Chapter 9

Molecular Geometry and Covalent Bonding Models

In Chapter 8 "Ionic versus Covalent Bonding", we described the interactions that hold atoms together in chemical substances, focusing on the lattice energy of ionic compounds and the bond energy of covalent compounds. In the process, we introduced Lewis electron structures, which provide a simple method for predicting the number of bonds in common substances. As you learned in Chapter 8 "Ionic versus Covalent Bonding", the dots in Lewis structures represent the valence electrons of the constituent atoms and are paired according to the octet rule. As you will soon discover, however, the bonding in more complex molecules, such as those with multiple bonds or an odd number of electrons, cannot be explained with this simple approach. The purpose of this chapter is to introduce you to conceptual models used by chemists to describe the bonding in more complex compounds.
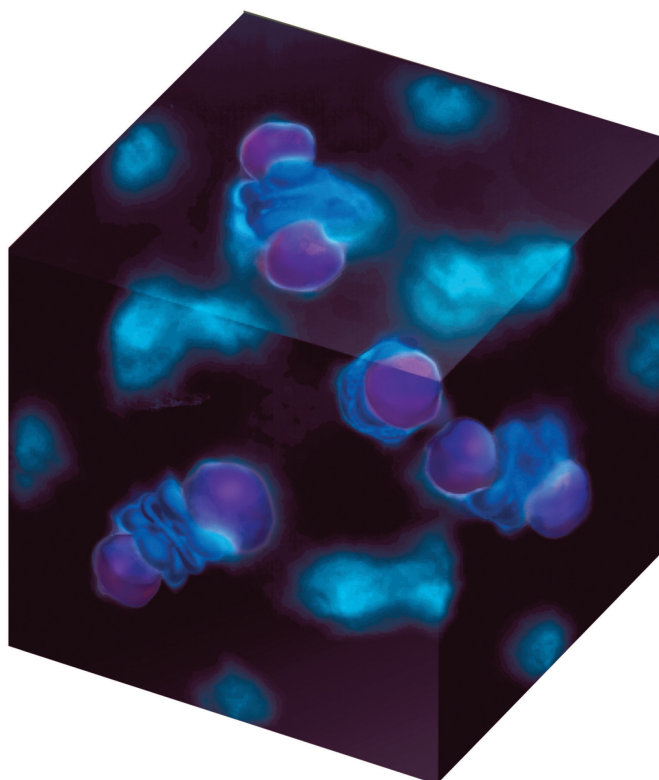
An experimental image of a covalent bond. This image shows that the bonding electrons on the copper atom in Cu_2O occupy d_{z^2} orbitals that point toward the oxygen atoms located at the center and corners of a cube.

In this chapter, we begin with a general method for predicting the structures of simple covalent molecules and polyatomic ions; then we discuss the actual distribution of electrons in covalent bonds. We apply two distinct approaches for describing covalent bonds: (1) a localized model to describe bonding in molecules with two or more atoms attached to a central atom and (2) a delocalized model to explain and predict which diatomic species exist and which do not exist. We conclude by describing more complex molecules and ions with multiple bonds. The tools you acquire in this chapter will enable you to explain why Ca_2 is too unstable to exist in nature and why the unpaired electrons on O_2 are crucial to the existence of life as we know it. You will also discover why carbon, the basic component of all organic compounds, forms four bonds despite having only two unpaired electrons in its valence electron configuration and how the structure of retinal, the key light-sensing component in our eyes, allows us to detect visible light.

9.1 Predicting the Geometry of Molecules and Polyatomic Ions

> ### LEARNING OBJECTIVES
>
> 1. To use the VSEPR model to predict molecular geometries.
> 2. To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach described in <u>Chapter 8 "Ionic versus Covalent Bonding"</u> can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion (VSEPR) model**[1] (pronounced "vesper"), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The VSEPR model is *not* a theory; it does not attempt to explain observations. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

> ## Note the Pattern
>
> Lewis electron structures predict the number and types of bonds, whereas VSEPR can predict the shapes of many molecules and polyatomic ions.

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing on only the number of electron pairs around the *central atom*,

1. A model used to predict the shapes of many molecules and polyatomic ions, based on the idea that the lowest-energy arrangement for a compound is the one in which its electron pairs (bonding and nonbonding) are as far apart as possible.

ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms" and Figure 9.2 "Geometries for Species with Two to Six Electron Groups".

Figure 9.1   Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms
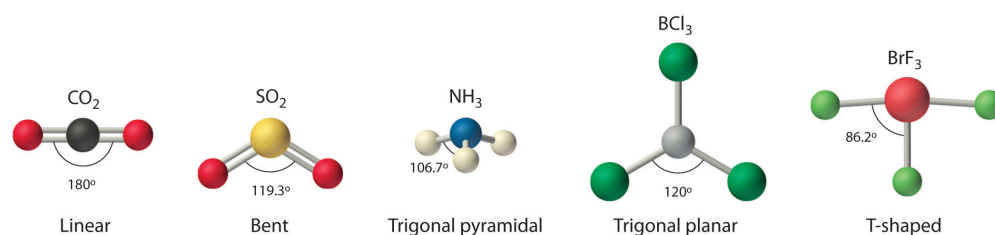
The VSEPR model explains these differences in molecular geometry.

Figure 9.2   Geometries for Species with Two to Six Electron Groups

Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Predicted Bond Angles	180°	120°	109.5°	90°, 120°	90°

Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy. That is, the one that minimizes repulsions.

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group
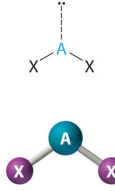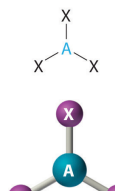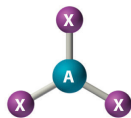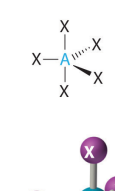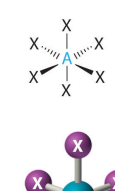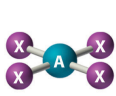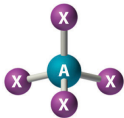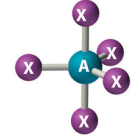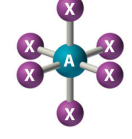
around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**[2]. Using this information, we can describe the **molecular geometry**[3], the arrangement of the *bonded atoms* in a molecule or polyatomic ion. This procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 9.2 "Geometries for Species with Two to Six Electron Groups" and Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*", which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

2. The angle between bonds.

3. The arrangement of the bonded atoms in a molecule or a polyatomic ion in space.

Figure 9.3 *Common Molecular Geometries for Species with Two to Six Electron Groups**

AX_mE_n Notation	AX_2	AX_2E	AX_3	AX_3E
Geometry	Linear	Bent (V-shaped)	Trigonal planar	Trigonal pyramidal
Idealized Bond Angles	180°	<180°	120°	<120°

AX_mE_n Notation	AX_4E_2	AX_4	AX_5	AX_6
Geometry	Square planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Idealized Bond Angles	90°	109.5°	90°, 120°	90°

Lone pairs are shown using a dashed line.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

$$H:Be:H \quad \text{or} \quad H—Be—H$$

Lewis structure
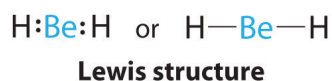
2. There are two electron groups around the central atom. We see from Figure 9.2 "Geometries for Species with Two to Six Electron Groups" that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*" we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is

$$\ddot{O}\!::\!C\!::\!\ddot{O}$$

2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"). The structure of CO_2 is shown in Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms" .

Three Electron Groups
AX_3: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is
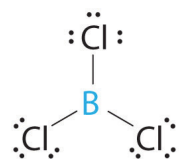
Lewis structure

2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (<u>Figure 9.2 "Geometries for Species with Two to Six Electron Groups"</u>).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From <u>Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"</u> we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in <u>Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms"</u>.

AX_3: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned in <u>Chapter 8 "Ionic versus Covalent Bonding"</u>, the Lewis electron structure of one of three resonance forms is represented as
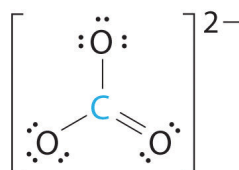
Lewis structure

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of $1 \frac{1}{3}$. We minimize repulsions by placing the three groups 120° apart (<u>Figure 9.2 "Geometries for Species with Two to Six Electron Groups"</u>).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from <u>Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"</u> that the molecular geometry of CO_3^{2-} is trigonal planar.
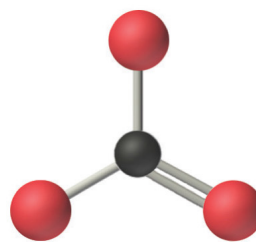
Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX$_2$E: SO$_2$

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.
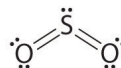
2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (<u>Figure 9.2 "Geometries for Species with Two to Six Electron Groups"</u>).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX$_2$E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (<u>Figure 9.4 "The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair"</u>). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO$_2$, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (<u>Figure 9.1 "Common Structures for Molecules and Polyatomic Ions</u>

That Consist of a Central Atom Bonded to Two or Three Other Atoms" and Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*").

Figure 9.4 *The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair*
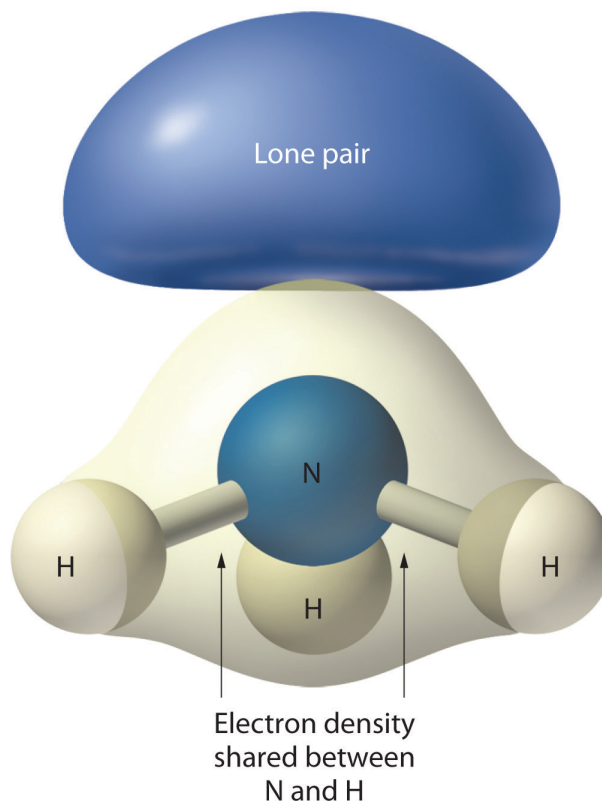
As with SO$_2$, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH$_2$O (AX$_3$), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

116.5°
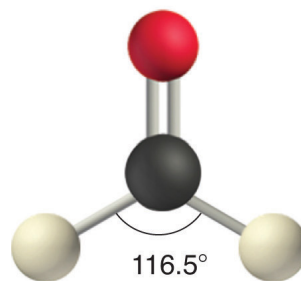
Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX$_4$: CH$_4$

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is
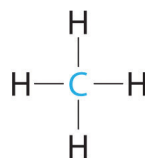
Lewis structure

2. There are four electron groups around the central atom. As shown in <u>Figure 9.2 "Geometries for Species with Two to Six Electron Groups"</u>, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX$_4$.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (<u>Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"</u>).
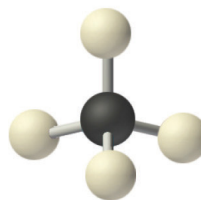
Molecular geometry
(tetrahedral)

AX$_3$E: NH$_3$

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure
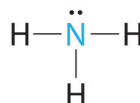
Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX$_3$E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*" and Figure 9.4 "The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair").

AX$_2$E$_2$: H$_2$O

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

$$H - \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - H$$
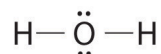
2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron <u>Figure 9.2 "Geometries for Species with Two to Six Electron Groups"</u>.

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.

104.5°
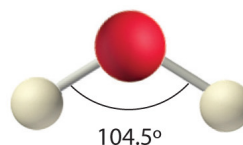
Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5: PCl_5

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is
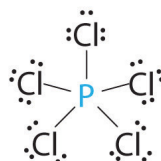
2. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (<u>Figure 9.2 "Geometries for Species with Two to Six Electron Groups"</u>):

3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in <u>Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"</u>. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.

PCl_5
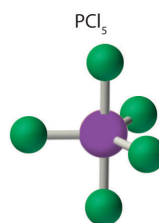
AX_4E: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is
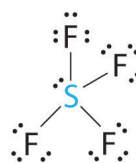
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in <u>Figure 9.2 "Geometries for Species with Two to Six Electron Groups"</u>.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at 90°. If we place it in the axial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the equatorial position is more stable than the one with the lone pair in the axial position. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

Figure 9.5 *Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them*
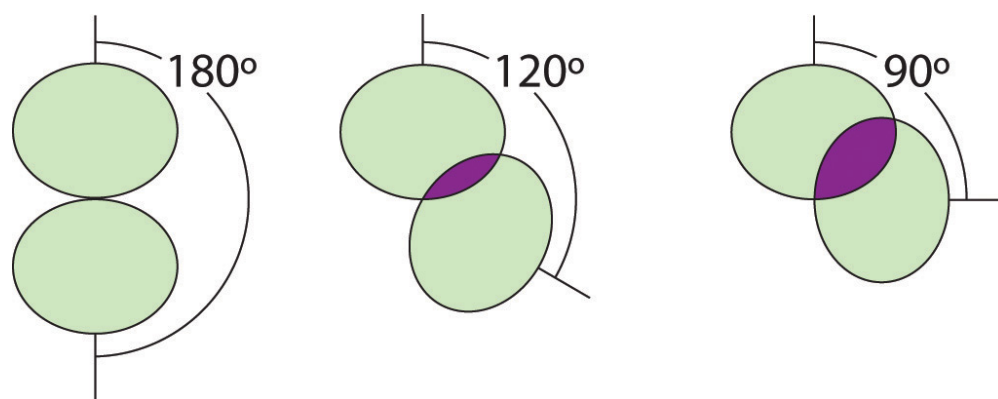
At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.
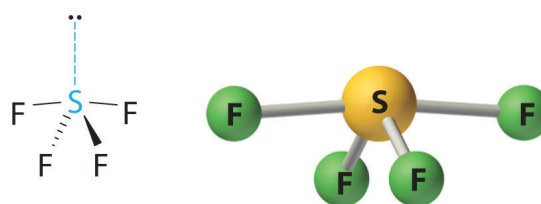
Molecular geometry (seesaw)

AX₃E₂: BrF₃

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is
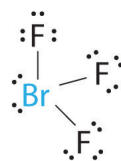
Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:

	Lone pairs axial	Lone pairs equatorial	Lone pairs axial and equatorial
	(a)	(b)	(c)
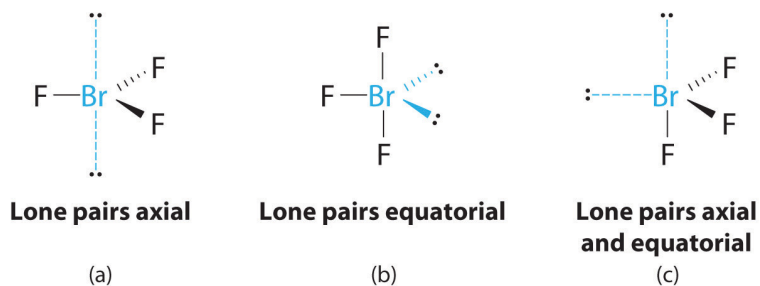
Interactions

90° LP–LP	0	0	1
90° LP–BP	6	4	3

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we

predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped.* This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions ([Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms"](#)).

Note the Pattern

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

AX_2E_3: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is

$$: \ddot{I} \, {-}{\cdot} \, \underset{\cdot\cdot}{I} \, {\cdot}{-} \, \ddot{I} :$$

2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.
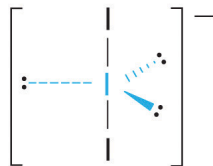
The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

I_3^-
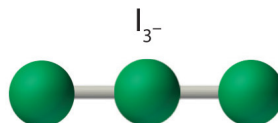
Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 9.2 "Geometries for Species with Two to Six Electron Groups").

AX$_6$: SF$_6$

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is
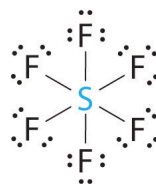
Lewis structure

With an expanded valence, we know from Chapter 8 "Ionic versus Covalent Bonding", Section 8.6 "Exceptions to the Octet Rule" that this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 9.2 "Geometries for Species with Two to Six Electron Groups" that the geometry that minimizes repulsions is *octahedral.*

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.
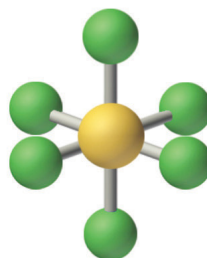
Molecular geometry
(octahedral)

AX_5E: BrF_5

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is
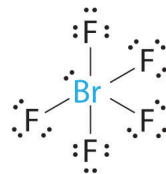
Lewis structure

With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:
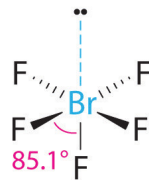
3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal.* The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.
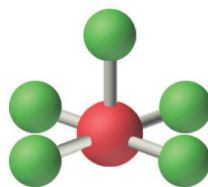
Molecular geometry
(square pyramidal)

AX_4E_2: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is
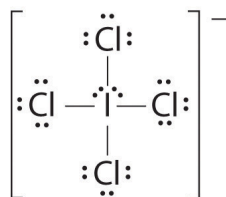
2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is

$$\left[\begin{array}{c} Cl_{\cdots} \ddot{} \cdots Cl \\ Cl \ddot{} Cl \end{array}\right]^{-}$$
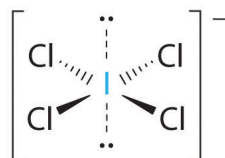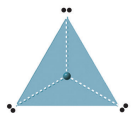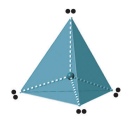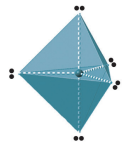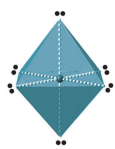
3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl_4^- ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.
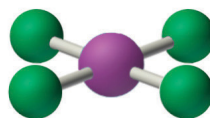
The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 9.6 "Overview of Molecular Geometries".

