1.1 INTRODUCTION

A. What Is Organic Chemistry?

Organic chemistry is the branch of science that deals generally with compounds of carbon. Yet the name organic seems to imply a connection with living things. Let’s explore this connection, for the emergence of organic chemistry as a science is linked to the early evolution of the life sciences.

B. Emergence of Organic Chemistry

As early as the sixteenth century, scholars seem to have had some realization that the phenomenon of life has chemical attributes. Theophrastus Bombastus von Hohenheim, a Swiss physician and alchemist (ca. 1493–1541) better known as Paracelsus, sought to deal with medicine in terms of its “elements” mercury, sulfur, and salt. An ailing person was thought to be deficient in one of these elements and therefore in need of supplementation with the missing substance. Paracelsus was said to have effected some dramatic “cures” based on this idea.

By the eighteenth century, chemists were beginning to recognize the chemical aspects of life processes in a modern sense. Antoine Laurent Lavoisier (1743–1794) recognized the similarity of respiration to combustion in the uptake of oxygen and expiration of carbon dioxide.

At about the same time, it was found that certain compounds are associated with living systems and that these compounds generally contain carbon. They were thought to have arisen from, or to be a consequence of, a “vital force” responsible for the life process. The term organic was applied to substances isolated from living things by Jöns Jacob Berzelius (1779–1848). Somehow, the fact that these chemical substances were organic in nature was thought to put them beyond the scope of the experimentalist. The logic of the time seems to have been that life is not understandable; organic compounds spring from life; therefore, organic compounds are not understandable.
The barrier between organic (living) and inorganic (nonliving) chemistry began to crumble in 1828 because of a serendipitous (accidental) discovery by Friedrich Wöhler (1800–1882), a German analyst originally trained in medicine. When Wöhler heated ammonium cyanate, an inorganic compound, he isolated urea, a known urinary excretion product of mammals.

\[ \text{ammonium cyanate} \rightarrow \text{heat} \rightarrow \text{urea} \]

\[ \text{an inorganic compound} \rightarrow \text{an organic compound} \]  

Wöhler recognized that he had synthesized this biological material “without the use of kidneys, nor an animal, be it man or dog.” Not long thereafter followed the synthesis of acetic acid by Hermann Kolbe in 1845 and the preparation of acetylene and methane by Marcellin Berthelot in the period 1856–1863. Although “vitalism” was not so much a widely accepted formal theory as an intuitive idea that something might be special and beyond human grasp about the chemistry of living things, Wöhler did not identify his urea synthesis with the demise of the vitalistic idea; rather, his work signaled the start of a period in which the synthesis of so-called organic compounds was no longer regarded as something outside the province of laboratory investigation. Organic chemists now investigate not only molecules of biological importance, but also intriguing molecules of bizarre structure and purely theoretical interest. Thus, organic chemistry deals with compounds of carbon regardless of their origin. Wöhler seems to have anticipated these developments when he wrote to his mentor Berzelius, “Organic chemistry appears to be like a primeval tropical forest, full of the most remarkable things.”

C. Why Study Organic Chemistry?

The study of organic chemistry is important for several reasons. First, the field has an independent vitality as a branch of science. Organic chemistry is characterized by continuing development of new knowledge, a fact evidenced by the large number of journals devoted exclusively or in large part to the subject. Second, organic chemistry lies at the heart of a substantial fraction of the modern chemical industry and therefore contributes to the economies of many nations. Third, many students who take organic chemistry nowadays are planning careers in the biological sciences or in allied health disciplines, such as medicine or pharmacy. Organic chemistry is immensely important as a foundation to these fields, and its importance is sure to increase. One need only open modern textbooks or journals of biochemistry or biology to appreciate the sophisticated organic chemistry that is central to these areas. Finally, even for those who do not plan a career in any of the sciences, a study of organic chemistry is important. We live in a technological age that is made possible in large part by applications of organic chemistry to industries as diverse as plastics, textiles, communications, transportation, food, and clothing. In addition, problems of pollution and depletion of resources are all around us. If organic chemistry has played a part in creating these problems, it will surely have a role in their solutions.

As a science, organic chemistry lies at the interface of the physical and biological sciences. Research in organic chemistry is a mixture of sophisticated logic and empirical observation. At its best, it takes on artistic dimensions. You can use the study of organic chemistry to develop and apply basic skills in problem solving and, at the same time, to learn a subject of immense practical value. Thus, to develop as a chemist, to remain in the mainstream of a health profession, or to be a well-informed citizen in a technological age, you will find value in the study of organic chemistry.

In this text we have several objectives. We’ll present the “nuts and bolts”—the nomenclature, classification, structure, and properties of organic compounds. We’ll also cover the principal reactions and the syntheses of organic molecules. But, more than this, we’ll develop underlying principles that allow us to understand, and sometimes to predict, reactions rather than
simply memorizing them. We’ll consider some of the organic chemistry that is industrially im-
portant. Finally, we’ll examine some of the beautiful applications of organic chemistry in bi-
ology, such as how nature does organic chemistry and how the biological world has inspired a
great deal of the research in organic chemistry.

1.2 CLASSICAL THEORIES OF CHEMICAL BONDING

To understand organic chemistry, it is necessary to have some understanding of the chemical
bond—the forces that hold atoms together within molecules. First, we’ll review some of the
older, or “classical,” ideas of chemical bonding—ideas that, despite their age, remain useful
today. Then, in the last part of this chapter, we’ll consider more modern ways of describing the
chemical bond.

A. Electrons in Atoms

Chemistry happens because of the behavior of electrons in atoms and molecules. The basis of
this behavior is the arrangement of electrons within atoms, an arrangement suggested by the
periodic table. Consequently, let’s first review the organization of the periodic table (see page
facing inside back cover). The shaded elements are of greatest importance in organic chem-
istry, knowing their atomic numbers and relative positions will be valuable later on. For the
moment, however, consider the following details of the periodic table because they were im-
portant in the development of the concepts of bonding.

A neutral atom of each element contains a number of both protons and electrons equal to
its atomic number. The periodic aspect of the table—its organization into groups of elements
with similar chemical properties—led to the idea that electrons reside in layers, or shells,
about the nucleus. The outermost shell of electrons in an atom is called its valence shell,
and the electrons in this shell are called valence electrons. The number of valence electrons for
any neutral atom in an A group of the periodic table (except helium) equals its group number.
Thus, lithium, sodium, and potassium (Group 1A) have one valence electron, whereas carbon
( Group 4A) has four, the halogens (Group 7A) have seven, and the noble gases (except he-
lium) have eight. Helium has two valence electrons.

Walter Kossel (1888–1956) noted in 1916 that when atoms form ions they tend to gain or
lose valence electrons so as to have the same number of electrons as the noble gas of closest
atomic number. Thus, potassium, with one valence electron (and 19 total electrons), tends to
lose an electron to become K⁺, the potassium ion, which has the same number of electrons
(18) as the nearest noble gas (argon). Chlorine, with seven valence electrons (and 17 total elec-
trons) tends to accept an electron to become the 18-electron chloride ion, Cl⁻, which also has
the same number of electrons as argon. Because the noble gases have an octet of electrons
(that is, eight electrons) in their valence shells, the tendency of atoms to gain or lose valence
electrons to form ions with the noble-gas configuration has been called the octet rule.

B. The Ionic Bond

A chemical compound in which the component atoms exist as ions is called an ionic com-
 pound. Potassium chloride, KCl, is a common ionic compound. The electronic configurations
of the potassium and chloride ions obey the octet rule.

The structure of crystalline KCl is shown in Fig. 1.1 on p. 4. In the KCl structure, which is
typical of many ionic compounds, each positive ion is surrounded by negative ions, and each
negative ion is surrounded by positive ions. The crystal structure is stabilized by an interaction
between ions of opposite charge. Such a stabilizing interaction between opposite charges is
called an **electrostatic attraction.** An electrostatic attraction that holds ions together, as in crystalline KCl, is called an **ionic bond.** Thus, the crystal structure of KCl is maintained by ionic bonds between potassium ions and chloride ions. The ionic bond is the same in all directions; that is, a positive ion has the same attraction for each of its neighboring negative ions, and a negative ion has the same attraction for each of its neighboring positive ions.

When an ionic compound such as KCl dissolves in water, it dissociates into free ions (each surrounded by water). (We’ll consider this process further in Sec. 8.4.) Each potassium ion moves around in solution more or less independently of each chloride ion. The conduction of electricity by KCl solutions shows that the ions are present. Thus, the ionic bond is broken when KCl dissolves in water.

To summarize, the ionic bond

1. is an electrostatic attraction between ions;
2. is the same in all directions—that is, it has no preferred orientation in space; and
3. is broken when an ionic compound dissolves in water.

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**PROBLEMS**

1.1 How many valence electrons are found in each of the following species?

(a) Na  
(b) Ca  
(c) O\(^{2-}\)  
(d) Br\(^+\)

1.2 When two different species have the same number of electrons, they are said to be **isoelectronic.** Name the species that satisfies each of the following criteria:

(a) the singly charged negative ion isoelectronic with neon  
(b) the singly charged positive ion isoelectronic with neon  
(c) the dipositive ion isoelectronic with argon  
(d) the neon species that is isoelectronic with neutral fluorine

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* The solutions to problems or problem parts labeled with boldface blue numbers or letters can be found in the *Study Guide and Solutions Manual* supplement.
C. The Covalent Bond

Many compounds contain bonds that are very different from the ionic bond in KCl. Neither these compounds nor their solutions conduct electricity. This observation indicates that these compounds are not ionic. How are the bonding forces that hold atoms together in such compounds different from those in KCl? In 1916, G. N. Lewis (1875–1946), an American physical chemist, proposed an electronic model for bonding in nonionic compounds. According to this model, the chemical bond in a nonionic compound is a covalent bond, which consists of an electron pair that is shared between bonded atoms. Let’s examine some of the ideas associated with the covalent bond.

Lewis Structures  One of the simplest examples of a covalent bond is the bond between the two hydrogen atoms in the hydrogen molecule.

\[
\begin{align*}
\text{covalent bond} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

The symbols “-” and “—” are both used to denote an electron pair. A shared electron pair is the essence of the covalent bond. Molecular structures that use this notation for the electron-pair bond are called Lewis structures. In the hydrogen molecule, an electron-pair bond holds the two hydrogen atoms together. Conceptually, the bond can be envisioned to come from the pairing of the valence electrons of two hydrogen atoms:

\[
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\]

Both electrons in the covalent bond are shared equally between the hydrogen atoms. Even though electrons are mutually repulsive, bonding occurs because the electron of each hydrogen atom is attracted to both hydrogen nuclei (protons) simultaneously.

An example of a covalent bond between two different atoms is provided by methane (CH₄), the simplest stable organic molecule. We can form methane conceptually by pairing each of the four carbon valence electrons with a hydrogen valence electron to make four C—H electron-pair bonds.

\[
\begin{align*}
\text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

In the previous examples, all valence electrons of the bonded atoms are shared. In some covalent compounds, such as water (H₂O), however, some valence electrons remain unshared. In the water molecule, oxygen has six valence electrons. Two of these combine with hydrogens to make two O—H covalent bonds; four of the oxygen valence electrons are left over. These are represented in the Lewis structure of water as electron pairs on the oxygen. In general, unshared valence electrons in Lewis structures are depicted as paired dots and referred to as unshared pairs.

Although we often write water as H—O—H, or even H₂O, it is a good habit to indicate all unshared pairs with paired dots until you remember instinctively that they are there.

The foregoing examples illustrate an important point: The sum of all shared and unshared valence electrons around each atom in many stable covalent compounds is eight (two for the
hydrogen atom). This is the **octet rule** for covalent bonding, and *it will prove to be extremely important for understanding chemical reactivity*. It is reminiscent of the octet rule for ion formation (Sec. 1.2A), except that in ionic compounds, valence electrons belong completely to a particular ion. In covalent compounds, shared electrons are counted twice, once for each of the sharing partner atoms.

Notice how the covalent compounds we’ve just considered follow the octet rule. In the structure of methane (Eq. 1.3), four shared pairs surround the carbon atom—that is, eight shared electrons, an octet. Each hydrogen shares two electrons, the “octet rule” number for hydrogen. Similarly, the oxygen of the water molecule has four shared electrons and two unshared pairs for a total of eight, and again the hydrogens have two shared electrons.

Two atoms in covalent compounds may be connected by more than one covalent bond. The following compounds are common examples:

- **Ethylene and formaldehyde** each contain a **double bond**—a bond consisting of two electron pairs. **Acetylene** contains a **triple bond**—a bond involving three electron pairs.

  Covalent bonds are especially important in organic chemistry because *all organic molecules contain covalent bonds*.

