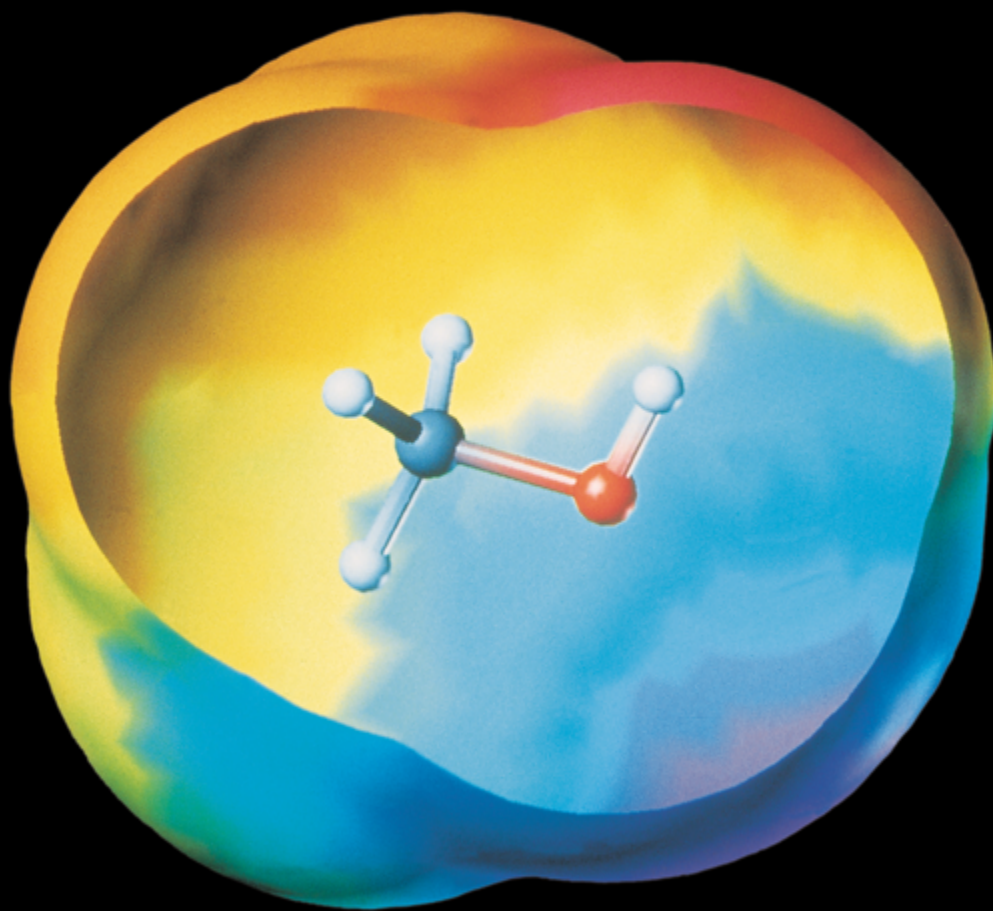
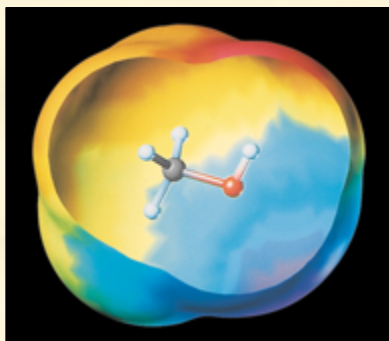


Molecular Structure and Covalent Bonding Theories

8





A computer model of a polar molecule of wood alcohol, or methanol, CH_3OH (C, gray; H, white; O, red). The ball-and-stick model is shown inside a computer-generated molecular surface. The surface is color-coded to show how charge ranges from very positive (red) to very negative (blue).

OUTLINE

- | | | | |
|-------------------------------------|--|------|---|
| 8-1 | A Preview of the Chapter | 8-9 | Tetrahedral Electronic Geometry: AB_2U_2 Species (Two Lone Pairs of Electrons on A) |
| 8-2 | Valence Shell Electron Pair Repulsion (VSEPR) Theory | 8-10 | Tetrahedral Electronic Geometry: ABU_3 Species (Three Lone Pairs of Electrons on A) |
| 8-3 | Polar Molecules: The Influence of Molecular Geometry | 8-11 | Trigonal Bipyramidal Electronic Geometry: AB_5 , AB_4U , AB_3U_2 , and AB_2U_3 |
| 8-4 | Valence Bond (VB) Theory | 8-12 | Octahedral Electronic Geometry: AB_6 , AB_5U , and AB_4U_2 |
| Molecular Shapes and Bonding | | | |
| 8-5 | Linear Electronic Geometry: AB_2 Species (No Lone Pairs of Electrons on A) | 8-13 | Compounds Containing Double Bonds |
| 8-6 | Trigonal Planar Electronic Geometry: AB_3 Species (No Lone Pairs of Electrons on A) | 8-14 | Compounds Containing Triple Bonds |
| 8-7 | Tetrahedral Electronic Geometry: AB_4 Species (No Lone Pairs of Electrons on A) | 8-15 | A Summary of Electronic and Molecular Geometries |
| 8-8 | Tetrahedral Electronic Geometry: AB_3U Species (One Lone Pair of Electrons on A) | | |

OBJECTIVES

After you have studied this chapter, you should be able to

- Describe the basic ideas of the valence shell electron pair repulsion (VSEPR) theory
- Use the VSEPR theory to predict the electronic geometry of polyatomic molecules and ions
- Use the VSEPR theory to predict the molecular geometry of polyatomic molecules and ions
- Describe the relationships between molecular shapes and molecular polarities
- Predict whether a molecule is polar or nonpolar
- Describe the basic ideas of the valence bond (VB) theory
- Analyze the hybrid orbitals used in bonding in polyatomic molecules and ions
- Use hybrid orbitals to describe the bonding in double and triple bonds

We know a great deal about the molecular structures of many thousands of compounds, all based on reliable experiments. In our discussion of theories of covalent bonding, we must keep in mind that the theories represent *an attempt to explain and organize experimental observations*. For bonding theories to be valid, they must be consistent with the large body of experimental observations about molec-

ular structure. In this chapter we will study two theories of covalent bonding, which usually allow us to predict correct structures and properties. Like any simplified theories, they are not entirely satisfactory in describing *every* known structure; however, their successful application to many thousands of structures justifies their continued use.

8-1 A PREVIEW OF THE CHAPTER

The electrons in the outer shell, or **valence shell**, of an atom are the electrons involved in bonding. In most of our discussion of covalent bonding, we will focus attention on these electrons. Valence shell electrons are those that were not present in the *preceding* noble gas, ignoring *filled* sets of *d* and *f* orbitals. Lewis formulas show the number of valence shell electrons in a polyatomic molecule or ion (Sections 7-4 through 7-7). We will write Lewis formulas for each molecule or polyatomic ion we discuss. The theories introduced in this chapter apply equally well to polyatomic molecules and to ions.

Two theories go hand in hand in a discussion of covalent bonding. The *valence shell electron pair repulsion (VSEPR) theory* helps us to understand and predict the spatial arrangement of atoms in a polyatomic molecule or ion. It does not, however, explain *how* bonding occurs, just *where* it occurs and where unshared pairs of valence shell electrons are directed. The *valence bond (VB) theory* describes *how* the bonding takes place, in terms of *overlapping atomic orbitals*. In this theory, the atomic orbitals discussed in Chapter 5 are often “mixed,” or *hybridized*, to form new orbitals with different spatial orientations. Used together, these two simple ideas enable us to understand the bonding, molecular shapes, and properties of a wide variety of polyatomic molecules and ions.

We will first discuss the basic ideas and application of these two theories. Then we will learn how an important molecular property, *polarity*, depends on molecular shape. Most of this chapter will then be devoted to studying how these ideas are applied to various types of polyatomic molecules and ions.

In Chapter 7 we used valence bond terminology to discuss the bonding in H_2 although we did not name the theory there.

IMPORTANT NOTE

Different instructors prefer to cover these two theories in different ways. Your instructor will tell you the order in which you should study the material in this chapter. Regardless of how you study this chapter, Tables 8-1, 8-2, 8-3, and 8-4 are important summaries, and you should refer to them often.

1. One approach is to discuss both the VSEPR theory and the VB theory together, emphasizing how they complement each other. If your instructor prefers this parallel approach, you should study the chapter in the order in which it is presented.
2. An alternative approach is to first master the VSEPR theory and the related topic of molecular polarity for different structures, and then learn how the VB theory describes the overlap of bonding orbitals in these structures. If your instructor takes this approach, you should study this chapter in the following order:
 - a. Read the summary material under the main heading “Molecular Shapes and Bonding” preceding Section 8-5.
 - b. *VSEPR theory, molecular polarity*. Study Sections 8-2 and 8-3; then in Sections 8-5 through 8-12, study only the subsections marked A and B.
 - c. *VB theory*. Study Section 8-4; then in Sections 8-5 through 8-12, study the Valence Bond Theory subsections, marked C; then study Sections 8-13 and 8-14.

No matter which order your instructor prefers, the following procedure will help you analyze the structure and bonding in any compound.

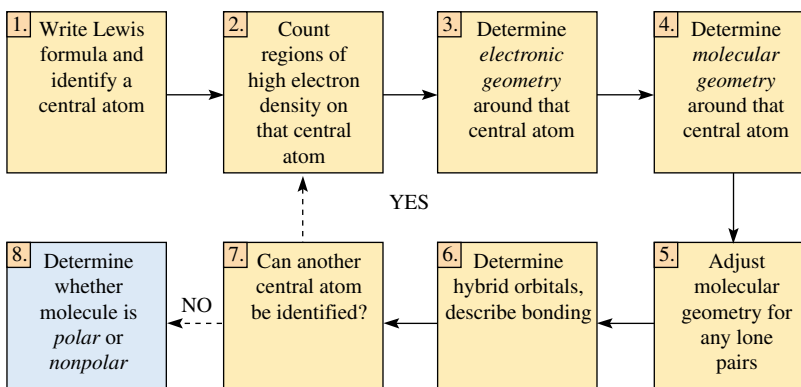
Never skip to step 4 until you have done step 3. The electronic geometry and the molecular geometry may or may not be the same; knowing the electronic geometry first will enable you to find the correct molecular geometry.

*Many chemists use the terms *lone pair* and *unshared pair* interchangeably, as we will do throughout this discussion.*

1. Write the Lewis formula for the molecule or polyatomic ion, and identify a *central atom*—an atom that is bonded to more than one other atom (Section 8-2).
2. Count the *number of regions of high electron density* on the central atom (Section 8-2).
3. Apply the VSEPR theory to determine the arrangement of the *regions of high electron density* (the *electronic geometry*) about the central atom (Section 8-2; Tables 8-1 and 8-4).
4. Using the Lewis formula as a guide, determine the arrangement of the *bonded atoms* (the *molecular geometry*) about the central atom, as well as the location of the unshared valence electron pairs on that atom (parts B of Sections 8-5 through 8-12; Tables 8-3 and 8-4). This description includes ideal bond angles.
5. If there are lone (unshared) pairs of valence shell electrons on the central atom, consider how their presence might modify somewhat the *ideal* molecular geometry and bond angles deduced in step 4 (Section 8-2; of Sections 8-8 through 8-12).
6. Use the VB theory to determine the *hybrid orbitals* utilized by the central atom; describe the overlap of these orbitals to form bonds; describe the orbitals that contain unshared pairs of valence shell electrons on the central atom (parts C of Sections 8-5 through 8-12; Sections 8-13; 8-14; Tables 8-2 and 8-4).
7. If more than one atom can be identified as a central atom, repeat steps 2 through 6 for each central atom, to build up a picture of the geometry and bonding in the entire molecule or ion.
8. When all central atoms in the molecule or ion have been accounted for, use the entire molecular geometry, electronegativity differences, and the presence of lone pairs of valence shell electrons on the central atom to predict *molecular polarity* (Section 8-3; parts B of Sections 8-5 through 8-12).

The following diagram summarizes this procedure.

Learn this procedure, and use it as a mental “checklist.” Trying to do this reasoning in a different order often leads to confusion or wrong answers.



In Section 7-4 we showed that Lewis formulas of polyatomic ions can be constructed in the same way as those of neutral molecules. Once the Lewis formula of an ion is known, we use the VSEPR and VB theories to deduce its electronic geometry, shape, and hybridization, just as for neutral molecules.

Recall that we must take into account the “extra” electrons on anions and the “missing” electrons of cations.

8-2 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The basic ideas of the **valence shell electron pair repulsion (VSEPR) theory** are:

Each set of valence shell electrons on a central atom is significant. The sets of valence shell electrons on the *central atom* repel one another. They are arranged about the *central atom* so that repulsions among them are as small as possible.

This results in maximum separation of the regions of high electron density about the central atom.

A **central atom** is any atom that is bonded to more than one other atom. In some molecules, more than one central atom may be present. In such cases, we determine the arrangement around each in turn, to build up a picture of the overall shape of the entire molecule or ion. We first count the number of **regions of high electron density** around the *central atom*, as follows:

1. Each bonded atom is counted as *one* region of high electron density, *whether the bonding is single, double, or triple*.
2. Each unshared pair of valence electrons on the central atom is counted as *one* region of high electron density.

The VSEPR theory assumes that regions of high electron density (electron pairs) on the central atom will be as far from one another as possible.

Consider the following molecules and polyatomic ions as examples.

Formula:	CO ₂	NH ₃	CH ₄	SO ₄ ²⁻
Lewis dot formula:	$\text{:O}=\text{C}=\text{O:}$	$\begin{array}{c} \text{H} \\ \\ \text{:N}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\left[\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \\ \text{:}\ddot{\text{O}}-\text{S}-\ddot{\text{O}}\text{:} \\ \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^{2-}$
Central atom:	C	N	C	S
Number of atoms bonded to <i>central atom</i> :	2	3	4	4
Number of unshared pairs on <i>central atom</i> :	0	1	0	0
Total number of regions of high electron density on <i>central atom</i> :	2	4	4	4

According to VSEPR theory, the structure is most stable when the regions of high electron density on the central atom are as far apart as possible. The arrangement of these *regions of high electron density* around the central atom is referred to as the **electronic geometry** of the central atom.

Although the terminology is not as precise as we might wish, we use “molecular geometry” to describe the arrangement of atoms in *polyatomic ions* as well as in molecules.

For instance, two regions of high electron density are most stable on opposite sides of the central atom (the linear arrangement). Three regions are most stable when they are arranged at the corners of an equilateral triangle. Each different number of regions of high electron density corresponds to a most stable arrangement of those regions. Table 8-1 shows the relationship between the common numbers or regions of high electron density and their corresponding electronic geometries. After we know the electronic geometry (and *only then*), we consider how many of these regions of high electron density connect (bond) the central atom to other atoms. This lets us deduce the arrangement of *atoms* around the central atom, called the **molecular geometry**. If necessary, we repeat this procedure for each central atom in the molecule or ion. These procedures are illustrated in parts B of Section 8-5 through 8-12.

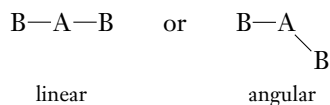
8-3 POLAR MOLECULES: THE INFLUENCE OF MOLECULAR GEOMETRY

In Chapter 7 we saw that the unequal sharing of electrons between two atoms with different electronegativities, $\Delta(\text{EN}) > 0$, results in a *polar bond*. For heteronuclear diatomic molecules such as HF, this bond polarity results in a *polar molecule*. Then the entire molecule acts as a dipole, and we would find that the molecule has a measurable *dipole moment*, that is, greater than zero.

When a molecule consists of more than two atoms joined by polar bonds, we must also take into account the *arrangement* of the resulting bond dipoles in deciding whether or not a molecule is polar. For such a case, we first use the VSEPR theory to deduce the molecular geometry (arrangement of atoms), as described in the preceding section and exemplified in parts A and B of Sections 8-5 through 8-12. Then we determine whether the bond dipoles are arranged in such a way that they cancel (so that the resulting molecule is *nonpolar*) or do not cancel (so that the resulting molecule is *polar*).

In this section we will discuss the ideas of cancellation of dipoles in general terms, using general atomic symbols A and B. Then we will apply these ideas to specific molecular geometries and molecular polarities in parts B of Sections 8-5 through 8-12.

Let us consider a heteronuclear triatomic molecule with the formula AB_2 (A is the central atom). Such a molecule must have one of the following two molecular geometries:



The angular form could have different angles, but either the molecule is linear or it is not. The angular arrangement is sometimes called *V-shaped* or *bent*.

Suppose that atom B has a higher electronegativity than atom A. Then each A—B bond is polar, with the negative end of the bond dipole pointing toward B. We can view each bond dipole as an *electronic vector*, with a *magnitude* and a *direction*. In the linear AB_2 arrangement, the two bond dipoles are *equal* in magnitude and *opposite* in direction. They therefore cancel to give a nonpolar molecule (dipole moment equal to zero).

TABLE 8-1 Number of Regions of High Electron Density About a Central Atom

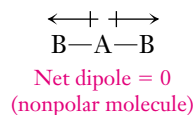
No. Regions of High Electron Density	Electronic Geometry*				
	Description; Angles†	Line Drawing‡			Stereo View§
2	linear; 180°				
3	trigonal planar; 120°				
4	tetrahedral; 109.5°				
5	trigonal bipyramidal; 90°, 120°, 180°				
6	octahedral; 90°, 180°				

*Electronic geometries are illustrated here using only single pairs of electrons as regions of high electron density. Each orange sphere represents a region of high electron density about the central atom (gray sphere). Each may represent either an atom bonded to the central atom or a lone pair on the central atom.

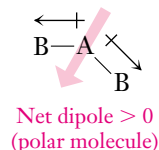
†Angles made by imaginary lines through the nucleus and the centers of regions of high electron density.

‡By convention, a line in the plane of the drawing is represented by a solid line —, a line behind this plane is shown as a dashed line -----, and a line in front of this plane is shown as a wedge — with the fat end of the wedge nearest the viewer.

§View the three-dimensional drawings with the aid of the viewer inside the cover of the text.



In the case of the angular arrangement, the two equal dipoles *do not cancel*, but add to give a dipole moment greater than zero. The angular molecular arrangement represents a polar molecule.



If the electronegativity differences were reversed in this B—A—B molecule—that is, if A were more electronegative than B—the directions of all bond polarities would be reversed. But the bond polarities would still cancel in the linear arrangement to give a nonpolar molecule. In the angular arrangement, bond polarities would still add to give a polar molecule, but with the net dipole pointing in the opposite direction from that described earlier.

We can make similar arguments based on addition of bond dipoles for other arrangements. As we will see in Section 8-8, lone pairs on the central atom can also affect the direction and the magnitude of the net molecular dipole, so the presence of lone pairs on the central atom must always be taken into account.

