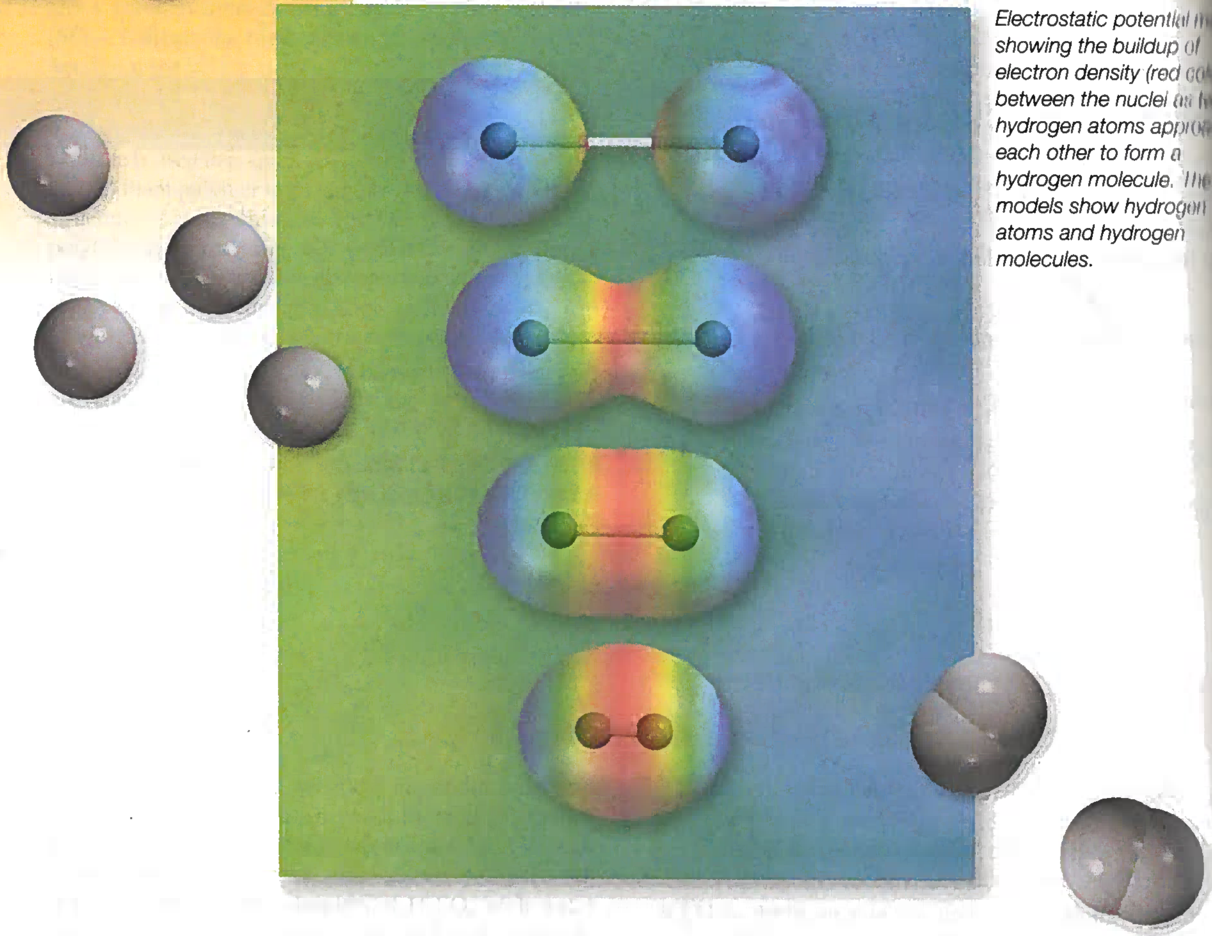
10



Electrostatic potential map showing the buildup of electron density (red color) between the nuclei as two hydrogen atoms approach each other to form a hydrogen molecule. The models show hydrogen atoms and hydrogen molecules.

Chemical Bonding II

Molecular Geometry and Hybridization of Atomic Orbitals

A LOOK AHEAD

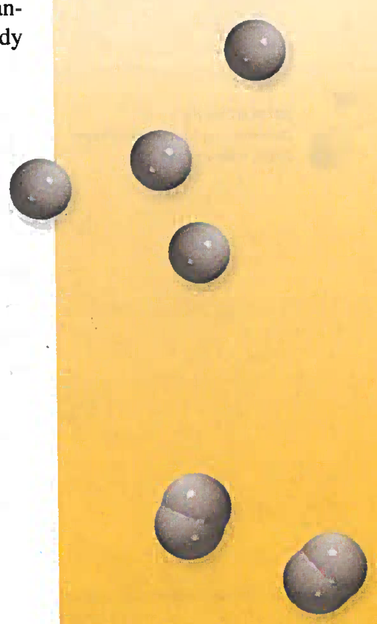
- We first examine the role of chemical bonds and lone pairs on the geometry of a molecule in terms of a simple approach called the VSEPR model (10.1)
- We then learn the factors that determine whether a molecule possesses a dipole moment and how its measurement can help us in the study of molecular geometry. (10.2)
- Next, we learn a quantum mechanical approach, called the valence bond (VB) theory, in the study of chemical bonds. The VB theory explains why and how chemical bonds form in terms of atomic orbital overlaps. (10.3)
- We see that the VB approach, in terms of the concept of mixing or hybridization of atomic orbitals, accounts for both chemical bond formation and molecular geometry. (10.4 and 10.5)
- We then examine another quantum mechanical treatment of the chemical bond, called the molecular orbital (MO) theory. The MO theory considers the formation of molecular orbitals as a result of the overlap of atomic orbitals, and is able to explain the paramagnetism of the oxygen molecule. (10.6)
- We see that writing molecular orbital configuration is analogous to writing electron configuration for atoms in that both the Pauli exclusion principle and Hund's rule apply. Using homonuclear diatomic molecules as examples, we can learn about the strength of a bond as well as general magnetic properties from the molecular orbital configurations. (10.7)
- Finally, the concept of molecular orbital formation is extended to delocalized molecular orbitals, which cover three or more atoms. We see that these delocalized orbitals impart extra stability to molecules like benzene. (10.8)

Interactive Activity Summary

1. Animation: VSEPR (10.1)
2. Interactivity: Determining Molecular Shape (10.1)
3. Animation: Polarity of Molecules (10.2)
4. Interactivity: Molecular Polarity (10.2)
5. Animation: Hybridization (10.4)
6. Interactivity: Determining Orbital Hybridization (10.4)
7. Animation: Sigma and Pi Bonds (10.5)

In Chapter 9 we discussed bonding in terms of the Lewis theory. Here we will study the shape, or geometry, of molecules. Geometry has an important influence on the physical and chemical properties of molecules, such as melting point, boiling point, and reactivity. We will see that we can predict the shapes of molecules with considerable accuracy using a simple method based on Lewis structures.

The Lewis theory of chemical bonding, although useful and easy to apply, does not tell us how and why bonds form. A proper understanding of bonding comes from quantum mechanics. Therefore, in the second part of this chapter, we will apply quantum mechanics to the study of the geometry and stability of molecules.



10.1 Molecular Geometry

The term "central atom" means an atom that is not a terminal atom in a polyatomic molecule.

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.*

VSEPR is pronounced "vesper."

Animation:
VSEPR
ARIS, Animations

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

Interactivity:
Determining Molecular Shape
ARIS, Interactives

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

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\!-\!\mathrm{Be}\!-\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$$

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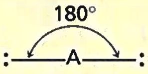
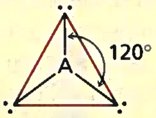
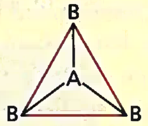
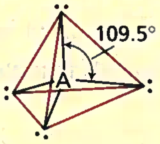
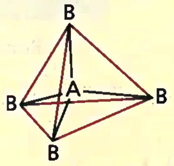
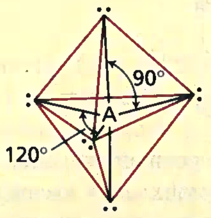
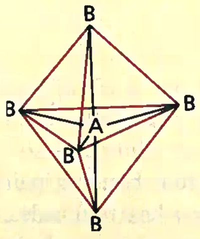
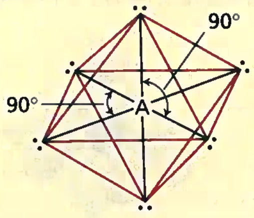
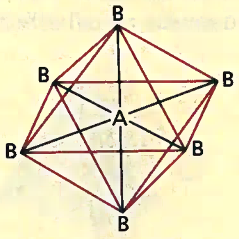
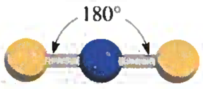
TABLE 10.1 Arrangement of Electron Pairs About a Central Atom (A) in a Molecule and Geometry of Some Simple Molecules and Ions in Which the Central Atom Has No Lone Pairs

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.

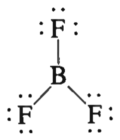
Because the bonding pairs repel each other, they must be at opposite ends of a straight line in order for them to be as far apart as possible. Thus, the ClBeCl angle is predicted to be 180°, and the molecule is linear (see Table 10.1). The "ball-and-stick" model of $BeCl_2$ is



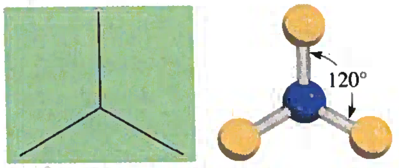
The blue and yellow spheres are for atoms in general.

AB_3: Boron Trifluoride (BF_3)

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



According to Table 10.1, the geometry of BF_3 is *trigonal planar* because the end atoms are at the corners of an equilateral triangle which is planar:

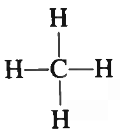


Planar

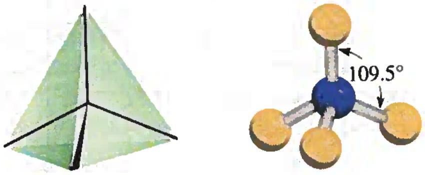
Thus, each of the three FBF angles is 120°, and all four atoms lie in the same

AB_4: Methane (CH_4)

The Lewis structure of methane is



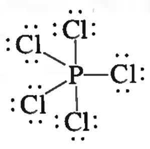
Because there are four bonding pairs, the geometry of CH_4 is tetrahedral (see 10.1). A *tetrahedron* has four sides (the prefix *tetra* means "four"), or faces, all which are equilateral triangles. In a tetrahedral molecule, the central atom (C in case) is located at the center of the tetrahedron and the other four atoms are at corners. The bond angles are all 109.5°.



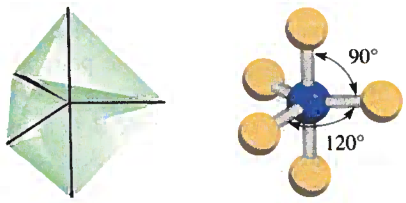
Tetrahedral

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 arrange the PCl bonds in the form of a trigonal bipyramid (see Table 10.1). A trigon bipyramid can be generated by joining two tetrahedrons along a common triangular base:

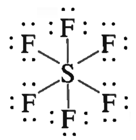


Trigonal bipyramidal

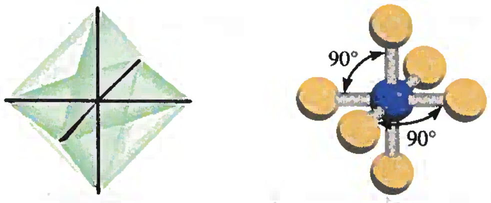
The central atom (P in this case) is at the center of the common triangle with the surrounding atoms positioned at the five corners of the trigonal bipyramid. The atoms that are above and below the triangular plane are said to occupy *axial* positions, and those that are in the triangular plane are said 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:

lone-pair vs. lone-pair repulsion > lone-pair vs. bonding-pair repulsion > bonding-pair vs. bonding-pair repulsion

For $x = 1$ we have a diatomic molecule, which by definition has a linear geometry.

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.

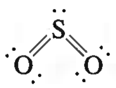
As the following examples show, in most cases the presence of lone pairs on the central atom makes it difficult to predict the bond angles accurately.

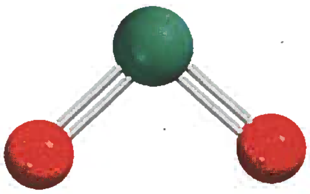
AB_2E: Sulfur Dioxide (SO_2)

The Lewis structure of sulfur dioxide is

$$\underset{\cdot\cdot}{\ddot{O}}=\ddot{S}=\underset{\cdot\cdot}{\ddot{O}}$$

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.



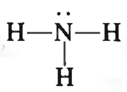


SO_2

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°.

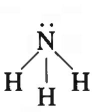
AB_3E: Ammonia (NH_3)

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

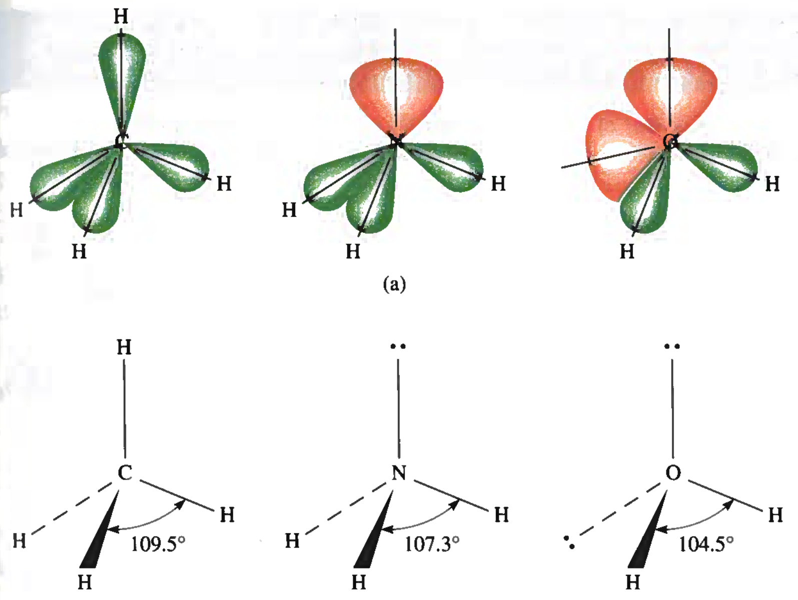


$$H-\underset{\displaystyle H}{\underset{|}{\ddot{N}}}-H$$

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:



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



(a)

(b)

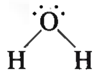
Figure 10.1 *(a) The relative sizes of bonding pairs and lone pairs in CH_4, NH_3, and H_2O. (b) The bond angles in CH_4, NH_3, and H_2O. Note that the dashed lines represent bond axes behind the plane of the paper, the wedged lines represent bond axes in front of the plane of the paper, and the thin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

AB_2E_2: Water (H_2O)

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

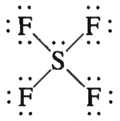
$$\mathrm{H}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-\mathrm{H}$$

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:

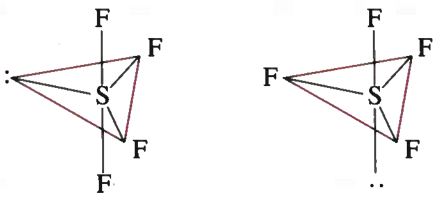


AB_4E: Sulfur Tetrafluoride (SF_4)

The Lewis structure of SF_4 is

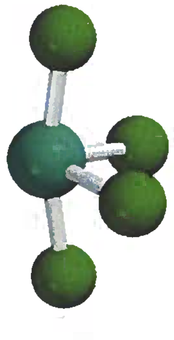


The central sulfur atom has five electron pairs whose arrangement, according to Table 10.1, is trigonal bipyramidal. In the SF_4 molecule, however, one of the electron pairs is a lone pair, so the molecule must have one of the following geometries:



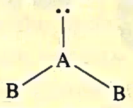
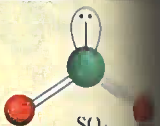
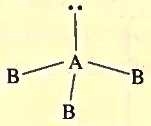
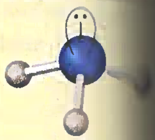
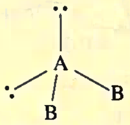
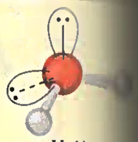
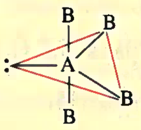
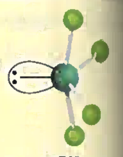
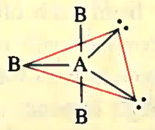
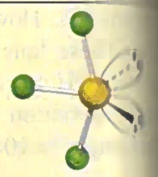
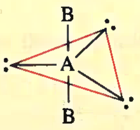
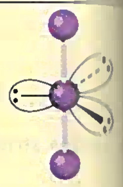
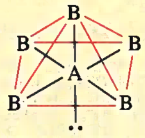
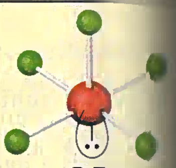
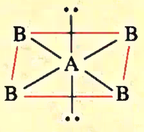
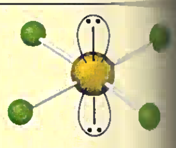
(a)

(b)

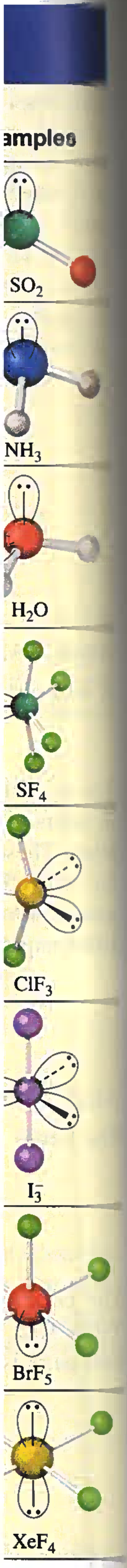


SF$_4$

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 of Molecule or Ion	Exampl
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 shape, not bonds.

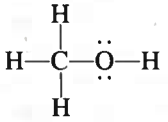


In (a) the lone pair occupies an equatorial position, and in (b) it occupies an axial position. The axial position has three neighboring pairs at 90° and one at 180°, while the equatorial position has two neighboring pairs at 90° and two more at 120°. The repulsion is smaller for (a), and indeed (a) is the structure observed experimentally. This shape is sometimes described as a distorted tetrahedron (or seesaw if you turn the structure 90° to the right 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 only describe the shape around each of the central atoms. For example, consider methanol, CH_3OH, whose Lewis structure is shown below:



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

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).

