Earlier we referred to the forces that hold nonmetal atoms to one another, covalent bonds. These bonds consist of an electron pair shared between two atoms. To represent the covalent bond in the H₂ molecule, two structures can be written:

\[ \text{H} : \text{H} \quad \text{or} \quad \text{H} - \text{H} \]

These structures can be misleading if they are taken to mean that the two electrons are fixed in position between the two nuclei. A more accurate picture of the electron density in H₂ is shown in Figure 7.1. At a given instant, the two electrons may be located at any of various points about the two nuclei. However, they are more likely to be found between the nuclei than at the far ends of the molecule.

To understand the stability of the electron-pair bond, consider the graph shown in Figure 7.2, p. 164, where we plot the energy of interaction between two hydrogen atoms as a function of distance. At large distances of separation (far right) the system consists of two isolated H atoms that do not interact with each other. As the atoms come closer together (moving to the left in Figure 7.2), they experience an attraction that leads gradually to an energy minimum. At an internuclear distance of 0.074 nm and an attractive energy of 436 kJ, the system is in its most stable state; we refer to that state as the H₂ molecule. If the atoms are brought closer together, forces of repulsion become increasingly important and the energy curve rises steeply.

The existence of the energy minimum shown in Figure 7.2 is directly responsible for the stability of the H₂ molecule. The attractive forces that bring about this minimum result from two factors:

1. Locating two electrons between the two protons of the H₂ molecule lowers the electrostatic energy of the system. Attractive energies between oppositely charged particles (electron-proton) slightly exceed the repulsive energies between particles of like charge (electron-electron, proton-proton).

2. When two hydrogen atoms come together to form a molecule, the electrons are spread over the entire volume of the molecule instead of being confined to a particular atom. As pointed out in Chapter 6, quantum mechanics tells us that increasing the volume available to an electron decreases its kinetic energy. We often describe this situation by saying that the two 1s orbitals of the hydrogen atom “overlap” to form a new bonding orbital. At any rate, calculations suggest that this is the principal factor accounting for the stability of the H₂ molecule.

This chapter is devoted to the covalent bond as it exists in molecules and polyatomic ions. We consider—

- the distribution of outer level (valence) electrons in species in which atoms are joined by covalent bonds. These distributions are most simply described by Lewis structures (Section 7.1).
- molecular geometries. The so-called VSEPR model can be used to predict the angles between covalent bonds formed by a central atom (Section 7.2).
- the polarity of covalent bonds and the molecules they form (Section 7.3). Most bonds and many molecules are polar in the sense that they have a positive and a negative pole.
- the distribution of valence electrons among atomic orbitals, using the valence bond approach (Section 7.4).
The idea of the covalent bond was first suggested by the American physical chemist G. N. Lewis in 1916. He pointed out that the electron configuration of the noble gases appears to be a particularly stable one. Noble-gas atoms are themselves extremely unreactive. Moreover, as pointed out in Chapter 6, a great many monatomic ions have noble-gas structures. Lewis suggested that nonmetal atoms, by sharing electrons to form an electron-pair bond, can acquire a stable noble-gas structure. Consider, for example, two hydrogen atoms, each with one electron. The process by which they combine to form an H₂ molecule can be shown as using dots to represent electrons; the circles emphasize that the pair of electrons in the covalent bond can be considered to occupy the 1s orbital of either hydrogen atom. In that sense, each atom in the H₂ molecule has the electronic structure of the noble gas helium, with the electron configuration 1s².

These structures (without the circles) are referred to as Lewis structures.

