1 FOCUS

Objectives

- **8.3.1 Describe** the relationship between atomic and molecular orbitals.
- **8.3.2 Describe** how VSEPR theory helps predict the shapes of molecules.
- **8.3.3 Identify** ways in which orbital hybridization is useful in describing molecules.

Guide for Reading

Build Vocabulary

Paraphrase The hybridization of atomic orbitals is the combining of two or more orbitals to form a single orbital that is different from those that were combined.

Reading Strategy

Compare and Contrast As students read about atomic and molecular orbitals encourage them to make a table in which to list similarities and differences. Have them extend the list to include hybrid orbitals.

INSTRUCT

Connecting to Your World

Have students read the opening paragraph. Ask, Why is very little paint wasted when a car is electrostatically spray painted? (The droplets of paint are attracted to the auto body and don't fall to the floor.) Can you infer the charge on the auto body? (positive)

Molecular Orbitals Use Visuals

Figure 8.13 Have students note the positions of the two nuclei in the two hydrogen atomic orbitals. Ask, Where is the electron most likely to be in the hydrogen atomic orbital? (In the sphere, close to the nucleus.) Where are the two shared electrons likely to be in the H₂ molecular orbital? (In the region between the two nuclei.)

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

L2

L2

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.



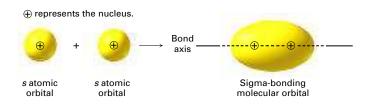
Molecular Orbitals

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 (H₂). In a bonding molecular orbital, the electron density between the nuclei is high.



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— Section Resources ——

Print

- Guided Reading and Study Workbook, Section 8.3
- Core Teaching Resources, Section 8.3 Review, Interpreting Graphics
- Laboratory Manual, Lab 11
- Small-Scale Chemistry Laboratory Manual, Lab 11
- Transparencies, T90–T92

Technology

- Interactive Textbook with ChemASAP, Simulation 7, Assessment 8.3
- Go Online, Section 8.3



p atomic orbital



Sigma-bonding molecular orbital

Figure 8.14 Two p atomic

orbitals can combine to form

orbital, as in the case of fluorine

(F2). Notice that the sigma bond

is symmetrical around the bond

a sigma-bonding molecular

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 H₂.

Atomic p orbitals can also overlap to form molecular orbitals. A fluorine atom, for example, has a half-filled 2p 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 (F2). The overlap of the 2p orbitals produces a bonding molecular orbital that is symmetrical when viewed around the F-F bond axis connecting the nuclei.

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.

Therefore, the F—F bond is a sigma bond.

represents the nucleus.

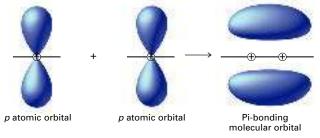


Figure 8.15 The side-by-side overlap of two p atomic orbitals produces a pi-bonding molecular orbital. Together, the two sausage-shaped regions in which the bonding electron pair is most likely to be found constitute one pi-bonding molecular orbital.

Section 8.3 Bonding Theories 231

Differentiated Instruction

Gifted and Talented



Molecular orbital theory is a third way of treating chemical bonding in addition to the valence bond approach and VESPR theory, both of which are covered in this text. Each approach to bonding contributes different important ideas. Molecular orbital theory is a

quantum mechanical approach involving not just localized bonds but bonds that bind entire molecules. Students may want to access a college text and learn more about this theory and how it explains the paradox of bonding in the oxygen molecule.

Discuss

Ask, How can you visualize the formation of the covalent bond in H2 as two separated hydrogen atoms move closer together? (As the distance between them decreases, each nucleus is attracted by both electrons, and the potential energy of the system decreases.) Explain that repulsive forces also come into play as the nuclei and the electrons of both atoms begin to repel each other. An interatomic distance is reached at which the potential energy is at a minimum. If the distance decreases beyond this point, the potential energy increases because of increased repulsion. Thus, a chemical bond forms with a bond length equal

to the interatomic distance at which

the potential energy is a minimum.

