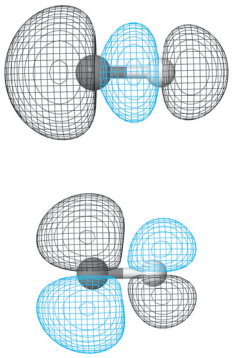
Chapter 5

Molecular Orbitals



Molecular orbital theory uses group theory to describe the bonding in molecules; it complements and extends the introductory bonding models in Chapter 3. In molecular orbital theory the symmetry properties and relative energies of atomic orbitals determine how these orbitals interact to form molecular orbitals. The molecular orbitals are then occupied by the available electrons according to the same rules used for atomic orbitals as described in Sections 2.2.3 and 2.2.4. The total energy of the electrons in the molecular orbitals is compared with the initial total energy of electrons in the atomic orbitals. If the total energy of the electrons in the molecular orbitals is less than in the atomic orbitals, the molecule is stable relative to the separate atoms; if not, the molecule is unstable and predicted not to form. We will first describe the bonding, or lack of it, in the first 10 homonuclear diatomic molecules (H_2 through Ne_2) and then expand the discussion to heteronuclear diatomic molecules and molecules having more than two atoms.

A less rigorous pictorial approach is adequate to describe bonding in many small molecules and can provide clues to more complete descriptions of bonding in larger ones. A more elaborate approach, based on symmetry and employing group theory, is essential to understand orbital interactions in more complex molecular structures. In this chapter, we describe the pictorial approach and develop the symmetry methodology required for complex cases.

5.1 Formation of Molecular Orbitals from Atomic Orbitals

As with atomic orbitals, Schrödinger equations can be written for electrons in molecules. Approximate solutions to these molecular Schrödinger equations can be constructed from **linear combinations of atomic orbitals (LCAO)**, the sums and differences of the atomic wave functions. For diatomic molecules such as H_2, such wave functions have the form

$$\Psi = c_a\psi_a + c_b\psi_b$$

where Ψ is the molecular wave function, ψ_a and ψ_b are atomic wave functions for atoms a and b, and c_a and c_b are adjustable coefficients that quantify the contribution of each atomic orbital to the molecular orbital. The coefficients can be equal or unequal, positive or negative, depending on the individual orbitals and their energies. As the distance between two atoms is decreased, their orbitals overlap, with significant probability for electrons from both atoms being found in the region of overlap. As a result, **molecular orbitals** form. Electrons in bonding molecular orbitals have a high probability of occupying the space between the nuclei; the electrostatic forces between the electrons and the two positive nuclei hold the atoms together.

Three conditions are essential for overlap to lead to bonding. First, the symmetry of the orbitals must be such that regions with the same sign of ψ overlap. Second, the atomic orbital energies must be similar. When the energies differ greatly, the change in the energy of electrons upon formation of molecular orbitals is small, and the net reduction in energy

of the electrons is too small for significant bonding. Third, the distance between the atoms must be short enough to provide good overlap of the orbitals, but not so short that repulsive forces of other electrons or the nuclei interfere. When these three conditions are met, the overall energy of the electrons in the occupied molecular orbitals is lower in energy than the overall energy of the electrons in the original atomic orbitals, and the resulting molecule has a lower total energy than the separated atoms.

5.1.1 Molecular Orbitals from *s* Orbitals

Consider the interactions between two *s* orbitals, as in H_2. For convenience, we label the atoms of a diatomic molecule *a* and *b*, so the atomic orbital wave functions are $\psi(1s_a)$ and $\psi(1s_b)$. We can visualize the two atoms approaching each other, until their electron clouds overlap and merge into larger molecular electron clouds. The resulting molecular orbitals are linear combinations of the atomic orbitals, the sum of the two orbitals and the difference between them.

In general terms	for H_2

$$\Psi(\sigma) = N[c_a\psi(1s_a) + c_b\psi(1s_b)] = \frac{1}{\sqrt{2}}[\psi(1s_a) + \psi(1s_b)](H_a + H_b)$$

$$\text{and } \Psi(\sigma^*) = N[c_a\psi(1s_a) - c_b\psi(1s_b)] = \frac{1}{\sqrt{2}}[\psi(1s_a) - \psi(1s_b)](H_a - H_b)$$

where N = normalizing factor, so $\int \Psi\Psi^* \, d\tau = 1$

c_a and c_b = adjustable coefficients

In this case, the two atomic orbitals are identical, and the coefficients are nearly identical as well.* These orbitals are depicted in **Figure 5.1**. In this diagram, as in all the orbital diagrams in this book (such as Table 2.3 and Figure 2.6), the signs of orbital lobes are indicated by shading or color. Light and dark lobes or lobes of different color indicate opposite signs of Ψ. The choice of positive and negative for specific atomic orbitals is arbitrary; what is important is how they combine to form molecular orbitals. In the diagrams in **Figure 5.2**, the different colors show opposite signs of the wave function, both

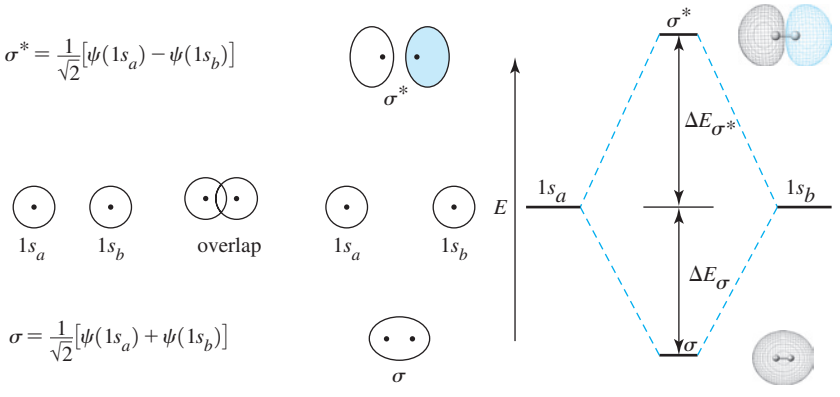


FIGURE 5.1 Molecular Orbitals from Hydrogen 1*s* Orbitals. The σ molecular orbital is a bonding molecular orbital, and has a lower energy than the original atomic orbitals, since this combination of atomic orbitals results in an increased concentration of electrons between the two nuclei. The σ^* orbital is an antibonding orbital at higher energy since this combination of atomic orbitals results in a node with zero electron density between the nuclei.

*More precise calculations show that the coefficients of the σ^* orbital are slightly larger than those for the σ orbital; but for the sake of simplicity, we will generally not focus on this. For identical atoms, we will use $c_a = c_b = 1$ and $N = \frac{1}{\sqrt{2}}$. The difference in coefficients for the σ and σ^* orbitals also results in a larger change in energy (increase) from the atomic to the σ^* molecular orbitals than for the σ orbitals (decrease). In other words, $\Delta E_{\sigma^*} > \Delta E_\sigma$, as shown in Figure 5.1.

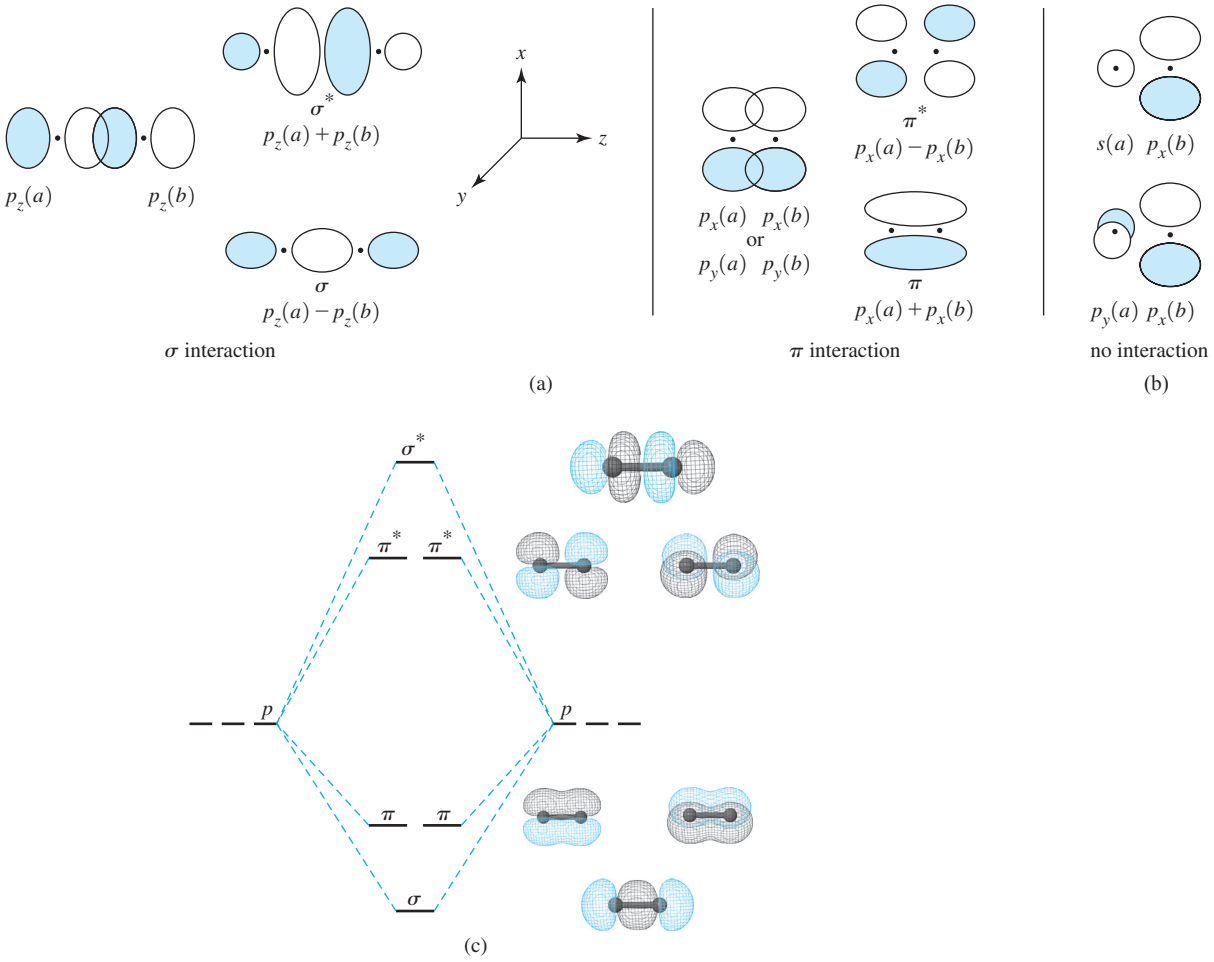


FIGURE 5.2 Interactions of *p* Orbitals. (a) Formation of molecular orbitals. (b) Orbitals that do not form molecular orbitals. (c) Energy-level diagram.

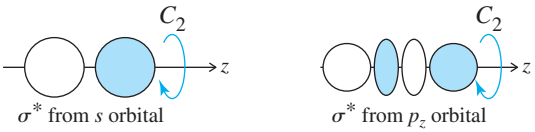
in the schematic sketches on the left of the energy level diagram and in the calculated molecular orbital images on the right.*

Because the σ molecular orbital is the sum of two atomic orbitals, $\frac{1}{\sqrt{2}}[\psi(1s_a) + \psi(1s_b)]$, and results in an increased concentration of electrons between the two nuclei, it is a **bonding molecular orbital** and has a lower energy than the original atomic orbitals. The σ^* molecular orbital is the difference of the two atomic orbitals, $\frac{1}{\sqrt{2}}[\psi(1s_a) - \psi(1s_b)]$. It has a node with zero electron density between the nuclei, due to cancellation of the two wave functions, and a higher energy; it is therefore called an **antibonding orbital**. Electrons in bonding orbitals are concentrated between the nuclei and attract the nuclei, holding them together. Antibonding orbitals have one or more nodes between the nuclei; electrons in these orbitals are destabilized relative to the parent atomic orbitals; the electrons do not have access to the region between the nuclei where they could experience the maximum

*Molecular orbital images in this chapter were prepared using Scigress Explorer Ultra, Version 7.7.0.47, © 2000–2007 Fujitsu Limited, © 1989–2000 Oxford Molecular Ltd.

nuclear attraction. **Nonbonding orbitals** are also possible. The energy of a nonbonding orbital is essentially that of an atomic orbital, either because the orbital on one atom has a symmetry that does not match any orbitals on the other atom or the orbital on one atom has a severe energy mismatch with symmetry-compatible orbitals on the other atom.

The σ (sigma) notation indicates orbitals that are symmetric to rotation about the line connecting the nuclei:



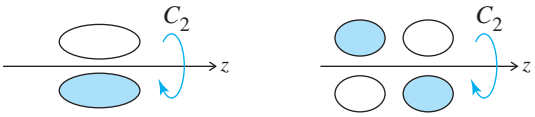
An asterisk is frequently used to indicate antibonding orbitals. Because the bonding, nonbonding, or antibonding nature of a molecular orbital is not always straightforward to assign in larger molecules, we will use the asterisk notation only for those molecules where bonding and antibonding orbital descriptions are unambiguous.

The pattern described for H_2 is the usual model for combining two orbitals: two atomic orbitals combine to form two molecular orbitals, one bonding orbital with a lower energy and one antibonding orbital with a higher energy. Regardless of the number of orbitals, the number of resulting molecular orbitals is always the same as the initial number of atomic orbitals; the total number of orbitals is always conserved.

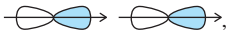
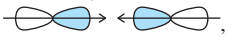
5.1.2 Molecular Orbitals from *p* Orbitals

Molecular orbitals formed from p orbitals are more complex since each p orbital contains separate regions with opposite signs of the wave function. When two orbitals overlap, and the overlapping regions have the same sign, the sum of the two orbitals has an increased electron probability in the overlap region. When two regions of opposite sign overlap, the combination has a decreased electron probability in the overlap region. Figure 5.1 shows this effect for the 1s orbitals of H_2; similar effects result from overlapping lobes of p orbitals with their alternating signs. The interactions of p orbitals are shown in Figure 5.2. For convenience, we will choose a common z axis connecting the nuclei and assign x and y axes as shown in the figure.

When we draw the z axes for the two atoms pointing in the same direction,* the p_z orbitals subtract to form σ and add to form σ^* orbitals, both of which are symmetric to rotation about the z axis, with nodes perpendicular to the line that connects the nuclei. Interactions between p_x and p_y orbitals lead to π and π^* orbitals. The π (pi) notation indicates a change in sign of the wave function with C_2 rotation about the bond axis:



As with the s orbitals, the overlap of two regions with the same sign leads to an increased concentration of electrons, and the overlap of two regions of opposite signs leads to a node of zero electron density. In addition, the nodes of the atomic orbitals become the

*The choice of direction of the z axes is arbitrary. When both are positive in the same direction  , the difference between the p_z orbitals is the bonding combination. When the positive z axes are chosen to point toward each other,  , the sum of the p_z orbitals is the bonding combination. We have chosen to have the p_z orbitals positive in the same direction for consistency with our treatment of triatomic and larger molecules.

nodes of the resulting molecular orbitals. In the π^* antibonding case, four lobes result that are similar in appearance to a d orbital, as in Figure 5.2(c).

The p_x, p_y, and p_z orbital pairs need to be considered separately. Because the z axis was chosen as the internuclear axis, the orbitals derived from the p_z orbitals are symmetric to rotation around the bond axis and are labeled σ and σ^* for the bonding and antibonding orbitals, respectively. Similar combinations of the p_y orbitals form orbitals whose wave functions change sign with C_2 rotation about the bond axis; they are labeled π and π^*. In the same way, the p_x orbitals also form π and π^* orbitals.

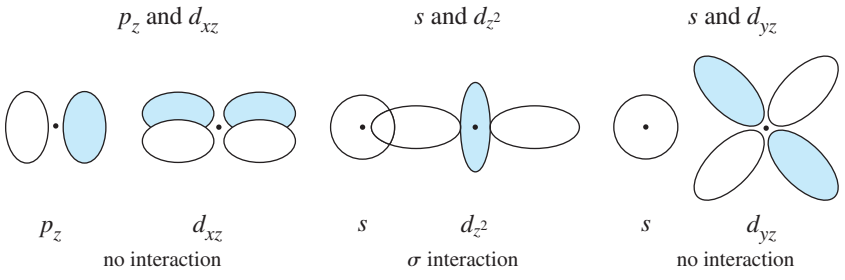
It is common for s and p atomic orbitals on different atoms to be sufficiently similar in energy for their combinations to be considered. However, if the symmetry properties of the orbitals do not match, no combination is possible. For example, when orbitals overlap equally with both the same and opposite signs, as in the $s + p_x$ example in Figure 5.2(b), the bonding and antibonding effects cancel, and no molecular orbital results. If the symmetry of an atomic orbital does not match *any* orbital of the other atom, it is called a nonbonding orbital. Homonuclear diatomic molecules have only bonding and antibonding molecular orbitals; nonbonding orbitals are described further in Sections 5.1.4, 5.2.2, and 5.4.3.

5.1.3 Molecular Orbitals from *d* Orbitals

In the heavier elements, particularly the transition metals, d orbitals can be involved in bonding. **Figure 5.3** shows the possible combinations. When the z axes are collinear, two d_{z^2} orbitals can combine end-on for σ bonding. The d_{xz} and d_{yz} orbitals form π orbitals. When atomic orbitals meet from two parallel planes and combine side to side, as do the $d_{x^2-y^2}$ and d_{xy} orbitals with collinear z axes, they form (δ) delta orbitals (Figure 1.2). (The δ notation indicates sign changes on C_4 rotation about the bond axis.) Sigma orbitals have no nodes that include the line connecting the nuclei, pi orbitals have one node that includes the line connecting the nuclei, and delta orbitals have two nodes that include the line connecting the nuclei. Again, some orbital interactions are forbidden on the basis of symmetry; for example, p_z and d_{xz} have zero net overlap if the z axis is chosen as the bond axis since the p_z would approach the d_{xz} orbital along a d_{xz} node (Example 5.1). It is noteworthy in this case that p_x and d_{xz} would be eligible to interact in a π fashion on the basis of the assigned coordinate system. This example emphasizes the importance of maintaining a consistent coordinate system when assessing orbital interactions.

EXAMPLE 5.1

Sketch the overlap regions of the following combination of orbitals, all with collinear z axes, and classify the interactions.



EXERCISE 5.1 Repeat the process in the preceding example for the following orbital combinations, again using collinear z axes.

p_x and d_{xz} $\quad$ p_z and d_{z^2} $\quad$ s and $d_{x^2-y^2}$

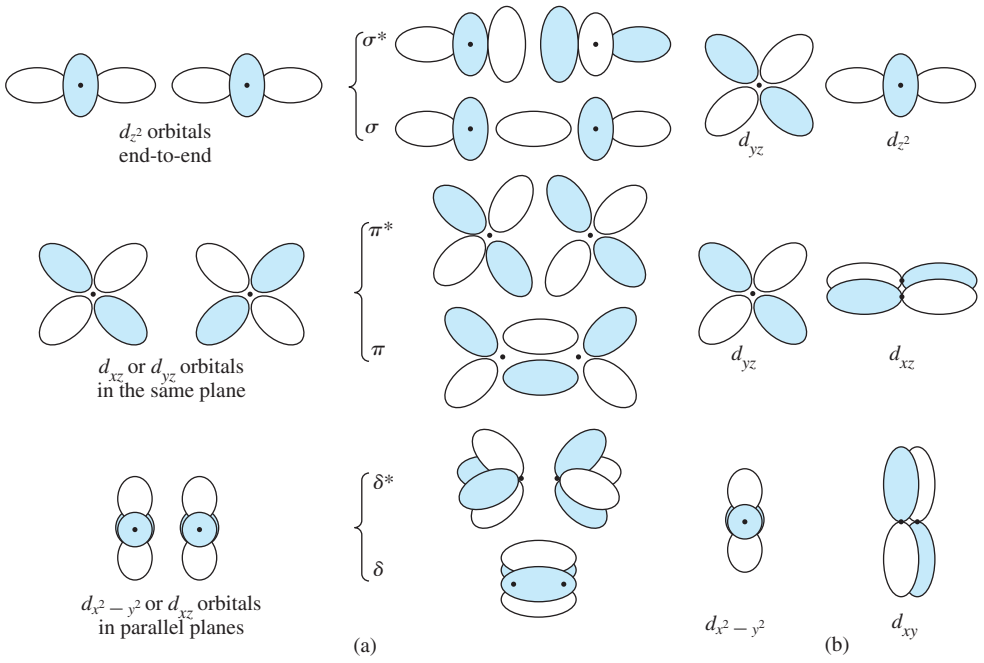


FIGURE 5.3 Interactions of *d* Orbitals. (a) Formation of molecular orbitals. (b) Atomic orbital combinations that do not form molecular orbitals.

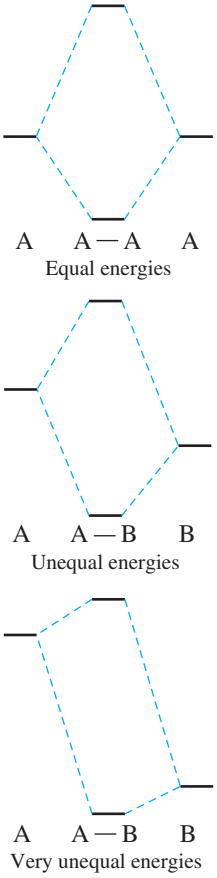


FIGURE 5.4 Energy Match and Molecular Orbital Formation.

5.1.4 Nonbonding Orbitals and Other Factors

As mentioned previously, nonbonding molecular orbitals have energies essentially equal to that of atomic orbitals. These can form in larger molecules, for example when there are three atomic orbitals of the same symmetry and similar energies, a situation that requires the formation of three molecular orbitals. Most commonly, one molecular orbital formed is a low-energy bonding orbital, one is a high-energy antibonding orbital, and one is of intermediate energy and is a nonbonding orbital. Examples will be considered in Section 5.4 and in later chapters.

In addition to symmetry, the second major factor that must be considered in forming molecular orbitals is the relative energy of the atomic orbitals. As shown in **Figure 5.4**, when the interacting atomic orbitals have the same energy, the interaction is strong, and the resulting molecular orbitals have energies well below (bonding) and above (antibonding) that of the original atomic orbitals. When the two atomic orbitals have quite different energies, the interaction is weaker, and the resulting molecular orbitals have energies and shapes closer to the original atomic orbitals. For example, although they have the same symmetry, 1*s* orbitals do not combine significantly with 2*s* orbitals of the other atom in diatomic molecules such as N_2, because their energies are too far apart. The general rule is that the closer the energy match, the stronger the interaction.

5.2 Homonuclear Diatomic Molecules

Because of their simplicity, diatomic molecules provide convenient examples to illustrate how the orbitals of individual atoms interact to form orbitals in molecules. In this section, we will consider **homonuclear** diatomic molecules such as H_2 and O_2; in Section 5.3 we will examine **heteronuclear** diatomics such as CO and HF.