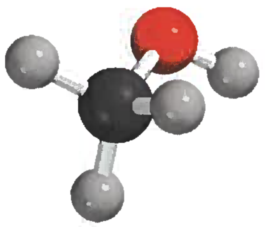


Figure 10.2 *The geometry of CH_3OH.*

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.
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.

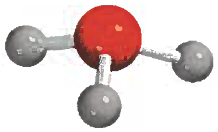
The VSEPR model generates reliable predictions of the geometries of a variety of molecular structures. Chemists use the VSEPR approach because of its simplicity. Although there are some theoretical concerns about whether "electron-pair repulsion" actually determines molecular shapes, the assumption that it does leads to useful (and generally reliable) predictions. We need not ask more of any model at this 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 ion (a) AsH_3, (b) OF_2, (c) $AlCl_4^-$, (d) I_3^-, (e) C_2H_4.

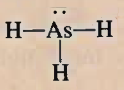
Strategy The sequence of steps in determining molecular geometry is as follow

draw Lewis structure ⟶ find arrangement of electron pairs ⟶ find arrangement of bonding pairs ⟶ determine geom based on bonding p



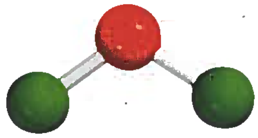
AsH_3

Solution (a) The Lewis structure of AsH_3 is



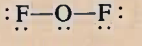
$$\mathrm{H-\overset{\cdot\cdot}{\underset{\underset{\displaystyle H}{|}}{As}}-H}$$

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.



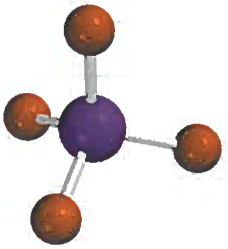
OF_2

(b) The Lewis structure of OF_2 is



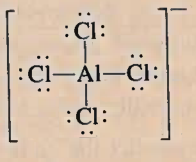
$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:$$

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.



$AlCl_4^-$

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

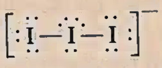


$$\left[\begin{array}{c} :\overset{\cdot\cdot}{\mathrm{Cl}}: \\ | \\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}-\mathrm{Al}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \\ | \\ :\underset{\cdot\cdot}{\mathrm{Cl}}: \end{array}\right]^-$$

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

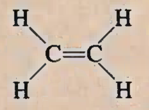


$$\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}:\right]^-$$

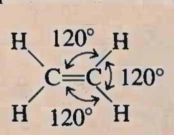
(Continued)

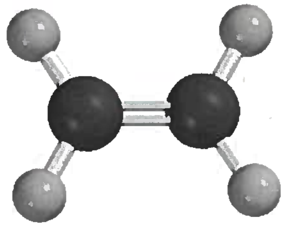
There are five electron pairs around the central I atom; therefore, the electron pair arrangement is trigonal bipyramidal. Of the five electron pairs, three are lone pairs and two are bonding pairs. Recall that the lone pairs preferentially occupy the equatorial positions in a trigonal bipyramid (see 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) 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°.





C_2H_4

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 9.4 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 9.4). 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,

$$\overset{+\!\!\longrightarrow}{H-\ddot{\underset{\cdot\cdot}{F}}:}$$

The consequent charge separation can be represented as

$$\overset{\delta+}{H}-\overset{\delta-}{\ddot{\underset{\cdot\cdot}{F}}:}$$

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)**, which is *the product of the charge Q and the distance r between the charges:*

$$\mu = Q \times r \tag{10.1}$$

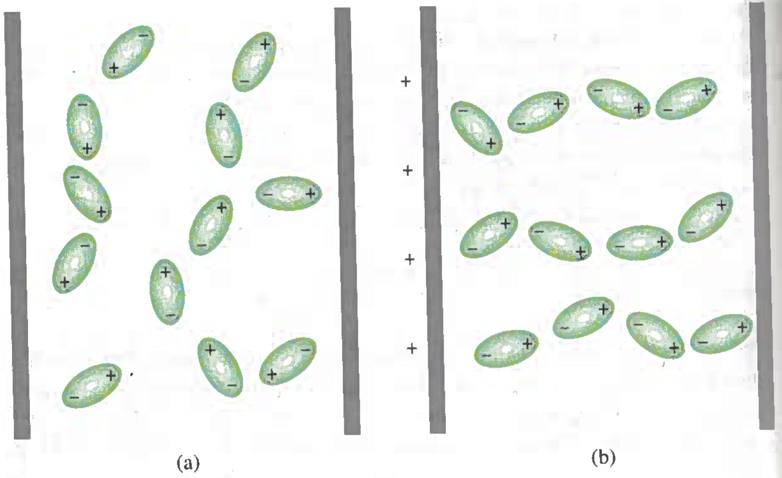


Figure 10.3 *Behavior of polar molecules (a) in the absence of an external electric field and (b) when the electric field is turned on. Nonpolar molecules are not affected by an electric field.*

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

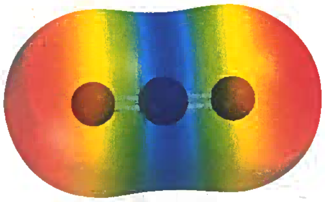
To maintain electrical neutrality, the charges on both ends of an electrically neut diatomic molecule must be equal in magnitude and opposite in sign. However, i Equation (10.1), Q refers only to the magnitude of the charge and not to its sign, s μ is always positive. Dipole moments are usually expressed in debye units (D), named for Peter Debye.[†] The conversion factor is

$$1\ \text{D} = 3.336 \times 10^{-30}\ \text{C m}$$

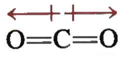
where C is coulomb and m is meter.

Animation:
Polarity of Molecules
ARIS, Animations

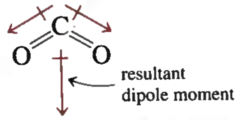
Diatomic molecules containing atoms of *different* elements (for example, HI, CO, and NO) *have dipole moments* and are called ***polar molecules.*** Diatomic mol ecules containing atoms of the *same* element (for example, H_2, O_2, and F_2) are examples of ***nonpolar molecules*** because they *do not 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 present, the molecule will not necessarily have a dipole moment. Car bon dioxide (CO_2), for example, is a triatomic molecule, so its geometry is either linear or bent:



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 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

Interactivity:
Molecular Polarity
ARIS, Interactives

[†] Peter Joseph William Debye (1884–1966). American chemist and physicist of Dutch origin. Debye made many significant contributions in the study of molecular structure, polymer chemistry, X-ray analysis, and electrolyte solution. He was awarded the Nobel Prize in Chemistry in 1936.

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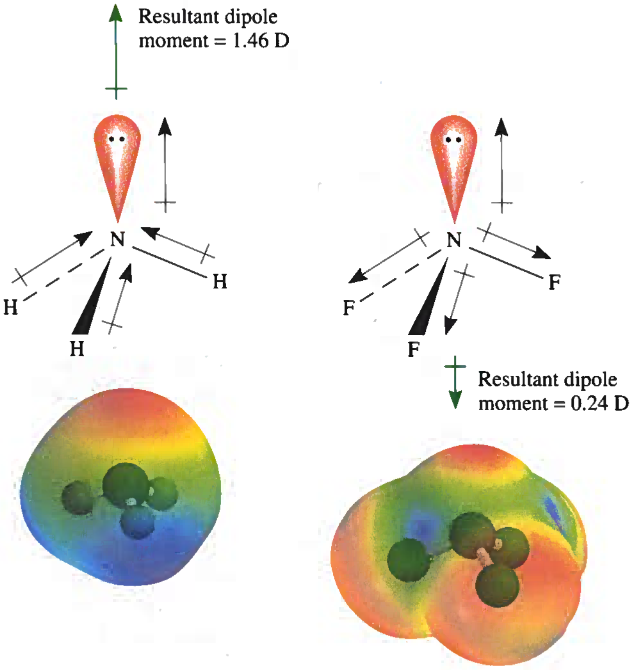


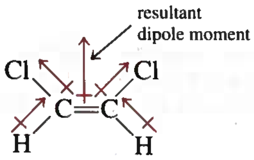
Figure 10.4 *Bond moments and resultant dipole moments in NH_3 and NF_3. The electrostatic potential maps show the electron density distributions in these molecules.*

m or resultant dipole moment would be zero. On the other hand, if the CO_2 mole- ule were bent, the two bond moments would partially reinforce each other, so that e molecule would have a dipole moment. Experimentally it is found that carbon ioxide has no dipole moment. Therefore, we conclude that the carbon dioxide mol- ule is linear. The linear nature of carbon dioxide has been confirmed through other xperimental measurements.

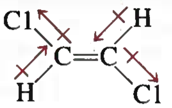
The VSEPR model predicts that CO_2 is a linear molecule.

Next let us consider the NH_3 and NF_3 molecules shown in Figure 10.4. In both ses, the central N atom has a lone pair, whose charge density is away from the N om. From Figure 9.5 we know that N is more electronegative than H, and F is more ectronegative than N. For this reason, the shift of electron density in NH_3 is toward N and so contributes a larger dipole moment, whereas the NF bond moments are irected away from the N atom and so together they offset the contribution of the one pair to the dipole moment. Thus, the resultant dipole moment in NH_3 is larger an that in NF_3.

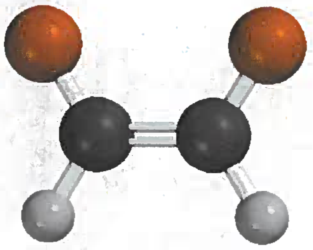
Dipole moments can be used to distinguish between molecules that have the same rmula but different structures. For example, the following molecules both exist; they ave the same molecular formula ($C_2H_2Cl_2$), the same number and type of bonds, but ifferent molecular structures:



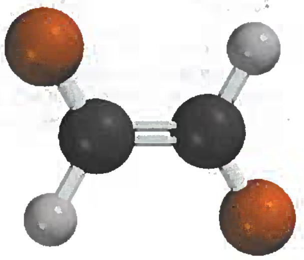
cis-dichloroethylene
$\mu = 1.89$ D



trans-dichloroethylene
$\mu = 0$

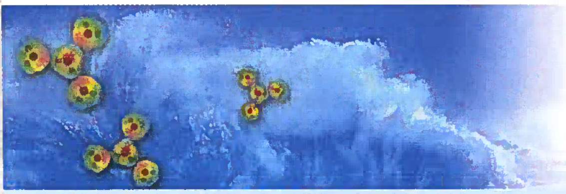


cis-dichloroethylene



trans-dichloroethylene

cause *cis*-dichloroethylene is a polar molecule but *trans*-dichloroethylene is not, ey can readily be distinguished by a dipole moment measurement. Additionally, as

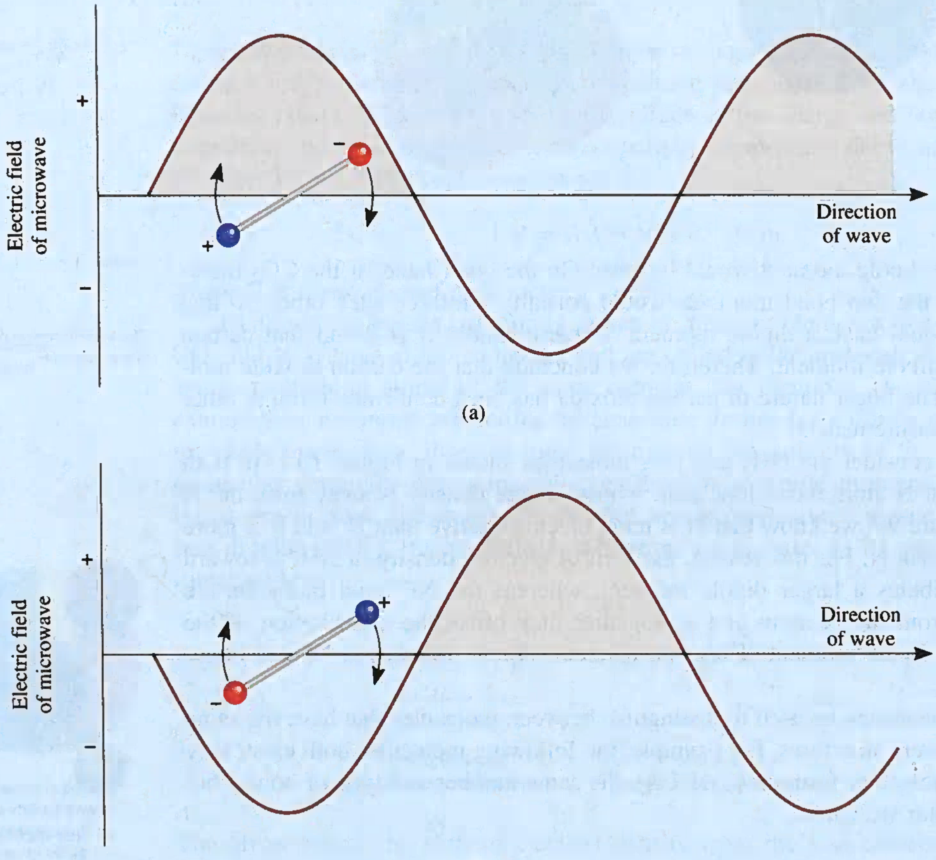


CHEMISTRY in Action

Microwave Ovens—Dipole Moments at Work

In the last 20 years the microwave oven has become a ubiquitous appliance. Microwave technology enables us to thaw and cook food much more rapidly than conventional appliances do. How do microwaves heat food so quickly?

In Chapter 7 we saw that microwaves are a form of electromagnetic radiation (see Figure 7.3). Microwaves are generated by a magnetron, which was invented during World when radar technology was being developed. The is a hollow cylinder encased in a horseshoe-shaped the center of the cylinder is a cathode rod. The cylinder act as an anode. When heated, the cathode trons that travel toward the anode. The magnetic field



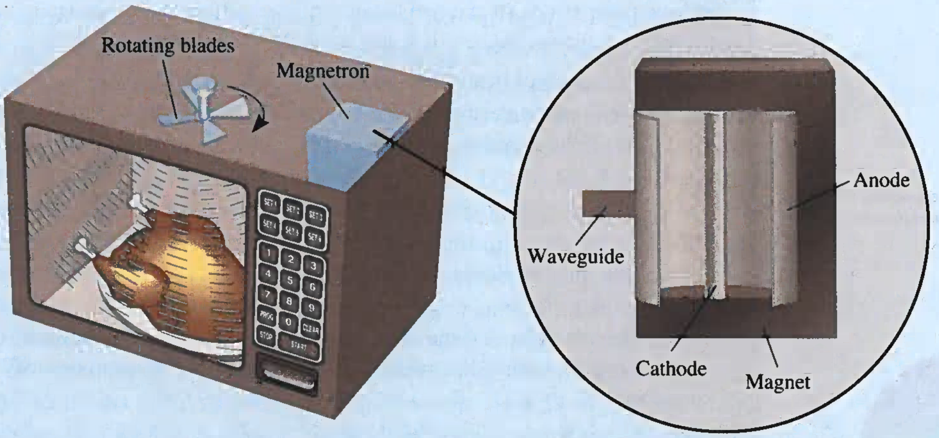
Interaction between the electric field component of the microwave and a polar molecule. (a) The negative end of the dipole follows the propagation of the (the positive region) and rotates in a clockwise direction. (b) If, after the molecule has rotated to the new position the radiation has also moved along to its cle, the positive end of the dipole will move into the negative region of the wave while the negative end will be pushed up. Thus, the molecule will rotate such interaction can occur with nonpolar molecules.

the electrons to move in a circular path. This motion of charged particles generates microwaves, which are adjusted to a frequency of 2.45 GHz (2.45×10^9 Hz) for cooking. A "waveguide" directs the microwaves into the cooking compartment. Rotating fan blades reflect the microwaves to all parts of the oven.

The cooking action in a microwave oven results from the interaction between the electric field component of the radiation with the polar molecules—mostly water—in food. All molecules rotate at room temperature. If the frequency of the radiation and that of the molecular rotation are equal, energy can be transferred from microwave to the polar molecule. As a result, the molecule will rotate faster. This is what happens in a gas. In the condensed state (for example, in food), a molecule cannot execute the free rotation. Nevertheless, it still experiences a torque (a force that causes rotation) that tends to align its dipole moment with the oscillating field of the microwave. Consequently, there is friction between the molecules, which appears as heat in the food.

The reason that a microwave oven can cook food so fast is that the radiation is not absorbed by nonpolar molecules and can therefore reach different parts of food at the same time. (Depending on the amount of water present, microwaves can penetrate food to a depth of several inches.) In a conventional oven, heat can affect the center of foods only by conduction (that is, by transfer of heat from hot air molecules to cooler molecules in food in a layer-by-layer fashion), which is a very slow process.

The following points are relevant to the operation of a microwave oven. Plastics and Pyrex glasswares do not contain polar molecules and are therefore not affected by microwave radiation. (Styrofoam and certain plastics cannot be used in microwaves because they melt from the heat of the food.) Metals, however, reflect microwaves, thereby shielding the food and possibly returning enough energy to the microwave emitter to overload it. Because microwaves can induce a current in the metal, this action can lead to sparks jumping between the container and the bottom or walls of the oven. Finally, although water molecules in ice are locked in position and therefore cannot rotate, we routinely thaw food in a microwave oven. The reason is that at room temperature a thin film of liquid water quickly forms on the surface of frozen food and the mobile molecules in that film can absorb the radiation to start the thawing process.



A microwave oven. The microwaves generated by the magnetron are reflected to all parts of the oven by the rotating fan blades.

TABLE 10.3 Dipole Moments of Some Polar Molecules

Molecule	Geometry	Dipole Moment
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

we will see in Chapter 11, the strength of intermolecular forces is partially dete by whether molecules possess a dipole moment. Table 10.3 lists the dipole mom of several polar molecules.

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

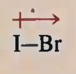
Example 10.2

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

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 m not possess a dipole moment if it has a highly symmetrical geometry.

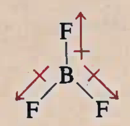
Solution (a) Because IBr (iodine bromide) is diatomic, it has a linear geometry. Bromine is more electronegative than iodine (see Figure 9.5), so IBr is polar with bromine at the negative end.

All diatomic molecules containing different elements possess a dipole moment.



