As shown in the diagram, the\(^3\)s\(^-\) and \(^3\)p\(^-\) electrons are the valence electrons of sulfur; the \(^3\)s and \(^3\)p orbitals are the valence orbitals.

1.8 ANOTHER LOOK AT THE COVALENT BOND: MOLECULAR ORBITALS

A. Molecular Orbital Theory

One way to think about chemical bonding is to assume that a bond consists of two electrons localized between two specific atoms. This is the simplest view of a Lewis electron-pair bond. As useful as this picture is, it is sometimes too restrictive. When atoms combine into a molecule, the electrons contributed to the chemical bonds by each atom are no longer localized on individual atoms but “belong” to the entire molecule. Consequently, atomic orbitals are no longer appropriate descriptions for the state of electrons in molecules. Instead, molecular orbitals, nicknamed MOs, which are orbitals for the entire molecule, are used.

Determining the electronic configuration of a molecule is a lot like determining the electronic configuration of an atom, except that molecular orbitals are used instead of atomic orbitals. The following four steps summarize conceptually how we start with two isolated hydrogen atoms and end up with the electronic configuration of the dihydrogen molecule, H\(_2\).

**Step 1.** Start with the isolated atoms of the molecule and bring them together to the positions that they have in the molecule. Their valence atomic orbitals will overlap.

For H\(_2\), this means bringing the two hydrogen atoms together until the nuclei are separated by the length of the H—H bond (Fig. 1.13a). At this distance, the 1s orbitals of the atoms overlap.

**Step 2.** Allow the overlapping valence atomic orbitals to interact to form molecular orbitals (MOs). This step implies that MOs of H\(_2\) are derived by combining the 1s atomic orbitals of the two hydrogen atoms in a certain way. Conceptually, this is reasonable: molecules result from a combination of atoms, so molecular orbitals result from a combination of atomic orbitals. We’ll shortly learn the process for combining atomic orbitals to form molecular orbitals.

1.18 Give the electronic configurations of each of the following atoms and ions. Identify the valence electrons and valence orbitals in each.

(a) oxygen atom  (b) chloride ion, Cl\(^-\)  (c) potassium ion, K\(^+\)  (d) sodium atom
Step 3. Arrange the MOs in order of increasing energy.
Steps 1 and 2 will yield two MOs for H₂ that differ in energy. We’ll also learn how to determine relative energies of these MOs.

Step 4. Determine the electronic configuration of the molecule by redistributing the electrons from the constituent atoms into the MOs in order of increasing MO energy; the Pauli principle and Hund’s rules are used.
We redistribute the two electrons (one from each starting hydrogen atom) into the MOs of H₂ to give the electronic configuration of the molecule.

How to carry out steps 2 and 3 is the key to understanding the formation of molecular orbitals. Quantum theory gives us a few simple rules that allow us to derive the essential features of molecular orbitals without any calculations. We’ll state these rules as they apply to H₂ and other cases involving the overlap of two atomic orbitals. (These rules will require only slight modification for more complex cases.)
Rules for forming molecular orbitals:

1. The combination of two atomic orbitals gives two molecular orbitals.
   For $\text{H}_2$, this rule means that the overlap of two $1s$ orbitals from the constituent hydrogen atoms gives two molecular orbitals. Later, we’ll have situations in which we combine more than two atomic orbitals. When we combine $j$ atomic orbitals, we always obtain $j$ molecular orbitals.

2. One molecular orbital is derived by the addition of the two atomic orbitals in the region of overlap.
   To apply this to $\text{H}_2$, remember that the $1s$ orbital is a wave peak. When we add two wave peaks, they reinforce. When we add two $1s$ orbitals in the overlap region, they reinforce to form a continuous orbital that includes the region between the two nuclei (Fig. 1.13b). This molecular orbital is called a bonding molecular orbital, or bonding MO. The reason for the name is that, when electrons occupy this MO, they are attracted to both nuclei simultaneously. In other words, the electrons occupy not only the region around the nuclei but also the region between the nuclei, thus providing “electron cement” that holds the nuclei together, just as mortar between two bricks holds the bricks together.

3. The other molecular orbital is derived by subtraction of the two atomic orbitals in the region of overlap.
   To subtract the two $1s$ orbitals, we change one of the $1s$ orbitals from a peak to a trough. (This is equivalent to changing the mathematical sign of the $1s$ wavefunction.) Then we add the two resulting orbitals. This process is illustrated in Fig. 1.13c. Adding a wave peak to a wave trough results in cancellation of the two waves in the region of overlap and formation of a node—a region in which the wave is zero. In this case, the node is a plane. The resulting orbital is called an antibonding molecular orbital or antibonding MO. Electrons that occupy this MO decrease bonding because the region between the nuclei contains no electron density.

