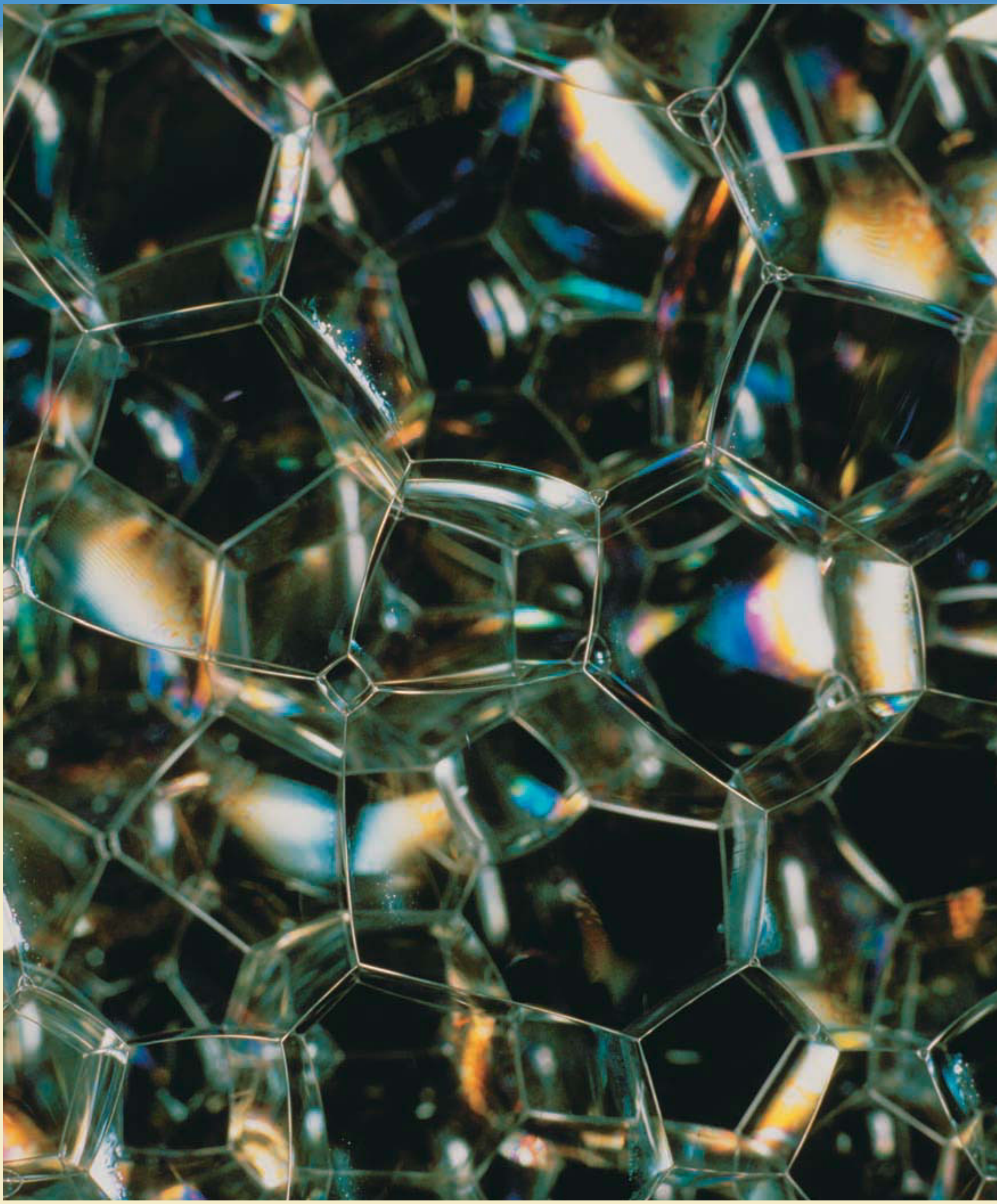
9 Covalent Bonding: Orbitals

Contents



A close-up of soap bubbles reveals their geometric shapes.

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 allowing 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.

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 arrangement of valence electrons is represented by the Lewis structure (or structures, where resonance 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.

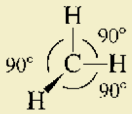
sp^3 Hybridization

Visualization: Hybridization: *sp*^{3}

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

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 valence orbitals. This means that the hydrogen atoms in methane use 1*s* orbitals. The valence orbitals of a carbon atom are the 2*s* and 2*p* 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:

1. Using the 2*p* and 2*s* atomic orbitals will lead to two different types of C—H bonds: (a) those from the overlap of a 2*p* orbital of carbon and a 1*s* orbital of hydrogen (there will be three of these) and (b) those from the overlap of a 2*s* orbital of carbon and a 1*s* 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 2*p* orbitals are mutually perpendicular, we might expect the three C—H bonds formed with these orbitals to be oriented at 90-degree angles:



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

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.

sp^3 hybridization gives a tetrahedral set of orbitals.

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” 2*s* and 2*p* orbitals to bond to the hydrogen atoms in forming the methane molecule. The second conclusion seems more reasonable. The 2*s* and 2*p* orbitals present on an *isolated* carbon atom may not be the best set of orbitals for bonding; a new set of atomic

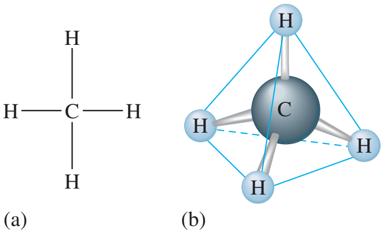


FIGURE 9.1
(a) The Lewis structure of the methane molecule. (b) The tetrahedral molecular geometry of the methane molecule.

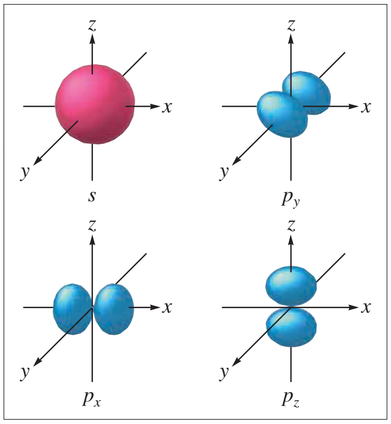


FIGURE 9.2
The valence orbitals on a free carbon atom: 2*s*, $2p_x$, $2p_y$, and $2p_z$.

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 orbitals, arranged tetrahedrally. In fact, such a set of orbitals can be obtained quite readily by combining the carbon 2*s* and 2*p* orbitals, as shown schematically in Fig. 9.3. This mixing of the native atomic orbitals to form special orbitals for bonding is called **hybridization.** The four new orbitals are called sp^3 orbitals because they are formed from one 2*s* and three 2*p* orbitals (s^1p^3). We say that the carbon atom undergoes **sp^3 hybridization** or is **sp^3 hybridized.** The four sp^3 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 2*s* and 2*p* orbitals also can be represented by an orbital 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 atoms—it is the total number of electrons and the arrangement of these electrons in the *molecule* that are important. We are assuming that carbon's atomic orbitals are rearranged to accommodate the best electron arrangement for the molecule as a whole. The new sp^3 atomic orbitals on carbon are used to share electron pairs with the 1*s* orbitals from the four hydrogen atoms, as shown in Fig. 9.6 on page 393.

At this point let's summarize the bonding in the methane molecule. The experimentally known structure of this molecule can be explained if we assume that the carbon atom adopts a special set of atomic orbitals. These new orbitals are obtained by combining the 2*s* and the three 2*p* orbitals of the carbon atom to produce four identically shaped orbitals that are oriented toward the corners of a tetrahedron and are used to bond to the hydrogen atoms. Thus the four sp^3 orbitals on carbon in methane are postulated to account for its known structure.

Remember this principle: *Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, this model assumes that the atom adopts a set of sp^3 orbitals; the atom becomes sp^3 hybridized.*

It is really not surprising that an atom in a molecule might adopt a different set of atomic orbitals (called **hybrid orbitals**) from those it has in the free state. It does not seem unreasonable that to achieve minimum energy, an atom uses one set of atomic orbitals in the free state and a different set in a molecule. This is consistent with the idea that a molecule is more than simply a sum of its parts. What the atoms in a molecule were

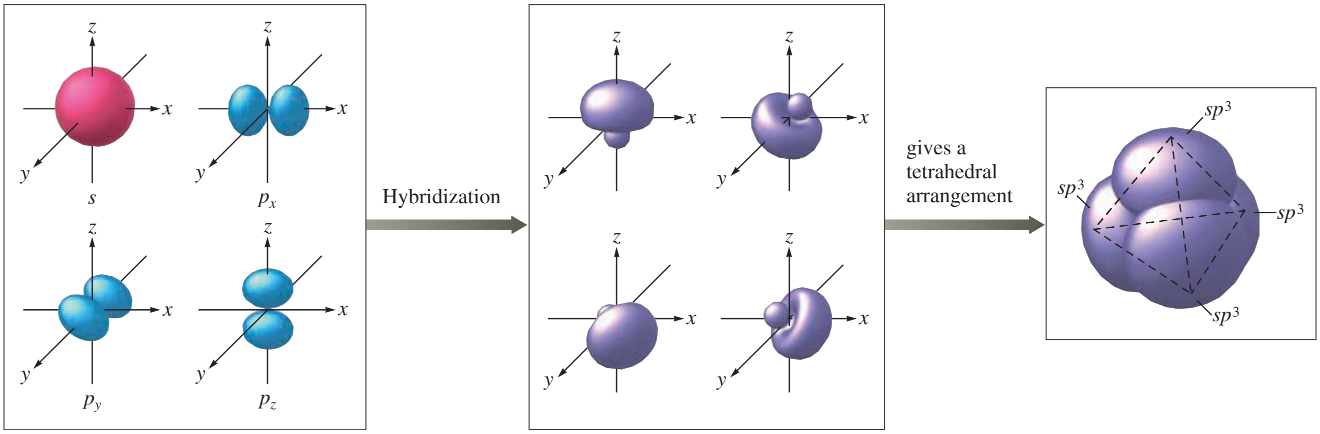


FIGURE 9.3
The "native" 2*s* and three 2*p* atomic orbitals characteristic of a free carbon atom are combined to form a new set of four sp^3 orbitals. The small lobes of the orbitals are usually omitted from diagrams for clarity.

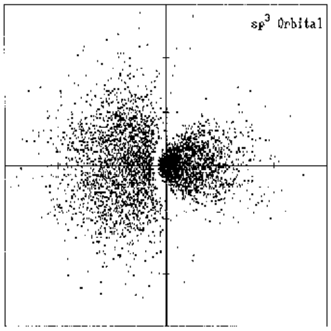


FIGURE 9.4
Cross section of an sp^3 orbital. This shows a "slice" of the electron density of the sp^3 orbitals illustrated in the center diagram of Fig. 9.3.
(Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC2402; printed with permission.)

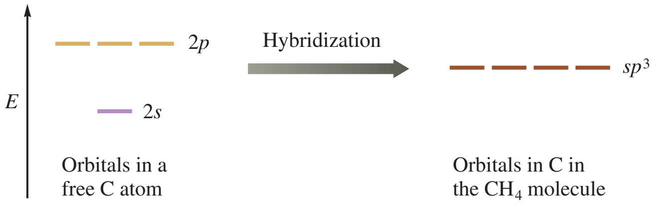


FIGURE 9.5
An energy-level diagram showing the formation of four sp^3 orbitals.

like before the molecule was formed is not as important as how the electrons are best arranged in the molecule. Therefore, this model assumes that the individual atoms respond as needed to achieve the minimum energy for the molecule.

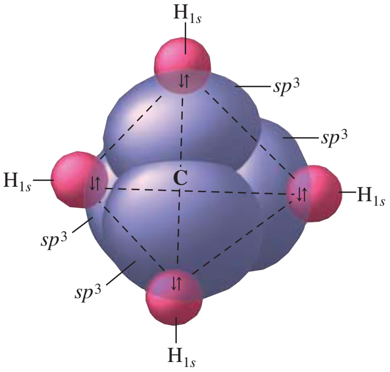


FIGURE 9.6
The tetrahedral set of four sp^3 orbitals of the carbon atom are used to share electron pairs with the four 1s orbitals of the hydrogen atoms to form the four equivalent C—H bonds. This accounts for the known tetrahedral structure of the CH_4 molecule.

Sample Exercise 9.1

The Localized Electron Model I

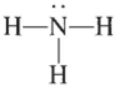
Describe the bonding in the ammonia molecule using the localized electron model.

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 NH_3 is



The four electron pairs around the nitrogen atom require a tetrahedral arrangement to minimize repulsions. We have seen that a tetrahedral set of sp^3 hybrid orbitals is obtained by combining the 2s and three 2p orbitals. In the NH_3 molecule three of the sp^3 orbitals are used to form bonds to the three hydrogen atoms, and the fourth sp^3 orbital holds the lone pair, as shown in Fig. 9.7.

See Exercise 9.15.

