8.3 Bonding Theories

Guide for Reading

Key Concepts

- How are atomic and molecular orbitals related?
- How does VSEPR theory help predict the shapes of molecules?
- In what ways is orbital hybridization useful in describing molecules?

Vocabulary

molecular orbitals
bonding orbital
sigma bond
pi bond
tetrahedral angle
VSEPR theory
hybridization

Reading Strategy

Summarizing When you summarize, you review and state, in the correct order, the main points you have read. As you read about bonding theories, write a brief summary of the text following each heading. Your summary should include only the most important information.

Connecting to Your World This car is being painted by a process called electrostatic spray painting. A custom-designed spray nozzle wired up to an electric power supply imparts a negative charge to the paint droplets as they exit the spray gun. The negatively charged droplets are attracted to the auto body. Painting with attractive forces is very efficient, because almost all the paint is applied to the car body and very little is wasted. In this section, you will learn how attractive and repulsive forces influence the shapes of molecules.

Molecular Orbitals

The model for covalent bonding you have been using assumes that the orbitals are those of the individual atoms. There is a quantum mechanical model of bonding, however, that describes the electrons in molecules using orbitals that exist only for groupings of atoms. When two atoms combine, this model assumes that their atomic orbitals overlap to produce **molecular orbitals,** or orbitals that apply to the entire molecule.

In some ways, atomic orbitals and molecular orbitals are similar. **Just as an atomic orbital belongs to a particular atom, a molecular orbital belongs to a molecule as a whole.** Each atomic orbital is filled if it contains two electrons. Similarly, two electrons are required to fill a molecular orbital. A molecular orbital that can be occupied by two electrons of a covalent bond is called a **bonding orbital.**

Sigma Bonds When two atomic orbitals combine to form a molecular orbital that is symmetrical around the axis connecting two atomic nuclei, a **sigma bond** is formed, as illustrated in Figure 8.13. The symbol for this bond is the Greek letter sigma (σ).

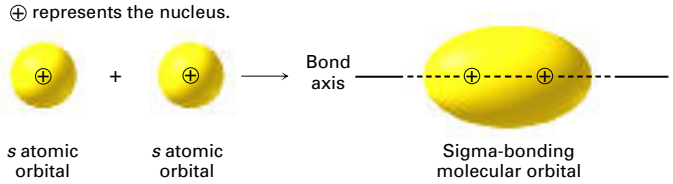

Figure 8.13 Two *s* atomic orbitals can combine to form a molecular orbital, as in the case of hydrogen (H_2). In a bonding molecular orbital, the electron density between the nuclei is high.

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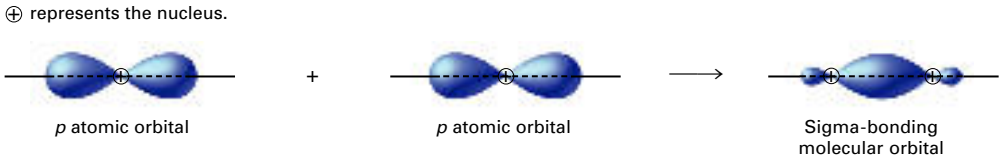

Figure 8.14 Two *p* atomic orbitals can combine to form a sigma-bonding molecular orbital, as in the case of fluorine (F_2). Notice that the sigma bond is symmetrical around the bond axis connecting the nuclei.

In general, covalent bonding results from an imbalance between the attractions and repulsions of the nuclei and electrons involved. Because their charges have opposite signs, the nuclei and electrons attract each other. Because their charges have the same sign, nuclei repel other nuclei and electrons repel other electrons. In a hydrogen molecule, the nuclei repel each other, as do the electrons. In a bonding molecular orbital of hydrogen, however, the attractions between the hydrogen nuclei and the electrons are stronger than the repulsions. The balance of all the interactions between the hydrogen atoms is thus tipped in favor of holding the atoms together. The result is a stable diatomic molecule of H_2.

Atomic *p* orbitals can also overlap to form molecular orbitals. A fluorine atom, for example, has a half-filled 2*p* orbital. When two fluorine atoms combine, as shown in Figure 8.14, the *p* orbitals overlap to produce a bonding molecular orbital. There is a high probability of finding a pair of electrons between the positively charged nuclei of the two fluorines. The fluorine nuclei are attracted to this region of high electron density. This attraction holds the atoms together in the fluorine molecule (F_2). The overlap of the 2*p* orbitals produces a bonding molecular orbital that is symmetrical when viewed around the F—F bond axis connecting the nuclei. Therefore, the F—F bond is a sigma bond.