4. The two molecular orbitals have different energies. Orbital energy increases with the number of nodes. The bonding MO has a lower energy than the isolated $1s$ orbitals and the antibonding MO has a higher energy than the isolated $1s$ orbitals.
   The orbital energies are summarized in an orbital interaction diagram, shown in Fig. 1.14. This diagram is a plot of orbital energy versus the position of the two interacting nuclei. The isolated atomic orbitals and their energies are shown on the left and right sides of the diagram, and the molecular orbitals and their energies are shown in the center, where the separation of the atoms corresponds to the bond length. The number of nodes tells us the relative energies of the MOs: the more nodes an MO has, the higher is its energy. The bonding MO has no nodes and therefore has the lower energy. The antibonding MO has one node and has the higher energy. Notice that the energies of the two MOs “spread” about the energy of the isolated $1s$ orbitals—the energy of the bonding MO is lowered by a certain amount and the energy of the antibonding MO is raised by the same amount.

Now that we’ve described how to form the MOs and rank their energies, we’re ready to populate these MOs with electrons. We apply the aufbau principle. We have two electrons—one from each hydrogen atom—to redistribute. Both can be placed in the bonding MO with opposite spins. Electron occupancy of the bonding MO is also shown in Fig. 1.14.

When we talk about the energy of an orbital, what we are really talking about is the energy of an electron that occupies the orbital. It follows, then, that the electrons in the bonding MO have lower energy than two electrons in their parent $1s$ orbitals. In other words, chemical bonding is an energetically favorable process. Each electron in the bonding MO of $\text{H}_2$ contributes about half to the stability of the $\text{H}—\text{H}$ bond. It takes about 435 kJ (104 kcal) to dissociate a mole of $\text{H}_2$ into hydrogen atoms, or about 218 kJ (52 kcal) per bonding electron. This a lot of...
energy on a chemical scale—more than enough to raise the temperature of a kilogram of water from freezing to boiling.

According to the picture just developed, the chemical bond in a hydrogen molecule results from the occupancy of a bonding molecular orbital by two electrons. You may wonder why we concern ourselves with the antibonding molecular orbital if it is not occupied. The reason is that it can be occupied! If a third electron were introduced into the hydrogen molecule, then the antibonding molecular orbital would be occupied. The resulting three-electron species is the hydrogen molecule anion, $\text{H}_2^-$ (see Prob. 1.19b, p. 36). $\text{H}_2^-$ exists because each electron in the bonding molecular orbital of the hydrogen molecule contributes equally to the stability of the molecule. The third electron in $\text{H}_2^-$, the one in the antibonding molecular orbital, has a high energy that offsets the stabilization afforded by one of the bonding electrons. However, the stabilization due to the second bonding electron remains. Thus, $\text{H}_2^-$ is a stable species, but only about half as stable as the hydrogen molecule. In terms of our brick-and-mortar analogy, if electrons in a bonding MO bind the two nuclei together as mortar binds two bricks, then electrons in an antibonding MO act as “anti-mortar”: not only do they not bind the two nuclei together, but they oppose the binding effect of the bonding electrons. The importance of the antibonding MO is particularly evident when we attempt to construct diatomic helium, $\text{He}_2$, as shown in Study Problem 1.5.
Use molecular orbital theory to explain why \( \text{He}_2 \) does not exist. The molecular orbitals of \( \text{He}_2 \) are formed in the same way as those of \( \text{H}_2 \).

**Solution**  
The orbital interaction diagram for the MOs of \( \text{He}_2 \) is conceptually the same as for \( \text{H}_2 \) (Fig. 1.14). However, \( \text{He}_2 \) contains four electrons—two from each \( \text{He} \) atom. According to the aufbau principle, two electrons are placed into the bonding MO, but the other two must occupy the antibonding MO. Any stability contributed by the bonding electrons is offset by the instability contributed by the antibonding electrons. Hence, formation of \( \text{He}_2 \) has no energetic advantage. As a result, \( \text{He} \) is monatomic.