**Formal Charge** The Lewis structures considered in the previous discussion are those of neutral molecules. However, many familiar ionic species, such as \([\text{SO}_4]^{2-}\), \([\text{NH}_4]^+\), and \([\text{BF}_4]^-\), also contain covalent bonds. Consider the tetrafluoroborate anion, which contains covalent \(\text{B}—\text{F}\) bonds:

Because the ion bears a negative charge, one or more of the atoms within the ion must be charged—but which one(s)? The rigorous answer is that the charge is shared by all of the atoms. However, chemists have adopted a useful and important procedure for electronic bookkeeping that assigns a charge to specific atoms. The charge on each atom thus assigned is called its **formal charge**. The sum of the formal charges on the individual atoms must equal the total charge on the ion.
Computation of formal charge on an atom involves dividing the total number of valence electrons between the atom and its bonding partners. Each atom receives all of its unshared electrons and half of its bonding electrons. To assign a formal charge to an atom, then, use the following procedure:

1. Write down the group number of the atom from its column heading in the periodic table. This is equal to the number of valence electrons in the neutral atom.
2. Determine the valence electron count for the atom by adding the number of unshared valence electrons on the atom to the number of covalent bonds to the atom. Counting the covalent bonds in effect adds half the bonding electrons—one electron for each bond.
3. Subtract the valence electron count from the group number. The result is the formal charge.

This procedure is illustrated in Study Problem 1.1.

**Study Problem 1.1**

Assign a formal charge to each of the atoms in the tetrafluoroborate ion, \([\text{BF}_4]^-\), which has the structure shown above.

**Solution** Let’s first apply the procedure outlined above to fluorine:

- **Group number of fluorine:** 7
- **Valence-electron count:** 7
  
  (Unshared pairs contribute 6 electrons; the covalent bond contributes 1 electron.)
- **Formal charge on fluorine:** Group number − Valence-electron count = 7 − 7 = 0

Because all fluorine atoms in \([\text{BF}_4]^-\) are equivalent, they all must have the same formal charge—zero. It follows that the boron must bear the formal negative charge. Let’s compute it to be sure.

- **Group number of boron:** 3
- **Valence-electron count:** 4
  
  (Four covalent bonds contribute 1 electron each.)
- **Formal charge on boron:** Group number − Valence-electron count = 3 − 4 = −1

Because the formal charge of boron is −1, the structure of \([\text{BF}_4]^-\) is written with the minus charge assigned to boron:

When indicating charge on a compound, we can show the formal charges on each atom, or we can show the formal charge on the ion as a whole, **but we should not show both.**

*Study Guide Links are short discussions in the Study Guide and Solutions Manual supplement that provide extra hints or shortcuts that can help you master the material more easily.*
Rules for Writing Lewis Structures  The previous two sections can be summarized in the following rules for writing Lewis structures.

1. Hydrogen can share no more than two electrons.
2. The sum of all bonding electrons and unshared pairs for atoms in the second period of the periodic table—the row beginning with lithium—is never greater than eight (octet rule). These atoms may, however, have fewer than eight electrons.
3. In some cases, atoms below the second period of the periodic table may have more than eight electrons. However, rule 2 should also be followed for these cases until exceptions are discussed later in the text.
4. Nonvalence electrons are not shown in Lewis structures.
5. The formal charge on each atom is computed by the procedure illustrated in Study Problem 1.1 and, if not equal to zero, is indicated with a plus or minus sign on the appropriate atom(s).

Here’s something very important to notice: There are two types of electron counting. When we want to know whether an atom has a complete octet, we count all unshared valence electrons and all bonding electrons (rule 2 in the previous list). When we want to determine formal charge, we count all unshared valence electrons and half of the bonding electrons.

Study Problem 1.2  Draw a Lewis structure for the covalent compound methanol, CH₄O. Assume that the octet rule is obeyed, and that none of the atoms have formal charges.

Solution  For carbon to be both neutral and consistent with the octet rule, it must have four covalent bonds:

There is also only one way each for oxygen and hydrogen to have a formal charge of zero and simultaneously not violate the octet rule:

If we connect the carbon and the oxygen, and fill in the remaining bonds with hydrogens, we obtain a structure that meets all the criteria in the problem:

PROBLEMS

1.3 Draw a Lewis structure for each of the following species. Show all unshared pairs and the formal charges, if any. Assume that bonding follows the octet rule in all cases.
(a) HCCl₃  (b) NH₃  (c) [NH₄]⁺  (d) [H₂O]⁺

1.4 Write two reasonable structures corresponding to the formula C₃H₆O. Assume that all bonding adheres to the octet rule, and that no atom bears a formal charge.
1.5 Draw a Lewis structure for acetonitrile, \( \text{C}_2\text{H}_3\text{N} \), assuming that all bonding obeys the octet rule, and that no atom bears a formal charge. Acetonitrile contains a carbon–nitrogen triple bond.

1.6 Compute the formal charges on each atom of the following structures. In each case, what is the charge on the entire structure?

(a) \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{B} \\
\text{N} \\
\text{H} \\
\text{H}
\end{array}
\]

(b) \[
\begin{array}{c}
\ddot{\text{O}} \\
\ddot{\text{O}} \\
\ddot{\text{P}} \\
\ddot{\text{O}} \\
\text{H}
\end{array}
\]

---

**D. The Polar Covalent Bond**

In many covalent bonds the electrons are not shared equally between two bonded atoms. Consider, for example, the covalent compound hydrogen chloride, HCl. (Although HCl dissolves in water to form \( \text{H}_3\text{O}^+ \) and \( \text{Cl}^- \) ions, in the gaseous state pure HCl is a covalent compound.) The electrons in the H—Cl covalent bond are *unevenly* distributed between the two atoms; they are polarized, or “pulled,” toward the chlorine and away from the hydrogen. A bond in which electrons are shared unevenly is called a *polar bond*. The H—Cl bond is an example of a polar bond.

How can we determine whether a bond is polar? Think of the two atoms at each end of the bond as if they were engaging in a tug-of-war for the bonding electrons. *The tendency of an atom to attract electrons to itself in a covalent bond is indicated by its electronegativity.* The electronegativities of a few elements that are important in organic chemistry are shown in Table 1.1. Notice the trends in this table. Electronegativity increases to the top and to the right of the periodic table. The more an atom attracts electrons, the more *electronegative* it is. Fluorine is the most electronegative element. Electronegativity decreases to the bottom and to the left of the periodic table. The less an atom attracts electrons, the more *electropositive* it is. Of the common stable elements, cesium is the most electropositive.

### TABLE 1.1  
**Average Pauling Electronegativities of Some Main-Group Elements**

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Li 0.98</th>
<th>Be 1.57</th>
<th>B 2.04</th>
<th>C 2.55</th>
<th>N 3.04</th>
<th>O 3.44</th>
<th>F 3.98</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.93</td>
<td>Mg 1.31</td>
<td>Al 1.61</td>
<td>Si 1.90</td>
<td>P 2.19</td>
<td>S 2.58</td>
<td>Cl 3.16</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.82</td>
<td>Ca 1.00</td>
<td>Se 2.55</td>
<td>Br 2.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>0.82</td>
<td>I 1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
If two bonded atoms have equal electronegativities, then the bonding electrons are shared equally. But if two bonded atoms have considerably different electronegativities, then the electrons are unequally shared, and the bond is polar. (We might think of a polar covalent bond as a covalent bond that is trying to become ionic!) Thus, a polar bond is a bond between atoms with significantly different electronegativities.

Sometimes we indicate the polarity of a bond in the following way:

\[
\delta^+ \quad \delta^- 
\]

In this notation, the delta (\(\delta\)) is read as “partially” or “somewhat,” so that the hydrogen atom of HCl is “partially positive,” and the chlorine atom is “partially negative.”

Another more graphical way that we’ll use to show polarities is the electrostatic potential map. An electrostatic potential map (EPM) of a molecule starts with a map of the total electron density. This is a picture of the spatial distribution of the electrons in the molecule that comes from molecular orbital theory, which we’ll learn about in Sec. 1.8. Think of this as a picture of “where the electrons are.” The EPM is a map of total electron density that has been color-coded for regions of local positive and negative charge. Areas of greater negative charge are colored red, and areas of greater positive charge are colored blue. Areas of neutrality are colored green.

This is called a “potential map” because it represents the interaction of a test positive charge with the molecule at various points in the molecule. When the test positive charge encounters negative charge in the molecule, an attractive potential energy occurs; this is color-coded red. When the test positive charge encounters positive charge, a repulsive potential energy results, and this is color-coded blue.

The EPM of H—Cl shows the red region over the Cl and the blue region over the H, as we expect from the greater electronegativity of Cl versus H. In contrast, the EPM of dihydrogen shows the same color on both hydrogens because the two atoms share the electrons equally. The green color indicates that neither hydrogen atom bears a net charge.

How can bond polarity be measured experimentally? The uneven electron distribution in a compound containing covalent bonds is measured by a quantity called the dipole moment, which is abbreviated with the Greek letter \(\mu\) (mu). The dipole moment is commonly given in derived units called debyes, abbreviated D, and named for the physical chemist Peter Debye (1884–1966), who won the 1936 Nobel Prize in Chemistry. For example, the HCl molecule has a dipole moment of 1.08 D, whereas dihydrogen (H₂), which has a uniform electron distribution, has a dipole moment of zero.

* Further Explorations are brief sections in the Study Guide and Solutions Manual supplement that cover the subject in greater depth.
The dipole moment is defined by the following equation:

$$\mu = qr$$  \hspace{1cm} (1.4)$$

In this equation, $q$ is the magnitude of the separated charge and $r$ is a vector from the site of the positive charge to the site of the negative charge. For a simple molecule like HCl, the magnitude of the vector $r$ is merely the length of the HCl bond, and it is oriented from the H (the positive end of the dipole) to the Cl (the negative end). The dipole moment is a \textit{vector quantity}, and $\mu$ and $r$ have the same direction—from the positive to the negative end of the dipole.

As a result, the dipole moment vector for the HCl molecule is oriented along the H—Cl bond from the H to the Cl:

Notice that the magnitude of the dipole moment is affected not only by the \textit{amount} of charge that is separated ($q$) but also by \textit{how far} the charges are separated ($r$). Consequently, a molecule in which a relatively small amount of charge is separated by a large distance can have a dipole moment as great as one in which a large amount of charge is separated by a small distance.

Molecules that have permanent dipole moments are called \textbf{polar molecules}. HCl is a polar molecule, whereas H$_2$ is a nonpolar molecule. Some molecules contain several polar bonds. Each polar bond has associated with it a dipole moment contribution, called a \textbf{bond dipole}. The net dipole moment of such a polar molecule is the vector sum of its bond dipoles. (Because HCl has only one bond, its dipole moment is equal to the H—Cl bond dipole.) Dipole moments of typical polar organic molecules are in the 1–3 D range.

The vectorial aspect of bond dipoles can be illustrated in a relatively simple way with the carbon dioxide molecule, CO$_2$:

Because the CO$_2$ molecule is \textit{linear}, the C—O bond dipoles are oriented in opposite directions. Because they have equal magnitudes, they \textit{exactly cancel}. (Two vectors of equal magnitude oriented in opposite directions always cancel.) Consequently, CO$_2$ is a nonpolar molecule, \textit{even though it has polar bonds}. In contrast, if a molecule contains several bond dipoles that do not cancel, the various bond dipoles add vectorially to give the overall resultant dipole moment. For example, in the water molecule, which has a bond angle of 104.5°, the O—H bond dipoles add vectorially to give a resultant dipole moment of 1.84 D, which bisects the bond angle. The EPM of water shows the charge distribution suggested by the dipole vectors—a concentration of negative charge on oxygen and positive charge on hydrogen.
Polarity is an important concept because the polarity of a molecule can significantly influence its chemical and physical properties. For example, a molecule’s polarity may give some indication of how it reacts chemically. Returning to the HCl molecule, we know that HCl in water dissociates to its ions in a manner suggested by its bond polarity.

\[ \text{H}_2\text{O} + \text{HCl} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]  

(1.5)

We’ll find many similar examples in organic chemistry in which bond polarity provides a clue to chemical reactivity.

Bond polarity is also useful because it gives us some insight that we can apply to the concept of formal charge. It’s important to keep in mind that formal charge is only a bookkeeping device for keeping track of charge. In some cases, formal charge corresponds to the actual charge. For example, the actual negative charge on the hydroxide ion, \( \text{OH}^- \), is on the oxygen, because oxygen is much more electronegative than hydrogen. In this case, the locations of the formal charge and actual charge are the same. But in other cases the formal charge does not correspond to the actual charge. For example, in the \( \text{BF}_4^- \) anion, fluorine is much more electronegative than boron (Table 1.1). So, most of the charge should actually be situated on the fluorines. In fact, the actual charges on the atoms of the tetrafluoroborate ion are in accord with this intuition:

Because the Lewis structure doesn’t provide a simple way of showing this distribution, we assign the charge to the boron by the formal-charge rules. An analogy might help. Let’s say a big corporation arbitrarily chalks up all of its receipts to its sales department. This is a bookkeeping device. Everyone in the company knows that the receipts are in reality due to a company-wide effort. As long as no one forgets the reality, the administrative convenience of showing receipts in one place makes keeping track of the money a little simpler. Thus, showing formal charge on single atoms makes our handling of Lewis structures much simpler, but applying what we know about bond polarities helps us to see where the charge really resides.

