

# 12

## Diatomic Molecules

- 
- Key Concepts**
- 12-1** Molecular orbitals. Bond length. Orbital overlap and bonding orbitals. Nodal planes and antibonding orbitals. Sigma ( $\sigma$ ) orbitals. Pauli *aufbau* process. Net bonding.
  - 12-2** Homonuclear diatomic molecules. Pi ( $\pi$ ) orbitals. Degenerate energy levels. Paramagnetism and diamagnetism.
  - 12-3** Heteronuclear diatomic molecules. Electric dipole moments. Ionic character.

*A theory is not an ultimate goal; its object is physical rather than metaphysical. From the point of view of the physicist, a theory is a matter of policy rather than a creed.*

**J. J. Thomson (1856–1940)**

The language of chemistry is filled with Lewis line and dot structural formulas. If we know the Lewis structure for a molecule, we can say something about the stability, bond orders, bond energies, and bond lengths of that molecule. And, if we use the VSEPR method, we often can predict the geometry of the molecule. In this chapter we shall see that it is possible to go even further in formulating the electronic structures of molecules, by considering the actual shapes and energies of the valence orbitals that are involved in chemical bond formation. This more advanced method of analysis is known as the **molecular orbital theory**.

---

## 12-1 MOLECULAR ORBITALS

In Chapter 9, we used atomic orbitals to explain the properties of atoms. From the Schrödinger equation (Chapter 8) we obtained a set of wave functions,  $\psi_{(x,y,z)}$ , of such a nature that  $|\psi_{(x,y,z)}|^2$  at any point is the electron probability density at that point. If the electron is in the quantum state described by  $n$ ,  $l$ , and  $m$ , the probability of finding the electron within a small element of volume  $dv$  at  $(x, y, z)$  is

$$|\psi_{n,l,m(x,y,z)}|^2 dv$$

In building a picture of many-electron atoms, we envisioned the probability functions or orbitals as if they had a shadowy existence of their own and

then we filled these orbitals by adding electrons like peas dropped into cups. To build a picture of a molecule, we need to find a set of **molecular orbitals** for a given arrangement of atoms and then fill the orbitals with the available electrons, no more than two to an orbital as before. But before we do this, let's look at what happens when two hydrogen atoms come together to make a molecule.

### Bonding in the H<sub>2</sub> Molecule

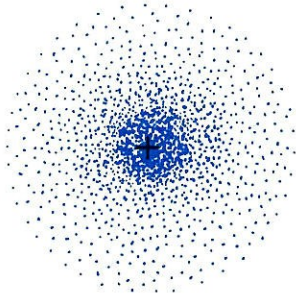
If two hydrogen atoms are far apart, they have no effect on one another. But as they are brought closer together, they begin to exert an effect. The two nuclei, having the same positive charge, repel one another, and the two electron clouds also repel one another. However, most important of all is the attraction between the nucleus of one atom and the electron cloud of the other atom. As the atoms approach, the electron clouds are pulled toward the region between the nuclei (Figure 12-1d). The combination of two nuclei and two electrons is more stable (has lower energy) than two isolated nuclei, each with its electron. The closer the nuclei come, the more electron density is attracted between them, the lower the energy falls, and the more stable the assembly (which can now be called a molecule) becomes. However, there is a limit to this process. If the nuclei are too close, the repulsion between them begins to dominate. Beyond this limit, the nuclear repulsion is greater than the nucleus–electron cloud attraction.

The potential energy of an H<sub>2</sub> molecule as a function of the distance between the two H atoms is shown in Figure 12-2. There is an intermediate *equilibrium* distance at which the attractive and repulsive forces are balanced. Pull the atoms apart, and attractive forces pull them back again. Push them together, and repulsive forces push back. The two atoms act very much as if they were tied together by a spring. This condition of balance, or equilibrium distance, is what we normally mean when we speak of the **bond length** (Figures 12-1e and 12-2).

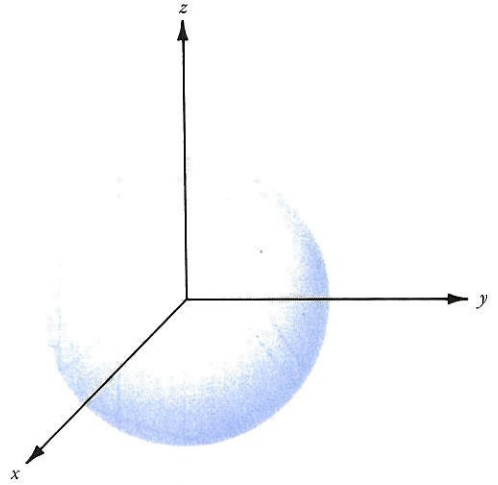
The attraction that makes the molecule stable is the attraction of the nuclei for the electron density concentrated between them. We can think of this concentration as an **overlap** of the 1s atomic orbitals. If, for convenience, we represent the atomic wave function  $\psi_{1s}$  simply by the symbol 1s, then electron density in the atom is represented by  $[1s]^2$ . [Square brackets

**Figure 12-1**

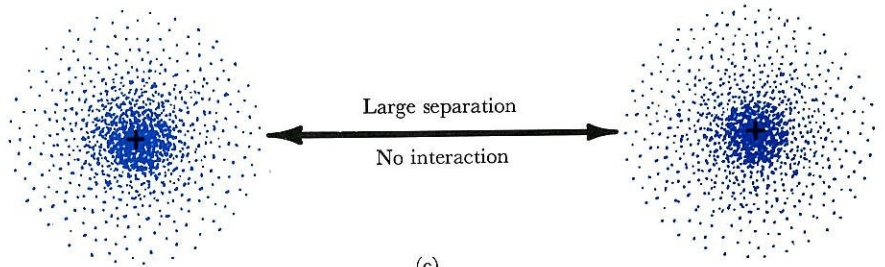
Bonding in the H<sub>2</sub> molecule. (a) Probability density in the 1s atomic orbital of hydrogen. (b) The spherical surface that encloses 99% of the probability density. (c) Two hydrogen atoms sufficiently far apart will exert no effect on one another. (d) As the atoms are brought together, each electron cloud begins to respond to the attraction of the nucleus of the other atom. The electron clouds become distorted, and electron density increases in the region between the nuclei. (e) At closer proximity, repulsion between the nuclei becomes significant. The equilibrium bond distance in the H<sub>2</sub> molecule is the point of balance between this attraction and repulsion. ►



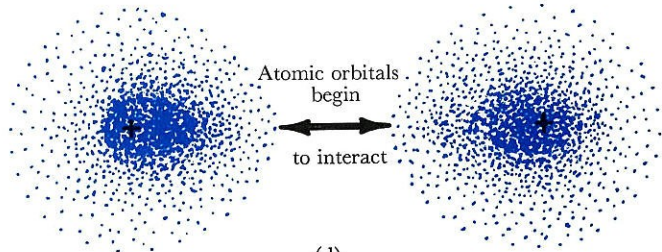
(a)



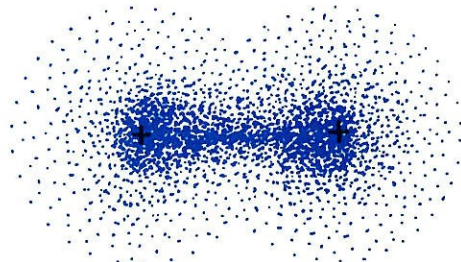
(b)



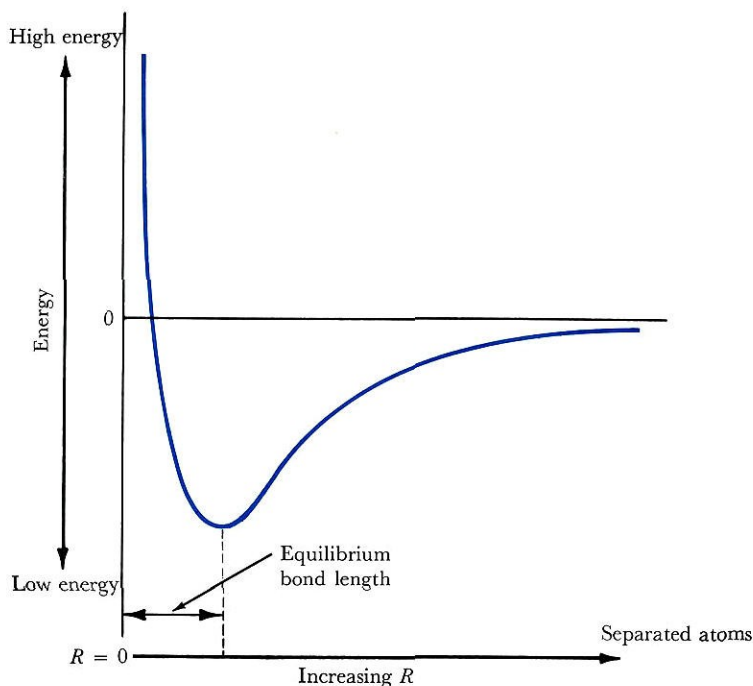
(c)



(d)



(e)

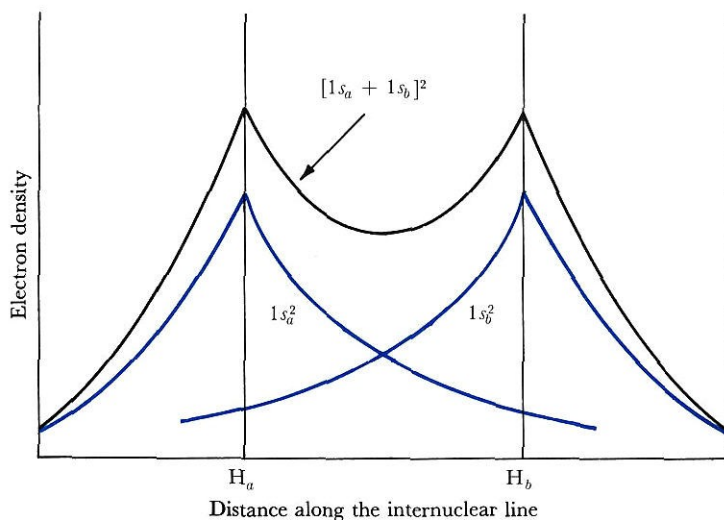


**Figure 12-2**

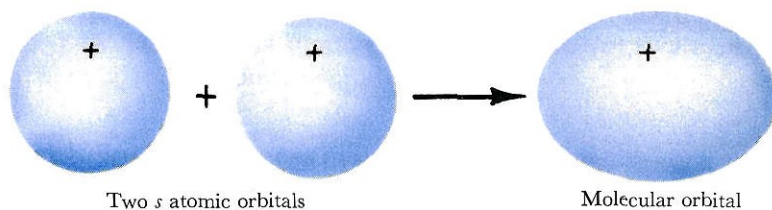
Potential-energy curve for the  $\text{H}_2$  molecule. As atoms come closer together and the distance between nuclei ( $R$ ) decreases, the potential energy decreases because of electron cloud–nucleus attraction, and then increases because of nucleus–nucleus repulsion. The equilibrium bond length is the bond length at the minimum value of the potential energy (where attraction and repulsion are balanced and the molecule is stable).

are used here to avoid confusion with the notation for electronic configuration in atoms:  $(1s)^2(2s)^1$ , and so on.] We can construct a molecular orbital (which we shall sometimes abbreviate MO) by adding the two atomic wave functions from atoms  $a$  and  $b$  to produce the molecular wave function  $1s_a + 1s_b$ . The electron probability density in such a molecular state is given by the square of the molecular wave function:  $[1s_a + 1s_b]^2$ . As you can see in Figure 12-3a, such a combination of atomic orbitals produces the pileup of electron density that we have been using to explain bonding. In the hydrogen molecule, this molecular orbital is filled with the two electrons having opposite spins (paired), and a single covalent bond is formed. This type of molecular orbital is a **bonding orbital**.

