Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

Chapter Outline

Essential Concepts

Molecular Geometry Molecular geometry refers to the three-dimensional arrangement of atoms in a molecule. For relatively small molecules, in which the central atom contains two to six bonds, geometries can be reliably predicted by the valence-shell electron-pair repulsion (VSEPR) model. This model is based on the assumption that chemical bonds and lone pairs tend to remain as far apart as possible to minimize repulsion.

Dipole Moments In a diatomic molecule the difference in the electronegativities of bonding atoms results in a polar bond and a dipole moment. The dipole moment of a molecule made up of three or more atoms depends on both the polarity of the bonds and molecular geometry. Dipole moment measurements can help us distinguish between different possible geometries of a molecule.

Hybridization of Atomic Orbitals Hybridization is the quantum mechanical description of chemical bonding. Atomic orbitals are hybridized, or mixed, to form hybrid orbitals. These orbitals then interact with other atomic orbitals to form chemical bonds. Various molecular geometries can be generated by different hybridizations. The hybridization concept accounts for the exception to the octet rule and also explains the formation of double and triple bonds.

10.1 Molecular Geometry

Molecular geometry is the three-dimensional arrangement of atoms in a molecule. A molecule's geometry affects its physical and chemical properties, such as melting point, boiling point, density, and the types of reactions it undergoes. In general, bond lengths and bond angles must be determined by experiment. However, there is a simple procedure that enables us to predict with considerable success the overall geometry of a molecule or ion if we know the number of electrons surrounding a central atom in its Lewis structure. The basis of this approach is the assumption that electron pairs in the valence shell of an atom repel one another. The ***valence shell*** is *the outermost electron-occupied shell of an atom; it holds the electrons that are usually involved in bonding.* In a covalent bond, a pair of electrons, often called the *bonding pair,* is responsible for holding two atoms together. However, in a polyatomic molecule, where there are two or more bonds between the central atom and the surrounding atoms, the repulsion between electrons in different bonding pairs causes them to remain as far apart as possible. The geometry that the molecule ultimately assumes (as defined by the positions of all the atoms) minimizes the repulsion. This approach to the study of molecular geometry is called the ***valence-shell electron-pair repulsion (VSEPR) model,*** because *it accounts for the geometric arrangements of electron pairs around a central atom in terms of the electrostatic repulsion between electron pairs.*

Two general rules govern the use of the VSEPR model:

1. As far as electron-pair repulsion is concerned, double bonds and triple bonds can be treated like single bonds. This approximation is good for qualitative purposes. However, you should realize that in reality multiple bonds are "larger" than single bonds; that is, because there are two or three bonds between two atoms, the electron density occupies more space.
2. If a molecule has two or more resonance structures, we can apply the VSEPR model to any one of them. Formal charges are usually not shown.

With this model in mind, we can predict the geometry of molecules (and ions) in a systematic way. For this purpose, it is convenient to divide molecules into two categories, according to whether or not the central atom has lone pairs.

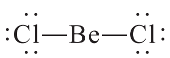
Molecules in Which the Central Atom Has No Lone Pairs

For simplicity we will consider molecules that contain atoms of only two elements, A and B, of which A is the central atom. These molecules have the general formula AB_x, where x is an integer 2, 3, ... (If $x = 1$, we have the diatomic molecule AB, which is linear by definition.) In the vast majority of cases, x is between 2 and 6.

Table 10.1 shows five possible arrangements of electron pairs around the central atom A. As a result of mutual repulsion, the electron pairs stay as far from one another as possible. Note that the table shows arrangements of the electron pairs but not the positions of the atoms that surround the central atom. Molecules in which the central atom has no lone pairs have one of these five arrangements of bonding pairs. Using Table 10.1 as a reference, let us take a close look at the geometry of molecules with the formulas AB_2, AB_3, AB_4, AB_5, and AB_6.

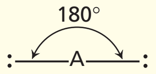
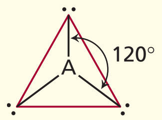
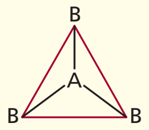
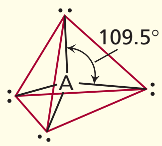
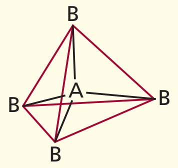
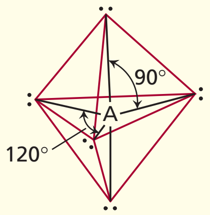
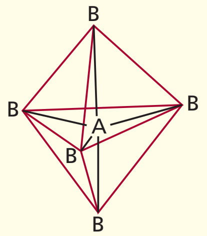
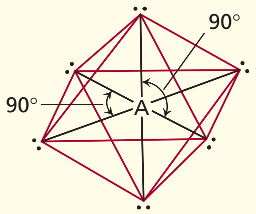
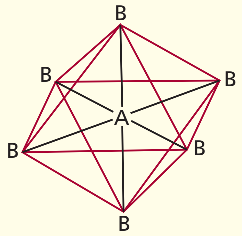
AB_2: Beryllium Chloride ($BeCl_2$)

The Lewis structure of beryllium chloride in the gaseous state is



$$:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}-\mathrm{Be}-\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$$

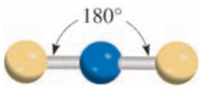
TABLE 10.1 **Arrangement of Electron Pairs About a Central Atom (A) in a Molecule and Geometry of Some Simple Molecules and Ions in Which the Central Atom Has No Lone Pairs**

Number of Electron Pairs	Arrangement of Electron Pairs*	Molecular Geometry*	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

*The colored lines are used only to show the overall shapes; they do not represent bonds.

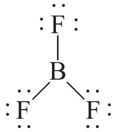
Because the bonding pairs repel each other, they must be at opposite ends of a straight line in order for them to be as far apart as possible. Thus, the ClBeCl angle is predicted to be 180°, and the molecule is linear (see Table 10.1). The "ball-and-stick" model of $BeCl_2$ is

The blue and yellow spheres are for atoms in general.

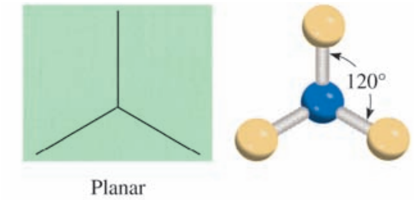


AB$_3$: Boron Trifluoride (BF$_3$)

Boron trifluoride contains three covalent bonds, or bonding pairs. In the most stable arrangement, the three BF bonds point to the corners of an equilateral triangle with B in the center of the triangle:



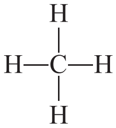
According to Table 10.1, the geometry of BF$_3$ is *trigonal planar* because the three end atoms are at the corners of an equilateral triangle that is planar:



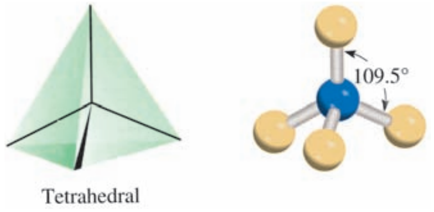
Thus, each of the three FBF angles is 120°, and all four atoms lie in the same plane.

AB$_4$: Methane (CH$_4$)

The Lewis structure of methane is

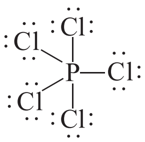


Because there are four bonding pairs, the geometry of CH$_4$ is tetrahedral (see Table 10.1). A *tetrahedron* has four sides (the prefix *tetra* means "four"), or faces, all of which are equilateral triangles. In a tetrahedral molecule, the central atom (C in this case) is located at the center of the tetrahedron and the other four atoms are at the corners. The bond angles are all 109.5°.

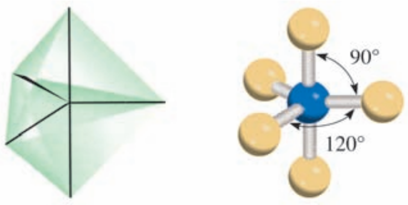


AB$_5$: Phosphorus Pentachloride (PCl$_5$)

The Lewis structure of phosphorus pentachloride (in the gas phase) is



The only way to minimize the repulsive forces among the five bonding pairs is to arrange the PCl bonds in the form of a trigonal bipyramid (see Table 10.1). A trigonal bipyramid can be generated by joining two tetrahedrons along a common triangular base:

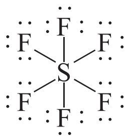


Trigonal bipyramidal

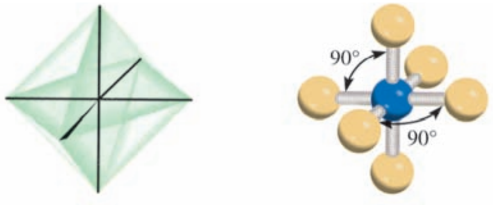
The central atom (P in this case) is at the center of the common triangle with the surrounding atoms positioned at the five corners of the trigonal bipyramid. The atoms that are above and below the triangular plane are said to occupy *axial* positions, and those that are in the triangular plane are said to occupy *equatorial* positions. The angle between any two equatorial bonds is 120°; that between an axial bond and an equatorial bond is 90°, and that between the two axial bonds is 180°.

AB_6: Sulfur Hexafluoride (SF_6)

The Lewis structure of sulfur hexafluoride is



The most stable arrangement of the six SF bonding pairs is in the shape of an octahedron, shown in Table 10.1. An octahedron has eight sides (the prefix *octa* means "eight"). It can be generated by joining two square pyramids on a common base. The central atom (S in this case) is at the center of the square base and the surrounding atoms are at the six corners. All bond angles are 90° except the one made by the bonds between the central atom and the pairs of atoms that are diametrically opposite each other. That angle is 180°. Because the six bonds are equivalent in an octahedral molecule, we cannot use the terms "axial" and "equatorial" as in a trigonal bipyramidal molecule.



Octahedral

Molecules in Which the Central Atom Has One or More Lone Pairs

Determining the geometry of a molecule is more complicated if the central atom has both lone pairs and bonding pairs. In such molecules there are three types of repulsive forces—those between bonding pairs, those between lone pairs, and those between a bonding pair and a lone pair. In general, according to the VSEPR model, the repulsive forces decrease in the following order:

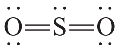
$$\text{lone-pair vs. lone-pair repulsion} > \text{lone-pair vs. bonding-pair repulsion} > \text{bonding-pair vs. bonding-pair repulsion}$$

Electrons in a bond are held by the attractive forces exerted by the nuclei of the two bonded atoms. These electrons have less "spatial distribution" than lone pairs; that is, they take up less space than lone-pair electrons, which are associated with only one particular atom. Because lone-pair electrons in a molecule occupy more space, they experience greater repulsion from neighboring lone pairs and bonding pairs. To keep track of the total number of bonding pairs and lone pairs, we designate molecules with lone pairs as AB_xE_y, where A is the central atom, B is a surrounding atom, and E is a lone pair on A. Both x and y are integers; $x = 2, 3, \ldots,$ and $y = 1, 2, \ldots.$ Thus, the values of x and y indicate the number of surrounding atoms and number of lone pairs on the central atom, respectively. The simplest such molecule would be a triatomic molecule with one lone pair on the central atom and the formula is AB_2E.