5.2.1 Molecular Orbitals

Although apparently satisfactory Lewis electron-dot structures of N_2, O_2, and F_2 can be drawn, the same is not true with Li_2, Be_2, B_2, and C_2, which violate the octet rule. In addition, the Lewis structure of O_2 predicts a double-bonded, diamagnetic (all electrons paired) molecule (:O=O:), but experiment has shown O_2 to have two unpaired electrons, making it paramagnetic. As we will see, the molecular orbital description predicts this paramagnetism, and is more in agreement with experiment. **Figure 5.5** shows the full set of molecular orbitals for the homonuclear diatomic molecules of the first 10 elements, based on the energies appropriate for O_2. The diagram shows the order of energy levels for the molecular orbitals, assuming significant interactions only between atomic orbitals of identical energy. The energies of the molecular orbitals change in a periodic way with atomic number, since the energies of the interacting atomic orbitals decrease across a period (**Figure 5.7**), but the general order of the molecular orbitals remains similar (with some subtle changes, as will be described in several examples) even for heavier atoms lower in the periodic table. Electrons fill the molecular orbitals according to the same rules that govern the filling of atomic orbitals, filling from lowest to highest energy (aufbau principle), maximum spin

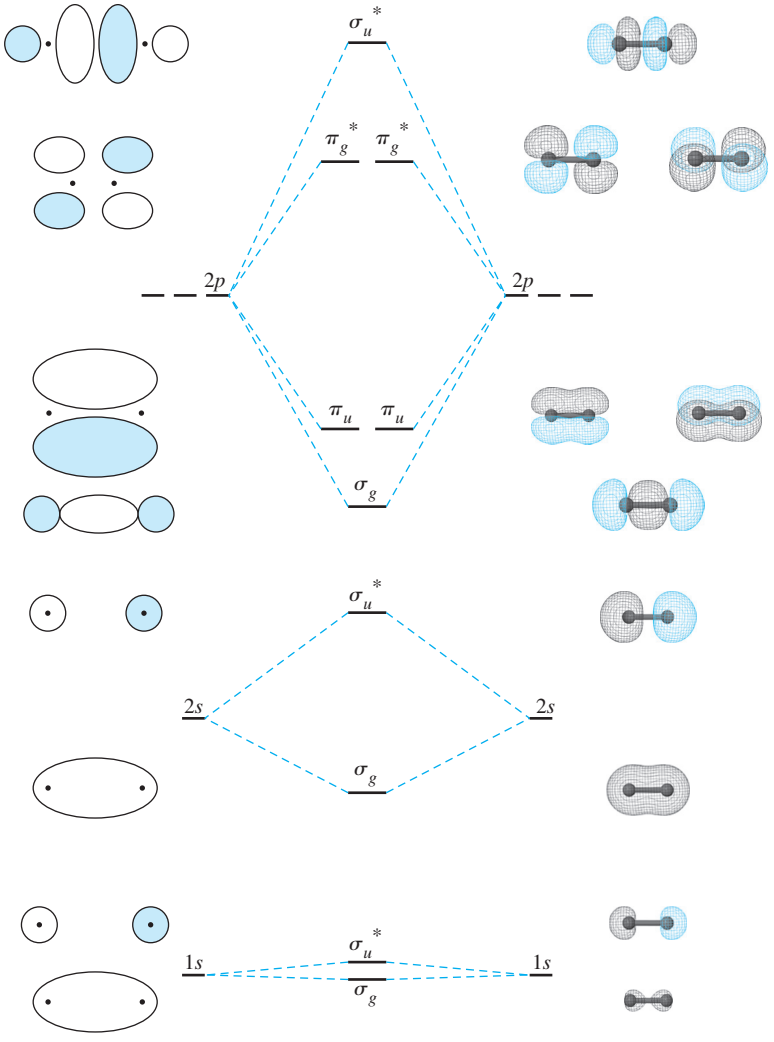


FIGURE 5.5 Molecular Orbitals for the First 10 Elements, Assuming Significant Interactions Only between the Valence Atomic Orbitals of Identical Energy.

multiplicity consistent with the lowest net energy (Hund's rules), and no two electrons with identical quantum numbers (Pauli exclusion principle). The most stable configuration of electrons in the molecular orbitals is always the configuration with minimum energy, and the greatest net stabilization of the electrons.

The overall number of bonding and antibonding electrons determines the number of bonds (bond order):

$$\text{Bond order} = \frac{1}{2}\left[\begin{pmatrix}\text{number of electrons}\\ \text{in bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{number of electrons}\\ \text{in antibonding orbitals}\end{pmatrix}\right]$$

It is generally sufficient to consider only valence electrons. For example, O_2, with 10 electrons in bonding orbitals and 6 electrons in antibonding orbitals, has a bond order of 2, a double bond. Counting only valence electrons, 8 bonding and 4 antibonding, gives the same result. Because the molecular orbitals derived from the 1*s* orbitals have the same number of bonding and antibonding electrons, they have no net effect on the bond order. Generally electrons in atomic orbitals lower in energy than the valence orbitals are considered to reside primarily on the original atoms and to engage only weakly in bonding and antibonding interactions, as shown for the 1*s* orbitals in Figure 5.5; the difference in energy between the σ_g and σ_u^* orbitals is slight. Because such interactions are so weak, we will not include them in other molecular orbital energy level diagrams.

Additional labels describe the orbitals. The subscripts *g* for *gerade*, orbitals symmetric to inversion, and *u* for *ungerade*, orbitals antisymmetric to inversion (those whose signs change on inversion), are commonly used.* The *g* or *u* notation describes the symmetry of the orbitals without a judgment as to their relative energies. Figure 5.5 has examples of both bonding and antibonding orbitals with *g* and *u* designations.

EXAMPLE 5.2

Add a *g* or *u* label to each of the molecular orbitals in the energy-level diagram in Figure 5.2.

From top to bottom, the orbitals are σ_u^*, π_g^*, π_u, and σ_g.

EXERCISE 5.2 Add a *g* or *u* label to each of the molecular orbitals in Figure 5.3(a).

5.2.2 Orbital Mixing

In Figure 5.5, we only considered interactions between atomic orbitals of identical energy. However, atomic orbitals with similar, but unequal, energies can interact if they have appropriate symmetries. We now outline two approaches to analyzing this phenomenon, one in which we first consider the atomic orbitals that contribute most to each molecular orbital before consideration of additional interactions and one in which we consider all atomic orbital interactions permitted by symmetry simultaneously.

Figure 5.6(a) shows the familiar energy levels for a homonuclear diatomic molecule where only interactions between **degenerate** (having the same energy) atomic orbitals are considered. However, when two molecular orbitals of the same symmetry have similar energies, they interact to lower the energy of the lower orbital and raise the energy of the higher orbital. For example, in the homonuclear diatomics, the $\sigma_g(2s)$ and $\sigma_g(2p)$ orbitals both have σ_g symmetry (symmetric to infinite rotation and inversion); these orbitals

*See the end of Section 4.3.3 for more details on symmetry labels.

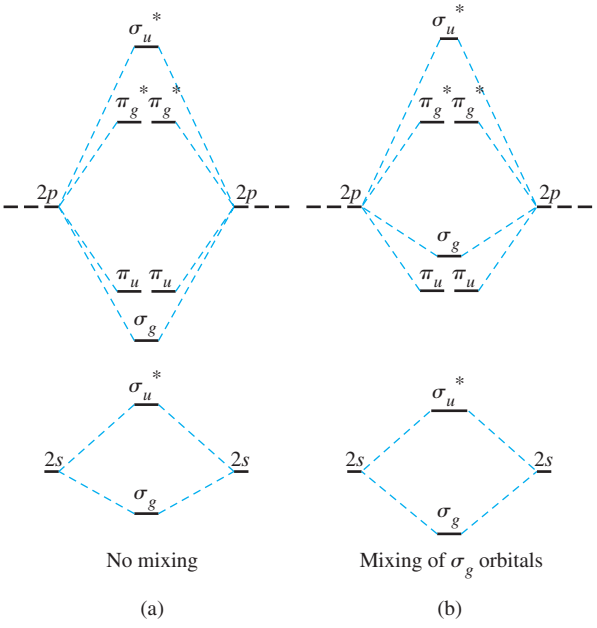


FIGURE 5.6 Interaction between Molecular Orbitals. Mixing molecular orbitals of the same symmetry results in a greater energy difference between the orbitals. The σ orbitals mix strongly; the σ^* orbitals differ more in energy and mix weakly.

interact to lower the energy of the $\sigma_g(2s)$ and to raise the energy of the $\sigma_g(2p)$ as shown in Figure 5.6(b). Similarly, the $\sigma_u^*(2s)$ and $\sigma_u^*(2p)$ orbitals interact to lower the energy of the $\sigma_u^*(2s)$ and to raise the energy of the $\sigma_u^*(2p)$. This phenomenon is called **mixing**, which takes into account that molecular orbitals with similar energies interact if they have appropriate symmetry, a factor ignored in Figure 5.5. When two molecular orbitals of the same symmetry mix, the one with higher energy moves still higher in energy, and the one with lower energy moves lower. Mixing results in additional electron stabilization, and enhances the bonding.

A perhaps more rigorous approach to explain mixing considers that the four σ molecular orbitals (MOs) result from combining the four atomic orbitals (two $2s$ and two $2p_z$) that have similar energies. The resulting molecular orbitals have the following general form, where a and b identify the two atoms, with appropriate normalization constants for each atomic orbital:

$$\Psi = c_1\psi(2s_a) \pm c_2\psi(2s_b) \pm c_3\psi(2p_a) \pm c_4\psi(2p_b)$$

For homonuclear diatomic molecules, $c_1 = c_2$ and $c_3 = c_4$ in each of the four MOs. The lowest energy MO has larger values of c_1 and c_2, the highest has larger values of c_3 and c_4, and the two intermediate MOs have intermediate values for all four coefficients. The symmetry of these four orbitals is the same as those without mixing, but their shapes are changed somewhat by having significant contributions from both the s and p atomic orbitals. In addition, the energies are shifted relative to their placement if the upper two exhibited nearly exclusive contribution from $2p_z$ while the lower two exclusive contribution from $2s$, as shown in Figure 5.6.

It is clear that s-p mixing often has a detectable influence on molecular orbital energies. For example, in early second period homonuclear diatomics (Li_2 to N_2), the σ_g orbital formed from $2p_z$ orbitals is higher in energy than the π_u orbitals formed from the $2p_x$ and $2p_y$ orbitals. This is an inverted order from that expected without s-p mixing (Figure 5.6). For B_2 and C_2, s-p mixing affects their magnetic properties. Mixing also changes the bonding–antibonding nature of some orbitals. The orbitals with intermediate energies may,

on the basis of *s-p* mixing, gain either a slightly bonding or slightly antibonding character and contribute in minor ways to the bonding. Each orbital must be considered separately on the basis of its energy and electron distribution.

5.2.3 Diatomic Molecules of the First and Second Periods

Before proceeding with examples of homonuclear diatomic molecules, we must define two types of magnetic behavior, **paramagnetic** and **diamagnetic**. Paramagnetic compounds are attracted by an external magnetic field. This attraction is a consequence of one or more unpaired electrons behaving as tiny magnets. Diamagnetic compounds, on the other hand, have no unpaired electrons and are repelled slightly by magnetic fields. (An experimental measure of the magnetism of compounds is the **magnetic moment**, a concept developed in Chapter 10 in the discussion of the magnetic properties of coordination compounds.)

H_2, He_2, and the homonuclear diatomic species shown in **Figure 5.7** will now be discussed. As previously discussed, atomic orbital energies decrease across a row in the Periodic Table as the increasing effective nuclear charge attracts the electrons more strongly. The result is that the molecular orbital energies for the corresponding homonuclear

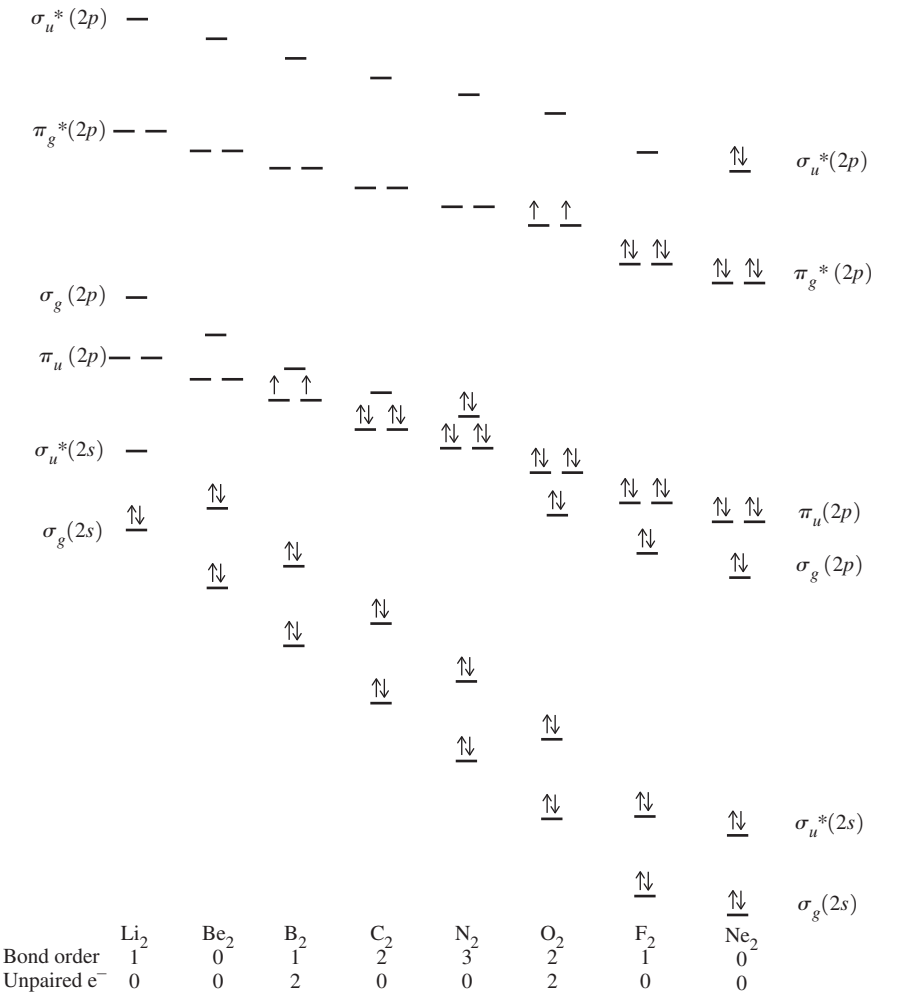


FIGURE 5.7 Energy Levels of the Homonuclear Diatomics of the Second Period.

diatomics also decrease across the row. As shown in Figure 5.7, this decrease in energy is larger for σ orbitals than for π orbitals, due to the greater overlap of the atomic orbitals that participate in σ interactions.

$H_2[\sigma_g^2(1s)]$

This is the simplest diatomic molecule. The MO description (Figure 5.1) shows a single σ orbital containing one electron pair; the bond order is 1, representing a single bond. The ionic species H_2^+, with a single electron in the a σ orbital and a bond order of $\frac{1}{2}$, has been detected in low-pressure gas-discharge systems. As expected, H_2^+ has a weaker bond than H_2 and therefore a considerably longer bond distance than H_2 (105.2 pm vs. 74.1 pm).

$He_2[\sigma_g^2\sigma_u^{*2}(1s)]$

The molecular orbital description of He_2 predicts two electrons in a bonding orbital and two in an antibonding orbital, with a bond order of zero—in other words, no bond. This is what is observed experimentally. The noble gas He has no significant tendency to form diatomic molecules and, like the other noble gases, exists in the form of free atoms. He_2 has been detected only in very low-pressure and low-temperature molecular beams. It has an extremely low binding energy,[1] approximately 0.01 J/mol; for comparison, H_2 has a bond energy of 436 kJ/mol.

$Li_2[\sigma_g^2(2s)]$

As shown in Figure 5.7, the MO model predicts a single Li—Li bond in Li_2, in agreement with gas-phase observations of the molecule.

$Be_2[\sigma_g^2\sigma_u^{*2}(2p)]$

Be_2 has the same number of antibonding and bonding electrons and consequently a bond order of zero. Hence, like He_2, Be_2 is an unstable species.*

$B_2[\pi_u^1\pi_u^1(2p)]$

Here is an example in which the MO model has a distinct advantage over the Lewis dot model. B_2 is a gas-phase species; solid boron exists in several forms with complex bonding, primarily involving B_{12} icosahedra.

B_2 is paramagnetic. This behavior can be explained if its two highest energy electrons occupy separate π orbitals, as shown. The Lewis dot model cannot account for the paramagnetic behavior of this molecule.

The energy-level shift caused by *s*-*p* mixing is vital to understand the bonding in B_2. In the absence of mixing, the $\sigma_g(2p)$ orbital would be expected to be lower in energy than the $\pi_u(2p)$ orbitals, and the molecule would likely be diamagnetic.** However, mixing of the $\sigma_g(2s)$ orbital with the $\sigma_g(2p)$ orbital (Figure 5.6b) lowers the energy of the $\sigma_g(2s)$ orbital and increases the energy of the $\sigma_g(2p)$ orbital to a higher level than the π orbitals, giving the order of energies shown in Figure 5.7. As a result, the last two electrons are unpaired in the degenerate π orbitals, as required by Hund's rule of maximum multiplicity, and the molecule is paramagnetic. Overall, the bond order is one, even though the two π electrons are in different orbitals.

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*Be_2 is calculated to have a very weak bond when effects of higher energy, unoccupied orbitals are taken into account. See A. Krapp, F. M. Bickelhaupt, and G. Frenking, *Chem. Eur. J.*, **2006**, *12*, 9196.

**This presumes that the energy difference between $\sigma_g(2p)$ and $\pi_u(2p)$ would be greater than Π_c (Section 2.2.3), a reliable expectation for molecular orbitals discussed in this chapter, but sometimes not true in transition metal complexes, as discussed in Chapter 10.

$C_2[\pi_u^2\pi_u^2(2p)]$

The MO model of C_2 predicts a doubly bonded molecule, with all electrons paired, but with both **highest occupied molecular orbitals (HOMOs)** having π symmetry. C_2 is unusual because it has two π bonds and no σ bond. Although C_2 is a rarely encountered allotrope of carbon (carbon is significantly more stable as diamond, graphite, fullerenes and other polyatomic forms described in Chapter 8), the acetylide ion, C_2^{2-}, is well known, particularly in compounds with alkali metals, alkaline earths, and lanthanides. According to the molecular orbital model, C_2^{2-} should have a bond order of 3 (configuration $\pi_u^2\pi_u^2\sigma_g^2$). This is supported by the similar C—C distances in acetylene and calcium carbide (acetylide)[2,3].

C—C Distance	(pm)
C=C (gas phase)	124.2
H—C≡C—H	120.5
CaC_2	119.1

$N_2[\pi_u^2\pi_u^2\sigma_g^2(2p)]$

N_2 has a triple bond according to both the Lewis and the molecular orbital models. This agrees with its very short N—N distance (109.8 pm) and extremely high bond-dissociation energy (942 kJ/mol). Atomic orbitals decrease in energy with increasing nuclear charge Z as discussed in Section 2.2.4, and further described in Section 5.3.1; as the effective nuclear charge increases, the energies of all orbitals are reduced. The varying shielding abilities of electrons in different orbitals and electron–electron interactions cause the difference between the 2*s* and 2*p* energies to increase as Z increases, from 5.7 eV for boron to 8.8 eV for carbon and 12.4 eV for nitrogen. (These energies are given in Table 5.2 in Section 5.3.1.) The radial probability functions (Figure 2.7) indicate that 2*s* electrons have a higher probability of being close to the nucleus relative to 2*p* electrons, rendering the 2*s* electrons more susceptible to the increasing nuclear charge as Z increases. As a result, the $\sigma_g(2s)$ and $\sigma_g(2p)$ levels of N_2 interact (mix) less than the corresponding B_2 and C_2 levels, and the N_2 $\sigma_g(2p)$ and $\pi_u(2p)$ are very close in energy. The order of energies of these orbitals has been controversial and will be discussed in more detail in Section 5.2.4.

$O_2[\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*1}\pi_g^{*1}(2p)]$

O_2 is paramagnetic. As for B_2, this property cannot be explained by the Lewis dot structure :O=O:, but it is evident from the MO picture, which assigns two electrons to the degenerate π_g^* orbitals. The paramagnetism can be demonstrated by pouring liquid O_2 between the poles of a strong magnet; O_2 will be held between the pole faces until it evaporates. Several charged forms of diatomic oxygen are known, including O_2^+, O_2^-, and O_2^{2-}. The internuclear O—O distance can be conveniently correlated with the bond order predicted by the molecular orbital model, as shown in the following table.*

	Bond Order	Internuclear Distance (pm)
O_2^+ (dioxygenyl)	2.5	111.6
O_2 (dioxygen)	2.0	120.8
O_2^- (superoxide)	1.5	135
O_2^{2-} (peroxide)	1.0	150.4

Oxygen–oxygen distances in O_2^- and O_2^{2-} are influenced by the cation. This influence is especially strong in the case of O_2^{2-} and is one factor in its unusually long bond distance, which should be considered approximate. The disproportionation of KO_2 to O_2 and O_2^{2-} in the presence of hexacarboximide cryptand (similar molecules will be discussed in Chapter 8) results in encapsulation of O_2^{2-} in the cryptand via hydrogen-bonding interactions. This O—O peroxide distance was determined as 150.4(2) pm.[4]

*See Table 5.1 for references.

The extent of mixing is not sufficient in O_2 to push the $\sigma_g(2p)$ orbital to higher energy than the $\pi_u(2p)$ orbitals. The order of molecular orbitals shown is consistent with the photoelectron spectrum, discussed in Section 5.2.4.

$F_2[\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}(2p)]$

The MO model of F_2 shows a diamagnetic molecule having a single fluorine–fluorine bond, in agreement with experimental data.

The bond order in N_2, O_2, and F_2 is the same whether or not mixing is taken into account, but the order of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals is different in N_2 than in O_2 and F_2. As stated previously and further described in Section 5.3.1, the energy difference between the 2*s* and 2*p* orbitals of the second row main group elements increases with increasing *Z*, from 5.7 eV in boron to 21.5 eV in fluorine. As this difference increases, the *s*-*p* interaction (mixing) decreases, and the "normal" order of molecular orbitals returns in O_2 and F_2. The higher $\sigma_g(2p)$ orbital (relative to $\pi_u(2p)$) occurs in many heteronuclear diatomic molecules, such as CO, described in Section 5.3.1.

Ne_2

All the molecular orbitals are filled, there are equal numbers of bonding and antibonding electrons, and the bond order is therefore zero. The Ne_2 molecule is a transient species, if it exists at all.

One triumph of molecular orbital theory is its prediction of two unpaired electrons for O_2. Oxygen had long been known to be paramagnetic, but early explanations for this phenomenon were unsatisfactory. For example, a special "three-electron bond"[5] was proposed. The molecular orbital description directly explains why two unpaired electrons are required. In other cases, experimental observations (paramagnetic B_2, diamagnetic C_2) require a shift of orbital energies, raising σ_g above π_u, but they do not require major modifications of the model.

Bond Lengths in Homonuclear Diatomic Molecules

Figure 5.8 shows the variation of bond distance with the number of valence electrons in second-period *p*-block homonuclear diatomic molecules having 6 to 14 valence electrons. Beginning at the left, as the number of electrons increases the number in bonding orbitals also increases; the bond strength becomes greater, and the bond length becomes shorter.

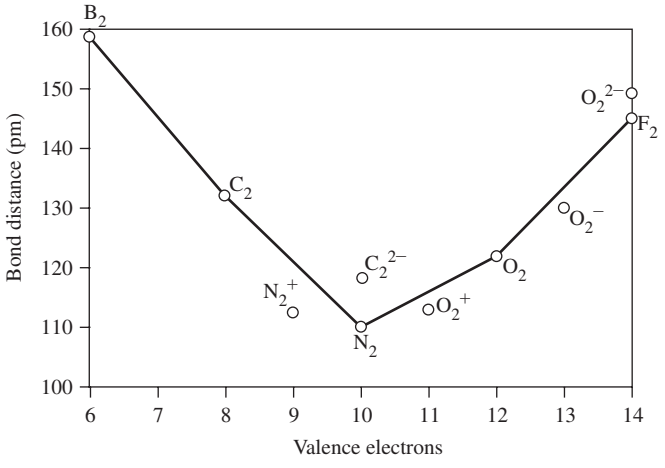


FIGURE 5.8 Bond Distances of Homonuclear Diatomic Molecules and Ions.

