figure 6.16b: A Hybridization Used by Atoms Obeying the Octet Rule

Four sp^3 (spoken “sp three”) hybrid orbitals are produced by combining the s and all three p orbitals. There are no p orbitals available to form π bonds, so sp^3 hybridized atoms form only single bonds and have bond angles of 109° .

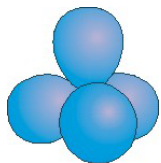


Figure 6.16c: A Hybridization Used by Atoms Obeying the Octet Rule

6.4-10. Using Valence Bond Theory to Explain the Structure of Allene

We conclude our discussion of valence bond theory by using it to explain why the planes of the two CH_2 groups of allene are perpendicular.

A video or simulation is available online.

We start by determining the hybridization of each carbon atom. The central atom is surrounded by two electron groups and is involved in two bonds, so it is sp hybridized. If the bonding axis is the z -axis, then the p_z orbital must be used to construct the hybrid orbitals, which leaves the p_x and p_y orbitals available to form the two bonds. Each of the terminal carbon atoms (C_A and C_B) is surrounded by three electron groups and is involved in one bond, so each is sp^2 hybridized. The sp^2 hybrid orbitals of C_A lie in the xz -plane because that is the plane defined by the C-H bonds, so the s, p_x and p_z orbitals are used to construct them.

This leaves the p_y orbital available to form a bond with the central carbon. If the central carbon uses its p_y orbital to bond to C_A , then it must use its p_x orbital to bond with C_B . If C_B uses its p_x orbital to form a bond, then it must use its s, p_y , and p_z orbitals to form the sp^2 hybrid orbitals, which lie in the yz -plane and are perpendicular to the sp^2 plane of C_A . Thus, the two CH_2 groups must be perpendicular if the central atom is to bond to both terminal carbon atoms because each bond requires a different p orbital. Figure 6.17 shows the bonding geometry in allene.

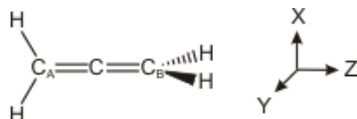


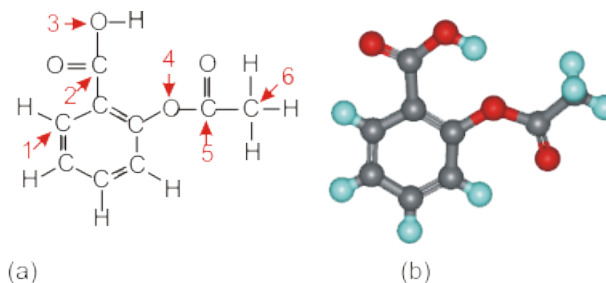
Figure 6.17: Coordinate System Used in Allene

Bonding and Hybridization Examples

6.4-11. Aspirin

EXERCISE 6.6:

Indicate the hybridization as sp , sp^2 , or sp^3 at each of the labeled atoms in the Lewis structure of the aspirin molecule shown below. Note that the lone pairs have been omitted, but C and O do obey the octet rule.



C₁

sp
 sp^2
 sp^3

O₄

sp
 sp^2
 sp^3

C₂

sp
 sp^2
 sp^3

C₅

sp
 sp^2
 sp^3

O₃

sp
 sp^2
 sp^3

C₆

sp
 sp^2
 sp^3

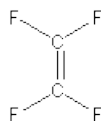
6.4-12. C₂F₄

EXERCISE 6.7:

Lewis structure and bonding in **tetrafluoroethylene (C₂F₄)**:

- ER = 6(8) = 48 electrons required with no sharing
- VE = 2(4) from C + 4(7) from F = 36 valence electrons
- SP = 1/2(48 - 36) = 6 shared pairs

The Lewis structure is the following.



The double bond must go between the carbon atoms because double bonds are never drawn to fluorine as that places positive formal charge on the fluorine atom. Note that each fluorine atom has three lone pairs, which are not shown.

Determine the following for C₂F₄.

C-C bond order _____

the hybridization of each carbon atom:

sp
 sp^2
 sp^3

the number of σ bonds _____

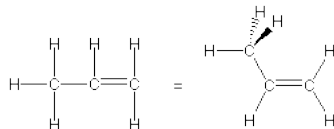
the number of π bonds _____

6.4-13. C₃H₆

EXERCISE 6.8:

Lewis structure and bonding in **propene (C₃H₆)**:

- ER = 3(8) + 6(2) = 36 electrons required with no sharing
- VE = 3(4) from C + 6(1) from H = 18 valence electrons
- SP = 1/2(36 - 18) = 9 shared pairs



The six C-H bonds must all be single bonds, two more bonds are required to connect the three carbon atoms for a total of eight shared pairs. The Lewis structure requires nine shared pairs, so one C-C double bond is required.

