Chapter 9

Covalent Bonding: Orbitals

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Chili peppers taste hot because of capsaicin, a complex molecule containing atoms with many different hybridizations.

In Chapter 8 we discussed the fundamental concepts of bonding and introduced the most widely used simple model for covalent bonding: the localized electron model. We saw the usefulness of a bonding model as a means for systematizing chemistry by allow-

ing us to look at molecules in terms of individual bonds. We also saw that molecular structure can be predicted by minimizing electron-pair repulsions. In this chapter we will examine bonding models in more detail, particularly focusing on the role of orbitals.

//Heading

9.1 Hybridization and the Localized Electron Model

As we saw in Chapter 8, the localized electron model views a molecule as a collection of atoms bound together by sharing electrons between their atomic orbitals. The arrange- ment of valence electrons is represented by the Lewis structure (or structures, where res- onance occurs), and the molecular geometry can be predicted from the VSEPR model. In this section we will describe the atomic orbitals used to share electrons and hence to form the bonds.

//Sub Heading

sp3 Hybridization

Let us reconsider the bonding in methane, which has the Lewis structure and molecular geometry shown in Fig. 9.1. In general, we assume that bonding involves only the va- lence orbitals. This means that the hydrogen atoms in methane use 1s orbitals. The va- lence orbitals of a carbon atom are the 2s and 2p orbitals shown in Fig. 9.2. In thinking about how carbon can use these orbitals to bond to the hydrogen atoms, we can see two related problems:

//Image

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Figure 9.1

(a) The Lewis structure of the methane molecule.

(b) The tetrahedral molecular geometry of the methane molecule

Figure 9.2

The valence orbitals on a free carbon atom: 2s, 2px, 2py, and 2pz.

//Quote

The valence orbitals are the orbitals associated with the highest principal quantum level that contains electrons on a given atom.

//Image

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Figure 9.3

The “native” 2s and three 2p atomic orbitals characteristic of a free carbon atom are combined to form a new set of four sp3 orbitals. The small lobes of the orbitals are usually omitted from diagrams for clarity.

1. Using the 2p and 2s atomic orbitals will lead to two different types of C¬H bonds:

(a) those from the overlap of a 2p orbital of carbon and a 1s orbital of hydrogen (there will be three of these) and (b) those from the overlap of a 2s orbital of carbon and a 1s orbital of hydrogen (there will be one of these). This is a problem because methane is known to have four identical C¬H bonds.

2. Since the carbon 2p orbitals are mutually perpendicular, we might expect the three C¬H bonds formed with these orbitals to be oriented at 90-degree angles:

//Image

IMG9.3(a)

Figure 9.4

Cross section of an sp3 orbital. This shows a “slice” of the electron density of the sp3 orbitals illustrated in the center diagram of Fig. 9.3.

(Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC2402; printed with permission.)

//Image

IMG9.4

However, the methane molecule is known by experiment to be tetrahedral with bond angles of 109.5 degrees.

This analysis leads to one of two conclusions: Either the simple localized electron model is wrong or carbon adopts a set of atomic orbitals other than its “native” 2s and 2p orbitals to bond to the hydrogen atoms in forming the methane molecule. The second con- clusion seems more reasonable. The 2s and 2p orbitals present on an isolated carbon atom may not be the best set of orbitals for bonding; a new set of atomic orbitals might better serve the carbon atom in forming molecules. To account for the known structure of methane, it makes sense to assume that the carbon atom has four equivalent atomic or- bitals, arranged tetrahedrally. In fact, such a set of orbitals can be obtained quite readily by combining the carbon 2s and 2p orbitals, as shown schematically in Fig. 9.3. This mix- ing of the native atomic orbitals to form special orbitals for bonding is called hybridiza- tion. The four new orbitals are called sp3 orbitals because they are formed from one 2s and three 2p orbitals (s1p3). We say that the carbon atom undergoes sp3 hybridization or is sp3 hybridized. The four sp3 orbitals are identical in shape, each one having a large lobe and a small lobe (see Fig. 9.4). The four orbitals are oriented in space so that the large lobes form a tetrahedral arrangement, as shown in Fig. 9.3.

The hybridization of the carbon 2s and 2p orbitals also can be represented by an or- bital energy-level diagram, as shown in Fig. 9.5. Note that electrons have been omitted because we do not need to be concerned with the electron arrangements on the individual

//Quote

Hybridization is a modification of the localized electron model to account for the observation that atoms often seem to use special atomic orbitals in forming molecules.

sp3 hybridization gives a tetrahedral set of orbitals.

Note that the shapes of the hybrid orbitals shown in Figure 9.3 are “mushroom-like,” calculated from wave functions.

Figure 9.6

An energy-level diagram showing the formation of four sp3 orbitals.

//Image

IMG9.5

Figure 9.7

The tetrahedral set of four sp3 orbitals of the carbon atom are used to share electron pairs with the four 1s orbitals of the hydrogen atoms to form the four equivalent C¬H bonds. This accounts for the known tetrahedral structure of the CH4 molecule.

//Image

IMG9.6

//Example

EXAMPLE 9.1 The Localized Electron Model I

Describe the bonding in the ammonia molecule using the localized electron model

//Solution

A complete description of the bonding involves three steps:

1. Writing the Lewis structure

2. Determining the arrangement of electron pairs using the VSEPR model

3. Determining the hybrid atomic orbitals needed to describe the bonding in the molecule

The Lewis structure for NH3 is

//Image

IMG9.7

//Image

IMG9.8

Figure 9.7

The nitrogen atom in ammonia is sp3

hybridized.

The four electron pairs around the nitrogen atom require a tetrahedral arrangement to minimize repulsions. We have seen that a tetrahedral set of sp3 hybrid orbitals is ob- tained by combining the 2s and three 2p orbitals. In the NH3 molecule three of the sp3 or- bitals are used to form bonds to the three hydrogen atoms, and the fourth sp3 orbital holds

the lone pair, as shown in Fig. 9.7.

//Image

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Figure 9.8

The hybridization of the s, px, and py atomic orbitals results in the formation of three sp2 orbitals centered in the xy plane. The large lobes of the orbitals lie in the plane at angles of 120 degrees and point toward the corners of a triangle.

//Sub Heading

sp2 Hybridization

Ethylene (C2H4) is an important starting material in the manufacture of plastics. The C2H4 molecule has 12 valence electrons and the following Lewis structure:

//Image

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//Quote

A double bond acts as one effective electron pair.

We saw in Chapter 8 that a double bond acts as one effective pair, so in the ethylene mol- ecule each carbon is surrounded by three effective pairs. This requires a trigonal planar arrangement with bond angles of 120 degrees. What orbitals do the carbon atoms in this molecule employ? The molecular geometry requires a set of orbitals in one plane at angles of 120 degrees. Since the 2s and 2p valence orbitals of carbon do not have the required arrangement, we need a set of hybrid orbitals.

//Quote

sp2 hybridization gives a trigonal planar arrangement of atomic orbitals.

The sp3 orbitals we have just considered will not work because they are at angles of

109.5 degrees rather than the required 120 degrees. In ethylene the carbon atom must hy- bridize in a different manner. A set of three orbitals arranged at 120-degree angles in the same plane can be obtained by combining one s orbital and two p orbitals, as shown in Fig. 9.8. The orbital energy-level diagram for this arrangement is shown in Fig. 9.9. Since one 2s and two 2p orbitals are used to form these hybrid orbitals, this is called sp2 hy- bridization. Note from Fig. 9.8 that the plane of the sp2 hybridized orbitals is determined by which p orbitals are used. Since in this case we have arbitrarily decided to use the px and py orbitals, the hybrid orbitals are centered in the xy plane.

//Quote

Note in Fig. 9.10 and the figures that follow that the orbital lobes are artificially narrowed to more clearly show their relative orientations.

In forming the sp2 orbitals, one 2p orbital on carbon has not been used. This remain-

ing p orbital (pz) is oriented perpendicular to the plane of the sp2 orbitals, as shown in Fig. 9.10.

Now we will see how these orbitals can be used to account for the bonds in ethyl- ene. The three sp2 orbitals on each carbon can be used to share electrons, as shown in figure 9.11

//Image

IMG9.11

Figure 9.9

An orbital energy-level diagram for sp2 hybridization. Note that one p orbital remains unchanged.

//Image

IMG9.12

Figure 9.10

When an s and two p orbitals are mixed to form a set of three sp2 orbitals, one p orbital remains unchanged and is perpen- dicular to the plane of the hybrid orbitals. Note that in this figure and those that follow, the orbitals are drawn with nar- rowed lobes to show their orientations more clearly.

//Image

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Figure 9.11

The u bonds in ethylene. Note that for each bond the shared electron pair occupies the region directly between the atoms.

//Image

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Figure 9.12

A carbon–carbon double bond consists of a u bond and a 1r bond. In the u bond the shared electrons occupy the space directly between the atoms. The 1r bond is formed from the unhybridized p orbitals on the two

carbon atoms. In a 1r bond the shared electron pair occupies the space above and below a line joining the atoms.