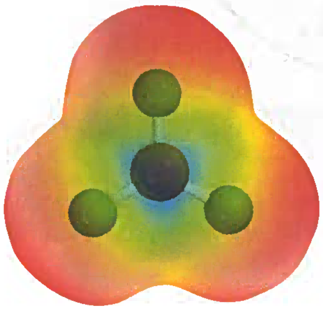
Thus, the molecule does have a dipole moment.

(b) Because fluorine is more electronegative than boron, each B—F bond in BF_3 (boro 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:



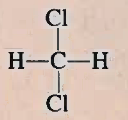
An analogy is an object that is pulled in the directions shown by the three bond moments. If the forces are equal, the object will not move. Consequently, BF_3 has no dipole moment; it is a nonpolar molecule.

(Continued)



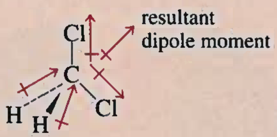
Electrostatic potential map shows that the electron density is symmetrically distributed in the BF_3 molecule.

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



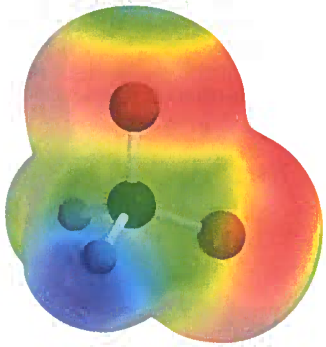
$$\begin{array}{c} Cl \\ | \\ H-C-H \\ | \\ Cl \end{array}$$

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

Similar problems: 10.21, 10.22, 10.23.

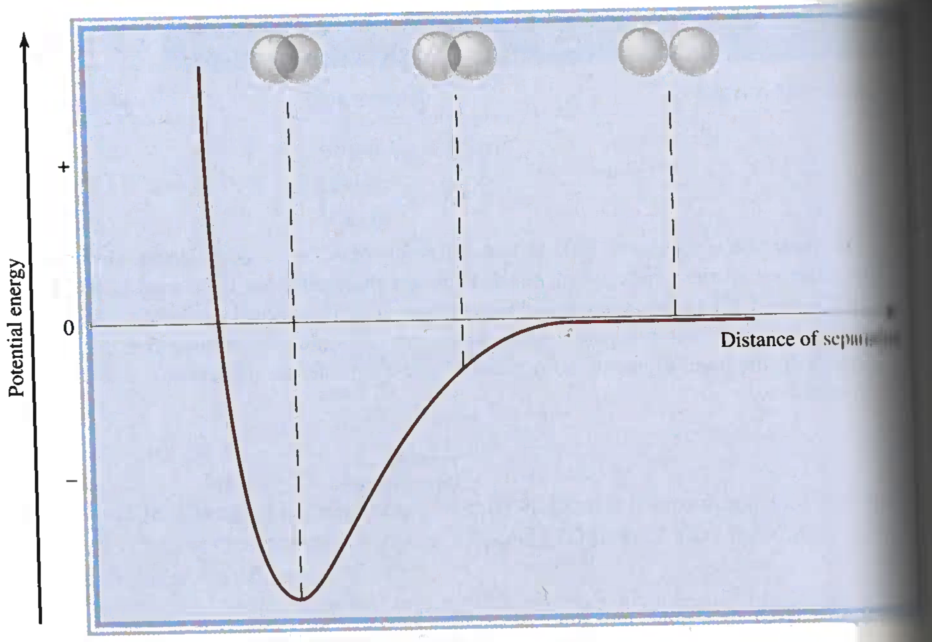
10.3 Valence Bond Theory

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.

Figure 10.5 *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.*



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 10.5). 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 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 10.6 is another way of viewing the formation of an H_2 molecule.

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

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. 297.

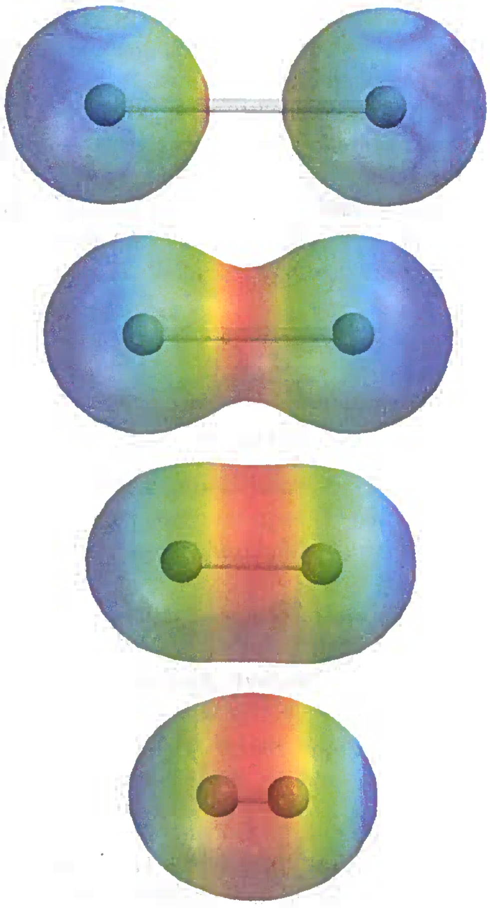


Figure 10.6 *Top to bottom: As two H atoms approach each other, their 1s orbitals begin to interact and each electron begins to feel the attraction of the other proton. Gradually, the electron density builds up in the region between the two nuclei (red color). Eventually, a stable H_2 molecule is formed when the internuclear distance is 74 pm.*

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

Animation: Hybridization ARIS, Animations

Interactivity: Determining Orbital Hybridization ARIS, Interactives

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

$$\begin{array}{cc} \boxed{\uparrow\downarrow} & \boxed{\uparrow}\boxed{\uparrow}\boxed{} \\ 2s & 2p \end{array}$$

Because the carbon atom has two unpaired electrons (one in each of the two $2p$ 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 $2s$ orbital to the $2p$ orbital:

$$\begin{array}{cc} \boxed{\uparrow} & \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow} \\ 2s & 2p \end{array}$$

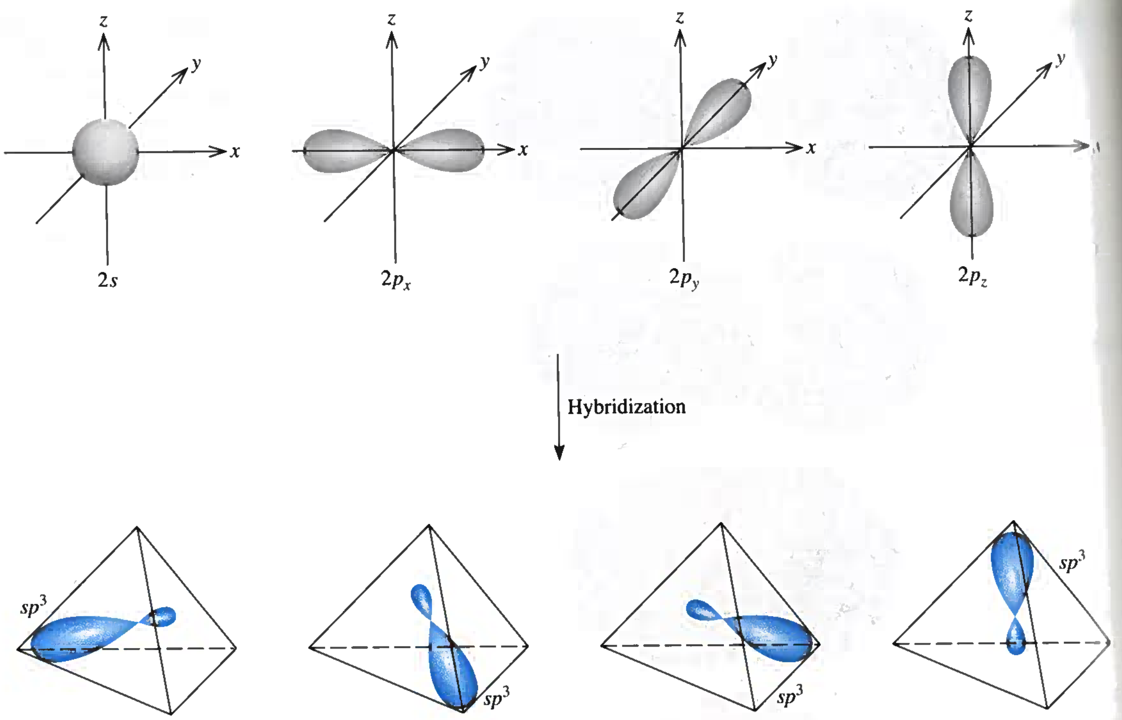


Figure 10.7 *Formation of four sp^3 hybrid orbitals from one 2s and three 2p orbitals. The sp^3 orbitals point to the corners of a tetrahedron.*

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:

sp^3 is pronounced "*s*-*p* three."

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

Because the new orbitals are formed from one *s* and three *p* orbitals, they are called sp^3 hybrid orbitals. Figure 10.7 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 10.8 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.)

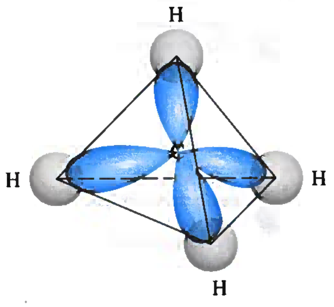


Figure 10.8 *Formation of four bonds between the carbon sp^3 hybrid orbitals and the hydrogen 1s orbitals in CH_4. The smaller lobes are not shown.*

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 rep

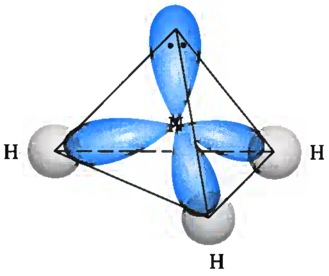
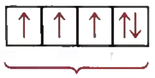


Figure 10.9 *The sp^3-hybridized N atom in NH_3. Three sp^3 hybrid orbitals form bonds with the H atoms. The fourth is occupied by nitrogen's lone pair.*

ent three $2p$ 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



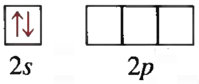
sp^3 orbitals

Three of the four hybrid orbitals form covalent N—H bonds, and the fourth hybrid orbital accommodates the lone pair on nitrogen (Figure 10.9). 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.

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



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

Now there are two Be orbitals available for bonding, the $2s$ and $2p$. However, if two Cl atoms were to combine with Be in this excited state, one Cl atom would share a $2s$ electron and the other Cl would share a $2p$ 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 $2s$ and $2p$ orbitals must be mixed, or hybridized, to form two equivalent sp hybrid orbitals:

sp orbitals   empty $2p$ orbitals

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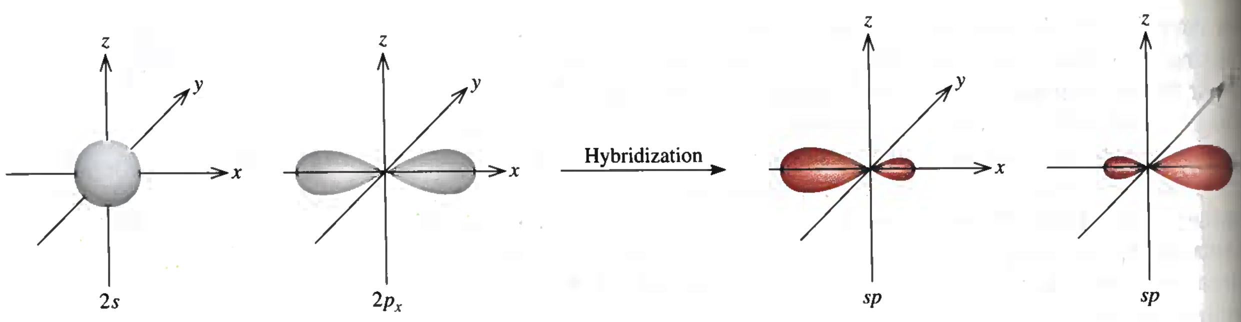


Figure 10.10 *Formation of sp hybrid orbitals.*

Figure 10.10 shows the shape and orientation of the *sp* orbitals. These two hy orbitals lie on the same line, the *x*-axis, so that the angle between them is 180°. of the BeCl bonds is then formed by the overlap of a Be *sp* hybrid orbital and $3p$ orbital, and the resulting $BeCl_2$ molecule has a linear geometry (Figure 10.1

sp^2 Hybridization

Next we will look at the BF_3 (boron trifluoride) molecule, known to have a planar ge try. 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:

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

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

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

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

These three sp^2 orbitals lie in the same plane, and the angle between any two of th is 120° (Figure 10.12). Each of the BF bonds is formed by the overlap of a boron hybrid orbital and a fluorine 2*p* orbital (Figure 10.13). The BF_3 molecule is pl with all the FBF angles equal to 120°. This result conforms to experimental findi and also to VSEPR predictions.

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

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

Figure 10.11 *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.*

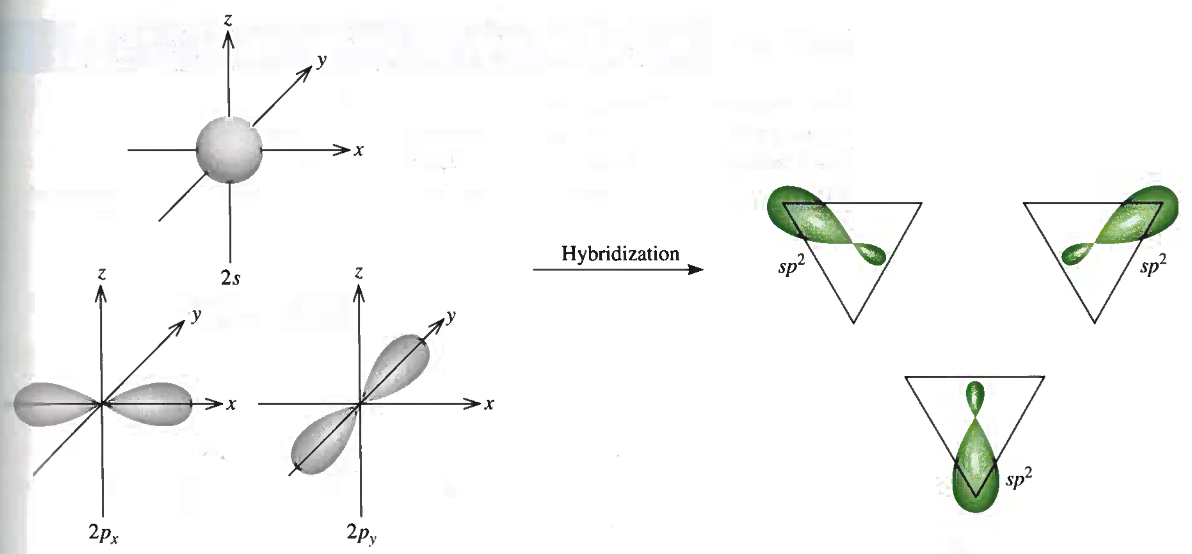


Figure 10.12 *Formation of sp^2 hybrid orbitals from one 2s and two 2p orbitals. The sp^2 orbitals point to the corners of an equilateral triangle.*

To summarize our discussion of hybridization, we note that

- The concept of hybridization is not applied to isolated atoms. It is a theoretical model used only to explain covalent bonding.
- 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.
- The number of hybrid orbitals generated is equal to the number of pure atomic orbitals that participate in the hybridization process.
- Hybridization requires an input of energy; however, the system more than recovers this energy during bond formation.
- 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.

Table 10.4 summarizes *sp*, sp^2, and sp^3 hybridization (as well as other types that we will discuss shortly).

Procedure for Hybridizing Atomic Orbitals

Before going on to discuss the hybridization of *d* orbitals, let us specify what we need to know in order 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 illustrates this procedure.

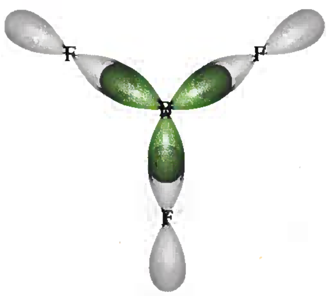
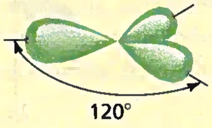
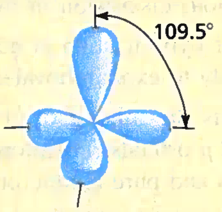
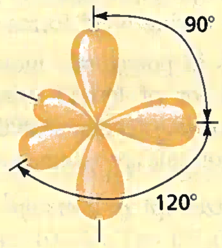
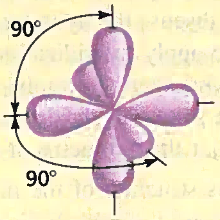


Figure 10.13 *The sp^2 hybrid orbitals of boron overlap with the 2p orbitals of fluorine. The BF_3 molecule is planar, and all the FBF angles are 120°.*

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
s, p, p, p, d	sp^3d	5	 Trigonal bipyramidal	PCl_5
s, p, p, p, d, d	sp^3d^2	6	 Octahedral	SF_6

Example 10.3

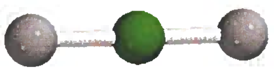
Determine the hybridization state of the central (underlined) atom in each of the following molecules: (a) $\underline{\text{Be}}H_2$, (b) $\underline{\text{Al}}I_3$, and (c) $\underline{\text{P}}F_3$. Describe the hybridization process and determine the molecular geometry in each case.

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

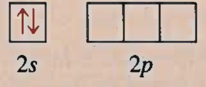
draw Lewis structure of the molecule ⟶ use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1) ⟶ use Table 10.4 to determine the hybridization state of the central atom

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

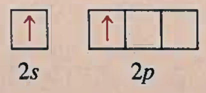
$$\text{H}-\text{Be}-\text{H}$$


BeH_2

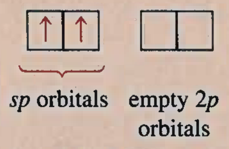
There are two bonding pairs around Be; therefore, the electron pair arrangement is linear. We conclude that Be uses *sp* hybrid orbitals in bonding with H, because *sp* orbitals have a linear arrangement (see Table 10.4). The hybridization process can be imagined as follows. First, we draw the orbital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



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

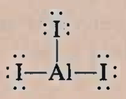


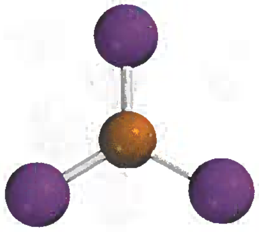
The 2*s* and 2*p* orbitals then mix to form two hybrid orbitals:



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.