As the following examples show, in most cases the presence of lone pairs on the central atom makes it difficult to predict the bond angles accurately.

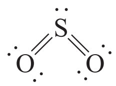
AB_2E: Sulfur Dioxide (SO_2)

The Lewis structure of sulfur dioxide is

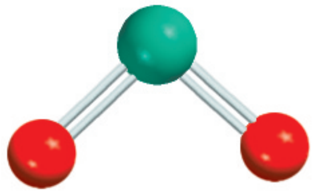


$$O=S=O$$

Because VSEPR treats double bonds as though they were single, the SO_2 molecule can be viewed as consisting of three electron pairs on the central S atom. Of these, two are bonding pairs and one is a lone pair. In Table 10.1 we see that the overall arrangement of three electron pairs is trigonal planar. But because one of the electron pairs is a lone pair, the SO_2 molecule has a "bent" shape.



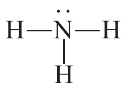
Because the lone-pair versus bonding-pair repulsion is greater than the bonding-pair versus bonding-pair repulsion, the two sulfur-to-oxygen bonds are pushed together slightly and the OSO angle is less than 120°.



SO_2

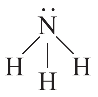
AB_3E: Ammonia (NH_3)

The ammonia molecule contains three bonding pairs and one lone pair:



$$H-\underset{\displaystyle H}{\underset{|}{\ddot{N}}}-H$$

As Table 10.1 shows, the overall arrangement of four electron pairs is tetrahedral. But in NH_3 one of the electron pairs is a lone pair, so the geometry of NH_3 is trigonal pyramidal (so called because it looks like a pyramid, with the N atom at the apex). Because the lone pair repels the bonding pairs more strongly, the three NH bonding pairs are pushed closer together:



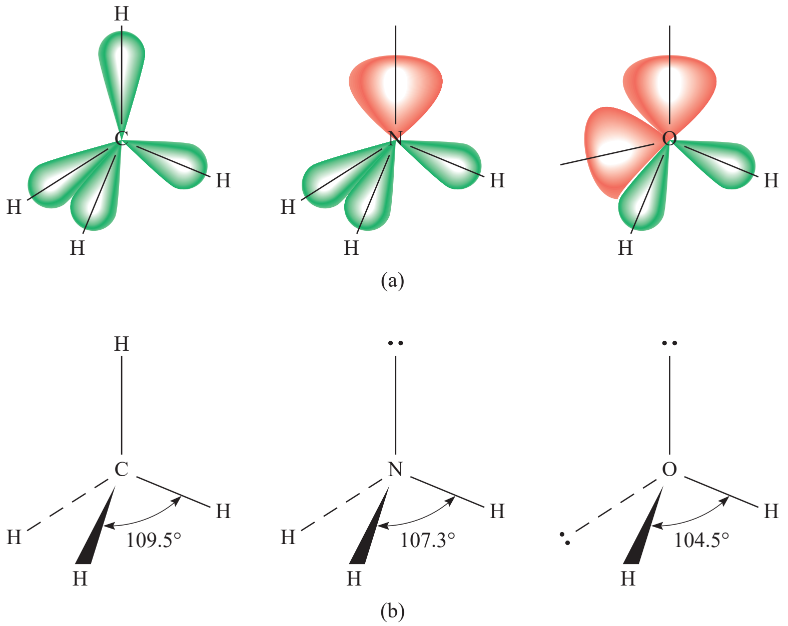


Figure 10.1
(a) The relative sizes of bonding pairs and lone pairs in CH_4, NH_3, and H_2O. (b) The bond angles in CH_4, NH_3, and H_2O. Note that the dashed lines represent a bond axes behind the plane of the paper, the wedged lines represent a bond axes in front of the plane of the paper, and the thin solid lines represent bonds in the plane of the paper.

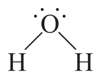
Thus, the HNH angle in ammonia is smaller than the ideal tetrahedral angle of 109.5° (Figure 10.1).

AB_2E_2: Water (H_2O)

A water molecule contains two bonding pairs and two lone pairs:

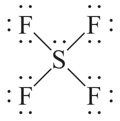
$$\mathrm{H-\underset{..}{\ddot{O}}-H}$$

The overall arrangement of the four electron pairs in water is tetrahedral, the same as in ammonia. However, unlike ammonia, water has two lone pairs on the central O atom. These lone pairs tend to be as far from each other as possible. Consequently, the two OH bonding pairs are pushed toward each other, and we predict an even greater deviation from the tetrahedral angle than in NH_3. As Figure 10.1 shows, the HOH angle is 104.5°. The geometry of H_2O is bent:

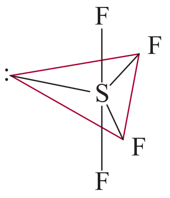


AB_4E: Sulfur Tetrafluoride (SF_4)

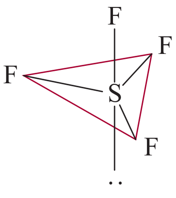
The Lewis structure of SF_4 is



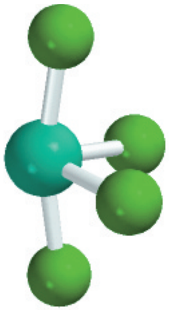
The central sulfur atom has five electron pairs whose arrangement, according to Table 10.1, is trigonal bipyramidal. In the SF_4 molecule, however, one of the electron pairs is a lone pair, so the molecule must have one of the following geometries:



(a)



(b)



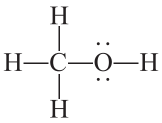
SF$_4$

In (a) the lone pair occupies an equatorial position, and in (b) it occupies an axial position. The axial position has three neighboring pairs at 90° and one at 180°, while the equatorial position has two neighboring pairs at 90° and two more at 120°. The repulsion is smaller for (a), and indeed (a) is the structure observed experimentally. This shape is sometimes described as a seesaw (if you turn the structure 90° clockwise to view it). The angle between the axial F atoms and S is 173°, and that between the equatorial F atoms and S is 102°.

Table 10.2 shows the geometries of simple molecules in which the central atom has one or more lone pairs, including some that we have not discussed.

Geometry of Molecules with More Than One Central Atom

So far we have discussed the geometry of molecules having only one central atom. The overall geometry of molecules with more than one central atom is difficult to define in most cases. Often we can describe only the shape around each of the central atoms. For example, consider methanol, CH_3OH, whose Lewis structure is shown next:



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}\ddot{\underset{\cdot\cdot}{O}}{-}H}$$

The two central (nonterminal) atoms in methanol are C and O. We can say that the three CH and the CO bonding pairs are tetrahedrally arranged about the C atom. The HCH and OCH bond angles are approximately 109°. The O atom here is like the one in water in that it has two lone pairs and two bonding pairs. Therefore, the HOC portion of the molecule is bent, and the angle HOC is approximately equal to 105° (Figure 10.2).

Guidelines for Applying the VSEPR Model

Having studied the geometries of molecules in two categories (central atoms with and without lone pairs), let us consider some rules for applying the VSEPR model to all types of molecules:

1. Write the Lewis structure of the molecule, considering only the electron pairs around the central atom (that is, the atom that is bonded to more than one other atom).
2. Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double and triple bonds as though they were single bonds. Refer to Table 10.1 to predict the overall arrangement of the electron pairs.
3. Use Tables 10.1 and 10.2 to predict the geometry of the molecule.

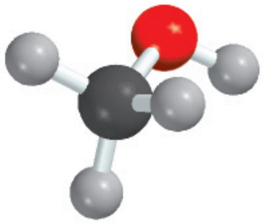
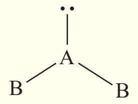
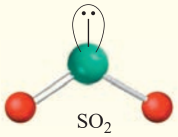
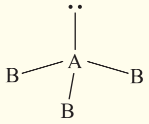
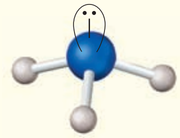
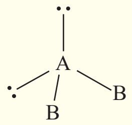
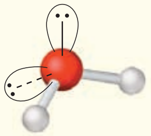
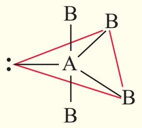
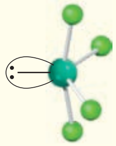
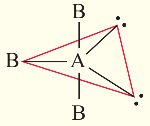
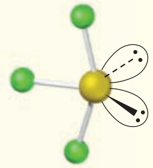
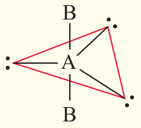
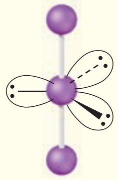
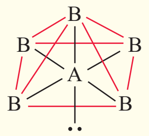
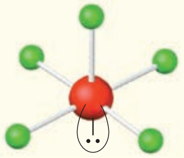
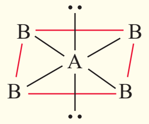
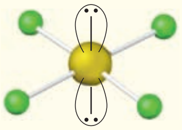


Figure 10.2
The geometry of CH_3OH*.*

TABLE 10.2 Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs

Class of molecule	Total number of electron pairs	Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs*	Geometry	Examples
AB_2E	3	2	1	 Trigonal planar	Bent	 SO_2
AB_3E	4	3	1	 Tetrahedral	Trigonal pyramidal	 NH_3
AB_2E_2	4	2	2	 Tetrahedral	Bent	 H_2O
AB_4E	5	4	1	 Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	 SF_4
AB_3E_2	5	3	2	 Trigonal bipyramidal	T-shaped	 ClF_3
AB_2E_3	5	2	3	 Trigonal bipyramidal	Linear	 I_3^-
AB_5E	6	5	1	 Octahedral	Square pyramidal	 BrF_5
AB_4E_2	6	4	2	 Octahedral	Square planar	 XeF_4

*The colored lines are used to show the overall shapes, not bonds.