In each of these bonds, the electron pair is shared in an area centered on a line running between the atoms. This type of covalent bond is called a sigma (u) bond. In the ethylene molecule, the u bonds are formed using sp2 orbitals on each carbon atom and the 1s orbital on each hydrogen atom.

How can we explain the double bond between the carbon atoms? In the u bond the electron pair occupies the space between the carbon atoms. The second bond must there- fore result from sharing an electron pair in the space above and below the u bond. This type of bond can be formed using the 2p orbital perpendicular to the sp2 hybrid orbitals on each carbon atom (refer to Fig. 9.10). These parallel p orbitals can share an electron pair, which occupies the space above and below a line joining the atoms, to form a pi (Tr) bond, as shown in Fig. 9.12.

Note that u bonds are formed from orbitals whose lobes point toward each other, but 1r bonds result from parallel orbitals. A double bond always consists of one u bond, where the electron pair is located directly between the atoms, and one 1r bond, where the shared pair occupies the space above and below the u bond.

We can now completely specify the orbitals that this model assumes are used to form the bonds in the ethylene molecule. As shown in Fig. 9.13, the carbon atoms use sp2 hybrid orbitals to form the u bonds to the hydrogen atoms and to each other, and they use p to form the 1r bond with each other. Note that we have accounted fully for the Lewis structure of ethylene with its carbon–carbon double bond and carbon–hydrogen single bonds.

This example illustrates an important general principle of this model: Whenever an atom is surrounded by three effective pairs, a set of sp2 hybrid orbitals is required.

//Image

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Figure 9.13

1. The orbitals used to form the bonds in ethylene. (b) The Lewis structure for ethylene

//Image

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Figure 9.14

When one s orbital and one p orbital are hybridized, a set of two sp orbitals oriented at 180 degrees results.

//Image

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Figure 9.15

The hybrid orbitals in the CO2 molecule

//Image

IMG9.18

Figure 9.16

The orbital energy-level diagram for the formation of sp hybrid orbitals on carbon.

//Sub Heading

sp Hybridization

Another type of hybridization occurs in carbon dioxide, which has the following Lewis structure:

//Quote

More rigorous theoretical models of CO2 indicate that each of the oxygen atoms uses two p orbitals simultaneously to form the pi bonds to the carbon atom, thus leading to unusually strong C“O bonds

In the CO2 molecule the carbon atom has two effective pairs that will be arranged at an angle of 180 degrees. We therefore need a pair of atomic orbitals oriented in opposite di- rections. This requires a new type of hybridization, since neither sp3 nor sp2 hybrid or- bitals will fit this case. To obtain two hybrid orbitals arranged at 180 degrees requires sp hybridization, involving one s orbital and one p orbital, as shown in Fig. 9.14.

In terms of this model, two effective pairs around an atom will always require sp

hybridization of that atom. The sp orbitals of carbon in carbon dioxide can be seen in Fig. 9.15, and the corresponding orbital energy-level diagram for their formation is given in Fig. 9.16. These sp hybrid orbitals are used to form the er bonds between the carbon and the oxygen atoms. Note that two 2p orbitals remain unchanged on the sp hybridized carbon. These are used to form the 1r bonds with the oxygen atoms.

In the CO2 molecule each oxygen atom\* has three effective pairs around it, requir- ing a trigonal planar arrangement of the pairs. Since a trigonal set of hybrid orbitals re- quires sp2 hybridization, each oxygen atom is sp2 hybridized. One p orbital on each oxygen is unchanged and is used for the 1r bond with the carbon atom.

Now we are ready to use our model to describe the bonding in carbon dioxide. The sp orbitals on carbon form er bonds with the sp2 orbitals on the two oxygen atoms (see Fig. 9.15). The remaining sp2 orbitals on the oxygen atoms hold lone pairs. The 1r bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel 2p orbitals. The sp hybridized carbon atom has two unhybridized p orbitals, pictured in Fig. 9.17. Each of these p orbitals is used to form a 1r bond with an oxygen atom (see

//Image

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Figure 9.17

The orbitals of an sp hybridized carbon atom.

\*We will assume that minimizing electron repulsions also is important for the peripheral atoms in a mol- ecule and apply the VSEPR model to these atoms as well.

//Image

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Figure 9.18

The orbital arrangement for an sp2 hybridized oxygen atom.

//Image

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Figure 9.19

(a)The orbitals used to form the bonds in carbon dioxide. Note that the carbon–oxygen double bonds each consist of one u bond and one Tr bond. (b) The Lewis structure for carbon dioxide.

Fig. 9.18). The total bonding picture for the CO2 molecule is shown in Fig. 9.19. Note that this picture of the bonding neatly explains the arrangement of electrons predicted by the Lewis structure.

Another molecule whose bonding can be described by sp hybridization is acetylene (C2H2), which has the systematic name ethyne. The Lewis structure for acetylene is

H¬C‚C¬H

Because the triple bond counts as one effective repulsive unit, each carbon has two effec- tive pairs, which requires a linear arrangement. Thus each carbon atom requires sp hybridiza- tion, leaving two unchanged p orbitals (see Fig. 9.16). One of the oppositely oriented (see Fig. 9.14) sp orbitals is used to form a bond to the hydrogen atom; the other sp orbital overlaps with the similar sp orbital on the other carbon to form the sigma bond. The two pi bonds are formed from the overlap of the two p orbitals on each carbon. This accounts for the triple bond (one sigma and two pi bonds) in acetylene.

//Example

Example 9.2 The Localized Electron Model II

//Solution

The Lewis structure for the nitrogen molecule is

//Image

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where each nitrogen atom is surrounded by two effective pairs. (Remember that a multi- ple bond counts as one effective pair.) This gives a linear arrangement (180 degrees) re- quiring a pair of oppositely directed orbitals. This situation requires sp hybridization. Each nitrogen atom in the nitrogen molecule has two sp hybrid orbitals and two unchanged p orbitals, as shown in Fig. 9.20(a). The sp orbitals are used to form the u bond between the nitrogen atoms and to hold lone pairs, as shown in Fig. 9.20(b). The p orbitals are used to form the two Tr bonds [see Fig. 9.20(c)]; each pair of overlapping parallel p or- bitals holds one electron pair. Such bonding accounts for the electron arrangement given by the Lewis structure. The triple bond consists of a u bond (overlap of two sp orbitals) and two Tr bonds (each one from an overlap of two p orbitals). In addition, a lone pair occupies an sp orbital on each nitrogen atom.

//Image

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Figure 9.20

(a) An sp hybridized nitrogen atom. There are two sp hybrid orbitals and two unhybridized p orbitals. (b) The er bond in the N2 molecule. (c) The two 7T bonds in N2 are formed when electron pairs are shared between two sets of parallel

p orbitals. (d) The total bonding picture for N2.

//Sub Heading

dsp3 Hybridization

To illustrate the treatment of a molecule in which the central atom exceeds the octet rule,

consider the bonding in the phosphorus pentachloride molecule (PCl5). The Lewis structure

//Image

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shows that the phosphorus atom is surrounded by five electron pairs. Since five pairs re- quire a trigonal bipyramidal arrangement, we need a trigonal bipyramidal set of atomic orbitals on phosphorus. Such a set of orbitals is formed by dsp3 hybridization of one d orbital, one s orbital, and three p orbitals, as shown in Fig. 9.21.

The dsp3 hybridized phosphorus atom in the PCl5 molecule uses its five dsp3 orbitals to share electrons with the five chlorine atoms. Note that a set of five effective pairs around

a given atom always requires a trigonal bipyramidal arrangement, which in turn requires

dsp3 hybridization of that atom.

The Lewis structure for PCl5 shows that each chlorine atom is surrounded by four electron pairs. This requires a tetrahedral arrangement, which in turn requires a set of four sp3 orbitals on each chlorine atom.

Now we can describe the bonding in the PCl5 molecule shown in Fig. 9.22. The five P¬Cl er bonds are formed by sharing electrons between a dsp3 orbital\* on the phosphorus atom and an orbital on each chlorine.

//Image

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Figure 9.21

A set of dsp3 hybrid orbitals on a phos- phorus atom. Note that the set of five dsp3 orbitals has a trigonal bipyramidal dsp3 arrangement. (Each dsp3 orbital also has a small lobe that is not shown in this diagram.)

//Image

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Figure 9.22

The structure of the PCI5 molecule.

\*There is considerable controversy about whether the d orbitals are as heavily involved in the bonding in these molecules as this model predicts. However, this matter is beyond the scope of this text.

//Example

Example 9.3 The Localized Electron Model III

Describe the bonding in the triiodide ion (I3 ).

//Solution

The Lewis structure for I3

//Image

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shows that the central iodine atom has five pairs of electrons (see Section 8.11). A set of five pairs requires a trigonal bipyramidal arrangement, which in turn requires a set of dsp3 orbitals. The outer iodine atoms have four pairs of electrons, which calls for a tetrahedral arrangement and sp3 hybridization.

