

Richard F. Daley and Sally J. Daley
www.ochem4free.com

Organic Chemistry

Chapter 1

Atoms, Orbitals, and Bonds

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Chapter 1

Atoms, Orbitals, and Bonds

Chapter Outline

- 1.1 The Periodic Table**
A review of the periodic table
- 1.2 Atomic Structure**
Subatomic particles and isotopes
- 1.3 Energy Levels and Atomic Orbitals**
A review of the energy levels and formation of atomic orbitals
- 1.4 How Electrons Fill Orbitals**
The Pauli Exclusion principle and Aufbau principle
- 1.5 Bond Formation**
An introduction to the various types of bonds
- 1.6 Molecular Orbitals**
Formation of molecular orbitals from the *1s* atomic orbitals of hydrogen
- 1.7 Orbital Hybridization**
The VSEPR model and the three-dimensional geometry of molecules
- 1.8 Multiple Bonding**
The formation of more than one molecular orbital between a pair of atoms
- 1.9 Drawing Lewis Structures**
Drawing structures showing the arrangement of atoms, bonds, and nonbonding pairs of electrons
- 1.10 Polar Covalent Bonds**
Polarity of bonds and bond dipoles
- 1.11 Inductive Effects on Bond Polarity**
An introduction to how inductive and field effects affect bond polarity
- 1.12 Formal Charges**
Finding the atom or atoms in a molecule that bear a charge
- 1.13 Resonance**
An introduction to resonance

Objectives

- ✓ Know how to use the periodic table
- ✓ Understand atomic structure of an atom including its mass number, isotopes, and orbitals
- ✓ Know how atomic orbitals overlap to form molecular orbitals
- ✓ Understand orbital hybridization
- ✓ Using the VSEPR model, predict the geometry of molecules
- ✓ Understand the formation of π molecular orbitals
- ✓ Know how to draw Lewis structures
- ✓ Predict the direction and approximate strength of a bond dipole
- ✓ Using a Lewis structure, find any atom or atoms in a molecule that has a formal charge
- ✓ Understand how to draw resonance structures

Concern for man and his fate must always form the chief interest of all technical endeavors. Never forget this in the midst of your diagrams and equations.

—Albert Einstein

To comprehend bonding and molecular geometry in organic molecules, you must understand the electron configuration of individual atoms. This configuration includes the distribution of electrons into different energy levels and the arrangement of electrons into atomic orbitals. Also, you must understand the rearrangement of the atomic orbitals into hybrid orbitals. Such an understanding is important, because hybrid orbitals usually acquire a structure different from that of simple atomic orbitals.

When an atomic orbital of one atom combines with an atomic orbital of another atom, they form a new orbital that bonds the two atoms into a molecule. Chemists call this new orbital a molecular orbital. A molecular orbital involves either the sharing of two electrons between two atoms or the transfer of one electron from one atom to another. You also need to know what factors affect the electron distribution in molecular orbitals to create polar bonds. These

factors include the electronegativity differences between the atoms involved in the bond and the effects of adjacent bonds.

1.1 The Periodic Table

The periodic table of the elements is a helpful tool for studying the characteristics of the elements and for comparing their similarities and differences. By looking at an element's position on the periodic table you can ascertain its electron configuration and make some intelligent predictions about its chemical properties. For example, you can determine such things as an atom's reactivity and its acidity or basicity relative to the other elements.

Dmitrii Mendeleev described the first periodic table at a meeting of the Russian Chemical Society in March 1869. He arranged the periodic table by empirically systematizing the elements known at that time according to their periodic relationships. He listed the elements with similar chemical properties in families, then arranged the families into groups, or periods, based on atomic weight. Mendeleev's periodic table contained numerous gaps. By considering the surrounding elements, chemists predicted specific elements that would fit into the gaps. They searched for and discovered many of these predicted elements, which led to the modern periodic table. A portion of the modern periodic table is shown in Figure 1.1.

The modern periodic table consists of 90 naturally occurring elements and a growing list of more than 20 synthetic elements. The elements in the vertical groups, or families, have similar atomic structures and chemical reactions. The elements in the horizontal groups, or periods, increase in atomic number from left to right across the periodic table.