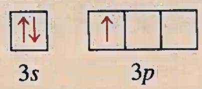
(b) The ground-state electron configuration of Al is $[\text{Ne}]3s^23p^1$. Therefore, the Al atom has three valence electrons. The Lewis structure of AlI_3 is



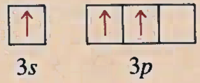

AlI_3

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

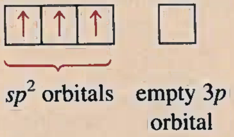
(Continued)



By promoting a 3s electron into the 3p orbital we obtain the following excit

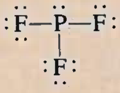


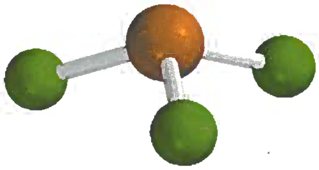
The 3s and two 3p orbitals then mix to form three sp^2 hybrid orbitals:



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

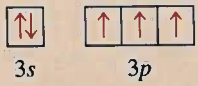
(c) The ground-state electron configuration of P is $[Ne]3s^23p^3$. Therefore, P atom five valence electrons. The Lewis structure of PF_3 is



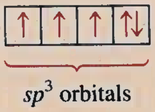


PF_3

There are four pairs of electrons around P; therefore, the electron pair arrangem is tetrahedral. We conclude that P uses sp^3 hybrid orbitals in bonding to F, becau 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°.

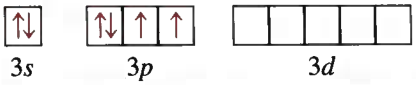
Similar problems: 10.33, 10.34.

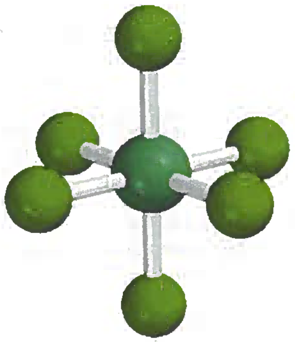
Practice Exercise Determine the hybridization state of the underlined atoms in the following compounds: (a) $SiBr_4$ and (b) BCl_3.

Hybridization of *s*, *p*, and *d* Orbitals

We have seen that hybridization neatly explains bonding that involves *s* and *p* orbit For elements in the third period and beyond, however, we cannot always account f molecular geometry by assuming that only *s* and *p* orbitals hybridize. To underst the formation of molecules with trigonal bipyramidal and octahedral geometries, for instance, we must include d orbitals in the hybridization concept.

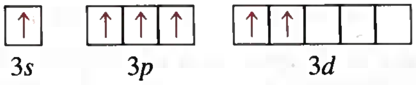
Consider the SF_6 molecule as an example. In Section 10.1 we saw that this molecule has octahedral geometry, which is also the arrangement of the six electron pairs. Table 10.4 shows that the S atom is sp^3d^2-hybridized in SF_6. The ground-state electron configuration of S is $[Ne]3s^23p^4$:



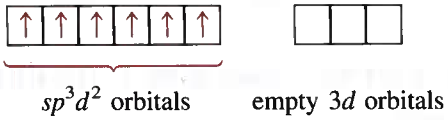


SF_6

Because the $3d$ level is quite close in energy to the $3s$ and $3p$ levels, we can promote $3s$ and $3p$ electrons to two of the $3d$ orbitals:



Mixing the $3s$, three $3p$, and two $3d$ orbitals generates six sp^3d^2 hybrid orbitals:



sp^3d^2 is pronounced "s-p three d two."

The six S—F bonds are formed by the overlap of the hybrid orbitals of the S atom with the $2p$ orbitals of the F atoms. Because there are 12 electrons around the S atom, the octet rule is violated. The use of d orbitals in addition to s and p orbitals to form an expanded octet (see Section 9.9) is an example of *valence-shell expansion.* Second-period elements, unlike third-period elements, do not have $2d$ energy levels, so they can never expand their valence shells. (Recall that when $n = 2$, $l = 0$ and 1. Thus, we can only have $2s$ and $2p$ orbitals.) Hence atoms of second-period elements can never be surrounded by more than eight electrons in any of their compounds.

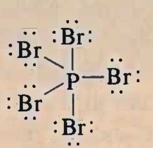
Example 10.4 deals with valence-shell expansion in a third-period element.

Example 10.4

Describe the hybridization state of phosphorus in phosphorus pentabromide (PBr_5).

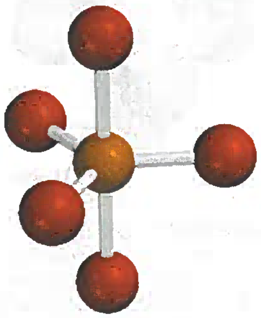
Strategy Follow the same procedure shown in Example 10.3.

Solution The ground-state electron configuration of P is $[Ne]3s^23p^3$. Therefore, the P atom has five valence electrons. The Lewis structure of PBr_5 is



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

(Continued)



PBr_5

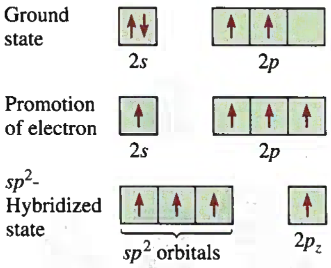
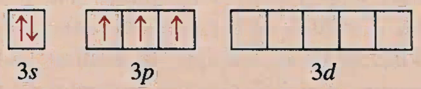
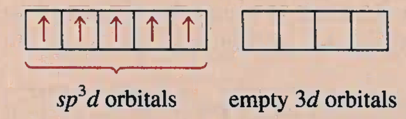


Figure 10.14 *The sp^2 hybridization of a carbon atom. The 2s orbital is mixed with only two 2p orbitals to form three equivalent sp^2 hybrid orbitals. This process leaves an electron in the unhybridized orbital, the $2p_z$ orbital.*



Promoting a 3*s* electron into a 3*d* orbital results in the following excited state:

Mixing the one 3*s*, three 3*p*, and one 3*d* orbitals generates five sp^3d hybrid orbitals:



These hybrid orbitals overlap the 4*p* orbitals of Br to form five covalent P—Br bonds. Because there are no lone pairs on the P atom, the geometry of PBr_5 is trigonal bipyramidal.

Similar problem: 10.42.

Practice Exercise Describe the hybridization state of Se in SeF_6.

10.5 Hybridization in Molecules Containing Double and Triple Bonds

Animation:
Sigma and Pi Bonds
ARIS, Animations

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 10.14 shows orbital diagrams of this hybridization process. We assume that only the $2p_x$ and $2p_y$ orbitals combine with the 2*s* orbital, and that the $2p_z$ orbital remains unchanged. Figure 10.15 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 10.16(a) shows, each carbon atom uses the three sp^2 hybrid orbitals to form two bonds with the two hydrogen 1*s* 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 10.16(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 10.16(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 10.16(b). It is this pi bond formation that gives ethylene its planar geometry. Figure 10.16(c) shows the orientation of the sigma and pi bonds. Figure 10.17 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.

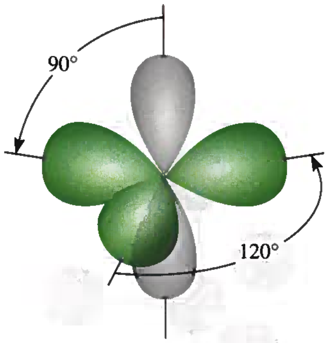


Figure 10.15 *Each carbon atom in the C_2H_4 molecule has three sp^2 hybrid orbitals (green) and one unhybridized $2p_z$ orbital (gray), which is perpendicular to the plane of the hybrid orbitals.*

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 2*s* with the $2p_x$ orbital (Figure 10.18). As

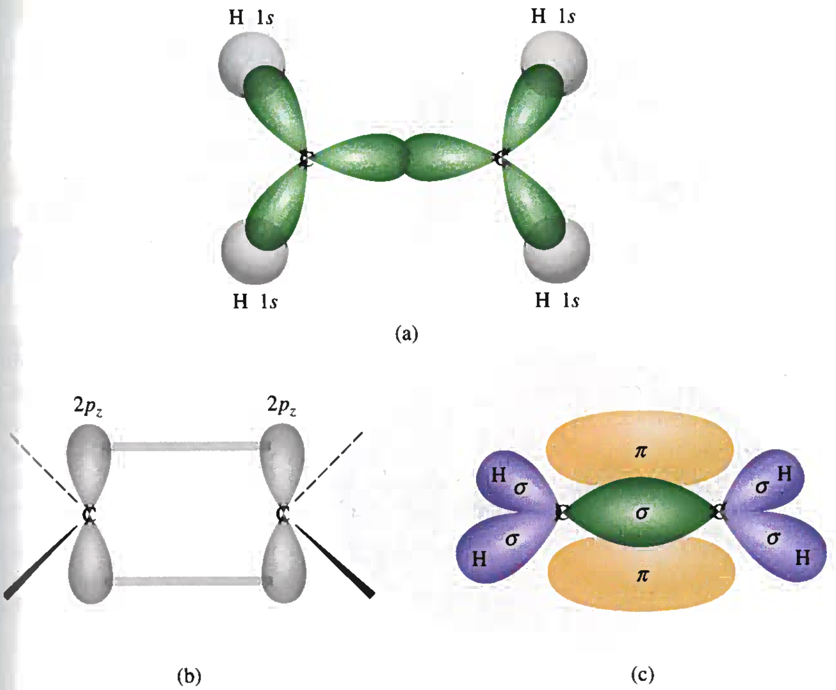


Figure 10.16 *Bonding in ethylene, C_2H_4. (a) Top view of the sigma bonds between carbon atoms and between carbon and hydrogen atoms. All the atoms lie in the same plane, making C_2H_4 a planar molecule. (b) Side view showing how the two $2p_z$ orbitals on the two carbon atoms overlap, leading to the 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.*

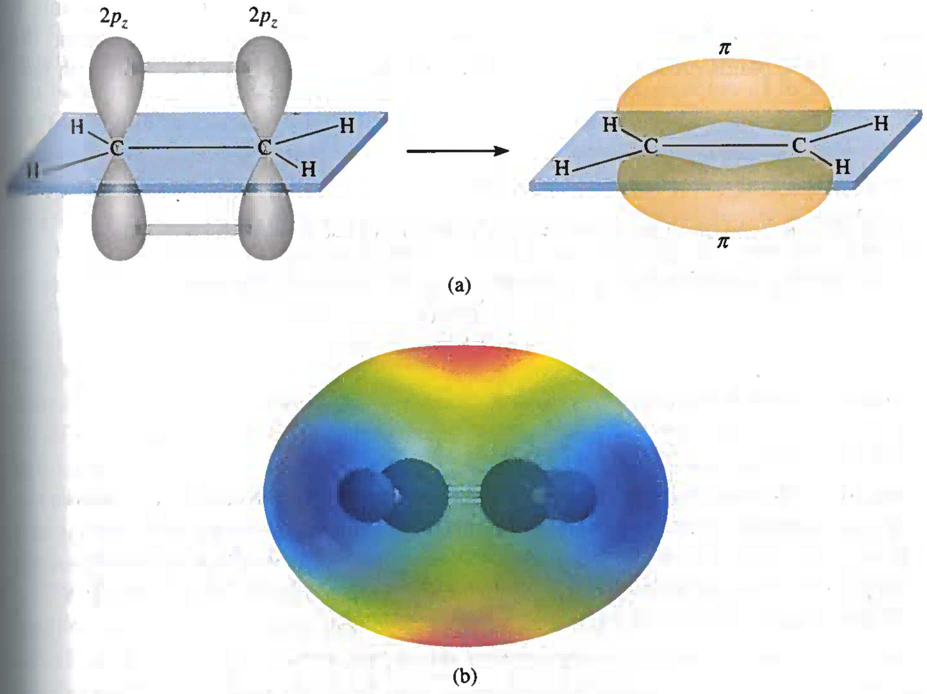


Figure 10.17 *(a) Another view of pi bond formation in the C_2H_4 molecule. Note that all six atoms are in the same plane. It is the overlap of the $2p_z$ orbitals that causes the molecule to assume a planar structure. (b) Electrostatic potential map of C_2H_4.*

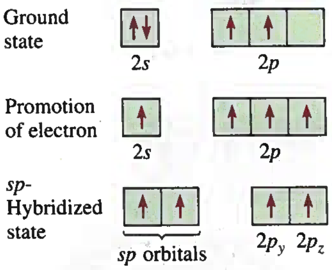


Figure 10.18 *The sp hybridization of a carbon atom. The 2s orbital is mixed with only one 2p orbital to form two sp hybrid orbitals. This process leaves an electron in each of the two unhybridized 2p orbitals, namely, the $2p_y$ and $2p_z$ orbitals.*

Figure 10.19 shows, the two *sp* hybrid orbitals of each C atom form one sigma bond with a hydrogen 1*s* 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

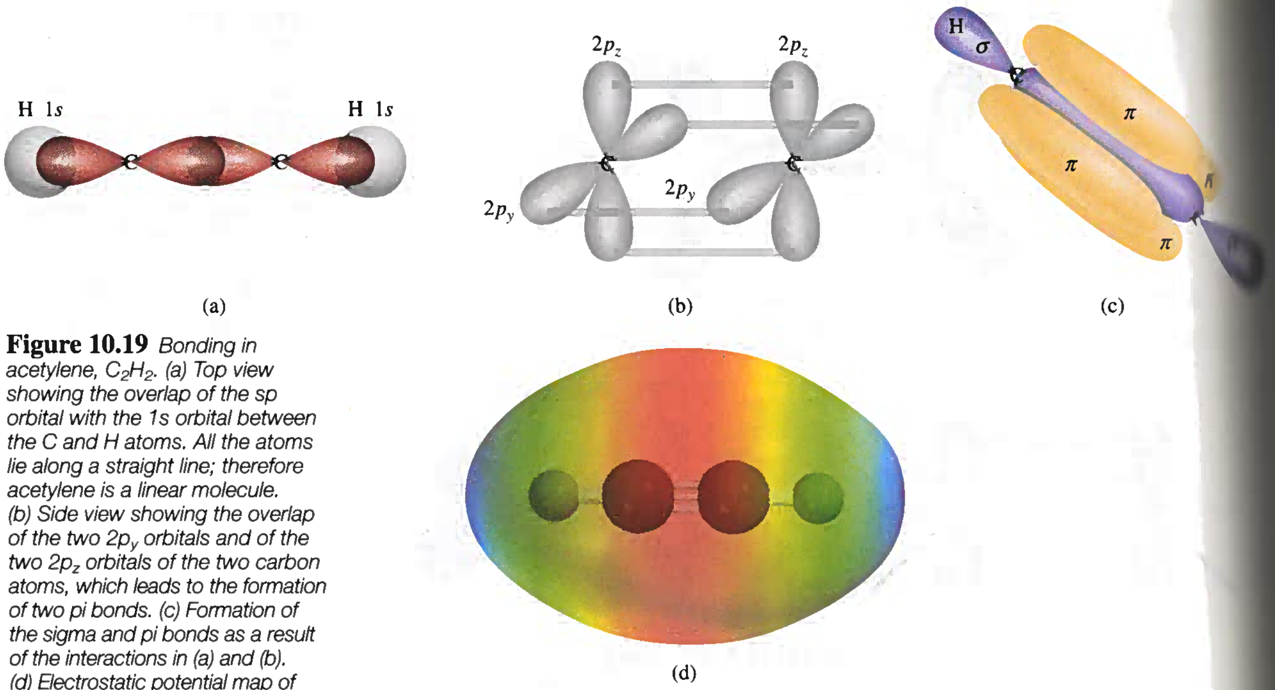
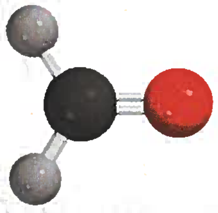


Figure 10.19 *Bonding in acetylene, C_2H_2. (a) Top view showing the overlap of the sp orbital with the 1s orbital between the C and H atoms. All the atoms lie along a straight line; therefore acetylene is a linear molecule. (b) Side view showing the overlap of the two $2p_y$ orbitals and of the two $2p_z$ 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.*

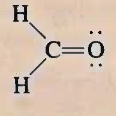
double bonds or a triple bond, it is *sp*-hybridized. Note that this rule applies only atoms of the second-period elements. Atoms of third-period elements and beyond the form multiple bonds present a more complicated picture and will not be dealt with here



CH_2O

Example 10.5

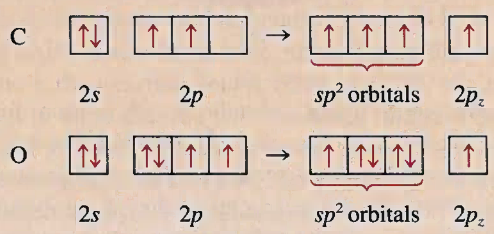
Describe the bonding in the formaldehyde molecule whose Lewis structure is



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

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:



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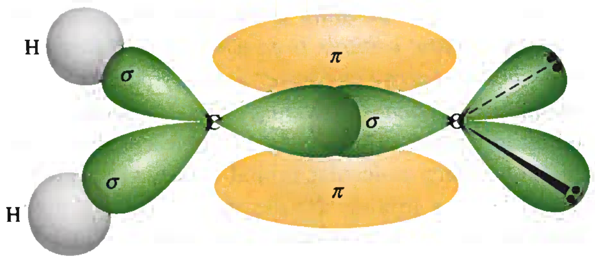


Figure 10.20 *Bonding in the formaldehyde molecule. A sigma bond is formed by the overlap of the sp^2 hybrid orbital of carbon and the sp^2 hybrid orbital of oxygen; a pi bond is formed by the overlap of the $2p_z$ orbitals of the carbon and oxygen atoms. The two lone pairs on oxygen are placed in the other two sp^2 orbitals of oxygen.*

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 10.20).

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

Similar problems: 10.38, 10.39, 10.41.

