

CHEMICAL PRINCIPLES

The Quest for Insight

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PETER ATKINS / LORETTA JONES

MOLECULAR SHAPE AND STRUCTURE

What Are the Key Ideas? The central ideas of this chapter are, first, that electrostatic repulsions between electron pairs determine molecular shapes and, second, that chemical bonds can be discussed in terms of two quantum mechanical theories that describe the distribution of electrons in molecules.

Why Do We Need to Know This Material? The shapes of molecules determine their odors, their tastes, and their actions as drugs. Molecular shape governs the reactions that take place throughout our bodies and are necessary for life. It also affects the properties of the materials around us, including their physical states and their solubilities. Perception, thinking, and learning depend on the shapes of molecules and how they change. Modern theories of the electronic structures of molecules can be extended to describe metals and semiconductors, and so the information in this chapter is also at the root of the development of new technologies.

What Do We Need to Know Already? This chapter uses atomic orbitals and electron configurations (Chapter 1). It also extends the concept of Lewis structures introduced in Chapter 2. The discussion of polar molecules develops the material on polar bonds described in Section 2.12.

The bright colors of flowers and the varied hues of autumn leaves have always been a cause for delight, but it was not until the twentieth century that chemists understood how these colors arise from the presence of organic compounds with common structural features. They discovered how small differences in the structures of the molecules of these compounds can enhance photosynthesis, produce important vitamins, and attract pollinating bees. They now know how the shapes of molecules and the orbitals occupied by their electrons explain the properties of these compounds and even the processes taking place in our eyes that allow us to see them.

The impact of modern theories of bonding, however, goes far beyond understanding the colors around us. Increasing knowledge of the electronic structures of the atoms and molecules in polymers and semiconductors has led to the development of new technologies. The pharmaceutical industry is increasingly turning to computer-aided design—in which molecular shape and the distribution of electrons play a crucial role—to discover new, more potent drugs (Box 3.1).

In this chapter we meet three increasingly sophisticated models of molecular shape. The first considers molecular shape to be a consequence merely of the electrostatic (Coulombic) interaction between pairs of electrons. The other two models are theories that describe the distribution of electrons and molecular shape in terms of the occupation of orbitals.

THE VSEPR MODEL

In this section, we construct a model of molecular shape empirically, which means that we base it on rules suggested by experimental observations rather than on more fundamental principles. We proceed in three steps. First, we set up the basic model for simple molecules without lone pairs on the central atom. Then, we include the effects of lone pairs. Finally, we explore some of the consequences of molecular shape.

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Chapter 3

THE VSEPR MODEL

- 3.1 The Basic VSEPR Model
- 3.2 Molecules with Lone Pairs on the Central Atom
- 3.3 Polar Molecules

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- 3.13 Bonding in the Solid State
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BOX 3.1 FRONTIERS OF CHEMISTRY: DRUGS BY DESIGN AND DISCOVERY

The search for new drugs relies not only on the skills of synthetic organic chemists but also on biologists, ethnobotanists, and medical researchers. Because there are so many millions of compounds, it would take too long to start with the elements, combine them in different ways, and then test them. Instead, chemists usually start either by *drug discovery*, the identification and possibly the modification of promising medicines that already exist, or by *rational drug design*, the identification of characteristics of a target enzyme, virus, bacterium, or parasite and the design of new compounds to react with it.

In drug discovery, a chemist usually begins by investigating compounds that have already shown medicinal value. A fruitful path is to find a *natural product*, an organic compound found in nature, that has been shown to have healing characteristics. Nature is the best of all synthetic chemists, with billions of chemicals that fulfill as many different needs. The challenge is to find compounds that have curative powers. These substances are found in different ways: random or "blind" collection of samples that are then tested, or collection of specific samples identified by native healers as medically effective.

Observation of the properties of plants and animals can help to guide a random search. For example, if certain types of fruits remain fresh while others rot, we might expect the former to contain antifungal agents. An example of this type of collection is the gathering of tunicates and sponges in the Caribbean. The chemists harvest the samples by diving from research vessels (see Fig. E.1). The samples are tested for antiviral and antitumor activity in a chemical laboratory on the ship. The antiviral drug didemnin-C and the anticancer drug bryostatins 1 were discovered in marine organisms.



A field biologist examines a plant in a South American rainforest. The plant produces chemicals that will be investigated for their medicinal value.

The guided route requires fewer samples for testing because the chemist works with a native healer, the ancient lore guiding the modern chemistry. Often an ethnobotanist, a specialist in plants used for native healing, joins the team. This approach saves time for the scientists and can provide an economic benefit for the healers and their nations as well. Drugs that have been discovered in this way include a variety of anticancer and antimalarial drugs, blood-clotting agents, antibiotics, and medicines for the heart and digestive system. Once the empirical and molecular formulas of the active compounds are determined, then their structural formulas are sought. At that point, synthetic work can begin. The chemist can identify compounds in the material that have medicinal value and find a way to *synthesize* them, or prepare them in the laboratory, so that they can be made available in large quantities.

In rational drug design, the chemist begins with the tumor or organism that the drug is intended to eradicate. Virtually all processes in living cells depend on specific *enzymes*, types of proteins with very large molecules having specific shapes. Usually there is an *active site* on the enzyme into which only specific molecules can fit and react. If the enzymes that control the growth of parasites or bacteria can be identified and their shapes known, compounds that fit into the active sites and block the reactions can be designed. The chemist taking this route begins by identifying key enzymes in the bacterium or parasite. Then the molecular structure of the enzyme is determined. A computer program is used to design molecules with structures that fit into the active site. The new compounds are synthesized, and their effects and side effects tested.

E How Might You Contribute?

Despite all the medicines in a modern pharmacy, there is still a great need for specific chemotherapeutic agents with few side effects. We are beginning to see the investigation of a wide array of natural products and the rational drug design of new therapeutic agents. The selection of good candidates for drug development from these large numbers of compounds and synthetic routes to duplicate them need to be optimized.

Related Exercises: 3.77 and 3.96

For Further Reading: D. Hart, "Designer drugs," *Science Spectra*, no. 8, 1997, p. 52. A. M. Rouhi, "Seeking drugs in natural products," *Chemical and Engineering News*, April 7, 1997, p. 14. J. Staunton and K. Weissman, "Medicines from nature," *The New Chemistry*, edited by N. Hall (Cambridge: Cambridge University Press, 2000), pp. 195-213. R. P. Saurami, V. Vinson, and E. Marshall, "Rethinking drug discovery," *Science*, vol. 303, p. 1795, March 19, 2004.

3.1 The Basic VSEPR Model

We begin by looking at molecules that consist of one central atom to which all the other atoms are attached. Many of these molecules have the shapes of the geometrical figures shown in Fig. 3.1; thus, CH_4 (1) is tetrahedral, SF_6 (2) is octahedral, and PCl_5 (3) is trigonal bipyramidal. In a number of these cases the bond angles

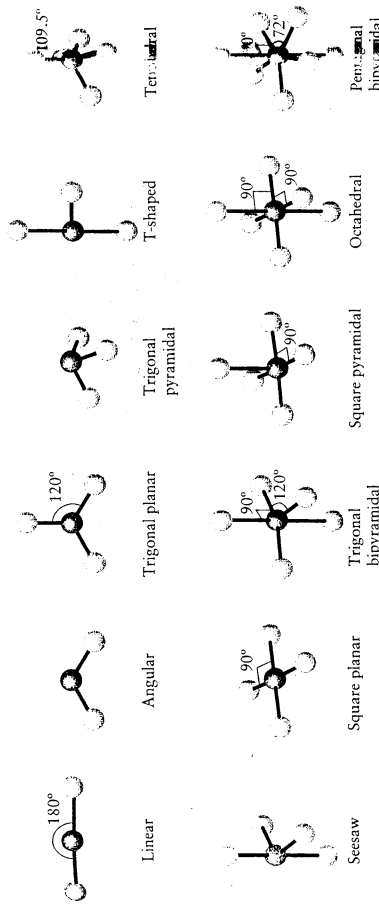


FIGURE 3.1 The names of the shapes of simple molecules and their bond angles. Lone pairs of electrons are not shown, because they are not included when identifying molecular shapes.

the angles between the bonds (the straight lines that join the atom centers), are fixed by the symmetry of the molecule; these bond angles are indicated in Fig. 3.1. Thus, the HCH angle in CH_4 is 109.5° (the "tetrahedral angle"), the FSF angles in SF_6 are 90° and 180° , and the ClPCl angles in PCl_5 are 90° , 120° , and 180° . The bond angles of molecules that are not fixed by symmetry must be determined experimentally. The HOH bond angle in the angular H_2O molecule, for instance, has been found to be 104.5° and the HNH angle in the trigonal pyramidal NH_3 molecule is measured as 107° . The principal technique for determining bond angles in small molecules is spectroscopy, especially rotational and vibrational spectroscopy; x-ray diffraction is used for larger molecules.

The Lewis structures encountered in Chapter 2 are two-dimensional representations of the links between atoms—their connectivity—and except in the simplest cases do not depict the arrangement of atoms in space. The valence-shell electron-pair repulsion model (VSEPR model) extends Lewis's theory of bonding to account for molecular shapes by adding rules that account for bond angles. The model starts from the idea that because electrons repel one another, the shapes of simple molecules correspond to arrangements in which pairs of bonding electrons lie as far apart as possible. Specifically:

Rule 1 Regions of high electron concentration (bonds and lone pairs on the central atom) repel one another and, to minimize their repulsions, these regions move as far apart as possible while maintaining the same distance from the central atom (Fig. 3.2).

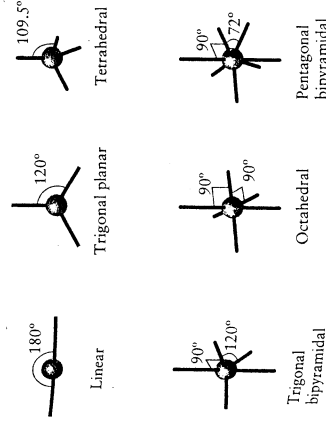


FIGURE 3.2 The positions that two to seven regions of high electron concentration (atoms and lone pairs) take around a central atom. The regions are denoted by the straight lines sticking out of the central atom. Use this diagram to identify the electron arrangement of a molecule, and then use Fig. 3.1 to identify the shape of the molecule from the locations of its atoms.

The VSEPR model was first explored by the British chemists Nevil Sidgwick and Herbert Powell and has been developed by the Canadian chemist Ronald Gillespie.

Once we have identified the arrangement of the "most distant" locations of these regions, which is called the **electron arrangement** of the molecule, we note where the atoms lie and identify the shape of the molecule by giving it the name of the corresponding shape in Fig. 3.1. In naming the molecular shape, we consider only the positions of atoms, not any lone pairs that may be present on the central atom, even though they affect the shape.

A molecule with only two atoms attached to the central atom is BeCl_2 . The Lewis structure is $\text{Cl}-\text{Be}-\text{Cl}$, and there are no lone pairs on the central atom. To be as far apart as possible, the two bonding pairs lie on opposite sides of the Be atom, and so the electron arrangement is linear. Because a Cl atom is attached to each bonding pair, the VSEPR model predicts a linear shape for the BeCl_2 molecule, with a bond angle of 180° (4). That shape is confirmed by experiment.

A boron trifluoride molecule, BF_3 , has the Lewis structure shown in (5). There are three bonding pairs attached to the central atom and no lone pairs. To be as far apart as possible, the three bonding pairs must lie at the corners of an equilateral triangle. The electron arrangement is trigonal planar. Because an F atom is attached to each bonding pair, the BF_3 molecule is trigonal planar (6), and all three BF angles are 120° , as confirmed experimentally.

Methane, CH_4 , has four bonding pairs on the central atom. To be as far apart as possible, the four pairs must take up a tetrahedral arrangement around the C atom. Because the electron arrangement is tetrahedral and an H atom is attached to each bonding pair, we expect the molecule to be tetrahedral (see 1), with bond angles of 109.5° . That is the shape found experimentally.

In a phosphorus pentachloride molecule, PCl_5 (7), there are five bonding pairs and no lone pairs on the central atom. According to the VSEPR model, the five pairs and the atoms that they carry are farthest apart in a trigonal bipyramidal arrangement (see Fig. 3.2). In this arrangement, three atoms lie at the corners of an equilateral triangle and the other two atoms lie above and below the plane of the triangle (see 3). This structure has three different bond angles: the bond angles in the equatorial plane are 120° ; the angle between the axial and the equatorial atoms is 90° ; the one axial ClPCl bond angle is 180° . This structure is also confirmed experimentally.

A sulfur hexafluoride molecule, SF_6 , has six atoms attached to the central S atom and no lone pairs on that atom (8). According to the VSEPR model, the electron arrangement is octahedral, with four pairs at the corners of a square on the equator and the remaining two pairs above and below the plane of the square (see Fig. 3.2). An F atom is attached to each electron pair, and so the molecule is predicted to be octahedral. All its bond angles are either 90° or 180° , and all the F atoms are equivalent.

The second rule of the VSEPR model concerns the treatment of multiple bonds:

Rule 2 There is no distinction between single and multiple bonds: a multiple bond is treated as a single region of high electron concentration.

That is, the two electron pairs in a double bond stay together and repel other bonds or lone pairs as a unit. The three electron pairs in a triple bond also stay together and act like a single region of high electron concentration. For instance, a carbon dioxide molecule, $\text{O}=\text{C}=\text{O}$, has a linear structure similar to that of BeCl_2 , even though both bonds are double bonds (9). One of the Lewis structures of a carbonate ion, CO_3^{2-} , is shown in (10). The two pairs of electrons in the double bond are treated as a unit, and the resulting shape (11) is trigonal planar. Because each bond, whether single or multiple, acts as a single unit, to count the number of regions of high electron concentration we simply count the number of atoms attached to the central atom and add the number of lone pairs.

When there is more than one central atom, we consider the bonding about each atom independently. For example, to predict the shape of an ethene (ethylene)

molecule, $\text{CH}_2=\text{CH}_2$, we consider each carbon atom separately. From the Lewis structure (12) we note that each carbon atom has three atoms attached but no lone pairs. The arrangement around each carbon atom is therefore trigonal planar. We predict that the HCH and HCC angles will both be 120° (13); this prediction is confirmed experimentally.

EXAMPLE 3.1 Predicting the shape of a molecule with no lone pairs on the central atom

Suggest a shape for the ethyne (acetylene) molecule, $\text{HC}\equiv\text{CH}$.

STRATEGY Write down the Lewis structure and identify the electron arrangement around each "central" atom (each C atom, in this case). Treat each multiple bond as a single unit. Then identify the overall shape of the molecule (refer to Fig. 3.2 if necessary).

SOLUTION

Write the Lewis structure of the molecule.



Identify the electron arrangement around each "central" atom.

Linear: Each C atom is attached to two other atoms (one H atom and one C atom), and there are no lone pairs.

Identify the arrangement of atoms around each C atom.

Linear, and the molecule is linear overall.

SELF-TEST 3.1A Predict the shape of an arsenic pentafluoride molecule, AsF_5 .

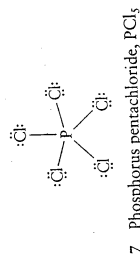
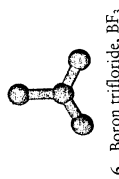
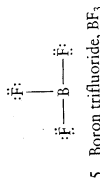
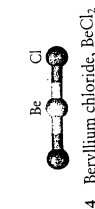
SELF-TEST 3.1B Predict the shape of a formaldehyde molecule, CH_2O .

Because we treat single bonds and multiple bonds as equivalent in the VSEPR model, it does not matter which of the Lewis structures contributing to a resonance structure we consider. For example, although we can write several different Lewis structures for a nitrate ion, all of them have three regions of electron concentration around the central N atom—all of them have three atoms attached to the central atom—and in each case we expect a trigonal planar structure (14). That the three N—O bonds are all equivalent is confirmed experimentally by the fact that all three have the same length and the three bond angles are identical. It is also confirmed by calculation: an electrostatic potential diagram (Section C) shows the symmetry of the calculated electron distribution (15). The equivalence of the three bonds is what we would expect in a resonance structure.

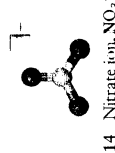
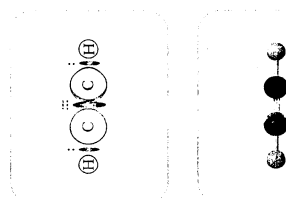
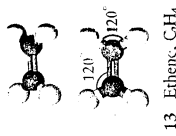
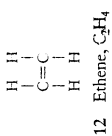
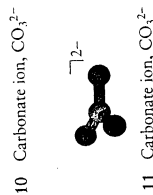
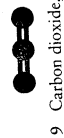
According to the VSEPR model, regions of high electron concentration take up positions that maximize their separations; electron pairs in a multiple bond are treated as a single unit. The shape of the molecule is then identified from the relative locations of its atoms.

3.2 Molecules with Lone Pairs on the Central Atom

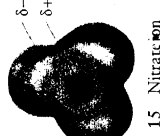
To help us predict the shapes of molecules, we use the generic "VSEPR formula" AX_mE_n to identify the different combinations of atoms and lone pairs attached to



All six terminal atoms are equivalent in a regular octahedral molecule.



Recall that red regions indicate negative potential (an accumulation of electrons) and blue regions indicate positive potential (a deficiency of electrons).



the central atom. We let A represent a central atom, X an attached atom, and E a lone pair. For example, the BF_3 molecule, with three attached fluorine atoms and no lone pairs on B, is an example of an AX_3 species. The sulfite ion, SO_3^{2-} (16), which has one lone pair, is an example of an AX_3E species. Molecules with the same VSEPR formula have essentially the same electron arrangement and the same shape; so by recognizing the formula we can immediately predict the shape (but not necessarily the precise numerical values of bond angles that are not governed by symmetry).

If there are no lone pairs on the central atom (an AX_n molecule), each region of high electron concentration corresponds to an atom, and so the molecular shape is the same as the electron arrangement. However, if lone pairs are present, the molecular shape differs from the electron arrangement because only the positions of the atoms are considered when naming the shape. For example, the four regions of high electron concentration in SO_3^{2-} are farthest apart if they adopt a tetrahedral arrangement (see Fig. 3.2). However, the *shape* of the ion is described by the locations of the atoms, not the lone pair. Because only three of the tetrahedral locations are occupied by atoms, the shape of an SO_3^{2-} ion is trigonal pyramidal (17). The rule to remember is

Rule 3 All regions of high electron density, lone pairs and bonds, are included in a description of the electronic arrangement, but *only the positions of atoms are considered when reporting the shape of a molecule.*

A single unpaired electron on the central atom also is a region of high electron density and is treated like a lone pair when determining molecular shape. For example, radicals such as NO_2 have a single nonbonding electron, a “lone half-pair.” Thus, NO_2 (18) has a trigonal planar electron arrangement (including the unpaired electron on N), but its shape is angular (19).

EXAMPLE 3.2 Predicting the shape of a molecule with lone pairs

Predict the electron arrangement and the shape of a nitrogen trifluoride molecule, NF_3 . **STRATEGY** For the electron arrangement, draw the Lewis structure and then use the VSEPR model to decide how the bonding pairs and lone pairs are arranged around the central (nitrogen) atom (consult Fig. 3.2 if necessary). Identify the molecular shape from the layout of atoms, as in Fig. 3.1.