Thus the central iodine is dsp3 hybridized. Three of these hybrid orbitals hold lone pairs, and two of them overlap with sp3 orbitals of the other two iodine atoms to form a- bonds.

//Sub Heading

d2sp3 Hybridization

Some molecules have six pairs of electrons around a central atom; an example is sulfur hexafluoride (SF6), which has the Lewis structure

//Quote

d 2sp3 hybridization gives six orbitals arranged octahedrally.

//Image

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//Image

IMG9.29

Figure 9.23

An octahedral set of d 2sp3 orbitals on a sulfur atom. The small lobe of each hybrid orbital has been omitted for clarity.

//Example

Example 9.4 The Localized Electron Model IV

How is the xenon atom in XeF4 hybridized?

//Solution

As seen in Example 8.13, XeF4 has six pairs of electrons around xenon that are arranged octahedrally to minimize repulsions. An octahedral set of six atomic orbitals is required to hold these electrons, and the xenon atom is d2sp3 hybridized.

//Image

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//Exercise

Exercise 9.26

The Localized Electron Model: A Summary

The description of a molecule using the localized electron model involves three distinct steps.

PROBLEM SOLVING STRATEGY

Using the Localized Electron Model

1 Draw the Lewis structure(s).

2 Determine the arrangement of electron pairs using the VSEPR model.

3 Specify the hybrid orbitals needed to accommodate the electron pairs.

It is important to do the steps in this order. For a model to be successful, it must fol- low nature’s priorities. In the case of bonding, it seems clear that the tendency for a molecule to minimize its energy is more important than the maintenance of the charac- teristics of atoms as they exist in the free state. The atoms adjust to meet the “needs” of the molecule. When considering the bonding in a particular molecule, therefore, we always start with the molecule rather than the component atoms. In the molecule the electrons will be arranged to give each atom a noble gas configuration, where possible, and to minimize electron-pair repulsions. We then assume that the atoms adjust their orbitals by hybridization to allow the molecule to adopt the structure that gives the min- imum energy.

In applying the localized electron model, we must remember not to overemphasize the characteristics of the separate atoms. It is not where the valence electrons originate that is important; it is where they are needed in the molecule to achieve stability. In the same vein, it is not the orbitals in the isolated atom that matter, but which orbitals the molecule requires for minimum energy.

The requirements for the various types of hybridization are summarized in Fig. 9.24 on the following page.

//Image

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Figure 9.24

The relationship of the number of effective pairs, their spatial arrangement, and the hybrid orbital set required.

//Example

Example 9.5 The Localized Electron Model V

For each of the following molecules or ions, predict the hybridization of each atom, and describe the molecular structure.

a. CO b. BF4 c. XeF2

//Solution

a. The CO molecule has 10 valence electrons, and its Lewis structure is

: C=O :

Each atom has two effective pairs, which means that both are sp hybridized. The triple bond consists of a a- bond produced by overlap of an sp orbital from each atom and

two 'TT bonds produced by overlap of 2p orbitals from each atom. The lone pairs are in

sp orbitals. Since the CO molecule has only two atoms, it must be linear.

//Image

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The BF4 ion has 32 valence electrons. The Lewis structure shows four pairs of elec- trons around the boron atom, which means a tetrahedral arrangement:

//Image

IMG9.33

This requires sp3 hybridization of the boron atom. Each fluorine atom also has four electron pairs and can be assumed to be sp3 hybridized (only one sp3 orbital is shown for each fluorine atom). The BF4 ion’s molecular structure is tetrahedral.

//Image

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C. The XeF2 molecule has 22 valence electrons. The Lewis structure shows five electron pairs on the xenon atom, which requires a trigonal bipyramidal arrangement:

//Image

IMG9.35

Note that the lone pairs are placed in the plane where they are 120 degrees apart. To accommodate five pairs at the vertices of a trigonal bipyramid requires that the xenon atom adopt a set of five dsp3 orbitals. Each fluorine atom has four electron pairs and can be assumed to be sp3 hybridized. The XeF2 molecule has a linear arrangement of atoms.

//Image

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//Heading

9.2 The Molecular Orbital Model

We have seen that the localized electron model is of great value in interpreting the struc- ture and bonding of molecules. However, there are some problems with this model. For example, it incorrectly assumes that electrons are localized, and so the concept of reso- nance must be added. Also, the model does not deal effectively with molecules containing unpaired electrons. And finally, the model gives no direct information about bond energies. Another model often used to describe bonding is the molecular orbital model. To introduce the assumptions, methods, and results of this model, we will consider the sim- plest of all molecules, H2, which consists of two protons and two electrons. A very sta- ble molecule, H2 is lower in energy than the separated hydrogen atoms by 432 kJ/mol. Since the hydrogen molecule consists of protons and electrons, the same components found in separated hydrogen atoms, it seems reasonable to use a theory similar to the atomic theory discussed in Chapter 7, which assumes that the electrons in an atom exist in orbitals of a given energy. Can we apply this same type of model to the hydrogen molecule? Yes. In fact, describing the H2 molecule in terms of quantum mechanics is

quite straightforward.

However, even though it is formulated rather easily, this problem cannot be solved exactly. The difficulty is the same as that in dealing with polyelectronic atoms—the elec- tron correlation problem. Since we do not know the details of the electron movements, we cannot deal with the electron–electron interactions in a specific way. We need to make approximations that allow a solution of the problem but do not destroy the model’s phys- ical integrity. The success of these approximations can only be measured by comparing predictions based on theory with experimental observations. In this case we will see that the simplified model works very well.

Just as atomic orbitals are solutions to the quantum mechanical treatment of atoms, molecular orbitals (MOs) are solutions to the molecular problem. Molecular orbitals have many of the same characteristics as atomic orbitals. Two of the most important are that they can hold two electrons with opposite spins and that the square of the molecular orbital wave function indicates electron probability.

We will now describe the bonding in the hydrogen molecule using this model. The first step is to obtain the hydrogen molecule’s orbitals, a process that is greatly simpli- fied if we assume that the molecular orbitals can be constructed from the hydrogen 1s atomic orbitals.

//Quote

Molecular orbital theory parallels the atomic theory discussed in Chapter 7.

When the quantum mechanical equations for the hydrogen molecule are solved, two molecular orbitals result, which can be represented as

//Image

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where 1sA and 1sB represent the 1s orbitals from the two separated hydrogen atoms. This

process is shown schematically in Fig. 9.25.

The orbital properties of most interest are size, shape (described by the electron probability

distribution), and energy. These properties for the hydrogen molecular orbitals are

represented in Fig. 9.26. From Fig. 9.26 we can note several important points:

1. The electron probability of both molecular orbitals is centered along the line passing

through the two nuclei. For MO1 the greatest electron probability is between the nuclei,

and for MO2 it is on either side of the nuclei. This type of electron distribution is

described as sigma (), as in the localized electron model. Accordingly, we refer to

MO1 and MO2 as sigma () molecular orbitals.

2. In the molecule only the molecular orbitals are available for occupation by electrons.

The 1s atomic orbitals of the hydrogen atoms no longer exist, because the H2 molecule—

a new entity—has its own set of new orbitals.

3. MO1 is lower in energy than the 1s orbitals of free hydrogen atoms, while MO2 is

higher in energy than the 1s orbitals. This fact has very important implications for

the stability of the H2 molecule, since if the two electrons (one from each hydrogen

atom) occupy the lower-energy MO1, they will have lower energy than they do in the

two separate hydrogen atoms. This situation favors molecule formation, because nature

tends to seek the lowest energy state. That is, the driving force for molecule formation

is that the molecular orbital available to the two electrons has lower energy

than the atomic orbitals these electrons occupy in the separated atoms. This situation

is favorable to bonding, or probonding.

On the other hand, if the two electrons were forced to occupy the higher-energy

MO2, they would be definitely antibonding. In this case, these electrons would have

lower energy in the separated atoms than in the molecule, and the separated state

would be favored. Of course, since the lower-energy MO1 is available, the two electrons

occupy that MO and the molecule is stable.

We have seen that the molecular orbitals of the hydrogen molecule fall into two

classes: bonding and antibonding. A bonding molecular orbital is lower in energy

than the atomic orbitals of which it is composed. Electrons in this type of orbital will

favor the molecule; that is, they will favor bonding. An antibonding molecular orbital

is higher in energy than the atomic orbitals of which it is composed. Electrons in this

type of orbital will favor the separated atoms (they are antibonding). Figure 9.27

illustrates these ideas.

4. Figure 9.26 shows that for the bonding molecular orbital in the H2 molecule the electrons

have the greatest probability of being between the nuclei. This is exactly what

we would expect, since the electrons can lower their energies by being simultaneously

attracted by both nuclei. On the other hand, the electron distribution for the

antibonding molecular orbital is such that the electrons are mainly outside the space

between the nuclei. This type of distribution is not expected to provide any bonding

force. In fact, it causes the electrons to be higher in energy than in the separated atoms.

