



This is “Molecular Geometry and Covalent Bonding Models”, chapter 9 from the book [Principles of General Chemistry \(index.html\)](#) (v. 1.0).

This book is licensed under a [Creative Commons by-nc-sa 3.0](http://creativecommons.org/licenses/by-nc-sa/3.0/) license. See the license for more details, but that basically means you can share this book as long as you credit the author (but see below), don't make money from it, and do make it available to everyone else under the same terms.

This content was accessible as of December 29, 2012, and it was downloaded then by [Andy Schmitz](#) (<http://lardbucket.org>) in an effort to preserve the availability of this book.

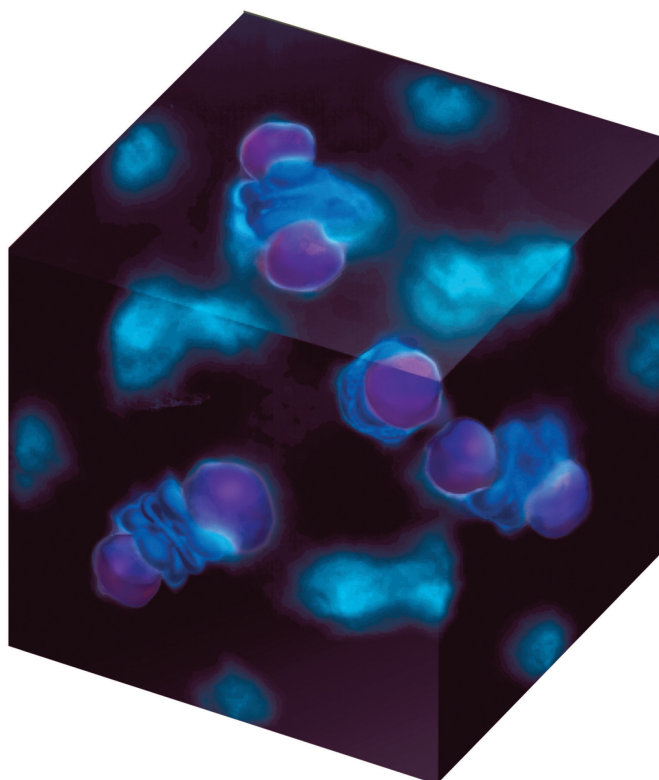
Normally, the author and publisher would be credited here. However, the publisher has asked for the customary Creative Commons attribution to the original publisher, authors, title, and book URI to be removed. Additionally, per the publisher's request, their name has been removed in some passages. More information is available on this project's [attribution page](http://2012books.lardbucket.org/attribution.html?utm_source=header).

For more information on the source of this book, or why it is available for free, please see [the project's home page](#) (<http://2012books.lardbucket.org/>). You can browse or download additional books there.

## 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  $\text{Cu}_2\text{O}$  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  $\text{Ca}_2$  is too unstable to exist in nature and why the unpaired electrons on  $\text{O}_2$  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 [Chapter 8 "Ionic versus Covalent Bonding"](#) 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**<sup>1</sup> (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

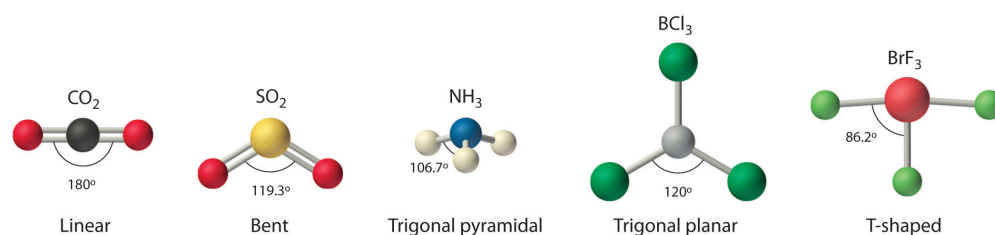
Lewis electron structures predict the number and types of bonds, whereas VSEPR can predict the shapes of many molecules and polyatomic ions.

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.

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*,

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


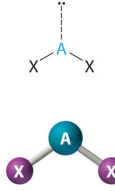
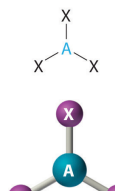

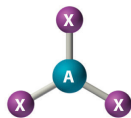

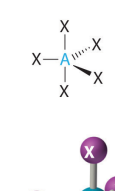
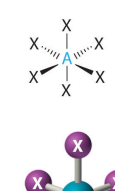
around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**<sup>2</sup>. Using this information, we can describe the **molecular geometry**<sup>3</sup>, 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\*

<b>AX<sub>m</sub>E<sub>n</sub> Notation</b>	AX <sub>2</sub>	AX <sub>2</sub> E	AX <sub>3</sub>	AX <sub>3</sub> E
<b>Geometry</b>	Linear X—A—X 	Bent (V-shaped) 	Trigonal planar 	Trigonal pyramidal 
<b>Idealized Bond Angles</b>	180°	<180°	120°	<120°
<b>AX<sub>m</sub>E<sub>n</sub> Notation</b>	AX <sub>4</sub> E <sub>2</sub>	AX <sub>4</sub>	AX <sub>5</sub>	AX <sub>6</sub>
<b>Geometry</b>	Square planar 	Tetrahedral 	Trigonal bipyramidal 	Octahedral 
<b>Idealized Bond Angles</b>	90°	109.5°	90°, 120°	90°

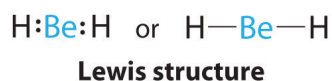
\*Lone pairs are shown using a dashed line.

## Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH<sub>2</sub>.

### AX<sub>2</sub>: BeH<sub>2</sub>

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



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  $180^\circ$  apart.

3. Both groups around the central atom are bonding pairs (BP). Thus  $\text{BeH}_2$  is designated as  $\text{AX}_2$ .

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  $\text{BeH}_2$  is *linear*.

### $\text{AX}_2$ : $\text{CO}_2$

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



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  $\text{BeH}_2$ , the arrangement that minimizes repulsions places the groups  $180^\circ$  apart.

3. Once again, both groups around the central atom are bonding pairs (BP), so  $\text{CO}_2$  is designated as  $\text{AX}_2$ .

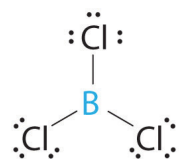
4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of  $\text{CO}_2$  is linear ([Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups\\*"](#)). The structure of  $\text{CO}_2$  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

#### $\text{AX}_3$ : $\text{BCl}_3$

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





Lewis structure

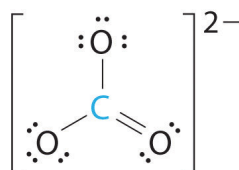
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed  $120^\circ$  apart ([Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#)).

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

4. From [Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups"](#) we see that with three bonding pairs around the central atom, the molecular geometry of  $BCl_3$  is *trigonal planar*, as 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"](#).

### $AX_3$ : $CO_3^{2-}$

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

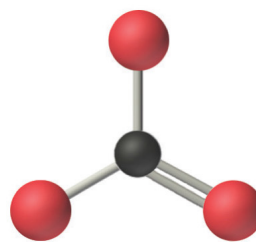


Lewis structure

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  $120^\circ$  apart ([Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#)).

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 [Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups"](#) that the molecular geometry of  $\text{CO}_3^{2-}$  is trigonal planar.

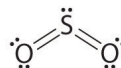


Molecular geometry  
(trigonal planar)

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

#### **AX<sub>2</sub>E: SO<sub>2</sub>**

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.



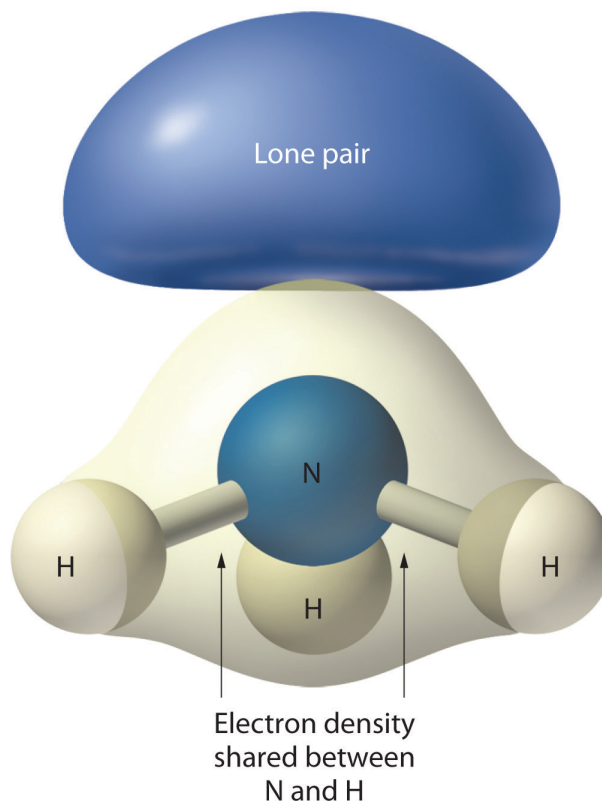
2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions ([Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#)).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX<sub>2</sub>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 ([Figure 9.4 "The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair"](#)). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO<sub>2</sub>, 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 ([Figure 9.1 "Common Structures for Molecules and Polyatomic Ions"](#)).

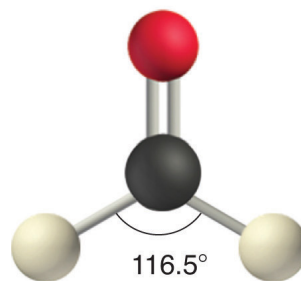
That Consist of a Central Atom Bonded to Two or Three Other Atoms" and Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups\*").

Figure 9.4 The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair



As with  $\text{SO}_2$ , 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  $\text{CH}_2\text{O}$  ( $\text{AX}_3$ ), 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  $\text{H-C-H}$  bond angle of  $116.5^\circ$  rather than  $120^\circ$ ).

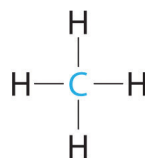


### Four Electron Groups

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<sub>4</sub>: CH<sub>4</sub>

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

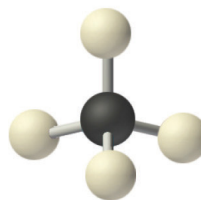


**Lewis structure**

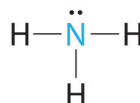
2. There are four electron groups around the central atom. As shown in [Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#), repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX<sub>4</sub>.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* ([Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups\\*"](#)).

Molecular geometry  
(tetrahedral)**AX<sub>3</sub>E: NH<sub>3</sub>**

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**

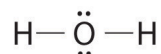
2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX<sub>3</sub>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<sub>2</sub>E<sub>2</sub>: H<sub>2</sub>O**

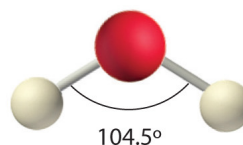
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



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 [Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#).

3. With two bonding pairs and two lone pairs, the structure is designated as AX<sub>2</sub>E<sub>2</sub> 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<sub>3</sub>, 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.

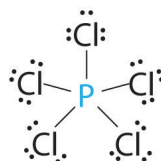


### Five Electron Groups

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<sub>5</sub>: PCl<sub>5</sub>

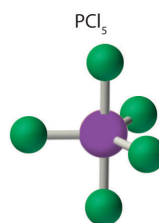
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl<sub>5</sub> is



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 ([Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#)):

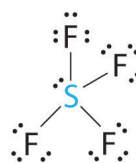
3. All electron groups are bonding pairs, so the structure is designated as AX<sub>5</sub>. There are no lone pair interactions.

4. The molecular geometry of PCl<sub>5</sub> is *trigonal bipyramidal*, as shown in [Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups\\*"](#). 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.



#### AX<sub>4</sub>E: SF<sub>4</sub>

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



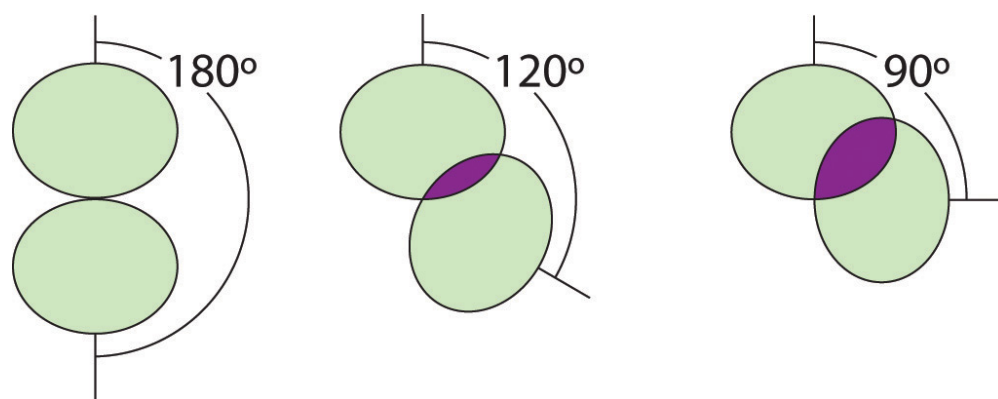
**Lewis structure**

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 [Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#).

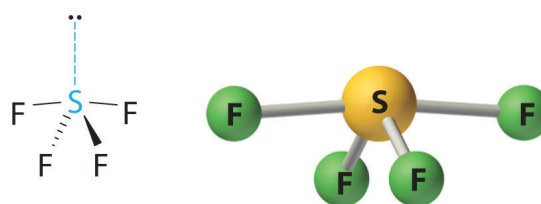
3. We designate  $\text{SF}_4$  as  $\text{AX}_4\text{E}$ ; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at  $90^\circ$ . If we place it in the axial position, we have two  $90^\circ$  LP–BP repulsions at  $90^\circ$ . With fewer  $90^\circ$  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  $90^\circ$ , 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  $\text{F}_{\text{axial}}\text{--S--F}_{\text{axial}}$  angle is  $173^\circ$  rather than  $180^\circ$  because of the lone pair of electrons in the equatorial plane.

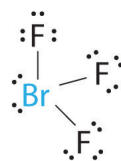


Molecular geometry (seesaw)



**AX<sub>3</sub>E<sub>2</sub>: BrF<sub>3</sub>**

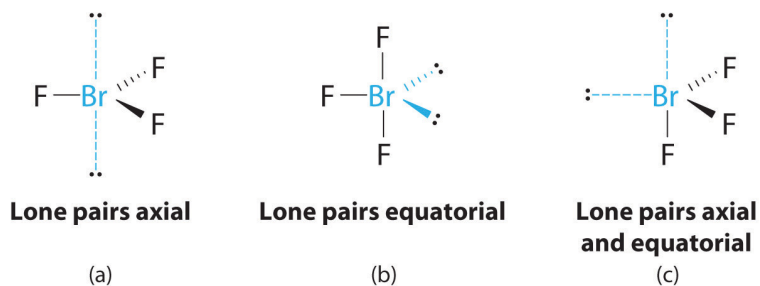
1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is

**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<sub>3</sub>E<sub>2</sub> 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°:

**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  $\text{BrF}_3$  determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The  $\text{F}_{\text{axial}}\text{-Br-F}_{\text{axial}}$  angle is  $172^\circ$ , less than  $180^\circ$  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.

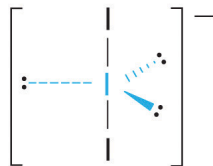
### $\text{AX}_2\text{E}_3: \text{I}_3^-$

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



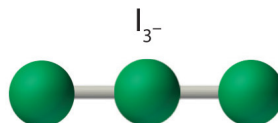
2. There are five electron groups about the central atom in  $\text{I}_3^-$ , two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs,  $\text{I}_3^-$  has a total of five electron pairs and is designated as  $\text{AX}_2\text{E}_3$ . 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  $90^\circ$  LP-LP repulsions and minimizes the number of  $90^\circ$  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  $180^\circ$ , as expected.

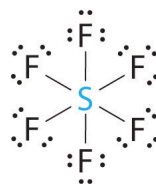


### Six Electron Groups

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



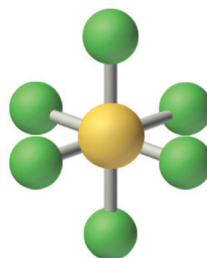
**Lewis structure**

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,  $\text{SF}_6$  is designated as  $\text{AX}_6$ . All positions are chemically equivalent, so all electronic interactions are equivalent.

4. There are six nuclei, so the molecular geometry of  $\text{SF}_6$  is octahedral.

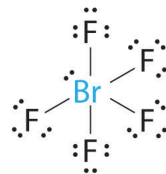


Molecular geometry  
(octahedral)

---

#### $\text{AX}_5\text{E}$ : $\text{BrF}_5$

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

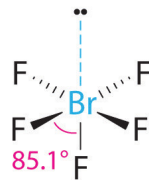


Lewis structure

---

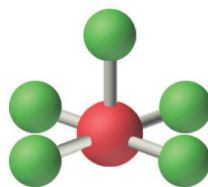
With its expanded valence, this species is an exception to the octet rule.

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,  $\text{BrF}_5$  is designated as  $\text{AX}_5\text{E}$ ; it has a total of six electron pairs. The  $\text{BrF}_5$  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  $\text{F}_{\text{axial}}\text{-Br-F}_{\text{equatorial}}$  angles to be less than  $90^\circ$  because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

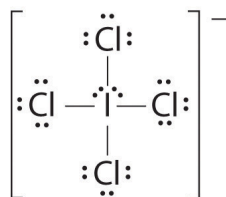
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The  $\text{F}_{\text{axial}}\text{-Br-F}_{\text{equatorial}}$  angles are  $85.1^\circ$ , less than  $90^\circ$  because of LP-BP repulsions.