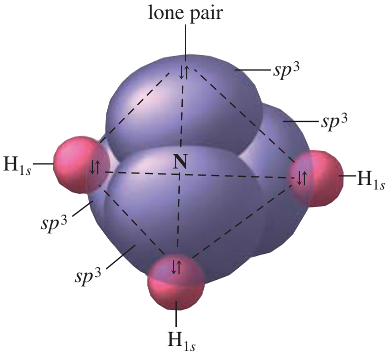
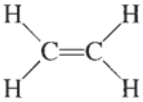


FIGURE 9.7
The nitrogen atom in ammonia is sp^3 hybridized.

sp^2 Hybridization

Ethylene (C_2H_4) is an important starting material in the manufacture of plastics. The C_2H_4 molecule has 12 valence electrons and the following Lewis structure:



We saw in Chapter 8 that a double bond acts as one effective pair, so in the ethylene molecule 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

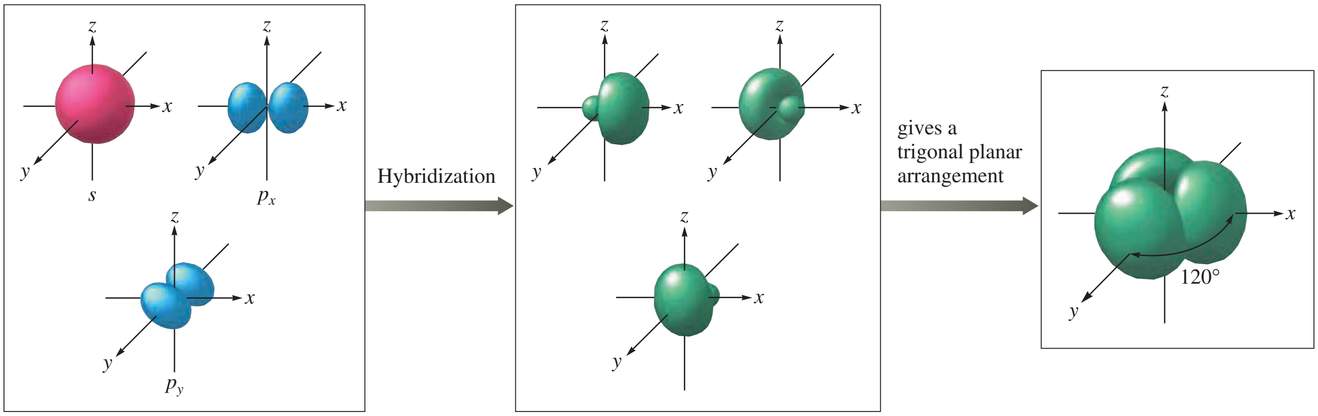


FIGURE 9.8
The hybridization of the s, p_x, and p_y atomic orbitals results in the formation of three sp^2 orbitals centered in the xy plane. The large lobes of the orbitals lie in the plane at angles of 120 degrees and point toward the corners of a triangle.

A double bond acts as one effective electron pair.

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.

The sp^3 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 hybridize 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 **sp^2 hybridization.** Note from Fig. 9.8 that the plane of the sp^2 hybridized orbitals is determined by which p orbitals are used. Since in this case we have arbitrarily decided to use the p_x and p_y orbitals, the hybrid orbitals are centered in the xy plane.

sp^2 hybridization gives a trigonal planar arrangement of atomic orbitals.

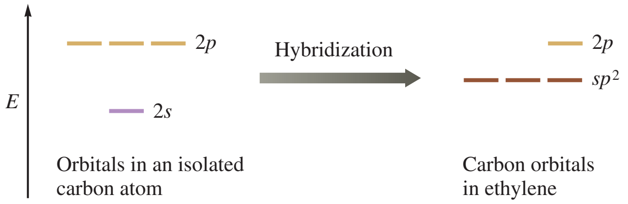
Note in Fig. 9.10 and the figures that follow that the orbital lobes are artificially narrowed to more clearly show their relative orientations.

In forming the sp^2 orbitals, one 2p orbital on carbon has not been used. This remaining p orbital (p_z) is oriented perpendicular to the plane of the sp^2 orbitals, as shown in Fig. 9.10.

Now we will see how these orbitals can be used to account for the bonds in ethylene. The three sp^2 orbitals on each carbon can be used to share electrons, as shown in Fig. 9.11. 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 (σ) bond.** In the ethylene molecule, the σ bonds are formed using sp^2 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 σ bond the electron pair occupies the space between the carbon atoms. The second bond must therefore result from sharing an electron pair in the space *above and below* the σ bond. This type of bond can be formed using the 2p orbital perpendicular to the sp^2 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 (π) bond,** as shown in Fig. 9.12.

FIGURE 9.9
An orbital energy-level diagram for sp^2 hybridization. Note that one p orbital remains unchanged.



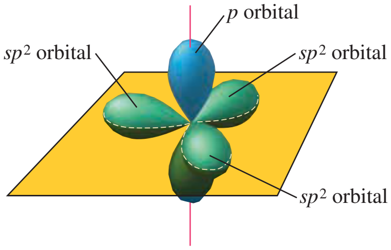


FIGURE 9.10
When an *s* and two *p* orbitals are mixed to form a set of three sp^2 orbitals, one *p* orbital remains unchanged and is perpendicular to the plane of the hybrid orbitals. Note that in this figure and those that follow, the orbitals are drawn with narrowed lobes to show their orientations more clearly.

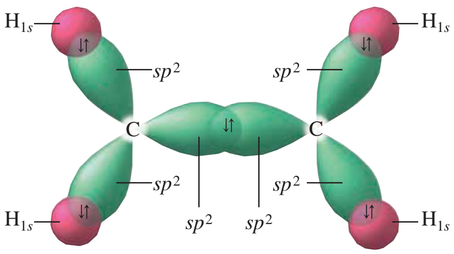


FIGURE 9.11
The σ bonds in ethylene. Note that for each bond the shared electron pair occupies the region directly between the atoms.

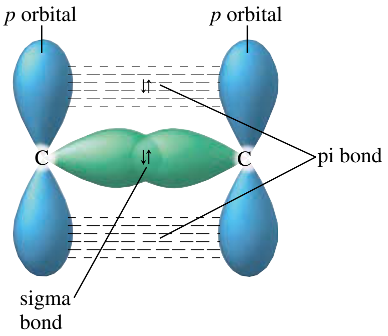


FIGURE 9.12
A carbon–carbon double bond consists of a σ bond and a π bond. In the σ bond the shared electrons occupy the space directly between the atoms. The π bond is formed from the unhybridized *p* orbitals on the two carbon atoms. In a π bond the shared electron pair occupies the space above and below a line joining the atoms.

Visualization: Hybridization: sp^2

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

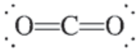
Visualization: Formation of C=C Double Bond in Ethylene

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 sp^2 hybrid orbitals to form the σ bonds to the hydrogen atoms and to each other, and they use *p* to form the π 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 sp^2 hybrid orbitals is required.*

sp Hybridization

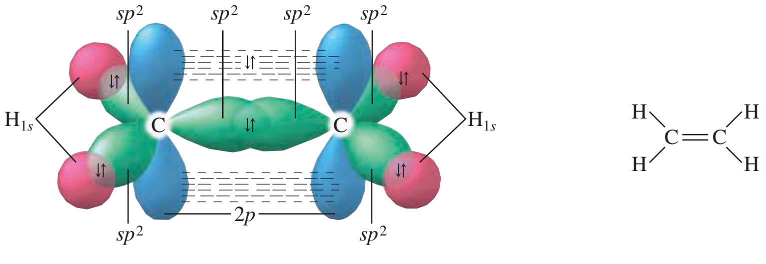
Another type of hybridization occurs in carbon dioxide, which has the following Lewis structure:



$$\ddot{O}=C=\ddot{O}$$

In the CO_2 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 directions. This requires a new type of hybridization, since neither sp^3 nor sp^2 hybrid

Visualization: Hybridization: *sp*



(a)

(b)

FIGURE 9.13
(a) The orbitals used to form the bonds in ethylene. (b) The Lewis structure for ethylene.

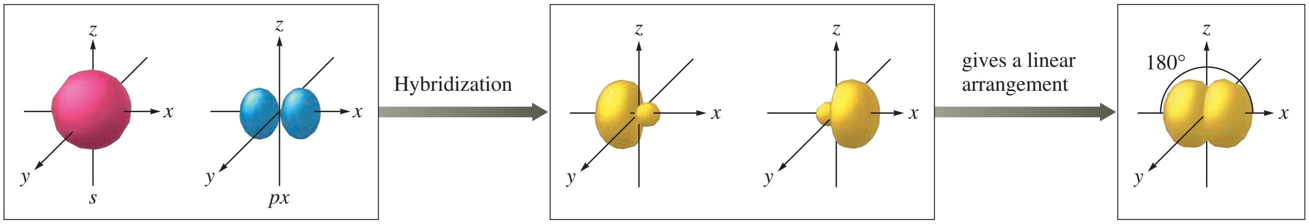


FIGURE 9.14
When one *s* orbital and one *p* orbital are hybridized, a set of two *sp* orbitals oriented at 180 degrees results.

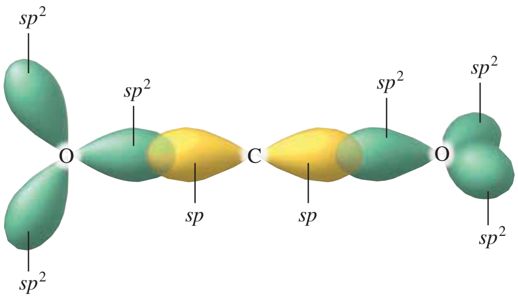


FIGURE 9.15
The hybrid orbitals in the CO_2 molecule.

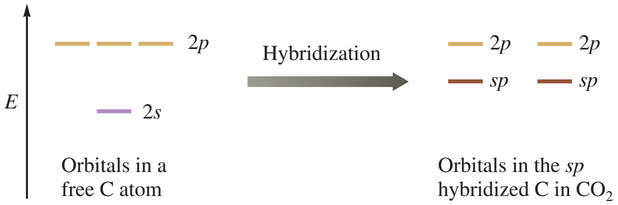


FIGURE 9.16
The orbital energy-level diagram for the formation of *sp* hybrid orbitals on carbon.

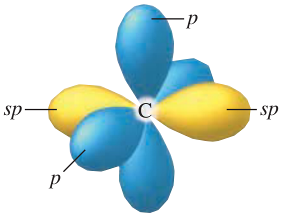


FIGURE 9.17
The orbitals of an *sp* hybridized carbon atom.

More rigorous theoretical models of CO_2 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.

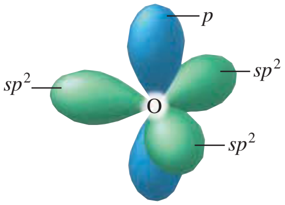


FIGURE 9.18
The orbital arrangement for an sp^2 hybridized oxygen atom.

orbitals 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 σ bonds between the carbon and the oxygen atoms. Note that two 2*p* orbitals remain unchanged on the *sp* hybridized carbon. These are used to form the π bonds with the oxygen atoms.

In the CO_2 molecule each oxygen atom* has three effective pairs around it, requiring a trigonal planar arrangement of the pairs. Since a trigonal set of hybrid orbitals requires sp^2 hybridization, each oxygen atom is sp^2 hybridized. One *p* orbital on each oxygen is unchanged and is used for the π 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 σ bonds with the sp^2 orbitals on the two oxygen atoms (Fig. 9.15). The remaining sp^2 orbitals on the oxygen atoms hold lone pairs. The π bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel 2*p* 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 π bond with an oxygen atom (see Fig. 9.18). The total bonding picture for the CO_2 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 (C_2H_2), which has the systematic name ethyne. The Lewis structure for acetylene is

$$H{-}C{\equiv}C{-}H$$

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

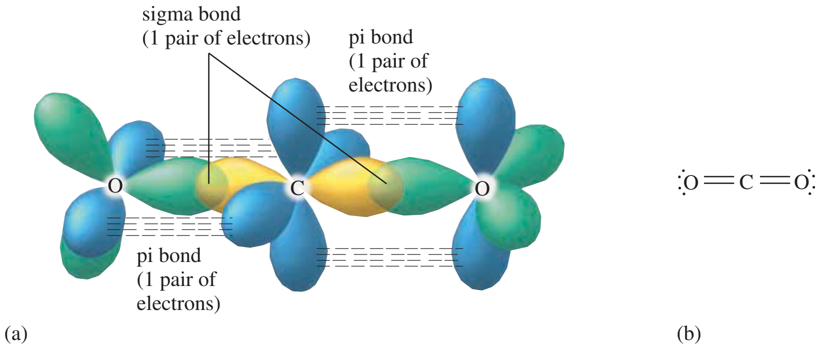


FIGURE 9.19 (a) The orbitals used to form the bonds in carbon dioxide. Note that the carbon–oxygen double bonds each consist of one σ bond and one π bond. (b) The Lewis structure for carbon dioxide.

Because the triple bond counts as one effective repulsive unit, each carbon has two effective pairs, which requires a linear arrangement. Thus each carbon atom requires *sp* hybridization, 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.

Sample Exercise 9.2

The Localized Electron Model II

Describe the bonding in the N_2 molecule.

Solution

The Lewis structure for the nitrogen molecule is

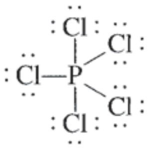
$$:N\equiv N:$$

where each nitrogen atom is surrounded by two effective pairs. (Remember that a multiple bond counts as one effective pair.) This gives a linear arrangement (180 degrees) requiring 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 σ 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 π bonds [see Fig. 9.20(c)]; each pair of overlapping parallel *p* orbitals holds one electron pair. Such bonding accounts for the electron arrangement given by the Lewis structure. The triple bond consists of a σ bond (overlap of two *sp* orbitals) and two π bonds (each one from an overlap of two *p* orbitals). In addition, a lone pair occupies an *sp* orbital on each nitrogen atom.