10.6 Molecular Orbital Theory

Valence bond theory is one of the two quantum mechanical approaches that explain bonding in molecules. It accounts, at least qualitatively, for the stability of the covalent bond in terms of overlapping atomic orbitals. Using the concept of hybridization, valence bond theory can explain molecular geometries predicted by the VSEPR model. However, the assumption that electrons in a molecule occupy atomic orbitals of the individual atoms can only be an approximation, because each bonding electron in a molecule must be in an orbital that is characteristic of the molecule as a whole.

In some cases, valence bond theory cannot satisfactorily account for observed properties of molecules. Consider the oxygen molecule, whose Lewis structure is

$$\underset{\cdot\cdot}{\ddot{\mathrm{O}}}{=}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$$

According to this description, all the electrons in O_2 are paired and oxygen should therefore be diamagnetic. But experiments have shown that the oxygen molecule has two unpaired electrons (Figure 10.21). This finding suggests a fundamental deficiency in valence bond theory, one that justifies searching for an alternative bonding approach that accounts for the properties of O_2 and other molecules that do not match the predictions of valence bond theory.

Magnetic and other properties of molecules are sometimes better explained by another quantum mechanical approach called *molecular orbital (MO) theory.* Molecular orbital theory describes covalent bonds in terms of ***molecular orbitals,*** which *result from interaction of the atomic orbitals of the bonding atoms and are associated with the entire molecule.* The difference between a molecular orbital and an atomic orbital is that an atomic orbital is associated with only one atom.

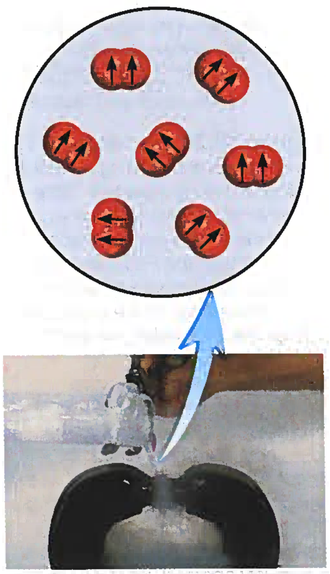
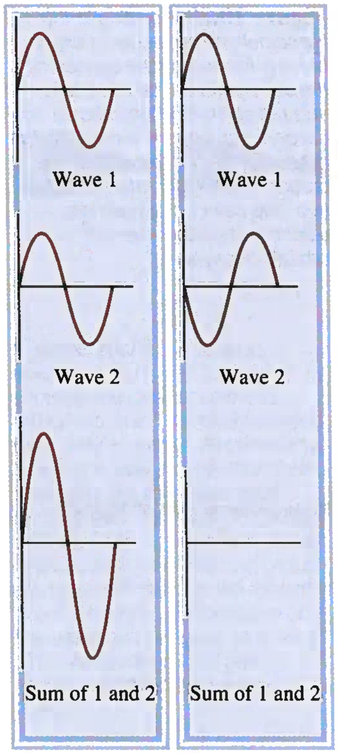


Figure 10.21 *Liquid oxygen caught between the poles of a magnet, because the O_2 molecules are paramagnetic, having two parallel spins.*

Bonding and Antibonding Molecular Orbitals

According to MO theory, the overlap of the 1*s* orbitals of two hydrogen atoms leads to the formation of two molecular orbitals: one bonding molecular orbital and one



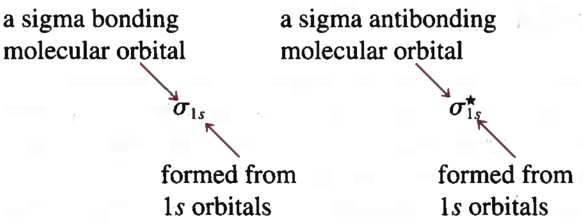
(a) (b)

Figure 10.22 *Constructive interference (a) and destructive interference (b) of two waves of the same wavelength and amplitude.*

antibonding molecular orbital. A ***bonding molecular orbital*** has *lower energy and greater stability than the atomic orbitals from which it was formed.* An ***antibonding molecular orbital*** has *higher energy and lower stability than the atomic orbitals from which it was formed.* As the names "bonding" and "antibonding" suggest, placing electrons in a bonding molecular orbital yields a stable covalent bond, whereas placing electrons in an antibonding molecular orbital results in an unstable bond.

In the bonding molecular orbital, the electron density is greatest between the nuclei of the bonding atoms. In the antibonding molecular orbital, on the other hand, the electron density decreases to zero between the nuclei. We can understand this distinction if we recall that electrons in orbitals have wave characteristics. A property unique to waves enables waves of the same type to interact in such a way that the resultant wave has either an enhanced amplitude or a diminished amplitude. In the former case, we call the interaction *constructive interference;* in the latter case, it is *destructive interference* (Figure 10.22).

The formation of bonding molecular orbitals corresponds to constructive interference (the increase in amplitude is analogous to the buildup of electron density between the two nuclei). The formation of antibonding molecular orbitals corresponds to destructive interference (the decrease in amplitude is analogous to the decrease in electron density between the two nuclei). The constructive and destructive interaction between the two 1*s* orbitals in the H_2 molecule, then, lead to the formation of a sigma bonding molecular orbital σ_{1s} and a sigma antibonding molecular orbital $\sigma^{\star}_{1s}$:



where the star denotes an antibonding molecular orbital.

In a ***sigma molecular orbital*** (bonding or antibonding) *the electron density is concentrated symmetrically around a line between the two nuclei of the bonding atoms.* Two electrons in a sigma molecular orbital form a sigma bond (see Section 10.5). Remember that a single covalent bond (such as H—H or F—F) is almost always a sigma bond.

Figure 10.23 shows the *molecular orbital energy level diagram*—that is, the relative energy levels of the orbitals produced in the formation of the H_2 molecule—and the constructive and destructive interferences between the two 1*s* orbitals. Notice that in the antibonding molecular orbital there is a *nodal plane* between the nuclei that signifies zero electron density. The nuclei are repelled by each other's positive charges rather than held together. Electrons in the antibonding molecular orbital have higher

The two electrons in the sigma molecular orbital are paired. The Pauli exclusion principle applies to molecules as well as to atoms.

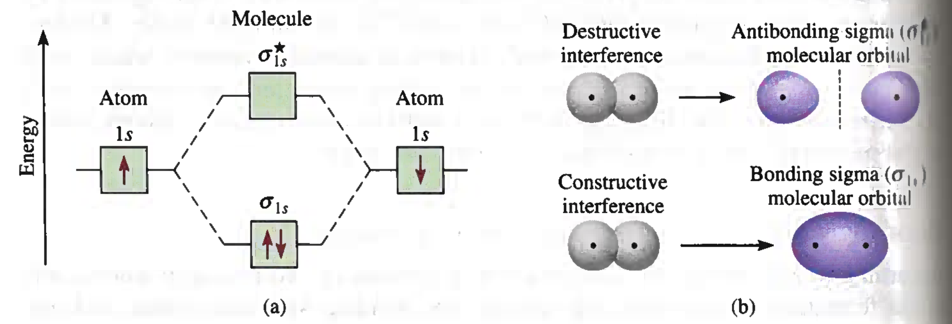


Figure 10.23 *(a) Energy levels of bonding and antibonding molecular orbitals in the H_2 molecule. Note that the two electrons in the σ_{1s} orbital must have opposite spins in accord with the Pauli exclusion principle. Keep in mind that the higher the energy of the molecular orbital, the less stable the electrons in that molecular orbital. (b) Constructive and destructive interferences between the two hydrogen 1s orbitals lead to the formation of a bonding and an antibonding molecular orbital. In the bonding molecular orbital, there is a buildup between the nuclei of electron density, which acts as a negatively charged "glue" to hold the positively charged nuclei together. In the antibonding molecular orbital, there is a nodal plane between the nuclei, where the electron density is zero.*

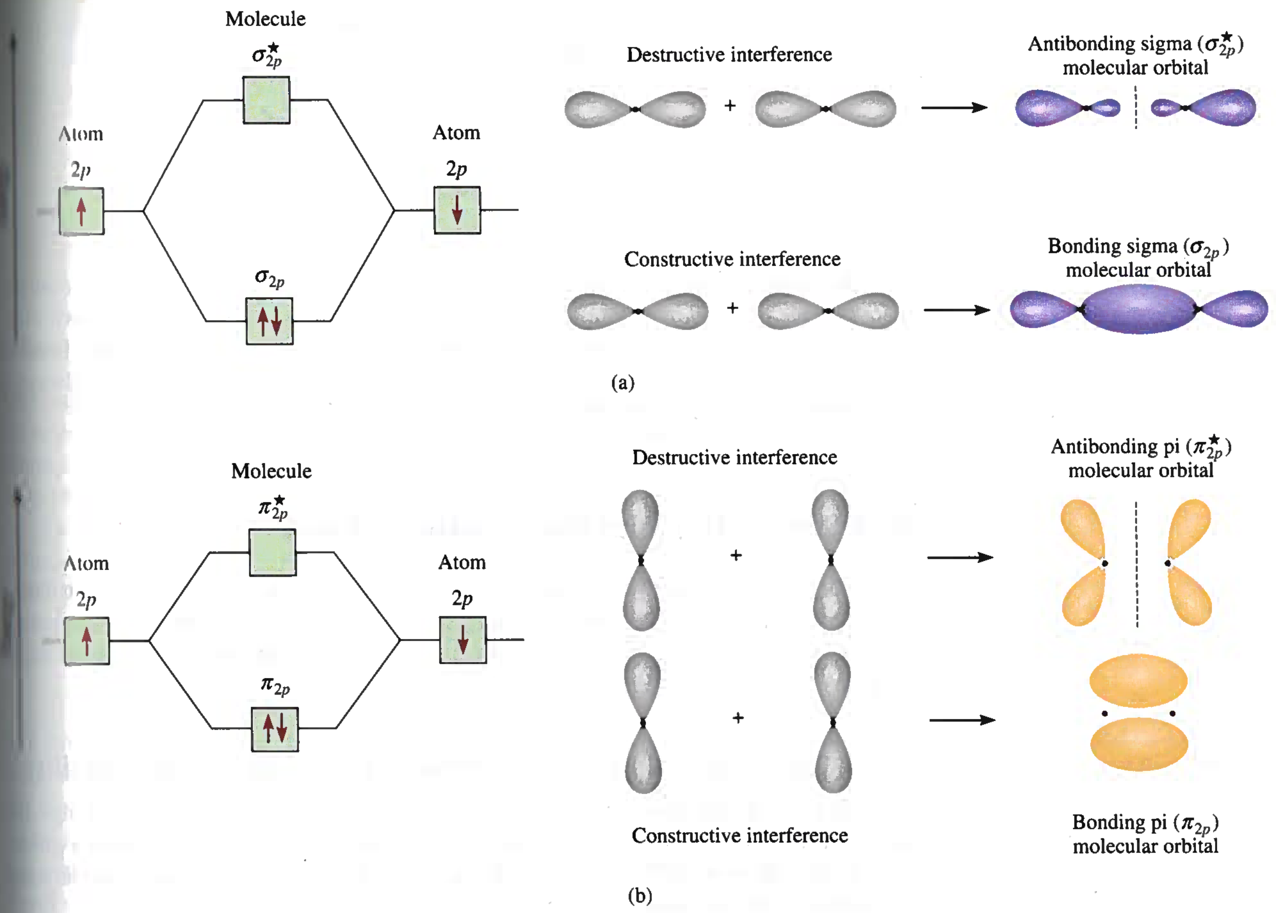


Figure 10.24 *Two possible interactions between two equivalent p orbitals and the corresponding molecular orbitals. (a) When the p orbitals overlap end-to-end, a sigma bonding and a sigma antibonding molecular orbital form. (b) When the p orbitals overlap side-to-side, a pi bonding and a pi antibonding molecular orbital form. Normally, a sigma bonding molecular orbital is more stable than a pi bonding molecular orbital, because side-to-side interaction leads to a smaller overlap of the p orbitals than does end-to-end interaction. We assume that the $2p_x$ orbitals take part in the sigma molecular orbital formation. The $2p_y$ and $2p_z$ orbitals can interact to form only π molecular orbitals. The behavior shown in (b) represents the interaction between the $2p_y$ orbitals or the $2p_z$ orbitals. In both cases, the dash line represents a nodal plane between the nuclei, where the electron density is zero.*

energy (and less stability) than they would have in the isolated atoms. On the other hand, electrons in the bonding molecular orbital have less energy (and hence greater stability) than they would have in the isolated atoms.

Although we have used the hydrogen molecule to illustrate molecular orbital formation, the concept is equally applicable to other molecules. In the H_2 molecule, we consider only the interaction between 1*s* orbitals; with more complex molecules we need to consider additional atomic orbitals as well. Nevertheless, for all *s* orbitals, the process is the same as for 1*s* orbitals. Thus, the interaction between two 2*s* or 3*s* orbitals can be understood in terms of the molecular orbital energy level diagram and the formation of bonding and antibonding molecular orbitals shown in Figure 10.23.

For *p* orbitals, the process is more complex because they can interact with each other in two different ways. For example, two 2*p* orbitals can approach each other end-to-end to produce a sigma bonding and a sigma antibonding molecular orbital, as shown in Figure 10.24(a). Alternatively, the two *p* orbitals can overlap sideways to generate a bonding and an antibonding pi molecular orbital [Figure 10.24(b)].

a pi bonding molecular orbital ↘ π_{2p} ↖ formed from 2*p* orbitals

a pi antibonding molecular orbital ↘ $\pi^{\star}_{2p}$ ↖ formed from 2*p* orbitals

In a ***pi molecular orbital*** (bonding or antibonding), *the electron density is concentrated above and below a line joining the two nuclei of the bonding atoms.* Two electrons in a pi molecular orbital form a pi bond (see Section 10.5). A double bond is almost always composed of a sigma bond and a pi bond; a triple bond is always a sigma bond plus two pi bonds.

10.7 Molecular Orbital Configurations

To understand properties of molecules, we must know how electrons are distributed among molecular orbitals. The procedure for determining the electron configuration of a molecule is analogous to the one we use to determine the electron configurations of atoms (see Section 7.8).

Rules Governing Molecular Electron Configuration and Stability

In order to write the electron configuration of a molecule, we must first arrange the molecular orbitals in order of increasing energy. Then we can use the following guidelines to fill the molecular orbitals with electrons. The rules also help us understand the stabilities of the molecular orbitals.

1. The number of molecular orbitals formed is always equal to the number of atomic orbitals combined.
2. The more stable the bonding molecular orbital, the less stable the corresponding antibonding molecular orbital.
3. The filling of molecular orbitals proceeds from low to high energies. In a stable molecule, the number of electrons in bonding molecular orbitals is always greater than that in antibonding molecular orbitals because we place electrons first in the lower-energy bonding molecular orbitals.
4. Like an atomic orbital, each molecular orbital can accommodate up to two electrons with opposite spins in accordance with the Pauli exclusion principle.
5. When electrons are added to molecular orbitals of the same energy, the most stable arrangement is predicted by Hund's rule; that is, electrons enter these molecular orbitals with parallel spins.
6. The number of electrons in the molecular orbitals is equal to the sum of all the electrons on the bonding atoms.

Hydrogen and Helium Molecules

Later in this section we will study molecules formed by atoms of the second-period elements. Before we do, it will be instructive to predict the relative stabilities of the simple species H_2^+, H_2, He_2^+, and He_2, using the energy-level diagrams shown in Figure 10.25. The σ_{1s} and $\sigma^{\star}_{1s}$ orbitals can accommodate a maximum of four electrons

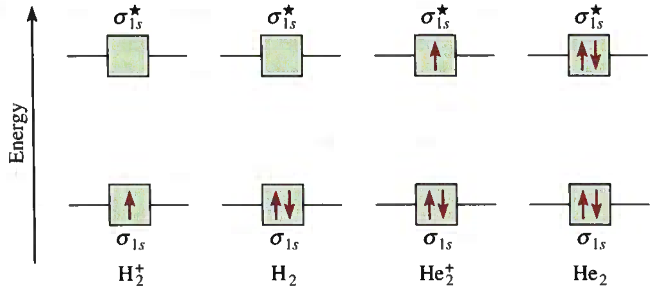


Figure 10.25 *Energy levels of the bonding and antibonding molecular orbitals in H_2^+, H_2, He_2^+, and He_2. In all these species, the molecular orbitals are formed by the interaction of two 1s orbitals.*

The total number of electrons increases from one for H_2^+ to four for He_2. The Pauli exclusion principle stipulates that each molecular orbital can accommodate a maximum of two electrons with opposite spins. We are concerned only with the ground-state electron configurations in these cases.

To evaluate the stabilities of these species we determine their ***bond order,*** defined as

$$\text{bond order} = \frac{1}{2}\left(\begin{array}{c}\text{number of electrons}\\ \text{in bonding MOs}\end{array} - \begin{array}{c}\text{number of electrons}\\ \text{in antibonding MOs}\end{array}\right) \qquad (10.2)$$

The bond order indicates the strength of a bond. For example, if there are two electrons in the bonding molecular orbital and none in the antibonding molecular orbital, the bond order is one, which means that there is one covalent bond and that the molecule is stable. Note that the bond order can be a fraction, but a bond order of zero (or a negative value) means the bond has no stability and the molecule cannot exist. Bond order can be used only qualitatively for purposes of comparison. For example, a bonding sigma molecular orbital with two electrons and a bonding pi molecular orbital with two electrons would each have a bond order of one. Yet, these two bonds must differ in bond strength (and bond length) because of the differences in the extent of atomic orbital overlap.

The quantitative measure of the strength of a bond is bond enthalpy (Section 9.10).

We are ready now to make predictions about the stability of H_2^+, H_2, He_2^+, and He_2 (see Figure 10.25). The H_2^+ molecular ion has only one electron in the σ_{1s} orbital. Because a covalent bond consists of two electrons in a bonding molecular orbital, H_2^+ has only half of one bond, or a bond order of $\frac{1}{2}$. Thus, we predict that the H_2^+ molecule may be a stable species. The electron configuration of H_2^+ is written as $(\sigma_{1s})^1$.

The superscript in $(\sigma_{1s})^1$ indicates that there is one electron in the sigma bonding molecular orbital.

The H_2 molecule has two electrons, both of which are in the σ_{1s} orbital. According to our scheme, two electrons equal one full bond; therefore, the H_2 molecule has a bond order of one, or one full covalent bond. The electron configuration of H_2 is $(\sigma_{1s})^2$.