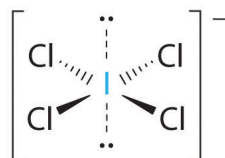
Molecular geometry  
(square pyramidal)

#### $\text{AX}_4\text{E}_2$ : $\text{ICl}_4^-$

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

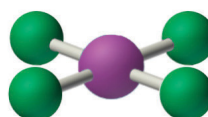


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP-LP, LP-BP, and BP-BP repulsions is



3.  $\text{ICl}_4^-$  is designated as  $\text{AX}_4\text{E}_2$  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  $\text{ICl}_4^-$  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
<b>Molecular Geometry</b>	 Linear	 Trigonal planar	 Tetrahedral	 Trigonal bipyramidal	 Octahedral
<b>Zero Lone Pairs</b>	$X-A-X$ Linear $AX_2$	 Trigonal planar $AX_3$	 Tetrahedral $AX_4$	 Trigonal bipyramidal $AX_5$	 Octahedral $AX_6$
<b>One Lone Pair</b>		 Bent (V-shaped) $AX_2E$	 Trigonal pyramidal $AX_3E$	 Seesaw $AX_4E$ One axial lone pair	 Square pyramidal $AX_5E$
<b>Two Lone Pairs</b>			 Bent (V-shaped) $AX_2E_2$	 T-shaped $AX_3E_2$ Two axial lone pairs	 Square planar $AX_4E_2$
<b>Three Lone Pairs</b>				 Linear $AX_2E_3$ Three axial lone pairs	

## EXAMPLE 1

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

- PF<sub>5</sub> (phosphorus pentafluoride, a catalyst used in certain organic reactions)
- H<sub>3</sub>O<sup>+</sup> (hydronium ion)

**Given:** two chemical species

**Asked for:** molecular geometry

**Strategy:**

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

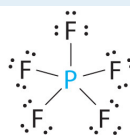
**B** Determine the electron group arrangement around the central atom that minimizes repulsions.

**C** Assign an AX<sub>m</sub>E<sub>n</sub> 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** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF<sub>5</sub> 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"](#)).

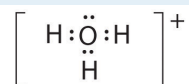


**C** All electron groups are bonding pairs, so  $\text{PF}_5$  is designated as  $\text{AX}_5$ . Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

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



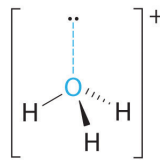
- b. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



**B** There are four electron groups around oxygen, three bonding pairs and one lone pair. Like  $\text{NH}_3$ , 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  $\text{AX}_3\text{E}$  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  $109.5^\circ$  because of LP-BP repulsions:



Exercise

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

- a.  $\text{XeO}_3$
- b.  $\text{PF}_6^-$
- c.  $\text{NO}_2^+$

**Answer:**

- a. trigonal pyramidal
- b. octahedral
- c. linear

## EXAMPLE 2

Predict the molecular geometry of each molecule.

- XeF<sub>2</sub>
- SnCl<sub>2</sub>

**Given:** two chemical compounds

**Asked for:** molecular geometry

**Strategy:**

Use the strategy given in Example 1.

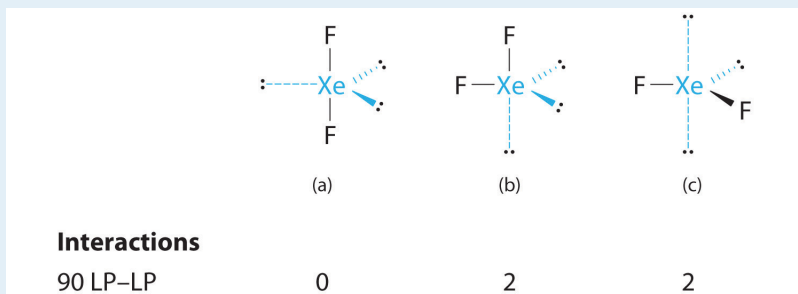
**Solution:**

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



**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.

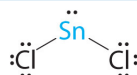
**C** From B, XeF<sub>2</sub> is designated as AX<sub>2</sub>E<sub>3</sub> and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



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  $95^\circ$ . The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

#### Exercise

Predict the molecular geometry of each molecule.

- $\text{SO}_3$
- $\text{XeF}_4$

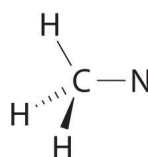
#### Answers:

- trigonal planar
- square planar

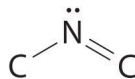
### Molecules with No Single Central Atom

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  $\text{AX}_m\text{E}_n$  fragments. We will demonstrate with methyl isocyanate ( $\text{CH}_3\text{-N=C=O}$ ), 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  $\text{AX}_m\text{E}_n$  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  $\text{AX}_4$ . We can therefore predict the  $\text{CH}_3\text{-N}$  portion of the molecule to be roughly tetrahedral, similar to methane:

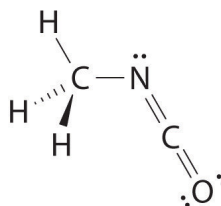


The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



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°.

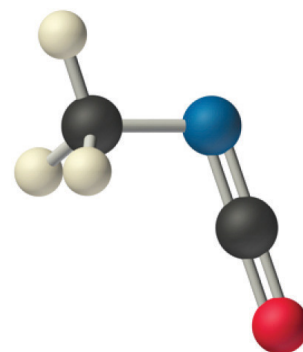
The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:



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 ([Figure 9.7 "The Experimentally Determined Structure of Methyl Isocyanate"](#)).

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  $\text{CO}_2$ , so its geometry, like that of  $\text{CO}_2$ , 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*



## EXAMPLE 3

Use the VSEPR model to predict the molecular geometry of propyne ( $\text{H}_3\text{C}-\text{C}\equiv\text{CH}$ ), 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 [Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups"](#) 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  $\text{C}-\text{C}\equiv\text{C}$  and  $\text{C}\equiv\text{C}-\text{H}$  angles of  $180^\circ$ .

Exercise

Predict the geometry of allene ( $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ ), 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  $\text{C}-\text{C}-\text{C}$  angle is  $180^\circ$ .

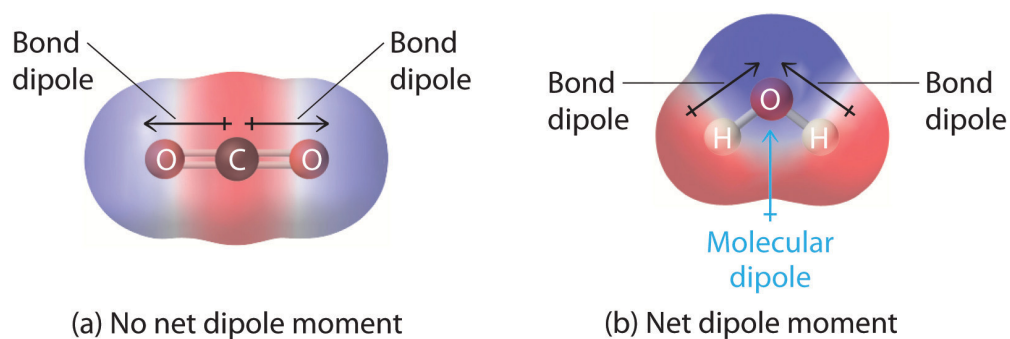
## Molecular Dipole Moments

In [Chapter 8 "Ionic versus Covalent Bonding"](#), 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  $\text{CO}_2$ , a linear molecule (part (a) in [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"](#)). Each C–O bond in  $\text{CO}_2$  is polar, yet experiments show that the  $\text{CO}_2$  molecule has no dipole moment. Because the two C–O bond dipoles in  $\text{CO}_2$  are equal in magnitude and oriented at  $180^\circ$  to each other, they cancel. As a result, the  $\text{CO}_2$  molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the  $\text{H}_2\text{O}$  molecule is not linear (part (b) in [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"](#)); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  to hydrogen-bond to other polarized or charged species, including other water molecules. (For more information on polar bonds, see [Chapter 4 "Reactions in Aqueous Solution"](#), [Section 4.1 "Aqueous Solutions"](#).)

*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*

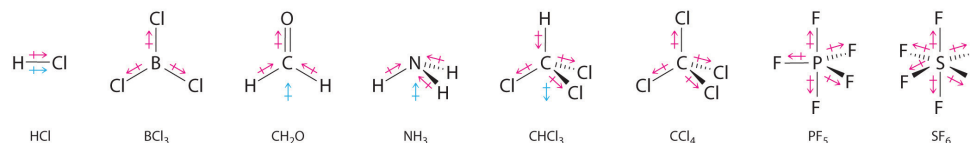


(a) In  $\text{CO}_2$ , the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at  $180^\circ$ ). Their vector sum is zero, so  $\text{CO}_2$  therefore has no net dipole. (b) In  $\text{H}_2\text{O}$ , the O–H bond dipoles are also equal in magnitude, but they are oriented at  $104.5^\circ$  to each other. Hence the vector sum is not zero, and  $\text{H}_2\text{O}$  has a net dipole moment.

Other examples of molecules with polar bonds are shown in [Figure 9.9 "Molecules with Polar Bonds"](#). 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  $\text{CHCl}_3$  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 ( $\text{HCl}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CHCl}_3$ ), indicated in blue, whereas others do not because the bond dipole moments cancel ( $\text{BCl}_3$ ,  $\text{CCl}_4$ ,  $\text{PF}_5$ , and  $\text{SF}_6$ ).

### Note the Pattern

Molecules with asymmetrical charge distributions have a net dipole moment.

## EXAMPLE 4

Which molecule(s) has a net dipole moment?

- $\text{H}_2\text{S}$
- $\text{NHF}_2$
- $\text{BF}_3$

**Given:** three chemical compounds

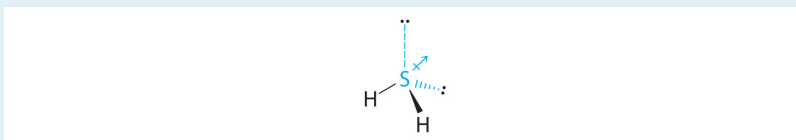
**Asked for:** net dipole moment

**Strategy:**

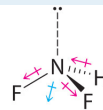
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

**Solution:**

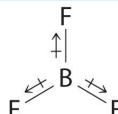
- The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of  $\text{H}_2\text{S}$  is bent ([Figure 9.6 "Overview of Molecular Geometries"](#)). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



- 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  $\text{NHF}_2$  cannot cancel one another. This means that  $\text{NHF}_2$  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  $\text{BF}_3$  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  $\text{BF}_3$  has a net dipole moment of zero:



### Exercise

Which molecule(s) has a net dipole moment?

- $\text{CH}_3\text{Cl}$
- $\text{SO}_3$
- $\text{XeO}_3$

**Answer:**  $\text{CH}_3\text{Cl}$ ;  $\text{XeO}_3$

## 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 VSEPR 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.  $\text{CH}_3\text{Cl}$
  - b.  $\text{PCl}_3$
  - c.  $\text{CO}$
  - d.  $\text{SF}_6$
  - e.  $\text{IF}_5$
  - f.  $\text{CH}_3\text{OCH}_3$
  - g.  $\text{CCl}_3\text{H}$
  - h.  $\text{H}_3\text{COH}$
15. The idealized molecular geometry of  $\text{BrF}_5$  is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of  $\text{BrF}_5$ ? If LP–BP repulsions were *weaker* than BP–BP repulsions, what would be the effect on the molecular geometry of  $\text{BrF}_5$ ?
16. Which has the smallest bond angle around the central atom— $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , or  $\text{H}_2\text{Te}$ ? 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.



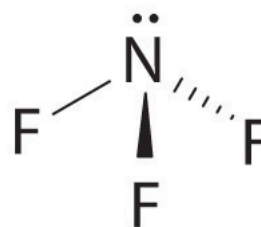
## NUMERICAL PROBLEMS

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.  $\text{BF}_3$
  - b.  $\text{PCl}_3$
  - c.  $\text{XeF}_2$
  - d.  $\text{AlCl}_4^-$
  - e.  $\text{CH}_2\text{Cl}_2$
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.  $\text{ICl}_3$
  - b.  $\text{CCl}_3^+$
  - c.  $\text{H}_2\text{Te}$
  - d.  $\text{XeF}_4$
  - e.  $\text{NH}_4^+$
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.  $\text{HCl}$
  - b.  $\text{NF}_3$
  - c.  $\text{ICl}_2^+$
  - d.  $\text{N}_3^-$
  - e.  $\text{H}_3\text{O}^+$
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.  $\text{SO}_3$
  - b.  $\text{NH}_2^-$
  - c.  $\text{NO}_3^-$
  - d.  $\text{I}_3^-$
  - e.  $\text{OF}_2$

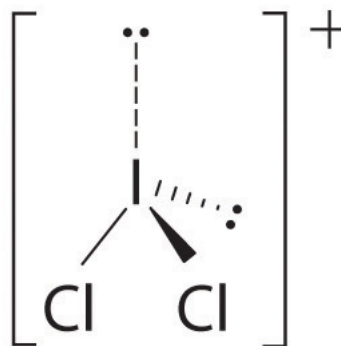
5. What is the molecular geometry of  $\text{ClF}_3$ ? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.
6. Predict the molecular geometry of each of the following.
  - a.  $\text{ICl}_3$
  - b.  $\text{AsF}_5$
  - c.  $\text{NO}_2^-$
  - d.  $\text{TeCl}_4$
7. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.
  - a.  $\text{NO}$
  - b.  $\text{HF}$
  - c.  $\text{PCl}_3$
  - d.  $\text{CO}_2$
  - e.  $\text{SO}_2$
  - f.  $\text{SF}_4$
8. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.
  - a.  $\text{OF}_2$
  - b.  $\text{BCl}_3$
  - c.  $\text{CH}_2\text{Cl}_2$
  - d.  $\text{TeF}_4$
  - e.  $\text{CH}_3\text{OH}$
  - f.  $\text{XeO}_4$
9. Of the molecules  $\text{Cl}_2\text{C}=\text{Cl}_2$ ,  $\text{IF}_3$ , and  $\text{SF}_6$ , which has a net dipole moment? Explain your reasoning.
10. Of the molecules  $\text{SO}_3$ ,  $\text{XeF}_4$ , and  $\text{H}_2\text{C}=\text{Cl}_2$ , which has a net dipole moment? Explain your reasoning.

## ANSWERS

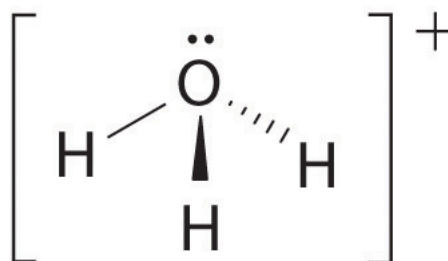
1.
  - a. trigonal planar (all electron groups are bonding pairs)
  - b. tetrahedral (one lone pair on P)
  - c. trigonal bipyramidal (three lone pairs on Xe)
  - d. tetrahedral (all electron groups on Al are bonding pairs)
  - e. tetrahedral (all electron groups on C are bonding pairs)
  
3.
  - a. four electron groups, linear molecular geometry
  - b. four electron groups, pyramidal molecular geometry



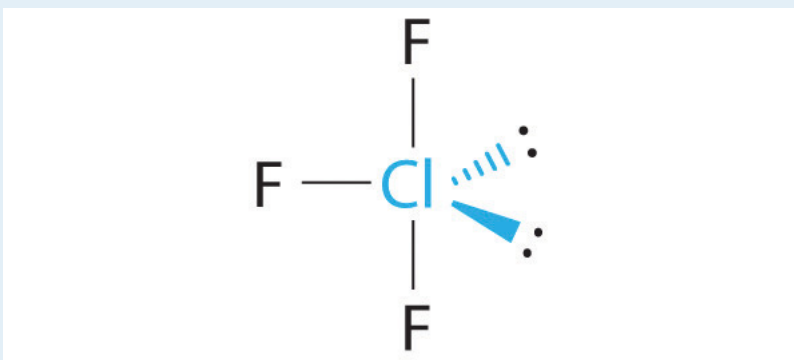
- c. four electron groups, bent molecular geometry



- d. two electron groups, linear molecular geometry
- e. four electron groups, pyramidal molecular geometry

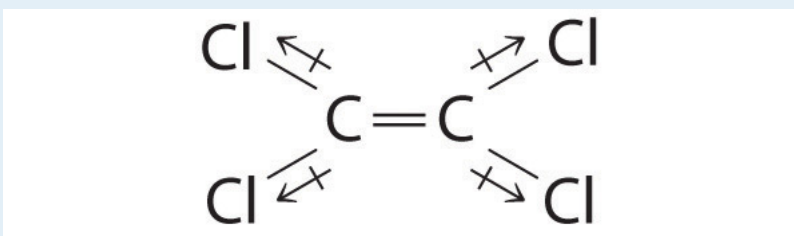


5.

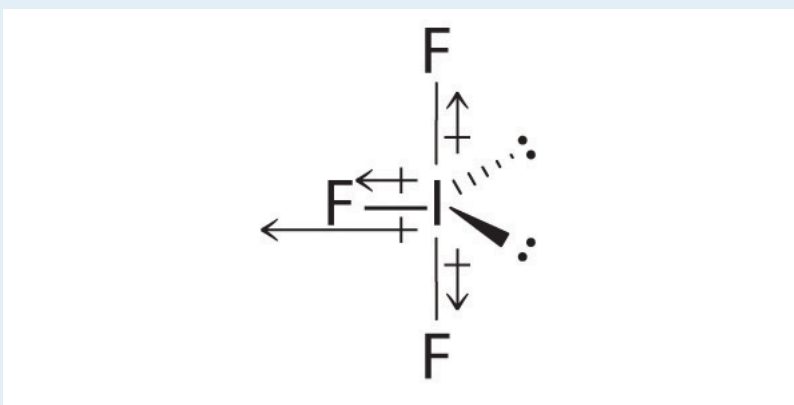


The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than  $180^\circ$ .

9.  $\text{Cl}_2\text{C}=\text{CCl}_2$ : Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and  $\text{Cl}_2\text{C}=\text{CCl}_2$  does not have a net dipole moment.



