GENERAL CHEMISTRY

THIRD EDITION

Some additional reading on molecular orbital theory if needed
See also lecture slides on this

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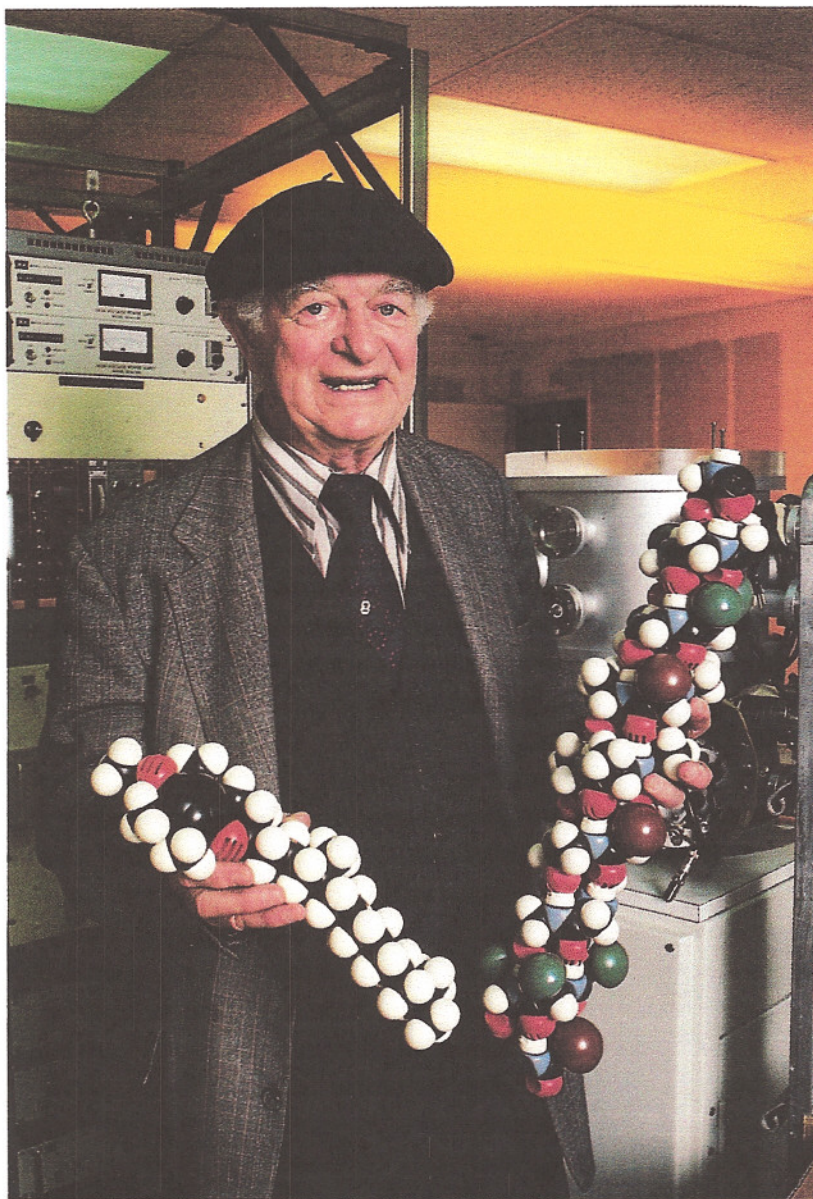
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13 COVALENT BONDING