Pi Bonds In the sigma bond of the fluorine molecule, the *p* atomic orbitals overlap end-to-end. In some molecules, however, orbitals can overlap side-by-side. As shown in Figure 8.15, the side-by-side overlap of atomic *p* orbitals produces what are called pi molecular orbitals. When a pi molecular orbital is filled with two electrons, a pi bond results. In a **pi bond** (symbolized by the Greek letter π), the bonding electrons are most likely to be found in sausage-shaped regions above and below the bond axis of the bonded atoms. It is not symmetrical around the F—F bond axis. Atomic orbitals in pi bonding overlap less than in sigma bonding. Therefore, pi bonds tend to be weaker than sigma bonds.

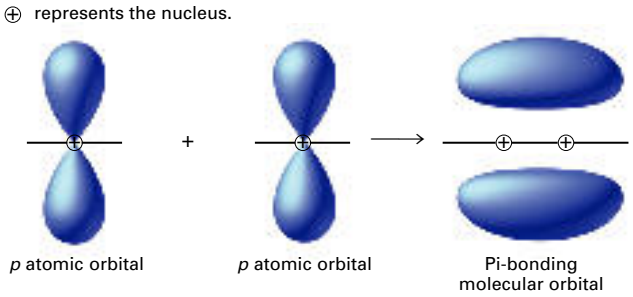

Figure 8.15 The side-by-side overlap of two *p* atomic orbitals produces a pi-bonding molecular orbital. Together, the two sausage-shaped regions in which the bonding electron pair is most likely to be found constitute one pi-bonding molecular orbital.

VSEPR Theory

A photograph or sketch may fail to do justice to your appearance. Similarly, electron dot structures fail to reflect the three-dimensional shapes of the molecules illustrated in Figure 8.16. The electron dot structure and structural formula of methane (CH_4), for example, show the molecule as if it were flat and merely two-dimensional.

Methane (electron dot structure) — Methane (structural formula)

In reality, methane molecules are three-dimensional. As Figure 8.16a shows, the hydrogens in a methane molecule are at the four corners of a geometric solid called a regular tetrahedron. In this arrangement, all of the H—C—H angles are 109.5°, the **tetrahedral angle.**

The valence-shell electron-pair repulsion theory, or **VSEPR theory,** explains the three-dimensional shape of methane. **According to VSEPR theory, the repulsion between electron pairs causes molecular shapes to adjust so that the valence-electron pairs stay as far apart as possible.** The methane molecule has four bonding electron pairs and no unshared pairs. The bonding pairs are farthest apart when the angle between the central carbon and its attached hydrogens is 109.5°. This is the H—C—H bond angle found experimentally.

Unshared pairs of electrons are also important in predicting the shapes of molecules. The nitrogen in ammonia (NH_3) is surrounded by four pairs of valence electrons, so you might predict the tetrahedral angle of 109.5° for the H—N—H bond angle. However, one of the valence-electron pairs shown in Figure 8.16b is an unshared pair. No bonding atom is vying for these unshared electrons. Thus they are held closer to the nitrogen than are the bonding pairs. The unshared pair strongly repels the bonding pairs, pushing them together. The measured H—N—H bond angle is only 107°.

Word *Origins*

Tetrahedral comes from the Greek *tetra-*, meaning "four," and *hedra*, meaning "face." The Greek *pod* means "foot." **What do you think *tetrapod* means?**