Thus the molecular orbital model produces electron distributions and energies that

agree with our basic ideas of bonding. This fact reassures us that the model is physically

reasonable.

5. The labels on molecular orbitals indicate their symmetry (shape), the parent atomic

orbitals, and whether they are bonding or antibonding. Antibonding character is indicated

//Image

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Figure 9.26

(a) The MO energy-level diagram for the H2 molecule. (b) The shapes of the MOs are obtained by squaring the wave func- tions for MO1 and MO2. The positions of the nuclei are indicated by •

//Image

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//Quote

Bonding will result if the molecule has lower energy than the separated atoms

by an asterisk. For the H2 molecule, both MOs have symmetry, and both are constructed

from hydrogen 1s atomic orbitals. The molecular orbitals for H2 are therefore

labelled as follows:

6. Molecular electron configurations can be written in much the same way as atomic

(electron) configurations. Since the H2 molecule has two electrons in the 1s molecular

orbital, the electron configuration is 1s

2.

7. Each molecular orbital can hold two electrons, but the spins must be opposite.

8. Orbitals are conserved. The number of molecular orbitals will always be the same as

the number of atomic orbitals used to construct them.

Many of the above points are summarized in Fig. 9.28.

Now suppose we could form the H2 ion from a hydride ion (H) and a hydrogen

atom. Would this species be stable? Since the H ion has the configuration 1s2 and the H

atom has a 1s1 configuration, we will use 1s atomic orbitals to construct the MO diagram

for the H2 ion, as shown in Fig. 9.29. The electron configuration for H2 is (1s)2(1s\*)1.

The key idea is that the H2 ion will be stable if it has a lower energy than its separated

parts. From Fig. 9.29 we see that in going from the separated H ion and H atom

to the H2 ion, the model predicts that two electrons are lowered in energy and one electron

is raised in energy. In other words, two electrons are bonding and one electron is antibonding.

Since more electrons favour bonding, H2 is predicted to be a stable entity—a

bond has formed. But how would we expect the bond strengths in the molecules of H2

and H2 to compare?

In the formation of the H2 molecule, two electrons are lowered in energy and no electrons

are raised in energy compared with the parent atoms. When H2 is formed, two

electrons are lowered in energy and one is raised, producing a net lowering of the energy

of only one electron. Thus the model predicts that H2 is twice as stable as H2 with respect

to their separated components. In other words, the bond in the H2 molecule is

predicted to be about twice as strong as the bond in the H2 ion.

//Image

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Figure 9.27

Bonding and antibonding molecular orbitals (MOs).

//Image

IMG9.41

Figure 9.28

A molecular orbital energy-level diagram for the H2 molecule.

//Sub Heading

Bond Order

To indicate bond strength, we use the concept of bond order. Bond order is the difference

between the number of bonding electrons and the number of antibonding electrons

divided by 2.

//Quote

Although the model predicts that H2 should be stable, this ion has never been observed, again emphasizing the perils of simple models.

//Image

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We divide by 2 because, from the localized electron model, we are used to thinking of bonds in terms of pairs of electrons.

Since the H2 molecule has two bonding electrons and no antibonding electrons, the bond order is

//Image

IMG9.43

The H2 ion has two bonding electrons and one antibonding electron; the bond order is

//Image

IMG9.44

Bond order is an indication of bond strength because it reflects the difference between the number of bonding electrons and the number of antibonding electrons. Larger bond order means greater bond strength.

//Image

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Figure 9.29

The molecular orbital energy-level diagram for the H2- ion.

We will now apply the molecular orbital model to the helium molecule (He2). Does

this model predict that this molecule will be stable? Since the He atom has a 1s2 configuration,

1s orbitals are used to construct the molecular orbitals, and the molecule will have

four electrons. From the diagram shown in Fig. 9.30 it is apparent that two electrons are

raised in energy and two are lowered in energy. Thus the bond order is zero:

//Image

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This implies that the He2 molecule is not stable with respect to the two free He atoms,

which agrees with the observation that helium gas consists of individual He atoms

//Image

IMG9.47

Figure 9.30

The molecular orbital energy-level diagram for the He2 molecule

//Heading

9.3 Bonding in Homonuclear Diatomic Molecules

In this section we consider homonuclear diatomic molecules (those composed of two iden- tical atoms) of elements in Period 2 of the periodic table. Since the lithium atom has a 1s22s1 electron configuration, it would seem that we should use the Li 1s and 2s orbitals to form the molecular orbitals of the Li2 molecule. However, the 1s orbitals on the lithium atoms are much smaller than the 2s orbitals and therefore do not overlap in space to any appreciable extent (see Fig. 9.31). Thus the two electrons in each 1s orbital can be as- sumed to be localized and not to participate in the bonding. To participate in molecular orbitals, atomic orbitals must overlap in space. This means that only the valence orbitals of the atoms contribute significantly to the molecular orbitals of a particular molecule. The molecular orbital diagram of the Li2 molecule and the shapes of its bonding and antibonding MOs are shown in Fig. 9.32. The electron configuration for Li2 (valence electrons only) is a2 2, and the bond order is

//Image

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//Image

IMG9.49

Li2 is a stable molecule (has lower energy than two separated lithium atoms). However, this does not mean that Li2 is the most stable form of elemental lithium. In fact, at normal temperature and pressure, lithium exists as a solid containing many lithium atoms bound to each other.

For the beryllium molecule (Be2) the bonding and antibonding orbitals both contain two electrons. In this case the bond order is (2 - 2)/2 = 0, and since Be2 is not more

stable than two separated Be atoms, no molecule forms. However, beryllium metal con- tains many beryllium atoms bonded to each other and is stable for reasons we will dis- cuss in Chapter 10.

Since the boron atom has a 1s22s22p1 configuration, we describe the B2 molecule by considering how p atomic orbitals combine to form molecular orbitals. Recall that p orbitals

have two lobes and that they occur in sets of three mutually perpendicular orbitals [see Fig. 9.33(a)]. When two B atoms approach each other, two pairs of p orbitals can overlap in a parallel fashion [Fig. 9.33(b) and (c)] and one pair can overlap head-on [Fig. 9.33(d)]. First, let’s consider the molecular orbitals from the head-on overlap. The bonding orbital is formed by reversing the sign of the right orbital so the positive phases of both orbitals match between the nuclei to produce constructive interference. This leads to enhanced electron probability between the nuclei. The antibonding orbital is formed by the direct combination of the orbitals, which gives destructive interference of the positive phase of one orbital with the negative phase of the second orbital. This produces a node between the nuclei, which gives decreased electron probability. Note that the electrons in the bonding MO are, as expected, concentrated between the nuclei, and the electrons in the antibonding MO are concentrated outside the area between the two nuclei. Also, both these

MOs are a molecular orbital.

//Image

IMG9.50

Beryllium metal

//Image

IMG9.51

Figure 9.32 The molecular orbital energy-level diagram for the Li2 molecule

//Image

IMG9.52

Figure 9.33

(a) The three mutually perpendicular 2p orbitals on two adjacent boron atoms. The signs indicate the orbital phases. Two pairs of parallel p orbitals can overlap, as shown in (b) and (c), and the third pair can overlap head-on, as shown in (d).

//Image

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When the parallel p orbitals are combined with the positive and negative phases matched, constructive interference occurs, giving a bonding orbital. When the orbitals have opposite phases (the signs of one orbital are reversed), destructive interference occurs, resulting in an antibonding orbital.

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//Image

IMG9.55

//Image

IMG9.56

Since the electron probability lies above and below the line between the nuclei, both

the orbitals are pi () molecular orbitals. They are designated as 2p for the bonding

MO and 2p\* for the antibonding MO. A similar set of molecular orbitals is formed

from overlap of the parallel pz atomic orbitals.

Let’s try to make an educated guess about the relative energies of the and molecular

orbitals formed from the 2p atomic orbitals. Would we expect the electrons to

prefer the bonding orbital (where the electron probability is concentrated in the area between

the nuclei) or the bonding orbital? The orbital would seem to have the lower

energy, since the electrons are closest to the two nuclei. This agrees with the observation

that interactions are stronger than interactions.

Figure 9.34 gives the molecular orbital energy-level diagram expected when the two

sets of 2p orbitals on the boron atoms combine to form molecular orbitals. Note that there

are two bonding orbitals at the same energy (degenerate orbitals) formed from the two

pairs of parallel p orbitals, and there are two degenerate antibonding orbitals. The energy

of the 2p orbitals is expected to be higher than that of the 2p orbital because

interactions are generally stronger than interactions.

To construct the total molecular orbital diagram for the B2 molecule, we make the assumption

that the 2s and 2p orbitals combine separately (in other words, there is no 2s2p

mixing). The resulting diagram is shown in Fig. 9.35. Note that B2 has six valence

electrons. (Remember the 1s orbitals and electrons are assumed not to participate in the

bonding.) This diagram predicts the bond order:

//Image

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//Image

IMG9.58

Therefore, B2 should be a stable molecule.