Determine the following for C₃H₆.

left C-C bond order _____ right C-C bond order _____

the hybridization of the leftmost carbon atom _____ the hybridization of the rightmost carbon atom _____

sp

sp²

sp³

sp

sp²

sp³

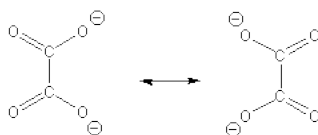
the number of σ bonds _____ the number of π bonds _____

6.4-14. C₂O₄²⁻

EXERCISE 6.9:

Lewis structure and bonding in the **oxalate ion (C₂O₄²⁻)**:

- ER = 6(8) = 48 electrons required with no sharing
- VE = 2(4) from C + 4(6) from O + 2 from charge = 34 valence electrons
- SP = 1/2(48 - 34) = 7 shared pairs



Five shared pairs are required for the sigma bonds, but seven shared pairs are required, so there must be two double bonds. This can only be accomplished while obeying the octet rule with one C=O double bond to each carbon.

Determine the following for C₂O₄²⁻.

C-C bond order _____ C-O bond order _____

the hybridization of each carbon atom _____

sp

sp²

sp³

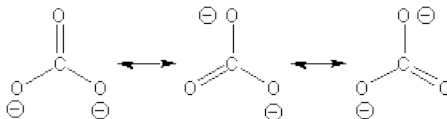
the number of σ bonds _____ the number of π bonds _____

6.4-15. CO_3^{2-}

EXERCISE 6.10:

Lewis structure and bonding in the **carbonate ion** (CO_3^{2-}):

- ER = $4(8) = 32$ electrons required with no sharing
- VE = 4 from C + $3(6)$ from O + 2 from charge = 24 valence electrons
- SP = $1/2(32 - 24) = 4$ shared pairs



The lone pairs on the O atoms have been omitted, but each O obeys the octet rule.

Determine the following for CO_3^{2-} .

C-O bond order _____

the hybridization of the carbon atom

- sp
- sp²
- sp³

the number of σ bonds _____

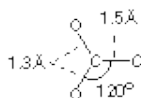
the number of π bonds _____

6.4-16. Bonding from Structure

EXERCISE 6.11:

X-rays are scattered from the atoms in molecules, and the manner in which they are scattered can be used to determine the relative positions of the atoms. Indeed, the structures of many molecules have been determined with this technique. However, x-rays are not scattered by electrons, and H atoms are usually too small to be seen. Consequently, lone pairs and H atoms must be added by the chemist. Determine the number of hydrogen atoms that must be added to the central carbon atom and the hybridization of the central atom of the structures given in the activity area. Hint:

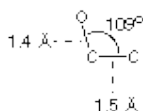
- use bond lengths (see table in the Resources) to determine bond orders and bond angles to determine hybridizations, and
- recall that C usually has no formal charge, which is the case when there are 4 bonds to it.



What is the hybridization on the central carbon atom?

- sp
- sp²
- sp³

How many hydrogen atoms must be added to the central carbon atom?



What is the hybridization on the central carbon atom?

- sp
- sp²
- sp³

How many hydrogen atoms must be added to the central carbon atom?

6.5 Molecular Orbital Theory and Delocalized Bonds

Introduction

In valence bond theory, orbitals on the same atom are combined to produce hybrid orbitals, which are then used to overlap an orbital on an adjacent atom to produce a bond that is localized between the two atoms. In **molecular orbital theory**, atomic orbitals on different atoms are mixed to produce bonds that can be localized between two atoms but are frequently **delocalized** over several. The rules presented in the previous section for mixing atomic orbitals that we used in the construction of hybrid orbitals will now be used to construct molecular orbitals.

Valence bond theory allows us to make predictions about bonding and structure from relatively simple considerations, but hybridization and resonance had to be invoked to account for some structural features. MO theory is more powerful in its predictive power, but it is somewhat more difficult to use. Thus, chemists use both theories, choosing the one that is easier to use while still providing sufficient predictive power. In this section, we present a qualitative introduction to molecular orbital theory; one that will introduce some important terms, present a more satisfying picture of delocalization, and explain the electronic structure of molecules.