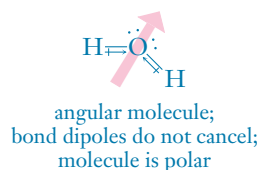
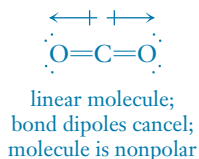
For a molecule to be polar, *two* conditions must be met:

1. There must be at least one polar bond or one lone (unshared) pair on the central atom.
- and*
2. a. The polar bonds, if there are more than one, must not be arranged so that their polarities (bond dipoles) cancel.
- or*
- b. If there are two or more lone (unshared) pairs on the central atom, they must not be arranged so that their polarities cancel.

Put another way, if there are no polar bonds or unshared pairs of electrons on the central atom, the molecule *cannot* be polar. Even if polar bonds or unshared pairs are present, they may be arranged so that their polarities cancel one another, resulting in a nonpolar molecule.

Carbon dioxide, CO₂, is a three-atom molecule in which each carbon–oxygen bond is *polar* because of the electronegativity difference between C and O. But the molecule *as a whole* is shown by experiment (dipole moment measurement) to be nonpolar. This tells us that the polar bonds are arranged in such a way that the bond polarities cancel. Water, H₂O, on the other hand, is a very polar molecule; this tells us that the H—O bond polarities do not cancel one another. Molecular shapes clearly play a crucial role in determining molecular dipole moments. We will develop a better understanding of molecular shapes in order to understand molecular polarities.

The logic used in deducing whether a molecule is polar or nonpolar is outlined in Figure 8-1. The approach described in this section will be applied to various electronic and molecular geometries in parts B of Sections 8-5 through 8-12.



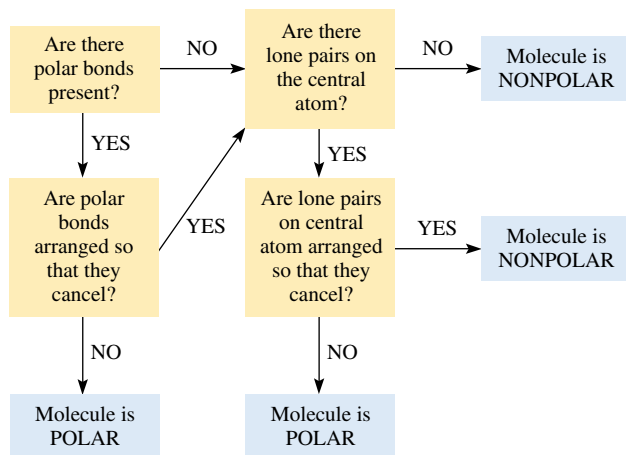


Figure 8-1 A guide to determining whether a polyatomic molecule is polar or nonpolar. Study the more detailed presentation in the text.

8-4 VALENCE BOND (VB) THEORY

In Chapter 7 we described covalent bonding as electron pair sharing that results from the overlap of orbitals from two atoms. This is the basic idea of the **valence bond (VB) theory**—it describes *how* bonding occurs. In many examples throughout this chapter, we first use the VSEPR theory to describe the *orientations* of the regions of high electron density. Then we use the VB theory to describe the atomic orbitals that overlap to produce the bonding with that geometry. We also assume that each lone pair occupies a separate orbital. Thus, the two theories work together to give a fuller description of the bonding.

We learned in Chapter 5 that an isolated atom has its electrons arranged in orbitals in the way that leads to the lowest total energy for the atom. Usually, however, these “pure atomic” orbitals do not have the correct energies or orientations to describe where the electrons are when an atom is bonded to other atoms. When other atoms are nearby as in a molecule or ion, an atom can combine its valence shell orbitals to form a new set of orbitals that is at a lower total energy in the presence of the other atoms than the pure atomic orbitals would be. This process is called **hybridization**, and the new orbitals that are formed are called **hybrid orbitals**. These hybrid orbitals can overlap with orbitals on other atoms to share electrons and form bonds. Such hybrid orbitals *usually* give an improved description of the experimentally observed geometry of the molecule or ion.

The designation (label) given to a set of hybridized orbitals reflects the *number and kind* of atomic orbitals that hybridize to produce the set (Table 8-2). Further details about hybridization and hybrid orbitals appear in the following sections. Throughout the text, hybrid orbitals are shaded in green.

TABLE 8-2 Relation Between Electronic Geometries and Hybridization

Regions of High Electron Density	Electronic Geometry	Atomic Orbitals Mixed from Valence Shell of Central Atom	Hybridization
2	linear	one <i>s</i> , one <i>p</i>	<i>sp</i>
3	trigonal planar	one <i>s</i> , two <i>p</i> 's	<i>sp</i> ²
4	tetrahedral	one <i>s</i> , three <i>p</i> 's	<i>sp</i> ³
5	trigonal bipyramidal	one <i>s</i> , three <i>p</i> 's, one <i>d</i>	<i>sp</i> ³ <i>d</i>
6	octahedral	one <i>s</i> , three <i>p</i> 's, two <i>d</i> 's	<i>sp</i> ³ <i>d</i> ²



We can describe hybridization as the mathematical combination of the waves that represent the orbitals of the atom. This is analogous to the formation of new waves on the surface of water when different waves interact.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 10.2, Models of Chemical Bonding, and Screen 10.3, Valence Bond Theory.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 10.6, Determining Hybrid Orbitals.

MOLECULAR SHAPES AND BONDING

We are now ready to study the structures of some simple molecules. We often refer to generalized chemical formulas in which “A” represents the central atom and “B” represents an atom bonded to A. We follow the eight steps of analysis outlined in Section 8-1. We first give the known (experimentally determined) facts about polarity and shape and write the Lewis formula (part A of each section). Then we explain these facts in terms of the VSEPR and VB theories. The simpler VSEPR theory will be used to explain (or predict) first the *electronic geometry* and then the *molecular geometry* in the molecule (part B). We then show how the molecular polarity of a molecule is a result of bond polarities, lone pairs, and molecular geometry. Finally, we use the VB theory to describe the bonding in molecules in more detail, usually using hybrid orbitals (part C). As you study each section, refer frequently to the summaries that appear in Table 8-4.

See the “Important Note” in Section 8-1; consult your instructor for guidance on the order in which you should study Sections 8-5 through 8-12.

8-5 LINEAR ELECTRONIC GEOMETRY: AB₂ SPECIES (NO LONE PAIRS OF ELECTRONS ON A)

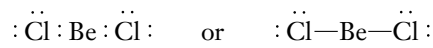
A. Experimental Facts and Lewis Formulas

Several linear molecules consist of a central atom plus two atoms of another element, abbreviated as AB₂. These compounds include gaseous BeCl₂, BeBr₂, and BeI₂, as well as CdX₂ and HgX₂, where X = Cl, Br, or I. All of these are known to be linear (bond angle = 180°), nonpolar, covalent compounds.

The high melting point of BeCl₂ is due to its polymeric nature in the solid state.

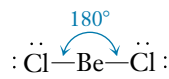
Let's focus on *gaseous* BeCl₂ molecules (mp 405°C). We wrote the Lewis formula for BeCl₂ in Example 7-5. It shows two single covalent bonds, with Be and Cl each contributing one electron to each bond.

In many of its compounds, Be does not satisfy the octet rule (see Section 7-7).

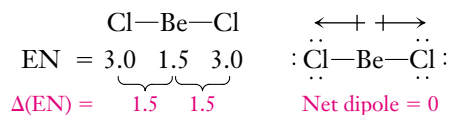


B. VSEPR Theory

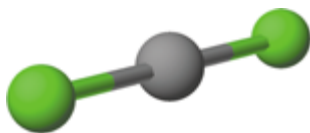
Valence shell electron pair repulsion theory places the two electron pairs on Be 180° apart, that is, with **linear** *electronic geometry*. Both electron pairs are bonding pairs, so VSEPR also predicts a linear atomic arrangement, or *linear molecular geometry*, for BeCl₂.



If we examine the bond dipoles, we see that the electronegativity difference (see Table 6-3) is large (1.5 units) and each bond is quite polar:



The VSEPR theory describes the locations of bonded atoms around the central atom, as well as where its lone pairs of valence shell electrons are directed.



A model of BeCl₂, a linear AB₂ molecule.

It is important to distinguish between *nonpolar bonds* and *nonpolar molecules*.

The two bond dipoles are *equal* in magnitude and *opposite* in direction. They therefore cancel to give a nonpolar molecule.

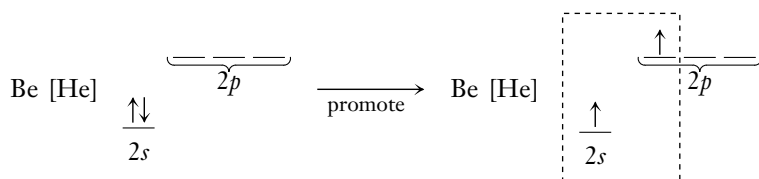
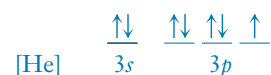
The difference in electronegativity between Be and Cl is so large that we might expect ionic bonding. The radius of Be²⁺ is so small (0.59 Å) and its **charge density** (ratio of charge to size) is so high, however, that most simple beryllium compounds are covalent rather than ionic. The high charge density of Be²⁺ causes it to attract and distort the electron cloud of monatomic anions of all but the most electronegative elements. As a result, the bonds in BeCl₂ are polar covalent rather than ionic. Two exceptions are BeF₂ and BeO. They are ionic compounds because they contain the two most electronegative elements bonded to Be.

We say that the Be²⁺ ion *polarizes* the anions, Cl⁻.

C. Valence Bond Theory

Consider the ground state electron configuration of Be. There are two electrons in the 1s orbital, but these nonvalence (inner) electrons are *not* involved in bonding. Two more electrons are *paired* in the 2s orbital. How, then, will a Be atom bond to two Cl atoms? The Be atom must somehow make available one orbital for each bonding Cl electron (the unpaired *p* electrons). The following *ground state* electron configuration for Be is the configuration for an isolated Be atom. Another configuration may be more stable when the Be atom is covalently bonded. Suppose that the Be atom “promoted” one of the paired 2s electrons to one of the 2*p* orbitals, the next higher energy orbitals.

Cl ground state configuration:



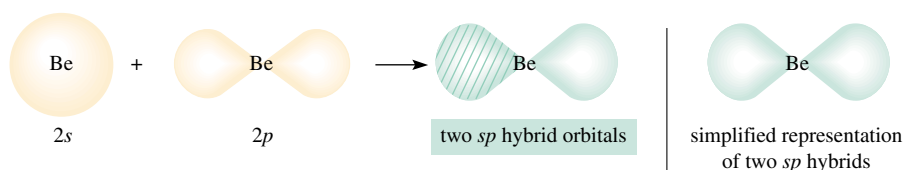
Then there would be two Be orbitals available for bonding. This description, however, is still not fully consistent with experimental fact. The Be 2s and 2*p* orbitals could not overlap a Cl 3*p* orbital with equal effectiveness; that is, this “promoted pure atomic” arrangement would predict two *nonequivalent* Be—Cl bonds. Yet we observe experimentally that the Be—Cl bonds are *identical* in bond length and bond strength.

For these two orbitals on Be to become equivalent, they must *hybridize* to give two orbitals intermediate between the *s* and *p* orbitals. These are called ***sp* hybrid orbitals**. Consistent with Hund’s Rule, each of these equivalent hybrid orbitals on Be would contain one electron.

Hund’s Rule is discussed in Section 5-17.

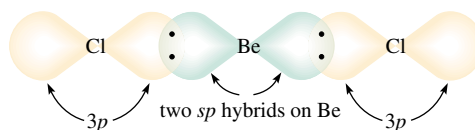


The *sp* hybrid orbitals are described as *linear orbitals*, and we say that Be has *linear electronic geometry*.



As we did for pure atomic orbitals, we often draw hybrid orbitals more slender than they actually are. Such drawings are intended to remind us of the orientations and general shapes of orbitals.

We can imagine that there is one electron in each of these hybrid orbitals on the Be atom. Recall that each Cl atom has a half-filled $3p$ orbital that can overlap with a half-filled sp hybrid of Be. We picture the bonding in BeCl_2 in the following diagram, in which only the bonding electrons are represented.



Unshared pairs of electrons on Cl atoms are not shown. The hybrid orbitals on the central atom are shown in green in this and subsequent drawings.

Thus, the Be and two Cl nuclei would lie on a straight line. *This is consistent with the experimental observation that the molecule is linear.*

The structures of beryllium bromide, BeBr_2 , and beryllium iodide, BeI_2 , are similar to that of BeCl_2 . The chlorides, bromides, and iodides of cadmium, CdX_2 , and mercury, HgX_2 , are also linear, covalent molecules (where X = Cl, Br, or I).

The two X's within one structure are identical.

sp Hybridization occurs at the central atom whenever there are two regions of high electron density around the central atom. AB_2 molecules and ions with no lone pairs on the central atom have linear electronic geometry, linear molecular geometry, and sp hybridization on the central atom.

✓ Problem-Solving Tip: Number and Kind of Hybrid Orbitals

One additional idea about hybridization is worth special emphasis:

The number of hybrid orbitals is always equal to the number of atomic orbitals that hybridize.

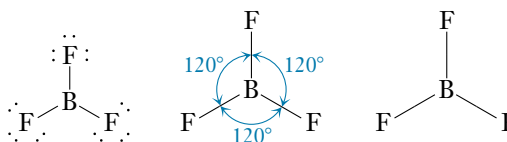
Hybrid orbitals are named by indicating the *number and kind* of atomic orbitals hybridized. Hybridization of *one s* orbital and *one p* orbital gives *two sp* hybrid orbitals. We shall see presently that hybridization of *one s* and *two p* orbitals gives *three sp²* hybrid orbitals; hybridization of *one s* orbital and *three p* orbitals gives *four sp³* hybrids, and so on (see Table 8-2).

Hybridization usually involves orbitals from the same main shell (same n).

8-6 TRIGONAL PLANAR ELECTRONIC GEOMETRY: AB_3 SPECIES (NO LONE PAIRS OF ELECTRONS ON A)

A. Experimental Facts and Lewis Formulas

Boron is a Group IIIA element that forms many covalent compounds by bonding to three other atoms. Typical examples include boron trifluoride, BF_3 (mp -127°C); boron trichloride, BCl_3 (mp -107°C); boron tribromide, BBr_3 (mp -46°C); and boron triiodide, BI_3 (mp 50°C). All are trigonal planar nonpolar molecules.



A trigonal planar molecule is a flat molecule in which all three bond angles are 120° .

The solid lines represent bonds between B and F atoms.

The Lewis formula for BF₃ is derived from the following: (a) each B atom has three electrons in its valence shell and (b) each B atom is bonded to three F (or Cl, Br, I) atoms. In Example 7-6 we wrote the Lewis formula for BCl₃. Both F and Cl are members of Group VIIA, and so the Lewis formulas for BF₃ and BCl₃ should be similar.

We see that BF₃ and other similar molecules have a central element that does *not* satisfy the octet rule. Boron shares only six electrons.

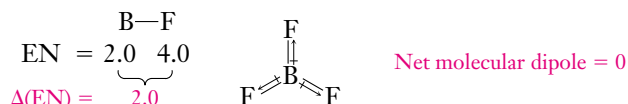


A model of BF₃, a trigonal planar AB₃ molecule.

B. VSEPR Theory

Boron, the central atom, has three regions of high electron density (three bonded atoms, no lone pairs on B). The VSEPR theory predicts **trigonal planar electronic geometry** for molecules such as BF₃ because this structure gives maximum separation among the three regions of high electron density. There are no lone pairs of electrons associated with the boron atom, so a fluorine atom is at each corner of the equilateral triangle, and the *molecular geometry* is also trigonal planar. The maximum separation of any three items (electron pairs) around a fourth item (B atom) is at 120° angles in a single plane. All four atoms are in the same plane. The three F atoms are at the corners of an equilateral triangle, with the B atom in the center. The structures of BCl₃, BBr₃, and BI₃ are similar.

Examination of the bond dipoles of BF₃ shows that the electronegativity difference (see Table 6-3) is very large (2.0 units) and that the bonds are very polar.



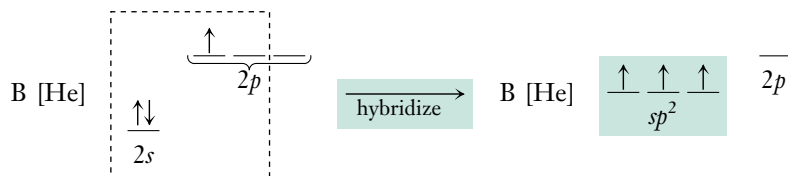
However, the three bond dipoles are symmetrical, so they cancel to give a nonpolar molecule.

Trigonal planar geometry is sometimes called *plane triangular* or, simply, *triangular*.

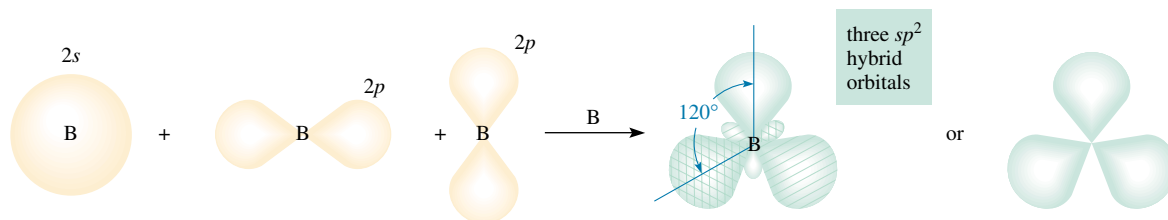
The B³⁺ ion is so small (radius = 0.20 Å) that boron does not form simple ionic compounds.

C. Valence Bond Theory

To be consistent with experimental findings and the predictions of the VSEPR theory, the VB theory must explain three *equivalent* B—F bonds. Again we use the idea of hybridization. Now the 2s orbital and two of the 2p orbitals of B hybridize to form a set of three equivalent *sp² hybrid orbitals*.