There is more than one way of combining two atomic wave functions,  $1s_a$  and  $1s_b$ . What if they were subtracted instead of added? Expressed dif-



(a)



(b)

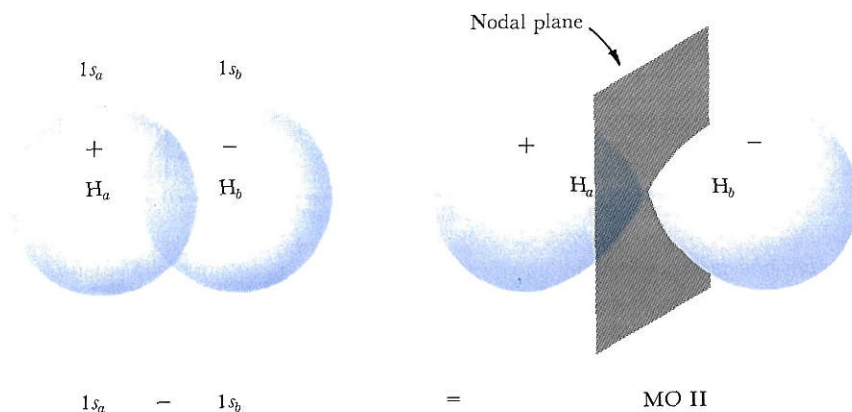
**Figure 12-3**

Molecular orbitals are obtained by taking linear combinations (sums and differences) of atomic orbitals. If the hydrogen  $1s$  wave function,  $\psi_{1s}$ , is represented simply by  $1s$ , the electron density is given by  $[1s]^2$ . Similarly, the electron density in the combined molecular orbital is given by  $[1s_a + 1s_b]^2$ , in which  $1s_a$  and  $1s_b$  are the wave functions of the individual atoms,  $H_a$  and  $H_b$ . (a) A plot of electron density in atomic orbitals (color) and the molecular orbital (black). (b) A conventional representation of the combination of two atomic orbitals to make a molecular orbital. Plus signs indicate signs of wave functions, not charge.

ferently, what if the atomic wave functions were combined with opposite sign, or were out of phase? The results are compared in Figure 12-4. The first drawing (Figure 12-4a) shows the addition of atomic wave functions to make the molecular orbital  $[1s_a + 1s_b]^2$ . The second drawing (Figure 12-4b) shows the subtraction of one from the other to make the molecular orbital  $[1s_a - 1s_b]^2$ . The wave function,  $1s_a - 1s_b$ , changes sign halfway from one



(a)



(b)

**Figure 12-4**

Two atomic  $1s$  orbitals give rise to two molecular orbitals (MO). (a) If the two atomic wave functions are added, or combined with the same sign, the resulting molecular orbital has high electron density between the nuclei. Electrons in such an orbital hold the molecule together, and it is called a *bonding* orbital. (b) If the two atomic functions are subtracted, or combined with opposite signs, the electron density in the molecular orbital is concentrated away from the internuclear region. There is zero probability of finding the electron in a nodal plane halfway between the nuclei. Electrons in such a molecular orbital pull the molecule apart, so it is called an *antibonding* orbital.

nucleus to the other, so its square falls to zero at the nodal plane. If electrons are in this molecular orbital in the molecule, there is *no* probability of finding them on a plane halfway between the nuclei. In fact, most of the electron density is concentrated outside the two nuclei. Rather than

being pulled together, the nuclei are pulled apart. This type of molecular orbital is an **antibonding orbital**.

The potential energies of the bonding and antibonding orbitals are shown in Figure 12-5a. The closer the nuclei come in the antibonding state, the more they are held back by the drag of their electron clouds and the higher the energy of the molecule is. At every point, the energy of the molecule is greater than that of two isolated atoms. The energies of the two molecular orbitals at the equilibrium bonding distance are plotted in Figure 12-5b and compared with the energy of the electrons in  $1s$  orbitals of isolated atoms.

In summary, the two atomic  $1s$  orbitals can be combined in two different ways to produce two molecular orbitals, one bonding and one antibonding. The bonding orbital concentrates electron density between the nuclei; the antibonding orbital concentrates it outside the two nuclei and has no density at all on a plane halfway between them. Both these molecular orbitals are symmetrical with respect to rotation around the line joining the nuclei; that is, when the orbital is spun around this line, neither the appearance of the electron-density cloud nor the sign of the wave function composing it is altered. Orbitals with such symmetry are called **sigma** ( $\sigma$ ) orbitals. The bonding orbital is given the superscript  $b$  and the superscript  $*$  is given to the antibonding orbital. (The types of molecular orbitals are described by the symbols sigma ( $\sigma$ ), pi ( $\pi$ ), delta ( $\delta$ ), . . . , by analogy with  $s$ ,  $p$ ,  $d$ , . . . for atomic orbitals.)

### The Pauli Buildup Process in Molecules

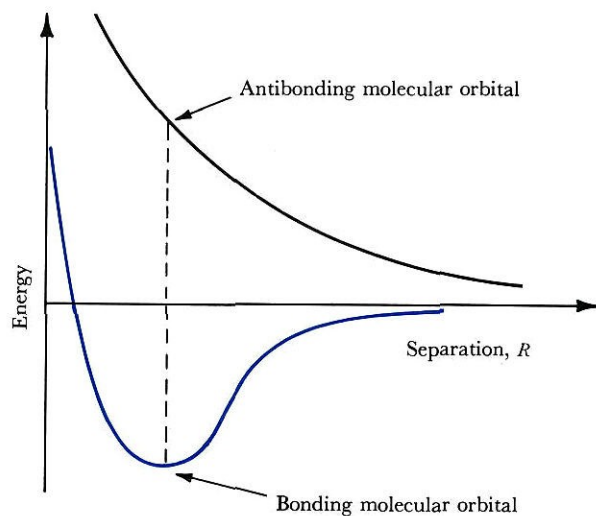
Now we can use an *aufbau* process to explain the occurrence or nonoccurrence of the molecules  $H_2^+$ ,  $H_2$ ,  $He_2^+$ , and  $He_2$ . The hydrogen molecule-ion,  $H_2^+$ , has two nuclei but only one electron. By Pauli's reasoning, this electron will be in the lowest-energy molecular orbital, which Figure 12-5b indicates is the bonding  $\sigma^b$  orbital. The  $H_2^+$  molecule-ion should be weakly stable.

The hydrogen molecule,  $H_2$ , has two nuclei and two electrons. Both electrons can be accommodated in the  $\sigma^b$  orbital if their spins are paired, and a covalent electron-pair bond is created. The bond energy (the energy needed to pull the atoms apart) should be substantially larger than that of the hydrogen molecule-ion.

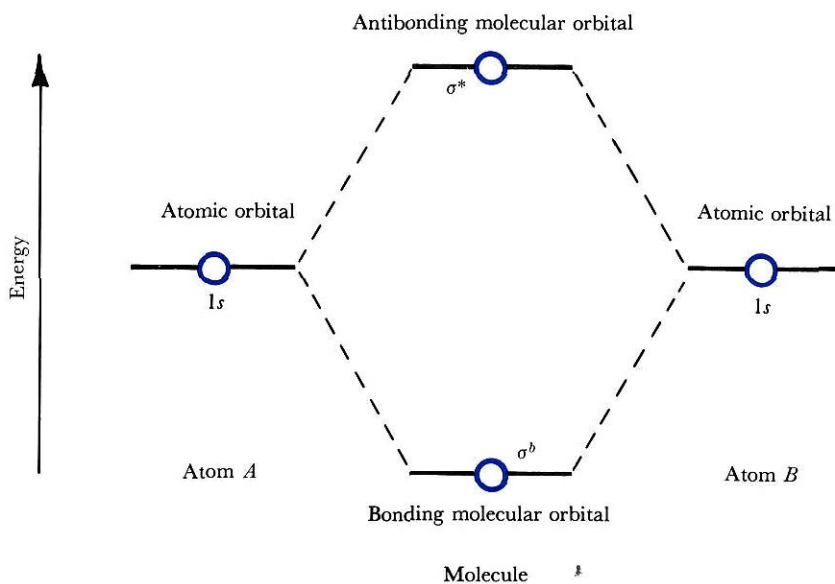
The helium molecule-ion,  $He_2^+$ , has two helium nuclei and three electrons. Although the energies of the helium orbitals, atomic and molecular, are different from those of hydrogen because of the different nuclear charge, the relative arrangement of atomic and molecular energy levels is similar. We can use Figure 12-5b for He as well as for H if we make the proper adjustments to the energy scale on the left.

The first two electrons in  $He_2^+$  pair their spins and fill the  $\sigma^b$  bonding orbital. But what happens to the third electron? By the Pauli exclusion principle, it cannot occupy the  $\sigma^b$  state, so it must go into the next lowest





(a)



(b)

**Figure 12-5**

(a) The energy of a molecule with electrons in the bonding orbital falls to a minimum at the observed interatomic distance. The energy of a molecule with electrons in the antibonding orbital is always greater than the energy of completely separated atoms; it increases steadily as the atoms are brought closer together. (b) The two lowest molecular orbitals for the hydrogen molecule, and the atomic  $1s$  orbitals from which they came. The symbol  $\sigma$  (sigma) indicates that the orbital is symmetrical around the line between the nuclei, and that the orbital could be spun around that line as an axis without changing the orbital's appearance. The superscript  $b$  indicates bonding character, and  $*$  indicates antibonding character.

Table 12-1

## Comparison of Predicted and Observed Bonding in Simple Diatomic Molecules

Molecular-orbital-theory predictions					Experimental observations	
Molecule	Molecular orbital configuration	Bonding electrons	Antibonding electrons	Net bonding electrons	Bond length (Å)	Bond energy (kJ mole <sup>-1</sup> )
H <sub>2</sub> <sup>+</sup>	(σ <sup>b</sup> ) <sup>2</sup>	1	0	1	1.06	255
H <sub>2</sub>	(σ <sup>b</sup> ) <sup>2</sup>	2	0	2	0.74	432
He <sub>2</sub> <sup>+</sup>	(σ <sup>b</sup> ) <sup>2</sup> (σ*) <sup>1</sup>	2	1	1	1.08	322
He <sub>2</sub>	(σ <sup>b</sup> ) <sup>2</sup> (σ*) <sup>2</sup>	2	2	0	none	none

energy level, which is the antibonding σ\* orbital. This third electron is pushed away from the region between the nuclei by the presence of the first two and is forced into the region outside the two nuclei. This electron is a disruptive influence; it pulls the nuclei apart. The molecule would be more stable if the third electron were not there. The electron effectively counteracts the contribution of one of the bonding electrons, thereby leaving a **net bonding action** of one electron, or half a covalent bond. The bond energy of He<sub>2</sub><sup>+</sup> should be less than that of H<sub>2</sub>.

In He<sub>2</sub>, the fourth electron also must go into the antibonding orbital. Now there are two bonding electrons and two antibonding electrons. The molecule is *no more stable than the isolated atoms and falls apart*. We should not expect to find an He<sub>2</sub> molecule.

Enough of theory for a moment. What actually happens? Table 12-1 lists the observed bond energies and bond lengths for H<sub>2</sub><sup>+</sup>, H<sub>2</sub>, and He<sub>2</sub><sup>+</sup>; as predicted, He<sub>2</sub> does not exist. Moreover, the measured bond energies are consistent with the number of net bonding electrons given by molecular orbital theory. Bond lengths, too, are consistent. The more bonding electrons, the tighter the interaction and the shorter the bond length.

## Example 1

What is the electronic configuration of H<sub>2</sub><sup>-</sup>? How many bonding electrons are there? How many antibonding electrons? What is the net number of bonds? Will the bond length of H<sub>2</sub><sup>-</sup> be longer or shorter than that of H<sub>2</sub>? What molecule-ion is H<sub>2</sub><sup>-</sup> isoelectronic with?

## Solution

The molecule-ion H<sub>2</sub><sup>-</sup> has three electrons. The ground state of H<sub>2</sub><sup>-</sup> is therefore (σ<sup>b</sup>)<sup>2</sup>(σ\*)<sup>1</sup>. There are two bonding electrons and one antibonding electron; there is a net of one bonding electron, or half a bond. The bond length

of  $\text{H}_2^-$  will be greater than that of  $\text{H}_2$ , because there is less net bonding in  $\text{H}_2^-$  (one half-bond versus one full bond). Finally,  $\text{H}_2^-$  is isoelectronic with  $\text{He}_2^+$  (each has three electrons).