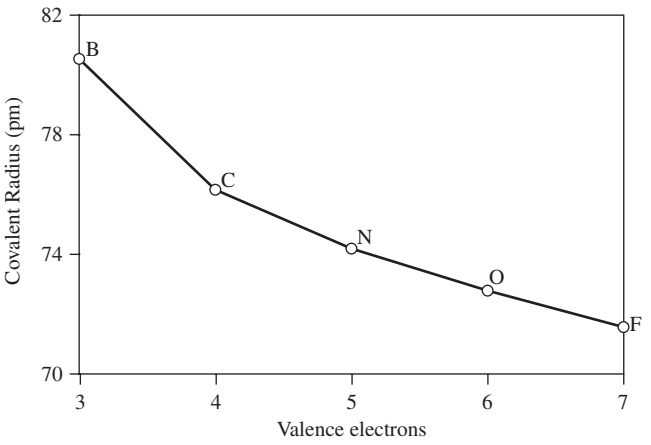


FIGURE 5.9 Covalent Radii of Second-Period Atoms.

This continues up to 10 valence electrons in N_2, where the trend reverses, because the additional electrons occupy antibonding orbitals. The ions N_2^+, O_2^+, O_2^-, and O_2^{2-} are also shown in the figure and follow a similar trend.

The minimum in Figure 5.8 occurs even though the radii of the free atoms decrease steadily from B to F. **Figure 5.9** shows the change in covalent radius for these atoms (defined for single bonds), decreasing as the number of valence electrons increases, primarily because the increasing nuclear charge pulls the electrons closer to the nucleus. For the elements boron through nitrogen, the trends shown in Figures 5.8 and 5.9 are similar: as the covalent radius of the atom decreases, the bond distance of the matching diatomic molecule also decreases. However, beyond nitrogen these trends diverge. Even though the covalent radii of the free atoms continue to decrease (N > O > F), the bond distances in their diatomic molecules increase ($N_2 < O_2 < F_2$) with the increasing population of antibonding orbitals. In general the bond order is the more important factor, overriding the covalent radii of the component atoms. Bond lengths of homonuclear and heteronuclear diatomic species are given in **Table 5.1**.

5.2.4 Photoelectron Spectroscopy

In addition to data on bond distances and energies, specific information about the energies of electrons in orbitals can be determined from photoelectron spectroscopy.[6] In this technique, ultraviolet (UV) light or X-rays eject electrons from molecules:

$$O_2 + h\nu(\text{photons}) \rightarrow O_2^+ + e^-$$

The kinetic energy of the expelled electrons can be measured; the difference between the energy of the incident photons and this kinetic energy equals the ionization energy (binding energy) of the electron:

$$\text{Ionization energy} = h\nu(\text{energy of photons}) - \text{kinetic energy of the expelled electron}$$

UV light removes outer electrons; X-rays are more energetic and can remove inner electrons. **Figures 5.10** and **5.11** show photoelectron spectra for N_2 and O_2, respectively, and the relative energies of the highest occupied orbitals of the ions. The lower energy peaks (at the top in the figure) are for the higher energy orbitals (less energy required to remove electrons). If the energy levels of the ionized molecule are assumed to be essentially the same as those of

TABLE 5.1 Bond Distances in Diatomic Species[a]

Formula	Valence Electrons	Internuclear Distance (pm)
H_2^+	1	105.2
H_2	2	74.1
B_2	6	159.0
C_2	8	124.2
C_2^{2-}	10	119.1[b]
N_2^+	9	111.6
N_2	10	109.8
O_2^+	11	111.6
O_2	12	120.8
O_2^-	13	135
O_2^{2-}	14	150.4[c]
F_2	14	141.2
CN	9	117.2
CN^-	10	115.9[d]
CO	10	112.8
NO^+	10	106.3
NO	11	115.1
NO^-	12	126.7

[a]Except as noted in footnotes, data are from K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*,Van Nostrand Reinhold Company, New York, 1979. Additional data on diatomic species can be found in R. Janoscheck, *Pure Appl. Chem.*, **2001**, *73*, 1521.
[b]Distance in CaC_2 in M. J. Atoji, *J. Chem. Phys.*, **1961**, *35*, 1950.
[c]Reference 4.
[d]Distance in low-temperature orthorhombic phase of NaCN in T. Schräder, A. Loidl, T. Vogt, *Phys. Rev. B*, **1989**, *39*, 6186.

the uncharged molecule,* the observed energies can be directly correlated with the molecular orbital energies. The levels in the N_2 spectrum are more closely spaced than those in the O_2 spectrum, and some theoretical calculations have disagreed about the order of the highest occupied orbitals in N_2. Stowasser and Hoffmann[7] have compared different calculation methods and showed that the different order of energy levels was simply a function of the calculation method; the methods favored by the authors agree with the experimental results, with σ_g above π_u.

The photoelectron spectrum shows the π_u lower than σ_g in N_2 (Figure 5.10). In addition to the ionization energies of the orbitals, the spectrum provides evidence of the quantized electronic and vibrational energy levels of the molecule. Because vibrational energy levels

*This perspective on photoelectron spectroscopy is oversimplified; a rigorous treatment of this technique is beyond the scope of this text. The interpretation of photoelectron specta is challenging since these spectra provide differences between energy levels of the ground electronic state in the neutral molecule and energy levels in the ground and excited electronic states of the ionized molecule. Rigorous interpretation of photoelectron spectra requires consideration of how the energy levels and orbital shapes vary between the neutral and ionized species.

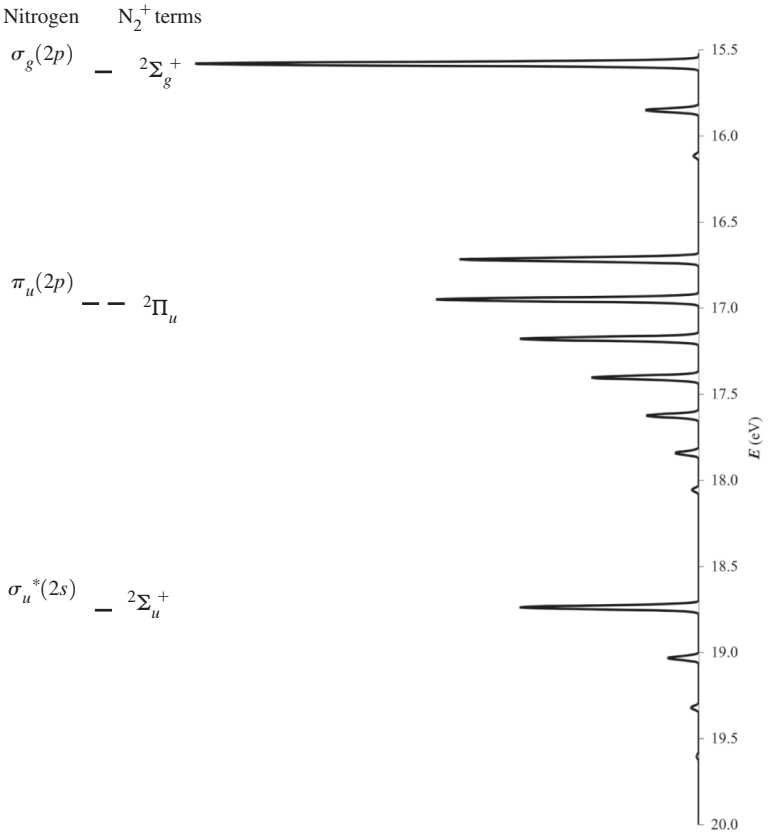


FIGURE 5.10 Photoelectron Spectrum and Molecular Orbital Energy Levels of N_2. Spectrum simulated by Susan Green using FCF program available at R. L. Lord, L. Davis, E. L. Millam, E. Brown, C. Offerman, P. Wray, S. M. E. Green, *J. Chem. Educ.*, **2008**, *85*, 1672 and data from "Constants of Diatomic Molecules" by K.P. Huber and G. Herzberg (data prepared by J.W. Gallagher and R.D. Johnson, III) in **NIST Chemistry WebBook, NIST Standard Reference Database Number 69,** Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved July 22, 2012).

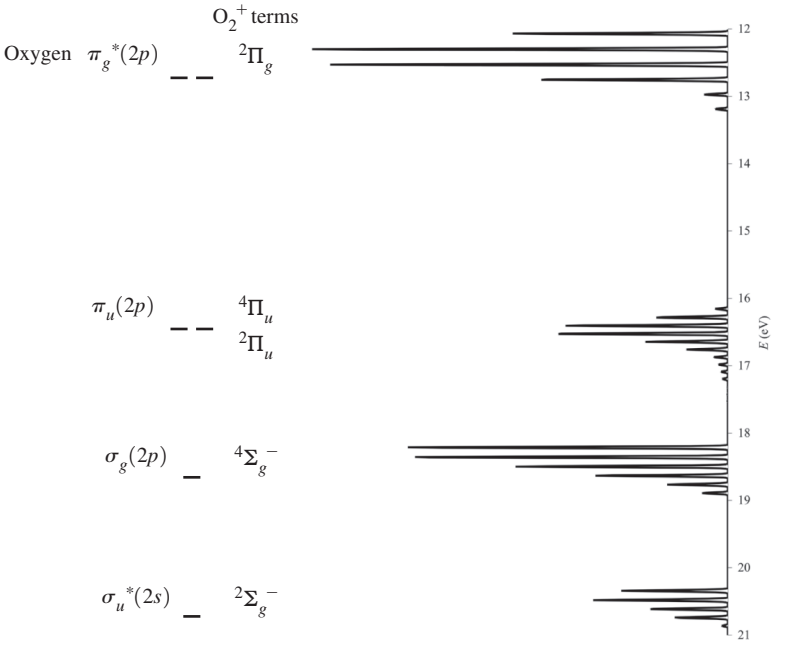


FIGURE 5.11 Photoelectron Spectrum and Molecular Orbital Energy Levels of O_2. Spectrum simulated by Susan Green using FCF program available at R. L. Lord, L. Davis, E. L. Millam, E. Brown, C. Offerman, P. Wray, S. M. E. Green, *J. Chem. Educ.*, **2008**, *85*, 1672 and data from "Constants of Diatomic Molecules" by K.P. Huber and G. Herzberg (data prepared by J.W. Gallagher and R.D. Johnson, III) in **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved July 22, 2012).

are much more closely spaced than electronic levels, any collection of molecules will include molecules with different vibrational energies even when the molecules are in the ground electronic state. Therefore, transitions from electronic levels can originate from different vibrational levels, resulting in multiple peaks for a single electronic transition. Orbitals that are strongly involved in bonding have vibrational fine structure (multiple peaks); orbitals that are less involved in bonding have only a few peaks at each energy level.[8] The N_2 spectrum indicates that the π_u orbitals are more involved in the bonding than either of the σ orbitals. The CO photoelectron spectrum (**Figure 5.13**) has a similar pattern. The O_2 photoelectron spectrum (Figure 5.11) has much more vibrational fine structure for all the energy levels, with the π_u levels again more involved in bonding than the other orbitals. The photoelectron spectra of O_2 and of CO show the expected order of energy levels for these molecules.[8]

5.3 Heteronuclear Diatomic Molecules

The homonuclear diatomic molecules discussed Section 5.2 are nonpolar molecules. The electron density within the occupied molecular orbitals is evenly distributed over each atom. A discussion of heteronuclear diatomic molecules provides an introduction into how molecular orbital theory treats molecules that are polar, with an unequal distribution of the electron density in the occupied orbitals.

5.3.1 Polar Bonds

The application of molecular orbital theory to heteronuclear diatomic molecules is similar to its application to homonuclear diatomics, but the different nuclear charges of the atoms require that interactions occur between orbitals of unequal energies and shifts the resulting molecular orbital energies. In dealing with these heteronuclear molecules, it is necessary to estimate the energies of the atomic orbitals that may interact. For this purpose, the orbital potential energies, given in **Table 5.2** and **Figure 5.12**, are useful.* These potential energies are negative, because they represent attraction between valence electrons and atomic nuclei. The values are the average energies for all electrons in the same level (for example, all 3*p* electrons), and they are weighted averages of all the energy states that arise due to electron–electron interactions discussed in Chapter 11. For this reason, the values do not

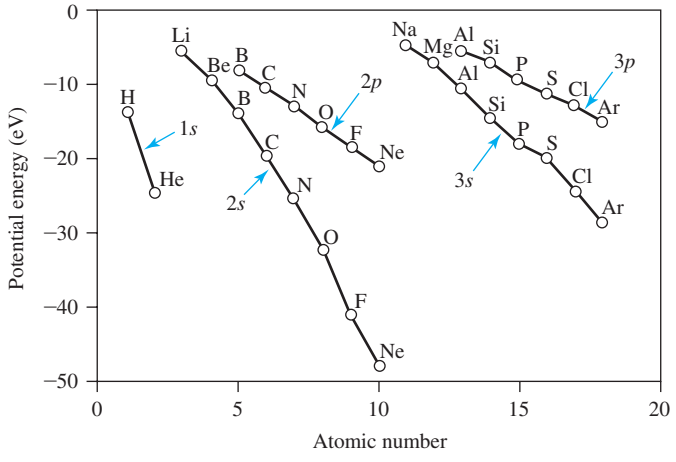


FIGURE 5.12 Orbital Potential Energies.

*A more complete listing of orbital potential energies is in Appendix B-9, available online at pearsonhighered.com/advchemistry

TABLE 5.2 Orbital Potential Energies

		Orbital Potential Energy (eV)						
Atomic Number	Element	1*s*	2*s*	2*p*	3*s*	3*p*	4*s*	4*p*
1	H	−13.61						
2	He	−24.59						
3	Li		−5.39					
4	Be		−9.32					
5	B		−14.05	−8.30				
6	C		−19.43	−10.66				
7	N		−25.56	−13.18				
8	O		−32.38	−15.85				
9	F		−40.17	−18.65				
10	Ne		−48.47	−21.59				
11	Na				−5.14			
12	Mg				−7.65			
13	Al				−11.32	−5.98		
14	Si				−15.89	−7.78		
15	P				−18.84	−9.65		
16	S				−22.71	−11.62		
17	Cl				−25.23	−13.67		
18	Ar				−29.24	−15.82		
19	K						−4.34	
20	Ca						−6.11	
30	Zn						−9.39	
31	Ga						−12.61	−5.93
32	Ge						−16.05	−7.54
33	As						−18.94	−9.17
34	Se						−21.37	−10.82
35	Br						−24.37	−12.49
36	Kr						−27.51	−14.22

J. B. Mann, T. L. Meek, L. C. Allen, *J. Am. Chem. Soc.*, 2000, *122*, 2780.

All energies are negative, representing average attractive potentials between the electrons and the nucleus for all terms of the specified orbitals.

Additional orbital potential energy values are available in the online Appendix B-9.

show the variations of the ionization energies seen in Figure 2.10 but steadily become more negative from left to right within a period, as the increasing nuclear charge attracts all the electrons more strongly.

The atomic orbitals of the atoms that form homonuclear diatomic molecules have identical energies, and both atoms contribute equally to a given MO. Therefore, in the molecular orbital equations, the coefficients associated with the same atomic orbitals of

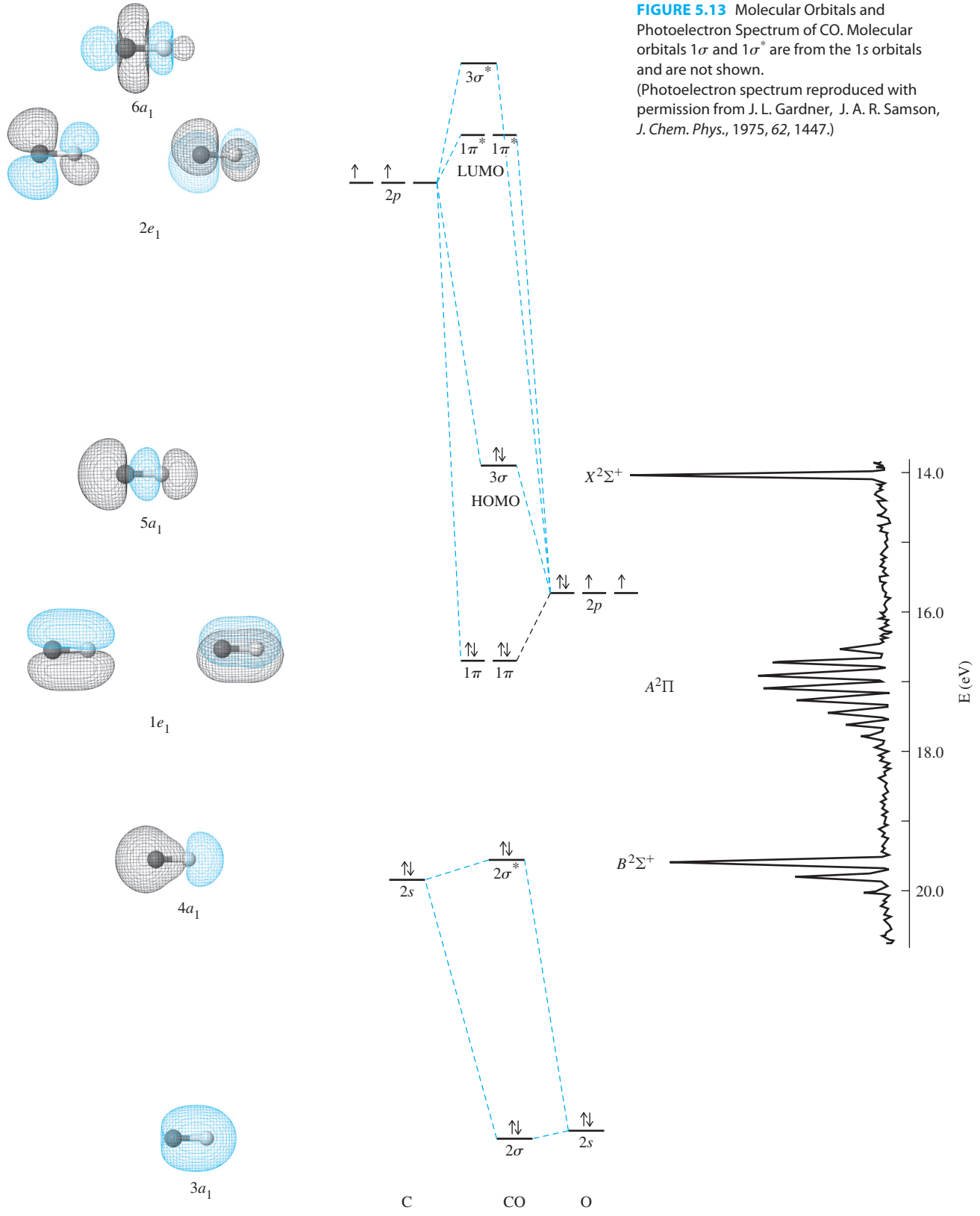


FIGURE 5.13 Molecular Orbitals and Photoelectron Spectrum of CO. Molecular orbitals 1σ and $1\sigma^*$ are from the $1s$ orbitals and are not shown. (Photoelectron spectrum reproduced with permission from J. L. Gardner, J. A. R. Samson, *J. Chem. Phys.*, 1975, *62*, 1447.)

each atom (such as the $2p_z$) are identical. In heteronuclear diatomic molecules, such as CO and HF, the atomic orbitals have different energies, and a given MO receives unequal contributions from these atomic orbitals; the MO equation has a different coefficient for each of the atomic orbitals that contribute to it. As the energies of the atomic orbitals get farther apart, the magnitude of the interaction decreases. The atomic orbital closer in energy to an MO contributes more to the MO, and its coefficient is larger in the wave equation.

Carbon Monoxide

The most efficient approach to bonding in heteronuclear diatomic molecules employs the same strategy as for homonuclear diatomics with one exception: the more electronegative element has atomic orbitals at lower potential energies than the less electronegative element. Carbon monoxide, shown in Figure 5.13, shows this effect, with oxygen having lower energies for its 2*s* and 2*p* orbitals than the matching orbitals of carbon. The result is that the orbital interaction diagram for CO resembles that for a homonuclear diatomic (Figure 5.5), with the right (more electronegative) side pulled down in comparison with the left. In CO, the lowest set of π orbitals (1π in Figure 5.13) is lower in energy than the lowest σ orbital with significant contribution from the 2*p* subshells (3σ in Figure 5.13); the same order occurs in N_2. This is the consequence of significant interactions between the $2p_z$ orbital of oxygen and both the 2*s* and $2p_z$ orbitals of carbon. Oxygen's $2p_z$ orbital (−15.85 eV) is intermediate in energy between carbon's 2*s* (−19.43 eV) and $2p_z$ (−10.66 eV), so the energy match for both interactions is favorable.

The 2σ orbital has more contribution from (and is closer in energy to) the lower energy oxygen 2*s* atomic orbital; the $2\sigma^*$ orbital has more contribution from (and is closer in energy to) the higher energy carbon 2*s* atomic orbital.* In the simplest case, the bonding orbital is similar in energy and shape to the lower energy atomic orbital, and the antibonding orbital is similar in energy and shape to the higher energy atomic orbital. In more complicated cases, such as the $2\sigma^*$ orbital of CO, other orbitals (the oxygen $2p_z$ orbital) also contribute, and the molecular orbital shapes and energies are not as easily predicted. As a practical matter, atomic orbitals with energy differences greater than about 10 eV to 14 eV usually do not interact significantly.

Mixing of the σ and σ^* levels, like that seen in the homonuclear σ_g and σ_u orbitals, causes a larger split in energy between the $2\sigma^*$ and 3σ, and the 3σ is higher than the 1π levels. The shape of the 3σ orbital is interesting, with a very large lobe on the carbon end. This is a consequence of the ability of both the 2*s* and $2p_z$ orbitals of carbon to interact with the $2p_z$ orbital of oxygen (because of the favorable energy match in both cases, as mentioned previously); the orbital has significant contributions from two orbitals on carbon but only one on oxygen, leading to a larger lobe on the carbon end. The pair of electrons in the 3σ orbital most closely approximates the carbon-based lone pair in the Lewis structure of CO, but the electron density is still delocalized over both atoms.