**PROBLEMS**

1.7 Analyze the polarity of each bond in the following organic compound. Which bond, other than the C—C bond, is the least polar one in the molecule? Which carbon has the most partial positive character?

1.8 For which of the following ions does the formal charge give a fairly accurate picture of where the charge really is? Explain in each case.

(a) \( \text{NH}_4^+ \)  
(b) \( \text{H}_2\text{O}^+ \)  
(c) \( \text{N}_2\text{H}_4 \)  
(d) \( \text{CH}_3^+ \)
1.9 Draw an appropriate bond dipole for the carbon–magnesium bond of dimethylmagnesium. Explain your reasoning.

\[ \text{dimethylmagnesium} \]

1.3 STRUCTURES OF COVALENT COMPOUNDS

We know the structure of a molecule containing covalent bonds when we know its atomic connectivity and its molecular geometry. Atomic connectivity is the specification of how atoms in a molecule are connected. For example, we specify the atomic connectivity within the water molecule when we say that two hydrogens are bonded to an oxygen. Molecular geometry is the specification of how far apart the atoms are and how they are situated in space.

Chemists learned about atomic connectivity before they learned about molecular geometry. The concept of covalent compounds as three-dimensional objects emerged in the latter part of the nineteenth century on the basis of indirect chemical and physical evidence. Until the early part of the twentieth century, however, no one knew whether these concepts had any physical reality, because scientists had no techniques for viewing molecules at the atomic level. By the second decade of the twentieth century, investigators could ask two questions: (1) Do organic molecules have specific geometries and, if so, what are they? (2) How can molecular geometry be predicted?

A. Methods for Determining Molecular Geometry

Among the greatest developments of chemical physics in the early twentieth century were the discoveries of ways to deduce the structures of molecules. Such techniques include various types of spectroscopy and mass spectrometry, which we’ll consider in Chapters 12–15. As important as these techniques are, they are used primarily to provide information about atomic connectivity. Other physical methods, however, permit the determination of molecular structures that are complete in every detail. Most complete structures today come from three sources: X-ray crystallography, electron diffraction, and microwave spectroscopy.

The arrangement of atoms in the crystalline solid state can be determined by X-ray crystallography. This technique, invented in 1915 and subsequently revolutionized by the availability of high-speed computers, uses the fact that X-rays are diffracted from the atoms of a crystal in precise patterns that can be mathematically deciphered to give a molecular structure. In 1930, electron diffraction was developed. With this technique, the diffraction of electrons by molecules of gaseous substances can be interpreted in terms of the arrangements of atoms in molecules. Following the development of radar in World War II came microwave spectroscopy, in which the absorption of microwave radiation by molecules in the gas phase provides detailed structural information.

Most of the spatial details of molecular structure in this book are derived from gas-phase methods: electron diffraction and microwave spectroscopy. For molecules that are not readily studied in the gas phase, X-ray crystallography is the most important source of structural information. No methods of comparable precision exist for molecules in solution, a fact that is unfortunate because most chemical reactions take place in solution. The consistency of gas-phase and crystal structures suggests, however, that molecular structures in solution probably differ little from those of molecules in the solid or gaseous state.
CHAPTER 1 • CHEMICAL BONDING AND CHEMICAL STRUCTURE

B. Prediction of Molecular Geometry

The way a molecule reacts is determined by the characteristics of its chemical bonds. The characteristics of the chemical bonds, in turn, are closely connected to molecular geometry. Molecular geometry is important, then, because it is a starting point for understanding chemical reactivity.

Given the connectivity of a covalent molecule, what else do we need to describe its geometry? Let’s start with a simple diatomic molecule, such as HCl. The structure of such a molecule is completely defined by the bond length, the distance between the centers of the bonded nuclei. Bond length is usually given in angstroms; 1 Å = 10^{-10} \text{ m} = 10^{-8} \text{ cm} = 100 \text{ pm} (picometers). Thus, the structure of HCl is completely specified by the H—Cl bond length, 1.274 Å.

When a molecule has more than two atoms, understanding its structure requires knowledge of not only each bond length, but also each bond angle, the angle between each pair of bonds to the same atom. The structure of water (H₂O) is completely determined, for example, when we know the O—H bond lengths and the H—O—H bond angle.

We can generalize much of the information that has been gathered about molecular structure into a few principles that allow us to analyze trends in bond length and to predict approximate bond angles.

**Bond Length**  The following three generalizations can be made about bond length, *in decreasing order of importance.*

1. **Bond lengths increase significantly toward higher periods (rows) of the periodic table.** This trend is illustrated in Fig. 1.2. For example, the H—S bond in hydrogen sulfide is longer than the other bonds to hydrogen in Fig. 1.2; sulfur is in the third period of the periodic table, whereas carbon, nitrogen, and oxygen are in the second period. Similarly, a C—H bond is shorter than a C—F bond, which is shorter than a C—Cl bond. These effects all reflect atomic size. Because bond length is the distance between the centers of bonded atoms, larger atoms form longer bonds.

![Figure 1.2](image.png)

**Figure 1.2** Effect of atomic size on bond length. (Within each structure, all bonds to hydrogen are equivalent. Dashed bonds are behind the plane of page, and wedged bonds are in front.) Compare the bond lengths in hydrogen sulfide with those of the other molecules to see that bond lengths increase toward higher periods of the periodic table. Compare the bond lengths in methane, ammonia, and water to see that bond lengths decrease toward higher atomic number within a period (row) of the periodic table.
1.3 STRUCTURES OF COVALENT COMPOUNDS

2. Bond lengths decrease with increasing bond order. Bond order describes the number of covalent bonds shared by two atoms. For example, a $\text{C}$—$\text{C}$ bond has a bond order of $1$, a $\text{C}$—$\text{C}$ bond has a bond order of $2$, and a $\text{C}$—$\text{C}$ bond has a bond order of $3$. The decrease of bond length with increasing bond order is illustrated in Fig. 1.3. Notice that the bond lengths for carbon–carbon bonds are in the order $\text{C}$—$\text{C}$ > $\text{C}$—$\text{N}$ > $\text{C}$—$\text{O}$.

3. Bonds of a given order decrease in length toward higher atomic number (that is, to the right) along a given row (period) of the periodic table. Compare, for example, the $\text{H}$—$\text{C}$, $\text{H}$—$\text{N}$, and $\text{H}$—$\text{O}$ bond lengths in Fig. 1.2. Likewise, the $\text{C}$—$\text{F}$ bond in $\text{H}_3\text{C}$—$\text{F}$, at $1.39$ Å, is shorter than the $\text{C}$—$\text{C}$ bond in $\text{H}_3\text{C}$—$\text{CH}_3$, at $1.54$ Å. Because atoms on the right of the periodic table in a given row are smaller, this trend, like that in item 1, also results from differences in atomic size. However, this effect is much less significant than the differences in bond length observed when atoms of different periods are compared.

**Bond Angle** The bond angles within a molecule determine its shape. For example, in the case of a triatomic molecule such as $\text{H}_2\text{O}$ or $\text{BeH}_2$, the bond angles determine whether it is bent or linear. To predict approximate bond angles, we rely on valence-shell electron-pair repulsion theory, or VSEPR theory, which you may have encountered in general chemistry. According to VSEPR theory, both the bonding electron pairs and the unshared valence electron pairs have a spatial requirement. The fundamental idea of VSEPR theory is that bonds and electron are arranged about a central atom so that the bonds are as far apart as possible. This arrangement minimizes repulsions between electrons in the bonds. Let’s first apply VSEPR theory to three situations involving bonding electrons: a central atom bound to four, three, and two groups, respectively.

When four groups are bonded to a central atom, the bonds are farthest apart when the central atom has tetrahedral geometry. This means that the four bound groups lie at the vertices of a tetrahedron. A tetrahedron is a three-dimensional object with four triangular faces (Fig. 1.4a, p. 16). Methane, $\text{CH}_4$, has tetrahedral geometry. The central atom is the carbon and the four groups are the hydrogens. The $\text{C}$—$\text{H}$ bonds of methane are as far apart as possible when the hydrogens lie at the vertices of a tetrahedron. Because the four $\text{C}$—$\text{H}$ bonds of methane are identical, the hydrogens lie at the vertices of a regular tetrahedron, a tetrahedron in which all edges are equal (Fig. 1.4b). The tetrahedral shape of methane requires a bond angle of $109.5^\circ$ (Fig. 1.4c).

In applying VSEPR theory for the purpose of predicting bond angles, we regard all groups as identical. For example, the groups that surround carbon in $\text{CH}_3\text{Cl}$ (methyl chloride) are treated as if they were identical, even though in reality the $\text{C}$—$\text{Cl}$ bond is considerably longer...
than the C—H bonds. Although the bond angles show minor deviations from the exact tetrahedral bond angle of 109.5°, methyl chloride in fact has the general tetrahedral shape.

Because you’ll see tetrahedral geometry repeatedly, it is worth the effort to become familiar with it. Tetrahedral carbons are often represented by line-and-wedge structures, as illustrated by the following structure of methylene chloride, CH₂Cl₂.

A good way to become familiar with the tetrahedral shape (or any other aspect of molecular geometry) is to use molecular models, which are commercially available scale models from which you can construct simple organic molecules. Perhaps your instructor has required that you purchase a set of models or can recommend a set to you. Almost all beginning students require models, at least initially, to visualize the three-dimensional aspects of organic chemistry. Some of the types of models available are shown in Fig. 1.5. In this text, we use ball-and-stick models (Fig. 1.5a) to visualize the directionality of chemical bonds, and we use space-filling models (Fig. 1.5c) to see the consequences of atomic and molecular volumes. You should obtain an inexpensive set of molecular models and use them frequently. Begin using them by building a model of the methylene chloride molecule discussed above and relating it to the line-and-wedge structure.
1.3 STRUCTURES OF COVALENT COMPOUNDS

When three groups surround an atom, the bonds are as far apart as possible when all bonds lie in the same plane with bond angles of 120°. This is, for example, the geometry of boron trifluoride:

In such a situation the surrounded atom (in this case boron) is said to have trigonal planar geometry.

When an atom is surrounded by two groups, maximum separation of the bonds demands a bond angle of 180°. This is the situation with each carbon in acetylene, $\text{H}_2\text{C}≡\text{C}_2\text{H}$. Each carbon is surrounded by two groups: a hydrogen and another carbon. Notice that the triple bond (as well as a double bond in other compounds) is considered as one bond for purposes of VSEPR theory, because all three bonds connect the same two atoms. Atoms with 180° bond angles are said to have linear geometry. Thus, acetylene is a linear molecule.

\[\text{boron trifluoride}\]

In such a situation the surrounded atom (in this case boron) is said to have trigonal planar geometry.

\[\text{acetylene}\]
Now let’s consider how unshared valence electron pairs are treated by VSEPR theory. An unshared valence electron pair is treated as if it were a bond without a nucleus at one end. For example, in VSEPR theory, the nitrogen in ammonia, $\text{NH}_3$, is surrounded by four “bonds”: three $\text{N—H}$ bonds and the unshared valence electron pair. These “bonds” are directed to the vertices of a tetrahedron so that the hydrogens occupy three of the four tetrahedral vertices. This geometry is called **trigonal pyramidal** because the three $\text{N—H}$ bonds also lie along the edges of a pyramid.

VSEPR theory also postulates that unshared valence electron pairs occupy more space than an ordinary bond. It’s as if the electron pair “spreads out” because it isn’t constrained by a second nucleus. As a result, the bond angle between the unshared pair and the other bonds are somewhat larger than tetrahedral, and the $\text{N—H}$ bond angles are correspondingly smaller. In fact, the $\text{H—N—H}$ bond angle in ammonia is $107.3^\circ$.

![Illustration of ammonia molecule with bond angles labeled]

**Study Problem 1.3**

Estimate each bond angle in the following molecule, and order the bonds according to length, beginning with the shortest.

