

Figure 10.21 Liquid oxygen caught between the poles of a magnet, because the O_2 molecules are paramagnetic, having two parallel spins.

10.6 Molecular Orbital Theory

Valence bond theory is one of the two quantum mechanical approaches that explain bonding in molecules. It accounts, at least qualitatively, for the stability of the covalent bond in terms of overlapping atomic orbitals. Using the concept of hybridization, valence bond theory can explain molecular geometries predicted by the VSEPR model. However, the assumption that electrons in a molecule occupy atomic orbitals of the individual atoms can only be an approximation, because each bonding electron in a molecule must be in an orbital that is characteristic of the molecule as a whole.

In some cases, valence bond theory cannot satisfactorily account for observed properties of molecules. Consider the oxygen molecule, whose Lewis structure is



According to this description, all the electrons in O_2 are paired and oxygen should therefore be diamagnetic. But experiments have shown that the oxygen molecule has two unpaired electrons (Figure 10.21). This finding suggests a fundamental deficiency in valence bond theory, one that justifies searching for an alternative bonding approach that accounts for the properties of O_2 and other molecules that do not match the predictions of valence bond theory.

Magnetic and other properties of molecules are sometimes better explained by another quantum mechanical approach called *molecular orbital (MO) theory*. Molecular orbital theory describes covalent bonds in terms of *molecular orbitals*, which result from interaction of the atomic orbitals of the bonding atoms and are associated with the entire molecule. The difference between a molecular orbital and an atomic orbital is that an atomic orbital is associated with only one atom.

Review of Concepts

One way to account for the fact that an O_2 molecule contains two unpaired electrons is to draw the following Lewis structure:



Suggest two reasons why this structure is unsatisfactory.

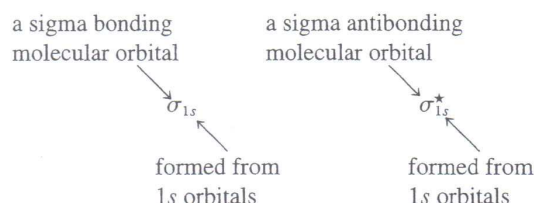
Bonding and Antibonding Molecular Orbitals

According to MO theory, the overlap of the $1s$ orbitals of two hydrogen atoms leads to the formation of two molecular orbitals: one bonding molecular orbital and one antibonding molecular orbital. A *bonding molecular orbital* has lower energy and greater stability than the atomic orbitals from which it was formed. An *antibonding molecular orbital* has higher energy and lower stability than the atomic orbitals from which it was formed. As the names “bonding” and “antibonding” suggest, placing electrons in a bonding molecular orbital yields a stable covalent bond, whereas placing electrons in an antibonding molecular orbital results in an unstable bond.

In the bonding molecular orbital, the electron density is greatest between the nuclei of the bonding atoms. In the antibonding molecular orbital, on the other hand, the electron density decreases to zero between the nuclei. We can understand this

distinction if we recall that electrons in orbitals have wave characteristics. A property unique to waves enables waves of the same type to interact in such a way that the resultant wave has either an enhanced amplitude or a diminished amplitude. In the former case, we call the interaction *constructive interference*; in the latter case, it is *destructive interference* (Figure 10.22).

The formation of bonding molecular orbitals corresponds to constructive interference (the increase in amplitude is analogous to the buildup of electron density between the two nuclei). The formation of antibonding molecular orbitals corresponds to destructive interference (the decrease in amplitude is analogous to the decrease in electron density between the two nuclei). The constructive and destructive interactions between the two $1s$ orbitals in the H_2 molecule, then, lead to the formation of a sigma bonding molecular orbital σ_{1s} and a sigma antibonding molecular orbital σ_{1s}^* .



where the star denotes an antibonding molecular orbital.

In a *sigma molecular orbital* (bonding or antibonding) the electron density is concentrated symmetrically around a line between the two nuclei of the bonding atoms. Two electrons in a sigma molecular orbital form a sigma bond (see Section 10.5). Remember that a single covalent bond (such as H—H or F—F) is almost always a sigma bond.

Figure 10.23 shows the *molecular orbital energy level diagram*—that is, the relative energy levels of the orbitals produced in the formation of the H_2 molecule—and the constructive and destructive interferences between the two $1s$ orbitals. Notice that in the antibonding molecular orbital there is a *nodal plane* between the nuclei that signifies zero electron density. The nuclei are repelled by each other's positive

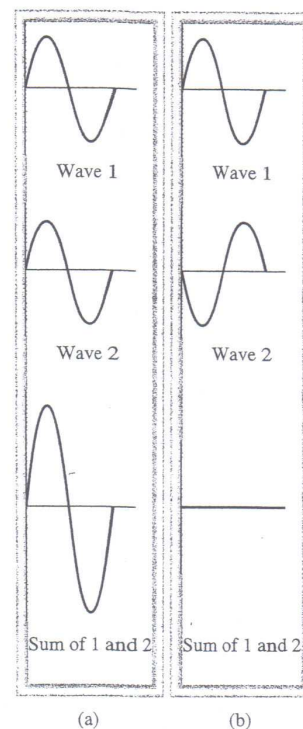


Figure 10.22 Constructive interference (a) and destructive interference (b) of two waves of the same wavelength and amplitude.

The two electrons in the sigma molecular orbital are paired. The Pauli exclusion principle applies to molecules as well as to atoms.