---

Thus far, molecular orbital theory explains the data well. How can we extend this explanation to more complicated molecules? The process that we shall use to explain first the diatomic molecules of heavier atoms and then more complicated molecules can be summarized as follows:

1. Combine atomic orbitals in a suitable way to obtain a set of molecular orbitals. The total number of molecular orbitals obtained will always be equal to the number of atomic orbitals that we began with.
  2. Decide the order of energies of these molecular orbitals.
  3. Feed all the electrons in the molecule into these molecular orbitals. Start from the lowest and work up; place no more than two electrons in any one orbital.
  4. Examine the filled bonding and antibonding orbitals to determine the net number of bonding electrons. (Some antibonding orbitals will have lower energy than other bonding orbitals and will be filled before these bonding orbitals are. The criterion for a bonding orbital is not that it have a low energy, but that it have a *minimum* in energy, as in Figure 12-5a, at some interatomic distance.) Two net bonding electrons correspond to what we have called a single bond in the Lewis model.
- 

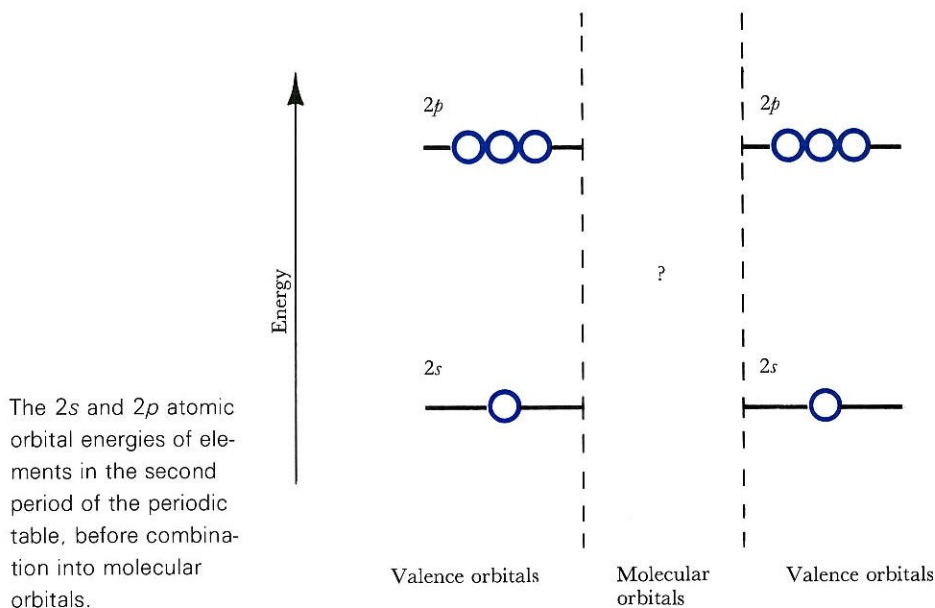
## 12-2 DIATOMIC MOLECULES WITH ONE TYPE OF ATOM

The  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{Cl}_2$  molecules, with only one type of atom, are called **homonuclear** molecules. In contrast,  $\text{HCl}$ ,  $\text{CO}$ , and  $\text{HI}$  are **heteronuclear**. We want to extend the simple molecular orbital treatment of  $\text{H}_2$  and  $\text{He}_2$  to homonuclear diatomic molecules of elements in the second period of the periodic table. Some of these molecules, such as  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{F}_2$ , are stable at STP. Others, such as  $\text{C}_2$  and  $\text{Li}_2$ , are found only at high temperatures. Some do not exist at all. What are the predictions of molecular orbital theory?

The first step in the treatment is to construct molecular orbitals. The atomic orbitals available are the  $2s$  and three  $2p$  orbitals from each of the two atoms. Their energies are diagrammed in Figure 12-6, and the molecular orbitals that result from their combination are shown in Figure 12-7.

The two  $2s$  atomic orbitals can be combined into a bonding  $\sigma_s^b$  and an antibonding  $\sigma_s^*$  orbital in the same manner as for the  $1s$ . If the line joining the nuclei is the  $z$  axis, then there are two kinds of  $2p$  orbitals: the  $2p_z$  orbital, which is parallel to the internuclear axis, and the  $2p_x$  and  $2p_y$  orbitals, which are perpendicular to it. The two  $2p_z$  orbitals from the two atoms can be combined with the same signs in the internuclear region, thereby pro-

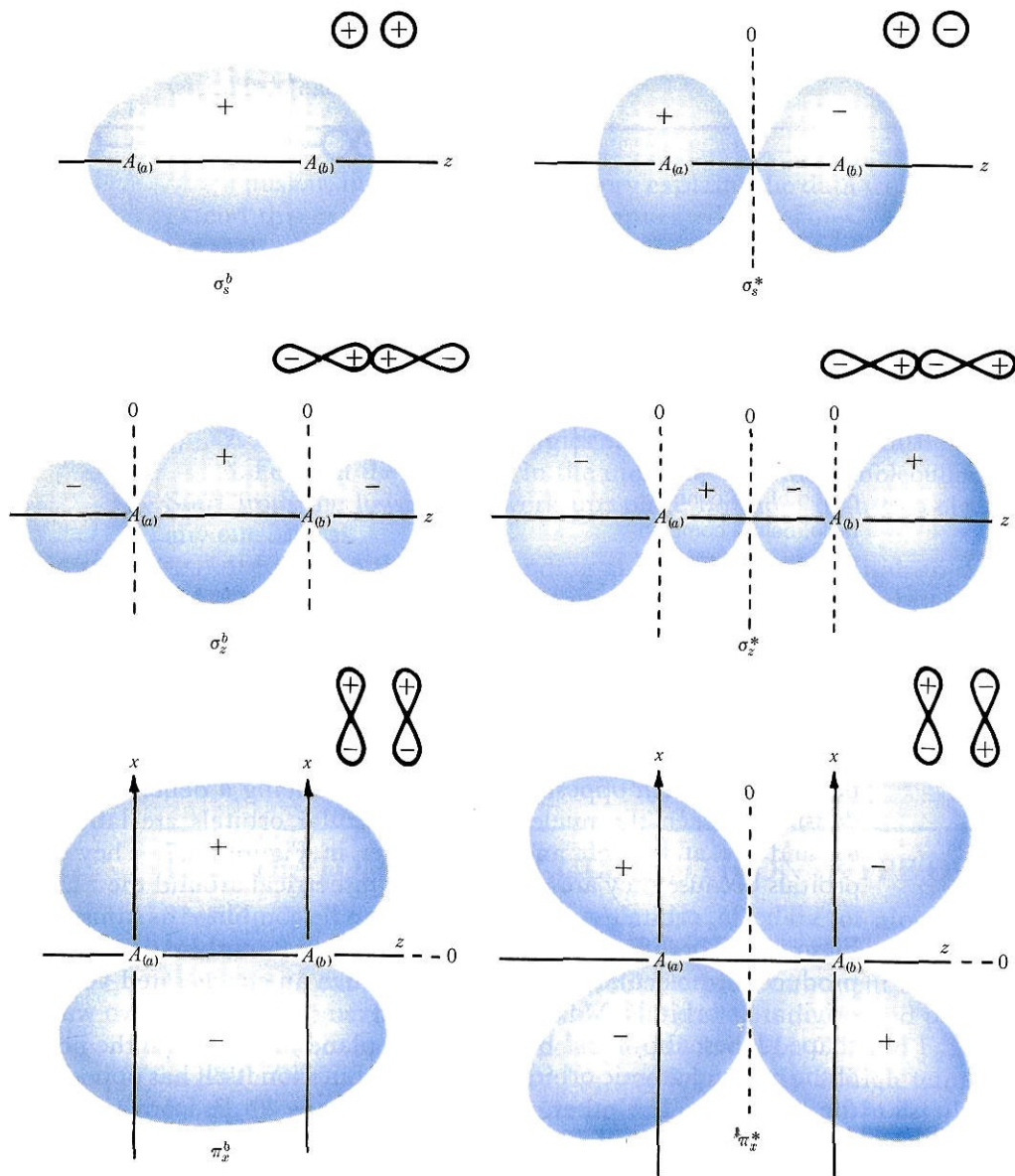
Figure 12-6



ducing a concentration of electron density between the nuclei. They can also be combined with opposing signs, thus producing a deficiency of electron density between the nuclei. These molecular orbitals are labeled  $\sigma_z^b$  and  $\sigma_z^*$ , and are at the left and right center in Figure 12-7. They are still  $\sigma$  orbitals because they are rotationally symmetrical around the  $z$  axis.

The  $2p_x$  orbitals on the two atoms can be combined as sums (lower left, Figure 12-7) or differences (lower right). The first combination,  $[2p_x + 2p_x]^2$ , produces a molecular orbital that looks like an exaggerated version of the original  $2p$  orbitals. Maximum electron density occurs in two watermelon-shaped lobes, above and below a nodal plane that was also the nodal plane of the original atomic orbitals. The wave function itself has opposite signs in the two lobes. The other combination,  $[2p_x - 2p_x]^2$ , leads to a molecular orbital with a second nodal plane, and four lobes whose electron densities lie mostly outside the internuclear region (lower right, Figure 12-7). The two-lobed orbital is bonding; the four-lobed orbital is antibonding. They are called  $\pi$  orbitals and have a different kind of symmetry around the  $z$  axis. If either orbital is rotated  $180^\circ$  around the  $z$  axis, the electron-density cloud has the same appearance, but the signs of the wave function in the different lobes are reversed. The two orbitals are labeled  $\pi_x^b$  and  $\pi_x^*$ . A corresponding pair,  $\pi_y^b$  and  $\pi_y^*$ , results from the two  $2p_y$  atomic orbitals.

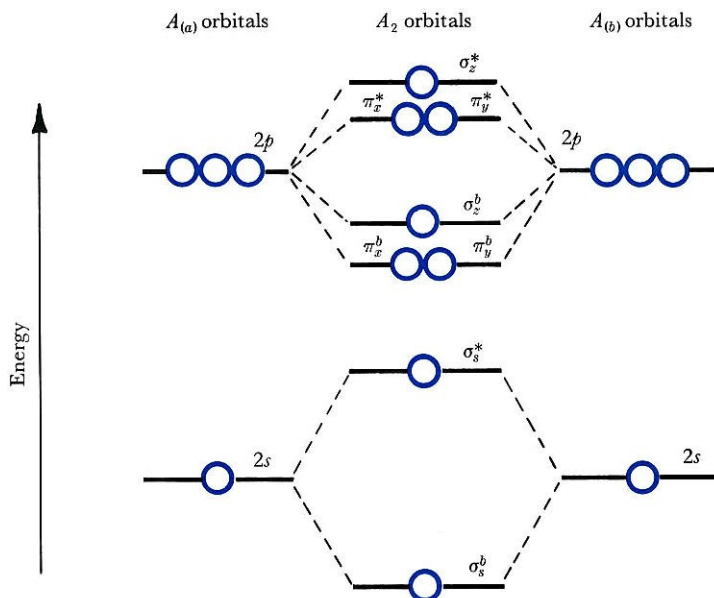
From eight atomic orbitals we have obtained eight molecular orbitals, four of them bonding ( $\sigma_s^b$ ,  $\sigma_z^b$ ,  $\pi_x^b$ ,  $\pi_y^b$ ) and the other four antibonding ( $\sigma_s^*$ ,  $\sigma_z^*$ ,  $\pi_x^*$ ,  $\pi_y^*$ ). What is the order of energy of these orbitals?



**Figure 12-7**

The six different kinds of molecular orbitals formed from the  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$  orbitals of two similar atoms in a diatomic molecule. The line drawn through the two nuclei is chosen as the  $z$  axis. The symbol  $\pi$  indicates that if the molecular orbital is rotated  $180^\circ$  around the axis the electron distribution is unchanged. The only effect is to reverse the signs of the parts of the wave function. Plus and minus signs represent only the signs on the wave function, and not electric charge. The atomic orbitals from which these are obtained are shown, with their appropriate signs, at the upper right of each molecular orbital. The atomic orbitals used are  $s$  (top row),  $p_z$  (middle row), and  $p_x$  (bottom row), which is equivalent to  $p_y$ . Bonding orbitals are in the left column; antibonding orbitals are in the right one. Dashed lines are nodal planes of zero electron density.

The orbitals derived from the  $s$  atomic orbitals will have lower energy than those from the  $p$  orbitals. Moreover, of two orbitals derived from the same atomic orbitals, the bonding orbital will lie lower than the antibonding orbital. Therefore, the first two most stable levels are the  $\sigma_s^b$  and  $\sigma_s^*$ . The most stable of the bonding orbitals obtained from  $2p$  orbitals are  $\pi_x^b$  and  $\pi_y^b$  rather than  $\sigma_z^b$ , which is contrary to earlier ideas and to the diagrams in many older texts. This order of levels has been found from recent, careful, spectroscopic and magnetic studies of  $B_2$  and  $N_2^+$ . It is reasonable, because electrons added to  $\pi_x^b$  are farther removed in space from those in filled  $\sigma_s^b$  and  $\sigma_s^*$  than they would be if they were in the  $\sigma_z^b$  orbital. (There is a crossover of energy levels at O, so in  $O_2$  and  $F_2$  the  $\sigma_z^b$  is more stable than  $\pi_x^b$  and  $\pi_y^b$ . This really does not matter in our discussion since all three levels are filled in  $O_2$  and  $F_2$  anyway.) The  $\pi_x^b$  and  $\pi_y^b$  orbitals have the same energy, and are said to be **degenerate** energy levels. Above these orbitals lies the  $\sigma_z^b$ , then the two antibonding  $\pi_x^*$  and  $\pi_y^*$ , and last of all the antibonding  $\sigma_z^*$ . The complete energy diagram of the molecular orbitals from  $2s$  and  $2p$  atomic orbitals appears in Figure 12-8.