SOLUTION

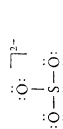
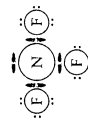
Draw the Lewis structure.



The central N atom has one electron pair and three bonds, corresponding to four regions of high electron density.

Assign the electron arrangement.

Tetrahedral



16 Sulfite ion, SO_3^{2-}



17 Sulfite ion, SO_3^{2-}



18 Nitrogen dioxide, NO_2



19 Nitrogen dioxide, NO_2

Identify the shape considering only atoms.



The three atoms bonded to N form a trigonal pyramid.

Note that only when using the type of representation on the right do we show the lone pair explicitly. Spectroscopic measurements confirm the prediction of a trigonal pyramidal shape for NF_3 .

SELF-TEST 3.2A Predict (a) the electron arrangement and (b) the shape of an IF_5 molecule.

[Answer: (a) Octahedral; (b) square pyramidal]

SELF-TEST 3.2B Predict (a) the electron arrangement and (b) the shape of an SO_2 molecule.

So far we have regarded lone pairs as equivalent to atoms, but is that really the case? We have predicted, for instance, that the electron arrangement of an SO_3^{2-} ion is tetrahedral, and so we might expect OSO angles of 109.5° . However, experimental findings have shown that, although the sulfite ion is indeed trigonal pyramidal, its bond angle is only 106° (20). Such experimental evidence tells us that the VSEPR model as we have described it is incomplete and needs to be refined.

The final rule of the VSEPR model takes note of the different effects of lone pairs and atoms. Because bond angles in molecules with lone pairs are typically smaller than expected, lone pairs are treated in the VSEPR model as having a more strongly repelling effect than do electrons in bonds. That is, the lone pairs push the atoms bonded to the central atom closer together. One possible rationalization for this effect is that the electron cloud of a lone pair can spread over a larger volume than a bonding pair, because a bonding pair (or several bonding pairs in a multiple bond) is pinned down by two atoms, not one (Fig. 3.3). In summary, the VSEPR model provides reasonably reliable predictions if we adopt the following rule:

Rule 4 The strengths of repulsions are in the order lone pair–lone pair > lone pair–atom > atom–atom

Therefore, the lowest energy is achieved when lone pairs are as far from each other as possible. The energy is also lowest if the atoms bonded to the central atom are far from lone pairs, even though that might bring the atoms closer to other atoms.

Our improved model helps to account for the bond angle of the AX_3E sulfite ion. The atoms and the lone pair adopt a tetrahedral arrangement around the S atom. However, the lone pair exerts a strong repulsion on the atoms, forcing them to move together slightly, reducing the OSO angle from the 109.5° of the regular tetrahedron to 106° . Note that, although the VSEPR model can predict the direction of the distortion, it cannot predict its extent. We can predict that, in any AX_3E species, the XAX angle will be less than 109.5° , but we cannot predict its actual value; we must measure it experimentally or calculate it by solving the Schrödinger equation numerically on a computer.

SELF-TEST 3.3A (a) Give the VSEPR formula of an NH_3 molecule. Predict (b) its electron arrangement and (c) its shape.

[Answer: (a) AX_3E ; (b) tetrahedral; (c) trigonal pyramidal (21, LP is lone pair), HNH angle less than 109.5°]



20 Sulfite ion, SO_3^{2-}



Bonding pairs

FIGURE 3.3 A possible explanation of why lone pairs have a stronger repelling effect than that of bonding electrons. A lone pair is less restrained than bonding pairs and so takes up more space; the bonding pairs (with their atoms) move away from the lone pair in an attempt to lower the repulsion that they experience, thus compressing the bond angle slightly.



21 Ammonia, NH_3

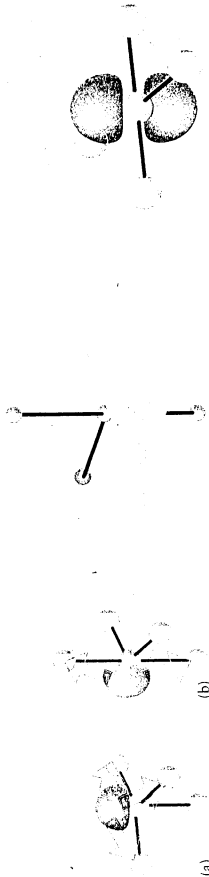


FIGURE 3.4 (a) A lone pair in an axial position is close to three equatorial atoms. (b) In an equatorial position, a lone pair is close to only two atoms, a more favorable arrangement.

FIGURE 3.5 Two lone pairs in an AX_2E_2 molecule adopt equatorial positions and move away from each other slightly. As a result, the molecule is approximately T-shaped.

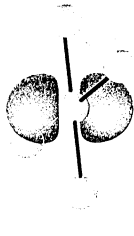


FIGURE 3.6 The square planar arrangement of atoms taken up in AX_2E_2 molecules; the two lone pairs are farthest apart when they are on opposite sides of the central atom.

SELF-TEST 3.3B (a) Give the VSEPR formula of a ClO_2^- ion. Predict (b) its electron arrangement and (c) its shape.

Rule 4 allows us to predict the position in which a lone pair will be found. For example, the electron arrangement in an AX_4E molecule or ion, such as PF_5 , is trigonal bipyramidal, but there are two different possible locations for the lone pair. An axial lone pair lies on the axis of the molecule, where it repels three electron pairs strongly; an equatorial lone pair lies on the molecule's equator, on the plane perpendicular to the molecular axis, where it repels only two electron pairs strongly (Fig. 3.4). Therefore, the lowest energy is achieved when a lone pair is equatorial, producing a seesaw-shaped molecule. An AX_3E_2 molecule, such as ClF_3 , also has a trigonal bipyramidal arrangement of electron pairs, but two of the pairs are lone pairs. These two pairs are farthest apart if they occupy two of the three equatorial positions but move away from each other slightly. The result is a T-shaped molecule (Fig. 3.5). Now consider an AX_2E_2 molecule, which has an octahedral arrangement of electron pairs, two of which are lone pairs. The two lone pairs are farthest apart when they lie opposite each other, and so the molecule is square planar (Fig. 3.6).

Molecules with the same VSEPR formula all have the same general shape, although their bond angles generally differ slightly. For example, O_3 is an AX_2E species ($:\ddot{O}-O=\ddot{O}:$); it has a trigonal planar electron arrangement and an angular, molecular shape (22). The nitrite ion, NO_2^- , has the same general formula ($:\ddot{O}-N=\ddot{O}:^-$) and the same shape (23); so too does sulfur dioxide, SO_2 ($:\ddot{O}-S=\ddot{O}:$, 24).



TOOLBOX 3.1

HOW TO USE THE VSEPR MODEL

CONCEPTUAL BASIS

Regions of high electron concentration—bonds to atoms and lone pairs attached to a central atom in a molecule—arrange themselves in such a way as to minimize mutual repulsions.

PROCEDURE

The general procedure for predicting the shape of a molecule is as follows:

Step 1 Decide how many atoms and lone pairs are present on the central atom by writing a Lewis structure for the molecule.

Step 2 Identify the electron arrangement, treating a multiple bond as equivalent to a single bond (see Fig. 3.2).

Step 3 Locate the atoms and identify the molecular shape (according to Fig. 3.1).

Step 4 Allow the molecule to distort so that lone pairs are as far from one another and from bonding pairs as possible. The repulsions are in the order

Lone pair–lone pair > lone pair–atom > atom–atom

Example 3.3 shows how this procedure is used.

EXAMPLE 3.3 Sample exercise: Predicting a molecular shape

Predict the shape of a sulfur tetrafluoride molecule, SF_4 .

SOLUTION

Step 1 Draw the Lewis structure.

Because we are focusing on the central atom, there is no need to show the lone pairs on the F atoms.



Step 2 Assign the electron arrangement around the central atom.

There are 5 regions of high electron density (4 atoms and 1 lone pair); so trigonal bipyramidal.

Step 3 Identify the molecular shape.

AX_4E . To minimize electron pair repulsions, the lone pair occupies an equatorial location. SF_4 has a seesaw shape.

Step 4 Allow for distortions.

The atoms move slightly away from the lone pair.

This shape (resembling a slightly bent seesaw) is the one found experimentally.

SELF-TEST 3.4A Predict the shape of an I_3^- ion.

[Answer: Linear]

SELF-TEST 3.4B Predict the shape of a xenon tetrafluoride molecule, XeF_4 .

In a molecule that has lone pairs or a single nonbonding electron on the central atom, the valence electrons contribute to the electron arrangement about the central atom but only bonded atoms are considered in the identification of the shape. Lone pairs distort the shape of a molecule so as to reduce lone pair–bonding pair repulsions.

3.3 Polar Molecules

In Section 2.12, we saw that a polar covalent bond in which electrons are not evenly distributed has a nonzero dipole moment. A polar molecule is a molecule with a nonzero dipole moment. All diatomic molecules are polar if their bonds are polar. An HCl molecule, with its polar covalent bond ($\delta^+H-Cl\delta^-$), is a polar molecule. Its dipole moment of 1.1 D is typical of polar diatomic molecules (Table 3.1). All diatomic molecules that are composed of atoms of different elements are at least slightly polar. A nonpolar molecule is a molecule that has no electric dipole moment. All homonuclear diatomic molecules, diatomic molecules containing atoms of only one element, such as O_2 , N_2 , and Cl_2 , are nonpolar, because their bonds are nonpolar.

A polyatomic molecule may be nonpolar even if its bonds are polar. For example, the two $\delta^+C-O\delta^-$ dipole moments in carbon dioxide, a linear molecule, point in opposite directions, and so they cancel each other (25) and CO_2 is a nonpolar



25 Carbon dioxide, CO_2

TABLE 3.1 Dipole Moments of Selected Molecules

Molecule	Dipole moment (D)	Molecule	Dipole moment (D)
HF	1.91	PH ₃	0.58
HCl	1.08	AsH ₃	0.20
HBr	0.80	SbH ₃	0.12
HI	0.42	O ₃	0.53
CO	0.12	CO ₂	0
ClF	0.88	BF ₃	0
NaCl*	9.00	CH ₄	0
CsCl*	10.42	<i>cis</i> -CHCl=CHCl	1.90
H ₂ O	1.85	<i>trans</i> -CHCl=CHCl	0
NH ₃	1.47		

*For pairs of ions in the gas phase, not the bulk ionic solid.

molecule. Even though there are positive and negative regions of charge within the molecule, the center of positive charge and the center of negative charge coincide, so the molecule itself is nonpolar. The electrostatic potential diagram (26) illustrates this conclusion. As noted in Section C, the colors show how electron density is distributed in the molecule. Partially positive regions are blue and partially negative regions are red. In contrast, the two $\delta^+H-\delta^-O$ dipole moments in H₂O lie at 104.5° to each other and do not cancel, and so H₂O is a polar molecule (27). This polarity is part of the reason why water is such a good solvent for ionic compounds.

As we have seen by comparing CO₂ and H₂O, the shape of a polyatomic molecule affects whether or not it is polar. The same is true of more complicated molecules. For instance, the atoms and bonds are the same in *cis*-dichloroethene (28) and *trans*-dichloroethene (29); but, in the latter, the C—Cl bonds point in opposite directions and the dipoles (which point along the C—Cl bonds) cancel. Thus, whereas *cis*-dichloroethene is polar, *trans*-dichloroethene is nonpolar. Because dipole moments are directional, we can treat each bond dipole moment as a vector. The molecule as a whole will be nonpolar if the vector sum of the dipole moments of the bonds is zero.

If the four atoms attached to the central atom in a tetrahedral molecule are the same, as in tetrachloromethane (carbon tetrachloride), CCl₄ (30), the dipole moments cancel and the molecule is nonpolar. However, if one or more of the atoms are replaced by different atoms, as in trichloromethane (chloroform), CHCl₃, or by lone pairs, as in NH₃, then the dipole moments associated with the bonds are not all the same, so they do not cancel. Thus, the CHCl₃ molecule is polar (31).

Figure 3.7 summarizes the shapes of simple molecules that result in them being polar or nonpolar.

EXAMPLE 3.4 Predicting the polar character of a molecule

Predict whether (a) a boron trifluoride molecule, BF₃, and (b) an ozone molecule, O₃, are polar.

STRATEGY In each case, we must decide on the shape of the molecule by using the VSEPR model and then decide whether the symmetry of the molecule results in the cancellation of the dipole moments associated with the bonds. If necessary, refer to Fig. 3.7.

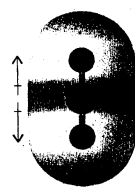
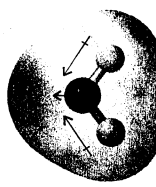
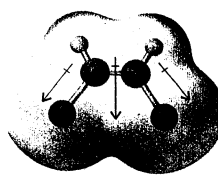
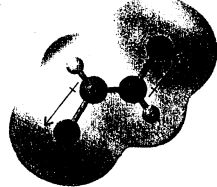
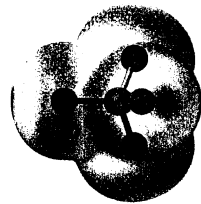
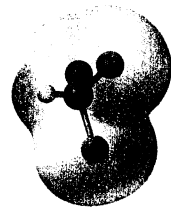
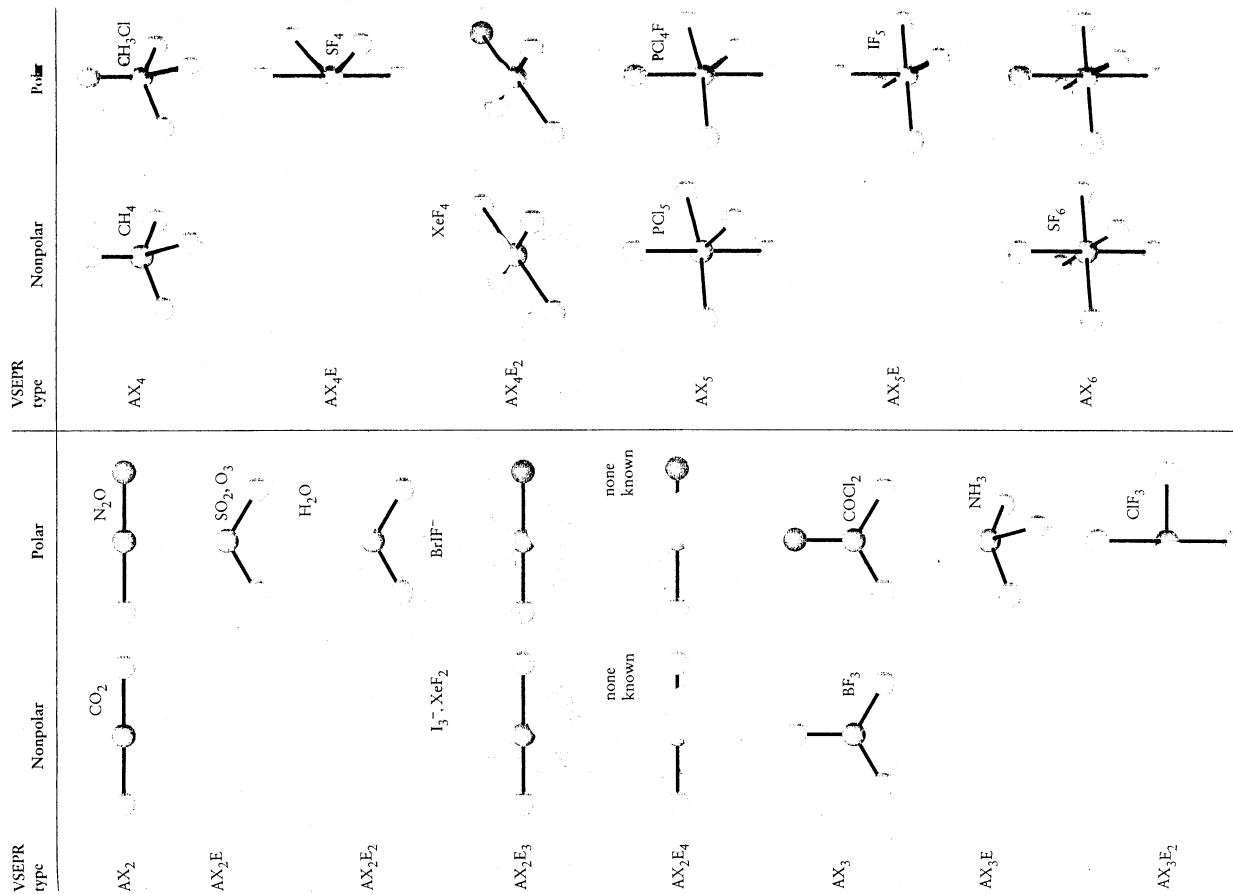
26 Carbon dioxide, CO₂27 Water, H₂O28 *cis*-Dichloroethene, CH₂CH₂Cl₂29 *trans*-Dichloroethene, CH₂CH₂Cl₂30 Tetrachloromethane, CCl₄31 Trichloromethane, CHCl₃

FIGURE 3.7 The arrangements of atoms that give rise to polar and nonpolar molecules. In these VSEPR formulas, A stands for a central atom, X for an attached atom, and E for a lone pair. Identical atoms are the same color; attached atoms colored differently belong to different elements. The green lobes represent lone pairs of electrons.



Animation: Figure 3.8 Formation of the hydrogen molecule

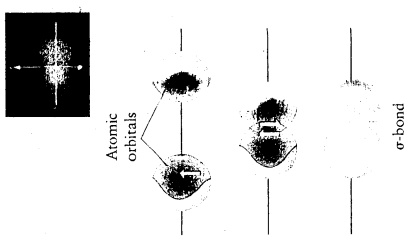


FIGURE 3.8 When electrons with opposite spins (depicted as ↑ and ↓) in two hydrogen 1s-orbitals pair and the s-orbitals overlap, they form a σ-bond, which is depicted here by the boundary surface of the electron cloud. The cloud has cylindrical symmetry around the internuclear axis and spreads over both nuclei. In the illustrations in this book, σ-bonds are usually colored blue.

The Greek letter sigma, σ, is the equivalent of our letters. It reminds us that, looking along the internuclear axis, the electron distribution resembles that of an s-orbital.

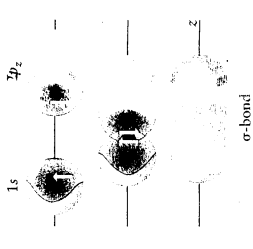


FIGURE 3.9 A π-bond is also formed when electrons in 1s- and 2p_y-orbitals pair (where z is the direction along the internuclear axis). The two electrons in the bond are spread over the entire region of space enclosed by the boundary surface.

By convention, the bond direction defines the z-axis.

The Greek letter pi, π, is the equivalent of our letters. When we imagine looking along the internuclear axis, a π-bond resembles a pair of electrons in a p-orbital.

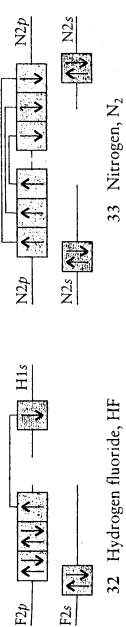
space defined by its orbital. The same principles apply to electrons in molecules, except that the electrons are distributed over a larger region.