Use Visuals



Figures 8.14 and 8.15 Ask, What is different about the ways that the two p orbitals overlap in the two **illustrations?** (In Figure 8.14, the p orbitals overlap end-to-end and form an orbital that is symmetrical around the axis joining the nuclei. In Figure 8.15, the p orbitals overlap side-by-side and form two areas of electron density, one above and another below the axis joining the nuclei.) Ask, What are the two bonds called? (Figure 8.14: sigma bond; Figure 8.15: pi bond)

Relate



Topographic maps are usually drawn as a series of lines tracing the elevations of a terrain. The more closely spaced the lines are, the steeper is the terrain. Scientists who wish to know the positions of atoms in crystals of molecules may use electron densities that are plotted in much the same way that a terrain is shown on a topographic map. From X-ray diffraction data, scientists can map the electron density at any position in a crystal of interest. Where the lines are closest in the map, the electron density of the molecule is greatest.

Section 8.3 (continued)

VSEPR Theory

Discuss

L2

Ask students to write out the electron configuration for carbon when it is forming bonds. $(1s^2, 2s^1, 2p^3)$ **How** many valence electrons does carbon have? (4) How many bonds does carbon form? (4) Have students describe the three p orbitals. (dumbbell-shaped orbitals containing two lobes; the three orbitals are perpendicular to each other, oriented on the x-, y-, and z-axes) Point out that if carbon forms three of its four bonds using p orbitals, it must form molecules that are three-dimensional.

CLASS Activity

Making Molecular Models

L2

Purpose Students achieve an understanding of simple molecular shapes and relate actual three-dimensional geometry to two-dimensional illustrations.

Materials ball-and-stick molecular model kits or foam balls and toothpicks

Procedure Have students make the tetrahedral model of methane. Have them examine the model and compare it with the illustrations in Figure 8.16. Ask them to draw the model and label it tetrahedral. Have students remove one ball leaving the stick in place. The stick can represent an unshared pair of electrons. This is a model for the ammonia molecule. Again have students compare their models with Figure 8.16 and make their own illustration, labeling it pyramidal. Have students remove a second ball. Now the model simulates the water molecule with two sticks (pairs of unshared electrons). Have students compare their models with Figure 8.17 and make their own illustration labeled bent triatomic.

Word Origins **L**

The word *tetrapod* means having four feet. Dogs, cats, and elephants are all tetrapods because they all have four feet.

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 (CH₄), for example, show the molecule as if it were flat and merely two-dimensional.

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 -C-H angles are 109.5°, the tetrahedral angle.

The valence-shell electron-pair repulsion theory, or VSEPR theory, 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 (NH₃) 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°.

Figure 8.16 Methane and ammonia, represented here, are three-dimensional molecules. 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?

Word Origins

Tetrahedral comes from

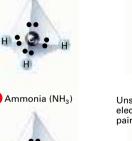
the Greek tetra-, meaning

"face." The Greek pod

"four," and hedra, meaning

means "foot." What do you

think tetrapod means?

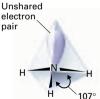








Methane (CH₄)





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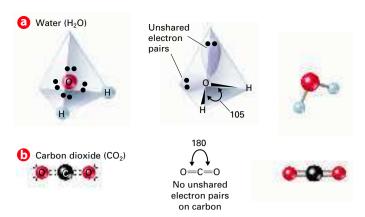
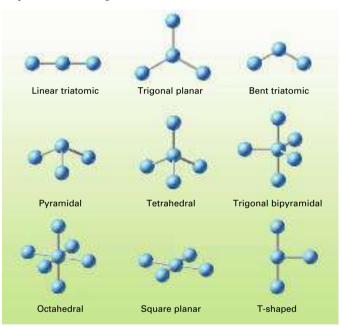


Figure 8.17 This comparison of water and carbon dioxide illustrates how unshared pairs of electrons can affect the shape of a molecule made of three atoms. The water molecule is bent because the two unshared pairs of electrons on oxygen repel the bonding electrons. In contrast, the carbon dioxide molecule 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.



Go nline

SSZ SCINKS

For: Links on VSEPR
Theory
Visit: www.SciLinks.org
Web Code: cdn-1083

Figure 8.18 Shown here are common molecular shapes.

Section 8.3 Bonding Theories 233

Differentiated Instruction

Less Proficient Readers

nos-

Give students as many opportunities as possible to see three-dimensional models of molecules. When you write formulas on the chalkboard, try to have a three-dimensional model to hold up or circulate around the class. This will help students interpret two-dimensional drawings.