**Figure 12-8**

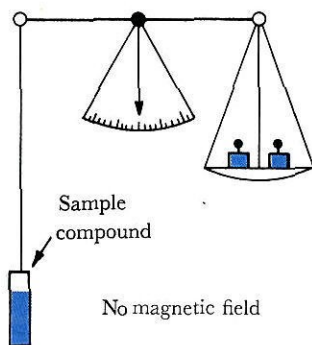
Energy levels for the molecular orbitals shown in Figure 12-7. Among the orbitals that come from either  $s$  or  $p$  atomic orbitals, bonding molecular orbitals are more stable than antibonding orbitals. The  $\pi_x^b$  and  $\pi_y^b$  orbitals are more stable than the  $\sigma_z^b$  because they permit the electrons to remain farther away from the filled  $\sigma_s^b$  orbital.

## Paramagnetism and Unpaired Electrons

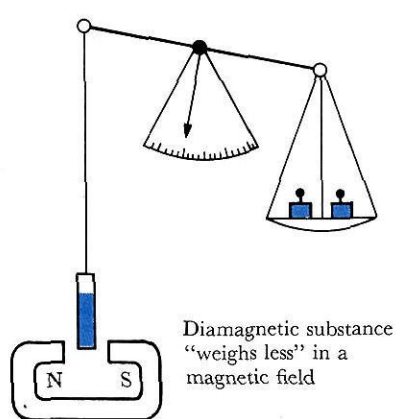
Substances whose molecules and ions have electrons with unpaired spins tend to be drawn into magnetic fields. The magnetic field aligns the spins and magnetizes the substance. Many substances, called **paramagnetic** substances, lose their magnetism when removed from the magnetic field. These materials have unpaired electrons, and the strength of the attraction by a magnetic field can be used to determine how many such unpaired electrons there are per mole of substance. If a molecule has no unpaired electrons, it is **diamagnetic** and is slightly repelled by a magnetic field because of the small opposing magnetic moments induced in it by the field. The number of unpaired electrons in a molecule of a substance can be determined with a magnetic balance as shown schematically in Figure 12-9. In the next section we shall see examples of both paramagnetic and diamagnetic molecules.

**Figure 12-9**

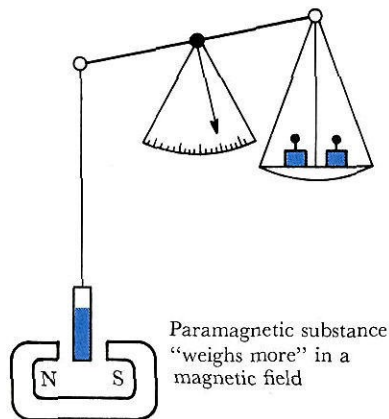
(a) The presence or absence of unpaired electron spins can be determined by a magnetic or Gouy balance. (b) A diamagnetic substance, with no unpaired electrons, is slightly repelled by a magnetic field. (c) A paramagnetic substance, with unpaired electron spins, is attracted into the magnetic field.



(a)



(b)



(c)

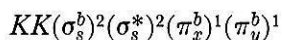
## Buildup of Diatomic Molecules

We are now ready to feed electrons into molecular orbitals, two electrons to an orbital, and to build the diatomic molecules from  $\text{Li}_2$  through  $\text{Ne}_2$ . There will always be four electrons from the lower  $n = 1$  atomic orbitals. In the diatomic molecule, two of these inner-shell electrons will be in the  $\sigma_{1s}^b$  bonding molecular orbital and two will be in the  $\sigma_{1s}^*$  antibonding orbital. However, it makes no difference to the net bonding whether we think of them as in  $1s$  atomic orbitals or in the molecular orbitals obtained from  $1s$  orbitals. The bonding properties of the molecule arise only from the outer shell of  $n = 2$  electrons, and we need to consider only the molecular orbitals derived from  $2s$  and  $2p$  atomic orbitals.

■ *Lithium.* The Li atom has one valence electron, so the  $\text{Li}_2$  molecule has two potential bonding electrons. These are paired in the lowest available molecular orbital,  $\sigma_s^b$ . Therefore, the  $\text{Li}_2$  molecule contains a single covalent bond. The bond length is longer than in  $\text{H}_2$ , 2.67 Å compared to 0.74 Å, because the larger  $n = 2$  orbitals are involved, rather than the  $n = 1$ . For the same reason the bond is weaker: 110 kJ mole<sup>-1</sup> rather than 432 kJ mole<sup>-1</sup> as in  $\text{H}_2$ . The nuclei are farther apart, the electron cloud is spread over a greater volume, and the overall attractive forces are weaker.

■ *Beryllium.* There are four valence electrons available in the  $\text{Be}_2$  molecule. Two are paired in the bonding  $\sigma_s^b$  molecular orbital, and two are paired in the antibonding  $\sigma_s^*$ . This configuration gives no net bonds, which is consistent with the absence of  $\text{Be}_2$  from the family of stable second-row diatomic molecules.

■ *Boron.* The two additional valence electrons of  $\text{B}_2$  go into the next lowest unfilled molecular orbitals,  $\pi_x^b$  and  $\pi_y^b$ . By Hund's rule, electron-electron repulsion ensures that one electron occupies each orbital rather than both being spin-paired in one. Whether or not the electrons are paired, the effect of two bonding electrons is a single covalent bond. The electronic configuration for  $\text{B}_2$  is



The symbol  $KK$  represents the four electrons in the inner  $n = 1$  shells that have no effect on bonding. The experimental bond length in  $\text{B}_2$ , 1.59 Å, is less than that in  $\text{Li}_2$ , 2.67 Å. The bond energy is greater; it is 274 kJ mole<sup>-1</sup> rather than 110 kJ mole<sup>-1</sup>. Both effects arise from the greater positive charge on the B nucleus and the tightness with which the electrons are held. Perhaps the most satisfying test of the molecular orbital theory is the finding of two unpaired electrons in  $\text{B}_2$  from magnetic measurements. This is a direct confirmation of the order of  $\sigma_s^b$  and  $\pi_x^b$  orbital energies in Figure 12-8; if the order were reversed, both electrons would be paired in  $\sigma_s^b$  and the molecule would have no unpaired spins. (As a matter of historical fact,



the unpaired electrons in  $B_2$  were not predicted in advance. The existence of the unpaired electrons compelled scientists to revise their original order of orbital energies to that of Figure 12-8.)

■ *Carbon.* The two additional electrons in carbon,  $C_2$ , complete the  $\pi_x^b$  and  $\pi_y^b$  molecular orbitals. There are four net bonding electrons, and hence two covalent bonds in Lewis' terminology. There should be no unpaired spins in the ground electronic state. True to predictions, the bond energy of  $C_2$  is twice that of  $B_2$  ( $603 \text{ kJ mole}^{-1}$  and  $274 \text{ kJ mole}^{-1}$ ), and the bond length is less ( $1.24 \text{ \AA}$  and  $1.59 \text{ \AA}$ ). Moreover,  $C_2$  is not paramagnetic.

■ *Nitrogen.* With nitrogen, all the bonding orbitals in Figure 12-8 are filled. The  $N_2$  molecule has the electronic configuration

$$KK(\sigma_s^b)^2(\sigma_s^*)^2(\pi_x^b)^2(\pi_y^b)^2(\sigma_z^b)^2 \quad \text{or} \quad KK(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^4(\sigma_z^b)^2$$

There are six net bonding electrons, so the  $N_2$  molecule contains a triple bond. Since there are no unpaired electrons, no paramagnetism is expected.

Nitrogen has the greatest bond energy and the shortest bond length of any element in the second period,  $942 \text{ kJ mole}^{-1}$  and  $1.10 \text{ \AA}$ . The increase in bond energy with theoretical bond order (single, double, or triple bonds), shown in Figure 12-10, is remarkably constant. As predicted,  $N_2$  is diamagnetic.

We now can interpret the Lewis structure of  $N_2$ ,



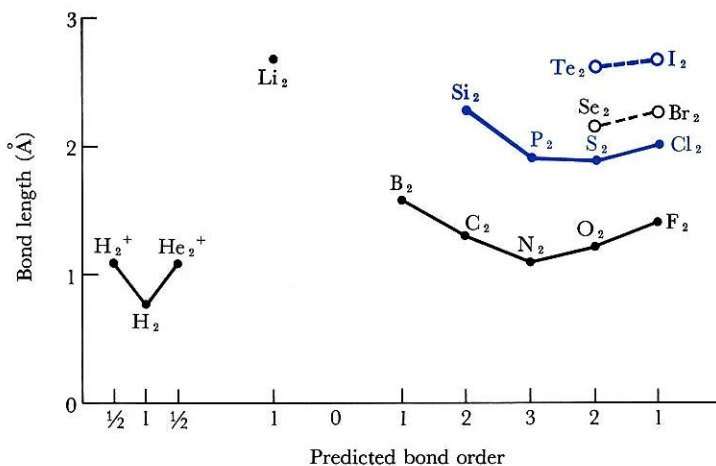
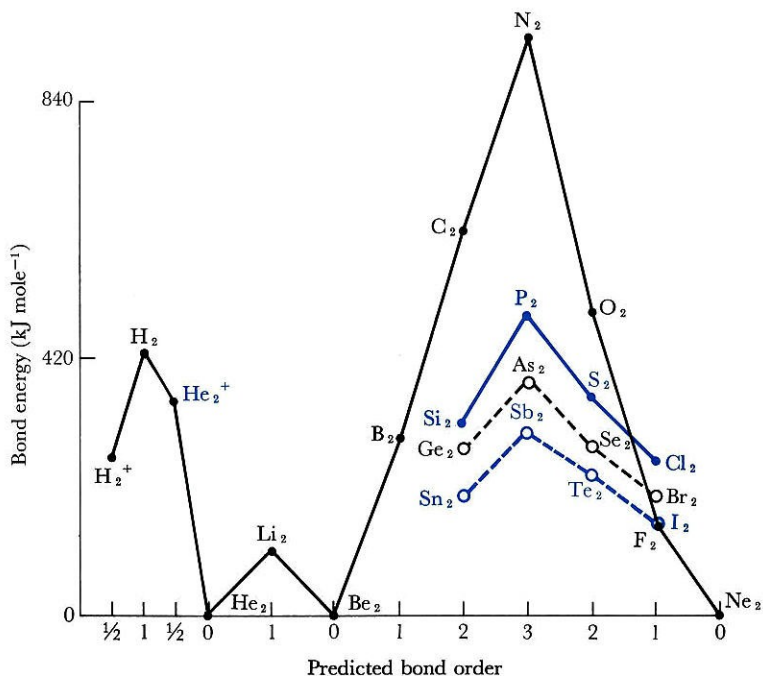
The three bonds involve the  $\pi_x^b$ ,  $\pi_y^b$ , and  $\sigma_z^b$  orbitals. The two lone pairs correspond, at least formally, to the self-canceling pair of orbitals:  $(\sigma_s^b)^2(\sigma_s^*)^2$ .

We did not try to write a Lewis structure for  $C_2$ . Nothing in Lewis' covalence theory suggests that it should exist. Now, by analogy with  $N_2$ , we would write the  $C_2$  molecule as



in which the bonds correspond to the filled  $\pi_x^b$  and  $\pi_y^b$  orbitals, and the lone pairs are as in  $N_2$ . But  $C_2$ , like  $BF_3$ , is electron-deficient; there are only six valence electrons around each carbon atom. We might expect that  $C_2$  would accept electron pairs from a donor in the way that  $BF_3$  accepts them from  $NH_3$  to make the addition compound  $BF_3NH_3$ . But  $C_2$  also has a lone pair and can play the role of donor as well. The  $C_2$  molecule is found only at high temperatures. At lower temperatures, each atom in  $C_2$  accepts electrons from one new C and donates electrons to another. The result is a network in which each C is covalently linked to at least three others (graphite) or, alternatively, to four (diamond).