See Exercises 9.17 and 9.18.

dsp^3 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 (PCl_5). The Lewis structure



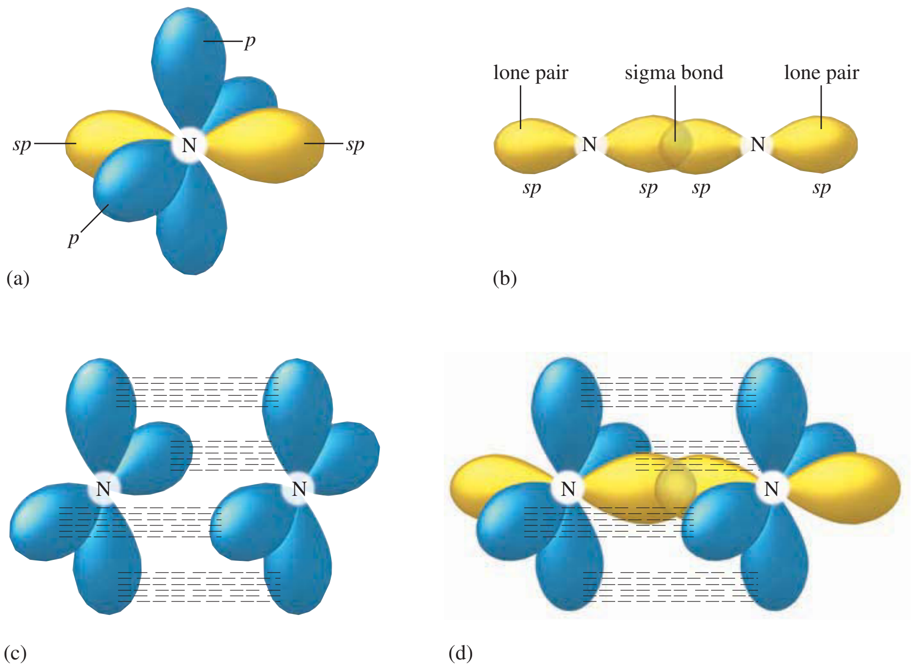


FIGURE 9.20
(a) An *sp* hybridized nitrogen atom. There are two *sp* hybrid orbitals and two unhybridized *p* orbitals. (b) The σ bond in the N_2 molecule. (c) The two π bonds in N_2 are formed when electron pairs are shared between two sets of parallel *p* orbitals. (d) The total bonding picture for N_2.

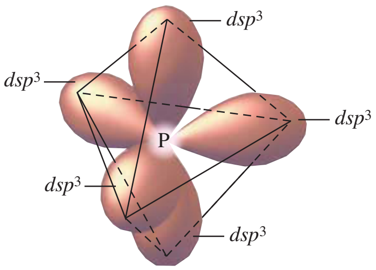


FIGURE 9.21
A set of dsp^3 hybrid orbitals on a phosphorus atom. Note that the set of five dsp^3 orbitals has a trigonal bipyramidal arrangement. (Each dsp^3 orbital also has a small lobe that is not shown in this diagram.)

shows that the phosphorus atom is surrounded by five electron pairs. Since five pairs require a trigonal bipyramidal arrangement, we need a trigonal bipyramidal set of atomic orbitals on phosphorus. Such a set of orbitals is formed by **dsp^3 hybridization** of one *d* orbital, one *s* orbital, and three *p* orbitals, as shown in Fig. 9.21.

The dsp^3 hybridized phosphorus atom in the PCl_5 molecule uses its five dsp^3 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 dsp^3 hybridization of that atom.*

The Lewis structure for PCl_5 shows that each chlorine atom is surrounded by four electron pairs. This requires a tetrahedral arrangement, which in turn requires a set of four sp^3 orbitals on each chlorine atom.

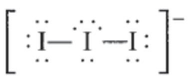
Now we can describe the bonding in the PCl_5 molecule. The five P—Cl σ bonds are formed by sharing electrons between a dsp^3 orbital* on the phosphorus atom and an sp^3 orbital on each chlorine.[†] The other sp^3 orbitals on each chlorine hold lone pairs. This is shown in Fig. 9.22.

Sample Exercise 9.3 The Localized Electron Model III

Describe the bonding in the triiodide ion (I_3^-).

Solution

The Lewis structure for I_3^-



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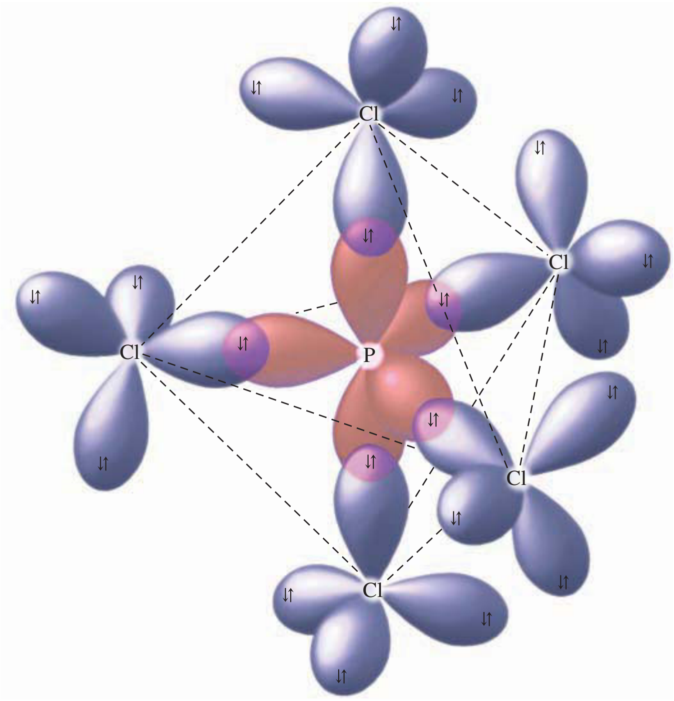
*There is considerable controversy about whether the *d* orbitals are as heavily involved in the bonding in these molecules as this model predicts. However, this matter is beyond the scope of this text.

[†] Although we have no way of proving conclusively that each chlorine is sp^3 hybridized, we assume that minimizing electron-pair repulsions is as important for peripheral atoms as for the central atom. Thus we will apply the VSEPR model and hybridization to both central and peripheral atoms.

(a)



(b)

FIGURE 9.22
(a) The structure of the PCl_5 molecule.
(b) The orbitals used to form the bonds in PCl_5. The phosphorus uses a set of five dsp^3 orbitals to share electron pairs with sp^3 orbitals on the five chlorine atoms. The other sp^3 orbitals on each chlorine atom hold lone pairs.

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 dsp^3 orbitals. The outer iodine atoms have four pairs of electrons, which calls for a tetrahedral arrangement and sp^3 hybridization.

Thus the central iodine is dsp^3 hybridized. Three of these hybrid orbitals hold lone pairs, and two of them overlap with sp^3 orbitals of the other two iodine atoms to form σ bonds.

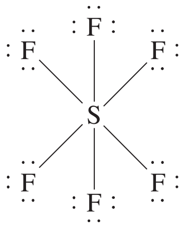
See Exercise 9.23.

---

d^2sp^3 hybridization gives six orbitals arranged octahedrally.

d^2sp^3 Hybridization

Some molecules have six pairs of electrons around a central atom; an example is sulfur hexafluoride (SF_6), which has the Lewis structure



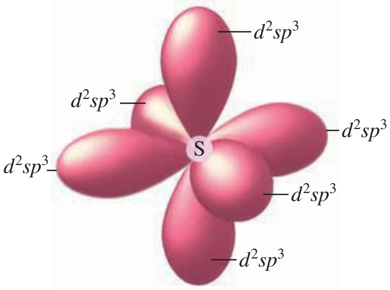


FIGURE 9.23
An octahedral set of d^2sp^3 orbitals on a sulfur atom. The small lobe of each hybrid orbital has been omitted for clarity.

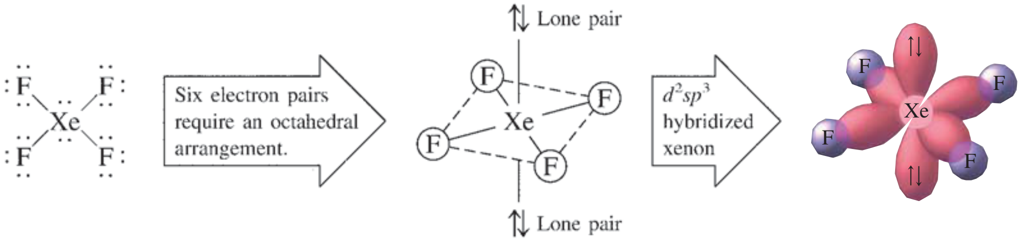
This requires an octahedral arrangement of pairs and in turn an octahedral set of six hybrid orbitals, or **d^2sp^3 hybridization,** in which two *d* orbitals, one *s* orbital, and three *p* orbitals are combined (see Fig. 9.23). Note that *six electron pairs around an atom are always arranged octahedrally and require d^2sp^3 hybridization of the atom.* Each of the d^2sp^3 orbitals on the sulfur atom is used to bond to a fluorine atom. Since there are four pairs on each fluorine atom, the fluorine atoms are assumed to be sp^3 hybridized.

Sample Exercise 9.4 The Localized Electron Model IV

How is the xenon atom in XeF_4 hybridized?

Solution

As seen in Sample Exercise 8.13, XeF_4 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 d^2sp^3 hybridized.



Lewis structure

Octahedral arrangement of six electron pairs.

Xenon uses six d^2sp^3 hybrid atomic orbitals to bond to the four fluorine atoms and to hold the two lone pairs.

See Exercise 9.24.

The Localized Electron Model: A Summary

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

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 follow 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 characteristics 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 minimum 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.

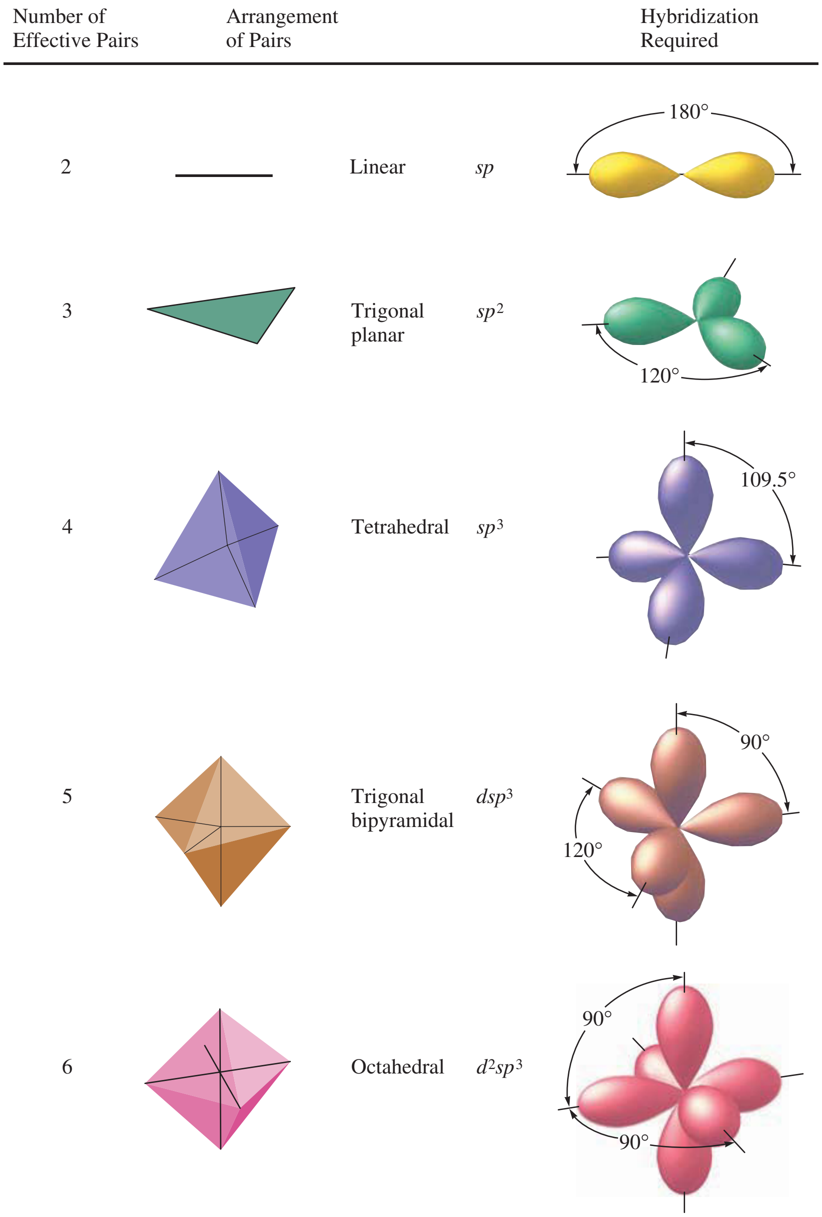


FIGURE 9.24
The relationship of the number of effective pairs, their spatial arrangement, and the hybrid orbital set required.

Sample Exercise 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.

