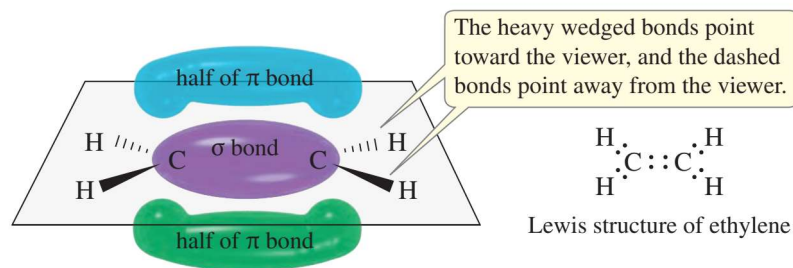
**FIGURE 1-17**

Pi bonding and antibonding molecular orbitals. The sideways overlap of two p orbitals leads to a π bonding MO and a π^* antibonding MO. A pi bond is not as strong as most sigma bonds.

FIGURE 1-18

Structure of the double bond in ethylene. The first pair of electrons forms a σ bond. The second pair forms a π bond. The π bond has its electron density centered in two lobes above and below the σ bond. Together, the two lobes of the π bonding molecular orbital constitute one bond.



1-14A Single and Double Bonds

A **double bond** requires the presence of four electrons in the bonding region between the nuclei. The first pair of electrons goes into the sigma bonding MO, forming a strong sigma bond. The second pair of electrons cannot go into the same orbital or the same space. It goes into a pi bonding MO, with its electron density centered above and below the sigma bond.

This combination of one sigma bond and one pi bond is the normal structure of a double bond. Figure 1-18 shows the structure of ethylene, an organic molecule containing a carbon–carbon double bond.

1-15 Hybridization and Molecular Shapes

Thus far, we have discussed bonds involving overlap of simple s and p atomic orbitals. Although these simple bonds are occasionally seen in organic compounds, they are not as common as bonds formed using **hybrid atomic orbitals**. Hybrid atomic orbitals result from the mixing of orbitals on the *same* atom. The geometry of these hybrid orbitals helps us to account for the actual structures and bond angles observed in organic compounds.

If we predict the bond angles of organic molecules using just the simple s and p orbitals, we expect bond angles of about 90° . The s orbitals are nondirectional, and the p orbitals are oriented at 90° to one another (see Figure 1-5). Experimental evidence shows, however, that bond angles in organic compounds are usually close

to 109° , 120° , or 180° (Figure 1-19). A common way of accounting for these bond angles is the **valence-shell electron-pair repulsion theory (VSEPR theory)**: Electron pairs repel each other, and the bonds and lone pairs around a central atom generally are separated by the largest possible angles. An angle of 109.5° is the largest possible separation for four pairs of electrons; 120° is the largest separation for three pairs; and 180° is the largest separation for two pairs. All the structures in Figure 1-19 have bond angles that separate their bonds about as far apart as possible.

The shapes of these molecules cannot result from bonding between simple s and p atomic orbitals. Although s and p orbitals have the lowest energies for isolated atoms in space, they are not the best for forming bonds. To explain the shapes of common organic molecules, we conclude that the s and p orbitals combine to form hybrid atomic orbitals that separate the electron pairs more widely in space and place more electron density in the bonding region between the nuclei.

1-15A sp Hybrid Orbitals

Orbitals can interact to form new orbitals. We have used this principle to form molecular orbitals by adding and subtracting atomic orbitals on *different* atoms. We can also add and subtract orbitals on the *same* atom. Consider the result, shown in Figure 1-20, when we combine a p orbital and an s orbital on the same atom.

The resulting orbital is called an **sp hybrid orbital**. Its electron density is concentrated toward one side of the atom. We started with two orbitals (s and p), so we must finish with two sp hybrid orbitals. The second sp hybrid orbital results if we add the p orbital with the opposite phase (Figure 1-20).