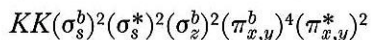
■ *Oxygen.* In oxygen, the next 2 electrons must go into the two antibonding orbitals  $\pi_x^*$  and  $\pi_y^*$ , one in each by Hund's rule. Of the 12 valence



**Figure 12-10**

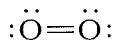
Plot of bond energies and bond lengths against predicted bond order for homonuclear diatomic molecules. Bond energies increase with increasing bond order, and bond lengths decrease.

electrons in O<sub>2</sub>, a total of 8 are in bonding orbitals and 4 are in antibonding orbitals. There are 4 *net* bonding electrons, thus the molecule has a double bond. The two additional electrons, which go into antibonding orbitals, cancel the effects of two of the electrons in the orbitals that gave N<sub>2</sub> a triple bond. Both bond length and bond energy agree well with theory (Figure 12-10). The electronic configuration for O<sub>2</sub> is

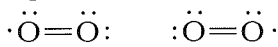


Notice that the relative order of energy levels  $\sigma_z^b$  and  $\pi_{x,y}^b$  has changed, as was mentioned previously.

Molecular orbital theory explains why  $O_2$  is paramagnetic, indicating two unpaired electrons, whereas the Lewis theory fails. The Lewis structure for  $O_2$  has no unpaired electrons:

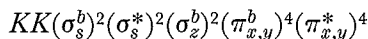


The only possible Lewis structures with a double bond and two unpaired electrons violate the symmetry of the molecule by making the oxygen atoms different, and make it appear that the unpaired electrons are both associated with a particular atom:



You can partially redeem the Lewis structures by saying that these two structures are the two resonance structures for  $O_2$ , and that the true structure is unrepresentable but has the character of both resonance structures in equal amounts. But this treatment hardly seems worth the effort. It is easier to abandon Lewis structures and to think in molecular orbital terms.

■ *Fluorine.* In  $F_2$ , all of the molecular orbitals in Figure 12-8 are occupied except the highest one. The molecule has one net covalent bond from its two net bonding electrons, and the electronic structure is



Bond energy and bond length are as expected for a single bond, and the  $F_2$  molecule is diamagnetic.

■ *Neon.* The  $Ne_2$  molecule would have all the molecular orbitals in the center of Figure 12-8 filled, and an equal number of bonding and antibonding electrons. There would be no net bonding electrons and no reason for the atoms to remain together. As predicted, there is no  $Ne_2$  molecule.

■ *Later periods in the table.* Experimental data on several diatomic molecules and molecule-ions are given in Table 12-2. Some of these data have been plotted in Figure 12-10 as well. The trends for the nonmetals are regular and understandable in terms of larger orbitals (in which  $n = 3, 4,$  and  $5$ ) and weaker forces holding the electrons. The unexpected weakness of the  $F_2$  bond is odd. The lone electron pairs in  $F_2$  are considerably closer together than they are in the larger halogens, and we think that such close lone-pair repulsion may be at least part of the reason for the weak  $F_2$  bond.

### Example 2

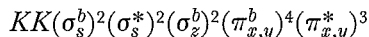
Write the molecular orbital electronic structure of the molecule-ion  $O_2^-$ . What is the bond order, and how many unpaired electrons are there?

**Table 12-2****Bond Properties of Some Homonuclear Diatomic Molecules and Ions**

Molecule	Bond length (Å)	Bond energy (kJ mole <sup>-1</sup> )
Ag <sub>2</sub>	—	161.9
As <sub>2</sub>	2.288	382.0
Au <sub>2</sub>	2.472	225.5
B <sub>2</sub>	1.589	274.0
Bi <sub>2</sub>	—	195.0
Br <sub>2</sub>	2.2809	190.1
C <sub>2</sub>	1.2425	602.5
Cl <sub>2</sub>	1.988	239.2
Cl <sub>2</sub> <sup>+</sup>	1.8917	415.0
Cs <sub>2</sub>	—	43.5
Cu <sub>2</sub>	2.2195	197.9
F <sub>2</sub>	1.417	138.9
Ge <sub>2</sub>	—	272
H <sub>2</sub>	0.74116	432.0
H <sub>2</sub> <sup>+</sup>	1.06	255.5
He <sub>2</sub> <sup>+</sup>	1.080	322.2
I <sub>2</sub>	2.6666	148.7
K <sub>2</sub>	3.923	49.4
Li <sub>2</sub>	2.672	110.0
N <sub>2</sub>	1.0976	941.7
N <sub>2</sub> <sup>+</sup>	1.116	842.2
Na <sub>2</sub>	3.078	72.4
O <sub>2</sub>	1.20741	493.5
O <sub>2</sub> <sup>+</sup>	1.1227	—
O <sub>2</sub> <sup>-</sup>	1.26	392.9
O <sub>2</sub> <sup>2-</sup>	1.49	—
P <sub>2</sub>	1.8937	477.0
Pb <sub>2</sub>	—	96.2
Rb <sub>2</sub>	—	47.3
S <sub>2</sub>	1.889	421.3
Sb <sub>2</sub>	2.21	298.3
Se <sub>2</sub>	2.1663	324.7
Si <sub>2</sub>	2.246	314
Sn <sub>2</sub>	—	192
Te <sub>2</sub>	2.5574	260.7

**Solution**

The ion has 6 valence electrons from each oxygen atom plus 1 extra for the  $-1$  charge, or 13 valence electrons. Filling orbitals in Figure 12-8 from the bottom, we find an electronic structure of



There are three net bonding electrons, hence a bond order of  $1\frac{1}{2}$ . The molecule has one unpaired electron.

**Example 3**

With what neutral molecule is  $O_2^{2-}$  isoelectronic? Explain the fact that the O—O bond lengths increase in the following order:

**Solution**

The molecular orbital configuration of  $O_2^{2-}$  is  $KK(\sigma_s^b)^2(\sigma_s^*)^2(\sigma_z^b)^2(\pi_{x,y}^b)^4(\pi_{x,y}^*)^4$ ;  $O_2^{2-}$  is isoelectronic with  $F_2$  and has two net bonding electrons, corresponding to a single bond (bond order of 1). As electrons are removed from the antibonding  $\pi_{x,y}^*$  level, the bond order increases as follows:  $O_2^{2-}$ , 1;  $O_2^-$ ,  $1\frac{1}{2}$ ;  $O_2$ , 2;  $O_2^+$ ,  $2\frac{1}{2}$ . As the bond order increases, the bond length shortens. Thus we would predict the O—O bond length to increase in the order observed.

## 12-3 DIATOMIC MOLECULES WITH DIFFERENT ATOMS

Keeping the methods used for homonuclear diatomic molecules in mind, let's examine the molecular orbital treatment of heteronuclear molecules, those with two different atoms.

### Hydrogen Fluoride and Potassium Chloride

When we carry out the mathematical operations that are behind the expression, "combining two atomic orbitals to produce an antibonding and a bonding molecular orbital," we find that the two atomic orbitals should be reasonably close in energy. In the  $H_2$  molecule, each of the two molecular orbitals has a 50% contribution from each of the two hydrogen  $1s$  atomic orbitals. At the other extreme, if in a molecule of the type  $AB$  we combined an orbital from  $A$  having extremely high energy with one from  $B$  of quite low energy, we would find at the end of the mathematical analysis that the antibonding molecular orbital was almost pure  $A$ , and the bonding orbital was almost pure  $B$ . Then a pair of electrons in this "bonding" orbital would not be in a true covalent bonding orbital at all. It would be a lone electron pair in a  $B$  orbital. The interaction of these two atomic orbitals would be negligible. We shall see, for the HF molecule, what this means in terms of partial ionic character in a bond.

In HF, the energies of the hydrogen  $1s$  and fluorine  $1s$  atomic orbitals are so different that there is effectively no interaction between them. The fluorine  $2s$  orbital has too low an energy as well. Only the  $2p$  orbitals are

close enough in energy to the hydrogen  $1s$  to effect an appreciable combination into molecular orbitals. Moreover, the  $2p_x$  and  $2p_y$  orbitals have the wrong symmetry for combining with hydrogen  $1s$ , as Figure 12-11 shows. The total overlap of either  $p$  with the  $1s$  is zero if proper account is taken of the signs of the wave functions. The molecular orbitals in HF are obtained by a combination of hydrogen  $1s$  and fluorine  $2p_z$  atomic orbitals. This combination produces two orbitals with  $\sigma$  symmetry, one bonding ( $\sigma^b$ ) and one antibonding ( $\sigma^*$ ).

The energy levels for HF appear in Figure 12-12. The  $\pi_x$  and  $\pi_y$  orbitals are essentially lone-pair orbitals on fluorine and might just as well be designated  $2p_x$  and  $2p_y$ . A third lone pair occupies the fluorine  $2s$  orbital. There are eight valence electrons in HF; seven from F and one from H. These electrons fill all the HF orbitals except the highest antibonding  $\sigma^*$ . In the HF molecule this assignment produces one covalent bond and three lone pairs on F. The Lewis structure is

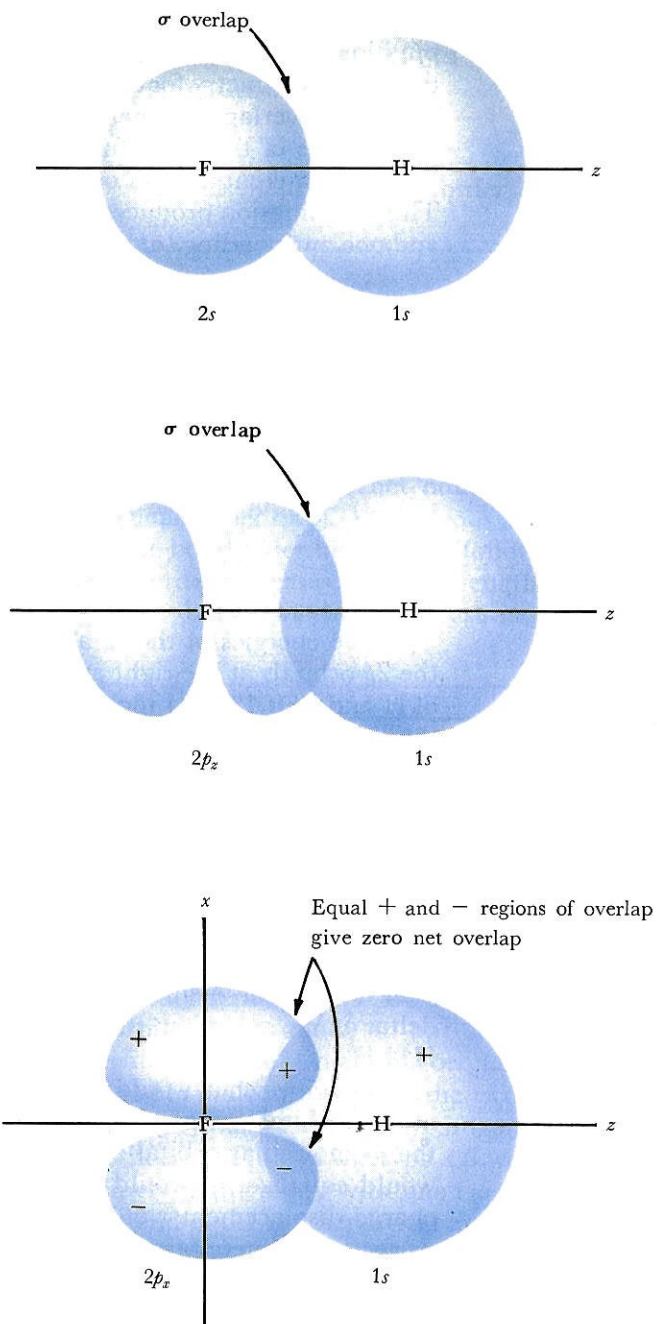


and it is accurate.

The energies of the  $1s$  atomic orbital at the left of Figure 12-12 and the  $2p$  orbitals at the right are obtainable from the first ionization energies of H and F. If  $1310 \text{ kJ mole}^{-1}$  are required to remove the electron from H, the energy of the electron before removal is  $-1310 \text{ kJ mole}^{-1}$ . Similarly, the first ionization energy of F is  $1682 \text{ kJ mole}^{-1}$ , so the energy of the  $2p$  levels is  $-1682 \text{ kJ mole}^{-1}$ . The two atomic levels differ by  $372 \text{ kJ mole}^{-1}$ . The  $\sigma^b$  molecular orbital is closer in energy to the fluorine  $2p$  than to the hydrogen  $1s$ . This means that there will be more of a fluorine  $2p$  character to the  $\sigma^b$  orbital. The covalent bond is not perfectly symmetrical; there is a small inequality in charge distribution and a partial ionic character to the bond. Electrons in the  $\sigma^b$  orbital will have a greater probability of being near the F atom. A small charge displacement is represented by a lowercase delta,  $\delta$ . We can show the partial ionic character of the HF molecule by  $\text{H}^{\delta+} \text{F}^{\delta-}$ .