Prerequisites

- 5.7 Resonance (Describe resonance and determine the bond order of bonds involved in resonance structures.)
- 2.6 Orbital Shapes and Sizes

Objectives

- Explain the difference between bonding and antibonding orbitals and show how s orbitals combine to produce MO's.
- Show how p orbitals can be used to construct σ and σ^* MO's.
- Show how p orbitals can be used to construct π and π^* MO's.
- Predict the relative energies the bonding MO, the antibonding MO, and the atomic orbitals used to construct them.
- Define HOMO and LUMO.
- Use an MO diagram to predict whether a diatomic molecule can form.
- Determine the bond order of a bond from the number of bonding and antibonding pairs of electrons.
- Use an MO diagram to predict the number of unpaired electrons in a molecule.
- Explain how to determine the relative phases of the atomic orbitals used to construct the molecular orbitals for molecules with more than two atoms.
- Determine whether a molecular orbital is bonding, nonbonding, or antibonding from the phases of the atomic orbitals used to construct it.

- Explain how MO theory explains resonance.
- Show how MO theory explains delocalized pi systems.

6.5-1. Bonding Versus Antibonding Orbitals

Bonding MO's increase the electron density between the nuclei, while antibonding MO's contain nodal planes perpendicular to the internuclear axis.

A video or simulation is available online.

In MO theory, atomic orbitals (AO's) are combined to form molecular orbitals (MO's). The number of MO's created is always equal to the number of AO's used to create them. Thus, combining two AO's produces two MO's, which differ in the way in which the AO's are combined.

- 1 **Bonding MO's:** A combination of two AO's that have the same phase in the region between the two nuclei results in a bonding MO. Bonding MO's are characterized by an accumulation of electron density between the two atoms.
- 2 **Antibonding MO's:** A combination of two AO's of opposite phase in the region between the two nuclei results in an antibonding MO. Antibonding MO's are characterized by an annihilation of electron density between the two atoms. That is, antibonding interactions contain nodal planes perpendicular to the bonding axis. Antibonding MO's are designated with a star (*). For example, the σ^* and π^* (pronounced "sigma star" and "pi star") are the antibonding combinations that contain nodal planes perpendicular to the bonding axis.

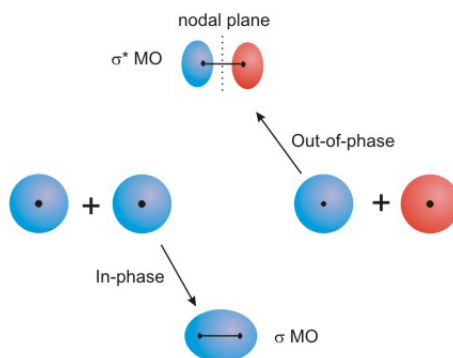


Figure 6.18: Combining Two s Orbitals

6.5-2. End-on Interactions of p Orbitals Produce σ and σ^* MO's

Head-on combination of two p orbitals results in electron density on the bonding axis, so both combinations are classified as σ . The combination of orbitals of the same phase increases electron density on the bonding axis, so it is the bonding σ orbital. The combination of opposite phases produces a nodal plane perpendicular to the bonding axis, so it is the antibonding σ^* orbital.

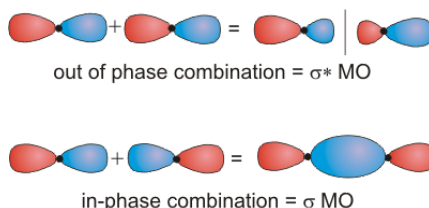


Figure 6.19: Head-on Combination of Two p Orbitals

6.5-3. Side-on Interactions of p Orbitals Produce π and π^* MO's

A video or simulation is available online.

The side-on combination of two p orbitals results in no electron density on the bonding axis, so both combinations are classified as π . The combination of orbitals of the same phase increases electron density between the bound atoms, so it is the π bonding orbital. The combination in which lobes of opposite phase interact produces a nodal plane perpendicular to the bonding axis, so it is an antibonding π^* orbital.

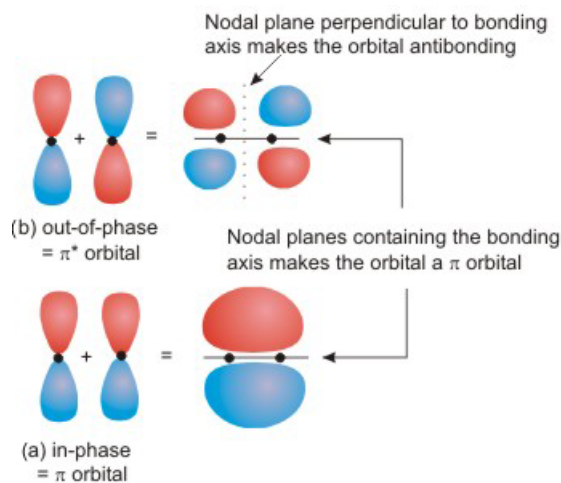


Figure 6.20: Side-on Combinations of Two p Orbitals

6.5-4. Energy

Each molecular orbital is characterized by an energy level, and the electrons in a molecule fill the molecular energy levels in the same manner that they fill atomic orbitals. That is, the electrons fill the molecular energy levels at lowest energy while obeying both Hund's Rule and the Pauli Exclusion Principle.