4. In predicting bond angles, note that a lone pair repels another lone pair or a bonding pair more strongly than a bonding pair repels another bonding pair. Remember that in general there is no easy way to predict bond angles accurately when the central atom possesses one or more lone pairs.

The VSEPR model generates reliable predictions of the geometries of a variety of molecular structures. Chemists use the VSEPR approach because of its simplicity. Although there are some theoretical concerns about whether "electron-pair repulsion" actually determines molecular shapes, the assumption that it does leads to useful (and generally reliable) predictions. We need not ask more of any model at this stage in the study of chemistry. Example 10.1 illustrates the application of VSEPR.

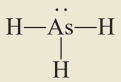
Example 10.1

Use the VSEPR model to predict the geometry of the following molecules and ions: (a) AsH_3, (b) OF_2, (c) $AlCl_4^-$, (d) I_3^-, (e) C_2H_4.

Strategy The sequence of steps in determining molecular geometry is as follows:

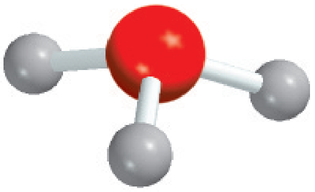
$$\begin{array}{c}\text{draw Lewis}\\ \text{structure}\end{array} \longrightarrow \begin{array}{c}\text{find arrangement}\\ \text{of electron pairs}\end{array} \longrightarrow \begin{array}{c}\text{find arrangement}\\ \text{of bonding pairs}\end{array} \longrightarrow \begin{array}{c}\text{determine geometry}\\ \text{based on bonding pairs}\end{array}$$

Solution (a) The Lewis structure of AsH_3 is



$$\begin{array}{c}\mathrm{H{-}\ddot{As}{-}H}\\ |\\ \mathrm{H}\end{array}$$

There are four electron pairs around the central atom; therefore, the electron pair arrangement is tetrahedral (see Table 10.1). Recall that the geometry of a molecule is determined only by the arrangement of atoms (in this case the As and H atoms). Thus, removing the lone pair leaves us with three bonding pairs and a trigonal pyramidal geometry, like NH_3. We cannot predict the HAsH angle accurately, but we know that it is less than 109.5° because the repulsion of the bonding electron pairs in the As—H bonds by the lone pair on As is greater than the repulsion between the bonding pairs.

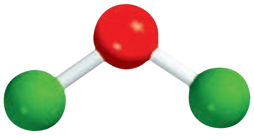


AsH_3

(b) The Lewis structure of OF_2 is

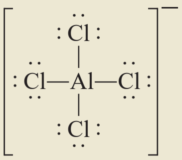
$$:\underset{..}{\ddot{\mathrm{F}}}{-}\underset{..}{\ddot{\mathrm{O}}}{-}\underset{..}{\ddot{\mathrm{F}}}:$$

There are four electron pairs around the central atom; therefore, the electron pair arrangement is tetrahedral (see Table 10.1). Recall that the geometry of a molecule is determined only by the arrangement of atoms (in this case the O and F atoms). Thus, removing the two lone pairs leaves us with two bonding pairs and a bent geometry, like H_2O. We cannot predict the FOF angle accurately, but we know that it must be less than 109.5° because the repulsion of the bonding electron pairs in the O—F bonds by the lone pairs on O is greater than the repulsion between the bonding pairs.



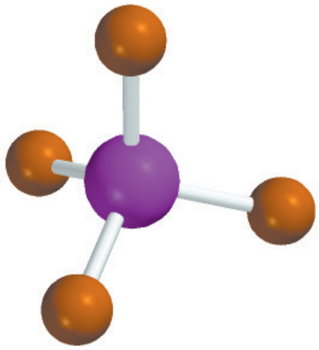
OF_2

(c) The Lewis structure of $AlCl_4^-$ is



$$\left[\begin{array}{c}:\underset{}{\ddot{\mathrm{Cl}}}:\\ |\\ :\underset{..}{\ddot{\mathrm{Cl}}}{-}\mathrm{Al}{-}\underset{..}{\ddot{\mathrm{Cl}}}:\\ |\\ :\underset{..}{\mathrm{Cl}}:\end{array}\right]^-$$

(Continued)

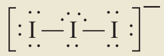


$AlCl_4^-$

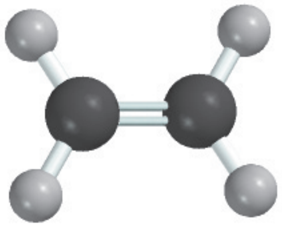
There are four electron pairs around the central atom; therefore, the electron pair arrangement is tetrahedral. Because there are no lone pairs present, the arrangement of the bonding pairs is the same as the electron pair arrangement. Therefore, $AlCl_4^-$ has a tetrahedral geometry and the ClAlCl angles are all 109.5°.

I_3^-

(d) The Lewis structure of I_3^- is

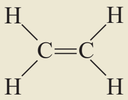


There are five electron pairs around the central I atom; therefore, the electron pair arrangement is trigonal bipyramidal. Of the five electron pairs, three are lone pairs and two are bonding pairs. Recall that the lone pairs preferentially occupy the equatorial positions in a trigonal bipyramid (see Table 10.2). Thus, removing the lone pairs leaves us with a linear geometry for I_3^-, that is, all three I atoms lie in a straight line.

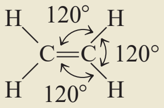


C_2H_4

(e) The Lewis structure of C_2H_4 is



The C=C bond is treated as though it were a single bond in the VSEPR model. Because there are three electron pairs around each C atom and there are no lone pairs present, the arrangement around each C atom has a trigonal planar shape like BF_3, discussed earlier. Thus, the predicted bond angles in C_2H_4 are all 120°.



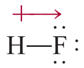
Comment (1) The I_3^- ion is one of the few structures for which the bond angle (180°) can be predicted accurately even though the central atom contains lone pairs. (2) In C_2H_4, all six atoms lie in the same plane. The overall planar geometry is not predicted by the VSEPR model, but we will see why the molecule prefers to be planar later. In reality, the angles are close, but not equal, to 120° because the bonds are not all equivalent.

Similar problems: 10.7, 10.8, 10.9.

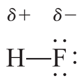
Practice Exercise Use the VSEPR model to predict the geometry of (a) $SiBr_4$, (b) CS_2, and (c) NO_3^-.

10.2 Dipole Moments

In Section 9.2, we learned that hydrogen fluoride is a covalent compound with a polar bond. There is a shift of electron density from H to F because the F atom is more electronegative than the H atom (see Figure 9.3). The shift of electron density is symbolized by placing a crossed arrow (+⟶) above the Lewis structure to indicate the direction of the shift. For example,



The consequent charge separation can be represented as



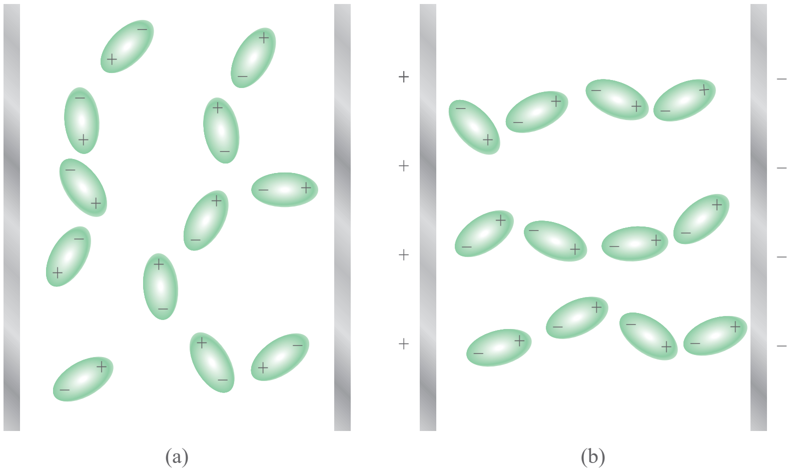


Figure 10.3
Behavior of polar molecules (a) in the absence of an external electric field and (b) when the electric field is turned on. Nonpolar molecules are not affected by an electric field.

where δ (delta) denotes a partial charge. This separation of charges can be confirmed in an electric field (Figure 10.3). When the field is turned on, HF molecules orient their negative ends toward the positive plate and their positive ends toward the negative plate. This alignment of molecules can be detected experimentally.

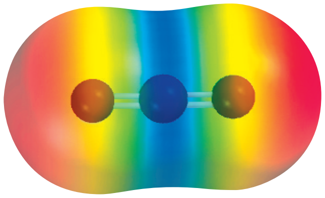
A quantitative measure of the polarity of a bond is its ***dipole moment (μ),***

To maintain electrical neutrality, the charges on both ends of an electrically neutral diatomic molecule must be equal in magnitude and opposite in sign. Dipole moments are usually expressed in debye units (D), named for the Dutch-American chemist and physicist Peter Debye.

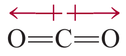
In a diatomic molecule like HF, the charge Q is equal to $\delta+$ and $\delta-$.

Diatomic molecules containing atoms of *different* elements (for example, HCl, CO, and NO) *have dipole moments* and are called ***polar molecules.*** Diatomic molecules containing atoms of the *same* element (for example, H_2, O_2, and F_2) are examples of ***nonpolar molecules*** because they *do not have dipole moments.* For a molecule made up of three or more atoms, both the polarity of the bonds and the molecular geometry determine whether there is a dipole moment. **Even if polar bonds are pres-ent, the molecule will not necessarily have a dipole moment.** Carbon dioxide (CO_2), for example, is a triatomic molecule, so its geometry is either linear or bent:

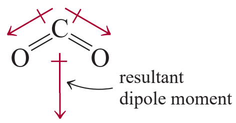
Animation:
Polarity of Molecules
ARIS, Animations



Each carbon-to-oxygen bond is polar, with the electron density shifted toward the more electronegative oxygen atom. However, the linear geometry of the molecule results in the cancellation of the two bond moments.



linear molecule
(no dipole moment)



bent molecule
(would have a dipole moment)

The arrows show the shift of electron density from the less electronegative carbon atom to the more electronegative oxygen atom. In each case, the dipole moment of the entire molecule is made up of two *bond moments,* that is, individual dipole

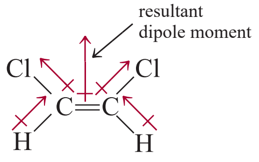
TABLE 10.3 Dipole Moments of Some Polar Molecules

Molecule	Geometry	Dipole Moment (D)
HF	Linear	1.92
HCl	Linear	1.08
HBr	Linear	0.78
HI	Linear	0.38
H_2O	Bent	1.87
H_2S	Bent	1.10
NH_3	Trigonal pyramidal	1.46
SO_2	Bent	1.60

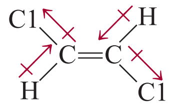
moments in the polar C═O bonds. The bond moment is a *vector quantity,* which means that it has both magnitude and direction. The measured dipole moment is equal to the vector sum of the bond moments. The two bond moments in CO_2 are equal in magnitude. Because they point in opposite directions in a linear CO_2 molecule, the sum or resultant dipole moment would be zero. On the other hand, if the CO_2 molecule were bent, the two bond moments would partially reinforce each other, so that the molecule would have a dipole moment. Experimentally it is found that carbon dioxide has no dipole moment. Therefore, we conclude that the carbon dioxide molecule is linear. The linear nature of carbon dioxide has been confirmed through other experimental measurements.