Imagine what would happen to the H—F bond if the hydrogen  $1s$  atomic orbital energy were to fall slowly. The energy separations between the  $\sigma^b$  molecular orbital and the two atomic orbitals from which it came would equalize;  $\sigma^b$  would assume an equal contribution from each. The charge displacement would diminish, and the bond would approach the perfectly symmetrical covalent bond of  $\text{F}_2$  or  $\text{H}_2$ . This is more nearly the situation for HCl, in which the first ionization energies of H and Cl are close:  $1310 \text{ kJ mole}^{-1}$  and  $1255 \text{ kJ mole}^{-1}$ . In HCl, HBr, and HI the bonds are much more covalent and the charge separation in the molecule much less than in HF.

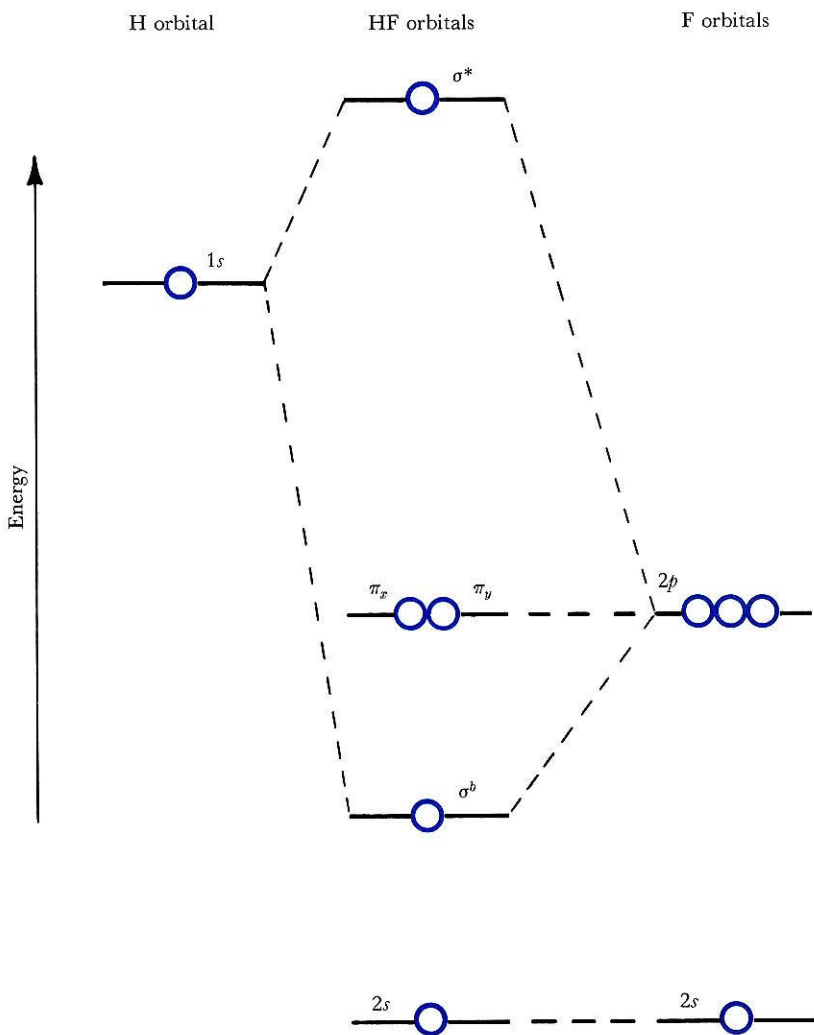
In the HCl example, the numbers just given make it appear that the electrons would be more attracted to H than to Cl since the first ionization energy of H ( $1310 \text{ kJ mole}^{-1}$ ) is larger than that of Cl ( $1255 \text{ kJ mole}^{-1}$ ). But ionization energies are only part of the story; relative electron affinities

**Figure 12-11**

Overlap of the hydrogen  $1s$  atomic orbital with the valence orbitals of fluorine. The net overlap of a  $2p_x$  or  $2p_y$  orbital of fluorine with the hydrogen  $1s$  orbital is zero, and these two  $p$  orbitals cannot be used in forming molecular orbitals.

must also be considered. The electron affinity of Cl ( $356 \text{ kJ mole}^{-1}$ ) is so much larger than that of H ( $67 \text{ kJ mole}^{-1}$ ) that the prediction based on ionization energies alone is reversed. The combination of ionization energy and electron affinity—the electronegativity of each atom—is the true deciding factor in determining charge distribution in the bond.

Now imagine instead that the H orbital at the left of Figure 12-12 is raised from its present position of  $1310 \text{ kJ mole}^{-1}$  toward an eventual limit of zero energy. As this happens, the  $\sigma^b$  molecular orbital becomes even more like the original  $2p_z$ . The limit of this trend is for the hydrogen  $1s$  orbital to go to zero energy (which means complete dissociation of the electron) and for the  $\sigma^b$  containing the two bonding electrons to become the  $2p_z$  of F



**Figure 12-12**

Relative energies of atomic and molecular orbitals in HF. The energy of an electron in the hydrogen atom  $1s$  orbital is  $-1310 \text{ kJ mole}^{-1}$  (the first ionization energy of H is  $+1310 \text{ kJ mole}^{-1}$ ), and the energy in the  $2p$  orbitals in F is  $-1682 \text{ kJ mole}^{-1}$  (first ionization energy of  $+1682 \text{ kJ mole}^{-1}$ ).



(which means the formation of a  $F^-$  anion). This behavior is approached in KF. Here the first ionization energy of K is only 418 kJ mole $^{-1}$ , and the energy of the K 3s level is  $-418$  kJ mole $^{-1}$ .

### Dipole Moments

A heteronuclear diatomic molecule such as HF possesses an **electric dipole moment** caused by the separation of positive and negative charges. If a positive and a negative charge of magnitude  $q$  are separated by a distance  $r$ , the dipole moment,  $\mu$  (the Greek letter mu), is

$$\mu = qr$$

The measured experimental dipole moment of HF is 1.82 debye units. [One debye (D) unit is  $10^{-20}$  esu (or electrostatic unit) m. Since the charge on an electron in the electrostatic system of units is  $4.80 \times 10^{-10}$  esu, two unit charges of opposite sign separated by 1 Å will have a dipole moment of  $4.80 \times 10^{-10} \times 10^{-10}$  esu m =  $4.80 \times 10^{-20}$  esu m = 4.80 D.] If H really had a full +1 charge and F had a full  $-1$  charge, and if these charges were separated by the true bond length of 0.92 Å, the dipole moment of HF would be calculated as 4.4 D, from the formula just given. The separated partial charges on the HF molecule are given by the ratio of true or experimental dipole moment ( $\mu_e$ ) to calculated dipole moment ( $\mu_c$ ):  $1.82/4.4 = 0.41$ . We say that the HF bond has 41% ionic character.

The **percent ionic characters** of several other diatomic molecules are listed in Table 12-3. The HCl bond has only 17% ionic character, and the KF bond is 83% ionic by the dipole-moment criterion.

This treatment of HF indicates that no bond is purely ionic or purely covalent. These are not two different mechanisms of bonding but only two extreme examples of a continuous range of polarity. What matters in molecular orbital theory is the degree of match or mismatch of energy levels from the two atoms. This match or mismatch is related to the electronegativities of the atoms.

#### Example 4

The dipole moment of the diatomic KBr molecule is 10.41 D, and that of KCl is 10.27 D. Which bond has greater ionic character?

#### Solution

The bond length of KBr is 2.82 Å; that of KCl is 2.67 Å (Table 12-4). The ionic structures have the following calculated dipole moments,  $\mu_c$ :

$$\begin{aligned}\mu_c(\text{KBr}) &= 4.80(2.82) = 13.5 \text{ D} \\ \mu_c(\text{KCl}) &= 4.80(2.67) = 12.8 \text{ D}\end{aligned}$$

Using the formula  $\mu_e/\mu_c \times 100\%$ , we find the percent ionic character in each case to be

Table 12-3

## Percent Ionic Character of Bonds, from Dipole Moments

Molecule	Bond length, $r$ (Å)	Calculated dipole moment, $\mu_c$	Experimental dipole moment, $\mu_e$	Percent ionic character, $\mu_e/\mu_c \times 100$
H <sub>2</sub>	0.74	3.6	0.00	0
F <sub>2</sub>	1.42	6.82	0.00	0
HI	1.60	7.68	0.38	5
BrCl	2.14	10.3	0.57	5
ICl	2.32	11.1	0.65	6
FCI	1.63	7.82	0.88	11
HBr	1.41	6.77	0.79	12
FBr	1.76	8.45	1.29	15
HCl	1.27	6.10	1.07	17
HF	0.92	4.4	1.82	41
KI	3.05	14.6	9.24	63
LiH	1.60	7.68	5.88	77
KF	2.17	10.4	8.60	83

$$\text{KBr: } 10.41/13.5 \times 100\% = 77\%$$

$$\text{KCl: } 10.27/12.8 \times 100\% = 80\%$$

The KCl bond is more ionic than the KBr bond, which is consistent with the fact that Cl is more electronegative than Br.

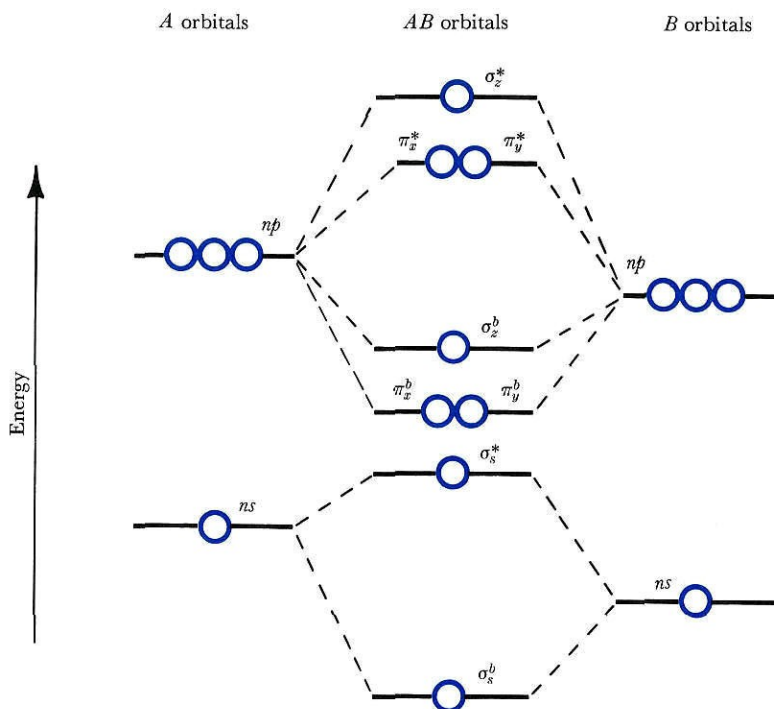
### A General $AB$ Type Diatomic Molecule

The treatment of heteronuclear diatomic molecules of the general  $AB$  type is similar to that of homonuclear molecules. The energy-level diagram is similar, except that the atomic levels of the more electronegative atom are lower than those of the more electropositive atom (Figure 12-13). Therefore, bonding orbitals have more of the character of the electronegative atom, and antibonding orbitals, of the electropositive atom. The molecular orbitals are skewed toward one or the other atom, as shown in Figure 12-14.

Filling of orbitals with electrons occurs exactly as before. The BN molecule is isoelectronic with C<sub>2</sub>, except that the  $\pi_{x,y}^b$  and  $\sigma_z^b$  levels are so close together that the energy required to promote one electron to the  $\sigma_z^b$  orbital can be provided by the energy gained in unpairing two electrons. The electronic configuration of BN is

$$KK(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^3(\sigma_3^b)^1$$

The BN bond energy of 385 kJ mole<sup>-1</sup> is suspiciously low in comparison



**Figure 12-13**

Energy levels for a general  $AB$  molecule, in which  $B$  is more electronegative than  $A$ . Compare with the homonuclear  $AA$  molecular levels in Figure 12-8. As atom  $B$  becomes more electronegative, its atomic energy levels decrease in energy and the bonding molecular orbitals assume more  $B$ -atom character.

with  $603 \text{ kJ mole}^{-1}$  for  $\text{C}_2$ . Further experimental work is necessary to verify the  $\text{BN}$  bond energy.