As for the He_2^+ molecular ion, we place the first two electrons in the σ_{1s} orbital and the third electron in the $\sigma^\star_{1s}$ orbital. Because the antibonding molecular orbital is destabilizing, we expect He_2^+ to be less stable than H_2. Roughly speaking, the instability resulting from the electron in the $\sigma^\star_{1s}$ orbital is balanced by one of the σ_{1s} electrons. The bond order is $\frac{1}{2}(2 - 1) = \frac{1}{2}$ and the overall stability of He_2^+ is similar to that of the H_2^+ molecule. The electron configuration of He_2^+ is $(\sigma_{1s})^2(\sigma^\star_{1s})^1$.

In He_2 there would be two electrons in the σ_{1s} orbital and two electrons in the $\sigma^\star_{1s}$ orbital, so the molecule would have a bond order of zero and no net stability. The electron configuration of He_2 would be $(\sigma_{1s})^2(\sigma^\star_{1s})^2$.

To summarize, we can arrange our examples in order of decreasing stability:

$$H_2 > H_2^+, He_2^+ > He_2$$

We know that the hydrogen molecule is a stable species. Our simple mo orbital method predicts that H_2^+ and He_2^+ also possess some stability, becau have bond orders of $\frac{1}{2}$. Indeed, their existence has been confirmed by experim turns out that H_2^+ is somewhat more stable than He_2^+, because there is only one tron in the hydrogen molecular ion and therefore it has no electron-electron sion. Furthermore, H_2^+ also has less nuclear repulsion than He_2^+. Our pre about He_2 is that it would have no stability, but in 1993 He_2 gas was found to The "molecule" is extremely unstable and has only a transient existence und cially created conditions.

Homonuclear Diatomic Molecules of Second-Period Elements

We are now ready to study the ground-state electron configuration of molecules taining second-period elements. We will consider only the simplest case, th ***homonuclear diatomic molecules,*** or *diatomic molecules containing atoms same elements.*

Figure 10.26 shows the molecular orbital energy level diagram for the first ber of the second period, Li_2. These molecular orbitals are formed by the overl $1s$ and $2s$ orbitals. We will use this diagram to build up all the diatomic mole as we will see shortly.

The situation is more complex when the bonding also involves *p* orbitals. orbitals can form either a sigma bond or a pi bond. Because there are three *p* o for each atom of a second-period element, we know that one sigma and two pi ular orbitals will result from the constructive interaction. The sigma molecular is formed by the overlap of the $2p_x$ orbitals along the internuclear axis, that is, th axis. The $2p_y$ and $2p_z$ orbitals are perpendicular to the *x*-axis, and they will ov sideways to give two pi molecular orbitals. The molecular orbitals are called σ_{2p}

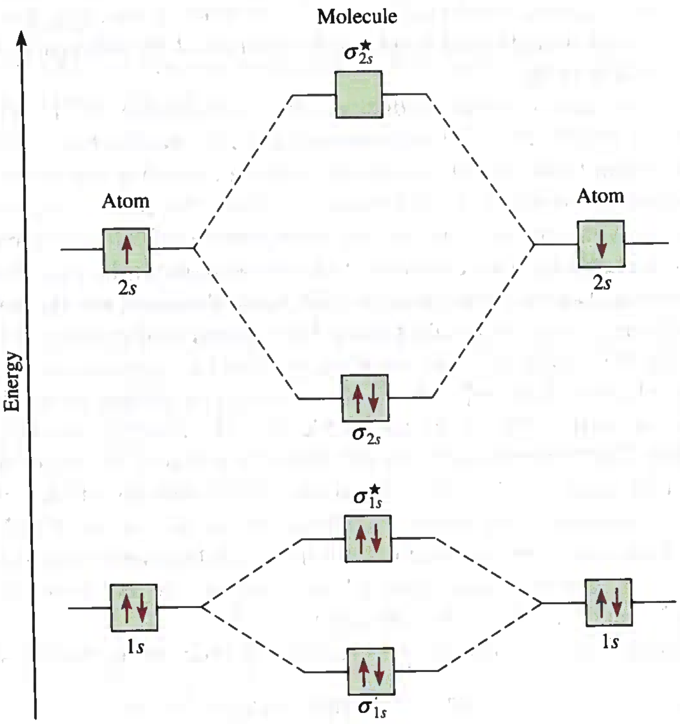


Figure 10.26 *Molecular orbital energy level diagram for the Li_2 molecule. The six electrons in Li_2 (Li's electron configuration is $1s^2 2s^1$) are in the σ_{1s}, $\sigma^\star_{1s}$, and σ_{2s} orbitals. Because there are two electrons each in σ_{1s} and $\sigma^\star_{1s}$ (just as in He_2), there is no net bonding or antibonding effect. Therefore, the single covalent bond in Li_2 is formed by the two electrons in the bonding molecular orbital σ_{2s}. Note that although the antibonding orbital ($\sigma^\star_{1s}$) has higher energy and is thus less stable than the bonding orbital (σ_{1s}), this antibonding orbital has less energy and greater stability than the σ_{2s} bonding orbital.*

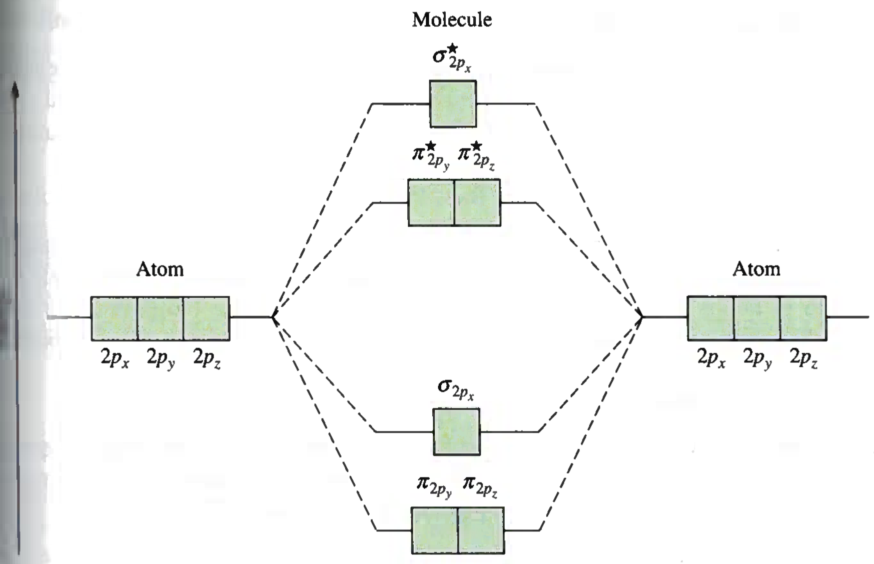


Figure 10.27 *General molecular orbital energy level diagram for the second-period homonuclear diatomic molecules Li_2, Be_2, B_2, C_2, and N_2. For simplicity, the σ_{1s} and σ_{2s} orbitals have been omitted. Note that in these molecules the σ_{2p_x} orbital is higher in energy than either the π_{2p_y} or the π_{2p_z} orbitals. This means that electrons in the σ_{2p_x} orbitals are less stable than those in π_{2p_y} and π_{2p_z}. For O_2 and F_2, the σ_{2p_x} orbital is lower in energy than π_{2p_y} and π_{2p_z}.*

and π_{2p_z} orbitals, where the subscripts indicate which atomic orbitals take part in forming the molecular orbitals. As shown in Figure 10.24, overlap of the two p orbitals is normally greater in a σ molecular orbital than in a π molecular orbital, so we would expect the former to be lower in energy. However, the energies of molecular orbitals actually increase as follows:

$$\sigma_{1s} < \sigma^{\star}_{1s} < \sigma_{2s} < \sigma^{\star}_{2s} < \pi_{2p_y} = \pi_{2p_z} < \sigma_{2p_x} < \pi^{\star}_{2p_y} = \pi^{\star}_{2p_z} < \sigma^{\star}_{2p_x}$$

The inversion of the σ_{2p_x} orbital and the π_{2p_y} and π_{2p_z} orbitals is due to the interaction between the $2s$ orbital on one atom with the $2p$ orbital on the other. In MO terminology, we say there is mixing between these orbitals. The condition for mixing is that the $2s$ and $2p$ orbitals must be close in energy. This condition is met for the lighter molecules B_2, C_2, and N_2 with the result that the σ_{2p_x} orbital is raised in energy relative to the π_{2p_y} and π_{2p_z} orbitals as already shown. The mixing is less pronounced for O_2 and F_2 so the σ_{2p_x} orbital lies lower in energy than the π_{2p_y} and π_{2p_z} orbitals in these molecules.

With these concepts and Figure 10.27, which shows the order of increasing energies for $2p$ molecular orbitals, we can write the electron configurations and predict the magnetic properties and bond orders of second-period homonuclear diatomic molecules. We will consider a few examples.

The Lithium Molecule (Li_2)

The electron configuration of Li is $1s^22s^1$, so Li_2 has a total of six electrons. According to Figure 10.26, these electrons are placed (two each) in the σ_{1s}, $\sigma^{\star}_{1s}$, and σ_{2s} molecular orbitals. The electrons of σ_{1s} and $\sigma^{\star}_{1s}$ make no net contribution to the bonding in Li_2. Thus, the electron configuration of the molecular orbitals in Li_2 is $(\sigma_{1s})^2(\sigma^{\star}_{1s})^2(\sigma_{2s})^2$. Since there are two more electrons in the bonding molecular orbitals than in antibonding orbitals, the bond order is 1 [see Equation (10.2)]. We conclude that the Li_2 molecule is stable, and because it has no unpaired electron spins, it should be diamagnetic. Indeed, diamagnetic Li_2 molecules are known to exist in the vapor phase.

The Carbon Molecule (C_2)

The carbon atom has the electron configuration $1s^22s^22p^2$; thus, there are 12 el in the C_2 molecule. From the bonding scheme for Li_2, we place four additional electrons in the π_{2p_y} and π_{2p_z} orbitals. Therefore, C_2 has the electron configura

$$(\sigma_{1s})^2(\sigma_{1s}^{\star})^2(\sigma_{2s})^2(\sigma_{2s}^{\star})^2(\pi_{2p_y})^2(\pi_{2p_z})^2$$

Its bond order is 2, and the molecule has no unpaired electrons. Again, diam C_2 molecules have been detected in the vapor state. Note that the double bonds are both pi bonds because of the four electrons in the two pi molecular orbit most other molecules, a double bond is made up of a sigma bond and a pi bon

The Oxygen Molecule (O_2)

As we stated earlier, valence bond theory does not account for the magnetic pro ties of the oxygen molecule. To show the two unpaired electrons on O_2, we nee draw an alternative to the resonance structure present on p. 429:

$$\cdot\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\!-\!\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\cdot$$

This structure is unsatisfactory on at least two counts. First, it implies the pres of a single covalent bond, but experimental evidence strongly suggests that there double bond in this molecule. Second, it places seven valence electrons around oxygen atom, a violation of the octet rule.

The ground-state electron configuration of O is $1s^22s^22p^4$; thus, there are 16 trons in O_2. Using the order of increasing energies of the molecular orbitals disc above, we write the ground-state electron configuration of O_2 as

$$(\sigma_{1s})^2(\sigma_{1s}^{\star})^2(\sigma_{2s})^2(\sigma_{2s}^{\star})^2(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi_{2p_y}^{\star})^1(\pi_{2p_z}^{\star})^1$$

TABLE 10.5 Properties of Homonuclear Diatomic Molecules of the Second-Period Elements*

	Li_2	B_2	C_2	N_2	O_2	F_2	
$\sigma_{2p_x}^{\star}$	☐	☐	☐	☐	☐	☐	$\sigma_{2p_x}^{\star}$
$\pi_{2p_y}^{\star}, \pi_{2p_z}^{\star}$	☐☐	☐☐	☐☐	☐☐	↑ ↑	↑↓ ↑↓	$\pi_{2p_y}^{\star}, \pi_{2p_z}^{\star}$
σ_{2p_x}	☐	☐	☐	↑↓	↑↓ ↑↓	↑↓ ↑↓	π_{2p_y}, π_{2p_z}
π_{2p_y}, π_{2p_z}	☐☐	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	↑↓	↑↓	σ_{2p_x}
$\sigma_{2s}^{\star}$	☐	↑↓	↑↓	↑↓	↑↓	↑↓	$\sigma_{2s}^{\star}$
σ_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	σ_{2s}
Bond order	1	1	2	3	2	1	
Bond length (pm)	267	159	131	110	121	142	
Bond enthalpy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9	
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	

*For simplicity the σ_{1s} and $\sigma_{1s}^{\star}$ orbitals are omitted. These two orbitals hold a total of four electrons. Remember that for O_2 and F_2, σ_{2p_x} is lower in energy than π_{2p_y} and π_{2p_z}.

According to Hund's rule, the last two electrons enter the $\pi^\star_{2p_y}$ and $\pi^\star_{2p_z}$ orbitals with parallel spins. Ignoring the σ_{1s} and σ_{2s} orbitals (because their net effects on bonding are zero), we calculate the bond order of O_2 using Equation (10.2):

$$\text{bond order} = \tfrac{1}{2}(6 - 2) = 2$$

Therefore, the O_2 molecule has a bond order of 2 and oxygen is paramagnetic, a prediction that corresponds to experimental observations.

Table 10.5 summarizes the general properties of the stable diatomic molecules of the second period.

Example 10.6 shows how MO theory can help predict molecular properties of ions.

Example 10.6

The N_2^+ ion can be prepared by bombarding the N_2 molecule with fast-moving electrons. Predict the following properties of N_2^+: (a) electron configuration, (b) bond order, (c) magnetic properties, and (d) bond length relative to the bond length of N_2 (is it longer or shorter?).

Strategy From Table 10.5 we can deduce the properties of ions generated from the homonuclear molecules. How does the stability of a molecule depend on the number of electrons in bonding and antibonding molecular orbitals? From what molecular orbital is an electron removed to form the N_2^+ ion from N_2? What properties determine whether a species is diamagnetic or paramagnetic?

Solution From Table 10.5 we can deduce the properties of ions generated from the homonuclear diatomic molecules.

(a) Because N_2^+ has one fewer electron than N_2, its electron configuration is

$$(\sigma_{1s})^2(\sigma^\star_{1s})^2(\sigma_{2s})^2(\sigma^\star_{2s})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^1$$

(b) The bond order of N_2^+ is found by using Equation (10.2):

$$\text{bond order} = \tfrac{1}{2}(9 - 4) = 2.5$$

(c) N_2^+ has one unpaired electron, so it is paramagnetic.

(d) Because the electrons in the bonding molecular orbitals are responsible for holding the atoms together, N_2^+ should have a weaker and, therefore, longer bond than N_2. (In fact, the bond length of N_2^+ is 112 pm, compared with 110 pm for N_2.)

Check Because an electron is removed from a bonding molecular orbital, we expect the bond order to decrease. The N_2^+ ion has an odd number of electrons (13), so it should be paramagnetic.

Similar problems: 10.57, 10.58.

Practice Exercise Which of the following species has a longer bond length: F_2 or F_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.

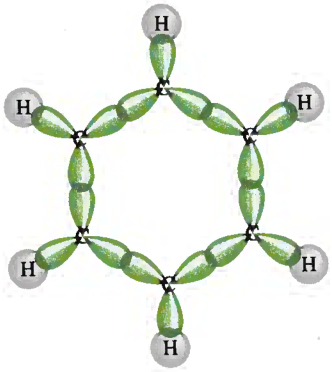
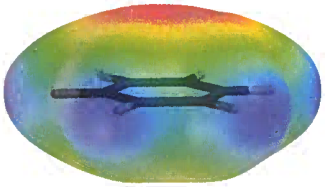


Figure 10.28 *The sigma bond framework in the benzene molecule. Each carbon atom is* sp^2*-hybridized and forms sigma bonds with two adjacent carbon atoms and another sigma bond with a hydrogen atom.*

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.

Because of their similar shape and orientation, each $2p_z$ orbital overlaps two others, one on each adjacent carbon atom. According to the rules listed on p. 431, the interaction of six $2p_z$ orbitals leads to the formation of six pi molecular orbitals, of which three are bonding and three antibonding. A benzene molecule in the ground state therefore has six electrons in the three pi bonding molecular orbitals, two electrons with paired spins in each orbital (Figure 10.29).



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.

Unlike the pi bonding molecular orbitals in ethylene, those in benzene form **delocalized molecular orbitals,** which *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. Thus, molecular orbital theory offers an alternative to the resonance approach, which is based on valence bond theory. (The resonance structures of benzene are shown on p. 379.)

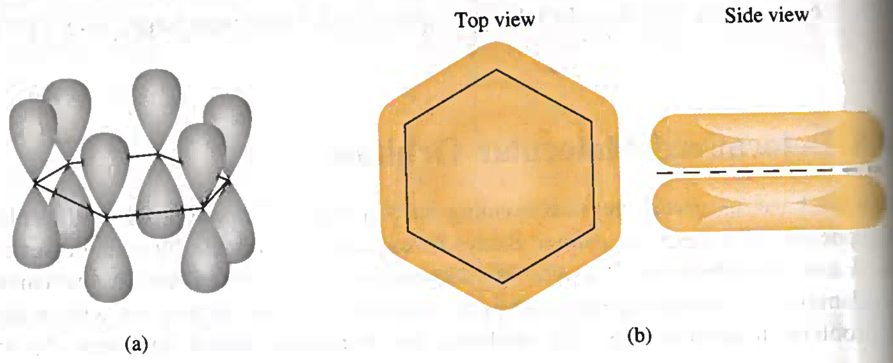


Figure 10.29 *(a) The six* $2p_z$ *orbitals on the carbon atoms in benzene. (b) The delocalized molecular orbital formed by the overlap of the* $2p_z$ *orbitals. The delocalized molecular orbital possesses pi symmetry and lies above and below the plane of the benzene ring. Actually, these* $2p_z$ *orbitals 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.*

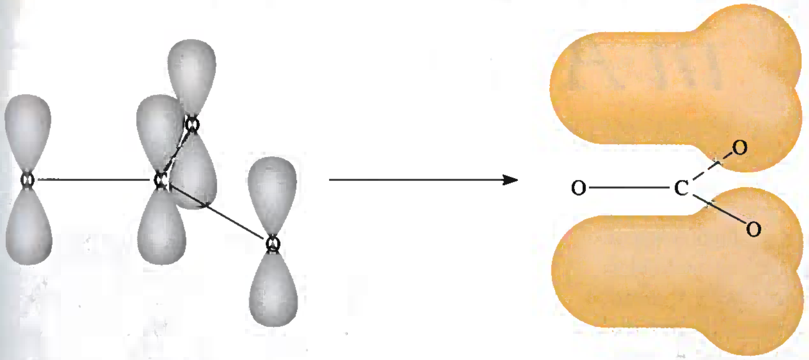


Figure 10.30 *Bonding in the carbonate ion. The carbon atom forms three sigma bonds with the three oxygen atoms. In addition, the $2p_z$ orbitals of the carbon and oxygen atoms overlap to form delocalized molecular orbitals, so that there is also a partial pi bond between the carbon atom and each of the three oxygen atoms.*

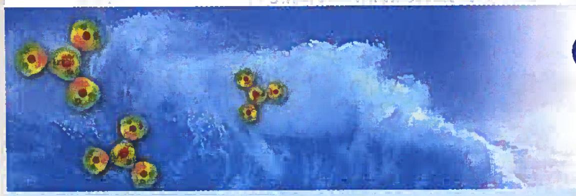
The Carbonate Ion

Cyclic compounds like benzene are not the only ones with delocalized molecular orbitals. Let's look at bonding in the carbonate ion (CO_3^{2-}). VSEPR predicts a trigonal 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 (Figure 10.30). The result is a delocalized molecular orbital that extends over all four nuclei in such a way that the electron densities (and hence the bond orders) in the carbon-to-oxygen bonds are all the same. Molecular orbital theory therefore provides an acceptable alternative explanation of the properties of the carbonate ion as compared with the resonance structures of the ion shown on p. 378.