The VSEPR model predicts that CO_2 is a linear molecule.

Dipole moments can be used to distinguish between molecules that have the same formula but different structures. For example, the following molecules both exist; they have the same molecular formula ($C_2H_2Cl_2$), the same number and type of bonds, but different molecular structures:



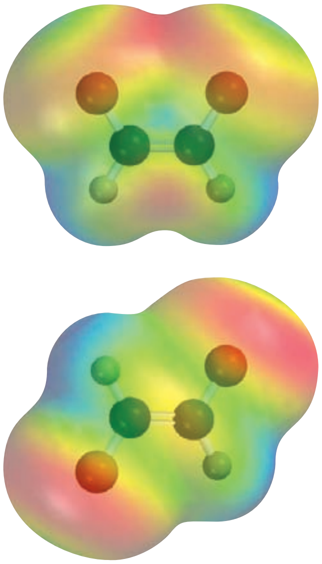
cis-dichloroethylene
$\mu = 1.89$ D



trans-dichloroethylene
$\mu = 0$

Because *cis*-dichloroethylene is a polar molecule but *trans*-dichloroethylene is not, they can readily be distinguished by a dipole moment measurement. Additionally, as we will see in Chapter 11, the strength of intermolecular forces is partially determined by whether molecules possess a dipole moment. Table 10.3 lists the dipole moments of several polar molecules.

Example 10.2 shows how we can predict whether a molecule possesses a dipole moment if we know its molecular geometry.



In *cis*-dichloroethylene (top), the bond moments reinforce one another and the molecule is polar. The opposite holds for *trans*-dichloroethylene (bottom) and the molecule is nonpolar.

Example 10.2

Predict whether each of the following molecules has a dipole moment: (a) IBr, (b) BF_3 (trigonal planar), (c) CH_2Cl_2 (tetrahedral).

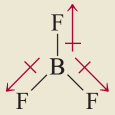
(*Continued*)

Strategy Keep in mind that the dipole moment of a molecule depends on both the difference in electronegativities of the elements present and its geometry. A molecule can have polar bonds (if the bonded atoms have different electronegativities), but it may not possess a dipole moment if it has a highly symmetrical geometry.

Solution (a) Because IBr (iodine bromide) is diatomic, it has a linear geometry. Bromine is more electronegative than iodine (see Figure 9.4), so IBr is polar with bromine at the negative end.

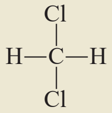
Thus, the molecule does have a dipole moment.

(b) Because fluorine is more electronegative than boron, each B—F bond in BF_3 (boron trifluoride) is polar and the three bond moments are equal. However, the symmetry of a trigonal planar shape means that the three bond moments exactly cancel one another:



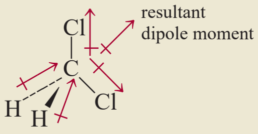
An analogy is an object that is pulled in the directions shown by the three bond moments. If the forces are equal, the object will not move. Consequently, BF_3 has no dipole moment; it is a nonpolar molecule.

(c) The Lewis structure of CH_2Cl_2 (methylene chloride) is



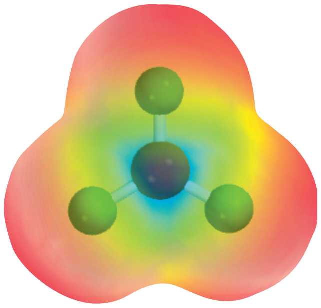
$$\begin{array}{c} \text{Cl} \\ | \\ \text{H—C—H} \\ | \\ \text{Cl} \end{array}$$

This molecule is similar to CH_4 in that it has an overall tetrahedral shape. However, because not all the bonds are identical, there are three different bond angles: HCH, HCCl, and ClCCl. These bond angles are close to, but not equal to, 109.5°. Because chlorine is more electronegative than carbon, which is more electronegative than hydrogen, the bond moments do not cancel and the molecule possesses a dipole moment:

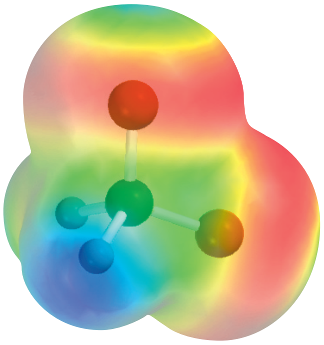


Thus, CH_2Cl_2 is a polar molecule.

Practice Exercise Does the $AlCl_3$ molecule have a dipole moment?



Electrostatic potential map shows that the electron density is symmetrically distributed in the BF_3 molecule.



Electrostatic potential map of CH_2Cl_2. The electron density is shifted toward the electronegative Cl atoms.

Similar problems: 10.19, 10.21, 10.22.

10.3 Valence Bond Theory

The VSEPR model, based largely on Lewis structures, provides a relatively simple and straightforward method for predicting the geometry of molecules. But as we noted earlier, the Lewis theory of chemical bonding does not clearly explain why chemical bonds exist. Relating the formation of a covalent bond to the pairing of electrons was a step in the right direction, but it did not go far enough. For example, the Lewis theory describes the single bond between the H atoms in H_2 and that between the F atoms in F_2 in essentially the same way—as the pairing of two electrons. Yet these two molecules have quite different bond enthalpies and bond lengths (436.4 kJ/mol and 74 pm for H_2 and 150.6 kJ/mol and 142 pm for F_2). These and many other facts cannot be explained by the Lewis theory. For a more complete explanation of chemical bond formation we look to quantum mechanics. In fact, the quantum mechanical study of chemical bonding also provides a means for understanding molecular geometry.

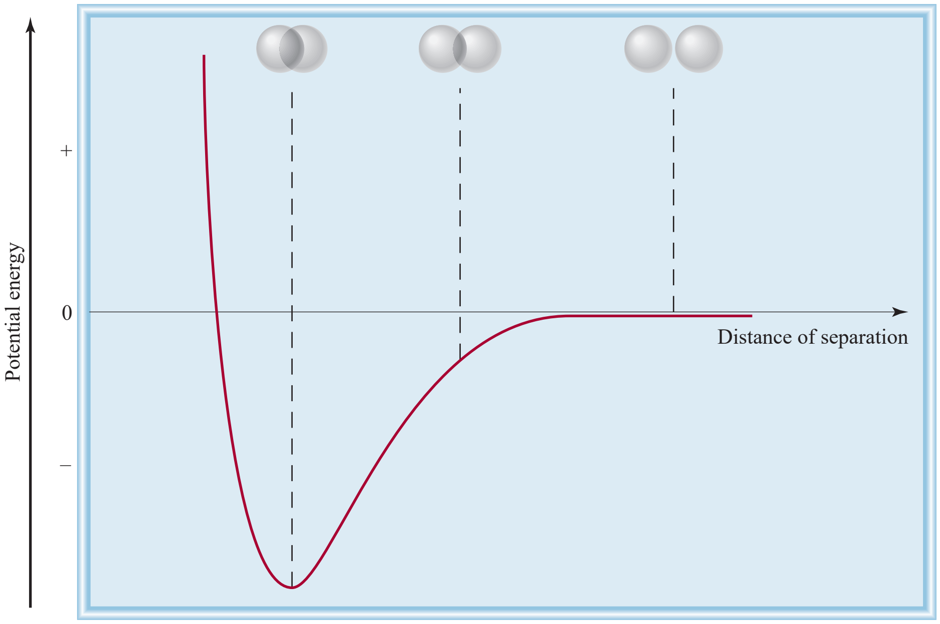
At present, two quantum mechanical theories are used to describe covalent bond formation and the electronic structure of molecules. *Valence bond (VB) theory* assumes that the electrons in a molecule occupy atomic orbitals of the individual atoms. It enables us to retain a picture of individual atoms taking part in the bond formation. The second theory, called *molecular orbital (MO) theory,* assumes the formation of molecular orbitals from the atomic orbitals. Neither theory perfectly explains all aspects of bonding, but each has contributed something to our understanding of many observed molecular properties.

Let us start our discussion of valence bond theory by considering the formation of a H_2 molecule from two H atoms. The Lewis theory describes the H—H bond in terms of the pairing of the two electrons on the H atoms. In the framework of valence bond theory, the covalent H—H bond is formed by the *overlap* of the two 1*s* orbitals in the H atoms. By overlap, we mean that the two orbitals share a common region in space.

Recall that an object has potential energy by virtue of its position.

What happens to two H atoms as they move toward each other and form a bond? Initially, when the two atoms are far apart, there is no interaction. We say that the potential energy of this system (that is, the two H atoms) is zero. As the atoms approach each other, each electron is attracted by the nucleus of the other atom; at the same time, the electrons repel each other, as do the nuclei. While the atoms are still separated, attraction is stronger than repulsion, so that the potential energy of the system *decreases* (that is, it becomes negative) as the atoms approach each other (Figure 10.4). This trend continues until the potential energy reaches a minimum value. At this point, when the system has the lowest potential energy, it is most stable. This condition corresponds to substantial overlap of the 1*s* orbitals and the formation of a

Figure 10.4
Change in potential energy of two H atoms with their distance of separation. At the point of minimum potential energy, the H_2 molecule is in its most stable state and the bond length is 74 pm. The spheres represent the 1s orbitals.