$\text{IF}_3$ : In this structure, the individual I–F bond dipoles cannot cancel one another, giving  $\text{IF}_3$  a net dipole moment.



$\text{SF}_6$ : The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus,  $\text{SF}_6$  has no net dipole moment.



## 9.2 Localized Bonding and Hybrid Atomic Orbitals

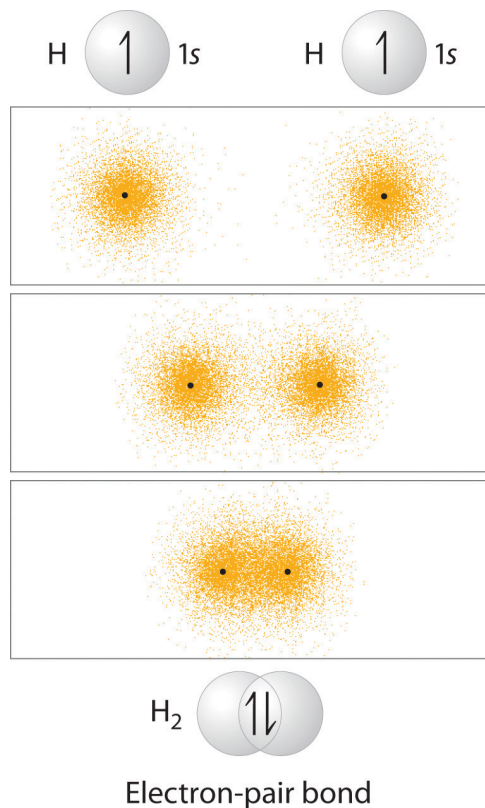
### LEARNING OBJECTIVE

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  $\text{H}_2\text{S}$  and  $\text{PH}_3$  should have structures similar to those of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than  $12^\circ$  smaller than the corresponding bond angles in  $\text{H}_2\text{O}$  and  $\text{NH}_3$ . More disturbing, the VSEPR model predicts that the simple group 2 halides ( $\text{MX}_2$ ), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including  $\text{SrF}_2$  and  $\text{BaF}_2$ , 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 H<sub>2</sub>*

The formation of H<sub>2</sub> 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 H<sub>2</sub> 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**<sup>4</sup>, which is built on two assumptions:

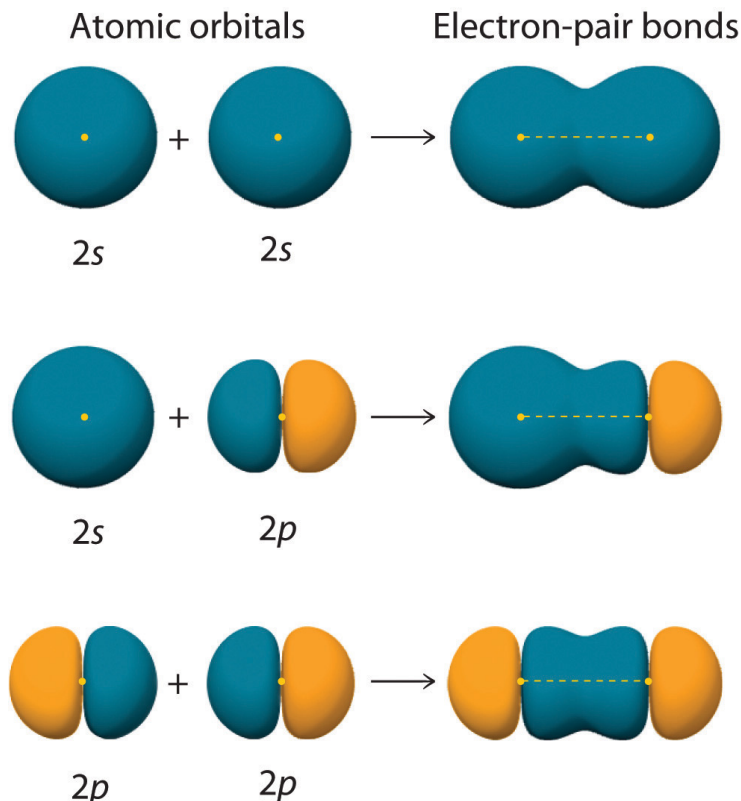
4. A localized bonding model that assumes that the strength of a covalent bond is proportional to the amount of overlap between atomic orbitals and that an atom can use different combinations of atomic orbitals (hybrids) to maximize the overlap between bonded atoms.

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.

**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.

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

Let's examine the bonds in  $\text{BeH}_2$ , for example. According to the VSEPR model,  $\text{BeH}_2$  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**<sup>5</sup>:





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<sub>2</sub>, 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<sub>2</sub> form, scientists developed the concept of hybridization.

### Hybridization of s and p Orbitals

The localized bonding approach uses a process called **hybridization**<sup>6</sup>, 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**<sup>7</sup> because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

In BeH<sub>2</sub>, 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<sub>z</sub> atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the z-axis, as shown in [Figure 9.12 "The Formation of "](#). Because the difference A – B can also be written as A + (–B), in [Figure 9.12 "The Formation of "](#) 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 [Equation 9.1](#), where the value  $\frac{1}{\sqrt{2}}$  is needed

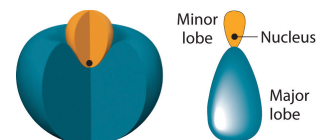
mathematically to indicate that the 2s and 2p orbitals contribute equally to each hybrid orbital.

*Equation 9.1*

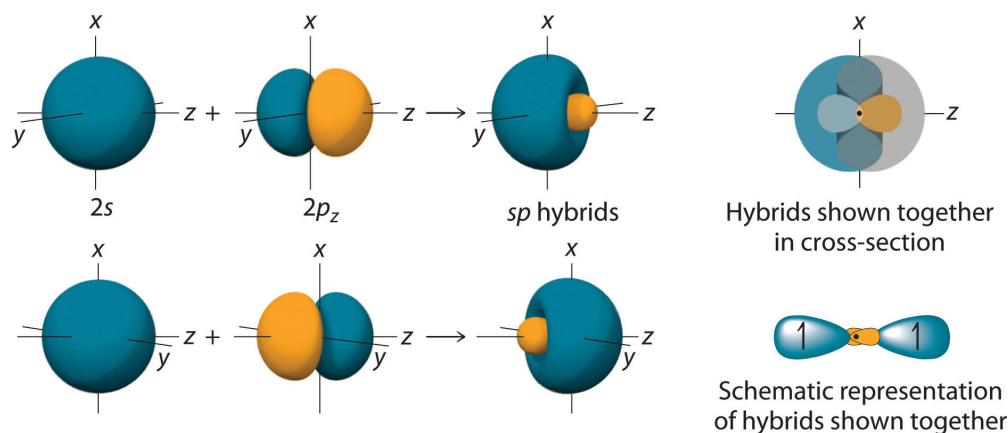
$$sp = \frac{1}{\sqrt{2}} (2s + 2p_z) \quad \text{and} \quad sp = \frac{1}{\sqrt{2}} (2s - 2p_z)$$

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.

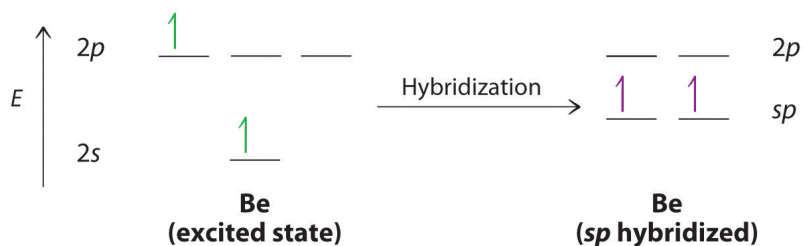
Figure 9.12 The Formation of  $sp$  Hybrid Orbitals


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.



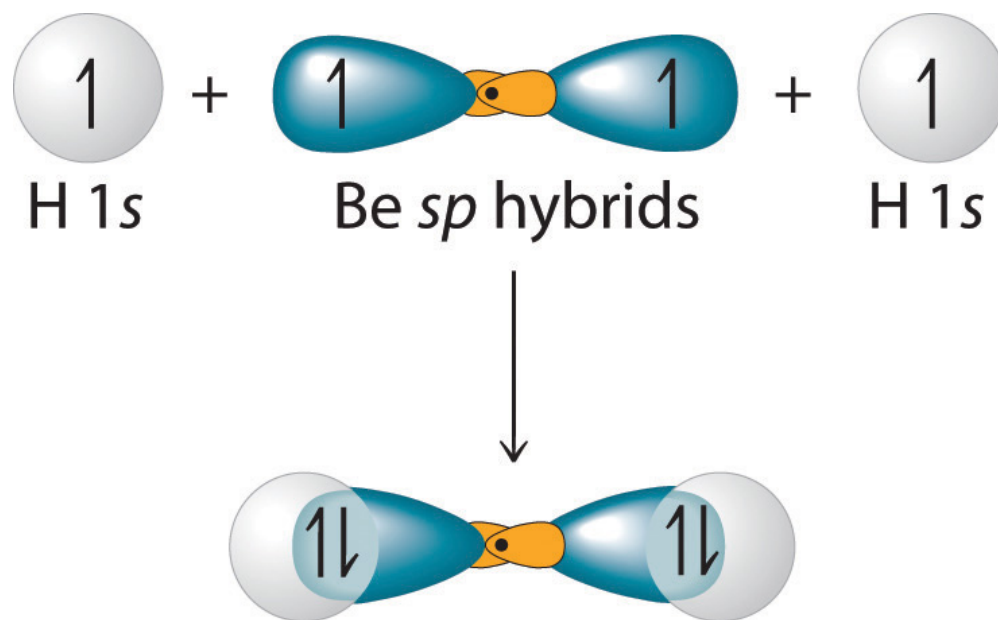
Taking the mathematical sum and difference of an  $ns$  and an  $np$  atomic orbital where  $n = 2$  gives two equivalent  $sp$  hybrid orbitals oriented at  $180^\circ$  to each other.

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:



Each singly occupied ***sp* hybrid orbital**<sup>8</sup> can now form an electron-pair bond with the singly occupied 1s atomic orbital of one of the H atoms. As shown in [Figure 9.13 "Explanation of the Bonding in BeH"](#), 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<sub>2</sub> 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<sub>2</sub> are equivalent in energy and why BeH<sub>2</sub> has a linear geometry.

Figure 9.13 Explanation of the Bonding in BeH<sub>2</sub> Using *sp* Hybrid Orbitals

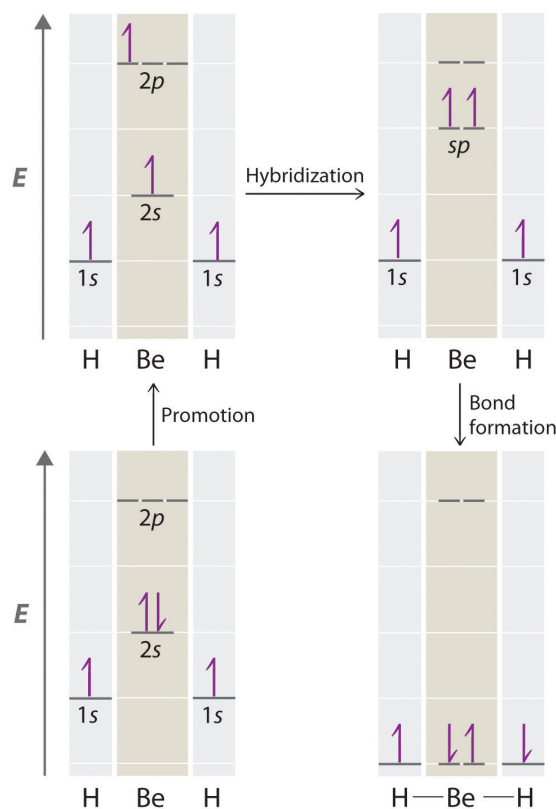


Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1s orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH<sub>2</sub> molecule is linear.

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.

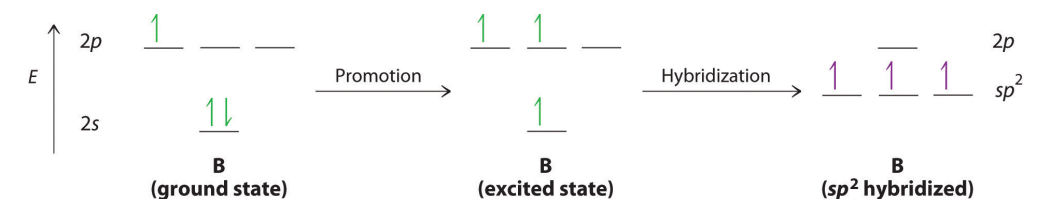
Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals ([Figure 9.14 "A Hypothetical Stepwise Process for the Formation of BeH"](#)). 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  $\text{BeH}_2$  from a Gaseous Be Atom and Two Gaseous H Atoms



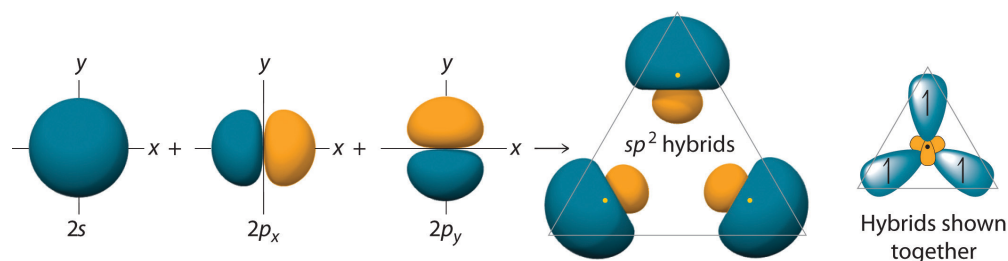
The promotion of an electron from the  $2s$  orbital of beryllium to one of the  $2p$  orbitals is energetically uphill. The overall process of forming a  $\text{BeH}_2$  molecule from a Be atom and two H atoms will therefore be energetically favorable only if the amount of energy released by the formation of the two  $\text{Be-H}$  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  $\text{BF}_3$ , 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  $120^\circ$  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<sup>9</sup> 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.

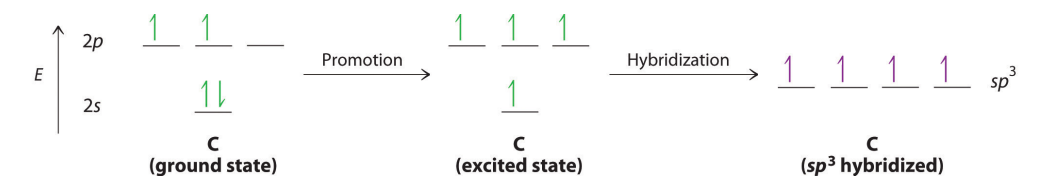
Figure 9.15 Formation of  $sp^2$  Hybrid Orbitals



Combining one  $ns$  and two  $np$  atomic orbitals gives three equivalent  $sp^2$  hybrid orbitals in a trigonal planar arrangement; that is, oriented at  $120^\circ$  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:

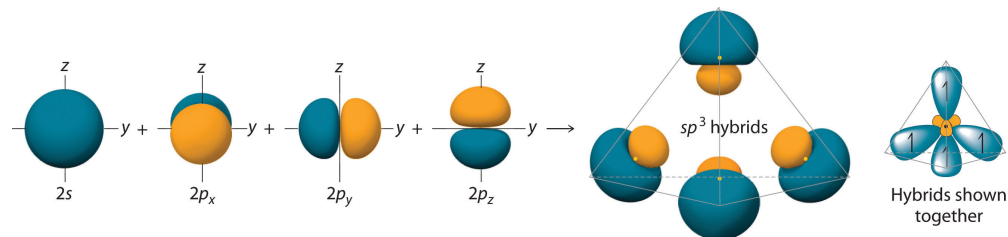
9. The three equivalent hybrid orbitals that result when one  $ns$  orbital and two  $np$  orbitals are combined (hybridized). The three  $sp^2$  hybrid orbitals are oriented in a plane at  $120^\circ$  from each other. They are equivalent in energy, and their energy is between the energy values associated with pure  $s$  and pure  $p$  orbitals.



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with  $109.5^\circ$  angles between them (Figure 9.16 "Formation of "). Like all

the hybridized orbitals discussed earlier, the  $sp^3$  hybrid atomic orbitals<sup>10</sup> 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  $109.5^\circ$  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  $\text{CH}_2$  or  $\text{CF}_2$ ), 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  $109.5^\circ$  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  $\text{NH}_3$  or  $\text{H}_2\text{O}$ , which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In  $\text{NH}_3$ , 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:



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.

## 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.  $\text{H}_2\text{S}$
- b.  $\text{CHCl}_3$

**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**  $\text{H}_2\text{S}$  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  $3s^2 3p^4$  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  $\text{CHCl}_3$  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  $2s^2 2p^2$  valence electron configuration. By hybridizing its 2s and 2p orbitals, it can form



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.

- the  $\text{BF}_4^-$  ion
- hydrazine ( $\text{H}_2\text{N}-\text{NH}_2$ )

#### Answer:

- 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.
- 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.

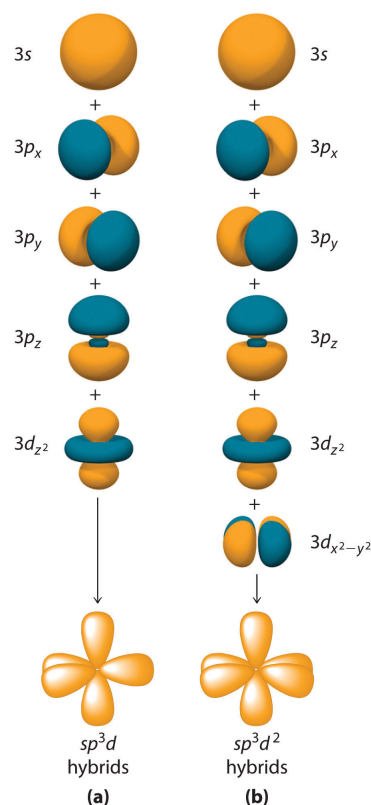
### Hybridization Using *d* Orbitals

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  $\text{PF}_5$  and  $\text{SF}_6$ ). Using the  $ns$  orbital, all three  $np$  orbitals, and one  $(n - 1)d$  orbital gives a set of five

**$sp^3d$  hybrid orbitals**<sup>11</sup> 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  $120^\circ$  angles, and the other two are oriented at  $90^\circ$  to the first three and at  $180^\circ$  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**<sup>12</sup> 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



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).