The energy changes resulting from the combinations of two s orbitals are shown in an MO diagram like the one shown in Figure 6.21. Three important characteristics of these diagrams are:

- the energy of bonding interactions is lower than that of the atomic orbitals by ΔE .
- the energy of antibonding orbitals is higher than that of the atomic orbitals by (ΔE^*) .
- $\Delta E^* > \Delta E$.

Many of the properties of a molecule are dictated by the nature of and energy difference between the occupied MO that is highest in energy and the unoccupied MO that is lowest in energy. These two orbitals are referred to as the HOMO and LUMO.

- **HOMO**; The **H**ighest **O**ccupied **M**O
- **LUMO**; The **L**owest **U**noccupied **M**O

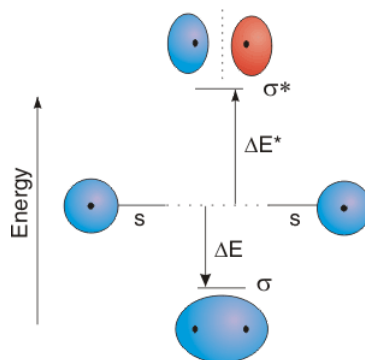


Figure 6.21: An MO Energy Diagram An MO diagram for the combination of two s orbitals of the same energy. Note that $\Delta E^* > \Delta E$.

Electrons that occupy bonding orbitals lower the energy of the system and make the MO more bonding, while those occupying antibonding orbitals raise the energy and make the MO less bonding. Indeed the bond order (BO) is defined in terms of the difference between the number of bonding and antibonding electrons in the bond as follows.

$$\text{BO} = \frac{1}{2}(\text{number of bonding electrons} - \text{number of antibonding electrons})$$

6.5-5. MO Diagrams for H₂ and He₂

As an example of the use of a diagram such as the one shown in Figure 6.21, we examine the differences predicted for the H₂ and He₂ molecules.

H + H → H₂: Each H atom has one electron in the 1s orbital, so the two-atom system has two electrons to place in the MO diagram. Both electrons would enter the σ bonding orbital. Their energy in a sigma orbital of H₂ is less than that of two electrons in two 1s orbitals of separated H atoms, so H₂ is a stable molecule. The bond order of the H-H bond is $1/2(2 - 0) = 1$, a single bond.

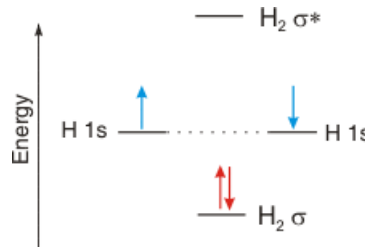


Figure 6.22a: MO Diagram for H₂

He + He → He₂: Each He atom has two electrons in its 1s orbital, so the two-atom system has four electrons. Two electrons would be placed in the σ orbital and two would be placed in the σ^* . However, $\Delta E^* > \Delta E$, so the energy of four electrons in He₂ is greater than in two separated He atoms. The bond order of the He-He bond would be $1/2(2 - 2) = 0$, no bond. Consequently, He₂ does not form.

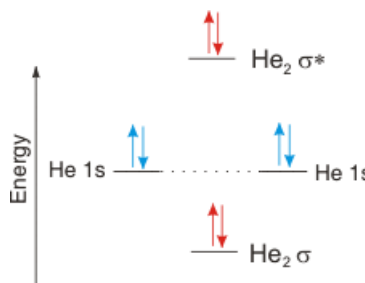


Figure 6.22b: MO Diagram He₂

6.5-6. Relative Orbital Energies in O₂

Consider the interaction of the valence orbitals of two oxygen atoms to form an oxygen molecule.

- The 2s orbitals interact to form σ and σ^* orbitals as shown in the Combining Two s Orbitals video. We use the notation σ (2s) and σ^* (2s) to show that these MO's are derived from the 2s interaction. The 2s orbitals are the lowest energy valence orbitals in an oxygen atom, so the two MO's are also low in energy.
- The 2p orbitals that are directed along the bonding axis interact in a head-on manner similar to that shown in Figure 6.19 to produce the σ (2p) and σ^* (2p) orbitals. Head-on interactions are stronger than side-on interactions, so the σ (2p) is the lowest energy MO derived from the 2p interactions, while the σ^* (2p) is the highest energy MO.
- The remaining 2p orbitals interact in a side-on fashion as shown in the Side-on Combinations of Two p Orbitals video to produce a pair of π (2p) and a pair of π^* (2p) orbitals. Note that the members of each pair have the same energy because there the two π (2p) orbitals are identical except for their orientation relative to one another.