In writing Lewis structures, only the valence electrons written above are shown, because they are the ones that participate in covalent bonding. For the main-group elements, the only ones dealt with here, the number of valence electrons is

\[
\text{H} \cdot + \text{H} \cdot \rightarrow \text{H} \cdot \cdot \cdot \text{H} \cdot
\]

The combination of a hydrogen with a fluorine atom leads to

\[
\text{H} \cdot + \cdot \text{F} : \rightarrow \text{H} \cdot \cdot \text{F} : \cdot
\]

As you can see, the fluorine atom "owns" six valence electrons outright and shares two others. Putting it another way, the F atom is surrounded by eight valence electrons; its electron configuration has become 1s²2s²2p⁶, which is that of the noble gas neon. This, according to Lewis, explains why the HF molecule is stable in contrast to species such as H₂F, H₃F, ... none of which exist.

These structures (without the circles) are referred to as Lewis structures.
equal to the last digit of the group number in the periodic table (Table 7.1). Notice that elements in a given main group all have the same number of valence electrons. This explains why such elements behave similarly when they react to form covalently bonded species.

In the Lewis structure of a molecule or polyatomic ion, valence electrons ordinarily occur in pairs. There are two kinds of electron pairs.

1. A pair of electrons shared between two atoms is a **covalent bond**, ordinarily shown as a straight line between bonded atoms.

2. An **unshared pair** of electrons, owned entirely by one atom, is shown as a pair of dots on that atom. (An unshared pair is often referred to, more picturesquely, as a **lone pair**.)

   The Lewis structures for the species $\text{OH}^-$, $\text{H}_2\text{O}$, $\text{NH}_3$, and $\text{NH}_4^+$ are

   
   ![Lewis Structures](image)

   Notice that in each case the oxygen or nitrogen atom is surrounded by eight valence electrons. In each species, a single electron pair is shared between two bonded atoms. These bonds are called **single bonds**. There is one single bond in the $\text{OH}^-$ ion, two in the $\text{H}_2\text{O}$ molecule, three in $\text{NH}_3$, and four in $\text{NH}_4^+$. There are three unshared pairs in the hydroxide ion, two in the water molecule, one in the ammonia molecule, and none in the ammonium ion.

   Bonded atoms can share more than one electron pair. A **double bond** occurs when bonded atoms share two electron pairs; in a **triple bond**, three pairs of electrons are shared. In ethylene ($\text{C}_2\text{H}_4$) and acetylene ($\text{C}_2\text{H}_2$), the carbon atoms are linked by a double bond and triple bond, respectively. Using two parallel lines to represent a double bond and three for a triple bond, we write the structures of these molecules as

   ![Double and Triple Bonds](image)

   Note that each carbon is surrounded by eight valence electrons and each hydrogen by two.

   These examples illustrate the principle that atoms in covalently bonded species tend to have noble-gas electronic structures. This generalization is often referred to as the **octet rule**. Nonmetals, except for hydrogen, achieve a noble-gas structure by sharing in an **octet** of electrons (eight). Hydrogen atoms, in molecules or polyatomic ions, are surrounded by a **duet** of electrons (two).

   ![Octet Rule](image)
Writing Lewis Structures

For very simple species, Lewis structures can often be written by inspection. Usually, though, you will save time by following these steps:

1. **Count the number of valence electrons.** For a molecule, simply sum up the valence electrons of the atoms present. For a polyatomic anion, one electron is added for each unit of negative charge. For a polyatomic cation, a number of electrons equal to the positive charge must be subtracted.

2. **Draw a skeleton structure for the species, joining atoms by single bonds.** In some cases, only one arrangement of atoms is possible; in others, there are two or more alternative structures. Most of the molecules and polyatomic ions dealt with in this chapter consist of a central atom bonded to two or more terminal atoms, located at the outer edges of the molecule or ion. For such species (e.g., \( \text{NH}_4^+ \), \( \text{SO}_2 \), \( \text{CCl}_4 \)), it is relatively easy to derive the skeleton structure. The central atom is usually the one written first in the formula (\( N \) in \( \text{NH}_4^+ \), \( S \) in \( \text{SO}_2 \), \( C \) in \( \text{CCl}_4 \)); put this in the center of the molecule or ion. Terminal atoms are most often hydrogen, oxygen, or a halogen; bond these atoms to the central atom.