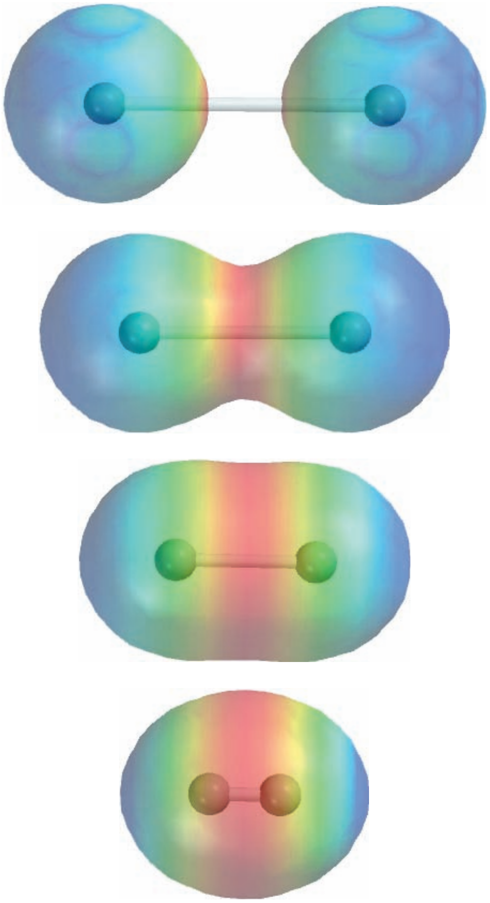


Figure 10.5
Top to bottom: As two H atoms approach each other, their 1s orbitals begin to interact and each electron begins to feel the attraction of the other proton. Gradually, the electron density builds up in the region between the two nuclei (red color). Eventually, a stable H_2 molecule is formed when the internuclear distance is 74 pm.

stable H_2 molecule. If the distance between nuclei were to decrease further, the potential energy would rise steeply and finally become positive as a result of the increased electron-electron and nuclear-nuclear repulsions. In accord with the law of conservation of energy, the decrease in potential energy as a result of H_2 formation must be accompanied by a release of energy. Experiments show that as a H_2 molecule is formed from two H atoms, heat is given off. The converse is also true. To break a H—H bond, energy must be supplied to the molecule. Figure 10.5 is another way of viewing the formation of an H_2 molecule.

Thus, valence bond theory gives a clearer picture of chemical bond formation than the Lewis theory does. Valence bond theory states that a stable molecule forms from reacting atoms when the potential energy of the system has decreased to a minimum; the Lewis theory ignores energy changes in chemical bond formation.

The concept of overlapping atomic orbitals applies equally well to diatomic molecules other than H_2. Thus, a stable F_2 molecule forms when the 2*p* orbitals (containing the unpaired electrons) in the two F atoms overlap to form a covalent bond. Similarly, the formation of the HF molecule can be explained by the overlap of the 1*s* orbital in H with the 2*p* orbital in F. In each case, VB theory accounts for the changes in potential energy as the distance between the reacting atoms changes. Because the orbitals involved are not the same kind in all cases, we can see why the bond enthalpies and bond lengths in H_2, F_2, and HF might be different. As we stated earlier, Lewis theory treats *all* covalent bonds the same way and offers no explanation for the differences among covalent bonds.

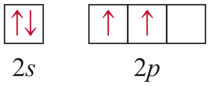
The orbital diagram of the F atom is shown on p. 231.

10.4 Hybridization of Atomic Orbitals

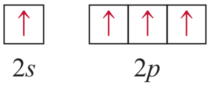
The concept of atomic orbital overlap should apply also to polyatomic molecules. However, a satisfactory bonding scheme must account for molecular geometry. We will discuss three examples of VB treatment of bonding in polyatomic molecules.

sp^3 Hybridization

Consider the CH_4 molecule. Focusing only on the valence electrons, we can represent the orbital diagram of C as

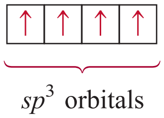


Because the carbon atom has two unpaired electrons (one in each of the two 2*p* orbitals), it can form only two bonds with hydrogen in its ground state. Although the species CH_2 is known, it is very unstable. To account for the four C—H bonds in methane, we can try to promote (that is, energetically excite) an electron from the 2*s* orbital to the 2*p* orbital:



Now there are four unpaired electrons on C that could form four C—H bonds. However, the geometry is wrong, because three of the HCH bond angles would have to be 90° (remember that the three 2*p* orbitals on carbon are mutually perpendicular), and yet *all* HCH angles are 109.5°.

To explain the bonding in methane, VB theory uses hypothetical ***hybrid orbitals,*** which are *atomic orbitals obtained when two or more nonequivalent orbitals of the same atom combine in preparation for covalent bond formation.* ***Hybridization*** is the term applied to *the mixing of atomic orbitals in an atom (usually a central atom) to generate a set of hybrid orbitals.* We can generate four equivalent hybrid orbitals for carbon by mixing the 2*s* orbital and the three 2*p* orbitals:



Because the new orbitals are formed from one *s* and three *p* orbitals, they are called *sp*^{3} hybrid orbitals. Figure 10.6 shows the shape and orientations of the *sp*^{3} orbitals. These four hybrid orbitals are directed toward the four corners of a regular tetrahedron. Figure 10.7 shows the formation of four covalent bonds between the carbon *sp*^{3} hybrid orbitals and the hydrogen 1*s* orbitals in CH_4. Thus, CH_4 has a tetrahedral shape, and all the HCH angles are 109.5°. Note that although energy is required to bring about hybridization, this input is more than compensated for by the energy released upon the formation of C—H bonds. (Recall that bond formation is an exothermic process.)

The following analogy is useful for understanding hybridization. Suppose that we have a beaker of a red solution and three beakers of blue solutions and that the volume of each is 50 mL. The red solution corresponds to one 2*s* orbital, the blue solutions represent three 2*p* orbitals, and the four equal volumes symbolize four separate orbitals. By mixing the solutions we obtain 200 mL of a purple solution, which can be divided into four 50-mL portions (that is, the hybridization process generates four sp^3 orbitals). Just as the purple color is made up of the red and blue components of the original solutions, the sp^3 hybrid orbitals possess both s and p orbital characteristics.

Another example of sp^3 hybridization is ammonia (NH_3). Table 10.1 shows that the arrangement of four electron pairs is tetrahedral, so that the bonding in NH_3 can be explained by assuming that N, like C in CH_4, is sp^3-hybridized. The ground-state electron configuration of N is $1s^22s^22p^3$, so that the orbital diagram for the sp^3 hybridized N atom is

$$\underbrace{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow\downarrow}}_{sp^3\text{ orbitals}}$$

Three of the four hybrid orbitals form covalent N—H bonds, and the fourth hybrid orbital accommodates the lone pair on nitrogen (Figure 10.8). Repulsion between the lone-pair electrons and electrons in the bonding orbitals decreases the HNH bond angles from 109.5° to 107.3°.

It is important to understand the relationship between hybridization and the VSEPR model. We use hybridization to describe the bonding scheme only when the arrangement of electron pairs has been predicted using VSEPR. If the VSEPR model predicts a tetrahedral arrangement of electron pairs, then we assume that one s and three p orbitals are hybridized to form four sp^3 hybrid orbitals. The following are examples of other types of hybridization.

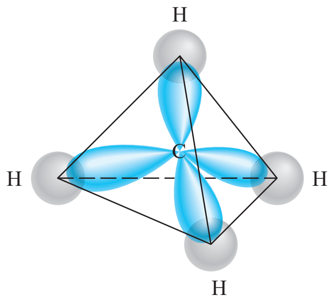


Figure 10.7
Formation of four bonds between the carbon sp^3 hybrid orbitals and the hydrogen 1s orbitals in CH_4.

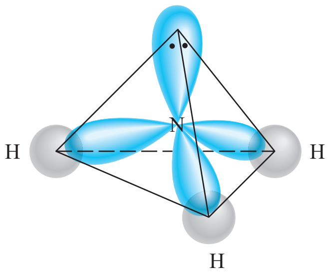


Figure 10.8
The sp^3-hybridized N atom in NH_3. Three sp^3 hybrid orbitals form bonds with the H atoms. The fourth is occupied by nitrogen's lone pair.

sp Hybridization

The beryllium chloride ($BeCl_2$) molecule is predicted to be linear by VSEPR. The orbital diagram for the valence electrons in Be is

$$\underset{2s}{\boxed{\uparrow\downarrow}} \qquad \underset{2p}{\boxed{}\boxed{}\boxed{}}$$

We know that in its ground state Be does not form covalent bonds with Cl because its electrons are paired in the 2*s* orbital. So we turn to hybridization for an explanation of Be's bonding behavior. First, we promote a 2*s* electron to a 2*p* orbital, resulting in

$$\underset{2s}{\boxed{\uparrow}} \qquad \underset{2p}{\boxed{\uparrow}\boxed{}\boxed{}}$$

Now there are two Be orbitals available for bonding, the 2*s* and 2*p*. However, if two Cl atoms were to combine with Be in this excited state, one Cl atom would share a 2*s* electron and the other Cl would share a 2*p* electron, making two nonequivalent BeCl bonds. This scheme contradicts experimental evidence. In the actual $BeCl_2$ molecule, the two BeCl bonds are identical in every respect. Thus, the 2*s* and 2*p* orbitals must be mixed, or hybridized, to form two equivalent *sp* hybrid orbitals:

$$\underbrace{\boxed{\uparrow}\boxed{\uparrow}}_{sp\ \text{orbitals}} \qquad \underset{\text{empty } 2p \text{ orbitals}}{\boxed{}\boxed{}}$$

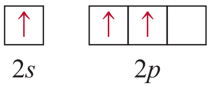
Figure 10.9 shows the shape and orientation of the *sp* orbitals. These two hybrid orbitals lie on the same line, the *x*-axis, so that the angle between them is 180°. Each of the BeCl bonds is then formed by the overlap of a Be *sp* hybrid orbital and a Cl 3*p* orbital, and the resulting $BeCl_2$ molecule has a linear geometry (Figure 10.10).

sp^2 Hybridization

Next we will look at the BF_3 (boron trifluoride) molecule, known to have planar geometry based on VSEPR. Considering only the valence electrons, the orbital diagram of B is

$$\underset{2s}{\boxed{\uparrow\downarrow}} \qquad \underset{2p}{\boxed{\uparrow}\boxed{}\boxed{}}$$

First, we promote a 2*s* electron to an empty 2*p* orbital:



Mixing the 2*s* orbital with the two 2*p* orbitals generates three sp^2 hybrid orbitals:

sp^2 is pronounced "*s-p* two."

These three sp^2 orbitals lie in the same plane, and the angle between any two of them is 120° (Figure 10.11). Each of the BF bonds is formed by the overlap of a boron sp^2 hybrid orbital and a fluorine 2*p* orbital (Figure 10.12). The BF_3 molecule is planar with all the FBF angles equal to 120°. This result conforms to experimental findings and also to VSEPR predictions.