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  $n = 4$ .

## EXAMPLE 6

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

- XeF<sub>4</sub>
- SO<sub>4</sub><sup>2-</sup>
- SF<sub>4</sub>

**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** Using the VSEPR model, we find that Xe in XeF<sub>4</sub> 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.
- A** The S in the SO<sub>4</sub><sup>2-</sup> 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.
- A** The S atom in SF<sub>4</sub> 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.

- $\text{PCl}_4^+$
- $\text{BrF}_3$
- $\text{SiF}_6^{2-}$

### Answer:

- $sp^3$  with four P–Cl bonds
- $sp^3d$  with three Br–F bonds and two lone pairs
- $sp^3d^2$  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 ( $\text{CF}_4$  and  $\text{SiF}_4$ ), only  $\text{SiF}_4$  reacts with  $\text{F}^-$  to give a stable hexafluoro dianion,  $\text{SiF}_6^{2-}$ . Because there are no  $2d$  atomic orbitals, the formation of octahedral  $\text{CF}_6^{2-}$  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  $\text{CF}_6^{2-}$  have never been prepared.

## EXAMPLE 7

What is the hybridization of the oxygen atom in  $\text{OF}_4$ ? Is  $\text{OF}_4$  likely to exist?

**Given:** chemical compound

**Asked for:** hybridization and stability

**Strategy:**

**A** Predict the geometry of  $\text{OF}_4$  using the VSEPR model.

**B** From the number of electron pairs around O in  $\text{OF}_4$ , 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  $\text{OF}_4$  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  $\text{OF}_4$  molecule is unlikely to exist. In fact, it has not been detected.

Exercise

What is the hybridization of the boron atom in  $\text{BF}_6^{3-}$ ? 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  $180^\circ$ , whereas the combination of an  $ns$  and two or three  $np$  orbitals produces three equivalent  **$sp^2$  hybrids** or four equivalent  **$sp^3$  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  **$sp^3d$  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  $\text{BeF}_2$ , 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  $\text{CCl}_6^{2-}$  ion does not exist.
11. Species such as  $\text{NF}_5^{2-}$  and  $\text{OF}_4^{2-}$  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?

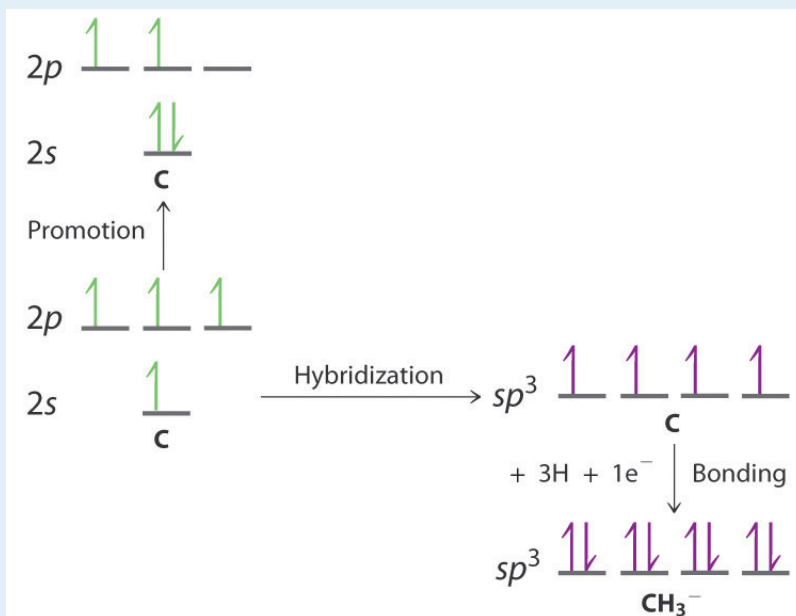
## NUMERICAL PROBLEMS

1. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in  $\text{CH}_3^-$ . 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  $\text{CH}_3^+$ . 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.  $\text{BBr}_3$
  - b.  $\text{PCl}_3$
  - c.  $\text{NO}_3^-$
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.  $\text{AsBr}_3$
  - b.  $\text{CF}_3^+$
  - c.  $\text{H}_2\text{O}$
5. What is the hybridization of the central atom in each of the following?
  - a.  $\text{CF}_4$
  - b.  $\text{CCl}_2^{2-}$
  - c.  $\text{IO}_3^-$
  - d.  $\text{SiH}_4$
6. What is the hybridization of the central atom in each of the following?
  - a.  $\text{CCl}_3^+$
  - b.  $\text{CBr}_2\text{O}$
  - c.  $\text{CO}_3^{2-}$
  - d.  $\text{IBr}_2^-$
7. What is the hybridization of the central atom in  $\text{PF}_6^-$ ? 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  $\text{SF}_5^-$ ? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?



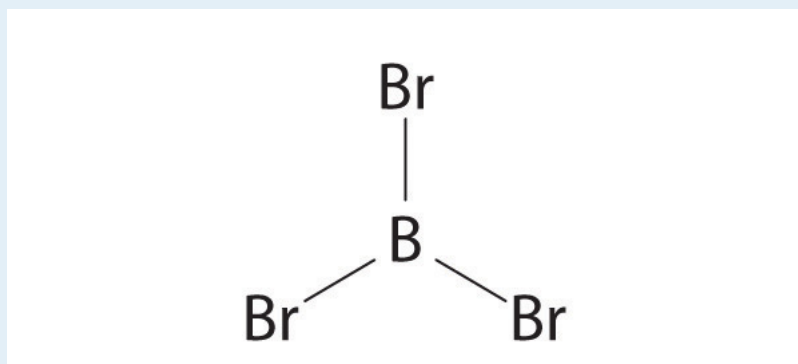
## ANSWERS

1.



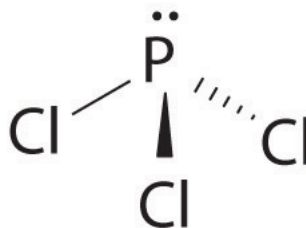
The promotion and hybridization process is exactly the same as shown for  $\text{CH}_4$  in the chapter. The only difference is that the C atom uses the four singly occupied  $sp^3$  hybrid orbitals to form electron-pair bonds with only *three* H atoms, and an electron is added to the fourth hybrid orbital to give a charge of  $1^-$ . The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in  $\text{NH}_3$ .

3.



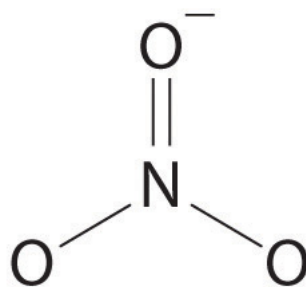
a.

 $sp^2$ , trigonal planar



b.

$sp^3$ , pyramidal



c.

$sp^2$ , trigonal planar

5. The central atoms in  $\text{CF}_4$ ,  $\text{CCl}_2^{2-}$ ,  $\text{IO}_3^-$ , and  $\text{SiH}_4$  are all  $sp^3$  hybridized.
7. The phosphorus atom in the  $\text{PF}_6^-$  ion is  $sp^3d^2$  hybridized, and the ion is octahedral. The  $\text{PF}_6^-$  ion is isoelectronic with  $\text{SF}_6$  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)**<sup>13</sup>—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**<sup>14</sup>, 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<sub>2</sub>, formed from two isolated hydrogen atoms, each with a 1s<sup>1</sup> electron configuration. As we explained in [Chapter 6 "The Structure of Atoms"](#), 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 [Chapter 6 "The Structure of Atoms"](#), [Section 6.5 "Atomic Orbitals and Their Energies"](#).) 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

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

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

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

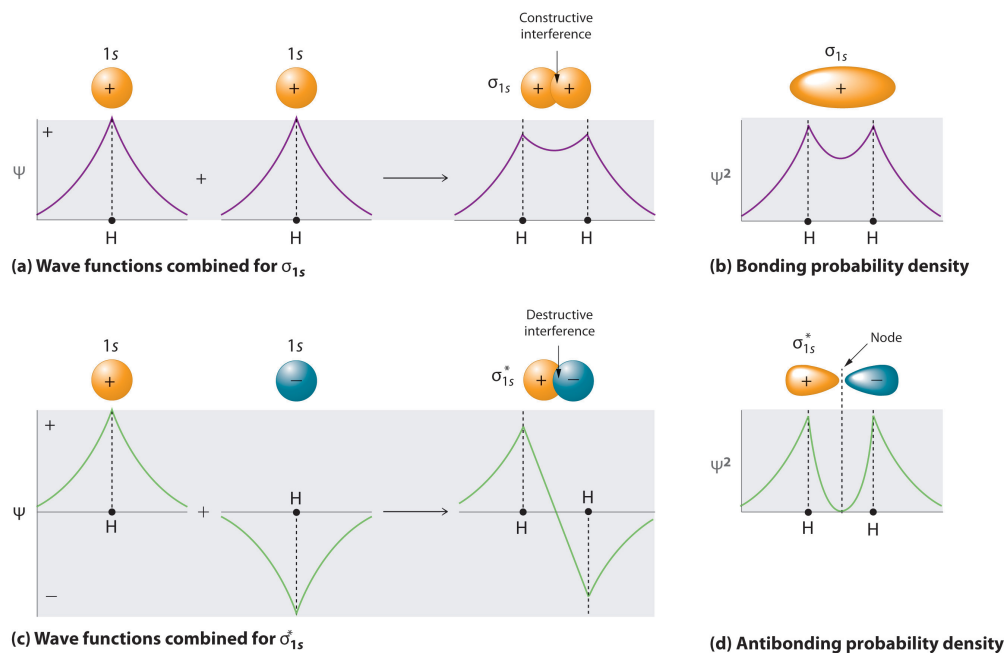
15. Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals).

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

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  $\sigma_{1s}$  combination (pronounced "sigma one ess") (part (a) and part (b) in [Figure 9.18 "Molecular Orbitals for the H"](#)). In a **sigma ( $\sigma$ ) orbital**<sup>16</sup>, 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

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) This diagram shows the formation of a bonding  $\sigma_{1s}$  molecular orbital for  $H_2$  as the sum of the wave functions ( $\Psi$ ) of two  $H$   $1s$  atomic orbitals. (b) This plot of the square of the wave function ( $\Psi^2$ ) for the bonding  $\sigma_{1s}$  molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall from [Chapter 6 "The Structure of Atoms"](#) that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding  $\sigma_{1s}^*$  molecular orbital for  $H_2$  as the difference of the wave functions ( $\Psi$ ) of two  $H$   $1s$  atomic orbitals. (d) This plot of the square of the wave function ( $\Psi^2$ ) for the antibonding  $\sigma_{1s}^*$  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 [Figure 9.18 "Molecular Orbitals for the H"](#)). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called  $\sigma_{1s}^*$  ("sigma one ess star"). In a **sigma star ( $\sigma^*$ ) orbital**<sup>17</sup>, 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  $\sigma_{1s}$  molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the  $\sigma_{1s}$  orbital represents a **bonding molecular orbital**<sup>18</sup>. In contrast, electrons in the  $\sigma_{1s}^*$  orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the  $\sigma_{1s}^*$  orbital is an **antibonding molecular orbital**<sup>19</sup>.

### Note the Pattern

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

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.

### Energy-Level Diagrams

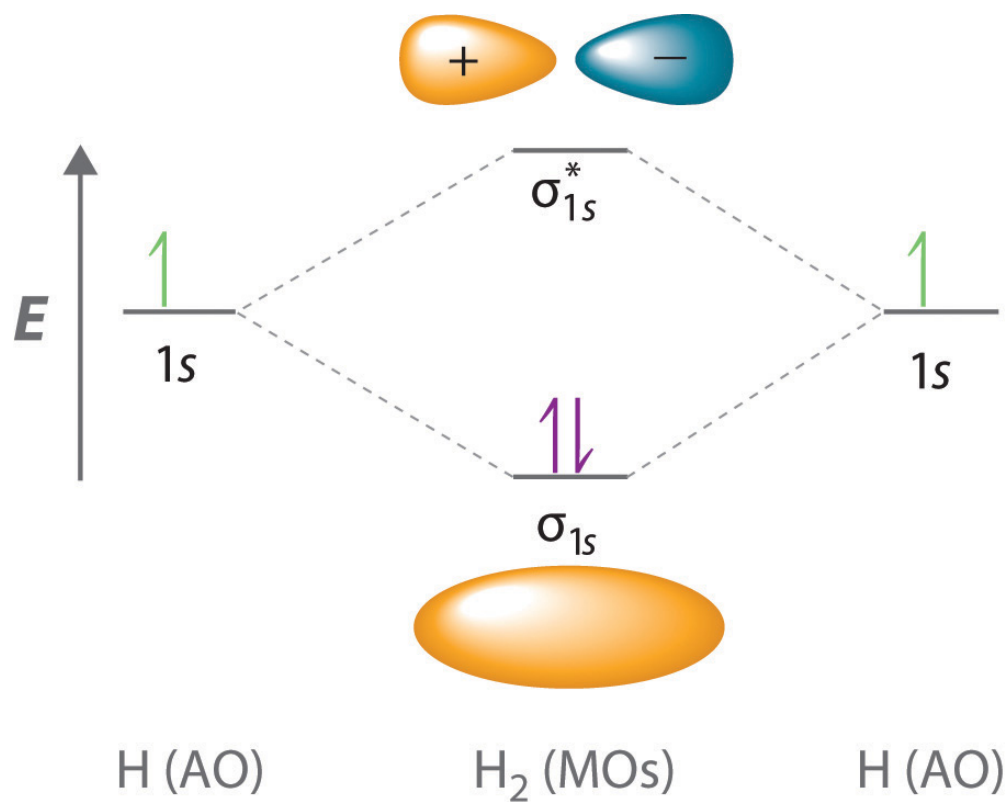
Because electrons in the  $\sigma_{1s}$  orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the  $\sigma_{1s}$  molecular orbital has a *lower* energy than either of the hydrogen 1s atomic orbitals. Conversely, electrons in the  $\sigma_{1s}^*$  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  $\sigma_{1s}^*$  molecular orbital has a *higher* energy than either of the hydrogen 1s atomic orbitals. The  $\sigma_{1s}$  (bonding) molecular orbital is *stabilized* relative to the 1s atomic orbitals,

and the  $\sigma_{1s}^*$  (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the **energy-level diagram**<sup>20</sup> 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<sub>2</sub>



20. A schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals.

The two available electrons (one from each H atom) in this diagram fill the bonding  $\sigma_{1s}$  molecular orbital. Because the energy of the  $\sigma_{1s}$  molecular orbital is lower than that of the two H 1s atomic orbitals, the H<sub>2</sub> molecule is more stable (at a lower energy) than the two isolated H atoms.

To describe the bonding in a **homonuclear diatomic molecule**<sup>21</sup> such as H<sub>2</sub>, 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  $\sigma_{1s}$  bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H<sub>2</sub> molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H<sub>2</sub> 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**<sup>22</sup> 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<sub>2</sub>, we see from [Figure 9.19 "Molecular Orbital Energy-Level Diagram for H"](#) that the  $\sigma_{1s}$  (bonding) molecular orbital contains two electrons, while the  $\sigma_{1s}^*$  (antibonding) molecular orbital is empty. The bond order of H<sub>2</sub> 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.

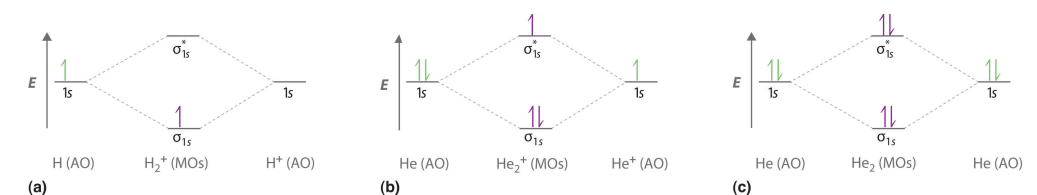


We can use energy-level diagrams such as the one in [Figure 9.19 "Molecular Orbital Energy-Level Diagram for H"](#) to describe the bonding in other pairs of atoms and ions where  $n = 1$ , such as the  $\text{H}_2^+$  ion, the  $\text{He}_2^+$  ion, and the  $\text{He}_2$  molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

Part (a) in [Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1"](#) shows the energy-level diagram for the  $\text{H}_2^+$  ion, which contains two protons and only one electron. The single electron occupies the  $\sigma_{1s}$  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  $\text{H}_2^+$  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  $\text{H}_2^+$ . With a bond order of only  $\frac{1}{2}$ , the bond in  $\text{H}_2^+$  should be weaker than in the  $\text{H}_2$  molecule, and the H–H bond should be longer. As shown in [Table 9.1 "Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions"](#), these predictions agree with the experimental data.

Part (b) in [Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1"](#) is the molecular orbital energy-level diagram for  $\text{He}_2^+$ . This ion has a total of three valence electrons. Because the first two electrons completely fill the  $\sigma_{1s}$  molecular orbital, the Pauli principle states that the third electron must be in the  $\sigma_{1s}^*$  antibonding orbital, giving a  $(\sigma_{1s})^2 (\sigma_{1s}^*)^1$  electron configuration. This electron configuration gives a bond order of  $(2 - 1) \div 2 = \frac{1}{2}$ . As with  $\text{H}_2^+$ , the  $\text{He}_2^+$  ion should be stable, but the He–He bond should be weaker and longer than in  $\text{H}_2$ . In fact, the  $\text{He}_2^+$  ion can be prepared, and its properties are consistent with our predictions ([Table 9.1 "Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions"](#)).