Figure 9.6 *Overview of Molecular Geometries*

Electron Groups	2	3	4	5	6
Molecular Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Zero Lone Pairs	X—A—X Linear AX_2	Trigonal planar AX_3	Tetrahedral AX_4	Trigonal bipyramidal AX_5	Octahedral AX_6
One Lone Pair		Bent (V-shaped) AX_2E	Trigonal pyramidal AX_3E	Seesaw AX_4E One axial lone pair	Square pyramidal AX_5E
Two Lone Pairs			Bent (V-shaped) AX_2E_2	T-shaped AX_3E_2 Two axial lone pairs	Square planar AX_4E_2
Three Lone Pairs				Linear AX_2E_3 Three axial lone pairs	

EXAMPLE 1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
b. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A Draw the Lewis electron structure of the molecule or polyatomic ion.

B Determine the electron group arrangement around the central atom that minimizes repulsions.

C Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.

D Describe the molecular geometry.

Solution:

a. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is
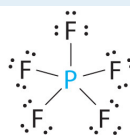
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 9.6 "Overview of Molecular Geometries").

C All electron groups are bonding pairs, so PF$_5$ is designated as AX$_5$. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF$_5$ molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.

b. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is
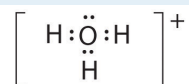
B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH$_3$, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX$_3$E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:
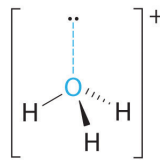
Exercise

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer:

a. trigonal pyramidal
b. octahedral
c. linear

EXAMPLE 2

Predict the molecular geometry of each molecule.

a. XeF_2
b. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example 1.

Solution:

a. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is

$$:\!\ddot{F}\!-\!\dot{\underset{..}{X}e}\!-\!\ddot{F}\!:$$

B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:

Interactions			
90 LP–LP	0	2	2
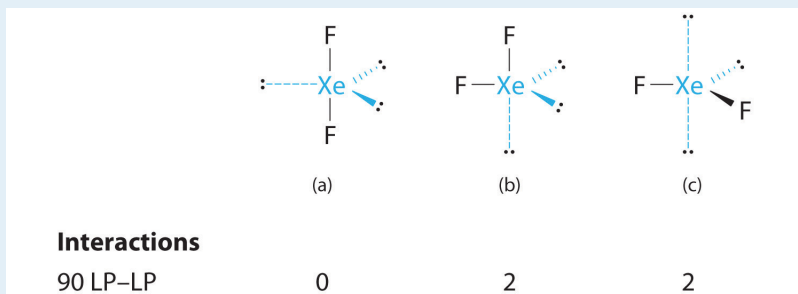
The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

b. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is
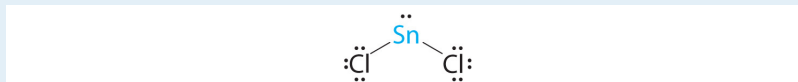
B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but

with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answers:

a. trigonal planar
b. square planar

Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate ($CH_3–N=C=O$), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the $CH_3–N$ portion of the molecule to be roughly tetrahedral, similar to methane:
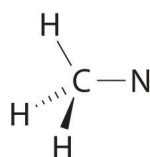
The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:

$$\overset{\displaystyle \ddot{N}}{\underset{\displaystyle C}{}} \quad C$$
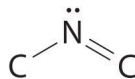
Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:
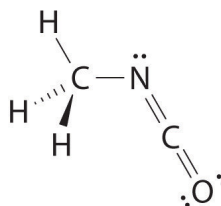
We predict that all four nonhydrogen atoms lie in a single plane, with a C–N–C angle of approximately 120°. The experimentally determined structure of methyl isocyanate confirms our prediction (<u>Figure 9.7 "The Experimentally Determined Structure of Methyl Isocyanate"</u>).

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

Figure 9.7 The Experimentally Determined Structure of Methyl Isocyanate

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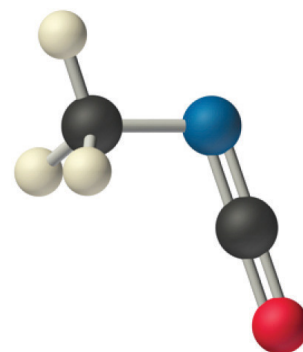
EXAMPLE 3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C\equiv CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use <u>Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"</u> to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with $C–C\equiv C$ and $C\equiv C–H$ angles of 180°.

Exercise

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer: The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

Molecular Dipole Moments

In <u>Chapter 8 "Ionic versus Covalent Bonding"</u>, you learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole

moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (part (a) in <u>Figure 9.8 "How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures"</u>). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (part (b) in <u>Figure 9.8 "How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures"</u>); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules. (For more information on polar bonds, see <u>Chapter 4 "Reactions in Aqueous Solution"</u>, <u>Section 4.1 "Aqueous Solutions"</u>.)

Figure 9.8   How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures

(a) No net dipole moment

(b) Net dipole moment
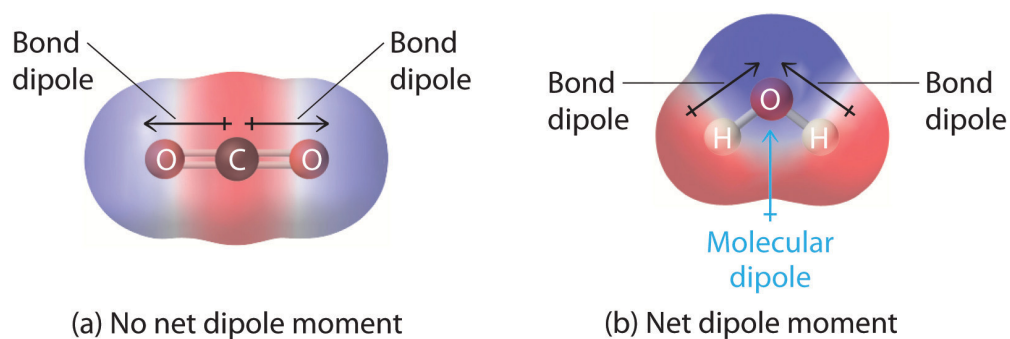
(a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in <u>Figure 9.9 "Molecules with Polar Bonds"</u>. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms

bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment.

Figure 9.9 *Molecules with Polar Bonds*
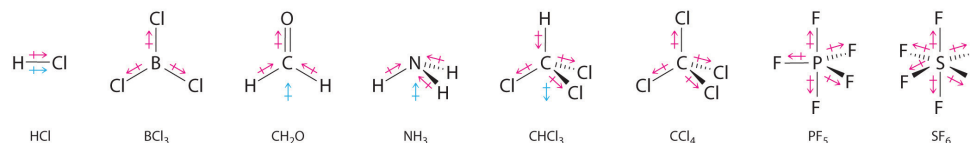
Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

Note the Pattern

Molecules with asymmetrical charge distributions have a net dipole moment.

EXAMPLE 4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

Asked for: net dipole moment

Strategy:

For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

a. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 9.6 "Overview of Molecular Geometries"). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.
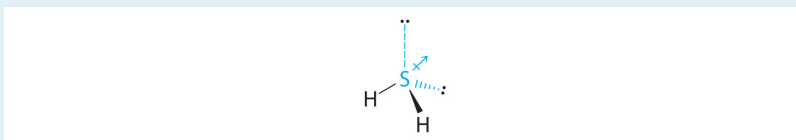
b. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.
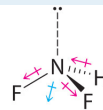
c. The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:
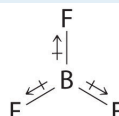
Exercise

Which molecule(s) has a net dipole moment?

a. CH_3Cl
b. SO_3
c. XeO_3

Answer: CH_3Cl; XeO_3

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. A combination of VSEPR and a bonding model, such as Lewis electron structures, however, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

KEY TAKEAWAY

- The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds.

CONCEPTUAL PROBLEMS

1. What is the main difference between the VSEPR model and Lewis electron structures?

2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.

3. How does the VSEPR model deal with the presence of multiple bonds?

4. Three molecules have the following generic formulas: AX_2, AX_2E, and AX_2E_2. Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.

5. Which has the smaller angles around the central atom—H_2S or SiH_4? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?

6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?

7. When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.

8. How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?

9. Straight-chain alkanes do not have linear structures but are "kinked." Using *n*-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of *n*-hexane.

10. How is molecular geometry related to the presence or absence of a molecular dipole moment?

11. How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?

12. What two features of a molecule's structure and bonding are required for a molecule to be considered polar? Is COF_2 likely to have a significant dipole moment? Explain your answer.

13. When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?

14. Use the VSPER model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.

    a. CH_3Cl
    b. PCl_3
    c. CO
    d. SF_6
    e. IF_5
    f. CH_3OCH_3
    g. CCl_3H
    h. H_3COH

15. The idealized molecular geometry of BrF_5 is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of BrF_5? If LP–BP repulsions were *weaker* than BP–BP repulsions, what would be the effect on the molecular geometry of BrF_5?

16. Which has the smallest bond angle around the central atom—H_2S, H_2Se, or H_2Te? the largest? Justify your answers.

17. Which of these molecular geometries *always* results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

ANSWERS

3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.

11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.

13. The term "polar" is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.

NUMERICAL PROBLEMS

1. Give the number of electron groups around the central atom and the molecular geometry for each molecule. Classify the electron groups in each species as bonding pairs or lone pairs.

   a. BF_3
   b. PCl_3
   c. XeF_2
   d. $AlCl_4^-$
   e. CH_2Cl_2

2. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.

   a. ICl_3
   b. CCl_3^+
   c. H_2Te
   d. XeF_4
   e. NH_4^+

3. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

   a. HCl
   b. NF_3
   c. ICl_2^+
   d. N_3^-
   e. H_3O^+

4. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

   a. SO_3
   b. NH_2^-
   c. NO_3^-
   d. I_3^-
   e. OF_2

5. What is the molecular geometry of ClF_3? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.

6. Predict the molecular geometry of each of the following.

    a. ICl_3
    b. AsF_5
    c. NO_2^-
    d. $TeCl_4$

7. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

    a. NO
    b. HF
    c. PCl_3
    d. CO_2
    e. SO_2
    f. SF_4

8. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

    a. OF_2
    b. BCl_3
    c. CH_2Cl_2
    d. TeF_4
    e. CH_3OH
    f. XeO_4

9. Of the molecules $Cl_2C=Cl_2$, IF_3, and SF_6, which has a net dipole moment? Explain your reasoning.

10. Of the molecules SO_3, XeF_4, and $H_2C=Cl_2$, which has a net dipole moment? Explain your reasoning.

ANSWERS

1. a. trigonal planar (all electron groups are bonding pairs)
    b. tetrahedral (one lone pair on P)
    c. trigonal bipyramidal (three lone pairs on Xe)
    d. tetrahedral (all electron groups on Al are bonding pairs)
    e. tetrahedral (all electron groups on C are bonding pairs)

3. a. four electron groups, linear molecular geometry

    b. four electron groups, pyramidal molecular geometry
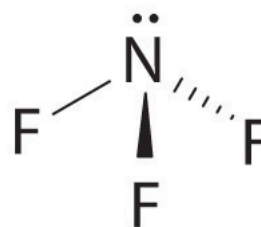
    c. four electron groups, bent molecular geometry
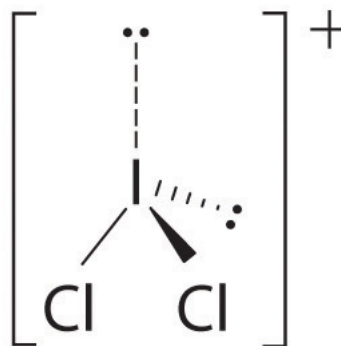
    d. two electron groups, linear molecular geometry

    e. four electron groups, pyramidal molecular geometry
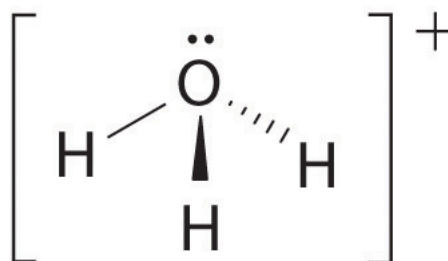
5.
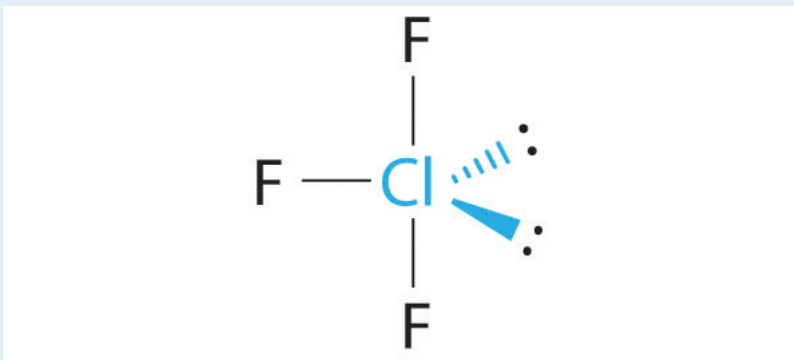
The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.

9. $Cl_2C=CCl_2$: Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C=CCl_2$ does not have a net dipole moment.
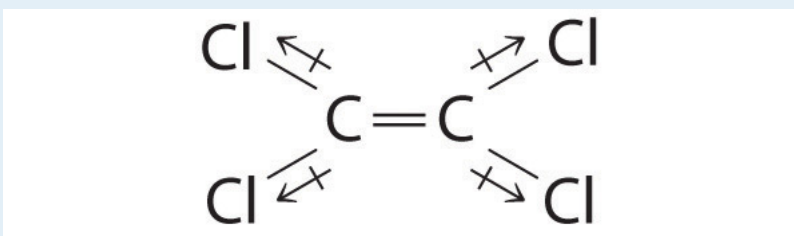
IF_3: In this structure, the individual I–F bond dipoles cannot cancel one another, giving IF_3 a net dipole moment.
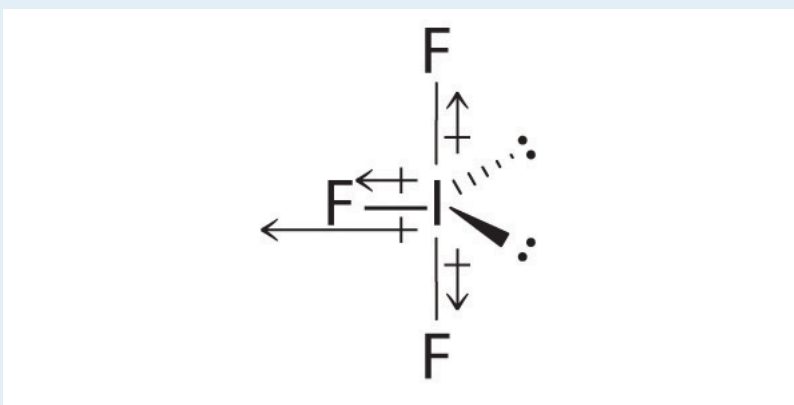
SF_6: The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, SF_6 has no net dipole moment.

9.2 Localized Bonding and Hybrid Atomic Orbitals

> **LEARNING OBJECTIVE**
>
> 1. To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

Valence Bond Theory: A Localized Bonding Approach

In Chapter 8 "Ionic versus Covalent Bonding", you learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure 8.9 "A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms"). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a maximum of two electrons with opposite spin, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1s atomic orbital of one hydrogen atom overlaps with the singly occupied 1s atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure 9.10 "Overlap of Two Singly Occupied Hydrogen 1").

Figure 9.10 *Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in H₂*
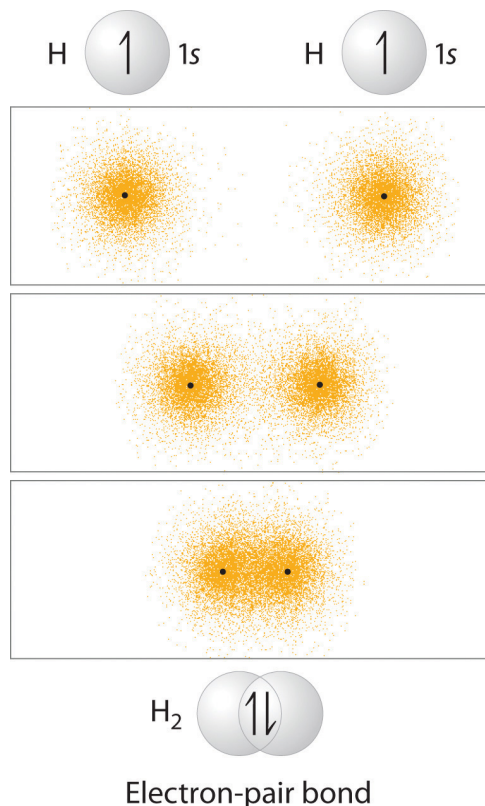
Electron-pair bond

The formation of H₂ from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H₂ molecule increases the electron density in the region between the two positively charged nuclei.

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as **valence bond theory**[4], which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

4. A localized bonding model that assumes that the strength of a covalent bond is proportional to the amount of overlap between atomic orbitals and that an atom can use different combinations of atomic orbitals (hybrids) to maximize the overlap between bonded atoms.

Figure 9.11 "Three Different Ways to Form an Electron-Pair Bond" shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic

orbitals, and an *ns* and an *np* orbital where *n* = 2. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

Figure 9.11 *Three Different Ways to Form an Electron-Pair Bond*
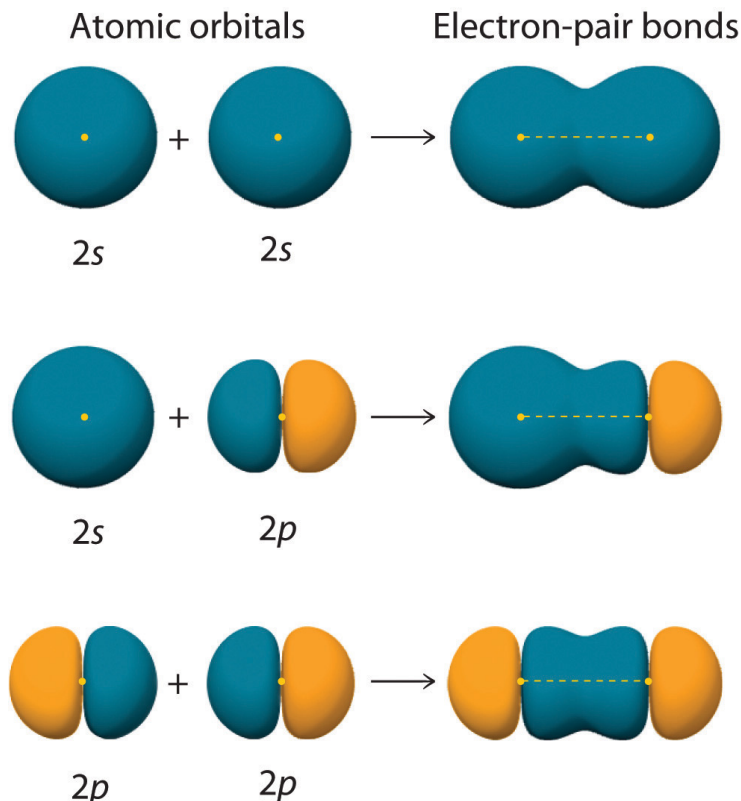
An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where n = 2. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2s subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1s orbitals on the H atoms. If a singly occupied 1s orbital on hydrogen were to overlap with a filled 2s orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2s electrons into an empty 2p orbital and reverse its spin, in a process called **promotion**[5]:

5. The excitation of an electron from a filled ns^2 atomic orbital to an empty np or $(n-1)d$ valence orbital.

In this excited state, the Be atom would have two singly occupied atomic orbitals (the $2s$ and one of the $2p$ orbitals), each of which could overlap with a singly occupied $1s$ orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the $1s$ orbital of one hydrogen atom would overlap with a Be $2s$ orbital, and the $1s$ orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be $2p$ orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Hybridization of s and p Orbitals

The localized bonding approach uses a process called **hybridization**[6], in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called **hybrid atomic orbitals**[7] because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

In BeH_2, we can generate two equivalent orbitals by combining the $2s$ orbital of beryllium and any one of the three degenerate $2p$ orbitals. By taking the sum and the difference of Be $2s$ and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the z-axes, as shown in <u>Figure 9.12 "The Formation of "</u>.Because the difference A – B can also be written as A + (–B), in <u>Figure 9.12 "The Formation of "</u> and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by –1 and adding. This gives us <u>Equation 9.1</u>, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the $2s$ and $2p$ orbitals contribute equally to each hybrid orbital.