The energy level diagram for the MO's in O₂ is shown in Figure 6.23.

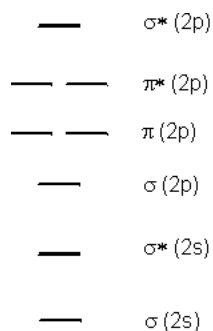


Figure 6.23

6.5-7. Predictions for O₂

Each oxygen atom has six valence electrons, so a total of 12 electrons must be placed into the energy diagram. The electrons are placed in the same manner as they are into the orbitals of an atom: lowest energy orbitals are occupied first and the Pauli Exclusion Principle and Hund's Rule are obeyed. The result of placing 12 electrons in the diagram is shown in Figure 6.24. Note that the π^* MO constructed from the 2p orbitals is the HOMO, while the σ^* MO constructed from the 2p is the LUMO. Two important predictions can be made based on this diagram:

- 1 **O-O bond order is 2.** Recall that the bond order of a bond is determined as $BO = 1/2(\text{number bonding electrons} - \text{number antibonding electrons})$, so the O-O bond order is $1/2(8 - 4) = 2$, which is the same conclusion we made from the Lewis structure.
- 2 **Oxygen molecules are paramagnetic.** Oxygen molecules are paramagnetic (deflected in a magnetic field), which means that O₂ must have unpaired electrons. The Lewis structure we drew in Section 5.5 had no unpaired electrons, which indicates a flaw in the bonding theory used in the previous chapter. However, paramagnetism in O₂ is readily explained with MO theory. The two highest energy electrons must be placed into the two π^* orbitals, and, since they must obey Hund's Rule, they must be unpaired. The presence of two unpaired electrons in O₂ makes it paramagnetic. This prediction was a major success for the MO theory.

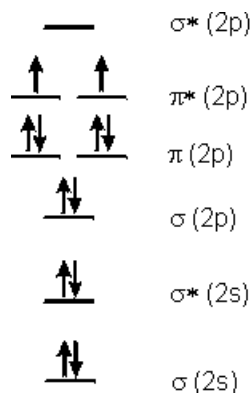


Figure 6.24: Molecular Orbital Occupancy for an O₂ Molecule

6.5-8. Heteronuclear Diatomic Molecules

The two nuclei in heteronuclear diatomic molecules are nuclei of different elements, so the AO's that mix to form the bonding MO are at different energies. Whereas the two atoms of a homonuclear diatomic molecule like H₂ and O₂ make equal contributions to each MO in the molecule, the energy difference between the AO's in a heteronuclear diatomic molecule results in MO's that are not composed of equal amounts of the AO's. Instead, the AO's mix in the ratio that achieves the lowest energy possible for the bonding MO. The lowest energy MO is produced when the AO at lower energy contributes more to the MO than does the AO at higher energy. We now examine the bonding between an s orbital on atom X with the s orbitals on atoms A, B, and C, which are at different energies.

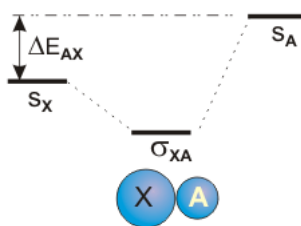


Figure 6.25a: Mixing AO's of Different Energy

The energy of s_X (the s orbital on atom X) is less than that of s_A by an amount ΔE_{XA} . s_X is the lower energy AO, so it contributes more to the bonding MO (σ_{XA}) than does s_A , which is shown by the relative sizes of the spheres describing the MO. The larger sphere on X means that there is more electron density on atom X in the bond, so the XA bond is polar with atom X carrying the negative charge.

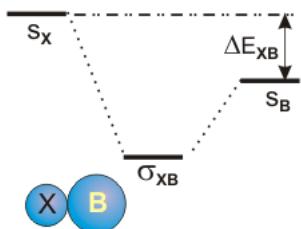


Figure 6.25b: Mixing AO's of Different Energy

s_B is lower in energy than s_X by an amount ΔE_{XB} . s_B is the lower energy orbital, so it contributes more to the bonding MO (σ_{XB}). The XB bond is therefore polar with atom B carrying the negative charge.