Molecular orbitals, like atomic orbitals, have shapes that correspond to regions of significant electron density. Consider the shape of the bonding molecular orbital of \( \text{H}_2 \), shown in both Figs 1.13b and 1.14. In this molecular orbital the electrons occupy an ellipsoidal region of space. No matter how we turn the hydrogen molecule about a line joining the two nuclei, its electron density looks the same. This is another way of saying that the bond in the hydrogen molecule has **cylindrical symmetry**. Other cylindrically symmetrical objects are shown in Fig. 1.15. Bonds in which the electron density is cylindrically symmetrical about the internuclear axis are called **sigma bonds** (abbreviated \( \sigma \) bonds). The bond in the hydrogen molecule is thus a \( \sigma \) bond. The lower-case Greek letter sigma was chosen to describe the bonding molecular orbital of hydrogen because it is the Greek letter equivalent of \( s \), the letter used to describe the atomic orbital of lowest energy.

**PROBLEMS**

1.19 Draw an orbital interaction diagram corresponding to Fig. 1.14 for each of the following species. Indicate which are likely to exist as diatomic species, and which would dissociate into monatomic fragments. Explain.

(a) the \( \text{He}^+_2 \) ion  
(b) the \( \text{H}_2^- \) ion  
(c) \( \text{Li}_2 \)  
(d) the \( \text{H}_2^- \) ion  
(e) the \( \text{He}^+_2 \) ion

1.20 The bond dissociation energy of \( \text{H}_2 \) is 435 kJ mol\(^{-1}\) (104 kcal mol\(^{-1}\)); that is, it takes this amount of energy to dissociate \( \text{H}_2 \) into its atoms. Estimate the bond dissociation energy of \( \text{H}_2^+ \) and explain your answer.

**B. Molecular Orbital Theory and the Lewis Structure of \( \text{H}_2 \)**

Let’s now relate the quantum-mechanical description of \( \text{H}_2 \) to the concept of the Lewis electron-pair bond. In the Lewis structure of \( \text{H}_2 \), the bond is represented by an electron pair shared between the two nuclei. In the quantum-mechanical description, the bond is the result of the presence of two electrons in a bonding molecular orbital and the resulting electron density between the two nuclei. Both electrons are attracted to each nucleus, and these electrons thus serve as the “cement” that holds the nuclei together. Thus, for \( \text{H}_2 \), the **Lewis electron-pair bond is equivalent to the quantum-mechanical idea of a bonding molecular orbital occupied by a pair of electrons**. The Lewis picture places the electrons squarely between the nuclei. Quantum theory says that, although the electrons have a high probability of being between the bound nuclei, they can also occupy other regions of space.

Molecular orbital theory shows, however, that a chemical bond need not be an electron *pair*. For example, \( \text{H}_2^+ \) (the hydrogen molecule cation, which we might represent in the Lewis sense as \( \text{H}^+\text{H}^- \)) is a stable species in the gas phase (see Prob. 1.19e). It is not so stable as the hydrogen molecule itself because the ion has only one electron in the bonding molecular orbital, rather than the two found in a neutral hydrogen molecule. The hydrogen molecule anion,
1.9 HYBRID ORBITALS

A. Bonding in Methane

We ultimately want to describe the chemical bonding in organic compounds, and our first step in this direction is to understand the bonding in methane, CH₄. Before quantum theory was applied to the bonding problem, it was known experimentally that the hydrogens in methane, and thus the bonds to these hydrogens, were oriented tetrahedrally about the central carbon. The valence orbitals in a carbon atom, however, are not directed tetrahedrally. The 2s orbital, as you’ve learned, is spherically symmetrical (see Fig. 1.8), and the 2p orbitals are perpendicular (see Fig. 1.10). If the valence orbitals of carbon aren’t directed tetrahedrally, why is methane a tetrahedral molecule?

The modern solution to this problem is to apply molecular orbital theory. You can’t do this with just the simple rules that we applied to H₂, but it can be done. The result is that the combination of one carbon 2s and three carbon 2p orbitals with four tetrahedrally placed hydrogen 1s orbitals gives four bonding MOs and four antibonding MOs. (The combination of eight atomic orbitals give eight molecular orbitals; rule 1, p. 34, with \( j = 8 \).) Eight electrons (four from carbon and one from each of the four hydrogens) are just sufficient to fill the four bonding MOs with electron pairs. This molecular orbital description of methane accounts accurately for its electronic properties.

The conceptual difficulty with the molecular orbital description of methane is that we can’t associate a given pair of electrons in the molecule with any one bond. Instead, the electrons from all of the atoms are redistributed throughout the entire molecule. We can’t even tell where atoms begin or end! If we add up all of the contributions of the electrons in the four bonding MOs of methane, we obtain a picture of the total electron density—that is, the prob-