9-4. Molecular Orbital Theory Predicts the Electron Configurations of Diatomic Molecules

When we wrote electron configurations for multielectron atoms in Chapter 5, we used the ordering of the energies of the atomic orbitals shown in Figures 5.11 and 5.12. Recall that the order of the energies of the orbitals for multielectron atoms does not follow the order of the energies of the hydrogen atomic orbitals. For instance, the energy of the 4*s* orbital is less than that of the 3*d* orbitals for multielectron atoms. A similar thing happens when we use the H_2^+ molecular orbitals that we have constructed from the combination of hydrogen atomic orbitals. The ordering of the molecular orbitals shown in Figure 9.2 can be used for the homonuclear diatomic molecules H_2 through N_2, that is, for $Z = 1$ through $Z = 7$ (recall from Chapter 2 that Z is the atomic number or number of protons in an atom). However, for $Z > 7$, the σ_{2p} and π_{2p} orbitals interchange energies so that the energy of the σ_{2p} orbital is less than that of the π_{2p} orbitals. The ordering of the energies of the molecular orbitals that we use to write electron configuration of the second-row homonuclear diatomic molecules Li_2 through Ne_2 is shown in Figure 9.11. Observe that the order of the σ_{2p} and π_{2p} orbitals changes in going from N_2 to O_2 molecules. Figure 9.11 is, in a sense, the homonuclear diatomic molecule analog of Figures 5.11 and 5.12 for multielectron atoms. We have already discussed the homonuclear molecules H_2 through He_2, so now we'll use Figure 9.11 to write electron configurations for the homonuclear diatomic molecules Li_2 through Ne_2 and use these electron configurations to discuss the bonding in these molecules.

Lithium vapor contains diatomic lithium molecules, Li_2. A lithium atom has three electrons, so a Li_2 molecule has a total of six electrons. In the ground state of a Li_2 molecule, the six electrons occupy the lowest molecular orbitals shown in Figure 9.11, in accord with the Pauli exclusion principle. The ground state electron configuration of a Li_2 molecule is $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$. There are four bonding electrons and two antibonding electrons, so the bond order is 1

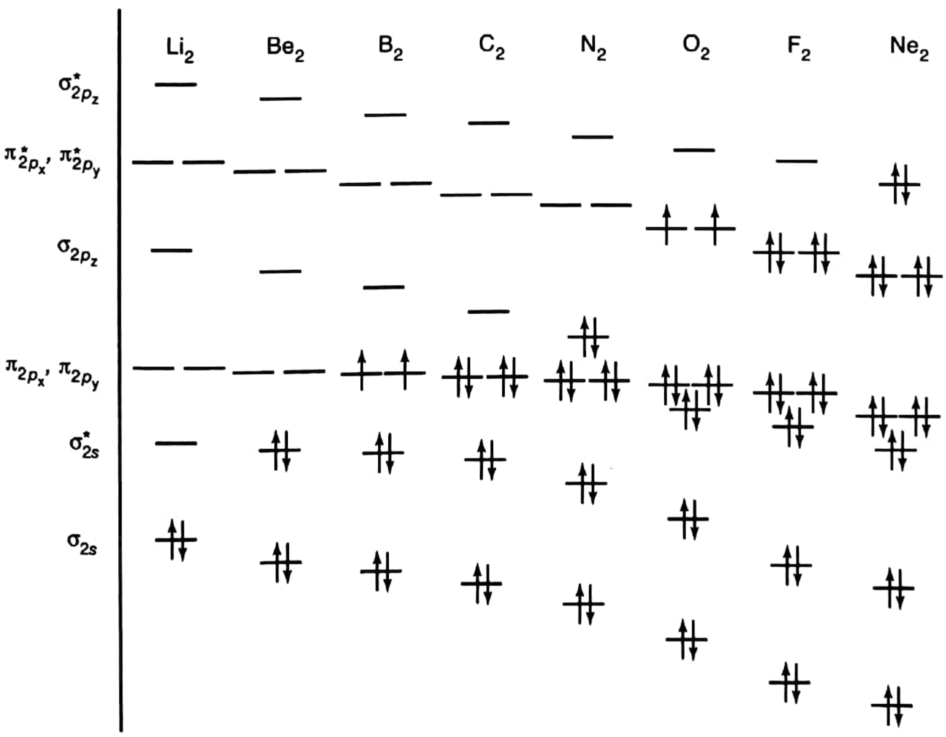

Figure 9.11 The relative energies (not to scale) of the molecular orbitals for the homonuclear diatomic molecules Li_2 through Ne_2. Notice that for O_2 through Ne_2 the energy of the σ_{2p_z} orbital is below that of the π_{2p} orbitals.