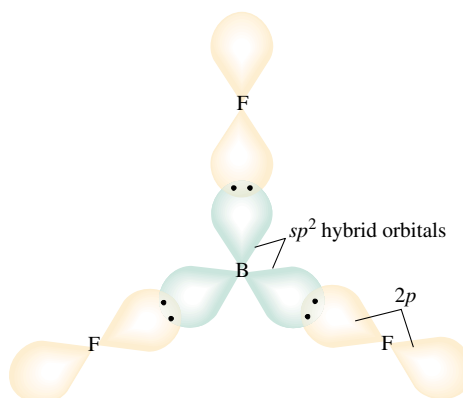


Three *sp²* hybrid orbitals point toward the corners of an equilateral triangle:



We can imagine that there is one electron in each of these hybrid orbitals. Each of the three F atoms has a $2p$ orbital with one unpaired electron. The $2p$ orbitals can overlap the three sp^2 hybrid orbitals on B. Three electron pairs are shared among one B and three F atoms:

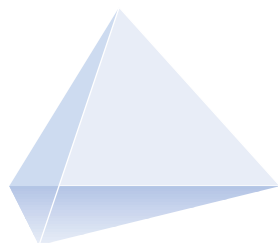
Lone pairs of electrons are not shown for the F atoms.



sp^2 Hybridization occurs at the central atom whenever there are three regions of high electron density around the central atom. AB_3 molecules and ions with no unshared pairs on the central atom have trigonal planar electronic geometry, trigonal planar molecular geometry, and sp^2 hybridization on the central atom.

8-7 TETRAHEDRAL ELECTRONIC GEOMETRY: AB_4 SPECIES (NO LONE PAIRS OF ELECTRONS ON A)

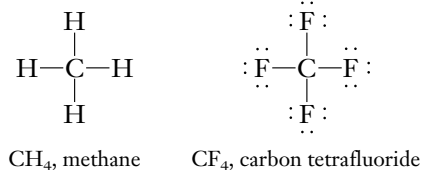
A. Experimental Facts and Lewis Formulas



The names of many solid figures are based on the numbers of plane faces they have. A *regular* tetrahedron is a three-dimensional figure with four equal-sized equilateral triangular faces (the prefix *tetra-* means “four”).

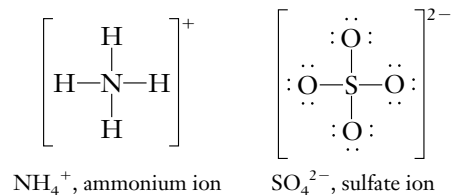
Each Group IVA element has four electrons in its highest occupied energy level. The Group IVA elements form many covalent compounds by sharing those four electrons with four other atoms. Typical examples include CH_4 (mp $-182^\circ C$), CF_4 (mp $-184^\circ C$), CCl_4 (mp $-23^\circ C$), SiH_4 (mp $-185^\circ C$), and SiF_4 (mp $-90^\circ C$). All are tetrahedral, nonpolar molecules (bond angles = 109.5°). In each, the Group IVA atom is located in the center of a regular tetrahedron. The other four atoms are located at the four corners of the tetrahedron.

The Group IVA atom contributes four electrons to the bonding in a tetrahedral AB_4 molecule, and the other four atoms contribute one electron each. The Lewis formulas for methane, CH_4 , and carbon tetrafluoride, CF_4 , are typical.



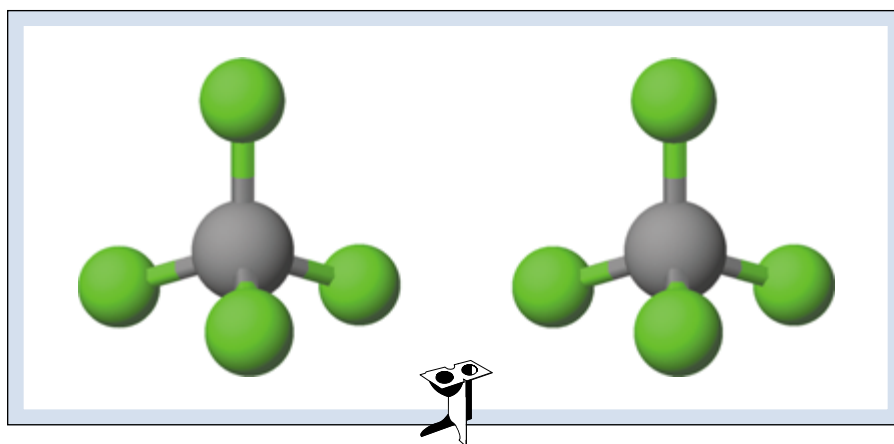
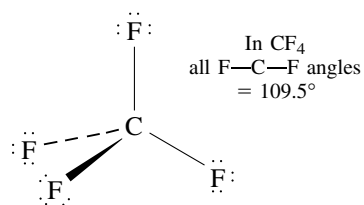
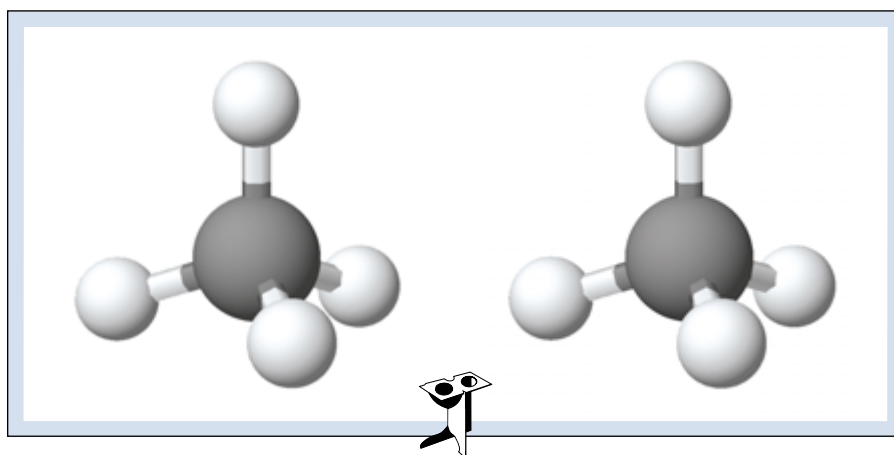
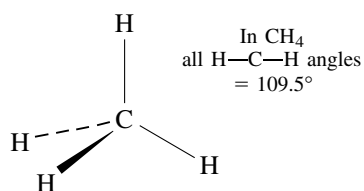
The ammonium ion, NH_4^+ , and the sulfate ion, SO_4^{2-} , are familiar examples of polyatomic ions of this type. In each of these ions, the central atom is located at the center of

a regular tetrahedron with the other atoms at the corners (H—N—H and O—S—O bond angles = 109.5°).



B. VSEPR Theory

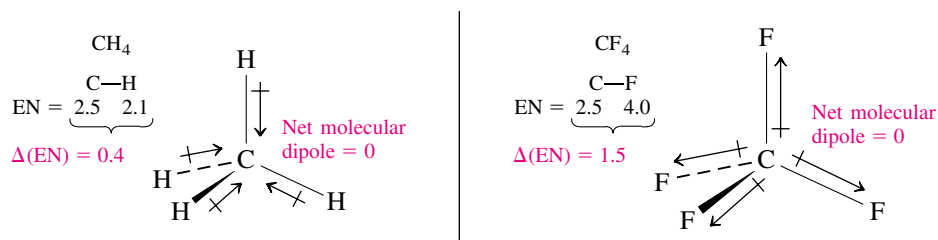
VSEPR theory predicts that four valence shell electron pairs are directed toward the corners of a regular tetrahedron. That shape gives the maximum separation for four electron pairs around one atom. Thus, VSEPR theory predicts **tetrahedral electronic geometry** for an AB₄ molecule that has no unshared electrons on A. There are no lone pairs of electrons on the central atom, so another atom is at each corner of the tetrahedron. VSEPR theory predicts a *tetrahedral molecular geometry* for each of these molecules.



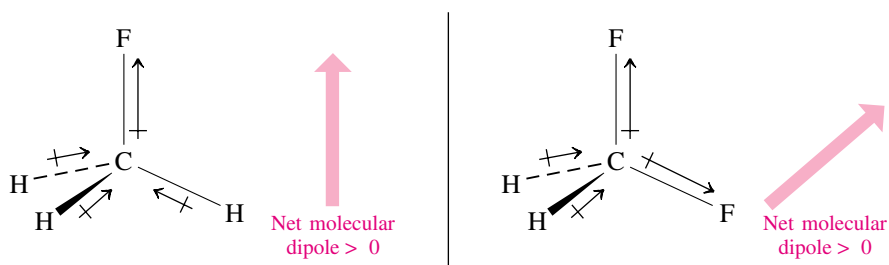
The results that we discussed in Sections 8-5 (BeX_2 , CdX_2 , and HgX_2 , where $X = \text{Cl}$, Br , or I), and 8-6 (BX_3 , where $X = \text{F}$, Cl , Br , or I), and in this section (CH_4 , CF_4 , CCl_4 , SiH_4 , SiF_4 , NH_4^+ , and SO_4^{2-}) illustrate an important generalization:

When a molecule or polyatomic ion has no unshared pairs of valence electrons on the central atom, the *electronic geometry* and the *molecular geometry* are the same.

Examination of bond dipoles shows that in CH_4 the individual bonds are only slightly polar, whereas in CF_4 the bonds are quite polar. In CH_4 the bond dipoles are directed toward carbon, but in CF_4 they are directed away from carbon. Both molecules are very symmetrical, so the bond dipoles cancel, and both molecules are nonpolar. This is true for all AB_4 molecules in which there are *no unshared electron pairs on the central element* and all four B atoms are identical.



In some tetrahedral molecules, the atoms bonded to the central atom are not all the same. Such molecules are usually polar, with the degree of polarity depending on the relative sizes of the bond dipoles present. In CH_3F or CH_2F_2 , for example, the addition of unequal dipoles makes the molecule polar.



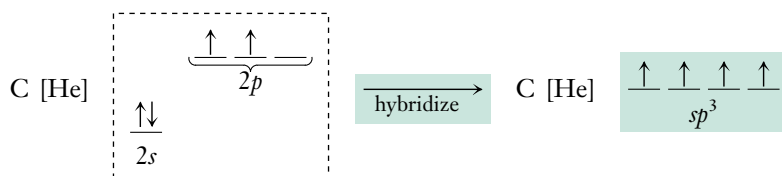
The VSEPR theory also predicts that NH_4^+ and SO_4^{2-} ions have tetrahedral electronic geometry. Each region of high electron density bonds the central atom to another atom (H in NH_4^+ , O in SO_4^{2-}) at the corner of the tetrahedral arrangement. We describe the molecular geometry of each of these ions as tetrahedral.

You may wonder whether square planar AB_4 molecules exist. We will discuss some examples of square planar AB_4 species in Section 8-12. The bond angles in square planar

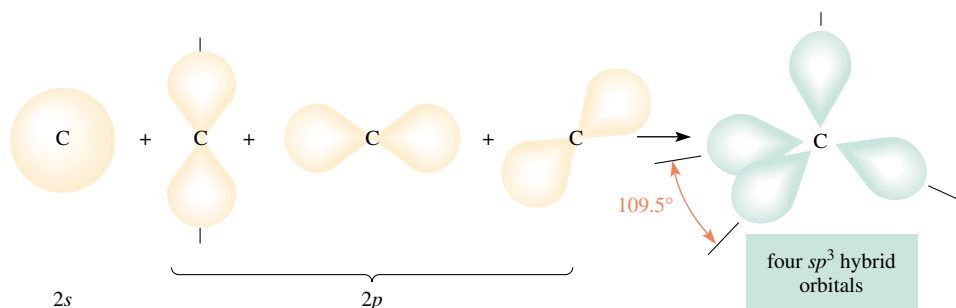
molecules are only 90°. Most AB₄ molecules are tetrahedral, however, with larger bond angles (109.5°) and greater separation of valence electron pairs around A.

C. Valence Bond Theory

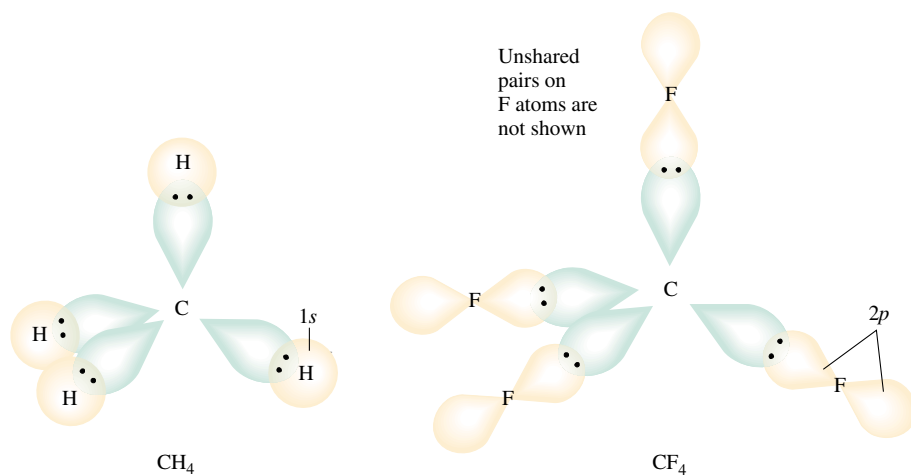
According to VB theory, each Group IVA atom (C in our example) must make four equivalent orbitals available for bonding. To do this, C forms four **sp³ hybrid orbitals** by mixing the *s* and all three *p* orbitals in its outer (*n* = 2) shell. This results in four unpaired electrons.





These sp³ hybrid orbitals are directed toward the corners of a regular tetrahedron, which has a 109.5° angle from any corner to the center to any other corner.



Each of the four atoms that bond to C has a half-filled atomic orbital; these can overlap the half-filled sp³ hybrid orbitals, as is illustrated for CH₄ and CF₄.



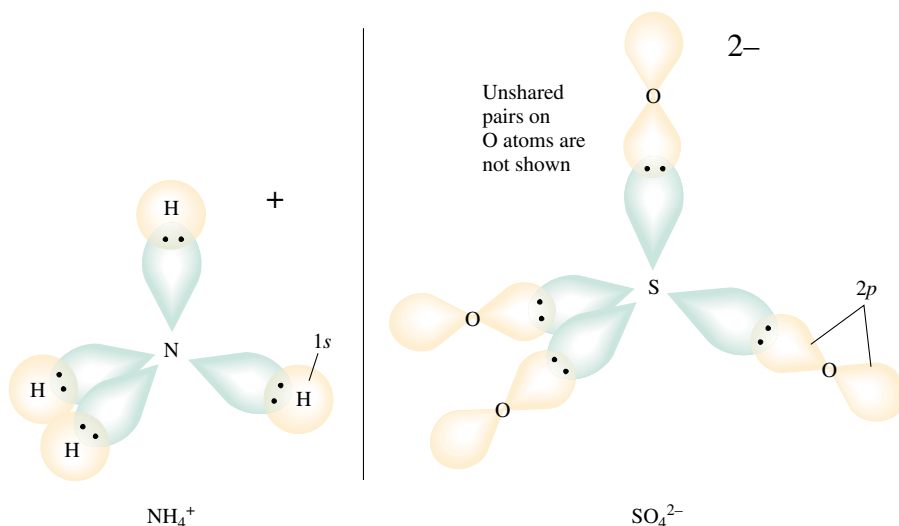
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 10.4, Hybrid Orbitals. Be sure to see the animation of sp³ orbital formation on that screen. See also the hybridization tool in Screen 10.6, which you can use to build hybrid orbitals.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 10.5, Sigma Bonds.

✓ Problem-Solving Tip: Use Periodic Relationships

Because F, Cl, Br, and I are all in the same group of the periodic table, we know that their compounds would be similar. We expect that the detailed descriptions we have seen for CF_4 would also apply to CCl_4 , CBr_4 , and CI_4 , and we do not need to go through the entire reasoning for each one. Thus, we can say that each of the CX_4 molecules ($X = \text{F, Cl, Br, or I}$) also has tetrahedral electronic geometry, tetrahedral molecular geometry, sp^3 hybridization on the carbon atom, zero dipole moment, and so on.

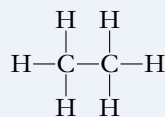
We can give the same VB description for the hybridization of the central atoms in polyatomic ions. In NH_4^+ and SO_4^{2-} , the N and S atoms, respectively, form four sp^3 hybrid orbitals directed toward the corners of a regular tetrahedron. Each of these sp^3 hybrid orbitals overlaps with an orbital on a neighboring atom (H in NH_4^+ , O in SO_4^{2-}) to form a bond.



sp^3 Hybridization occurs at the central atom whenever there are four regions of high electron density around the central atom. AB_4 molecules and ions with no unshared pairs on the central atom have tetrahedral electronic geometry, tetrahedral molecular geometry, and sp^3 hybridization on the central atom.

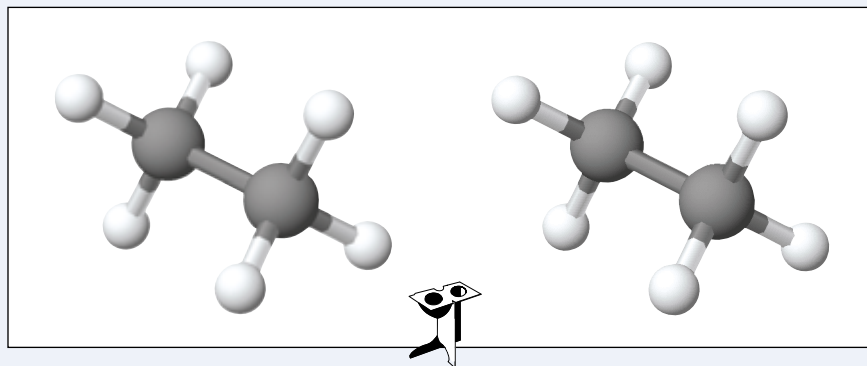
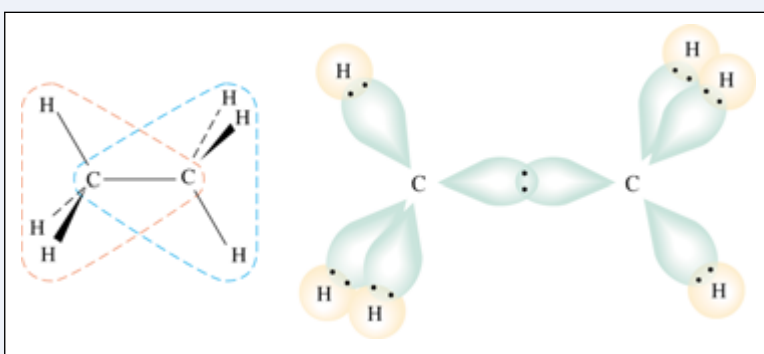
✓ Problem-Solving Tip: Often There Is More Than One Central Atom

Many molecules contain more than one central atom, that is, there is more than one atom that is bonded to several other atoms. We can analyze such molecules one central atom at a time, to build up a picture of the three-dimensional aspects of the molecule. An example is ethane, C_2H_6 ; its Lewis formula is



Let us first consider the left-hand carbon atom. The arrangements of its regions of high electron density allows us to locate the other C and three H atoms with respect to that C atom (the atoms outlined in red). Then we carry out a similar analysis for the right-hand C atom to deduce the arrangements of *its* neighbors (outlined in blue).