![Chemical structure with bonds labeled]

**Solution** Because carbon-2 is bound to two groups (H and C), its geometry is linear. Similarly, carbon-3 also has linear geometry. The remaining carbon (carbon-4) is bound to three groups (C, O, and Cl); therefore, it has approximately trigonal planar geometry. To arrange the bonds in order of length, recall the order of importance of the bond-length rules. The major influence on length is the row in the periodic table from which the bonded atoms are taken. Hence, the $\text{H—C}$ bond is shorter than all carbon–carbon or carbon-oxygen bonds, which are shorter than the $\text{C—Cl}$ bond. The next major effect is the bond order. Hence, the $\text{C≡C}$ bond is shorter than the $\text{C==O}$ bond, which is shorter than the $\text{C—C}$ bond. Putting these conclusions together, the required order of bond lengths is

$$(a) < (b) < (e) < (c) < (d)$$

**PROBLEMS**

1.10 Predict the approximate geometry in each of the following molecules.

- (a) water
- (b) $[\text{BF}_3]^-$
- (c) $\text{H}_2\text{C}==\text{O}$
- (d) $\text{H}_3\text{C}==\text{C}==\text{N}$

formaldehyde

acetonitrile
1.11 Estimate each of the bond angles and order the bond lengths (smallest first) for each of the following molecules. For molecule (b), state any points of ambiguity and explain.

(a)  

(b)  

Dihedral Angles To completely describe the shapes of molecules that are more complex than the ones we’ve just discussed, we need to specify not only the bond lengths and bond angles, but also the spatial relationship of the bonds on adjacent atoms.

To illustrate this problem, consider the molecule hydrogen peroxide, \( \text{H}---\hat{\text{O}}---\hat{\text{O}}---\text{H} \). Both \( \text{O}---\text{O}---\text{H} \) bond angles are 96.5°. However, knowledge of these bond angles is not sufficient to describe completely the shape of the hydrogen peroxide molecule. To understand why, imagine two planes, each containing one of the oxygens and its two bonds (Fig. 1.6). To completely describe the structure of hydrogen peroxide, we need to know the angle between these two planes. This angle is called the \textbf{dihedral angle} or \textbf{torsion angle}. Three possibilities for the dihedral angle are shown in Fig. 1.6. You can also visualize these dihedral angles using a model of hydrogen peroxide by holding one \( \text{O}---\hat{\text{O}}---\text{H} \) bond fixed and rotating the remaining oxygen and its bonded hydrogen about the \( \text{O}---\text{O} \) bond. (The actual dihedral angle in hydrogen peroxide is addressed in Problem 1.43, p. 44.) Molecules containing many bonds typically contain many dihedral angles to be specified. We’ll begin to learn some of the principles that allow us to predict dihedral angles in Chapter 2.

Let’s summarize: The geometry of a molecule is completely determined by three elements: its bond lengths, its bond angles, and its dihedral angles. The geometries of diatomic molecules are completely determined by their bond lengths. The geometries of molecules in which a central atom is surrounded by two or more other atoms are determined by both bond lengths and bond angles. Bond lengths, bond angles, and dihedral angles are required to specify the geometry of more complex molecules.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{dihedral_angles}
\caption{The concept of dihedral angle illustrated for the hydrogen peroxide molecule, \( \text{H}---\hat{\text{O}}---\hat{\text{O}}---\text{H} \). Knowledge of the bond angles does not define the dihedral angle. Three possibilities for the dihedral angle (0°, 90°, and 180°) are shown.}
\end{figure}
PROBLEMS

1.12 The dihedral angles in ethane, $\text{H}_3\text{C}—\text{CH}_3$, relate the planes containing the $\text{H}—\text{C}—\text{C}$ bonds centered on the two carbons. Prepare models of ethane in which this dihedral angle is (a) $0^\circ$; (b) $60^\circ$; (c) $180^\circ$. Two of these models are identical; explain.

1.13 (a) Give the $\text{H}—\text{C}═\text{O}$ bond angle in methyl formate.

(b) One dihedral angle in methyl formate relates the plane containing the $\text{O}═\text{C}—\text{O}$ bonds to the plane containing the $\text{C}—\text{O}—\text{C}$ bonds. Sketch two structures of methyl formate: one in which this dihedral angle is $0^\circ$ and the other in which it is $180^\circ$.

1.4 RESONANCE STRUCTURES

Some compounds are not accurately described by a single Lewis structure. Consider, for example, the structure of nitromethane, $\text{H}_3\text{C}—\text{NO}_2$.

This Lewis structure shows an $\text{N}—\text{O}$ single bond and an $\text{N}═\text{O}$ double bond. From the preceding section, we expect double bonds to be shorter than single bonds. However, it is found experimentally that the two nitrogen–oxygen bonds of nitromethane have the same length, and this length is intermediate between the lengths of single and double nitrogen–oxygen bonds found in other molecules. We can convey this idea by writing the structure of nitromethane as follows:

\[
\begin{align*}
\text{H}_3\text{C} & \longrightarrow \text{N} & \text{O} \\
& \amentimes & \text{:O:} \\
\text{H}_3\text{C} & \longrightarrow \text{N} & \text{O} \\
& \text{O} & \amentimes \\
\end{align*}
\]

The double-headed arrow (\(\leftrightarrow\)) means that nitromethane is a single compound that is the “average” of both structures; nitromethane is said to be a resonance hybrid of these two structures. Note carefully that the double-headed arrow (\(\leftrightarrow\)) is different from the arrows used in chemical equilibria, (\(\rightleftharpoons\)). The two structures for nitromethane are not rapidly interconverting and they are not in equilibrium. Rather, they are alternative representations of one molecule. In this text, resonance structures will be enclosed in brackets to emphasize this point. Resonance structures are necessary because of the inadequacy of a single Lewis structure to represent nitromethane accurately.

The two resonance structures in Eq. 1.6 are fictitious, but nitromethane is a real molecule. Because we have no way to describe nitromethane accurately with a single Lewis structure, we must describe it as the hybrid of two fictitious structures. An analogy to this situation is a description of Fred Flatfoot, a real detective. Lacking words to describe Fred, we picture him as a resonance hybrid of two fictional characters:

Fred Flatfoot = [Sherlock Holmes \(\leftrightarrow\) James Bond]
This suggests that Fred is a dashing, violin-playing, pipe-smoking, highly intelligent British agent with an assistant named Watson, and that Fred likes his martinis shaken, not stirred.

When two resonance structures are identical, as they are for nitromethane, they are equally important in describing the molecule. We can think of nitromethane as a 1:1 average of the structures in Eq. 1.6. For example, each oxygen bears half a negative charge, and each nitrogen-oxygen bond is neither a single bond nor a double bond, but a bond halfway in between.

If two resonance structures are not identical, then the molecule they represent is a weighted average of the two. That is, one of the structures is more important than the other in describing the molecule. Such is the case, for example, with the methoxymethyl cation:

\[
\begin{align*}
\text{methoxymethyl cation}
\end{align*}
\]

It turns out that the structure on the right is a better description of this cation because all atoms have complete octets. Hence, the C—O bond has significant double-bond character, and most of the formal positive charge resides on the oxygen.

Formal charge has the same limitations as a bookkeeping device in resonance structures that it does in other structures. Although most of the formal charge in the methoxymethyl cation resides on oxygen, the CH₂ carbon bears more of the actual positive charge, because oxygen is more electronegative than carbon.

The hybrid character of some molecules is sometimes conveyed in a single structure in which dashed lines are used to represent partial bonds. For example, nitromethane can be represented in this notation in either of the following ways:

\[
\begin{align*}
\text{or }
\end{align*}
\]

In the hybrid structure on the left, the locations of the shared negative charge are shown explicitly with partial charges. In the hybrid structure on the right, the locations of the shared negative charge are not shown. Although the use of hybrid structures is sometimes convenient, it is difficult to apply electron-counting rules and the curved-arrow notation to them. To avoid confusion, we’ll use conventional resonance structures in these situations.

Another very important aspect of resonance structures is that they have implications for the stability of the molecule they represent. A molecule represented by resonance structures is more stable than its fictional resonance contributors. For example, the actual molecule nitromethane is more stable than either one of the fictional molecules described by the contributing resonance structures in Eq. 1.6. Nitromethane is thus said to be a resonance-stabilized molecule, as is the methoxymethyl cation.

How do we know when to use resonance structures, how to draw them, or how to assess their relative importance? In Chapter 3, we’ll learn a technique for deriving resonance structures, and in Chapter 15, we’ll return to a more detailed study of the other aspects of resonance. In the meantime, we’ll draw resonance structures for you and tell you when they’re important. Just try to remember the following points:

1. Resonance structures are used for compounds that are not adequately described by a single Lewis structure.
2. Resonance structures are not in equilibrium; that is, the compound they describe is not one resonance structure part of the time and the other resonance structure part of the time, but rather a single structure.
3. The structure of a molecule is the weighted average of its resonance structures. When resonance structures are identical, they are equally important descriptions of the molecule.

4. Resonance hybrids are more stable than any of the fictional structures used to describe them. Molecules described by resonance structures are said to be resonance-stabilized.

**PROBLEMS**

1.14 (a) Draw a resonance structure for the allyl anion that shows, along with the following structure, that the two CH₂ carbons are equivalent and indistinguishable.

   \[
   \text{allyl anion} \quad \text{H}_2\text{C} = \text{CH} = \text{CH}_2
   \]

   (b) According to the resonance structures, how much negative charge is on each of the CH₂ carbons?

   (c) Draw a single hybrid structure for the allyl anion that shows shared bonds as dashed lines and charges as partial charges.

1.15 The compound benzene has only one type of carbon–carbon bond, and this bond has a length intermediate between that of a single bond and a double bond. Draw a resonance structure of benzene that, taken with the following structure, accounts for the carbon–carbon bond length.

**1.5 WAVE NATURE OF THE ELECTRON**

You’ve learned that the covalent chemical bond can be viewed as the sharing of one or more electron pairs between two atoms. Although this simple model of the chemical bond is very useful, in some situations it is inadequate. A deeper insight into the nature of the chemical bond can be obtained from an area of science called quantum mechanics. Quantum mechanics deals in detail with, among other things, the behavior of electrons in atoms and molecules. Although the theory involves some sophisticated mathematics, we need not explore the mathematical detail to appreciate some general conclusions of the theory. The starting point for quantum mechanics is the idea that small particles such as electrons also have the character of waves. How did this idea evolve?

As the twentieth century opened, it became clear that certain things about the behavior of electrons could not be explained by conventional theories. There seemed to be no doubt that the electron was a particle; after all, both its charge and mass had been measured. However, electrons could also be diffracted like light, and diffraction phenomena were associated with waves, not particles. The traditional views of the physical world treated particles and waves as unrelated phenomena. In the mid-1920s, this mode of thinking was changed by the advent of quantum mechanics. This theory holds that, in the submicroscopic world of the electron and other small particles, there is no real distinction between particles and waves. The behavior of small particles such as the electron can be described by the physics of waves. In other words, matter can be regarded as a wave-particle duality.
How does this wave-particle duality require us to alter our thinking about the electron? In our everyday lives, we’re accustomed to a deterministic world. That is, the position of any familiar object can be measured precisely, and its velocity can be determined, for all practical purposes, to any desired degree of accuracy. For example, we can point to a baseball resting on a table and state with confidence, “That ball is at rest (its velocity is zero), and it is located exactly 1 foot from the edge of the table.” Nothing in our experience indicates that we couldn’t make similar measurements for an electron. The problem is that humans, chemistry books, and baseballs are of a certain scale. Electrons and other tiny objects are of a much smaller scale. A central principle of quantum mechanics, the Heisenberg uncertainty principle, tells us that the accuracy with which we can determine the position and velocity of a particle is inherently limited. For “large” objects, such as basketballs, organic chemistry textbooks, and even molecules, the uncertainty in position is small relative to the size of the object and is inconsequential. But for very small objects such as electrons, the uncertainty is significant. As a result, the position of an electron becomes “fuzzy.” According to the Heisenberg uncertainty principle, we are limited to stating the probability that an electron is occupying a certain region of space.

In summary:

1. Electrons have wavelike properties.
2. The exact position of an electron cannot be specified; only the probability that it occupies a certain region of space can be specified.
numbers have mathematical significance in the wave equations of the electron, for us they serve as labels, or designators, for the various orbitals, or wave motions, available to the electron. These quantum numbers can have only certain values, and the values of some quantum numbers depend on the values of others.

The **principal quantum number**, abbreviated \( n \), can have any integral value greater than zero—that is, \( n = 1, 2, 3, \ldots \).

The **angular momentum quantum number**, abbreviated \( l \), depends on the value of \( n \). The \( l \) quantum number can have any integral value from zero through \( n - 1 \), that is, \( l = 0, 1, 2, \ldots, n - 1 \). So that they are not confused with the principal quantum number, the values of \( l \) are encoded as letters. To \( l = 0 \) is assigned the letter \( s \); to \( l = 1 \), the letter \( p \); to \( l = 2 \), the letter \( d \); and to \( l = 3 \), the letter \( f \). The values of \( l \) are summarized in Table 1.2. It follows that there can be only one orbital, or wavefunction, with \( n = 1 \): this is the orbital with \( l = 0 \)—a \( 1s \) orbital. However, two values of \( l \), that is, 0 and 1, are allowed for \( n = 2 \). Consequently, an electron in the hydrogen atom can exist in either a \( 2s \) or a \( 2p \) orbital.