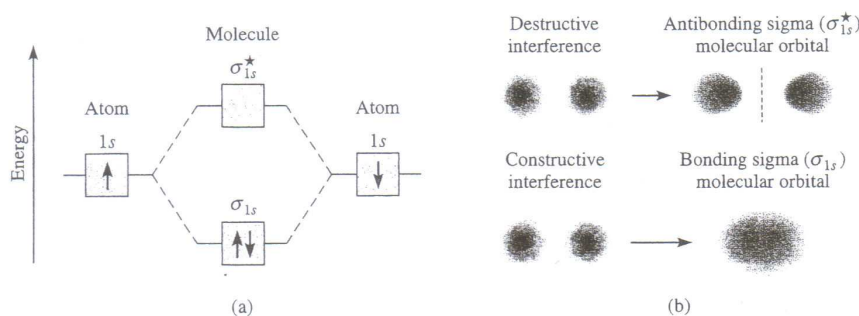


Figure 10.23 (a) Energy levels of bonding and antibonding molecular orbitals in the H_2 molecule. Note that the two electrons in the σ_{1s} orbital must have opposite spins in accord with the Pauli exclusion principle. Keep in mind that the higher the energy of the molecular orbital, the less stable the electrons in that molecular orbital. (b) Constructive and destructive interferences between the two hydrogen $1s$ orbitals lead to the formation of a bonding and an antibonding molecular orbital. In the bonding molecular orbital, there is a buildup between the nuclei of electron density, which acts as a negatively charged "glue" to hold the positively charged nuclei together. In the antibonding molecular orbital, there is a nodal plane between the nuclei, where the electron density is zero.

charges, rather than held together. Electrons in the antibonding molecular orbital have higher energy (and less stability) than they would have in the isolated atoms. On the other hand, electrons in the bonding molecular orbital have less energy (and hence greater stability) than they would have in the isolated atoms.

Although we have used the hydrogen molecule to illustrate molecular orbital formation, the concept is equally applicable to other molecules. In the H_2 molecule, we consider only the interaction between $1s$ orbitals; with more complex molecules we need to consider additional atomic orbitals as well. Nevertheless, for all s orbitals, the process is the same as for $1s$ orbitals. Thus, the interaction between two $2s$ or $3s$ orbitals can be understood in terms of the molecular orbital energy level diagram and the formation of bonding and antibonding molecular orbitals shown in Figure 10.23.

For p orbitals, the process is more complex because they can interact with each other in two different ways. For example, two $2p$ orbitals can approach each other end-to-end to produce a sigma bonding and a sigma antibonding molecular orbital, as shown in Figure 10.24(a). Alternatively, the two p orbitals can

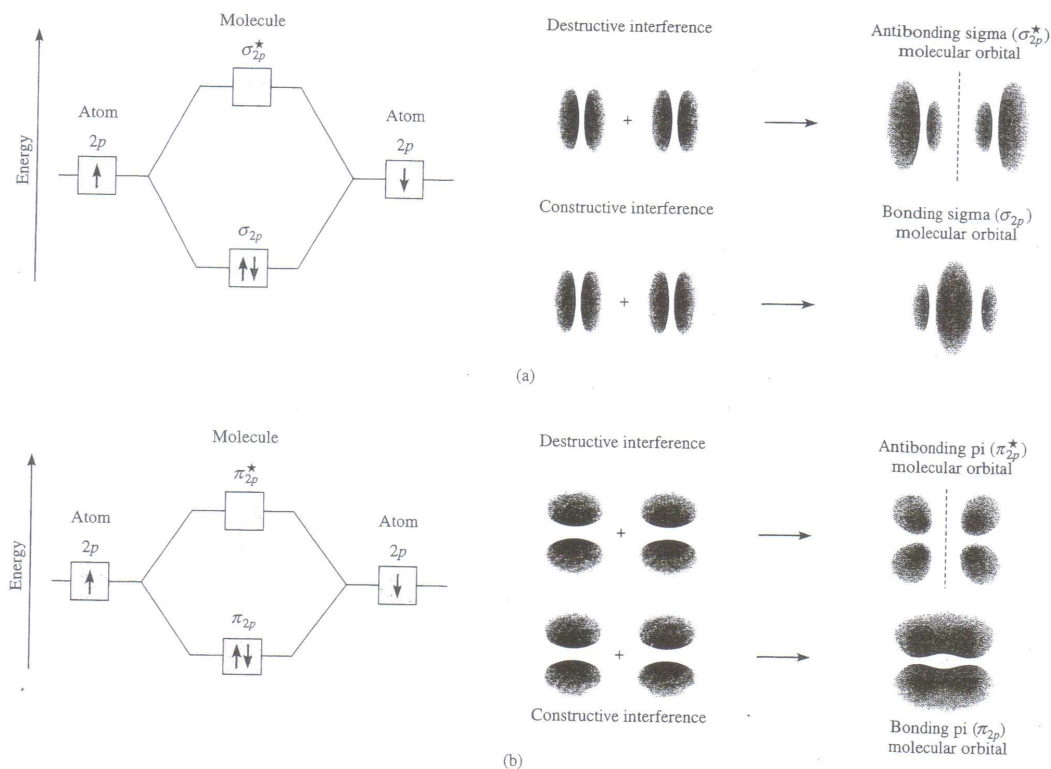
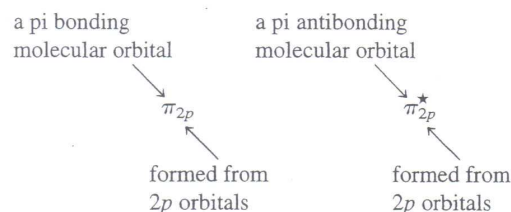


Figure 10.24 Two possible interactions between two equivalent p orbitals and the corresponding molecular orbitals. (a) When the p orbitals overlap end-to-end, a sigma bonding and a sigma antibonding molecular orbital form. (b) When the p orbitals overlap side-to-side, a pi bonding and a pi antibonding molecular orbital form. Normally, a sigma bonding molecular orbital is more stable than a pi bonding molecular orbital, because side-to-side interaction leads to a smaller overlap of the p orbitals than does end-to-end interaction. We assume that the $2p_x$ orbitals take part in the sigma molecular orbital formation. The $2p_y$ and $2p_z$ orbitals can interact to form only π molecular orbitals. The behavior shown in (b) represents the interaction between the $2p_y$ orbitals or the $2p_z$ orbitals. In both cases, the dashed line represents a nodal plane between the nuclei, where the electron density is zero.

overlap sideways to generate a bonding and an antibonding pi molecular orbital [Figure 10.24(b)].