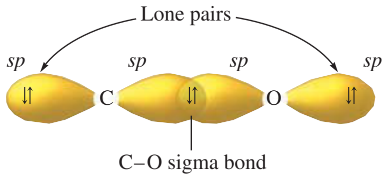
a. CO **b.** BF_4^- **c.** XeF_2

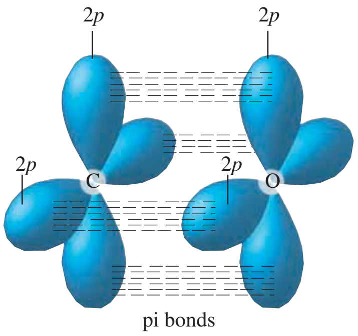
Solution

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

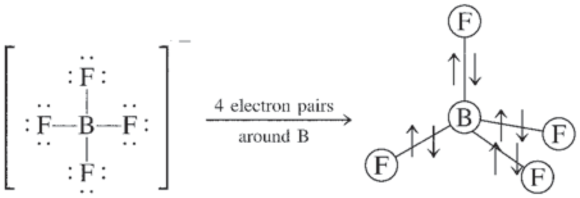
$$:\mathrm{C}\equiv\mathrm{O}:$$

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

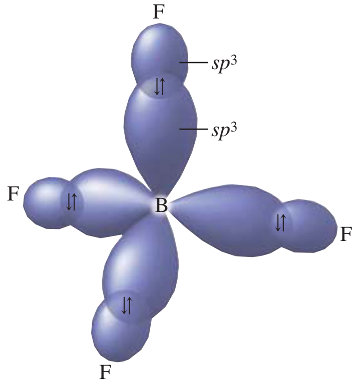




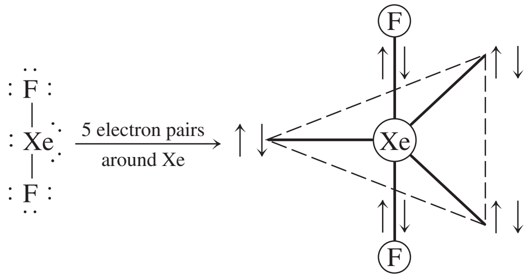
b. The BF_4^- ion has 32 valence electrons. The Lewis structure shows four pairs of electrons around the boron atom, which means a tetrahedral arrangement:



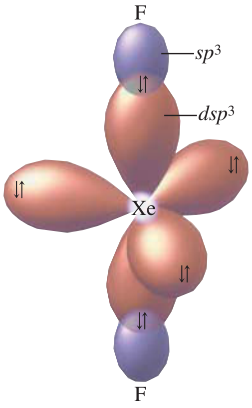
This requires sp^3 hybridization of the boron atom. Each fluorine atom also has four electron pairs and can be assumed to be sp^3 hybridized (only one sp^3 orbital is shown for each fluorine atom). The BF_4^- ion's molecular structure is tetrahedral.



c. The XeF_2 molecule has 22 valence electrons. The Lewis structure shows five electron pairs on the xenon atom, which requires a trigonal bipyramidal arrangement:



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 dsp^3 orbitals. Each fluorine atom has four electron pairs and can be assumed to be sp^3 hybridized. The XeF_2 molecule has a linear arrangement of atoms.



See Exercises 9.27 and 9.28.

9.2 The Molecular Orbital Model

We have seen that the localized electron model is of great value in interpreting the structure 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 resonance 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.

Visualization: Bonding in H_2

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 simplest of all molecules, H_2, which consists of two protons and two electrons. A very stable molecule, H_2 is lower in energy than the separated hydrogen atoms by 432 kJ/mol.

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

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 H_2 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 electron 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 physical 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

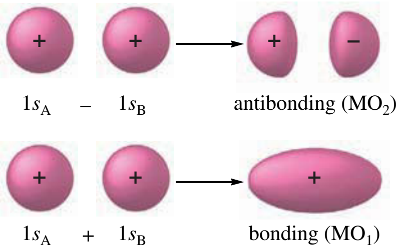


FIGURE 9.25
The combination of hydrogen 1*s* atomic orbitals to form MOs. The phases of the orbitals are shown by signs inside the boundary surfaces. When the orbitals are added, the matching phases produce constructive interference, which give enhanced electron probability between the nuclei. This results in a bonding molecular orbital. When one orbital is subtracted from the other, destructive interference occurs between the opposite phases, leading to a node between the nuclei. This is an antibonding MO.

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 simplified if we assume that the molecular orbitals can be constructed from the hydrogen 1*s* atomic orbitals.

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

$$MO_1 = 1s_A + 1s_B$$
$$MO_2 = 1s_A - 1s_B$$

where $1s_A$ and $1s_B$ represent the 1*s* 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:

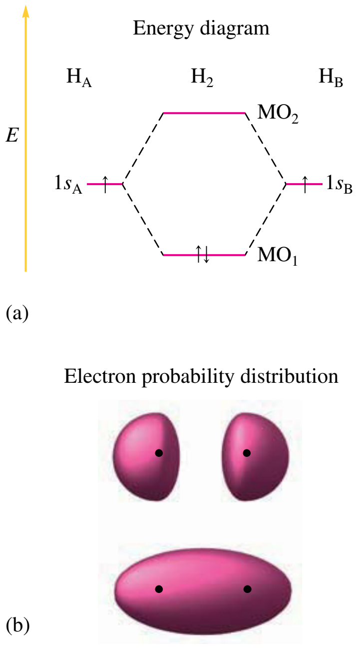


FIGURE 9.26
(a) The MO energy-level diagram for the H_2 molecule. (b) The shapes of the MOs are obtained by squaring the wave functions for MO_1 and MO_2. The positions of the nuclei are indicated by •.

1. The electron probability of both molecular orbitals is centered along the line passing through the two nuclei. For MO_1 the greatest electron probability is *between* the nuclei, and for MO_2 it is on *either side* of the nuclei. This type of electron distribution is described as *sigma* (σ), as in the localized electron model. Accordingly, we refer to MO_1 and MO_2 as **sigma (σ) molecular orbitals.**

2. In the molecule only the molecular orbitals are available for occupation by electrons. The 1*s* atomic orbitals of the hydrogen atoms no longer exist, because the H_2 molecule—a new entity—has its own set of new orbitals.

3. MO_1 is lower in energy than the 1*s* orbitals of free hydrogen atoms, while MO_2 is higher in energy than the 1*s* orbitals. This fact has very important implications for the stability of the H_2 molecule, since if the two electrons (one from each hydrogen atom) occupy the lower-energy MO_1, 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 MO_2, 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 MO_1 *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 H_2 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

Visualization: Sigma Bonding and Antibonding Orbitals 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.

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

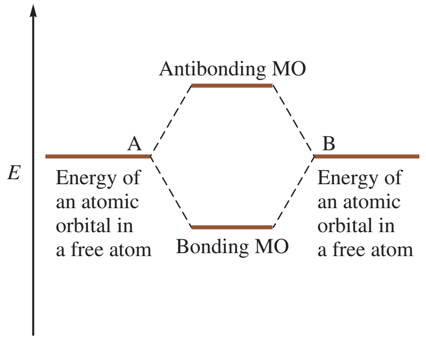


FIGURE 9.27
Bonding and antibonding molecular orbitals (MOs).

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 by an asterisk. For the H_2 molecule, both MOs have σ symmetry, and both are constructed from hydrogen 1*s* atomic orbitals. The molecular orbitals for H_2 are therefore labeled as follows:

$$\mathrm{MO}_1 = \sigma_{1s}$$
$$\mathrm{MO}_2 = \sigma_{1s}{}^*$$

6. Molecular electron configurations can be written in much the same way as atomic (electron) configurations. Since the H_2 molecule has two electrons in the σ_{1s} molecular orbital, the electron configuration is $\sigma_{1s}{}^2$.
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.

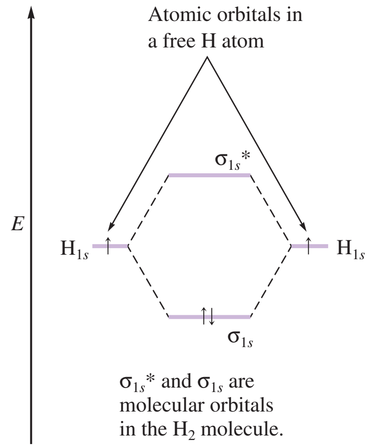


FIGURE 9.28
A molecular orbital energy-level diagram for the H_2 molecule.

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

Now suppose we could form the H_2^- ion from a hydride ion (H^-) and a hydrogen atom. Would this species be stable? Since the H^- ion has the configuration $1s^2$ and the H atom has a $1s^1$ configuration, we will use 1*s* atomic orbitals to construct the MO diagram for the H_2^- ion, as shown in Fig. 9.29. The electron configuration for H_2^- is $(\sigma_{1s})^2(\sigma_{1s}{}^*)^1$.

The key idea is that the H_2^- 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 H_2^- 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 favor bonding, H_2^- is predicted to be a stable entity—a bond has formed. But how would we expect the bond strengths in the molecules of H_2 and H_2^- to compare?

Although the model predicts that H_2^- should be stable, this ion has never been observed, again emphasizing the perils of simple models.

In the formation of the H_2 molecule, two electrons are lowered in energy and no electrons are raised in energy compared with the parent atoms. When H_2^- 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 H_2 is *twice as stable* as H_2^- with respect to their separated components. In other words, the bond in the H_2 molecule is predicted to be about twice as strong as the bond in the H_2^- ion.

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.*

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

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

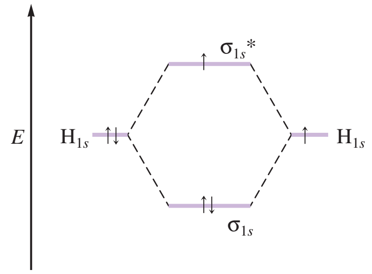


FIGURE 9.29
The molecular orbital energy-level diagram for the H_2^- ion.

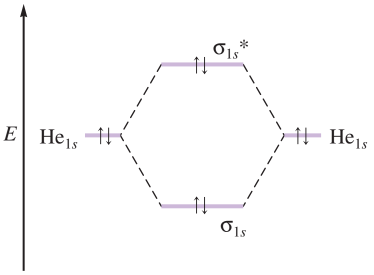


FIGURE 9.30
The molecular orbital energy-level diagram for the He_2 molecule.

Since the H_2 molecule has two bonding electrons and no antibonding electrons, the bond order is

$$\text{Bond order} = \frac{2 - 0}{2} = 1$$

The H_2^- ion has two bonding electrons and one antibonding electron; the bond order is

$$\text{Bond order} = \frac{2 - 1}{2} = \frac{1}{2}$$

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.*

We will now apply the molecular orbital model to the helium molecule (He_2). Does this model predict that this molecule will be stable? Since the He atom has a $1s^2$ 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:

$$\frac{2 - 2}{2} = 0$$

This implies that the He_2 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.

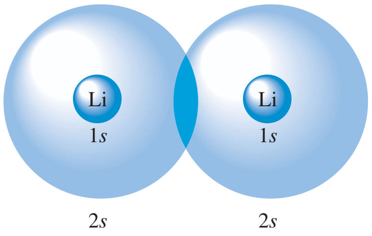


FIGURE 9.31
The relative sizes of the lithium $1s$ and $2s$ atomic orbitals.

9.3 Bonding in Homonuclear Diatomic Molecules

In this section we consider *homonuclear diatomic molecules* (those composed of two identical atoms) of elements in Period 2 of the periodic table. Since the lithium atom has a $1s^2 2s^1$ electron configuration, it would seem that we should use the Li $1s$ and $2s$ orbitals to form the molecular orbitals of the Li_2 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 assumed 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.

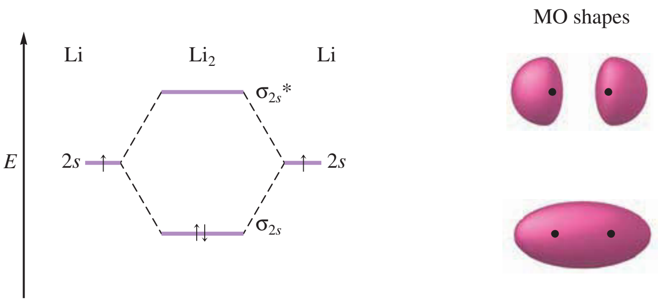
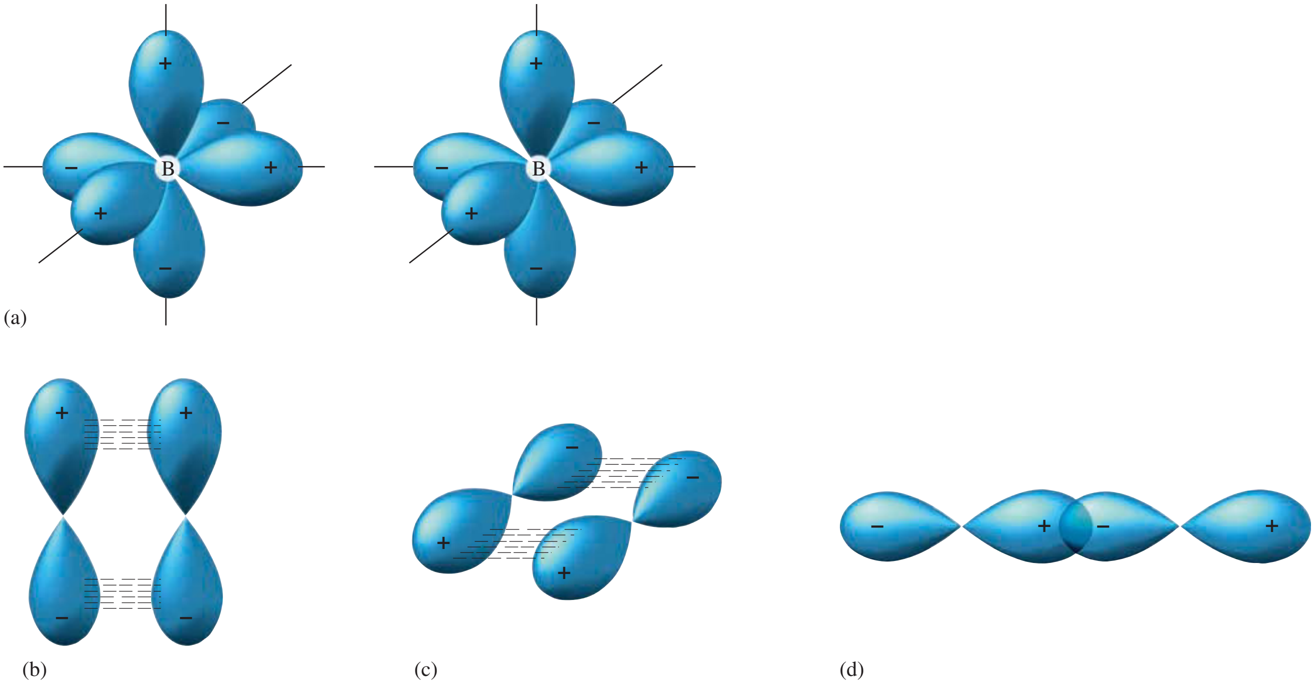


FIGURE 9.32
The molecular orbital energy-level diagram for the Li_2 molecule.