Linus Pauling, one of America's greatest chemists, was a pioneer in the development of the theory and understanding of chemical bonding. His book, *The Nature of the Chemical Bond,* first published in 1939, is one of the most influential chemistry texts of the twentieth century. During the 1950s, Pauling was in the forefront of the fight against nuclear bomb testing. He was awarded the Nobel Prize for chemistry in 1954 and the Nobel Peace Prize in 1963.
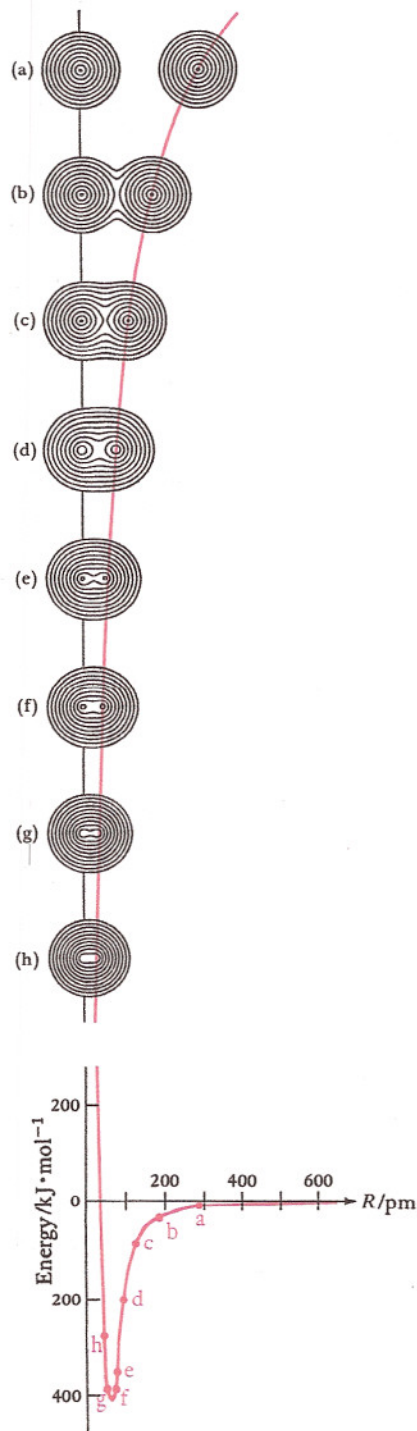
The VSEPR theory allows us to predict how bonds are arranged, but not how and why bonds form in the first place. Why, for example, *does hydrogen exist as a diatomic molecule and helium as a monatomic gas?* Why has the species He_2 never been observed? To answer these and similar questions, we need a more fundamental theory of covalent bonding. We showed in Chapter 9 how the quantum theory describes the electrons in atoms in terms of atomic orbitals. Now we will discuss how molecular orbitals are formed from overlapping atomic orbitals from different atoms. In the first few sections, we apply a theory called molecular orbital theory to homonuclear diatomic molecules (diatomic molecules in which the two atoms are the same), describing how to write electron configurations for these molecules and how to predict relative bond lengths and bond energies. Then after applying molecular orbital theory to heteronuclear diatomic molecules (diatomic molecules in which the two atoms are different), we go on to discuss polyatomic molecules. A **polyatomic molecule** can be pictured as a group of atoms held together by covalent bonds. The bonding in polyatomic molecules can be described using molecular orbitals in a manner similar to that used for diatomic molecules. In many instances, however, a simpler picture can be obtained if the covalent bonds are considered to be localized between adjacent atoms. To describe these localized covalent bonds, we introduce the idea of hybrid orbitals, which are combinations of atomic orbitals of the same atom. This approach is called valence-bond theory and is mathematically equivalent to the more elaborate molecular orbital theory. In those instances where a localized bond model is inappropriate, the molecular orbital theory will be used.

13-1. A MOLECULAR ORBITAL IS A COMBINATION OF ATOMIC ORBITALS ON DIFFERENT ATOMS

The simplest neutral molecule is diatomic hydrogen, H_2, which has only two electrons. The Schrödinger equation (Section 9-12) that describes the motion of the electrons in H_2 can be solved with a computer to a high degree of accuracy. The results are valuable because they are similar to the results for more complicated molecules. Let's look, therefore, at the approach of quantum theory in more detail. As a first step in setting up the Schrödinger equation for H_2, the two nuclei are fixed at some given separation. Then the two electrons are included, and the equation is solved to give the wave functions and energies that describe the two electrons. The wave function that corresponds to the lowest energy, the **ground-state wave function,** can be used to compute contour diagrams, much like the maps used to show peaks and valleys in hilly terrain. These diagrams show the distribution of electron density around the two nuclei.

Figure 13-1 shows contour diagrams of the ground-state electron density as a function of the separation of the two nuclei of the hydrogen atoms. Note that at large separations the two atoms hardly interact, so the electron density is just that of two electrons, each in a $1s$ orbital about each of the hydrogen atoms. As the separation decreases, how-

ever, the two $1s$ orbitals overlap, combining into one orbital that is distributed around both nuclei. Such an orbital is called a **molecular orbital,** because it extends over both nuclei in the molecule. Throughout this chapter, we will build molecular orbitals by overlapping atomic orbitals on different atoms. The buildup of electron density between the nuclei results in a covalent bond. Note how the detailed quantum theoretical results shown in Figure 13-1 correspond to the Lewis formula; both approaches picture a covalent bond as the sharing of an electron pair between two nuclei.

The lower part of Figure 13-1 shows the energies that correspond to the electron densities. Notice that interaction energies are negative for any distances at which the atoms attract each other. These negative values mean that energy is released when the H_2 bond is formed. The graph shows that, for H_2, the interaction energy has a minimum at the internuclear separation $R = 74$ pm. This value of R is the predicted length of a bond and is in excellent agreement with the experimental value.

13-2. THE HYDROGEN MOLECULAR ION H_2^+ IS THE SIMPLEST DIATOMIC SPECIES

In this section we discuss a theory of bonding, called **molecular orbital theory,** that gives us insight into why, for example, two hydrogen atoms join to form a stable molecule whereas two helium atoms do not. This theory was developed in the 1930s by the German scientist Friedrich Hund and the American scientist Robert Mullikin. Although molecular orbital theory can be applied to all molecules, for simplicity we will consider only diatomic molecules.