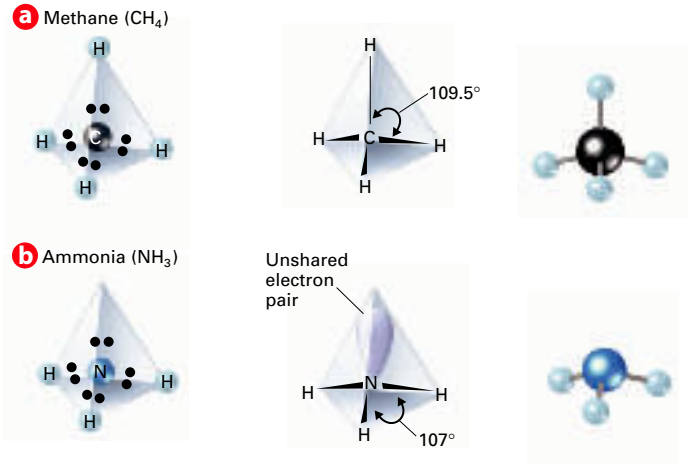

Figure 8.16 Methane and ammonia, represented here, are three-dimensional molecules. **a** Methane is a tetrahedral molecule. The hydrogens in methane are at the four corners of a regular tetrahedron, and the bond angles are all 109.5°. **b** An ammonia molecule is pyramidal. The unshared pair of electrons repels the bonding pairs. **Interpreting Diagrams** ***How do the resulting H—N—H bond angles compare to the tetrahedral angle?***

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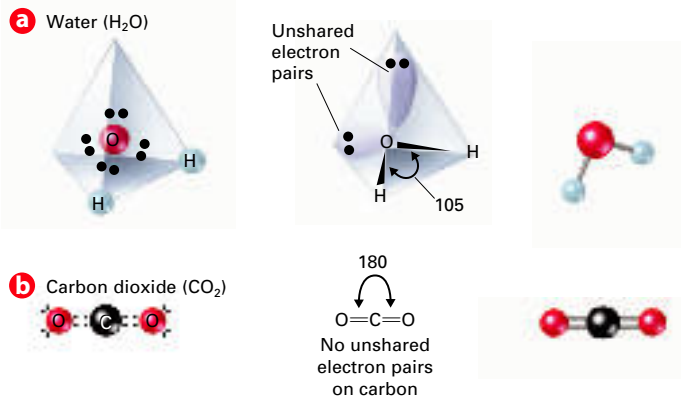

Figure 8.17 This comparison of water and carbon dioxide illustrates how unshared pairs of electrons can affect the shape of a molecule made of three atoms. **a** The water molecule is bent because the two unshared pairs of electrons on oxygen repel the bonding electrons. **b** In contrast, the carbon dioxide molecule is linear. The carbon atom has no unshared electron pairs.

In a water molecule, oxygen forms single covalent bonds with two hydrogen atoms. The two bonding pairs and the two unshared pairs of electrons form a tetrahedral arrangement around the central oxygen. Thus the water molecule is planar (flat) but bent. With two unshared pairs repelling the bonding pairs, the H—O—H bond angle is compressed in comparison with the H—C—H bond angle in methane. The experimentally measured bond angle in water is about 105°, as shown in Figure 8.17a.

In contrast, the carbon in a carbon dioxide molecule has no unshared electron pairs. The double bonds joining the oxygens to the carbon are farthest apart when the O═C═O bond angle is 180° as illustrated in Figure 8.17b. Thus CO_2 is a linear molecule. Nine of the possible molecular shapes are shown in Figure 8.18.

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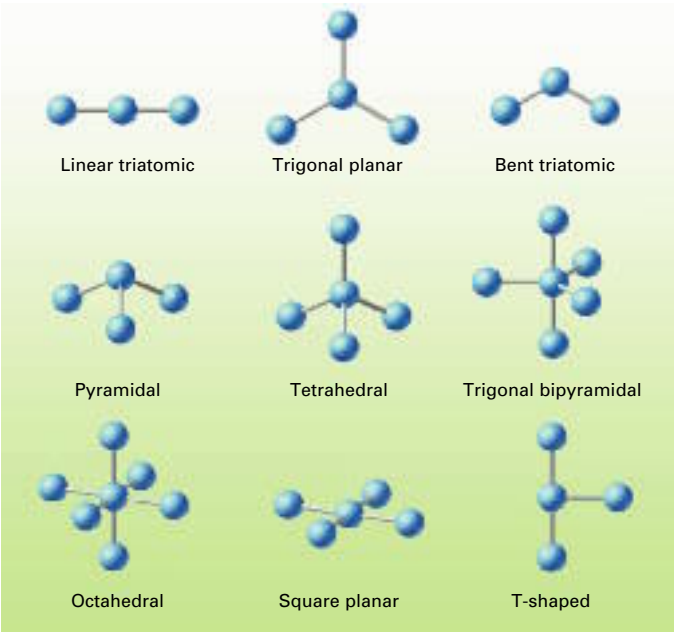

Figure 8.18 Shown here are common molecular shapes.