In a *pi molecular orbital* (bonding or antibonding), the electron density is concentrated above and below a line joining the two nuclei of the bonding atoms. Two electrons in a pi molecular orbital form a pi bond (see Section 10.5). A double bond is almost always composed of a sigma bond and a pi bond; a triple bond is always a sigma bond plus two pi bonds.

10.7 Molecular Orbital Configurations

To understand properties of molecules, we must know how electrons are distributed among molecular orbitals. The procedure for determining the electron configuration of a molecule is analogous to the one we use to determine the electron configurations of atoms (see Section 7.8).

Rules Governing Molecular Electron Configuration and Stability

In order to write the electron configuration of a molecule, we must first arrange the molecular orbitals in order of increasing energy. Then we can use the following guidelines to fill the molecular orbitals with electrons. The rules also help us understand the stabilities of the molecular orbitals.

1. The number of molecular orbitals formed is always equal to the number of atomic orbitals combined.
2. The more stable the bonding molecular orbital, the less stable the corresponding antibonding molecular orbital.
3. The filling of molecular orbitals proceeds from low to high energies. In a stable molecule, the number of electrons in bonding molecular orbitals is always greater than that in antibonding molecular orbitals because we place electrons first in the lower-energy bonding molecular orbitals.
4. Like an atomic orbital, each molecular orbital can accommodate up to two electrons with opposite spins in accordance with the Pauli exclusion principle.
5. When electrons are added to molecular orbitals of the same energy, the most stable arrangement is predicted by Hund's rule; that is, electrons enter these molecular orbitals with parallel spins.
6. The number of electrons in the molecular orbitals is equal to the sum of all the electrons on the bonding atoms.

Hydrogen and Helium Molecules

Later in this section we will study molecules formed by atoms of the second-period elements. Before we do, it will be instructive to predict the relative stabilities of the simple species H_2^+ , H_2 , He_2^+ , and He_2 , using the energy-level diagrams shown in

Figure 10.25 Energy levels of the bonding and antibonding molecular orbitals in H_2^+ , H_2 , He_2^+ , and He_2 . In all these species, the molecular orbitals are formed by the interaction of two $1s$ orbitals.

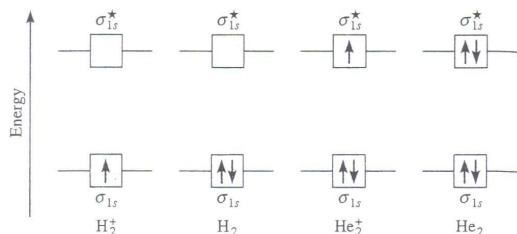


Figure 10.25. The σ_{1s} and σ_{1s}^* orbitals can accommodate a maximum of four electrons. The total number of electrons increases from one for H_2^+ to four for He_2 . The Pauli exclusion principle stipulates that each molecular orbital can accommodate a maximum of two electrons with opposite spins. We are concerned only with the ground-state electron configurations in these cases.

To evaluate the stabilities of these species we determine their **bond order**, defined as

$$\text{bond order} = \frac{1}{2} \left(\begin{array}{c} \text{number of electrons} \\ \text{in bonding MOs} \end{array} - \begin{array}{c} \text{number of electrons} \\ \text{in antibonding MOs} \end{array} \right) \quad (10.2)$$

The quantitative measure of the strength of a bond is bond enthalpy (Section 9.10).

The bond order indicates the approximate strength of a bond. For example, if there are two electrons in the bonding molecular orbital and none in the antibonding molecular orbital, the bond order is one, which means that there is one covalent bond and that the molecule is stable. Note that the bond order can be a fraction, but a bond order of zero (or a negative value) means the bond has no stability and the molecule cannot exist. Bond order can be used only qualitatively for purposes of comparison. For example, a bonding sigma molecular orbital with two electrons and a bonding pi molecular orbital with two electrons would each have a bond order of one. Yet, these two bonds must differ in bond strength (and bond length) because of the differences in the extent of atomic orbital overlap.

We are ready now to make predictions about the stability of H_2^+ , H_2 , He_2^+ , and He_2 (see Figure 10.25). The H_2^+ molecular ion has only one electron in the σ_{1s} orbital. Because a covalent bond consists of two electrons in a bonding molecular orbital, H_2^+ has only half of one bond, or a bond order of $\frac{1}{2}$. Thus, we predict that the H_2^+ molecule may be a stable species. The electron configuration of H_2^+ is written as $(\sigma_{1s})^1$.

The H_2 molecule has two electrons, both of which are in the σ_{1s} orbital. According to our scheme, two electrons equal one full bond; therefore, the H_2 molecule has a bond order of one, or one full covalent bond. The electron configuration of H_2 is $(\sigma_{1s})^2$.