Figure 9.20 Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals



(a) The  $\text{H}_2^+$  ion, (b) the  $\text{He}_2^+$  ion, and (c) the  $\text{He}_2$  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)
$\text{H}_2^+$	$(\sigma_{1s})^1$	$\frac{1}{2}$	106	269
$\text{H}_2$	$(\sigma_{1s})^2$	1	74	436
$\text{He}_2^+$	$(\sigma_{1s})^2 (\sigma_{1s}^*)^1$	$\frac{1}{2}$	108	251
$\text{He}_2$	$(\sigma_{1s})^2 (\sigma_{1s}^*)^2$	0	not observed	not observed

Finally, we examine the  $\text{He}_2$  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  $\text{He}_2$ . With a total of four valence electrons, both the  $\sigma_{1s}$  bonding and  $\sigma_{1s}^*$  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  $\text{He}_2$  molecule has no net bond and is not a stable species. Experiments show that the  $\text{He}_2$  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  $\text{H}_2^+$  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 [Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1"](#), to predict the bond order in the  $\text{He}_2^{2+}$  ion. Is this a stable species?

**Given:** chemical species

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

**Strategy:**

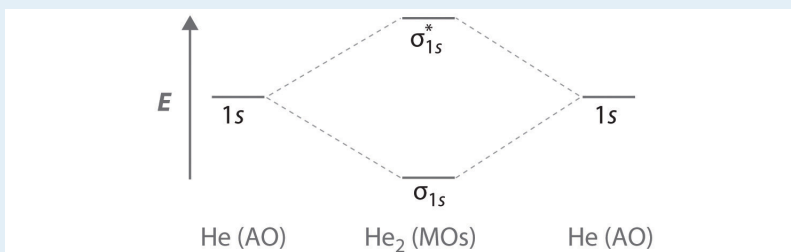
**A** Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.

**B** Determine the total number of valence electrons in the  $\text{He}_2^{2+}$  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.

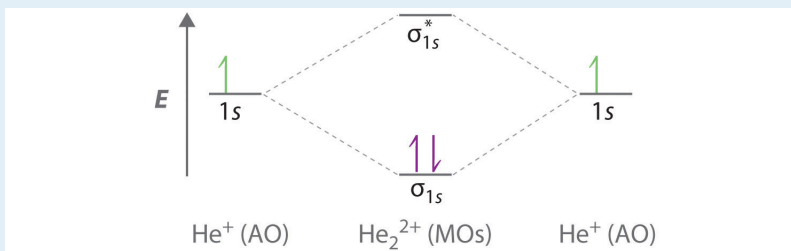
**Solution:**

**A** Two He 1s atomic orbitals combine to give two molecular orbitals: a  $\sigma_{1s}$  bonding orbital at lower energy than the atomic orbitals and a  $\sigma_{1s}^*$  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  $\text{He}_2^{2+}$  ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view  $\text{He}_2^{2+}$  as being formed from

two  $\text{He}^+$  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 ( $\sigma_{1s}$ ) 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

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

$\text{He}_2^{2+}$  is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

#### Exercise

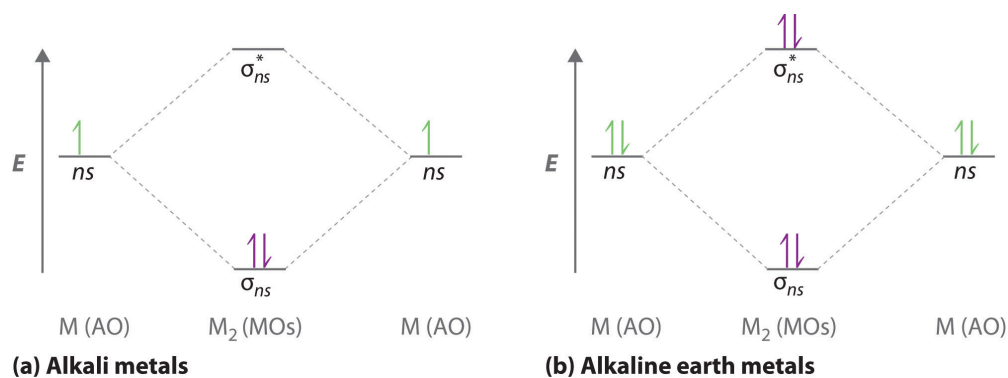
Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the  $\text{H}_2^{2-}$  ion. Is this a stable species?

**Answer:**  $\text{H}_2^{2-}$  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 ( $\text{Li}_2$  and  $\text{Cs}_2$ , for example) is shown in part (a) in [Figure 9.21 "Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic \(M"](#), where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a  $\sigma_{ns}$  bonding molecular orbital and a  $\sigma_{ns}^*$  antibonding molecular orbital. Because each alkali metal (M) has an  $ns^1$  valence electron configuration, the  $\text{M}_2$  molecule has two valence electrons that fill the  $\sigma_{ns}$  bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals ( $\text{Li}_2$ ,  $\text{Na}_2$ ,  $\text{K}_2$ ,  $\text{Rb}_2$ , and  $\text{Cs}_2$ ). The general features of these  $\text{M}_2$  diagrams are identical to the diagram for the  $\text{H}_2$  molecule in [Figure 9.19 "Molecular Orbital Energy-Level Diagram for H"](#). Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

**Figure 9.21** Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic ( $\text{M}_2$ ) Molecules



(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the  $\sigma_{ns}$  (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the  $\sigma_{ns}$  (bonding) and the  $\sigma_{ns}^*$  (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  $\text{Be}_2$ ), in which each metal atom has an  $ns^2$  valence electron configuration, resemble the diagram for the  $\text{He}_2$  molecule in part (c) in [Figure 9.20 "Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1"](#). As shown in part (b) in [Figure 9.21 "Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic \(M"](#), this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the  $\sigma_{ns}$  bonding orbital and the  $\sigma_{ns}^*$  antibonding orbital and give a bond order of 0. Thus  $\text{Be}_2$ ,  $\text{Mg}_2$ ,  $\text{Ca}_2$ ,  $\text{Sr}_2$ , and  $\text{Ba}_2$  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,  $\text{Be}_2$  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  $\text{Na}_2^-$  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.

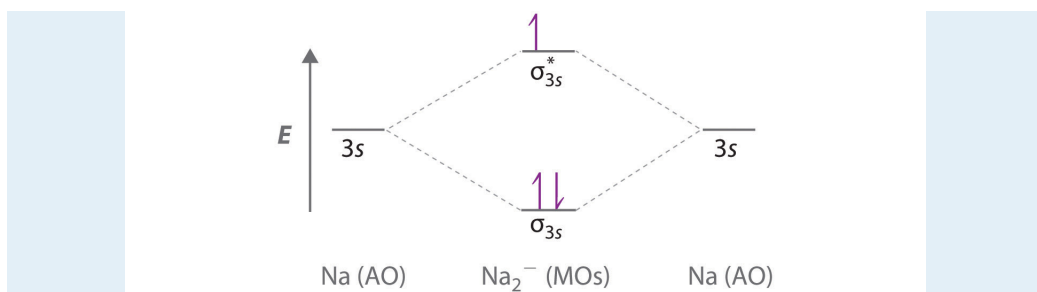
**B** Determine the total number of valence electrons in the  $\text{Na}_2^-$  ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

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

**Solution:**

**A** Because sodium has a  $[\text{Ne}]3s^1$  electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two  $1s$  atomic orbitals. **B** The  $\text{Na}_2^-$  ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled  $\sigma_{3s}$  molecular orbital, a half-filled  $\sigma_{3s}^*$  molecular orbital, and a  $(\sigma_{3s})^2 (\sigma_{3s}^*)^1$  electron configuration.





C The bond order is  $(2 - 1) \div 2 = \frac{1}{2}$ . With a fractional bond order, we predict that the  $\text{Na}_2^-$  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  $\text{Ca}_2^+$  ion.

**Answer:**  $\text{Ca}_2^+$  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 [Chapter 6 "The Structure of Atoms", Section 6.5 "Atomic Orbitals and Their Energies"](#) that for each  $np$  subshell, for example, there are  $np_x$ ,  $np_y$ , and  $np_z$  orbitals ([Figure 6.25 "The Three Equivalent 2"](#)). 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 [Figure 9.22 "Formation of Molecular Orbitals from "](#), 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  $\sigma_{np_z}$

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

Equation 9.7

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

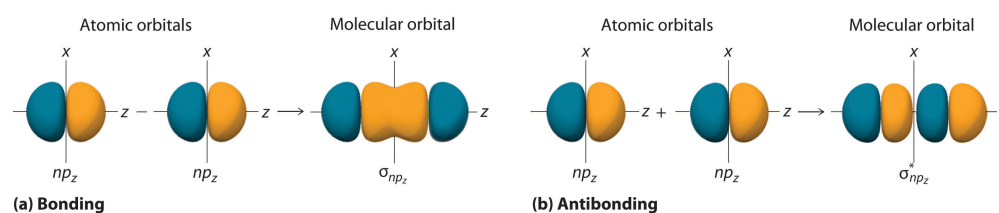
The other possible combination of the two  $np_z$  orbitals is the mathematical sum:

Equation 9.8

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

In this combination, shown in part (b) in [Figure 9.22 "Formation of Molecular Orbitals from Atomic Orbitals from"](#), 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  $\sigma$  (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  $\sigma^*$  (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 [Figure 9.23 "Formation of  \$\pi\$  Molecular Orbitals from "](#), 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  $\sigma$  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 ( $\pi$ ) orbital**<sup>23</sup>. 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 ( $\pi^*$ ) orbital**<sup>24</sup>.

Equation 9.9

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

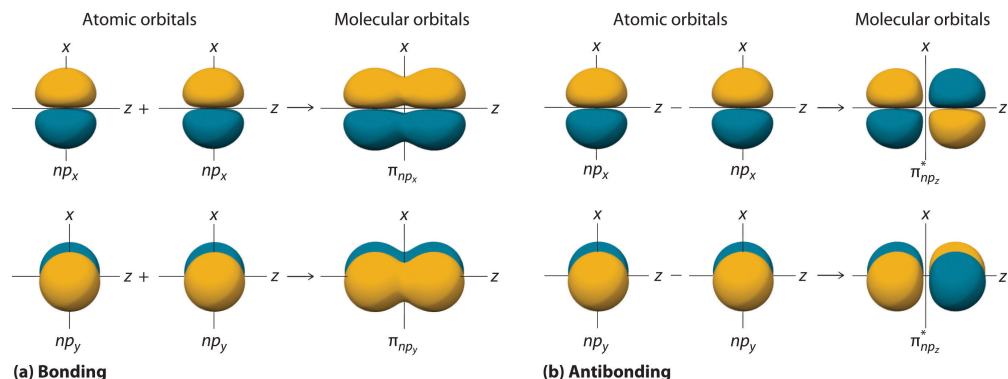
23. A bonding molecular orbital formed from the side-to-side interactions of two or more parallel  $np$  atomic orbitals.

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.

Equation 9.10

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

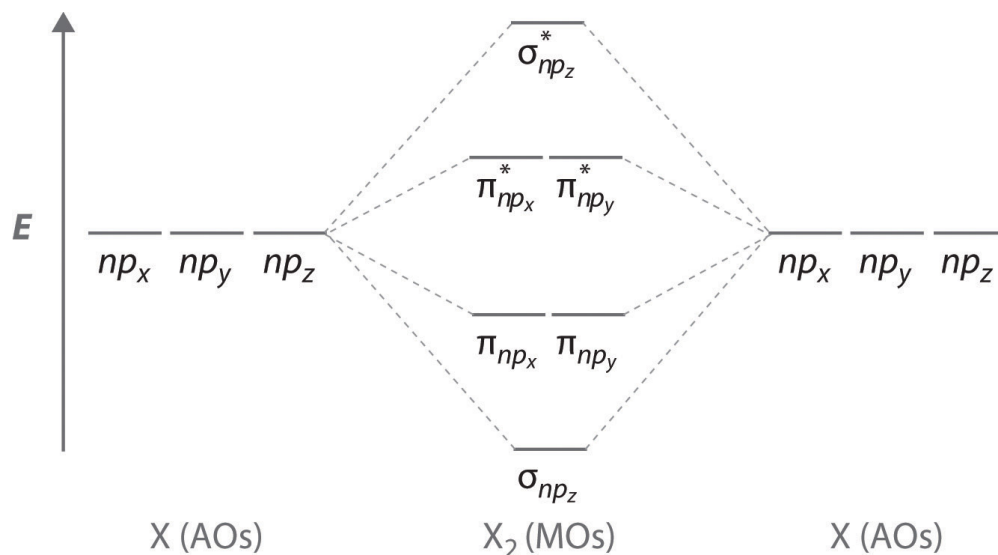
The two  $np_y$  orbitals can also combine using side-to-side interactions to produce a bonding  $\pi_{np_y}$  molecular orbital and an antibonding  $\pi_{np_y}^*$  molecular orbital. Because the  $np_x$  and  $np_y$  atomic orbitals interact in the same way (side-to-side) and have the same energy, the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

Figure 9.23 Formation of  $\pi$  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  $\pi$  (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a  $\pi^*$  (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

**Figure 9.24 "The Relative Energies of the  $\sigma$  and  $\pi$  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  $\sigma$  and  $\sigma^*$  molecular orbitals is significantly greater than the difference between the two  $\pi$  and  $\pi^*$  sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a  $\sigma$  bond than a  $\pi$  bond, which means that the  $\sigma$  molecular orbital is more stable (lower in energy) than the  $\pi$  molecular orbitals.

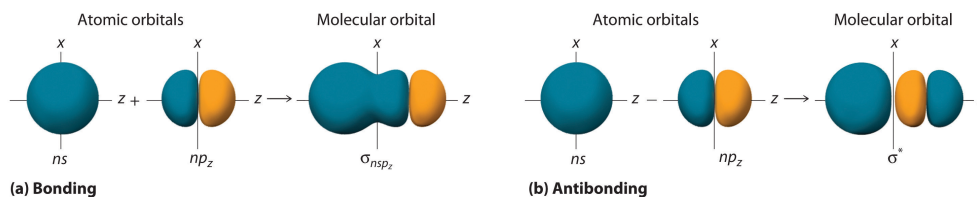
Figure 9.24 The Relative Energies of the  $\sigma$  and  $\pi$  Molecular Orbitals Derived from  $np_x$ ,  $np_y$ , and  $np_z$  Orbitals on Identical Adjacent Atoms



Because the two  $np_z$  orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the  $\sigma$  and  $\sigma^*$  molecular orbitals is greater than the energy difference between the  $\pi$  and  $\pi^*$  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 [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"](#), the sum of the two atomic wave functions ( $ns + np_z$ ) produces a  $\sigma$  bonding molecular orbital. Their difference ( $ns - np_z$ ) produces a  $\sigma^*$  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  $\sigma$  (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a  $\sigma^*$  (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**<sup>25</sup>).
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.

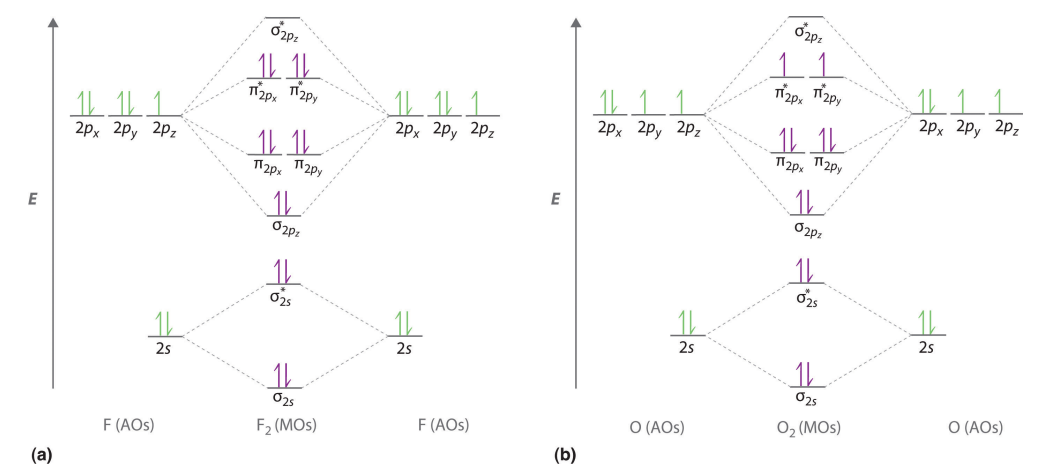
We illustrate how to use these points by constructing a molecular orbital energy-level diagram for  $F_2$ . We use the diagram in part (a) in [Figure 9.26 "Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules"](#); the  $n = 1$  orbitals ( $\sigma_{1s}$  and  $\sigma_{1s}^*$ ) are located well below those of the  $n = 2$  level and are not shown. As illustrated in the diagram, the  $\sigma_{2s}$  and  $\sigma_{2s}^*$  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  $\sigma_{2p_z}$ , and the next most stable are the two degenerate orbitals,  $\pi_{2p_x}$  and  $\pi_{2p_y}$ . 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  $\sigma_{2s}$  and  $\sigma_{2s}^*$  orbitals, 2 fill the  $\sigma_{2p_z}$  orbital, 4 fill the two degenerate  $\pi$  orbitals, and 4 fill the two degenerate  $\pi^*$  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  $(8 - 6) \div 2 = 1$ . 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  $\sigma_{2s}$  and  $\sigma_{2s}^*$  orbitals, 2 more to fill the  $\sigma_{2p_z}$  orbital, and 4 to fill the degenerate  $\pi_{2p_x}$  and  $\pi_{2p_y}$  orbitals. According to Hund's rule, the last 2 electrons must be placed in separate  $\pi^*$  orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of  $(8 - 4) \div 2 = 2$ , 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  $(\pi_{2p_x}^*, \pi_{2p_y}^*)$  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 [Figure 9.27 "Liquid O"](#), 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.