(a)

(b)

(c)

(d)

FIGURE 9.33
(a) The three mutually perpendicular 2*p* 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).

The molecular orbital diagram of the Li_2 molecule and the shapes of its bonding and antibonding MOs are shown in Fig. 9.32. The electron configuration for Li_2 (valence electrons only) is $\sigma_{2s}{}^2$, and the bond order is

$$\frac{2-0}{2} = 1$$

Beryllium metal.

The Li_2 is a stable molecule (has lower energy than two separated lithium atoms). However, this does not mean that Li_2 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 (Be_2) the bonding and antibonding orbitals both contain two electrons. In this case the bond order is $(2 - 2)/2 = 0$, and since Be_2 is not more stable than two separated Be atoms, no molecule forms. However, beryllium metal contains many beryllium atoms bonded to each other and is stable for reasons we will discuss in Chapter 10.

Since the boron atom has a $1s^22s^22p^1$ configuration, we describe the B_2 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)].

Visualization: Pi Bonding and Antibonding Orbitals

First, let's consider the molecular orbitals from the head-on overlap, as shown in Fig. 9.34(a). 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 σ molecular orbitals. The

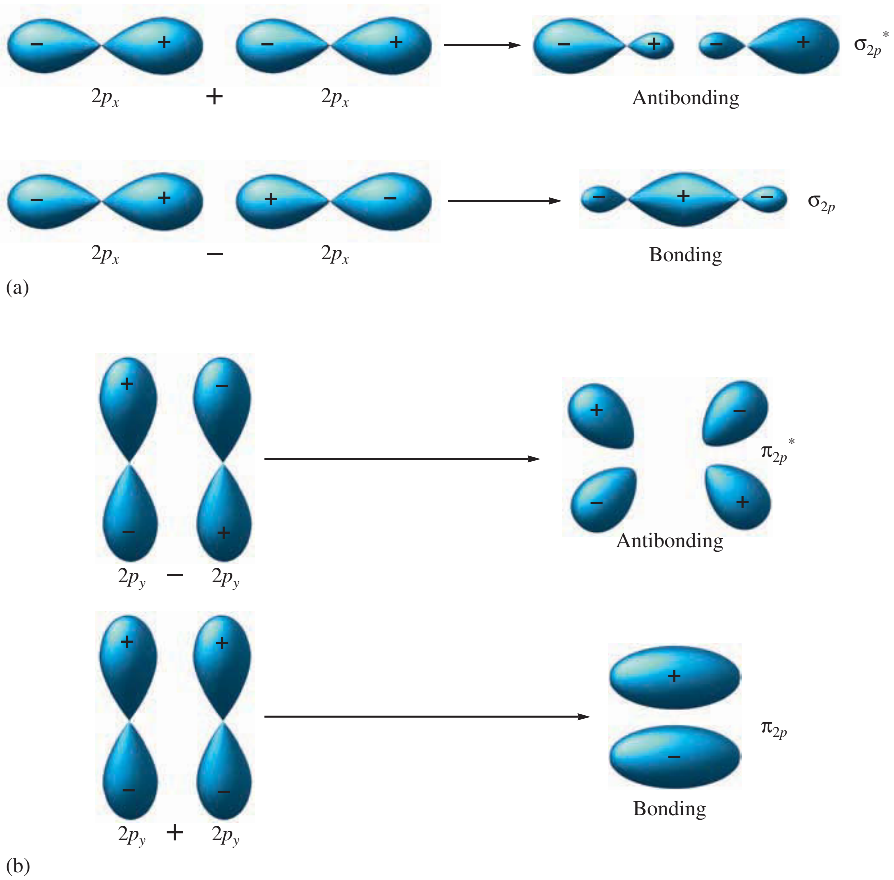


FIGURE 9.34
(a) The two *p* orbitals on the boron atoms that overlap head-on combine to form σ bonding and antibonding orbitals. The bonding orbital is formed by reversing the sign of the right orbital so the positive phases of both orbitals match between the nuclei to produce constructive interference. 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. (b) When the parallel *p* orbitals are combined with the positive and negative phases matched, constructive interference occurs, giving a bonding π orbital. When the orbitals have opposite phases (the signs of one orbital are reversed), destructive interference occurs, resulting in an antibonding π orbital.

p orbitals that overlap in a parallel fashion also produce bonding and antibonding orbitals [Fig. 9.34(b)]. Since the electron probability lies above and below the line between the nuclei, both the orbitals are **pi (π) molecular orbitals.** They are designated as π_{2p} for the bonding MO and π_{2p}^* for the antibonding MO.

Let's try to make an educated guess about the relative energies of the σ and π molecular orbitals formed from the 2*p* atomic orbitals. Would we expect the electrons to prefer the σ bonding orbital (where the electron probability is concentrated in the area between the nuclei) or the π bonding orbital? The σ orbital would seem to have the lower energy, since the electrons are closest to the two nuclei. This agrees with the observation that σ interactions are stronger than π interactions.

Figure 9.35 gives the molecular orbital energy-level diagram *expected* when the two sets of 2*p* orbitals on the boron atoms combine to form molecular orbitals. Note that there are two π bonding orbitals at the same energy (degenerate orbitals) formed from the two pairs of parallel *p* orbitals, and there are two degenerate π antibonding orbitals. The energy of the π_{2p} orbitals is expected to be higher than that of the σ_{2p} orbital because σ interactions are generally stronger than π interactions.

To construct the total molecular orbital diagram for the B_2 molecule, we make the assumption that the 2*s* and 2*p* orbitals combine separately (in other words, there is no 2*s*–2*p* mixing). The resulting diagram is shown in Fig. 9.36. Note that B_2 has six *valence* electrons. (Remember the 1*s* orbitals and electrons are assumed not to participate in the bonding.) This diagram predicts the bond order:

$$\frac{4-2}{2} = 1$$

Therefore, B_2 should be a stable molecule.

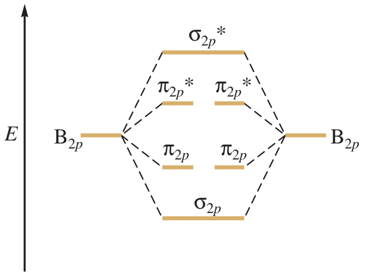


FIGURE 9.35
The *expected* molecular orbital energy-level diagram resulting from the combination of the 2*p* orbitals on two boron atoms.

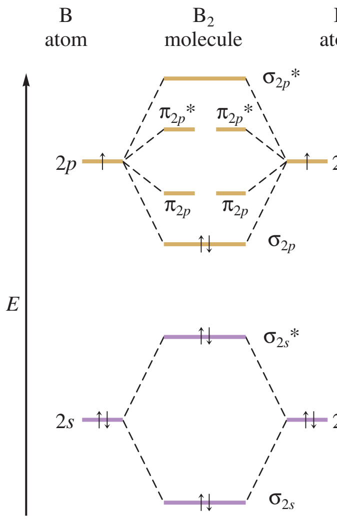


FIGURE 9.36
The *expected* molecular orbital energy-level diagram for the B_2 molecule.

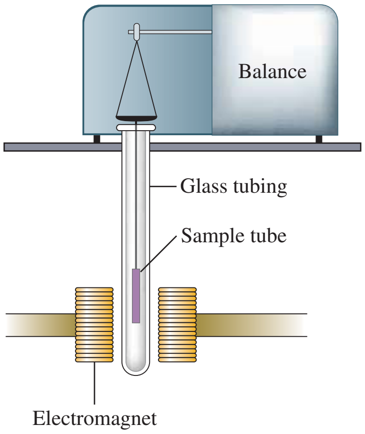


FIGURE 9.37
Diagram of the kind of apparatus used to measure the paramagnetism of a sample. A paramagnetic sample will appear heavier when the electromagnet is turned on because the sample is attracted into the inducing magnetic field.

Paramagnetism

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 9.37 illustrates how 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. 9.36 predicts that the B_2 molecule will be diamagnetic, since the MOs contain only paired electrons. However, experiments show that B_2 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 B_2, it certainly is suspect if it cannot describe the B_2 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 B_2, 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 B_2 (see Fig. 9.38). 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 π_{2p} and σ_{2p} orbitals are reversed by *p–s* mixing, and the σ_{2s} and the σ_{2s}^* orbitals are no longer equally spaced relative to the energy of the free 2*s* orbital.

When the six valence electrons for the B_2 molecule are placed in the modified energy-level diagram, each of the last two electrons goes into one of the degenerate π_{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 C_2 and N_2 molecules use the same set of orbitals as for B_2 (see Fig. 9.38). Because the importance of 2*s*–2*p* mixing decreases across the period, the σ_{2p} and π_{2p} orbitals revert to the order expected in the absence of 2*s*–2*p* mixing for the molecules O_2 and F_2, as shown in Fig. 9.39.

Several significant points arise from the orbital diagrams, bond strengths, and bond lengths summarized in Fig. 9.39 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 B_2 and F_2 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 B_2 appears to be about twice as strong as the bond in F_2. As we will see in our later discussion of the halogens, F_2 has an unusually weak single bond due to larger than usual electron–electron repulsions (there are 14 valence electrons on the small F_2 molecule).

3. Note the very large bond energy associated with the N_2 molecule, which the molecular orbital model predicts will have a bond order of 3, a triple bond. The very strong bond in N_2 is the principal reason that many nitrogen-containing compounds are used as high explosives. The reactions involving these explosives give the very stable N_2 molecule as a product, thus releasing large quantities of energy.

Visualization: Magnetic Properties of Liquid Nitrogen and Oxygen

4. The O_2 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. 9.40. 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.

Sample Exercise 9.6 The Molecular Orbital Model I

For the species O_2, O_2^+, and O_2^-, give the electron configuration and the bond order for each. Which has the strongest bond?

Solution

The O_2 molecule has 12 valence electrons (6 + 6); O_2^+ has 11 valence electrons (6 + 6 − 1); and O_2^- has 13 valence electrons (6 + 6 + 1). We will assume that the ions

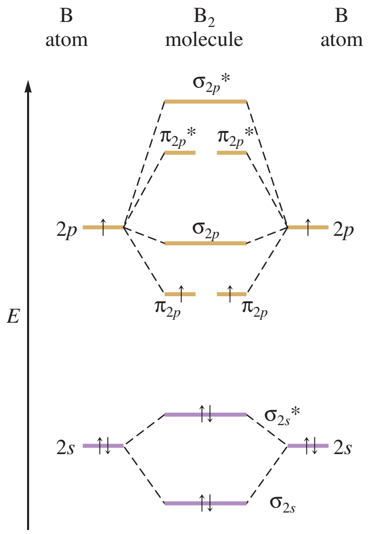
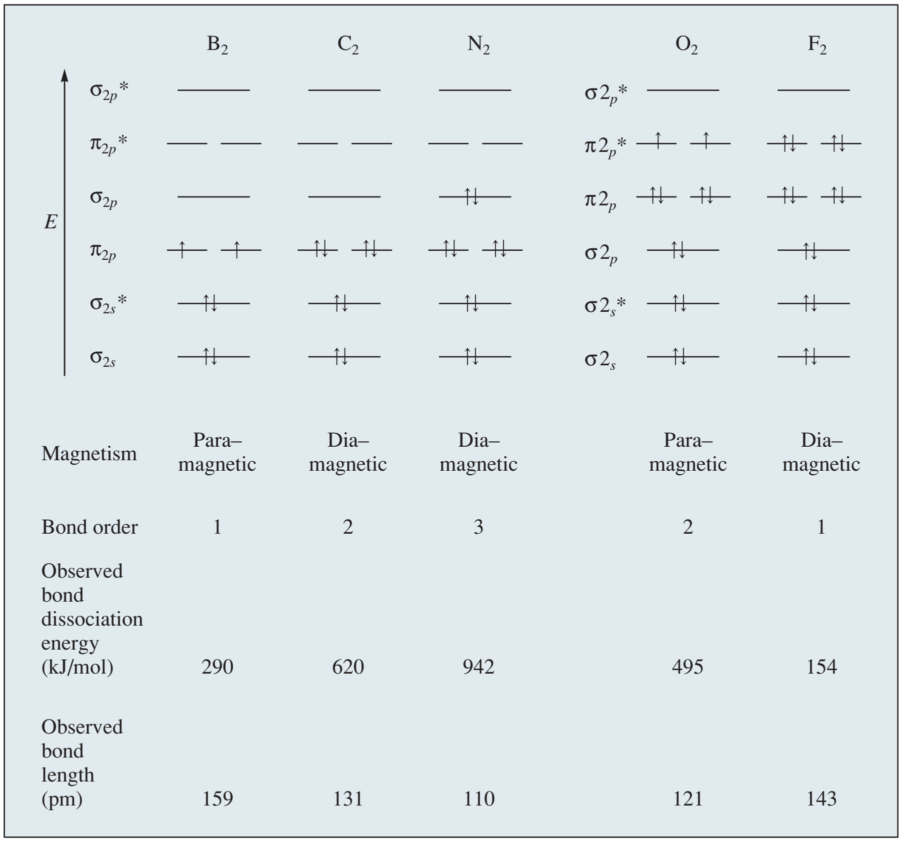


FIGURE 9.38
The *correct* molecular orbital energy-level diagram for the B_2 molecule. When *p–s* mixing is allowed, the energies of the σ_{2p} and π_{2p} orbitals are reversed. The two electrons from the B 2*p* orbitals now occupy separate, degenerate π_{2p} molecular orbitals and thus have parallel spins. Therefore, this diagram explains the observed paramagnetism of B_2.