As for the He_2^+ molecular ion, we place the first two electrons in the σ_{1s} orbital and the third electron in the σ_{1s}^* orbital. Because the antibonding molecular orbital is destabilizing, we expect He_2^+ to be less stable than H_2 . Roughly speaking, the instability resulting from the electron in the σ_{1s}^* orbital is balanced by one of the σ_{1s} electrons. The bond order is $\frac{1}{2}(2 - 1) = \frac{1}{2}$ and the overall stability of He_2^+ is similar to that of the H_2^+ molecule. The electron configuration of He_2^+ is $(\sigma_{1s})^2(\sigma_{1s}^*)^1$.

In He_2 there would be two electrons in the σ_{1s} orbital and two electrons in the σ_{1s}^* orbital, so the molecule would have a bond order of zero and no net stability. The electron configuration of He_2 would be $(\sigma_{1s})^2(\sigma_{1s}^*)^2$.

The superscript in $(\sigma_{1s})^1$ indicates that there is one electron in the sigma bonding molecular orbital.

To summarize, we can arrange our examples in order of decreasing stability:



We know that the hydrogen molecule is a stable species. Our simple molecular orbital method predicts that H_2^+ and He_2^+ also possess some stability, because both have bond orders of $\frac{1}{2}$. Indeed, their existence has been confirmed by experiment. It turns out that H_2^+ is somewhat more stable than He_2^+ , because there is only one electron in the hydrogen molecular ion and therefore it has no electron-electron repulsion. Furthermore, H_2^+ also has less nuclear repulsion than He_2^+ . Our prediction about He_2 is that it would have no stability, but in 1993 He_2 gas was found to exist. The “molecule” is extremely unstable and has only a transient existence under specially created conditions.

Review of Concepts

Estimate the bond enthalpy (kJ/mol) of the H_2^+ ion.

Homonuclear Diatomic Molecules of Second-Period Elements

We are now ready to study the ground-state electron configuration of molecules containing second-period elements. We will consider only the simplest case, that of *homonuclear diatomic molecules*, or *diatomic molecules containing atoms of the same elements*.

Figure 10.26 shows the molecular orbital energy level diagram for the first member of the second period, Li_2 . These molecular orbitals are formed by the overlap of $1s$ and $2s$ orbitals. We will use this diagram to build up all the diatomic molecules, as we will see shortly.

The situation is more complex when the bonding also involves p orbitals. Two p orbitals can form either a sigma bond or a pi bond. Because there are three p orbitals for each atom of a second-period element, we know that one sigma and

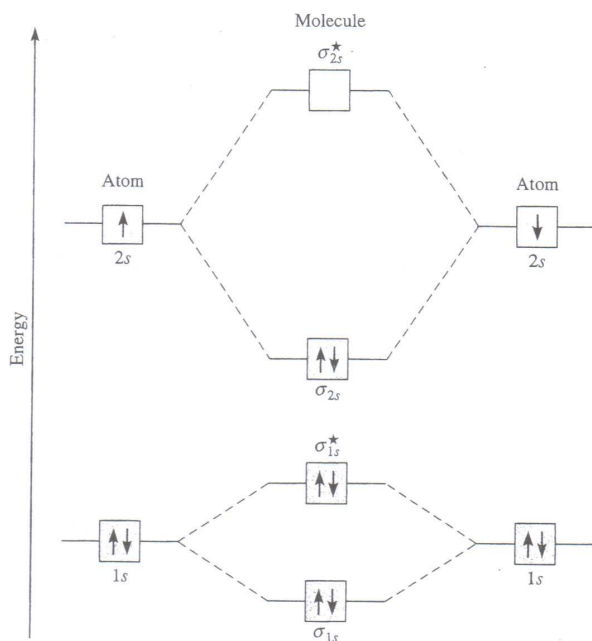


Figure 10.26 Molecular orbital energy level diagram for the Li_2 molecule. The six electrons in Li_2 (Li 's electron configuration $1s^2 2s^1$) are in the σ_{1s} , σ_{1s}^* , and σ_{2s} orbitals. Because there are two electrons each in σ_{1s} and σ_{1s}^* (just as in He_2), there is no net bonding or antibonding effect. Therefore, the single covalent bond in Li_2 is formed by the two electrons in the bonding molecular orbital σ_{2s} . Note that although the antibonding orbital (σ_{1s}^*) has higher energy and is thus less stable than the bonding orbital (σ_{1s}), this antibonding orbital has less energy and greater stability than the σ_{2s} bonding orbital.

two pi molecular orbitals will result from the constructive interaction. The sigma molecular orbital is formed by the overlap of the $2p_x$ orbitals along the internuclear axis, that is, the x -axis. The $2p_y$ and $2p_z$ orbitals are perpendicular to the x -axis, and they will overlap sideways to give two pi molecular orbitals. The molecular orbitals are called σ_{2p_x} , π_{2p_y} , and π_{2p_z} orbitals, where the subscripts indicate which atomic orbitals take part in forming the molecular orbitals. As shown in Figure 10.24, overlap of the two p orbitals is normally greater in a σ molecular orbital than in a π molecular orbital, so we would expect the former to be lower in energy. However, the energies of molecular orbitals actually increase as follows:

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_y} = \pi_{2p_z} < \sigma_{2p_x} < \pi_{2p_y}^* = \pi_{2p_z}^* < \sigma_{2p_x}^*$$