Recall that we describe the electronic structure of atoms in terms of atomic orbitals, which are based on the set of orbitals that were given for a hydrogen atom. Because a hydrogen atom has only one electron, its atomic orbitals are relatively simple to calculate from the Schrödinger equation and serve as approximate orbitals for more complicated atoms. A one-electron system that applies to homonuclear diatomic molecules is the **hydrogen molecular ion,** H_2^+, which consists of two protons and one electron. The H_2^+ ion is stable relative to a separated H and H^+; its bond length is 106 pm and its bond energy is 255 kJ·mol^{-1}.

Figure 13-1 Electron density contour diagrams of two hydrogen atoms as a function of their separation (upper part). At large separations, as in (a), the two orbitals appear simply as those of two separate atoms. As the atoms come together, the two separate atomic orbitals combine into one molecular orbital encompassing both nuclei, as in (b) through (h).

The lower part of the figure shows the energy of two hydrogen atoms as a function of their separation R. The labels (a) through (h) correspond to those in the upper part of the figure. At large distances (a), the two hydrogen atoms do not interact, so their interaction energy is zero. As the two atoms come together, they attract each other, and so their interaction energy becomes negative. When they are less than 74 pm apart, the interaction energy increases and they repel each other. The bond length of H_2 is the distance at which the energy is a minimum, that is, 74 pm. The energy at this distance is -436 kJ·mol^{-1}, which is the energy required to dissociate the H_2 molecule into two separate hydrogen atoms.

The Schrödinger equation for H_2^+, like that for a hydrogen atom, is relatively easy to solve, and we obtain a set of wave functions, or orbitals, and a corresponding set of energies. As noted earlier, these orbitals extend over both nuclei in H_2^+ and therefore are called molecular orbitals. In Chapter 9 we discussed the shapes of the various hydrogen atomic orbitals and then used them to build up the electronic structures of more complicated atoms. In just the same way we now use the various H_2^+ molecular orbitals to build up the electronic structures of more complicated diatomic molecules.

Figure 13-2 shows the shapes of the first several molecular orbitals of H_2^+. Each shape represents the three-dimensional surface that encloses
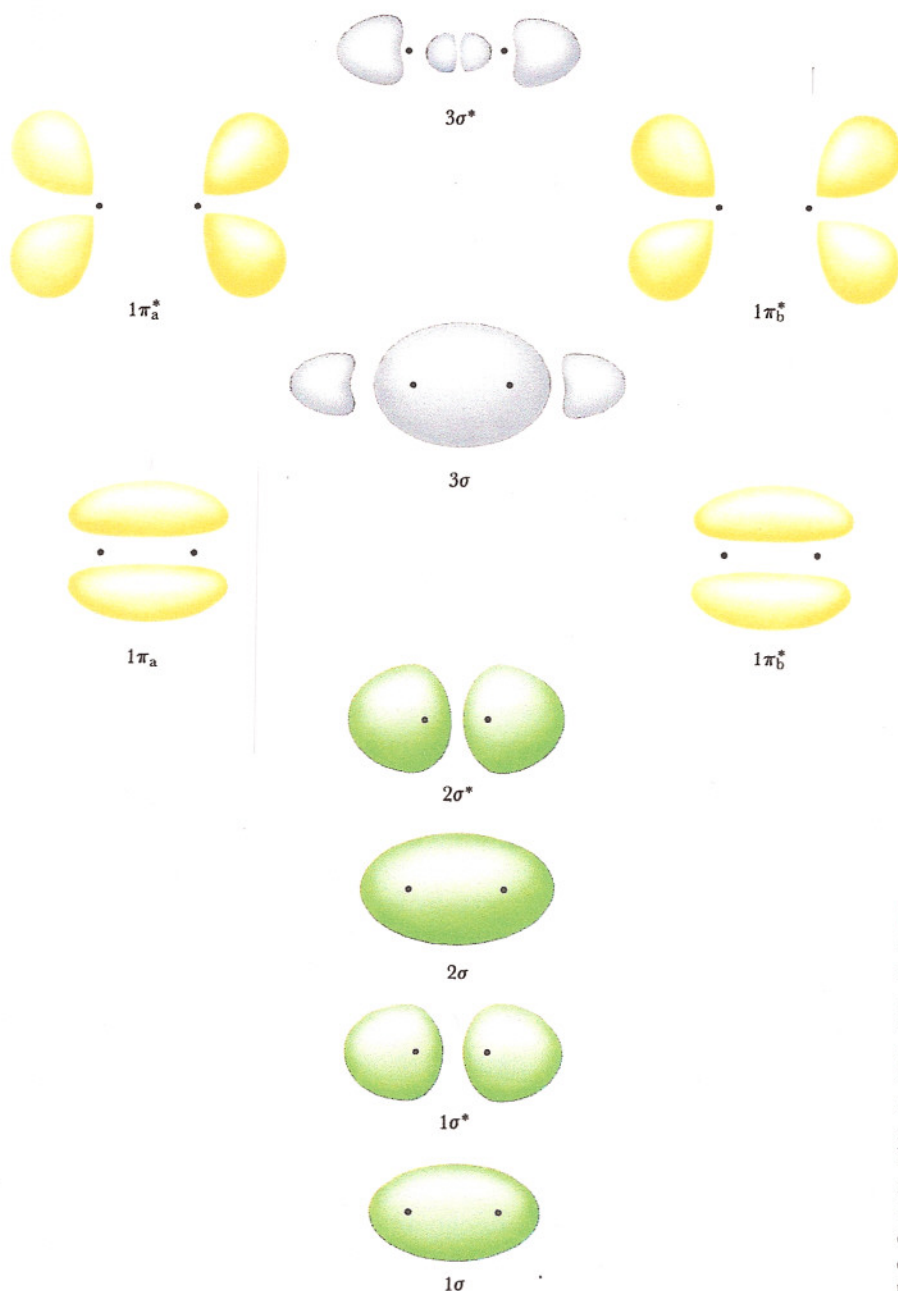
Figure 13-2 The three-dimensional surfaces that depict the shapes but not the relative sizes of the first few H_2^+ molecular orbitals. The orbitals are listed in order of increasing energy. Note that some molecular orbitals have nodal planes between the two nuclei, which are shown as heavy black dots. Also note that the two molecular orbitals designated by $1\pi_a$ and $1\pi_b$ have the same energy and that the two designated by $1\pi_a^*$ and $1\pi_b^*$ have the same energy.