Each C atom in C_2H_6 has four regions of high electron density. The VSEPR theory tells us that each C atom has tetrahedral electronic geometry; the resulting atomic arrangement around each C atom has one C and three H atoms at the corners of this tetrahedral arrangement. The VB interpretation is that each C atom is sp^3 hybridized. The C—C bond is formed by overlap of a half-filled sp^3 hybrid orbital of one C atom with a half-filled sp^3 hybrid orbital of the other C atom. Each C—H bond is formed by the overlap of a half-filled sp^3 hybrid orbital on C with the half-filled $1s$ orbital of an H atom.



8-8 TETRAHEDRAL ELECTRONIC GEOMETRY: AB_3U SPECIES (ONE LONE PAIR OF ELECTRONS ON A)

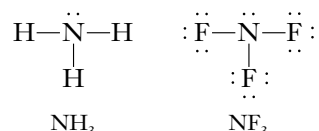
We are now ready to study the structures of some simple molecules with unshared valence electron pairs (lone pairs) on the central atom. In this and subsequent sections, we use generalized chemical formulas in which “A” represents the central atom, “B” represents an atom bonded to A, and “U” represents an unshared valence shell electron pair (lone pair) on the central atom A. For instance, AB_3U would represent any molecule with three B atoms bonded to a central atom A, with one unshared valence pair on A.

Some Group VA elements also form covalent compounds by sharing all five valence electrons (Sections 7-7 and 8-11).

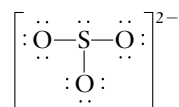
A. Experimental Facts and Lewis Formulas

Each Group VA element has five electrons in its valence shell. The Group VA elements form some covalent compounds by sharing three of those electrons with three other atoms. Let us describe two examples: ammonia, NH_3 , and nitrogen trifluoride, NF_3 . Each is a trigonal pyramidal, polar molecule with an unshared pair on the nitrogen atom. Each has a nitrogen atom at the apex and the other three atoms at the corners of the triangular base of the pyramid.

The Lewis formulas for NH_3 and NF_3 are

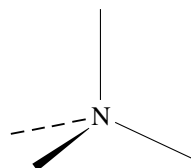


Sulfite ion, SO_3^{2-} , is an example of a polyatomic ion of the AB_3U type. It is a trigonal pyramidal ion with an unshared pair on the sulfur atom.

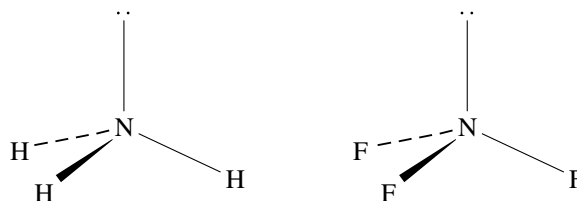


B. VSEPR Theory

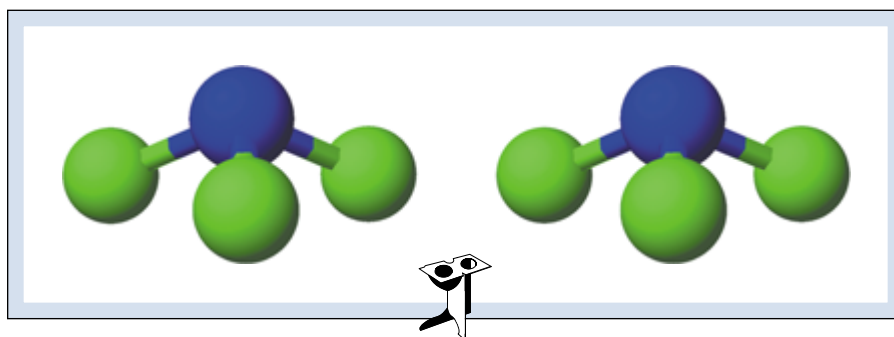
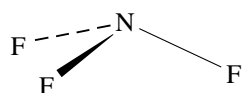
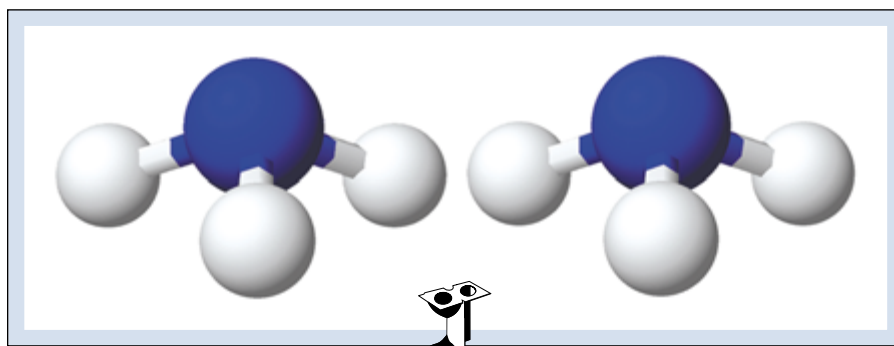
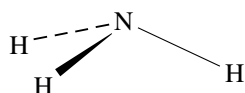
As in Section 8-7, VSEPR theory predicts that the *four* regions of high electron density around a central atom will be directed toward the corners of a tetrahedron, because this gives maximum separation. So N has tetrahedral electronic geometry in NH_3 and NF_3 . We must reemphasize the distinction between electronic geometry and molecular geometry. *Electronic geometry* refers to the geometric arrangement of the *regions of electron density* around the central atom. But the *molecular geometry* excludes the unshared pairs on the central atom, and describes only the arrangement of *atoms* (i.e., nuclei) around the central atom. We can represent the tetrahedral electronic geometry around N in NH_3 or NF_3 as follows.



We then use the Lewis formula as a guide to put the bonded atoms and the lone pairs in these tetrahedral sites around the nitrogen atom.



Then we describe the *molecular geometry* as the arrangement of the *atoms*. In each of these molecules, the N atom is at the apex of a (shallow) trigonal pyramidal arrangement and the other three atoms are at the corners of the triangular base of the pyramid. Thus, the molecular geometry of each molecule is described as *trigonal pyramidal*.

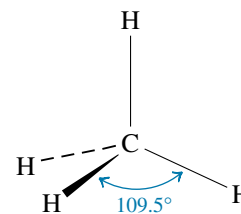


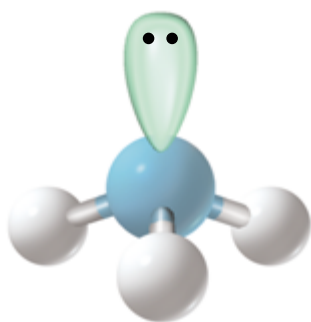
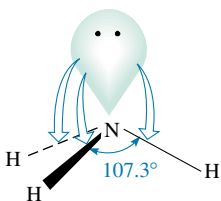
We have seen that CH₄, CF₄, NH₃, and NF₃ all have tetrahedral electronic geometry. But CH₄ and CF₄ (AB₄) have tetrahedral molecular geometry, whereas NH₃ and NF₃ (AB₃U) have trigonal pyramidal molecular geometry.

In molecules or polyatomic ions that contain lone (unshared) pairs of valence electrons on the central atom, the *electronic geometry* and the *molecular geometry* cannot be the same.

Because this trigonal pyramidal molecular geometry is a fragment of tetrahedral electronic geometry, we expect that the H—N—H angle would be close to the tetrahedral value, 109.5°. In CH₄ (a tetrahedral AB₄ molecule), all H—C—H bond angles are observed to be this ideal value, 109.5°. In NH₃, however, the H—N—H bond angles are observed to be less than this, 107.3°. How can we explain this deviation?

A lone pair is a pair of valence electrons that is associated with only one nucleus in contrast to a bonded pair, which is associated with two nuclei. The known geometries of many molecules and polyatomic ions, based on measurements of bond angles, show that *lone pairs of electrons occupy more space than bonding pairs*. A lone pair has only one atom



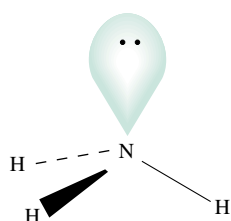


A model of NH_3 , a trigonal pyramidal AB_3U molecule, showing the lone pair.

exerting strong attractive forces on it, so it resides closer to the nucleus than do bonding electrons. The relative magnitudes of the repulsive forces between pairs of electrons on an atom are

$$lp/lp \gg lp/bp > bp/bp$$

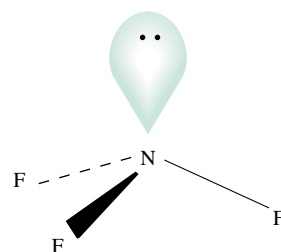
where lp refers to lone (unshared) pairs and bp refers to bonding pairs of valence shell electrons. We are most concerned with the repulsions among the electrons in the valence shell of the *central atom* of a molecule or polyatomic ion. The angles at which repulsive forces among valence shell electron pairs are minimized are the angles at which the bonding pairs and unshared pairs (and therefore nuclei) are found in covalently bonded molecules and polyatomic ions. Due to lp/bp repulsions in NH_3 and NF_3 , their bond angles are *less* than the angles of 109.5° we observed in CH_4 and CF_4 molecules.



In NH_3 , H-N-H angle = 107.3°

Tetrahedral
electronic geometry

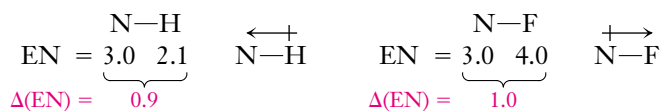
Trigonal pyramidal
molecular geometry



In NF_3 , F-N-F angle = 102.1°

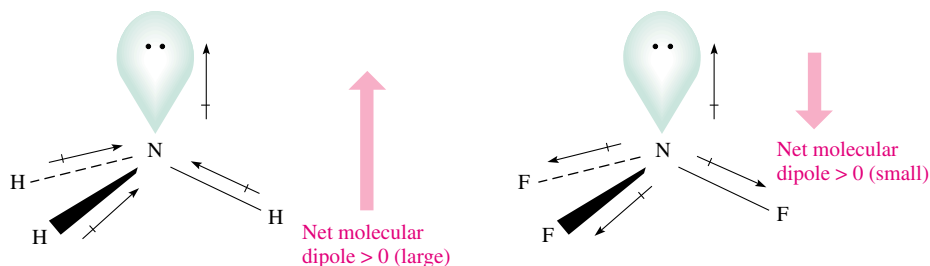
The formulas are frequently written as $:\text{NH}_3$ and $:\text{NF}_3$ to emphasize the unshared pairs of electrons. The unshared pairs must be considered as the polarities of these molecules are examined; they are extremely important in chemical reactions. This is why NH_3 is a base, as we saw in Section 4-2.4 and as we shall discuss more fully in Chapter 10. The contribution of each unshared pair to polarity can be depicted as shown in the margin.

The electronegativity differences in NH_3 and NF_3 are nearly equal, *but* the resulting nearly equal bond polarities are in opposite directions.



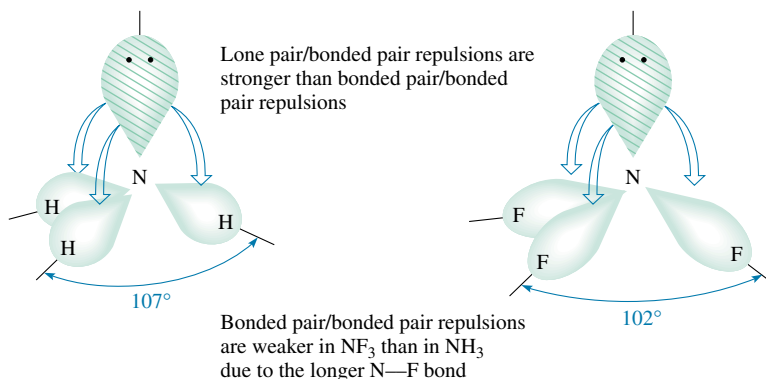
Thus, we have

In NH_3 the bond dipoles *reinforce* the effect of the unshared pair, so NH_3 is very polar ($\mu = 1.47$ D). In NF_3 the bond dipoles *oppose* the effect of the unshared pair, so NF_3 is only slightly polar ($\mu = 0.23$ D).



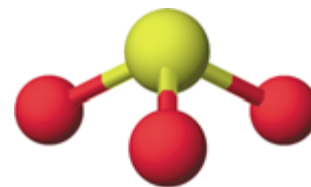
We can now use this information to explain the bond angles observed in NF_3 and NH_3 . Because of the direction of the bond dipoles in NH_3 , the electron-rich end of each N-H bond is at the central atom, N. On the other hand, the fluorine end of each bond in NF_3 is the electron-rich end. As a result, the lone pair can more closely approach the N in

NF₃ than in NH₃. In NF₃ the lone pair therefore exerts greater repulsion toward the bonded pairs than in NH₃. In addition, the longer N—F bond length makes the *bp*–*bp* distance greater in NF₃ than in NH₃, so that the *bp/bp* repulsion in NF₃ is less than that in NH₃. The net effect is that the bond angles are reduced more in NF₃. We can represent this situation as:



We might expect the larger F atoms ($r = 0.72 \text{ \AA}$) to repel each other more strongly than the H atoms ($r = 0.37 \text{ \AA}$), leading to larger bond angles in NF₃ than in NH₃. This is not the case, however, because the N—F bond is longer than the N—H bond. The N—F bond density is farther from the N than the N—H bond density.

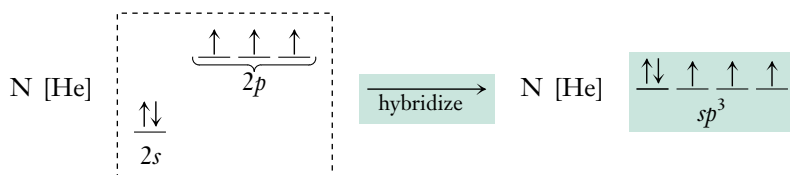
With the same kind of reasoning, VSEPR theory predicts that sulfite ion, SO₃²⁻, has tetrahedral electronic geometry. One of these tetrahedral locations is occupied by the sulfur lone pair, and oxygen atoms are at the other three locations. The molecular geometry of this ion is trigonal pyramidal, the same as for other AB₃U species.



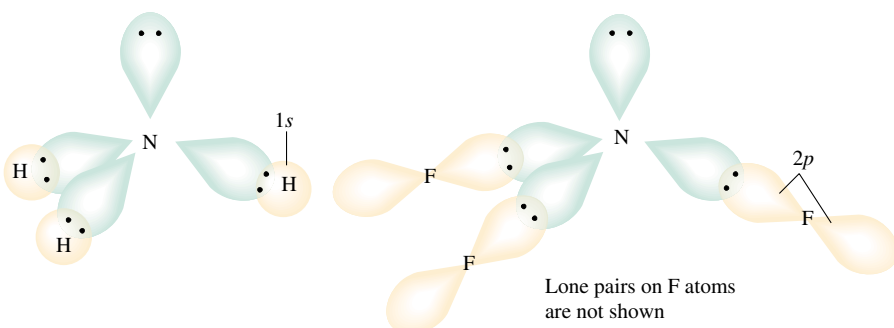
A model of sulfite ion, SO₃²⁻.

C. Valence Bond Theory

Experimental results suggest four nearly equivalent orbitals (three involved in bonding, a fourth to accommodate the lone pair), so we again need four *sp*³ hybrid orbitals.



In both NH₃ and NF₃ the lone pair of electrons occupies one of the *sp*³ hybrid orbitals. Each of the other three *sp*³ orbitals participates in bonding by sharing electrons with another atom. They overlap with half-filled H 1*s* orbitals and F 2*p* orbitals in NH₃ and NF₃, respectively.



The sulfur atom in the sulfite ion, SO_3^{2-} , can be described as sp^3 hybridized. One of these hybrid orbitals contains the sulfur lone pair, and the remaining three overlap with oxygen orbitals to form bonds.

AB_3U molecules and ions, each having four regions of high electron density around the central atom, *usually* have tetrahedral electronic geometry, trigonal pyramidal molecular geometry, and sp^3 hybridization on the central atom.

We must remember that *theory* (and its application) depends on fact, not the other way around. Sometimes the experimental facts are not consistent with the existence of hybrid orbitals. In PH_3 and AsH_3 , each H—P—H bond angle is 93.7° , and each H—As—H bond angle is 91.8° . These angles very nearly correspond to three p orbitals at 90° to each other. Thus, there appears to be no need to use the VSEPR theory or hybridization to describe the bonding in these molecules. In such cases, we just use the “pure” atomic orbitals rather than hybrid orbitals to describe the bonding.



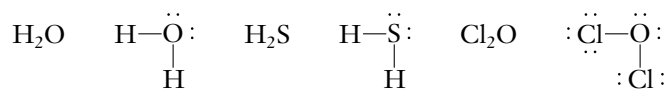
Problem-Solving Tip: *When Do We Not Need To Describe Hybrid Orbitals?*

Students often wonder how to recognize when hybridization does not apply, as in the PH_3 and AsH_3 cases just described and in H_2S (see Section 8-9). Remember that models such as hybridization are our attempts to explain observations such as bond angles. At the level of our studies, we will be given information about the observed molecular geometry, such as measured bond angles. If these are near the angles of pure (unhybridized) orbitals, then hybridization is not needed; if they are near the predicted angles for hybridized orbitals, then hybridization should be used in our explanation. If no information about observed molecular geometry (molecular shape, bond angles, etc.) is supplied, you should assume that the VSEPR and hybridization approaches presented in this chapter should be used.

8-9 TETRAHEDRAL ELECTRONIC GEOMETRY: AB_2U_2 SPECIES (TWO LONE PAIRS OF ELECTRONS ON A)

A. Experimental Facts and Lewis Formulas

Each Group VIA element has six electrons in its valence shell. The Group VIA elements form many covalent compounds by sharing a pair of electrons with each of two other atoms. Typical examples are H_2O , H_2S , and Cl_2O . The Lewis formulas for these molecules are

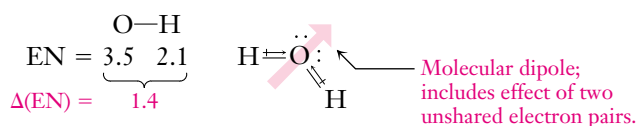


All are angular, polar molecules. The bond angle in water, for example, is 104.5° , and the molecule is very polar with a dipole moment of 1.85 D.

B. VSEPR Theory

The VSEPR theory predicts that the four electron pairs around the oxygen atom in H₂O should be 109.5° apart in a tetrahedral arrangement. The observed H—O—H bond angle is 104.5°. The two lone (unshared) pairs strongly repel each other and the bonding pairs of electrons. These repulsions force the bonding pairs closer together and result in the decreased bond angle. The decrease in the H—O—H bond angle (from 109.5° to 104.5°) is greater than the corresponding decrease in the H—N—H bond angles in ammonia (from 109.5° to 107.3°) because of the *lp/lp* repulsion in H₂O.