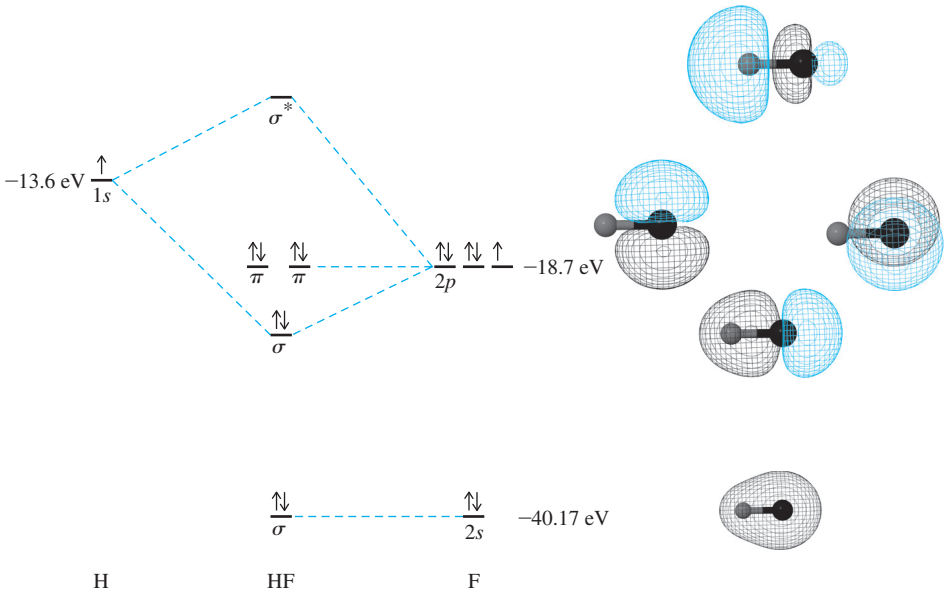
The p_x and p_y orbitals also form four molecular orbitals, two bonding (1π) and two antibonding ($1\pi^*$). In the bonding orbitals the larger lobes are concentrated on the side of the more electronegative oxygen, reflecting the better energy match between these orbitals and the $2p_x$ and $2p_y$ orbitals of oxygen. In contrast, the larger lobes of the π^* orbitals are on carbon, a consequence of the better energy match of these antibonding orbitals with the $2p_x$

*Molecular orbitals are labeled in different ways. Most in this book are numbered within each set of the same symmetry ($1\sigma_g$, $2\sigma_g$ and $1\sigma_u$, $2\sigma_u$). In some figures of homonuclear diatomics, $1\sigma_g$ and $1\sigma_u$ MOs from 1*s* atomic orbitals are understood to be at lower energies than the MOs from the valence orbitals and are omitted. It is noteworthy that interactions involving core orbitals are typically very weak; these interactions feature sufficiently poor overlap that the energies of the resulting orbitals are essentially the same as the energies of the original atomic orbitals.

and $2p_y$ orbitals of carbon. The distribution of electron density in the 3σ and $1\pi^*$ orbitals is vital to understand how CO binds to transition metals, a topic to be discussed further in this section. When the electrons are filled in, as in Figure 5.13, the valence orbitals form four bonding pairs and one antibonding pair for a net bond order of 3.*

EXAMPLE 5.3

Molecular orbitals for HF can be found by using the approach used for CO. The $2s$ orbital of the fluorine atom is more than 26 eV lower than that of the hydrogen $1s$, so there is very little interaction between these orbitals. The fluorine $2p_z$ orbital (−18.65 eV) and the hydrogen $1s$ (−13.61 eV), on the other hand, have similar energies, allowing them to combine into bonding and antibonding σ^* orbitals. The fluorine $2p_x$ and $2p_y$ orbitals remain nonbonding, each with a pair of electrons. Overall, there is one bonding pair and three lone pairs; however, the lone pairs are not equivalent, in contrast to the Lewis dot approach. The occupied molecular orbitals of HF predict a polar bond since all of these orbitals are biased toward the fluorine atom. The electron density in HF is collectively distributed with more on the fluorine atom relative to the hydrogen atom, and fluorine is unsurprisingly the negative end of the molecule.



EXERCISE 5.3 Use a similar approach to the discussion of HF to explain the bonding in the hydroxide ion OH^-.

The molecular orbitals that are typically of greatest interest for reactions are the **highest occupied molecular orbital (HOMO)** and the **lowest unoccupied molecular orbital (LUMO)**, collectively known as **frontier orbitals** because they lie at the occupied–unoccupied frontier. The MO diagram of CO helps explain its reaction chemistry with transition metals, which is different than that predicted by electronegativity considerations that would suggest more electron density on the oxygen. On the sole basis of the carbon–oxygen electronegativity

*The classification of the filled σ orbitals as "bonding" and "antibonding" in CO is not as straightforward as in, for example, H_2, since the 2σ and $2\sigma^*$ orbitals are only changed modestly in energy relative to the $2s$ orbitals of oxygen and carbon, respectively. However, these orbital classifications are consistent with a threefold bond order for CO.

difference (and without considering the MO diagram), compounds in which CO is bonded to metals, called *carbonyl complexes*, would be expected to bond as M—O—C with the more electronegative oxygen attached to the electropositive metal. One impact of this electronegativity difference within the MO model is that the 2σ and 1π molecular orbitals in CO feature greater electron density on the more electronegative oxygen (Figure 5.13). However, the structure of the vast majority of metal carbonyl complexes, such as $Ni(CO)_4$ and $Mo(CO)_6$, has atoms in the order M—C—O. The HOMO of CO is 3σ, with a larger lobe, and therefore higher electron density, on the carbon (as explained above on the basis of *s-p* mixing). The electron pair in this orbital is more concentrated on the carbon atom, and can form a bond with a vacant orbital on the metal. The electrons of the HOMO are of highest energy (and least stabilized) in the molecule; these are generally the most energetically accessible for reactions with empty orbitals of other reactants. The LUMOs are the $1\pi^*$ orbitals; like the HOMO, these are concentrated on the less electronegative carbon, a feature that also predisposes CO to coordinate to metals via the carbon atom. Indeed, the frontier orbitals can both donate electrons (HOMO) and accept electrons (LUMO) in reactions. These tremendously important effects in organometallic chemistry are discussed in more detail in Chapters 10 and 13.

5.3.2 Ionic Compounds and Molecular Orbitals

Ionic compounds can be considered the limiting form of polarity in heteronuclear diatomic molecules. As mentioned previously, as the atoms forming bonds differ more in electronegativity, the energy gap between the interacting atomic orbitals also increases, and the concentration of electron density is increasingly biased toward the more electronegative atom in the bonding molecular orbitals. At the limit, the electron is transferred completely to the more electronegative atom to form a negative ion, leaving a positive ion with a high-energy vacant orbital. When two elements with a large difference in their electronegativities (such as Li and F) combine, the result is an ionic bond. However, in molecular orbital terms, we can treat an ion pair like we do a covalent compound. In **Figure 5.14**, the atomic orbitals and an approximate indication of molecular orbitals for such a diatomic molecule, LiF, are given. On formation of the diatomic molecule LiF, the electron from the Li 2*s*

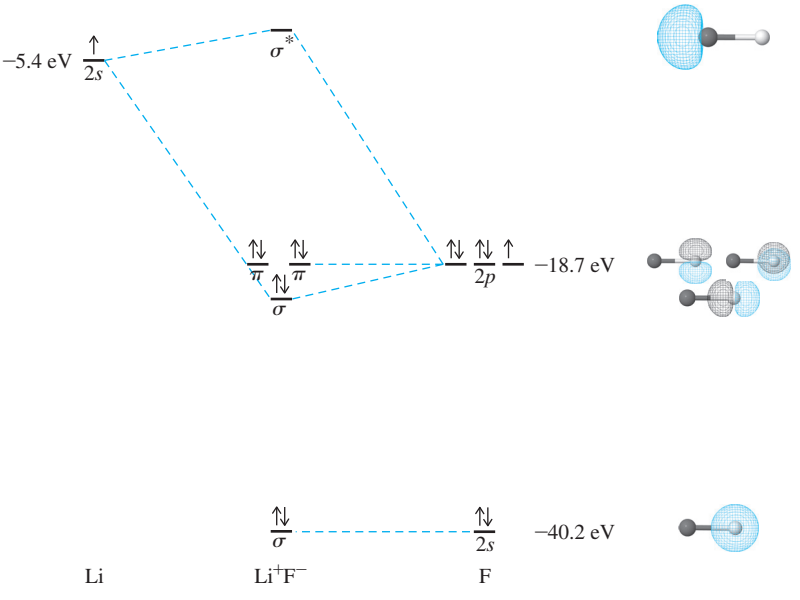


FIGURE 5.14 Approximate LiF Molecular Orbitals.

orbital is transferred to the bonding orbital formed from interaction between the Li $2s$ orbital and the F $2p_z$ orbital. Indeed, the σ orbital deriving from the $2s/2p_z$ interaction has a significantly higher contribution from $2p_z$ relative to $2s$ on the basis of the large energy gap. Both electrons, the one originating from Li and the one originating from the F $2p_z$ orbital, are stabilized. Note that the level of theory used to calculate the orbital surfaces in Figure 5.14 suggests essentially no covalency in diatomic LiF.

Lithium fluoride exists as a crystalline solid; this form of LiF has significantly lower energy than diatomic LiF. In a three-dimensional crystalline lattice containing many formula units of a salt, the ions are held together by a combination of electrostatic (ionic) attraction and covalent bonding. There is a small covalent bonding contribution in all ionic compounds, but salts do not exhibit directional bonds, in contrast to molecules with highly covalent bonds that adopt geometries predicted by the VSEPR model. In the highly ionic LiF, each Li^+ ion is surrounded by six F^- ions, each of which in turn is surrounded by six Li^+ ions. The orbitals in the crystalline lattice form energy bands, described in Chapter 7.

Addition of these elementary steps, beginning with solid Li and gaseous F_2, results in formation of the corresponding gas-phase ions, and provides the net enthalpy change for this chemical change:

Elementary Step	Chemical/Physical Change	$\Delta H°$(kJ/mol)*
$Li(s) \longrightarrow Li(g)$	Sublimation	161
$Li(g) \longrightarrow Li^+(g) + e^-$	Ionization	520
$\frac{1}{2}F_2(g) \longrightarrow F(g)$	Bond dissociation	79
$F(g) + e^- \longrightarrow F^-(g)$	–Electron affinity	–328
$Li(s) + \frac{1}{2}F_2(g) \longrightarrow Li^+(g) + F^-(g)$	Formation of gas-phase ions from the elements in their standard states	432

The free energy change $(\Delta G = \Delta H - T\Delta S)$ must be negative for a reaction to proceed spontaneously. The very large and positive ΔH (432 kJ/mol) associated with the formation of these gas-phase ions renders the ΔG positive for this change despite its positive ΔS. However, if we combine these isolated ions, the large coulombic attraction between them results in a dramatic decrease in electronic energy, releasing 755 kJ/mol on formation of gaseous Li^+F^- ion pairs and 1050 kJ/mol on formation of a LiF crystal containing 1 mol of each ion.

Elementary Step	Chemical Change	$\Delta H°$(kJ/mol)
$Li^+(g) + F^-(g) \longrightarrow LiF(g)$	Formation of gaseous ion pairs	–755
$Li^+(g) + F^-(g) \longrightarrow LiF(s)$	Formation of crystalline solid	–1050

The **lattice enthalpy** for crystal formation is sufficiently large and negative to render ΔG for $Li(s) + \frac{1}{2}F_2(g) \longrightarrow LiF(s)$ negative. Consequently, the reaction is spontaneous,

*While ionization energy and electron affinity are formally internal energy changes (ΔU), these are equivalent to enthalpy changes since $\Delta H = \Delta U + P\Delta V$ and $\Delta V = 0$ for the processes that define ionization energy and electron affinity.

despite the net endothermic contribution for generating gaseous ions from the parent elements and the negative entropy change associated with gas-phase ions coalescing into a crystalline solid.

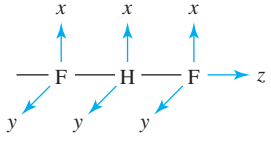
5.4 Molecular Orbitals for Larger Molecules

The methods described previously for diatomic molecules can be extended to molecules consisting of three or more atoms, but this approach becomes more challenging as molecules become more complex. We will first consider several examples of linear molecules to illustrate the concept of group orbitals and then proceed to molecules that benefit from the application of formal group theory methods.

5.4.1 FHF^-

The linear ion FHF^-, an example of very strong hydrogen bonding that can be described as a covalent interaction,[9] provides a convenient introduction to the concept of **group orbitals**, collections of matching orbitals on outer atoms. To generate a set of group orbitals, we will use the valence orbitals of the fluorine atoms, as shown in Figure 5.15. We will then examine which central-atom orbitals have the proper symmetry to interact with the group orbitals.

The lowest energy group orbitals are composed of the 2*s* orbitals of the fluorine atoms. These orbitals either have matching signs of their wave functions (group orbital 1) or opposite signs (group orbital 2). These group orbitals should be viewed as sets of orbitals that potentially could interact with central atom orbitals. Group orbitals are the same combinations that formed bonding and antibonding orbitals in diatomic molecules (e.g., $p_{xa} + p_{xb}$, $p_{xa} - p_{xb}$), but now are separated by the central hydrogen atom. Group orbitals 3 and 4 are derived from the fluorine $2p_z$ orbitals, in one case having lobes with matching signs pointing toward the center (orbital 3), and in the other case having opposite signs pointing toward the center (orbital 4). Group orbitals 5 through 8 are derived from the $2p_x$ and $2p_y$ fluorine orbitals, which are mutually parallel and can be paired according to matching (orbitals 5 and 7) or opposite (orbitals 6 and 8) signs of their wave functions.



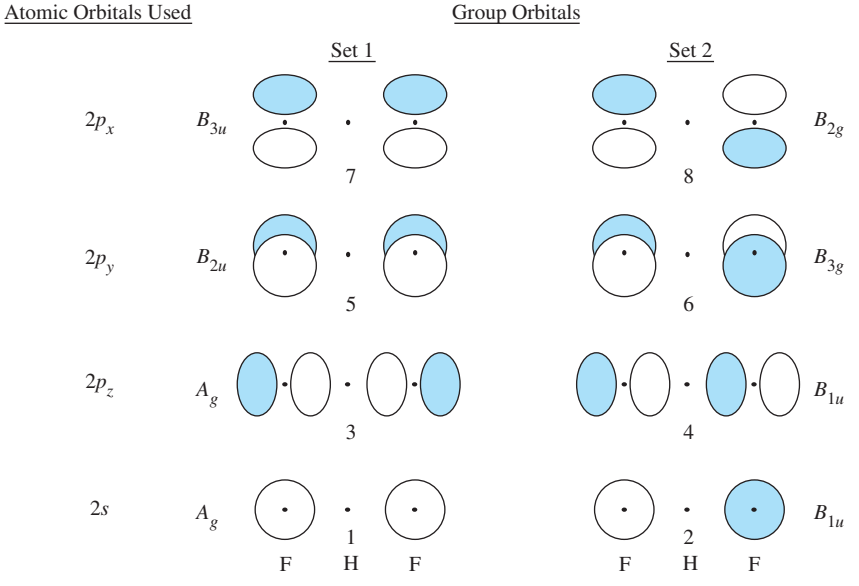


FIGURE 5.15 Group Orbitals.

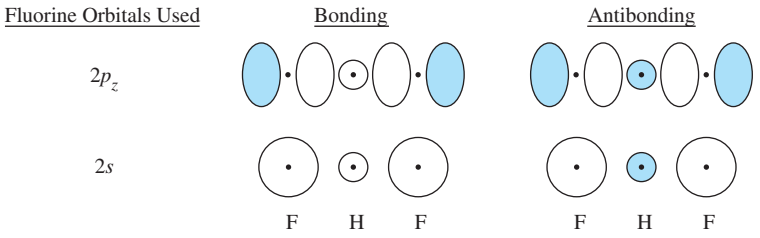


FIGURE 5.16 Interaction of Fluorine Group Orbitals with the Hydrogen 1*s* Orbital.

The central hydrogen atom in FHF^-, with only its 1*s* orbital available for bonding, is only eligible on the basis of its symmetry to interact with group orbitals 1 and 3; the 1*s* orbital is nonbonding with respect to the other group orbitals. These bonding and antibonding combinations are shown in **Figure 5.16**.

Which interaction, the hydrogen 1*s* orbital with group orbital 1 or 3, respectively, is likely to be stronger? The potential energy of the 1*s* orbital of hydrogen (−13.61 eV) is a much better match for the fluorines' $2p_z$ orbitals (−18.65 eV) than their 2*s* orbitals (−40.17 eV). Consequently, we expect the interaction with the $2p_z$ orbitals (group orbital 3) to be stronger than with the 2*s* orbitals (group orbital 1). The 1*s* orbital of hydrogen cannot interact with group orbitals 5 through 8; these orbitals are nonbonding.

The molecular orbitals for FHF^- are shown in **Figure 5.17**. In sketching molecular orbital energy diagrams of polyatomic species, we will show the orbitals of the central atom on the far left, the group orbitals of the surrounding atoms on the far right, and the resulting molecular orbitals in the middle.

Five of the six group orbitals derived from the fluorine 2*p* orbitals do not interact with the central atom; these orbitals remain essentially nonbonding and contain lone pairs of electrons.

It is important to recognize that these "lone pairs" are each delocalized over two fluorine atoms, a different perspective from that afforded by the Lewis dot model where these pairs are associated with single atoms. There is a slight interaction between orbitals on the non-neighboring fluorine atoms, but not enough to change their energies significantly because the fluorine atoms are so far apart (229 pm, more than twice the 91.7 pm distance between hydrogen and fluorine in HF). As already described, the sixth 2*p* group orbital, the remaining $2p_z$ (number 3), interacts with the 1*s* orbital of hydrogen to give two molecular orbitals, one bonding and one antibonding. An electron pair occupies the bonding orbital. The group orbitals from the 2*s* orbitals of the fluorine atoms are much lower in energy than the 1*s* orbital of the hydrogen atom and are essentially nonbonding. Group orbitals 2 and 4, while both essentially nonbonding, are slightly stabilized, and destabilized, respectively, due to a mixing phenomenon analogous to *s*-*p* mixing. These group orbitals are eligible to interact since they possess the same symmetry; this general issue will be discussed later in this chapter.

The Lewis approach to bonding requires two electrons to represent a single bond between two atoms and would result in four electrons around the hydrogen atom of FHF^-. The molecular orbital model, on the other hand, suggests a 2-electron bond delocalized over *three* atoms (a 3-center, 2-electron bond). The bonding MO in Figure 5.17 formed from group orbital 3 shows how the molecular orbital approach represents such a bond: two electrons occupy a low-energy orbital formed by the interaction of all three atoms (a central atom and a two-atom group orbital). The remaining electrons are in the group orbitals derived from the 2*s*, p_x, and p_y orbitals of the fluorine at essentially the same energy as that of the atomic orbitals.

In general, bonding molecular orbitals derived from three or more atoms, like the one in Figure 5.17, are stabilized more relative to their parent orbitals than bonding molecular

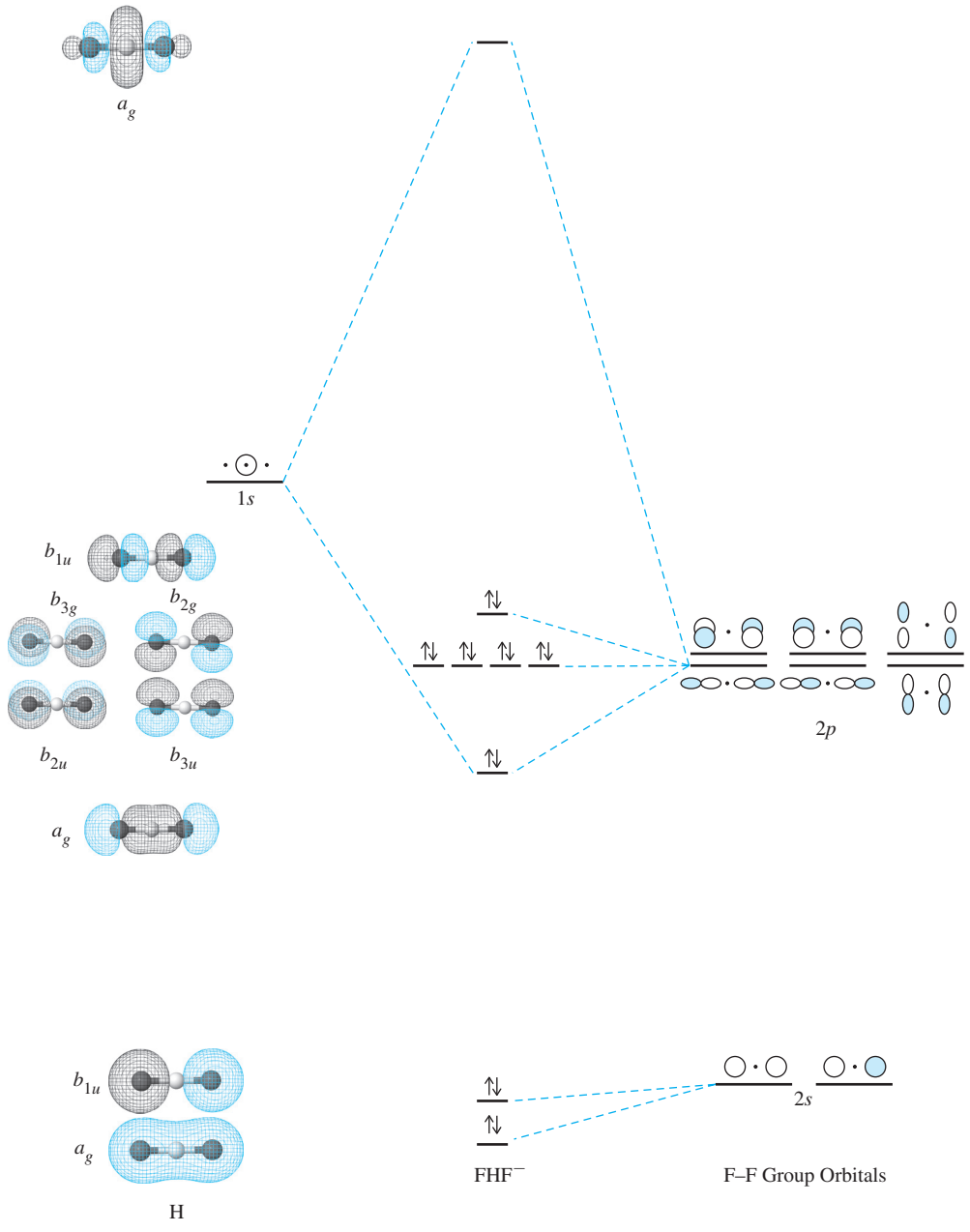


FIGURE 5.17 Molecular Orbital Diagram of FHF^-.

orbitals that arise from orbitals on only two atoms. Electrons in bonding molecular orbitals consisting of more than two atoms experience attraction from multiple nuclei, and are delocalized over more space relative to electrons in bonding MOs composed of two atoms. Both of these features lead to additional stabilization in larger systems. However, the total energy of a molecule is the sum of the energies of *all* of the electrons in *all* the occupied orbitals. FHF^- has a bond energy of 212 kJ/mol and F—H distances of 114.5 pm. HF has a bond energy of 574 kJ/mol and an F—H bond distance of 91.7 pm.[10]

EXERCISE 5.4

Sketch the energy levels and the molecular orbitals for the linear H_3^+ ion.

5.4.2 CO_2

The approach used so far can be applied to other linear species—such as CO_2, N_3^-, and BeH_2—to consider how molecular orbitals can be constructed on the basis of interactions of group orbitals with central atom orbitals. However, we also need a method to understand the bonding in more complex molecules. We will first illustrate this approach using carbon dioxide, another linear molecule with a more complicated molecular orbital description than FHF^-. The following stepwise approach permits examination of more complex molecules:

1. Determine the point group of the molecule. If it is linear, substituting a simpler point group that retains the symmetry of the orbitals (ignoring the wave function signs) makes the process easier. It is useful to substitute D_{2h} for $D_{\infty h}$ and C_{2v} for $C_{\infty v}$. This substitution retains the symmetry of the orbitals without the need to use infinite-fold rotation axes.*
2. Assign x, y, and z coordinates to the atoms, chosen for convenience. Experience is the best guide here. A general rule is that *the highest order rotation axis of the molecule is assigned as the z axis of the central atom.* In nonlinear molecules, the y axes of the outer atoms are chosen to point toward the central atom.
3. Construct a (reducible) representation for the combination of the valence s orbitals on the outer atoms. If the outer atom is not hydrogen, repeat the process, finding the representations for each of the other sets of outer atom orbitals (for example, p_x, p_y, and p_z). As in the case of the vectors described in Chapter 4, any orbital that changes position during a symmetry operation contributes zero to the character of the resulting representation; any orbital that remains in its original position—such as a p orbital that maintains its position and direction (signs of its orbital lobes)—contributes 1; and any orbital that remains in the original position, with the signs of its lobes reversed, contributes -1.
4. Reduce each representation from Step 3 to its irreducible representations. This is equivalent to finding the symmetry of the **group orbitals** or the **symmetry-adapted linear combinations (SALCs)** of the orbitals. The group orbitals are then the combinations of atomic orbitals that match the symmetry of the irreducible representations.
5. Identify the atomic orbitals of the central atom with the same symmetries (irreducible representations) as those found in Step 4.
6. Combine the atomic orbitals of the central atom and those of the group orbitals with matching symmetry and similar energy to form molecular orbitals. The total number of molecular orbitals formed must equal the number of atomic orbitals used from all the atoms.**

In summary, the process used in creating molecular orbitals is to match the symmetries of the group orbitals, using their irreducible representations, with the symmetries of the central atom orbitals. If the symmetries match and the energies are similar, there is an interaction—both bonding and antibonding—if not, there is no interaction.