The first description of covalent bonding to be devised in terms of atomic orbitals, by Walter Heitler, Fritz London, John Slater, and Linus Pauling in the late 1920s, is called **valence-bond theory** (VB theory). This theory is a quantum mechanical description of the distribution of electrons in bonds that goes beyond Lewis's theory and the VSEPR model by providing a way of calculating the numerical values of bond angles and bond lengths. We shall not go into the actual calculations, which are very complicated, but shall concentrate instead on some of the qualitative concepts. These bonding concepts are used throughout chemistry, so it is important to know how to apply them.

3.4 Sigma and Pi Bonds

We begin with H₂, the simplest molecule of all, and start by thinking about the two hydrogen atoms from which it is formed. Each hydrogen atom in its ground state has one electron in a 1s-orbital. In valence-bond theory, we suppose that, as two H atoms come together, their 1s-electrons pair (denoted ↑↓, as in the discussion of atomic structure in Section 1.10), and the atomic orbitals merge together (Fig. 3.8). The resulting sausage-shaped distribution of electrons, with an accumulation of electron density between the nuclei, is called a "σ-bond" (a sigma bond). More formally, a σ-bond is cylindrically symmetrical (the same in all directions around the long axis of the bond), with no nodal planes containing the internuclear axis. A hydrogen molecule is held together by a σ-bond. The merging of the two atomic orbitals is called the **overlap of orbitals**. A general point to keep in mind throughout this section is that, the greater the extent of orbital overlap, the stronger the bond.

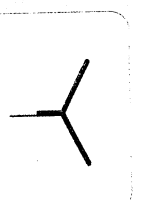
Much the same kind of σ-bond formation ("σ-bonding") occurs in the hydrogen halides. For example, before the H and F atoms combine to form hydrogen fluoride, the unpaired electron on the fluorine atom occupies a 2p_z-orbital, and the unpaired electron on the hydrogen atom occupies a 1s-orbital. These two electrons are the ones that pair to form a bond (32). They pair as the orbitals that they occupy overlap and merge into a cloud that spreads over both atoms (Fig. 3.9). When viewed from the side, the resulting bond has a more complicated shape than that of the σ-bond in H₂; however, the bond looks much the same—it has cylindrical symmetry and no nodal planes containing the internuclear axis—when viewed along the internuclear (z) axis; hence it too is a σ-bond. All *single* covalent bonds are σ-bonds.



We encounter a different type of bond in a nitrogen molecule, N₂. There is a single electron in each of the three 2p-orbitals on each atom (33). However, when we try to pair them and form three bonds, only one of the three orbitals on each atom can overlap end to end to form a σ-bond (Fig. 3.10). Two of the 2p-orbitals on each atom (2p_x and 2p_y) are perpendicular to the internuclear axis, and each one contains an unpaired electron (Fig. 3.11, top). When the electrons in one of these p-orbitals on each N atom pair, the orbitals can overlap only in a side-by-side arrangement. This overlap results in a "π-bond," a bond in which the two electrons lie in two lobes, one on each side of the internuclear axis (Fig. 3.11, bottom). More formally, a π-bond has a single nodal plane containing the internuclear axis. Although a π-bond has electron density on each side of the internuclear axis, it is only one bond, with the electron cloud in the form of two lobes, just as a p-orbital is one orbital with two lobes. In a molecule with two π-bonds, such as N₂, the

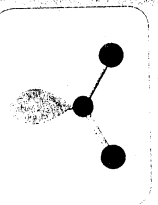
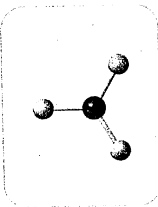
SOLUTION

Draw the Lewis structure.

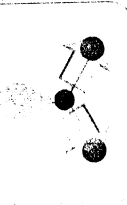
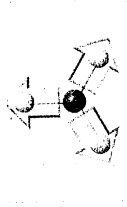


Assign the electron arrangement.

Identify the VSEPR formula.



Name the molecular shape.



Identify the polarity.

This example shows that a homonuclear polyatomic molecule (O₃) can be polar: shape is more important than differences in atoms and O₃ is polar despite all three atoms being oxygen. In this case, the central O atom has a different electron density associated with it than the outer two O atoms: it is bonded to two O atoms whereas the outer atoms are bonded only to one O atom.

SELF-TEST 3.5A Predict whether (a) SF₄, (b) SF₆ is polar or nonpolar. [Answer: (a) Polar; (b) nonpolar]

SELF-TEST 3.5B Predict whether (a) PCl₃, (b) IF₅ is polar or nonpolar.

A diatomic molecule is polar if its bond is polar. A polyatomic molecule is polar if it has polar bonds arranged in space in such a way that the dipole moments associated with the bonds do not cancel.

VALENCE-BOND THEORY

The Lewis model of the chemical bond assumes that each bonding electron pair is located between the two bonded atoms—it is a *localized electron model*. However, we know from the wave-particle duality of the electron (Sections 1.5–1.7) that the location of an electron in an atom cannot be described in terms of a precise position, but only in terms of the *probability* of finding it somewhere in a region of

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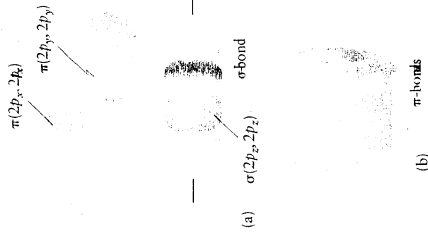


FIGURE 3.12 The bonding pattern in a nitrogen molecule, N_2 . (a) The two atoms are held together by one σ -bond (blue) and two perpendicular π -bonds (yellow). (b) When the three bonds are put together, the two π -bonds merge to form a long doughnut-shaped cloud surrounding the σ -bond cloud, so the overall structure resembles a cylindrical hot dog.

electron is possible if the overall change, taking account of all contributions to the energy and especially the greater number of bonds that can thereby be formed, is toward lower energy. Boron, $[He]2s^2 2p^1$, like carbon, is an element in which promotion can lead to the formation of more bonds (three in its case), and boron does typically form three bonds.

At this stage, it looks as though electron promotion should result in two different types of bonds in methane, one bond from the overlap of a hydrogen $1s$ -orbital and a carbon $2s$ -orbital, and three more bonds from the overlap of hydrogen $1s$ -orbitals with each of the three carbon $2p$ -orbitals. The overlap with the $2p$ -orbitals should result in three σ -bonds at 90° to one another. However, this arrangement is inconsistent with the known tetrahedral structure of methane with four equivalent bonds.

To improve our model we note that s - and p -orbitals are waves of electron density centered on the nucleus of an atom. We imagine that the four orbitals interfere with one another and produce new patterns where they intersect, like waves in water. Where the wavefunctions are all positive or all negative, the amplitudes are increased by this interference; where the wavefunctions have opposite signs, the overall amplitude is reduced and might even be canceled completely. As a result, the interference between the atomic orbitals results in new patterns. These new patterns are called hybrid orbitals. Each of the four hybrid orbitals, designated h_n , is formed from a linear combination of the four atomic orbitals:

$$h_1 = s + p_x + p_y + p_z$$

$$h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z$$

$$h_4 = s + p_x - p_y - p_z$$

For instance, in h_1 the s - and p -orbitals all have their usual signs and their amplitudes add together where they are all positive. In h_2 , however, the signs of p_x and p_y are reversed, and so the resulting interference pattern is different.

The four hybrid orbitals that we have constructed differ only in their orientation, with one pointing toward each corner of a tetrahedron (Fig. 3.13); in all other respects, they are identical. These four hybrid orbitals are called sp^3 hybrids because they are formed from one s -orbital and three p -orbitals. In an orbital-energy diagram, we represent the hybridization as the formation of four orbitals of equal energy intermediate between the energies of the s - and p -orbitals from which they are constructed (37). The hybrids are colored green to remind us that they are a blend of (blue) s -orbitals and (yellow) p -orbitals. An sp^3 hybrid orbital has two lobes, but one lobe extends farther than those of the contributing p -orbitals and the other lobe is shortened. The fact that hybrid orbitals have their amplitudes concentrated on one side of the nucleus allows them to overlap more effectively with other orbitals, and as a result the bonds that they form are stronger than in the absence of hybridization.

We are now ready to account for the bonding in methane. In the promoted, hybridized atom each of the electrons in the four sp^3 hybrid orbitals can pair with an electron in a hydrogen $1s$ -orbital. Their overlapping orbitals form four σ -bonds that point toward the corners of a tetrahedron (Fig. 3.14). The valence-bond description is now consistent with experimental data on molecular geometry.

When there is more than one "central" atom in a molecule, we concentrate on each atom in turn and match the hybridization of each atom to the shape at that atom predicted by VSEPR. For example, in ethane, C_2H_6 (38), the two carbon atoms are both "central" atoms. According to the VSEPR model, the four electron pairs around each carbon atom take up a tetrahedral arrangement. This arrangement suggests sp^3 hybridization of the carbon atoms, as shown in Fig. 3.14. Each

Animation: Figure 3.13 Hybridization: sp^3 orbitals

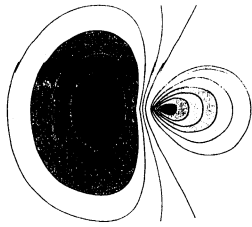


FIGURE 3.13 These contours indicate the amplitude of the sp^3 hybrid orbital wavefunction in a plane that bisects it and passes through the nucleus. Each sp^3 hybrid orbital points toward the corner of a tetrahedron.

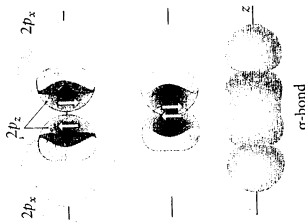
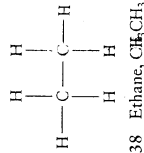
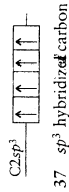
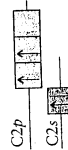


FIGURE 3.10 A σ -bond is formed by the pairing of electron spins in two $2p_z$ orbitals on neighboring atoms. At this stage, we are ignoring the interactions of any $2p_x$ and $2p_y$ orbitals that also contain unpaired electrons, because they cannot form σ -bonds. The electron pair may be found anywhere within the boundary surface shown in the bottom diagram. Notice that the nodal plane of each p_z orbital survives in the σ -bond.

There are a few exceptions to the rule about double bonds: in a very few instances both bonds of a double bond are π bonds.



Carbon monoxide, CO , is the only common exception to the tetravalence of carbon.

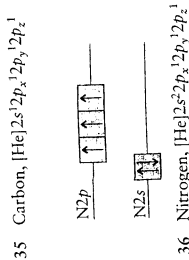


FIGURE 3.11 A π -bond is formed when electrons in two $2p$ -orbitals pair and overlap side by side. The middle diagram shows the extent of the overlap, and the bottom diagram shows the corresponding boundary surface. Even though the bond has a complicated shape, with two lobes, it is occupied by one pair of electrons and counts as one bond. In this text, π -bonds are usually colored yellow.

electron densities in the two π -bonds merge, and the two atoms appear to be surrounded by a cylinder of electron density (Fig. 3.12).

We can generalize from these examples to the description of a multiply bonded species according to valence-bond theory:

A single bond is a σ -bond.

A double bond is a σ -bond plus one π -bond.

A triple bond is a σ -bond plus two π -bonds.

SELF-TEST 3.6A How many σ -bonds and how many π -bonds are there in (a) CO_2 and (b) CO ?
[Answer: (a) Two σ , two π ; (b) one σ , two π]

SELF-TEST 3.6B How many σ -bonds and how many π -bonds are there in (a) NH_3 and (b) HCN ?

In valence-bond theory, we assume that bonds form when unpaired electrons in valence-shell atomic orbitals pair; the atomic orbitals overlap end to end to form σ -bonds or side by side to form π -bonds.

3.5 Electron Promotion and the Hybridization of Orbitals

When we try to apply VB theory to methane we run into difficulties. A carbon atom has the configuration $[He]2s^2 2p_x^1 2p_y^1$ with four valence electrons (34). However, two valence electrons are already paired and only the two half-filled $2p$ -orbitals appear to be available for bonding. It looks as though a carbon atom should have a valence of 2 and form two perpendicular bonds, but in fact it almost always has a valence of 4 (it is commonly "tetravalent") and in CH_4 has a tetrahedral arrangement of bonds.

To overcome this difficulty we note that a carbon atom would have four unpaired electrons available for bonding if an electron is promoted—that is, has been relocated to a higher-energy orbital. When we promote a $2s$ -electron into an empty $2p$ -orbital, we get the configuration $[He]2s^1 2p_x^1 2p_y^1 2p_z^1$ (35). Without promotion, a carbon atom can form only two bonds; after promotion, it can form four bonds. Although it takes energy to promote an electron, the overall energy of the CH_4 molecule is lower than if carbon formed only two C—H bonds.

The characteristic tetravalence of carbon is due to the small promotion energy of a carbon atom. The promotion energy is small because a $2s$ -electron is transferred from an orbital that it shares with another electron to an empty $2p$ -orbital. Although the promoted electron enters an orbital of higher energy, it experiences less repulsion from other electrons than before it was promoted. As a result, only a small energy is needed to promote the electron. Nitrogen, carbon's neighbor, cannot use promotion to increase the number of bonds that it can form, because it has no empty p -orbitals (36). The same is true of oxygen and fluorine. Promotion of an

Animation: Figure 3.16 Hybridization: sp^2 and sp orbitals

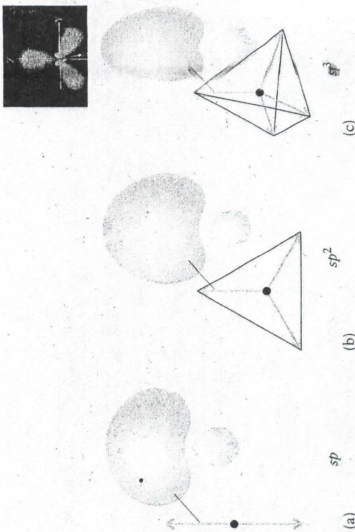


FIGURE 3.16 Three common hybridization schemes shown as outlines of the amplitude of the wavefunction and in terms of the orientations of the hybrid orbitals. (a) An s -orbital and a p -orbital hybridize into two sp hybrid orbitals that point in opposite directions, forming a linear molecular shape. (b) An s -orbital and two p -orbitals can blend together to give three sp^2 hybrid orbitals that point to the corners of an equilateral triangle. (c) An s -orbital and three p -orbitals can blend together to give four sp^3 hybrid orbitals that point to the corners of a tetrahedron.

Animation: Figure 3.17 Hybridization: sp^3d orbitals

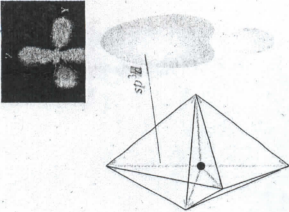


FIGURE 3.17 One of the five sp^3d hybrid orbitals, and their five directions, that account for a trigonal bipyramidal arrangement of electron pairs. The sp^3d hybridization scheme can be applied only when d -orbitals are available on the central atom.

Animation: Figure 3.18 Hybridization: sp^3d^2 orbitals

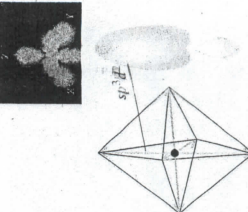


FIGURE 3.18 One of the six sp^3d^2 hybrid orbitals, and their six directions, that may be formed when d -orbitals are available and we need to account for an octahedral arrangement of electron pairs.

these types of bonds by using the d -orbitals of the central atom. To account for a trigonal bipyramidal arrangement of five electron pairs, we use one d -orbital as well as all the valence s - and p -orbitals of the atom. The resulting five orbitals are called sp^3d hybrid orbitals (Fig. 3.17).

We need six orbitals to accommodate six electron pairs around an atom in an octahedral arrangement, as in SF_6 and XeF_4 , and so we need to use two d -orbitals in addition to the valence s - and p -orbitals to form six sp^3d^2 hybrid orbitals (Fig. 3.18). These identical orbitals point toward the six corners of a regular octahedron.

Table 3.2 summarizes the relation between electron arrangement and hybridization type. No matter how many atomic orbitals we mix together, the number of hybrid orbitals is always the same as the number of atomic orbitals with which we started:

N atomic orbitals always produce N hybrid orbitals.

So far, we have not considered whether terminal atoms, such as the Cl atoms in PCl_5 , are hybridized. Because they are bonded to only one other atom, we can not use bond angles to predict a hybridization scheme. However, spectroscopic data and calculation suggest that both s - and p -orbitals of terminal atoms take part in bond formation, and so it is reasonable to suppose that their orbitals are hybridized. The simplest model is to suppose that the three lone pairs and the bonding pair are arranged tetrahedrally and therefore that the chlorine atoms bond to the phosphorus atom by using sp^3 hybrid orbitals.

TABLE 3.2 Hybridization and Molecular Shape*

Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	2	sp	2
trigonal planar	3	sp^2	3
tetrahedral	4	sp^3	4
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

*Other combinations of s -, p -, and d -orbitals can give rise to the same or different shapes, but the combinations in the table are the most common.

C atom has one unpaired electron in each of its four sp^3 hybrid orbitals and can therefore form four σ -bonds that point toward the corners of a regular tetrahedron. The C-C bond is formed by spin-pairing of the electrons in one sp^3 hybrid orbital of each C atom. We label this bond $\sigma(C2sp^3, C2sp^3)$ to show its composition: $C2sp^3$ denotes an sp^3 hybrid orbital composed of $2s$ - and $2p$ -orbitals on a carbon atom, and the parentheses show which orbitals on each atom overlap (Fig. 3.15). Each C-H bond is formed by spin-pairing of an electron in one of the remaining sp^3 hybrid orbitals with an electron in a $1s$ -orbital of an H atom (denoted $H1s$). These bonds are denoted $\sigma(C2sp^3, H1s)$.

We can extend these ideas to molecules, such as ammonia, that have a lone pair of electrons on the central atom. According to the VSEPR model, the four electron pairs in NH_3 take up a tetrahedral electron arrangement, so we describe the nitrogen atom in terms of four sp^3 hybrid orbitals. Because nitrogen has five valence electrons, one of these hybrid orbitals is already doubly occupied (39). The $1s$ -electrons of the three hydrogen atoms pair with the three unpaired electrons in the remaining sp^3 hybrid orbitals. This pairing and overlap result in the formation of three N-H σ -bonds. Whenever an atom in a molecule has a tetrahedral electron arrangement, we say that it is sp^3 hybridized.



39 Ammonia, NH_3
The promotion of electrons will occur if, overall, it leads to a lowering of energy by permitting the formation of more bonds. Hybrid orbitals are constructed or an atom to reproduce the electron arrangement characteristic of the experimentally determined shape of a molecule.