The electronegativity difference is large (1.4 units), and so the bonds are quite polar. Additionally, the bond dipoles *reinforce* the effect of the two unshared pairs, so the H₂O molecule is very polar. Its dipole moment is 1.8 D. Water has unusual properties, which can be explained in large part by its high polarity.

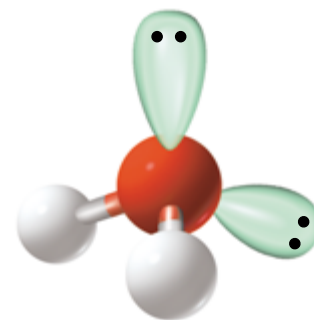
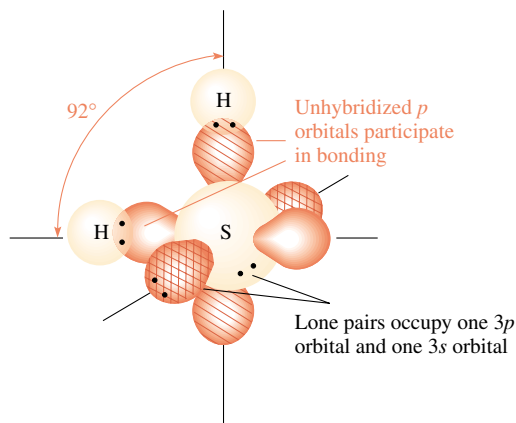


C. Valence Bond Theory

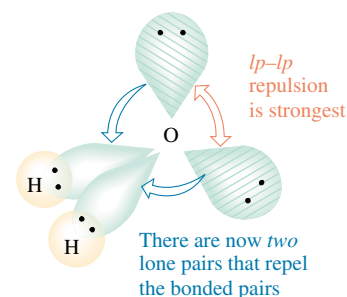
The bond angle in H₂O (104.5°) is closer to the tetrahedral value (109.5°) than to the 90° angle that would result from bonding by pure 2*p* atomic orbitals on O. Valence bond theory therefore postulates four *sp*³ hybrid orbitals centered on the O atom: two to participate in bonding and two to hold the two unshared pairs.

AB₂U₂ molecules and ions, each having four regions of high electron density around the central atom, *usually* have tetrahedral electronic geometry, angular molecular geometry, and *sp*³ hybridization on the central atom.

Hydrogen sulfide, H₂S, is also an angular molecule, but the H—S—H bond angle is 92.2°. This is very close to the 90° angles between two unhybridized 3*p* orbitals of S. We therefore *do not* propose hybrid orbitals to describe the bonding in H₂S. The two H atoms are able to exist at approximately right angles to each other when they are bonded to the larger S atom. The bond angles in H₂Se and H₂Te are 91° and 89.5°, respectively.



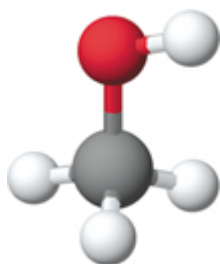
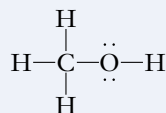
A model of H₂O, an angular AB₂U₂ molecule, showing the lone pairs.



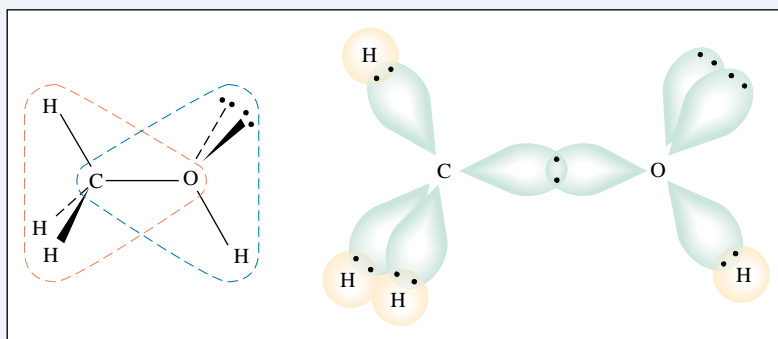
Sulfur is located directly below oxygen in Group VIA.

 **Problem-Solving Tip:** *Some Molecules Have Two Central Atoms and Lone Pairs*

Methanol, CH_3OH , is a simple molecule that has more than one central atom *and* two lone pairs. It is the simplest member of a family of organic molecules called *alcohols*; all alcohols contain the atom grouping $\text{C}-\text{O}-\text{H}$. The Lewis formula for methanol is

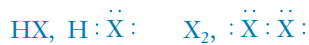


Again, we consider the arrangements around two central atoms in sequence. The carbon atom (outlined in red) has four regions of high electron density. VSEPR theory tells us that this atom has tetrahedral *electronic* geometry; the resulting atomic arrangement around the C atom has four atoms (O and three H) at the corners of this tetrahedral arrangement, so the molecular geometry about the C atom is tetrahedral. The oxygen atom (outlined in blue) has four regions of high electron density, so it, too, has tetrahedral *electronic* geometry. Thus, the $\text{C}-\text{O}-\text{H}$ arrangement is angular and there are two unshared pairs on O. The VB interpretation is that both atoms are sp^3 hybridized. The $\text{C}-\text{O}$ bond is formed by overlap of a half-filled sp^3 hybrid orbital on the C atom with a half-filled sp^3 hybrid orbital on the O atom. Each covalent bond to an H is formed by the overlap of a half-filled sp^3 hybrid orbital with the half-filled $1s$ orbital on an H atom. Each unshared pair of electrons on O is in an sp^3 hybrid orbital.



8-10 **TETRAHEDRAL ELECTRONIC GEOMETRY: ABU_3 SPECIES (THREE LONE PAIRS OF ELECTRONS ON A)**

We represent the halogen as X.



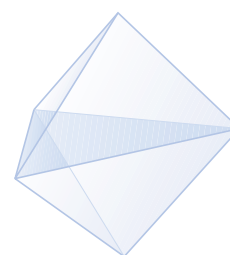
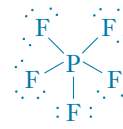
In latter case, either halogen may be considered the “A” atom of AB.

Each Group VIIA element has seven electrons in its highest occupied energy level. The Group VIIA elements form molecules such as $\text{H}-\text{F}$, $\text{H}-\text{Cl}$, $\text{Cl}-\text{Cl}$, and $\text{I}-\text{I}$ by sharing one of their electrons with another atom. The other atom contributes one electron to the bonding. Lewis dot formulas for these molecules are shown in the margin. Any diatomic molecule must be linear. Neither VSEPR theory nor VB theory adds anything to what we already know about the molecular geometry of such molecules.

8-11 TRIGONAL BIPYRAMIDAL ELECTRONIC GEOMETRY: AB₅, AB₄U, AB₃U₂, AND AB₂U₃

A. Experimental Facts and Lewis Formulas

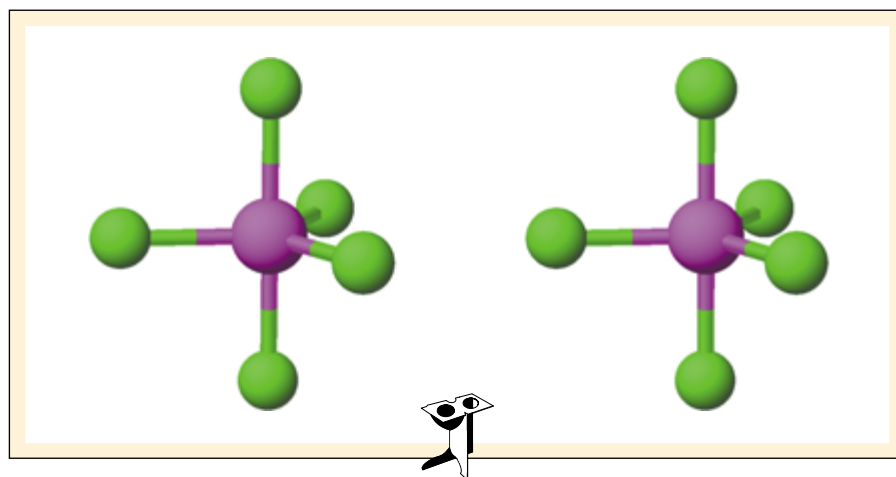
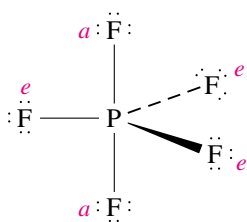
In Section 8-8 we saw that the Group VA elements have five electrons in their outermost occupied shells and form some molecules by sharing only three of these electrons with other atoms (e.g., NH₃, NF₃, and PCl₃). Group VA elements (P, As, and Sb) beyond the second period also form some covalent compounds by sharing all five of their valence electrons with five other atoms (see Section 7-7). Phosphorus pentafluoride, PF₅ (mp -83°C), is such a compound. Each P atom has five valence electrons to share with five F atoms. The Lewis formula for PF₅ (see Example 7-7) is shown in the margin. PF₅ molecules are *trigonal bipyramidal* nonpolar molecules. A **trigonal bipyramid** is a six-sided polyhedron consisting of two pyramids joined at a common triangular (trigonal) base.



A trigonal bipyramid.

B. VSEPR Theory

The VSEPR theory predicts that the five regions of high electron density around the phosphorus atom in PF₅ should be as far apart as possible. Maximum separation of five items around a sixth item is achieved when the five items (bonding pairs) are placed at the corners and the sixth item (P atom) is placed in the center of a trigonal bipyramid. This is in agreement with experimental observation.

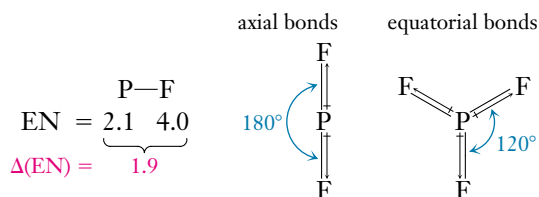


The three F atoms marked *e* are at the corners of the common base, in the same plane as the P atom. These are called *equatorial* F atoms (*e*). The other two F atoms, one above and one below the plane, are called *axial* F atoms (*a*). The F—P—F bond angles are 90° (axial to equatorial), 120° (equatorial to equatorial), and 180° (axial to axial).

The large electronegativity difference between P and F (1.9) suggests very polar bonds. Let's consider the bond dipoles in two groups, because there are two different kinds of P—F bonds in PF₅ molecules, axial and equatorial.

As an exercise in geometry, in how many different ways can five fluorine atoms be arranged *symmetrically* around a phosphorus atom? Compare the hypothetical bond angles in such arrangements with those in a trigonal bipyramidal arrangement.

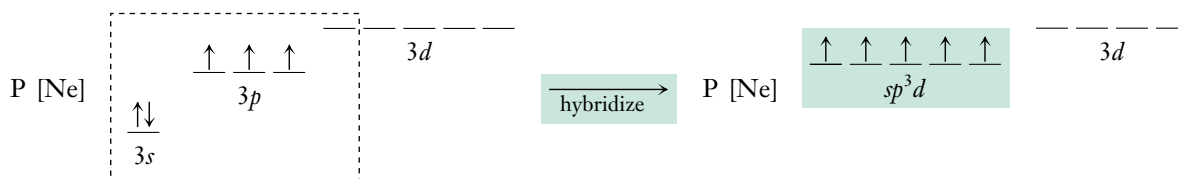
The two axial bonds are in a linear arrangement, like the two bonds in BeCl_2 (see Section 8-5); the three equatorial bonds are in a trigonal planar arrangement, like the three bonds in BF_3 (see Section 8-6).



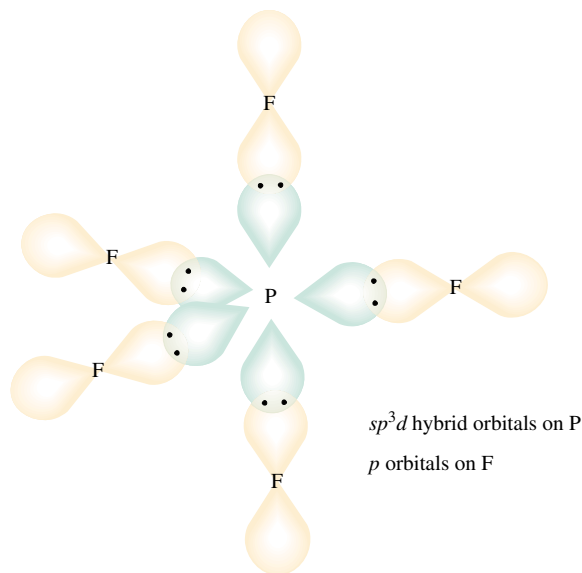
The two axial bond dipoles cancel each other, and the three equatorial bond dipoles cancel, so PF_5 molecules are nonpolar.

C. Valence Bond Theory

Because phosphorus is the central atom in a PF_5 molecule, it must have available five half-filled orbitals to form bonds with five F atoms. Hybridization involves one d orbital from the vacant set of $3d$ orbitals along with the $3s$ and $3p$ orbitals of the P atom.



The five sp^3d hybrid orbitals on P point toward the corners of a trigonal bipyramid. Each is overlapped by a singly occupied $2p$ orbital of an F atom. The resulting pairing of P and F electrons forms five covalent bonds.



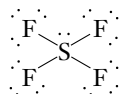
sp^3d Hybridization occurs at the central atom whenever there are five regions of high electron density around the central atom. AB₅ molecules and ions with no unshared pairs on the central atom have trigonal bipyramidal electronic geometry, trigonal bipyramidal molecular geometry, and sp^3d hybridization on the central atom.

We see that sp^3d hybridization uses an available d orbital in the outermost occupied shell of the central atom. The heavier Group VA elements—P, As, and Sb—can form five covalent bonds using this hybridization. But nitrogen, also in Group VA, cannot form five covalent bonds, because the valence shell of N has only one s and three p orbitals (and no d orbitals). The set of s and p orbitals in a given energy level (and therefore any set of hybrids composed only of s and p orbitals) can accommodate a *maximum* of eight electrons and participate in a *maximum* of four covalent bonds. The same is true of all elements of the second period, because they have only s and p orbitals in their valence shells. No atoms in the first and second periods can exhibit expanded valence.

The P atom is said to have an *expanded valence shell* (see Section 7-7).

D. Unshared Valence Electron Pairs in Trigonal Bipyramidal Electronic Geometry

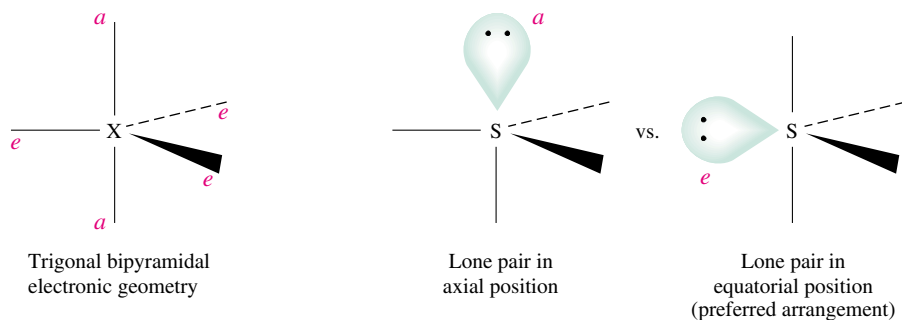
As we saw in Sections 8-8 and 8-9, lone pairs of electrons occupy more space than bonding pairs, resulting in increased repulsions from lone pairs. What happens when one or more of the five regions of high electron density on the central atom are lone pairs? Let us first consider a molecule such as SF₄, for which the Lewis formula is



Reminder: The relative magnitudes of repulsive forces are:

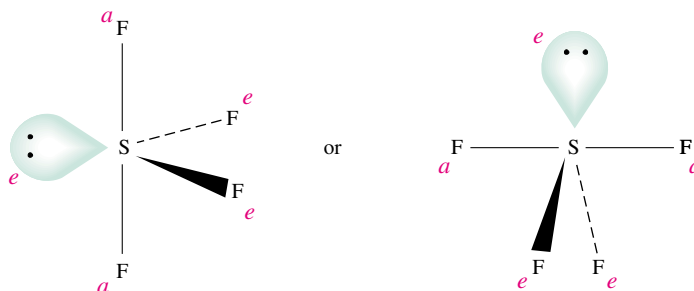
$$lp/lp \gg lp/bp > bp/bp$$

The central atom, S, is bonded to four atoms and has one lone pair. This is an example of the general formula AB₄U. Sulfur has five regions of high electron density, so we know that the electronic geometry is trigonal bipyramidal and that the bonding orbitals are sp^3d hybrids. But now a new question arises: Is the lone (unshared) pair more stable in an axial (a) or in an equatorial (e) position? If it were in an axial position, it would be 90° from



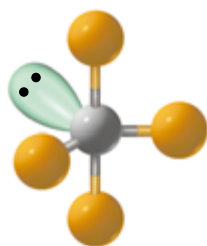
the *three* closest other pairs (the pairs bonding three F atoms in equatorial positions) and 180° from the other axial pair. If it were in an equatorial position, only the *two* axial pairs would be at 90° , and the other two equatorial pairs would be less crowded at 120° apart. The lone pair would be less crowded in an *equatorial* position. The four F atoms then occupy the remaining four positions. We describe the resulting arrangement of *atoms* as a **seesaw arrangement**.

Imagine rotating the arrangement so that the line joining the two axial positions is the board on which the two seesaw riders sit, and the two bonded equatorial positions are the pivot of the seesaw.



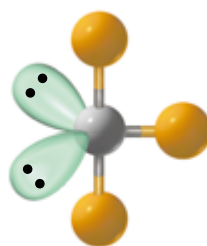
As we saw in Sections 8-8 and 8-9, the differing magnitudes of repulsions involving lone pairs and bonding pairs often result in observed bond angles that are slightly different from idealized values. For instance, *lp/bp* repulsion in the seesaw molecule SF_4 causes distortion of the axial S—F bonds away from the lone pair, to an angle of 177° ; the two equatorial S—F bonds, ideally at 120° , move much closer together to an angle of 101.6° .

By the same reasoning, we understand why additional lone pairs also take equatorial positions (AB_3U_2 with both lone pairs equatorial or AB_2U_3 with all three lone pairs equatorial). These arrangements are summarized in Figure 8-2.