In CO_2 the group orbitals for the oxygen atoms are identical to the group orbitals for the fluorine atoms in FHF^- (Figure 5.15), but the central carbon atom in CO_2 has both *s and p* orbitals capable of interacting with the oxygen atom group orbitals. As in the discussion of FHF^-, the group orbital–atomic orbital interactions of CO_2 will be the focus.

1. **Point Group:** CO_2 has $D_{\infty h}$ symmetry so the D_{2h} point group will be used.
2. **Coordinate System:** The z axis is chosen as the C_∞ axis, and the y and z coordinates are chosen similarly to the FHF^- example (**Figure 5.18**).

*This approach is sometimes referred to as a "Descent in Symmetry."

**We use lowercase labels on the molecular orbitals, with uppercase for the atomic orbitals and for representations in general. This practice is common but not universal.

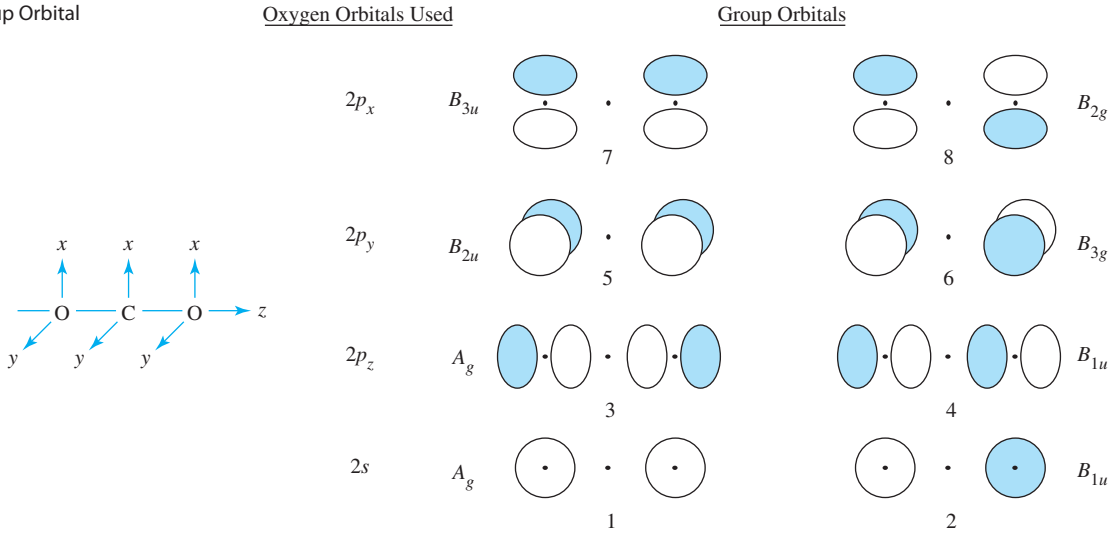


FIGURE 5.18 Group Orbital Symmetry in CO_2.

3. **Reducible Representations for Outer Atom Orbitals:** In CO_2 these are the $2s$ and $2p$ oxygen orbitals. These can be grouped into four sets (Figure 5.18). For example, the pair of $2s$ orbitals on the oxygen atoms has the following representation:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma(2s)$	2	2	0	0	0	0	2	2

The other group orbitals have the following representations:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma(2p_z)$	2	2	0	0	0	0	2	2
$\Gamma(2p_x)$	2	−2	0	0	0	0	2	−2
$\Gamma(2p_y)$	2	−2	0	0	0	0	−2	2

4. **Group Orbitals from Reducible Representations:** Each of the representations from Step 3 can be reduced by the procedure described in Section 4.4.2. For example, the representation $\Gamma(2s)$ reduces to $A_g + B_{1u}$:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
A_g	1	1	1	1	1	1	1	1
B_{1u}	1	1	−1	−1	−1	−1	1	1

When this procedure is conducted for each representation, the representations describe the symmetry properties of the oxygen atom group orbitals for CO_2, shown with the appropriate D_{2h} labels in Figure 5.18. Note that these group orbitals are the same as those deduced by inspection for the fluorine atoms in FHF^-.

EXERCISE 5.5

Using the D_{2h} character table shown, verify that the group orbitals in Figure 5.18 match their irreducible representations.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

5. **Matching Orbitals on the Central Atom:** To determine which atomic orbitals of carbon are of correct symmetry to interact with the group orbitals, we will consider each group orbital separately. The carbon atomic orbitals are shown in **Figure 5.19** with their symmetry labels within the D_{2h} point group.

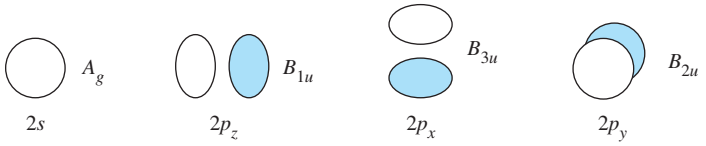


FIGURE 5.19 Symmetry of the Carbon Atomic Orbitals in the D_{2h} Point Group.

The D_{2h} character table shows the symmetry of these orbitals. For example, B_{1u} has the symmetry of the z axis and of the p_z oxygen orbitals; they are unchanged by the E, $C_2(z)$, $\sigma(xz)$, and $\sigma(yz)$ operations, and the $C_2(y)$, $C_2(x)$, i, and $\sigma(xy)$ operations reverse their signs.

6. **Formation of Molecular Orbitals:** Group orbitals 1 and 2 in **Figure 5.20**, formed by adding and subtracting the oxygen 2s orbitals, have A_g and B_{1u} symmetry, respectively. Group orbital 1 is of appropriate symmetry to interact with the 2s orbital of carbon (both have A_g symmetry), and group orbital 2 is of appropriate symmetry to interact with the $2p_z$ orbital of carbon (both have B_{1u} symmetry).

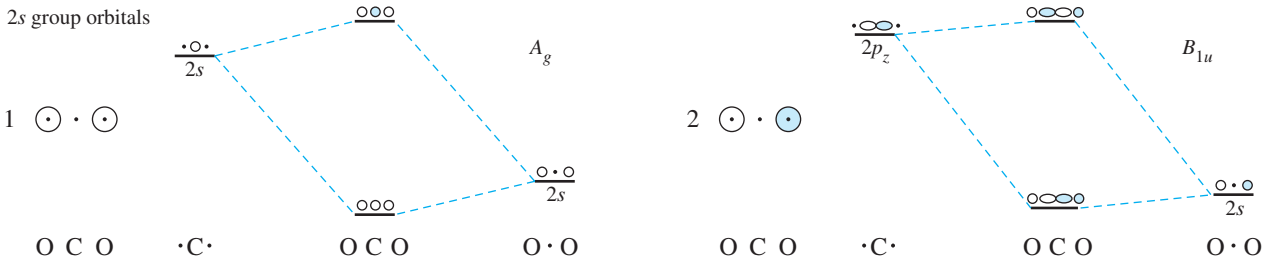


FIGURE 5.20 Group Orbitals 1 and 2 for CO_2.

Group orbitals 3 and 4 in **Figure 5.21**, formed by adding and subtracting the oxygen $2p_z$ orbitals, also have A_g and B_{1u} symmetries. Therefore, group orbital 3 can also interact with the 2s of carbon, and group orbital 4 can also interact with the carbon $2p_z$.

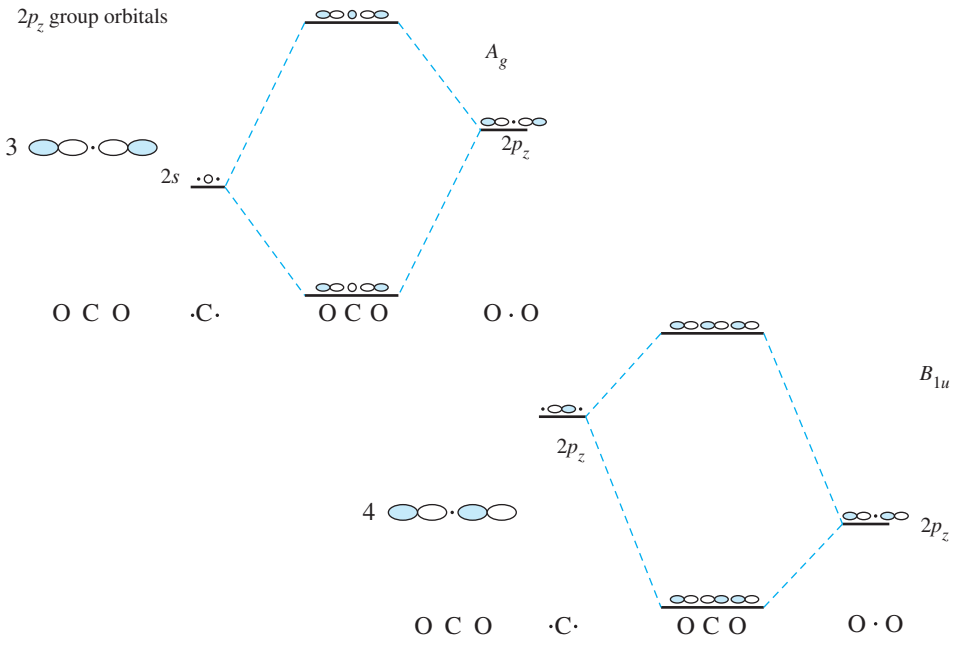


FIGURE 5.21 Group Orbitals 3 and 4 for CO_2.

Indeed, the $2s$ and $2p_z$ orbitals of carbon have two possible sets of group orbitals with which they may interact; all four interactions in Figures 5.20 and 5.21 are symmetry allowed. It is necessary to estimate which interactions are expected to be the strongest from the potential energies of the $2s$ and $2p$ orbitals of carbon and oxygen given in **Figure 5.22**.

Orbital	2s	2p
Carbon	−19.43 eV	−10.66 eV
Oxygen	−32.38 eV	−15.85 eV

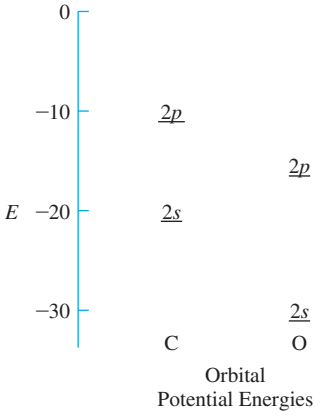


FIGURE 5.22 Orbital Potential Energies of Carbon and Oxygen.

Interactions are strongest between orbitals having similar energies. The energy match between group orbital 3 and the $2s$ orbital of carbon is much better (a difference of 3.58 eV) than the energy match between group orbital 1 and the $2s$ of carbon (a difference of 12.95 eV); therefore, the primary interaction is between the $2p_z$ orbitals of oxygen and the $2s$ orbital of carbon. Group orbital 2 also has an energy too low for strong interaction with the carbon p_z (a difference of 21.72 eV), so the final molecular orbital diagram in Figure 5.25 shows only a slight interaction with carbon orbitals for group orbital 2.

EXERCISE 5.6

Using orbital potential energies, show that group orbital 4 is more likely than group orbital 2 to interact strongly with the $2p_z$ orbital of carbon.

The $2p_y$ orbital of carbon has B_{2u} symmetry and interacts with group orbital 5 (**Figure 5.23**). The result is the formation of two π molecular orbitals, one bonding and one antibonding. However, there is no carbon orbital with B_{3g} symmetry to interact with group orbital 6, also formed by combining $2p_y$ orbitals of oxygen. Therefore, group orbital 6 is nonbonding.

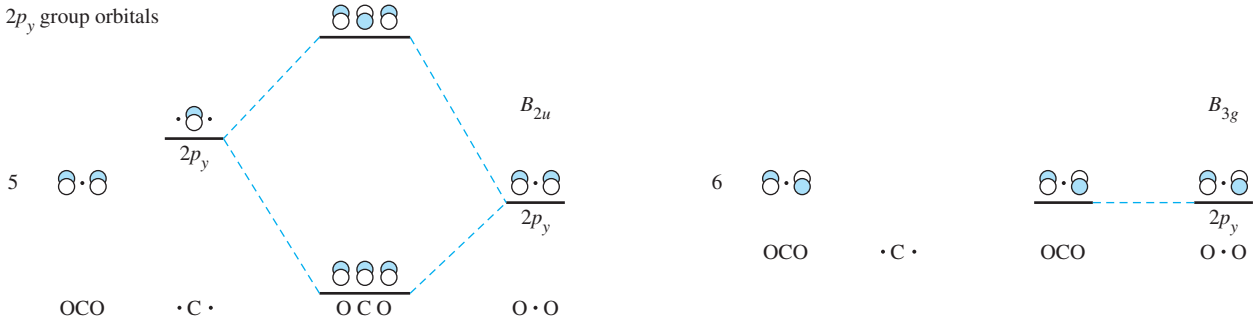


FIGURE 5.23 Group Orbitals 5 and 6 for CO_2.

Interactions of the $2p_x$ orbitals are similar to those of the $2p_y$ orbitals. Group orbital 7, with B_{3u} symmetry, interacts with the $2p_x$ orbital of carbon to form π bonding and antibonding orbitals, whereas group orbital 8 is nonbonding (**Figure 5.24**).

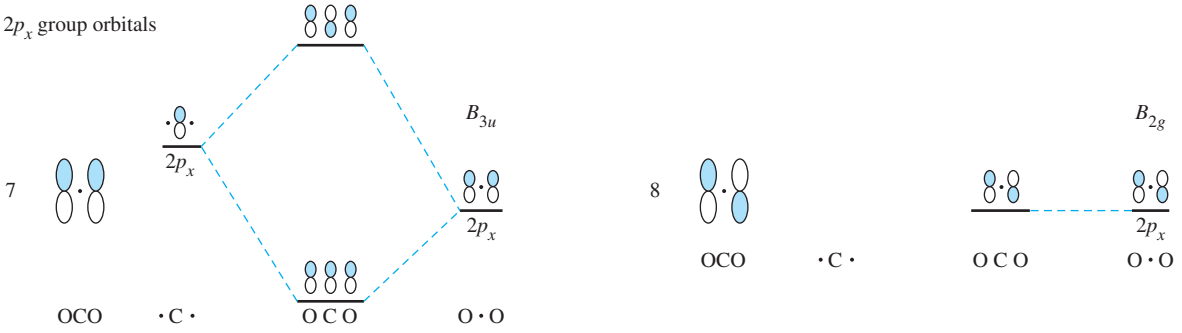


FIGURE 5.24 Group Orbitals 7 and 8 for CO_2.

The molecular orbital diagram of CO_2 is shown in **Figure 5.25**. The 16 valence electrons occupy, from the bottom, two essentially nonbonding σ orbitals, two bonding σ orbitals, two bonding π orbitals, and two nonbonding π orbitals. In other words, two of the bonding electron pairs are in σ orbitals, two are in π orbitals, and there are four bonds in the molecule, as expected. As in FHF^-, all the occupied molecular orbitals are 3-center, 2-electron orbitals.

The molecular orbitals of related linear triatomic species—such as N_3^-, CS_2, and OCN^- —can be determined similarly. The molecular orbitals of longer polyatomic species can be determined by a similar method. Examples of bonding in linear and cyclic π systems are considered in Chapter 13.

EXERCISE 5.7

Prepare a molecular orbital diagram for the azide ion, N_3^-.

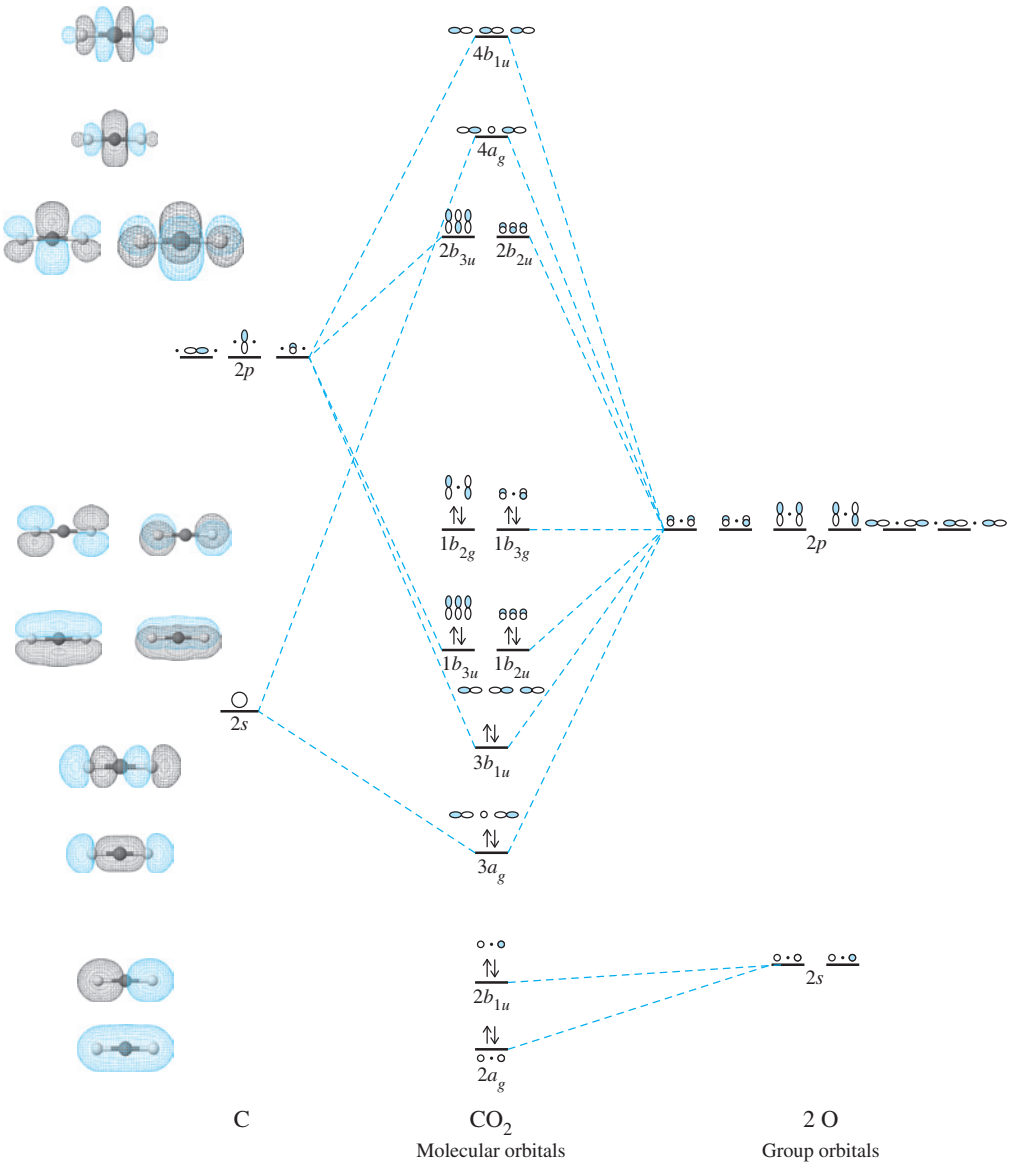


FIGURE 5.25 Molecular Orbitals of CO_2.

EXERCISE 5.8

Prepare a molecular orbital diagram for the BeH_2 molecule. (Assume an orbital potential energy of –6.0 eV for 2*p* orbitals of Be. This orbital set should be taken into account, even though it is unoccupied in a free Be atom.)

This process can be extended to obtain numerical values of the coefficients of the atomic orbitals used in the molecular orbitals.[11,12] The coefficients may be small or large, positive or negative, similar or quite different, depending on the characteristics of the orbital under consideration. Computer software packages are available to calculate these coefficients and generate the pictorial diagrams that describe the molecular orbitals. Examples of problems that use molecular modeling software to generate molecular orbitals of a variety of molecules are included in the problems at the end of this chapter and in later chapters. Discussion of these computational methods is beyond the scope of this text.

5.4.3 H_2O

Molecular orbitals of nonlinear molecules can be determined by similar procedures. Water is a useful example:

1. Water is a bent molecule with a C_2 axis through the oxygen and two mirror planes that intersect along this axis (Figure 5.26). The point group is C_{2v}.
2. The C_2 axis is chosen as the z axis and the xz plane as the plane of the molecule.* Because the hydrogen 1s orbitals have no directionality, it is not necessary to assign axes to the hydrogen atoms.
3. The hydrogen atoms determine the symmetry of the molecule, and their 1s orbitals form the basis of a reducible representation. The characters for each operation for the hydrogen atom 1s orbitals are readily obtained, Γ. The sum of the contributions to the character (1, 0, or −1, as described previously) for each symmetry operation is the character for that operation in the representation. The complete list for all operations of the group is the reducible representation for the atomic orbitals:

   The E operation leaves both hydrogen orbitals unchanged, for a character of 2.

   C_2 rotation interchanges the orbitals, so each contributes 0, for a total character of 0.

   Reflection in the plane of the molecule (σ_v) leaves both hydrogens unchanged, for a character of 2.

   Reflection perpendicular to the plane (σ_v') switches the two orbitals, for a character of 0.

   Step 3 is summarized in Table 5.3.

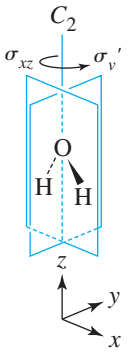


FIGURE 5.26 Symmetry of the Water Molecule.

TABLE 5.3 Representations for C_{2v} Symmetry Operations for Hydrogen Atoms in Water

C_{2v} Character Table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

$$\begin{bmatrix} H_a' \\ H_b' \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} H_a \\ H_b \end{bmatrix} \text{ for the identity operation}$$

$$\begin{bmatrix} H_a' \\ H_b' \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} H_a \\ H_b \end{bmatrix} \text{ for the } C_2 \text{ operation}$$

$$\begin{bmatrix} H_a' \\ H_b' \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} H_a \\ H_b \end{bmatrix} \text{ for the } \sigma_v \text{ reflection } (xz) \text{ plane}$$

$$\begin{bmatrix} H_a' \\ H_b' \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} H_a \\ H_b \end{bmatrix} \text{ for the } \sigma_v' \ (yz \text{ plane})$$

The reducible representation $\Gamma = A_1 + B_1$:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
Γ	2	0	2	0	
A_1	1	1	1	1	z
B_1	1	−1	1	−1	x

*One can also select the yz plane as the plane of the molecule. This results in $\Gamma = A_1 + B_2$ and switches the b_1 and b_2 labels of the molecular orbitals.

4. The representation Γ can be reduced to the irreducible representations $A_1 + B_1$, representing the symmetries of the group orbitals. In Step 5 these group orbitals will be matched with oxygen orbitals of matching symmetries.