Visualization: Molecular Orbital Diagram (N_2)



	B_2	C_2	N_2	O_2	F_2
Magnetism	Para–magnetic	Dia–magnetic	Dia–magnetic	Para–magnetic	Dia–magnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

FIGURE 9.39
The molecular orbital energy-level diagrams, bond orders, bond energies, and bond lengths for the diatomic molecules B_2 through F_2. Note that for O_2 and F_2 the σ_{2p} orbital is lower in energy than the π_{2p} orbitals.

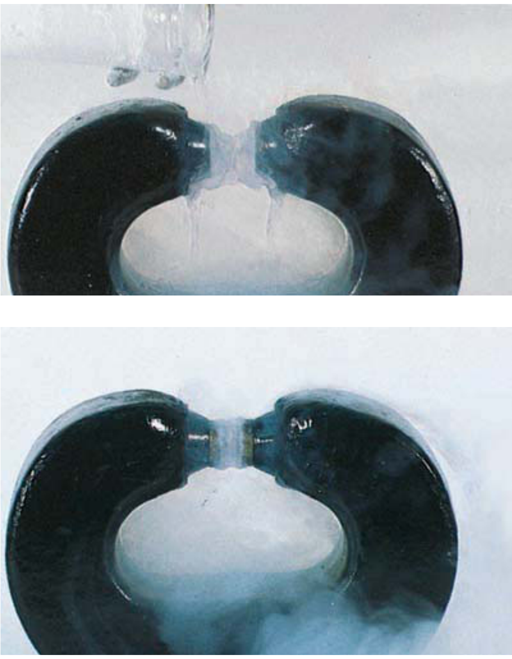
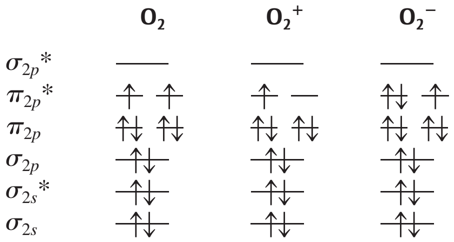


FIGURE 9.40
When liquid oxygen is poured into the space between the poles of a strong magnet, it remains there until it boils away. This attraction of liquid oxygen for the magnetic field demonstrates the paramagnetism of the O_2 molecule.

can be treated using the same molecular orbital diagram as for the neutral diatomic molecule:



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

$$O_2: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$$
$$O_2^+: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$$
$$O_2^-: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$$

The bond orders are:

$$\text{For } O_2: \quad \frac{8-4}{2} = 2$$

$$\text{For } O_2^+: \quad \frac{8-3}{2} = 2.5$$

$$\text{For } O_2^-: \quad \frac{8-5}{2} = 1.5$$

Thus O_2^+ is expected to have the strongest bond of the three species.

See Exercises 9.39 and 9.40.

Sample Exercise 9.7 The Molecular Orbital Model II

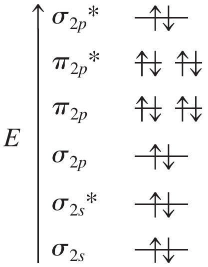
Use the molecular orbital model to predict the bond order and magnetism of each of the following molecules.

a. Ne_2
b. P_2

Visualization: Magnetic Properties of Liquid Nitrogen and Oxygen

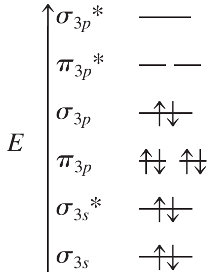
Solution

a. The valence orbitals for Ne are 2*s* and 2*p*. Thus we can use the molecular orbitals we have already constructed for the diatomic molecules of the Period 2 elements. The Ne_2 molecule has 16 valence electrons (8 from each atom). Placing these electrons in the appropriate molecular orbitals produces the following diagram:



The bond order is $(8 - 8)/2 = 0$, and Ne_2 does not exist.

b. The P_2 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 P_2 analogous to that for N_2. The only change will be that the molecular orbitals will be formed from 3*s* and 3*p* atomic orbitals. The P_2 model has 10 valence electrons (5 from each phosphorus atom). The resulting molecular orbital diagram is



The molecule has a bond order of 3 and is expected to be diamagnetic.

See Exercises 9.37 through 9.42.

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 example, 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. 9.41. The molecule should be paramagnetic and has a bond order of

$$\frac{8-3}{2} = 2.5$$

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.

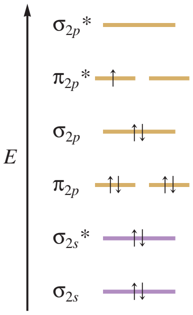


FIGURE 9.41
The molecular orbital energy-level diagram for the NO molecule. We assume that orbital order is the same as that for N_2. The bond order is 2.5.

Sample Exercise 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

$$\frac{8-2}{2} = 3$$

The molecular orbital diagram for these two ions is the same (see Fig. 9.42).

See Exercises 9.43 and 9.44.

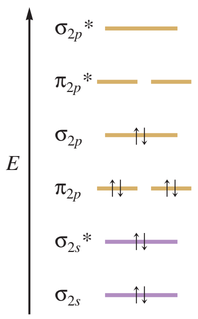


FIGURE 9.42
The molecular orbital energy-level diagram for both the NO^+ and CN^- ions.

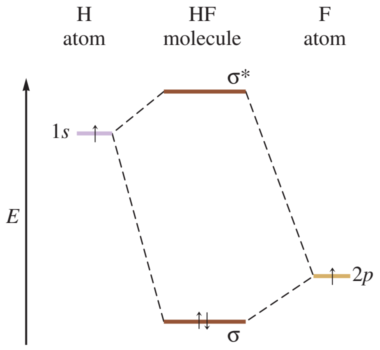


FIGURE 9.43
A partial molecular orbital energy-level diagram for the HF molecule.

When the two atoms of a diatomic molecule are very different, the energy-level diagram 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 $1s^1$ and $1s^22s^22p^5$, 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 9.43 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.

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 σ molecular orbital containing the bonding electron pair shows greater electron probability close to the fluorine (see Fig. 9.44). 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.

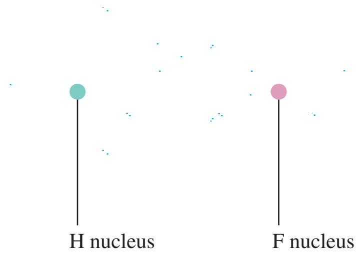


FIGURE 9.44
The electron probability distribution in the bonding molecular orbital of the HF molecule. Note the greater electron density close to the fluorine atom.

9.5 Combining the Localized Electron and Molecular Orbital Models

One of the main difficulties with the localized electron model is its assumption that electrons 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 O_3 and NO_3^- 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 require resonance. Note that for species such as O_3 and NO_3^- the double bond changes position in the resonance structures (see Fig. 9.45). Since a double bond involves one σ and one π bond, there is a σ bond between all bound atoms in each resonance structure. It is really the π bond that has different locations in the various resonance structures.

Therefore we conclude that the σ bonds in a molecule can be described as being localized with no apparent problems. It is the π bonding that must be treated as being

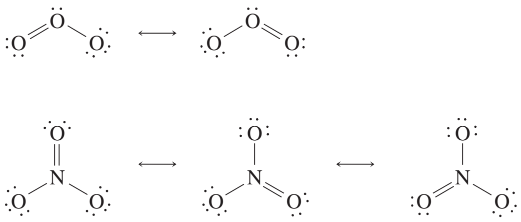


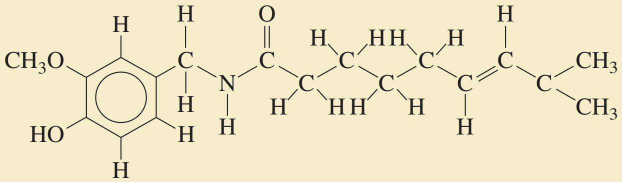
FIGURE 9.45
The resonance structures for O_3 and NO_3^-. Note that it is the double bond that occupies various positions in the resonance structures.

CHEMICAL IMPACT

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 repellant 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.

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

delocalized. Thus, for molecules that require resonance, we will use the localized electron model to describe the σ bonding and the molecular orbital model to describe the π 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 (C_6H_6) consists of a planar hexagon of carbon atoms with one hydrogen atom bound to each carbon atom, as shown in Fig. 9.46(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. 9.46(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 σ bonds of carbon involve sp^2 orbitals, as shown in Fig. 9.47. These σ bonds are all centered in the plane of the molecule.

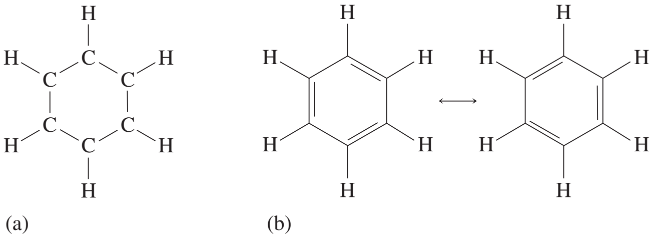


FIGURE 9.46
(a) The benzene molecule consists of a ring of six carbon atoms with one hydrogen atom bound to each carbon; all atoms are in the same plane. All the C—C bonds are known to be equivalent. (b) Two of the resonance structures for the benzene molecule. The localized electron model must invoke resonance to account for the six equal C—C bonds.

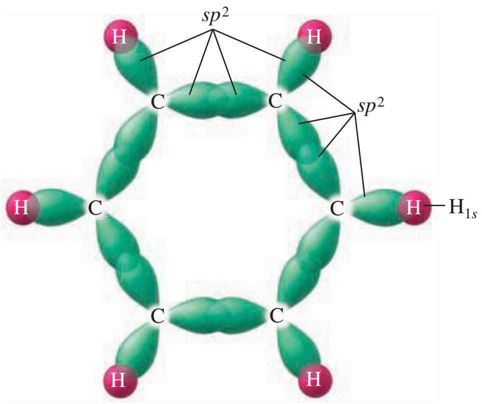


FIGURE 9.47
The σ bonding system in the benzene molecule.

Since each carbon atom is sp^2 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 π molecular orbitals, as shown in Fig. 9.48(a). The electrons in the resulting π molecular orbitals are delocalized above and below the plane of the ring, as shown in Fig. 9.48(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

to indicate the **delocalized π bonding** in the molecule.

Very similar treatments can be applied to other planar molecules for which resonance is required by the localized electron model. For example, the NO_3^- ion can be described using the π molecular orbital system shown in Fig. 9.49. In this molecule each atom is assumed to be sp^2 hybridized, which leaves one p orbital on each atom perpendicular to the plane of the ion. These p orbitals can combine to form the π molecular orbital system.

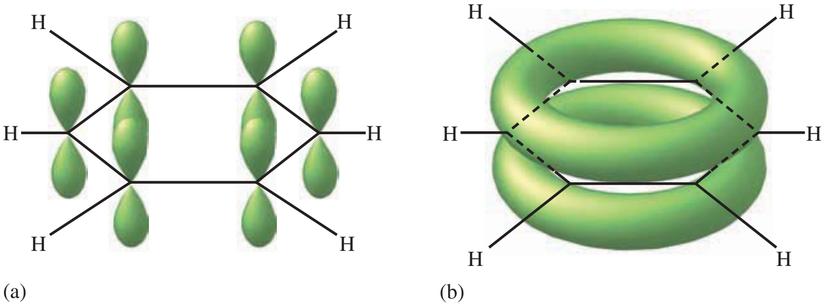


FIGURE 9.48
(a) The π molecular orbital system in benzene is formed by combining the six p orbitals from the six sp^2 hybridized carbon atoms. (b) The electrons in the resulting π molecular orbitals are delocalized over the entire ring of carbon atoms, giving six equivalent bonds. A composite of these orbitals is represented here.

Visualization: Pi Bonding in the Nitrate Ion

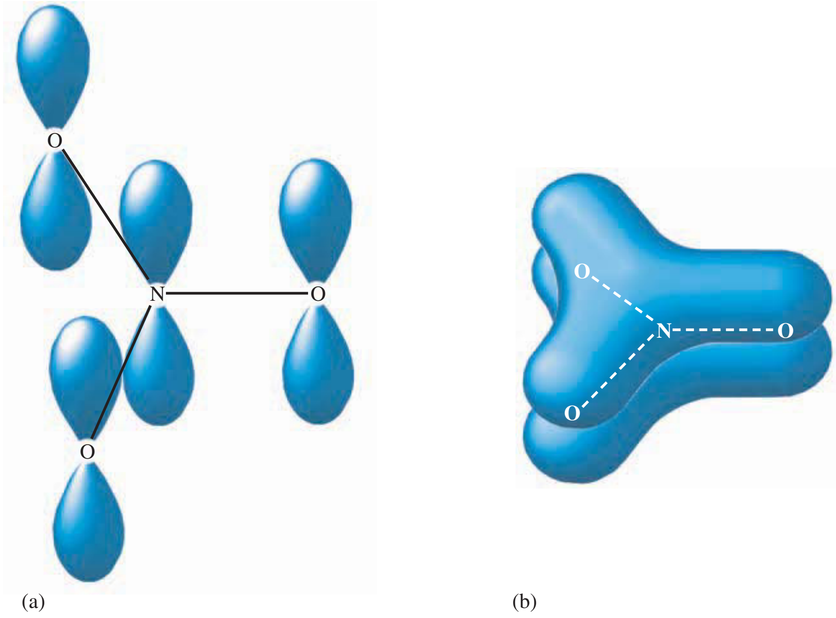


FIGURE 9.49
(a) The p orbitals used to form the π bonding system in the NO_3^- ion. (b) A representation of the delocalization of the electrons in the π molecular orbital system of the NO_3^- ion.