6. A process in which two or more atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds.

7. New atomic orbitals formed from the process of hybridization.

Equation 9.1

$$sp = \frac{1}{\sqrt{2}}\left(2s + 2p_z\right) \text{ and } sp = \frac{1}{\sqrt{2}}\left(2s - 2p_z\right)$$

Figure 9.12 *The Formation of sp Hybrid Orbitals*
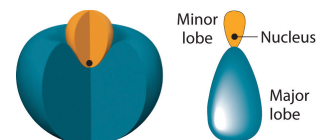
The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

2s   2p$_z$ sp hybrids   Hybrids shown together in cross-section

Schematic representation of hybrids shown together
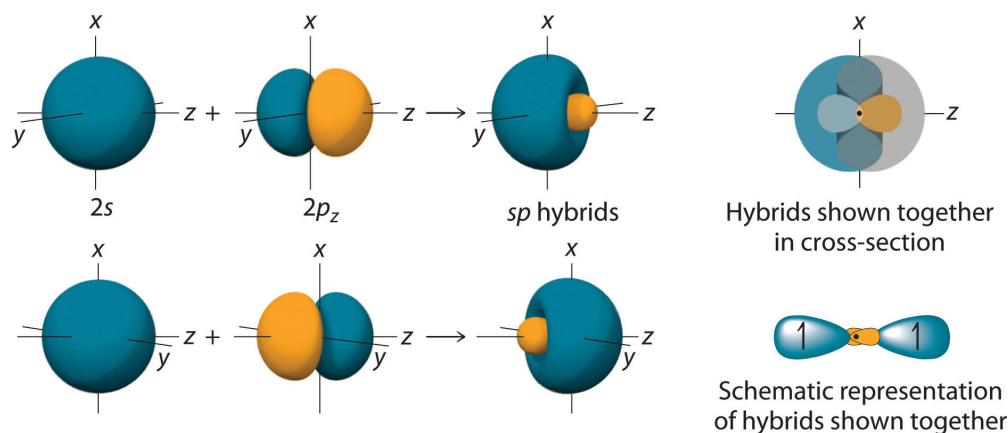
Taking the mathematical sum and difference of an ns and an np atomic orbital where n = 2 gives two equivalent sp hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:

Be (excited state)   Hybridization   **Be** (*sp* hybridized)
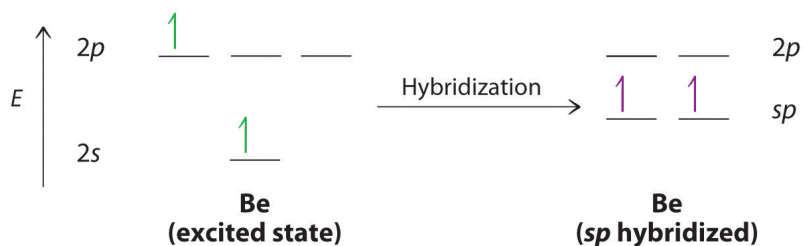
Each singly occupied **sp hybrid orbital**[8] can now form an electron-pair bond with the singly occupied $1s$ atomic orbital of one of the H atoms. As shown in <u>Figure 9.13 "Explanation of the Bonding in BeH"</u>, each sp orbital on Be has the correct orientation for the major lobes to overlap with the $1s$ atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

Figure 9.13   Explanation of the Bonding in BeH$_2$ Using sp Hybrid Orbitals
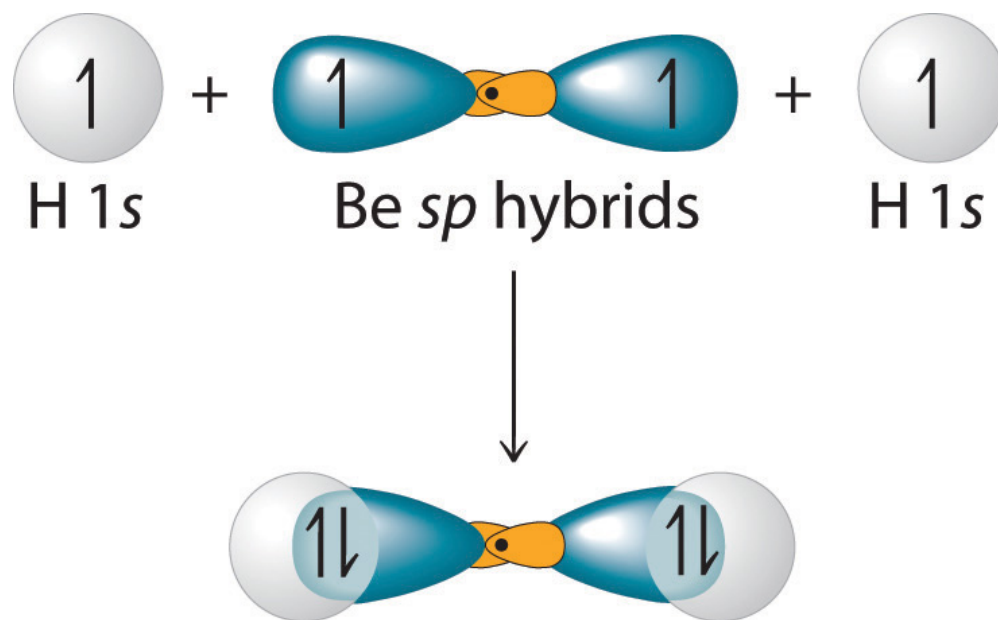
Each singly occupied sp hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1s orbital of a hydrogen atom. Because the two sp hybrid orbitals are oriented at a 180° angle, the BeH$_2$ molecule is linear.

8. The two equivalent hybrid orbitals that result when one ns orbital and one np orbital are combined (hybridized). The two sp hybrid orbitals are oriented at 180° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure s and pure p orbitals.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (<u>Figure 9.14 "A Hypothetical Stepwise Process for the Formation of BeH"</u>). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

Figure 9.14 *A Hypothetical Stepwise Process for the Formation of BeH$_2$ from a Gaseous Be Atom and Two Gaseous H Atoms*
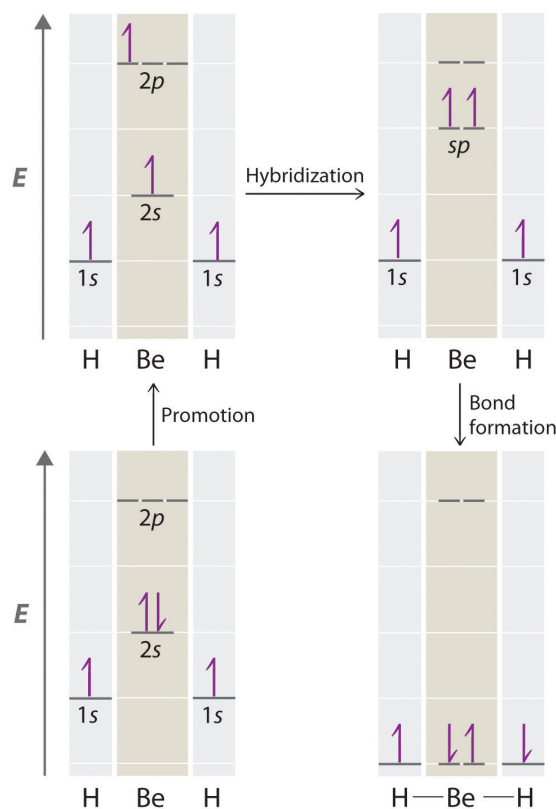
The promotion of an electron from the 2s orbital of beryllium to one of the 2p orbitals is energetically uphill. The overall process of forming a BeH$_2$ molecule from a Be atom and two H atoms will therefore be energetically favorable only if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF$_3$, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2s electrons to an unoccupied 2p orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2s and two 2p orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:
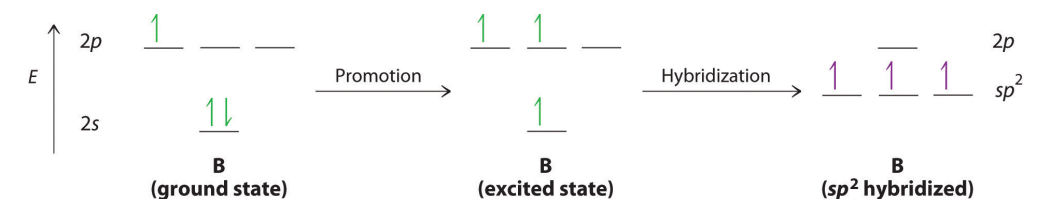
The hybrid orbitals are degenerate and are oriented at 120° angles to each other (Figure 9.15 "Formation of "). Because the hybrid atomic orbitals are formed from one s and two p orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied **sp^2 hybrid atomic orbitals**[9] can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

Figure 9.15 *Formation of sp^2 Hybrid Orbitals*
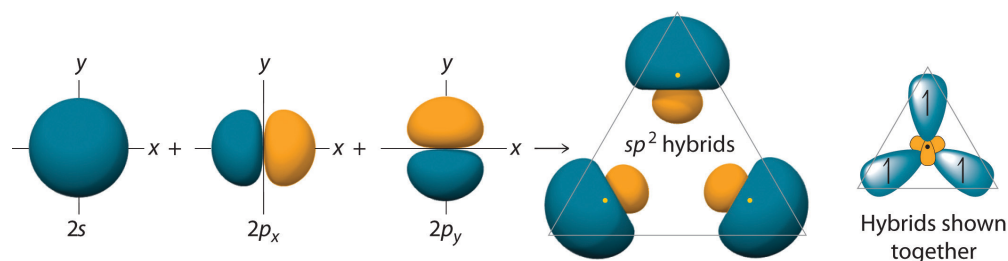
Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the $2s^2 2p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired $2p$ electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the $2s$ orbital and the three $2p$ orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:

9. The three equivalent hybrid orbitals that result when one ns orbital and two np orbitals are combined (hybridized). The three sp^2 hybrid orbitals are oriented in a plane at 120° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure s and pure p orbitals.
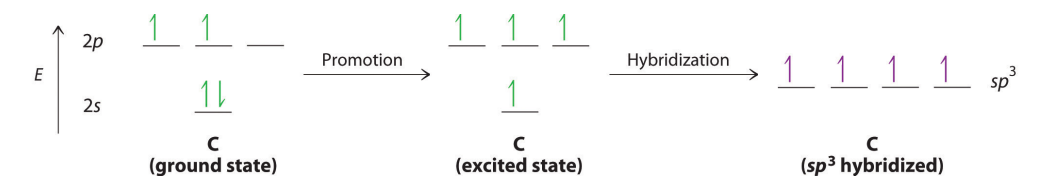
The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 9.16 "Formation of "). Like all

the hybridized orbitals discussed earlier, the **sp^3 hybrid atomic orbitals**[10] are predicted to be equal in energy.

Figure 9.16   *Formation of sp^3 Hybrid Orbitals*
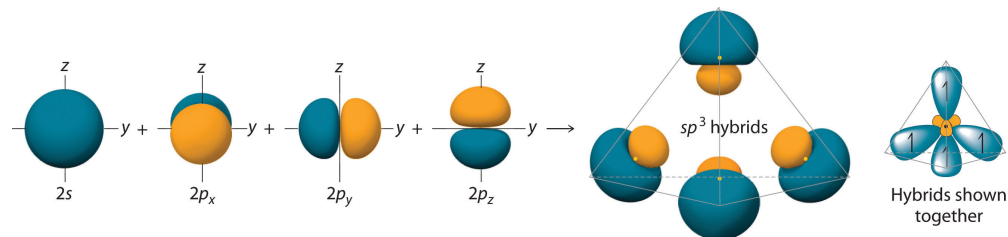
Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Note the Pattern

Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.

10. The four equivalent hybrid orbitals that result when one ns orbital and three np orbitals are combined (hybridized). The four sp^3 hybrid orbitals point at the vertices of a tetrahedron, so they are oriented at 109.5° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure s and pure p orbitals.

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^2 2p^3$ valence electron configuration, can hybridize its $2s$ and $2p$ orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:

$$\underline{\uparrow\downarrow}\ \ \underline{\uparrow}\ \ \underline{\uparrow}\ \ \underline{\uparrow}\ \ \ sp^3$$

The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in CH_4 and NH_3, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

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EXAMPLE 5

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A Using the approach from Example 1, determine the number of electron pairs and the molecular geometry of the molecule.

B From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

a. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^23p^4$ valence electron configuration with six electrons, but by hybridizing its 3s and 3p orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
b. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^22p^2$ valence electron configuration. By hybridizing its 2s and 2p orbitals, it can form

</div>

four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3s and 3p valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine (H_2N–NH_2)

Answer:

a. B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.
b. Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

Note the Pattern

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

Hybridization Using d Orbitals

Hybridization is not restricted to the ns and np atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n - 1)d$ orbitals as well as its ns and np orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the ns orbital, all three np orbitals, and one $(n - 1)d$ orbital gives a set of five

sp^3d **hybrid orbitals**[11] that point toward the vertices of a trigonal bipyramid (part (a) in Figure 9.17 "Hybrid Orbitals Involving "). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent sp^3d^2 **hybrid orbitals**[12] oriented toward the vertices of an octahedron (part (b) in Figure 9.17 "Hybrid Orbitals Involving "). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

Figure 9.17 Hybrid Orbitals Involving d Orbitals

The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from ns, np, and nd atomic orbitals where n = 4.
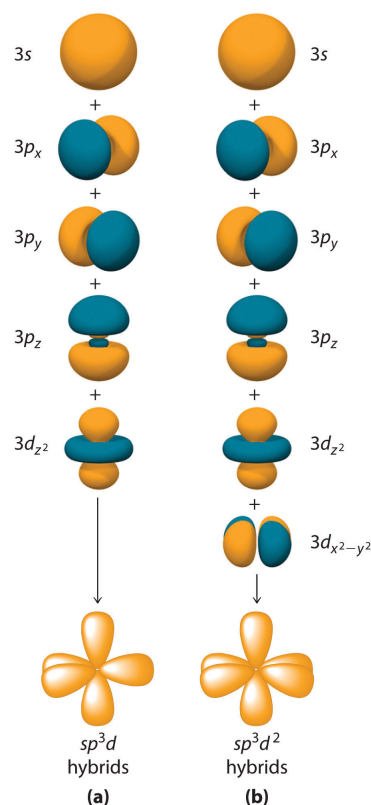
11. The five hybrid orbitals that result when one ns, three np and one $(n-1)d$ orbitals are combined (hybridized).

12. The six equivalent hybrid orbitals that result when one ns, three np, and two $(n-1)d$ orbitals are combined (hybridized).

EXAMPLE 6

What is the hybridization of the central atom in each species? Describe the bonding in each species.

a. XeF_4
b. SO_4^{2-}
c. SF_4

Given: three chemical species

Asked for: hybridization of the central atom

Strategy:

A Determine the geometry of the molecule using the strategy in Example 1. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.

B Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

a. **A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.
b. **A** The S in the SO_4^{2-} ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S–O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.

c. **A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:

To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

Exercise

What is the hybridization of the central atom in each species? Describe the bonding.

a. PCl_4^+
b. BrF_3
c. SiF_6^{2-}

Answer:

a. sp^3 with four P–Cl bonds
b. sp^3d with three Br–F bonds and two lone pairs
c. sp^3d^2 with six Si–F bonds

Hybridization using d orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F⁻ to give a stable hexafluoro dianion, SiF_6^{2-}. Because there are no $2d$ atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from $2s$, $2p$, and $3d$ atomic orbitals. The $3d$ orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.

EXAMPLE 7

What is the hybridization of the oxygen atom in OF_4? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

A Predict the geometry of OF_4 using the VSEPR model.

B From the number of electron pairs around O in OF_4, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be sp^3d hybridized. The only d orbital available for forming a set of sp^3d hybrid orbitals is a $3d$ orbital, which is *much* higher in energy than the $2s$ and $2p$ valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise

What is the hybridization of the boron atom in $BF_6{}^{3-}$? Is this ion likely to exist?

Answer: sp^3d^2 hybridization; no

Summary

The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty np or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an ns and an np orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an ns and two or three np orbitals produces three equivalent $\textbf{\textit{sp}}^{\textbf{2}}$ **hybrids** or four equivalent $\textbf{\textit{sp}}^{\textbf{3}}$ **hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five sp^3d or six $\textbf{\textit{sp}}^{\textbf{3}}\textbf{\textit{d}}^{\textbf{2}}$ **hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

KEY TAKEAWAY

- Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach.

CONCEPTUAL PROBLEMS

1. Arrange sp, sp^3, and sp^2 in order of increasing strength of the bond formed to a hydrogen atom. Explain your reasoning.

2. What atomic orbitals are combined to form sp^3, sp, sp^3d^2, and sp^3d? What is the maximum number of electron-pair bonds that can be formed using each set of hybrid orbitals?

3. Why is it incorrect to say that an atom with sp^2 hybridization will form only three bonds? The carbon atom in the carbonate anion is sp^2 hybridized. How many bonds to carbon are present in the carbonate ion? Which orbitals on carbon are used to form each bond?