5. The first step in deducing the molecular orbitals is to combine the two hydrogen 1*s* orbitals to afford group orbitals. Their sum, $\frac{1}{\sqrt{2}}[\Psi(H_a) + \Psi(H_b)]$, has A_1 symmetry (this is the group orbital in which the 1*s* wave functions have matching signs); their difference, $\frac{1}{\sqrt{2}}[(\Psi(H_a) - \Psi(H_b)]$, has symmetry B_1 (the group orbital in which the 1*s* wave functions have opposite signs) as shown in **Figure 5.27**. These equations define the group orbitals, or symmetry-adapted linear combinations. In this case, the combining 1*s* atomic orbitals are identical and contribute equally to each group orbital. This means that the coefficients for each unique 1*s* atomic orbital in the group orbital equations have the same magnitude. These coefficients also reflect the normalization requirement discussed in Section 2.2; the sum of squares of the coefficients for each atomic orbital must equal 1 when all group orbitals including a given atomic orbital are considered. In this case, the normalizing factor is $\frac{1}{\sqrt{2}}$. In general, the normalizing factor (N) for a group orbital is

$$N = \frac{1}{\sqrt{\sum c_i^2}}$$

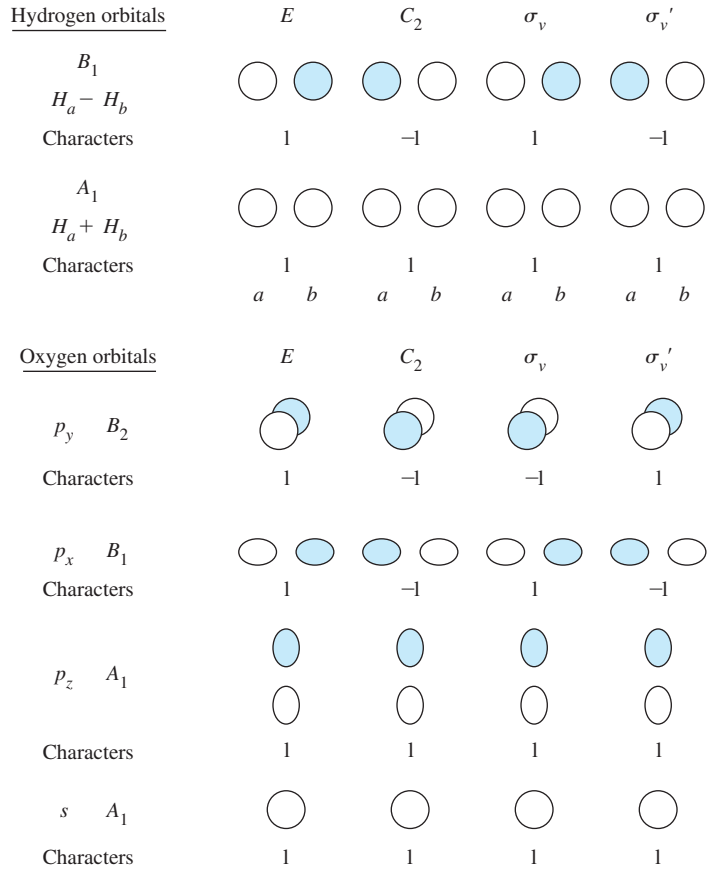


FIGURE 5.27 Symmetry of Atomic and Group Orbitals in the Water Molecule.

TABLE 5.4 Molecular Orbitals for Water

Symmetry	Molecular Orbitals		Oxygen Atomic Orbitals		Group Orbitals from Hydrogen Atoms	Description
B_1	ψ_6	=	$c_9\psi(p_x)$	+	$c_{10}[\psi(H_a) - \psi(H_b)]$	Antibonding (c_{10} is negative)
A_1	ψ_5	=	$c_7\psi(s)$	+	$c_8[\psi(H_a) + \psi(H_b)]$	Antibonding (c_8 is negative)
B_2	ψ_4	=	$\psi(p_y)$			Nonbonding
A_1	ψ_3	=	$c_5\psi(p_z)$	+	$c_6[\psi(H_a) + \psi(H_b)]$	Slightly bonding (c_6 is small)
B_1	ψ_2	=	$c_3\psi(p_x)$	+	$c_4[\psi(H_a) - \psi(H_b)]$	Bonding (c_4 is positive)
A_1	ψ_1	=	$c_1\psi(s)$	+	$c_2[\psi(H_a) + \psi(H_b)]$	Bonding (c_2 is positive)

where c_i = the coefficients on the atomic orbitals. Each group orbital is treated as a single orbital for combination with the oxygen atomic orbitals.

The symmetries of oxygen's 2*s* and 2*p* atomic orbitals can be assigned and confirmed using the C_{2v} character table. The *x*, *y*, and *z* axes and the more complex functions assist in assigning representations to the atomic orbitals. In this case:

The *s* orbital is unchanged by all the operations, so it has A_1 symmetry; an *s* orbital is totally symmetric.

The p_x orbital has the B_1 symmetry of the *x* axis.

The p_y orbital has the B_2 symmetry of the *y* axis.

The p_z orbital has the A_1 symmetry of the *z* axis.

6. The atomic and group orbitals with the same symmetry are combined into molecular orbitals, as listed in **Table 5.4** and shown in **Figure 5.28**. They are numbered Ψ_1 through Ψ_6 in order of their energy, with 1 the lowest and 6 the highest.

The A_1 group orbital combines with the *s* and p_z orbitals of the oxygen to form three molecular orbitals (three atomic or group orbitals forming three molecular orbitals), Ψ_1, Ψ_3, and Ψ_5. The energy of molecular orbital Ψ_1 is only slightly lower in energy relative the oxygen 2*s* orbital; Ψ_1 can be regarded as relatively nonbonding.[13] The electrons that occupy Ψ_1 represent one of the lone pairs in the Lewis electron-dot structure of water, a pair with high probability of being found on the oxygen. As expected on the basis of the relatively close energy match between the oxygen 2*p* subshell and the hydrogen group orbitals, Ψ_3 has significant contribution from oxygen p_z; Ψ_3 is a bonding orbital. Ψ_5 is antibonding and has significantly more contribution from the oxygen p_z relative to the oxygen 2*s*.

The hydrogen B_1 group orbital combines with the oxygen p_x orbital to form two MOs, one bonding and one antibonding (Ψ_2 and Ψ_6). The oxygen p_y (Ψ_4, with B_2 symmetry) does not match the symmetry of the hydrogen 1*s* group orbitals and is therefore nonbonding. This pair of electrons represents the second lone pair in the Lewis structure of water. It is noteworthy that the nonbonding pairs afforded by the MO model of water are not equivalent as in the Lewis model. Overall, there are two bonding orbitals (Ψ_2, Ψ_3), one nonbonding (Ψ_4), one essentially nonbonding orbital (Ψ_1), and two antibonding orbitals (Ψ_5, Ψ_6). The oxygen 2*s* orbital (−32.38 eV) is nearly 20 eV below the hydrogen orbitals in energy (−13.61 eV), so it has very little interaction with the group orbitals. The oxygen 2*p* orbitals (−15.85 eV) are a good match for the hydrogen 1*s* energy, allowing formation of the bonding b_1 and a_1 molecular orbitals. When the eight valence electrons are added, two pairs occupy bonding orbitals, and two pairs occupy nonbonding orbitals; this complements the two bonds and two lone pairs of the Lewis electron-dot structure.

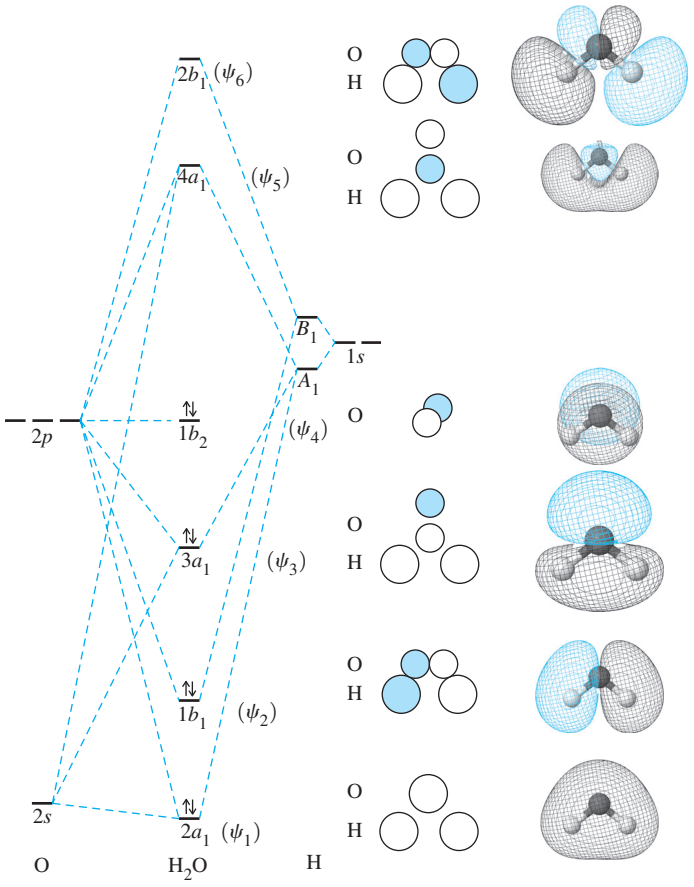


FIGURE 5.28 Molecular Orbitals of H_2O.

As mentioned previously, the molecular orbital perspective differs from the common conception of the water molecule as having two equivalent lone electron pairs and two equivalent O—H bonds. In the MO model, the highest energy electron pair, designated b_2, is truly nonbonding, occupying the oxygen $2p_y$ orbital with its axis perpendicular to the plane of the molecule. The two pairs next highest in energy are bonding pairs, resulting from overlap of the $2p_z$ and $2p_x$ orbital with the 1*s* orbitals of the hydrogen atoms. The lowest energy pair is concentrated on the 2*s* orbital of oxygen. All four occupied molecular orbitals are different.

5.4.4 NH_3

The VSEPR approach describes ammonia as a pyramidal molecule with a lone pair of electrons and C_{3v} symmetry. To obtain a molecular orbital description of NH_3, it is convenient to view this molecule down the C_3, or *z*, axis and with the *yz* plane passing through one of the hydrogen atoms, as shown in **Figure 5.29**. The reducible representation for the three hydrogen atom 1*s* orbitals is given in **Table 5.5**. It can be reduced to the A_1 and E irreducible representations. Because three hydrogen 1*s* orbitals are considered, there must be three group orbitals formed from them, one with A_1 symmetry and two with E symmetry.

Deducing group orbitals thus far has been relatively straightforward; each polyatomic example considered (FHF^-, CO_2, H_2O) has two atoms attached to the central atom, and the group orbitals could be obtained by combining identical atomic orbitals on the terminal atoms in both a bonding and antibonding sense. This is no longer possible with NH_3. To address situations such as NH_3, the **projection operator method**, a systematic approach for deduction of group orbitals, is the preferred strategy.

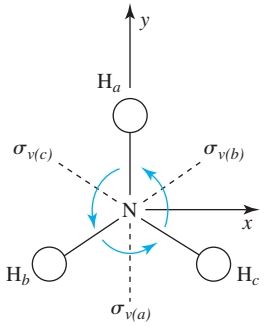


FIGURE 5.29 Coordinate System for NH_3.

TABLE 5.5 Representations for Atomic Orbitals in Ammonia

C_{3v} Character Table

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1		
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

The reducible representation $\Gamma = A_1 + E$:

C_{3v}	E	$2C_3$	$3\sigma_v$		
Γ	3	0	1		
A_1	1	1	1	z	$x^2 + y^2, z^2$
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

The projection operator method permits elucidation of how atomic orbitals should be combined to afford the symmetry-adapted linear combinations (SALCs) that define the group orbitals. This method requires determining the impact of each point group symmetry operation on one atomic orbital (e.g., the hydrogen 1*s* orbital of H_a) within a set of identical atomic orbitals (e.g., the set of three hydrogen 1*s* orbitals in Figure 5.29). For example, the E operation leaves hydrogen 1*s* orbital H_a unchanged while C_3 transforms H_a to H_b. These outcomes are best tabulated; note that each unique symmetry operation is considered without their usual groupings into classes as in Table 5.5.

Original Orbital	E	C_3	C_3^2	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{v(c)}$
H_a becomes…	H_a	H_b	H_c	H_a	H_c	H_b

Linear combinations of these hydrogen 1*s* atomic orbitals that match the symmetries of the A_1, A_2, and E irreducible representations can be obtained via

(1) multiplication of each outcome by the characters associated with each operation for these irreducible representations, followed by

(2) addition of the results. This approach affords the following:

	E C_3 C_3^2 $\sigma_{v(a)}$ $\sigma_{v(b)}$ $\sigma_{v(c)}$
A_1	$H_a + H_a + H_c + H_a + H_c + H_b = 2H_a + 2H_b + 2H_c$
A_2	$H_a + H_b + H_c - H_a - H_c - H_b = 0$
E	$2H_a - H_b - H_c + 0 \quad + 0 \quad + 0 \quad = 2H_a - H_b - H_c$

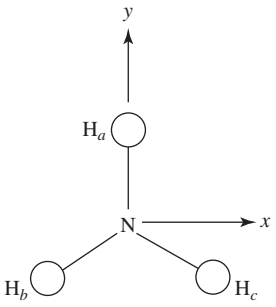
EXERCISE 5.9

The same general SALCs are obtained regardless of the initial atomic orbital examined. Show that if hydrogen 1*s* orbital H_b is chosen as the basis (instead of H_a), the resulting A_1 and A_2 linear combinations would be identical to those shown previously, and the E linear combination would feature the same relative contributions and signs of the three wave functions as in SALC(E) generated via H_a.

The zero sum associated with A_2 confirms that a group orbital of this symmetry cannot be obtained using these three hydrogen 1*s* orbitals, consistent with the $A_1 + E$ reducible representation for the group orbitals. The symmetry-adapted linear combination for A_1

(SALC(A_1)) indicates that each 1*s* orbital contributes equally to this group orbital, as one would visualize for SALC(A_1), a situation not the case with *E*.

Recall that the sum of the squares of the coefficients of each unique atomic orbital in the SALCs must equal 1. To meet this requirement, it is necessary that each group orbital equation be normalized, so that the sum of the squares of the coefficients within each equation affords 1. This requires that the wave functions for the 1*s* orbitals of H_a, H_b, and H_c each have a contribution of $\frac{1}{\sqrt{3}}$ in the normalized A_1 group orbital.

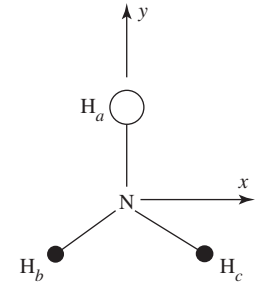


A_1 group orbital

$$\frac{1}{\sqrt{3}}\left[\Psi(H_a) + \Psi(H_b) + \Psi(H_c)\right]$$

As described in Section 5.4.3, the normalization factor is formally calculated via $N = \left(\sqrt{(c_a^2 + c_b^2 + c_c^2)}\right)^{-1} = \left(\sqrt{(1^2 + 1^2 + 1^2)}\right)^{-1} = \frac{1}{\sqrt{3}}$, where c_a, c_b, and c_c are the lowest common integer coefficients for the hydrogen 1*s* atomic orbital wave functions within SALC(A_1). This uniform contribution for each atomic orbital is expected for a totally symmetric group orbital. The SALC(A_1) equation $\frac{1}{\sqrt{3}}\left[\Psi(H_a) + \Psi(H_b) + \Psi(H_c)\right]$ also indicates that each 1*s* atomic orbital in the A_1 group orbital will exhibit the same wave function sign, since the signs of all three terms are positive.

Normalization of SALC(*E*) derived from the projection operator method must account for the doubled contribution of H_a relative to H_b and H_c, while maintaining the opposite wave function signs for H_a relative to H_b and H_c.



$E(y)$ group orbital

$$\frac{1}{\sqrt{6}}\left[2\Psi(H_a) - \Psi(H_b) - \Psi(H_c)\right]$$

$$N = \left(\sqrt{(c_a^2 + c_b^2 + c_c^2)}\right)^{-1} = \left(\sqrt{(2^2 + (-1)^2 + (-1)^2)}\right)^{-1} = \frac{1}{\sqrt{6}}$$

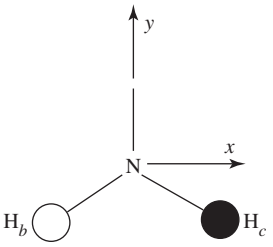
The second *E* group orbital can be motivated by remembering that the symmetry of central atom orbitals (in this case the N atom) must match the symmetry of the group orbitals with which they are combined to form molecular orbitals. The C_{3v} character table indicates that *E* describes the symmetries of the pair of atomic orbitals p_x and p_y, so the *E* group orbitals must be compatible with these orbitals. On the basis of the coordinate system defined in Figure 5.29, the *E* group orbital shown previously has the same symmetry as p_y (with the *xz* plane defining a node); it will interact with the N p_y orbital to create molecular orbitals. In this way, we see that hydrogen 1*s* orbital H_a was the most convenient basis for deduction of the SALCs; since hydrogen 1*s* orbital H_a lies on the *y* axis, the first *E* group orbital is compatible with this axis. The other *E* group orbital must match the symmetry of *x*, requiring zero contribution from H_a due to the orthogonal node defined by the *yz* plane; this means that only H_b and H_c can contribute to the second *E* group orbital. The H_b and H_c wave function contributions can be deduced by cataloging the squares of the coefficients for the normalized equations (**Table 5.6**). The coefficients for H_b and H_c must be $\frac{1}{\sqrt{2}}$ and $-\frac{1}{\sqrt{2}}$, respectively, to satisfy the normalization requirement while leading to identical total contributions from all three 1*s* wave functions across the three group orbitals. The positive and negative coefficients are necessary to match the symmetry of the p_x atomic orbital.

TABLE 5.6 SALC Coefficients and Evidence of Normalization

	Coefficients in Normalized SALCs			Squares of SALC Coefficients			Sum of the Squares = 1 for Normalization Requirement
	c_a	c_b	c_c	c_a^2	c_b^2	c_c^2	
A_1	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	1
$E(y)$	$\frac{2}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{2}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	1
$E(x)$	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1
Sum of the squares for each 1s wave function must total 1 for an identical contribution of each atomic orbital to the group orbitals				1	1	1	

$$\frac{1}{\sqrt{2}}[\Psi(H_b) - \Psi(H_c)]$$

$$N = \left(\sqrt{(c_a^2 + c_b^2 + c_c^2)}\right)^{-1} = \left(\sqrt{0^2 + 1^2 + (-1)^2}\right)^{-1} = \frac{1}{\sqrt{2}}$$



$E(x)$ group orbital

The s and p_z orbitals of nitrogen both have A_1 symmetry, and the pair p_x, p_y has E symmetry, exactly the same as the representations for the hydrogen 1s group orbitals; there are symmetry matches for both A_1 and E. As with the previous examples, each group orbital is treated as a single orbital in combining with the nitrogen orbitals (**Figure 5.30**). The nitrogen s and p_z orbitals combine with the hydrogen A_1 group orbital to give three a_1 orbitals, one bonding, one nonbonding, and one antibonding. The nonbonding orbital is almost entirely nitrogen p_z, with the nitrogen s orbital combining with the hydrogen group orbital for the bonding and antibonding orbitals. The nitrogen p_x and p_y orbitals combine with the E group orbitals to form four e orbitals, two bonding and two antibonding (e has a dimension of 2, which requires a pair of degenerate orbitals).

When eight electrons are put into the lowest energy levels, three bonds and one essentially nonbonding pair are indicated. The 1s orbital energies $(-13.61\ \text{eV})$ of the hydrogen atoms match well with the energies of the nitrogen 2p orbitals $(-13.18\ \text{eV})$, resulting in large differences between the bonding and antibonding orbital energies. The nitrogen 2s has such a sufficiently low energy $(-25.56\ \text{eV})$ that its interaction with the hydrogen orbitals is quite small, and the $2a_1$ molecular orbital has nearly the same energy as the nitrogen 2s orbital.

The HOMO of NH_3 is slightly bonding, because it contains an electron pair in an orbital resulting from interaction of the $2p_z$ orbital of nitrogen with the 1s orbitals of the hydrogens (from the zero-node A_1 group orbital). The $2p_z$ orbital participates in weak overlap with the A_1 group orbital. One half of the $2p_z$ orbital points away from the hydrogen atoms, while the other half points at the center of the triangle formed by the three hydrogen nuclei. The HOMO is the lone pair of the electron-dot and VSEPR models. It is also the pair donated by ammonia when it functions as a Lewis base (discussed in Chapter 6).

5.4.5 CO_2 Revisited with Projection Operators

Section 5.4.2 outlines the process for determining group orbitals in the linear case where the outer atoms employ both s and p orbitals; Figure 5.18 illustrates the group orbitals comprised of $2p_x$, $2p_y$, $2p_z$, and 2s orbitals, respectively. While these orbitals can be deduced by

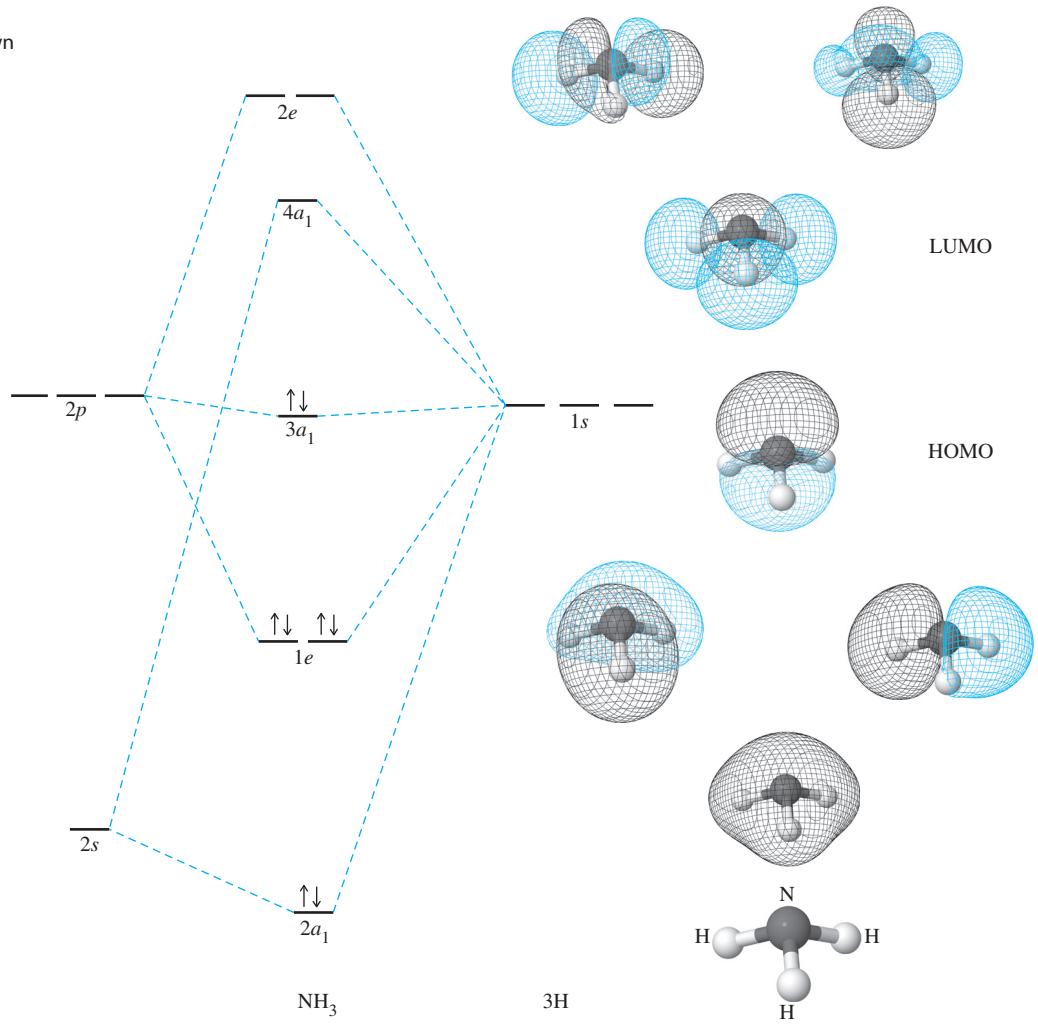
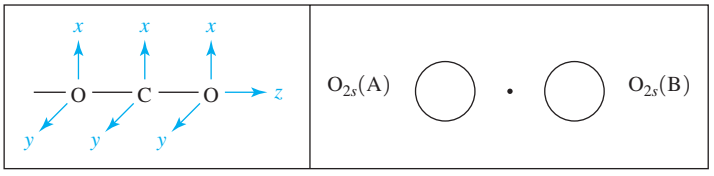


FIGURE 5.30 Molecular Orbitals of NH_3. All are shown with the orientation of the molecule at the bottom.

matching their symmetries to the corresponding irreducible representations, a complementary strategy is to employ projection operators. For example, the group orbitals composed of oxygen atom 2*s* atomic orbitals have A_g and B_{1u} symmetry in the D_{2h} point group.* As in the NH_3 example, consider the impact of each D_{2h} point group symmetry operation on one atomic orbital (in this case the oxygen 2*s* orbital of O_A) within a set of two 2*s* atomic orbitals. With linear molecules, the group orbital with matching orbital lobe signs toward the center is always chosen as the basis, in this case the A_g orbital. This general strategy was also employed in Section 5.4.4, where the A_1 group orbital (Figure 5.29) was used as the basis.