3.6 Other Common Types of Hybridization

We use different hybridization schemes to describe other arrangements of electron pairs (Fig. 3.16). For example, to explain a trigonal planar electron arrangement, like that in BF_3 and each carbon atom in ethene, we mix one s -orbital with two p -orbitals and so produce three sp^2 hybrid orbitals:

$$h_1 = s + 2^{1/2}p_y$$

$$h_2 = s + (\frac{2}{3})^{1/2}p_x - (\frac{1}{3})^{1/2}p_y$$

$$h_3 = s - (\frac{2}{3})^{1/2}p_x - (\frac{1}{3})^{1/2}p_y$$

These identical orbitals all lie in the same plane and point toward the corners of an equilateral triangle.

A linear arrangement of electron pairs requires two hybrid orbitals, and so we mix an s -orbital with a p -orbital to obtain two sp -hybrid orbitals:

$$h_1 = s + p$$

$$h_2 = s - p$$

These two sp -hybrid orbitals point away from each other at 180° , and result in bonds that form a straight line. This is the arrangement we see in CO_2 .

SELF-TEST 3.7A Suggest a structure in terms of hybrid orbitals for BF_3 .

[Answer: Three σ -bonds formed from $F2p_z$ orbitals and $B2sp^2$ hybrids in a trigonal planar arrangement]

SELF-TEST 3.7B Suggest a structure in terms of hybrid orbitals for each carbon atom in ethyne, C_2H_2 .

Some of the elements in Period 3 and later periods can accommodate five or more electron pairs, as in PCl_5 . We can devise a hybridization scheme to describe

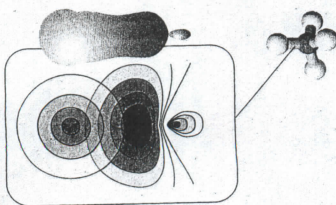


FIGURE 3.14 Each C-H bond in methane is formed by the pairing of an electron in a hydrogen $1s$ -orbital and an electron in one of the four sp^3 hybrid orbitals of carbon. Therefore, valence-bond theory predicts four equivalent σ -bonds in a tetrahedral arrangement, which is consistent with experimental results.

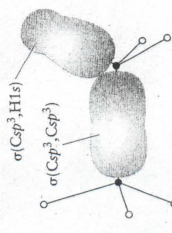


FIGURE 3.15 The valence-bond description of bonding in an ethane molecule, C_2H_6 . The boundary surfaces of only two of the bonds are shown. Each pair of neighboring atoms is linked by a σ -bond formed by the pairing of electrons in either $H1s$ -orbitals or $C2sp^3$ hybrid orbitals. All the bond angles are close to 109.5° (the tetrahedral angle).

EXAMPLE 3.5 Sample exercise: Assigning a hybridization scheme

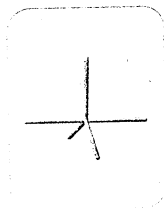
What is the hybridization of sulfur in PF_5 ?

SOLUTION

Draw the Lewis structure.

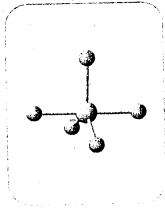
Determine the electron arrangement about the central atom.

Trigonal bipyramidal



Identify the molecular shape.

Trigonal bipyramidal

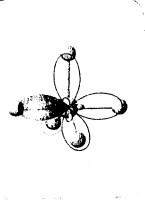


Select the same number of atomic orbitals as there are hybrid orbitals.

5

Construct the hybrid orbitals, starting with the s -orbital, and proceeding to the p - and d -orbitals.

sp^3d



SELF-TEST 3.8A Describe (a) the electron arrangement, (b) the molecular shape, and (c) the hybridization of the central chlorine atom in chlorine trifluoride.

Answer: (a) Trigonal bipyramidal; (b) T-shaped; (c) sp^3d

SELF-TEST 3.8B Describe (a) the electron arrangement, (b) the molecular shape, and (c) the hybridization of the central atom in BrF_4^- .

A hybridization scheme is adopted to match the electron arrangement of the molecule. Valence-shell expansion requires the use of d -orbitals.

3.7 Characteristics of Multiple Bonds

Atoms of the Period 2 elements C, N, and O readily form double bonds with one another, with themselves, and (especially for oxygen) with atoms of elements in later periods. However, double bonds are rarely found between atoms of elements in Period 3 and later periods, because the atoms are so large and bond lengths consequently so great that it is difficult for their p -orbitals to take part in effective side-by-side overlap.

To describe carbon-carbon double bonds, we use the pattern provided by ethene, $\text{CH}_2=\text{CH}_2$. We know from experimental data that all six atoms in ethene

lie in the same plane, with HCH and CCH bond angles of 120° . This angle suggests a trigonal planar electron arrangement and sp^2 hybridization for each C atom (40). Each of the three hybrid orbitals on the C atom has one electron available for bonding; the fourth valence electron of each C atom occupies the unhybridized $2p$ -orbital, which is perpendicular to the plane formed by the hybrids. The two carbon atoms form a σ -bond by overlap of an sp^2 hybrid orbital on each atom. The H atoms form σ -bonds with the remaining lobes of the sp^2 hybrids. The electrons in the two unhybridized $2p$ -orbitals form a π -bond through side-by-side overlap. Figure 3.19 shows that the electron density in the π -bond lies above and below the axis of the C-C σ -bond.

In benzene, the C atoms and their attached H atoms all lie in the same plane, with the C atoms forming a hexagonal ring. To describe the bonding in the Kekulé structures of benzene (Section 2.8) in terms of VB theory, we need hybrid orbitals that match the 120° bond angles of the hexagonal ring. Therefore, we take each carbon atom to be sp^2 hybridized, as in ethene (Fig. 3.20). There is one electron in each of the three hybrid orbitals and one electron in an unhybridized $2p$ -orbital perpendicular to the plane of the hybrids. Spin-pairing and overlap of the sp^2 hybrid orbitals on neighboring carbon atoms results in six σ -bonds between them, and spin pairing and overlap between the remaining sp^2 hybrid and hydrogen $1s$ -electrons results in six carbon-hydrogen bonds. Finally, spin pairing and side-by-side overlap of the $2p$ -orbitals on each C atom results in a π -bond between each carbon atom and one of its neighbors (Fig. 3.21). The resulting pattern of π -bonds matches either of the two Kekulé structures, and the overall structure is a resonance hybrid of the two. This resonance ensures that the electrons in the π -bonds are spread around the entire ring (Fig. 3.22).

The presence of a carbon-carbon double bond strongly influences the shape of a molecule because it prevents one part of a molecule from rotating relative to another part. The double bond of ethene, for example, holds the entire molecule flat. Figure 3.19 shows that the two $2p$ -orbitals overlap best if the two CH_2 groups lie in the same plane. In order for the molecule to rotate about the double bond, the π -bond would need to break and reform.

Double bonds and their influence on molecular shape are vitally important for living organisms. For instance, they enable you to read these words. Vision depends on the shape of the molecule retinal in the retina of the eye. *cis*-Retinal is held rigid by its double bonds (41). When light enters the eye, it excites an electron out of the π -bond marked by the arrow. The double bond is now weaker, and the molecule is free to rotate about the remaining σ -bond. When the excited electron falls back, the molecule has rotated about the double



Animation: Figure 3.19 Ethene bond formation

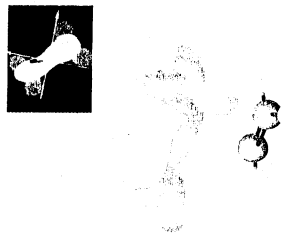
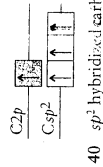


FIGURE 3.19 A view of the bonding pattern in ethene (ethylene), showing the framework of σ -bonds and the single π -bond formed by side-to-side overlap of unhybridized $2p$ -orbitals. The double bond is resistant to twisting because twisting would reduce the overlap between the two $2p$ -orbitals and weaken the π -bond.



40 sp^2 hybridized carbon



41 *cis*-Retinal



Animation: Figure 3.22 Benzene representations

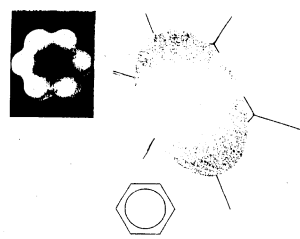


FIGURE 3.22 As a result of resonance between two structures like the one shown in Fig. 3.21 (corresponding to resonance of the two Kekulé structures), the π -electrons form a diffuse doughnut-shaped cloud above and below the plane of the ring.

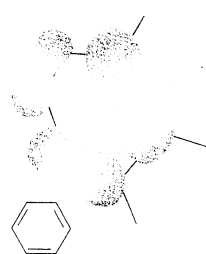


FIGURE 3.21 Unhybridized carbon $2p$ -orbitals can form a π -bond with either of their immediate neighbors. Two arrangements are possible, each one corresponding to a different Kekulé structure. One Kekulé structure and the corresponding π -bonds are shown here.

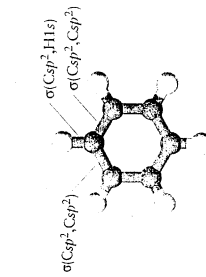


FIGURE 3.20 The framework of σ -bonds in benzene: each carbon atom is sp^2 hybridized, and the array of hybrid orbitals matches the bond angles (of 120°) in the hexagonal molecule. The bonds around only one carbon atom are labeled; all the others are the same.

FIGURE 3.23 The pattern of bonding in ethyne (acetylene). The carbon atoms are sp hybridized, and the two remaining p -orbitals on each C atom form two π -bonds. (a) The resulting pattern is very similar to that for N_2 (Fig. 3.12), but C—H groups replace the two N atoms. (b) Although the two π orbitals are built from p -orbitals, the overall electron density turns out to have cylindrical symmetry.

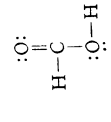
bond and is now trapped in its trans shape (42). This change in shape triggers a signal along the optic nerve and is interpreted by the brain as the sensation of vision.

Now consider the alkynes, hydrocarbons with carbon-carbon triple bonds. The Lewis structure of the linear molecule ethyne (acetylene) is $H-C\equiv C-H$. To describe the bonding in a linear molecule, we need a hybridization scheme that produces two equivalent orbitals at 180° from each other: this is sp hybridization. Each C atom has one electron in each of its two sp hybrid orbitals and one electron in each of its two perpendicular unhybridized $2p$ -orbitals (43). The electrons in the sp hybrid orbitals on the two carbon atoms pair and form a carbon-carbon σ -bond. The electrons in the remaining sp hybrid orbitals pair with hydrogen $1s$ -electrons to form two carbon-hydrogen σ -bonds. The electrons in the two perpendicular sets of $2p$ -orbitals pair with a side-by-side overlap, forming two π -bonds at 90° to each other. As in the N_2 molecule, the electron density in the σ -bonds forms a cylinder about the C—C bond axis. The resulting bonding pattern is shown in Fig. 3.23.

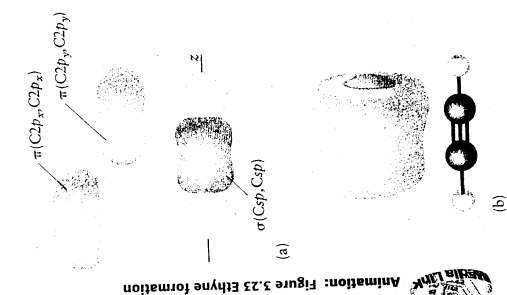
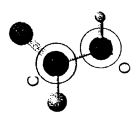
A carbon-carbon double bond is stronger than one carbon-carbon single bond but weaker than the sum of two single bonds (Section 2.15): A carbon-carbon triple bond is weaker than the sum of three carbon-carbon single bonds. Recall that a single C—C bond is a σ -bond, but the additional bonds in a multiple bond are π -bonds. One reason for the difference in strength is that the side-by-side overlap of p -orbitals that results in a π -bond is not as great as the end-to-end overlap that results in a σ -bond.

EXAMPLE 3.6 Accounting for the structure of a molecule with multiple bonds
Account for the structure of a formic acid molecule, $HCOOH$, in terms of hybrid orbitals, bond angles, and σ - and π -bonds. The C atom is attached to an H atom, a terminal O atom, and an —OH group.

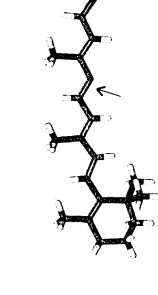
STRATEGY Use the VSEPR model to identify the shape of the molecule and then assign the hybridization consistent with that shape. All single bonds are σ -bonds and multiple bonds are composed of a σ -bond and one or more π -bonds. Because the C atom is attached to three atoms, we anticipate that its hybridization scheme is sp^2 and that one unhybridized p -orbital remains. Finally, we form σ - and π -bonds by allowing the orbitals to overlap.



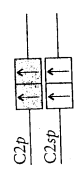
The C atom is bonded to 3 atoms and has no lone pairs; therefore, it has a trigonal planar arrangement. The O atom in the —OH group has two single bonds and two lone pairs; thus, it has a tetrahedral electron arrangement.



Animation: Figure 3.23 Ethyne formation



42 *trans*-Retinal



43 sp hybridized carbon

SOLUTION

Draw the Lewis structure.

Use the VSEPR model to identify the electron arrangements around the central C and O atoms.

C atom: trigonal planar, so 120° bond angle; sp^2 hybridized.
O atom of the —OH group: tetrahedral, so bond angles close to 109.5° ; sp^3 hybridized.

Form the bonds.
A π -bond forms by the overlap of the p -orbital on the C atom with the p -orbital on the terminal O atom.

SELF-TEST 3.9A Describe the structure of the carbon suboxide molecule, C_3O_2 , in terms of hybrid orbitals, bond angles, and σ - and π -bonds. The atoms lie in the order OCCO.
[Answer: Linear; bond angles all 180° ; each C atom is sp hybridized and forms one σ -bond and one π -bond to each adjacent C or O atom.]

SELF-TEST 3.9B Describe the structure of the propene molecule, $CH_3-CH=CH_2$, in terms of hybrid orbitals, bond angles, and σ - and π -bonds.

Multiple bonds are formed when an atom forms a σ -bond by using an sp or sp^2 hybrid orbital and one or more π -bonds by using unhybridized p -orbitals. The side-by-side overlap that forms a π -bond makes a molecule resistant to twisting, results in bonds weaker than σ -bonds, and prevents atoms with large radii from forming multiple bonds.

MOLECULAR ORBITAL THEORY

Lewis's theory of the chemical bond was brilliant, but it was little more than guesswork inspired by insight. Lewis had no way of knowing why an electron pair was so important for the formation of covalent bonds. Valence-bond theory explained the importance of the electron pair in terms of spin-pairing but it could not explain the properties of some molecules. Molecular orbital theory, which is also based on quantum mechanics and was introduced in the late 1920s by Mulliken and Hund, has proved to be the most successful theory of the chemical bond; it overcomes all the deficiencies of Lewis's theory and is easier to use in calculations than valence-bond theory.

3.8 The Limitations of Lewis's Theory

According to Lewis's approach and valence-bond theory, we should describe the bonding in O_2 as having all the electrons paired. However, oxygen is a paramagnetic gas (Fig. 3.24 and Box 3.2), and paramagnetism is a property of unpaired electrons. The paramagnetism of O_2 , therefore contradicts both the Lewis structure and the valence-bond description of the molecule.

Lewis's theory also fails to account for the compound diborane, B_2H_6 , a colorless gas that bursts into flame on contact with air. The problem is that diborane has only 12 valence electrons (three from each B atom, one from each H atom); but, for a Lewis structure, it needs at least seven bonds, and therefore 14 electrons, to bind the eight atoms together! Diborane is an example of an electron-deficient compound, a compound with too few valence electrons to be assigned a valid Lewis structure. Valence-bond theory can account for the structures of electron-deficient compounds in terms of resonance, but the explanation is not straightforward.

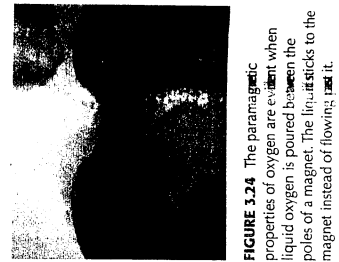


FIGURE 3.24 The paramagnetic properties of oxygen are evident when liquid oxygen is poured between the poles of a magnet. The liquid sticks to the magnet instead of flowing past it.

しっかり勉強する

theory and is the procedure almost universally used in calculations of molecular structures, like those described in Major Technique 5 following Chapter 13.

Unlike Lewis's theory, molecular-orbital theory can account for the existence of electron-deficient compounds and the paramagnetism of oxygen.

3.9 Molecular Orbitals

In molecular orbital theory, electrons occupy orbitals called molecular orbitals that spread throughout the entire molecule. In other words, whereas in the Lewis and valence-bond models of molecular structure the electrons are localized on atoms or between pairs of atoms, in molecular orbital theory all valence electrons are delocalized over the whole molecule, not confined to individual bonds.

In this section we start, as in valence-bond theory, with a simple molecule, H₂, and in the following sections extend the same principles to more complex molecules and solids. In every case, molecular orbitals are built by adding together—the technical term is superimposing—atomic orbitals belonging to the valence shells of the atoms in the molecule. For example, a molecular orbital for H₂ is

$$\psi = \psi_{A1s} + \psi_{B1s} \quad (1)^*$$

where ψ_{A1s} is a 1s-orbital centered on one atom (A) and ψ_{B1s} is a 1s-orbital centered on the other atom (B). The molecular orbital ψ is called a linear combination of atomic orbitals (LCAO). Any molecular orbital formed from a linear combination of atomic orbitals on different atoms is called an LCAO-MO. Note that at this stage there are no electrons in the molecular orbital: a molecular orbital is just a combination—in this case, a sum—of wavefunctions. Like atomic orbitals, the molecular orbital in Eq. 1 is a well-defined mathematical function that can be evaluated at each point in space and pictured in three dimensions.

The LCAO-MO in Eq. 1 turns out to have a lower energy than either of the atomic orbitals used in its construction. The two atomic orbitals are like waves centered on different nuclei. Between the nuclei, the waves interfere constructively with each other in the sense that the total amplitude of the wavefunction is increased where they overlap (Fig. 3.25). The increased amplitude in the internuclear region means that there is an enhanced probability density between the nuclei. Any electron that occupies that molecular orbital, therefore, is attracted to both nuclei and so has a lower energy than when it is confined to an atomic orbital on one atom. Moreover, because the electron now occupies a greater volume than when it is confined to a single atom, it also has a lower kinetic energy, just like a particle confined to a bigger box (Section 1.7). A combination of atomic orbitals that results in an overall lowering of energy, like that in Eq. 1, is called a bonding orbital.

An important feature of MO theory is that

When N atomic orbitals overlap, they form N molecular orbitals.

In molecular hydrogen, where we are building LCAO-MOs from two atomic orbitals, we expect two molecular orbitals. In the second molecular orbital, the two atomic orbitals interfere destructively where they overlap. This orbital has the form

$$\psi = \psi_{A1s} - \psi_{B1s} \quad (2)^*$$

The negative sign indicates that the amplitude of ψ_{B1s} subtracts from the amplitude of ψ_{A1s} where they overlap (Fig. 3.26), and there is a nodal surface where the atomic orbitals cancel completely. In a hydrogen molecule, the nodal surface is a plane that lies halfway between the two nuclei. If an electron occupies this orbital, it is largely excluded from the internuclear region and consequently has a higher energy than when it occupies one of the atomic orbitals alone. A combination of atomic orbitals that results in an overall raising of energy, like that in Eq. 2, is called an antibonding orbital.