You may have noticed an interesting connection between hybridization and the octet rule. Regardless of the type of hybridization, an atom starting with one *s* and three *p* orbitals would still possess four orbitals, enough to accommodate a total of eight electrons in a compound. For elements in the second period of the periodic table, eight is the maximum number of electrons that an atom of any of these elements can accommodate in the valence shell. This is the reason that the octet rule is usually obeyed by the second-period elements.

The situation is different for an atom of a third-period element. If we use only the 3*s* and 3*p* orbitals of the atom to form hybrid orbitals in a molecule, then the octet rule applies. However, in some molecules the same atom may use one or more 3*d* orbitals, in addition to the 3*s* and 3*p* orbitals, to form hybrid orbitals. In these cases, the octet rule does not hold. We will see specific examples of the participation of the 3*d* orbital in hybridization shortly.

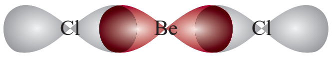


Figure 10.10
The linear geometry of $BeCl_2$ can be explained by assuming that Be is sp-hybridized. The two sp hybrid orbitals overlap with the two chlorine 3p orbitals to form two covalent bonds.

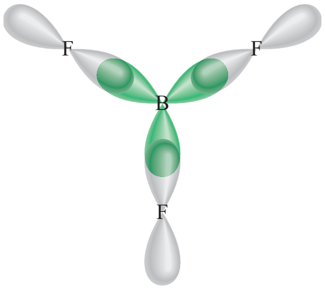


Figure 10.12
The sp^2 hybrid orbitals of boron overlap with the 2p orbitals of fluorine. The BF_3 molecule is planar, and all the FBF angles are 120°.

To summarize our discussion of hybridization, we note that

1. The concept of hybridization is not applied to isolated atoms. It is a theoretical model used only to explain covalent bonding.
2. Hybridization is the mixing of at least two nonequivalent atomic orbitals, for example, *s* and *p* orbitals. Therefore, a hybrid orbital is not a pure atomic orbital. Hybrid orbitals and pure atomic orbitals have very different shapes.
3. The number of hybrid orbitals generated is equal to the number of pure atomic orbitals that participate in the hybridization process.
4. Hybridization requires an input of energy; however, the system more than recovers this energy during bond formation.
5. Covalent bonds in polyatomic molecules and ions are formed by the overlap of hybrid orbitals, or of hybrid orbitals with unhybridized ones. Therefore, the hybridization bonding scheme is still within the framework of valence bond theory; electrons in a molecule are assumed to occupy hybrid orbitals of the individual atoms.

Procedure for Hybridizing Atomic Orbitals

Before going on to discuss the hybridization of *d* orbitals, let us specify what we need to know to apply hybridization to bonding in polyatomic molecules in general. In essence, hybridization simply extends Lewis theory and the VSEPR model. To assign a suitable state of hybridization to the central atom in a molecule, we must have some idea about the geometry of the molecule. The steps are as follows:

1. Draw the Lewis structure of the molecule.
2. Predict the overall arrangement of the electron pairs (both bonding pairs and lone pairs) using the VSEPR model (see Table 10.1).
3. Deduce the hybridization of the central atom by matching the arrangement of the electron pairs with those of the hybrid orbitals shown in Table 10.4.

Example 10.3

Determine the hybridization state of the central (underlined) atom in each of the following molecules: (a) <u>Be</u>H_2, (b) <u>Al</u>I_3, and (c) <u>P</u>F_3. Describe the hybridization process and determine the molecular geometry in each case.

Strategy The steps for determining the hybridization of the central atom in a molecule are:

draw Lewis structure of the molecule ⟶ use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1) ⟶ use Table 10.4 to determine the hybridization state of the central atom

Solution (a) The ground-state electron configuration of Be is $1s^22s^2$ and the Be atom has two valence electrons. The Lewis structure of BeH_2 is

$$H—Be—H$$

(*Continued*)

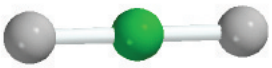
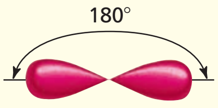
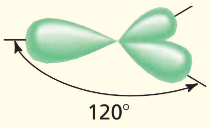
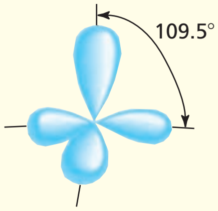

BeH_2

TABLE 10.4 Important Hybrid Orbitals and Their Shapes

Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
s, *p*	*sp*	2	 Linear	$BeCl_2$
s, *p*, *p*	sp^2	3	 Trigonal planar	BF_3
s, *p*, *p*, *p*	sp^3	4	 Tetrahedral	CH_4, NH_4^+

There are two bonding pairs around Be; therefore, the electron pair arrangement is linear. We conclude that Be uses *sp* hybrid orbitals in bonding with H, because *sp* orbitals have a linear arrangement (see Table 10.4). The hybridization process can be imagined as follows. First we draw the orbital diagram for the ground state of Be:

$$\underset{2s}{\boxed{\uparrow\downarrow}}\qquad\underset{2p}{\boxed{}\boxed{}\boxed{}}$$

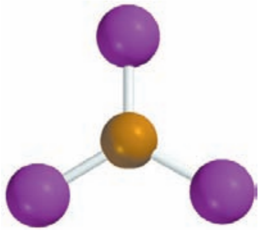
By promoting a 2*s* electron to the 2*p* orbital, we get the excited state:

$$\underset{2s}{\boxed{\uparrow}}\qquad\underset{2p}{\boxed{\uparrow}\boxed{}\boxed{}}$$

The 2*s* and 2*p* orbitals then mix to form two hybrid orbitals:

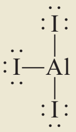
$$\underbrace{\boxed{\uparrow}\boxed{\uparrow}}_{sp\text{ orbitals}}\qquad\underset{\substack{\text{empty }2p\\ \text{orbitals}}}{\boxed{}\boxed{}}$$

The two Be—H bonds are formed by the overlap of the Be *sp* orbitals with the 1*s* orbitals of the H atoms. Thus, BeH_2 is a linear molecule.



AlI_3

(b) The ground-state electron configuration of Al is $[Ne]3s^23p^1$. Therefore, the Al atom has three valence electrons. The Lewis structure of AlI_3 is



There are three pairs of electrons around Al; therefore, the electron pair arrangement is trigonal planar. We conclude that Al uses sp^2 hybrid orbitals in bonding with I because sp^2 orbitals have a trigonal planar arrangement (see Table 10.4). The orbital diagram of the ground-state Al atom is

$$\underset{3s}{\boxed{\uparrow\downarrow}}\qquad\underset{3p}{\boxed{\uparrow}\boxed{}\boxed{}}$$

By promoting a 3*s* electron into the 3*p* orbital we obtain the following excited state:

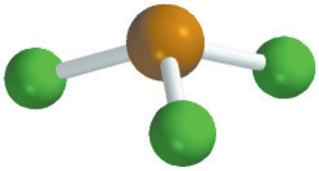
$$\underset{3s}{\boxed{\uparrow}}\qquad\underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}}$$

The 3*s* and two 3*p* orbitals then mix to form three sp^2 hybrid orbitals:

$$\underbrace{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}_{sp^2\text{ orbitals}}\qquad\underset{\substack{\text{empty }3p\\ \text{orbitals}}}{\boxed{}}$$

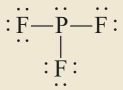
The sp^2 hybrid orbitals overlap with the 5*p* orbitals of I to form three covalent Al—I bonds. We predict that the AlI_3 molecule is trigonal planar and all the IAlI angles are 120°.

(Continued)



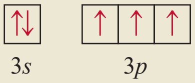
PF$_3$

(c) The ground-state electron configuration of P is [Ne]$3s^2 3p^3$. Therefore, the P atom has five valence electrons. The Lewis structure of PF$_3$ is

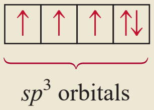


$$\begin{array}{c} :\underset{\cdot\cdot}{\ddot{F}}-\ddot{P}-\ddot{F}: \\ | \\ :\underset{\cdot\cdot}{F}: \end{array}$$

There are four pairs of electrons around P; therefore, the electron pair arrangement is tetrahedral. We conclude that P uses sp^3 hybrid orbitals in bonding to F, because sp^3 orbitals have a tetrahedral arrangement (see Table 10.4). The hybridization process can be imagined to take place as follows. The orbital diagram of the ground-state P atom is



By mixing the $3s$ and $3p$ orbitals, we obtain four sp^3 hybrid orbitals.



As in the case of NH$_3$, one of the sp^3 hybrid orbitals is used to accommodate the lone pair on P. The other three sp^3 hybrid orbitals form covalent P—F bonds with the $2p$ orbitals of F. We predict the geometry of the molecule to be trigonal pyramidal; the FPF angle should be somewhat less than 109.5°.

Practice Exercise Determine the hybridization state of the underlined atoms in the following compounds: (a) $\underline{Si}Br_4$ and (b) $\underline{B}Cl_3$.

10.5 Hybridization in Molecules Containing Double and Triple Bonds

The concept of hybridization is useful also for molecules with double and triple bonds. Consider the ethylene molecule, C_2H_4, as an example. In Example 10.1 we saw that C_2H_4 contains a carbon-carbon double bond and has planar geometry. Both the geometry and the bonding can be understood if we assume that each carbon atom is sp^2-hybridized. Figure 10.13 shows orbital diagrams of this hybridization process. We assume that only the $2p_x$ and $2p_y$ orbitals combine with the $2s$ orbital, and that the $2p_z$ orbital remains unchanged. Figure 10.14 shows that the $2p_z$ orbital is perpendicular to the plane of the hybrid orbitals. Now, how do we account for the bonding of the C atoms? As Figure 10.15(a) shows, each carbon atom uses the three sp^2 hybrid orbitals to form two bonds with the two hydrogen $1s$ orbitals and one bond with the sp^2 hybrid orbital of the adjacent C atom. In addition, the two unhybridized $2p_z$ orbitals of the C atoms form another bond by overlapping sideways [Figure 10.15(b)].