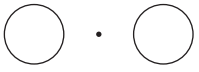
*We "descend in symmetry" from $D_{\infty h}$ to D_{2h} for convenience.

Original Orbital	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$O_{2s(A)}$ becomes…	$O_{2s(A)}$	$O_{2s(A)}$	$O_{2s(B)}$	$O_{2s(B)}$	$O_{2s(B)}$	$O_{2s(B)}$	$O_{2s(A)}$	$O_{2s(A)}$

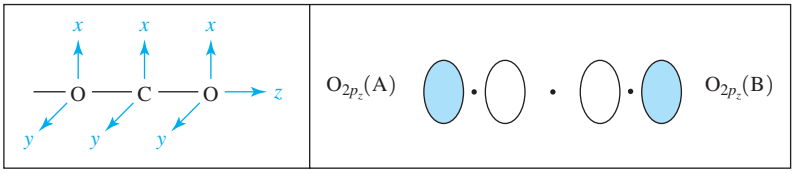
In this D_{2h} case, unlike in the C_{3v} point group, each operation is in its own class, and the number of columns above is identical to that in the D_{2h} character table. SALC(A_g) and SALC(B_{1u}) of these oxygen 2s wave functions can be obtained by multiplication of each outcome by the characters associated with each operation of these irreducible representations, followed by addition of the results:

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
A_g	$O_{2s(A)}$ +	$O_{2s(A)}$ +	$O_{2s(B)}$ +	$O_{2s(B)}$ +	$O_{2s(B)}$ +	$O_{2s(B)}$ +	$O_{2s(A)}$ +	$O_{2s(A)}$	$= 4(O_{2s(A)}) + 4(O_{2s(B)})$
B_{1u}	$O_{2s(A)}$ +	$O_{2s(A)}$ −	$O_{2s(B)}$ −	$O_{2s(B)}$ −	$O_{2s(B)}$ −	$O_{2s(B)}$ +	$O_{2s(A)}$ +	$O_{2s(A)}$	$= 4(O_{2s(A)}) - 4(O_{2s(A)})$

Normalization results in the expected group orbitals. In all molecules with two identical outer atoms, normalization always leads to $\pm\frac{1}{\sqrt{2}}$ coefficients as two atomic orbitals equally contribute toward two different SALCs.

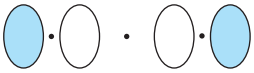
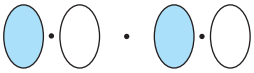
A_g	$O_{2s(A)}$		$O_{2s(B)}$	$\frac{1}{\sqrt{2}}[\psi(O_{2s(A)}) + \psi(O_{2s(B)})]$
B_{1u}	$O_{2s(A)}$		$O_{2s(B)}$	$\frac{1}{\sqrt{2}}[\psi(O_{2s(A)}) - \psi(O_{2s(B)})]$

The $2p_z$ group orbitals also possess A_g and B_{1u} symmetry. The basis for the projection operator method is again the A_g group orbital, with the same signs of the orbital lobes pointing toward the center.

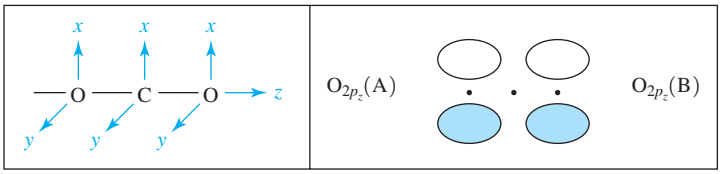


Original Orbital	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$O_{2p_z(A)}$ becomes…	$O_{2p_z(A)}$	$O_{2p_z(A)}$	$O_{2p_z(B)}$	$O_{2p_z(B)}$	$O_{2p_z(B)}$	$O_{2p_z(B)}$	$O_{2p_z(A)}$	$O_{2p_z(A)}$

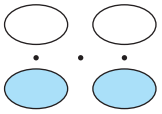
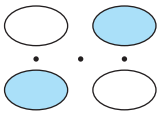
Extension to the SALCs affords the anticipated wave function equations and group orbitals; the signs are defined on the basis of the orientation of the orbitals relative to the central atom.

A_g	$O_{2p_z(A)}$		$O_{2p_z(B)}$	$\frac{1}{\sqrt{2}}[\psi(O_{2p_z(A)} + \psi(O_{2p_z(B)})]$
B_{1u}	$O_{2p_z(A)}$		$O_{2p_z(B)}$	$\frac{1}{\sqrt{2}}[\psi(O_{2p_z(A)}) - \psi(O_{2p_z(B)})]$

The SALCs for the $2p_x$ orbitals exhibit B_{3u} and B_{2g} symmetries. With the B_{3u} orbital as the basis, we encounter situations, common with group orbitals designated for π bonding, where the original orbital (in this case $O_{2p_z(A)}$) becomes its own inverse or the inverse of another orbital upon transformation by some symmetry operations.



Original Orbital	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$O_{2p_x(A)}$ becomes…	$O_{2p_x(A)}$	$-O_{2p_x(A)}$	$-O_{2p_x(B)}$	$O_{2p_x(B)}$	$-O_{2p_x(B)}$	$O_{2p_x(B)}$	$O_{2p_x(A)}$	$-O_{2p_x(A)}$
B_{3u}	$O_{2p_x(A)} + O_{2p_x(A)} + O_{2p_x(B)} + O_{2p_x(B)} + O_{2p_x(B)} + O_{2p_x(B)} + O_{2p_x(A)} + O_{2p_x(A)} = 4(O_{2p_x(A)}) + 4(O_{2p_x(B)})$							
B_{2g}	$O_{2p_x(A)} + O_{2p_x(A)} - O_{2p_x(B)} - O_{2p_x(B)} - O_{2p_x(B)} - O_{2p_x(B)} + O_{2p_x(A)} + O_{2p_x(A)} = 4(O_{2p_x(A)}) - 4(O_{2p_x(B)})$							

B_{3u}	$O_{2p_x(A)}$		$O_{2p_x(B)}$	$\frac{1}{\sqrt{2}}[\psi(O_{2p_x(A)}) + \psi(O_{2p_x(B)})]$
B_{2g}	$O_{2p_x(A)}$		$O_{2p_x(B)}$	$\frac{1}{\sqrt{2}}[\psi(O_{2p_x(A)}) - \psi(O_{2p_x(B)})]$

EXERCISE 5.10

Use the projection operator method to derive normalized SALCs that define the group orbitals for CO_2 based on the $2p_y$ orbitals.

5.4.6 BF_3

Boron trifluoride is a Lewis acid, an electron-pair acceptor. Molecular orbital theory of BF_3 must provide an orbital capable of acting as such an acceptor to be consistent with this chemical property. The VSEPR-predicted shape is trigonal, consistent with experimental observations.

The procedure for describing molecular orbitals of BF_3 differs from NH_3, because the fluorine atoms surrounding the central boron atom have $2p$ as well as $2s$ electrons to be considered. We assign the highest order rotation axis, the C_3, to be the z axis. The fluorine p_y axes are chosen to point toward the boron atom; the p_x axes are in the molecular plane. The group orbitals and their symmetry in the D_{3h} point group are shown in **Figure 5.31**. The molecular orbitals are shown in **Figure 5.32**.

As discussed in Chapter 3, consideration of all resonance structures for BF_3 suggests that this molecule possesses some double-bond character in the B—F bonds. The molecular orbital view of BF_3 has an electron pair in a bonding π orbital with a_2'' symmetry delocalized over all four atoms; this is the orbital slightly lower in energy than the five nonbonding electron pairs. Overall, BF_3 has three bonding σ orbitals (a_1' and e') and one slightly bonding π orbital (a_2'') occupied by electron pairs, together with eight nonbonding pairs on the fluorine atoms. The greater than 10 eV difference between the boron and fluorine p orbital energies renders this π orbital weakly bonding, but not insignificant.

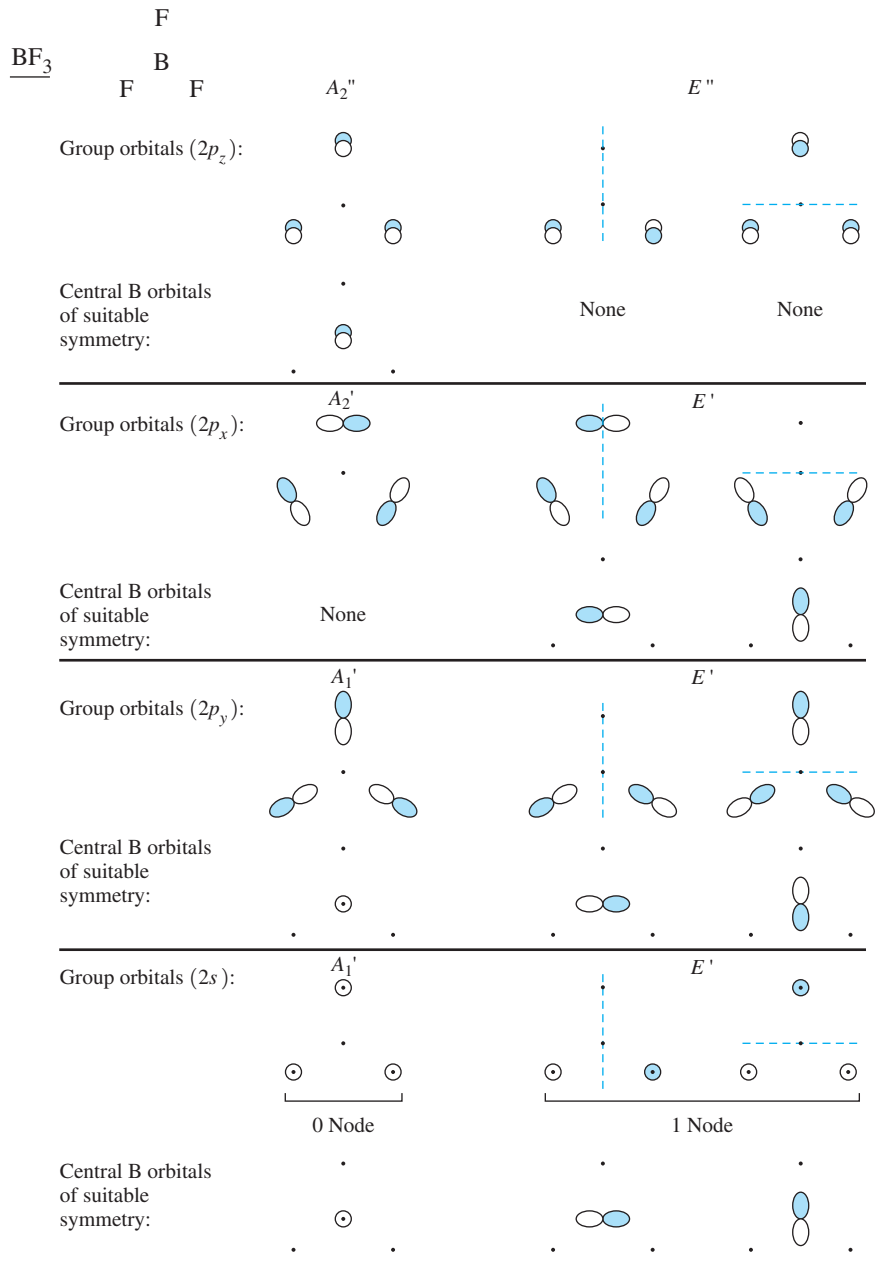


FIGURE 5.31 Group Orbitals for BF_3.

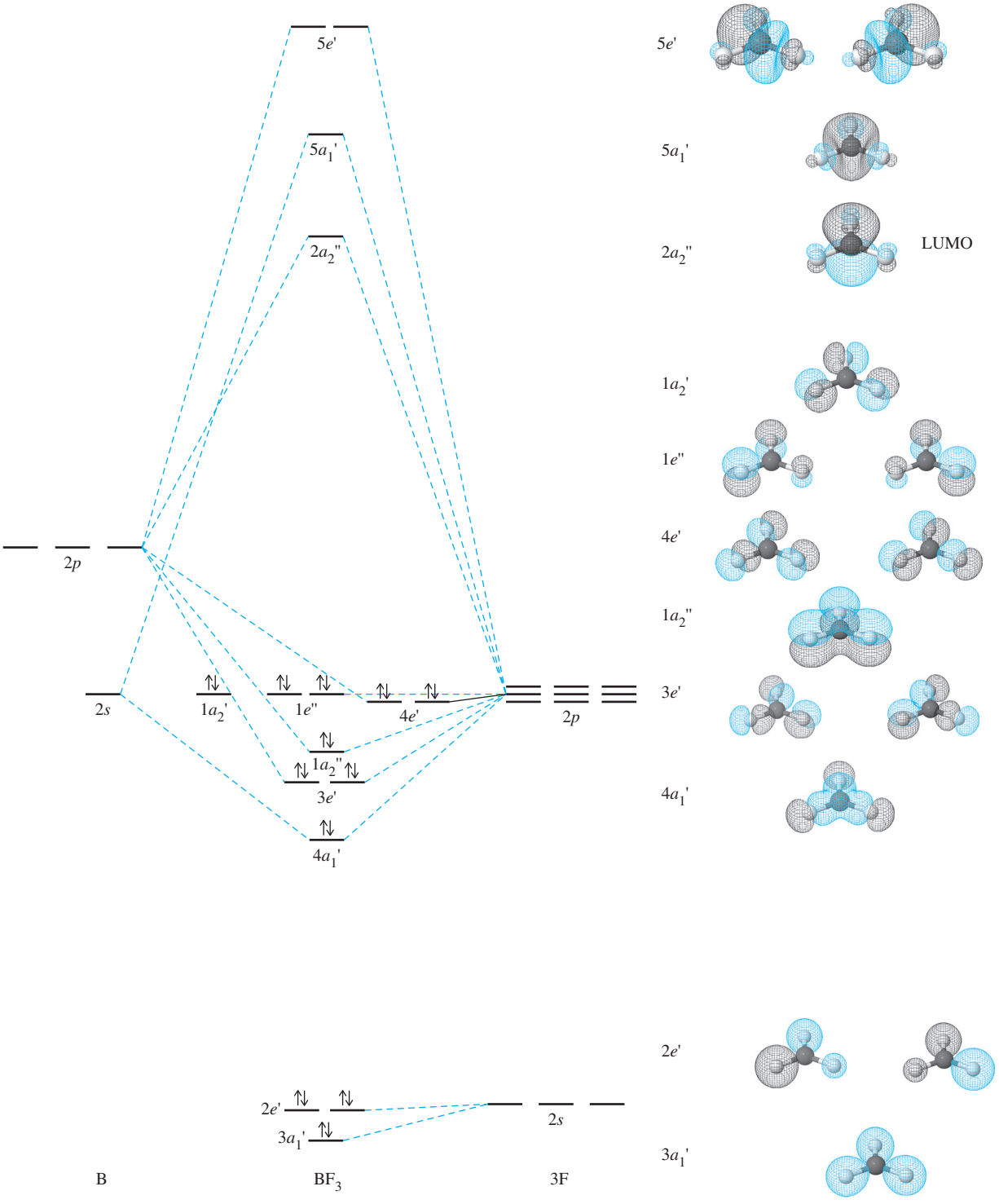


FIGURE 5.32 Molecular Orbitals of BF_3.

The LUMO of BF_3 is noteworthy. It is an empty π orbital (a_2''), which has antibonding interactions between the $2p_z$ orbital on boron and the $2p_z$ orbitals of the surrounding fluorines. This orbital has large, empty lobes on boron and can act as an electron-pair

acceptor (for example, from the HOMO of NH_3) using these lobes in Lewis acid–base interactions.

Other trigonal species can be treated using this molecular orbital theory approach. The trigonal planar SO_3, NO_3^-, and CO_3^{2-} are isoelectronic with BF_3, with three electron pairs in σ-bonding orbitals and one pair in a π-bonding orbital with contributions from all four atoms. The resonance forms of these oxygen-containing species all predict delocalized π-electron density as an important aspect of their electronic ground states.

Because the extent of orbital overlap in π interactions is generally less than that in most σ interactions, a double bond composed of one filled σ orbital and one filled π orbital is not twice as strong as a single bond. Single bonds between the same atoms, but within different chemical environments in different molecules, can have widely different energies. An "average" C—C bond is usually described as having an approximate energy of 345 kJ/mol; a large number of molecules containing C—C bonds in different environments contribute to this average energy. These individual values vary tremendously; some are as low as 69 and as high as 649 kJ/mol.[14] The low value is for hexaphenyl ethane, $(C_6H_5)_3C—C(C_6H_5)_3$, and the high is for diacetylene, H—C≡C—C≡C—H, examples of extremes in steric crowding and bonding, respectively, adjacent to the C—C bond.

The group orbital approach described in this chapter, despite its modest use of group theory, conveniently provides a qualitatively useful description of bonding in simple molecules. Computational chemistry methods are necessary for more complex molecules and to obtain wave equations for the molecular orbitals. These advanced methods also apply molecular symmetry and group theory concepts.

While a qualitative group orbital approach does not allow the determination of the precise energies of molecular orbitals, we can generally place the MOs in approximate order on the basis of their shapes and expected orbital overlaps. Relatively nonbonding energy levels at intermediate energies can be particularly difficult to rank in energy. Proficiency at estimating orbital energies is only gained by experience, and by always attempting to correlate molecular orbitals and their energies with experimental properties of the molecules under consideration. Mastery of the interactions that define the basic molecular shapes described in this chapter provides a foundation that can be extended to other geometries.

5.4.7 Hybrid Orbitals

An oversimplified bonding model, and one engrained in the chemistry vernacular, that also employs molecular symmetry and group theory involves **hybrid orbitals**. The merits of hybrid atomic orbital theory have been recently debated.[15] While the modern inorganic literature almost exclusively employs molecular orbital theory to gain insights regarding structure and bonding, chemists evoke the hydridization model when it is convenient to help visualize an interaction. In the hybrid concept, the orbitals of the central atom are combined into sets of equivalent hybrids. These hybrid orbitals form bonds with orbitals of other atoms. The hybrid model is especially useful in organic chemistry where, for example, it predicts four equivalent C—H bonds in methane. A traditional criticism of the hybrid orbital description of methane was its alleged inconsistency with photoelectron spectroscopic data. However, the assumptions associated with these conclusions have been criticized, and the utility of the hybrid orbital model in the interpretation of methane's photoelectron spectrum has been validated.[16] Like all bonding models, hybrids are useful so long as their limits are recognized.

Hybrid orbitals are localized in space and are directional, pointing in a specific direction. In general, these hybrids point from a central atom toward surrounding atoms or lone pairs. Therefore, the symmetry properties of a set of hybrid orbitals will be identical to the properties of a set of vectors with origins at the nucleus of the central atom and pointing toward the surrounding atoms.

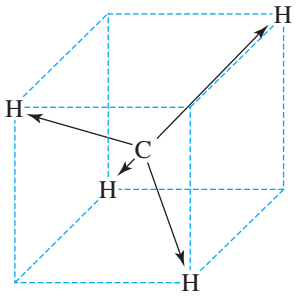


FIGURE 5.33 Bond Vectors in Methane.

For example, in methane, the vectors point at the corners of a tetrahedron or at alternate corners of a cube (**Figure 5.33**).

Using the T_d point group, these four vectors form the basis of a reducible representation. As usual, the character for each vector is 1 if it remains unchanged by the symmetry operation, and 0 if it changes position (reversing direction is not an option for hybrids). The reducible representation for these four vectors is $\Gamma = A_1 + T_2$:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ	4	1	0	0	2		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

In terms of hybrids, this means that the atomic orbitals of carbon used in the hybrids *must* have symmetry matching $A_1 + T_2$; more specifically, one orbital must match A_1, and a set of three (degenerate) orbitals must match T_2.

A_1, the totally symmetric representation, has the same symmetry as the 2*s* orbital of carbon; T_2 has the same symmetry as the three 2*p* orbitals taken together (x, y, z) or the d_{xy}, d_{xz}, and d_{yz} orbitals taken together. Because the 3*d* orbitals of carbon are at much higher energy, and are therefore a poor match for the energies of the 1*s* orbitals of the hydrogens, the hybridization for methane must be sp^3, combining four atomic orbitals—one 2*s* and three 2*p*—into four equivalent hybrid orbitals, one directed toward each hydrogen atom.

Ammonia fits the same pattern. Bonding in NH_3 uses all the nitrogen valence orbitals, so the hybrids are sp^3, incorporating one *s* orbital and all three *p* orbitals, with overall tetrahedral symmetry. The predicted HNH angle is 109.5°, reduced to the actual 106.6° by repulsion from the lone pair, which is also viewed to occupy an sp^3 orbital.

There are two hybridization descriptions for the water molecule. A commonly taught idea in general chemistry is that the electron pairs around the oxygen atom in water can be considered as adopting nearly tetrahedral symmetry (counting the two lone pairs and the two bonds equally). All four valence orbitals of oxygen are used, and the hybrid orbitals are sp^3. The predicted bond angle is then the tetrahedral angle of 109.5°, compared with the experimental value of 104.5°. Repulsion by the lone pairs explains this smaller angle.

In another approach, which complements the molecular orbital description of Section 5.4.3, the bent planar shape indicates that the oxygen orbitals used in molecular orbital bonding in water are the 2*s*, $2p_x$, and $2p_z$ (in the plane of the molecule). As a result, the hybrids could be described as sp^2, a combination of one *s* orbital and two *p* orbitals. Three sp^2 orbitals have trigonal symmetry and a predicted H—O—H angle of 120°, considerably larger than the experimental value. Repulsion by the lone pairs on the oxygen—one in an sp^2 orbital, one in the remaining p_y orbital—forces the angle to be smaller. Note that the $1b_2$ orbital in the molecular orbital picture of H_2O (Figure 5.28) is a filled nonbonding $2p_y$ orbital.