Of all the elements the one of greatest importance to organic chemists is carbon (C). It is so important that many chemists define organic chemistry as the study of carbon and its interactions with other elements. Carbon forms compounds with nearly all the other elements, but this text considers only the elements of most concern to organic chemists. These elements are mainly hydrogen (H), nitrogen (N), oxygen (O), chlorine (Cl), bromine (Br), and iodine (I). Lithium (Li), boron (B), fluorine (F), magnesium (Mg), phosphorus (P), silicon (Si), and sulfur (S) are also significant.

1 H Hydrogen 1.01							2 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01	5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.00	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31	13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95

Figure 1.1. Abbreviated periodic table with each element's atomic number, symbol, name, and atomic weight.

1.2 Atomic Structure

To understand the elements of the periodic table, you must consider the subatomic particles that make up atoms. Atoms consist of three types of subatomic particles. These are **protons**, **neutrons**, and **electrons**. The protons and neutrons are located in the nucleus of the atom. The electrons fill "clouds" in the space surrounding the nucleus. Protons are positively charged, while electrons have a negative charge that is equal but opposite to the charge on the protons. As the name implies, neutrons are neutral. They have neither a positive nor a negative charge.

The number of protons in an atom identifies which element that atom is and gives that element its atomic number. The number of protons in the nucleus and the corresponding number of electrons around the nucleus controls each element's chemical properties. However, the electrons are the active portion of an atom when it chemically bonds with another atom. The electrons determine the structure of the newly formed molecule. Thus, of the three types of subatomic particles, electrons are the most important to your study of organic chemistry.

Each element has more than one energy level. An element's lowest energy level is its **ground state**. In each element, the ground state of the atom contains a fixed and equal number of protons and electrons.

Protons, neutrons, and electrons are subatomic particles that make up the majority of atoms. Protons are positively charged, neutrons have no charge, and electrons are negatively charged.

The ground state of an element is its lowest energy level.

Isotopes are atoms with the same number of protons but with a different number of neutrons.

Mass number is the total number of neutrons and protons in the nucleus.

Many chemists refer to ^2H as deuterium and ^3H as tritium.

The number of protons in the atoms that make up a sample of a particular element is always the same, but the number of neutrons can vary. Each group of atoms of an element with the same number of protons is an **isotope** of that element. For example, hydrogen has three isotopes. The most common isotope of hydrogen contains a single proton, but no neutrons. This isotope has a **mass number** of 1. The atomic symbol for hydrogen is H, so the symbol for hydrogen's most common isotope is ^1H (read as "hydrogen one"). A very small portion of hydrogen, less than 0.1%, has one neutron and one proton in the nucleus. Its mass number is 2, and its symbol is ^2H . A third isotope of hydrogen has two neutrons and one proton. Its mass number is 3, and its symbol is ^3H . The ^3H isotope is radioactive with a half-life of 12.26 years. Because the ^3H isotope is radioactive, chemists use it to label molecules to study their characteristics or to follow their reactions with other molecules.

1.3 Energy Levels and Atomic Orbitals

An atomic orbital is the region of space where the electrons of an atom or molecule are found.

Electron density is a measure of the probability of finding an electron in an orbital.

The wave function is the mathematical description of the volume of space occupied by an electron having a certain amount of energy.

A node in an orbital is the place where a crest and a trough meet. At that point ψ is equal to 0 because it is neither positive nor negative.

In the early 1900s Niels Bohr developed the theory of an atom with a central nucleus around which one or more electrons revolved. From his model, chemists came to view **atomic orbitals** as specific paths on which the electrons travel about the nucleus. A common analogy is that of a miniature solar system with the electron "planets" in orbit around a nuclear "sun." Using quantum mechanics, Erwin Schrödinger showed this picture to be simplistic and inaccurate. In Schrödinger's model the orbitals of electrons are not like miniature solar systems, but are regions of **electron density** with the location and route of the electron described as probabilities.

Quantum mechanics describes orbitals by the mathematical **wave function** ψ (spelled psi and pronounced "sigh"). The wave function is useful here because orbitals have all the properties associated with waves on a body of water or sound waves. They have a crest and a trough (that is, they can be either positive or negative), and they have a **node**. There is zero probability of finding an electron at the node.