A note on good practice: What the negative sign in Eq. 2 really represents is that we reverse the sign of ψ_{B1s} everywhere (so a peak becomes a trough and vice versa), then superimpose the resulting wavefunction on ψ_{A1s} .

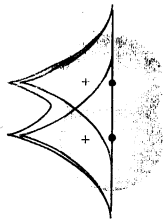


FIGURE 3.25 When two 1s-orbitals overlap in the same region of space in such a way that their wavefunctions have the same signs in that region, their wavefunctions (red lines) interfere constructively and give rise to a region of enhanced amplitude between the two nuclei (blue line).

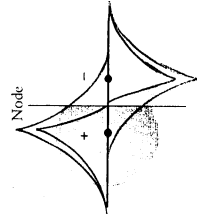
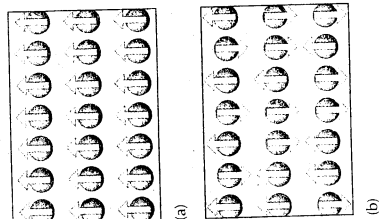


FIGURE 3.26 When two 1s-orbitals overlap in the same region of space in such a way that their wavefunctions have opposite signs, the wavefunctions (red and orange lines) interfere destructively and give rise to a region of diminished amplitude and a node between the two nuclei (blue line).

BOX 3.2 HOW DO WE KNOW... THAT ELECTRONS ARE NOT PAIRED?

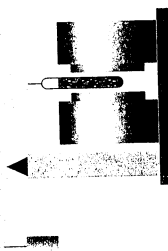
that can line up in this way, the greater the lowering of energy and the stronger the tendency of the sample to move into the applied field. Oxygen is a paramagnetic substance because it has two unpaired electrons; this property is used to detect the concentration of oxygen in incubators. All radicals are paramagnetic. Many compounds of the d-block elements are paramagnetic because they have various numbers of unpaired d-electrons.

The modern approach to measuring magnetic properties is to use a *superconducting quantum interference device* (SQUID), which is highly sensitive to small magnetic fields and can make very precise measurements on small samples.



(a) In a magnetic field, the spins of electrons in both paramagnetic and ferromagnetic substances are aligned (ferromagnetism is described in Chapter 16). (b) The spins of electrons in a paramagnetic substance return to a random orientation after an applied magnetic field is removed. However, the spins of electrons in a ferromagnetic substance remain aligned after a magnetic field is removed.

A Gouy balance is used to observe the magnetic character of a sample by detecting the extent to which it is drawn into (paramagnetic substances) or driven out of (diamagnetic substances) a magnetic field.



The development of molecular orbital theory (MO theory) in the late 1920s overcame these difficulties. It explains why the electron pair is so important for bond formation and predicts that oxygen is paramagnetic. It accommodates electron-deficient compounds such as the boranes just as naturally as it deals with methane and water. Furthermore, molecular orbital theory can be extended to account for the structures and properties of metals and semiconductors. It can also be used to account for the electronic spectra of molecules, which arise when an electron makes a transition from an occupied molecular orbital to a vacant molecular orbital.

The VB and MO theories are both procedures for constructing approximations to the wavefunctions of electrons, but they construct these approximations in different ways. The language of valence-bond theory, in which the focus is on bonds between pairs of atoms, pervades the whole of organic chemistry, where chemists speak of σ - and π -bonds between particular pairs of atoms, hybridization, and resonance. However, molecular orbital theory, in which the focus is on electrons that spread throughout the nuclear framework and bind the entire collection of atoms together, has been developed far more extensively than valence-bond

Most common materials are *diamagnetic*, which means that a sample of the material tends to move out of a magnetic field. The effect is quite small, but it can be detected by hanging a long, thin sample from the pan of a balance and letting it lie between the poles of an electromagnet. This arrangement, which was once the primary technique used to measure the magnetic properties of samples, is called a *Gouy balance*. When the electromagnet is turned on, a diamagnetic sample tends to move upward, out of the field, so it appears to weigh less than in the absence of the field. The diamagnetism arises from the effect of the magnetic field on the electrons in the molecule: the field forces the electrons to circulate through the nuclear framework. Because electrons are charged particles, this circulation corresponds to an electric current circulating within the molecule. That current gives rise to its own magnetic field, which opposes the applied field. The sample tends to move out of the field so as to minimize this opposing field.

Compounds with unpaired electrons are *paramagnetic*. They tend to move into a magnetic field and can be identified because they seem to weigh more in a Gouy balance when a magnetic field is applied than when it is absent. Paramagnetism arises from the electron spins, which behave like tiny bar magnets that tend to line up with the applied field. The more

The relative energies of the original atomic orbitals and the bonding and antibonding molecular orbitals are shown in a molecular orbital energy-level diagram like that in Fig. 3.27. The increased energy of an antibonding orbital is about equal to or a little greater than the lowering of the energy of the corresponding bonding orbital.

Molecular orbitals are formed by combining atomic orbitals: when atomic orbitals interfere constructively, they give rise to bonding orbitals; when they interfere destructively, they give rise to antibonding orbitals. N atomic orbitals combine to give N molecular orbitals.

3.10 The Electron Configurations of Diatomic Molecules

In the molecular orbital description of homonuclear diatomic molecules, we first build all possible molecular orbitals from the available valence-shell atomic orbitals. Then we accommodate the valence electrons in molecular orbitals by using the same procedure we used in the building-up principle for atoms (Section 1.13). That is,

- 1 Electrons are accommodated in the lowest-energy molecular orbital, then in orbitals of increasingly higher energy.
- 2 According to the Pauli exclusion principle, each molecular orbital can accommodate up to two electrons. If two electrons are present in one orbital, they must be paired.
- 3 If more than one molecular orbital of the same energy is available, the electrons enter them singly and adopt parallel spins (Hund's rule).

We shall illustrate these rules first with H_2 and then with other diatomic molecules. The same principles apply to polyatomic molecules, but their molecular orbitals are more complicated and their energies are harder to predict. Mathematical software for calculating the molecular orbitals and their energies is now widely available, and we shall show some of the results that it provides.

In H_2 , two $1s$ -orbitals (one on each atom) merge to form two molecular orbitals. We denote the bonding orbital σ_{1s} and the antibonding orbital σ_{1s}^* . The $1s$ in the notation shows the atomic orbitals from which the molecular orbitals are formed. The σ indicates that we have built a " σ -orbital," a sausage-shaped orbital. More formally, a σ -orbital is a molecular orbital that has cylindrical symmetry and no nodal plane that contains the internuclear axis. Two electrons, one from each H atom, are available. Both occupy the bonding orbital (the lower-energy orbital) and result in the configuration σ_{1s}^2 (Fig. 3.28). Because only the bonding orbital is occupied, the energy of the molecule is lower than that of the separate atoms, and hydrogen exists as H_2 molecules. Two electrons in a σ -orbital form a σ -bond, like the σ -bond in VB theory. However, even a single electron may be able to hold two atoms together with about half the strength of an electron pair for a bond. According to Lewis's theory and VB theory—an electron pair is not required for a bond. A pair is just the maximum number of electrons allowed by the Pauli exclusion principle to occupy any one molecular orbital. Even a single electron can act to bond atoms together.

Now we extend these ideas to other homonuclear diatomic molecules of Period 2 elements. The first step is to build up the molecular orbital energy-level diagram from the valence-shell atomic orbitals provided by the atoms. Because Period 2 atoms have $2s$ - and $2p$ -orbitals in their valence shells, we form molecular orbitals from the overlap of these atomic orbitals. There are a total of eight atomic orbitals (one $2s$ - and three $2p$ -orbitals on each atom); so we can expect to build eight molecular orbitals. The two $2s$ -orbitals overlap to form two σ -orbitals, one bonding (the σ_{2s} -orbital) and the other antibonding (the σ_{2s}^* -orbital); these orbitals resemble the σ_{1s} - and σ_{1s}^* -orbitals in H_2 . The six $2p$ -orbitals (three on each neighboring atom) form the remaining six molecular orbitals. They can overlap in two distinct ways. The two $2p$ -orbitals that are

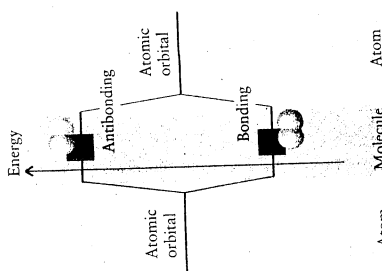


FIGURE 3.27 A molecular orbital energy-level diagram for the bonding and antibonding molecular orbitals that can be built from two s -orbitals. Different signs of the s -orbitals (reflecting how they are combined together to form the molecular orbital) are depicted by the different shades of blue.

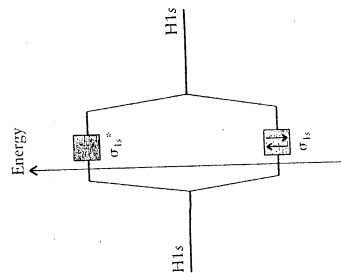


FIGURE 3.28 The two electrons in an H_2 molecule occupy the lower-energy (bonding) molecular orbital and result in a stable molecule.

directed toward each other along the internuclear axis form a bonding σ -orbital (σ_{2p}) and an antibonding σ^* -orbital (σ_{2p}^*) where they overlap (Fig. 3.29). The two $2p$ -orbitals on each atom that are perpendicular to the internuclear axis overlap side by side to form bonding and antibonding " π -orbitals" (Fig. 3.30). A π -orbital is a molecular orbital with one nodal plane that contains the internuclear axis. There are two perpendicular $2p$ -orbitals on each atom, and so four molecular orbitals—two bonding π_{2p} -orbitals and two antibonding π_{2p}^* -orbitals—are formed by their overlap.

Detailed calculation shows that there are some small differences in the order of energy levels from molecule to molecule (Box 3.3). Figure 3.31 shows the order for the Period 2 elements with the exception of O_2 and F_2 , which lie in the order shown in Fig. 3.32. The order of energy levels is easy to explain for these two molecules. First, because each atom has many electrons that contribute to shielding, the $2s$ -orbitals lie well below the $2p$ -orbitals and we can think of building σ -orbitals from the two sets of atomic orbitals separately. However, because the atoms of elements earlier in the period have fewer electrons, their $2s$ - and $2p$ -orbitals have more similar energies than in O and F. As a result, it is no longer possible to think of a σ -orbital as being formed from either the $2s$ -orbitals or the $2p$ -orbitals separately, and all four of these orbitals must be used to build the four σ -orbitals. It is then hard to predict without detailed calculation where these four orbitals will lie, and it turns out that they in fact lie where we show them in Fig. 3.31.

Once we know what molecular orbitals are available, we can construct the ground-state electron configurations of the molecules by using the building-up principle. For example, consider N_2 . Because nitrogen belongs to Group 15/V, each atom supplies five valence electrons. A total of ten electrons must therefore be assigned to the eight molecular orbitals shown in Fig. 3.31. Two fill the σ_{2s} -orbital. The next two fill the σ_{2s}^* -orbital. Next in line for occupation are the two π_{2p} -orbitals, which can hold a total of four electrons. The last two electrons then enter the σ_{2p} -orbital. The ground configuration is therefore

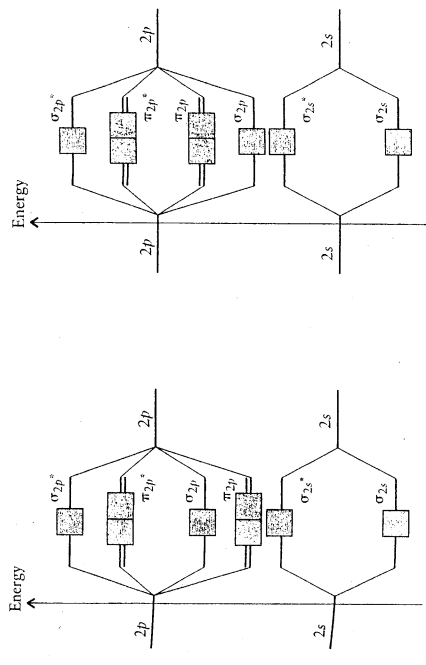
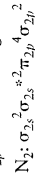


FIGURE 3.31 A typical molecular orbital energy-level diagram for the homonuclear diatomic molecules Li_2 through N_2 . Each box represents one molecular orbital and can accommodate up to two electrons.

FIGURE 3.32 The molecular orbital energy-level diagram for the homonuclear diatomic molecules on the right-hand side of Period 2, specifically O_2 and F_2 .

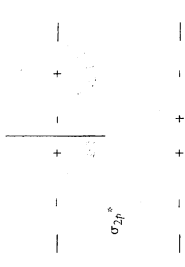


FIGURE 3.29 Two p -orbitals can overlap to give bonding (lower) and antibonding (upper) σ -orbitals. Note that the antibonding combination has a node between the two nuclei. If all σ -orbitals have nodes passing through the nuclei, but no nodes along the x -axis, the bond.

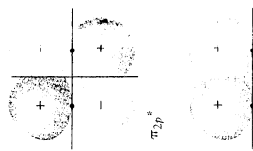


FIGURE 3.30 Two p -orbitals can overlap side by side to give bonding π -orbitals and antibonding (above) π^* -orbitals. Note that the latter has a nodal plane between the two nuclei. Both orbitals have a nodal plane through the two nuclei and look like p -orbitals when viewed along the internuclear axis.

BOX 3.3 HOW DO WE KNOW... THE ENERGIES OF MOLECULAR ORBITALS?

The energies of orbitals are calculated today by solving the Schrödinger equation with computer software. The commercial software available is now so sophisticated that this approach can be as easy as typing in the name of the molecule or drawing it on screen. But these values are theoretical. How do we determine orbital energies experimentally?

One of the most direct methods is photoelectron spectroscopy (PES), an adaptation of the photoelectric effect (Section 1.2). A photoelectron spectrometer (see illustration below) contains a source of high-frequency, short-wavelength radiation. Ultraviolet radiation is used most often for molecules, but x-rays are used to explore orbitals buried deeply inside solids. Photons in both frequency ranges have so much energy that they can eject electrons from the molecular orbitals they occupy.

Let's suppose that the frequency of the radiation is ν (nu), so each photon has an energy $h\nu$. An electron occupying a molecular orbital lies at an energy E_{orbital} below the zero of energy (corresponding to an electron far removed from the molecule). A photon that collides with the electron can eject it from the molecule if the photon can supply at least that much energy. The remaining energy of the photon, $h\nu - E_{\text{orbital}}$, then appears as the kinetic energy, E_K , of the ejected electron:

$$h\nu - E_{\text{orbital}} = E_K$$

We know ν , the frequency of the radiation being used to bombard the molecules; so, if we could measure the kinetic energy of the ejected electron, E_K , we could solve this expression to find the orbital energy, E_{orbital} .

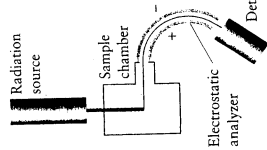
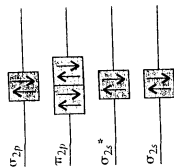


Diagram of a photoelectron spectrometer.



44 Nitrogen, N₂

This configuration is shown as (44), where the boxes represent molecular orbitals. At first sight, the molecular orbital description of N₂ looks quite different from the Lewis description (N≡N:). However, it is, in fact, very closely related. We can see their similarity by defining the bond order (b) in molecular orbital theory as the net number of bonds, allowing for the cancellation of bonds by antibonds:

$$\text{Bond order} = \frac{1}{2} \times (\text{number of electrons in bonding orbitals} - \text{number of electrons in antibonding orbitals}) \quad (3)$$

$$b = \frac{1}{2} \times (N - N^*)$$

Here N is the number of electrons in bonding molecular orbitals and N* is the number of electrons in antibonding molecular orbitals. This definition of bond order is the generalization of the one given in Section 2.6, where we simply counted shared pairs. In N₂, there are eight electrons in bonding orbitals and two in antibonding orbitals, and so the bond order is $\frac{1}{2}(8 - 2) = 3$. Because its bond order is 3, N₂ effectively has three bonds between the N atoms, just as the Lewis structure suggests.

TOOLBOX 3.2 HOW TO DETERMINE THE ELECTRON CONFIGURATION AND BOND ORDER OF A HOMONUCLEAR DIATOMIC SPECIES

CONCEPTUAL BASIS

When N valence atomic orbitals overlap, they form N molecular orbitals. The ground-state electron configuration of a molecule is deduced by using the building-up principle to accommodate all the valence electrons in the available molecular orbitals. The bond order is the net number of bonds that hold the molecule together.

PROCEDURE

- Step 1 Identify all the atomic orbitals in the valence shells, ignoring how many electrons they contain.
- Atoms of Period 1 elements (H and He) have one valence atomic orbital each, and atoms of Period 2 and Period 3 elements (Li through Ne, Na through Ar) have four (one s and three p).

- Step 2 Use matching valence-shell atomic orbitals to build bonding and antibonding molecular orbitals and draw the resulting molecular orbital energy-level diagram (Figs. 3.31 and 3.32).
- Step 3 Note the total number of electrons present in the valence shells of the two atoms. If the species is an ion, adjust the number of electrons to account for the charge.
- Step 4 Accommodate the electrons in the molecular orbitals according to the building-up principle.
- Step 5 To determine the bond order, subtract the number of electrons in antibonding orbitals from the number in bonding orbitals and divide the result by 2 (Eq. 3).

This procedure is illustrated in Example 3.7.

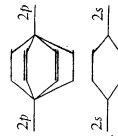
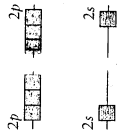
EXAMPLE 3.7 Sample exercise: Deducing the ground-state electron configuration of a diatomic molecule

Deduce the ground-state electron configuration of the fluorine molecule and calculate its bond order.

SOLUTION The Lewis structure of F₂ is :F—F:, and so we anticipate that its bond order is 1. To calculate the bond order formally, we proceed as in Toolbox 3.2.

- Step 1 Identify the valence atomic orbitals.

Each atom contributes a 2s-orbital and three 2p-orbitals, for a total of 8 orbitals.



- Step 2 Construct the molecular orbital energy-level diagram.

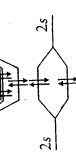
See Fig. 3.32.

- Step 3 Count the valence electrons.

$$2 \times 7 = 14$$

Step 4 Construct the electron configuration.

Fill the orbitals in order of increasing energy: $\sigma_{2s}^2 \sigma_{2s}^* \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^* \sigma_{2p}^2$.



Step 5 Determine the bond

We conclude that F_2 is a singly bonded molecule, in agreement with the Lewis structure. Notice that the first ten electrons repeat the N_2 configuration (apart from the change in order of the σ_{2p}^* and π_{2p} -orbitals).

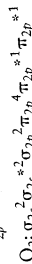
$$b = \frac{1}{2} \times [(2 + 2 + 4) - (2 + 4)] = 1$$

order from $b = \frac{1}{2} (N - N^*)$.