Key Terms

Section 9.1

hybridization
sp^3 hybridization
hybrid orbitals
sp^2 hybridization
sigma (σ) bond
pi (π) bond
sp hybridization
dsp^3 hybridization
d^2sp^3 hybridization

Section 9.2

molecular orbital model
molecular orbital (MO)
sigma (σ) molecular orbital
bonding molecular orbital
antibonding molecular orbital
bond order

Section 9.3

pi (π) molecular orbital
paramagnetism
diamagnetism

Section 9.4

heteronuclear diatomic molecule

Section 9.5

delocalized π bonding

For Review

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
  - Four electron pairs (tetrahedral arrangement) require sp^3 orbitals
  - Three electron pairs (trigonal planar arrangement) require sp^2 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 constructed. 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 (σ) MOs have their electron probability centered on a line passing through the nuclei
  - Pi (π) MOs have their electron probability concentrated above and below the line connecting the nuclei

Bond order is an index of bond strength

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

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 σ bonds are localized
- The π bonds are delocalized

REVIEW QUESTIONS

1. Why do we hybridize atomic orbitals to explain the bonding in covalent compounds? What type of bonds form from hybrid orbitals, sigma or pi? Explain.
2. What hybridization is required for central atoms that have a tetrahedral arrangement of electron pairs? A trigonal planar arrangement of electron pairs? A linear arrangement of electron pairs? How many unhybridized *p* atomic orbitals are present 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 H_2S, CH_4, H_2CO, 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 PF_5, SF_4, SF_6, and IF_5 using the localized electron model.
5. Electrons in σ bonding molecular orbitals are most likely to be found in the region between the two bonded atoms. Why does this arrangement favor bonding? In a σ antibonding orbital, where are the electrons most likely to be found in relation to the nuclei in a bond?
6. Show how 2*s* orbitals combine to form σ bonding and σ antibonding molecular orbitals. Show how 2*p* orbitals overlap to form σ bonding, π bonding, π antibonding, and σ 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. H_2 is stable, while He_2 is unstable.
   b. B_2 and O_2 are paramagnetic, while C_2, N_2, and F_2 are diamagnetic.
   c. N_2 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 molecular orbital theory is applied to describe the bonding in HF.
10. What is delocalized π bonding and what does it explain? Explain the delocalized π bonding system in C_6H_6 (benzene) and O_3 (ozone).

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

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

2. Explain the difference between the σ and π MOs for homonuclear diatomic molecules. How are bonding and antibonding orbitals different? Why are there two π MOs and one σ MO? Why are the π MOs degenerate?

3. Compare Figs. 9.36 and 9.38. Why are they different? Because B_2 is known to be paramagnetic, the π_{2p} and σ_{2p} molecular orbitals must be switched from the first prediction. What is the rationale for this? Why might one expect the σ_{2p} to be lower in energy than the π_{2p}? Why can't we use diatomic oxygen to help us decide whether the σ_{2p} or π_{2p} is lower in energy?

4. Which of the following would you expect to be more favorable energetically? Explain.
   a. An H_2 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, labeling each bond as σ or π.

6. Which is the more correct statement: "The methane molecule (CH_4) is a tetrahedral molecule because it is sp^3 hybridized" or "The methane molecule (CH_4) is sp^3 hybridized because it is a tetrahedral molecule"? What, if anything, is the difference between these two statements?

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*.

Questions

7. In the hybrid orbital model, compare and contrast σ bonds versus π bonds. What orbitals form the σ bonds and what orbitals form the π bonds? Assume the z-axis is the internuclear axis.

8. In the molecular orbital model, compare and contrast σ versus π bonds. What orbitals form the σ bonds and what orbitals form the π bonds? Assume the z-axis is the internuclear axis.

9. 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 (3*d*, 4*d*, 5*d*, or 6*d*) would sulfur use to form hybrid orbitals requiring *d* atomic orbitals? Answer the same question for arsenic and for iodine.

10. 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?

11. Compare and contrast bonding versus antibonding molecular orbitals.

12. What modification to the molecular orbital model was made from the experimental evidence that B_2 is paramagnetic?

13. Why does the molecular orbital model do a better job in explaining the bonding in NO^- and NO than the hybrid orbital model?

14. The three NO bonds in NO_3^- are all equivalent in length and strength. How is this explained even though any valid Lewis structure for NO_3^- 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

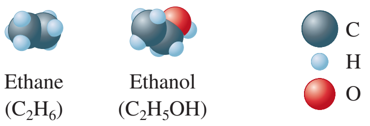
15. Use the localized electron model to describe the bonding in H_2O.

16. Use the localized electron model to describe the bonding in CCl_4.

17. Use the localized electron model to describe the bonding in H_2CO (carbon is the central atom).

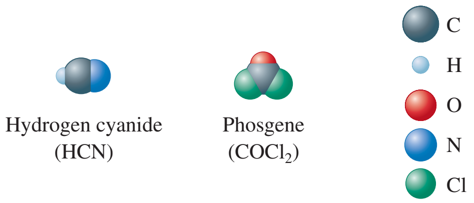
18. Use the localized electron model to describe the bonding in C_2H_2 (exists as HCCH).

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



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

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



Use the localized electron model to describe the bonding in hydrogen cyanide and phosgene.

21. Give the expected hybridization of the central atom for the molecules or ions in Exercises 67 and 73 from Chapter 8.

22. Give the expected hybridization of the central atom for the molecules or ions in Exercises 68 and 74 from Chapter 8.

23. Give the expected hybridization of the central atom for the molecules or ions in Exercise 71 from Chapter 8.

24. Give the expected hybridization of the central atom for the molecules in Exercise 72 from Chapter 8.

25. Give the expected hybridization of the central atom for the molecules in Exercises 91 and 92 from Chapter 8.

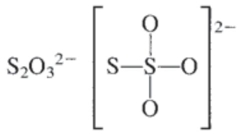
26. Give the expected hybridization of the central atom for the molecules in Exercises 93 and 94 from Chapter 8.

27. 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.

a. CF_4 **e.** BeH_2 **i.** KrF_4
b. NF_3 **f.** TeF_4 **j.** SeF_6
c. OF_2 **g.** AsF_5 **k.** IF_5
d. BF_3 **h.** KrF_2 **l.** IF_3

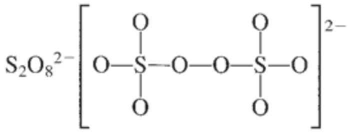
28. For each of the following molecules or ions that contain sulfur, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybrid orbitals for sulfur.

a. SO_2
b. SO_3
c.



$$S_2O_3^{2-}\quad\left[\begin{array}{c}\mathrm{O}\\ |\\ \mathrm{S{-}S{-}O}\\ |\\ \mathrm{O}\end{array}\right]^{2-}$$

d.

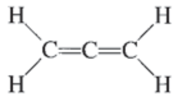


$$S_2O_8^{2-}\quad\left[\begin{array}{c}\mathrm{O}\qquad\qquad\qquad\mathrm{O}\\ |\qquad\qquad\qquad\;|\\ \mathrm{O{-}S{-}O{-}O{-}S{-}O}\\ |\qquad\qquad\qquad\;|\\ \mathrm{O}\qquad\qquad\qquad\mathrm{O}\end{array}\right]^{2-}$$

e. SO_3^{2-}
f. SO_4^{2-}
g. SF_2
h. SF_4
i. SF_6
j. $F_3S{-}SF$
k. SF_5^+

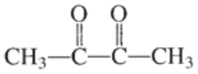
29. Why must all six atoms in C_2H_4 be in the same plane?

30. The allene molecule has the following Lewis structure:

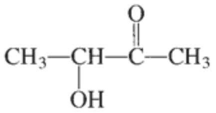


Are all four hydrogen atoms in the same plane? If not, what is their spatial relationship? Explain.

31. Biacetyl and acetoin are added to margarine to make it taste more like butter.



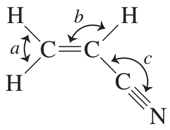
Biacetyl



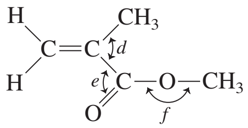
Acetoin

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. Are the four carbons and two oxygens in biacetyl in the same plane? How many σ bonds and how many π bonds are there in biacetyl and acetoin?

32. Many important compounds in the chemical industry are derivatives of ethylene (C_2H_4). Two of them are acrylonitrile and methyl methacrylate.



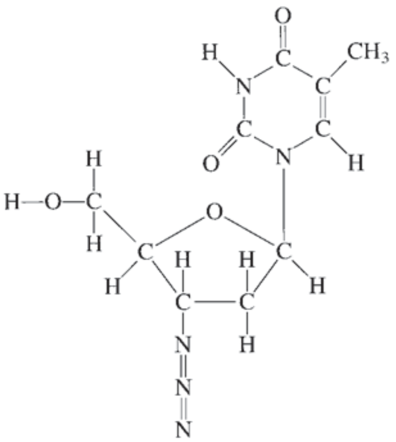
Acrylonitrile



Methyl methacrylate

Complete the Lewis structures, showing all lone pairs. Give approximate values for bond angles *a* through *f*. Give the hybridization of all carbon atoms. In acrylonitrile, how many of the atoms in the molecule lie in the same plane? How many σ bonds and how many π bonds are there in methyl methacrylate and acrylonitrile?

33. 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.



a. How many carbon atoms are sp^3 hybridized?

b. How many carbon atoms are sp^2 hybridized?

c. Which atom is *sp* hybridized?

d. How many σ bonds are in the molecule?

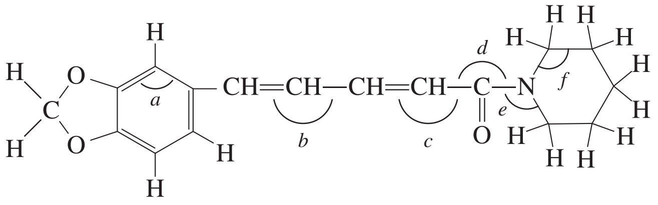
e. How many π bonds are in the molecule?

f. What is the N—N—N bond angle in the azide (—N_3) group?

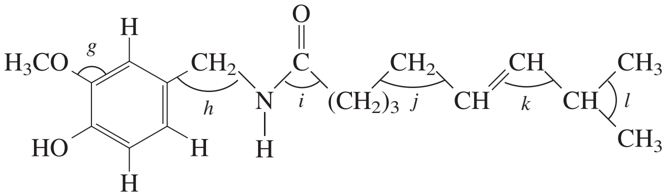
g. What is the H—O—C bond angle in the side group attached to the five-membered ring?

h. What is the hybridization of the oxygen atom in the —CH_2OH group?

34. Hot and spicy foods contain molecules that stimulate pain-detecting nerve endings. Two such molecules are piperine and capsaicin:



Piperine



Capsaicin

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*, sp^2, and sp^3 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

35. Which of the following are predicted by the molecular orbital model to be stable diatomic species?

a. H_2^+, H_2, H_2^-, H_2^{2-}

b. He_2^{2+}, He_2^+, He_2

36. Which of the following are predicted by the molecular orbital model to be stable diatomic species?

a. N_2^{2-}, O_2^{2-}, F_2^{2-} **b.** Be_2, B_2, Ne_2

37. Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic?

a. Li_2 **b.** C_2 **c.** S_2

38. Consider the following electron configuration:

$$(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^4$$

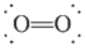
Give four species that, in theory, would have this electron configuration

39. Using molecular orbital theory, explain why the removal of one electron in O_2 strengthens bonding, while the removal of one electron in N_2 weakens bonding.

40. Using the molecular orbital model to describe the bonding in F_2^+, F_2, and F_2^-, predict the bond orders and the relative bond lengths for these three species. How many unpaired electrons are present in each species?

41. Which charge(s) for the N_2 molecule would give a bond order of 2.5?

42. A Lewis structure obeying the octet rule can be drawn for O_2 as follows:



Use the molecular orbital energy-level diagram for O_2 to show that the above Lewis structure corresponds to an excited state.

43. 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.** CO^{2+}

44. 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. NO^+ **b.** NO **c.** NO^-

45. In which of the following diatomic molecules would the bond strength be expected to weaken as an electron is removed to form the positive charged ion?

a. H_2 **c.** C_2^{2-}
b. B_2 **d.** OF

46. 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.

CN or NO
O_2^{2+} or N_2^{2+}

47. Show how two 2*p* atomic orbitals can combine to form a σ or a π molecular orbital.

48. Show how a hydrogen 1*s* atomic orbital and a fluorine 2*p* atomic orbital overlap to form bonding and antibonding molecular orbitals in the hydrogen fluoride molecule. Are these molecular orbitals σ or π molecular orbitals?

49. Use Figs. 9.43 and 9.44 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 2*p* character, greater hydrogen 1*s* character, or an equal contribution from both? Why?

c. Answer the previous two questions for the antibonding molecular orbital in HF.

50. 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 p_z orbital from oxygen with the higher-energy 1*s* orbital of hydrogen (the O—H bond lies along the *z*-axis).

a. Which of the two molecular orbitals will have the greater hydrogen 1*s* character?

b. Can the $2p_x$ orbital of oxygen form molecular orbitals with the 1*s* orbital of hydrogen? Explain.

c. Knowing that only the 2*p* orbitals of oxygen will interact significantly with the 1*s* 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.

51. Describe the bonding in the O_3 molecule and the NO_2^- ion using the localized electron model. How would the molecular orbital model describe the π bonding in these two species?

52. Describe the bonding in the CO_3^{2-} ion using the localized electron model. How would the molecular orbital model describe the π bonding in this species?