3. **Determine the number of valence electrons still available for distribution.** To do this, deduct two valence electrons for each single bond written in step 2.

4. **Determine the number of valence electrons required to fill out an octet for each atom** (except H), in the skeleton. Remember that shared electrons are counted for both atoms.
   - (a) If the number of electrons available (step 3) is equal to the number required (step 4), distribute the available electrons as unshared pairs, satisfying the octet rule for each atom.
   - (b) If the number of electrons available (step 3) is less than the number required (step 4), the skeleton structure must be modified by changing single to multiple bonds. If you are two electrons short, convert a single bond to a double bond; if there is a deficiency of four electrons, convert a single bond to a triple bond (or two single bonds to double bonds). Multiple bond formation is pretty much limited to the four atoms: C, N, O, and S. Hydrogen and halogen atoms never form double bonds.

The application of these steps and some further guiding principles are shown in Examples 7.1 and 7.2.

**EXAMPLE 7.1** Draw Lewis structures of

(a) the hypochlorite ion, \( \text{OCl}^- \)  
(b) ethane, \( \text{C}_2\text{H}_6 \)

**Strategy** Follow the steps described above. For the \( \text{OCl}^- \) ion, only one skeleton is possible. For ethane keep in mind that the carbon atom ordinarily forms four bonds. Hydrogen must be a terminal atom because it forms only one bond.

**Solution**

(a) (1) The number of valence electrons is 6 (from O) + 7 (from Cl) + 1 (from the −1 charge) = 14.
   (2) The skeleton structure is \( [\text{O}—\text{Cl}]^- \).
   (3) The number of electrons available for distribution is 14 (originally) − 2 (used in skeleton) = 12.
   (4) The number of electrons required to give each atom an octet is 6 (for O) + 6 (for Cl) = 12.

The number of available electrons is the same as the number required. This skeleton structure is correct; there are no multiple bonds. The Lewis structure is

\[ [\text{O}—\text{Cl}]^- \]
(b) (1) the number of valence electrons is 8 (from the two carbon atoms) + 6 (from the six hydrogen atoms) for a total of 14.
(2) Because carbon forms four bonds and hydrogen must be a terminal atom, the only reasonable skeleton is

(3) The skeleton contains seven single bonds, using up $7 \times 2e^- = 14e^-$. This is exactly the number available, as shown in (1). It follows that the skeleton is also the Lewis structure:

There are no unshared electron pairs.

**Reality Check** Whenever you write a Lewis structure, check to see if it follows the octet rule. The structures written for $\text{OCl}^-$ and $\text{C}_2\text{H}_6$ do just that; each atom except H is surrounded by eight electrons.

---

**EXAMPLE 7.2** Draw Lewis structures for
(a) $\text{SO}_2$  (b) $\text{N}_2$

**Strategy** Follow the four steps for writing Lewis structures.

**Solution**
(a) (1) There are 18 valence electrons. Both sulfur (two atoms) and oxygen (one atom) are in Group 16; $3 \times 6 = 18$.
(2) The skeleton structure, with sulfur as the central atom, is

The two single bonds account for four electrons.
(3) There are $18 - 4 = 14$ electrons available for distribution.
(4) Sixteen electrons are required to give each atom an octet (four for S and six for each O). There is a deficiency of two electrons. This means that a single bond in the skeleton must be converted to a double bond. The Lewis structure of $\text{SO}_2$ is

(b) (1) There are ten valence electrons; nitrogen is in Group 15.
(2) The skeleton structure is

(3) There are $10 - 2 = 8$ electrons available for distribution.
(4) Each N needs six electrons for an octet, so 12 electrons are needed. This means that there is a deficiency of $12 - 8 = 4$ electrons. Convert the single bond between the two N atoms to a triple bond. The Lewis structure is

**Resonance Forms**

In certain cases, the Lewis structure does not adequately describe the properties of the ion or molecule that it represents. Consider, for example, the $\text{SO}_2$ structure derived in Example 7.2. This structure implies that there are two different kinds of
sulfur-to-oxygen bonds in SO₂. One of these appears to be a single bond, the other a double bond. Yet experiment shows that there is only one kind of bond in the molecule.