a certain probability of finding the electron within the volume enclosed by that surface. The first two H_2^+ molecular orbitals shown in Figure 13-2 are cylindrically symmetric; that is, they have circular cross sections when viewed along a line joining the two hydrogen atoms (the **internuclear axis**). Because atomic s orbitals have a circular cross section, molecular orbitals that have a circular cross section when viewed along the internuclear axis are called $\boldsymbol{\sigma}$ **orbitals** (sigma, σ, is the Greek letter corresponding to s). Figure 13-2 shows, however, that these two orbitals are different. The first molecular orbital, the one that corresponds to the lowest energy of H_2^+, is concentrated between the two nuclei. An electron in this molecular orbital is likely to be found in the region between the two nuclei and so draws the two nuclei toward each other. Such a molecular orbital is called a **bonding orbital.**

The H_2^+ molecular orbital that corresponds to the second-lowest energy (that is, the second-lowest one in Figure 13-2) is concentrated more on the far sides of the two nuclei. An electron in this orbital is unlikely to be found in the region between the two nuclei. Thus, electrons in this orbital tend to draw the nuclei away from each other. Such a molecular orbital is called an **antibonding orbital.** In addition, on all points of a plane perpendicular to the internuclear axis and midway between the nuclei, the antibonding orbital has a value of 0. Recall from Chapter 9 that surfaces on which an orbital has zero value are called **nodal surfaces** and that the more nodal surfaces an orbital has, the greater is its corresponding energy. As we shall see repeatedly, antibonding molecular orbitals have one or more nodal planes. A bonding orbital is designated simply by its Greek letter, that is, σ orbital; and an antibonding orbital is designated by its Greek letter with an asterisk superscript, that is, $\boldsymbol{\sigma}$*** orbital.** Thus, we designate the two H_2^+ molecular orbitals of lowest energy by 1σ ("the one sigma orbital") and 1σ* ("the one sigma star orbital"), indicating the first σ orbital and the first σ* orbital in order of increasing energy. The next two orbitals in Figure 13-2 also have circular cross sections and thus also are σ orbitals. We designate these orbitals, respectively, the 2σ orbital and the 2σ* orbital; in other words, they are the second σ orbital and the second σ* orbital in order of increasing energy.

The next orbitals in Figure 13-2, again in order of increasing energy, are a pair with the same shape and, consequently, the same energy. But, the shape of these orbitals is different from that of the σ and σ* orbitals; they are not cylindrically symmetric when viewed along the internuclear axis. Instead, their cross section is similar to that of an atomic p orbital. These two orbitals are called $\boldsymbol{\pi}$ **orbitals** (pi, π, is the Greek letter that corresponds to p). We designate them as 1π orbitals, a name indicating that they are the first π orbitals in order of increasing energy.