Use of Plus and Minus Signs

Do not confuse these positive and negative signs with ionic charges. They are the mathematical signs of the wave function. You will see their importance later in this chapter when you study bonding.

Now, apply these principles to a review of the energy levels and atomic orbitals of a simple atom. As you study organic chemistry, there are three energy levels, or shells, and five sets of atomic orbitals

that are the most important for you to understand. These are the first, second, and third levels and the $1s$, $2s$, $2p$, $3s$, and $3p$ orbitals.

The $1s$ orbital, like all s orbitals, is spherically symmetrical. You can picture it shaped like a fuzzy hollow ball with the nucleus at the center. As you see in Figure 1.2, the probability of finding an electron decreases as the distance from the nucleus increases. The probability becomes zero at an infinite distance from the nucleus. The probability of finding an electron in an orbital at some distance from the nucleus is often called its electron density. The $1s$ orbital contains no nodes. Because the $1s$ orbital is closest to the nucleus and has no nodes, it has the lowest energy of all the atomic orbitals. Figure 1.3 is a representation of the $1s$ orbital.

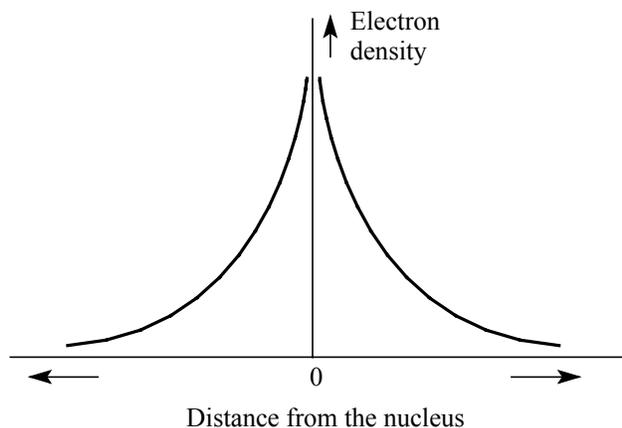


Figure 1.2. Graphical representation of the $1s$ atomic orbital.

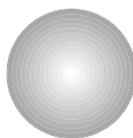


Figure 1.3. Representation of the $1s$ orbital.

The second level, or shell, of electrons contains two sets of orbitals: the $2s$ and $2p$ orbitals. The $2s$ orbital, like the $1s$, is spherically symmetrical. However, its graphical representation does not have the simple exponential function shape of the $1s$ orbital. While some electron density is found close to the nucleus, most is farther from the nucleus past a node where there is no electron density. Figure 1.4 is a graphical representation of the $2s$ orbital and Figure 1.5 is a cross section through the $2s$ orbital.

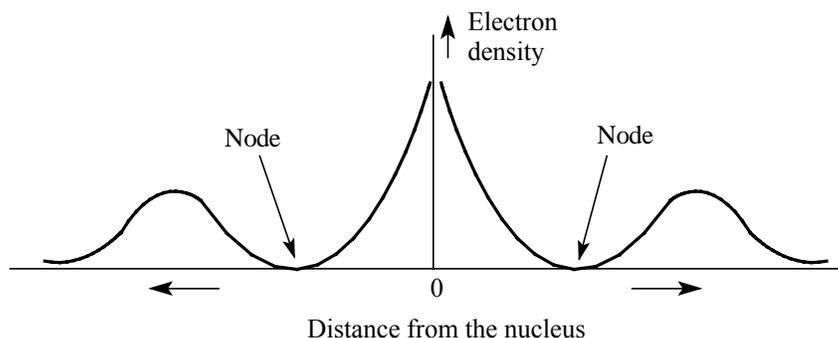


Figure 1.4. Graphical representation of the 2s atomic orbital. The 2s atomic orbital has a small region of electron density surrounding the nucleus, but most of the electron density is farther from the nucleus, beyond a node.

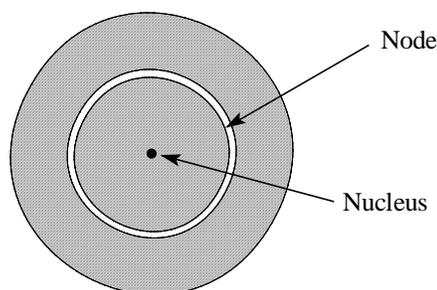


Figure 1.5. A cross section of the 2s atomic orbital.