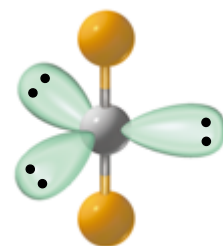
AB_4U 4 bonded atoms (B)
1 lone pair (U) in
equatorial position

Seesaw molecular geometry
Example: SF_4



AB_3U_2 3 bonded atoms (B)
2 lone pairs (U) in
equatorial positions

T-shaped molecular geometry
Examples: ClF_3 , BrF_3



AB_2U_3 2 bonded atoms (B)
3 lone pairs (U) in
equatorial positions

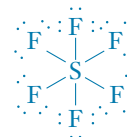
Linear molecular geometry
Examples: XeF_2 , I_3^-

Figure 8-2 Arrangements of bonded atoms and lone pairs (five regions of high electron density—trigonal pyramidal electronic geometry).

8-12 OCTAHEDRAL ELECTRONIC GEOMETRY: AB_6 , AB_5U , AND AB_4U_2

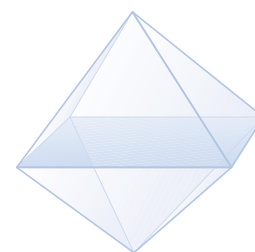
A. Experimental Facts and Lewis Formulas

The Group VIA elements below oxygen form some covalent compounds of the AB_6 type by sharing their six valence electrons with six other atoms. Sulfur hexafluoride, SF_6 (mp -51°C), an unreactive gas, is an example. Sulfur hexafluoride molecules are nonpolar octahedral molecules. The hexafluorophosphate ion, PF_6^- , is an example of a polyatomic ion of the type AB_6 .

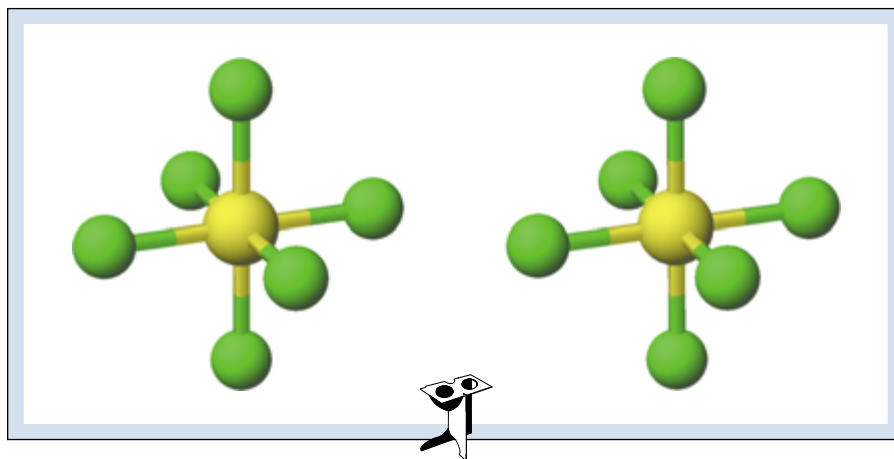
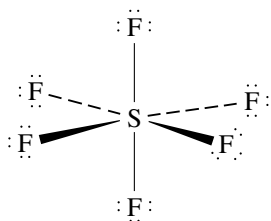


B. VSEPR Theory

In an SF_6 molecule we have six valence shell electron pairs and six F atoms surrounding one S atom. Because the valence shell of sulfur contains no lone pairs, the electronic and molecular geometries in SF_6 are identical. The maximum separation possible for six electron pairs around one S atom is achieved when the electron pairs are at the corners and the S atom is at the center of a regular octahedron. Thus, VSEPR theory is consistent with the observation that SF_6 molecules are **octahedral**.



In a regular octahedron, each of the eight faces is an equilateral triangle.

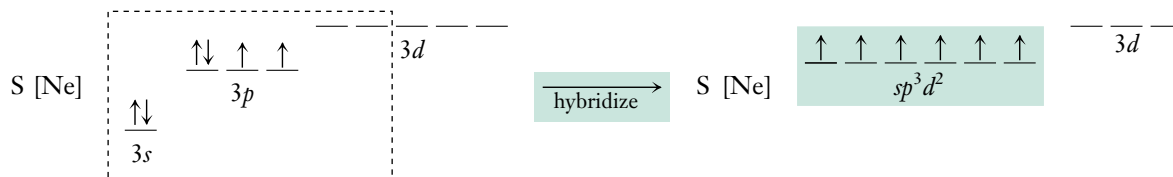


In this octahedral molecule the $F-S-F$ bond angles are 90° and 180° . Each $S-F$ bond is quite polar, but each bond dipole is canceled by an equal dipole at 180° from it. So the large bond dipoles cancel and the SF_6 molecule is nonpolar.

By similar reasoning, VSEPR theory predicts octahedral electronic geometry and octahedral molecular geometry for the PF_6^- ion, which has six valence shell electron pairs and six F atoms surrounding one P atom.

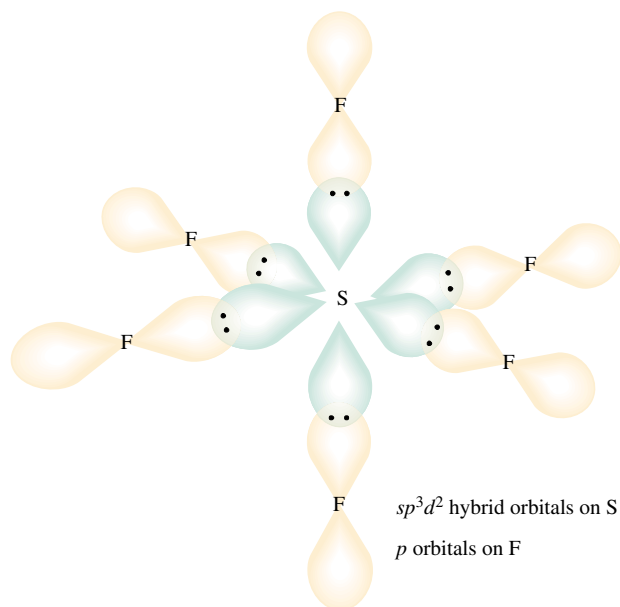
C. Valence Bond Theory

Sulfur atoms can use one $3s$, three $3p$, and two $3d$ orbitals to form six hybrid orbitals that accommodate six electron pairs:



The six sp^3d^2 hybrid orbitals are directed toward the corners of a regular octahedron. Each sp^3d^2 hybrid orbital is overlapped by a half-filled $2p$ orbital from fluorine, to form a total of six covalent bonds.

Se and Te, in the same group, form analogous compounds. O cannot do so, for the same reasons as discussed earlier for N (see Section 8-11).



An analogous picture could be drawn for the PF_6^- ion.

sp^3d^2 Hybridization occurs at the central atom whenever there are six regions of high electron density around the central atom. AB_6 molecules and ions with no lone pairs on the central atom have octahedral electronic geometry, octahedral molecular geometry, and sp^3d^2 hybridization on the central atom.

D. Unshared Valence Electron Pairs in Octahedral Electronic Geometry

We can reason along the lines used in part D of Section 8-11 to predict the preferred locations of lone pairs on the central atom in octahedral electronic geometry. Because of the high symmetry of the octahedral arrangement, all six positions are equivalent, so it does not matter in which position in the drawing we put the first lone pair. AB_5U molecules and ions are described as having **square pyramidal** molecular geometry. When a second lone pair is present, the most stable arrangement has the two lone pairs in two octahedral positions at 180° angles from each other. This leads to a **square planar** molecular geometry for AB_4U_2 species. These arrangements are shown in Figure 8-3. Table 8-3 summarizes a great deal of information—study this table carefully.

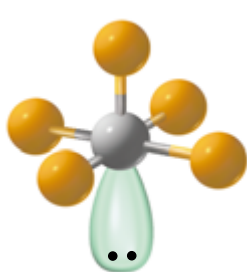
Two lone pairs at 90° from each other would be much more crowded.

✓ Problem-Solving Tip: Placing Lone Pairs on the Central Atom

Remember that lone pairs occupy more space than bonded pairs, so the lone pairs are always put in positions where they will be least crowded.

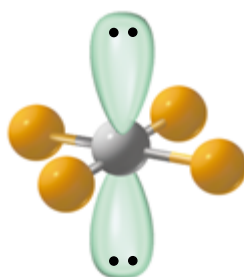
If the Lewis formula for a molecule or ion shows only one lone pair: In linear, trigonal planar, tetrahedral, or octahedral electronic geometry, all positions are equivalent, so it doesn't matter where we place the lone pair. In trigonal bipyramidal electronic geometry, place the lone pair in the equatorial position where it is least crowded, and put the bonded atoms in the other positions.

If the Lewis formula shows two lone pairs: In trigonal planar or tetrahedral electronic geometry, we can place the lone pairs in any two positions and the bonded atoms in the other position(s). In trigonal bipyramidal electronic geometry, place the two lone pairs in two equatorial positions (120° apart) where they are least crowded, and put the bonded atoms in the other positions. In octahedral electronic geometry, place the two lone pairs in two positions *across* (180°) from each other, and put the bonded atoms in the other positions.



AB_5U 5 bonded atoms (B)
1 lone pair (U)

Square pyramidal molecular geometry
Examples: IF_5 , BrF_5



AB_4U_2 4 bonded atoms (B)
2 lone pairs (U)

Square planar molecular geometry
Examples: XeF_4 , IF_4^-

Figure 8-3 Arrangements of bonded atoms and lone pairs (six regions of high electron density—octahedral electronic geometry).

TABLE 8-3 *Molecular Geometry of Species with Lone Pairs (U) on the Central Atom*


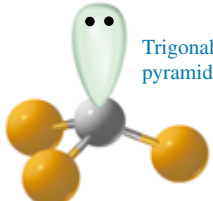
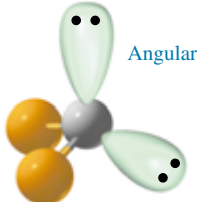
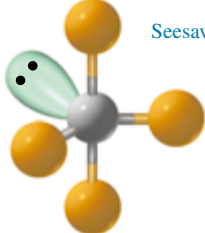
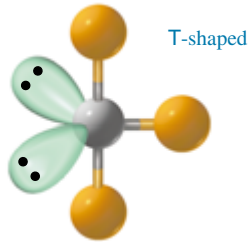
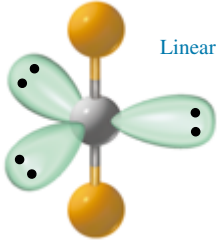
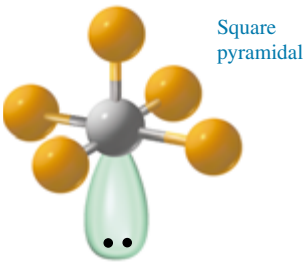
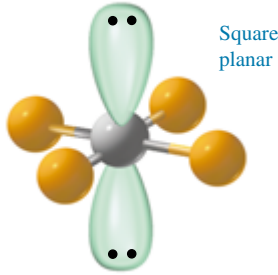
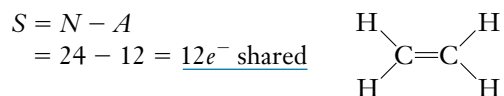
General Formula	Regions of High Electron Density	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB_2U	3	trigonal planar	sp^2	1	Angular 	O_3 , NO_2^- , SO_2
AB_3U	4	tetrahedral	sp^3	1	Trigonal pyramidal 	NH_3 , SO_3^{2-}
AB_2U_2	4	tetrahedral	sp^3	2	Angular 	H_2O , NH_2^-
AB_4U	5	trigonal bipyramidal	sp^3d	1	Seesaw 	SF_4

TABLE 8-3 (continued)

General Formula	Regions of High Electron Density	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB ₃ U ₂	5	trigonal bipyramidal	sp^3d	2	 T-shaped	ICl ₃ , ClF ₃
AB ₂ U ₃	5	trigonal bipyramidal	sp^3d	3	 Linear	XeF ₂ , I ₃ ⁻
AB ₅ U	6	octahedral	sp^3d^2	1	 Square pyramidal	IF ₅ , BrF ₅
AB ₄ U ₂	6	octahedral	sp^3d^2	2	 Square planar	XeF ₄ , IF ₄ ⁻

8-13 COMPOUNDS CONTAINING DOUBLE BONDS

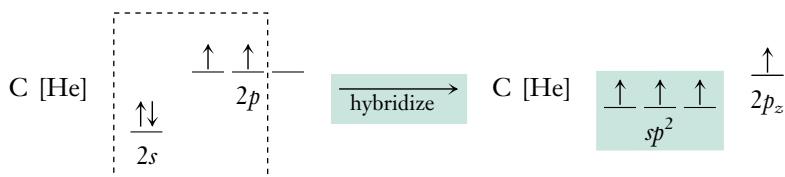
In Chapter 7 we constructed Lewis formulas for some molecules and polyatomic ions that contain double and triple bonds. We have not yet considered bonding and shapes for such species. Let us consider ethylene (ethene), C_2H_4 , as a specific example. Its dot formula is



Here each C atom is considered a central atom. Remember that each bonded atom counts as *one* region of high electron density.

Each atom has three regions of high electron density. The VSEPR theory tells us that each C atom is at the center of a trigonal plane.

Valence bond theory pictures each doubly bonded carbon atom as sp^2 hybridized, with one electron in each sp^2 hybrid orbital and one electron in the unhybridized $2p$ orbital. This $2p$ orbital is perpendicular to the plane of the three sp^2 hybrid orbitals:



An important use of ethylene, C_2H_4 , is in the manufacture of polyethylene, a nonbreakable, nonreactive plastic.

Recall that sp^2 hybrid orbitals are directed toward the corners of an equilateral triangle. Figure 8-4 shows top and side views of these hybrid orbitals.

The two C atoms interact by head-on (end-to-end) overlap of sp^2 hybrids pointing toward each other to form a *sigma* (σ) bond and by side-on overlap of the unhybridized $2p$ orbitals to form a *pi* (π) bond.

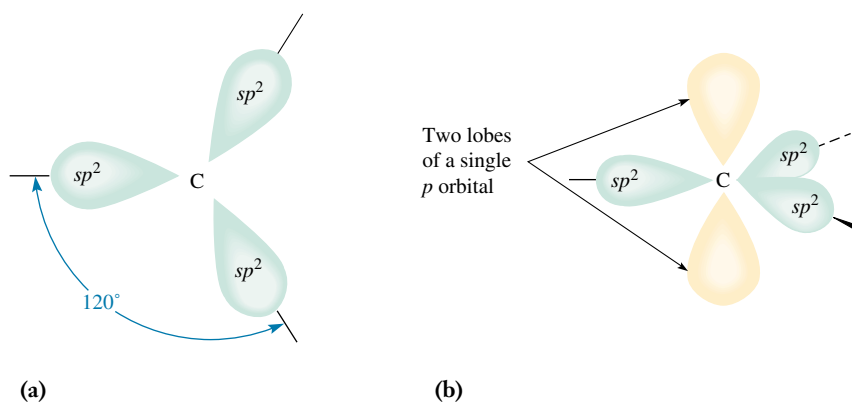


Figure 8-4 (a) A top view of three sp^2 hybrid orbitals (*green*). The remaining unhybridized p orbital (not shown in this view) is perpendicular to the plane of the drawing. (b) A side view of a carbon atom in a trigonal planar (sp^2 -hybridized) environment, showing the remaining p orbital (*tan*). This p orbital is perpendicular to the plane of the three sp^2 hybrid orbitals.

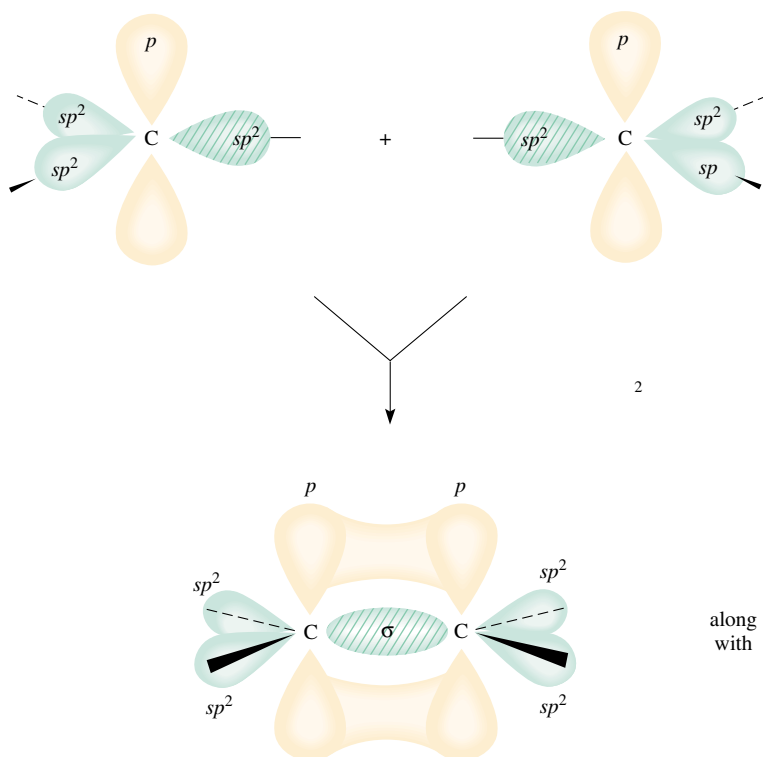


Figure 8-5 A schematic representation of the formation of a carbon-carbon double bond. Two sp^2 -hybridized carbon atoms form a sigma (σ) bond by overlap of two sp^2 orbitals (green, hatched) and a pi (π) bond by overlap of properly aligned p orbitals (tan). All orbitals are fatter than shown here.

A **sigma bond** is a bond resulting from head-on overlap of atomic orbitals. *The region of electron sharing is along and cylindrically around an imaginary line connecting the bonded atoms.*

See the Saunders Interactive General Chemistry CD-ROM, Screen 10.5, Sigma Bonds.

All single bonds are sigma bonds. Many kinds of pure atomic orbitals and hybridized orbitals can be involved in sigma bond formation.

A **pi bond** is a bond resulting from side-on overlap of atomic orbitals. *The regions of electron sharing are on opposite sides of an imaginary line connecting the bonded atoms and parallel to this line.*

See the Saunders Interactive General Chemistry CD-ROM, Screen 10.7, Multiple Bonding.

A pi bond can form *only* if there is *also* a sigma bond between the same two atoms. The sigma and pi bonds together make a double bond (Figure 8-5). The $1s$ orbitals (with one e^- each) of four hydrogen atoms overlap the remaining four sp^2 orbitals (with one e^- each) on the carbon atoms to form four C—H sigma bonds (Figure 8-6).