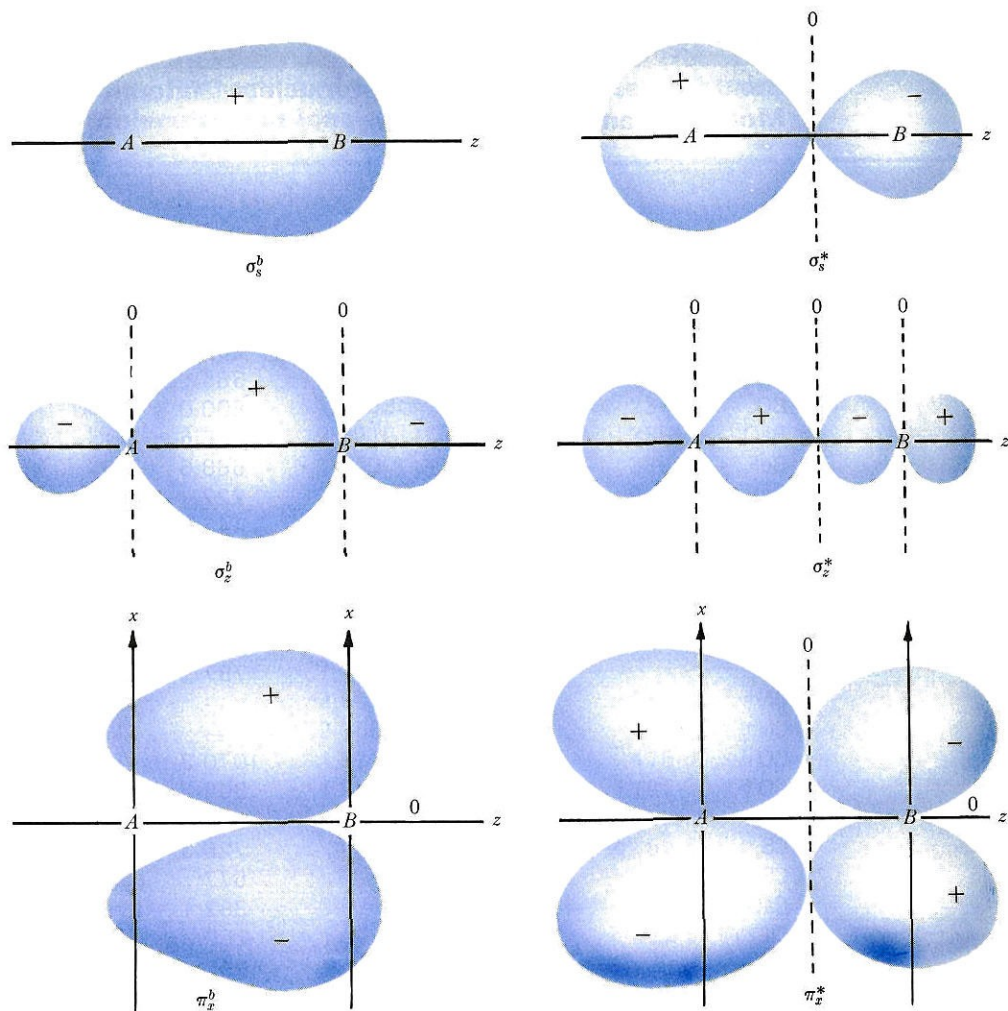
The species  $\text{BO}$ ,  $\text{CN}$ , and  $\text{CO}^+$  have 9 valence electrons. From molecular orbital theory we can predict a bond order of  $2\frac{1}{2}$  for them. The ions and molecules  $\text{NO}^+$ ,  $\text{CO}$ , and  $\text{CN}^-$  have 10 valence electrons and are isoelectronic with  $\text{N}_2$ . Nitric oxide,  $\text{NO}$ , has 11 electrons and is one of the few common gases with an odd number of electrons. The electronic configuration of  $\text{NO}$  is

$$KK(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^4(\sigma_z^b)^2(\pi_{x,y}^*)^1$$

It has a bond order of  $2\frac{1}{2}$ , and both its bond energy and its bond length are intermediate between those of  $\text{N}_2$  and  $\text{O}_2$ . Data on other  $AB$  diatomic molecules are in Table 12-4.

### Example 5

What is the electronic configuration of  $\text{CF}$ ? What is its bond order? Does it have unpaired electrons?

**Figure 12-14**

Molecular orbitals in an  $AB$  molecule, in which  $B$  is more electronegative than  $A$ . Compare with Figure 12-7. Note the increased electron probability near the more electronegative atom in bonding orbitals, and the opposite trend in antibonding orbitals.

**Solution**

$CF$  has 11 valence electrons (it is isoelectronic with  $NO$ ). Therefore its electronic configuration is  $KK(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^4(\sigma_z^b)^2(\pi_{x,y}^*)^1$ , with a bond order of  $2\frac{1}{2}$ . It has one unpaired electron.

Table 12-4

**Bond Properties of Some Heteronuclear Diatomic Molecules and Ions**

Molecule	Bond length (Å)	Bond energy (kJ mole <sup>-1</sup> )
AsN	1.620	481
AsO	1.623	473
BF	1.262	548
BH	1.2325	293
BN	1.281	385
BO	1.2043	800.0
BaO	1.940	545.6
BeF	1.3614	568.6
BeH	1.297	222
BeO	1.3308	443.9
BrCl	2.138	218
BrF	1.7555	230
CF	1.2718	443
CH	1.1202	335
CN	1.1719	787
CN <sup>+</sup>	1.1727	—
CN <sup>-</sup>	1.14	—
CO	1.1283	1070.3
CO <sup>+</sup>	1.1152	805.0
CP	1.5583	510.9
CS	1.5349	726.3
CSe	1.66	577
CaO	1.822	382.1
ClF	1.6281	252.3
CsBr	3.072	382.8
CsCl	2.9062	425.5
CsF	2.345	510
CsH	2.494	176
CsI	3.315	315.5
GeO	1.650	657
HBr	1.4145	361.9
HBr <sup>+</sup>	1.459	—
HCl	1.2744	427.6
HCl <sup>+</sup>	1.3153	453.1
HF	0.91680	565.3
HI	1.6090	295.0
HS	1.3503	340.6
IBr	2.485	175.3
ICI	2.32070	207.6
IF	1.908	191.2
KBr	2.8207	382.4
KCl	2.6666	421.8
KF	2.1715	497.5

**Table 12-4 (Continued)****Bond Properties of Some Heteronuclear Diatomic Molecules and Ions**

Molecule	Bond length (Å)	Bond energy (kJ mole <sup>-1</sup> )
KH	2.244	180
KI	3.0478	323.0
LiBr	2.1704	423
LiCl	2.018	473.8
LiF	1.5639	568.2
LiH	1.5953	234
Lil	2.3919	339
MgO	1.749	339
NH	1.045	356
NH <sup>+</sup>	1.081	—
NO	1.1508	678
NO <sup>+</sup>	1.0619	—
NP	1.4910	—
NS	1.495	481
NS <sup>+</sup>	1.25	—
NaBr	2.502	368
NaCl	2.3606	412
NaF	1.9260	476.6
NaH	1.8873	197
NaI	2.7115	289
NaK	—	59.8
NaRb	—	57.7
OH	0.9706	424.7
OH <sup>+</sup>	1.0289	422.6
PH	1.4328	—
PN	1.4869	730.5
PO	1.473	519
RbBr	2.9448	380.3
RbCl	2.7868	430.1
RbF	2.2704	500.0
RbH	2.367	163
RbI	3.1769	325.1
SO	1.4810	517.4
SbO	1.848	310
SiF	1.6008	541.8
SiH	1.5201	310
SiN	1.575	435
SiO	1.5097	764.8
SiS	1.929	619
SnH	1.785	310
SnO	1.838	529.3
SnS	2.209	461.5
SrO	1.9199	415.0

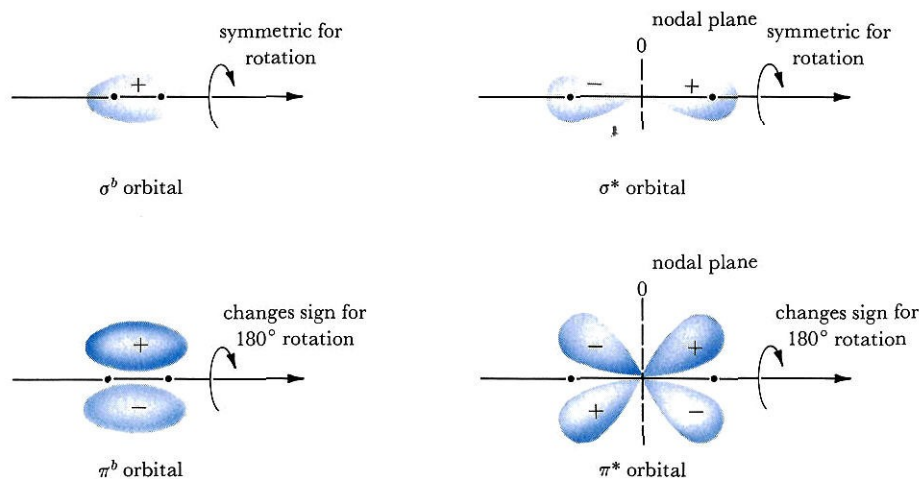
## Summary

A **molecular orbital** is a wave function for an electron in a molecule. It is usually an additive or subtractive combination of atomic orbitals on the atomic centers that are bound together in the molecule. Orbitals on different atoms often overlap, particularly in the region between the nuclei. Such overlap is called **orbital overlap**.

The wave function of a **bonding orbital** is additive in the overlap region. As a result, electron density is concentrated between the nuclei, and a bonding orbital is of lower energy than its atomic-orbital components. The energy of an electron in a bonding orbital goes through a minimum as the internuclear separation decreases. Placement of an electron in a bonding orbital enhances bond strength and stabilizes a molecule.

The wave function of an **antibonding orbital** is subtractive in the overlap region; such an orbital does *not* concentrate electron density between the nuclei. Rather, it forces electron density outside this region. An antibonding orbital has a **nodal plane**, or a plane at which the molecular wave function (and the electron density) is zero. This plane lies between the nuclei and is perpendicular to the internuclear axis. The energy of an electron in an antibonding orbital is greater than that of an electron in either of its atomic-orbital components; this energy does not go through a minimum, but continuously increases as the internuclear separation decreases. Placement of an electron in an antibonding orbital decreases bond strength and decreases the stability of a molecule.

Wave functions that are completely symmetric about the internuclear axis are called **sigma** ( $\sigma$ ) orbitals. Those whose wave functions change sign on a  $180^\circ$  rotation about the internuclear axis are called **pi** ( $\pi$ ) orbitals. Both  $\sigma$  and  $\pi$  orbitals can be bonding ( $\sigma^b$  or  $\pi^b$ ), or antibonding ( $\sigma^*$  or  $\pi^*$ ), as shown:



A **homonuclear** diatomic molecule is one in which the two atoms are the same; a **heteronuclear** diatomic molecule contains two different atoms. The molecular orbitals of a homonuclear diatomic molecule with  $ns$  and  $np$  valence orbitals increase in energy according to  $\sigma_s^b < \sigma_s^* < \pi_{x,y}^b < \sigma_z^b < \pi_{x,y}^* < \sigma_z^*$  (except for the molecules  $O_2$  and  $F_2$ , for which  $\sigma_z^b$  is below  $\pi_{x,y}^b$ ). The  $\pi_x^b$  and  $\pi_y^b$  orbitals have the same energy; orbitals with the same energy are said to be **degenerate**. The  $\pi_x^b$  and  $\pi_y^b$  orbitals correspond to a **degenerate energy level** that is denoted  $\pi_{x,y}^b$ ;  $\pi_{x,y}^*$  also is a degenerate energy level composed of  $\pi_x^*$  and  $\pi_y^*$  orbitals.