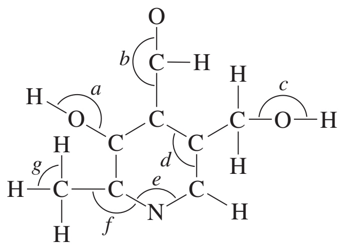
Additional Exercises

53. 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. XeO_3 **d.** $XeOF_2$
b. XeO_4 **e.** XeO_3F_2
c. $XeOF_4$

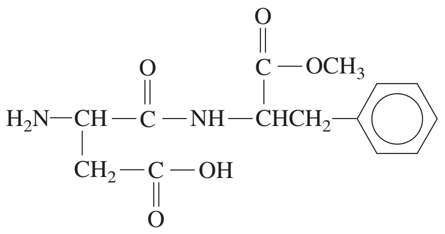
54. $FClO_2$ and F_3ClO can both gain a fluoride ion to form stable anions. F_3ClO and F_3ClO_2 will both lose a fluoride ion to form stable cations. Draw the Lewis structures and describe the hybrid orbitals used by chlorine in these ions.

55. Vitamin B_6 is an organic compound whose deficiency in the human body can cause apathy, irritability, and an increased susceptibility to infections. Below is an incomplete Lewis structure for vitamin B_6. Complete the Lewis structure and answer the following questions. *Hint:* Vitamin B_6 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.



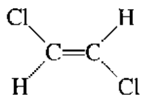
- **a.** How many σ bonds and π bonds exist in vitamin B_6?
- **b.** Give approximate values for the bond angles marked *a* through *g* in the structure.
- **c.** How many carbon atoms are sp^2 hybridized?
- **d.** How many carbon, oxygen, and nitrogen atoms are sp^3 hybridized?
- **e.** Does vitamin B_6 exhibit delocalized π bonding? Explain.

56. Aspartame is an artificial sweetener marketed under the name Nutra-Sweet. A partial Lewis structure for aspartame is shown below.

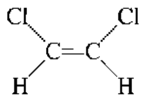


Note that the six-sided ring is shorthand notation for a benzene ring ($—C_6H_5$). Benzene is discussed in Section 9.5. Complete the Lewis structure for aspartame. How many C and N atoms exhibit sp^2 hybridization? How many C and O atoms exhibit sp^3 hybridization? How many σ and π bonds are in aspartame? Aspartame is an organic compound and the Lewis structure follows the guidelines outlined in Exercise 55.

57. Using bond energies from Table 8.4, estimate the barrier to rotation about a carbon–carbon double bond. To do this, consider what must happen to go from

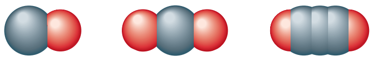


to



in terms of making and breaking chemical bonds; that is, what must happen in terms of the π bond?

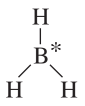
58. The three most stable oxides of carbon are carbon monoxide (CO), carbon dioxide (CO_2), and carbon suboxide (C_3O_2). The space-filling models for these three compounds are



For each oxide, draw the Lewis structure, predict the molecular structure, and describe the bonding (in terms of the hybrid orbitals for the carbon atoms).

59. Complete the Lewis structures of the following molecules. Predict the molecular structure, polarity, bond angles, and hybrid orbitals used by the atoms marked by asterisks for each molecule.

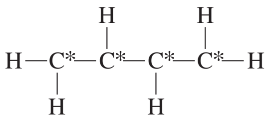
- **a.** BH_3



- **b.** N_2F_2

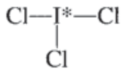
F—N*—N*—F

- **c.** C_4H_6



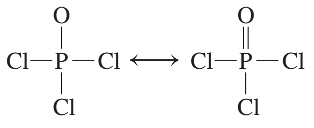
$H-\underset{H}{C^*}-\overset{H}{C^*}-\underset{H}{C^*}-\overset{H}{C^*}-H$

- **d.** ICl_3



$Cl-\underset{Cl}{I^*}-Cl$

60. Complete the following resonance structures for $POCl_3$.



$$Cl-\overset{O}{\underset{Cl}{P}}-Cl \longleftrightarrow Cl-\overset{\overset{O}{\|}}{\underset{Cl}{P}}-Cl$$

(A) (B)

- **a.** Would you predict the same molecular structure from each resonance structure?
- **b.** What is the hybridization of P in each structure?
- **c.** What orbitals can the P atom use to form the π bond in structure B?
- **d.** Which resonance structure would be favored on the basis of formal charges?

61. The N_2O molecule is linear and polar.

- **a.** On the basis of this experimental evidence, which arrangement, NNO or NON, is correct? Explain your answer.
- **b.** On the basis of your answer to part a, write the Lewis structure of N_2O (including resonance forms). Give the formal charge on each atom and the hybridization of the central atom.
- **c.** How would the multiple bonding in $:N\equiv N-\underset{..}{\ddot{O}}:$ be described in terms of orbitals?

62. 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.

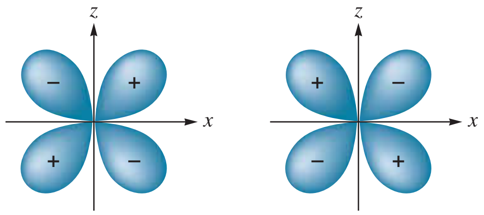
63. Describe the bonding in the first excited state of N_2 (the one closest in energy to the ground state) using the molecular orbital model. What differences do you expect in the properties of the molecule in the ground state as compared to the first excited state? (An excited state of a molecule corresponds to an electron arrangement other than that giving the lowest possible energy.)

64. Acetylene (C_2H_2) can be produced from the reaction of calcium carbide (CaC_2) with water. Use both the localized electron and molecular orbital models to describe the bonding in the acetylide anion (C_2^{2-}).

65. Using an MO energy-level diagram, would you expect F_2 to have a lower or higher first ionization energy than atomic fluorine? Why?

66. Show how a d_{xz} atomic orbital and a p_z atomic orbital combine to form a bonding molecular orbital. Assume the *x*-axis is the internuclear axis. Is a σ or a π molecular orbital formed? Explain.

67. What type of molecular orbital would result from the in phase combination of two d_{xz} atomic orbitals shown below? Assume the x-axis is the internuclear axis.

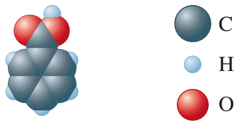


68. Consider three molecules: A, B, and C. Molecule A has a hybridization of sp^3. Molecule B has two more effective pairs (electron pairs around the central atom) than molecule A. Molecule C consists of two σ bonds and two π bonds. Give the molecular structure, hybridization, bond angles, and an example for each molecule.

Challenge Problems

69. Consider your Lewis structure for the computer-generated model of caffeine shown in Exercise 130 of Chapter 8. How many C and N atoms are sp^2 hybridized in your Lewis structure for caffeine? How many C and N atoms are sp^3 hybridized? sp hybridized? How many σ and π bonds are in your Lewis structure?

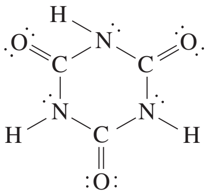
70. The space-filling model for benzoic acid is shown below.

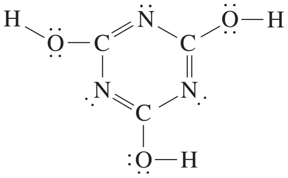


Benzoic acid
($C_6H_5CO_2H$)

Describe the bonding in benzoic acid using the localized electron model combined with the molecular orbital model.

71. Two structures can be drawn by cyanuric acid:



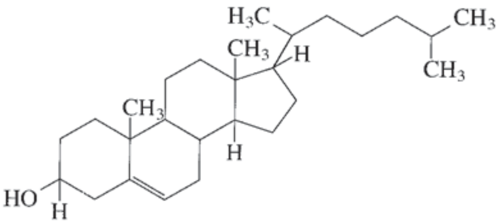


a. Are these two structures the same molecule? Explain.

b. Give the hybridization of the carbon and nitrogen atoms in each structure.

c. Use bond energies (Table 8.4) to predict which form is more stable; that is, which contains the strongest bonds?

72. Cholesterol ($C_{27}H_{46}O$) has the following structure:



In such shorthand structures, each point where lines meet represents a carbon atom and most H atoms are not shown. Draw the complete structure showing all carbon and hydrogen atoms. (There will be four bonds to each carbon atom.) Indicate which carbon atoms use sp^2 or sp^3 hybrid orbitals. Are all carbon atoms in the same plane, as implied by the structure?

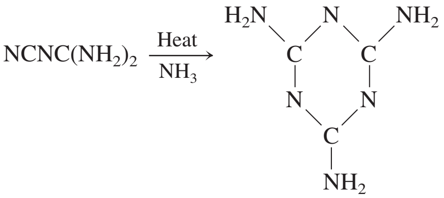
73. Cyanamide (H_2NCN), an important industrial chemical, is produced by the following steps:

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

$$CaNCN \xrightarrow{\text{Acid}} \underset{\text{Cyanamide}}{H_2NCN}$$

Calcium cyanamide (CaNCN) is used as a direct-application fertilizer, weed killer, and cotton defoliant. It is also used to make cyanamide, dicyandiamide, and melamine plastics:

$$H_2NCN \xrightarrow{\text{Acid}} \underset{\text{Dicyandiamide}}{NCNC(NH_2)_2}$$



Melamine
(π bonds
not shown)

a. Write Lewis structures for NCN^{2-}, H_2NCN, dicyandiamide, and melamine, including resonance structures where appropriate.

b. Give the hybridization of the C and N atoms in each species.

c. How many σ bonds and how many π bonds are in each species?

d. Is the ring in melamine planar?

e. There are three different C—N bond distances in dicyandiamide, $NCNC(NH_2)_2$, and the molecule is nonlinear. Of all the resonance structures you drew for this molecule, predict which should be the most important.

74. In Exercise 75 in Chapter 8, the Lewis structures for benzene (C_6H_6) were drawn. Using one of the Lewis structures, estimate ΔH_f° for $C_6H_6(g)$ using bond energies and given that the standard enthalpy of formation of $C(g)$ is 717 kJ/mol. The experimental ΔH_f° value of $C_6H_6(g)$ is 83 kJ/mol. Explain the discrepancy between the experimental value and the calculated ΔH_f° value for $C_6H_6(g)$.

75. A flask containing gaseous N_2 is irradiated with 25-nm light.

a. Using the following information, indicate what species can form in the flask during irradiation.

$$\begin{aligned} N_2(g) &\longrightarrow 2N(g) && \Delta H = 941 \text{ kJ/mol} \\ N_2(g) &\longrightarrow N_2^+(g) + e^- && \Delta H = 1501 \text{ kJ/mol} \\ N(g) &\longrightarrow N^+(g) + e^- && \Delta H = 1402 \text{ kJ/mol} \end{aligned}$$

b. What range of wavelengths will produce atomic nitrogen in the flask but will not produce any ions?

c. Explain why the first ionization energy of N_2 (1501 kJ/mol) is greater than the first ionization energy of atomic nitrogen (1402 kJ/mol).

76. As compared with CO and O_2, CS and S_2 are very unstable molecules. Give an explanation based on the relative abilities of the sulfur and oxygen atoms to form π bonds.

77. Values of measured bond energies may vary greatly depending on the molecule studied. Consider the following reactions:

$$\begin{aligned} NCl_3(g) &\longrightarrow NCl_2(g) + Cl(g) && \Delta H = 375 \text{ kJ/mol} \\ ONCl(g) &\longrightarrow NO(g) + Cl(g) && \Delta H = 158 \text{ kJ/mol} \end{aligned}$$

Rationalize the difference in the values of ΔH for these reactions, even though each reaction appears to involve only the breaking of one N—Cl bond. (*Hint:* Consider the bond order of the NO bond in ONCl and in NO.)

78. Use the MO model to explain the bonding in BeH_2. When constructing the MO energy-level diagram, assume that the Be's 1*s* electrons are not involved in bond formation.

79. 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:

$$\text{M—C}\equiv\text{O}$$

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, Figs. 9.43 and 9.44.) 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.

80. Arrange the following from lowest to highest ionization energy: O, O_2, O_2^-, O_2^+. Explain your answer.

81. Use the MO model to determine which of the following has the smallest ionization energy: N_2, O_2, N_2^{2-}, N_2^-, O_2^+, Explain your answer.

82. Given that the ionization energy of F_2^- is 290 kJ, do the following:

a. Calculate the bond energy of F_2^-. You will need to look up the bond energy of F_2 and ionization energy of F^-.

b. Explain the difference in bond energy between F_2^- and F_2 using MO theory.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

83. As the head engineer of your starship in charge of the warp drive, you notice that the supply of dilithium is critically low. While searching for a replacement fuel, you discover some diboron, B_2.

a. What is the bond order in Li_2 and B_2?

b. How many electrons must be removed from B_2 to make it isoelectronic with Li_2 so that it might be used in the warp drive?

c. The reaction to make B_2 isoelectronic with Li_2 is generalized (where n = number of electrons determined in part b) as follows:

$$B_2 \rightarrow B_2^{n+} + ne^- \qquad \Delta H = 6455 \text{ kJ/mol}$$

How much energy is needed to ionize 1.5 kg of B_2 to the desired isoelectronic species?

84. An unusual category of acids known as superacids, which are defined as any acid stronger than 100% sulfuric acid, can be prepared by seemingly simple reactions similar to the one below. In this example, the reaction of anhydrous HF with SbF_5 produces the superacid $[H_2F]^+[SbF_6]^-$:

$$2HF(l) + SbF_5(l) \rightarrow [H_2F]^+[SbF_6]^-(l)$$

a. What are the molecular structures of all species in this reaction? What are the hybridizations of the central atoms in each species?

b. What mass of $[H_2F]^+[SbF_6]^-$ can be prepared when 2.93 mL of anhydrous HF (density = 0.975 g/mL) and 10.0 mL of SbF_5 (density = 3.10 g/mL) are allowed to react?

85. Determine the molecular structure and hybridization of the central atom X in the polyatomic ion XY_3^+ given the following information: A neutral atom of X contains 36 electrons, and the element Y makes an anion with a 1– charge, which has the electron configuration $1s^22s^22p^6$.

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl7e.**