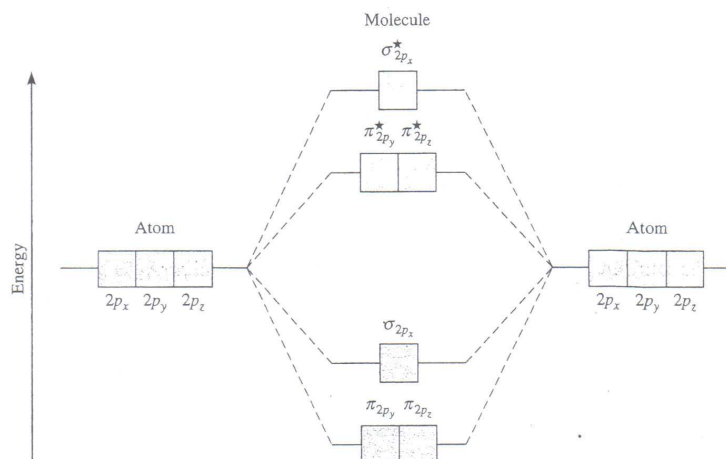
The inversion of the σ_{2p_x} orbital and the π_{2p_y} and π_{2p_z} orbitals is due to the interaction between the $2s$ orbital on one atom with the $2p$ orbital on the other. In MO terminology, we say there is mixing between these orbitals. The condition for mixing is that the $2s$ and $2p$ orbitals must be close in energy. This condition is met for the lighter molecules B_2 , C_2 , and N_2 with the result that the σ_{2p_x} orbital is raised in energy relative to the π_{2p_y} and π_{2p_z} orbitals as already shown. The mixing is less pronounced for O_2 and F_2 so the σ_{2p_x} orbital lies lower in energy than the π_{2p_y} and π_{2p_z} orbitals in these molecules.

With these concepts and Figure 10.27, which shows the order of increasing energies for $2p$ molecular orbitals, we can write the electron configurations and predict the magnetic properties and bond orders of second-period homonuclear diatomic molecules. We will consider a few examples.

The Lithium Molecule (Li_2)

The electron configuration of Li is $1s^2 2s^1$, so Li_2 has a total of six electrons. According to Figure 10.26, these electrons are placed (two each) in the σ_{1s} , σ_{1s}^* , and σ_{2s} molecular orbitals. The electrons of σ_{1s} and σ_{1s}^* make no net contribution to the bonding in Li_2 . Thus, the electron configuration of the molecular orbitals in Li_2 is $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2$. Since there are two more electrons in the bonding molecular orbitals than in antibonding orbitals, the bond order is 1 [see Equation (10.2)]. We conclude that the Li_2 molecule is stable, and because it has no unpaired electron spins, it should be diamagnetic. Indeed, diamagnetic Li_2 molecules are known to exist in the vapor phase.

Figure 10.27 General molecular orbital energy level diagram for the second-period homonuclear diatomic molecules Li_2 , Be_2 , B_2 , C_2 , and N_2 . For simplicity, the σ_{1s} and σ_{2s} orbitals have been omitted. Note that in these molecules, the σ_{2p_x} orbital is higher in energy than either the π_{2p_y} or the π_{2p_z} orbitals. This aberration stems from the different interactions between the electrons in the σ_{2p_x} orbital, on one hand, and π_{2p_y} and π_{2p_z} orbitals, on the other hand, with the electrons in the lower-energy σ_s orbitals. For O_2 and F_2 , the σ_{2p_x} orbital is lower in energy than π_{2p_y} and π_{2p_z} .



The Carbon Molecule (C₂)

The carbon atom has the electron configuration $1s^2 2s^2 2p^2$; thus, there are 12 electrons in the C₂ molecule. Referring to Figures 10.26 and 10.27, we place the last four electrons in the π_{2p_y} and π_{2p_z} orbitals. Therefore, C₂ has the electron configuration

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_y})^2(\pi_{2p_z})^2$$

Its bond order is 2, and the molecule has no unpaired electrons. Again, diamagnetic C₂ molecules have been detected in the vapor state. Note that the double bonds in C₂ are both pi bonds because of the four electrons in the two pi molecular orbitals. In most other molecules, a double bond is made up of a sigma bond and a pi bond.

The Oxygen Molecule (O₂)

The ground-state electron configuration of O is $1s^2 2s^2 2p^4$; thus, there are 16 electrons in O₂. Using the order of increasing energies of the molecular orbitals discussed above, we write the ground-state electron configuration of O₂ as

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi_{2p_y}^*)^1(\pi_{2p_z}^*)^1$$

According to Hund's rule, the last two electrons enter the $\pi_{2p_y}^*$ and $\pi_{2p_z}^*$ orbitals with parallel spins. Ignoring the σ_{1s} and σ_{2s} orbitals (because their net effects on bonding are zero), we calculate the bond order of O₂ using Equation (10.2):

$$\text{bond order} = \frac{1}{2}(6 - 2) = 2$$

Therefore, the O₂ molecule has a bond order of 2 and oxygen is paramagnetic, a prediction that corresponds to experimental observations.

Table 10.5 summarizes the general properties of the stable diatomic molecules of the second period.

TABLE 10.5 Properties of Homonuclear Diatomic Molecules of the Second-Period Elements*

	Li ₂	B ₂	C ₂	N ₂	O ₂	F ₂	
$\sigma_{2p_x}^*$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	$\sigma_{2p_x}^*$
$\pi_{2p_y}^*, \pi_{2p_z}^*$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	$\pi_{2p_y}^*, \pi_{2p_z}^*$
σ_{2p_x}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	π_{2p_y}, π_{2p_z}
π_{2p_y}, π_{2p_z}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	σ_{2p_x}
σ_{2s}^*	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	σ_{2s}^*
σ_{2s}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	σ_{2s}
Bond order	1	1	2	3	2	1	
Bond length (pm)	267	159	131	110	121	142	
Bond enthalpy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9	
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	

For simplicity the σ_{1s} and σ_{1s}^ orbitals are omitted. These two orbitals hold a total of four electrons. Remember that for O₂ and F₂, σ_{2p} is lower in energy than π_{2p_y} and π_{2p_z} .

Example 10.6 shows how MO theory can help predict molecular properties of ions.