Similarly, CO_2 uses *sp* hybrids, and SO_3 uses sp^2 hybrids. Only the σ bonding is considered when determining the orbitals used in hybridization; *p* orbitals not used in the hybrids are available for π interactions. The number of atomic orbitals used in the hybrids is frequently the same as the steric number in the VSEPR method. The common hybrids are summarized in **Figure 5.34**. The group theory approach to hybridization is described in the following example.

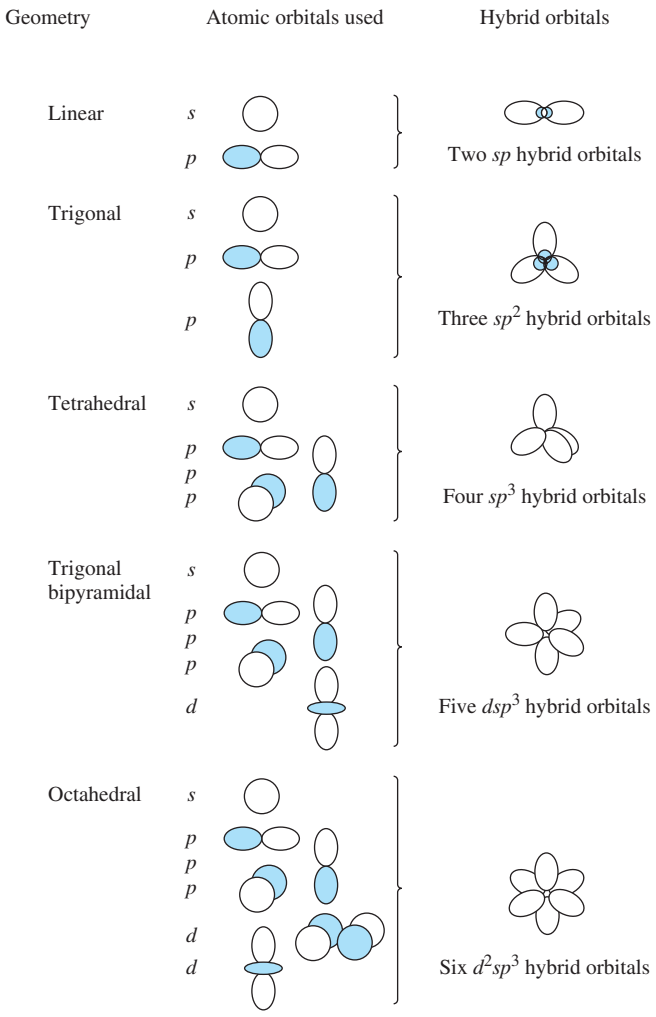


FIGURE 5.34 Hybrid Orbitals. Each single hybrid has the general shape . The figures here show all the resulting hybrids combined, omitting the smaller lobe in the sp^3 and higher orbitals.

EXAMPLE 5.11

Determine the hybrid orbitals for boron in BF_3.

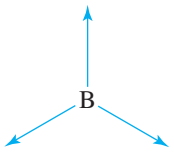
For a trigonal planar molecule such as BF_3, the orbitals likely to be involved in bonding are the $2s$, $2p_x$, and $2p_y$. This can be confirmed by finding the reducible representation in the D_{3h} point group of vectors pointing at the three fluorines and reducing it to its irreducible representations. The procedure is as follows.

Step 1 Determine the shape of the molecule (VSEPR), considering each sigma bond and lone pair on the central atom to be a vector pointing out from the center.

Step 2 Determine the reducible representation for the vectors, and deduce the irreducible representations that combine to form the reducible representation.

Step 3 The atomic orbitals that match the irreducible representations are those used in the hybrid orbitals.

Using the symmetry operations of the D_{3h} group, we find that the reducible representation $\Gamma = A_1' + E'$.



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
Γ	3	0	1	3	0	1		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$

The atomic orbitals that combine to afford the hybrids must have the same symmetry as A_1' and E'. One orbital must have A_1' symmetry and two orbitals must have E' symmetry. We must therefore select one orbital with A_1' symmetry and one *pair* of orbitals that collectively have E' symmetry. Examining the functions in the right-hand column of the character table, we see that the *s* orbital (not listed, but understood to be present for the totally symmetric representation) and the d_{z^2} orbital possess A_1' symmetry. However, the 3*d* orbitals, the lowest energy *d* orbitals, are too high in energy for bonding in BF_3 compared with the 2*s*. Therefore, the 2*s* orbital is the A_1' contributor.

The functions listed for E' symmetry match the p_x, p_y set and the $d_{x^2-y^2}$, d_{xy} set. The *d* orbitals are energetically inaccessible; the $2p_x$ and $2p_y$ orbitals are used by the central atom.*

Overall, the orbitals used in the hybridization are the 2*s*, $2p_x$, and $2p_y$ orbitals of boron, comprising the familiar sp^2 hybrids. The difference between this approach and the molecular orbital approach is that these orbitals are combined to form the hybrids before considering their interactions with the fluorine orbitals. Because the overall symmetry is trigonal planar, the resulting hybrids must have that same symmetry, so the three sp^2 orbitals point at the three corners of a triangle, and each interacts with a fluorine *p* orbital to form the three σ bonds. The $2p_z$ orbital is not involved in the bonding and, according to the hybrid approach, is empty; this orbital serves as an acceptor in acid–base reactions.

EXERCISE 5.11 Determine the types of hybrid orbitals that are consistent with the symmetry of the central atom in

a. PF_5

b. $[PtCl_4]^{2-}$, a square planar ion

The procedure for determining hybrids is in some respects similar to that used in the molecular orbital approach. Hybridization uses vectors pointing toward the outlying atoms and usually deals only with σ bonding. Once the σ hybrids are known, π bonding is added, using orbitals that do not participate in the hybridization. It is also possible to use hybridization techniques for π bonding.[17] As an approximate approach, hybridization may be quicker than the molecular orbital approach, because the molecular orbital approach uses all the atomic orbitals of the atoms and includes both σ and π bonding directly. Molecular orbital theory has gained prominence on the basis of its ability to predict the relative energies of electrons in molecules much more successfully than the hybrid orbital approach.[17]

EXERCISE 5.12

Determine the reducible representation for all the σ bonds, reduce it to its irreducible representations, and determine the sulfur orbitals used in bonding for $SOCl_2$.

*A combination of one *p* orbital and one *d* orbital cannot be chosen, because orbitals in parentheses must always be taken together.

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General References

There are many books describing bonding and molecular orbitals, with levels ranging from those even more descriptive and qualitative than the treatment in this chapter to those designed for the theoretician interested in the latest methods. A classic that starts at the level of this chapter and includes many more details is R. McWeeny's revision of *Coulson's Valence*, 3rd ed., Oxford University Press, Oxford, 1979. A different approach that uses the concept of generator orbitals is that of J. G. Verkade in *A Pictorial Approach to Molecular Bonding and Vibrations*, 2nd ed., Springer-Verlag, New York, 1997. The group theory approach in this chapter is similar to that of F. A. Cotton in *Chemical Applications of Group Theory*, 3rd ed., John Wiley & Sons, New York, 1990. A more recent book that extends the description is Y. Jean and F. Volatron, *An Introduction to Molecular Orbitals*, translated and edited by J. K. Burdett, Oxford University Press, Oxford, 1993. J. K. Burdett's *Molecular Shapes*, John Wiley & Sons, New York, 1980, and B. M. Gimarc's, *Molecular Structure and Bonding*, Academic Press, New York, 1979, are both good introductions to the qualitative molecular orbital description of bonding.

This is the first chapter that includes problems involving molecular modeling software. Discussion of such software is beyond the scope of this text. E. G. Lewars, *Computational Chemistry*, 2nd ed., Springer, New York, 2011 provides a readable introduction to the theory and applications of molecular modeling. In addition, examples of uses of molecular modeling in chemistry curricula are discussed in L. E. Johnson, T. Engel, *J. Chem. Educ.*, **2011**, *88*, 569 and references cited therein.

Problems

5.1 Expand the list of orbitals considered in Figures 5.2 and 5.3 by using all three *p* orbitals of atom A and all five *d* orbitals of atom B. Which of these have the necessary match of symmetry for bonding and antibonding orbitals? These combinations are rarely seen in simple molecules but can be important in transition metal complexes.

5.2 On the basis of molecular orbitals, predict the shortest bond, and provide a brief explanation.

a. Li_2^+ Li_2

b. F_2^+ F_2

c. He_2^+ HHe^+ H_2^+

5.3 On the basis of molecular orbitals, predict the weakest bond, and provide a brief explanation.

a. P_2 S_2 Cl_2

b. S_2^+ S_2 S_2^-

c. NO^- NO NO^+

5.4 Compare the bonding in O_2^{2-}, O_2^-, and O_2. Include Lewis structures, molecular orbital structures, bond lengths, and bond strengths in your discussion.

5.5 Although the peroxide ion, O_2^{2-}, and the acetylide ion, C_2^{2-}, have long been known, the diazenide ion N_2^{2-} has only been prepared much more recently. By comparison with the other diatomic species, predict the bond order,

bond distance, and number of unpaired electrons for N_2^{2-}. (See G. Auffermann, Y. Prots, R. Kniep, *Angew. Chem., Int. Ed.*, **2001**, *40*, 547.)

5.6 High-resolution photoelectron spectroscopy has provided information on the energy levels and bond distance in the ion Ar_2^+. Prepare a molecular orbital energy-level diagram for this ion. How would you expect the bond distance in Ar_2^+ to compare with 198.8 pm, the bond distance in Cl_2? (See A. Wüst, F. Merkt, *J. Chem. Phys.*, **2004**, *120*, 638.)

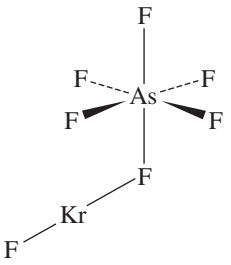
5.7 **a.** Prepare a molecular orbital energy-level diagram for NO, showing clearly how the atomic orbitals interact to form MOs.
b. How does your diagram illustrate the difference in electronegativity between N and O?
c. Predict the bond order and the number of unpaired electrons.
d. NO^+ and NO^- are also known. Compare the bond orders of these ions with the bond order of NO. Which of the three would you predict to have the shortest bond? Why?

5.8 **a.** Prepare a molecular orbital energy-level diagram for the cyanide ion. Use sketches to show clearly how the atomic orbitals interact to form MOs.
b. What is the bond order for cyanide, and how many unpaired electrons does cyanide have?
c. Which molecular orbital of CN^- would you predict to interact most strongly with a hydrogen 1*s* orbital to form an H—C bond in the reaction $CN^- + H^+ \rightarrow HCN$? Explain.

5.9 NF is a known molecule!
a. Construct a molecular orbital energy-level diagram for NF, being sure to include sketches that show how the valence orbitals of N and F interact to form molecular orbitals.
b. What is the most likely bond order for NF?
c. What are the point groups of the molecular orbitals of this molecule?
(See D. J. Grant, T-H. Wang, M. Vasiliu, D. A. Dixon, K. O. Christe, *Inorg. Chem.* **2011**, *50*, 1914 for references and theoretical calculations of numerous small molecules and ions having formula N_xF_y.)

5.10 The hypofluorite ion, OF^-, can be observed only with difficulty.
a. Prepare a molecular orbital energy level diagram for this ion.
b. What is the bond order, and how many unpaired electrons are in this ion?
c. What is the most likely position for adding H^+ to the OF^- ion? Explain your choice.

5.11 Reaction of KrF_2 with AsF_5 at temperatures between −78 and −53 °C yields $[KrF][AsF_6]$, a compound in which KrF^+ interacts strongly with AsF_6^- through a fluorine bridge, as shown. Would you predict the Kr—F bond to be shorter in KrF^+ or in KrF_2? Provide a brief explanation. (See J. F. Lehmann, D. A. Dixon, G. J. Schrobilgen, *Inorg. Chem.,* **2001**, *40*, 3002.)



5.12 Although KrF^+ and XeF^+ have been studied, $KrBr^+$ has not yet been prepared. For $KrBr^+$:
a. Propose a molecular orbital diagram, showing the interactions of the valence shell *s* and *p* orbitals to form molecular orbitals.
b. Toward which atom would the HOMO be polarized? Why?
c. Predict the bond order.
d. Which is more electronegative, Kr or Br? Explain your reasoning.

5.13 Prepare a molecular orbital energy level diagram for SH^-, including sketches of the orbital shapes and the number of electrons in each of the orbitals. If a program for calculating molecular orbitals is available, use it to confirm your predictions or to explain why they differ.

5.14 Methylene, CH_2, plays an important role in many reactions. One possible structure of methylene is linear.
a. Construct a molecular orbital energy-level diagram for this species. Include sketches of the group orbitals, and indicate how they interact with the appropriate orbitals of carbon.
b. Would you expect linear methylene to be diamagnetic or paramagnetic?

5.15 Beryllium hydride, BeH_2, is linear in the gas phase.
a. Construct a molecular orbital energy level diagram for BeH_2. Include sketches of the group orbitals, and indicate how they interact with the appropriate orbitals of Be.
b. If you have worked Problem 5.14, compare the results of these two problems.

5.16 In the gas phase, BeF_2 forms linear monomeric molecules. Prepare a molecular orbital energy-level diagram for BeF_2, showing clearly which atomic orbitals are involved in bonding and which are nonbonding.

5.17 For the compound XeF_2 do the following:
a. Sketch the valence shell group orbitals for the fluorine atoms (with the *z* axes collinear with the molecular axis).
b. For each of the group orbitals, determine which outermost *s*, *p*, and *d* orbitals of xenon are of suitable symmetry for interaction and bonding.

5.18 TaH_5 has been predicted to have C_{4v} symmetry, with a calculated axial H—Ta—H angle of approximately 117.5°. Using the six-step approach described in Section 5.4.2, describe the bonding in TaH_5 on the basis of matching group orbitals and central atom orbitals according to their symmetry. (See C. A. Bayse, M. B. Hall, *J. Am. Chem. Soc.*, **1999**, *121*, 1348.)

5.19 Describe the bonding in ozone, O_3, on the basis of matching group orbitals and central-atom orbitals according to their symmetry. Include both σ and π interactions, and try to put the resulting orbitals in approximate order of energy.

5.20 Describe the bonding in SO_3 by using group theory to find the molecular orbitals. Include both σ and π interactions, and try to put the resulting orbitals in approximate order of energy. (The actual results are more complex because of mixing of orbitals, but a simple description can be found by the methods given in this chapter.)

5.21 The ion H_3^+ has been observed, but its structure has been the subject of some controversy. Prepare a molecular orbital energy level diagram for H_3^+, assuming a cyclic structure. (The same problem for a linear structure is given in Exercise 5.4 in Section 5.4.2.)

5.22 Use molecular orbital arguments to explain the structures of SCN^-, OCN^-, and CNO^-, and compare the results with the electron-dot pictures of Chapter 3.

5.23 Thiocyanate and cyanate ions both bond to H^+ through the nitrogen atoms (HNCS and HNCO), whereas SCN^- forms bonds with metal ions through either nitrogen or sulfur, depending on the rest of the molecule. What does this suggest about the relative importance of S and N orbitals in the MOs of SCN^-? (Hint: See the discussion of CO_2 bonding in Section 5.4.2.)

5.24 The thiocyanate ion, SCN^-, can form bonds to metals through either S or N (see Problem 5.23). What is the likelihood of cyanide, CN^-, forming bonds to metals through N as well as C?

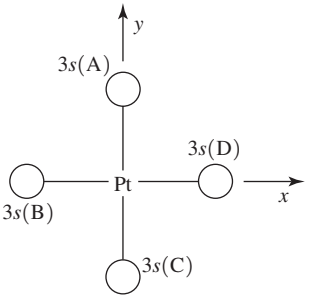
5.25 The isomeric ions NSO^- (thiazate) and SNO^- (thionitrite) ions have been reported. (S. P. So, *Inorg. Chem.*, **1989**, *28*, 2888).

- **a.** On the basis of the resonance structures of these ions, predict which would be more stable.
- **b.** Sketch the approximate shapes of the π and π^* orbitals of these ions.
- **c.** Predict which ion would have the shorter N—S bond and which would have the higher energy N—S stretching vibration? (Stronger bonds have higher energy vibrations.)

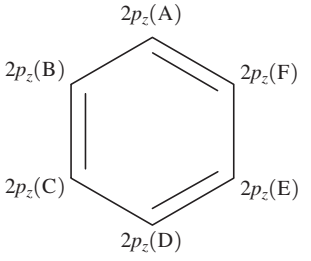
5.26 Apply the projection operator method to derive the group orbital SALCs for H_2O given in Section 5.4.3. Confirm using the squares of the coefficients that the group orbital wave function equations are normalized and that each 1*s* orbital contributes equally to the two group orbitals.

5.27 Apply the projection operator method to derive the group orbital SALCs for BF_3 on the basis of the irreducible representations given in Figure 5.31 for sets of $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals, respectively. Employ a set of three identical orbitals where all have the same bias (i.e., the group orbitals with A_1', A_2', and A_2'' symmetry in Figure 5.31) as a starting point. For each determination, provide a table like that in Section 5.4.4 to tabulate wave function coefficients, their squares, and how these values simultaneously satisfy the normalization requirement and confirm that each atomic orbital contributes equally to each set of group orbitals.

5.28 A set of four group orbitals derived from four 3*s* atomic orbitals is necessary to examine the bonding in $[PtCl_4]^-$, a square planar complex. Deduce the wave function equations for these four SALCs using the 3*s* labeling scheme specified, starting with the irreducible representations for these group orbitals. Using sketches of the deduced orbitals, symmetry characteristics of the representations, and a coefficient table like that in Section 5.4.4, deduce the SALCs not derived initially from the character table analysis. Provide normalized equations and a sketch for each group orbital.



5.29 The projection operator method has applications beyond the deduction of group orbital SALCs. Deduce the wave function equations for the six π molecular orbitals of benzene, using the labels specified for each $2p_z$ orbital. First, derive initial SALCs using *each* representation of the D_{6h} point group; some combinations will afford zero. Using sketches of the deduced orbitals, symmetry characteristics of the representations, and a coefficient table like that in Section 5.4.4, deduce the SALCs not derived initially from the character table analysis. Provide normalized equations and a sketch for each π molecular orbital.



5.30 Although the Cl_2^+ ion has not been isolated, it has been detected in the gas phase by UV spectroscopy. An attempt to prepare this ion by reaction of Cl_2 with IrF_6 yielded not Cl_2^+, but the rectangular ion Cl_4^+. (See S. Seidel, K. Seppelt, *Angew. Chem., Int. Ed.*, **2000**, *39*, 3923.)

- **a.** Compare the bond distance and bond energy of Cl_2^+ with Cl_2.

b. Account for the bonding in Cl_4^+. This ion contains two short Cl—Cl bonds and two much longer ones. Would you expect the shorter Cl—Cl distances in Cl_4^+ to be longer or shorter than the Cl—Cl distance in Cl_2? Explain.

5.31 BF_3 is often described as a molecule in which boron is electron deficient, with an electron count of six. However, resonance structures can be drawn in which boron has an octet, with delocalized π electrons.
a. Draw these structures.
b. Find the molecular orbital in Figure 5.32 that shows this delocalization and explain your choice.
c. BF_3 is *the* classic Lewis acid, accepting a pair of electrons from molecules with lone pairs. Find the orbital in Figure 5.32 that is this acceptor; explain your choice, including why it looks like a good electron acceptor.
d. What is the relationship between the orbitals identified in Parts b and c?

5.32 SF_4 has C_{2v} symmetry. Predict the possible hybridization schemes for the sulfur atom in SF_4.

5.33 Consider a square pyramidal AB_5 molecule. Using the C_{4v} character table, determine the possible hybridization schemes for central atom A. Which of these would you expect to be most likely?

5.34 In coordination chemistry, many square-planar species are known (for example, $[PtCl_4]^{2-}$). For a square planar molecule, use the appropriate character table to determine the types of hybridization possible for a metal surrounded in a square-planar fashion by four ligands; consider hybrids used in σ bonding only.

5.35 For the molecule PCl_5:
a. Using the character table for the point group of PCl_5, determine the possible type(s) of hybrid orbitals that can be used by P in forming σ bonds to the five Cl atoms.
b. What type(s) of hybrids can be used in bonding to the axial chlorine atoms? To the equatorial chlorine atoms?
c. Considering your answer to part b, explain the experimental observation that the axial P—Cl bonds (219 pm) are longer than the equatorial bonds (204 pm).

The following problems require the use of molecular modeling software.

5.36 **a.** Identify the point group of the $1a_2''$, $2a_2''$, $1a_2'$, and $1e''$ molecular orbitals in Figure 5.32.
b. Use molecular modeling software to calculate and view the molecular orbitals of BF_3.
c. Do any of the molecular orbitals show interactions between B and F?
d. Print out the contributions of the atomic orbitals to the $3a_1'$, $4a_1'$, $1a_2''$, $1a_2'$, and $2a_2''$ molecular orbitals, confirming (if you can) the atomic orbital combinations shown in Figure 5.32.

5.37 The ions and molecules NO^+, CN^-, CO, and N_2 and N_2 form an isoelectronic series. The changing nuclear charges will also change the molecular energy levels of the orbitals formed from the $2p$ atomic orbitals (1π, 3σ, and $1\pi^*$). Use molecular modeling software for the following:
a. Calculate and display the shapes of these three molecular orbitals for each species (CO and N_2 are included in this chapter).
b. Compare the shapes of each of the orbitals for each of the species (for example, the shapes of the 1π orbitals for each). What trends do you observe?
c. Compare the energies of each of the orbitals. For which do you see evidence of mixing?

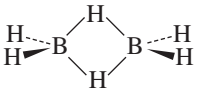
5.38 Molecular modeling software is typically capable of calculations on molecules that are hypothetical, even seemingly bizarre, in their structures. Beginning with N_2, calculate and display molecular orbitals of the isoelectronic CO, BF, and BeNe (which is truly hypothetical!). Compare the shapes of the matching molecular orbital in this series What trends do you observe?

5.39 Calculate and display the orbitals for the linear molecule BeH_2. Describe how they illustrate the interaction of the outer group orbitals with the orbitals on the central atom. Compare your results with the answer to Problem 5.15.

5.40 Calculate and display the orbitals for the linear molecule BeF_2. Compare the orbitals and their interactions with those of BeH_2 from Problem 5.39. In particular, indicate the outer group orbitals that do not interact with orbitals on the central atom.

5.41 The azide ion, N_3^-, is another linear triatomic species. Calculate and display the orbitals for this ion, and compare the three highest energy occupied orbitals with those of BeF_2. How do the outer atom group orbitals differ in their interactions with the central atom orbitals? How do the orbitals compare with the CO_2 orbitals discussed in Section 5.4.2?

5.42 Calculate and display the molecular orbitals of the ozone molecule, O_3. Which orbitals show π interactions? Compare your results with your answer to Problem 5.19.

5.43 **a.** Calculate and display the molecular orbitals for linear and cyclic H_3^+.
b. Which species is more likely to exist (i.e., which is more stable)?

5.44 Diborane, B_2H_6, has the structure shown.
a. Using the point group of the molecule, create a representation using the $1s$ orbitals on the hydrogens as a basis. Reduce this representation, and sketch group orbitals matching each of the irreducible representations. (Suggestion: Treat the bridging and terminal hydrogens separately.)
b. Calculate and display the molecular orbitals. Compare the software-generated images with the group orbital sketches from part a, and explain how hydrogen can form "bridges" between two B atoms. (This type of bonding is discussed in Chapter 8.)