Discuss

L2

In predicting molecular shapes, students may find it helpful to start with an electron dot structure. The electron dot structure shows both the bonding and nonbonding pairs of electrons around the central atom. Point out that when using VSEPR theory to predict molecular shape, double and triple bonds are viewed as single bonds. Each group of electrons in the electron dot structure must be accommodated around the central atom. Because electrons repel each other, they will stay as far apart as possible. When four pairs must be accommodated, the pairs have maximum space when they are arranged tetrahedrally with an angle of 109.5° between them. When three pairs or groups must be accommodated, a trigonal planar arrangement provides the most space with 120° separating them. Finally, when only two groups are present, they will adopt a linear arrangement in which they are separated by 180°. Have students predict the shapes of H₂S and BF₃. (bent and trigonal planar respectively)



Download a worksheet on **VSEPR Theory** for students to complete, and find additional teacher support from NSTA SciLinks.

Answers to...

Figure 8.16 They are smaller.

Section 8.3 (continued)

Hybrid Orbitals

Relate

L2

Students are aware that third row nonmetals such as phosphorus and sulfur, in Groups 5A and 6A respectively, can form more bonds than the number predicted by the octet rule. For example, phosphorus can form PCI₅ as well as PCl₃, and sulfur can form SF₆ as well as SF₂. Second row elements in the same groups, nitrogen and oxygen, do not form compounds that violate the octet rule. The difference lies in the fact that third row elements can promote electrons to empty 3d orbitals. Second row elements have no 2d orbitals. Bonding in phosphorus and sulfur in compounds such as PCI₅ and SF₆ involves hybrid orbitals. For phosphorus, one s, three p, and one d orbitals combine to form five dsp3 hybrid orbitals. The geometry of a set of five dsp³ orbitals is trigonal byprimidal. For sulfur, one s, three p, and two d orbitals combine to form six d^2sp^3 hybrid orbitals. The geometry of six d^2sp^3 orbitals is octahedral.

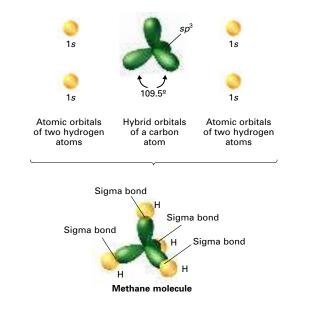
Hybrid Orbitals

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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Facts and Figures –

Towering 20th Century Chemist

An esteemed chemist and dedicated humanitarian, Linus Pauling (1916–1994) is the only person to have won two Nobel prizes that were unshared. In 1954 he won the prize for chemistry; in 1962 he won the prize for peace. The peace prize recognized his efforts to bring nuclear weapons under international control and halt nuclear testing. Much of his scientific work involved the structure of simple and complex molecules. His book

The Nature of the Chemical Bond and the Structure of Molecules and Crystals is one of the most important texts of the century. Pauling introduced the idea of hybrid orbitals to explain why the four bonds around a carbon atom are equivalent. He invented the concept of electronegativity and proposed that most covalent bonds have some ionic character. He also taught that the structures of some compounds must be described by two or more resonance hybrids.

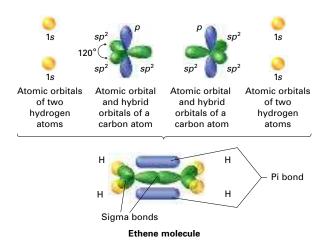


Figure 8.20 In an ethene molecule, two sp² hybrid orbitals from each carbon overlap with a 1s orbital of hydrogen to form a sigma bond. The other sp2 orbitals overlap to form a carbon-carbon sigma bond. The p atomic orbitals overlap to form a pi bond. Inferring What region of space does the pi bond occupy 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.

$$C = C$$
 H
Ethene

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 2s and two 2p 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 1s orbitals. The third sp^2 orbitals of each of the two carbons overlap to form a carbon-carbon sigma-bonding orbital. The nonhybridized 2p 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 carboncarbon 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 (C₂H₂), 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 2s atomic orbital of carbon mixes with only one of the three 2p atomic orbitals. The result is two sp hybrid orbitals for each carbon.