SELF-TEST 3.10A Deduce the electron configuration and bond order of the ion C_2^{2-} .
 [Answer: $\sigma_{2s}^2 \sigma_{2s}^* \sigma_{2p}^2 \pi_{2p}^4 \sigma_{2p}^2 \pi_{2p}^* \sigma_{2p}^*$, $b = 3$]

SELF-TEST 3.10B Suggest a configuration for the O_2^+ ion and state its bond order.

We find the ground-state electron configuration of O_2 by adding its twelve valence electrons (six from each atom) to the molecular orbitals shown in Fig. 3.32. The first ten electrons repeat the F_2 configuration, as in Example 3.7. According to the building-up principle, the last two electrons occupy the two separate π_{2p}^* -orbitals and do so with parallel spins. The configuration is therefore



as shown in (45). This conclusion is a minor triumph for molecular orbital theory, because the last two spins are not paired, their magnetic fields do not cancel, and the molecule is predicted to be paramagnetic, exactly as observed. The bond order of O_2 is

$$b = \frac{1}{2} \times [(2 + 2 + 4) - (2 + 1 + 1)] = 2$$

The double bond in this molecule is actually a σ -bond plus two "half π -bonds," each "half bond" consisting of a pair of bonding electrons and one antibonding electron.

The ground-state electron configurations of diatomic molecules are deduced by forming molecular orbitals from all the valence-shell atomic orbitals of the two atoms and adding the valence electrons to the molecular orbitals in order of increasing energy, in accord with the building-up principle.

3.11 Bonding in Heteronuclear Diatomic Molecules

The bond in a heteronuclear diatomic molecule, a diatomic molecule built from atoms of two different elements, is polar, with the electrons shared unequally by the two atoms. We therefore rewrite Eq. 1 as

$$\psi = c_A \psi_A + c_B \psi_B \quad (4)$$

where the coefficients c_A and c_B are not equal. Because we always take the squares of wavefunctions when interpreting them in terms of probabilities, if c_A is large, then the molecular orbital looks more like the atomic orbital of A and the electron density is greater near A; if c_B is large, it looks more like the atomic orbital of B and the electron density is greater near B. In general, the atom with the atomic orbitals of lower energy dominate the molecular orbitals and the electron density is greater closer to that atom. The relative values of c_A and c_B determine the type of bond:

- In a *nonpolar covalent bond*, $c_A^2 = c_B^2$ and the electron pair is shared equally between the two atoms.

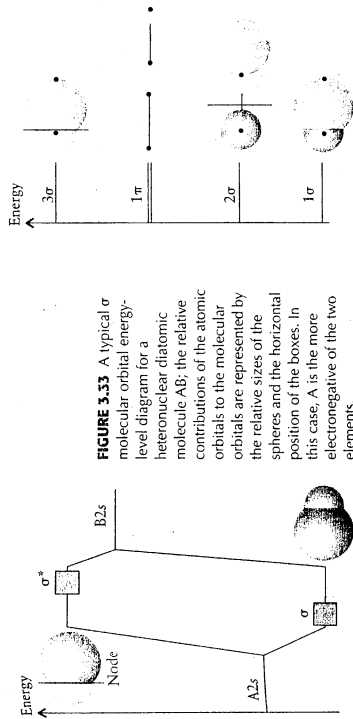


FIGURE 3.33 A typical σ molecular orbital energy-level diagram for a heteronuclear diatomic molecule AB; the relative contributions of the atomic orbitals to the molecular orbitals are represented by the relative sizes of the spheres and the horizontal position of the boxes. In this case, A is the more electronegative of the two elements.

- In an *ionic bond*, the coefficient belonging to one ion is nearly zero because the other ion captures almost all the electron density.

- In a *polar covalent bond*, the atomic orbital belonging to the more electronegative atom has the lower energy, and so it makes the larger contribution to the lowest energy molecular orbital (Fig. 3.33). Conversely, the contribution to the highest-energy (most antibonding) orbital is greater for the higher-energy atomic orbital, which belongs to the less electronegative atom.

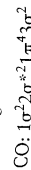
To find the ground-state electron configurations of heteronuclear diatomic molecules, we use the same approach that we used for homonuclear diatomic molecules; but first we must modify the energy-level diagrams. For example, consider the HF molecule. The σ -bond in this molecule consists of an electron pair in a σ -orbital built from the $F2p_z$ -orbital and the $H1s$ -orbital. Because the electronegativity of fluorine is 4.0 and that of hydrogen is 2.2, we can expect the bonding σ -orbital to be mainly $F2p_z$ and the antibonding σ^* -orbital to be mainly $H1s$ in character. These expectations are confirmed by calculation (Fig. 3.34). Because the two electrons in the bonding orbital are more likely to be found in the $F2p_z$ -orbital than in the $H1s$ -orbital, there is a partial negative charge on the F atom and a partial positive charge on the H atom.

The molecular orbital energy-level diagrams of heteronuclear diatomic molecules are much harder to predict qualitatively and we have to calculate each one explicitly because the atomic orbitals contribute differently to each one. Figure 3.35 shows the calculated scheme typically found for CO and NO. We can use this diagram to state the electron configuration by using the same procedure as for homonuclear diatomic molecules.

EXAMPLE 3.8 Sample exercise: Writing the configuration of a heteronuclear diatomic molecule or ion

Write the configuration of the ground state of the carbon monoxide molecule.

SOLUTION There are $4 + 6 = 10$ valence electrons to accommodate in the orbitals shown in Fig. 3.35. The resulting configuration is shown in the illustration, and is



SELF-TEST 3.11A Write the configuration of the ground state of the nitric oxide (nitrogen monoxide) molecule.

[Answer: $1\sigma^2 2\sigma^* 2\pi^4 3\sigma^2 2\pi^{*1}$]

SELF-TEST 3.11B Write the configuration of the ground state of the cyanide ion, CN^- , assuming that its molecular orbital energy-level diagram is the same as that for CO.

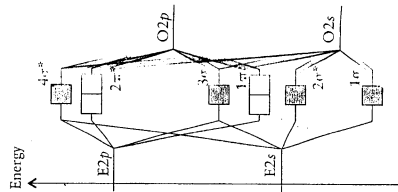


FIGURE 3.35 The molecular orbital schemes typical of those calculated for a diatomic oxide molecule, EO (where E is C for CO and E = N for NO). Note that the σ -orbitals are formed from mixtures of s - and p_z -orbitals on both atoms; accordingly, we label them simply 1σ , 2σ , etc. in order of increasing energy.

FIGURE 3.4 Schematic diagram of the molecular orbitals of F_2 . The orbitals are labeled by using a standard convention. The two 1π -orbitals are nonbonding; the three σ -orbitals are progressively more antibonding (1σ , bonding; 3σ , antibonding).

Bonding in heteronuclear diatomic molecules involves an unequal sharing of the bonding electrons. The more electronegative element contributes more strongly to the bonding orbitals, whereas the less electronegative element contributes more strongly to the antibonding orbitals.

3.12 Orbitals in Polyatomic Molecules

The molecular orbital theory of polyatomic molecules follows the same principles as those outlined for diatomic molecules, but the molecular orbitals spread over all the atoms in the molecule. An electron pair in a bonding orbital helps to bind together the whole molecule, not just an individual pair of atoms. The energies of molecular orbitals in polyatomic molecules can be studied experimentally by using ultraviolet and visible spectroscopy (see Major Technique 2, following this chapter).

The description of bonding in polyatomic molecules can be quite complex. However, we can illustrate qualitatively how to use molecular orbital theory to describe bonding in one of the simplest but most important polyatomic molecules, water. A water molecule has six atomic orbitals (one $O2s$, three $O2p$, and two $H1s$). These six orbitals are used to build six molecular orbitals in which the degree of net bonding character is related to the number of internuclear nodes (Fig. 3.36). The molecular orbital with no nodes between neighboring atoms is fully bonding and, when occupied, contributes to holding all the atoms together; the one with a node between all neighboring pairs of atoms is fully antibonding and, if occupied, contributes to pushing all the atoms apart. There are eight electrons to accommodate: six are provided by the O atom and one comes from each H atom. Two electrons in the lowest energy, most bonding, orbital pull all three atoms together. Two electrons in the orbital composed purely of the $O2p_x$ -orbital (where x lies perpendicular to the molecular plane) are localized completely on the oxygen atom and do not contribute directly to the bonding. An orbital such as this one that, when occupied, contributes to neither bonding nor antibonding is classified as a nonbonding orbital. In some cases, a nonbonding orbital is a single atomic orbital; in others, it may consist of a linear combination of atomic orbitals on atoms that are not neighbors and so overlap to a negligible extent.

When we apply molecular orbital theory to methane we see that valence bond theory misses an interesting point. Valence bond theory predicts that all eight bonding electrons in methane are in identical sp^3 -orbitals and should therefore have the same energy. However, although all four bonds are identical, one of the electron pairs is actually slightly lower in energy than the others. This finding is easily explained by molecular orbital theory. In methane eight molecular orbitals are constructed from the four carbon valence orbitals and the four $1s$ -orbitals from the four hydrogen atoms. These molecular orbitals have the energies shown in Fig. 3.37; we see that one bonding orbital lies lower in energy than the other three. Therefore, two of the electrons have a lower energy than the others. However, the overall electron density is the same in each bonding region because the molecular orbitals are delocalized and the electron density is spread out uniformly over all C—H regions.

A note on good practice: The concepts of promotion, hybridization, and resonance belong to valence bond theory, not molecular orbital theory. Instead, molecular orbitals are built from all the available atomic orbitals by noting whether or not they have the right shape to overlap with one another.

Another important polyatomic molecule is benzene, C_6H_6 , the parent of the aromatic compounds. In the molecular orbital description of benzene, all thirty $C2s$ -, $C2p$ -, and $H1s$ -orbitals contribute to molecular orbitals spreading over all twelve atoms (six C plus six H). The orbitals in the plane of the ring (the $C2s$ -, $C2p_x$ -, and $C2p_y$ -orbitals on each carbon atom and all six $H1s$ -orbitals) form delocalized σ -orbitals that bind the C atoms together and link the H atoms to the atoms. The six $C2p_z$ -orbitals, which are perpendicular to the ring, contribute to six delocalized π -orbitals that spread all the way around the ring. However, chemists

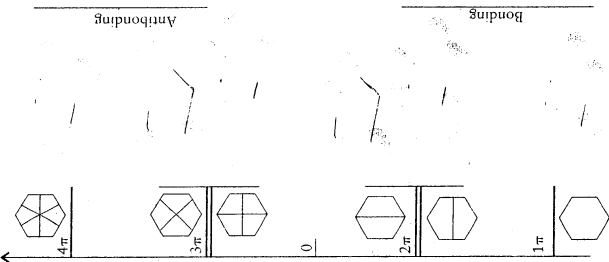


FIGURE 3.38 The six π -orbitals of benzene: locations of nodes, are shown on the left. Note that the orbitals range from fully bonding (no internuclear nodes) to fully antibonding (six internuclear nodes). The zero of energy corresponds to the total energy of the separated atoms. The three orbitals with negative energies have net bonding character.

(other than those carrying out detailed calculations, who use a pure MO scheme) commonly mix MO and VB descriptions when discussing organic molecules. Because the language of hybridization and orbital overlap is well suited to the description of σ -bonds, chemists typically express the σ -framework of molecules in VB terms. Thus, they think of the σ -framework of benzene as formed by the overlap of sp^2 hybridized orbitals on neighboring atoms. Then, because delocalization has such an important feature of the π -bonding component of conjugated double bonds, which alternate as in $-C=C-C=C-C=C-$, they treat such π -bonds in terms of MO theory. We shall do the same.

First, the VB part of the description of benzene. Each C atom is sp^2 hybridized, with one electron in each hybrid orbital. Each C atom has a p_z -orbital perpendicular to the plane defined by the hybrid orbitals, and it contains one electron. Two sp^2 hybrid orbitals on each C atom overlap and form σ -bonds with similar orbitals on the two neighboring C atoms, forming the 120° internal angle of the benzene hexagon. The third, outward-pointing sp^2 hybrid orbital on each C atom forms a σ -bond with a hydrogen atom. The resulting σ -framework is the same as that illustrated in Fig. 3.20.

Now for the MO part of the description. From the six $C2p_z$ -orbitals, we form six delocalized π -orbitals: their shapes are shown in Fig. 3.38 and their energies are shown in Fig. 3.39. The character of the orbitals changes from net bonding to net antibonding as the number of internuclear nodes increases from none (fully bonding) to six (fully antibonding).

Each carbon atom provides one electron for the π -orbitals. Two electrons occupy the lowest energy, most bonding orbital; and the remaining four electrons occupy the next higher energy orbitals (two orbitals of the same energy). Figure 3.39 shows one of the reasons for benzene's great stability: the π -electrons occupy only orbitals with a net bonding effect; none of the destabilizing antibonding orbitals are occupied.

The delocalization of electrons accounts for the existence of electron-deficient molecules. Because the bonding influence of an electron pair is spread over all the atoms in the molecule, there is no need to provide one pair of electrons for each pair of atoms. A smaller number of pairs of electrons spread throughout the molecule may be able to bind all the atoms together, particularly if the nuclei are not highly charged and so do not repel one another strongly. This is the case in diborane, B_2H_6 (Section 14.14), where six electron pairs can hold the eight nuclei together.

Another mystery solved by molecular orbital theory is the existence of hyper-valent compounds, compounds in which a central atom forms more bonds than allowed by the octet rule (recall Section 2.10). In valence bond theory, hybridization schemes are required to make sense of these compounds. For example, the expanded valence shell of Period 3 elements in compounds like SF_6 is explained as sp^3d hybridization. However, the d -orbitals of sulfur lie at relatively high energies and may not be accessible for bonding. In molecular orbital theory a bonding scheme can be devised for SF_6 that does not involve d -orbitals. The four valence orbitals provided by the sulfur atom and the six orbitals of the fluorine atoms that point toward the sulfur atom, for a total of 10 atomic orbitals, result in 10 molecular orbitals with the energies shown in Fig. 3.40. The 12 electrons occupy the lowest six orbitals, which are either bonding or nonbonding, and so bind all the atoms together without needing to use d -orbitals. Because four bonding orbitals are occupied, the average bond order of each of the six S—F links is $\frac{3}{2}$.

Finally, we return to the opening remarks of the chapter and see how molecular orbital theory explains the colors of vegetation. The presence of highly delocalized electrons in the large molecules found in the petals of flowers and in fruit and

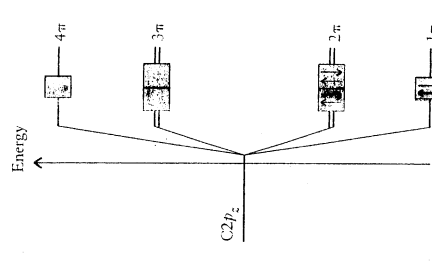


FIGURE 3.39 The molecular orbital energy-level diagram for the π -orbitals of benzene. In the ground state of the molecule, only the net bonding orbitals are occupied.

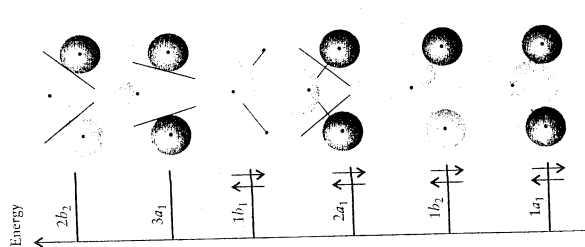


FIGURE 3.36 A schematic diagram of the molecular orbitals of H_2O . The orbitals are labeled according to the conventional notation for angular triatomic molecules. The orbitals become progressively more antibonding ($1a_1$, bonding; $2b_2$, antibonding). The orbital labeled $1b_2$ is nonbonding, because it is composed of an orbital ($O2p_x$) that does not overlap either hydrogen atom.

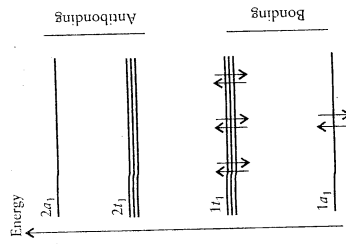


FIGURE 3.37 The molecular orbital energy-level diagram for methane and the occupation of the orbitals by the eight valence electrons of the atoms.

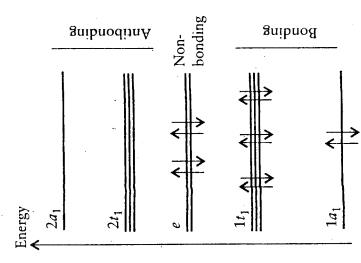
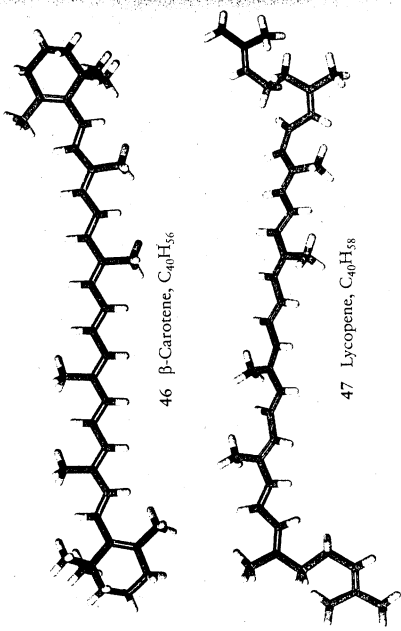


FIGURE 3.40 The molecular orbital energy-level diagram for SF₆ and the occupation of the orbitals by the 12 valence electrons of the atoms. Note that no antibonding orbitals are occupied and that there is a net bonding interaction even though no d-orbitals are involved.

vegetables is largely responsible for their colors. Because many carbon atoms contribute p-orbitals to the π system of these molecules, there are many molecular orbitals. An electron in a π system of such a molecule is like a particle in a large one-dimensional box. Because the “box” is very large, the energy levels are very close together. In these large molecules, the highest occupied molecular orbital (HOMO) is very close in energy to the lowest unoccupied molecular orbital (LUMO). As a result, it takes very little energy to excite an electron from a HOMO to a LUMO (Fig. 3.41). Photons of visible light have enough energy to excite the electrons across this energy gap, and the absorption of these photons results in the colors that we perceive. The coloring agent of carrots and the precursor of vitamin A, β-carotene (46), has a highly delocalized π system, as does lycopene (47), the red compound that gives tomatoes their color.



According to molecular orbital theory, the delocalization of electrons in a polyatomic molecule spreads the bonding effects of electrons over the entire molecule.

IMPACT ON MATERIALS: ELECTRONIC CONDUCTION IN SOLIDS

Molecular orbital theory explains the electrical properties of solids by treating them as one huge molecule and supposing that their valence electrons occupy “molecular orbitals” that spread throughout the solid.

3.13 Bonding in the Solid State

Metals and semiconductors are electronic conductors in which an electric current is carried by delocalized electrons. A metallic conductor is an electronic conductor in which the electrical conductivity decreases as the temperature is raised. A semiconductor is an electronic conductor in which the electrical conductivity increases as the temperature is raised. In most cases, a metallic conductor has a much higher electrical conductivity than a semiconductor, but it is the temperature dependence of the conductivity that distinguishes the two types of conductors. An insulator does not conduct electricity. A superconductor is a solid that has zero resistance to an electric current. Some metals become superconductors at very low temperatures, at about 20 K or less, and some compounds also show superconductivity (see Box 5.2). High-temperature superconductors have enormous technological potential because they offer the prospect of more efficient power transmission and the generation of high magnetic fields for use in transport systems (Fig. 3.42).