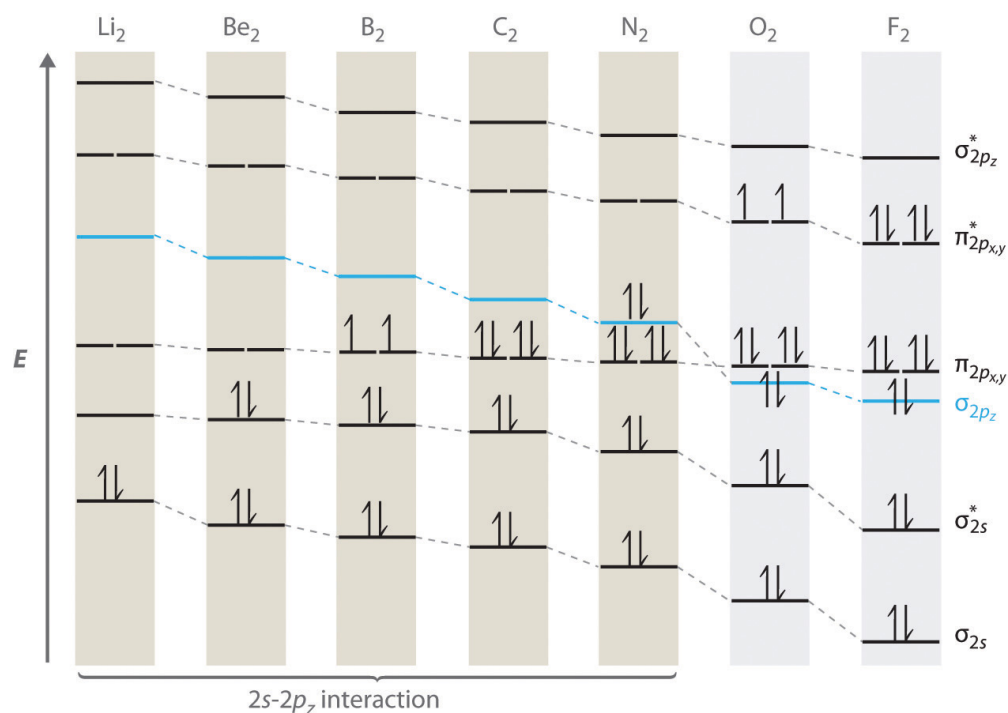
Because the  $O_2$  molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

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  $\sigma_{2p_z}$  molecular orbital is slightly *higher* in energy than the degenerate  $\pi_{2p_x}$  and  $\pi_{2p_y}$



orbitals. The difference in energy between the 2s and 2p atomic orbitals increases from  $\text{Li}_2$  to  $\text{F}_2$  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 2p<sub>z</sub> orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the  $\sigma_{2s}$  orbital and increases the energy of the  $\sigma_{2p_z}$  orbital. Thus for  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ , and  $\text{N}_2$ , the  $\sigma_{2p_z}$  orbital is higher in energy than the  $\sigma_{3p_z}$  orbitals, as shown in **Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"**. Experimentally, it is found that the energy gap between the ns and np atomic orbitals *increases* as the nuclear charge increases (**Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"**). Thus for example, the  $\sigma_{2p_z}$  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  $\text{Li}_2$  through  $\text{N}_2$ , the  $\sigma_{2p_z}$  orbital is higher in energy than the  $\pi_{2p_{x,y}}$  orbitals. In contrast, the  $\sigma_{2p_z}$  orbital is lower in energy than the  $\pi_{2p_{x,y}}$  orbitals for  $\text{O}_2$  and  $\text{F}_2$  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  $S_2$ .

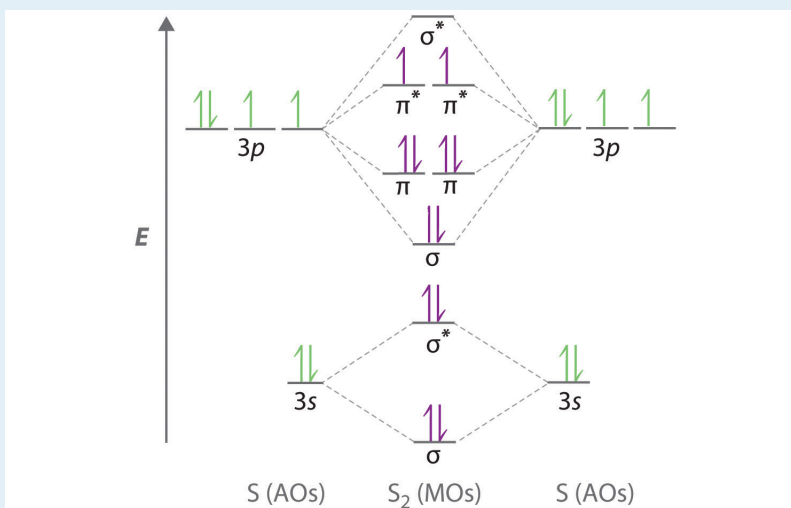
**C** Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.

**D** Calculate the bond order and describe the bonding.

**Solution:**

**A** Sulfur has a  $[Ne]3s^23p^4$  valence electron configuration. To create a molecular orbital energy-level diagram similar to those in [Figure 9.26 "Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules"](#) and [Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"](#), 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  $\sigma_{3p_z}$  molecular orbital is higher in energy. Because the  $ns-np$  energy gap *increases* as the nuclear charge increases ([Figure 9.28 "Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements"](#)), the  $\sigma_{3p_z}$  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  $\pi_{3p_x}$  and  $\pi_{3p_y}$ , 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

$$(\sigma_{3s})^2 (\sigma_{3s}^*)^2 (\sigma_{3p_z})^2 (\pi_{3p_{x,y}})^4 (\pi_{3p_{x,y}}^*)^2 \text{ with 2 unpaired electrons.}$$

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

#### Exercise

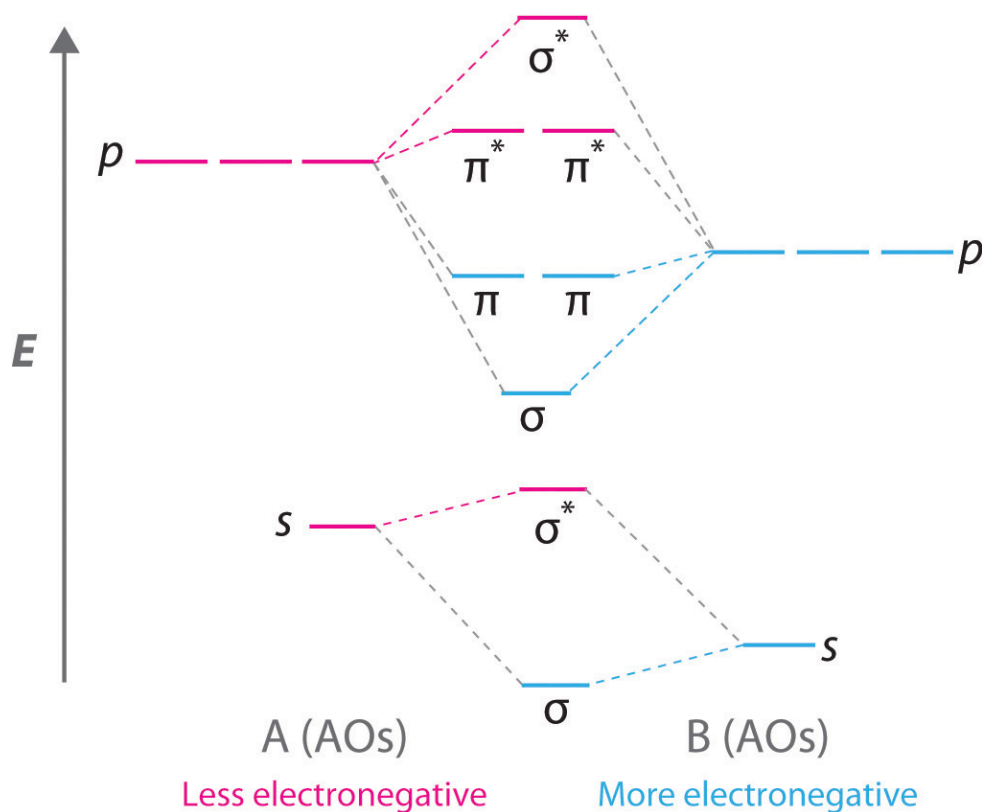
Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion ( $O_2^{2-}$ ).

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

## Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called **heteronuclear diatomic molecules**<sup>26</sup>. 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 **Figure 9.29** “**Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where  $\chi$** ”. 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

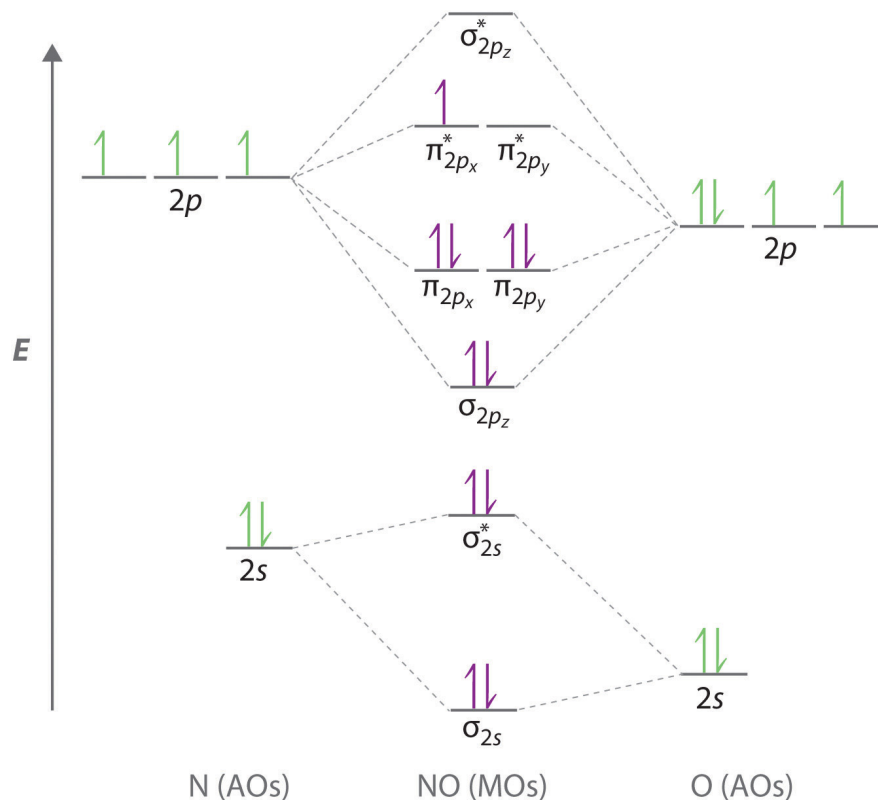
A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

### 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  $\pi^*$  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  $(\pi_{2p_x}^*, \pi_{2p_y}^*)$  pair of orbitals.

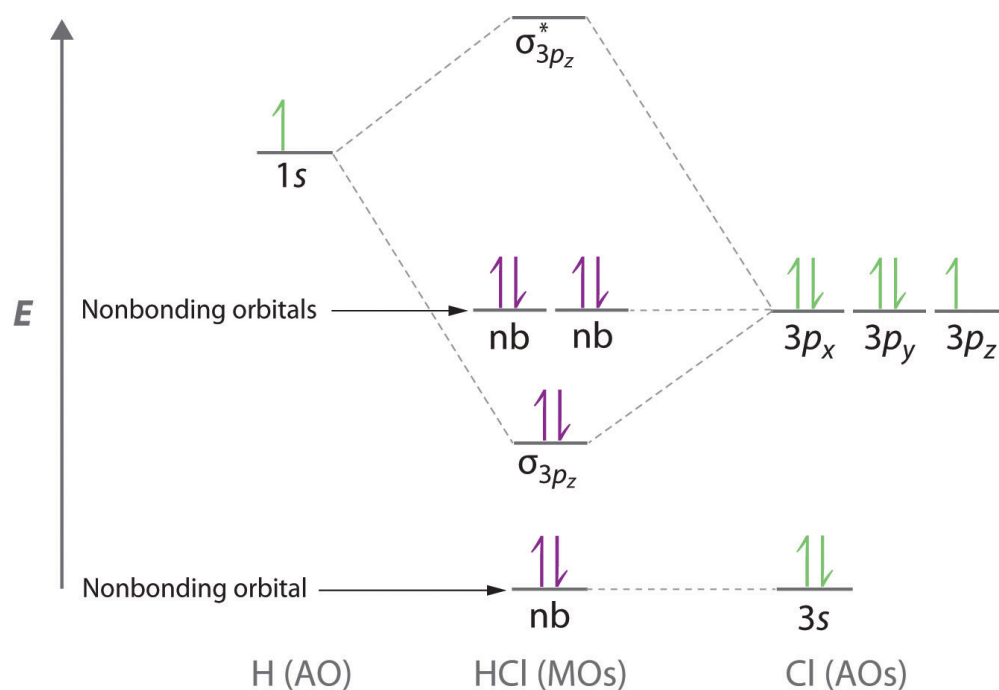
Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in [Figure 9.30 "Molecular Orbital Energy-Level Diagram for NO"](#), NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the  $\text{NO}^+$  cation, which is isoelectronic with  $\text{N}_2$  and has a bond order of 3, corresponding to an  $\text{N}=\text{O}$  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 [Figure 9.31 "Molecular Orbital Energy-Level Diagram for HCl"](#) that the 1s 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**<sup>27</sup>. 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  $\sigma$  bonding molecular orbital is closer in energy to the Cl  $3p_z$  than to the H  $1s$  atomic orbital, the electrons in the  $\sigma$  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  $\text{H}^{\delta+}-\text{Cl}^{\delta-}$  as described in [Chapter 8 "Ionic versus Covalent Bonding"](#).

Figure 9.31 Molecular Orbital Energy-Level Diagram for HCl



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.

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  $\sigma$  orbital is occupied by electrons, giving a bond order of 1.



**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  \$\chi\$ "](#) to describe the bonding in the cyanide ion ( $\text{CN}^-$ ). What is the bond order?

**Given:** chemical species

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

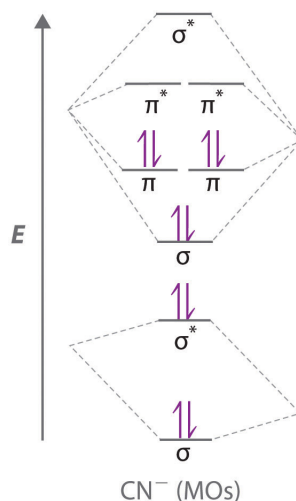
**Strategy:**

**A** Calculate the total number of valence electrons in  $\text{CN}^-$ . 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  \$\chi\$ "](#) 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  $\text{CN}^-$ .

**Solution:**

**A** The  $\text{CN}^-$  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  \$\chi\$ "](#) fills the five lowest-energy orbitals, as shown here:



Because  $\chi_{\text{N}} > \chi_{\text{C}}$ , 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  $\text{CN}^-$  ion has a triple bond, analogous to that in  $\text{N}_2$ .

#### Exercise

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

**Answer:** All molecular orbitals except the highest-energy  $\sigma^*$  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 ( $\sigma$ ) orbital** (bonding) or a **sigma star ( $\sigma^*$ ) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a  **$\pi$**

**( $\pi$ ) orbital** (bonding) and a **pi star ( $\pi^*$ ) 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.

KEY TAKEAWAY

- 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  $\sigma$  orbital? How are the two similar?
7. Why is a  $\sigma_{1s}$  molecular orbital lower in energy than the two  $s$  atomic orbitals from which it is derived? Why is a  $\sigma_{1s}^*$  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  $\sigma$  and  $\pi$  molecular orbitals. Which type of molecular orbital typically results in a stronger bond?

13. What is the minimum number of nodes in  $\sigma$ ,  $\pi$ ,  $\sigma^*$ , and  $\pi^*$ ? How are the nodes in bonding orbitals different from the nodes in antibonding orbitals?
14. It is possible to form both  $\sigma$  and  $\pi$  molecular orbitals with the overlap of a  $d$  orbital with a  $p$  orbital, yet it is possible to form only  $\sigma$  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  $\pi$  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  $\sigma$  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  $\text{AlCl}_3$  stronger, the same strength, or weaker than the Al–Br bonds in  $\text{AlBr}_3$ ? Why?
22. Are the Ga–Cl bonds in  $\text{GaCl}_3$  stronger, the same strength, or weaker than the Sb–Cl bonds in  $\text{SbCl}_3$ ? 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  $\sigma$  versus  $\pi$ ,  $\pi$  versus  $\sigma^*$ , and  $\sigma^*$  versus  $\pi^*$ , which of the resulting molecular orbitals is lower in energy?
27. The energy of a  $\sigma$  molecular orbital is usually lower than the energy of a  $\pi$  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  $\sigma_{2p_z}$  molecular orbital stabilized or destabilized by interaction with the  $\sigma_{2s}$  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.