(Equation 9.1). Thus, we predict (correctly) that a Li_2 molecule is more stable than two separated lithium atoms. Table 9.2 shows that a Li_2 molecule has a bond length of 267 pm and a bond energy of 0.174 aJ.

We write π_{2p} and π^*_{2p} for convenience instead of π_{2p_x}, π_{2p_y} and $\pi^*_{2p_x}$, $\pi^*_{2p_y}$. We use the full notation only when we need to denote specific electron configurations.

EXAMPLE 9-1: Use Figure 9.11 to write the ground-state electron configuration of a N_2 molecule. Calculate the bond order of a N_2 molecule and compare your result with its Lewis formula.

Solution: There are 14 electrons in a N_2 molecule. Using Figure 9.11, we see that its ground state electron configuration is $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$. According to Equation 9.1, the bond order in a N_2 molecule is

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

The Lewis formula for a N_2 molecule, :N≡N:, is thus in agreement with molecular orbital theory. The triple bond in a N_2 molecule accounts for its short bond length (110 pm) and its unusually large bond energy (1.57 aJ). The bond in a N_2 molecule is one of the strongest known bonds.

PRACTICE PROBLEM 9-1: Use molecular orbital theory to explain why neon does not form a stable diatomic molecule under normal conditions.

Answer: Using Figure 9.13, we see that the ground state electron configuration of a Ne_2 molecule is $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4(\sigma^*_{2p})^2$, giving a bond order of $(10-10)/2 = 0$. Like a He_2 molecule, a Ne_2 molecule does not exist under normal conditions.

One of the most impressive aspects of molecular orbital theory is its ability to predict that oxygen molecules are **paramagnetic**. This property means that

TABLE 9.2 Properties of the homonuclear diatomic molecules of the second-row elements

Species	Ground state configuration	Bond order	Bond length/pm	Bond energy/aJ
Li_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$	1	267	0.174
Be_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2$	0	245	≈0.01
B_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x})^1(\pi_{2p_y})^1$	1	159	0.493
C_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4$	2	124	1.01
N_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$	3	110	1.57
O_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p_x})^1(\pi^*_{2p_y})^1$	2	121	0.827
F_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	141	0.264
Ne_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4(\sigma^*_{2p})^2$	0	not observed	not observed

oxygen is weakly attracted to a region between the poles of a magnet (Figure 9.12). Most substances are **diamagnetic**, meaning that they are slightly repelled by a magnetic field. Let's see how the paramagnetism of $O_2(g)$ is related to its electron structure.

Each oxygen atom has eight electrons; thus, an O_2 molecule has a total of 16 electrons. When the 16 electrons are placed according to the molecular orbital diagram given in Figure 9.11, the last two go into the π^*_{2p} orbitals. As in the atomic case, we apply Hund's rule (Section 5.8). Because the two π^*_{2p} orbitals have the same energy, we place one electron in each π^*_{2p} orbital such that the two electrons have unpaired spins, as shown in Figure 9.11. The ground state electron configuration of an O_2 molecule is $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2px})^1(\pi^*_{2py})^1$. According to Hund's rule, each π^*_{2p} orbital is occupied by one electron and the spins are unpaired. Therefore, an oxygen molecule has a net electron spin and so acts like a tiny magnet. Thus, $O_2(g)$ is attracted into a region between the poles of a magnet (Figure 9.12).

The amount of oxygen in air can be monitored by measuring its paramagnetism. Because oxygen is the only major component of air that is paramagnetic, the measured paramagnetism of air is directly proportional to the amount of oxygen present. Linus Pauling (Frontispiece) 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 an O_2 molecule does not account for the paramagnetism of $O_2(g)$. According to the octet rule, we should write the Lewis formula of an O_2 molecule as $:\ddot{O}=\ddot{O}:$, but this formula implies incorrectly 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 molecular oxygen.

Table 9.2 gives the ground state electron configurations of the homonuclear diatomic molecules Li_2 through Ne_2.

Figure 9.12 Liquid oxygen is attracted to the magnetic field between the poles of a magnet because oxygen is paramagnetic. The attraction of paramagnetic materials to a magnetic field is much weaker than that of ferromagnetic materials (such as iron), and so a strong magnet is used to illustrate this effect.