One way to explain this situation is to assume that each of the bonds in SO₂ is intermediate between a single and a double bond. To express this concept, two structures, separated by a double-headed arrow, are written

\[
\begin{align*}
\text{O} & \text{S} \quad \text{O} \\
\text{O} & \text{S} \quad \text{O}
\end{align*}
\]

with the understanding that the true structure is intermediate between them. These are referred to as resonance forms. The concept of resonance is invoked whenever a single Lewis structure does not adequately reflect the properties of a substance.

Another species for which it is necessary to invoke the idea of resonance is the nitrate ion. Here three equivalent structures can be written

\[
\begin{align*}
\left[ \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}
\end{array} \right] & \quad \left[ \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}
\end{array} \right]^- & \quad \left[ \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}
\end{array} \right]^- \\
\text{N} & \quad \text{N} & \quad \text{N}
\end{align*}
\]

to explain the experimental observation that the three nitrogen-to-oxygen bonds in the NO₃⁻ ion are identical in all respects.

Resonance can also occur with many organic molecules, including benzene, C₆H₆, which is known to have a hexagonal ring structure. Benzene can be considered a resonance hybrid of the two forms

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

These structures are commonly abbreviated as

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

with the understanding that, at each corner of the hexagon, a carbon is attached to a hydrogen atom.

We will encounter other examples of molecules and ions whose properties can be interpreted in terms of resonance. In all such species,

1. Resonance forms do not imply different kinds of molecules with electrons shifting eternally between them. There is only one type of SO₂ molecule; its structure is intermediate between those of the two resonance forms drawn for sulfur dioxide.

2. Resonance can be anticipated when it is possible to write two or more Lewis structures that are about equally plausible. In the case of the nitrate ion, the three structures we have written are equivalent. One could, in principle, write many other structures, but none of them would put eight electrons around each atom.

3. Resonance forms differ only in the distribution of electrons, not in the arrangement of atoms. The molecule

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

is not a resonance structure of benzene, even though it has the same molecular formula, C₆H₆. Indeed, it is an entirely different substance with different chemical and physical properties.
EXAMPLE 7.3  Write two resonance structures for the NO$_2^-$ ion.

**Strategy**  Write a Lewis structure for the NO$_2^-$ ion, following the usual steps. Then write the other resonance form by changing the position of the multiple bond. Do not change the skeleton structure.

**Solution**  The Lewis structures of the two resonance forms are

\[
\begin{array}{c}
\text{NO}_2^-
\end{array}
\]

---

**Formal Charge**

Often it is possible to write two different Lewis structures for a molecule differing in the arrangement of atoms, that is,

\[
A-B-A \quad \text{or} \quad A-A-B
\]

Sometimes both structures represent real compounds that are isomers of each other. More often, only one structure exists in nature. For example, methyl alcohol (CH$_4$O) has the structure

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

In contrast, the structure

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

does not correspond to any real compound even though it obeys the octet rule.

There are several ways to choose the more plausible of two structures differing in their arrangement of atoms. As pointed out in Example 7.1, the fact that carbon almost always forms four bonds leads to the correct structure for ethane. Another approach involves a concept called **formal charge**, which can be applied to any atom within a Lewis structure. The formal charge is the difference between the number of valence electrons in the free atom and the number assigned to that atom in the Lewis structure. The assigned electrons include—

- all the unshared electrons owned by that atom.
- one half of the bonding electrons shared by that atom.

This definition of formal charge, $C_f$, leads to the following equation

\[
C_f = X - (Y + Z/2)
\]

where $X$ = the number of valence $e^-$ in the free atom, which is equal to the last digit of the group number in the periodic table;

$Y$ = the number of unshared $e^-$ owned by the atom in the Lewis structure;

$Z$ = the number of bonding $e^-$ shared by the atom in the Lewis structure.