The **magnetic quantum number**, abbreviated \( m_l \), is the third orbital quantum number. Its values depend on the value of \( l \). The \( m_l \) quantum number can be zero as well as both positive and negative integers up to \( \pm l \)—that is, 0, \( \pm 1, \pm 2, \ldots, \pm l \). Thus, for \( l = 0 \) (an \( s \) orbital), \( m_l \) can only be 0. For \( l = 1 \) (a \( p \) orbital), \( m_l \) can have the values \( -1, 0, \) and \( +1 \). In other words, there is one \( s \) orbital with a given principal quantum number, but (for \( n > 1 \)) there are three \( p \) orbitals with a given principal quantum number, one corresponding to each value of \( m_l \). Because of the multiple possibilities for \( l \) and \( m_l \), the number of orbitals becomes increasingly large as \( n \) increases. This point is illustrated in Table 1.2 up to \( n = 3 \).

Just as an electron in the hydrogen atom can exist only in certain states, or orbitals, it can also have only certain allowed energies. Each orbital is associated with a characteristic electron energy. The *energy of an electron in a hydrogen atom is determined by the principal quantum number \( n \) of its orbital*. This is one of the central ideas of quantum theory. The energy of the electron is said to be quantized, or limited to certain values. This feature of the atomic electron is a direct consequence of its wave properties. An electron in the hydrogen atom resides in an orbital with \( n = 1 \) (a \( 1s \) orbital) and remains in that state unless the atom is subjected to the exact amount of energy (say, from light) required to increase the energy of the electron to a state with a higher \( n \), say \( n = 2 \):

![Diagram of electron energy levels](image-url)

If that happens, the electron absorbs energy and instantaneously assumes the new, more energetic, wave motion characteristic of the orbital with \( n = 2 \). (Such energy-absorption experiments gave the first clues to the quantized nature of the atom.) An analogy to this may be familiar. If you have ever blown across the opening of a soda-pop bottle (or a flute, which is a more sophisticated example of the same thing), you know that only a certain pitch can be produced...
1.6 ELECTRONIC STRUCTURE OF THE HYDROGEN ATOM

by a bottle of a given size. If you blow harder, the pitch does not rise, but only becomes louder. However, if you blow hard enough, the sound suddenly jumps to a note of higher pitch. The pitch is quantized; only certain sound frequencies (pitches) are allowed. Such phenomena are observed because sound is a wave motion of the air in the bottle, and only certain pitches can exist in a cavity of given dimensions without canceling themselves out. The progressively higher pitches you hear as you blow harder (called overtones of the lowest pitch) are analogous to the progressively higher energy states (orbitals) of the electron in the atom. Just as each overtone in the bottle is described by a wavefunction with higher “quantum number,” each orbital of higher energy is described by a wavefunction of higher principal quantum number \( n \).

B. Spatial Characteristics of Orbitals

One of the most important aspects of atomic structure for organic chemistry is that each orbital is characterized by a three-dimensional region of space in which the electron is most likely to exist. That is, orbitals have spatial characteristics. The size of an orbital is governed mainly by its principal quantum number \( n \): the larger \( n \) is, the greater the region of space occupied by the corresponding orbital. The shape of an orbital is governed by its angular momentum quantum number \( l \). The directionality of an orbital is governed by its magnetic quantum number \( m_l \). These points are best illustrated by example.

When an electron occupies a \( 1s \) orbital, it is most likely to be found in a sphere surrounding the atomic nucleus (Fig. 1.7, p. 26). We cannot say exactly where in that sphere the electron is by the uncertainty principle; locating the electron is a matter of probability. The mathematics of quantum theory indicates that the probability is about 90% that an electron in a \( 1s \) orbital will be found within a sphere of radius 1.4 Å about the nucleus. This “90% probability level” is taken as the approximate size of an orbital. Thus, we can depict an electron in a \( 1s \) orbital as a smear of electron density, most of which is within 1.4 Å of the nucleus.

Because orbitals are actually mathematical functions of three spatial dimensions, it would take a fourth dimension to plot the value of the orbital (or the electron probability) at each point in space. (See Further Exploration 1.2 for an additional discussion of electron probability.) Because we are limited to three spatial dimensions, Fig. 1.7 and the other orbital pictures presented subsequently show each orbital as a geometric figure that encloses some fraction (in our case, 90%) of the electron probability. The detailed quantitative distribution of electron probability within each figure is not shown.

When an electron occupies a \( 2s \) orbital, it also lies in a sphere, but the sphere is considerably larger—about three times the radius of the \( 1s \) orbital (Fig. 1.8, p. 26). A \( 3s \) orbital is even
larger still. The size of the orbital reflects the fact that the electron has greater energy; a more energetic electron can escape the attraction of the positive nucleus to a greater extent.

The 2s orbital also illustrates a node, another very important spatial aspect of orbitals. You may be familiar with a simple wave motion, such as the wave in a vibrating string, or waves in a pool of water. If so, you know that waves have peaks and troughs, regions where the waves are at their maximum and minimum heights, respectively. As you know from trigonometry, a simple sine wave $\psi = \sin x$ has a positive sign at its peak and a negative sign at its trough (Fig. 1.9). Because the wave is continuous, it has to have a zero value somewhere in between the peak and the trough. A node is a point or, in a three-dimensional wave, a surface, at which the wave is zero.

Figure 1.7 A 1s orbital. Most (90%) of the electron density lies in a sphere within 1.4 Å of the nucleus.

Figure 1.8 A 2s orbital in a cutaway view, showing the positive (peak-containing) region of the electron wave in blue and the negative (trough-containing) region in green. This orbital can be described as two concentric spheres of electron density. A 2s orbital is considerably larger than a 1s orbital; most (90%) of the electron density of a 2s orbital lies within 3.9 Å of the nucleus.
As you can see from Fig. 1.8 and the subsequent figures, the peaks and troughs are color-coded: peaks are blue and troughs are green. When the nodal properties of orbitals aren’t important for the discussion, the orbitals will be colored grey.

Pay very careful attention to one point of potential confusion. The sign of the wavefunction for an electron is not the same as the charge on the electron. Electrons always bear a negative charge. The sign of the wavefunction refers to the sign of the mathematical expression that describes the wave. By convention, a wave peak (color-coded blue) has a positive (+) sign and a wave trough (color-coded green) has a negative (−) sign.

As shown in Fig. 1.8, the 2s orbital has one node. This node separates a wave peak near the nucleus from a wave trough further out. Because the 2s orbital is a three-dimensional wave, its node is a surface. The nodal surface in the 2s orbital is an infinitely thin sphere. Thus, the 2s orbital has the characteristics of two concentric balls of electron density.

In the 2s orbital, the wave peak corresponds to a positive value in the 2s wavefunction, and the wave trough corresponds to a negative value. The node—the spherical shell of zero electron density—lies between the peak and the trough. Some students ask, “If the electron cannot exist at the node, how does it cross the node?” The answer is that the electron is a wave, and the node is part of its wave motion, just as the node is part of the wave in a vibrating string. The electron is not analogous to the string; it is analogous to the wave in the string.

We turn next to the 2p orbitals (Fig. 1.10, p. 28), which are especially important in organic chemistry. The 2p orbital illustrates how the l quantum number governs the shape of an orbital. All s orbitals are spheres. In contrast, all p orbitals have dumbbell shapes and are directed in space (that is, they lie along a particular axis). One lobe of the 2p orbital corresponds to a wave peak, and the other to a wave trough; the electron density, or probability of finding the electron, is identical in corresponding parts of each lobe. Note that the two lobes are parts of the same orbital. The node in the 2p orbital, which passes through the nucleus and separates the two lobes, is a plane. The size of the 2p orbital, like that of other orbitals, is governed by its principal quantum number; it extends about the same distance from the nucleus as a 2s orbital.

Fig. 1.10b illustrates a drawing convention for 2p orbitals. Quite often the lobes of these orbitals are drawn in a less rounded, “teardrop” shape. (This shape is derived from the square of the wavefunction, which is proportional to the actual electron density.) This shape is useful because it emphasizes the directionality of the 2p orbital. This convention is so commonly adopted that we’ll often use it in this text.
Recall (Table 1.2) that there are three $2p$ orbitals, one for each allowed value of the quantum number $m_l$. The three $2p$ orbitals illustrate how the $m_l$ quantum number governs the directionality of orbitals. The axes along which each of the $2p$ orbitals “points” are mutually perpendicular. For this reason, the three $2p$ orbitals are sometimes differentiated with the labels $2p_x$, $2p_y$, and $2p_z$. The three $2p$ orbitals are shown superimposed in Fig. 1.10c.

Let’s examine one more atomic orbital, the $3p$ orbital (Fig. 1.11). First, notice the greater size of this orbital, which is a consequence of its greater principal quantum number. The 90% probability level for this orbital is almost 10 Å from the nucleus. Next, notice the shape of the $3p$ orbital. It is generally lobe-shaped, and it consists of four regions separated by nodes. The two inner regions resemble the lobes of a $2p$ orbital. The outer regions, however, are large and diffuse, and resemble mushroom caps. Finally, notice the number and the character of the nodes. A $3p$ orbital contains two nodes. One node is a plane through the nucleus, much like the node of a $2p$ orbital. The other is a spherical node, shown in Fig. 1.11b, that separates the inner part of each lobe from the larger outer part. An orbital with principal quantum number $n$ has $n - 1$ nodes. Because the $3p$ orbital has $n = 3$, it has $(3 - 1) = 2$ nodes. The greater number of nodes in orbitals with higher $n$ is a reflection of their higher energies. Again, the analogy to sound waves is striking: overtones of higher pitch have larger numbers of nodes.

**C. Summary: Atomic Orbitals of Hydrogen**

Here are the important points about orbitals in the hydrogen atom:

1. An orbital is an allowed state for the electron. It is a description of the wave motion of the electron. The mathematical description of an orbital is called a wavefunction.

2. Electron density within an orbital is a matter of probability, by the Heisenberg uncertainty principle. We can think of an orbital as a “smear” of electron density.

3. Orbitals are described by three quantum numbers:
   a. The principal quantum number $n$ governs the energy of an orbital; orbitals of higher $n$ have higher energy.
   b. The angular momentum quantum number $l$ governs the shape of an orbital. Orbitals with $l = 0$ ($s$ orbitals) are spheres; orbitals with $l = 1$ ($p$ orbitals) have lobes oriented along an axis.
   c. The magnetic quantum number $m_l$ governs the orientation of an orbital.
1.7 ELECTRONIC STRUCTURES OF MORE COMPLEX ATOMS

The orbitals available to electrons in atoms with atomic number greater than 1 are, to a useful approximation, essentially like those of the hydrogen atom. This similarity includes the shapes and nodal properties of the orbitals. There is, however, one important difference: In atoms other than hydrogen, electrons with the same principal quantum number \( n \) but with different values of \( l \) have different energies. For example, carbon and oxygen, like hydrogen, have \( 2s \) and \( 2p \) orbitals, but, unlike hydrogen, electrons in these orbitals differ in energy. The ordering of energy levels for atoms with more than one electron is illustrated schematically in Fig. 1.12, p. 30. As this figure shows, the gaps between energy levels become progressively

**PROBLEMS**

1.16 Sketch a plot of the wavefunction \( \psi = \sin nx \) for the domain \( 0 \leq x \leq \pi \) for \( n = 1, 2, \) and \( 3 \). What is the relationship between the "quantum number" \( n \) and the number of nodes in the wavefunction?

1.17 Use the trends in orbital shapes you’ve just learned to describe the general features of

(a) a 3s orbital

(b) a 4s orbital

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**Figure 1.11**

(a) Perspective representation of a 3p orbital; only the planar node is shown. There are three such orbitals, and they are mutually perpendicular. Notice that a 3p orbital is much larger than a 2p orbital in Fig 1.10. Most (90%) of the electron density lies within 9.75 Å of the nucleus; about 60% of the electron density lies in the large outer lobes. (b) Schematic planar representation of a 3p orbital showing both the planar and the spherical nodes.

4. Orbitals with \( n > 1 \) contain nodes, which are surfaces of zero electron density. The nodes separate peaks of electron density from troughs, or, equivalently, regions in which the wavefunction describing an orbital has opposite sign. Orbitals with principal quantum number \( n \) have \( n - 1 \) nodes.

5. Orbital size increases with increasing \( n \).
smaller as the principal quantum number increases. Furthermore, the energy gap between orbitals that differ in principal quantum number is greater than the gap between two orbitals within the same principal quantum level. Thus, the difference in energy between 2s and 3s orbitals is greater than the difference in energy between 3s and 3p orbitals.