A distinction is made between the two types of covalent bonds in C_2H_4. The three bonds formed by each C atom in Figure 10.15(a) are all ***sigma bonds (σ bonds),*** *covalent bonds formed by orbitals overlapping end-to-end, with the electron density concentrated between the nuclei of the bonding atoms.* The second type is called a ***pi bond (π bond),*** which is defined as *a covalent bond formed by sideways overlapping orbitals with electron density concentrated above and below the plane of the nuclei of the bonding atoms.* The two C atoms form a pi bond, as shown in Figure 10.15(b). This pi bond formation gives ethylene its planar geometry. Figure 10.15(c) shows the orientation of the sigma and pi bonds. Figure 10.16 is yet another way of looking at the planar C_2H_4 molecule and the formation of the pi bond. Although we normally represent the carbon-carbon double bond as C═C (as in a Lewis structure), it is important to keep in mind that the two bonds are different types: One is a sigma bond and the other is a pi bond. In fact, the bond enthalpies of the carbon-carbon pi and sigma bonds are about 270 kJ/mol and 350 kJ/mol, respectively.

The acetylene molecule (C_2H_2) contains a carbon-carbon triple bond. Because the molecule is linear, we can explain its geometry and bonding by assuming that each C atom is sp-hybridized by mixing the $2s$ with the $2p_x$ orbital (Figure 10.17). As Figure 10.18 shows, the two sp hybrid orbitals of each C atom form one sigma bond with a hydrogen $1s$ orbital and another sigma bond with the other C atom. In addition, two pi bonds are formed by the sideways overlap of the unhybridized $2p_y$ and $2p_z$ orbitals. Thus, the C≡C bond is made up of one sigma bond and two pi bonds.

The following rule helps us predict hybridization in molecules containing multiple bonds: If the central atom forms a double bond, it is sp^2-hybridized; if it forms two double bonds or a triple bond, it is sp-hybridized. Note that this rule applies only to atoms of the second-period elements. Atoms of third-period elements and beyond that form multiple bonds present a more complicated picture and will not be dealt with here.

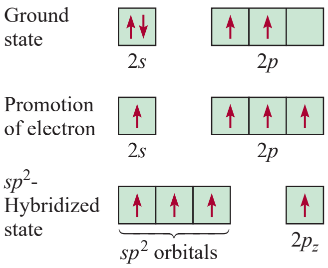
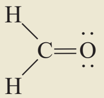


Figure 10.13
The sp^2 hybridization of a carbon atom. The 2s orbital is mixed with only two 2p orbitals to form three equivalent sp^2 hybrid orbitals. This process leaves an electron in the unhybridized orbital, the $2p_z$ orbital.

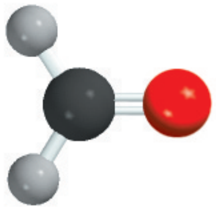
Example 10.5

Describe the bonding in the formaldehyde molecule whose Lewis structure is



Assume that the O atom is sp^2-hybridized.

(*Continued*)



CH_2O

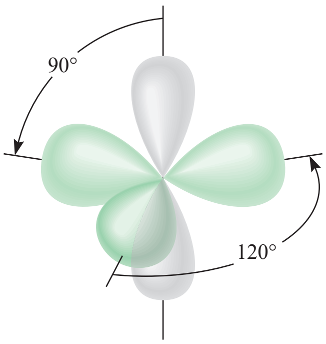


Figure 10.14
Each carbon atom in the C_2H_4 molecule has three sp^2 hybrid orbitals (green) and one unhybridized $2p_z$ orbital (gray), which is perpendicular to the plane of the hybrid orbitals.

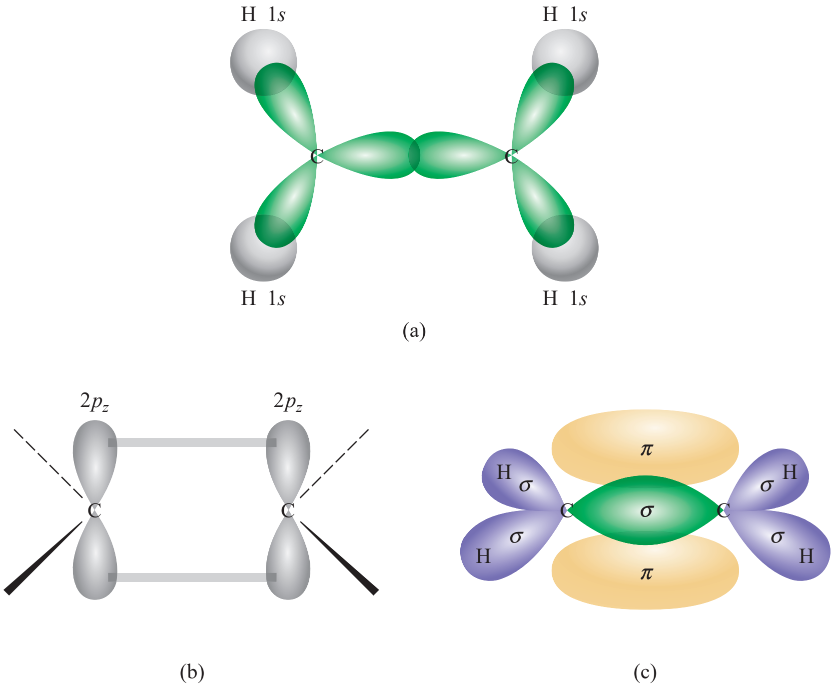
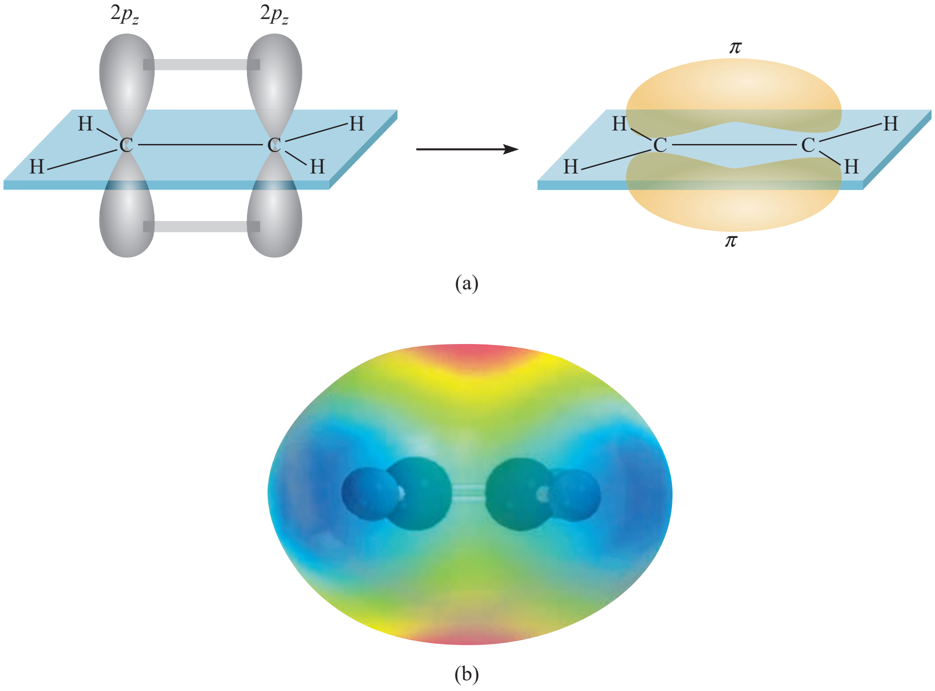


Figure 10.15
Bonding in ethylene, C_2H_4. (a) Top view of the sigma bonds between carbon atoms and between carbon and hydrogen atoms. All the atoms lie in the same plane, making C_2H_4 a planar molecule. (b) Side view showing how the two $2p_z$ orbitals on the two carbon atoms overlap, leading to the formation of a pi bond. (c) The interactions in (a) and (b) lead to the formation of the sigma bonds and the pi bond in ethylene. Note that the pi bond lies above and below the plane of the molecule.

Figure 10.16
(a) Another view of pi bond formation in the C_2H_4 molecule. Note that all six atoms are in the same plane. It is the overlap of the $2p_z$ orbitals that causes the molecule to assume a planar structure. (b) Electrostatic potential map of C_2H_4.



Strategy Follow the procedure shown in Example 10.3.

Solution There are three pairs of electrons around the C atom; therefore, the electron pair arrangement is trigonal planar. (Recall that a double bond is treated as a single bond in the VSEPR model.) We conclude that C uses sp^2 hybrid orbitals in bonding, because sp^2 hybrid orbitals have a trigonal planar arrangement (see Table 10.4). We can imagine the hybridization processes for C and O as follows:

$$\text{C}\quad \underset{2s}{\boxed{\uparrow\downarrow}}\quad \underset{2p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}}\ \rightarrow\ \underbrace{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}_{sp^2\text{ orbitals}}\quad \underset{2p_z}{\boxed{\uparrow}}$$

$$\text{O}\quad \underset{2s}{\boxed{\uparrow\downarrow}}\quad \underset{2p}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}}\ \rightarrow\ \underbrace{\boxed{\uparrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}_{sp^2\text{ orbitals}}\quad \underset{2p_z}{\boxed{\uparrow}}$$

Carbon has one electron in each of the three sp^2 orbitals, which are used to form sigma bonds with the H atoms and the O atom. There is also an electron in the $2p_z$ orbital, which forms a pi bond with oxygen. Oxygen has two electrons in two of its sp^2 hybrid orbitals. These are the lone pairs on oxygen. Its third sp^2 hybrid orbital with one electron is used to form a sigma bond with carbon. The $2p_z$ orbital (with one electron) overlaps with the $2p_z$ orbital of C to form a pi bond (Figure 10.19).

Practice Exercise Describe the bonding in the hydrogen cyanide molecule, HCN. Assume that N is *sp*-hybridized.

Similar problems: 10.36, 10.39.