//Sub Heading

Paramagnetism

At this point we need to discuss an additional molecular property—magnetism. Most

materials have no magnetism until they are placed in a magnetic field. However, in the

presence of such a field, magnetism of two types can be induced. Paramagnetism causes

the substance to be attracted into the inducing magnetic field. Diamagnetism causes the

substance to be repelled from the inducing magnetic field. Figure 9.36 illustrates how

//Image

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Figure 9.36

Diagram of the kind of apparatus used to measure the paramagnetism of a sample. A paramagnetic sample will appear heavier when the electromagnet is turned on because the sample is attracted into the inducing magnetic field.

paramagnetism is measured. The sample is weighed with the electromagnet turned off

and then weighed again with the electromagnet turned on. An increase in weight when

the field is turned on indicates the sample is paramagnetic. Studies have shown that

paramagnetism is associated with unpaired electrons and diamagnetism is associated

with paired electrons. Any substance that has both paired and unpaired electrons will exhibit

a net paramagnetism, since the effect of paramagnetism is much stronger than that

of diamagnetism.

The molecular orbital energy-level diagram represented in Fig. 9.35 predicts that the

B2 molecule will be diamagnetic, since the MOs contain only paired electrons. However,

experiments show that B2 is actually paramagnetic with two unpaired electrons. Why does

the model yield the wrong prediction? This is yet another illustration of how models are

developed and used. In general, we try to use the simplest possible model that accounts

for all the important observations. In this case, although the simplest model successfully

describes the diatomic molecules up to B2, it certainly is suspect if it cannot describe

the B2 molecule correctly. This means we must either discard the model or find a way to

modify it.

Let’s consider one assumption that we made. In our treatment of B2, we have assumed

that the s and p orbitals combine separately to form molecular orbitals. Calculations

show that when the s and p orbitals are allowed to mix in the same molecular

orbital, a different energy-level diagram results for B2 (see Fig. 9.37). Note that even

though the s and p contributions to the MOs are no longer separate, we retain the simple

orbital designations. The energies of 2p and 2p orbitals are reversed by p–s mixing, and

the 2s and the 2s\* orbitals are no longer equally spaced relative to the energy of the

free 2s orbital.

When the six valence electrons for the B2 molecule are placed in the modified energy level

diagram, each of the last two electrons goes into one of the degenerate 2p orbitals.

This produces a paramagnetic molecule in agreement with experimental results. Thus,

when the model is extended to allow p–s mixing in molecular orbitals, it predicts the correct

magnetism. Note that the bond order is (4 2)2 1, as before.

The remaining diatomic molecules of the elements in Period 2 can be described using

similar ideas. For example, the C2 and N2 molecules use the same set of orbitals as

for B2 (see Fig. 9.37). Because the importance of 2s–2p mixing decreases across the period,

the 2p and 2p orbitals revert to the order expected in the absence of 2s–2p mixing

for the molecules O2 and F2, as shown in Fig. 9.38.

Several significant points arise from the orbital diagrams, bond strengths, and bond

lengths summarized in Fig. 9.38 for the Period 2 diatomics:

1. There are definite correlations between bond order, bond energy, and bond length. As

the bond order predicted by the molecular orbital model increases, the bond energy

increases and the bond length decreases. This is a clear indication that the bond order

predicted by the model accurately reflects bond strength, and it strongly supports

the reasonableness of the MO model.

2. Comparison of the bond energies of the B2 and F2 molecules indicates that bond order

cannot automatically be associated with a particular bond energy. Although both

molecules have a bond order of 1, the bond in B2 appears to be about twice as strong

as the bond in F2. As we will see in our later discussion of the halogens, F2 has an

unusually weak single bond due to larger than usual electron–electron repulsions (there

are 14 valence electrons on the small F2 molecule).

3. Note the very large bond energy associated with the N2 molecule, which the molecular

orbital model predicts will have a bond order of 3, a triple bond. The very strong

bond in N2 is the principal reason that many nitrogen-containing compounds are used

as high explosives. The reactions involving these explosives give the very stable N2 molecule as a product, thus releasing large quantities of energy.

//Image

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Figure 9.37

The correct molecular orbital energy-level diagram for the B2 molecule. When p–s mixing is allowed, the energies of the 2p and 2p orbitals are reversed. The two electrons from the B 2p orbitals now occupy separate, degenerate 2p molecular orbitals and thus have parallel spins. Therefore, this diagram explains the observed paramagnetism of B2.

//Image

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Figure 9.38

The molecular orbital energy-level diagrams, bond orders, bond energies, and bond lengths for the diatomic

molecules B2 through F2. Note that for O2 and F2 the 2p orbital is lower in energy than the 2p orbitals.

4. The O2 molecule is known to be paramagnetic. This can be very convincingly demonstrated

by pouring liquid oxygen between the poles of a strong magnet, as shown in Fig. 9.39. The oxygen remains there until it evaporates. Significantly, the molecular orbital model correctly predicts oxygen’s paramagnetism, while the localized electron model predicts a diamagnetic molecule.

//Image

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Figure 9.39

When liquid oxygen is poured into the space between the poles of a strong magnet, it remains there until it boils away. This attraction of liquid oxygen for the magnetic field demonstrates the paramagnetism of the O2 molecule.

//Example

Example 9.6 The Molecular Orbital Model I

For the species O2, O2 , and O2 , give the electron configuration and the bond order for each. Which has the strongest bond?

//Solution

The O2 molecule has 12 valence electrons (6 + 6); O2+ has 11 valence electrons (6 + 6 - 1); and O2- has 13 valence electrons (6 + 6 + 1). We will assume that the ions can be treated using the same molecular orbital diagram as for the neutral diatomic molecule:

//Image

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The electron configuration for each species can then be taken from the diagram:

//Image

IMG9.64

The bond orders are:

//Image

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Thus O2 is expected to have the strongest bond of the three species.

//Example

Example 9.7 The Molecular Orbital Model II

Use the molecular orbital model to predict the bond order and magnetism of each of the following molecules.

a. Ne2

b. P2

//Solution

1. The valence orbitals for Ne are 2s and 2p. Thus we can use the molecular orbitals we have already constructed for the diatomic molecules of the Period 2 elements. The Ne2 molecule has 16 valence electrons (8 from each atom). Placing these electrons in the appropriate molecular orbitals produces the following diagram:

//Image

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The bond order is (8 - 8)/2 = 0, and Ne2 does not exist.

b. The P2 molecule contains phosphorus atoms from the third row of the periodic table. We will assume that the diatomic molecules of the Period 3 elements can be treated in a way very similar to that which we have used so far. Thus we will draw the MO diagram for P2 analogous to that for N2. The only change will be that the molecular orbitals will be formed from 3s and 3p atomic orbitals. The P2 model has 10 valence electrons (5 from each phosphorus atom). The resulting molecular orbital diagram is

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//Heading

9.4 Bonding in Heteronuclear Diatomic Molecules

In this section we will deal with selected examples of heteronuclear (different atoms) diatomic molecules. A special case involves molecules containing atoms adjacent to each other in the periodic table. Since the atoms involved in such a molecule are so similar, we can use the molecular orbital diagram for homonuclear molecules. For ex- ample, we can predict the bond order and magnetism of nitric oxide (NO) by placing its 11 valence electrons (5 from nitrogen and 6 from oxygen) in the molecular orbital energy-level diagram shown in Fig. 9.40. The molecule should be paramagnetic and has a bond order of

//Image

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//Image

IMG9.69

Figure 9.40

The molecular orbital energy-level diagram for the NO molecule. We assume that orbital order is the same as that for N2. The bond order is 2.5.

Experimentally, nitric oxide is indeed found to be paramagnetic. Notice that this odd electron molecule is described very naturally by the MO model. In contrast, the localized electron model, in the simple form used in this text, cannot be used readily to treat such molecules.

//Example

Example 9.8 The Molecular Orbital Model III

Use the molecular orbital model to predict the magnetism and bond order of the NO and

CN ions.

//Solution

The NO+ ion has 10 valence electrons (5 + 6 - 1). The CN- ion also has 10 valence electrons (4 + 5 + 1). Both ions are therefore diamagnetic and have a bond order derived from the equation

//Image

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The molecular orbital diagram for these two ions is the same (see Fig. 9.41).

//Image

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Figure 9.41

The molecular orbital energy-level diagram for both the NO and CN ions.