Hybrid Orbitals

The VSEPR theory works well when accounting for molecular shapes, but it does not help much in describing the types of bonds formed. **Orbital hybridization provides information about both molecular bonding and molecular shape.** In **hybridization,** several atomic orbitals mix to form the same total number of equivalent hybrid orbitals.

Hybridization Involving Single Bonds

Recall that the carbon atom's outer electron configuration is $2s^2\,2p^2$, but one of the $2s$ electrons is promoted to a $2p$ orbital to give one $2s$ electron and three $2p$ electrons, allowing it to bond to four hydrogen atoms in methane. You might suspect that one bond would be different from the other three. In fact, all the bonds are identical. This is explained by orbital hybridization.

The one $2s$ orbital and three $2p$ orbitals of a carbon atom mix to form four sp^3 hybrid orbitals. These are at the tetrahedral angle of 109.5°. As you can see in Figure 8.19, the four sp^3 orbitals of carbon overlap with the $1s$ orbitals of the four hydrogen atoms. The sp^3 orbitals extend farther into space than either s or p orbitals, allowing a great deal of overlap with the hydrogen $1s$ orbitals. The eight available valence electrons fill the molecular orbitals to form four C—H sigma bonds. The extent of overlap results in unusually strong covalent bonds.

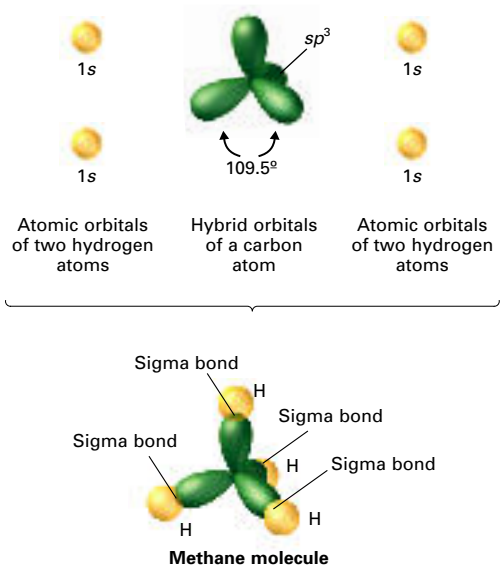

Figure 8.19 In methane, each of the four sp^3 hybrid orbitals of carbon overlaps with a $1s$ orbital of hydrogen.

Checkpoint ***Why are the bonds formed by the 2s and the 2p electrons of carbon the same in methane?***

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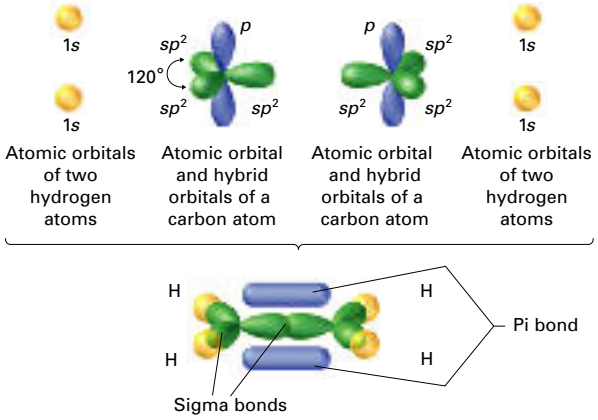
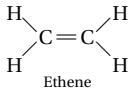


Figure 8.20 In an ethene molecule, two sp^2 hybrid orbitals from each carbon overlap with a 1*s* orbital of hydrogen to form a sigma bond. The other sp^2 orbitals overlap to form a carbon–carbon sigma bond. The *p* atomic orbitals overlap to form a pi bond. **Inferring** ***What region of space does the pi bond occupy relative to the carbon atoms?***

Hybridization Involving Double Bonds Hybridization is also useful in describing double covalent bonds. Ethene is a relatively simple molecule that has one carbon–carbon double bond and four carbon–hydrogen single bonds.