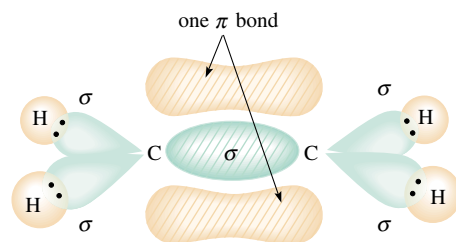


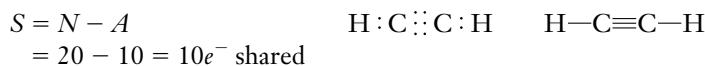
Figure 8-6 Four C—H σ bonds, one C—C σ bond (green, hatched), and one C—C π bond (tan, hatched) in the planar C_2H_4 molecule.

A double bond consists of one sigma bond and one pi bond.

As a consequence of the sp^2 hybridization of C atoms in carbon-carbon double bonds, each carbon atom is at the center of a trigonal plane. The p orbitals that overlap to form the π bond must be parallel to each other for effective overlap to occur. This adds the further restriction that these trigonal planes (sharing a common corner) must also be *coplanar*: Thus, all four atoms attached to the doubly bonded C atoms lie in the same plane (see Figure 8-6). Many other important organic compounds contain carbon-carbon double bonds. Several are described in Chapter 27.

8-14 COMPOUNDS CONTAINING TRIPLE BONDS

One compound that contains a triple bond is ethyne (acetylene), C_2H_2 . Its Lewis formula is



The VSEPR theory predicts that the two regions of high electron density around each carbon atom are 180° apart.

Each triple-bonded carbon atom has two regions of high electron density, so valence bond theory postulates that each is sp hybridized (see Section 8-5). Let us designate the p_x orbitals as the ones involved in hybridization. Carbon has one electron in each sp hybrid orbital and one electron in each of the $2p_y$ and $2p_z$ orbitals (before bonding is considered). See Figure 8-7.

The three p orbitals in a set are indistinguishable. We can label the one involved in hybridization as " p_x " to help us visualize the orientations of the two unhybridized p orbitals on carbon.

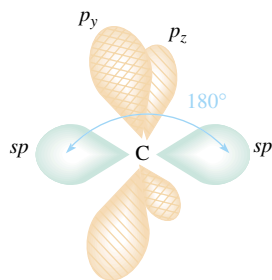
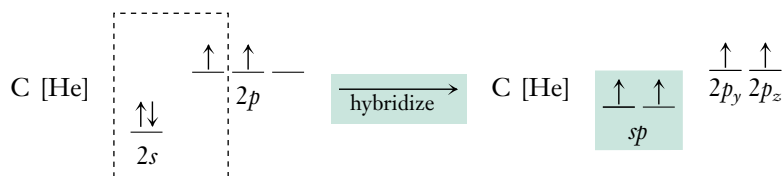


Figure 8-7 Diagram of the two linear hybridized sp orbitals (green) of an atom. These lie in a straight line, and the two unhybridized p orbitals p_y (tan, cross-hatched) and p_z (tan, hatched) lie in the perpendicular plane and are perpendicular to each other.

The two carbon atoms form one sigma bond by head-on overlap of the sp hybrid orbitals; each C atom also forms a sigma bond with one H atom. The sp hybrids on each atom are 180° apart. Thus, the entire molecule must be linear.



The unhybridized atomic $2p_y$ and $2p_z$ orbitals are perpendicular to each other and to the line through the centers of the two sp hybrid orbitals (Figure 8-8). The side-on overlap of the $2p_y$ orbitals on the two C atoms forms one pi bond; the side-on overlap of the $2p_z$ orbitals forms another pi bond.

A triple bond consists of one sigma bond and two pi bonds.

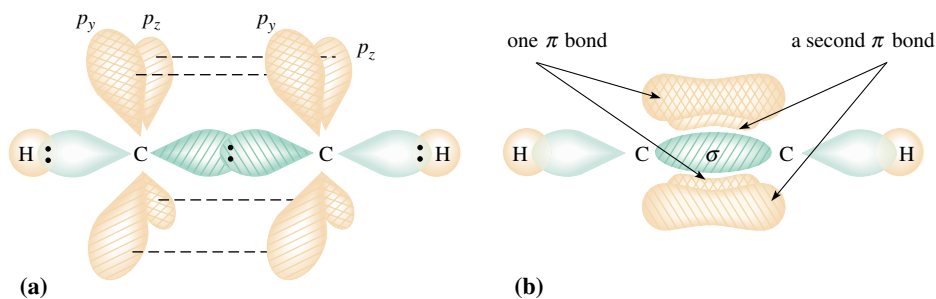


Figure 8-8 The acetylene molecule, C₂H₂. (a) The overlap diagram of two *sp*-hybridized carbon atoms and two *s* orbitals from two hydrogen atoms. The hybridized *sp* orbitals on each C are shown in green and the unhybridized *p* orbitals are shown in tan. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized *p* orbitals to form two π bonds. There are two C—H σ bonds, one C—C σ bond (*green, hatched*), and two C—C π bonds (*hatched and cross-hatched*). This makes the net carbon–carbon bond a triple bond. (b) The π bonding orbitals (*tan*) are positioned with one above and below the line of the σ bonds (*green*) and the other behind and in front of the line of the σ bonds.

Some other molecules containing triply bonded atoms are nitrogen, :N≡N:, hydrogen cyanide, H—C≡N:, and propyne, CH₃—C≡C—H. In each case, both atoms involved in the triple bonds are *sp* hybridized. In the triple bond, each atom participates in one sigma and two pi bonds. The C atom in carbon dioxide, :O=C=O:, must participate in two pi bonds (to two different O atoms). It also participates in two sigma bonds, so it is also *sp* hybridized and the molecule is linear.

In propyne, the C atom in the CH₃ group is *sp*³ hybridized and at the center of a tetrahedral arrangement.

8-15 A SUMMARY OF ELECTRONIC AND MOLECULAR GEOMETRIES

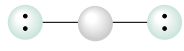

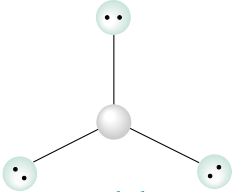
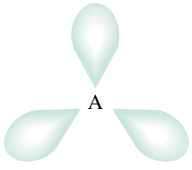
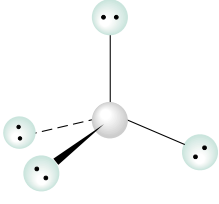
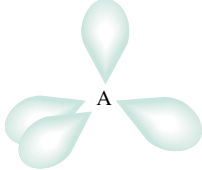
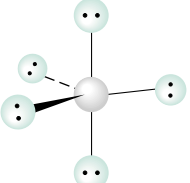
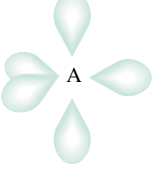
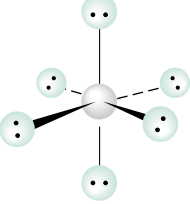
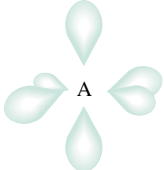
We have discussed several common types of polyatomic molecules and ions, and provided a reasonable explanation for the observed structures and polarities of these species. Table 8-4 provides a summation.

Our discussion of covalent bonding illustrates two important points:

1. Molecules and polyatomic ions have definite shapes.
2. The properties of molecules and polyatomic ions are determined to a great extent by their shapes. Incompletely filled electron shells and unshared pairs of electrons on the central element are very important.

Our ideas about chemical bonding have developed over many years. As experimental techniques for determining the *structures* of molecules have improved, our understanding of chemical bonding has improved also. Experimental observations on molecular geometry support our ideas about chemical bonding. The ultimate test for any theory is this: Can

TABLE 8-4 A Summary of Electronic and Molecular Geometries of Polyatomic Molecules and Ions

Regions of High Electron Density ^a	Electronic Geometry	Hybridization at Central Atom (Angles)	Hybridized Orbital Orientation	Examples	Molecular Geometry
2	 linear	sp (180°)		BeCl ₂ HgBr ₂ CdI ₂ CO ₂ ^b C ₂ H ₂ ^c	linear linear linear linear
3	 trigonal planar	sp^2 (120°)		BF ₃ BCl ₃ NO ₃ ^{-e} SO ₂ ^{d,e} NO ₂ ^{-d,e} C ₂ H ₄ ^f	trigonal planar trigonal planar trigonal planar angular (AB ₂ U) angular (AB ₂ U) planar (trig. planar at each C)
4	 tetrahedral	sp^3 (109.5°)		CH ₄ CCl ₄ NH ₄ ⁺ SO ₄ ²⁻ CHCl ₃ NH ₃ ^d SO ₃ ^{2-d} H ₃ O ^{+d} H ₂ O ^d	tetrahedral tetrahedral tetrahedral tetrahedral distorted tet. pyramidal (AB ₃ U) pyramidal (AB ₃ U) pyramidal (AB ₃ U) angular (AB ₂ U ₂)
5	 trigonal bipyramidal	sp^3d (90°, 120°, 180°)		PF ₅ SbCl ₅ SF ₄ ^d ClF ₃ ^d XeF ₂ ^d I ₃ ^{-d}	trigonal bipyramidal trigonal bipyramidal seesaw (AB ₄ U) T-shaped (AB ₃ U ₂) linear (AB ₂ U ₃) linear (AB ₂ U ₃)
6	 octahedral	sp^3d^2 (90°, 180°)		SF ₆ SeF ₆ PF ₆ ⁻ BrF ₅ ^d XeF ₄ ^d	octahedral octahedral octahedral square pyramidal (AB ₅ U) square planar (AB ₄ U ₂)

^aThe number of locations of high electron density around the central atom. A region of high electron density may be a single bond, a double bond, a triple bond, or an unshared pair. These determine the electronic geometry, and thus the hybridization of the central atom.

^bContains two double bonds.

^cContains a triple bond.

^dCentral atom in molecule or ion has unshared pair(s) of electrons.

^eBonding involves resonance.

^fContains one double bond.

it correctly predict the results of experiments before they are performed? When the answer is *yes*, we have confidence in the theory. When the answer is *no*, the theory must be modified. Current theories of chemical bonding enable us to make predictions that are usually accurate.

Key Terms

- Angular** A term used to describe the molecular geometry of a molecule that has two atoms bonded to a central atom and one or more unshared pairs on the central atom (AB_2U or AB_2U_2). Also called *V-shaped* or *bent*.
- Central atom** An atom in a molecule or polyatomic ion that is bonded to more than one other atom.
- Electronic geometry** The geometric arrangement of orbitals containing the shared and unshared electron pairs surrounding the central atom of a molecule or polyatomic ion.
- Hybridization** The mixing of a set of atomic orbitals on an atom to form a new set of hybrid orbitals with the same total electron capacity and with properties and energies intermediate between those of the original unhybridized orbitals.
- Hybrid orbitals** Orbitals formed on an atom by the process of hybridization.
- Lewis formula** A method of representing a molecule or formula unit by showing atoms and only outer-shell electrons; does not show shape.
- Linear** A term used to describe the electronic geometry around a central atom that has two regions of high electron density. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to two atoms on opposite sides (180°) of the central atom (AB_2 or AB_2U_3).
- Molecular geometry** The arrangement of atoms (*not* unshared pairs of electrons) around a central atom of a molecule or polyatomic ion.
- Octahedral** A term used to describe the electronic geometry around a central atom that has six regions of high electron density. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to six atoms at the corners of an octahedron (AB_6).
- Octahedron** A polyhedron with eight equal-sized, equilateral triangular faces and six apices (corners).
- Overlap of orbitals** The interaction of orbitals on different atoms in the same region of space.
- Pi (π) bond** A bond resulting from the side-on overlap of atomic orbitals, in which the regions of electron sharing are on opposite sides of and parallel to an imaginary line connecting the bonded atoms.
- Seesaw** A term used to describe the molecular geometry of a molecule or polyatomic ion that has four atoms bonded to a central atom and one unshared pair on the central atom (AB_4U).
- Sigma (σ) bond** A bond resulting from the head-on overlap of atomic orbitals, in which the region of electron sharing is along and (cylindrically) symmetrical to an imaginary line connecting the bonded atoms.
- Square planar** A term used to describe molecules and polyatomic ions that have one atom in the center and four atoms at the corners of a square.
- Square pyramidal** A term used to describe the molecular geometry of a molecule or polyatomic ion that has five atoms bonded to a central atom and one unshared pair on the central atom (AB_5U).
- Tetrahedral** A term used to describe the electronic geometry around a central atom that has four regions of high electron density. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to four atoms at the corners of a tetrahedron (AB_4).
- Tetrahedron** A polyhedron with four equal-sized, equilateral triangular faces and four apices (corners).
- Trigonal bipyramid** A six-sided polyhedron with five apices (corners), consisting of two pyramids sharing a common triangular base.
- Trigonal bipyramidal** A term used to describe the electronic geometry around a central atom that has five regions of high electron density. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to five atoms at the corners of a trigonal bipyramid (AB_5).
- Trigonal planar (also plane triangular)** A term used to describe the electronic geometry around a central atom that has three regions of high electron density. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to three atoms at the corners of an equilateral triangle (AB_3).
- Trigonal pyramidal** A term used to describe the molecular geometry of a molecule or polyatomic ion that has three atoms bonded to a central atom and one unshared pair on the central atom (AB_3U).
- T-shaped** A term used to describe the molecular geometry of a molecule or polyatomic ion that has three atoms bonded to a central atom and two unshared pairs on the central atom (AB_3U_2).
- Valence bond (VB) theory** Assumes that covalent bonds are formed when atomic orbitals on different atoms overlap and electrons are shared.
- Valence shell** The outermost occupied electron shell of an atom.
- Valence shell electron pair repulsion (VSEPR) theory** Assumes that valence electron pairs are arranged around the central element of a molecule or polyatomic ion so that there is maximum separation (and minimum repulsion) among regions of high electron density.

Exercises

VSEPR Theory: General Concepts

1. State in your own words the basic idea of the VSEPR theory.
2. (a) Distinguish between “lone pairs” and “bonding pairs” of electrons. (b) Which has the greater spatial requirement? How do we know this? (c) Indicate the order of increasing repulsions among lone pairs and bonding pairs of electrons.
3. Identify the central atom (or atoms) in each of the following compounds or ions: (a) H_2SO_4 ; (b) NH_3 ; (c) NH_4^+ ; (d) AlCl_3 ; (e) CH_3NH_2 ; (f) CdCl_2 .
4. Identify the central atom (or atoms) in each of the following compounds or ions: (a) HCO_3^- ; (b) SiO_2 ; (c) SO_3 ; (d) $\text{Al}(\text{OH})_4^-$; (e) BeBr_2 ; (f) $(\text{CH}_3)_4\text{Pb}$.
5. Distinguish between electronic geometry and molecular geometry.
6. Under what conditions is molecular (or ionic) geometry identical to electronic geometry about a central atom?
7. What two shapes can a triatomic species have? How would the electronic geometries for the two shapes differ?
8. How are double and triple bonds treated when the VSEPR theory is used to predict molecular geometry? How is a single unshared electron treated?
9. Sketch the three different possible arrangements of the three B atoms around the central atom A for the molecule AB_3U_2 . Which of these structures correctly describes the molecular geometry? Why? What are the predicted ideal bond angles? How would observed bond angles deviate from these values?
10. Sketch the three different possible arrangements of the two B atoms around the central atom A for the molecule AB_2U_3 . Which of these structures correctly describes the molecular geometry? Why?

Valence Bond Theory: General Concepts

11. What are hybridized atomic orbitals? How is the theory of hybridized orbitals useful?
12. (a) What is the relationship between the number of regions of high electron density on an atom and the number of its pure atomic orbitals that hybridize? (b) What is the relationship between the number of atomic orbitals that hybridize and the number of hybrid orbitals formed?
13. (a) What is the maximum number of bonds that an atom can form without expanding its valence shell? (b) What must be true of the electron configuration of an element for it to be able to expand its valence shell? (c) Tell which of the following elements can expand its valence shell: N, O, F, P, S, Cl.
14. Prepare sketches of the overlaps of the following atomic orbitals: (a) s with s ; (b) s with p along the bond axis; (c) p with p along the bond axis (head-on overlap); (d) p with p perpendicular to the bond axis (side-on overlap).
15. Prepare a sketch of the cross-section (through the atomic centers) taken between two atoms that have formed (a) a single σ bond, (b) a double bond consisting of a σ bond and a π bond, and (c) a triple bond consisting of a σ bond and two π bonds.
16. Prepare sketches of the orbitals around atoms that are (a) sp , (b) sp^2 , (c) sp^3 , (d) sp^3d , and (e) sp^3d^2 hybridized. Show in the sketches any unhybridized p orbitals that might participate in multiple bonding.
17. What hybridization is associated with these electronic geometries: trigonal planar; linear; tetrahedral; octahedral; trigonal bipyramidal?
18. What angles are associated with orbitals in the following sets of hybrid orbitals? (a) sp ; (b) sp^2 ; (c) sp^3 ; (d) sp^3d ; (e) sp^3d^2 . Sketch each.
19. What types of hybridization would you predict for molecules having the following general formulas? (a) AB_4 ; (b) AB_2U_3 ; (c) AB_3U ; (d) ABU_4 ; (e) ABU_3 .
20. Repeat Exercise 19 for (a) ABU_5 ; (b) AB_2U_4 ; (c) AB_3 ; (d) AB_3U_2 ; (e) AB_5 .
21. What are the primary factors on which we base a decision on whether the bonding in a molecule is better described in terms of simple orbital overlap or overlap involving hybridized atomic orbitals?

Electronic and Molecular Geometry

22. Write a Lewis formula for each of the following species. Indicate the number of regions of high electron density and the electronic and molecular or ionic geometries. (a) CdCl_2 ; (b) SnCl_4 ; (c) BrF_3 ; (d) SbF_6^- .
23. Write a Lewis formula for each of the following species. Indicate the number of regions of high electron density and the electronic and molecular or ionic geometries. (a) BF_3 ; (b) SO_2 ; (c) IO_3^- ; (d) SiCl_4 ; (e) SeF_6 .
24. (a) What would be the ideal bond angles in each molecule or ion in Exercise 22, ignoring lone pair effects? (b) How do these differ, if at all, from the actual values? Why?
25. (a) What would be the ideal bond angles in each molecule or ion in Exercise 23, ignoring lone pair effects? (b) Are these values greater than, less than, or equal to the actual values? Why?
26. The elements in Group IIA form compounds, such as Cl—Be—Cl , that are linear and, therefore, nonpolar. What is the hybridization at the central atoms?
27. The elements in Group IIIA form compounds, such as AlCl_3 , that are planar and, therefore, nonpolar. What is the hybridization at the central atoms?
28. Carbon forms two common oxides, CO and CO_2 . It also forms a third (very uncommon) oxide, carbon suboxide, C_3O_2 , which is linear. The structure has terminal oxygen atoms on both ends. Write the Lewis formula for C_3O_2 .