Atoms beyond hydrogen have more than one electron. Let’s now consider the electronic configurations of these atoms—that is, the way their electrons are distributed among their atomic orbitals. To describe electronic configurations we need to introduce the concept of electron spin, which is a magnetic property of the electron. An electron can have only two values of spin, sometimes described as “up” and “down.” Spin is characterized by a fourth quantum number $m_s$, which, in quantum theory, can have the values $+\frac{1}{2}$ (“up”) and $-\frac{1}{2}$ (“down”). Four quantum numbers, then, are associated with any electron in an atom: the three orbital quantum numbers $n$, $l$, and $m_l$, and the spin quantum number $m_s$.

The **aufbau principle** (German, meaning “buildup principle”) tells us how to determine electronic configurations. According to this principle, electrons are placed one by one into orbitals of the lowest possible energy in a manner consistent with the Pauli exclusion principle and Hund’s rules. The **Pauli exclusion principle** states that no two electrons may have all four quantum numbers the same. As a consequence of this principle, a maximum of two electrons may be placed in any one orbital, and these electrons must have different spins. To illustrate, consider the electronic configuration of the helium atom, which contains two electrons. Both electrons can be placed into the 1s orbital as long as they have differing spin. Consequently, we can write the electronic configuration of helium as follows:

$$\text{helium, He: (1s)}^2$$

This notation means that helium has two electrons of differing spin in a 1s orbital.

To illustrate Hund’s rules, consider the electronic configuration of carbon, obviously a very important element in organic chemistry. A carbon atom has six electrons. The first two electrons (with opposite spins) go into the 1s orbital; the next two (also with opposite spins) go into
In accordance with Hund’s rules, the electrons in the carbon 2p orbitals are unpaired with identical spin. Placing two electrons in different 2p orbitals ensures that repulsions between electrons are minimized, because electrons in different 2p orbitals occupy different regions of space. (Recall from Fig. 1.10c that the three 2p orbitals are mutually perpendicular.) As shown above, we can also write the electronic configuration of carbon more concisely as (1s)²(2s)²(2px)¹(2py)¹, which shows the two 2p electrons in different orbitals. (The choice of x and y as subscripts is arbitrary; 2px and 2py, or other combinations, are equally valid; the important point about this notation is that the two half-populated 2p orbitals are different.)

Let’s now re-define the term valence electrons, first defined in Sec. 1.2A, in light of what we’ve learned about quantum theory. The valence electrons of an atom are the electrons that occupy the orbitals with the highest principal quantum number. (Note carefully that this definition applies only to elements in the “A” groups—that is, the nontransition groups—of the periodic table.) For example, the 2s and 2p electrons of carbon are its valence electrons. A neutral carbon atom, therefore, has four valence electrons. The valence orbitals of an atom are the orbitals that contain the valence electrons. Thus, the 2s and 2p orbitals are the valence orbitals of carbon. It is important to be able to identify the valence electrons of common atoms because chemical interactions between atoms involve their valence electrons and valence orbitals.

**Study Problem 1.4**

Describe the electronic configuration of the sulfur atom. Identify the valence electrons and valence orbitals.

**Solution** Because sulfur has an atomic number of 16, a neutral sulfur atom has 16 electrons. Following the aufbau principle, the first two electrons occupy the 1s orbital with opposite spins. The next two, again with opposite spins, occupy the 2s orbital. The next six occupy the three 2p orbitals, with each 2p orbital containing two electrons of opposite spin. The next two electrons go into the 3s orbital with paired spins. The remaining four electrons are distributed among the three 3p orbitals. Taking Hund’s rules into account, the first three of these electrons are placed, unpaired and with identical spin, into the three equivalent 3p orbitals: 3px, 3py, and 3pz. The one remaining electron is then placed, with opposite spin, into the 3pz orbital. To summarize:
As shown in the diagram, the 3s and 3p electrons are the valence electrons of sulfur; the 3s and 3p orbitals are the valence orbitals.

A. Molecular Orbital Theory

One way to think about chemical bonding is to assume that a bond consists of two electrons localized between two specific atoms. This is the simplest view of a Lewis electron-pair bond. As useful as this picture is, it is sometimes too restrictive. When atoms combine into a molecule, the electrons contributed to the chemical bonds by each atom are no longer localized on individual atoms but “belong” to the entire molecule. Consequently, atomic orbitals are no longer appropriate descriptions for the state of electrons in molecules. Instead, molecular orbitals, nicknamed MOs, which are orbitals for the entire molecule, are used.

Determining the electronic configuration of a molecule is a lot like determining the electronic configuration of an atom, except that molecular orbitals are used instead of atomic orbitals. The following four steps summarize conceptually how we start with two isolated hydrogen atoms and end up with the electronic configuration of the dihydrogen molecule, H₂.

Step 1. Start with the isolated atoms of the molecule and bring them together to the positions that they have in the molecule. Their valence atomic orbitals will overlap.

For H₂, this means bringing the two hydrogen atoms together until the nuclei are separated by the length of the H—H bond (Fig. 1.13a). At this distance, the 1s orbitals of the atoms overlap.

Step 2. Allow the overlapping valence atomic orbitals to interact to form molecular orbitals (MOs).

This step implies that MOs of H₂ are derived by combining the 1s atomic orbitals of the two hydrogen atoms in a certain way. Conceptually, this is reasonable: molecules result from a combination of atoms, so molecular orbitals result from a combination of atomic orbitals. We’ll shortly learn the process for combining atomic orbitals to form molecular orbitals.

PROBLEM

1.18 Give the electronic configurations of each of the following atoms and ions. Identify the valence electrons and valence orbitals in each.

(a) oxygen atom (b) chloride ion, Cl⁻ (c) potassium ion, K⁺ (d) sodium atom
1.8 ANOTHER LOOK AT THE COVALENT BOND: MOLECULAR ORBITALS

Step 3. Arrange the MOs in order of increasing energy. Steps 1 and 2 will yield two MOs for H₂ that differ in energy. We’ll also learn how to determine relative energies of these MOs.

Step 4. Determine the electronic configuration of the molecule by redistributing the electrons from the constituent atoms into the MOs in order of increasing MO energy; the Pauli principle and Hund’s rules are used. We redistribute the two electrons (one from each starting hydrogen atom) into the MOs of H₂ to give the electronic configuration of the molecule.

How to carry out steps 2 and 3 is the key to understanding the formation of molecular orbitals. Quantum theory gives us a few simple rules that allow us to derive the essential features of molecular orbitals without any calculations. We’ll state these rules as they apply to H₂ and other cases involving the overlap of two atomic orbitals. (These rules will require only slight modification for more complex cases.)
Rules for forming molecular orbitals:

1. The combination of two atomic orbitals gives two molecular orbitals.
   For H₂, this rule means that the overlap of two 1s orbitals from the constituent hydrogen atoms gives two molecular orbitals. Later, we’ll have situations in which we combine more than two atomic orbitals. When we combine \( j \) atomic orbitals, we always obtain \( j \) molecular orbitals.

2. One molecular orbital is derived by the addition of the two atomic orbitals in the region of overlap.
   To apply this to H₂, remember that the 1s orbital is a wave peak. When we add two wave peaks, they reinforce. When we add two 1s orbitals in the overlap region, they reinforce to form a continuous orbital that includes the region between the two nuclei (Fig. 1.13b). This molecular orbital is called a bonding molecular orbital, or bonding MO. The reason for the name is that, when electrons occupy this MO, they are attracted to both nuclei simultaneously. In other words, the electrons occupy not only the region around the nuclei but also the region between the nuclei, thus providing “electron cement” that holds the nuclei together, just as mortar between two bricks holds the bricks together.

3. The other molecular orbital is derived by subtraction of the two atomic orbitals in the region of overlap.
   To subtract the two 1s orbitals, we change one of the 1s orbitals from a peak to a trough. (This is equivalent to changing the mathematical sign of the 1s wavefunction.) Then we add the two resulting orbitals. This process is illustrated in Fig. 1.13c. Adding a wave peak to a wave trough results in cancellation of the two waves in the region of overlap and formation of a node—a region in which the wave is zero. In this case, the node is a plane. The resulting orbital is called an antibonding molecular orbital or antibonding MO. Electrons that occupy this MO decrease bonding because the region between the nuclei contains no electron density.

4. The two molecular orbitals have different energies. Orbital energy increases with the number of nodes. The bonding MO has a lower energy than the isolated 1s orbitals and the antibonding MO has a higher energy than the isolated 1s orbitals.
   The orbital energies are summarized in an orbital interaction diagram, shown in Fig. 1.14. This diagram is a plot of orbital energy versus the position of the two interacting nuclei. The isolated atomic orbitals and their energies are shown on the left and right sides of the diagram, and the molecular orbitals and their energies are shown in the center, where the separation of the atoms corresponds to the bond length. The number of nodes tells us the relative energies of the MOs: the more nodes an MO has, the higher is its energy. The bonding MO has no nodes and therefore has the lower energy. The antibonding MO has one node and has the higher energy. Notice that the energies of the two MOs “spread” about the energy of the isolated 1s orbitals—the energy of the bonding MO is lowered by a certain amount and the energy of the antibonding MO is raised by the same amount.

Now that we’ve described how to form the MOs and rank their energies, we’re ready to populate these MOs with electrons. We apply the aufbau principle. We have two electrons—one from each hydrogen atom—to redistribute. Both can be placed in the bonding MO with opposite spins. Electron occupancy of the bonding MO is also shown in Fig. 1.14.

When we talk about the energy of an orbital, what we are really talking about is the energy of an electron that occupies the orbital. It follows, then, that the electrons in the bonding MO have lower energy than two electrons in their parent 1s orbitals. In other words, chemical bonding is an energetically favorable process. Each electron in the bonding MO of H₂ contributes about half to the stability of the H—H bond. It takes about 435 kJ (104 kcal) to dissociate a mole of H₂ into hydrogen atoms, or about 218 kJ (52 kcal) per bonding electron. This a lot of
energy on a chemical scale—more than enough to raise the temperature of a kilogram of water from freezing to boiling.

According to the picture just developed, the chemical bond in a hydrogen molecule results from the occupancy of a bonding molecular orbital by two electrons. You may wonder why we concern ourselves with the antibonding molecular orbital if it is not occupied. The reason is that it can be occupied! If a third electron were introduced into the hydrogen molecule, then the antibonding molecular orbital would be occupied. The resulting three-electron species is the hydrogen molecule anion, $\text{H}_2^-$ (see Prob. 1.19b, p. 36). $\text{H}_2^-$ exists because each electron in the bonding molecular orbital of the hydrogen molecule contributes equally to the stability of the molecule. The third electron in $\text{H}_2^-$, the one in the antibonding molecular orbital, has a high energy that offsets the stabilization afforded by one of the bonding electrons. However, the stabilization due to the second bonding electron remains. Thus, $\text{H}_2^-$ is a stable species, but only about half as stable as the hydrogen molecule. In terms of our brick-and-mortar analogy, if electrons in a bonding MO bind the two nuclei together as mortar binds two bricks, then electrons in an antibonding MO act as “anti-mortar”: not only do they not bind the two nuclei together, but they oppose the binding effect of the bonding electrons. The importance of the antibonding MO is particularly evident when we attempt to construct diatomic helium, $\text{He}_2$, as shown in Study Problem 1.5.

Figure 1.14 An orbital interaction diagram for the formation of the $\text{H}_2$ molecular orbitals from interacting $1s$ orbitals of two hydrogen atoms. The dashed lines show schematically how the two $1s$ orbitals interact as the internuclear distance changes from very large ($\infty$) to the $\text{H}--\text{H}$ bond length. The bonding MO has lower energy than the $1s$ orbitals and the antibonding MO has higher energy. Both electrons occupy the bonding MO.
Study Problem 1.5

Use molecular orbital theory to explain why He$_2$ does not exist. The molecular orbitals of He$_2$ are formed in the same way as those of H$_2$.

**Solution** The orbital interaction diagram for the MOs of He$_2$ is conceptually the same as for H$_2$ (Fig. 1.14). However, He$_2$ contains four electrons—two from each He atom. According to the aufbau principle, two electrons are placed into the bonding MO, but the other two must occupy the antibonding MO. Any stability contributed by the bonding electrons is offset by the instability contributed by the antibonding electrons. Hence, formation of He$_2$ has no energetic advantage. As a result, He is monatomic.

Molecular orbitals, like atomic orbitals, have shapes that correspond to regions of significant electron density. Consider the shape of the bonding molecular orbital of H$_2$, shown in both Figs 1.13b and 1.14. In this molecular orbital the electrons occupy an ellipsoidal region of space. No matter how we turn the hydrogen molecule about a line joining the two nuclei, its electron density looks the same. This is another way of saying that the bond in the hydrogen molecule has *cylindrical symmetry*. Other cylindrically symmetrical objects are shown in Fig. 1.15. Bonds in which the electron density is cylindrically symmetrical about the internuclear axis are called *sigma bonds* (abbreviated *s* bonds). The bond in the hydrogen molecule is thus a *s* bond. The lower-case Greek letter sigma was chosen to describe the bonding molecular orbital of hydrogen because it is the Greek letter equivalent of *s*, the letter used to describe the atomic orbital of lowest energy.