The next orbitals shown in Figure 13-2 are a 3σ (the third σ orbital) and two 1π* ("one pi star orbitals"). Note that, like the 1σ* orbital, the 1π*** orbitals** have a nodal plane between the nuclei. The orbital of highest energy shown in Figure 13-2 is the 3σ* orbital. Just as a hydrogen atom has atomic orbitals of ever-increasing energy, H_2^+ has molecular orbitals of higher energy also. We require only those shown in Figure 13-2, however, for our subsequent discussion of diatomic molecules from the second row of the periodic table. Note that the molecular orbitals shown in Figure 13-2 come in bonding-antibonding pairs.

Thus, we have both a 1σ (first σ orbital) and a $1\sigma*$ (first $\sigma*$ orbital) orbital, a 3σ and a $3\sigma*$ orbital, and so on.

Just as we were able to write electron configurations for multielectron atoms using the set of atomic orbitals obtained from the solution of the Schrödinger equation for the hydrogen atom, so we can use the set of molecular orbitals derived from the H_2^+ molecule-ion to write electron configurations for multielectron diatomic molecules. As in the atomic case, each of these molecular orbitals is occupied by a maximum of two electrons, in accord with the Pauli exclusion principle. The hydrogen molecule, H_2, has two electrons. According to the Pauli exclusion principle, we place two electrons of opposite spins in the 1σ orbital and write the electron configuration of H_2 as $(1\sigma)^2$. The ground-state electron configuration of H_2 is illustrated in Figure 13-3, where, for simplicity, only the first two energy levels are shown. The two electrons in the bonding orbital constitute the single bond of H_2.

What about the possibility of a species He_2, which would have four electrons? According to our procedure, two of the electrons of He_2 should occupy the 1σ orbital and two should occupy the $1\sigma*$ orbital (Figure 13-4). Thus, we place two electrons in a bonding orbital and two in an antibonding orbital. Electrons in a bonding orbital tend to draw the nuclei together, whereas electrons in an antibonding orbital tend to draw the nuclei away from each other. The two effects cancel, so there is no net bonding. The species He_2 has never been observed experimentally.

To make our theory more quantitative, we can define a quantity called **bond order** by the equation

$$\text{bond order} = \frac{\left(\begin{array}{c}\text{number of}\\\text{electrons in}\\\text{bonding orbitals}\end{array}\right) - \left(\begin{array}{c}\text{number of}\\\text{electrons in}\\\text{antibonding orbitals}\end{array}\right)}{2} \quad (13\text{-}1)$$

A bond order of $\frac{1}{2}$ indicates a one-electron bond (one half of an electron pair), a bond order of 1 indicates a single bond (one pair of electrons), a bond order of 2 (two pairs of electrons) indicates a double bond, and so on. Table 13-1 summarizes the properties of the molecular species, H_2^+, H_2, He_2^+, and He_2. The bond order of 0 for He_2 indicates that there is no helium-helium covalent bond. Note from Table 13-1 that bond lengths decrease and bond energies increase with increasing bond order.
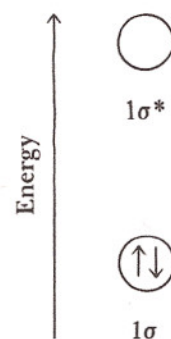

Figure 13-3 The electron configuration of H_2. The two electrons occupy the molecular orbital corresponding to the lowest energy and have opposite spins in accord with the Pauli exclusion principle.
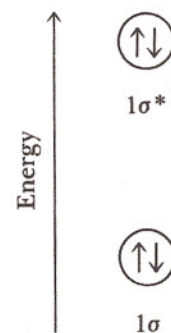
Figure 13-4 The electron configuration of the hypothetical molecule He_2. There are two electrons in a bonding orbital and two in an antibonding orbital, so He_2 has no net bonding. The molecule He_2 has never been detected experimentally.

Table 13-1 Molecular properties of H_2^+, H_2, He_2^+, and He_2

Species	Number of electrons	Ground-state electron configuration	Bond order	Bond length/pm	Bond energy/ kJ·mol^{-1}
H_2^+	1	$(1\sigma)^1$	$\frac{1}{2}$	106	255
H_2	2	$(1\sigma)^2$	1	74	436
He_2^+	3	$(1\sigma)^2(1\sigma*)^1$	$\frac{1}{2}$	108	251
He_2	4	$(1\sigma)^2(1\sigma*)^2$	0	not observed	not observed

13-3. MOLECULAR ORBITAL THEORY PREDICTS MOLECULAR ELECTRON CONFIGURATIONS

Figure 13-5 lists the molecular orbitals 1σ to $3\sigma*$ listed in order of increasing energy. We can use Figure 13-5 to write ground-state electron configurations for the homonuclear diatomic molecules Li_2 through Ne_2.