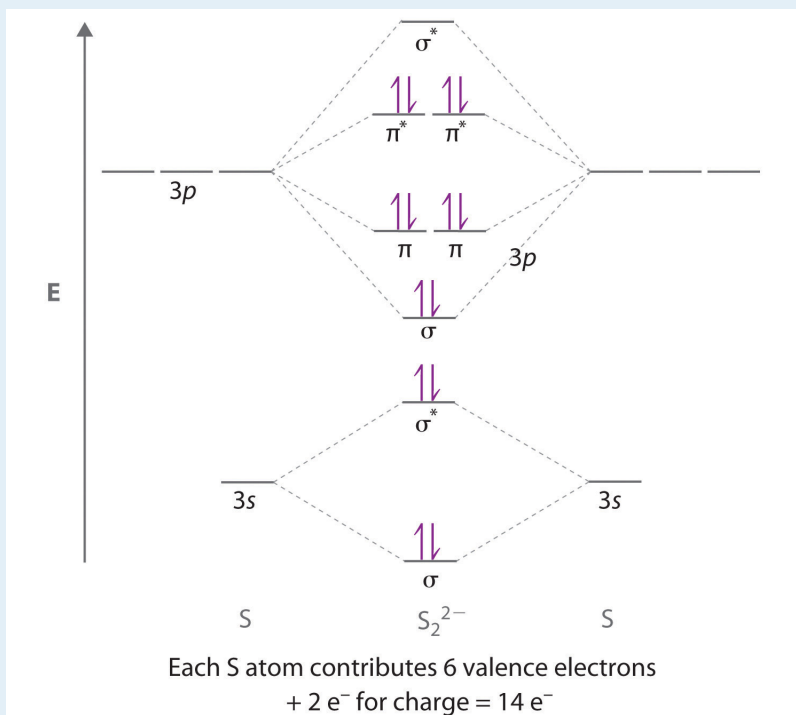
## NUMERICAL PROBLEMS

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  $\text{Na}_2^+$ . 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  $\text{Na}_2^+$ ,  $\text{Na}_2$ , or  $\text{Na}_2^-$  be the most stable? Why?
12. Draw a molecular orbital energy-level diagram for  $\text{Xe}_2^+$ , 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  $\text{Xe}_2^{2+}$ ,  $\text{Xe}_2^+$ , or  $\text{Xe}_2$  be most stable? Why?
13. Draw a molecular orbital energy-level diagram for  $\text{O}_2^{2-}$  and predict its valence electron configuration, bond order, and stability.
14. Draw a molecular orbital energy-level diagram for  $\text{C}_2^{2-}$  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  $\pi$  orbitals (and the corresponding antibonding orbitals) from the set of six  $p$  orbitals?
16. Draw a complete energy-level diagram for  $\text{B}_2$ . 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.  $\text{NO}^+$
  - b.  $\text{NO}^-$
18. The diatomic molecule  $\text{BN}$  has never been detected. Assume that its molecular orbital diagram would be similar to that shown for  $\text{CN}^-$  in [Section 9.3 "Delocalized Bonding and Molecular Orbitals"](#) but that the  $\sigma_{2p_z}$  molecular orbital is higher in energy than the  $\pi_{2p_{z,y}}$  molecular orbitals.
  - a. Sketch a molecular orbital diagram for  $\text{BN}$ .
  - b. Based on your diagram, what would be the bond order of this molecule?
  - c. Would you expect  $\text{BN}$  to be stable? Why or why not?
19. Of the species  $\text{BN}$ ,  $\text{CO}$ ,  $\text{C}_2$ , and  $\text{N}_2$ , which are isoelectronic?
20. Of the species  $\text{CN}^-$ ,  $\text{NO}^+$ ,  $\text{B}_2^{2-}$ , and  $\text{O}_2^+$ , which are isoelectronic?

## ANSWERS

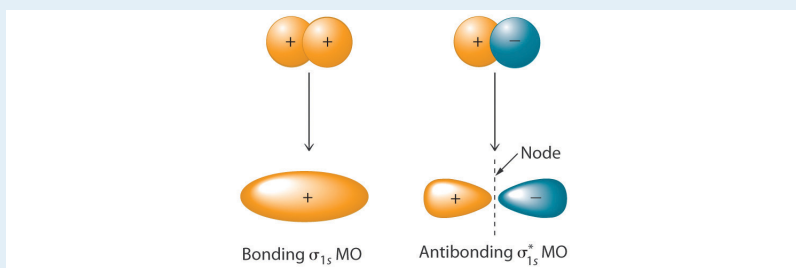
1.



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.

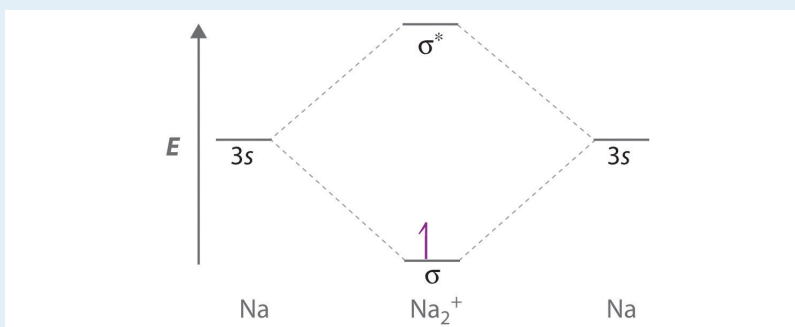
5.



Combining two atomic  $s$  orbitals gives two molecular orbitals, a  $\sigma$  (bonding) orbital with no nodal planes, and a  $\sigma^*$  (antibonding) orbital with a nodal plane perpendicular to the internuclear axis.

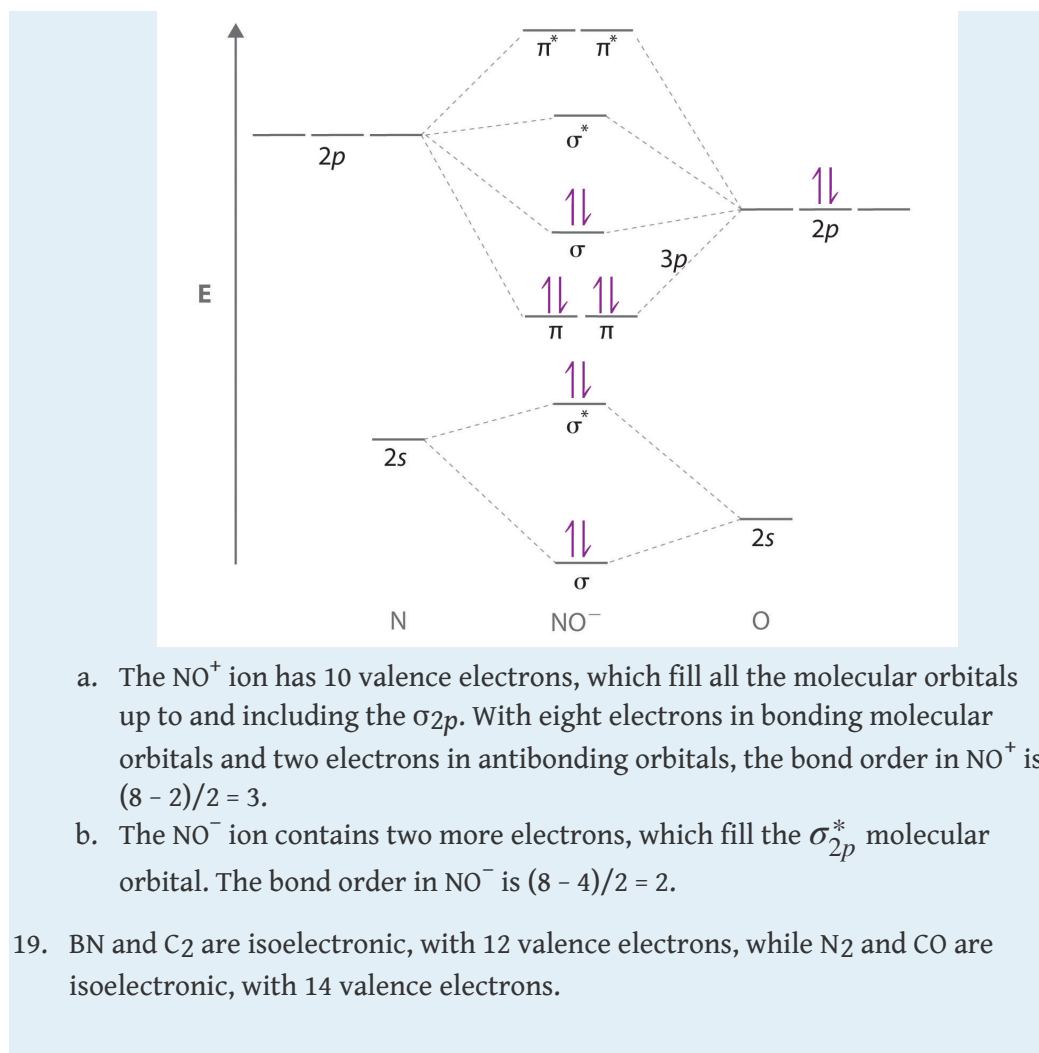
9.

- 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  $\sigma$  (bonding) orbital and a  $\sigma^*$  (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  $\sigma_{3s}^1$  electronic configuration and a bond order of 0.5. Consequently,  $\text{Na}_2^+$  should be a stable species. Oxidizing  $\text{Na}_2^+$  by one electron to give  $\text{Na}_2^{2+}$  would remove the electron in the  $\sigma_{3s}$  molecular orbital, giving a bond order of 0. Conversely, reducing  $\text{Na}_2^+$  by one electron to give  $\text{Na}_2$  would put an additional electron into the  $\sigma_{3s}$  molecular orbital, giving a bond order of 1. Thus, reduction to  $\text{Na}_2$  would produce a more stable species than oxidation to  $\text{Na}_2^{2+}$ . The  $\text{Na}_2^-$  ion would have two electrons in the bonding  $\sigma_{3s}$  molecular orbital and one electron in the antibonding  $\sigma_{3s}^*$  molecular orbital, giving a bond order of 0.5. Thus,  $\text{Na}_2$  is the most stable of the three species.

17.



## 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  $\sigma$  bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and  $\pi$  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  $120^\circ$ . 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  $\sigma$  bonds: two C-H ( $sp^2 + s$ ) and one C-C ( $sp^2 + sp^2$ ) (part (a) in [Figure 9.32 "Bonding in Ethylene"](#)). The  $sp^2$  hybridization can be represented as follows:

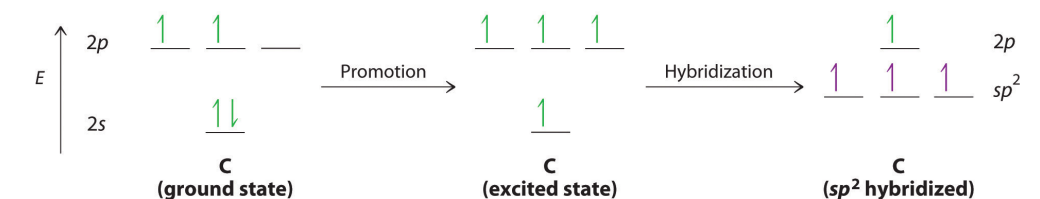
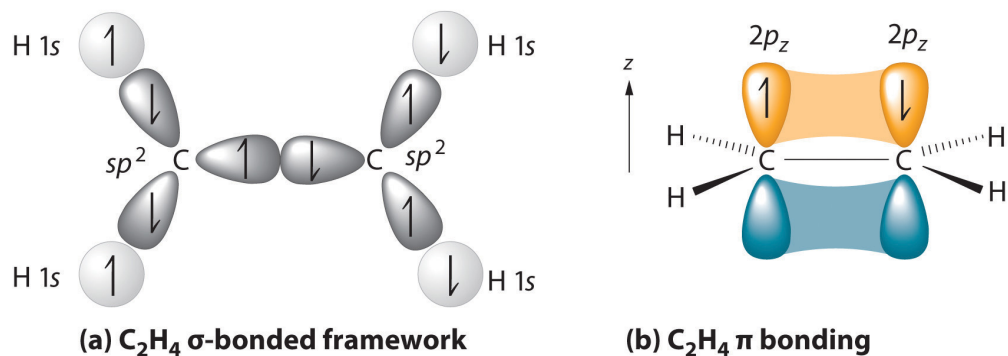


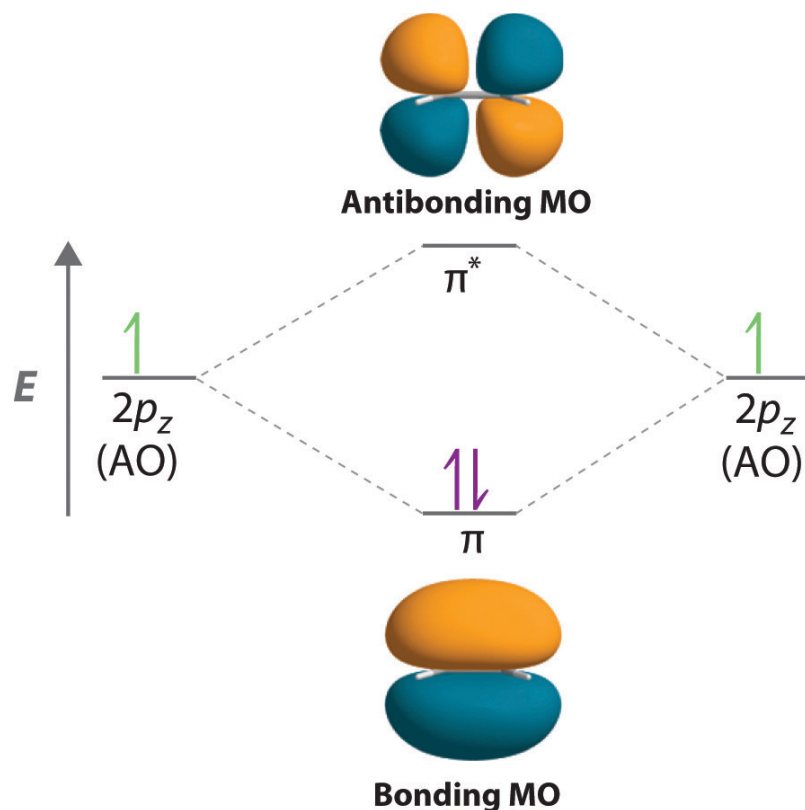
Figure 9.32 Bonding in Ethylene



(a) The  $\sigma$ -bonded framework is formed by the overlap of two sets of singly occupied carbon  $sp^2$  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  $\sigma$  bonds (four C-H bonds and one C-C bond). (b) One singly occupied unhybridized  $2p_z$  orbital remains on each carbon atom to form a carbon-carbon  $\pi$  bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the  $z$ -axis.)

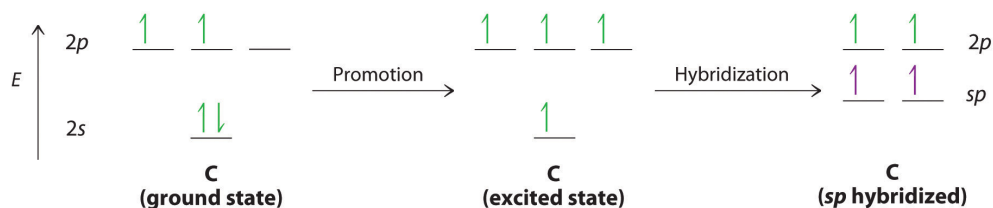
After hybridization, each carbon still has one unhybridized  $2p_z$  orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in [Figure 9.32 "Bonding in Ethylene"](#)). The two singly occupied  $2p_z$  orbitals can overlap to form a  $\pi$  bonding orbital and a  $\pi^*$  antibonding orbital, which produces the energy-level diagram shown in [Figure 9.33 "Molecular Orbital Energy-Level Diagram for  \$\pi\$  Bonding in Ethylene"](#). With the formation of a  $\pi$  bonding orbital, electron density increases in the plane between the carbon nuclei. The  $\pi^*$  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 ( $\pi$ ) level, leaving the  $\pi^*$  orbital empty. Consequently, the C-C bond in ethylene consists of a  $\sigma$  bond and a  $\pi$  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  $\text{CH}_2$  fragments are coplanar, which maximizes the overlap of the two singly occupied  $2p_z$  orbitals.



Figure 9.33 Molecular Orbital Energy-Level Diagram for  $\pi$  Bonding in Ethylene

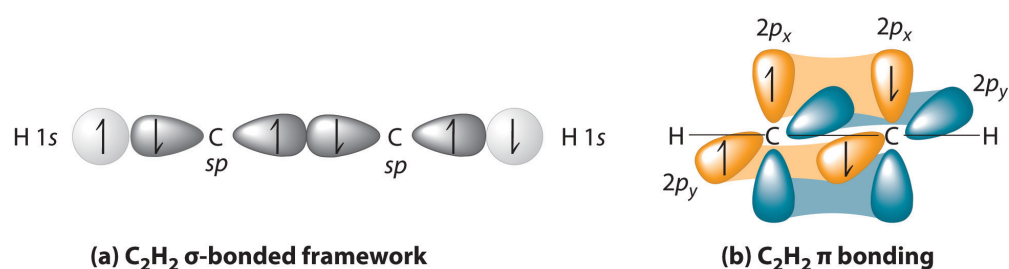
As in the diatomic molecules discussed previously, the singly occupied  $2p_z$  orbitals in ethylene can overlap to form a bonding/antibonding pair of  $\pi$  molecular orbitals. The two electrons remaining are enough to fill only the bonding  $\pi$  orbital. With one  $\sigma$  bond plus one  $\pi$  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  $\sigma$  bond and one is used to form the C-H  $\sigma$  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  $\pi$  bonds (part (b) in [Figure 9.34 "Bonding in Acetylene"](#)). Because each of the unhybridized  $2p$  orbitals has a single electron, four electrons are available for  $\pi$  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  $\sigma$  bond and two mutually perpendicular  $\pi$  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) In the formation of the  $\sigma$ -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  $\pi$  bonds in acetylene, two singly occupied unhybridized  $2p_{x,y}$  orbitals on each carbon atom overlap. With one  $\sigma$  bond plus two  $\pi$  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  $\sigma$  bonding, and unhybridized  $\pi$  orbitals and molecular orbital theory can be used to describe  $\pi$  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:**

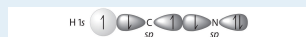
**A** From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the  $\sigma$ -bonded framework of the molecule and determine the number of valence electrons that are used for  $\sigma$  bonding.