PROBLEMS

1.19 Draw an orbital interaction diagram corresponding to Fig. 1.14 for each of the following species. Indicate which are likely to exist as diatomic species, and which would dissociate into monatomic fragments. Explain.
   
   (a) the He$_2^+$ ion  (b) the H$_2^+$ ion  (c) Li$_2$  (d) the H$_2^-$ ion  (e) the H$_2^-$ ion

1.20 The bond dissociation energy of H$_2$ is 435 kJ mol$^{-1}$ (104 kcal mol$^{-1}$); that is, it takes this amount of energy to dissociate H$_2$ into its atoms. Estimate the bond dissociation energy of H$_2^+$ and explain your answer.

B. **Molecular Orbital Theory and the Lewis Structure of H$_2$**

Let’s now relate the quantum-mechanical description of H$_2$ to the concept of the Lewis electron-pair bond. In the Lewis structure of H$_2$, the bond is represented by an electron pair shared between the two nuclei. In the quantum-mechanical description, the bond is the result of the presence of two electrons in a bonding molecular orbital and the resulting electron density between the two nuclei. Both electrons are attracted to each nucleus, and these electrons thus serve as the “cement” that holds the nuclei together. Thus, for H$_2$, the *Lewis electron-pair bond is equivalent to the quantum-mechanical idea of a bonding molecular orbital occupied by a pair of electrons*. The Lewis picture places the electrons squarely between the nuclei. Quantum theory says that, although the electrons have a high probability of being between the bound nuclei, they can also occupy other regions of space.

Molecular orbital theory shows, however, that a chemical bond need not be an electron *pair*. For example, H$_2^+$ (the hydrogen molecule cation, which we might represent in the Lewis sense as H$^+$H) is a stable species in the gas phase (see Prob. 1.19e). It is not so stable as the hydrogen molecule itself because the ion has only one electron in the bonding molecular orbital, rather than the two found in a neutral hydrogen molecule. The hydrogen molecule anion,
H2, discussed in the previous section, might be considered to have a three-electron bond consisting of two bonding electrons and one antibonding electron. The electron in the antibonding orbital is also shared by the two nuclei, but shared in a way that reduces the energetic advantage of bonding. (H2 is not so stable as H2; Sec. 1.8A.) This example demonstrates that the sharing of electrons between nuclei in some cases does not contribute to bonding. Nevertheless, the most stable arrangement of electrons in the dihydrogen molecular orbitals occurs when the bonding MO contains two electrons and the antibonding MO is empty—in other words, when there is an electron-pair bond.

1.9 HYBRID ORBITALS

A. Bonding in Methane

We ultimately want to describe the chemical bonding in organic compounds, and our first step in this direction is to understand the bonding in methane, CH4. Before quantum theory was applied to the bonding problem, it was known experimentally that the hydrogens in methane, and thus the bonds to these hydrogens, were oriented tetrahedrally about the central carbon. The valence orbitals in a carbon atom, however, are not directed tetrahedrally. The 2s orbital, as you've learned, is spherically symmetrical (see Fig. 1.8), and the 2p orbitals are perpendicular (see Fig. 1.10). If the valence orbitals of carbon aren’t directed tetrahedrally, why is methane a tetrahedral molecule?

The modern solution to this problem is to apply molecular orbital theory. You can’t do this with just the simple rules that we applied to H2, but it can be done. The result is that the combination of one carbon 2s and three carbon 2p orbitals with four tetrahedrally placed hydrogen 1s orbitals gives four bonding MOs and four antibonding MOs. (The combination of eight atomic orbitals give eight molecular orbitals; rule 1, p. 34, with j = 8.) Eight electrons (four from carbon and one from each of the four hydrogens) are just sufficient to fill the four bonding MOs with electron pairs. This molecular orbital description of methane accounts accurately for its electronic properties.

The conceptual difficulty with the molecular orbital description of methane is that we can’t associate a given pair of electrons in the molecule with any one bond. Instead, the electrons from all of the atoms are redistributed throughout the entire molecule. We can’t even tell where atoms begin or end! If we add up all of the contributions of the electrons in the four bonding MOs of methane, we obtain a picture of the total electron density—that is, the prob-
ability of finding electrons in the methane molecule. (The electrostatic potential maps, or EPMs, introduced in Sec. 1.2D, are superimposed on such pictures of total electron density.)

In this picture of total electron density, methane looks like an “electron pudding” containing the nuclei. Although this electron density has a tetrahedral shape, there are no discrete C—H bonds. In contrast, because H₂ has only one bond, we can associate the total electron density in H₂ with the H—H bond, as shown in the previous section.

Historically, chemists have liked to think that molecules are made up of atoms connected by individual bonds. We like to build models, hold them in our hands, and manipulate chemical bonds by plucking off certain atoms and replacing them by others. Although the molecular orbital description of methane certainly describes bonding, it suggests that the discrete chemical bond between individual atoms is something rationally conceivable but not rigorously definable (except perhaps for simple molecules like H₂). Nevertheless, the concept of the chemical bond is so useful in organic chemistry that we can’t ignore it! The problem, then, is this: Is there an electronic theory of bonding in methane that allows us to retain the notion of discrete C—H bonds?

To use a bonding theory that we know isn’t quite right may seem inappropriate, but science works this way. A theory is a framework for unifying a body of knowledge in such a way that we can use it to make useful predictions. An example you’re probably familiar with is the ideal gas law, \( PV = nRT \). Most real gases don’t follow this law exactly, but it can be used to make some useful predictions. For example, if you’re wondering what will happen to the pressure in your automobile tires when the temperature drops in winter, this law gives a perfectly useful answer: the pressure drops. If you’re interested in calculating exactly how much the pressure will drop per degree, you might need a more exact theory. We’ll find it necessary to use molecular orbital theory to explain certain phenomena, but in many cases we can get by with a simpler but less accurate theory that is attractive because it allows us to think in terms of discrete chemical bonds.

An electronic description of bonding in methane that retains the C—H bonds was developed in 1928 by Linus Pauling (1901–1994), a chemist at the California Institute of Technology who won the 1954 Nobel Prize in Chemistry for his work on chemical bonding. Pauling’s theory started with the premise that the valence orbitals of the carbon in methane are different from the orbitals in atomic carbon. However, the orbitals of carbon in methane can be derived simply from those of atomic carbon. For carbon in methane, we imagine that the 2s orbital and the three 2p orbitals are mixed to give four new equivalent orbitals, each with a character intermediate between pure s and pure p. It’s as if we mixed a blue dog and three yellow cats and ended up with four identical yellowish-green animals, each of which is three-fourths cat and one-fourth dog. This mixing process applied to orbitals is called hybridization, and the new orbitals are called hybrid orbitals. More specifically, hybrid orbitals result from the mixing of atomic orbitals with different l quantum numbers. Because each of the new hybrid carbon orbitals is one part s and three parts p, it is called an sp³ orbital (pronounced “s-p-three,” not
“s-p-cubed”). The six carbon electrons in this orbital picture are distributed between one 1s orbital and four equivalent $sp^3$ hybrid orbitals in quantum level 2. This mental transformation can be summarized as follows:

This orbital mixing can be done mathematically, and it yields the perspective drawing of an $sp^3$ hybrid orbital shown in Fig. 1.16a on p. 40. A simpler representation used in most texts is shown in Fig. 1.16b. As you can see from these pictures, an $sp^3$ orbital consists of two lobes separated by a node, much like a 2p orbital. However, one of the lobes is very small, and the other is very large. In other words, the electron density in an $sp^3$ hybrid orbital is highly directed in space. This directional character is ideal for bond formation along the axis of the large lobe.

The number of hybrid orbitals (four in this case) is the same as the number of orbitals that are mixed to obtain them. (One $s$ orbital + three $p$ orbitals = four $sp^3$ orbitals.) It turns out that the large lobes of the four carbon $sp^3$ orbitals are directed to the corners of regular tetrahedron, as shown in Figure 1.16c. In hybridization theory, each of the four electron-pair bonds in methane results from the overlap of a hydrogen 1s orbital containing one electron with a carbon $sp^3$ orbital, also containing a single electron. The resulting bond is a $\sigma$ bond.

This overlap looks a lot like the overlap of two atomic orbitals that we carried out in constructing the molecular orbitals of $H_2$. However, the hybrid orbital treatment is not a molecular orbital treatment because it deals with each bond in isolation. The hybrid orbital bonding picture for methane is shown in Fig. 1.16d.

The hybridization of carbon itself actually costs energy. (If this weren’t so, carbon atoms would exist in a hybridized configuration.) Remember, though, that this is a model for carbon in methane. Hybridization allows carbon to form four bonds to hydrogen that are much stronger than the bonds that would be formed without hybridization, and the strength of these bonds more than offsets the energy required for hybridization. Why does hybridization make these bonds stronger? First, the bonds are as far apart as possible, and repulsion between electron pairs in the bonds is therefore minimized. The pure $s$ and $p$ orbitals available on nonhybridized carbon, in contrast, are not directed tetrahedrally. Second, in each hybridized orbital,
the bulk of the electron density is directed toward the bound hydrogen. This directional character provides more electron “cement” between the carbon and hydrogen nuclei, and this results in stronger (that is, more stable) bonds.

B. Bonding in Ammonia

The hybrid orbital picture is readily extended to compounds containing unshared electron pairs, such as ammonia, \( \text{NH}_3 \). The valence orbitals of nitrogen in ammonia are, like the carbon in methane, hybridized to yield four \( sp^3 \) hybrid orbitals; however, unlike the corresponding carbon orbitals, one of these hybrid orbitals is fully occupied with a pair of electrons.

Each of the \( sp^3 \) orbitals on nitrogen containing one electron can overlap with the \( 1s \) orbital of a hydrogen atom, also containing one electron, to give one of the three \( N—H \) \( \sigma \) bonds of ammonia. The electrons in the filled \( sp^3 \) orbital on nitrogen become the unshared electron pair in ammonia. The unshared pair and the three \( N—H \) bonds, because they are made up of \( sp^3 \) hybrid orbitals, are directed to the corners of a regular tetrahedron (Fig. 1.17). The advantage of orbital hybridization in ammonia is the same as in carbon: hybridization accommodates the maximum separation of the unshared pair and the three hydrogens and, at the same time, provides strong, directed \( N—H \) bonds.

You may recall from Sec. 1.3B that the \( H—N—H \) bond angle in ammonia is 107.3°, a little smaller than tetrahedral (109.5°). Our hybrid-orbital picture can accommodate this struc-
tural refinement as well. Unshared electron pairs prefer $s$ orbitals, because $s$ orbitals have lower energy than $p$ orbitals. Or, to look at it another way, there’s no energetic advantage to putting an unshared pair in a spatially directed orbital if it’s not going to be involved in a chemical bond. But if the unshared pair were left in an unhybridized $2s$ orbital, each bond to hydrogen would have to be derived from a pure nitrogen $2p$ orbital. In such a bond, half of the electron density ("electron cement") would be directed away from the hydrogen, and the bond would be weak. In such a case, the $H—N—H$ bond angle would be $90^\circ$, the same as the angle between the $2p$ orbitals used to form the bonds. The actual geometry of ammonia is a compromise between the preference of unshared pairs for orbitals of high $s$ character and the preference of bonds for hybrid character. The orbital containing the unshared pair has a little more $s$ character than the bonding orbitals. Because $s$ orbitals cover an entire sphere (see Fig. 1.16, p. 26), orbitals with more $s$ character occupy more space. Hence, unshared pairs have a greater spatial requirement than bonds. Hence, the angle between the unshared pair and each of the $N—H$ bonds is somewhat greater than tetrahedral, and the bond angles between the $N—H$ bonds, as a consequence, are somewhat less than tetrahedral. This is the same conclusion we obtained from the application of VSEPR theory to ammonia (p. 18).

A connection exists between the hybridization of an atom and the arrangement in space of the bonds around that atom. Atoms surrounded by four groups (including unshared pairs) in a tetrahedral arrangement are $sp^3$-hybridized. The converse is also true: $sp^3$-hybridized atoms always have tetrahedral bonding geometry. A trigonal planar bonding arrangement is associated with a different hybridization, and a linear bonding arrangement with yet a third type of hybridization. (These types of hybridization are discussed in Chapters 4 and 14.) In other words, hybridization and molecular geometry are closely correlated.