When the two atoms of a diatomic molecule are very different, the energy-level dia- gram for homonuclear molecules can no longer be used. A new diagram must be devised for each molecule. We will illustrate this case by considering the hydrogen fluoride (HF) molecule. The electron configurations of the hydrogen and fluorine atoms are 1s1 and 1s22s22p5, respectively. To keep things as simple as possible, we will assume that fluorine uses only one of its 2p orbitals to bond to hydrogen. Thus the molecular orbitals for HF will be composed of fluorine 2p and hydrogen 1s orbitals. Figure 9.42 gives the partial molecular orbital energy-level diagram for HF, focusing only on the orbitals involved in the bonding. We are assuming that fluorine’s other valence electrons remain localized on the fluorine. The 2p orbital of fluorine is shown at a lower energy than the 1s orbital of hydrogen on the diagram because fluorine binds its valence electrons more tightly. Thus the 2p electron on a free fluorine atom is at lower energy than the 1s electron on a free hydrogen atom. The diagram predicts that the HF molecule should be stable because both electrons are lowered in energy relative to their energy in the free hydrogen and fluorine atoms, which is the driving force for bond formation.

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Figure 9.42

A partial molecular orbital energy-level diagram for the HF molecule.

//Image

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Figure 9.43

The electron probability distribution in the bonding molecular orbital of the HF molecule. Note the greater electron density close to the fluorine atom.

Because the fluorine 2p orbital is lower in energy than the hydrogen 1s orbital, the electrons prefer to be closer to the fluorine atom. That is, the u molecular orbital containing the bonding electron pair shows greater electron probability close to the fluorine (see Fig. 9.43). The electron pair is not shared equally. This causes the fluorine atom to have a slight excess of negative charge and leaves the hydrogen atom partially positive. This is exactly the bond polarity observed for HF. Thus the molecular orbital model accounts in a straightforward way for the different electronegativities of hydrogen and fluorine and the resulting unequal charge distribution.

//Heading

9.5 Combining the Localized Electron and Molecular Orbital Models

One of the main difficulties with the localized electron model is its assumption that elec- trons are localized. This problem is most apparent with molecules for which several valid Lewis structures can be drawn. It is clear that none of these structures taken alone adequately describes the electronic structure of the molecule. The concept of resonance was invented to solve this problem. However, even with resonance included, the localized electron model does not describe molecules and ions such as O3 and NO3 in a very satisfying way.

It would seem that the ideal bonding model would be one with the simplicity of the

localized electron model but with the delocalization characteristic of the molecular orbital model. We can achieve this by combining the two models to describe molecules that re- quire resonance. Note that for species such as O3 and NO3 the double bond changes

//Chemical Connections

What’s Hot?

One of the best things about New Mexico is the food. Authentic New Mexican cuisine

employs liberal amounts of green and red chilies—often called chili peppers. Chilies apparently originated in parts of South America and were spread north by birds. When Columbus came to North America, which he originally thought was India, he observed the natives using chilies for spicing foods. When he took chilies back to Europe, Columbus mistakenly called them peppers and the name stuck.

The spicy payload of chilies is delivered mainly by the chemical capsaicin, which has the following structure:

Capsaicin was isolated as a pure substance by L. T. Thresh in 1846. Since then substituted capsaicins have also been found in chilies. The spicy power of chilies derives mostly from capsaicin and dihydrocapsaicin.

The man best known for explaining the “heat” of chilies is Wilbur Scoville, who defined the Scoville unit for measuring chili power. He arbitrarily established the hotness of pure capsaicin as 16 million. On this scale a typical green or red chili has a rating of about 2500 Scoville units. You may have had an encounter with habanero chilies that left you looking for a firehose to put out the blaze in your mouth—habaneros have a Scoville rating of about 500,000!

Capsaicin has found many uses outside of cooking. It is used in pepper sprays and repellent sprays for many garden pests, although birds are unaffected by capsaicin. Capsaicin also stimulates the body’s circulation and causes pain receptors to release endorphins, similar to the effect produced by intense exercise. Instead of jogging you may want to sit on the couch eating chilies. Either way you are going to sweat

//Image

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position in the resonance structures (see Fig. 9.44). Since a double bond involves one u and one Tr bond, there is a u bond between all bound atoms in each resonance structure. It is really the Tr bond that has different locations in the various resonance structures.

Therefore, we conclude that the u bonds in a molecule can be described as being localized with no apparent problems. It is the Tr bonding that must be treated as being delocalized. Thus, for molecules that require resonance, we will use the localized electron model to describe the u bonding and the molecular orbital model to describe the Tr bonding. This allows us to keep the bonding model as simple as possible and yet give a more physically accurate description of such molecules.

We will illustrate the general method by considering the bonding in benzene, an important industrial chemical that must be handled carefully because it is a known carcinogen The benzene molecule (C6H6) consists of a planar hexagon of carbon atoms with one hydrogen atom bound to each carbon atom, as shown in Fig. 9.45(a). In the molecule all six C—C bonds are known to be equivalent. To explain this fact, the localized electron model must invoke resonance [see Fig. 9.45(b)]. A better description of the bonding in benzene results when we use a combination of

the models, as described above. In this description it is assumed that the bonds of carbon

involve sp2 orbitals, as shown in Fig. 9.46. These bonds are all cantered in the plane

of the molecule.

Since each carbon atom is sp2 hybridized, a p orbital perpendicular to the plane of the ring remains on each carbon atom. These six p orbitals can be used to form molecular orbitals, as shown in Fig. 9.47(a). The electrons in the resulting molecular orbitals are delocalized above and below the plane of the ring, as shown in Fig. 9.47(b). This gives six equivalent C—C bonds, as required by the known structure of the benzene molecule. The benzene structure is often written as

//Quote

In molecules that require resonance, it is the Tr bonding that is most clearly delocalized.

//Image

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Figure 9.44

The resonance structures for O3 and NO3. Note that it is the double bond that occupies various positions in the resonance structures.

//Image

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Figure 9.45

(a) The benzene molecule consists of a ring of six carbon atoms with one hydrogen atom bound to each carbon; all

atoms are in the same plane. All the C—Cbonds are known to be equivalent. (b) Two of the resonance structures for the benzene molecule. The localized electron model must invoke resonance to account for the six equal C—C bonds. as required by the known structure of the benzene molecule. The benzene structure is often written as to indicate the delocalized bonding in the molecule.

//Image

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Figure 9.46

The bonding system in the benzene molecule.

//Image

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Very similar treatments can be applied to other planar molecules for which resonance

is required by the localized electron model. For example, the NO3 ion can be described using the molecular orbital system shown in Fig. 9.48. In this molecule each atom is assumed to be sp2 hybridized, which leaves one p orbital on each atom perpendicular to the plane of the ion. These p orbitals can combine to form the molecular orbital system.

//Image

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Figure 9.47

(a) The molecular orbital system in benzene is formed by combining the six p orbitals from the six sp2 hybridized

carbon atoms. (b) The electrons in the resulting molecular orbitals are delocalized over the entire ring of carbon atoms, giving six equivalent bonds. A composite of these orbitals is represented here.

//Image

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//For Reviwe

//Key Terms

Section 9.1

hybridization

sp3 hybridization

hybrid orbitals

sp2 hybridization

sigma bond

pi bond

sp hybridization

dsp3 hybridization

d2sp3 hybridization

Section 9.2

molecular orbital model

molecular orbital (MO)

sigma molecular orbital

bonding molecular orbital

antibonding molecular orbital

bond order

Section 9.3

pi molecular orbital

paramagnetism

diamagnetism

Section 9.4

heteronuclear diatomic molecule

Section 9.5

delocalized bonding

Two widely used bonding models

• Localized electron model

• Molecular orbital model

Localized electron model

• Molecule is pictured as a group of atoms sharing electron pairs between atomic orbitals

• Hybrid orbitals, which are combinations of the “native” atomic orbitals, are often required to account for the molecular structure

• Six electron pairs (octahedral arrangement) requires d2sp3 orbitals

• Five electron pairs (trigonal bipyramidal arrangement) requires dsp3 orbitals

• Four electron pairs (tetrahedral arrangement) require sp3 orbitals

• Three electron pairs (trigonal planar arrangement) require sp2 orbitals

• Two electron pairs (linear arrangement) requires sp orbitals

Two types of bonds

• Sigma: electrons are shared in the area centered on a line joining the atoms

• Pi: a shared electron pair occupies the space above and below the line joining the atoms

Molecular orbital model

• A molecule is assumed to be a new entity consisting of positively charged nuclei and electrons

• The electrons in the molecule are contained in molecular orbitals, which in the simplest form of the model are constructed from the atomic orbitals of the constituent atoms

• The model correctly predicts relative bond strength, magnetism, and bond polarity

• It correctly portrays electrons as being delocalized in polyatomic molecules

• The main disadvantage of the model is that it is difficult to apply qualitatively to polyatomic molecules

Molecular orbitals are classified in two ways: energy and shape

• Energy

• A bonding MO is lower in energy than the atomic orbitals from which it is con- structed. Electrons in this type of MO are lower in energy in the molecule than in the separated atoms and thus favor molecule formation.

• An antibonding MO is higher in energy than the atomic orbitals from which it is constructed. Electrons in this type of MO are higher in energy in the molecule than in the separated atoms and thus do not favor molecule formation.