4. If hybridization did not occur, how many bonds would N, O, C, and B form in a neutral molecule, and what would be the approximate molecular geometry?

5. How are hybridization and molecular geometry related? Which has a stronger correlation—molecular geometry and hybridization or Lewis structures and hybridization?

6. In the valence bond approach to bonding in BeF_2, which step(s) require(s) an energy input, and which release(s) energy?

7. The energies of hybrid orbitals are intermediate between the energies of the atomic orbitals from which they are formed. Why?

8. How are lone pairs on the central atom treated using hybrid orbitals?

9. Because nitrogen bonds to only three hydrogen atoms in ammonia, why doesn't the nitrogen atom use sp^2 hybrid orbitals instead of sp^3 hybrids?

10. Using arguments based on orbital hybridization, explain why the $CCl_6{}^{2-}$ ion does not exist.

11. Species such as $NF_5{}^{2-}$ and $OF_4{}^{2-}$ are unknown. If $3d$ atomic orbitals were much lower energy, low enough to be involved in hybrid orbital formation, what effect would this have on the stability of such species? Why? What molecular geometry, electron-pair geometry, and hybridization would be expected for each molecule?

NUMERICAL PROBLEMS

1. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^-. How does your diagram compare with that for methane? What is the molecular geometry?

2. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^+. How does your diagram compare with that for methane? What is the molecular geometry?

3. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each molecule.

   a. BBr_3
   b. PCl_3
   c. NO_3^-

4. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each species.

   a. $AsBr_3$
   b. CF_3^+
   c. H_2O

5. What is the hybridization of the central atom in each of the following?

   a. CF_4
   b. CCl_2^{2-}
   c. IO_3^-
   d. SiH_4

6. What is the hybridization of the central atom in each of the following?

   a. CCl_3^+
   b. CBr_2O
   c. CO_3^{2-}
   d. IBr_2^-

7. What is the hybridization of the central atom in PF_6^-? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

8. What is the hybridization of the central atom in SF_5^-? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

ANSWERS

1.
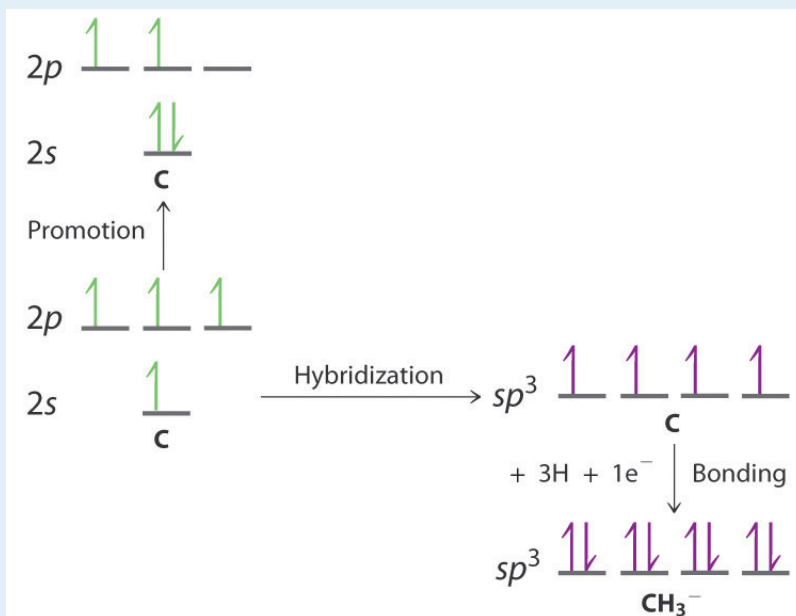
The promotion and hybridization process is exactly the same as shown for CH_4 in the chapter. The only difference is that the C atom uses the four singly occupied sp^3 hybrid orbitals to form electron-pair bonds with only *three* H atoms, and an electron is added to the fourth hybrid orbital to give a charge of 1−. The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in NH_3.

3.
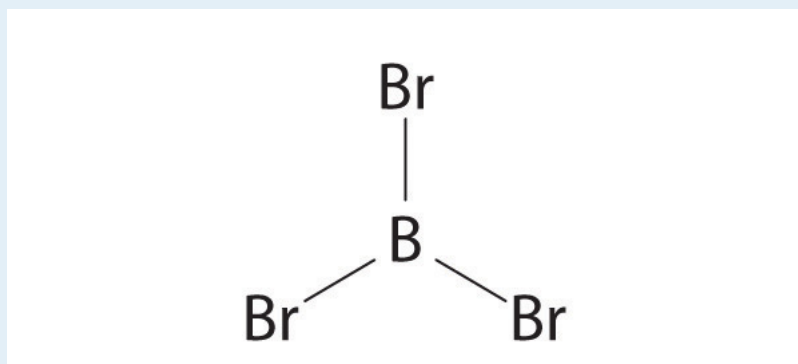
a.

sp^2, trigonal planar
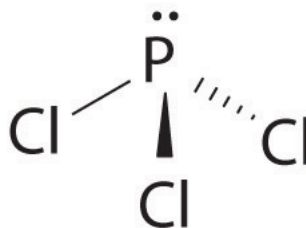
b.

sp^3, pyramidal
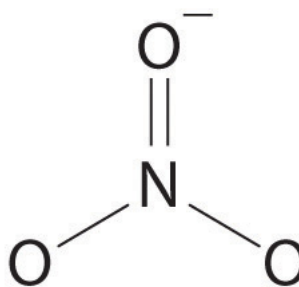
c.

sp^2, trigonal planar

5. The central atoms in CF_4, CCl_2^{2-}, IO_3^-, and SiH_4 are all sp^3 hybridized.

7. The phosphorus atom in the PF_6^- ion is sp^3d^2 hybridized, and the ion is octahedral. The PF_6^- ion is isoelectronic with SF_6 and has essentially the same structure. It should therefore be a stable species.

9.3 Delocalized Bonding and Molecular Orbitals

LEARNING OBJECTIVE
1. To use molecular orbital theory to predict bond order.

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. (For more information on semiconductors, see Chapter 12 "Solids", Section 12.6 "Bonding in Metals and Semiconductors".) These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

In Chapter 6 "The Structure of Atoms", we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of **molecular orbitals (MOs)**[13]—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called **molecular orbital theory**[14], is a *delocalized* approach to bonding.

> ## Note the Pattern
>
> Molecular orbital theory is a delocalized bonding approach that explains the colors of compounds, their stability, and resonance.

13. A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.

14. A delocalized bonding model in which molecular orbitals are created from the linear combination of atomic orbitals (LCAOs).

Molecular Orbital Theory: A Delocalized Bonding Approach

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in <u>Chapter 6 "The Structure of Atoms"</u>, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. (For more information on wave functions, see <u>Chapter 6 "The Structure of Atoms"</u>, <u>Section 6.5 "Atomic Orbitals and Their Energies"</u>.) The $1s$ atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H $1s$ wave functions, and the other produced by taking their *difference*:

Equation 9.2

$$MO\,(1) = AO\,(\text{atom A}) + AO\,(\text{atom B})$$
$$MO\,(2) = AO\,(\text{atom A}) - AO\,(\text{atom B})$$

The molecular orbitals created from <u>Equation 9.2</u> are called **linear combinations of atomic orbitals (LCAOs)**[15]. A molecule must have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H $1s$ orbitals is called a σ_{1s} combination (pronounced "sigma one ess") (part (a) and part (b) in <u>Figure 9.18 "Molecular Orbitals for the H"</u>). In a **sigma (σ) orbital**[16], the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript $1s$ denotes the atomic orbitals from which the molecular

15. Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals).

16. A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry.

orbital was derived:The $\approx$ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

Figure 9.18 *Molecular Orbitals for the H_2 Molecule*

(a) Wave functions combined for σ_{1s}

(b) Bonding probability density

(c) Wave functions combined for σ_{1s}^*

(d) Antibonding probability density
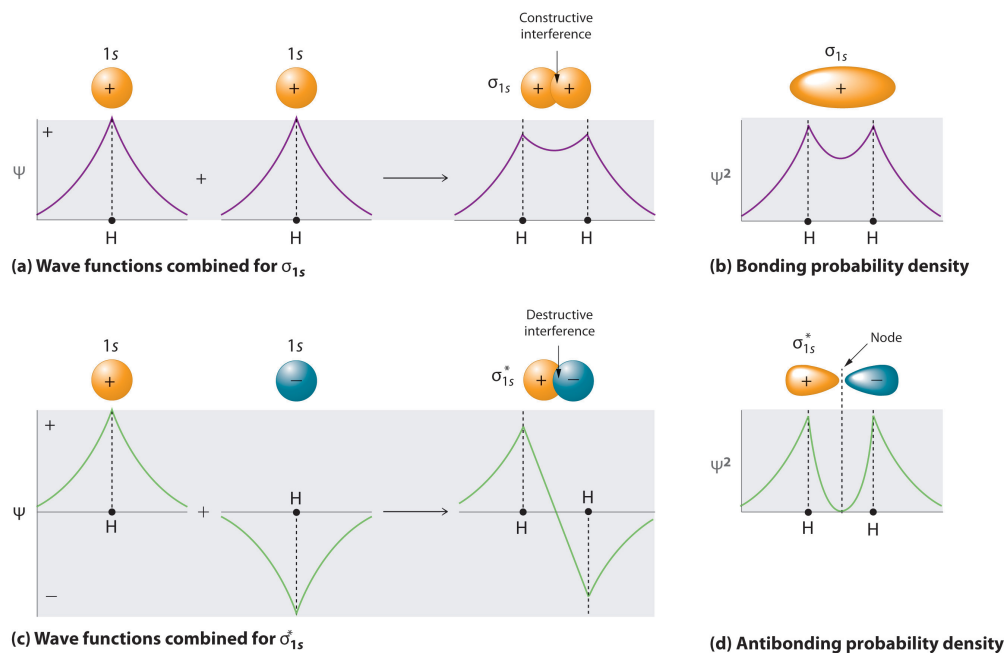
(a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall from <u>Chapter 6 "The Structure of Atoms"</u> that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ_{1s}^* molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the antibonding σ_{1s}^* molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

Equation 9.3

$$\sigma_{1s} \approx 1s(A) + 1s(B)$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in <u>Figure 9.18 "Molecular Orbitals for the H"</u>). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ_{1s}^* ("sigma one ess star"). In a **sigma star (σ*) orbital**[17], there

17. An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis.

is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

Equation 9.4

$$\sigma_{1s}^* \approx 1s(A) - 1s(B)$$

> **Note the Pattern**
>
> A molecule must have as many molecular orbitals as there are atomic orbitals.

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a **bonding molecular orbital**[18]. In contrast, electrons in the σ_{1s}^* orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ_{1s}^* orbital is an **antibonding molecular orbital**[19].

> **Note the Pattern**
>
> Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen $1s$ atomic orbitals. Conversely, electrons in the σ_{1s}^* orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen $1s$ atomic orbitals. Consequently, the σ_{1s}^* molecular orbital has a *higher* energy than either of the hydrogen $1s$ atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the $1s$ atomic orbitals,

18. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions.

19. A molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions.

and the σ_{1s}^* (antibonding) molecular orbital is *destabilized.* The relative energy levels of these orbitals are shown in the **energy-level diagram**[20] in Figure 9.19 "Molecular Orbital Energy-Level Diagram for H".

Note the Pattern

A bonding molecular orbital is *always* lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is *always* higher in energy (less stable).

Figure 9.19   Molecular Orbital Energy-Level Diagram for H_2

The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.
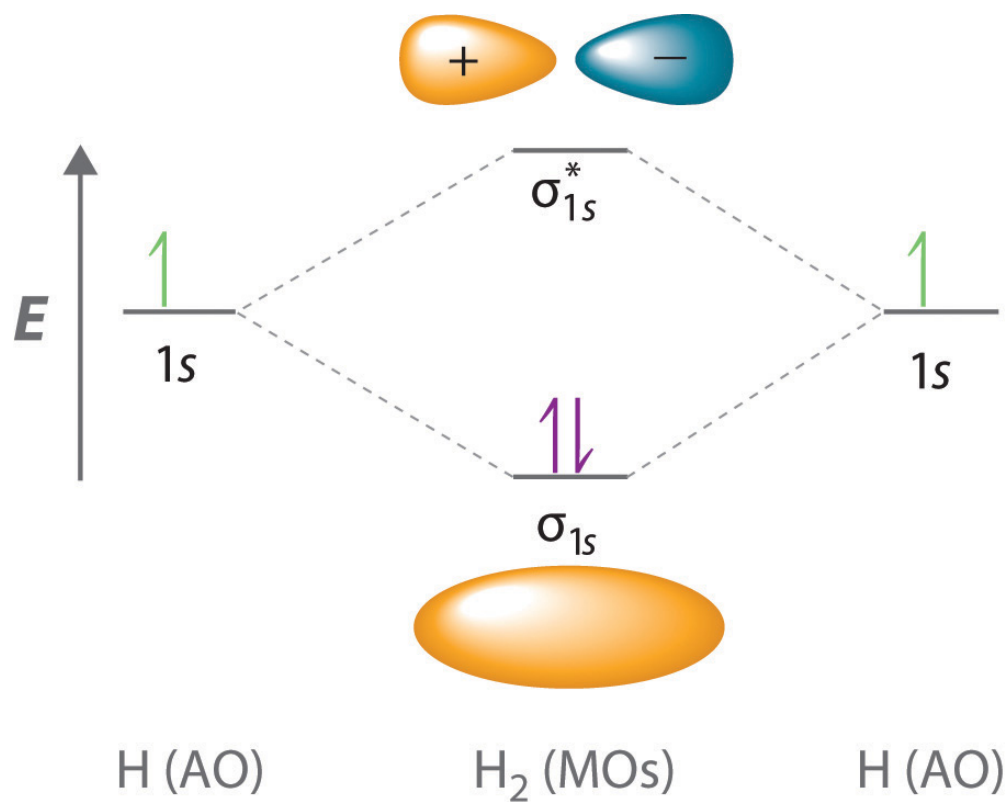
20. A schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals.

To describe the bonding in a **homonuclear diatomic molecule**[21] such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure 9.19 "Molecular Orbital Energy-Level Diagram for H"). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures described in Chapter 8 "Ionic versus Covalent Bonding", the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, **bond order**[22] is defined as one-half the *net* number of bonding electrons:

Equation 9.5

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

To calculate the bond order of H_2, we see from Figure 9.19 "Molecular Orbital Energy-Level Diagram for H" that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ_{1s}^{*} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

Equation 9.6

$$\frac{2 - 0}{2} = 1$$

21. A molecule that consists of two atoms of the same element.

22. One-half the net number of bonding electrons in a molecule.

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in <u>Figure 9.19 "Molecular Orbital Energy-Level Diagram for H"</u> to describe the bonding in other pairs of atoms and ions where $n = 1$, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

Part (a) in <u>Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1"</u> shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is $(1 - 0) \div 2 = \frac{1}{2}$ .Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only $\frac{1}{2}$,the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in <u>Table 9.1 "Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions"</u>, these predictions agree with the experimental data.

Part (b) in <u>Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1"</u> is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the σ_{1s}^* antibonding orbital, giving a $(\sigma_{1s})^2 \left(\sigma_{1s}^*\right)^1$ electron configuration. This electron configuration gives a bond order of $(2 - 1) \div 2 = \frac{1}{2}$ .As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (<u>Table 9.1 "Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions"</u>).

Figure 9.20 *Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals*
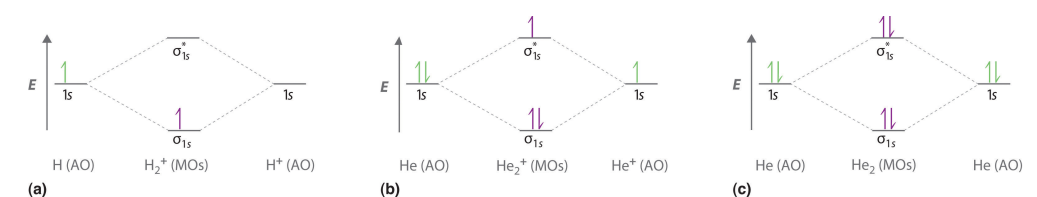
(a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Table 9.1 Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	$\frac{1}{2}$	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2 (\sigma_{1s}^*)^1$	$\frac{1}{2}$	108	251
He_2	$(\sigma_{1s})^2 (\sigma_{1s}^*)^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1" is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ_{1s}^* antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2 (\sigma_{1s}^*)^2$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

Note the Pattern

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

EXAMPLE 8

Use a molecular orbital energy-level diagram, such as those in <u>Figure 9.20</u> <u>"Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only</u> <u>1"</u>, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

A Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.

B Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

C Calculate the bond order and predict whether the species is stable.

Solution:

A Two He $1s$ atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ_{1s}^* antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:
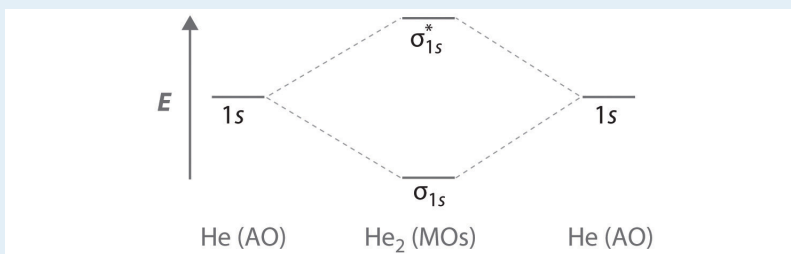
B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from

two He^+ ions, each of which has a single valence electron in the $1s$ atomic orbital. We can now fill the molecular orbital diagram:
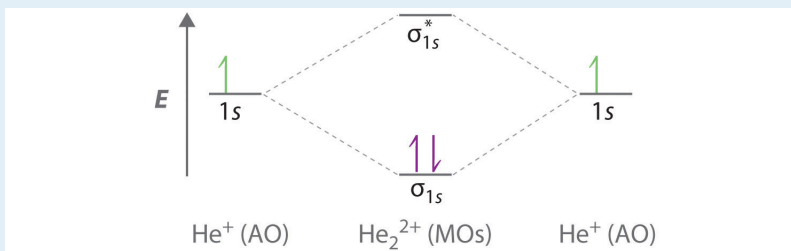
The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2 - 0}{2} = 1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer: H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2 (\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in <u>Figure 9.21 "Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M"</u>, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ_{ns}^* antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in <u>Figure 9.19 "Molecular Orbital Energy-Level Diagram for H"</u>. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

(a) Alkali metals   (b) Alkaline earth metals
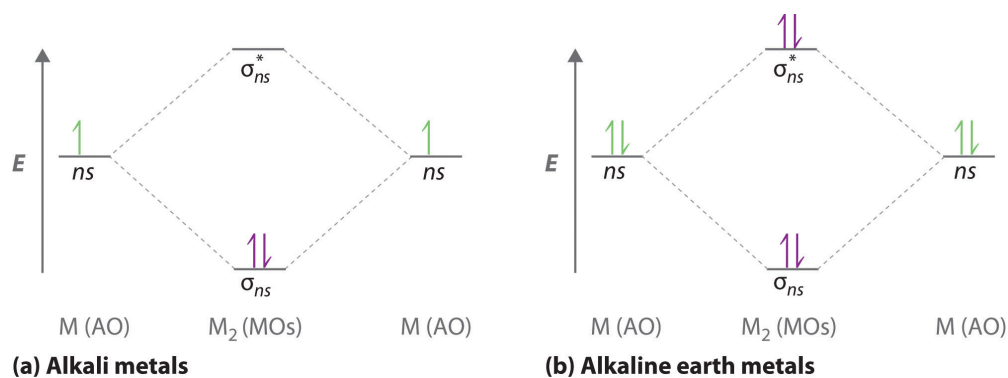
(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}^* (nonbonding) levels, leading to a predicted bond order of 0.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in <u>Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1"</u>. As shown in part (b) in <u>Figure 9.21 "Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M"</u>, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}^* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the

alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. (For more information on metallic bonding, see Chapter 12 "Solids", Section 12.6 "Bonding in Metals and Semiconductors".) At low temperatures, Be_2 is stable.