The hybridization picture of covalent bonding also drives home one of the most important differences between the ionic and covalent bond: the covalent bond has a definite direction in space, whereas the ionic bond is the same in all directions. The directionality of covalent bonding is responsible for molecular shape; and, as we shall see, molecular shape has some very important chemical consequences.

**PROBLEMS**

1.21 (a) Construct a hybrid orbital picture for the water molecule using oxygen $sp^3$ hybrid orbitals.
(b) Predict any departures from tetrahedral geometry that you might expect from the presence of two unshared electron pairs. Explain your answer.

1.22 (a) Construct a hybrid orbital picture for the hydronium ion ($H_3O^+$) using oxygen $sp^3$ hybrid orbitals.
(b) How would you expect the $H—O—H$ bond angles in hydronium ion to compare with those in water (larger or smaller)? Explain.
Chemical compounds can contain two types of bonds: ionic and covalent. In ionic compounds, ions are held together by electrostatic attraction (the attraction of opposite charges). In covalent compounds, atoms are held together by the sharing of electrons.

Both the formation of ions and bonding in covalent compounds tend to follow the octet rule: Each atom is surrounded by eight valence electrons (two electrons for hydrogen).

The formal-charge convention assigns charges within a given species to its constituent atoms. The calculation of formal charge is given in Study Problem 1.1. Formal charge is a bookkeeping device. In some cases the actual charge on an atom and the formal charge do not correspond.

In covalent compounds, electrons are shared unequally between bonded atoms with different electronegativities. This unequal sharing results in a bond dipole moment. The dipole moment of a molecule is the vector sum of its individual bond dipole moments. The local charge distribution in a molecule can be described graphically with an electrostatic potential map (EPM).

The structure of a molecule is determined by its connectivity and its geometry. The molecular geometry of a molecule is determined by its bond lengths, bond angles, and dihedral angles. Bond lengths are governed, in decreasing order of importance, by the period of the periodic table from which the bonded atoms are derived; by the bond order (whether the bond is single, double, or triple); and by the column (group) of the periodic table from which the atoms in the bond are derived. Approximate bond angles can be predicted by assuming that the groups surrounding a given atom are as far apart as possible. A complete description of geometry for complex molecules requires a knowledge of dihedral angles, which are the angles between bonds on adjacent atoms when the bonds are viewed in a planar projection.

Molecules that are not adequately described by a single Lewis structure are represented as resonance hybrids, which are weighted averages of two or more fictitious Lewis structures. Resonance hybrids are more stable than any of their contributing resonance structures.

As a consequence of their wave properties, electrons in atoms and molecules can exist only in certain allowed energy states, called orbitals. Orbitals are descriptions of the wave properties of electrons in atoms and molecules, including their spatial distribution. Orbitals are described mathematically by wavefunctions.

Electrons in orbitals are characterized by quantum numbers, which, for atoms, are designated \( n, l, \) and \( m_l \). Electron spin is described by a fourth quantum number \( m_s \). The higher the principal quantum number \( n \) of an electron, the higher its energy. In atoms other than hydrogen, the energy is also a function of the \( l \) quantum number.

Some orbitals contain nodes, which separate the wave peaks of the orbitals from the wave troughs. An atomic orbital of quantum number \( n \) has \( n-1 \) nodes.

The distribution of electron density in a given type of orbital has a characteristic arrangement in space governed by the \( l \) quantum number: all \( s \) orbitals are spheres, all \( p \) orbitals contain two equal-sized lobes, and so on. The orientation of an orbital is governed by its \( m_l \) quantum number.

Atomic orbitals and molecular orbitals are both populated with electrons according to the aufbau principle.

Covalent bonds are formed when the orbitals of different atoms overlap. In molecular orbital theory, covalent bonding arises from the filling of bonding molecular orbitals by electron pairs.

The directional properties of bonds can be understood by the use of hybrid orbitals. The hybridization of an atom and the geometry of the atoms attached to it are closely related. All \( sp^3 \)-hybridized atoms have tetrahedral geometry.
1.23 In each of the following sets, specify the one compound that is likely to have completely ionic bonds in its solid state.
(a) CCl₄  HCl  NaAt  K₂
(b) CS₂  CaF₂  HF  XeF₂  BF₃

1.24 Which of the atoms in each of the following species has a complete octet? What is the formal charge on each? Assume all unshared valence electrons are shown.
(a) CH₃  (b) NH₃  (c) CH₄
(d) BH₃  (e) H₃O⁺  (f) BH₄⁻

1.25 Draw one Lewis structure for each of the following compounds; show all unshared electron pairs. None of the atoms in the compounds bears a formal charge, and all atoms have octets (hydrogens have duets).
(a) C₂H₃Cl
(b) ketene, C₂H₂O, which has a carbon–carbon double bond

1.26 Draw two Lewis structures for a compound with the formula C₆H₁₀. No atom bears a charge, and all carbons have complete octets.

1.27 Give the formal charge on each atom and the net charge on each species in the following structures. All unshared valence electrons are shown.
(a) O∶Cl∶O;
(b) O∶Cl∶O∶;
(c) O∶O∶;
(d) H₂C∶N∶CH₃;
(e) O∶;
(f) H₃C∶C∶;
(g) H₃C∶N∶

1.28 Give the electronic configuration of (a) the chlorine atom; (b) the chloride ion; (c) the argon atom; (d) the magnesium atom.

1.29 Give the electronic configuration of silicon (Si). Indicate the valence electrons.

1.30 Which of the following orbitals is (are) not permitted by the quantum theory of the hydrogen atom? Explain.
2s  6s  5d  2d  3p

1.31 Predict the approximate bond angles in each of the following molecules.
(a) CH₄  (b) BeH₂  (c) CH₃⁺
(d) :ClSi  (e) O∶O∶;
(f) H₂C∶C∶CH₂  (Give H∶C∶C and C∶C∶C angles.)

1.32 The percent s character describes the hybridization of an orbital. For example, an sp³ orbital has 25% s character. Given the bond angles in each case, calculate the percent s character of (1) the orbital containing a lone pair and (2) the orbital used to form the bond to hydrogen in each of the following compounds. State any assumptions. (Hint: What would be the angle between bonds containing 0% s character?)
(a) NH₃, H∶N∶H bond angle 107.3°
(b) H₂O, H∶O∶H bond angle 105.5°

1.33 The allyl cation can be represented by the following resonance structures.

(a) What is the bond order of each carbon–carbon bond in the allyl cation?
(b) How much positive charge resides on each carbon of the allyl cation?
(c) Although the preceding structures are reasonable descriptions of the allyl cation, the following cation cannot be described by analogous resonance structures. Explain why the structure on the right is not a reasonable resonance structure.
1.34 Consider the resonance structures for the carbonate ion.

\[ \begin{array}{c}
\text{O}^- \quad \text{O}^- \quad \text{O}^- \\
\text{C} \quad \text{C} \quad \text{C}
\end{array} \]

(a) How much negative charge is on each oxygen of the carbonate ion?
(b) What is the bond order of each carbon–oxygen bond in the carbonate ion?

1.35 (a) Two types of nodes occur in atomic orbitals: spherical surfaces and planes. Examine the nodes in \( 2s \), \( 2p \), and \( 3p \) orbitals, and show that they agree with the following statements:
1. An orbital of principal quantum number \( n \) has \( n - 1 \) nodes.
2. The value of \( l \) gives the number of planar nodes.
(b) How many spherical nodes does a \( 5s \) orbital have? A \( 3d \) orbital? How many nodes of all types does a \( 3d \) orbital have?

1.36 The shape of one of the five energetically equivalent \( 3d \) orbitals follows. From your answer to Problem 1.35, sketch the nodes of this \( 3d \) orbital, and associate a wave peak or a wave trough with each lobe of the orbital. (Hint: It doesn’t matter where you put your first peak; you should be concerned only with the relative positions of peaks and troughs.)

1.37 Orbitals with \( l = 3 \) are called \( f \) orbitals.
(a) How many energetically equivalent \( f \) orbitals are there?
(b) In what principal quantum level do \( f \) orbitals first appear?
(c) How many nodes does a \( 5f \) orbital have?

1.38 Sketch a \( 4p \) orbital. Show the nodes and the regions of wave peaks and wave troughs. (Hint: Use Fig. 1.11 and the descriptions of nodes in Problem 1.35a.)

1.39 Account for the fact that \( \text{H}_3\text{C}—\text{Cl} \) (dipole moment 1.94 D) and \( \text{H}_3\text{C}—\text{F} \) (dipole moment 1.82 D) have almost identical dipole moments, even though fluorine is considerably more electronegative than chlorine.

1.40 The principles for predicting bond angles do not permit a distinction between the following two conceivable forms of ethylene.

- **Planar**
- **Staggered**

The dipole moment of ethylene is zero. Does this experimental fact provide a clue to the preferred dihedral angles in ethylene? Why or why not?

1.41 A well-known chemist, Havno Szents, has heard you apply the rules for predicting molecular geometry to water; you have proposed (Problem 1.10a, p. 18) a bent geometry for this compound. Dr. Szents is unconvinced by your arguments and continues to propose that water is a linear molecule. He demands that you debate the issue with him before a distinguished academy. You must therefore come up with *experimental* data that will prove to an objective body of scientists that water indeed has a bent geometry. Explain why the dipole moment of water, 1.84 D, could be used to support your case.

1.42 Use your knowledge of vectors to explain why, even though the \( \text{C}—\text{Cl} \) bond dipole is large, the dipole moment of carbon tetrachloride, \( \text{CCl}_4 \), is zero. (Hint: Take the resultant of any two \( \text{C}—\text{Cl} \) bond dipoles; then take the resultant of the other two. Now add the two resultants to get the dipole moment of the molecule. Use models!)

1.43 Three possible dihedral angles for \( \text{H}_2\text{O}_2 \) (0°, 90°, and 180°) are shown in Fig. 1.6 on p. 19.
(a) Assume that the \( \text{H}_2\text{O}_2 \) molecule exists predominantly in one of these arrangements. Which of the dihedral angles can be ruled out by the fact that \( \text{H}_2\text{O}_2 \) has a large dipole moment (2.13 D)? Explain.
(b) The bond dipole moment of the \( \text{O}—\text{H} \) bond is tabulated as 1.52 D. Use this fact and the overall dipole moment of \( \text{H}_2\text{O}_2 \) in part (a) to decide on the preferred dihedral angles in \( \text{H}_2\text{O}_2 \). Take the \( \text{H}—\text{O}—\text{O} \) bond angle to be the known value (96.5°). (Hint: Apply the law of cosines.)
1.44 Given the dipole moment of water (1.84 D) and the H—O—H bond angle (104.5°), justify the statement in Problem 1.43(b) that the bond dipole moment of the O—H bond is 1.52 D.

1.45 Consider two 2p orbitals, one on each of two atoms, oriented head-to-head as in Figure P1.45. Imagine bringing the nuclei closer together until the two wave peaks (the blue lobes) of the orbitals just overlap, as shown in the figure. A new system of molecular orbitals is formed by this overlap.

(a) Sketch the shape of the resulting bonding and antibonding molecular orbitals.
(b) Identify the nodes in each molecular orbital.
(c) Construct an orbital interaction diagram for molecular orbital formation.
(d) If two electrons occupy the bonding molecular orbital, is the resulting bond a σ bond? Explain.

1.46 Consider two 2p orbitals, one on each of two different atoms, oriented side-to-side, as in Figure P1.46. Imagine bringing these nuclei together so that overlap occurs as shown in the figure. This overlap results in a system of molecular orbitals.

(a) Sketch the shape of the resulting bonding and antibonding molecular orbitals.
(b) Identify the node(s) in each.
(c) Construct an orbital interaction diagram for molecular orbital formation.
(d) When two electrons occupy the bonding molecular orbital, is the resulting bond a σ bond? Explain.

1.47 When a hydrogen molecule absorbs light, an electron jumps from the bonding molecular orbital to the antibonding molecular orbital. Explain why this light absorption can lead to the dissociation of the hydrogen molecule into two hydrogen atoms. (This process, called photodissociation, can sometimes be used to initiate chemical reactions.)

1.48 Suppose you take a trip to a distant universe and find that the periodic table there is derived from an arrangement of quantum numbers different from the one on earth. The rules in that universe are:

1. principal quantum number \( n = 1, 2, \ldots \) (as on earth);
2. angular momentum quantum number \( l = 0, 1, 2, \ldots, n - 1 \) (as on earth);
3. magnetic quantum number \( m_l = 0, 1, 2, \ldots, l \) (that is, only positive integers up to and including \( l \) are allowed); and
4. spin quantum number \( m_s = -1, 0, +1 \) (that is, three allowed values of spin).

(a) Assuming that the Pauli exclusion principle remains valid, what is the maximum number of electrons that can populate a given orbital?
(b) Write the electronic configuration of the element with atomic number 8 in the periodic table.
(c) What is the atomic number of the second noble gas?
(d) What rule replaces the octet rule?