EXAMPLE 10.6

The N_2^+ ion can be prepared by bombarding the N_2 molecule with fast-moving electrons. Predict the following properties of N_2^+ : (a) electron configuration, (b) bond order, (c) magnetic properties, and (d) bond length relative to the bond length of N_2 (is it longer or shorter?).

Strategy From Table 10.5 we can deduce the properties of ions generated from the homonuclear molecules. How does the stability of a molecule depend on the number of electrons in bonding and antibonding molecular orbitals? From what molecular orbital is an electron removed to form the N_2^+ ion from N_2 ? What properties determine whether a species is diamagnetic or paramagnetic?

Solution From Table 10.5 we can deduce the properties of ions generated from the homonuclear diatomic molecules.

(a) Because N_2^+ has one fewer electron than N_2 , its electron configuration is

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\sigma_{2p_z})^1$$

(b) The bond order of N_2^+ is found by using Equation (10.2):

$$\text{bond order} = \frac{1}{2}(9 - 4) = 2.5$$

(c) N_2^+ has one unpaired electron, so it is paramagnetic.

(d) Because the electrons in the bonding molecular orbitals are responsible for holding the atoms together, N_2^+ should have a weaker and, therefore, longer bond than N_2 . (In fact, the bond length of N_2^+ is 112 pm, compared with 110 pm for N_2 .)

Check Because an electron is removed from a bonding molecular orbital, we expect the bond order to decrease. The N_2^+ ion has an odd number of electrons (13), so it should be paramagnetic.

Similar problems: 10.57, 10.58.



Practice Exercise Which of the following species has a longer bond length: F_2 or F_2^- ?

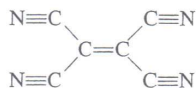
10.8 Delocalized Molecular Orbitals

So far we have discussed chemical bonding only in terms of electron pairs. However, the properties of a molecule cannot always be explained accurately by a single structure. A case in point is the O_3 molecule, discussed in Section 9.8. There we overcame the dilemma by introducing the concept of resonance. In this section we will tackle the problem in another way—by applying the molecular orbital approach. As in Section 9.8, we will use the benzene molecule and the carbonate ion as examples. Note that in discussing the bonding of polyatomic molecules or ions, it is convenient to determine first the hybridization state of the atoms present (a valence bond approach), followed by the formation of appropriate molecular orbitals.

The Benzene Molecule

Benzene (C_6H_6) is a planar hexagonal molecule with carbon atoms situated at the six corners. All carbon-carbon bonds are equal in length and strength, as are all carbon-hydrogen bonds, and the CCC and HCC angles are all 120° . Therefore, each carbon

- 10.42 How many pi bonds and sigma bonds are there in the tetracyanoethylene molecule?



- 10.43 Give the formula of a cation comprised of iodine and fluorine in which the iodine atom is sp^3d -hybridized.
- 10.44 Give the formula of an anion comprised of iodine and fluorine in which the iodine atom is sp^3d^2 -hybridized.

Molecular Orbital Theory

Review Questions

- 10.45 What is molecular orbital theory? How does it differ from valence bond theory?
- 10.46 Define the following terms: bonding molecular orbital, antibonding molecular orbital, pi molecular orbital, sigma molecular orbital.
- 10.47 Sketch the shapes of the following molecular orbitals: σ_{1s} , σ_{1s}^* , π_{2p} , and π_{2p}^* . How do their energies compare?
- 10.48 Explain the significance of bond order. Can bond order be used for quantitative comparisons of the strengths of chemical bonds?

Problems

- 10.49 Explain in molecular orbital terms the changes in H—H internuclear distance that occur as the molecular H_2 is ionized first to H_2^+ and then to H_2^{2+} .
- 10.50 The formation of H_2 from two H atoms is an energetically favorable process. Yet statistically there is less than a 100 percent chance that any two H atoms will undergo the reaction. Apart from energy considerations, how would you account for this observation based on the electron spins in the two H atoms?
- 10.51 Draw a molecular orbital energy level diagram for each of the following species: He_2 , HHe , He_2^+ . Compare their relative stabilities in terms of bond orders. (Treat HHe as a diatomic molecule with three electrons.)
- 10.52 Arrange the following species in order of increasing stability: Li_2 , Li_2^+ , Li_2^- . Justify your choice with a molecular orbital energy level diagram.
- 10.53 Use molecular orbital theory to explain why the Be_2 molecule does not exist.
- 10.54 Which of these species has a longer bond, B_2 or B_2^+ ? Explain in terms of molecular orbital theory.
- 10.55 Acetylene (C_2H_2) has a tendency to lose two protons (H^+) and form the carbide ion (C_2^{2-}), which is present in a number of ionic compounds, such as CaC_2 and MgC_2 . Describe the bonding scheme in the C_2^{2-} ion in terms of molecular orbital theory. Compare the bond order in C_2^{2-} with that in C_2 .

- 10.56 Compare the Lewis and molecular orbital treatments of the oxygen molecule.
- 10.57 Explain why the bond order of N_2 is greater than that of N_2^+ , but the bond order of O_2 is less than that of O_2^+ .
- 10.58 Compare the relative stability of the following species and indicate their magnetic properties (that is, diamagnetic or paramagnetic): O_2 , O_2^+ , O_2^- (superoxide ion), O_2^{2-} (peroxide ion).
- 10.59 Use molecular orbital theory to compare the relative stabilities of F_2 and F_2^+ .
- 10.60 A single bond is almost always a sigma bond, and a double bond is almost always made up of a sigma bond and a pi bond. There are very few exceptions to this rule. Show that the B_2 and C_2 molecules are examples of the exceptions.