We should note that molecules with delocalized molecular orbitals are generally more stable than those containing molecular orbitals extending over only two atoms. For example, the benzene molecule, which contains delocalized molecular orbitals, is chemically less reactive (and hence more stable) than molecules containing "localized" C=C bonds, such as ethylene.

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.
2. 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 forcefully than bonding pairs do and thus distort bond angles from the ideal geometry.
3. 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. Information about molecular geometry can be obtained from dipole moment measurements.
4. There are two quantum mechanical explanations for covalent bond formation: valence bond theory and molecular orbital theory. In valence bond theory, hybridized atomic orbitals are formed by the combination and rearrangement of orbitals from 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.
5. Valence-shell expansion can be explained by assuming hybridization of *s*, *p*, and *d* orbitals.
6. 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 an equilateral triangle; in sp^3 hybridization, the four hybrid orbitals are directed toward the corners of a tetrahedron; in sp^3d hybridization, the five hybrid orbitals are directed toward the corners of a trigonal bipyramid; in sp^3d^2 hybridization, the six hybrid orbitals are directed toward the corners of an octahedron.



CHEMISTRY *in Action*

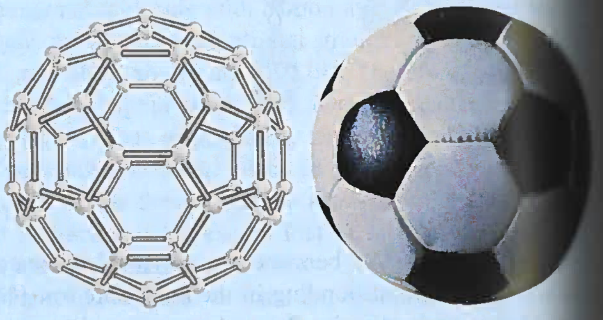
Buckyball, Anyone?

In 1985 chemists at Rice University in Texas used a high-powered laser to vaporize graphite in an effort to create unusual molecules believed to exist in interstellar space. Mass spectrometry revealed that one of the products was an unknown species with the formula C_{60}. Because of its size and the fact that it is pure carbon, this molecule has an exotic shape, which the researchers worked out using paper, scissors, and tape. Subsequent spectroscopic and X-ray measurements confirmed that C_{60} is shaped like a hollow sphere with a carbon atom at each of the 60 vertices. Geometrically, buckyball (short for "buckminsterfullerene") is the most symmetrical molecule known. In spite of its unique features, however, its bonding scheme is straightforward. Each carbon is sp^2-hybridized, and there are extensive delocalized molecular orbitals over the entire structure.

The discovery of buckyball generated tremendous interest within the scientific community. Here was a new allotrope of carbon with an intriguing geometry and unknown properties to investigate. Since 1985 chemists have created a whole class of *fullerenes,* with 70, 76, and even larger numbers of carbon atoms. Moreover, buckyball has been found to be a natural component of soot.

Buckyball and its heavier members represent a whole new concept in molecular architecture with far-reaching implications. For example, buckyball has been prepared with a helium atom trapped in its cage. Buckyball also reacts with potassium to give K_3C_{60}, which acts as a superconductor at 18 K. It is also possible to attach transition metals to buckyball. These derivatives show promise as catalysts. Because of its unique shape, buckyball can be used as a lubricant.

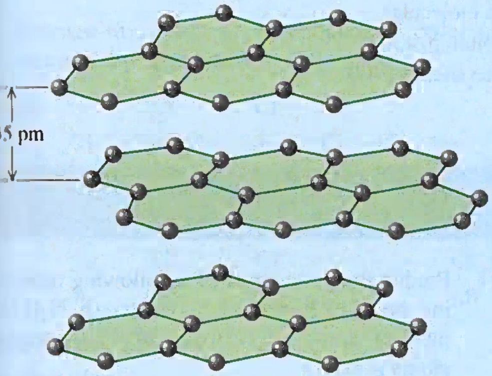
One fascinating discovery, made in 1991 by Japanese scientists, was the identification of structural relatives of buckyball. These molecules are hundreds of nanometers long with a tubular shape and an internal cavity about 15 nanometers in diameter. Dubbed "buckytubes" or "nanotubes" (because of their size), these molecules have two distinctly different structures. One is a single sheet of graphite that is capped at both with a kind of truncated buckyball. The other is a scroll tube having anywhere from 2 to 30 graphitelike layers. tubes are many times stronger than steel wires of similar sions. Numerous potential applications have been propo them, including conducting and high-strength materials, gen storage media, molecular sensors, semiconductor de and molecular probes. The study of these materials has a new field called *nanotechnology,* so called because scie can manipulate materials on a molecular scale to create devices.



The geometry of a buckyball C_{60} (left) resembles a soccer ball (right). tists arrived at this structure by fitting together paper cutouts of enou gons and pentagons to accommodate 60 carbon atoms at the poin they intersect.

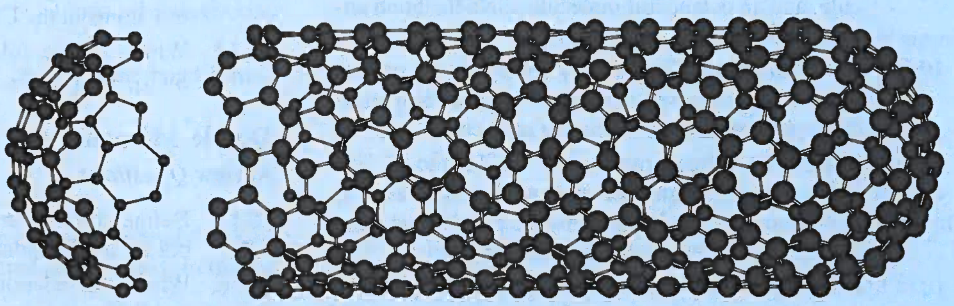
In the first biological application of buckyball, che at the University of California at San Francisco and Barbara made a discovery in 1993 that could help in desig drugs to treat AIDS. The human immunodeficiency (HIV) that causes AIDS reproduces by synthesizing a protein chain, which is cut into smaller segments by an zyme called HIV-protease. One way to stop AIDS, then,

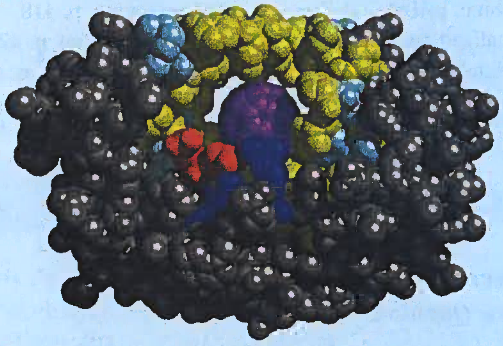
7. In an sp^2-hybridized atom (for example, carbon), the one unhybridized p orbital can form a pi bond with another p orbital. A carbon-carbon double bond consists of a sigma bond and a pi bond. In an sp-hybridized carbon atom, the two unhybridized p orbitals can form two pi bonds with two p orbitals on another atom (or atoms). A carbon-carbon triple bond consists of one sigma bond and two pi bonds.
8. Molecular orbital theory describes bonding in term the combination and rearrangement of atomic orbi to form orbitals that are associated with the molecul a whole.
9. Bonding molecular orbitals increase electron den between the nuclei and are lower in energy than vidual atomic orbitals. Antibonding molecular orbi have a region of zero electron density between



Graphite is made up of layers of six-membered rings of carbon.

The structure of a buckytube that consists of a single layer of carbon atoms. Note that the truncated buckyball "cap," which has been separated from the rest of the buckytube in this view, has a different structure than the graphitelike cylindrical portion of the tube. Chemists have devised ways to open the cap in order to place other molecules inside the tube.





Computer-generated model of the binding of a buckyball derivative to the site of HIV-protease that normally attaches to a protein needed for the reproduction of HIV. The buckyball structure (purple color) fits tightly into the active site, thus preventing the enzyme from carrying out its function.

to inactivate the enzyme. When the chemists reacted a water-soluble derivative of buckyball with HIV-protease, they found that it binds to the portion of the enzyme that would ordinarily cleave the reproductive protein, thereby preventing the HIV virus from reproducing. Consequently the virus could no longer infect the human cells they had grown in the laboratory. The buckyball compound itself is not a suitable drug for use against AIDS because of potential side effects and delivery difficulties, but it does provide a model for the development of such drugs.

nuclei, and an energy level higher than that of the individual atomic orbitals.

10. We write electron configurations for molecular orbitals as we do for atomic orbitals, filling in electrons in the order of increasing energy levels. The number of molecular orbitals always equals the number of atomic orbitals that were combined. The Pauli exclusion principle and Hund's rule govern the filling of molecular orbitals.
11. Molecules are stable if the number of electrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals.
12. Delocalized molecular orbitals, in which electrons are free to move around a whole molecule or group of atoms, are formed by electrons in p orbitals of adjacent atoms. Delocalized molecular orbitals are an alternative to resonance structures in explaining observed molecular properties.

Key Words

Antibonding molecular orbital, p. 430
Bond order, p. 433
Bonding molecular orbital, p. 430
Delocalized molecular orbital, p. 438
Dipole moment (μ), p. 409
Homonuclear diatomic molecule, p. 434
Hybrid orbital, p. 418
Hybridization, p. 418
Molecular orbital, p. 429
Nonpolar molecule, p. 410
Pi bond (π bond), p. 426
Pi molecular orbital, p. 432
Polar molecule, p. 410
Sigma bond (σ bond), p. 426
Sigma molecular orbital, p. 430
Valence shell, p. 400
Valence-shell elec repulsion (VSEPR) model, p. 400

Questions and Problems

Molecular Geometry

Review Questions

10.1 How is the geometry of a molecule defined and why is the study of molecular geometry important?

10.2 Sketch the shape of a linear triatomic molecule, a trigonal planar molecule containing four atoms, a tetrahedral molecule, a trigonal bipyramidal molecule, and an octahedral molecule. Give the bond angles in each case.

10.3 How many atoms are directly bonded to the central atom in a tetrahedral molecule, a trigonal bipyramidal molecule, and an octahedral molecule?

10.4 Discuss the basic features of the VSEPR model. Explain why the magnitude of repulsion decreases in the following order: lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair.

10.5 In the trigonal bipyramidal arrangement, why does a lone pair occupy an equatorial position rather than an axial position?

10.6 The geometry of CH_4 could be square planar, with the four H atoms at the corners of a square and the C atom at the center of the square. Sketch this geometry and compare its stability with that of a tetrahedral CH_4 molecule.

Problems

10.7 Predict the geometries of the following species using the VSEPR method: (a) PCl_3, (b) $CHCl_3$, (c) SiH_4, (d) $TeCl_4$.

10.8 Predict the geometries of the following species: (a) $AlCl_3$, (b) $ZnCl_2$, (c) $ZnCl_4^{2-}$.

10.9 Predict the geometry of the following molecules and ion using the VSEPR model: (a) CBr_4, (b) BCl_3, (c) NF_3, (d) H_2Se, (e) NO_2^-.

10.10 Predict the geometry of the following molecules and ion using the VSEPR model: (a) CH_3I, (b) ClF_3, (c) H_2S, (d) SO_3, (e) SO_4^{2-}.

10.11 Predict the geometry of the following molec ing the VSEPR method: (a) $HgBr_2$, (b) N_2O (ar ment of atoms is NNO), (c) SCN^- (arrange atoms is SCN).

10.12 Predict the geometries of the following ions: (a) (b) NH_2^-, (c) CO_3^{2-}, (d) ICl_2^-, (e) ICl_4^-, (f) (g) $SnCl_5^-$, (h) H_3O^+, (i) BeF_4^{2-}.

10.13 Describe the geometry around each of the th tral atoms in the CH_3COOH molecule.

10.14 Which of the following species are tetrah $SiCl_4$, SeF_4, XeF_4, CI_4, $CdCl_4^{2-}$

Dipole Moments

Review Questions

10.15 Define dipole moment. What are the units and bol for dipole moment?

10.16 What is the relationship between the dipole mo and the bond moment? How is it possible for a ecule to have bond moments and yet be nonpola

10.17 Explain why an atom cannot have a perman pole moment.

10.18 The bonds in beryllium hydride (BeH_2) molec are polar, and yet the dipole moment of the molec is zero. Explain.

Problems

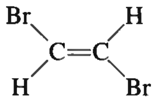
10.19 Referring to Table 10.3, arrange the following m cules in order of increasing dipole moment: H H_2S, H_2Te, H_2Se.

10.20 The dipole moments of the hydrogen halides crease from HF to HI (see Table 10.3). Explain trend.

10.21 List the following molecules in order of incre ing dipole moment: H_2O, CBr_4, H_2S, HF, NH CO_2.

10.22 Does the molecule OCS have a higher or lower pole moment than CS_2?

10.23 Which of the following molecules has a higher dipole moment?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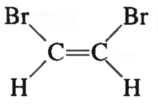
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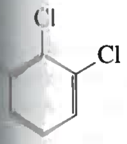
10.24 Arrange the following compounds in order of increasing dipole moment: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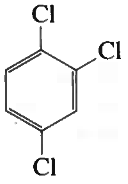
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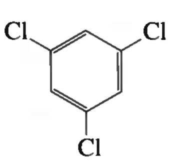
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Valence Bond Theory

Review Questions

10.25 What is valence bond theory? How does it differ from the Lewis concept of chemical bonding?

10.26 Use valence bond theory to explain the bonding in Cl_2 and HCl. Show how the atomic orbitals overlap when a bond is formed.

10.27 Draw a potential energy curve for the bond formation in F_2.

Hybridization

Review Questions

10.28 What is the hybridization of atomic orbitals? Why is it impossible for an isolated atom to exist in the hybridized state?

10.29 How does a hybrid orbital differ from a pure atomic orbital? Can two 2*p* orbitals of an atom hybridize to give two hybridized orbitals?

10.30 What is the angle between the following two hybrid orbitals on the same atom? (a) *sp* and *sp* hybrid orbitals, (b) sp^2 and sp^2 hybrid orbitals, (c) sp^3 and sp^3 hybrid orbitals

10.31 How would you distinguish between a sigma bond and a pi bond?

10.32 Which of the following pairs of atomic orbitals of adjacent nuclei can overlap to form a sigma bond? Which overlap to form a pi bond? Which cannot overlap (no bond)? Consider the *x*-axis to be the internuclear axis, that is, the line joining the nuclei of the two atoms. (a) 1*s* and 1*s*, (b) 1*s* and $2p_x$, (c) $2p_x$ and $2p_y$, (d) $3p_y$ and $3p_y$, (e) $2p_x$ and $2p_x$, (f) 1*s* and 2*s*

Problems

10.33 Describe the bonding scheme of the AsH_3 molecule in terms of hybridization.

10.34 What is the hybridization state of Si in SiH_4 and in $H_3Si{-}SiH_3$?

10.35 Describe the change in hybridization (if any) of the Al atom in the following reaction:

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

10.36 Consider the reaction

$$BF_3 + NH_3 \longrightarrow F_3B{-}NH_3$$

Describe the changes in hybridization (if any) of the B and N atoms as a result of this reaction.

10.37 What hybrid orbitals are used by nitrogen atoms in the following species? (a) NH_3, (b) $H_2N{-}NH_2$, (c) NO_3^-

10.38 What are the hybrid orbitals of the carbon atoms in the following molecules?

(a) $H_3C{-}CH_3$
(b) $H_3C{-}CH{=}CH_2$
(c) $CH_3{-}C{\equiv}C{-}CH_2OH$
(d) $CH_3CH{=}O$
(e) CH_3COOH

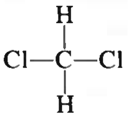
10.39 Specify which hybrid orbitals are used by carbon atoms in the following species: (a) CO, (b) CO_2, (c) CN^-.

10.40 What is the hybridization state of the central N atom in the azide ion, N_3^-? (Arrangement of atoms: NNN.)

10.41 The allene molecule $H_2C{=}C{=}CH_2$ is linear (the three C atoms lie on a straight line). What are the hybridization states of the carbon atoms? Draw diagrams to show the formation of sigma bonds and pi bonds in allene.

10.42 Describe the hybridization of phosphorus in PF_5.

10.43 How many sigma bonds and pi bonds are there in each of the following molecules?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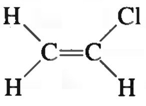
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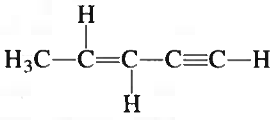
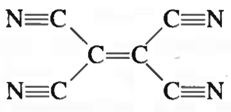

(c)

10.44 How many pi bonds and sigma bonds are there in the tetracyanoethylene molecule?



Molecular Orbital Theory

Review Questions

10.45 What is molecular orbital theory? How does it differ from valence bond theory?

10.46 Define the following terms: bonding molecular orbital, antibonding molecular orbital, pi molecular orbital, sigma molecular orbital.