EXAMPLE 9

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

A Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

B Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

C Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a $[Ne]3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two $1s$ atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s}^* molecular orbital, and a $(\sigma_{3s})^2 (\sigma_{3s}^*)^1$ electron configuration.

The energy-level diagram shows $3s$ atomic orbitals of Na on each side, combining to form Na_2^- molecular orbitals: σ_{3s}^* (upper, with one electron) and σ_{3s} (lower, with two electrons).
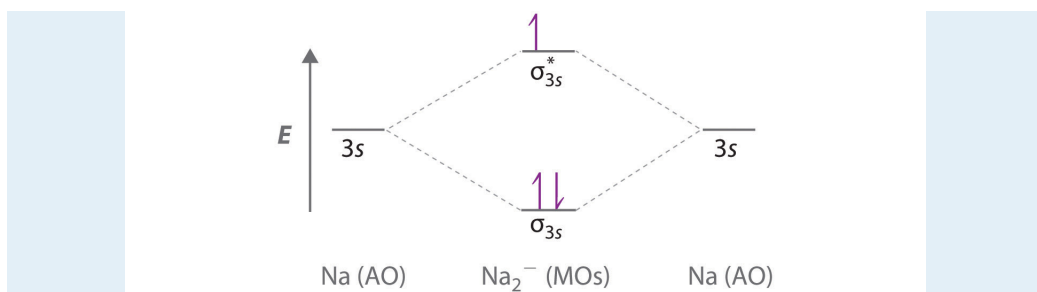
C The bond order is $(2 - 1) \div 2 = \frac{1}{2}$. With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer: Ca_2^+ has a $(\sigma_{4s})^2 (\sigma_{4s}^*)^1$ electron configuration and a bond order of $\frac{1}{2}$ and should exist.

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall from <u>Chapter 6 "The Structure of Atoms"</u>, <u>Section 6.5 "Atomic Orbitals and Their Energies"</u> that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals (<u>Figure 6.25 "The Three Equivalent 2"</u>). All have the same energy and are therefore degenerate, but they have different spatial orientations.

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in <u>Figure 9.22 "Formation of Molecular Orbitals from "</u>, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z}

bonding molecular orbital because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

Equation 9.7

$$\sigma_{np_z} = np_z(A) - np_z(B)$$

The other possible combination of the two np_z orbitals is the mathematical sum:

Equation 9.8

$$\sigma_{np_z} = np_z(A) + np_z(B)$$

In this combination, shown in part (b) in <u>Figure 9.22 "Formation of Molecular Orbitals from "</u>, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma^*_{np_z}$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

Figure 9.22 *Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms*
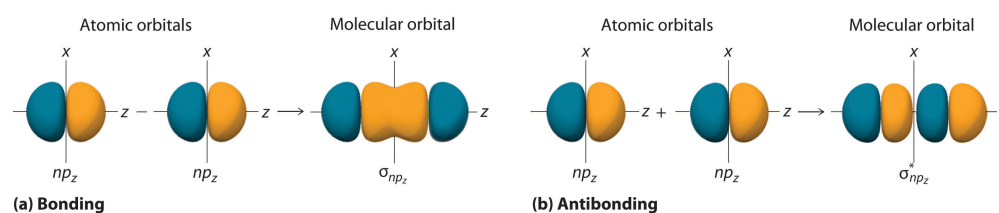
(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +z to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate - + - +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical difference, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical sum, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

Note the Pattern

Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining p orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in <u>Figure 9.23 "Formation of π Molecular Orbitals from "</u>, we see that we have two pairs of np orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a **pi (π) orbital**[23]. The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a **pi star (π*) orbital**[24].

Equation 9.9

$$\pi_{np_x} = np_x(\text{A}) + np_x(\text{B})$$

Equation 9.10

$$\pi^*_{np_x} = np_x(\text{A}) - np_x(\text{B})$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^*_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^*_{np_y}$ and π_{np_y} molecular orbitals.

23. A bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals.

24. An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel np atomic orbitals, creating a nodal plane perpendicular to the internuclear axis.

Figure 9.23 *Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms*
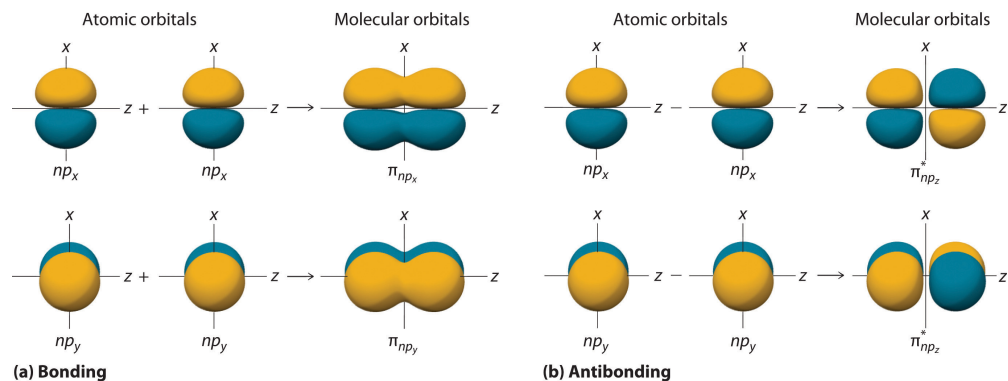
(a) *Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.*

Figure 9.24 "The Relative Energies of the σ and π Molecular Orbitals Derived from " is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

Figure 9.24   *The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms*
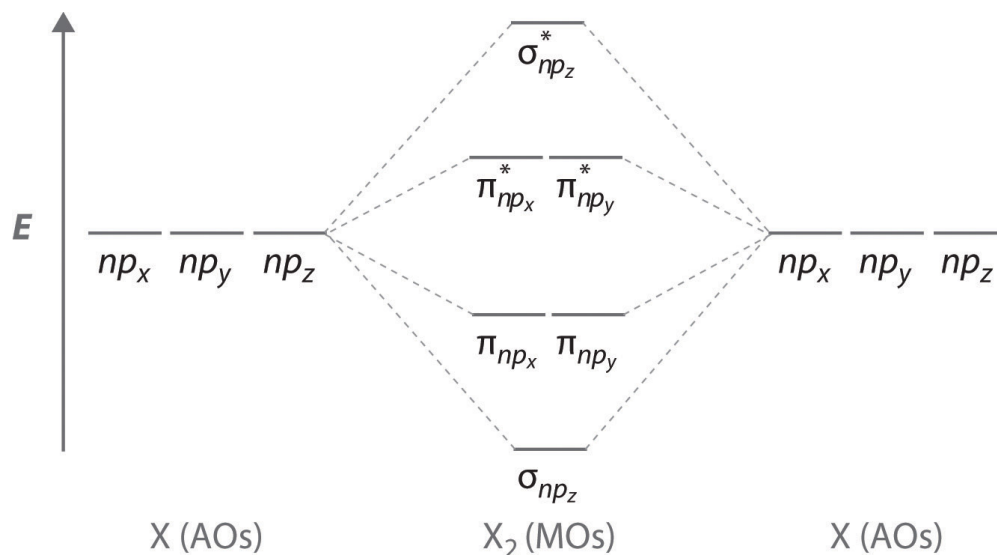
Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an ns atomic orbital on one atom with an np_z atomic orbital on another. As shown in <u>Figure 9.25 "Formation of Molecular Orbitals from an "</u>, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 9.25   *Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom*
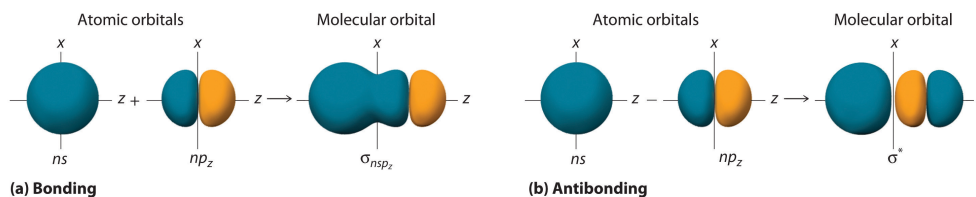
(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Molecular Orbital Diagrams for Period 2 Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the **law of conservation of orbitals**[25]).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Note the Pattern

The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 9.26 "Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules"; the $n = 1$ orbitals (σ_{1s} and σ_{1s}^*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}^* molecular orbitals are much lower in energy than the molecular orbitals derived from the $2p$ atomic orbitals because of the large difference in energy between the $2s$ and $2p$ atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three $2p$ orbitals on each F is σ_{2p_z}, and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma_{2p_z}^*$ orbital is higher in energy than either of the degenerate $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

25. A law that states that the number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}^* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of (8 − 6) ÷ 2 = 1. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 9.26 "Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules". We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}^* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate π_{2p_x} and π_{2p_y} orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of (8 − 4) ÷ 2 = 2, which corresponds to a double bond, in agreement with experimental data (Table 8.5 "Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K"): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

Figure 9.26 *Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules*
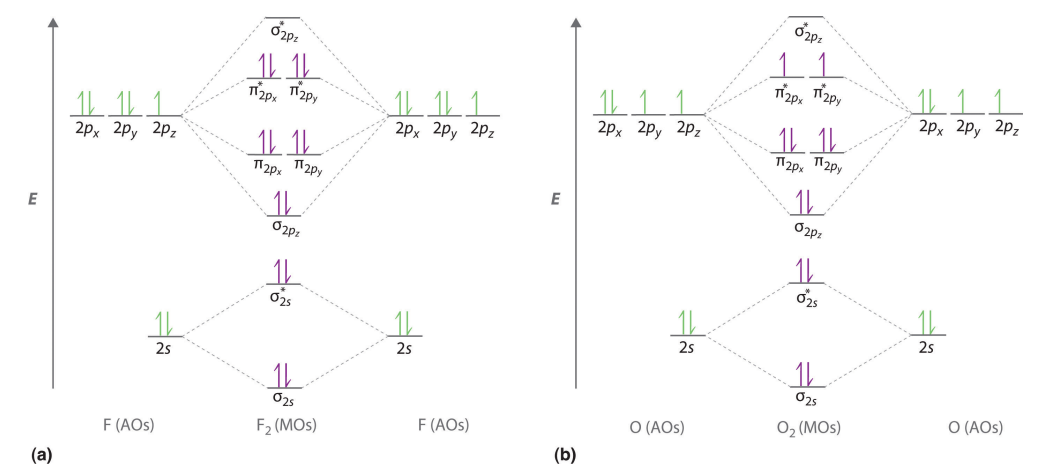
(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$, are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{2p_x},\ \pi^*_{2p_y} \right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in <u>Figure 9.27 "Liquid O"</u>, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

Figure 9.27 *Liquid O_2 Suspended between the Poles of a Magnet*

Sorry!

This image is permanently unavailable.

Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate π_{2p_x} and π_{2p_y}

9.3 Delocalized Bonding and Molecular Orbitals

orbitals. The difference in energy between the 2s and 2p atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2s electrons by electrons in the 2p subshell. The bonding interaction between the 2s orbital on one atom and the 2pz orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in <u>Figure 9.28</u> <u>"Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"</u>. Experimentally, it is found that the energy gap between the ns and np atomic orbitals *increases* as the nuclear charge increases (<u>Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"</u>). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

Figure 9.28   *Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements*
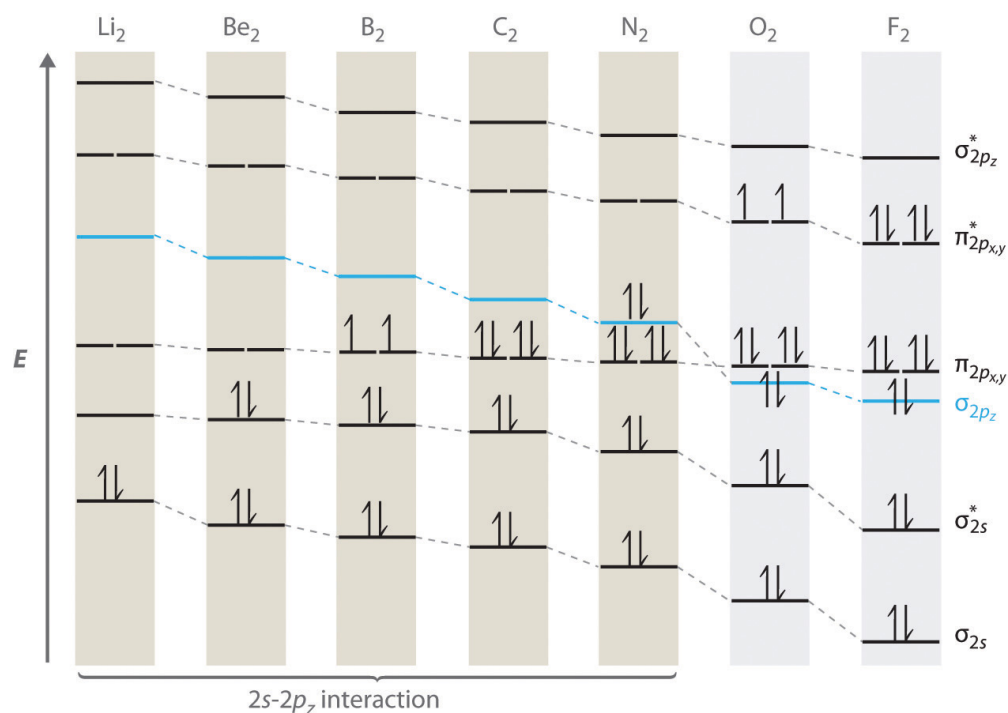
Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2s and 2p atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

EXAMPLE 10

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

Strategy:

A Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.

B Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.

C Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.

D Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in <u>Figure 9.26 "Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules"</u> and <u>Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"</u>, we need to know how close in energy the $3s$ and $3p$ atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z} molecular orbital is higher in energy. Because the ns–np energy gap *increases* as the nuclear charge increases (<u>Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"</u>), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:
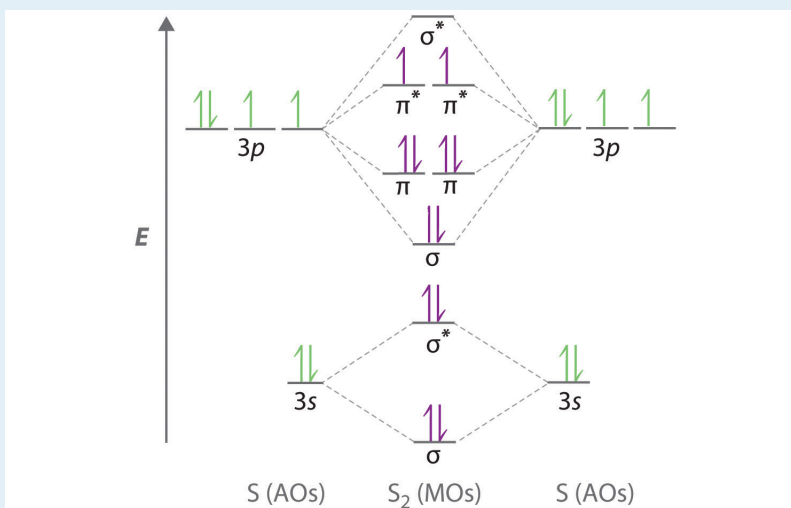
Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_x}$ and $\pi^*_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is

$$\left(\sigma_{3s}\right)^2 \left(\sigma^*_{3s}\right)^2 \left(\sigma_{3p_z}\right)^2 \left(\pi_{3p_{x,y}}\right)^4 \left(\pi^*_{3p_{x,y}}\right)^2$$ with 2 unpaired electrons.

The bond order is $(8 - 4) \div 2 = 2$, so we predict an S=S double bond.