To show how this works, let’s calculate the formal charges of carbon and oxygen in the two structures written above for methyl alcohol:

1. \[
\text{H} - \text{C} - \text{O} - \text{H}
\]
2. \[
\text{H} - \text{C} - \text{O} - \text{H}
\]
Ordinarily, the more likely Lewis structure is the one in which—

- the formal charges are as close to zero as possible.
- any negative formal charge is located on the most strongly electronegative atom.

Applying these rules, we can see that structure (1) for methyl alcohol is preferred over structure (2). In (1), both carbon and oxygen have formal charges of zero. In (2), a negative charge is assigned to carbon, which is actually less electronegative than oxygen (2.5 versus 3.5).

The concept of formal charge has a much wider applicability than this short discussion might imply. In particular, it can be used to predict situations in which conventional Lewis structures, written in accordance with the octet rule, may be incorrect (Table 7.2).

**Exceptions to the Octet Rule: Electron-Deficient Molecules**

Although most of the molecules and polyatomic ions referred to in general chemistry follow the octet rule, there are some familiar species that do not. Among these are molecules containing an odd number of valence electrons. Nitric oxide, NO, and nitrogen dioxide, NO₂, fall in this category:

\[
\text{NO} \quad \text{no. of valence electrons} = 5 + 6 = 11
\]

\[
\text{NO}_2 \quad \text{no. of valence electrons} = 5 + 6(2) = 17
\]

For such odd electron species (sometimes called free radicals) it is impossible to write Lewis structures in which each atom obeys the octet rule. In the NO molecule, the unpaired electron is put on the nitrogen atom, giving both atoms a formal charge of zero:

\[\cdot\text{N}\equiv\text{O}\]

In NO₂, the best structure one can write again puts the unpaired electron on the nitrogen atom:

Elementary oxygen, like NO and NO₂, is paramagnetic (Figure 7.3). Experimental evidence suggests that the O₂ molecule contains two unpaired electrons and a double bond. It is impossible to write a conventional Lewis structure for O₂ that has these two characteristics. A more sophisticated model of bonding, using molecular orbitals (Appendix 5), is required to explain the properties of oxygen.

There are a few species in which the central atom violates the octet rule in the sense that it is surrounded by two or three electron pairs rather than four. Examples include the fluorides of beryllium and boron, BeF₂ and BF₃. Although one could...
write multiple bonded structures for these molecules in accordance with the octet rule (Table 7.2), experimental evidence suggests the structures

\[
\begin{align*}
\text{F} & \text{Be} \text{F} \quad \text{and} \\
\text{F} & \text{B} \text{F} \\
\end{align*}
\]

in which the central atom is surrounded by four and six valence electrons, respectively, rather than eight. Another familiar substance in which boron is surrounded by only three pairs of electrons rather than four is boric acid, \( \text{H}_3\text{BO}_3 \), used as an insecticide and fungicide.

\[
\begin{align*}
\text{H} & - \text{O} - \text{B} - \text{O} - \text{H} \\
\text{H} & \\
\end{align*}
\]

Exceptions to the Octet Rule: Expanded Octets

The largest class of molecules to violate the octet rule consists of species in which the central atom is surrounded by more than four pairs of valence electrons. Typical molecules of this type are phosphorus pentachloride, \( \text{PCl}_5 \), and sulfur hexafluoride, \( \text{SF}_6 \). The Lewis structures of these molecules are

\[
\begin{align*}
\text{Cl} & \text{Cl} \text{Cl} \text{Cl} \text{Cl} \\
\text{P} & \\
\end{align*}
\]

\[
\begin{align*}
\text{F} & \text{F} \text{F} \text{F} \\
\text{S} & \text{F} \text{F} \\
\end{align*}
\]

As you can see, the central atoms in these molecules have expanded octets. In \( \text{PCl}_5 \), the phosphorus atom is surrounded by 10 valence electrons (5 shared pairs); in \( \text{SF}_6 \), there are 12 valence electrons (6 shared pairs) around the sulfur atom.