Delocalized Molecular Orbitals

Review Questions

- 10.61 How does a delocalized molecular orbital differ from a molecular orbital such as that found in H_2 or C_2H_4 ? What do you think are the minimum conditions (for example, number of atoms and types of orbitals) for forming a delocalized molecular orbital?
- 10.62 In Chapter 9 we saw that the resonance concept is useful for dealing with species such as the benzene molecule and the carbonate ion. How does molecular orbital theory deal with these species?

Problems

- 10.63 Both ethylene (C_2H_4) and benzene (C_6H_6) contain the $C=C$ bond. The reactivity of ethylene is greater than that of benzene. For example, ethylene readily reacts with molecular bromine, whereas benzene is normally quite inert toward molecular bromine and many other compounds. Explain this difference in reactivity.
- 10.64 Explain why the symbol on the left is a better representation of benzene molecules than that on the right.

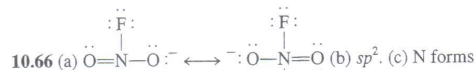


- 10.65 Determine which of these molecules has a more delocalized orbital and justify your choice.



(Hint: Both molecules contain two benzene rings. In naphthalene, the two rings are fused together. In biphenyl, the two rings are joined by a single bond, around which the two rings can rotate.)

10.24 (b) = (d) < (c) < (a). **10.32** sp^3 for both. **10.34** B: sp^2 to sp^3 ; N: remains at sp^3 . **10.36** From left to right. (a) sp^3 . (b) sp^3 , sp^2 , sp^2 . (c) sp^3 , sp , sp , sp^3 . (d) sp^3 , sp^2 . (e) sp^3 , sp^2 . **10.38** sp . **10.40** sp^3 . **10.42** 9 pi bonds and 9 sigma bonds. **10.44** IF_4^- . **10.50** Electron spins must be paired in H_2 . **10.52** $Li_2^- = Li_2^+ < Li_2$. **10.54** B_2^+ . **10.56** MO theory predicts O_2 is paramagnetic. **10.58** $O_2^{2-} < O_2^- < O_2 < O_2^+$. **10.60** B_2 contains a pi bond; C_2 contains 2 pi bonds. **10.64** The circle shows electron delocalization.



sigma bonds with F and O atoms. There is a pi molecular orbital delocalized over N and O atoms. **10.68** sp^2 . **10.70** Linear. Dipole moment measurement. **10.72** The large size of Si results in poor sideways overlap of p orbitals to form pi bonds. **10.74** XeF_4^+ : T-shaped; XeF_5^+ : square pyramidal; SbF_6^- : octahedral. **10.76** (a) 180° . (b) 120° . (c) 109.5° . (d) About 109.5° . (e) 180° . (f) About 120° . (g) About 109.5° . (h) 109.5° . **10.78** sp^3 . **10.80** ICl_2^- and $CdBr_2$. **10.82** (a) sp^2 . (b) Molecule on the right. **10.84** The pi bond in *cis*-dichloroethylene prevents rotation. **10.86** O_3 , CO, CO_2 , NO_2 , N_2O , CH_4 , $CFCl_3$. **10.88** C: all single-bonded C atoms are sp^3 , the double-bonded C atoms are sp^2 ; N: single-bonded N atoms are sp^3 , N atoms that form one double bond are sp^2 , N atom that forms two double bonds is sp . **10.90** Si has $3d$ orbitals so water can add to Si (valence shell expansion). **10.92** C: sp^2 ; N: N atom that forms a double bond is sp^2 , the others are sp^3 . **10.94** (a) Use a conventional oven. (b) No. Polar molecules would absorb microwaves. (c) Water molecules absorb part of microwaves. **10.96** The small size of F results in a shorter bond and greater lone pair repulsion. **10.98** 43.6%. **10.100** Second and third vibrations. CO, NO_2 , N_2O . **10.102** (a) The two 90° rotations will break and make the pi bond and convert *cis*-dichloroethylene to *trans*-dichloroethylene. (b) The pi bond is weaker because of the lesser extent of sideways orbital overlap. (c) 444 nm. **10.104** (a) H_2 . The electron is removed from the more stable bonding molecular orbital. (b) N_2 . Same as (a). (c) O. The atomic orbital in O is more stable than the antibonding molecular orbital in O_2 . (d) The atomic orbital in F is more stable than the antibonding molecular orbital in F_2 . **10.106** (a) $[Ne_2](\sigma_{3s})^2(\sigma_{3s}^*)^2(\pi_{3p})^2(\pi_{3p}^*)^2(\sigma_{3p})^2$. (b) 3. (c) Diamagnetic. **10.108** For all the electrons to be paired in O_2 (see Table 10.5), energy is needed to flip the spin of one of the electrons in the antibonding molecular orbitals. This arrangement is less stable according to Hund's rule. **10.110** (a) Planar and no dipole moment. (b) 20 sigma bonds and 6 pi bonds. **10.112** The negative formal charge is placed on the less electronegative carbon, so there is less charge separation and a smaller dipole moment. (b) Both the Lewis structure and the molecular orbital treatment predicts a triple bond. (c) C. **10.114** $O=C=C=C=O$. The molecule is linear and nonpolar.

CHAPTER 11

11.8 Methane. **11.10** (a) Dispersion forces. (b) Dispersion and dipole-dipole forces. (c) Same as (b). (d) Dispersion and ion-ion forces. (e) Same as (a). **11.12** (e). **11.14** Only 1-butanol can form hydrogen bonds. **11.16** (a) Xe. (b) CS_2 . (c) Cl_2 . (d) LiF. (e) NH_3 . **11.18** (a) Hydrogen bond and dispersion forces. (b) Dispersion forces. (c) Dispersion forces. (d) Covalent bond. **11.20** The compound on the left can form intramolecular hydrogen bond. **11.32** Between ethanol and glycerol. **11.38** scc: 1; bcc: 2; fcc: 4. **11.40** 6.20×10^{23} Ba atoms/mol. **11.42** 458 pm. **11.44** XY_3 .