To build up the electronic structures of homonuclear diatomic molecules, valence electrons are fed into the molecular orbitals  $\sigma_s^b$  through  $\sigma_z^*$ , in order of increasing energy. Thus  $Li_2$  has the molecular orbital configuration  $KK(\sigma_s^b)^2$  (one  $\sigma$  bond) and the  $N_2$  molecule has the configuration  $KK(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^4(\sigma_z^b)^2$ , with three net bonds (one  $\sigma$ , two  $\pi$ ). The net number of bonding electrons divided by 2 gives the conventional bond order:  $Li_2$  has a bond order of 1,  $N_2$  has a bond order of 3. As the bond order in a given homonuclear diatomic system increases, bond length decreases and bond energy increases.

Molecules with unpaired electrons (such as  $B_2$  and  $O_2$ ) are **paramagnetic**. Molecules with all their electrons paired (such as  $Li_2$  and  $N_2$ ) are **diamagnetic**.

In a heteronuclear diatomic molecule,  $AB$ , where  $B$  is more electronegative than  $A$ , the bonding molecular orbitals have more  $B$  atomic-orbital character, and the antibonding molecular orbitals are more closely associated with  $A$ . Where the difference in electronegativity is extremely large, such as in  $KF$ , the valence electrons become localized on the more electronegative atom ( $F$  in this case) and the concept of a covalent bonding orbital loses significance. In such a situation an ionic structure  $K^+F^-$  is appropriate. Most heteronuclear diatomic molecules are somewhere between ion pairs and covalently bound atoms; that is, they possess some degree of ionic character,  $A^{\delta+}B^{\delta-}$ .

A diatomic molecule with charge separation possesses an **electric dipole moment** ( $\mu$ ):

$$\mu = qr$$

If  $q$  is taken as  $4.80 \text{ debyes } \text{\AA}^{-1}$ , and  $r$  (distance between positive and negative charges) is taken in  $\text{\AA}$ , then the dipole moment,  $\mu$ , is in debye units ( $10^{-20} \text{ esu m} = 1 \text{ debye, D}$ ). That is, the dipole moment of a molecule in which unit positive and negative charges are separated by  $1 \text{ \AA}$  is  $4.80 \text{ D}$ .

The **percent ionic character** of a molecule may be evaluated by dividing the experimentally observed dipole moment ( $\mu_e$ ) by the calculated dipole moment ( $\mu_c$ ) for an ionic structure:

$$\text{Percent ionic character} = \mu_e / \mu_c \times 100\%$$

For example,  $HF$  has  $\mu_e = 1.82 \text{ D}$ , and  $\mu_c = 4.4 \text{ D}$  ( $4.80 \text{ D } \text{\AA}^{-1} \times 0.92 \text{ \AA} = 4.4 \text{ D}$ ); therefore  $HF$  has  $1.82/4.4 \times 100\% = 41\%$  ionic character.



## Self-Study Questions

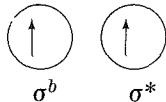
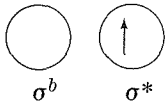
1. Why does the potential-energy curve in Figure 12-2 have a minimum?
2. Figure 12-3a shows profiles through the two atomic electron-density clouds,  $[1s_a]^2$  and  $[1s_b]^2$ , and the profile through the bonding molecular orbital formed from  $[1s_a + 1s_b]^2$ . What would profiles through the two atomic wave functions,  $1s_a$  and  $1s_b$ , look like? Draw the profile through the antibonding molecular wave function,  $1s_a - 1s_b$ , and through the resulting electron-density distribution in the antibonding molecular orbital,  $[1s_a - 1s_b]^2$ .
3. What do the symmetry symbols for molecular orbitals,  $\sigma$  and  $\pi$ , indicate?
4. Why does molecular orbital theory predict that  $\text{He}_2$  should not exist, whereas  $\text{He}_2^+$  should, under the right conditions?
5. What is the equivalent of a Lewis covalent bond in molecular orbital theory?
6. What is wrong with the general statement that bonding orbitals have low energies and antibonding orbitals have high energies? What feature of a bonding orbital makes it a bonding orbital?
7. What is the order of increasing energy among the molecular orbitals formed from the  $2s$  and  $2p$  atomic orbitals in diatomic molecules? What experimental evidence is there that this order is correct?
8. What are homonuclear and heteronuclear diatomic molecules?
9. What do the small positive and negative signs in the lobes of the orbitals in Figure 12-7 signify? What do the small line drawings at the upper right of each orbital drawing represent?
10. Why is the bond energy in  $\text{Li}_2$  less than in  $\text{H}_2$ ?
11. Each boron atom has three valence electrons. Why is the  $\text{B}_2$  molecule not held together by a triple bond as  $\text{N}_2$  is?
12. What is the ground-state configuration of the  $\text{C}_2$  molecule?
13. Why is  $\text{O}_2$  paramagnetic, whereas  $\text{N}_2$  is not? Support your argument with the ground-state electronic configurations of the two molecules.
14. Describe the electronic structure of the diatomic molecule  $\text{O}_2$  by using molecular orbitals. Is  $\text{O}_2$  paramagnetic, from predictions based on molecular orbital theory, and does this prediction agree with the possible predictions based on the Lewis structure? Which molecule would you expect to have the greater bond energy,  $\text{O}_2$  or  $\text{NO}$ ?
15. The molecular orbital description of the  $\text{B}_2$  molecule can be written  $KK(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^2$ . What does the  $KK$  symbol mean? In the same notation, what is the molecular orbital description of  $\text{F}_2$ ?
16. What are the molecular orbital descriptions of  $\text{Li}_2$  and  $\text{Be}_2$ ? Which molecule should not exist, and why?
17. What happens to the molecular orbitals when two atomic orbitals with radically different energies on two different atoms are combined? If we combine two atomic orbitals with drastically different energies, and

- place two electrons in the lower of the two resulting molecular orbitals, what will be the nature of the electrons? Will they be bonding electrons?
- Why can't the  $2p_x$  and  $1s$  atomic orbitals in Figure 12-11 be combined to produce two molecular orbitals?
  - In Figure 12-12, is the  $\sigma^b$  molecular orbital more like the hydrogen  $1s$  or the fluorine  $2p$  atomic orbital? Which atomic orbital makes more of a contribution to the  $\sigma^*$  molecular orbital?
  - What experimental data give us the relative positions of the hydrogen  $1s$  and fluorine  $2p$  atomic orbitals in Figure 12-12?
  - If the hydrogen  $1s$  and fluorine  $2p$  atomic orbitals were by some process made equal in energy, what effect would this have on the character of the bond in HF?
  - What is a purely ionic bond, in the language of molecular orbital theory and Figure 12-12?
  - How can dipole moments give us an estimate of the ionic character of a bond? How ionic is the HF bond?
  - Why do the orbital drawings for heteronuclear diatomic molecules in Figure 12-14 differ from those for homonuclear diatomic molecules in Figure 12-7?
  - Which of the following molecules are paramagnetic: CO, Cl<sub>2</sub>, NO, N<sub>2</sub>?

## Problems

### MO configuration and bond properties

- What is the molecular orbital configuration of the diatomic ion Li<sub>2</sub><sup>+</sup>?
- What is the bond order of Li<sub>2</sub><sup>+</sup>? Is the Li<sub>2</sub><sup>+</sup> ion paramagnetic?
- Describe the electronic structure of the diatomic molecule NO by using molecular orbitals. From the molecular orbital diagram, would you expect the molecule to be paramagnetic? Does your answer agree with the predictions that you can make from the Lewis structure? Would you predict the bond energy of NO to be greater than, equal to, or less than that of the ion NO<sup>+</sup>?
- Using molecular orbitals, describe the electronic structures of the peroxide ion, O<sub>2</sub><sup>2-</sup>, and the superoxide ion, O<sub>2</sub><sup>-</sup>. Are these ions diamagnetic, or paramagnetic? How does the strength of the oxygen–oxygen bond in each of these ions compare to that in O<sub>2</sub>?
- What is the molecular orbital configuration of the P<sub>2</sub> molecule? How many unpaired electrons does it have? What is its bond order? Would you expect its bond energy to be greater, or less, than that of S<sub>2</sub>? Why? Which should have the longer bond length, P<sub>2</sub> or S<sub>2</sub>?
- Write the molecular orbital configurations for the ground states of NF, NF<sup>+</sup>, and NF<sup>-</sup>. Which of these species are paramagnetic? How many unpaired electrons does each have? Predict the bond orders and relative bond lengths for each species.
- Which would you expect to have the greater bond energy, NF or NF<sup>+</sup>?

8. What is the bond order of  $\text{Cl}_2^+$ ? Should its bond energy be larger, or smaller, than that of  $\text{Cl}_2$ ? Why? Is  $\text{Cl}_2^+$  paramagnetic?
9. What is the molecular orbital configuration of  $\text{Br}_2^-$ ? Is  $\text{Br}_2^-$  paramagnetic?
10. Write the molecular orbital configuration of the SO molecule. How many unpaired electrons does it have? What is its bond order?
11. How many unpaired electrons does PO have? Would you expect the bond energy of PO to be greater, or smaller, than that of SO? Why? Should the bond length of PO be greater, or smaller, than that of SO?
12. Why is the bond energy of  $\text{B}_2$  greater than that of  $\text{F}_2$ ? Can you explain the fact that the  $\text{F}_2$  bond distance is *shorter* than the  $\text{B}_2$  bond distance?
13. The ground state of  $\text{H}_2$  has the molecular orbital configuration  $(\sigma^b)^2$ . In addition to the ground state there are excited states possessing the following configurations:
  - a) 
  
 $\sigma^b$        $\sigma^*$
  - b) 
  
 $\sigma^b$        $\sigma^*$

Predict which of these states is higher in energy and which is lower. Explain your reasoning. Would you expect the lower excited state of  $\text{H}_2$  to be paramagnetic or diamagnetic?
14. The neutral, diatomic OH molecule has been observed in outer space. Formulate its electronic structure in terms of molecular orbital theory using only the  $2p$  oxygen and the  $1s$  hydrogen orbitals. What type of molecular orbital contains the unpaired electron? Is this orbital associated with both oxygen and hydrogen atoms, or is it localized on a single atom? If it is localized, which atom is it on?

15. What type of molecular orbital contains the unpaired electron in  $\text{HF}^+$ ? Is it localized on H, or on F? What is the molecular configuration of  $\text{HF}^-$ ? What is the bond order of  $\text{HF}^-$ ? Of  $\text{HF}^+$ ? Which should have the larger bond energy,  $\text{HF}^+$  or  $\text{HF}^-$ ? Should  $\text{HF}^-$  be paramagnetic?

### Dipole moments and ionic character

16. Which of the following molecules will be expected to have a dipole moment:  $\text{H}_2$ ,  $\text{O}_2$ , HF, HI,  $\text{I}_2$ ? Assuming that the molecules with dipole moments are completely ionic, calculate their dipole moments. (Needed data are in Tables 12-2 and 12-4.)
17. The measured dipole moment of carbon monoxide (CO) is 0.112 D. What is the partial ionic character of the C—O bond?
18. Which substance has bonds of greater ionic character, KI or BaO? What is the percent ionic character of each? (Dipole-moment data are available in the *CRC Handbook of Chemistry and Physics*.)
19. Compare the percent ionic character of the bonds in HCl, CsCl, and TlCl. Can you interpret your results in terms of the periodic table? (The Tl—Cl bond length is 3.2 Å. Measured dipole moment for TlCl molecules in the gas phase is 4.44 D; for CsCl, 10.42 D.)
20. Predict the order of increasing ionic character of the following molecules: ClF, BrF, IF. Which should have the larger dipole moment, BrF or IF?
21. Which molecule has greater ionic character, LiH or CsH? Which should have the larger dipole moment?

## Suggested Reading

- C. A. Coulson, *Valence*, Oxford, New York, 1961, 2nd ed.
- H. B. Gray, *Chemical Bonds*, W. A. Benjamin, Menlo Park, Calif., 1973.
- H. B. Gray, *Electrons and Chemical Bonding*, W. A. Benjamin, Menlo Park, Calif., 1965.
- R. C. Johnson and R. R. Rettew, "Shapes of Atoms," *J. Chem. Educ.* **42**, 145 (1965).
- E. A. Ogryzlo and G. B. Porter, "Contour Surfaces for Atomic and Molecular Orbitals," *J. Chem. Educ.* **40**, 256 (1963).
- G. C. Pimentel and R. D. Spratley, *Chemical Bonding Clarified through Quantum Mechanics*, Holden-Day, San Francisco, 1969.
- G. E. Ryschkewitsch, *Chemical Bonding and the Geometry of Molecules*, Van Nostrand Reinhold, New York, 1972, 2nd ed.
- A. C. Wahl, "Chemistry by Computer," *Scientific American*, April 1970.