• Shape (symmetry)

• Sigma (u) MOs have their electron probability centered on a line passing through the nuclei

• Pi (1r) MOs have their electron probability concentrated above and below the line

connecting the nuclei

Bond order is an index of bond strength

//Image

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Molecules that require the concept of resonance in the localized electron model can be more accurately described by combining the localized electron and molecular orbital models

• The u bonds are localized

• The 1r bonds are delocalized

//Review Questions

1. Why do we hybridize atomic orbitals to explain the bonding in covalent com- pounds? What type of bonds form from hybrid orbitals, sigma or pi? Explain.

2. What hybridization is required for central atoms that have a tetrahedral arrange- ment of electron pairs? A trigonal planar arrangement of electron pairs? A linear arrangement of electron pairs? How many unhybridized p atomic orbitals are pres- ent when a central atom exhibits tetrahedral geometry? Trigonal planar geometry? Linear geometry? What are the unhybridized p atomic orbitals used for?

3. Describe the bonding in H2S, CH4, H2CO, and HCN using the localized electron model.

4. What hybridization is required for central atoms exhibiting trigonal bipyramidal geometry? Octahedral geometry? Describe the bonding of PF5, SF4, SF6, and IF5 using the localized electron model.

5. Electrons in u bonding molecular orbitals are most likely to be found in the re- gion between the two bonded atoms. Why does this arrangement favor bonding? In a u antibonding orbital, where are the electrons most likely to be found in re- lation to the nuclei in a bond?

6. Show how 2s orbitals combine to form u bonding and u antibonding molecular orbitals. Show how 2p orbitals overlap to form u bonding, 1T bonding, 1T antibond- ing, and u antibonding molecular orbitals.

7. What are the relationships among bond order, bond energy, and bond length? Which of these can be measured? Distinguish between the terms paramagnetic and diamagnetic. What type of experiment can be done to determine if a material is paramagnetic?

8. How does molecular orbital theory explain the following observations?

a. H2 is stable, while He2 is unstable.

b. B2 and O2 are paramagnetic, while C2, N2, and F2 are diamagnetic.

c. N2 has a very large bond energy associated with it.

d. NO+ is more stable than NO-.

9. Consider the heteronuclear diatomic molecule HF. Explain in detail how molecu- lar orbital theory is applied to describe the bonding in HF.

10. What is delocalized 1T bonding and what does it explain? Explain the delocalized 1T bonding system in C6H6 (benzene) and O3 (ozone).

//Active Learning Questions

These questions are designed to be used by groups of students in class.

1. What are molecular orbitals? How do they compare with atomic orbitals? Can you tell by the shape of the bonding and antibond- ing orbitals which is lower in energy? Explain.

2. Explain the difference between the u and 1T MOs for homonu- clear diatomic molecules. How are bonding and antibonding or- bitals different? Why are there two 1T MOs and one u MO? Why are the 1T MOs degenerate?

3. Compare Figs. 9.35 and 9.37. Why are they different? Because B2 is known to be paramagnetic, the 1T2p and u2p molecular orbitals must be switched from the first prediction. What is the rationale for this? Why might one expect the u2p to be lower in energy than the 1T2p? Why can’t we use diatomic oxygen to help us decide whether the u2p or 1T2p is lower in energy?

4. Which of the following would you expect to be more favorable energetically? Explain.

a. an H2 molecule in which enough energy is added to excite one electron from the bonding to the antibonding MO

b. two separate H atoms

5. Draw the Lewis structure for HCN. Indicate the hybrid orbitals, and draw a picture showing all the bonds between the atoms, la- beling each bond as u or 1T.

6. Which is the more correct statement: “The methane molecule (CH4) is a tetrahedral molecule because it is sp3 hybridized” or “The methane molecule (CH4) is sp3 hybridized because it is a tetrahedral molecule”? What, if anything, is the difference between these two statements?

7. Compare and contrast the MO model with the LE model. When is each useful?

8. What are the relationships among bond order, bond energy, and bond length? Which of these quantities can be measured?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the Solutions Guide, as found on Power Lecture.

//Questions

9. In the hybrid orbital model, compare and contrast a bonds with

1T bonds. What orbitals form the bonds and what orbitals form

the bonds? Assume the z-axis is the internuclear axis.

10. In the molecular orbital model, compare and contrast bonds with

bonds. What orbitals form the bonds and what orbitals form

the bonds? Assume the z-axis is the internuclear axis.

11. Why are d orbitals sometimes used to form hybrid orbitals? Which

period of elements does not use d orbitals for hybridization? If

necessary, which d orbitals (3d, 4d, 5d, or 6d) would sulfur use

to form hybrid orbitals requiring d atomic orbitals? Answer the

same question for arsenic and for iodine.

12. The atoms in a single bond can rotate about the internuclear

axis without breaking the bond. The atoms in a double and triple

bond cannot rotate about the internuclear axis unless the bond

is broken. Why?

13. Compare and contrast bonding molecular orbitals with antibonding

molecular orbitals.

14. What modification to the molecular orbital model was made from

the experimental evidence that B2 is paramagnetic?

15. Why does the molecular orbital model do a better job in explaining

the bonding in NO and NO than the hybrid orbital model?

16. The three NO bonds in NO3

are all equivalent in length and

strength. How is this explained even though any valid Lewis

structure for NO3

has one double bond and two single bonds to

nitrogen?

//Exercises

In this section similar exercises are paired.

The Localized Electron Model and Hybrid Orbitals

17. Use the localized electron model to describe the bonding in H2O.

18. Use the localized electron model to describe the bonding in CCl4.

19. Use the localized electron model to describe the bonding in H2CO

(carbon is the central atom).

20. Use the localized electron model to describe the bonding in C2H2

(exists as HCCH).

21. The space-filling models of ethane and ethanol are shown below

//Image

IMG9.82

Use the localized electron model to describe the bonding in ethane and ethanol

22. The space-filling models of hydrogen cyanide and phosgene are shown below

//Image

IMG9.83

Use the localized electron model to describe the bonding in hydrogen

cyanide and phosgene.

23. Give the expected hybridization of the central atom for the molecules

or ions in Exercises 81 and 87 from Chapter 8.

24. Give the expected hybridization of the central atom for the molecules

or ions in Exercises 82 and 88 from Chapter 8.

25. Give the expected hybridization of the central atom for the molecules

or ions in Exercise 85 from Chapter 8.

26. Give the expected hybridization of the central atom for the molecules

in Exercise 86 from Chapter 8.

27. Give the expected hybridization of the central atom for the molecules

in Exercises 107 and 108 from Chapter 8.

28. Give the expected hybridization of the central atom for the molecules

in Exercises 109 and 110 from Chapter 8.

29. For each of the following molecules, write the Lewis structure(s),

predict the molecular structure (including bond angles), give the

expected hybrid orbitals on the central atom, and predict the overall

polarity

//Image

IMG9.84

30. For each of the following molecules or ions that contain sulfur,

write the Lewis structure(s), predict the molecular structure (including

bond angles), and give the expected hybrid orbitals for

sulfur.

a. SO2

b. SO3

//Image

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e. SO3^2

f. SO4^2

g. SF2

h. SF4

i. SF6

j. F3S SF

k. SF5

31. Why must all six atoms in C2H4 lie in the same plane?

32. The allene molecule has the following Lewis structure:

//Image

IMG9.86

Must all hydrogen atoms lie the same plane? If not, what is their

spatial relationship? Explain.

33. Indigo is the dye used in colouring blue jeans. The term navy blue

is derived from the use of indigo to dye British naval uniforms in

the eighteenth century. The structure of the indigo molecule is

//Image

IMG9.87

a. How many Sigma bonds and pie bonds exist in the molecule?

b. What hybrid orbitals are used by the carbon atoms in the indigo

molecule?

34. Urea, a compound formed in the liver, is one of the ways humans

excrete nitrogen. The Lewis structure for urea is

//Image

IMG9.88

Using hybrid orbital theory, which orbitals overlap to form the

various bonds in urea?

35. Biacetyl and acetoin are added to margarine to make it taste more

like butter.

//Image

IMG9.89

Complete the Lewis structures, predict values for all C—C—O

bond angles, and give the hybridization of the carbon atoms in

these two compounds. Must the four carbon atoms and two oxygen

atoms in biacetyl lie the same plane? How many bonds and how

many bonds are there in biacetyl and acetoin?

36. Many important compounds in the chemical industry are derivatives

of ethylene (C2H4). Two of them are acrylonitrile and methyl

methacrylate.

//Image

IMG9.90

molecule must lie in the same plane? How many bonds and how

many bonds are there in methyl methacrylate and acrylonitrile?