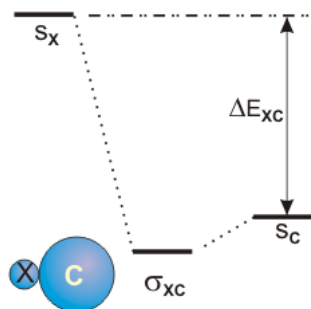


Figure 6.25c: Mixing AO's of Different Energy

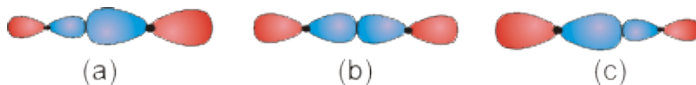
s_C is lower in energy than s_X by an amount ΔE_{XC} . $\Delta E_{XC} > \Delta E_{XB}$, so s_C contributes even more to the XC bond than did s_B to the XB bond. The small sphere representing the contribution of s_X to the σ_{XC} MO indicates that only a small amount of the electron density in the bond resides on atom X. The result is that the XC bond is more polar than the XB bond.

Recall that electronegativity is a measure of how well an atom attracts the bonding electrons, but, as shown in the preceding figure, the electron density in a bond is greater around the atom with the lower energy orbital; i.e., the atom with the lower energy orbital attracts the electrons more, so it is the more electronegative atom. This is why we used the energy of the unfilled orbitals to predict relative electronegativities in Chapter 3! Using the relative energies of atoms X, A, B, and C in Figures 6.25a, 6.25b, and 6.25c, we conclude that atom C is the most electronegative atom and atom A is the least electronegative. The bond dipole of the AX bond points toward atom X because X is more electronegative than A, but it points toward atom C in the XC bond because atom C is more electronegative than atom X.

6.5-9. Heteronuclear Bonding MO Exercise

EXERCISE 6.12:

Indicate which representation (a, b, or c) best describes the interaction of p orbitals in each of the following O-X bonds. Assume the oxygen orbital is on the left in each case.



an O-F bond

- a
- b
- c

an O-N bond

- a
- b
- c

an O-O bond

- a
- b
- c

6.5-10. Rules for MO Construction of Simple Systems

MO's can be bonding, nonbonding, or antibonding.

So far we have discussed the MO's formed by interacting only two atoms, but all of the atoms in a molecule can be involved in a single MO. Computers are used to determine the MO's of complicated molecules, so we will limit our discussion to the MO's of simple systems, which can be constructed with the following rules.

- 1 The number of MO's equals the number of atomic orbitals used to construct them.
- 2 Each MO contains one more nodal plane than the MO that it is immediately beneath it in energy. There are no nodal planes in the lowest energy MO, and there is a nodal plane between each pair of atoms in the highest energy MO.
- 3 The nodal planes are placed symmetrically even if it means placing them on an atom.
- 4 Nodal planes cannot be placed on adjacent atoms.

5 Nodal planes are not placed on terminal atoms.

The bonding character of an MO spread over several atoms depends upon the relative number of bonding and antibonding interactions. In the following discussion, we use \mathbf{B} = number of bonding interactions and \mathbf{A} = number of antibonding interactions.

- $\mathbf{B} > \mathbf{A}$: The MO is bonding, and its energy is lower than the energy of the AO's used to construct it.
- $\mathbf{B} < \mathbf{A}$: The MO is antibonding, and its energy is higher than the energy of the AO's used to construct it.
- $\mathbf{B} = \mathbf{A}$: The MO is nonbonding, and its energy is close to the energy of the AO's used to construct it.

A common way to draw MO's, and the one used in the following discussion, is to show only the relative phases of the AO's used to construct them. Thus, we will not be drawing the σ and π orbitals shown in the Combining Two s Orbitals video or the Side-on Combinations of Two p Orbitals video. Rather, we will represent them by the phases of the interacting orbitals.

6.5-11. Constructing the MO's for a Three-Atom System

A video or simulation is available online.

There are three atomic orbitals, so there must be three MO's. All of the atomic orbitals must be of the same phase in the lowest energy orbital, which produces an MO with two bonding interactions and no anti-bonding interactions. This orbital is a bonding orbital. The next highest orbital must contain one nodal plane placed in the center. This orbital contains no bonding or antibonding interactions between adjacent atoms, so it is nonbonding. The highest energy orbital requires one more nodal plane. The two nodal planes must be placed symmetrically. The resulting MO contains no bonding and two antibonding interactions, so it is an antibonding orbital. If we assume the system contains four electrons and place them the two lowest energy orbitals, then the nonbonding orbital is the HOMO and the antibonding orbital is the LUMO.