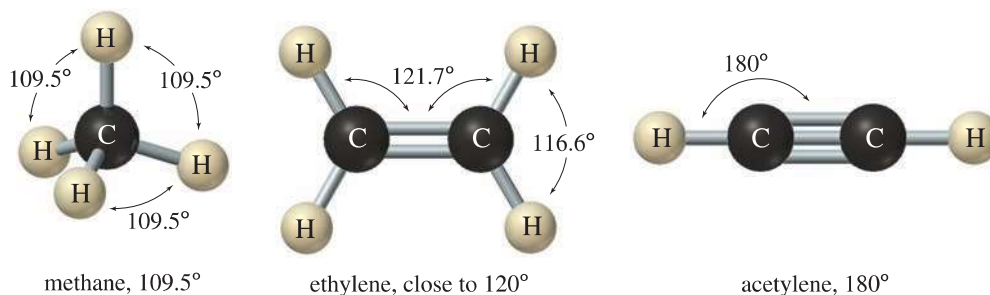


FIGURE 1-19
Common bond angles. Bond angles in organic compounds are usually close to 109° , 120° , or 180° .

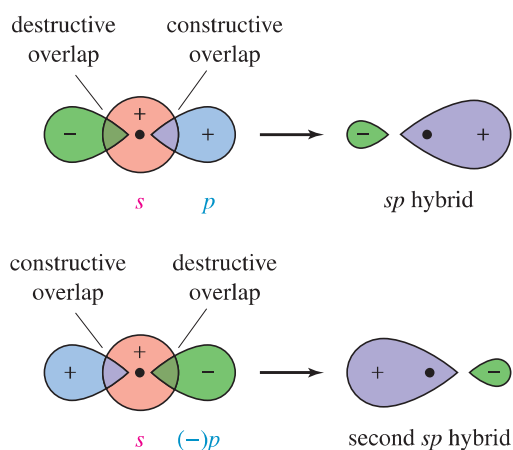


FIGURE 1-20
Formation of a pair of sp hybrid atomic orbitals. Addition of an s orbital to a p orbital gives an sp hybrid atomic orbital, with most of its electron density on one side of the nucleus. Adding the p orbital with opposite phase gives the other sp hybrid orbital, with most of its electron density on the opposite side of the nucleus from the first hybrid.

The result of this hybridization is a pair of directional sp hybrid orbitals pointed in opposite directions. These hybridized orbitals provide enhanced electron density in the bonding region for a sigma bond toward the left of the atom and for another sigma bond toward the right. They give a bond angle of 180° , separating the bonding electrons as much as possible. In general, sp hybridization results in this **linear** bonding arrangement.

SOLVED PROBLEM 1-7

Draw the Lewis structure for beryllium hydride, BeH_2 . Draw the orbitals that overlap in the bonding of BeH_2 , and label the hybridization of each orbital. Predict the $\text{H}-\text{Be}-\text{H}$ bond angle.

SOLUTION

First, draw a Lewis structure for BeH_2 .



There are only four valence electrons in BeH_2 (two from Be and one from each H), so the Be atom cannot have an octet. The bonding must involve orbitals on Be that give the strongest bonds (the most electron density in the bonding region) and also allow the two pairs of electrons to be separated as far as possible.

Hybrid orbitals concentrate the electron density in the bonding region, and sp hybrids give 180° separation for two pairs of electrons. Hydrogen cannot use hybridized orbitals, because the closest available p orbitals are the $2p$'s, and they are much higher in energy than the $1s$. The bonding in BeH_2 results from overlap of sp hybrid orbitals on Be with the $1s$ orbitals on hydrogen. Figure 1-21 shows how this occurs.

1-15B sp^2 Hybrid Orbitals

For three bonds to be oriented as far apart as possible, bond angles of 120° are required. When an s orbital combines with two p orbitals, the resulting three hybrid orbitals are oriented at 120° angles to each other (Figure 1-22). These orbitals are called **sp^2 hybrid orbitals** because they are composed of one s and two p orbitals. The 120° arrangement is called **trigonal** geometry, in contrast to the linear geometry associated with sp hybrid orbitals. There remains an unhybridized p orbital (p_z) perpendicular to the plane of the three sp^2 hybrid orbitals.

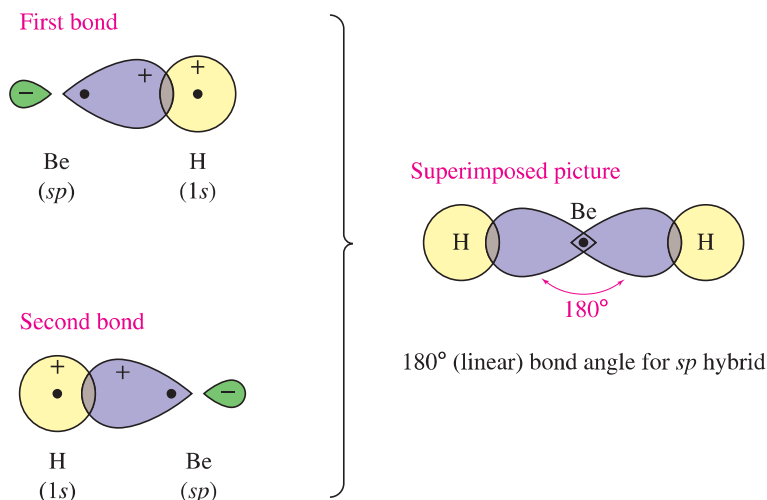


FIGURE 1-21

Linear geometry in the bonding of BeH_2 . To form two sigma bonds, the two sp hybrid atomic orbitals on Be overlap with the $1s$ orbitals of hydrogen. The bond angle is 180° (linear).

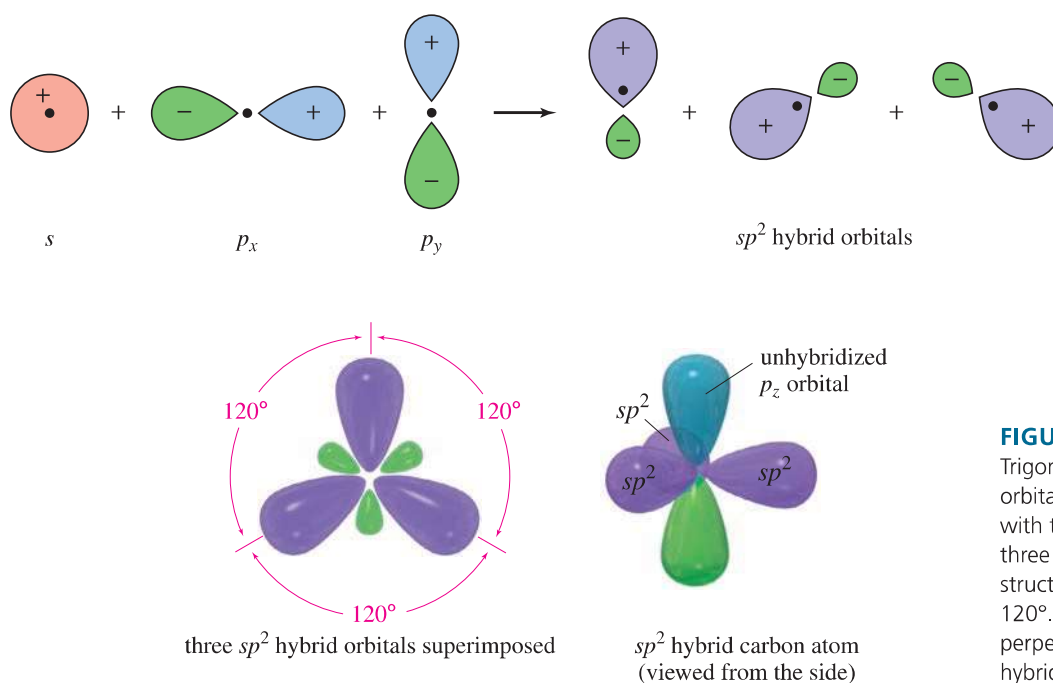


FIGURE 1-22

Trigonal geometry with sp^2 hybrid orbitals. Hybridization of an s orbital with two p orbitals gives a set of three sp^2 hybrid orbitals. This trigonal structure has bond angles of about 120° . The remaining p orbital is perpendicular to the plane of the three hybrid orbitals.

SOLVED PROBLEM 1-8

Borane (BH_3) is unstable under normal conditions, but it has been detected at low pressure.

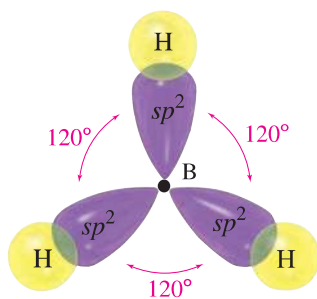
- Draw the Lewis structure for borane.
- Draw a diagram of the bonding in BH_3 , and label the hybridization of each orbital.
- Predict the $\text{H}-\text{B}-\text{H}$ bond angle.

SOLUTION

There are only six valence electrons in borane, so the boron atom cannot have an octet. Boron has a single bond to each of the three hydrogen atoms.



The best bonding orbitals are those that provide the greatest electron density in the bonding region while keeping the three pairs of bonding electrons as far apart as possible. Hybridization of an s orbital with two p orbitals gives three sp^2 hybrid orbitals directed 120° apart. Overlap of these orbitals with the hydrogen $1s$ orbitals gives a planar, trigonal molecule. (Note that the small back lobes of the hybrid orbitals have been omitted.)

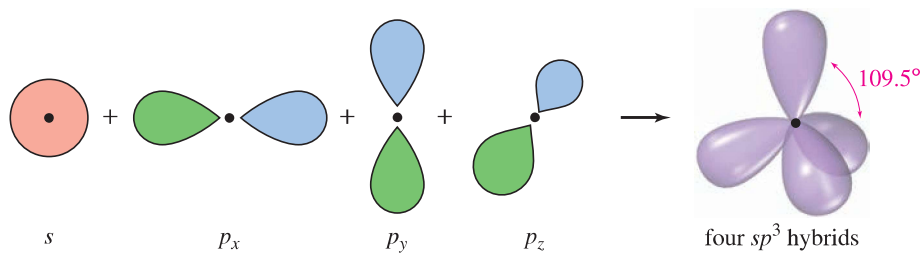
**PROBLEM-SOLVING HINT**

The number of hybrid orbitals formed is always the same as the total number of s and p orbitals hybridized.

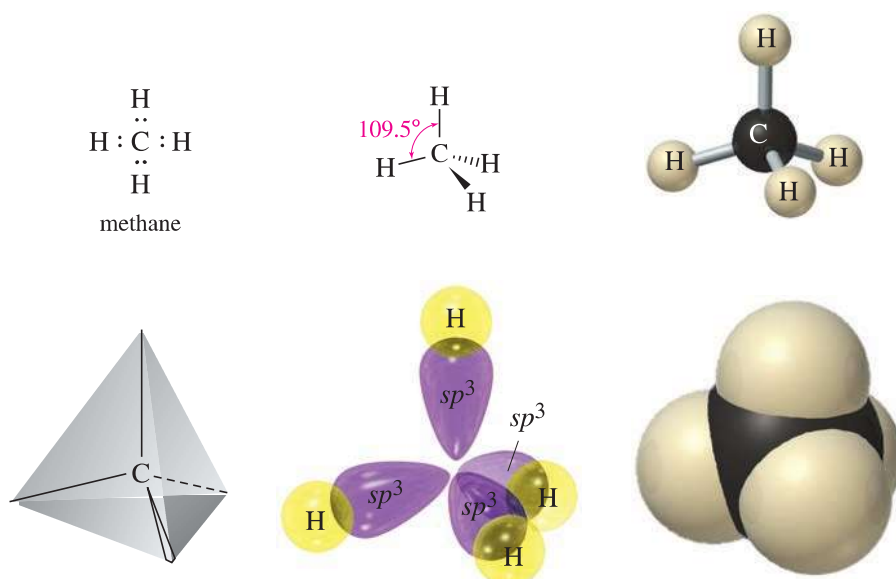
Number of Orbitals	Hybrid	Angle
2	sp	180°
3	sp^2	120°
4	sp^3	109.5°

FIGURE 1-23

Tetrahedral geometry with sp^3 hybrid orbitals. Hybridization of an s orbital with all three p orbitals gives four sp^3 hybrid orbitals with tetrahedral geometry corresponding to 109.5° bond angles.

**FIGURE 1-24**

Several views of methane. Methane has tetrahedral geometry, using four sp^3 hybrid orbitals to form sigma bonds to the four hydrogen atoms.



Application: Biology

Methanotrophs are bacteria or archaea that use methane as their source of carbon and energy. Those that live in the air use oxygen to oxidize methane to formaldehyde ($\text{H}_2\text{C}=\text{O}$) and CO_2 . Those that live in anoxic marine sediments use sulfate (SO_4^{2-}) to oxidize methane to formaldehyde and CO_2 , also reducing sulfate to H_2S .

1-15C sp^3 Hybrid Orbitals

Many organic compounds contain carbon atoms that are bonded to four other atoms. When four bonds are oriented as far apart as possible, they form a regular tetrahedron (109.5° bond angles), as pictured in Figure 1-23. This **tetrahedral** arrangement can be explained by combining the s orbital with all three p orbitals. The resulting four orbitals are called **sp^3 hybrid orbitals** because they are composed of one s and three p orbitals.

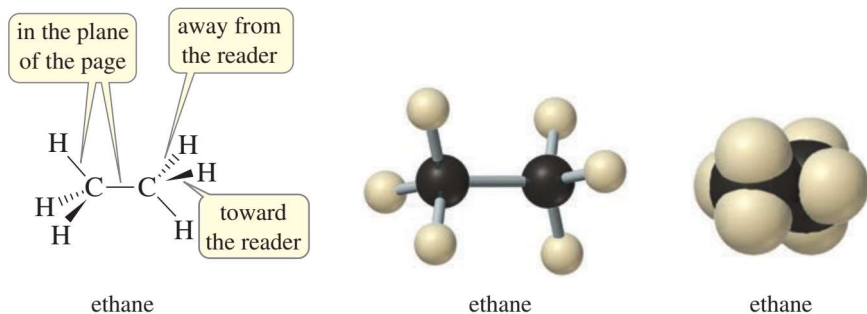
Methane (CH_4) is the simplest example of sp^3 hybridization (Figure 1-24). The Lewis structure for methane has eight valence electrons (four from carbon and one from each hydrogen), corresponding to four C—H single bonds. Tetrahedral geometry separates these bonds by the largest possible angle, 109.5° .

1-16 Drawing Three-Dimensional Molecules

Figures 1-23 and 1-24 are more difficult to draw than the earlier figures because they depict three-dimensional objects on a two-dimensional surface. The p_z orbital should look like it points in and out of the page, and the tetrahedron should look three-dimensional. These drawings use perspective and the viewer's imagination to add the third dimension.

The use of perspective is difficult when a molecule is large and complicated. Organic chemists have developed a shorthand notation to simplify three-dimensional drawings. Dashed lines indicate bonds that go backward, away from the reader. Heavy wedge-shaped lines depict bonds that come forward, toward the reader. Straight lines are bonds in the plane of the page. Dashed lines and wedges show perspective in the second drawing of methane in Figure 1-24.

The three-dimensional structure of ethane, C_2H_6 , has the shape of two tetrahedra joined together. Each carbon atom is sp^3 hybridized, with four sigma bonds formed by the four sp^3 hybrid orbitals. Dashed lines represent bonds that go away from the viewer, wedges represent bonds that come out toward the viewer, and other bond lines are in the plane of the page. All the bond angles are close to 109.5° .

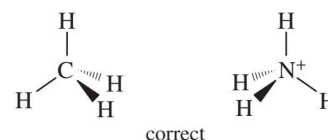
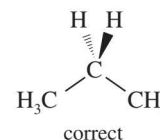
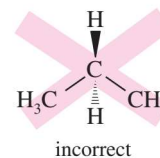


PROBLEM 1-15

- Use your molecular models to make ethane, and compare the model with the preceding structures.
- Make a model of propane (C_3H_8), and draw this model using dashed lines and wedges to represent bonds going back and coming forward.

PROBLEM-SOLVING HINT

When showing perspective, do not draw another bond between the two bonds in the plane of the paper. Such a drawing shows an incorrect shape.



1-17 General Rules of Hybridization and Geometry

At this point, we can consider some general rules for determining the hybridization of orbitals and the bond angles of atoms in organic molecules. After stating these rules, we solve some problems to show how to use these rules.

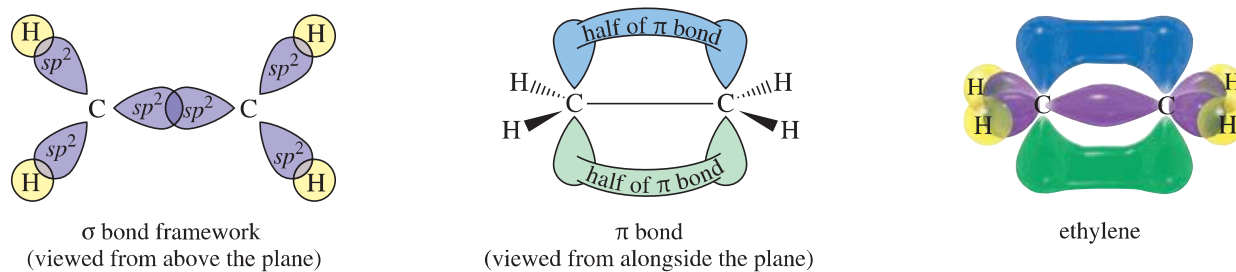
Rule 1: Both sigma bonding electrons and lone pairs can occupy hybrid orbitals. The number of hybrid orbitals on an atom is computed by adding the number of sigma bonds and the number of lone pairs of electrons on that atom.

Because the first bond to another atom is always a sigma bond, the number of hybrid orbitals may be computed by adding the number of lone pairs to the number of atoms bonded to the central atom.

Rule 2: Use the hybridization and geometry that give the widest possible separation of the calculated number of bonds and lone pairs.

SUMMARY Hybridization and Geometry

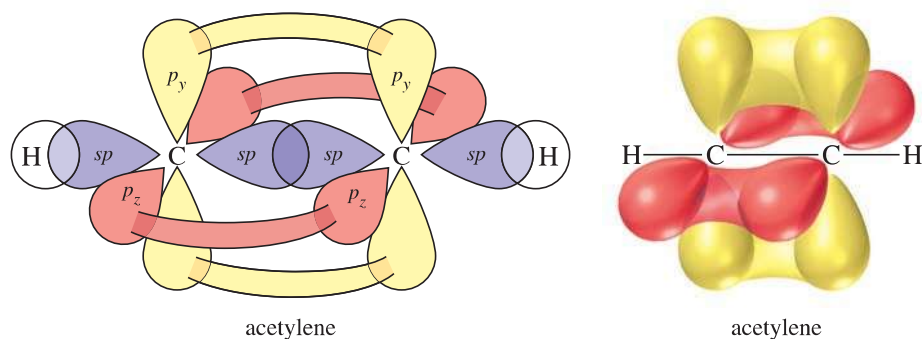
Hybrid Orbitals	Hybridization	Geometry	Approximate Bond Angles
2	$s + p = sp$	linear	180°
3	$s + p + p = sp^2$	trigonal	120°
4	$s + p + p + p = sp^3$	tetrahedral	109.5°

**FIGURE 1-25**

Planar geometry of ethylene. The carbon atoms in ethylene are sp^2 hybridized, with trigonal bond angles of about 120° . All the carbon and hydrogen atoms lie in the same plane.

FIGURE 1-26

Linear geometry of acetylene. The carbon atoms in acetylene are sp hybridized, with linear (180°) bond angles. The triple bond contains one sigma bond and two perpendicular pi bonds.



The number of hybrid orbitals obtained equals the number of atomic orbitals combined. Lone pairs of electrons take up more space than bonding pairs of electrons; thus, they compress the bond angles.

Rule 3: If two or three pairs of electrons form a multiple bond between two atoms, the first bond is a sigma bond formed by a hybrid orbital. The second bond is a pi bond, consisting of two lobes above and below the sigma bond, formed by two unhybridized p orbitals (see the structure of ethylene in Figure 1-25). The third bond of a triple bond is another pi bond, perpendicular to the first pi bond (shown in Figure 1-26).

Solved Problems 1-9 through 1-13 show how to use these rules to predict the hybridization and bond angles in organic compounds.

SOLVED PROBLEM 1-9

Predict the hybridization of the nitrogen atom in ammonia, NH_3 . Draw a picture of the three-dimensional structure of ammonia, and predict the bond angles.

SOLUTION

The hybridization depends on the number of sigma bonds plus lone pairs. A Lewis structure provides this information.