How many regions of high electron density are there about each of the three carbon atoms?

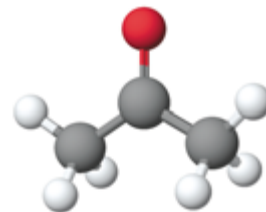
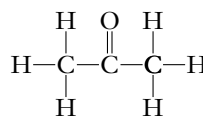
29. Pick the member of each pair that you would expect to have the smaller bond angles, if different, and explain why. (a) SF_2 and SO_2 ; (b) BF_3 and BCl_3 ; (c) SiF_4 and SF_4 ; (d) NF_3 and OF_2 .
30. Draw a Lewis formula, sketch the three-dimensional shape, and name the electronic and ionic geometries for the following polyatomic ions. (a) H_3O^+ ; (b) PCl_6^- ; (c) PCl_4^- ; (d) SbCl_4^+ .
31. As the name implies, the interhalogens are compounds that contain two halogens. Write Lewis formulas and three-dimensional structures for the following. Name the electronic and molecular geometries of each. (a) BrF_3 ; (b) BrF ; (c) BrF_5 .
32. A number of ions derived from the interhalogens are known. Write Lewis formulas and three-dimensional structures for the following ions. Name the electronic and molecular geometries of each. (a) IF_4^+ ; (b) ICl_4^- ; (c) BrF_4^- ; (d) ClF_3^{2-} .
- *33. (a) Write a Lewis formula for each of the following molecules: BF_3 ; NF_3 ; ClF_3 . (b) Contrast the molecular geometries of these three molecules. Account for differences in terms of the VSEPR theory.
- *34. (a) Write a Lewis formula for each of the following molecules: SiF_4 ; SF_4 ; XeF_4 . (b) Contrast the molecular geometries of these three molecules. Account for differences in terms of the VSEPR theory.
35. Write the Lewis formulas and predict the shapes of these very reactive carbon-containing species: H_3C^+ (a carbocation); H_3C^- (a carbanion); and $:\text{CH}_2$ (a carbene whose unshared electrons are paired).
36. Write the Lewis formulas and predict the shapes of (a) I_3^- ; (b) TeCl_4 ; (c) XeO_3 ; (d) NOBr (N is the central atom); (e) NO_2Cl (N is the central atom); (f) SOCl_2 (S is the central atom).
37. Describe the shapes of these polyatomic ions: (a) BO_3^{3-} ; (b) AsO_4^{3-} ; (c) SO_3^{2-} ; (d) NO_3^- .
38. Would you predict a nitrogen–oxygen bond to have the same magnitude of bond polarity as a hydrogen–oxygen bond? Explain your answer.
39. Which of the following molecules are polar? Why? (a) CH_4 ; (b) CH_3Br ; (c) CH_2Br_2 ; (d) CHBr_3 ; (e) CBr_4 .
40. Which of the following molecules are polar? Why? (a) CdI_2 ; (b) BCl_3 ; (c) AsCl_3 ; (d) H_2O ; (e) SF_6 .
41. Which of the following molecules are nonpolar? Justify your answer. (a) SO_3 ; (b) IF ; (c) Cl_2O ; (d) NF_3 ; (e) CHCl_3 .
42. The PF_2Cl_3 molecule is nonpolar. Use this information to sketch its three-dimensional shape. Justify your choice.
- *43. In what two major ways does the presence of unshared pairs of valence electrons affect the polarity of a molecule? Describe two molecules for which the presence of unshared pairs on the central atom helps to make the molecules polar. Can you think of a bonding arrangement that has

unshared pairs of valence electrons on the central atom but that is nonpolar?

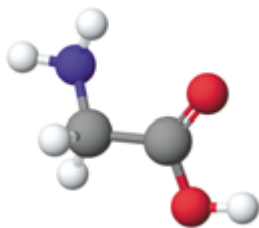
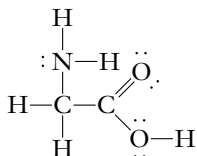
44. Is the phosphorus–chlorine bond in phosphorus trichloride a polar bond? Is phosphorus trichloride a polar molecule? Explain.
45. Is the phosphorus–chlorine bond in phosphorus pentachloride a polar bond? Is phosphorus pentachloride a polar molecule? Explain.
46. Write the Lewis formula for each of the following. Indicate which bonds are polar. (See Table 6-3.) Indicate which molecules are polar. (a) CS_2 ; (b) AlF_3 ; (c) H_2S ; (d) SnF_2 .
47. Write the Lewis formula for each of the following. Indicate which bonds are polar. (See Table 6-3.) Indicate which molecules are polar. (a) OF_2 ; (b) CH_4 ; (c) H_2SO_4 ; (d) SnF_4 .

Valence Bond Theory

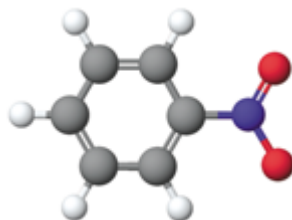
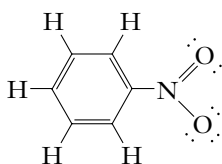
48. Describe the orbital overlap model of covalent bonding.
49. Briefly summarize the reasoning by which we might have predicted that the formula of the simplest stable hydrocarbon would be CH_2 , if we did not consider hybridization. Would this species satisfy the octet rule?
50. What is the hybridization of the central atom in each of the following? (a) NCl_3 ; (b) molecular AlCl_3 ; (c) CF_4 ; (d) SF_6 ; (e) IO_4^- .
51. What is the hybridization of the central atom in each of the following? (a) IF_4^- ; (b) SiO_4^{4-} ; (c) AlH_4^- ; (d) NH_4^+ ; (e) PCl_3 ; (f) ClO_3^- .
52. (a) Describe the hybridization of the central atom in each of these covalent species. (1) CHCl_3 ; (2) CH_2Cl_2 ; (3) NF_3 ; (4) PO_4^{3-} ; (5) IF_6^+ ; (6) SiF_6^{2-} . (b) Give the shape of each species.
53. Describe the hybridization of the underlined atoms in $\underline{\text{C}}_2\text{F}_6$, $\underline{\text{C}}_2\text{F}_2$, $\underline{\text{N}}_2\text{F}_4$, and $(\text{H}_2\underline{\text{N}})_2\underline{\text{C}}\text{O}$.
54. Prepare a sketch of the molecule $\text{CH}_3\text{CH}=\text{CH}_2$ showing orbital overlaps. Identify the type of hybridization of atomic orbitals on each carbon atom.
- *55. After comparing experimental and calculated dipole moments, Charles A. Coulson suggested that the Cl atom in HCl is sp hybridized. (a) Give the orbital electronic structure for an sp hybridized Cl atom. (b) Which HCl molecule would have a larger dipole moment—one in which the chlorine uses pure p orbitals for bonding with the H atom or one in which sp hybrid orbitals are used?
- *56. Predict the hybridization at each carbon atom in each of the following molecules.
(a) acetone (a common solvent)



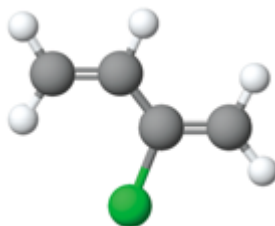
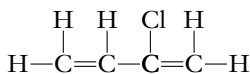
(b) glycine (an amino acid)



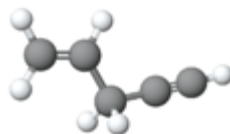
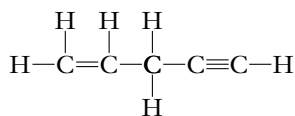
(c) nitrobenzene



(d) chloroprene (used to make neoprene, a synthetic rubber)

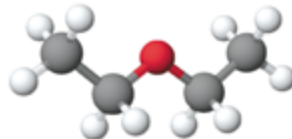
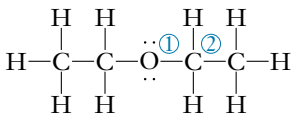


(e) 4-penten-1-yne

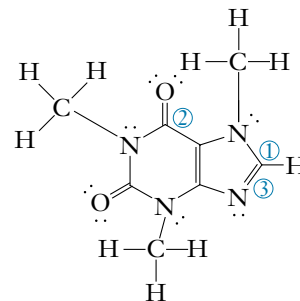


*57. Predict the hybridization at the numbered atoms (①, ②, and so on) in the following molecules and predict the approximate bond angles at those atoms.

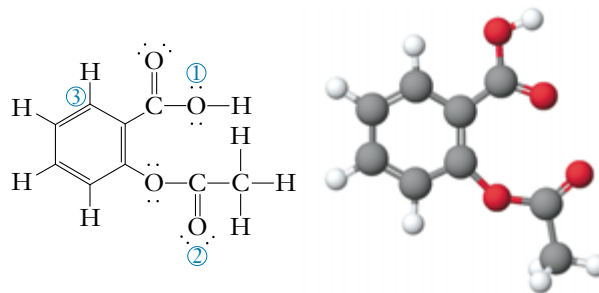
(a) diethyl ether, an anesthetic



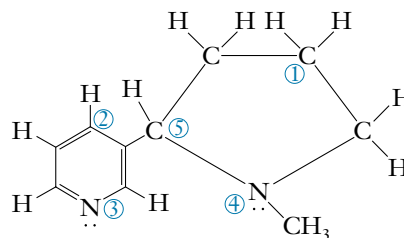
(b) caffeine, a stimulant in coffee and in many over-the-counter medicinals¹



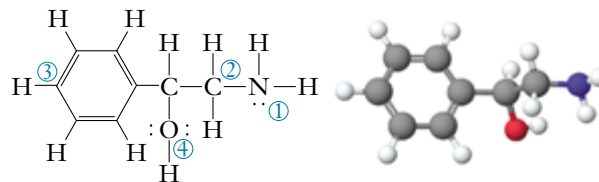
(c) acetylsalicylic acid (aspirin)¹



(d) nicotine¹

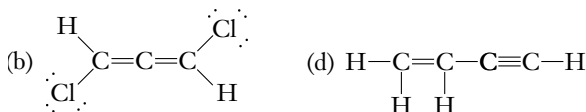
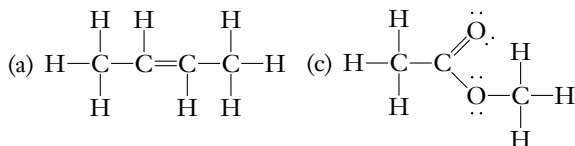


(e) ephedrine, a nasal decongestant¹

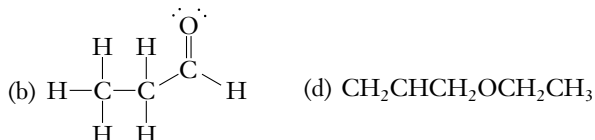
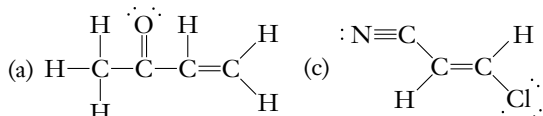


¹In these kinds of structural drawings, each intersection of lines represents a C atom.

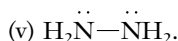
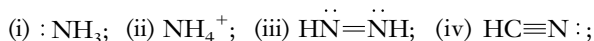
58. How many sigma and how many pi bonds are there in each of the following molecules?



- *59. How many sigma and how many pi bonds are there in each of the following molecules?



60. Describe the bonding in the carbide ion, C_2^{2-} , with a three-dimensional VB structure. Show the orbital overlap, and label the orbitals.
61. Write Lewis formulas for molecular oxygen and ozone. Assuming that all of the valence electrons in the oxygen atoms are in hybrid orbitals, what would be the hybridization of the oxygen atoms in each substance? Prepare sketches of the molecules.
- *62. Draw a Lewis formula and a three-dimensional structure for each of the following polycentered molecules. Indicate hybridizations and bond angles at each carbon atom. (a) butane, C_4H_{10} ; (b) propene, $\text{H}_2\text{C}=\text{CHCH}_3$; (c) 1-butyne, $\text{HC}\equiv\text{CCH}_2\text{CH}_3$; (d) acetaldehyde, CH_3CHO .
63. How many σ bonds and how many π bonds are there in each of the molecules of Exercise 62?
64. (a) Describe the hybridization of N in each of these species.

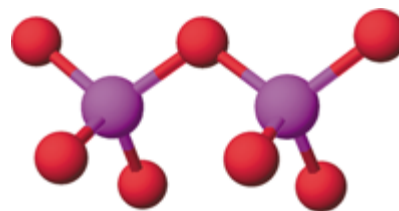


- (b) Give an orbital description for each species, specifying the location of any unshared pairs and the orbitals used for the multiple bonds.

65. Write the Lewis formulas and predict the hybrid orbitals and the shapes of these polyatomic ions and covalent molecules: (a) HgCl_2 ; (b) BF_3 ; (c) BF_4^- ; (d) SbCl_5 ; (e) SbF_6^- .
66. (a) What is the hybridization of each C in these molecules? (i) $\text{H}_2\text{C}=\text{O}$; (ii) $\text{HC}\equiv\text{N}$; (iii) $\text{CH}_3\text{CH}_2\text{CH}_3$; (iv) ketene, $\text{H}_2\text{C}=\text{C}=\text{O}$. (b) Describe the shape of each molecule.
- *67. The following fluorides of xenon have been well characterized: XeF_2 , XeF_4 , and XeF_6 . (a) Write Lewis formulas for these substances and decide what type of hybridization of the Xe atomic orbitals has taken place. (b) Draw all of the possible atomic arrangements of XeF_2 , and discuss your choice of molecular geometry. (c) What shape do you predict for XeF_4 ?
- *68. Iodine and fluorine form a series of interhalogen molecules and ions. Among these are IF (minute quantities observed spectroscopically), IF_3 , IF_4^- , IF_5 , IF_6^- , and IF_7 . (a) Write Lewis formulas for each of these species. (b) Identify the hybridization that the orbitals of the iodine atom have undergone in each substance. (c) Identify the shape of the molecule or ion.

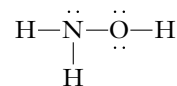
Mixed Exercises

69. In the pyrophosphate ion, $\text{P}_2\text{O}_7^{4-}$, one oxygen atom is bonded to both phosphorus atoms.

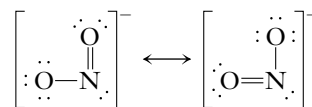


Write a Lewis formula, and sketch the three-dimensional shape of the ion. Describe the electronic and molecular geometries with respect to the central O atom and with respect to each P atom.

70. Briefly discuss the bond angles in the hydroxylamine molecule in terms of the ideal geometry and the small changes caused by electron-pair repulsions.



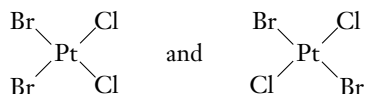
71. Repeat Exercise 70 for the nitrite ion.



- *72. The methyl free radical $\cdot\text{CH}_3$ has bond angles of about 120° , whereas the methyl carbanion :CH_3^- has bond

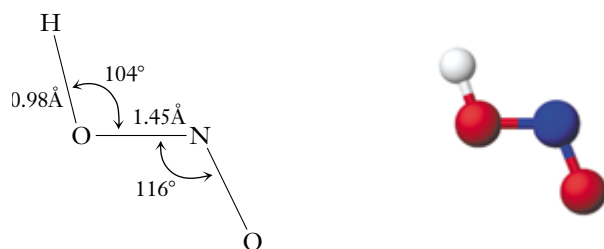
angles of about 109° . What can you infer from these facts about the repulsive force exerted by an unpaired, unshared electron as compared with that exerted by an unshared pair of electrons?

- *73. Two Lewis structures can be written for the square planar molecule PtCl_2Br_2 :

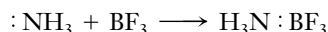


Show how a difference in dipole moments can distinguish between these two possible structures.

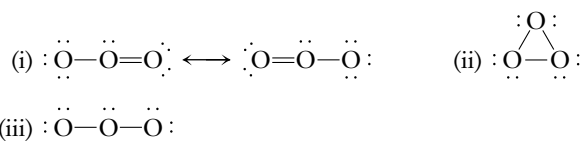
74. (a) Describe the hybridization of N in NO_2^+ and NO_2^- .
 (b) Predict the bond angle in each case.
- *75. The skeleton and a ball-and-stick model for the nitrous acid molecule, HNO_2 , are shown here. Draw the Lewis formula. What are the hybridizations at the middle O and N atoms?



76. Describe the change in hybridization that occurs at the central atom of the reactant at the left in each of the following reactions.
- $\text{PF}_5 + \text{F}^- \rightarrow \text{PF}_6^-$
 - $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$
 - $\text{AlI}_3 + \text{I}^- \rightarrow \text{AlI}_4^-$
 - What change in hybridization occurs in the following reaction?



- *77. Consider the following proposed Lewis formulas for ozone (O_3):



- Which of these correspond to a polar molecule?
- Which of these predict covalent bonds of equal lengths and strengths?
- Which of these predict a diamagnetic molecule?
- The properties listed in parts (a), (b), and (c) are those observed for ozone. Which structure correctly predicts all three?
- Which of these contain a considerable amount of "strain"? Explain.

78. What hybridizations are predicted for the central atoms in molecules having the formulas AB_2U_2 and AB_3U ? What are the predicted bond angles for these molecules? The observed bond angles for representative substances are

H_2O	104.5°	NH_3	106.7°
H_2S	92.2°	PH_3	93.7°
H_2Se	91.0°	AsH_3	91.8°
He_2Te	89.5°	SbH_3	91.3°

What would be the predicted bond angle if no hybridization occurred? What conclusion can you draw concerning the importance of hybridization for molecules of compounds involving elements with higher atomic numbers?

CONCEPTUAL EXERCISES

79. Draw and explain the difference in the three-dimensional shapes of $\text{CH}_3\text{CH}_2\text{CH}_3$ and CH_3COCH_3 .
80. Complete the following table.

Molecule or Ion	Electronic Geometry	Molecular Geometry	Hybridization of the Sulfur Atom
SO_2			
SCl_2			
SO_3			
SO_3^{2-}			
SF_4			
SO_4^{2-}			
SF_5^+			
SF_6			

81. Compare the shapes of the following pairs of molecules: (a) H_2CO and CH_4 ; (b) PbCl_4 and PbO_2 ; (c) CH_4 and PbCl_4 .
82. (a) Write two Lewis formulas for CO_3^{2-} . Do the two formulas represent resonance forms? (b) Do the same for HSO_4^- .
83. What advantages does the VSEPR model of chemical bonding have compared with Lewis formulas?
84. What evidence could you present to show that two carbon atoms joined by a single sigma bond are able to rotate about an axis that coincides with the bond, but two carbon atoms bonded by a double bond cannot rotate about an axis along the double bond?