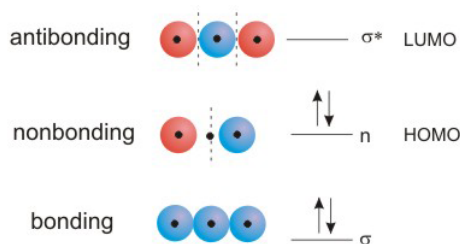


Figure 6.26

6.5-12. SO_2

The structural features that could only be explained by invoking resonance in Chapter 5 are readily understood in terms of delocalized MO's. Consider the case of SO_2 shown in Figure 6.27. Although the bond angles are 120° not 180° , the atomic orbitals are p orbitals not s orbitals, and the interactions are pi not sigma, the relative phases of the AO's are the same for SO_2 as for the three-atom system discussed above.

Two resonance structures (shown at the top of the figure) were used to account for the fact that the two S-O bonds are of equal length. The two structures differ in the position of the π bond, which is shared between the two bonds, and the location of one of the lone pairs, which appears to be shared by the oxygen atoms. The σ bonds and the lone pairs except the one that appears in different locations in the Lewis structure lie in the molecular plane and will be ignored in the following MO description discussion, which centers on the π system. Note that the term resonance is not required in the MO description.

The π system contains four electrons: the two in the π bond and two in the lone pair that appears to move in the two resonance forms. The AO's used to construct the π MO's are p orbitals that are perpendicular to the molecular plane. Placing four electrons into the system fills the π and n (nonbonding) orbitals. Note that there is one bonding orbital (the π bond) and one lone pair (nonbonding orbital) as shown in the Lewis structures. However, the π bond is delocalized over all three atoms, with no difference between the two S-O bonding regions, and the lone pair is

delocalized over both oxygen atoms. Thus, all of the features that caused us to invoke resonance with the earlier bonding theory are explained with molecular orbital theory.

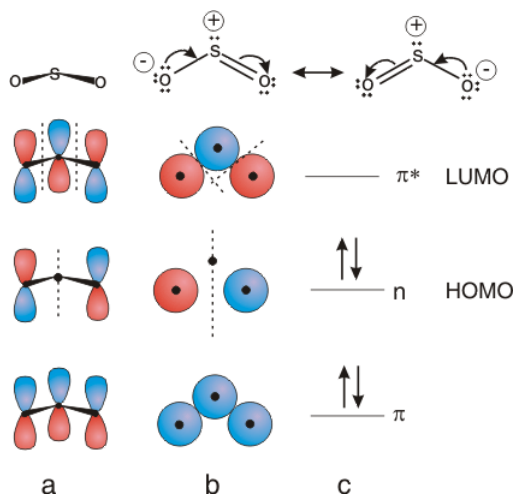
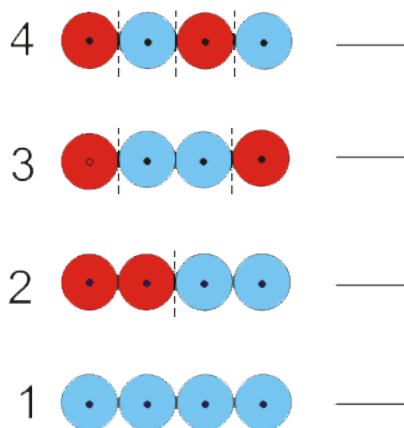


Figure 6.27: π MO's for Sulfur Dioxide (a) Viewing the p orbitals from the side; (b) Viewing the p orbitals from above so that only the top of the p orbitals can be seen; (c) Energy diagram showing two occupied MO's and identifying the HOMO and LUMO.

6.5-13. Orbital Types in a Delocalized Four-Atom System - Exercise

EXERCISE 6.13:

Use the MO diagram in the figure to determine the number of bonding interactions, the number of antibonding and orbital type for each of the four MO's of a delocalized four-atom system.



Orbital Number 4:

bonding interactions _____

antibonding interactions _____

orbital type:
bonding
antibonding
nonbonding

Orbital Number 3:

bonding interactions _____

antibonding interactions _____

orbital type:
bonding
antibonding
nonbonding

Orbital Number 2:

bonding interactions _____

antibonding interactions _____

orbital type:
bonding
antibonding
nonbonding

Orbital Number 1:

bonding interactions _____

antibonding interactions _____

orbital type:
bonding
antibonding
nonbonding

Assume a four-electron system to identify the orbital number of the HOMO and LUMO.