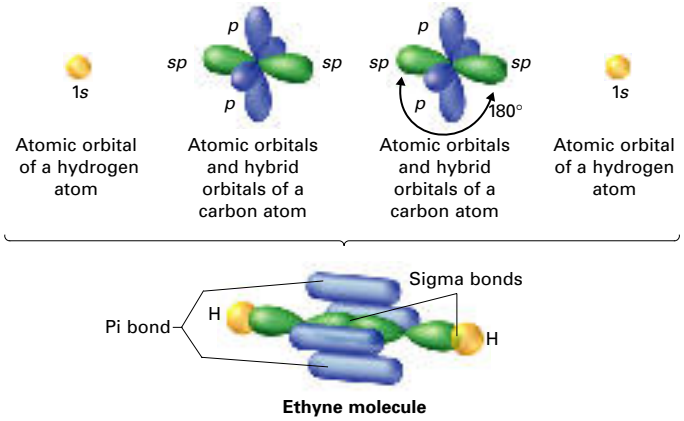
Experimental evidence indicates that the H—C—H bond angles in ethene are about 120°. In ethene, sp^2 hybrid orbitals form from the combination of one 2*s* and two 2*p* atomic orbitals of carbon. As you can see in Figure 8.20, each hybrid orbital is separated from the other two by 120°. Two sp^2 hybrid orbitals of each carbon form sigma-bonding molecular orbitals with the four available hydrogen 1*s* orbitals. The third sp^2 orbitals of each of the two carbons overlap to form a carbon–carbon sigma-bonding orbital. The non-hybridized 2*p* carbon orbitals overlap side-by-side to form a pi-bonding orbital. A total of twelve electrons fill six bonding molecular orbitals. Thus five sigma bonds and one pi bond hold the ethene molecule together. The sigma bonds and the pi bond are two-electron covalent bonds. Although they are drawn alike in structural formulas, pi bonds are weaker than sigma bonds. In chemical reactions that involve breaking one bond of a carbon–carbon double bond, the pi bond is more likely to break than the sigma bond.

Hybridization Involving Triple Bonds A third type of covalent bond is a triple bond, which is found in ethyne (C_2H_2), also called acetylene.

$$H-C\equiv C-H$$

As with other molecules, the hybrid orbital description of ethyne is guided by an understanding of the properties of the molecule. Ethyne is a linear molecule. The best hybrid orbital description is obtained if a 2*s* atomic orbital of carbon mixes with only one of the three 2*p* atomic orbitals. The result is two *sp* hybrid orbitals for each carbon.

Figure 8.21 In an ethyne molecule, one *sp* hybrid orbital from each carbon overlaps with a 1*s* orbital of hydrogen to form a sigma bond. The other *sp* hybrid orbital of each carbon overlaps to form a carbon–carbon sigma bond. The two *p* atomic orbitals from each carbon also overlap. **Interpreting Diagrams** ***How many pi bonds are formed in an ethyne molecule?***



The carbon–carbon sigma-bonding molecular orbital of the ethyne molecule in Figure 8.21 forms from the overlap of one *sp* orbital from each carbon. The other *sp* orbital of each carbon overlaps with the 1*s* orbital of each hydrogen, also forming sigma-bonding molecular orbitals. The remaining pair of *p* atomic orbitals on each carbon overlap side-by-side. They form two pi-bonding molecular orbitals that surround the central carbons. The ten available electrons completely fill five bonding molecular orbitals. The bonding of ethyne consists of three sigma bonds and two pi bonds.

Interactive Textbook

Simulation 7 Compare *sp*, sp^2, and sp^3 hybrid orbitals.

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8.3 Section Assessment

23. **Key Concept** How are atomic and molecular orbitals related?

24. **Key Concept** Explain how the VSEPR theory can be used to predict the shapes of molecules.

25. **Key Concept** How is orbital hybrization useful in describing molecules?

26. What shape would you expect a simple carbon-containing compound to have if the carbon atom has the following hybridizations?

a. sp^2 **b.** sp^3 **c.** *sp*

27. What is a sigma bond? Describe, with the aid of a diagram, how the overlap of two half-filled 1*s* orbitals produces a sigma bond?

28. How many sigma and how many pi bonds are in an ethyne molecule (C_2H_2)?

29. The BF_3 molecule is planar. The attachment of a fluoride ion to the boron in BF_3, through a coordinate covalent bond, creates the BF_4^- ion. What is the geometric shape of this ion?

Writing Activity

Molecular Bonding in Oxygen Research how chemists know that an oxygen molecule has unpaired electrons. Write a brief report on what you find.

Interactive Textbook

Assessment 8.3 Test yourself on the important concepts of Section 8.3.

with **ChemASAP**

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