Exercise

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer: $\left(\sigma_{2s}\right)^2 \left(\sigma^*_{2s}\right)^2 \left(\sigma_{2p_z}\right)^2 \left(\pi_{2p_{x,y}}\right)^4 \left(\pi^*_{2p_{x,y}}\right)^4$; bond order of 1; no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called **heteronuclear diatomic molecules**[26]. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in <u>Figure 9.29 "Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where χ"</u>. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

Figure 9.29   *Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$*
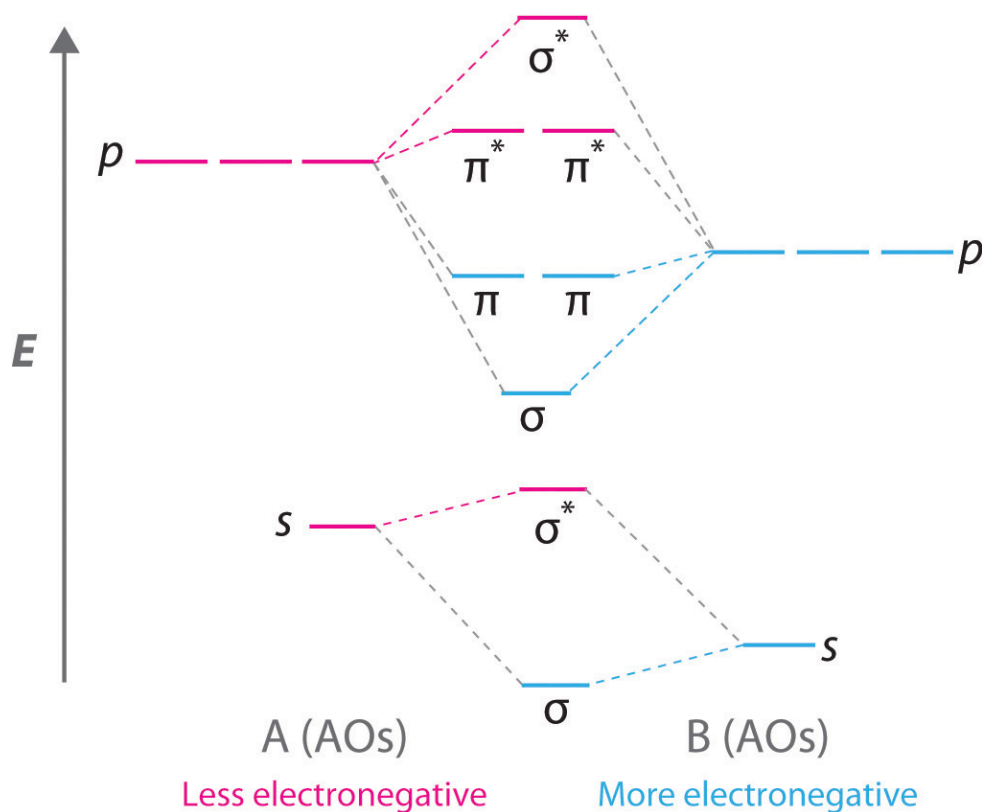
The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

26. A molecule that consists of two atoms of different elements.

> ## Note the Pattern
>
> A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 9.30 "Molecular Orbital Energy-Level Diagram for NO") shows that the general pattern is similar to that for the O_2 molecule (see Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from $2p$ atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore $(8 - 3) \div 2 = 2\frac{1}{2}$ Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

Figure 9.30 Molecular Orbital Energy-Level Diagram for NO
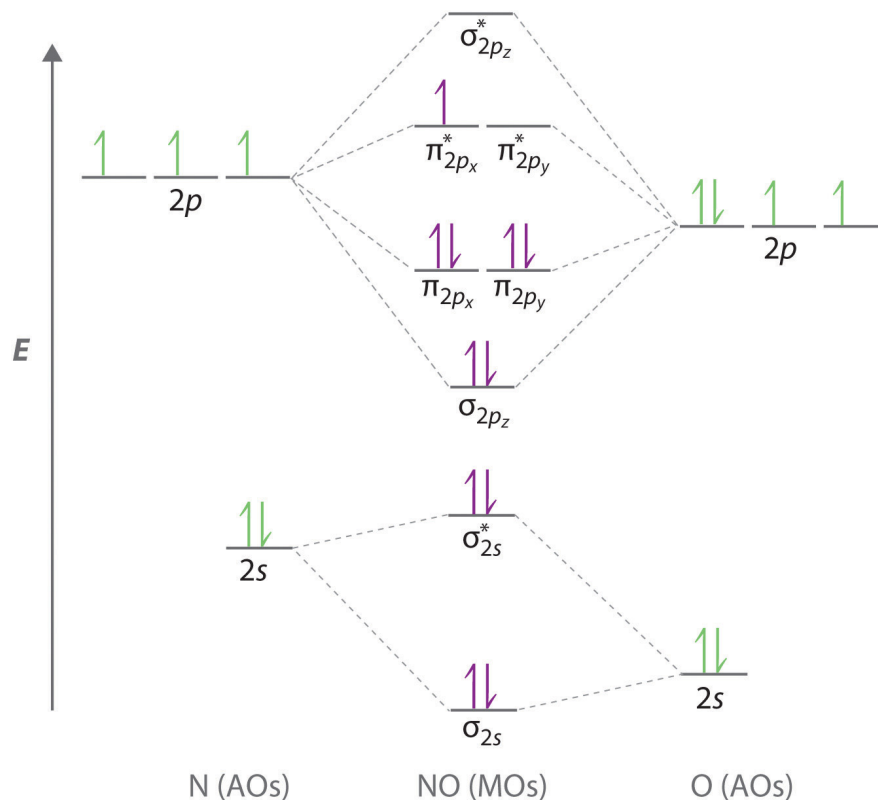
Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^*_{2p_x},\ \pi^*_{2p_y} \right)$ pair of orbitals.

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in <u>Figure 9.30 "Molecular Orbital Energy-Level Diagram for NO"</u>, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from <u>Figure 9.31 "Molecular Orbital Energy-Level Diagram for HCl"</u> that the 1*s* orbital of atomic hydrogen is

closest in energy to the $3p$ orbitals of chlorine. Consequently, the filled Cl $3s$ atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H $1s$ and Cl $3p$ orbitals. Of the three p orbitals, only one, designated as $3p_z$, can interact with the H $1s$ orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the $1s$ orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl $3s$, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**[27]. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is $(2 - 0) \div 2 = 1$. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H $1s$ atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}-Cl^{\delta-}$ as described in <u>Chapter 8 "Ionic versus Covalent Bonding"</u>.

Figure 9.31 Molecular Orbital Energy-Level Diagram for HCl

The hydrogen $1s$ atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/ antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.
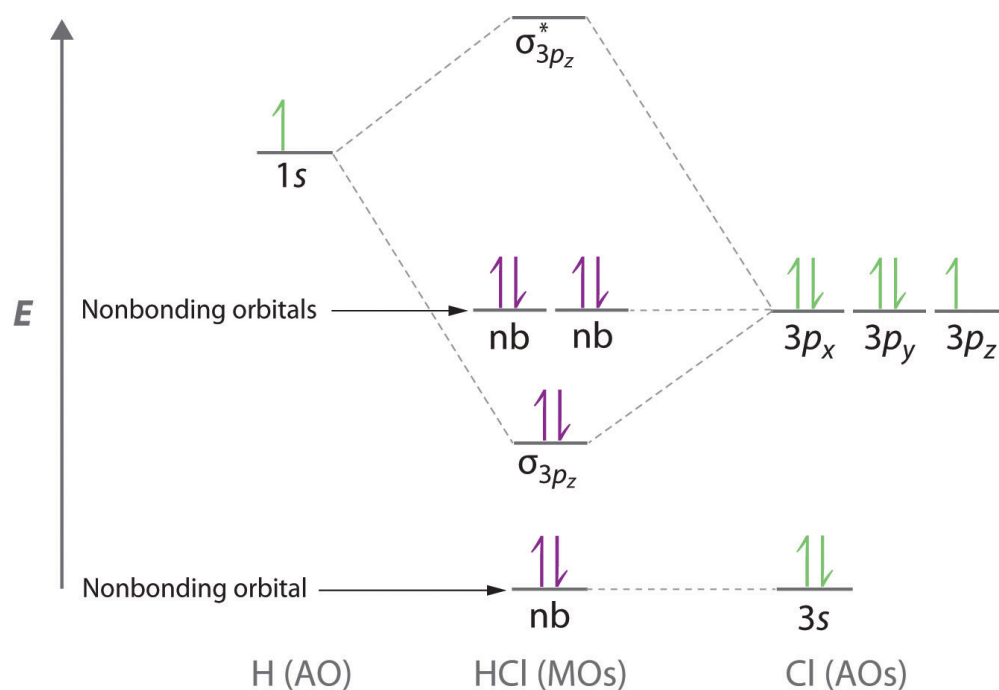
27. A molecular orbital that forms when atomic orbitals or orbital lobes interact only very weakly, creating essentially no change in the electron probability density between the nuclei.

> ## Note the Pattern
>
> Electrons in nonbonding molecular orbitals have no effect on bond order.

EXAMPLE 11

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 9.29 "Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where χ" to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 9.29 "Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where χ" in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

B Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the –1 charge. Placing these electrons in an energy-level diagram like Figure 9.29 "Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where χ" fills the five lowest-energy orbitals, as shown here:

CN^- (MOs)
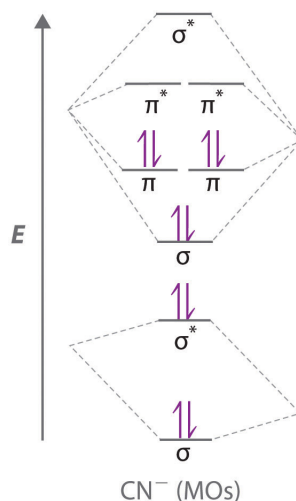
Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer: All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

Summary

A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.

2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.

3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi**

(π) **orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules,** using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

<div style="background:green">KEY TAKEAWAY</div>

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

CONCEPTUAL PROBLEMS

1. What is the distinction between an atomic orbital and a molecular orbital? How many electrons can a molecular orbital accommodate?

2. Why is the molecular orbital approach to bonding called a *delocalized* approach?

3. How is the energy of an electron affected by interacting with more than one positively charged atomic nucleus at a time? Does the energy of the system increase, decrease, or remain unchanged? Why?

4. Constructive and destructive interference of waves can be used to understand how bonding and antibonding molecular orbitals are formed from atomic orbitals. Does constructive interference of waves result in increased or decreased electron probability density between the nuclei? Is the result of constructive interference best described as a bonding molecular orbital or an antibonding molecular orbital?

5. What is a "node" in molecular orbital theory? How is it similar to the nodes found in atomic orbitals?

6. What is the difference between an *s* orbital and a σ orbital? How are the two similar?

7. Why is a σ_{1s} molecular orbital lower in energy than the two *s* atomic orbitals from which it is derived? Why is a σ_{1s}^* molecular orbital higher in energy than the two *s* atomic orbitals from which it is derived?

8. What is meant by the term *bond order* in molecular orbital theory? How is the bond order determined from molecular orbital theory different from the bond order obtained using Lewis electron structures? How is it similar?

9. What is the effect of placing an electron in an antibonding orbital on the bond order, the stability of the molecule, and the reactivity of a molecule?

10. How can the molecular orbital approach to bonding be used to predict a molecule's stability? What advantages does this method have over the Lewis electron-pair approach to bonding?

11. What is the relationship between bond length and bond order? What effect do antibonding electrons have on bond length? on bond strength?

12. Draw a diagram that illustrates how atomic *p* orbitals can form both σ and π molecular orbitals. Which type of molecular orbital typically results in a stronger bond?

13. What is the minimum number of nodes in σ, π, σ^*, and π^*? How are the nodes in bonding orbitals different from the nodes in antibonding orbitals?

14. It is possible to form both σ and π molecular orbitals with the overlap of a d orbital with a p orbital, yet it is possible to form only σ molecular orbitals between s and d orbitals. Illustrate why this is so with a diagram showing the three types of overlap between this set of orbitals. Include a fourth image that shows why s and d orbitals cannot combine to form a π molecular orbital.

15. Is it possible for an np_x orbital on one atom to interact with an np_y orbital on another atom to produce molecular orbitals? Why or why not? Can the same be said of np_y and np_z orbitals on adjacent atoms?

16. What is meant by *degenerate orbitals* in molecular orbital theory? Is it possible for σ molecular orbitals to form a degenerate pair? Explain your answer.

17. Why are bonding molecular orbitals lower in energy than the parent atomic orbitals? Why are antibonding molecular orbitals higher in energy than the parent atomic orbitals?

18. What is meant by the *law of conservation of orbitals*?

19. Atomic orbitals on different atoms have different energies. When atomic orbitals from nonidentical atoms are combined to form molecular orbitals, what is the effect of this difference in energy on the resulting molecular orbitals?

20. If two atomic orbitals have different energies, how does this affect the orbital overlap and the molecular orbitals formed by combining the atomic orbitals?

21. Are the Al–Cl bonds in $AlCl_3$ stronger, the same strength, or weaker than the Al–Br bonds in $AlBr_3$? Why?

22. Are the Ga–Cl bonds in $GaCl_3$ stronger, the same strength, or weaker than the Sb–Cl bonds in $SbCl_3$? Why?

23. What is meant by a *nonbonding* molecular orbital, and how is it formed? How does the energy of a nonbonding orbital compare with the energy of bonding or antibonding molecular orbitals derived from the same atomic orbitals?

24. Many features of molecular orbital theory have analogs in Lewis electron structures. How do Lewis electron structures represent

    a. nonbonding electrons?
    b. electrons in bonding molecular orbitals?

25. How does electron screening affect the energy difference between the 2s and 2p atomic orbitals of the period 2 elements? How does the energy difference between the 2s and 2p atomic orbitals depend on the effective nuclear charge?

26. For σ versus π, π versus σ*, and σ* versus π*, which of the resulting molecular orbitals is lower in energy?

27. The energy of a σ molecular orbital is usually lower than the energy of a π molecular orbital derived from the same set of atomic orbitals. Under specific conditions, however, the order can be reversed. What causes this reversal? In which portion of the periodic table is this kind of orbital energy reversal most likely to be observed?

28. Is the σ_{2p_z} molecular orbital stabilized or destabilized by interaction with the σ_{2s} molecular orbital in N_2? in O_2? In which molecule is this interaction most important?

29. Explain how the Lewis electron-pair approach and molecular orbital theory differ in their treatment of bonding in O_2.

30. Why is it crucial to our existence that O_2 is paramagnetic?

31. Will NO or CO react more quickly with O_2? Explain your answer.

32. How is the energy-level diagram of a heteronuclear diatomic molecule, such as CO, different from that of a homonuclear diatomic molecule, such as N_2?

33. How does molecular orbital theory describe the existence of polar bonds? How is this apparent in the molecular orbital diagram of HCl?

ANSWERS

1. An atomic orbital is a region of space around an atom that has a non-zero probability for an electron with a particular energy. Analogously, a molecular orbital is a region of space in a molecule that has a non-zero probability for an electron with a particular energy. Both an atomic orbital and a molecular orbital can contain two electrons.

15. No. Because an np_x orbital on one atom is perpendicular to an np_y orbital on an adjacent atom, the net overlap between the two is zero. This is also true for np_y and np_z orbitals on adjacent atoms.

NUMERICAL PROBLEMS

1. Use a qualitative molecular orbital energy-level diagram to describe the bonding in S_2^{2-}. What is the bond order? How many unpaired electrons does it have?

2. Use a qualitative molecular orbital energy-level diagram to describe the bonding in F_2^{2+}. What is the bond order? How many unpaired electrons does it have?

3. If three atomic orbitals combine to form molecular orbitals, how many molecular orbitals are generated? How many molecular orbitals result from the combination of four atomic orbitals? From five?

4. If two atoms interact to form a bond, and each atom has four atomic orbitals, how many molecular orbitals will form?

5. Sketch the possible ways of combining two $1s$ orbitals on adjacent atoms. How many molecular orbitals can be formed by this combination? Be sure to indicate any nodal planes.

6. Sketch the *four* possible ways of combining two $2p$ orbitals on adjacent atoms. How many molecular orbitals can be formed by this combination? Be sure to indicate any nodal planes.

7. If a diatomic molecule has a bond order of 2 and six bonding electrons, how many antibonding electrons must it have? What would be the corresponding Lewis electron structure (disregarding lone pairs)? What would be the effect of a one-electron reduction on the bond distance?

8. What is the bond order of a diatomic molecule with six bonding electrons and no antibonding electrons? If an analogous diatomic molecule has six bonding electrons and four antibonding electrons, which has the stronger bond? the shorter bond distance? If the highest occupied molecular orbital in both molecules is bonding, how will a one-electron oxidation affect the bond length?

9. Qualitatively discuss how the bond distance in a diatomic molecule would be affected by adding an electron to

    a. an antibonding orbital.
    b. a bonding orbital.

10. Explain why the oxidation of O_2 decreases the bond distance, whereas the oxidation of N_2 *increases* the N–N distance. Could Lewis electron structures be employed to answer this problem?

11. Draw a molecular orbital energy-level diagram for Na_2^+. What is the bond order in this ion? Is this ion likely to be a stable species? If not, would you recommend an oxidation or a reduction to improve stability? Explain your answer. Based on your answers, will Na_2^+, Na_2, or Na_2^- be the most stable? Why?

12. Draw a molecular orbital energy-level diagram for Xe_2^+, showing only the valence orbitals and electrons. What is the bond order in this ion? Is this ion likely to be a stable species? If not, would you recommend an oxidation or a reduction to improve stability? Explain your answer. Based on your answers, will Xe_2^{2+}, Xe_2^+, or Xe_2 be most stable? Why?

13. Draw a molecular orbital energy-level diagram for O_2^{2-} and predict its valence electron configuration, bond order, and stability.

14. Draw a molecular orbital energy-level diagram for C_2^{2-} and predict its valence electron configuration, bond order, and stability.

15. If all the p orbitals in the valence shells of two atoms interact, how many molecular orbitals are formed? Why is it not possible to form three π orbitals (and the corresponding antibonding orbitals) from the set of six p orbitals?

16. Draw a complete energy-level diagram for B_2. Determine the bond order and whether the molecule is paramagnetic or diamagnetic. Explain your rationale for the order of the molecular orbitals.

17. Sketch a molecular orbital energy-level diagram for each ion. Based on your diagram, what is the bond order of each species?

    a. NO^+
    b. NO^-

18. The diatomic molecule BN has never been detected. Assume that its molecular orbital diagram would be similar to that shown for CN^- in Section 9.3 "Delocalized Bonding and Molecular Orbitals" but that the σ_{2p_z} molecular orbital is higher in energy than the $\pi_{2p_{z,y}}$ molecular orbitals.

    a. Sketch a molecular orbital diagram for BN.
    b. Based on your diagram, what would be the bond order of this molecule?
    c. Would you expect BN to be stable? Why or why not?

19. Of the species BN, CO, C_2, and N_2, which are isoelectronic?

20. Of the species CN^-, NO^+, B_2^{2-}, and O_2^+, which are isoelectronic?

ANSWERS

1.