Lithium vapor contains diatomic lithium molecules, Li_2. A lithium atom has three electrons, so Li_2 has a total of six electrons. In the ground state of Li_2, the six electrons occupy the lowest three molecular orbitals in Figure 13-5, in accord with the Pauli exclusion principle. The ground-state electron configuration of Li_2 is $(1\sigma)^2(1\sigma*)^2(2\sigma)^2$. There is a net of two bonding electrons, so the bond order is 1. Thus, we predict that Li_2 is more stable than two separated lithium atoms. Table 13-2 shows that Li_2 has a bond length of 267 pm and a bond energy of 110 kJ·mol^{-1}. The process

$$Li_2(g) \rightarrow 2Li(g) \qquad \Delta H^\circ_{rxn} = 110 \text{ kJ}$$

is endothermic.

EXAMPLE 13-1: Use Figure 13-5 to write the ground-state electron configuration of N_2. Calculate the bond order of N_2 and compare your result with the Lewis formula for N_2.

Solution: There are 14 electrons in N_2. Using Figure 13-5, we see that its ground-state electron configuration is $(1\sigma)^2(1\sigma*)^2(2\sigma)^2(2\sigma*)^2(1\pi)^4(3\sigma)^2$. According to Equation (13-1), the bond order in N_2 is

$$\text{bond order} = \frac{10-4}{2} = 3$$

The Lewis formula for N_2, $:N\equiv N:$, is thus in agreement with molecular orbital theory. The triple bond in N_2 accounts for its short bond length (110 pm) and its unusually large bond energy (941 kJ·mol^{-1}). The bond in N_2 is one of the strongest known bonds.

PRACTICE PROBLEM 13-1: Use molecular orbital theory to explain why neon does not form a stable diatomic molecule.

Answer: Neon's ground-state electron configuration is
$(1\sigma)^2(1\sigma*)^2(2\sigma)^2(2\sigma*)^2(1\pi)^4(3\sigma)^2(1\pi*)^4(3\sigma*)^2$
giving a bond order of $(10-10)/2 = 0$.

One of the most impressive aspects of molecular orbital theory is its ability to predict that oxygen molecules will be **paramagnetic.** This property means that oxygen is attracted to a region between the poles of a magnet (Figure 13-6). Most substances are **diamagnetic,** meaning that they are slightly repelled by a magnetic field. Let's see how the paramagnetism of O_2 is related to its electron structure.

Each oxygen atom has 8 electrons; thus, O_2 has a total of 16 electrons. When the 16 electrons are placed according to the molecular orbital diagram given in Figure 13-5, the last 2 go into the $1\pi*$ orbitals. As in the atomic case, we apply Hund's rule (Section 9-19), because the two $1\pi*$ orbitals have the same energy. We, therefore, place one electron in each $1\pi*$ orbital such that the two electrons have unpaired spins as shown in Figure 13-7. The ground-state electron configuration of O_2
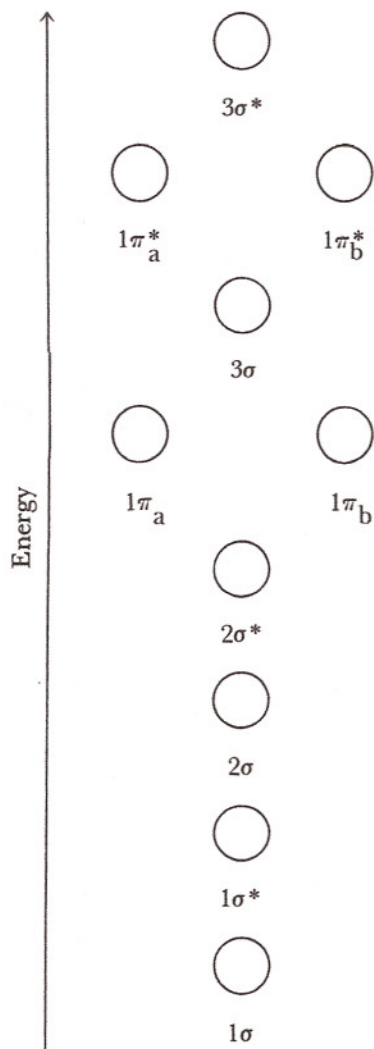

Figure 13-5 An energy-level diagram to be used for the homonuclear diatomic molecules H_2 through Ne_2. The orbitals are listed in order of increasing energy, $1\sigma < 1\sigma* < 2\sigma < 2\sigma* < 1\pi_a = 1\pi_b < 3\sigma < 1\pi_a^* = 1\pi_b^* < 3\sigma*$. Electrons occupy these orbitals in accord with the Pauli exclusion principle.

Figure 13-6 Liquid oxygen is attracted to the magnetic field between the poles of a magnet because oxygen is paramagnetic.

is $(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2(1\pi_a^*)^1(1\pi_b^*)^1$. Because each $1\pi^*$ orbital is occupied by one electron and the spins are unpaired, an oxygen molecule has a net electron spin; so it acts like a tiny magnet. Thus, O_2 is attracted into a region between the poles of a magnet.