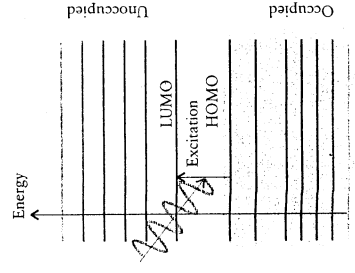


FIGURE 3.41 In large molecules, there are many closely spaced energy levels and the HOMO-LUMO gap is quite small. Such molecules are often colored because photons of visible light can be absorbed when electrons are excited from the HOMO to the LUMO.

FIGURE 3.42 Superconductors have the ability to levitate vehicles with embedded magnets. This picture shows an experimental zero-friction train in Japan, built to use helium-cooled metal superconductors.



Electrical conduction in metals can be explained in terms of molecular orbitals that spread throughout the solid. We have already seen that, when N atomic orbitals merge together in a molecule, they form N molecular orbitals. The same is true of a metal, but, for a metal, N is enormous (about 10²³ for 10 g of copper, for example). Instead of the few molecular orbitals with widely spaced energies typical of small molecules, the huge number of molecular orbitals in a metal are so close together in energy that they form a nearly continuous band (Fig. 3.43).

Consider a metal such as sodium. Each atom contributes one valence orbital (the 3s-orbital in this case) and one valence electron. If there are N atoms in the sample, then the N 3s-orbitals merge to form a band of N molecular orbitals, of which half are net bonding and half are net antibonding. We say “net” bonding or antibonding because, in general and as in benzene, a molecular orbital is bonding between some neighbors and antibonding between others, depending on where its internuclear nodes lie; only the molecular orbital of lowest energy, with no internuclear nodes, is bonding between all neighboring atoms. The N electrons contributed by the N atoms occupy the orbitals according to the building-up principle. Because two electrons can occupy each orbital, the N electrons occupy the lower ½N bonding orbitals.

An empty or incompletely filled band of molecular orbitals is called a conduction band. Because neighboring orbitals lie so close together in energy, it takes very little additional energy to excite the electrons from the topmost filled molecular orbitals to the empty orbitals of the conduction band. Electrons in the conduction band can move freely through the solid, and so they can carry an electric current. The resistance of the metal increases with temperature because, when it is heated, the atoms vibrate more vigorously. The passing electrons collide with the vibrating atoms and do not pass through the solid so easily.

In an insulator, the valence electrons fill all the available molecular orbitals to give a full band called a valence band. There is a substantial band gap, a range of energies for which there are no orbitals, before the next band, the empty orbitals that form the conduction band, begins (Fig. 3.44). The electrons in the valence band can be excited into the conduction band only by a very large injection of energy. Because the valence band is full and because the conduction band is separated from it by a large energy gap, the electrons are not mobile and the solid does not conduct electricity.

Bonding in solids may be described in terms of bands of molecular orbitals. In metals, the conduction bands are incompletely filled orbitals that allow electrons to flow. In insulators, the valence bands are full and the large band gap prevents the promotion of electrons to empty orbitals.

FIGURE 3.44 In a typical insulating solid, a full valence band is separated by a substantial energy gap from the empty conduction band. Note the break in the vertical scale.

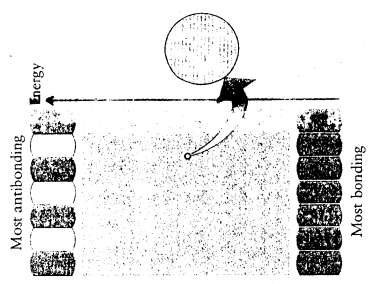
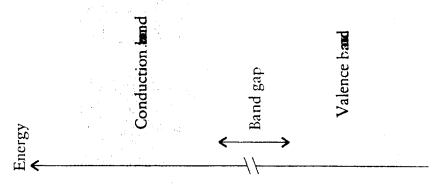


FIGURE 3.43 A line of atoms gives rise to an almost continuous band of molecular orbital energies. At the lower edge of the band, the molecular orbitals are fully bonding; at the upper edge, the molecular orbitals are fully antibonding. The enlargement shows that, although the band of allowed energies appears to be continuous, it is in fact composed of discrete, closely spaced levels.



SKILLS YOU SHOULD HAVE MASTERED

- 1 Explain the basis of the VSEPR model of bonding in terms of repulsions between electrons (Section 3.1).
- 2 Use the VSEPR model to predict the electron arrangement and shape of a molecule or polyatomic ion from its formula (Toolbox 3.1 and Examples 3.1, 3.2, and 3.3).
- 3 Predict the polar character of a molecule (Example 3.4).
- 4 Account for the structure of a molecule in terms of hybrid orbitals and σ - and π -bonds (Examples 3.5 and 3.6).
- 5 Construct and interpret a molecular orbital energy-level diagram for a homonuclear diatomic species (Sections 3.9 and 3.10).

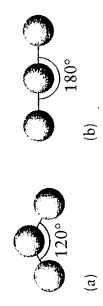
練習問題をレポート課題とします

EXERCISES

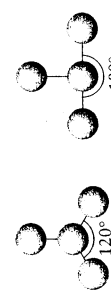
Exercises labeled □ require calculus.

The Shapes of Molecules and Ions

3.1 Below are ball-and-stick models of two molecules. In each case, indicate whether or not there must be, may be, or cannot be one or more lone pairs of electrons on the central atom:



3.2 Below are ball-and-stick models of two molecules. In each case, indicate whether or not there must be, may be, or cannot be one or more lone pairs of electrons on the central atom:



3.3 (a) What is the shape of the thionyl chloride molecule, SOCl_2 ? Sulfur is the central atom. (b) How many different OSCl bond angles are there in this molecule? (c) What values are expected for the OSCl and ClSCl bond angles?

3.4 (a) What is the shape of the ClO_3^- ion? (b) What values are expected for the ClO bond angles?

3.5 (a) What is the shape of the ClO_2^+ ion? (b) What is the OClO bond angle?

3.6 (a) What is the shape of the XeF_5^+ ion? (b) How many different FXeF bond angles are there in this molecule? (c) What values are expected for the FXeF bond angles?

3.7 (a) What is the shape of an ICl_2 molecule (iodine is the central atom)? (b) What value is expected for the ClICl angle?

3.14 Semiconductors

In a semiconductor, an empty conduction band lies close in energy to a full valence band. As a result, as the solid is warmed, electrons can be excited from the valence band into the conduction band, where they can travel throughout the solid. Hence, the resistance of a semiconductor decreases as its temperature is raised.

The ability of a semiconductor to carry an electric current can also be enhanced by adding electrons to the conduction band or by removing some from the valence band. This modification is carried out chemically by doping the solid, or spreading small amounts of impurities throughout it. In one example, a minute amount of a Group 15(V) element such as arsenic is added to very pure silicon. The arsenic increases the number of electrons in the solid: each Si atom (Group 14(IV) has four valence electrons, whereas each As atom (Group 15(V) has five. The additional electrons enter the upper, normally empty conduction band of silicon and allow the solid to conduct (Fig. 3.45). This type of material is called an n-type semiconductor because it contains excess negatively charged electrons. When silicon (Group 14(IV) is doped with indium (Group 13(III) instead of arsenic, the solid has fewer valence electrons than does pure silicon; so the valence band is no longer completely full (Fig. 3.46). We say that the valence band now contains "holes." Because the valence band is no longer full, it has been turned into a conduction band, and an electric current can flow. This type of semiconductor is called a p-type semiconductor, because the absence of negatively charged electrons is equivalent to the presence of positively charged holes. The doped solids are overall electrically neutral, because the nuclei of the doping atoms have a charge that matches the number of their electrons.

Solid-state electronic devices such as diodes, transistors, and integrated circuits contain p-n junctions in which a p-type semiconductor is in contact with an n-type semiconductor (Fig. 3.47). The structure of a p-n junction allows an electric current to flow in only one direction. When the electrode attached to the p-type semiconductor has a negative charge, the holes in the p-type semiconductor are attracted to it, the electrons in the n-type semiconductor are attracted to the other (positive) electrode, and current does not flow. When the polarity is reversed, with the negative electrode attached to the n-type semiconductor, electrons flow from the n-type semiconductor through the p-type semiconductor toward the positive electrode.

SELF-TEST 3.12A Which type of semiconductor is germanium doped with arsenic? [Answer: n-type]

SELF-TEST 3.12B Which type of semiconductor is antimony doped with tin?

In semiconductors, empty levels are close in energy to filled levels.

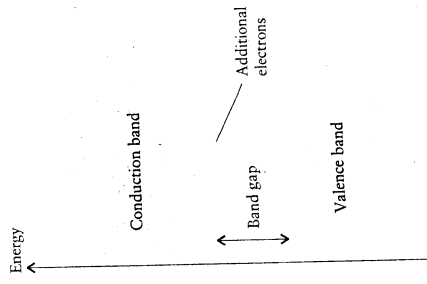


FIGURE 3.45 In an n-type semiconductor, the additional electrons supplied by the electron-rich dopant atoms enter the conduction band (forming the pink band at the bottom of the conduction band), where they can act as carriers for the current.

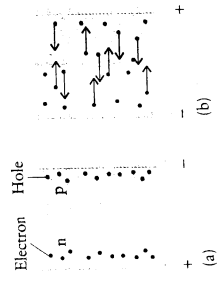
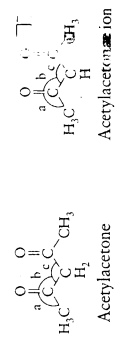


FIGURE 3.47 The structure of a p-n junction allows an electric current to flow in only one direction. (a) Reverse bias: the negative electrode is attached to the p-type semiconductor and current does not flow. (b) Forward bias: the electrodes are reversed to allow charge carriers to be regenerated.

FIGURE 3.46 In a p-type semiconductor, the electron-poor dopant atoms effectively remove electrons from the valence band, and the "holes" that result (blue band at the top of the valence band) enable the remaining electrons to become mobile and conduct electricity through the valence band.



3.8 (a) What is the shape of an SbF_6^{2-} ion? (b) How many different FSbF bond angles are there in this molecule? (c) What values are expected for the FSbF angles?

3.9 Using Lewis structures and VSEPR, give the VSEPR formula for each of the following species and predict its shape: (a) sulfur tetrachloride; (b) iodine trichloride; (c) IF_5 ; (d) xenon trioxide.

3.10 Using Lewis structures and VSEPR, give the VSEPR formula for each of the following species and predict its shape: (a) PF_5 ; (b) ICl_4 ; (c) phosphorus pentafluoride; (d) xenon tetrafluoride.

3.11 Give the VSEPR formula, molecular shape, and bond angles for each of the following species: (a) I_3^- ; (b) BCl_3 ; (c) IO_2 ; (d) NO_2 .

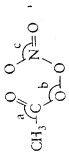
3.12 Give the VSEPR formula, molecular shape, and bond angles for each of the following species: (a) I_3^- ; (b) BCl_3 ; (c) SeO_3^{2-} ; (d) GeH_4 .

3.13 Write the Lewis structure and the VSEPR formula, list the shape, and predict the approximate bond angles for (a) CF_3Cl ; (b) TeCl_4 ; (c) COF_2 ; (d) CH_3 .

3.14 Write the Lewis structure and the VSEPR formula, list the shape, and predict the approximate bond angles for (a) PCl_2F_2 ; (b) SnF_4 ; (c) SnF_6^{2-} ; (d) IF_5 ; (e) XeO_4 .

3.15 The compound 2,4-pentanedione (also known as acetylacetone and abbreviated to acac) is acidic and can be deprotonated. The anion forms complexes with metals that are used in gasoline additives, lubricants, insecticides, and fungicides. (a) Estimate the bond angles marked with arcs and lowercase letters in 2,4-pentanedione and in the acac ion. (b) What are the differences, if any?

3.16 Estimate the bond angles marked with arcs and lowercase letters in peroxyacetyl nitrate, an eye irritant in smog:



3.17 Predict the bond angles at the central atom of the following molecules and ions: (a) ozone, O_3 ; (b) azide ion, N_3^- ; (c) cyanate ion, CNO^- ; (d) hydronium ion, H_3O^+ .

3.18 Predict the bond angles at the central atom of the following molecules and ions: (a) OF_2 ; (b) ClO_2 ; (c) NO_2 ; (d) $SeCl_2$.

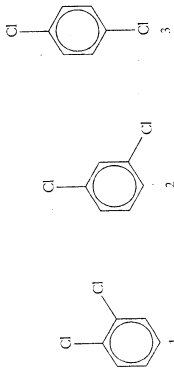
3.19 Write its Lewis structure and predict whether each of the following molecules is polar or nonpolar: (a) CH_2Cl_2 ; (b) CCl_4 ; (c) CS_2 ; (d) SF_4 .

3.20 Write its Lewis structure and predict whether each of the following molecules is polar or nonpolar: (a) BF_3 ; (b) PCl_3 ; (c) SiO_2 ; (d) H_2S .

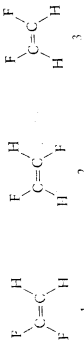
3.21 Predict whether each of the following molecules is likely to be polar or nonpolar: (a) C_2H_5N (pyridine), a molecule like benzene except that one $-CH_2-$ group is replaced by a nitrogen atom; (b) C_2H_6 (ethane); (c) $CHCl_3$ (trichloromethane, also known as chloroform, a common organic solvent and once used as an anesthetic).

3.22 Predict whether each of the following molecules is likely to be polar or nonpolar: (a) CCl_4 (tetrachloromethane); (b) $CH_3CHOHCH_3$ (2-propanol, rubbing alcohol); (c) CH_3COCH_3 (2-propanone, acetone, a common organic solvent used in nail polish remover).

3.23 There are three different dichlorobenzenes, $C_6H_4Cl_2$, which differ in the relative positions of the chlorine atoms on the benzene ring: (a) Which of the three forms are polar? (b) Which has the largest dipole moment?



3.24 There are three different difluoroethenes, $C_2H_2F_2$, which differ in the locations of the fluorine atoms: (a) Which of the forms are polar? (b) Which has the largest dipole moment?



3.25 Acrylonitrile, $CH_2=CHCN$, is used in the synthesis of acrylic fibers (polyacrylonitriles), such as Orlon. Write the Lewis structure of acrylonitrile and describe the hybrid orbitals on each carbon atom. What are the approximate values of the bond angles?

3.42 In the vapor phase, phosphorus can exist as P_2 molecules, which are highly reactive, whereas N_2 is relatively inert. Use valence-bond theory to explain this difference.

3.43 Noting that the bond angle of an sp^3 hybridized atom is 109.5° and that of an sp^2 hybridized atom is 120° , do you expect the bond angle between two hybrid orbitals to increase or decrease as the s-character of the hybrids is increased?

3.44 Both NH_2^- and NH_3^+ are angular species, but the bond angle in NH_2^- is less than that in NH_3^+ . (a) What is the reason for this difference in bond angles? (b) Take the x-axis as lying perpendicular to the plane of the molecule. Does the NH_2^- orbital participate in the hybridization for either species? Briefly explain your answer.

3.45 Given that the atomic orbitals used to form hybrids are normalized to 1 and mutually orthogonal, (a) show that the two tetrahedral hybrids $h_1 = s + p_x + p_y + p_z$ and $h_2 = s - p_x + p_y - p_z$ are orthogonal. (b) Construct the remaining two tetrahedral hybrids that are orthogonal to these two hybrids.

Hint: Two wavefunctions are orthogonal if $\int \psi_1 \psi_2 d\tau = 0$, where $\int \dots d\tau$ means "integrate over all space."

3.46 The hybrid orbital $h_1 = s + p_x + p_y + p_z$ referred to in Exercise 3.45 is not normalized. Find the normalization factor N , given that all the atomic orbitals are normalized to 1.

3.47 The composition of hybrids can be discussed quantitatively. The outcome is that, if two equivalent hybrids composed of an s-orbital and two p-orbitals make an angle θ to each other, then the hybrids can be regarded as sp^λ , with $\lambda = \cos \theta / \cos^2(\theta/2)$. What is the hybridization of the two O-H bonds in H_2O ?

3.48 Given the information in Exercise 3.47, plot a graph showing how the hybridization depends on the angle between two hybrids formed from an s-orbital and two p-orbitals, and confirm that λ ranges from 90° when no s-orbital is included in the mixture to 120° when the hybridization is sp^2 .

Molecular Orbital Theory

3.49 Draw a molecular orbital energy-level diagram and determine the bond order expected for each of the following diatomic species: (a) Li_2 ; (b) Li_2^+ ; (c) Li_2^- . State whether each molecule or ion will be paramagnetic or diamagnetic. If it is paramagnetic, give the number of unpaired electrons.

3.50 Draw a molecular orbital energy-level diagram and determine the bond order expected for the following diatomic species: (a) B_2 ; (b) B_2^+ ; (c) B_2^- . State whether each molecule or ion will be paramagnetic or diamagnetic. If it is paramagnetic, give the number of unpaired electrons.

3.51 (a) On the basis of the configuration of the neutral molecule F_2 , write the molecular orbital configuration of the valence molecular orbitals for (1) F_2 ; (2) F_2^+ ; (3) F_2^- . (b) For each species, give the expected bond order. (c) Which are paramagnetic, if any? (d) Is the highest-energy orbital that contains an electron σ or π in character?

3.52 (a) On the basis of the configuration for the neutral molecule N_2 , write the molecular orbital configuration of the valence molecular orbitals for (1) N_2^+ ; (2) N_2^- ; (3) N_2^{2+} ; (4) N_2^{2-} . (b) For each species, give the expected bond order. (c) Which are paramagnetic, if any? (d) Is the highest-energy orbital that contains an electron σ or π in character?

3.53 (a) Draw the molecular orbital energy-level diagram for N_2 and label the energy levels according to the type of orbitals from which they are made, whether they are σ - or π -orbitals and whether they are bonding or antibonding. (b) The orbital structure of the heteronuclear diatomic ion NO^- is similar to that of N_2 . How will the fact that the electronegativity of N differs from that of O affect the molecular orbital energy-level diagram of NO^- compared with that of N_2 ? Use this information to draw the energy-level diagram for NO^- . (c) In the molecular orbitals, will the electrons have a higher probability of being at N or at O? Why?

3.54 (a) How does molecular orbital theory make it possible to explain both ionic and covalent bonding? (b) The degree of ionic character in bonding was related to electronegativity in Chapter 2. How does electronegativity affect the molecular orbital diagram so that bonds become ionic?

3.55 Write the valence-shell electron configuration and bond orders of (a) B_2 ; (b) Be_2 ; (c) F_2 .

3.56 Write the valence-shell electron configuration and bond orders of (a) NO ; (b) N_2^+ ; (c) C_2^- .

3.57 Give the valence-shell electron configuration and bond orders for CO and CO^+ . Use that information to predict which species has the greater bond enthalpy.

3.58 Give the valence-shell electron configuration and bond orders for CN and CN^+ . Use that information to predict which species has the greater bond enthalpy.