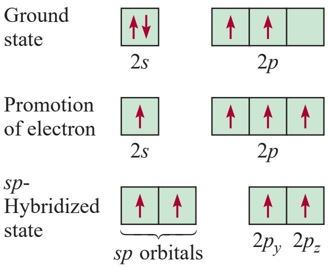
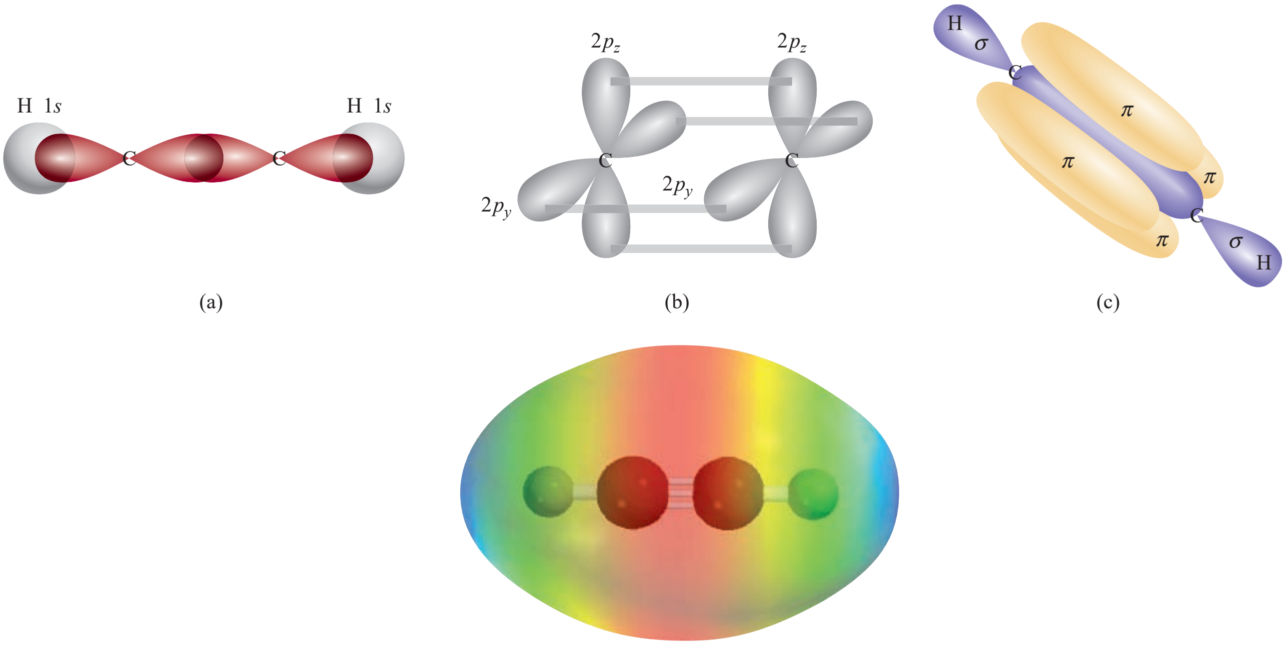


Figure 10.17
The sp hybridization of a carbon atom. The 2s orbital is mixed with only one 2p orbital to form two sp hybrid orbitals. This process leaves an electron in each of the two unhybridized 2p orbitals, namely, the $2p_y$ and $2p_z$ orbitals.



(a) (b) (c)

(d)

Figure 10.18
Bonding in acetylene, C_2H_2. (a) Top view showing the overlap of the sp orbitals between the C atoms and the overlap of the sp orbital with the 1s orbital between the C and H atoms. All the atoms lie along a straight line; therefore acetylene is a linear molecule. (b) Side view showing the overlap of the two $2p_y$ orbitals and of the two $2p_z$ orbitals of the two carbon atoms, which leads to the formation of two pi bonds. (c) Formation of the sigma and pi bonds as a result of the interactions in (a) and (b). (d) Electrostatic potential map of C_2H_2.

10.8 Delocalized Molecular Orbitals

So far we have discussed chemical bonding only in terms of electron pairs. However, the properties of a molecule cannot always be explained accurately by a single structure. A case in point is the O_3 molecule, discussed in Section 9.8. There we overcame the dilemma by introducing the concept of resonance. In this section we will tackle the problem in another way—by applying the molecular orbital approach. As in Section 9.8, we will use the benzene molecule and the carbonate ion as examples. Note that in discussing the bonding of polyatomic molecules or ions, it is convenient to determine first the hybridization state of the atoms present (a valence bond approach), followed by the formation of appropriate molecular orbitals.

The Benzene Molecule

Benzene (C_6H_6) is a planar hexagonal molecule with carbon atoms situated at the six corners. All carbon-carbon bonds are equal in length and strength, as are all carbon-hydrogen bonds, and the CCC and HCC angles are all 120°. Therefore, each carbon atom is sp^2-hybridized; it forms three sigma bonds with two adjacent carbon atoms and a hydrogen atom (Figure 10.28). This arrangement leaves an unhybridized $2p_z$ orbital on each carbon atom, perpendicular to the plane of the benzene molecule, or *benzene ring,* as it is often called. So far the description resembles the configuration of ethylene (C_2H_4), discussed in Section 10.5, except that in this case there are six unhybridized $2p_z$ orbitals in a cyclic arrangement.

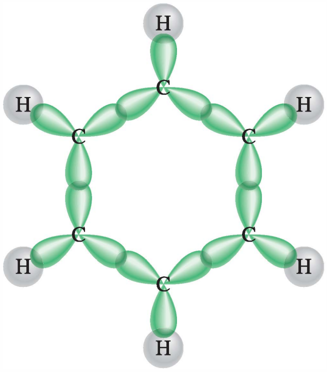
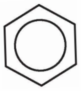


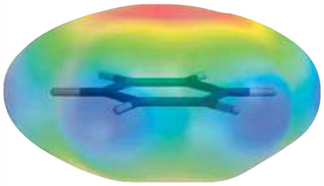
Figure 10.28 *The sigma bond framework in the benzene molecule. Each carbon atom is sp^2-hybridized and forms sigma bonds with two adjacent carbon atoms and another sigma bond with a hydrogen atom.*

Unlike the pi bonding in ethylene, those in benzene form ***delocalized orbitals,*** *are not confined between two adjacent bonding atoms, but actually extend over three or more atoms.* Therefore, electrons residing in any of these orbitals are free to move around the benzene ring. For this reason, the structure of benzene is sometimes represented as



in which the circle indicates that the pi bonds between carbon atoms are not confined to individual pairs of atoms; rather, the pi electron densities are evenly distributed throughout the benzene molecule. The carbon and hydrogen atoms are not shown in the simplified diagram.

We can now state that each carbon-to-carbon linkage in benzene contains a sigma bond and a "partial" pi bond. The bond order between any two adjacent carbon atoms is therefore between 1 and 2.

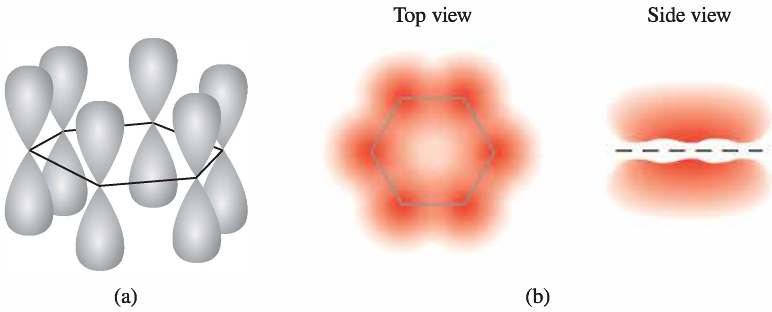


Electrostatic potential map of benzene shows the electron density (red color) above and below the plane of the molecule. For simplicity, only the framework of the molecule is shown.

The Carbonate Ion

Cyclic compounds like benzene are not the only ones with delocalized . Let's look at bonding in the carbonate ion (CO_3^{2-}). VSEPR predicts a trigoal planar geometry for the carbonate ion, like that for BF_3 The planar structure of

the carbonate ion can be explained by assuming that the carbon atom is sp^2-hybridized. The C atom forms sigma bonds with three O atoms. Thus, the unhybridized $2p_z$ orbital of the C atom can simultaneously overlap the $2p_z$ orbitals of all three O atoms



(a) (b)

Figure 10.29 *(a) The six $2p_z$ orbitals on the carbon atoms in benzene. (b) The delocalized molecular orbital formed by the overlap of the $2p_z$ orbitals. The delocalized molecular orbital possesses pi symmetry and lies above and below the plane of the benzene ring. Actually, these $2p_z$ orbitals can combine in six different ways to yield three bonding molecular orbitals and three antibonding molecular orbitals. The one shown here is the most stable.*

Summary of Facts and Concepts

1. The VSEPR model for predicting molecular geometry is based on the assumption that valence-shell electron pairs repel one another and tend to stay as far apart as possible. According to the VSEPR model, molecular geometry can be predicted from the number of bonding electron pairs and lone pairs. Lone pairs repel other pairs more strongly than bonding pairs do and thus distort bond angles from those of the ideal geometry.
2. The dipole moment is a measure of the charge separation in molecules containing atoms of different electronegativities. The dipole moment of a molecule is the resultant of whatever bond moments are present in a molecule. Information about molecular geometry can be obtained from dipole moment measurements.
3. In valence bond theory, hybridized atomic orbitals are formed by the combination and rearrangement of orbitals of the same atom. The hybridized orbitals are all of equal energy and electron density, and the number of hybridized orbitals is equal to the number of pure atomic orbitals that combine. Valence-shell expansion can be explained by assuming hybridization of *s*, *p*, and *d* orbitals.
4. In *sp* hybridization, the two hybrid orbitals lie in a straight line; in sp^2 hybridization, the three hybrid orbitals are directed toward the corners of a triangle; in sp^3 hybridization, the four hybrid orbitals are directed toward the corners of a tetrahedron;
5. In an sp^2-hybridized atom (for example, carbon), the one unhybridized *p* orbital can form a pi bond with another *p* orbital. A carbon-carbon double bond consists of a sigma bond and a pi bond. In an *sp*-hybridized carbon atom, the two unhybridized *p* orbitals can form two pi bonds with two *p* orbitals on another atom (or atoms). A carbon-carbon triple bond consists of one sigma bond and two pi bonds.

Key Words

Antibonding molecular orbital, p. 340
Bond order, p. 344
Bonding molecular orbital, p. 340
Dipole moment (μ), p. 323
Homonuclear diatomic molecule, p. 345
Hybrid orbital, p. 328
Hybridization, p. 328
Molecular orbital, p. 340
Nonpolar molecule, p. 323
Pi bond (π bond), p. 337
Pi molecular orbital, p. 342
Polar molecule, p. 323
Sigma bond (σ bond), p. 337
Sigma molecular orbital, p. 341
Valence shell, p. 313
Valence-shell electron-pair repulsion (VSEPR) model, p. 313

ANSWERS TO PRACTICE EXERCISES

10.1 (a) Tetrahedral, (b) linear, (c) trigonal planar. **10.2** No. **10.3** (a) sp^3, (b) sp^2. **10.4** sp^3d^2. **10.5** The C atom is *sp*-hybridized. It forms a sigma bond with the H atom and another sigma bond with the N atom. The two unhybridized *p* orbitals on the C atom are used to form two pi bonds with the N atom. The lone pair on the N atom is placed in the *sp* orbital. **10.6** F_2^-.