The amount of oxygen in air can be monitored by measuring its paramagnetism. Because oxygen is the only major component in air that is paramagnetic, the measured paramagnetism of air is directly proportional to the amount of oxygen present. Linus Pauling developed a method using the paramagnetism of oxygen to monitor oxygen levels in submarines and airplanes in World War II. A similar method is still used by physicians to monitor the oxygen content in blood during anesthesia.

The Lewis formula of O_2 does not account for the paramagnetism of O_2. According to the octet rule, we should write the Lewis formula of O_2 as $\ddot{O}=\ddot{O}$, but this formula incorrectly implies that all the electrons are paired. The oxygen molecule is an exception to the utility of Lewis formulas, whereas the more fundamental molecular orbital theory is able to account successfully for the distribution of the electrons in O_2.

Table 13-2 gives the ground-state electron configurations of the homonuclear diatomic molecules Li_2 through Ne_2.
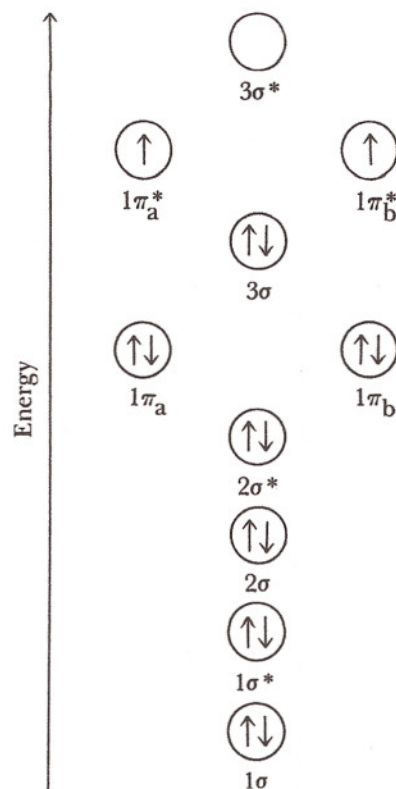

Figure 13-7 The ground-state electron configuration of O_2. There are 16 electrons in O_2, and they occupy the molecular orbitals as shown. Note that two of the electrons occupy the $1\pi^*$ orbitals in accord with Hund's rule, being placed in separate orbitals with unpaired spins. The molecule itself has a net electron spin, so it acts like a tiny magnet.

Table 13-2   Properties of the homonuclear diatomic molecules of the second-row elements

Species	Ground-state electron configuration	Bond order	Bond length/pm	Bond energy/kJ·mol^{-1}
Li_2	$(1\sigma)^2(1\sigma^*)^2(2\sigma)^2$	1	267	110
Be_2	$(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2$	0	not observed	not observed
B_2	$(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi_a)^1(1\pi_b)^1$	1	159	289
C_2	$(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^4$	2	124	599
N_2	$(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2$	3	110	941
O_2	$(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2(1\pi_a^*)^1(1\pi_b^*)^1$	2	121	494
F_2	$(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2(1\pi^*)^4$	1	142	154
Ne_2	$(1\sigma)^2(1\sigma^*)^2(2\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2(1\pi^*)^4(3\sigma^*)^2$	0	not observed	not observed

EXAMPLE 13-2: Use Figure 13-5 to determine which species has the greater bond length, F_2 or F_2^-.

Solution: The ground-state electron configurations of F_2 and F_2^- are

$$F_2: (1\sigma)^2(1\sigma*)^2(2\sigma)^2(2\sigma*)^2(1\pi)^4(3\sigma)^2(1\pi*)^4$$
$$F_2^-: (1\sigma)^2(1\sigma*)^2(2\sigma)^2(2\sigma*)^2(1\pi)^4(3\sigma)^2(1\pi*)^4(3\sigma*)^1$$
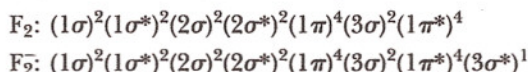
The bond orders are

$$\text{bond order } F_2 = \frac{10 - 8}{2} = 1$$

$$\text{bond order } F_2^- = \frac{10 - 9}{2} = \frac{1}{2}$$

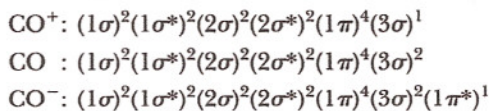Thus, we predict that F_2^- has a longer bond length than F_2.

PRACTICE PROBLEM 13-2: An excited state of O_2 has the electron configuration $(1\sigma)^2(1\sigma*)^2(2\sigma)^2(2\sigma*)^2(1\pi)^4(3\sigma)^1(1\pi*)^3$. Compare the bond length of O_2 in this excited state to the bond length of O_2 in its ground state.

Answer: The bond length of O_2 is shorter in its ground state.

Molecular orbital theory can also be applied to heteronuclear diatomic molecules. The energy-level scheme in Figure 13-5 can be used if the atomic numbers of the two atoms in the molecule differ by only one or two atomic numbers.