HOMO _____

LUMO _____

6.5-14. Four-atom Example: Butadiene

The Lewis structure of butadiene (Figure 6.28) shows two C=C double bonds and one C-C single bond, so we would expect two bond lengths of about 130 pm and one of about 150 pm. Experimentally, we find that there are two bonds of 134 pm and one of 135 pm, the approximate length of a C=C double bond. We now use an MO treatment of the π system to explain this observation. The relative phases of the p orbitals are the same as the s orbitals in the above exercise. Figure 6.28a views the molecule from the top so that only the top lobe of each orbital is shown, while Figure 6.28b shows the side-on view. There is one electron in each p orbital, so there are a total of four electrons in the π system, which are distributed into MO's as shown. Note that both pairs of electrons reside in π bonding orbitals, which is consistent with the two double bonds predicted by the Lewis structure. However, the π orbitals are delocalized over all four carbon atoms not localized between two atoms as shown in the Lewis structure, which explains why the bond lengths are nearly the same.

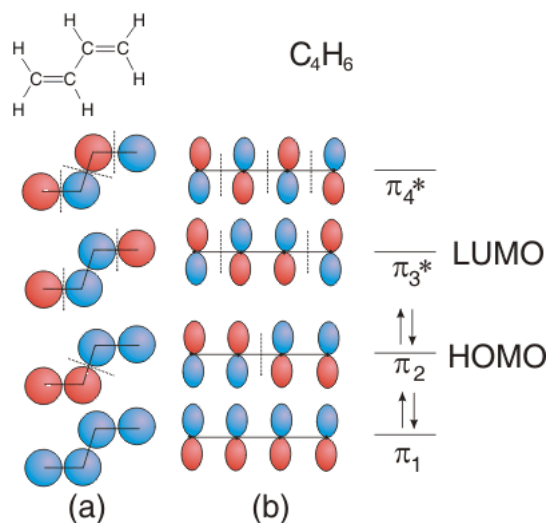


Figure 6.28: MO's for Butadiene (a) The circles represent the relative phases of the p orbitals (the orbitals viewed from the top). (b) Each p orbital represented by the traditional 'figure 8'.

6.5-15. Benzene

As our last example, we examine the delocalized π system in benzene (C_6H_6) shown in Figure 6.29. Recall that the double bonds in benzene are sometimes represented by a circle in Figure 6.8 due to resonance in the molecule. Although the construction of the MO's is beyond the scope of this text, an examination of them demonstrates the rules for construction and provides a better understanding of the bonding in this very important molecule. There are six carbon atoms and six p orbitals, so there are six π MO's. The lowest energy MO has no nodal planes and is a bonding orbital delocalized over all six atoms. The highest energy orbital has a nodal plane between each pair of atoms, but, due to the symmetry of benzene, this requires only three nodal planes. Thus, the four remaining MO's must contain either one or two nodal planes. In fact, two MO's have one nodal plane, and two MO's have two nodal planes. The π system has six electrons, so only the three bonding MO's are occupied, which gives rise to the three double bonds in the Lewis structure. The three MO's are delocalized over all six carbon atoms, so, consistent with representing the double bonds with a circle, the π electron density is spread over the entire molecule with no localized double bonds.

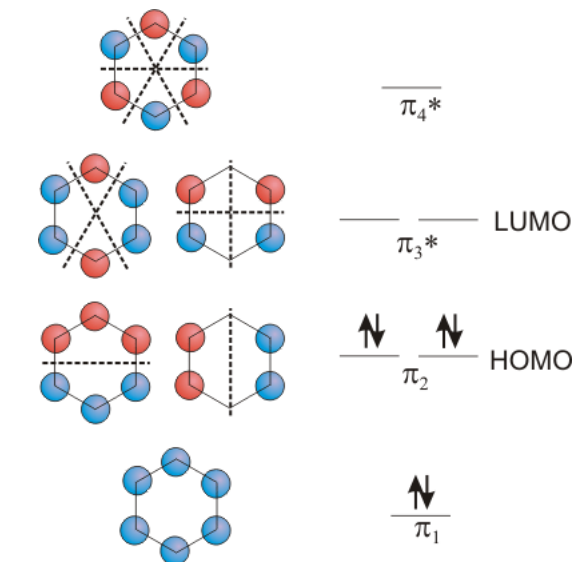


Figure 6.29: MO's for the π System of Benzene

6.5-16. Summary

Molecular orbital theory is a very powerful tool, and we will refer to the concepts and terms introduced here in subsequent chapters. However, the simple predications about geometry and bonding that we made in the previous chapter and most of this chapter are correct, and they are much easier to make using the bonding theory presented earlier. Thus, chemists often use a combination of the two theories when discussing molecular structure and bonding.

6.6 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.