Each S atom contributes 6 valence electrons
+ 2 e⁻ for charge = 14 e⁻
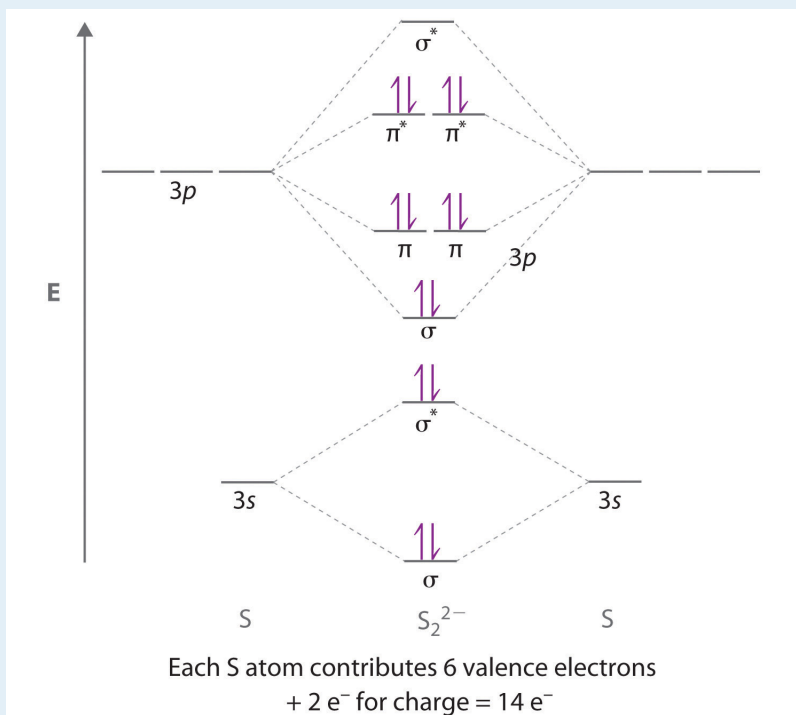
The bond order is 1, and the ion has no unpaired electrons.

3. The number of molecular orbitals is always equal to the number of atomic orbitals you start with. Thus, combining three atomic orbitals gives three molecular orbitals, and combining four or five atomic orbitals will give four or five molecular orbitals, respectively.

5.
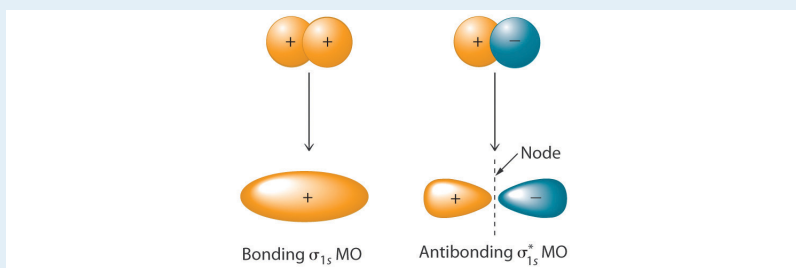
Combining two atomic *s* orbitals gives two molecular orbitals, a σ (bonding) orbital with no nodal planes, and a σ* (antibonding) orbital with a nodal plane perpendicular to the internuclear axis.
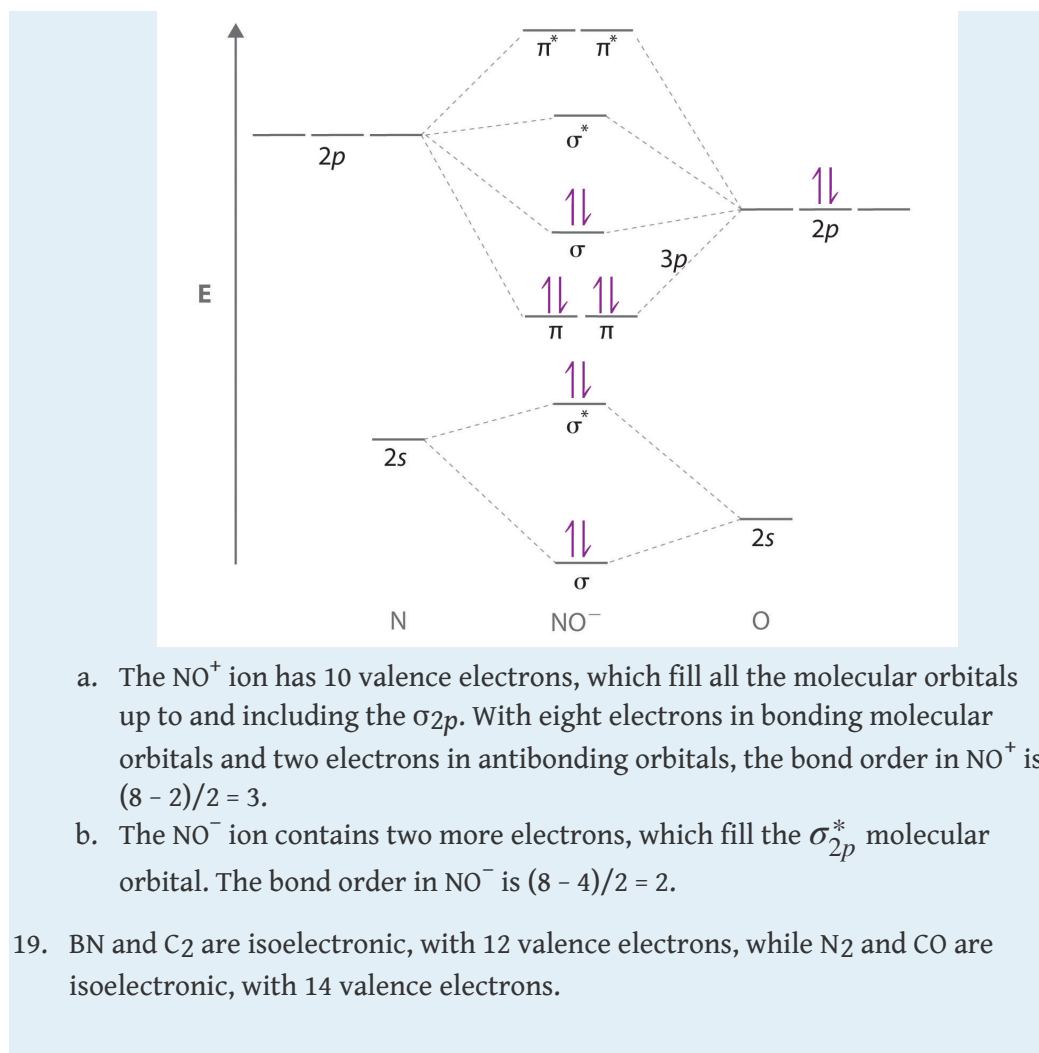
9.

a. Adding an electron to an antibonding molecular orbital will decrease the bond order, thereby increasing the bond distance.

b. Adding an electron to a bonding molecular orbital will increase the bond order, thereby decreasing the bond distance.

11. Sodium contains only a single valence electron in its $3s$ atomic orbital. Combining two $3s$ atomic orbitals gives two molecular orbitals; as shown in the diagram, these are a σ (bonding) orbital and a σ* (antibonding) orbital.
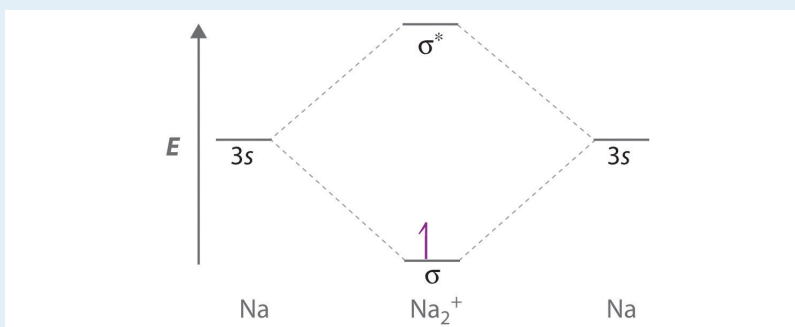
Although each sodium atom contributes one valence electron, the +1 charge indicates that one electron has been removed. Placing the single electron in the lowest energy molecular orbital gives a σ_{3s}^1 electronic configuration and a bond order of 0.5. Consequently, Na_2^+ should be a stable species. Oxidizing Na_2^+ by one electron to give Na_2^{2+} would remove the electron in the $\sigma 3s$ molecular orbital, giving a bond order of 0. Conversely, reducing Na_2^+ by one electron to give Na_2 would put an additional electron into the $\sigma 3s$ molecular orbital, giving a bond order of 1. Thus, reduction to Na_2 would produce a more stable species than oxidation to Na_2^{2+}. The Na_2^- ion would have two electrons in the bonding $\sigma 3s$ molecular orbital and one electron in the antibonding σ_{3s}^* molecular orbital, giving a bond order of 0.5. Thus, Na_2 is the most stable of the three species.

17.

a. The NO^+ ion has 10 valence electrons, which fill all the molecular orbitals up to and including the $\sigma 2p$. With eight electrons in bonding molecular orbitals and two electrons in antibonding orbitals, the bond order in NO^+ is $(8 - 2)/2 = 3$.

b. The NO^- ion contains two more electrons, which fill the σ_{2p}^* molecular orbital. The bond order in NO^- is $(8 - 4)/2 = 2$.

19. BN and C_2 are isoelectronic, with 12 valence electrons, while N_2 and CO are isoelectronic, with 14 valence electrons.

9.4 Polyatomic Systems with Multiple Bonds

LEARNING OBJECTIVE
1. To explain resonance structures using molecular orbitals.

So far in our molecular orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using molecular orbitals formed by unhybridized np atomic orbitals.

Multiple Bonds

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H ($sp^2 + s$) and one C–C ($sp^2 + sp^2$) (part (a) in <u>Figure 9.32 "Bonding in Ethylene"</u>). The sp^2 hybridization can be represented as follows:
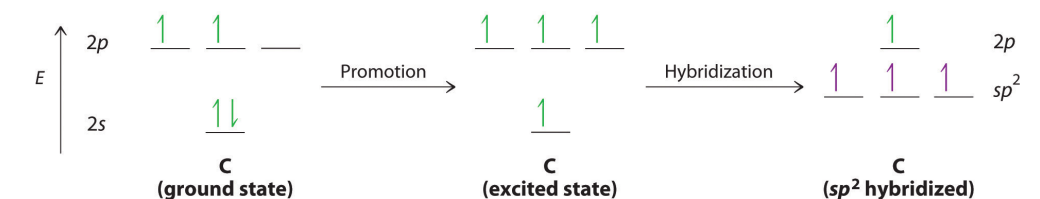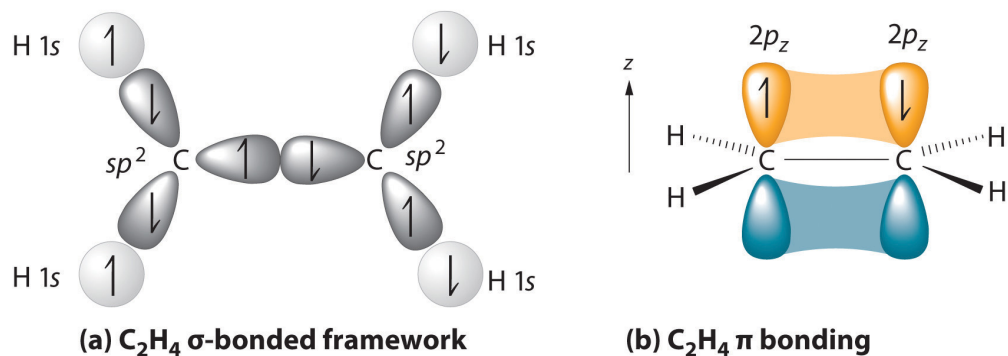
Figure 9.32 *Bonding in Ethylene*

**(a) C$_2$H$_4$ σ-bonded framework**   **(b) C$_2$H$_4$ π bonding**

(a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp² hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized 2pz orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the z-axis.)

After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure 9.32 "Bonding in Ethylene"). The two singly occupied $2p_z$ orbitals can overlap to form a π bonding orbital and a π* antibonding orbital, which produces the energy-level diagram shown in Figure 9.33 "Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene". With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH$_2$ fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.

Figure 9.33   *Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene*
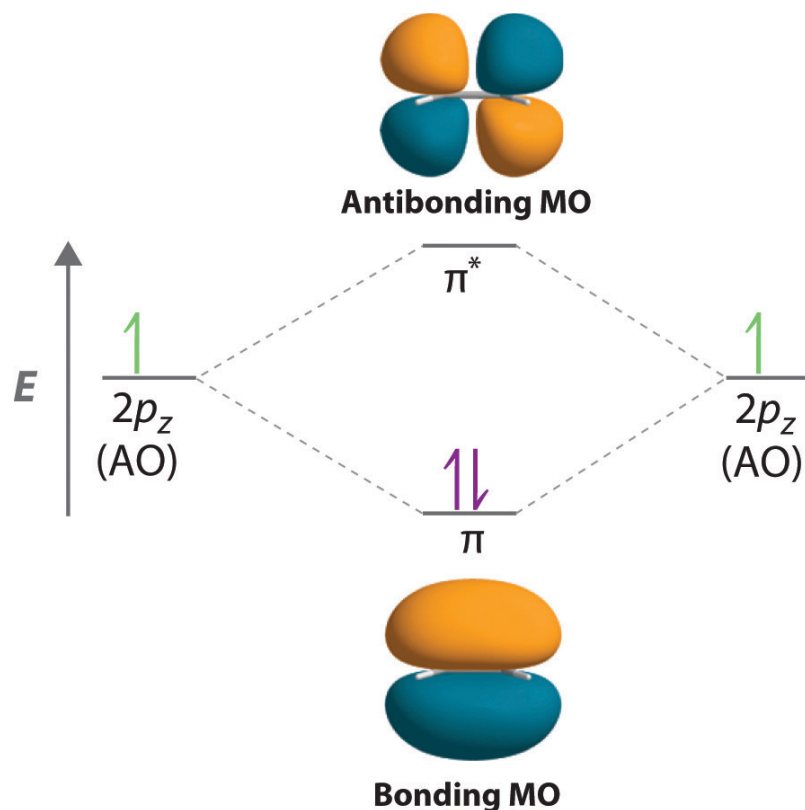

As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized $2p$ orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 9.34 "Bonding in Acetylene").
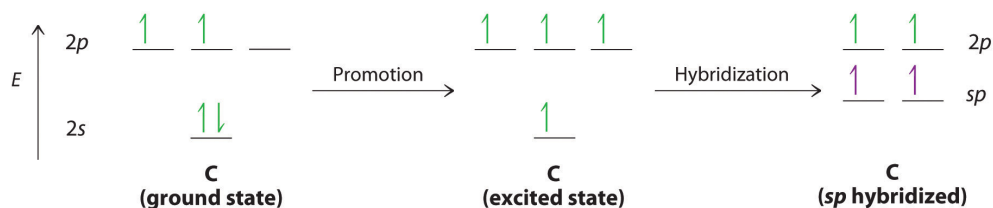
The two $2p$ orbitals on each carbon can align with the corresponding $2p$ orbitals on the adjacent carbon to simultaneously form a *pair* of π bonds (part (b) in <u>Figure 9.34 "Bonding in Acetylene"</u>). Because each of the unhybridized $2p$ orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

Figure 9.34   Bonding in Acetylene

(a) C$_2$H$_2$ σ-bonded framework   **(b) C$_2$H$_2$ π bonding**
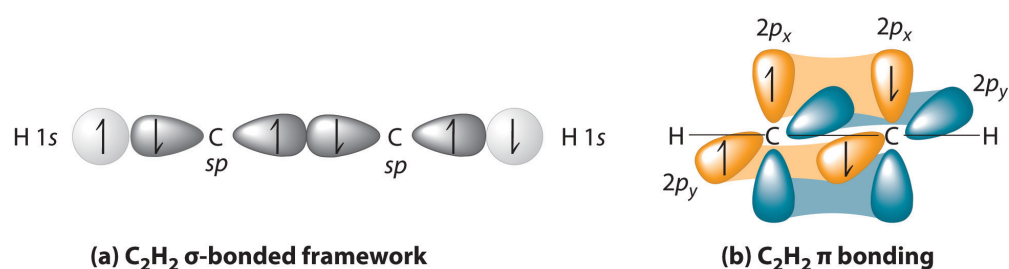
(a) In the formation of the σ-bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized 2p$_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

Note the Pattern

In complex molecules, hybrid orbitals and valence bond theory can be used to describe σ bonding, and unhybridized π orbitals and molecular orbital theory can be used to describe π bonding.

EXAMPLE 12

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

A From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.

B Determine the number of remaining valence electrons. Use any remaining unhybridized p orbitals to form π and π* orbitals.

**C** Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of sp hybridization at carbon. Because the nitrogen atom can also be described as sp hybridized, we can use one sp hybrid on each atom to form a C–N σ bond. This leaves one sp hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:
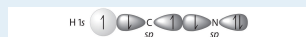
B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized $2p$ atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four $2p$ atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π* (antibonding)

orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.
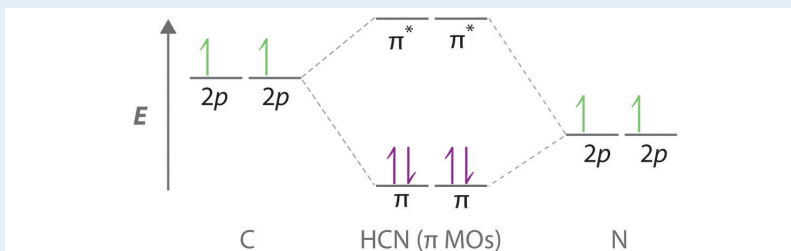
Exercise

Describe the bonding in formaldehyde ($H_2C=O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer:

σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.

π bonding: Unhybridized, singly occupied $2p$ atomic orbitals on carbon and oxygen interact to form π (bonding) and π* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

Molecular Orbitals and Resonance Structures

In Chapter 8 "Ionic versus Covalent Bonding", we used resonance structures to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). We showed that ozone can be represented by either of these Lewis electron structures:
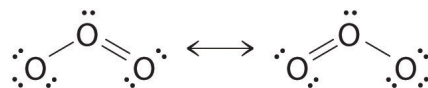

Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ-bonded framework shown in <u>Figure 9.35 "Bonding in Ozone"</u>. Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized $2p$ orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O_3 has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized $2p$ orbitals.

With a molecular orbital approach to describe the π bonding, three $2p$ atomic orbitals give us three molecular orbitals, as shown in <u>Figure 9.36 "π Bonding in Ozone"</u>. One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the O_3 plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O_3 plane and passes through the central O atom; it is a nonbonding molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

Figure 9.35 Bonding in Ozone
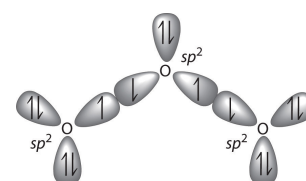
(a) O_3 σ-bond framework

(b) O_3 π bonding
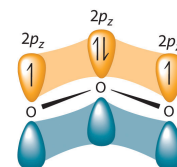
(a) In the formation of the σ-bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons.