3.59 Which of the following species are paramagnetic: (a) B_2 ; (b) B_2^+ ; (c) B_2^- ? If the species is paramagnetic, how many unpaired electrons does it possess?

3.60 Which of the following species are paramagnetic: (a) N_2^+ ; (b) F_2^+ ; (c) O_2^{2+} ? If the species is paramagnetic, how many unpaired electrons does it possess?

3.61 Determine the bond orders and use them to predict which species of each of the following pairs has the stronger bond: (a) F_2 or F_2^+ ; (b) B_2 or B_2^+ .

3.62 Determine the bond orders and use them to predict which species of each of the following pairs has the stronger bond: (a) C_2^- or C_2 ; (b) O_2 or O_2^+ .

3.63 Based on their valence-shell electron configurations which of the following species would you expect to have the lowest ionization energy? (a) C_2^+ ; (b) C_2 ; (c) C_2^- .

3.64 Based on their valence-shell electron configurations which of the following species would you expect to have the greatest electron affinity? (a) Be_2 ; (b) F_2 ; (c) B_2^+ ; (d) C_2^- .

3.65 How does the change in conductivity of a semiconductor differ from that of a metal as temperature is increased?

3.66 Normally, in conducting materials, we think of current as being carried by electrons as they move through a solid. In semiconductors, it is also common to talk about the current being carried by the "holes" in the valence band. (a) Explain how holes move through a solid material. (b) If, in a p -type semiconductor device, electric current is moving from left to right, in which direction will the holes be moving?

3.67 Germanium is a semiconductor. If small amounts of the elements In, P, Sb, and Ga are present as impurities, which of them will make germanium into (a) a p -type semiconductor; (b) an n -type semiconductor?

3.68 Gallium arsenide is a semiconducting material. If we wish to modify the sample by replacing a small amount of the arsenic with an element to produce an n -type semiconductor, which element would we choose: selenium, phosphorus, or silicon? Why?

□ 3.69 It is usually convenient to deal with wavefunctions that are "normalized," which means that the integral $\int \psi^2 dr = 1$.

The bonding orbital in Eq. 1 is not normalized. A wavefunction ψ can be normalized by writing it as $N\psi$ and finding the factor N which ensures that the integral over $(N\psi)^2$ is equal to 1. Find the factor N that normalizes the bonding orbital in Eq. 1, given that the individual atomic orbitals are each normalized. Express your answer in terms of the "overlap integral"

$$S = \int \psi_{A1s} \psi_{B1s} dr. \quad (\text{The notation is the same as in Exercise 3.45.})$$

□ 3.70 The antibonding orbital in Eq. 2 is not normalized (see Exercise 3.69). Find the factor that normalizes it to 1, given that the individual atomic orbitals are each normalized. Express your answer in terms of the overlap integral $S = \int \psi_{A1s} \psi_{B1s} dr$. (The notation is the same as in Exercise 3.45.) Confirm that the bonding and antibonding orbitals are mutually orthogonal—that is, that the integral over the product of the two wavefunctions is zero.

3.71 The two atomic orbitals that contribute to the antibonding orbital in Eq. 2 are each proportional to e^{-r/a_0} , where r is the distance of the point from its parent nucleus. Confirm that there is a nodal plane lying halfway between the two nuclei.

3.72 Use the plotting function on the Web site for this book to plot the amplitude of the bonding and antibonding orbitals in Eqs. 1 and 2, given the information in Exercise 3.71, on a line passing through the two nuclei. Ignore the normalization factors, and take the internuclear distance as (a) $4a_0$, (b) $2a_0$, (c) $5a_0$. Which of these three bond lengths is most likely to be close to the actual bond length?

Integrated Exercises

3.73 For each of the following species, write the Lewis structure, predict the shape and hybridization about each central atom, give the bond angles, and state whether it is polar or nonpolar: (a) GaCl_4^- ; (b) TeF_4 ; (c) SbCl_4^- ; (d) SiCl_4 .

3.74 For each of the following species, write the Lewis structure, predict the shape and hybridization about each central atom, give the bond angles, and state whether it is polar or nonpolar: (a) SnCl_3^- ; (b) TeO_3 ; (c) NO_3^- ; (d) ICl_3 .

3.75 Polar molecules attract other polar molecules through dipole-dipole intermolecular forces. Polar solutes tend to have higher solubilities in polar solvents than in nonpolar solvents. Which of the following pairs of compounds would be expected to have the higher solubility in hexafluorobenzene, C_6F_6 : (a) SiF_4 or PF_3 ; (b) SF_6 or SF_4 ; (c) IF_5 or AsF_3 ?

3.76 The halogens form compounds among themselves. These compounds, called the *interhalogens*, have the formulas XX'_2 , XX'_3 , and XX'_4 , where X is the heavier halogen atom. (a) Predict their structures and bond angles. (b) Which of them are polar? (c) Why is the lighter halogen atom not the central atom of such molecules?

3.77 An organic compound distilled from wood was found to have a molar mass of $32.04 \text{ g}\cdot\text{mol}^{-1}$ and the following composition by mass: 37.5% C, 12.6% H, and 49.9% O.

(a) Write the Lewis structure of the compound and determine the bond angles about the carbon and oxygen atoms. (b) Give the hybridization of the carbon and oxygen atoms. (c) Predict whether the molecule is polar or not.

3.78 Draw Lewis structures for each of the following species and predict the hybridization at each carbon atom: (a) H_2CCH^- ; (b) H_2CCH_3^+ ; (c) H_3CCH_2^- .

3.79 (a) Draw the bonding and antibonding orbitals that correspond to the σ -bond in H_2 . (b) Repeat this procedure for HF . (c) How do these orbitals differ?

3.80 (a) Consider a hypothetical species "HeH." What charge (magnitude and sign), if any, should be present on this combination of atoms to produce the most stable molecule or ion possible? (b) What is the maximum bond order that such a molecule or ion could have? (c) If the charge on this species were increased or decreased by one, what would be the effect on the bonding in the molecule?

3.81 (a) Order the following molecules according to increasing C—F bond length: CF_4 , CF_2F_2 . (b) Which of these molecules will be diamagnetic, if any? Explain your reasoning.

3.82 Describe as completely as you can the structure and bonding in carbamate ion, $\text{CO}(\text{NH}_2)_2$. The C—O bond lengths are both 128 pm, and the C—N bond length is 136 pm.

3.83 Borazine, $\text{B}_3\text{N}_3\text{H}_6$, a compound that has been called "inorganic benzene," because of its similar hexagonal structure (but with alternating B and N atoms in place of C atoms), is the basis of a large class of boron-nitrogen compounds. Write its Lewis structure and predict the composition of the hybrid orbitals used by each B and N atom.

3.84 Given that carbon has a valence of four in nearly all its compounds and can form chains and rings of C atoms, (a) draw any two of the three possible structures for C_3H_4 ; (b) determine all bond angles in each structure; (c) determine the hybridization of each carbon atom in the two structures; (d) ascertain whether the two structures are resonance structures and explain your reasoning.

3.85 (a) Draw a Lewis structure for each of the following species: CH_3^+ ; CH_4 ; CH_3^- ; CH_2 ; CH_2^+ ; CH_2^- . (b) Identify each as a radical or not. (c) Rank them in order of increasing HCH bond angles. Explain your choices.

3.86 Consider the molecules H_2CCH_2 , H_3CCCH_3 , and H_3COCCH_3 . (a) Draw Lewis structures for these molecules. (b) What is the hybridization at each C atom? (c) What type of bond connects the carbon atoms (single, double, etc.)? (d) What are the HCH, CCH, and CCC angles in these molecules? (e) Do all the hydrogen atoms lie in the same plane? (f) A generalized formula for molecules of this type is $\text{H}_3\text{C}(\text{C})_n\text{CH}_3$, where $x = 0, 1, 2$, etc. What can be said, if anything, about the relative orientation of the H atoms at the ends of the chain as a function of x ?

3.87 Acetylene (ethyne), C_2H_2 , can be polymerized. (a) Draw the Lewis structure for acetylene and draw a Lewis structure for the polymer that results when acetylene is polymerized. The polymer has formula $(\text{CH}_2)_n$, where n is large. (b) Consider the polymers polyacetylene and polyethylene. The latter has the formula $(\text{CH}_2)_n$ and is an insulating material (plastic wrap is made of polyethylene), whereas polyacetylene is a darkly colored material that can conduct electricity when properly treated. On the basis of your answer to part (a), suggest an explanation for the difference in the two polymers.

3.88 Dye molecules are of commercial importance because they are very intensely colored. Most dye molecules possess many multiple bonds and are often aromatic. Why is this important to the properties of the dye molecule?

3.89 Treat the π system of a dye molecule composed of a conjugated carbon chain of N carbon atoms as a box of length Nr , where R is the average C—C bond length. Given that each C atom contributes one electron and that each state of the box can accommodate two electrons, derive an expression for the wavelength of the light absorbed by the lowest-energy transition. Should you increase or decrease the number of carbon atoms in the chain to shift the wavelength to longer values? Refer to Major Technique 2, which follows these exercises.

3.90 Show that a molecule with configuration π^4 has a cylindrically symmetrical electron distribution. Hint: Take the π -orbitals to be equal to x^2 and y^2 , where f is a function that is independent of x and y .

3.91 In addition to forming σ and π types of bonds similar to p -orbitals, d -orbitals may overlap to form δ -bonds. (a) Draw overlap diagrams showing three different ways in which d -orbitals can combine to form bonds. (b) Place the three types of d - d bonds— σ , π , and δ —in order of strongest to weakest.

3.92 An s -orbital and a p -orbital on different atoms may overlap to form molecular orbitals. One of these interactions forms a bonding σ -orbital and the other is nonbonding. Draw diagrams to represent the two types of orbital overlap that give rise to σ -bonding and nonbonding orbitals.

3.93 (a) Describe the changes in bonding that would occur in benzene if two electrons were removed from the HOMO (highest occupied molecular orbital). This removal would correspond to an oxidation of benzene to $\text{C}_6\text{H}_6^{2+}$. (b) Describe

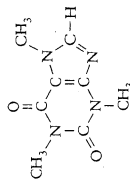
the changes in bonding that would occur if two electrons were added to the LUMO (lowest unoccupied molecular orbital). This addition would correspond to a reduction of benzene by two electrons to give $\text{C}_6\text{H}_6^{2-}$. Do you expect the anions to be diamagnetic or paramagnetic?

3.94 (a) Confirm, by using trigonometry, that the poles of the three bonds in a trigonal pyramidal AB_3 molecule do not cancel, resulting in a polar molecule. (b) Show that the dipoles of the four bonds in a tetrahedral AB_4 molecule cancel and the molecule is nonpolar.

3.95 Benzene, C_6H_6 , is a highly reactive molecule that is detected only at low temperatures. It is related to benzene in that it has a six-membered ring of carbon atoms, but, instead of three double bonds, the structure is normally drawn with two double bonds and a triple bond. (a) Draw a Lewis structure of the benzene molecule. Indicate on the structure the hybridization at each carbon atom. (b) On the basis of your understanding of bonding, explain why this molecule might be highly reactive.

3.96 The Lewis structure of caffeine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$, a common stimulant, is shown below. (a) Give the hybridization of each atom other than hydrogen and predict the bond angles about that atom. (b) On the basis of your answers in part (a), estimate the bond angles around each carbon and nitrogen atom.

(c) Search the chemical literature for the structure of caffeine, and compare the observed structural parameters with your predictions.



3.97 Cyclopropane, C_3H_6 , is a hydrocarbon composed of a three-membered ring of carbon atoms. (a) Determine the hybridization of the carbon atoms. (b) Predict the CCC and HCH bond angles at each carbon atom on the basis of your answer to part (a). (c) What must the "real" C—C bond angles in cyclopropane be? (d) What is the defining characteristic of a σ -bond compared with a π -bond, for example? (e) How do the C—C σ -bonds in cyclopropane extend the definition of conventional σ -bonds? (f) Draw a picture depicting the molecular orbitals to illustrate your answer.

3.98 The diameter of a C_{60} molecule (Section 1.4.3) is approximately 700 pm. (a) Could more than one lanthanum atom occupy the center of a C_{60} molecule? (b) Because it is possible for C_{60} to undergo reduction (six step-by-step reductions to give C_{60}^{6-} have been reported), it is also possible for a lanthanum ion, La^{3+} , to exist inside the C_{60} molecule. Could two La^{3+} ions be placed inside a C_{60} molecule?

3.99 In which of the following molecules could there be an π -to- π^* transition? Explain your choices. (a) Formic acid, HCOOH ; (b) ethyne, C_2H_2 ; (c) methanol, CH_3OH ; (d) hydrogen cyanide, HCN . Refer to Major Technique 2, which follows these exercises.

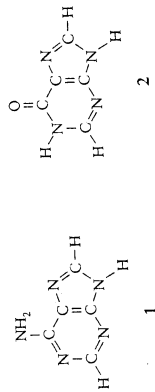
3.100 Aqueous solutions of compounds containing the Cu^{2+} ion are blue as a result of the presence of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex. Does this complex absorb in the visible region? Suggest an explanation. Refer to Major Technique 2, which follows these exercises.

3.101 Consider the bonding in $\text{CH}_2=\text{CHCHO}$. (a) Draw the most important Lewis structure. Include all nonzero formal charges. (b) Identify the composition of the bonds and the hybridization of each lone pair—for example, by writing $\sigma(\text{H}1s, \text{C}2sp^2)$.

3.102 Light-emitting diodes (LEDs) contain p-n junctions. The circuit in an LED is arranged so that electrons from the power source flow into the conduction band of the n-type side. As electrons continue to flow, they are pushed to the conduction band of the p-type side, which can hold more electrons. These electrons enter the conduction band of the p-type side, because they already occupy the higher-energy band in the n-type side. However, once the electrons are in the higher-energy band of the p-type side, they fall into the lower-energy band unless it is full. As these electrons make transitions to the lower-energy band, energy is released in the form of light. (a) Explain, in terms of the movement of electrons, why an LED cannot be made from the junction of pure silicon and silicon doped with phosphorus. (b) If the direction of the circuit in the LED is reversed, so that the electrons flow from the power source into the p-type side of the p-n junction directly, where would the electrons go once they enter the p-n junction? (That is, indicate which bands would receive the electrons and whether the electrons would then migrate to other bands.) (c) Would you expect the LED to emit light when it is placed in the reverse circuit described in part (b)? Explain your answer.

3.103 The reaction between SbF_3 and CsF produces, among other products, the anion $[\text{Sb}_2\text{F}_7]^-$. This anion has no F—F bonds and no Sb—Sb bonds. (a) Propose a Lewis structure for the ion. (b) Assign a hybridization scheme to the Sb atoms.

3.104 The following molecules are bases that are part of the nucleic acids involved in the genetic code. Identify (a) the hybridization of each C and N atom, (b) the number of σ - and π -bonds, and (c) the number of lone pairs of electrons in the molecule.



3.105 Just as AlCl_3 forms dimers (Section 2.11), in the $[\text{B}_2\text{Cl}_4]^{2-}$ ion two of the Cl atoms form “bridges” between the two B atoms. Propose a structure for the $[\text{B}_2\text{Cl}_4]^{2-}$ ion.

3.106 Germanium forms a series of anions called “germanides.” In the germanide ion Ge_4^{4-} the four Ge atoms form a tetrahedron in which each atom is bonded to the other three and each atom has a lone pair of electrons. What is the value of n , the charge on this anion? Explain your reasoning.

3.107 One form of the polyatomic ion I_5^- has an unusual V-shaped structure: one I atom lies at the point of the V, with a linear chain of two I atoms extending on each side. The bond angles are 88° at the central atom and 180° at the two atoms in the side chains. Draw a Lewis structure for I_5^- that explains its shape and indicate the hybridization you would assign to each nonterminal atom.

3.108 Molecules and ions, like atoms, can be isoelectronic. That is, they can have the same number of electrons. For example, CH_4 and NH_4^+ are isoelectronic. Therefore, they have the same molecular shape. Identify a molecule or ion that is isoelectronic with each of the following species and verify that each pair has the same shape: (a) CO_3^{2-} ; (b) O_3 ; (c) OH^- .

3.109 Is the Al_2Cl_6 molecule, described in Section 2.11, polar or nonpolar? Justify your conclusion.

3.110 The molecular structure of benzene, C_6H_6 , is planar. Is the molecular structure of cyclohexane, C_6H_{12} , planar as well? (a) Draw a Lewis structure for cyclohexane. (b) Indicate the bond angles about each carbon atom. (c) What is your conclusion about the shape of the cyclohexane molecule?

3.111 Complexes of d - and f -block metals can be described in terms of hybridization schemes, each associated with a particular shape. Bearing in mind that the number of atomic orbitals hybridized must be the same as the number of hybrid orbitals produced, match the hybrid orbitals sp^2 , d^2 , sp^3 , d^3 , and sp^2d^2 to the following shapes: (a) pentagonal bipyramidal; (b) cubic; (c) square planar.

Chemistry Connections

3.112 Hydrogen peroxide, H_2O_2 , is a nontoxic bleaching agent being used as a replacement for chlorine in industry and home laundries. The bleaching process is an oxidation and when hydrogen peroxide acts as a bleaching agent, the only waste it generates is H_2O .

(a) Draw the Lewis structure of hydrogen peroxide and determine the formal charge on each atom. What is the oxidation number of oxygen in hydrogen peroxide? Which is more useful in predicting the ability of H_2O_2 to act as an oxidizing agent, formal charge or oxidation number? Explain your reasoning.

(b) Predict the bond angles about each O atom in H_2O_2 . Are all the atoms in the same plane? Is the molecule polar or nonpolar? Explain your reasoning.

(c) Write the valence electron configuration of (1) O_3 ; (2) O_2^+ ; (3) O_2^- ; (4) O_2^{2-} . For each species, give the expected bond order and indicate which, if any, are paramagnetic.

(d) The following bond lengths have been reported: (1) O_2 , 121 pm; (2) O_2^- , 134 pm; (3) O_2^+ , 112 pm; (4) O_2^{2-} , 149 pm. Suggest a reason for the differences based on the configurations in part (c).

(e) One reaction in which H_2O_2 acts as an oxidizing agent is $\text{Fe}^{2+}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$. Balance the equation and determine what mass of iron(II) can be oxidized to iron(III) by 54.1 mL of 0.200 M $\text{H}_2\text{O}_2(\text{aq})$. *Hint:* Make sure you balance charge as well as mass.

(f) Hydrogen peroxide can also act as a reducing agent, as in $\text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$. Balance the equation and determine what mass of iron(III) can be reduced to iron(II) by 35.6 mL of 0.200 M $\text{H}_2\text{O}_2(\text{aq})$. *Hint:* Make sure you balance charge as well as mass.

(g) Hydrogen peroxide must be kept in brown bottles because in the presence of light it can *disproportionate*, which means that it oxidizes and reduces itself in the reaction $2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow$

$2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$. How many electrons are transferred in the reaction represented by this equation?

(h) Although peroxides do not generate hazardous waste, they can cause problems in the atmosphere. If it makes its way to the stratosphere, a hydrogen peroxide molecule can break into two OH radicals, which threaten the ozone layer that protects Earth from harmful radiation. Use data in Table 2.4 to calculate the minimum frequency of light needed to break the HO—OH bond.