11.48 0.220 nm. **11.52** Molecular solid. **11.54** Molecular solids: Se_8 , HBr, CO_2 , P_4O_6 , SiH_4 . Covalent solids: Si, C. **11.56** Each C atom in diamond is covalently bonded to four other C atoms. Graphite has delocalized electrons in two dimensions. **11.78** 2.67×10^3 kJ. **11.80** 47.03 kJ/mol. **11.82** Freezing, sublimation. **11.84** When steam condenses at $100^\circ C$, it releases heat equal to heat of vaporization. **11.86** 331 mmHg. **11.88** 75.9 kJ/mol. **11.92** Initially ice melts because of the increase in pressure. As the wire sinks into the ice, the water above it refreezes. In this way, the wire moves through the ice without cutting it in half. **11.94** (a) Ice melts. (b) Water vapor condenses to ice. (c) Water boils. **11.96** (d). **11.98** Covalent crystal. **11.100** CCl_4 . **11.102** 760 mmHg. **11.104** It is the critical point. **11.106** Crystalline SiO_2 . **11.108** (a), (b), (d). **11.110** 8.3×10^{-3} atm. **11.112** (a) K_2S . (b) Br_2 . **11.114** SO_2 . It is a polar molecule. **11.116** 62.4 kJ/mol. **11.118** Smaller ions have larger charge densities and a greater extent of hydration. **11.120** (a) 30.7 kJ/mol. (b) 192.5 kJ/mol. **11.122** (a) Decreases. (b) No change. (c) No change. **11.124** $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Three phases. **11.126** SiO_2 is a covalent crystal. CO_2 exists as discrete molecules. **11.128** 66.8%. **11.130** scc: 52.4%; bcc: 68.0%; fcc: 74.0%. **11.132** 1.69 g/cm³. **11.134** (a) Two (diamond/graphite/liquid and graphite/liquid/vapor). (b) Diamond. (c) Apply high pressure at high temperature. **11.136** Molecules in the cane are held together by intermolecular forces. **11.138** When the tungsten filament is heated to a high temperature (ca. $3000^\circ C$), it sublimates and condenses on the inside walls. The inert pressurized Ar gas retards sublimation. **11.140** When methane burns in air, it forms CO_2 and water vapor. The latter condenses on the outside of the cold beaker. **11.142** 6.019×10^{22} Fe atoms/mol. **11.144** Na (186 pm and 0.965 g/cm³). **11.146** (d). **11.148** 0.833 g/L. Hydrogen bonding in the gas phase.

CHAPTER 12

12.10 Cyclohexane cannot form hydrogen bonds. **12.12** The longer chains become more nonpolar. **12.16** (a) 25.9 g. (b) 1.72×10^3 g. **12.18** (a) 2.68 m. (b) 7.82 m. **12.20** 0.010 m. **12.22** 5.0×10^2 m; 18.3 M. **12.24** (a) 2.41 m. (b) 2.13 M. (c) 0.0587 L. **12.28** 45.9 g. **12.36** CO_2 pressure is greater at the bottom of the mine. **12.38** 0.28 L. **12.50** 1.3×10^3 g. **12.52** Ethanol: 30.0 mmHg; 1-propanol: 26.3 mmHg. **12.54** 128 g. **12.56** 0.59 m. **12.58** 120 g/mol. $C_4H_8O_4$. **12.60** $-8.6^\circ C$. **12.62** 4.3×10^2 g/mol. $C_{24}H_{20}P_4$. **12.64** 1.75×10^4 g/mol. **12.66** 343 g/mol. **12.70** Boiling point, vapor pressure, osmotic pressure. **12.72** 0.50 m glucose > 0.50 m acetic acid > 0.50 m HCl. **12.74** 0.9420 m. **12.76** 7.6 atm. **12.78** 1.6 atm. **12.82** 3.5 atm. **12.84** (a) 104 mmHg. (b) 116 mmHg. **12.86** 2.95×10^3 g/mol. **12.88** No. **12.90** $AlCl_3$ dissociates into Al^{3+} and 3 Cl^- ions. **12.92** NaCl: 143.8 g; $MgCl_2$: 5.14 g; Na_2SO_4 : 7.25 g; $CaCl_2$: 1.11 g; KCl: 0.67 g; $NaHCO_3$: 0.17 g. **12.94** The molar mass in B (248 g/mol) is twice as large as that in A (124 g/mol). A dimerization process. **12.96** (a) Last alcohol. (b) Methanol. (c) Last alcohol. **12.98** I_2 -water: weak dipole-induced dipole; I_3^- -water: favorable ion-dipole interaction. **12.100** (a) Same NaCl solution on both sides. (b) Only water would move from left to right. (c) Normal osmosis. **12.102** 12.3 M. **12.104** 14.2%. **12.106** (a) Decreases with lattice energy. (b) Increases with polarity of solvent. (c) Increases with enthalpy of hydration. **12.108** 1.80 g/mL. 5.0×10^2 m. **12.110** 0.815. **12.112** NH_3 can form hydrogen bonds with water. **12.114** 3%. **12.116** 1.2×10^2 g/mol. It forms a dimer in benzene. **12.118** (a) 1.1 m. (b) The protein prevents the formation of ice crystals. **12.120** It is due to the precipitated minerals that refract light and create an opaque appearance. **12.122** 1.9 m. **12.124** (a) $X_A = 0.524$, $X_B = 0.476$. (b) A: 50 mmHg; B: 20 mmHg.