37. Two molecules used in the polymer industry are azodicarbonamide

and methyl cyanoacrylate. Their structures are

//Image

IMG9.91

Azodicarbonamide is used in forming polystyrene. When added

to the molten plastic, it decomposes to nitrogen, carbon monoxide,

and ammonia gases, which are captured as bubbles in the

molten polymer. Methyl cyanoacrylate is the main ingredient in

super glue. As the glue sets, methyl cyanoacrylate polymerizes

across the carbon–carbon double bond. (See Chapter 22.)

a. Complete the Lewis structures showing all lone pairs of

electrons.

b. Which hybrid orbitals are used by the carbon atoms in each

molecule and the nitrogen atom in azodicarbonamide?

c. How many bonds are present in each molecule?

d. Give approximate values for the bond angles marked a through

h in the above structures.

38. Hot and spicy foods contain molecules that stimulate pain-detecting

nerve endings. Two such molecules are piperine and capsaicin:

//Image

IMG9.92

Piperine is the active compound in white and black pepper, and

capsaicin is the active compound in chili peppers. The ring structures

in piperine and capsaicin are shorthand notation. Each point

where lines meet represents a carbon atom.

a. Complete the Lewis structure for piperine and capsaicin showing

all lone pairs of electrons.

b. How many carbon atoms are sp, sp2, and sp3 hybridized in each

molecule?

c. Which hybrid orbitals are used by the nitrogen atoms in each

molecule?

d. Give approximate values for the bond angles marked a through

l in the above structures.

The Molecular Orbital Model

39. Which of the following are predicted by the molecular orbital

model to be stable diatomic species?

//Image

IMG9.93

40. Which of the following are predicted by the molecular orbital

model to be stable diatomic species?

//Image

IMG9.94

41. Using the molecular orbital model, write electron configurations

for the following diatomic species and calculate the bond orders.

Which ones are paramagnetic?

1. Li2 b. C2 c. S2

42. Consider the following electron configuration:

Give four species that, in theory, would have this electron

configuration.

//Image

IMG9.95

43. Using molecular orbital theory, explain why the removal of one

electron in O2 strengthens bonding, while the removal of one electron

in N2 weakens bonding.

44. Using the molecular orbital model to describe the bonding in F2-,F2, and F2+

, predict the bond orders and the relative bond lengths

for these three species. How many unpaired electrons are present

in each species?

45. Which charge(s) for the N2 molecule would give a bond order of 2.5?

46. A Lewis structure obeying the octet rule can be drawn for O2 as

follows:

//Image

IMG9.96

Use the molecular orbital energy-level diagram for O2 to show

that the above Lewis structure corresponds to an excited state.

47. Using the molecular orbital model, write electron configurations

for the following diatomic species and calculate the bond orders.

Which ones are paramagnetic? Place the species in order of increasing

bond length and bond energy.

a. CO b. CO+ c. CO2+

48. Using the molecular orbital model, write electron configurations

for the following diatomic species and calculate the bond orders.

Which ones are paramagnetic? Place the species in order of increasing

bond length and bond energy.

a. CN+ b. CN c. CN-

49. In which of the following diatomic molecules would the bond

strength be expected to weaken as an electron is removed?

a. H2 c. C 2-

b. B2 d. OF

50. In terms of the molecular orbital model, which species in each of

the following two pairs will most likely be the one to gain an electron?

Explain.

a. CN or NO

b. O2 or N2

51. Show how two 2p atomic orbitals can combine to form a Sigma or a

Pie molecular orbital.

52. Show how a hydrogen 1s atomic orbital and a fluorine 2p atomic

orbital overlap to form bonding and antibonding molecular orbitals

in the hydrogen fluoride molecule. Are these molecular

orbitals or molecular orbitals?

53. Use Figs. 9.42 and 9.43 to answer the following questions.

a. Would the bonding molecular orbital in HF place greater

electron density near the H or the F atom? Why?

b. Would the bonding molecular orbital have greater fluorine 2p

character, greater hydrogen 1s character, or an equal contribution

from both? Why?

c. Answer the previous two questions for the antibonding molecular

orbital in HF.

54. The diatomic molecule OH exists in the gas phase. The bond

length and bond energy have been measured to be 97.06 pm and

424.7 kJ/mol, respectively. Assume that the OH molecule is analogous

to the HF molecule discussed in the chapter and that molecular

orbitals result from the overlap of a lower-energy pz orbital

from oxygen with the higher-energy 1s orbital of hydrogen

(the O—H bond lies along the z-axis).

a. Which of the two molecular orbitals will have the greater

hydrogen 1s character?

b. Can the 2px orbital of oxygen form molecular orbitals with the

1s orbital of hydrogen? Explain.

c. Knowing that only the 2p orbitals of oxygen will interact significantly

with the 1s orbital of hydrogen, complete the molecular

orbital energy-level diagram for OH. Place the correct

number of electrons in the energy levels.

d. Estimate the bond order for OH.

e. Predict whether the bond order of OH will be greater than,

less than, or the same as that of OH. Explain.

Acetylene (C2H2) can be produced from the reaction of calcium

carbide (CaC2) with water. Use both the localized electron and

molecular orbital models to describe the bonding in the acetylide

anion (C2

2).

56. Describe the bonding in NO, NO, and NO using both the localized

electron and molecular orbital models. Account for any

discrepancies between the two models.

57. Describe the bonding in the O3 molecule and the NO2

ion using

the localized electron model. How would the molecular orbital

model describe the bonding in these two species?

58. Describe the bonding in the CO3

2 ion using the localized electron

model. How would the molecular orbital model describe the

bonding in this species?

//Connecting to Biochemistry

59. Vitamin B6 is an organic compound whose deficiency in the human

body can cause apathy, irritability, and an increased susceptibility

to infections. On the next page is an incomplete Lewis

structure for vitamin B6. Complete the Lewis structure and answer

the following questions. Hint: Vitamin B6 can be classified

as an organic compound (a compound based on carbon atoms).

The majority of Lewis structures for simple organic compounds

have all atoms with a formal charge of zero. Therefore, add lone

pairs and multiple bonds to the structure below to give each atom

a formal charge of zero.

//Image

IMG9.97

a. How many bonds and bonds exist in vitamin B6?

b. Give approximate values for the bond angles marked a through

g in the structure.

c. How many carbon atoms are sp2 hybridized?

d. How many carbon, oxygen, and nitrogen atoms are sp3

hybridized?

e. Does vitamin B6 exhibit delocalized bonding? Explain.

60. The antibiotic thiarubin-A was discovered by studying the feeding

habits of wild chimpanzees in Tanzania. The structure for

thiarubin-A is

//Image

IMG9.98

a. Complete the Lewis structure showing all lone pairs of electrons.

b. Indicate the hybrid orbitals used by the carbon and sulfur atoms

in thiarubin-A.

c. How many and bonds are present in this molecule?

61. One of the first drugs to be approved for use in treatment of acquired

immune deficiency syndrome (AIDS) was azidothymidine

(AZT). Complete the Lewis structure for AZT.

//Image

IMG9.99

a. How many carbon atoms are sp3 hybridized?

b. How many carbon atoms are sp2 hybridized?

c. Which atom is sp hybridized?

d. How many bonds are in the molecule?

e. How many bonds are in the molecule?

f. What is the N“N“N bond angle in the azide (—N3) group?

g. What is the H—O—C bond angle in the side group attached

to the five-membered ring?

h. What is the hybridization of the oxygen atom in the —CH2OH

group?

62. The transport of O2 in the blood is carried out by hemoglobin.

Carbon monoxide can interfere with oxygen transport because hemoglobin

has a stronger affinity for CO than for O2. If CO is present,

normal uptake of O2 is prevented, depriving the body of

needed oxygen. Using the molecular orbital model, write the electron

configurations for CO and for O2. From your configurations,

give two property differences between CO and O2.

63. Carbon monoxide (CO) forms bonds to a variety of metals and

metal ions. Its ability to bond to iron in hemoglobin is the reason

that CO is so toxic. The bond carbon monoxide forms to metals

is through the carbon atom:

a. On the basis of electronegativities, would you expect the carbon

atom or the oxygen atom to form bonds to metals?

b. Assign formal charges to the atoms in CO. Which atom would

you expect to bond to a metal on this basis?

c. In the MO model, bonding MOs place more electron density

near the more electronegative atom. (See the HF molecule in

Figs. 9.42 and 9.43.) Antibonding MOs place more electron

density near the less electronegative atom in the diatomic molecule.

Use the MO model to predict which atom of carbon

monoxide should form bonds to metals.

64. The space-filling model for benzoic acid, a food preservative, is

shown below.

//Image

IMG9.100

Describe the bonding in benzoic acid using the localized electron

model combined with the molecular orbital model.

Additional Exercises

65. Draw the Lewis structures, predict the molecular structures, and

describe the bonding (in terms of the hybrid orbitals for the central

atom) for the following.

a. XeO3 d. XeOF2

b. XeO4 e. XeO3F2

c. XeOF4

66. FClO2 and F3ClO can both gain a fluoride ion to form stable anions.

F3ClO and F3ClO2 will both lose a fluoride ion to form stable

cations. Draw the Lewis structures and describe the hybrid

orbitals used by chlorine in these ions.

67. Two structures can be drawn for cyanuric acid: