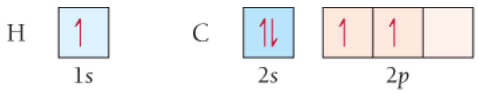
6.3: Valence Bond Theory: Hybridization of Atomic Orbitals

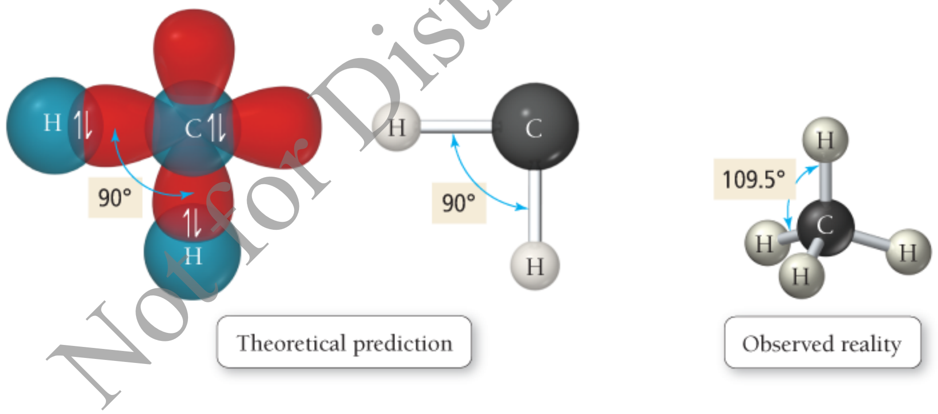
Key Concept Video **Valence Bond Theory: Hybridization**

Although the overlap of half-filled *standard* atomic orbitals adequately explains the bonding in H_2S, it cannot adequately explain the bonding in many other molecules. For example, suppose we try to explain the bonding between hydrogen and carbon using the same approach. The valence electron configurations of H and C are shown here:



Carbon has only two half-filled orbitals and should therefore form only two bonds with two hydrogen atoms. We would predict that carbon and hydrogen would form a molecule with the formula CH_2 and with a bond angle of 90° (corresponding to the angle between any two *p* orbitals).

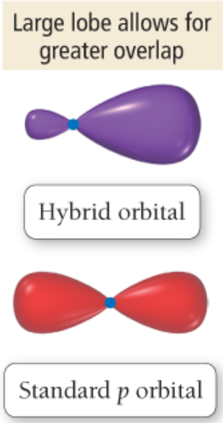
However, experiments show that the stable compound formed from carbon and hydrogen is CH_4 (methane), with bond angles of 109.5°. The experimental reality is different from our simple theoretical prediction in two ways. First, carbon forms bonds to four hydrogen atoms, not two. Second, the bond angles are much larger than the angle between two *p* orbitals.



Valence bond theory accounts for the bonding in CH_4 and many other polyatomic molecules by incorporating an additional concept called *orbital hybridization*. So far in the discussion in this chapter, we have assumed that the overlapping orbitals that form chemical bonds are simply the standard *s*, *p*, or *d* atomic orbitals, but this is an oversimplification. The concept of hybridization in valence bond theory is a step toward recognizing that *the orbitals in a molecule are not necessarily the same as the orbitals in an atom*. **Hybridization** is a mathematical procedure in which the standard atomic orbitals are combined to form new atomic orbitals called **hybrid orbitals** that correspond more closely to the actual distribution of electrons in chemically *bonded* atoms. Hybrid orbitals are still localized on individual atoms, but they have different shapes and energies from those of standard atomic orbitals.

Why does valence bond theory propose that electrons in some molecules occupy hybrid orbitals instead of the standard atomic orbitals? To answer this question, remember that, according to valence bond theory, a chemical bond is the overlap of two orbitals that together contain two electrons. The overlap of orbitals lowers the potential energy of the electrons in those orbitals. *The greater the overlap, the lower the energy and the stronger the* *bond*. Hybrid orbitals allow greater overlap because the electron density in a hybrid orbital is concentrated along a single directional lobe, as shown in Figure 6.2. This concentration of electron density in a single direction allows for greater overlap between orbitals. In other words, hybrid orbitals *minimize* the energy of the molecule by *maximizing* the orbital overlap in a bond.

Figure 6.2 Comparison of Standard Atomic Orbital and Hybrid Orbital



Hybridization, however, is not a free lunch—in most cases it actually costs some energy. So hybridization occurs only to the degree that the energy payback through bond formation is large. In general, therefore, the more bonds that an atom forms, the greater the tendency of its orbitals to hybridize. Central or interior atoms, which form the most bonds, have the greatest tendency to hybridize. Terminal atoms, which form the fewest bonds, have the least tendency to hybridize. *In this book, we focus on the hybridization of interior atoms and assume that all terminal atoms—those bonding to only one other atom—are unhybridized.* Hybridization is particularly important in carbon, which tends to form four bonds in its compounds and therefore always hybridizes.

> As we saw in Chapter 5, the word *hybrid* comes from breeding. A *hybrid* is an offspring of two animals or plants of different standard breeds. Similarly, a hybrid orbital is a product of mixing two or more standard atomic orbitals.

Although we cannot examine the procedure for obtaining hybrid orbitals in mathematical detail here, we can make the following general statements regarding hybridization:

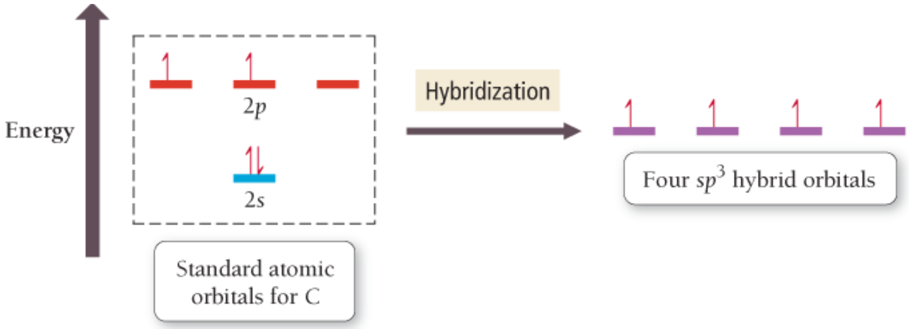
- The *number of standard atomic orbitals* added together always equals the *number of hybrid orbitals* formed. The total number of orbitals is conserved.
- The *particular combinations* of standard atomic orbitals added together determine the *shapes and energies* of the hybrid orbitals formed.
- The *particular type of hybridization that occurs* is the one that yields the *lowest overall energy for the molecule*. Since actual energy calculations are beyond the scope of this book, we use electron geometries as determined by VSEPR theory to predict the type of hybridization.

We now turn to examining the different types of hybridization that commonly occur in molecules.

> In a more nuanced treatment, hybridization is not an all-or-nothing process—it can occur to varying degrees that are not always easy to predict. We saw earlier, for example, that sulfur does not hybridize very much in forming H_2S.

sp^3 Hybridization

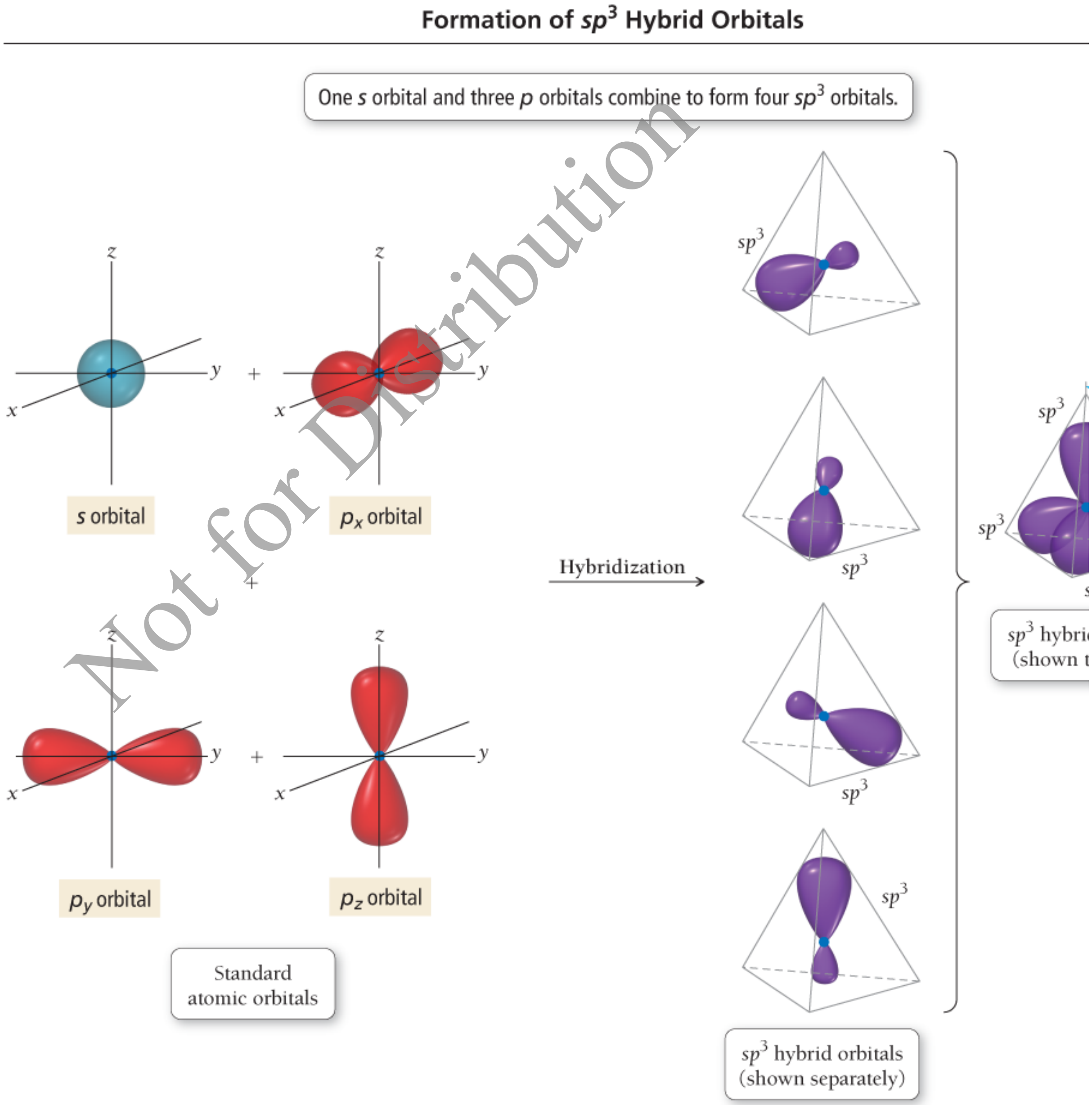
We can account for the tetrahedral geometry in CH_4 by the hybridization of the one 2*s* orbital and the three 2*p* orbitals on the carbon atom. The four new orbitals that result, called sp^3 hybrids, are shown in the following energy diagram:


Energy
2p
2s
Standard atomic orbitals for C
Hybridization
Four sp^3 hybrid orbitals

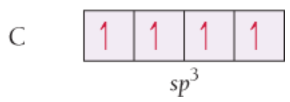
The notation sp^3 indicates that the hybrid orbitals are mixtures of one *s* orbital and three *p* orbitals. Notice that the hybrid orbitals all have the same energy—they are degenerate. The shapes of the sp^3 hybrid orbitals are shown in Figure 6.3. The four hybrid orbitals are arranged in a tetrahedral geometry with 109.5° angles between them as we just discussed.

Figure 6.3 sp^3 **Hybridization**

One *s* orbital and three *p* orbitals combine to form four sp^3 hybrid orbitals.

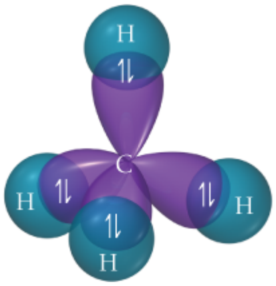

Formation of sp^3 Hybrid Orbitals
One s orbital and three p orbitals combine to form four sp^3 orbitals.
z
y
x
s orbital
+
p_x orbital
+
p_y orbital
p_z orbital
Standard atomic orbitals
Hybridization
sp^3
sp^3
sp^3
sp^3
sp^3 hybrid orbitals (shown separately)
sp^3
sp^3
sp^3 hybri
(shown t

We can write an orbital diagram for carbon using these hybrid orbitals:

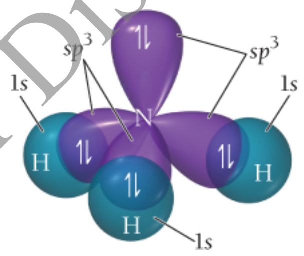


Carbon’s four valence electrons occupy the orbitals singly with parallel spins as dictated by Hund’s rule. With this electron configuration, carbon has four half-filled orbitals and can form four bonds with four hydrogen atoms.

The geometry of the *overlapping orbitals* (the hybrids) is tetrahedralwith angles of 109.5° between the orbitals. The *resulting geometry of the molecule* is therefore tetrahedral, with 109.5° bond angles, in agreement with the experimentally measured geometry of CH_4 and with the predicted VSEPR geometry.

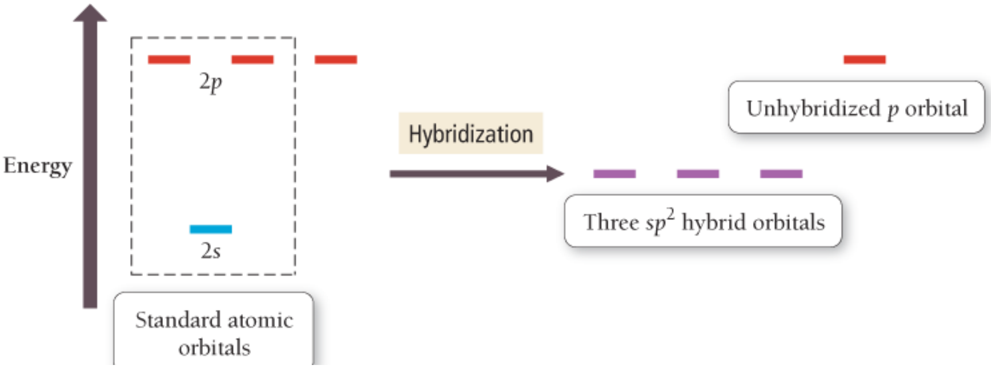


Hybridized orbitals readily form chemical bonds because they tend to maximize overlap with other orbitals. However, if the central atom of a molecule contains lone pairs, hybrid orbitals can also accommodate them. For example, the nitrogen orbitals in ammonia are sp^3 hybrids. Three of the hybrids are involved in bonding with three hydrogen atoms, but the fourth hybrid contains a lone pair. The presence of the lone pair lowers the tendency of nitrogen’s orbitals to hybridize. (Recall that the tendency to hybridize increases with the number of bonds formed.) Therefore, the bond angle in NH_3 is 107°, a bit closer to the unhybridized *p* orbital bond angle of 90°.



sp^2 Hybridization and Double Bonds

Hybridization of one *s* and two *p* orbitals results in three sp^2 hybrids and one leftover unhybridized *p* orbital, as shown in the following energy diagram:

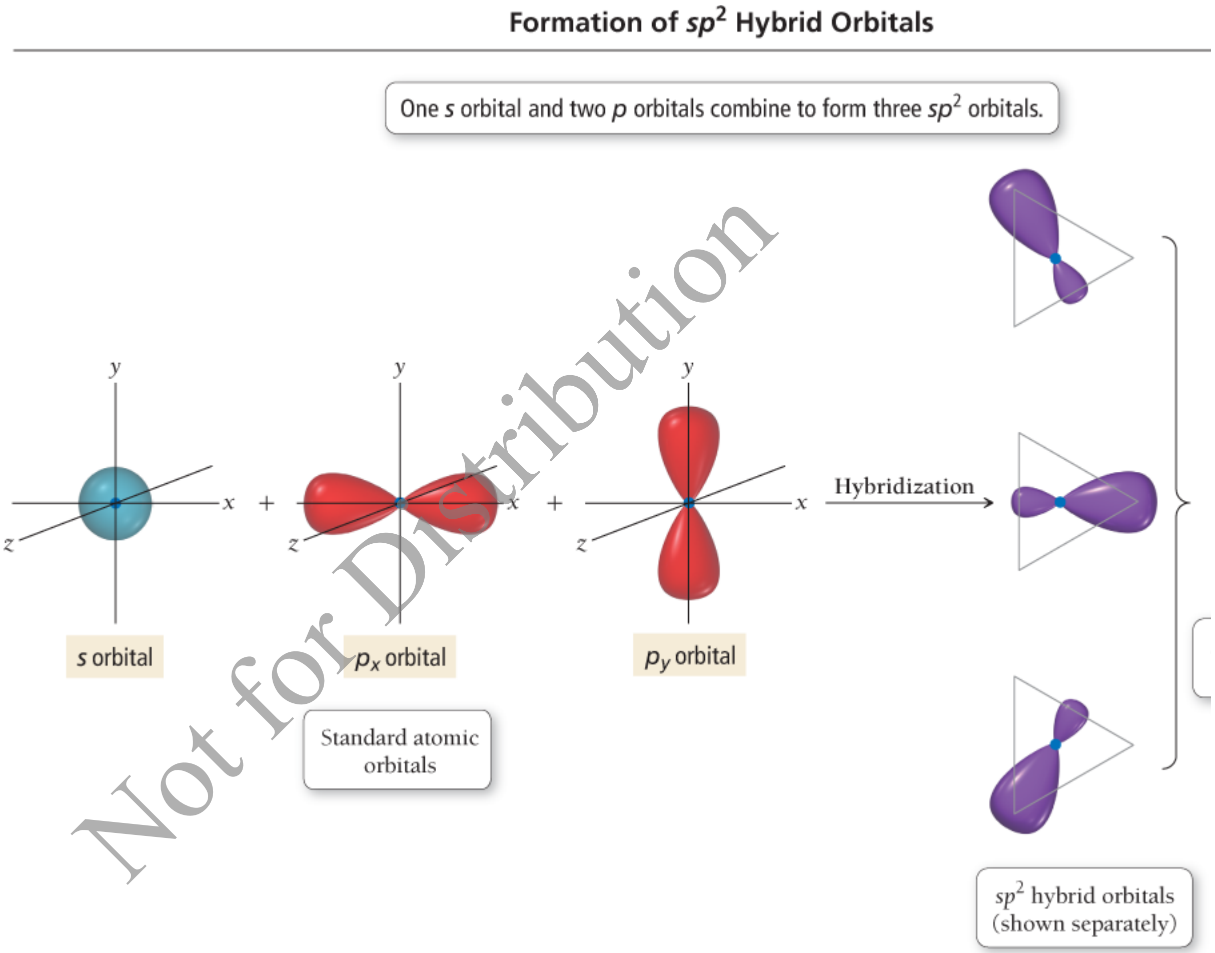


> In valence bond theory, the particular hybridization scheme (sp^2 versus sp^3, for example) for a given molecule is determined computationally, which is beyond our scope. In this book, we determine the particular hybridization scheme from the VSEPR geometry of the molecule, as shown later in this section.

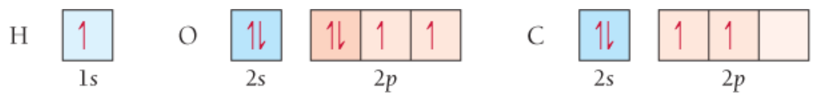
The notation sp^2 indicates that the hybrids are mixtures of one *s* orbital and two *p* orbitals. The shapes of the sp^2 hybrid orbitals are shown in Figure 6.4. Notice that the three hybrid orbitals have a trigonal planar geometry with 120° angles between them. The unhybridized *p* orbital, which is not shown in the figure, is oriented perpendicular to the three hybridized orbitals.

Figure 6.4 sp^2 **Hybridization**

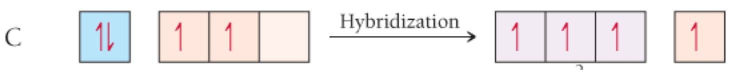
One *s* orbital and two *p* orbitals combine to form three sp^2 hybrid orbitals. One *p* orbital (not shown) remains unhybridized. (The small lobes of the sp^2 hybridized orbitals have been omitted for clarity in the far right image that shows the three orbitals together.)


Formation of sp^2 Hybrid Orbitals
One *s* orbital and two *p* orbitals combine to form three sp^2 orbitals.
y
x
z
+
y
x
z
+
y
x
z
Hybridization
s orbital
p_x orbital
p_y orbital
Standard atomic orbitals
sp^2 hybrid orbitals (shown separately)

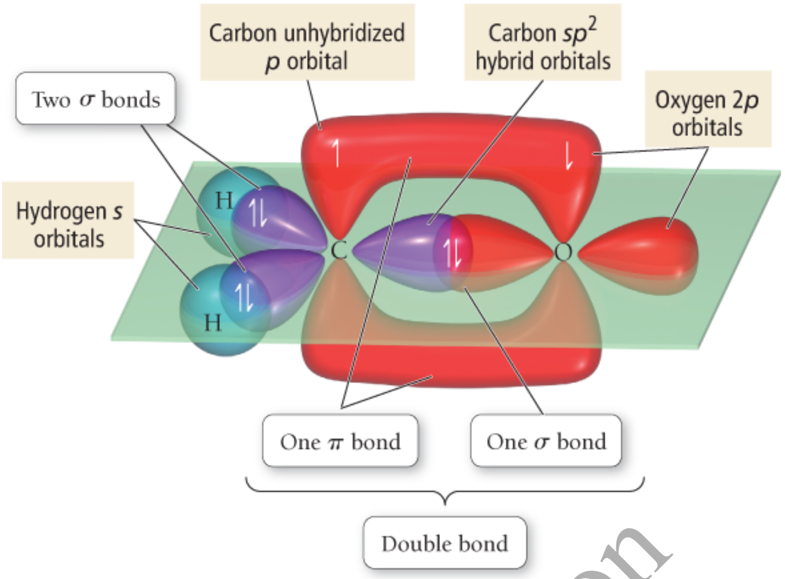
As an example of a molecule with sp^2 hybrid orbitals, consider H_2CO. The unhybridized valence electron configurations of each of the atoms are as follows:


H
↑
1s
O
↑↓
2s
↑↓ ↑ ↑
2p
C
↑↓
2s
↑ ↑
2p

Carbon is the central atom, and the hybridization of its orbitals is sp^2:


C
↑↓
↑ ↑
Hybridization
↑ ↑ ↑
↑

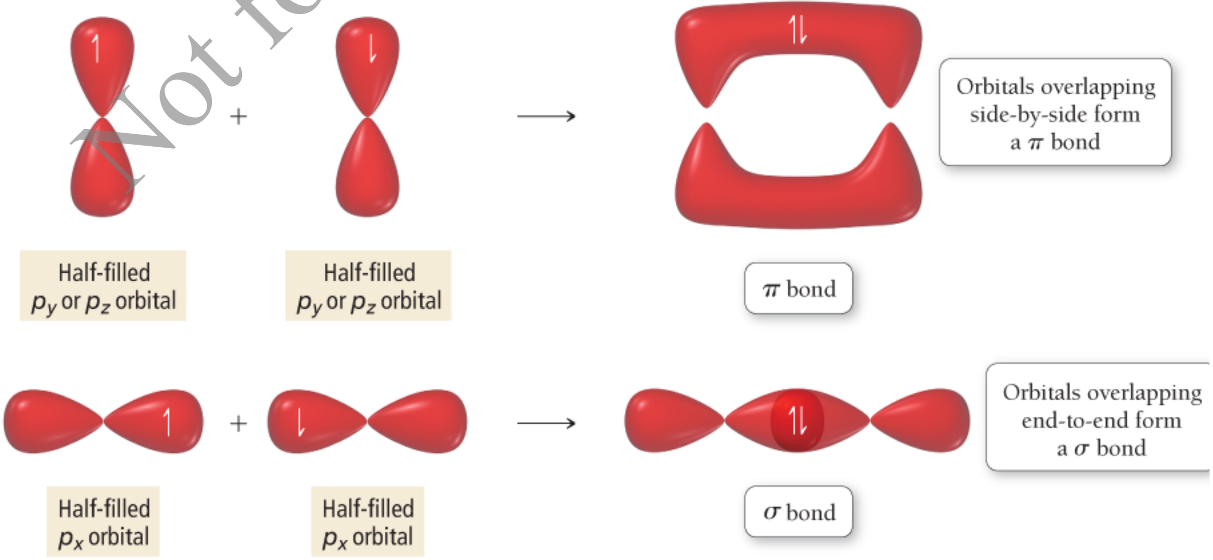
Note that each of the sp^2 orbitals is half-filled. The remaining electron occupies the leftover p orbital, even though it is slightly higher in energy. We can now see that the carbon atom has four half-filled orbitals and can therefore form four bonds: two with two hydrogen atoms and two (a double bond) with the oxygen atom. We draw the molecule and the overlapping orbitals as follows:


Carbon unhybridized p orbital
Carbon sp² hybrid orbitals
Two σ bonds
Oxygen 2p orbitals
Hydrogen s orbitals
H
H
C
O
One π bond
One σ bond
Double bond

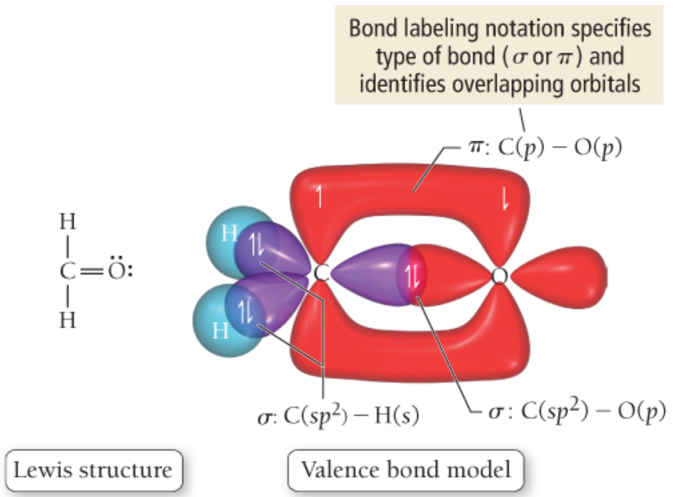
Notice the overlap between the half-filled p orbitals on the carbon and oxygen atoms. When p orbitals overlap this way (side by side), the resulting bond is a **pi (π) bond**, and the electron density is above and below the internuclear axis (the axis that connects the carbon atom and the oxygen atom). When orbitals overlap end to end, as in all the rest of the bonds in the molecule, the resulting bond is a **sigma (σ) bond** (Figure 6.5).

Figure 6.5 **Sigma and Pi Bonding**

When orbitals overlap side by side, the result is a pi (π) bond. When orbitals overlap end to end, they form a sigma (σ) bond. Two atoms can form only one sigma bond. A single bond is a sigma bond; a double bond consists of a sigma bond and a pi bond; a triple bond consists of a sigma bond and two pi bonds.


Orbitals overlapping side-by-side form a π bond
Half-filled p_y or p_z orbital
Half-filled p_y or p_z orbital
π bond
Orbitals overlapping end-to-end form a σ bond
Half-filled p_x orbital
Half-filled p_x orbital
σ bond

Even though we represent the two electrons in a π bond as two half arrows in the upper lobe, they are actually spread out over both the upper and lower lobes (this is one of the limitations we encounter when we try to represent electrons with arrows). We can label all the bonds in the molecule using a notation that specifies the represent electrons with arrows). We can label all the bonds in the molecule using a notation that specifies the type of bond (σ or π) as well as the type of overlapping orbitals. We have included this notation, as well as the Lewis structure of H_2CO for comparison, in the bonding diagram for H_2CO:


Bond labeling notation specifies type of bond (σ or π) and identifies overlapping orbitals
π: C(p) – O(p)
H
C=Ö:
H
H
H
σ: C(sp²) – H(s)
σ: C(sp²) – O(p)
Lewis structure
Valence bond model

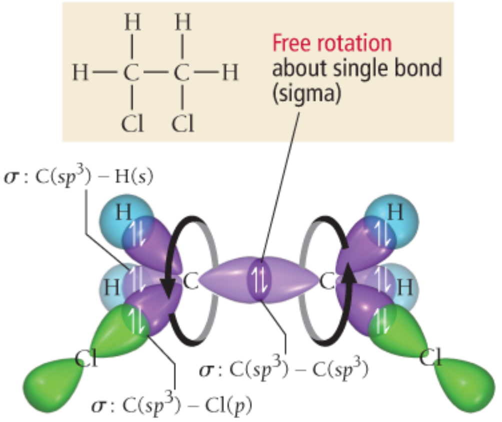
> In these drawings of the orbitals of H_2CO, the nonbonding electrons have been omitted (for clarity).

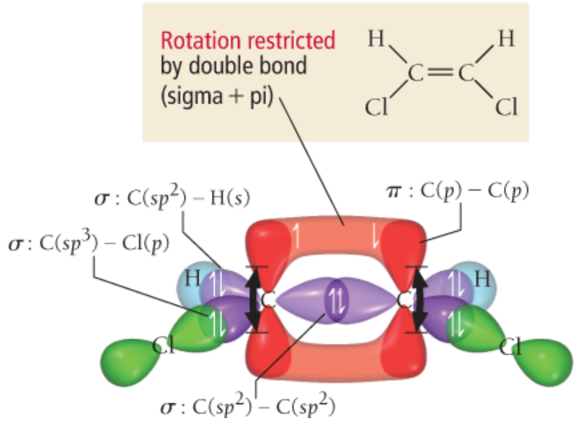
Notice the correspondence between the valence bond model and the Lewis structure. In both cases, the central carbon atom forms four bonds: two single bonds and one double bond. However, valence bond theory gives us more insight into the bonds. The double bond between carbon and oxygen according to valence bond theory consists of two different kinds of bonds—one σ and one π—while in the Lewis model the two bonds within the double bond appear identical. *A double bond in the Lewis model always corresponds to one σ and one π bond in valence bond theory*. In general, π bonds are weaker than σ bonds because the side-to-side orbital overlap tends to be less efficient than the end-to-end orbital overlap. Consequently, the π bond in a double bond is generally easier to break than the σ bond.

> One—and only one—σ bond forms between any two atoms. Additional bonds must be π bonds.

Valence bond theory allows us to see why the rotation about a double bond is severely restricted. Because of the side-by-side overlap of the p orbitals, the π bond must essentially break for rotation to occur. Valence bond theory shows us the types of orbitals involved in the bonding and their shapes. In H_2CO, the sp^2 hybrid orbitals on the central atom are trigonal planar with 120° angles between them, so the resulting predicted geometry of the molecule is trigonal planar with 120° bond angles. The experimentally measured bond angles in H_2CO, as discussed previously (see Section 5.7), are 121.9° for the HCO bond and 116.2° for the HCH bond angle, close to the predicted values.

Although rotation about a double bond is highly restricted, rotation about a single bond is relatively unrestricted. Consider, for example, the structures of two chlorinated hydrocarbons, 1,2-dichloroethane and 1,2-dichloroethene:

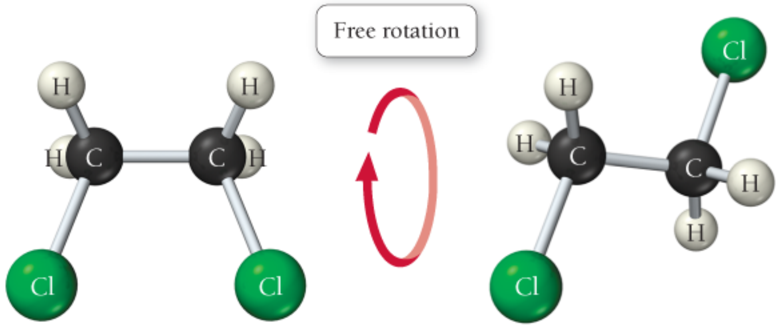

H H
H—C—C—H
Cl Cl
Free rotation about single bond (sigma)
σ: C(sp³) – H(s)
H
H
H
H
C
C
Cl
Cl
σ: C(sp³) – C(sp³)
σ: C(sp³) – Cl(p)


Rotation restricted by double bond (sigma + pi)
H H
C=C
Cl Cl
σ: C(sp²) – H(s)
π: C(p) – C(p)
σ: C(sp³) – Cl(p)
H
H
Cl
Cl
σ: C(sp²) – C(sp²)

1,2-Dichloroethane

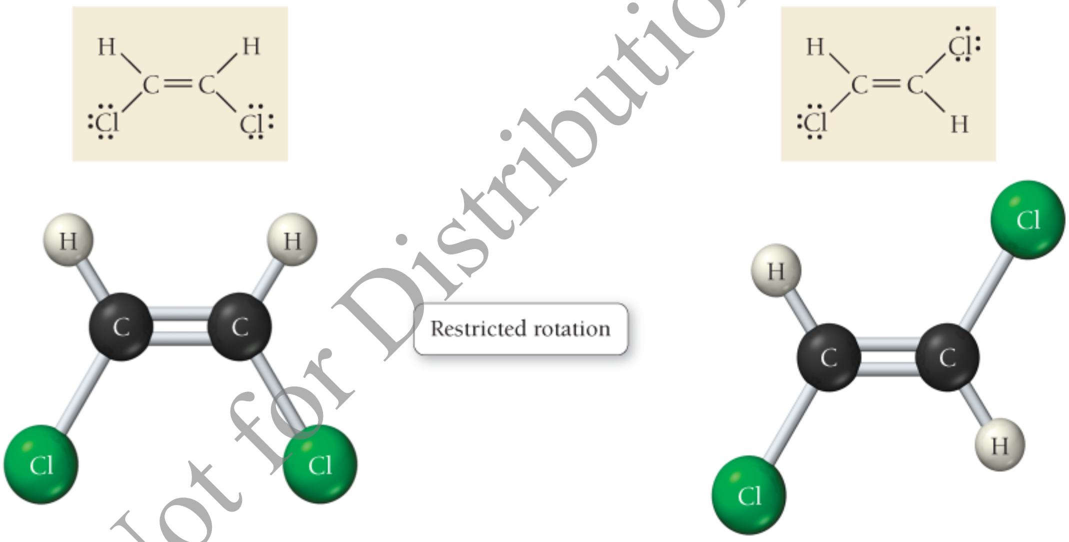
1,2-Dichloroethene

The hybridization of the carbon atoms in 1,2-dichloroethane is *sp*^{3}, resulting in relatively free rotation about the sigma single bond. Consequently, there is no difference between the following two structures at room temperature because they quickly interconvert:



Structures quickly interconvert.

In contrast, rotation about the double bond (sigma + pi) in 1,2-dichloroethene is restricted, so that, at room temperature, 1,2-dichloroethene exists in these two forms:



cis-1,2-Dichloroethene

trans-1,2-Dichloroethene

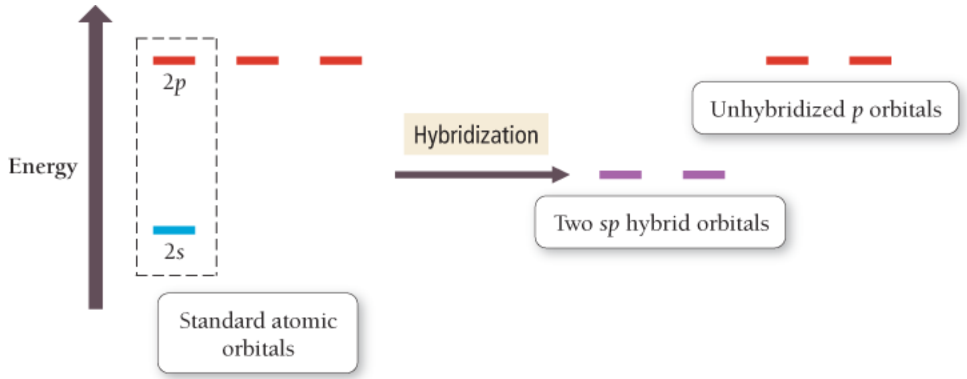
We distinguish between the two forms of 1,2-dichloroethene with the designations *cis* (meaning "same side") and *trans* (meaning "opposite sides"). These two forms have different structures and therefore different properties. For example, the *cis* form boils at 60.3 °C and the *trans* form boils at 47.2 °C. Notice that *structure* (in this case the nature of a double bond and the arrangement of the chlorine atoms) *affects properties* (boiling point). Compounds such as the two forms of 1,2-dichloroethene, with the same molecular formula but different structures or different spatial arrangement of atoms, are called **isomers**. Nature can—and does—make different compounds out of the same atoms by arranging the atoms in different ways. Isomerism is common throughout chemistry and is especially important in organic chemistry, as we will discuss in Chapter 21.

Conceptual Connection 6.2 **Single and Double Bonds**

sp Hybridization and Triple Bonds

sp Hybridization and Triple Bonds

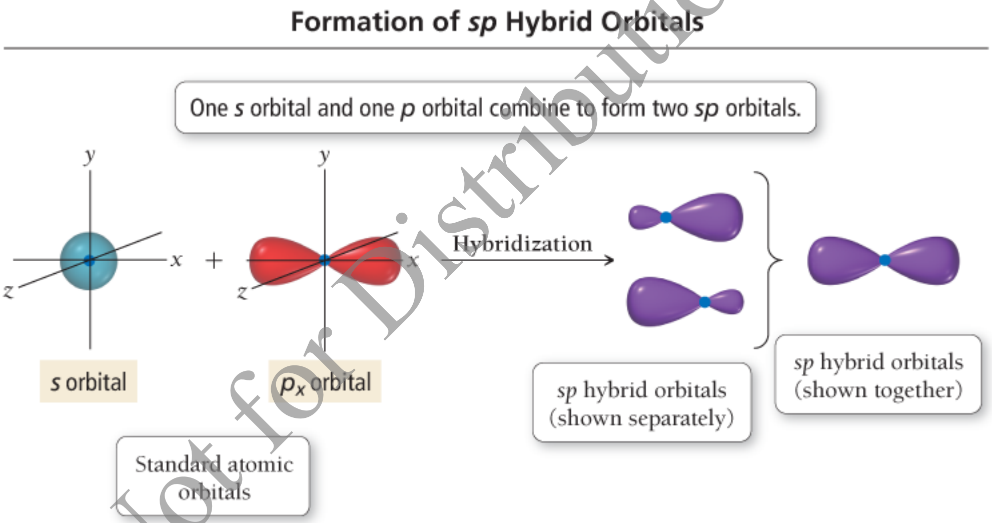
Hybridization of one *s* and one *p* orbital results in two *sp* hybrid orbitals and two leftover unhybridized *p* orbitals, as shown in the following energy diagram:


Energy
2p
2s
Standard atomic orbitals
Hybridization
Unhybridized p orbitals
Two sp hybrid orbitals

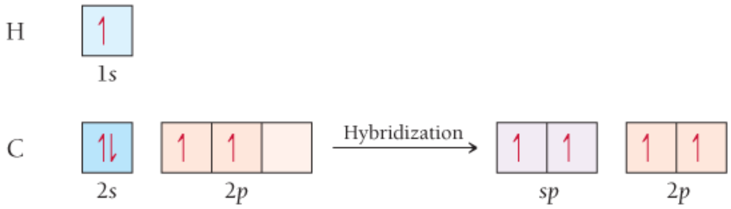
The shapes of the *sp* hybrid orbitals are shown in Figure 6.6. Notice that the two *sp* hybrid orbitals are arranged in a linear geometry with a 180° angle between them. The unhybridized *p* orbitals, which are not shown in the figure, are oriented in the plane that is perpendicular to the hybridized *sp* orbitals.

Figure 6.6 ***sp* Hybridization**

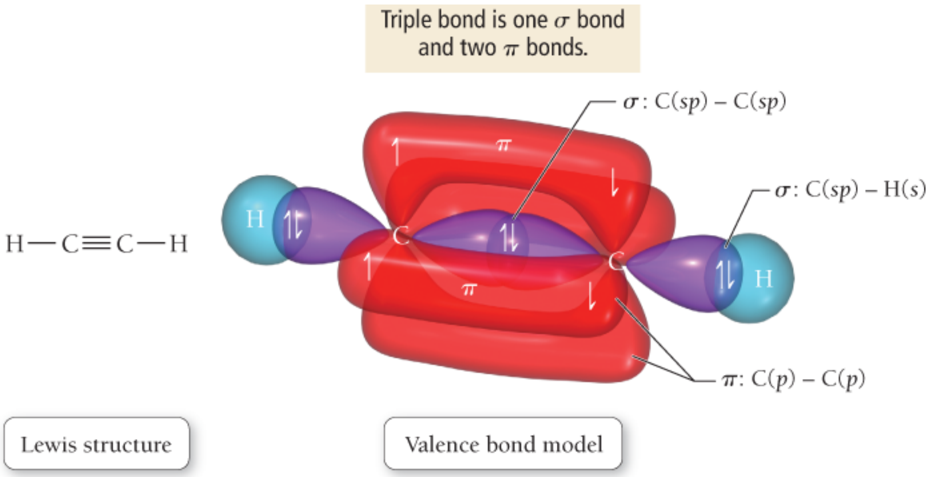
One *s* orbital and one *p* orbital combine to form two *sp* hybrid orbitals. Two *p* orbitals (not shown) remain unhybridized.


Formation of sp Hybrid Orbitals
One s orbital and one p orbital combine to form two sp orbitals.
y
x
z
+
y
x
z
Hybridization
s orbital
p_x orbital
Standard atomic orbitals
sp hybrid orbitals (shown separately)
sp hybrid orbitals (shown together)

The acetylene molecule, HC ≡ CH, has *sp* hybrid orbitals. The four valence electrons of carbon can distribute themselves among the two *sp* hybrid orbitals and the two *p* orbitals:


H
1s
C
2s
2p
Hybridization
sp
2p

Each carbon atom then has four half-filled orbitals and can form four bonds: one with a hydrogen atom and three (a triple bond) with the other carbon atom in HC ≡ CH. We draw the molecule and the overlapping orbitals as follows:


Triple bond is one σ bond and two π bonds.
σ: C(sp) – C(sp)
σ: C(sp) – H(s)
π: C(p) – C(p)
H—C≡C—H
H
C
π
C
H
Lewis structure
Valence bond model

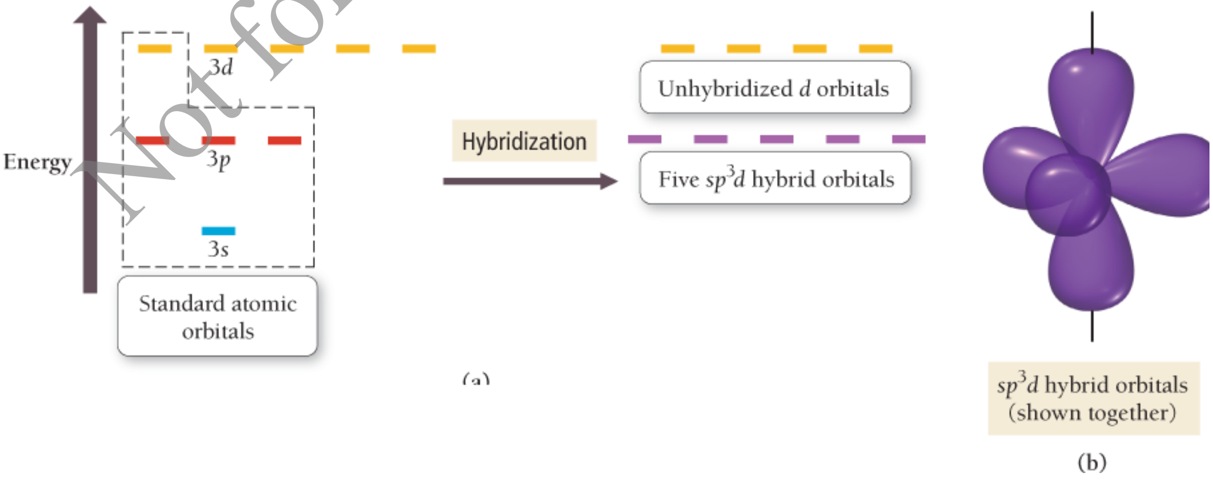
Notice that the triple bond between the two carbon atoms consists of two π bonds (overlapping p orbitals) and one σ bond (overlapping sp orbitals). The sp orbitals on the carbon atoms are linear with 180° between them, so the resulting geometry of the molecule is linear with 180° bond angles, in agreement with the experimentally measured geometry of HC ≡ CH and with the prediction of VSEPR theory.

sp^3d and sp^3d^2 Hybridization

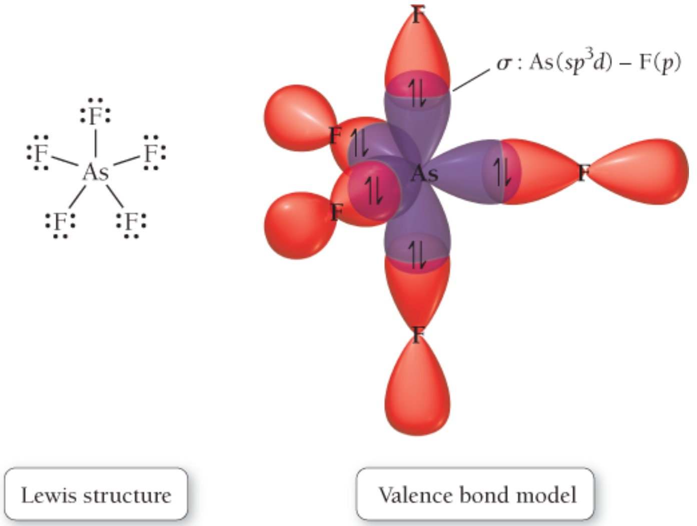
Recall that, according to the Lewis model, elements occurring in the third row of the periodic table (or below) can exhibit expanded octets (see Section 5.5). The equivalent concept in valence bond theory is hybridization involving the d orbitals. For third-period elements, the $3d$ orbitals are involved in hybridization because their energies are close to the energies of the $3s$ and $3p$ orbitals. The hybridization of one s orbital, three p orbitals, and one d orbital results in sp^3d hybrid orbitals, as shown in Figure 6.7a. The five sp^3d hybrid orbitals have a trigonal bipyramidal arrangement, as shown in Figure 6.7b. Arsenic pentafluoride, AsF_5 (shown in the margin), is an example of sp^3d hybridization. The arsenic atom bonds to five fluorine atoms by overlap between the sp^3d hybrid orbitals on arsenic and p orbitals on the fluorine atoms.

Figure 6.7 sp^3d **Hybridization**

One s orbital, three p orbitals, and one d orbital combine to form five sp^3d hybrid orbitals.


Energy
3d
3p
3s
Standard atomic orbitals
Hybridization
Unhybridized d orbitals
Five sp³d hybrid orbitals
(a)
sp³d hybrid orbitals (shown together)
(b)

The sp^3d orbitals on the arsenic atom are trigonal bipyramidal, so the molecular geometry is trigonal bipyramidal.

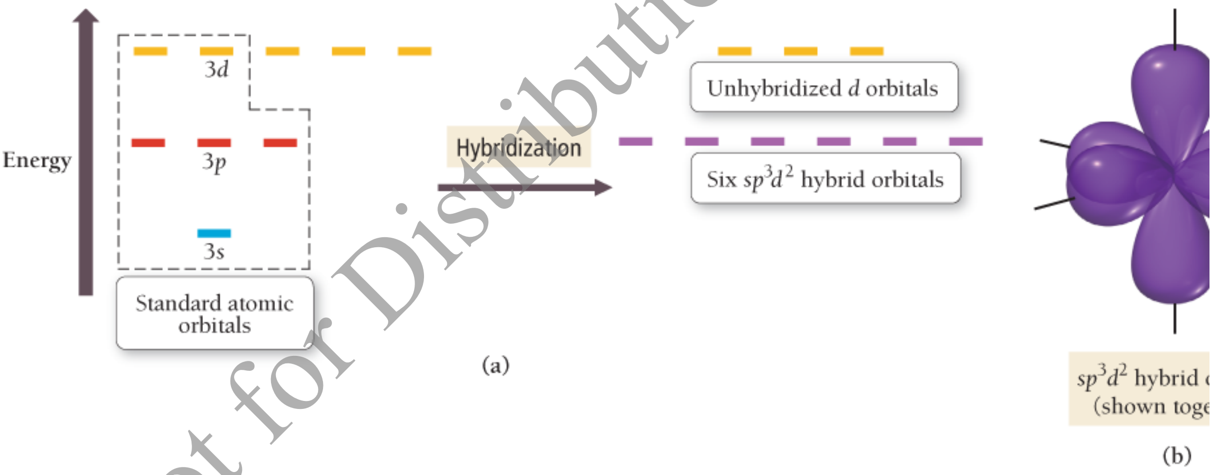


F
F
F
F
F
As
σ : As(sp3d) – F(p)
Lewis structure
Valence bond model

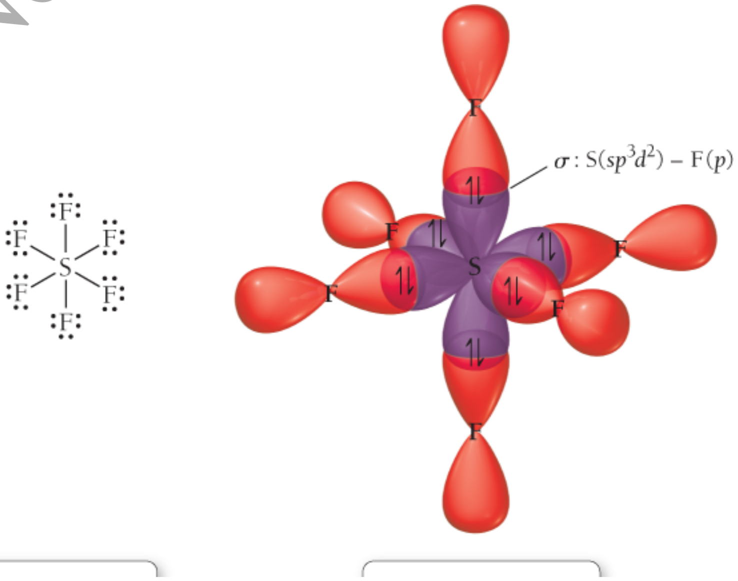
The hybridization of one *s* orbital, three *p* orbitals, and *two d* orbitals results in sp^3d^2 hybrid orbitals, as shown in Figure 6.8a. The six sp^3d^2 hybrid orbitals have an octahedral geometry, shown in Figure 6.8b. Sulfur hexafluoride, SF_6, is an example of sp^3d^2 hybridization. The sulfur atom bonds to six fluorine atoms by overlap between the sp^3d^2 hybrid orbitals on sulfur and *p* orbitals on the fluorine atoms.

Figure 6.8 sp^3d^2 **Hybridization**

One *s* orbital, three *p* orbitals, and two *d* orbitals combine to form six sp^3d^2 hybrid orbitals.



Energy
3d
3p
3s
Standard atomic orbitals
Hybridization
Unhybridized d orbitals
Six sp3d2 hybrid orbitals
(a)
sp3d2 hybrid
(shown toge
(b)



F
F
F
F
F
F
S
σ : S(sp3d2) – F(p)

Lewis structure
Valence bond model

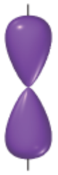
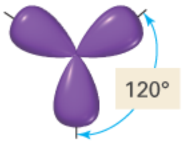
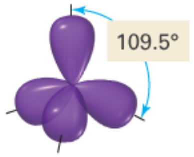
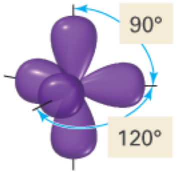
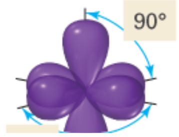
The sp^3d^2 orbitals on the sulfur atom are octahedral, so the molecular geometry is octahedral, again in agreement with VSEPR theory and with the experimentally observed geometry.

Writing Hybridization and Bonding Schemes

We have now studied examples of the five main types of atomic orbital hybridization. *But how do we know which hybridization scheme best describes the orbitals of a specific atom in a specific molecule?* In computational valence bond theory, the energy of the molecule is calculated using a computer; the degree of hybridization as well as the type of hybridization are varied to find the combination that gives the molecule the lowest overall energy. For our purposes, however, we can assign a hybridization scheme from the electron geometry—determined using VSEPR theory—of the central atom (or interior atoms) of the molecule.

The five VSEPR electron geometries and the corresponding hybridization schemes are shown in Table 6.1. For example, if the electron geometry of the central atom is tetrahedral, then the hybridization is sp^3, and if the electron geometry is octahedral, then the hybridization is sp^3d^2, and so on. Although this method of determining the hybridization scheme is not 100% accurate (for example, it predicts that H_2S should be sp^3 when in fact H_2S is largely unhybridized), it is the best we can do without more complex computer-based calculations.

Table 6.1 **Hybridization Scheme from Electron Geometry**

Number of Electron Groups	Electron Geometry (from VSEPR Theory)	Hybridization Scheme	Orbital Shapes and Relative Orientation
2	Linear	sp	
3	Trigonal planar	sp^2	
4	Tetrahedral	sp^3	
5	Trigonal bipyramidal	sp^3d	
6	Octahedral	sp^3d^2	

*As defined in the previous chapter, an *electron group* is a lone pair, bonding pair, or multiple bond.

Conceptual Connection 6.3 Hybridization

Interactive

We are now ready to put the Lewis model and valence bond theory together to describe bonding in molecules. In the procedure and examples that follow, we demonstrate how to write a *hybridization and bonding scheme* for a molecule. This involves drawing the Lewis structure for the molecule, determining its geometry using VSEPR theory, determining the hybridization of the interior atoms, drawing the molecule with its overlapping orbitals, and labeling each bond with the σ and π notation followed by the type of overlapping orbitals. This procedure involves virtually everything we have covered about bonding so far in this chapter and Chapter 5. The procedure for writing a hybridization and bonding scheme is shown in the left column, with two examples of how to apply the procedure in the columns to the right.

Example 6.1 Hybridization and Bonding Scheme

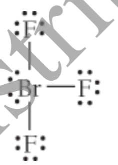
PROCEDURE FOR Hybridization and Bonding Scheme

Write a hybridization and bonding scheme for bromine trifluoride, BrF_3.

1. Draw the Lewis structure for the molecule.

SOLUTION

BrF_3 has 28 valence electrons and the following Lewis structure:



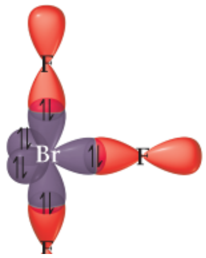
2. Apply VSEPR theory to predict the electron geometry about the central atom (or interior atoms).

The bromine atom has five electron groups and therefore has a trigonal bipyramidal electron geometry.

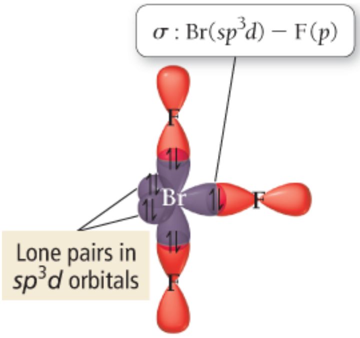
3. Select the correct hybridization for the central atom (or interior atoms) based on the electron geometry (refer to Table 6.1).

A trigonal bipyramidal electron geometry corresponds to sp^3d hybridization.

4. Sketch the molecule, beginning with the central atom and its orbitals. Show overlap with the appropriate orbitals on the terminal atoms.



5. Label all bonds using the σ or π notation followed by the type of overlapping orbitals.



$\sigma : \mathrm{Br}(sp^3d) - \mathrm{F}(p)$

Lone pairs in sp^3d orbitals

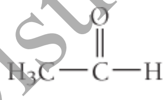
FOR PRACTICE 6.1

Write a hybridization and bonding scheme for XeF_4.

Example 6.2 Hybridization and Bonding Scheme

PROCEDURE FOR Hybridization and Bonding Scheme

Write a hybridization and bonding scheme for acetaldehyde.

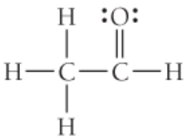


$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

1. Draw the Lewis structure for the molecule.

SOLUTION

Acetaldehyde has 18 valence electrons and the following Lewis structure:



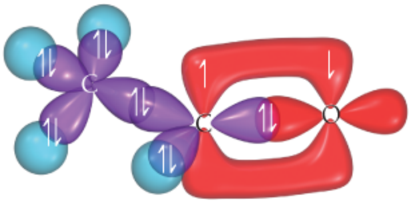
2. Apply VSEPR theory to predict the electron geometry about the central atom (or interior atoms).

The leftmost carbon atom has four electron groups and a tetrahedral electron geometry. The rightmost carbon atom has three electron groups and a trigonal planar geometry.

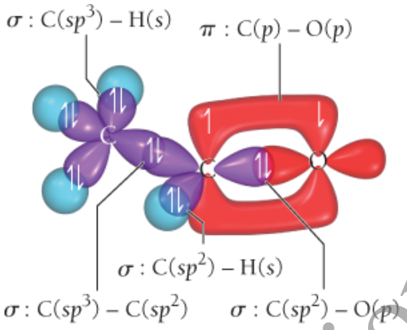
3. Select the correct hybridization for the central atom (or interior atoms) based on the electron geometry (refer to Table 6.1).

The leftmost carbon atom is sp^3 hybridized, and the rightmost carbon atom is sp^2 hybridized.

4. Sketch the molecule, beginning with the central atom and its orbitals. Show overlap with the appropriate orbitals on the terminal atoms.



5. Label all bonds using the σ or π notation followed by the type of overlapping orbitals.



σ : C(sp^3) – H(s)
π : C(p) – O(p)
σ : C(sp^2) – H(s)
σ : C(sp^3) – C(sp^2)
σ : C(sp^2) – O(p)

FOR PRACTICE 6.2

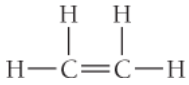
Write a hybridization and bonding scheme for HCN.

Example 6.3 Hybridization and Bonding Scheme

Apply valence bond theory to write a hybridization and bonding scheme for ethene, $H_2C=CH_2$.

SOLUTION

1. Draw the Lewis structure for the molecule.



$$H-\overset{\displaystyle H}{\overset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}-H$$

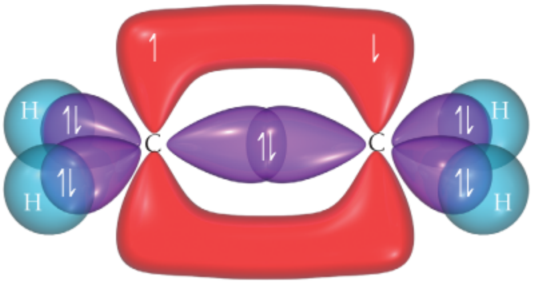
2. Apply VSEPR theory to predict the electron geometry about the central atom (or interior atoms).

The molecule has two interior atoms. Since each atom has three electron groups (one double bond and two single bonds), the electron geometry about each atom is trigonal planar.

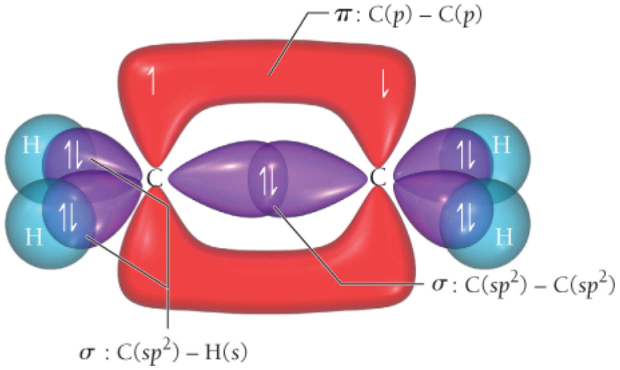
3. Select the correct hybridization for the central atom (or interior atoms) based on the electron geometry (refer to Table 6.1).

A trigonal planar geometry corresponds to sp^2 hybridization.

4. Sketch the molecule, beginning with the central atom and its orbitals. Show overlap with the appropriate orbitals on the terminal atoms.



5. Label all bonds using the σ or π notation followed by the type of overlapping orbitals.


π: C(p) – C(p)
H
H
C
C
H
H
σ : C(sp^2) – C(sp^2)
σ : C(sp^2) – H(s)

FOR PRACTICE 6.3 Apply valence bond theory to write a hybridization and bonding scheme for CO_2.

FOR MORE PRACTICE 6.3 What is the hybridization of the central iodine atom in I_3^-?

Interactive Worked Example 6.3 **Hybridization and Bonding Scheme**