EXAMPLE 13-3: Which of the following species would you expect to have the shortest bond length, CO^+, CO, or CO^-?

Solution: Using Figure 13-5, we see that the ground-state electron configurations of these three species are

$$CO^+: (1\sigma)^2(1\sigma*)^2(2\sigma)^2(2\sigma*)^2(1\pi)^4(3\sigma)^1$$
$$CO \ : (1\sigma)^2(1\sigma*)^2(2\sigma)^2(2\sigma*)^2(1\pi)^4(3\sigma)^2$$
$$CO^-: (1\sigma)^2(1\sigma*)^2(2\sigma)^2(2\sigma*)^2(1\pi)^4(3\sigma)^2(1\pi*)^1$$

with bond orders $2\frac{1}{2}$, 3, and $2\frac{1}{2}$, respectively. Thus, we predict that CO has the shortest bond, which is correct.

PRACTICE PROBLEM 13-3: Predict which of the following species has the largest bond energy, CN^+, CN, or CN^-?

Answer: CN^-

13-4. THE BONDING IN POLYATOMIC MOLECULES CAN BE DESCRIBED IN TERMS OF BOND ORBITALS

Molecular orbital theory can also be applied to polyatomic molecules. In doing so we construct molecular orbitals, this time by combining atomic orbitals from all the atoms in the molecule. Then, using the

corresponding energy-level diagram, we place electrons into the molecular orbitals in accord with the Pauli exclusion principle. Because molecular orbitals are combinations of atomic orbitals from all the atoms in a polyatomic molecule, they are often spread over the entire molecule.

There is an alternative theory, called valence-bond theory, that is mathematically equivalent to molecular orbital theory. It recognizes that many chemical bonds have properties such as bond lengths and bond energies that are fairly constant from molecule to molecule. For example, the carbon-hydrogen bond lengths in many molecules are about 110 pm and their bond energies are a little greater than 400 kJ·mol^{-1}. A large amount of experimental data such as these suggests that the bonding in many polyatomic molecules can be analyzed in terms of orbitals that are localized between pairs of bonded atoms.

Consider the methane molecule, CH_4, in which each hydrogen atom is joined to the central carbon atom by a covalent bond. As Figure 13-8 suggests, the bonding electrons, and hence the orbitals that describe them, are localized along the line joining the carbon and the hydrogen atoms. These electrons are said to occupy **localized bond orbitals,** and the two electrons that occupy a localized bond orbital are said to constitute a **localized covalent bond.** Note the similarity between this bonding picture in CH_4 and the Lewis formula for CH_4:

$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$
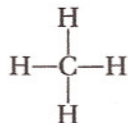
The localized bond orbital approach that we are describing is a simplified version of the **valence-bond theory,** which Linus Pauling developed in the 1930s. The valence-bond theory makes it possible to translate Lewis formulas into the mathematical formulas of the quantum theory. Although molecular orbital theory and valence-bond theory appear to be quite different, they lead to essentially the same results. In our treatment of polyatomic molecules, we use a mixture of both molecular orbital theory (delocalized bonds) and valence-bond theory (localized bonds). We use valence-bond theory to treat σ bonds and molecular orbital theory for π bonds. We use this mixed approach because of its close connection with Lewis formulas and because in a great many molecules the σ bonds are localized and the π bonds are delocalized.

13-5. HYBRID ORBITALS ARE COMBINATIONS OF ATOMIC ORBITALS ON THE SAME ATOM

The simplest neutral polyatomic molecule is BeH_2. Beryllium hydride is an electron-deficient compound. Its Lewis formula,

$$H-Be-H$$

does not satisfy the octet rule. According to VSEPR theory, beryllium hydride is a symmetric linear molecule; the two Be—H bonds are 180° apart and are equivalent. Therefore, according to valence-bond theory, we must form two equivalent bond orbitals that are localized along the H—Be—H axis.
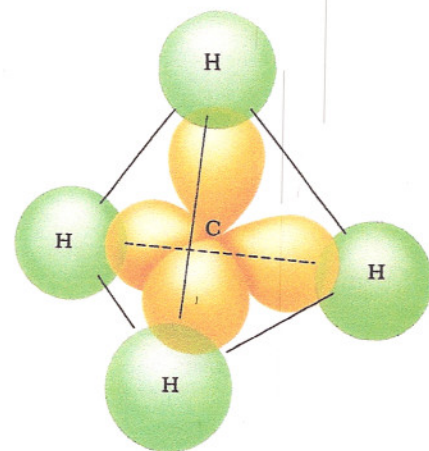

Figure 13-8 The bond orbitals in a methane molecule can be pictured as four carbon-hydrogen bond orbitals, directed toward the vertices of a tetrahedron. A localized bond orbital that is occupied by two electrons with opposite spins constitutes a covalent bond localized between two atoms.