Section 8.3 Bonding Theories 235

Facts and Figures

Ethene Ripens Tomatoes

Ethene, or ethylene $(H_2C = CH_2)$, is a gaseous hormone found in most plants. Tomatoes release ethene as they ripen, so a tomato placed in a container with unripe fruit can

hasten the ripening process. Because it's often convenient to pick and ship fruits and vegetables before they are ripe, the produce industry uses ethene to control how fast produce ripens.

Use Visuals

Figure 8.20 Direct student attention to the sigma bonds formed by the two carbon atoms in ethene. Each carbon forms three bonds using three sp² orbitals. Thus, the entire molecule is planar with the unhybridized p orbital forming lobes of electron density above and below the plane.

Discuss



Have students compare the shapes of the carbon hybrid orbitals in methane (sp^3) , ethene (sp^2) , and ethyne molecules (sp). The key concept in hybridization is that the atomic orbitals that combine to form the hybrid orbitals lose their identities. Entirely new orbitals form that have different characteristics. Emphasize that the shape and orientation of the hybrid orbitals cannot be predicted from the shapes of the combining atomic orbitals. Hybrid orbitals of a particular type $(sp^3, sp^2, or$ sp) are identical to one another in terms of shape and bonding properties.

B ASSESS

Evaluate Understanding



Have students compare and contrast the characteristics of sigma and pi bonds. (A sigma bond is formed when two atomic orbitals combine to form a molecular orbital that is symmetrical along the axis connecting the two atomic nuclei. The electrons tend to be found between the two nuclei. A pi bond is formed from the overlap of two p atomic orbitals. The electrons in a pi bond are found in sausage-shaped regions above and below the bond axis.) Ask how unshared pairs of electrons influence the shape of a molecule. (The unshared pairs take up space in the molecule. They repel the bonding pairs, pushing them closer together and decreasing the bond angle.)

Answers to...



orbital hybridization

Figure 8.20 the regions above and below the carbons

Section 8.3 (continued)

Reteach



Divide students into pairs to determine the shapes of molecules by means of the VSEPR theory. Give them the following information about the central atoms of five molecules and ask them to determine the geometry of each. Have them begin by writing electron dot structures.

• four bonding pairs + no nonbonding pairs (tetrahedral); • three bonding pairs + one nonbonding pair (pyramidal); • two bonding pairs + two nonbonding pairs (bent); • two bonding pairs + no nonbonding pair (linear); • one bonding pair + any number of nonbonding pairs (linear)

Writing Activity

Oxygen is paramagnetic, which means that it tends to be attracted to a magnetic field. This behavior is characteristic of substances that have unpaired electrons.



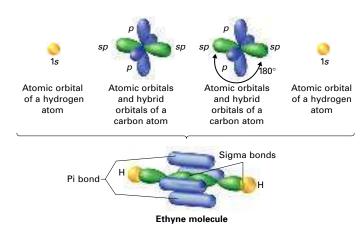
If your class subscribes to the Interactive Textbook, use it to review key concepts in Section 8.3

_with ChemASAP

Answers to ...

Figure 8.21 Two *pi* bonds are formed.

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?





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

with ChemASAP

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 1s 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.

8.3 Section Assessment

- 23. Key Concept How are atomic and molecular orbitals related?
- 25. Key Concept How is orbital hybrization useful in describing molecules?
- **26.** What shape would you expect a simple carboncontaining 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 1s 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?



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



Assessment 8.3 Test yourself on the important concepts of Section 8.3

with ChemASAP

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Section 8.3 Assessment

- **23.** When two atoms combine, their atomic orbitals overlap to produce molecular orbitals. An atomic orbital belongs to a particular atom, and a molecular orbital belongs to a molecule as a whole.
- 24. Each molecule assumes the shape that
- places valence-electron pairs as far apart as possible.
- **25.** Orbital hybridization provides information about both molecular bonding and molecular shape.
- 26. a. trigonal planar b. tetrahedral c. linear
- **27.** A sigma bond is formed by the overlap of two orbitals along the axis between two nuclei. See Figure 8.13.
- **28.** 3 sigma bonds and 2 pi bonds
- 29. tetrahedral