Figure 9.36 π *Bonding in Ozone*
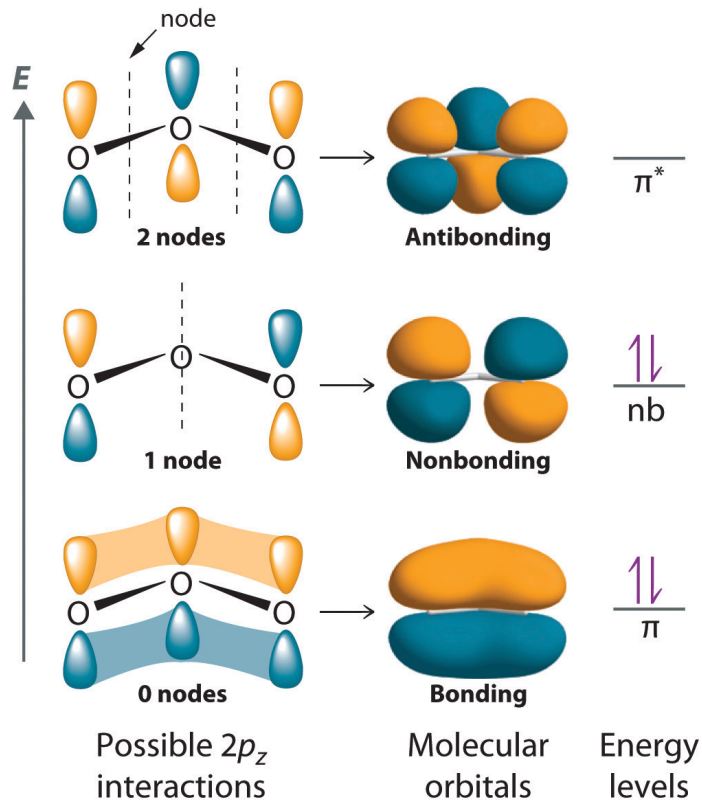
The three unhybridized $2p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is $\frac{1}{2}$ per O–O bond. The combined σ/π bond order is thus $1\frac{1}{2}$ for each O–O bond.

We can now place the remaining four electrons in the three energy levels shown in Figure 9.36 "π Bonding in Ozone", thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding *three* oxygen atoms together, or $\frac{1}{2}$ π bond per O–O. We therefore predict the overall O–O bond order to be $1\frac{1}{2}$ ($\frac{1}{2}$ πbond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital approach, however, shows that the π nonbonding orbital is localized on the *terminal* O atoms, which suggests that they are more electron rich than the central O atom. The reactivity of ozone is consistent with the predicted charge localization.

Note the Pattern

Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.

EXAMPLE 13

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

A Calculate the number of valence electrons in NO_2^-. From the structure, predict the type of atomic orbital hybridization in the ion.

B Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.

C If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

Solution:

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the –1 charge). The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized $2p$ orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three $2p$ orbitals interact to form bonding, nonbonding, and antibonding π molecular

orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.

C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of 1/2 per N–O bond. The overall N–O bond order is $1\frac{1}{2}$, consistent with a resonance structure.


NO_2 (π MOs)
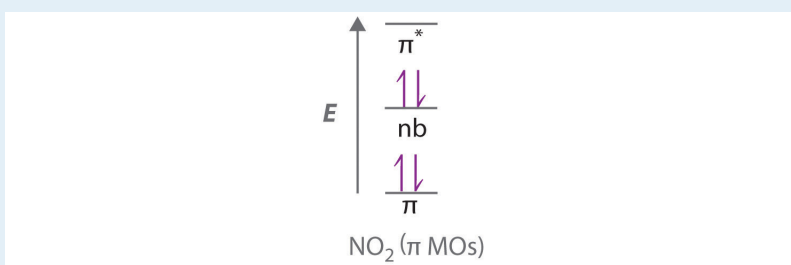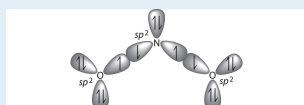
Exercise

Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer: Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized $2p$ orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore $1\frac{1}{2}$.

The Chemistry of Vision

Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds are generally more stable than expected because of resonance. Because the double bonds are close enough to interact electronically with one another, the π electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in <u>Figure 9.37 "π Bonding in 1,3-Butadiene"</u>.

As the number of interacting atomic orbitals increases, the number of molecular orbitals increases, the energy spacing between molecular orbitals decreases, and the systems become more stable (Figure 9.38 "Molecular Orbital Energy-Level Diagrams for a Chain of "). Thus as a chain of alternating double and single bonds becomes longer, the energy required to excite an electron from the highest-energy occupied (bonding) orbital to the lowest-energy unoccupied (antibonding) orbital decreases. If the chain is long enough, the amount of energy required to excite an electron corresponds to the energy of visible light. For example, vitamin A is yellow because its chain of five alternating double bonds is able to absorb violet light. Many of the colors we associate with dyes result from this same phenomenon; most dyes are organic compounds with alternating double bonds.

Figure 9.37   π Bonding in 1,3-Butadiene

(a) 1,3-Butadiene σ-bonded framework

(b) 1,3-Butadiene π bonding
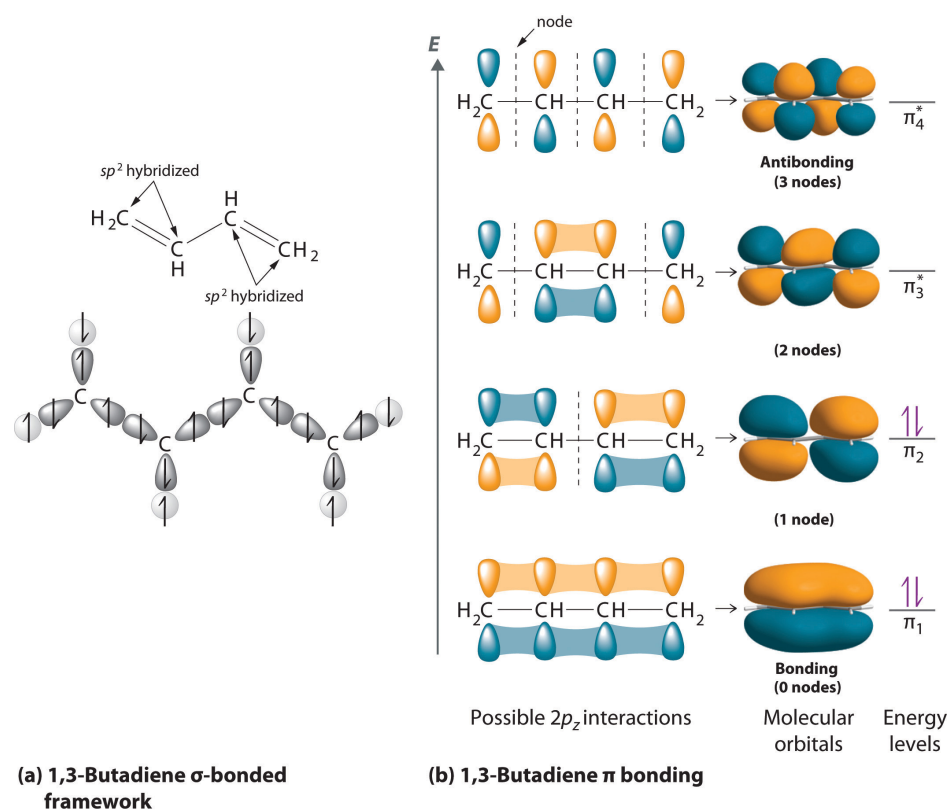
(a) If each carbon atom is assumed to be sp^2 hybridized, we can construct a σ-bonded framework that accounts for the C–H and C–C single bonds, leaving four singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, in this case to form four molecular orbitals. The molecular orbital at lowest energy is a bonding orbital with 0 nodes, the one at highest energy is antibonding with 3 nodes, and the two in the middle have 1 node and 2 nodes and are somewhere between bonding or antibonding and nonbonding, respectively. The energy of the molecular orbital increases with the number of nodes. With four electrons, only the two bonding orbitals are filled, consistent with the presence of two π bonds.

Figure 9.38 *Molecular Orbital Energy-Level Diagrams for a Chain of n Like Orbitals That Interact (n ≤ 5)*
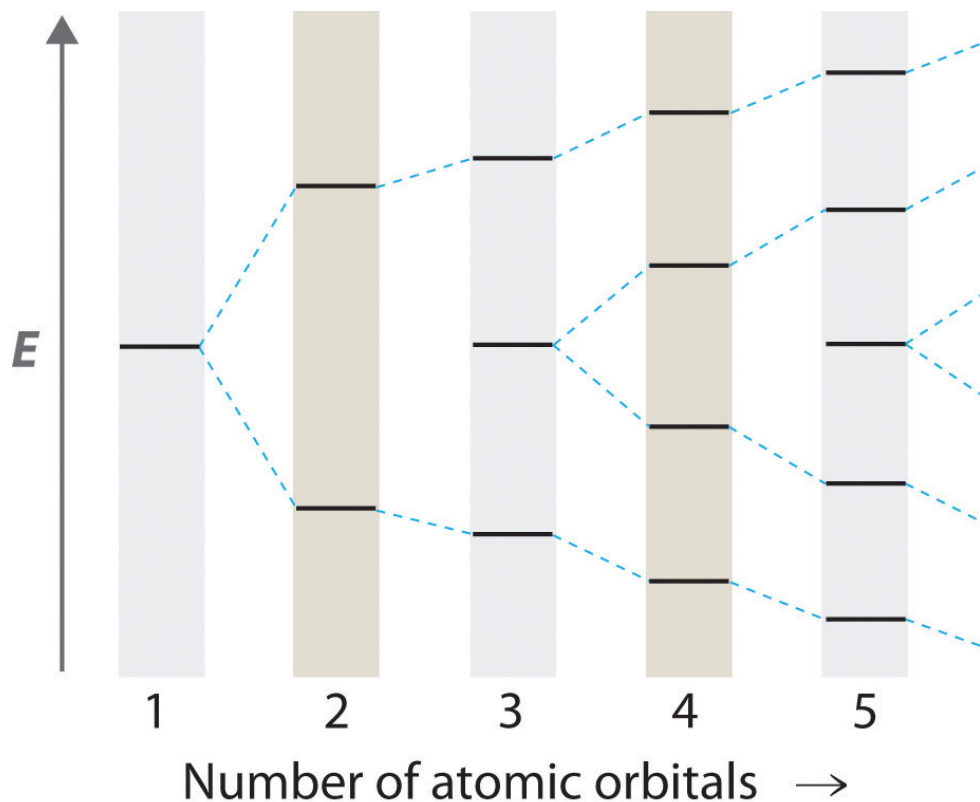
As the number of atomic orbitals increases, the difference in energy between the resulting molecular orbital energy levels decreases, which allows light of lower energy to be absorbed. As a result, organic compounds with long chains of carbon atoms and alternating single and double bonds tend to become more deeply colored as the number of double bonds increases.

Note the Pattern

As the number of interacting atomic orbitals increases, the energy separation between the resulting molecular orbitals steadily decreases.

A derivative of vitamin A called *retinal* is used by the human eye to detect light and has a structure with alternating C=C double bonds. When visible light strikes retinal, the energy separation between the molecular orbitals is sufficiently close that the energy absorbed corresponds to the energy required to change one double bond in the molecule from *cis*, where like groups are on the same side of the double

bond, to *trans*, where they are on opposite sides, initiating a process that causes a signal to be sent to the brain. If this mechanism is defective, we lose our vision in dim light. Once again, a molecular orbital approach to bonding explains a process that cannot be explained using any of the other approaches we have described.

Summary

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2. Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized *np* orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

KEY TAKEAWAY

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding.

CONCEPTUAL PROBLEMS

1. What information is obtained by using the molecular orbital approach to bonding in O_3 that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?

2. How is resonance explained using the molecular orbital approach?

3. Indicate what information can be obtained by each method:

|	Lewis Electron Structures	VSEPR Model	Valence Bond Theory	Molecular Orbital Theory
Geometry				
Resonance				
Orbital Hybridization				
Reactivity				
Expanded Valences				
Bond Order				

NUMERICAL PROBLEMS

1. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in BCl_3 and CS_3^{2-}.

2. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in CO_2 and N_3^-.

9.5 End-of-Chapter Material

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. ♦ Sulfur hexafluoride (SF_6) is a very stable gas that is used in a wide range of applications because it is nontoxic, nonflammable, and noncorrosive. Unfortunately, it is also a very powerful "greenhouse gas" that is about 22,000 times more effective at causing global warming than the same mass of CO_2.

   a. Draw the Lewis electron structure of SF_6 and determine the number of electron groups around the central atom, the molecular geometry, and the hybridization of the central atom.
   b. Suggest a reason for the extremely high stability of SF_6.
   c. Despite its rather high molecular mass (146.06 g/mol) and highly polar S–F bonds, SF_6 is a gas at room temperature (boiling point = –63°C). Why?

2. ♦ The elevated concentrations of chlorine monoxide (ClO) that accompany ozone depletions in Earth's atmosphere can be explained by a sequence of reactions. In the first step, chlorine gas is split into chlorine atoms by sunlight. Each chlorine atom then catalyzes the decomposition of ozone through a chlorine monoxide intermediate.

   a. Write balanced chemical equations showing this sequence of reactions.
   b. Sketch the molecular orbital energy-level diagram of ClO.
   c. Does ClO contain any unpaired electrons?
   d. Based on your molecular orbital diagram, is ClO likely to be a stable species? Explain your answer.

3. ♦ Saccharin is an artificial sweetener that was discovered in 1879. For several decades, it was used by people who had to limit their intake of sugar for medical reasons. Because it was implicated as a carcinogen in 1977, however, warning labels are now required on foods and beverages containing saccharin. The structure of this sweetener is as follows:
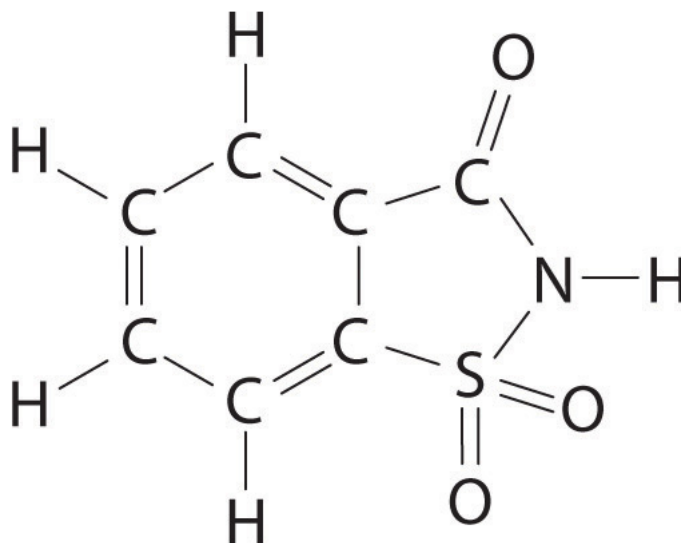
a. Give the hybridization of all five atoms shown in bold in the structure. Note: all five atoms in the five-membered ring are coplanar.

b. The carbon–oxygen bond is drawn as a double bond. If the nitrogen and the carbon attached to the $C=O$ group each contribute one electron to the bonding, use both a Lewis electron structure and a hybrid orbital approach to explain the presence of the double bond.

c. If sulfur and carbon each contribute one electron to nitrogen, how many lone pairs are present on the nitrogen?

d. What is the geometry of the sulfur atom?

e. The Lewis electron structure supports a single bond between the carbon and the nitrogen and a double bond between the carbon and the oxygen. In actuality, the C–O bond is longer than expected for a double bond, and the C–N bond is shorter. The nitrogen is also planar. Based on this information, what is the likely hybridization of the nitrogen? Using the concepts of molecular orbital theory, propose an explanation for this observation.

4. ♦ Pheromones are chemical signals used for communication between members of the same species. For example, the bark beetle uses an aggregation pheromone to signal other bark beetles to congregate at a particular site in a tree. Bark beetle infestations can cause severe damage because the beetles carry a fungal infection that spreads rapidly and can kill the tree. One of the components of this aggregation pheromone has the following structure:
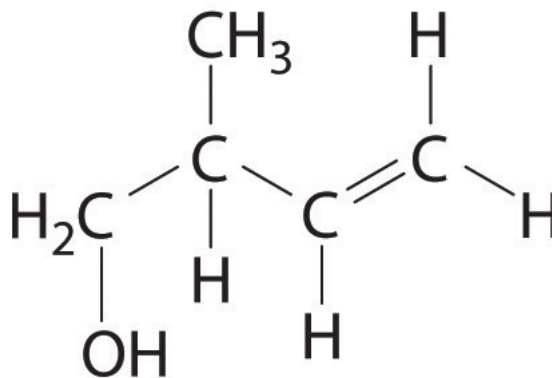
a. Give the hybridization of all atoms except hydrogen in this pheromone.
b. How many σ bonds are present in this molecule? How many π bonds are there?
c. Describe the bonding in this molecule using a combination of the localized and delocalized approaches.

5. Carbon monoxide is highly poisonous because it binds more strongly than O_2 to the iron in red blood cells, which transport oxygen in the blood. Consequently, a victim of CO poisoning suffocates from a lack of oxygen. Draw a molecular orbital energy-level diagram for CO. What is the highest occupied molecular orbital? Are any of the molecular orbitals degenerate? If so, which ones?

ANSWER

1.
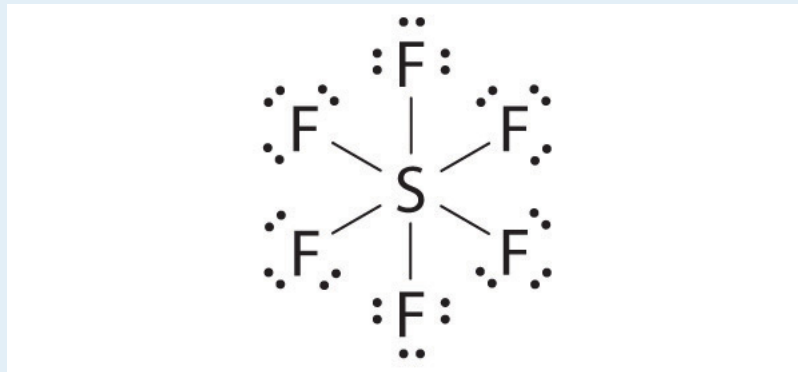
a. There are six electron groups, the molecular geometry is octahedral, and the hybridization of S is sp^3d^2.

b. With six fluorine atoms packed around the central sulfur atom, there is no room for another species to approach the sulfur to initiate a reaction. The polar S–F bonds are also expected to be quite strong, so breaking an S–F bond to initiate a reaction is unlikely under most conditions.

c. SF_6 is a gas at room temperature because it has no net dipole moment; the individual S–F bond dipoles cancel one another in this highly symmetrical structure. The absence of a dipole moment results in very weak interactions between SF_6 molecules, and as a result SF_6 is a gas rather than a liquid or a solid at room temperature.