10.47 Sketch the shapes of the following molecular orbitals: σ_{1s}, $\sigma^{\star}_{1s}$, π_{2p}, and $\pi^{\star}_{2p}$. How do their energies compare?

10.48 Explain the significance of bond order. Can bond order be used for quantitative comparisons of the strengths of chemical bonds?

Problems

10.49 Explain in molecular orbital terms the changes in H—H internuclear distance that occur as the molecular H_2 is ionized first to H_2^+ and then to H_2^{2+}.

10.50 The formation of H_2 from two H atoms is an energetically favorable process. Yet statistically there is less than a 100 percent chance that any two H atoms will undergo the reaction. Apart from energy considerations, how would you account for this observation based on the electron spins in the two H atoms?

10.51 Draw a molecular orbital energy level diagram for each of the following species: He_2, HHe, He_2^+. Compare their relative stabilities in terms of bond orders. (Treat HHe as a diatomic molecule with three electrons.)

10.52 Arrange the following species in order of increasing stability: Li_2, Li_2^+, Li_2^-. Justify your choice with a molecular orbital energy level diagram.

10.53 Use molecular orbital theory to explain why the Be_2 molecule does not exist.

10.54 Which of these species has a longer bond, B_2 or B_2^+? Explain in terms of molecular orbital theory.

10.55 Acetylene (C_2H_2) has a tendency to lose two protons (H^+) and form the carbide ion (C_2^{2-}), which is present in a number of ionic compounds, such as CaC_2 and MgC_2. Describe the bonding scheme in the C_2^{2-} ion in terms of molecular orbital theory. Compare the bond order in C_2^{2-} with that in C_2.

10.56 Compare the Lewis and molecular orbital treatments of the oxygen molecule.

10.57 Explain why the bond order of N_2 is greater than that of N_2^+, but the bond order of O_2 is less than that of O_2^+.

10.58 Compare the relative stability of the following species and indicate their magnetic properties (that is, diamagnetic or paramagnetic): O_2, O_2^+, O_2^- (superoxide ion), O_2^{2-} (peroxide ion).

10.59 Use molecular orbital theory to compare the relative stabilities of F_2 and F_2^+.

10.60 A single bond is almost always a sigma bond, and a double bond is almost always made up of a sigma bond and a pi bond. There are very few exceptions to this rule. Show that the B_2 and C_2 molecul
amples of the exceptions.

Delocalized Molecular Orbitals

Review Questions

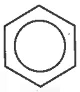
10.61 How does a delocalized molecular orbital
from a molecular orbital such as that foun
or C_2H_4? What do you think are the
conditions (for example, number of ato
types of orbitals) for forming a delocalized
ular orbital?

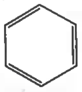
10.62 In Chapter 9 we saw that the resonance co
useful for dealing with species such as the
molecule and the carbonate ion. How does
lar orbital theory deal with these species?

Problems

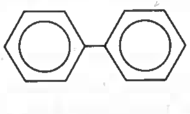
10.63 Both ethylene (C_2H_4) and benzene (C_6H_6)
the C=C bond. The reactivity of ethylene is
than that of benzene. For example, ethylene
reacts with molecular bromine, whereas ben
normally quite inert toward molecular bromi
many other compounds. Explain this differen
reactivity.

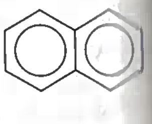
10.64 Explain why the symbol on the left is a better
sentation of benzene molecules than that
right.





10.65 Determine which of these molecules has a mor
localized orbital and justify your choice.





(*Hint:* Both molecules contain two benzene rin
naphthalene, the two rings are fused togeth
biphenyl, the two rings are joined by a single bo
around which the two rings can rotate.)

10.66 Nitryl fluoride (FNO_2) is very reactive chemic
The fluorine and oxygen atoms are bonded to the
trogen atom. (a) Write a Lewis structure for FN
(b) Indicate the hybridization of the nitrogen at
(c) Describe the bonding in terms of molecul
bital theory. Where would you expect delocali
molecular orbitals to form?

10.67 Describe the bonding in the nitrate ion NO
terms of delocalized molecular orbitals.

10.68 What is the state of hybridization of the central O atom in O_3? Describe the bonding in O_3 in terms of delocalized molecular orbitals.

Additional Problems

10.69 Which of the following species is not likely to have a tetrahedral shape? (a) $SiBr_4$, (b) NF_4^+, (c) SF_4, (d) $BeCl_4^{2-}$, (e) BF_4^-, (f) $AlCl_4^-$

10.70 Draw the Lewis structure of mercury(II) bromide. Is this molecule linear or bent? How would you establish its geometry?

10.71 Sketch the bond moments and resultant dipole moments for the following molecules: H_2O, PCl_3, XeF_4, PCl_5, SF_6.

10.72 Although both carbon and silicon are in Group 4A, very few Si=Si bonds are known. Account for the instability of silicon-to-silicon double bonds in general. (*Hint:* Compare the atomic radii of C and Si in Figure 8.5. What effect would the larger size have on pi bond formation?)

10.73 Predict the geometry of sulfur dichloride (SCl_2) and the hybridization of the sulfur atom.

10.74 Antimony pentafluoride, SbF_5, reacts with XeF_4 and XeF_6 to form ionic compounds, $XeF_3^+SbF_6^-$ and $XeF_5^+SbF_6^-$. Describe the geometries of the cations and anion in these two compounds.

10.75 Draw Lewis structures and give the other information requested for the following molecules: (a) BF_3. Shape: planar or nonplanar? (b) ClO_3^-. Shape: planar or nonplanar? (c) H_2O. Show the direction of the resultant dipole moment. (d) OF_2. Polar or nonpolar molecule? (e) NO_2. Estimate the ONO bond angle.

10.76 Predict the bond angles for the following molecules: (a) $BeCl_2$, (b) BCl_3, (c) CCl_4, (d) CH_3Cl, (e) Hg_2Cl_2 (arrangement of atoms: ClHgHgCl), (f) $SnCl_2$, (g) H_2O_2, (h) SnH_4.

10.77 Briefly compare the VSEPR and hybridization approaches to the study of molecular geometry.

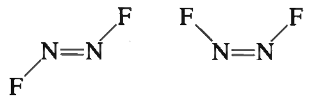
10.78 Describe the hybridization state of arsenic in arsenic pentafluoride (AsF_5).

10.79 Draw Lewis structures and give the other information requested for the following: (a) SO_3. Polar or nonpolar molecule? (b) PF_3. Polar or nonpolar molecule? (c) F_3SiH. Show the direction of the resultant dipole moment. (d) SiH_3^-. Planar or pyramidal shape? (e) Br_2CH_2. Polar or nonpolar molecule?

10.80 Which of the following molecules are linear? ICl_2^-, IF_2^+, OF_2, SnI_2, $CdBr_2$

10.81 Draw the Lewis structure for the $BeCl_4^{2-}$ ion. Predict its geometry and describe the hybridization state of the Be atom.

10.82 The N_2F_2 molecule can exist in either of the following two forms:

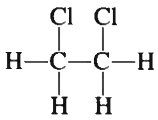


(a) What is the hybridization of N in the molecule?

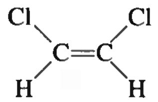
(b) Which structure has a dipole moment?

10.83 Cyclopropane (C_3H_6) has the shape of a triangle in which a C atom is bonded to two H atoms and two other C atoms at each corner. Cubane (C_8H_8) has the shape of a cube in which a C atom is bonded to one H atom and three other C atoms at each corner. (a) Draw Lewis structures of these molecules. (b) Compare the CCC angles in these molecules with those predicted for an sp^3-hybridized C atom. (c) Would you expect these molecules to be easy to make?

10.84 The compound 1,2-dichloroethane ($C_2H_4Cl_2$) is nonpolar, while *cis*-dichloroethylene ($C_2H_2Cl_2$) has a dipole moment:



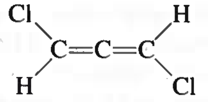
1,2-dichloroethane



cis-dichloroethylene

The reason for the difference is that groups connected by a single bond can rotate with respect to each other, but no rotation occurs when a double bond connects the groups. On the basis of bonding considerations, explain why rotation occurs in 1,2-dichloroethane but not in *cis*-dichloroethylene.

10.85 Does the following molecule have a dipole moment?

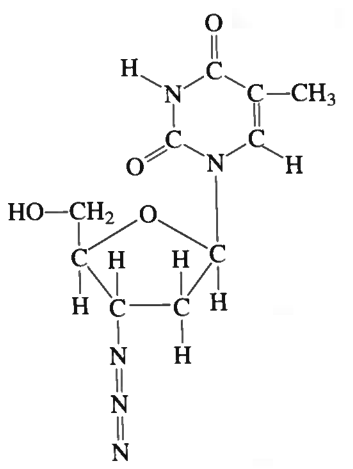


(*Hint:* See the answer to Problem 10.41.)

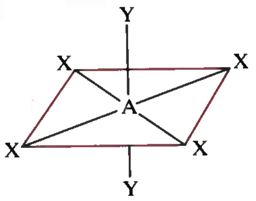
10.86 So-called greenhouse gases, which contribute to global warming, have a dipole moment or can be bent or distorted into shapes that have a dipole moment. Which of the following gases are greenhouse gases? N_2, O_2, O_3, CO, CO_2, NO_2, N_2O, CH_4, $CFCl_3$

10.87 The bond angle of SO_2 is very close to 120°, even though there is a lone pair on S. Explain.

10.88 3′-azido-3′-deoxythymidine, shown on p. 446, commonly known as AZT, is one of the drugs used to treat acquired immune deficiency syndrome (AIDS). What are the hybridization states of the C and N atoms in this molecule?



10.89 The following molecules (AX_4Y_2) all have octahedral geometry. Group the molecules that are equivalent to each other.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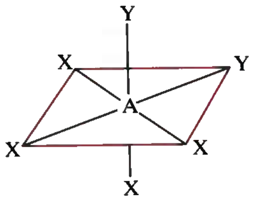
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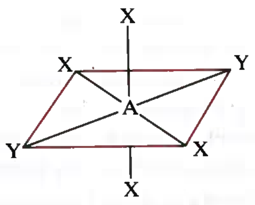
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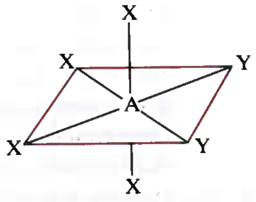
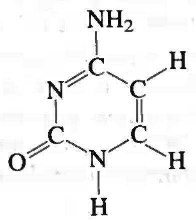

(d)

10.90 The compounds carbon tetrachloride (CCl_4) and silicon tetrachloride ($SiCl_4$) are similar in geometry and hybridization. However, CCl_4 does not react with water but $SiCl_4$ does. Explain the difference in their chemical reactivities. (*Hint:* The first step of the reaction is believed to be the addition of a water molecule to the Si atom in $SiCl_4$.)

10.91 Write the ground-state electron configuration for B_2. Is the molecule diamagnetic or paramagnetic?

10.92 What are the hybridization states of the C and N atoms in this molecule?



10.93 Use molecular orbital theory to explain
ence between the bond enthalpies of
Problem 9.110).

10.94 Referring to the Chemistry in Action on
swer the following questions: (a) If you
cook a roast (beef or lamb), would you
crowave oven or a conventional oven? (b)
means of locating an object by measuring
for the echo of a microwave from the object
to the source and the direction from which
Would radar work if oxygen, nitrogen,
dioxide were polar molecules? (c) In early
radar at the English Channel during World
the results were inconclusive even though
was no equipment malfunction. Why? (
weather is often foggy in the region.)

10.95 The stable allotropic form of phosphorus
which each P atom is bonded to three other
Draw a Lewis structure of this molecule
scribe its geometry. At high temperatures,
ciates to form P_2 molecules containing
bond. Explain why P_4 is more stable than

10.96 Referring to Table 9.4, explain why the
thalpy for Cl_2 is greater than that for F_2. (
bond lengths of F_2 and Cl_2 are 142 pm and
respectively.)

10.97 Use molecular orbital theory to explain the
the azide ion (N_3^-). (Arrangement of atoms

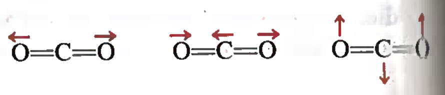
10.98 The ionic character of the bond in a diatomic
cule can be estimated by the formula

$$\frac{\mu}{ed} \times 100\%$$

where μ is the experimentally measured dipole
ment (in C m), e the electronic charge, and
bond length in meters. (The quantity ed is the
thetical dipole moment for the case in which
transfer of an electron from the less electro
to the more electronegative atom is com
Given that the dipole moment and bond len
HF are 1.92 D and 91.7 pm, respectively, cal
the percent ionic character of the molecule.

10.99 Draw three Lewis structures for compounds wi
formula $C_2H_2F_2$. Indicate which of the compou
are polar.

10.100 Greenhouse gases absorb (and trap) outgoing
radiation (heat) from Earth and contribute to
warming. The molecule of a greenhouse gas either
sesses a permanent dipole moment or has a
dipole moment during its vibrational motions.
sider three of the vibrational modes of carbon



where the arrows indicate the movement of the atoms. (During a complete cycle of vibration, the atoms move toward one extreme position and then reverse their direction to the other extreme position.) Which of the preceding vibrations are responsible for CO_2 to behave as a greenhouse gas? Which of the following molecules can act as a greenhouse gas: N_2, O_2, CO, NO_2, and N_2O?

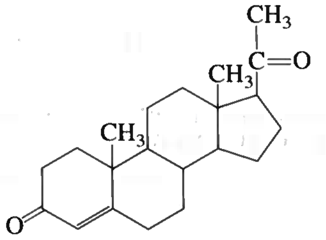
10.101 Aluminum trichloride ($AlCl_3$) is an electron-deficient molecule. It has a tendency to form a dimer (a molecule made of two $AlCl_3$ units):

$$AlCl_3 + AlCl_3 \longrightarrow Al_2Cl_6$$

(a) Draw a Lewis structure for the dimer. (b) Describe the hybridization state of Al in $AlCl_3$ and Al_2Cl_6. (c) Sketch the geometry of the dimer. (d) Do these molecules possess a dipole moment?

10.102 The molecules *cis*-dichloroethylene and *trans*-dichloroethylene shown on p. 411 can be interconverted by heating or irradiation. (a) Starting with *cis*-dichloroethylene, show that rotating the C═C bond by 180° will break only the pi bond but will leave the sigma bond intact. Explain the formation of *trans*-dichloroethylene from this process. (Treat the rotation as two stepwise 90° rotations.) (b) Account for the difference in the bond enthalpies for the pi bond (about 270 kJ/mol) and the sigma bond (about 350 kJ/mol). (c) Calculate the longest wavelength of light needed to bring about this conversion.

10.103 Progesterone is a hormone responsible for female sex characteristics. In the usual shorthand structure, each point where lines meet represent a C atom, and most H atoms are not shown. Draw the complete structure of the molecule, showing all C and H atoms. Indicate which C atoms are sp^2- and sp^3-hybridized.



Special Problems

10.104 For each pair listed here, state which one has a higher first ionization energy and explain your choice: (a) H or H_2, (b) N or N_2, (c) O or O_2, (d) F or F_2.

10.105 The molecule benzyne (C_6H_4) is a very reactive species. It resembles benzene in that it has a six-membered ring of carbon atoms. Draw a Lewis structure of the molecule and account for the molecule's high reactivity.

10.106 Assume that the third-period element phosphorus forms a diatomic molecule, P_2, in an analogous way as nitrogen does to form N_2. (a) Write the electronic configuration for P_2. Use $[Ne_2]$ to represent the electron configuration for the first two periods. (b) Calculate its bond order. (c) What are its magnetic properties (diamagnetic or paramagnetic)?

10.107 Consider a N_2 molecule in its first excited electronic state; that is, when an electron in the highest occupied molecular orbital is promoted to the lowest empty molecular obital. (a) Identify the molecular orbitals involved and sketch a diagram to show the transition. (b) Compare the bond order and bond length of N_2* with N_2, where the asterisk denotes the excited molecule. (c) Is N_2* diamagnetic or paramagnetic? (d) When N_2* loses its excess energy and converts to the ground state N_2, it emits a photon of wavelength 470 nm, which makes up part of the auroras lights. Calculate the energy difference between these levels.

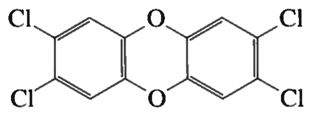
10.108 As mentioned in the chapter, the Lewis structure for O_2 is

$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$$

Use the molecular orbital theory to show that the structure actually corresponds to an excited state of the oxygen molecule.

10.109 Draw the Lewis structure of ketene (C_2H_2O) and describe the hybridization states of the C atoms. The molecule does not contain O—H bonds. On separate diagrams, sketch the formation of sigma and pi bonds.

10.110 TCDD, or 2,3,7,8-tetrachlorodibenzo-p-dioxin, is a highly toxic compound



It gained considerable notoriety in 2004 when it was implicated in the murder plot of a Ukrainian politician. (a) Describe its geometry and state whether the molecule has a dipole moment. (b) How many pi bonds and sigma bonds are there in the molecule?

10.111 Write the electron configuration of the cyanide ion (CN^-). Name a stable molecule that is isoelectronic with the ion.

10.112 Carbon monoxide (CO) is a poisonous compound due to its ability to bind strongly to Fe^{2+} in the hemoglobin molecule. The molecular orbitals of CO have the same energy order as those of the N_2 molecule, (a) Draw a Lewis structure of CO and assign formal charges. Explain why CO has a rather small dipole moment of 0.12 D. (b) Compare the bond order of CO with that from the molecular orbital theory. (c) Which of the atoms (C or O) is more likely to
bonds with the Fe^{2+} ion in hemoglobin?

10.113 The geometries discussed in this chapter all
themselves to fairly straightforward elucidation
bond angles. The exception is the tetrahedron, be
its bond angles are hard to visualize. Consider
CCl_4 molecule, which has a tetrahedral geometry
is nonpolar. By equating the bond moment of a p
ular C—Cl bond to the resultant bond moments of
other three C—Cl bonds in opposite directions,
that the bond angles are all equal to 109.5°.

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^-.