**B** Determine the number of remaining valence electrons. Use any remaining unhybridized  $p$  orbitals to form  $\pi$  and  $\pi^*$  orbitals.

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

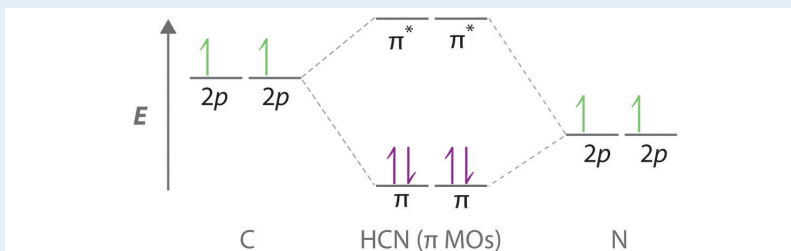
**Solution:**

**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  $\sigma$  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  $\sigma$  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  $\pi$  (bonding) orbitals and two  $\pi^*$  (antibonding)

orbitals. C With 4 electrons available, only the  $\pi$  orbitals are filled. The overall result is a triple bond (1  $\sigma$  and 2  $\pi$ ) between C and N.



### Exercise

Describe the bonding in formaldehyde ( $\text{H}_2\text{C}=\text{O}$ ), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

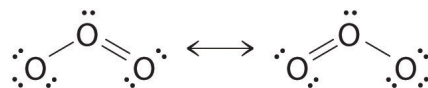
### Answer:

$\sigma$ -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  $\sigma$  bond.

$\pi$  bonding: Unhybridized, singly occupied  $2p$  atomic orbitals on carbon and oxygen interact to form  $\pi$  (bonding) and  $\pi^*$  (antibonding) molecular orbitals. With two electrons, only the  $\pi$  (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 ( $\text{O}_3$ ) and the nitrite ion ( $\text{NO}_2^-$ ). We showed that ozone can be represented by either of these Lewis electron structures:

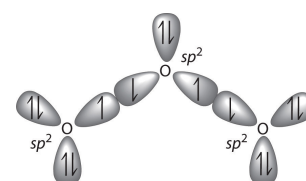


Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

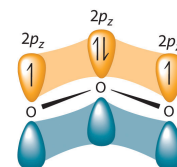
Experimental evidence indicates that ozone has a bond angle of  $117.5^\circ$ . Because this angle is close to  $120^\circ$ , it is likely that the central oxygen atom in ozone is trigonal planar and  $sp^2$  hybridized. If we assume that the terminal oxygen atoms are also  $sp^2$  hybridized, then we obtain the  $\sigma$ -bonded framework shown in [Figure 9.35 "Bonding in Ozone"](#). 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  $\sigma$  bonds and lone pairs account for a total of 14 electrons (five lone pairs and two  $\sigma$  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  $\pi$  bonding, three  $2p$  atomic orbitals give us three molecular orbitals, as shown in [Figure 9.36 " \$\pi\$  Bonding in Ozone"](#). One of the molecular orbitals is a  $\pi$  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  $\sigma$  bonds; it is a  $\pi^*$  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

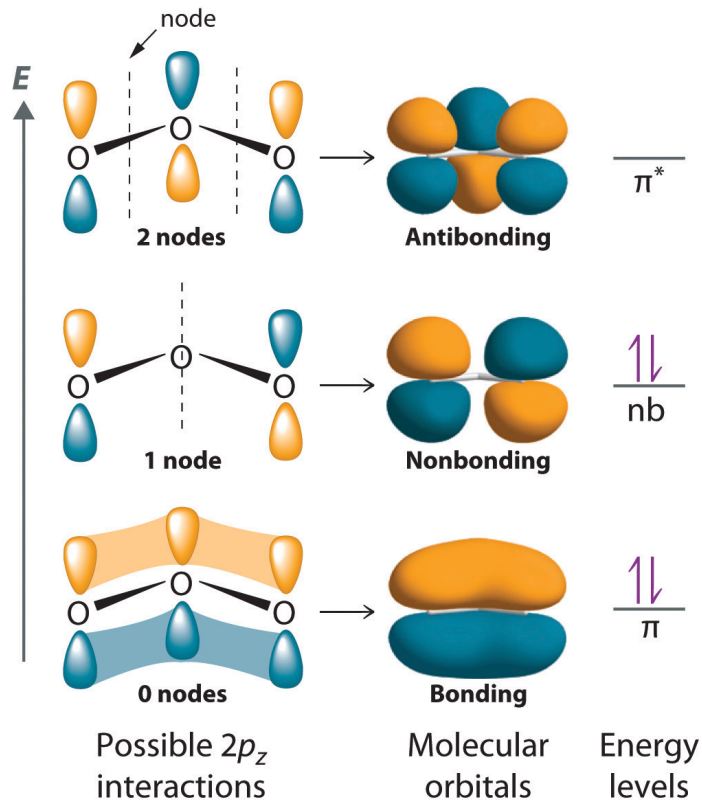


(a)  $O_3$   $\sigma$ -bond framework



(b)  $O_3$   $\pi$  bonding

(a) In the formation of the  $\sigma$ -bonded framework, three sets of oxygen  $sp^2$  hybrid orbitals overlap to give two O–O  $\sigma$  bonds and five lone pairs, two on each terminal O and one on the central O. The  $\sigma$  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  $\pi$  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  $\pi$  Bonding in Ozone

The three unhybridized  $2p_z$  atomic orbitals interact with one another to form three molecular orbitals: one  $\pi$  bonding orbital at lower energy, one  $\pi^*$  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  $\pi$  bonding orbital holding three atoms together, the net  $\pi$  bond order is  $\frac{1}{2}$  per O–O bond. The combined  $\sigma/\pi$  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  $\pi$  bonding and the nonbonding levels. The result is a single  $\pi$  bond holding *three* oxygen atoms together, or  $\frac{1}{2}$   $\pi$  bond per O–O. We therefore predict the overall O–O bond order to be  $1\frac{1}{2}$  ( $\frac{1}{2}$   $\pi$  bond plus 1  $\sigma$  bond), just as predicted using resonance structures. The molecular orbital approach, however, shows that the  $\pi$  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  $\text{NO}_2^-$  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  $\text{NO}_2^-$ . 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:**

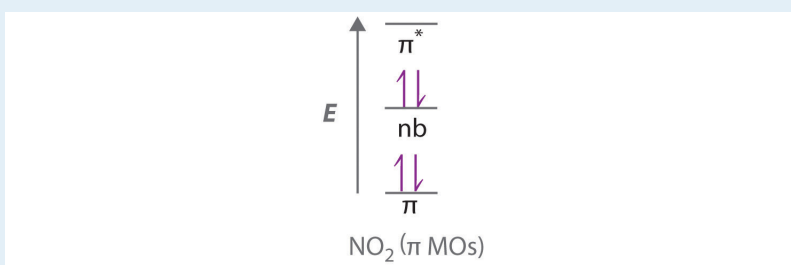
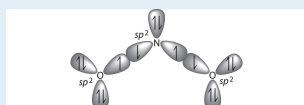
**A** The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in  $\text{NO}_2^-$  is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the -1 charge). The bent 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  $\sigma$  bonds with the remaining  $sp^2$  hybrid orbital on each oxygen. The  $\sigma$  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  $\pi$  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  $\pi$  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.



### Exercise

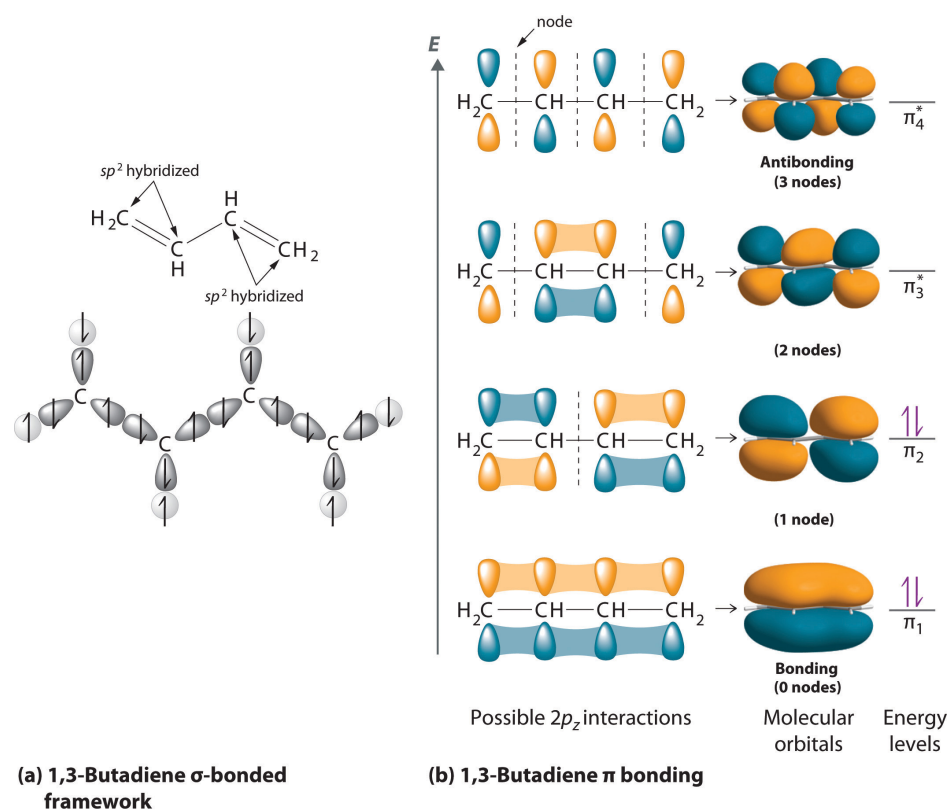
Describe the bonding in the formate ion ( $\text{HCO}_2^-$ ), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

**Answer:** Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The  $\sigma$  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  $\pi$  molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding  $\pi$  molecular orbitals. The overall C–O bond order is therefore  $1 \frac{1}{2}$ .

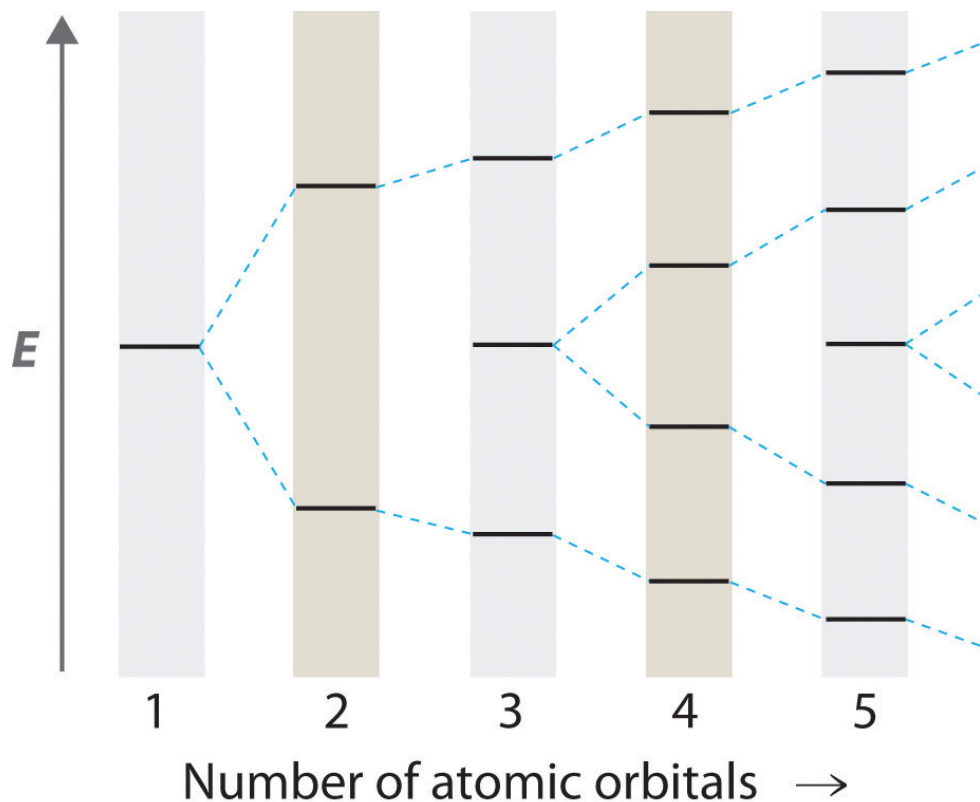
## The Chemistry of Vision

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  $\pi$  electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in [Figure 9.37 "π Bonding in 1,3-Butadiene"](#).

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  $\pi$  Bonding in 1,3-Butadiene

(a) If each carbon atom is assumed to be  $sp^2$  hybridized, we can construct a  $\sigma$ -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  $\pi$  bonds.

Figure 9.38 Molecular Orbital Energy-Level Diagrams for a Chain of  $n$  Like Orbitals That Interact ( $n \leq 5$ )

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  $\sigma$  bonding and molecular orbitals to describe the  $\pi$  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  $\pi$  bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the  $\pi$  molecular orbitals in diatomic molecules such as  $O_2$  and  $N_2$ . Applying the same approach to  $\pi$  bonding between three or four atoms requires combining three or four unhybridized  $np$  orbitals on adjacent atoms to generate  $\pi$  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  $\sigma$  bonding and molecular orbitals to describe  $\pi$  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

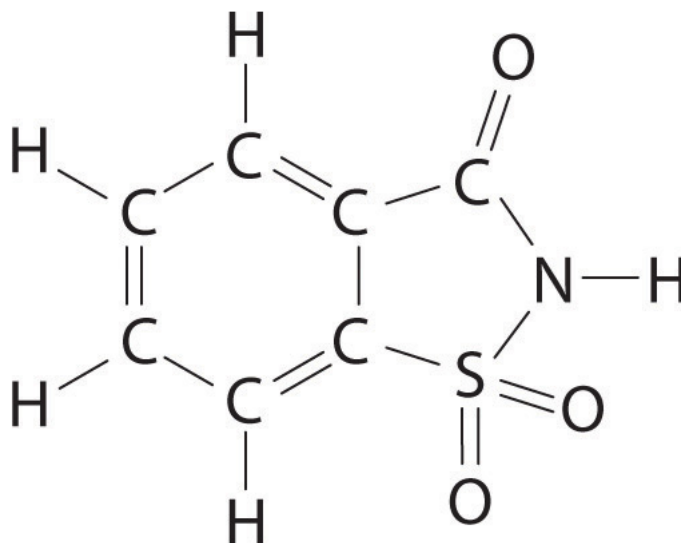
1. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in  $BCl_3$  and  $CS_3^{2-}$ .
2. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in  $CO_2$  and  $N_3^-$ .

## 9.5 End-of-Chapter Material

## APPLICATION PROBLEMS

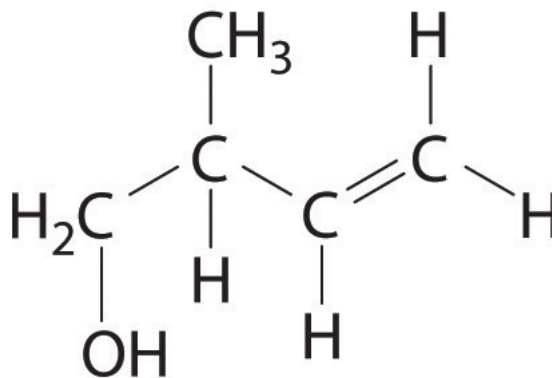
Problems marked with a ♦ involve multiple concepts.

1. ♦ Sulfur hexafluoride ( $\text{SF}_6$ ) 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  $\text{CO}_2$ .
  - a. Draw the Lewis electron structure of  $\text{SF}_6$  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  $\text{SF}_6$ .
  - c. Despite its rather high molecular mass (146.06 g/mol) and highly polar S–F bonds,  $\text{SF}_6$  is a gas at room temperature (boiling point =  $-63^\circ\text{C}$ ). Why?
2. ♦ The elevated concentrations of chlorine monoxide ( $\text{ClO}$ ) 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  $\text{ClO}$ .
  - c. Does  $\text{ClO}$  contain any unpaired electrons?
  - d. Based on your molecular orbital diagram, is  $\text{ClO}$  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:



- Give the hybridization of all five atoms shown in bold in the structure. Note: all five atoms in the five-membered ring are coplanar.
  - 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.
  - If sulfur and carbon each contribute one electron to nitrogen, how many lone pairs are present on the nitrogen?
  - What is the geometry of the sulfur atom?
  - 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:

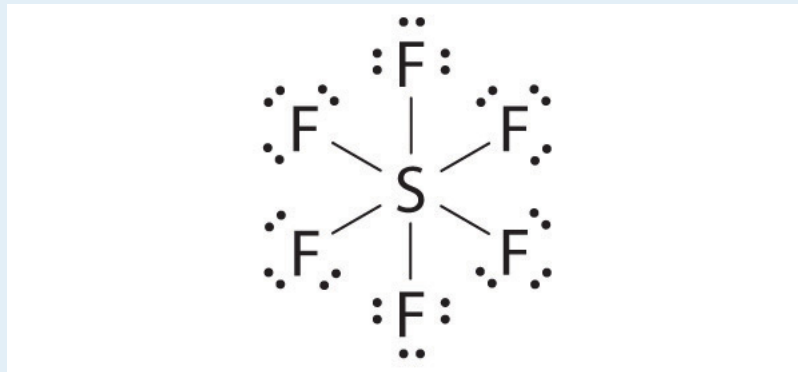




- Give the hybridization of all atoms except hydrogen in this pheromone.
  - How many  $\sigma$  bonds are present in this molecule? How many  $\pi$  bonds are there?
  - Describe the bonding in this molecule using a combination of the localized and delocalized approaches.
5. Carbon monoxide is highly 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.



- There are six electron groups, the molecular geometry is octahedral, and the hybridization of S is  $sp^3d^2$ .
- 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.
- $SF_6$  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.