In molecules of this type, the terminal atoms are most often halogens (F, Cl, Br, I); in a few molecules, oxygen is a terminal atom. The central atom is a nonmetal in the third, fourth, or fifth period of the periodic table. Most frequently, it is one of the following elements:

<table>
<thead>
<tr>
<th>Group 15</th>
<th>Group 16</th>
<th>Group 17</th>
<th>Group 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>3rd period</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td>4th period</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td>5th period</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
</tr>
</tbody>
</table>
All these atoms have d orbitals available for bonding (3d, 4d, 5d). These are the orbitals in which the extra pairs of electrons are located in such species as PCl$_5$ and SF$_6$. Because there is no 2d sublevel, C, N, and O never form expanded octets.

Sometimes, as with PCl$_5$ and SF$_6$, it is clear from the formula that the central atom has an expanded octet. Often, however, it is by no means obvious that this is the case. At first glance, formulas such as ClF$_3$ or XeF$_4$ look completely straightforward. However, when you try to draw the Lewis structure it becomes clear that an expanded octet is involved. The number of electrons available after the skeleton is drawn is greater than the number required to give each atom an octet. When that happens, distribute the extra electrons (two or four) around the central atom as unshared pairs.
EXAMPLE 7.4 Draw the Lewis structure of XeF₄.

Strategy Follow the usual four-step sequence. If there is an electron surplus, add the extra electrons to the central xenon atom as unshared pairs.

Solution
(1) The number of valence electrons is 8 (from Xe) + 28 (from four F atoms) = 36.
(2) The skeleton is

\[
\text{F} \quad \text{F} - \text{Xe} - \text{F} \\
\text{F}
\]

(3) The number of electrons available for distribution is 36 - 8 = 28.
(4) Each fluorine atom needs six electrons to complete its octet; the number of electrons required = 4(6) = 24.

There is a surplus of electrons; 28 are available and only 24 are required to fill out octets. The four extra electrons are added to the central Xe atom. The Lewis structure for XeF₄ is

\[
\text{F} \quad \text{F} \\
\text{F} \quad \text{Xe} \quad \text{F} \\
\text{F}
\]

In this molecule there are six pairs of electrons around the xenon atom.

7.2 Molecular Geometry

The geometry of a diatomic molecule such as Cl₂ or HCl can be described very simply. Because two points define a straight line, the molecule must be linear.

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

With molecules containing three or more atoms, the geometry is not so obvious. Here, the angles between bonds, called bond angles, must be considered. For example, a molecule of the type YX₂, where Y represents the central atom and X an atom bonded to it, can be—

- linear, with a bond angle of 180°: \( \text{X} - \text{Y} - \text{X} \)
- bent, with a bond angle less than 180°: \( \text{X} - \text{Y} - \text{X} \)

The major features of molecular geometry can be predicted on the basis of a quite simple principle—electron-pair repulsion. This principle is the essence of the valence-shell electron-pair repulsion (VSEPR) model, first suggested by N. V. Sidgwick and H. M. Powell in 1940. It was developed and expanded later by R. J. Gillespie and R. S. Nyholm. According to the VSEPR model, the valence electron pairs surrounding an atom repel one another. Consequently, the orbitals containing those electron pairs are oriented to be as far apart as possible.

In this section we apply this model to predict the geometry of some rather simple molecules and polyatomic ions. In all these species, a central atom is surrounded by from two to six pairs of electrons.

Ideal Geometries with Two to Six Electron Pairs on the Central Atom

We begin by considering species in which a central atom, A, is surrounded by from two to six electron pairs, all of which are used to form single bonds with terminal atoms, X. These species have the general formulas AX₂, AX₃, \ldots, AX₆. It is understood that there are no unshared pairs around atom A.