The three *p* orbitals in the second shell of electrons are totally different from the 1s and 2s orbitals. Each *p* orbital consists of a “teardrop” shape on either side of a **nodal plane** that runs through the center of the nucleus, as shown in Figure 1.6. The three 2*p* orbitals are oriented 90° from each other in the three spatial directions and have identical energies and shapes. Chemists call such orbitals **degenerate orbitals**. Figure 1.7 shows the spatial relationship of the three degenerate 2*p* orbitals. Figure 1.8 plots the electron density versus the distance from the nucleus for a *p* orbital. Because the electrons in the three 2*p* orbitals are farther from the nucleus than those in the 2s orbital, they are at a higher energy level.

A nodal plane is a plane between lobes of an orbital that has zero electron density.

Degenerate orbitals are two or more orbitals that have identical energies.

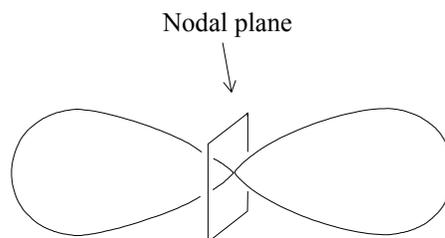


Figure 1.6. Representation of one of the $2p$ orbitals.

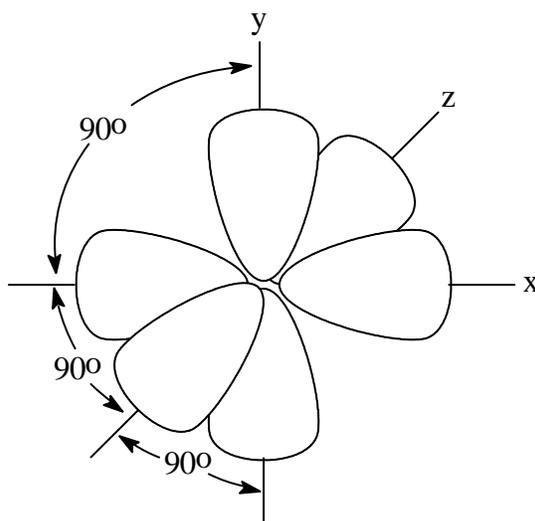


Figure 1.7. The three $2p$ orbitals are at 90° angles to one another. Here each is labeled with its orientation to the x, y, or z axis.

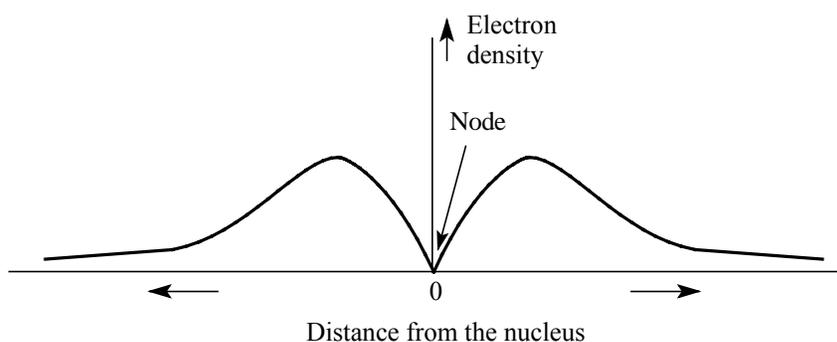


Figure 1.8. Graphical representation of a p orbital, showing that the node is at the nucleus.

The third energy level consists of nine orbitals. However, you only need to be familiar with the shapes of the s and p orbitals, because the orbitals beyond the $3p$ orbital are of less importance in the structure of organic molecules discussed in this book. The $3s$ and $3p$

orbitals resemble the $2s$ and $2p$ orbitals, respectively. Both third-level orbitals are larger than the second-level orbitals. The $3s$ orbital also adds another node, giving it a higher energy than the second-level orbitals.

Usually, the more nodes a wave function has the higher is its energy. In atoms with a number of electrons the energies of the atomic orbitals increases in the order of $1s < 2s < 2p < 3s < 3p$. Section 1.4 looks at how electrons fill these atomic orbitals.

1.4 How Electrons Fill the Orbitals

The Pauli Exclusion Principle states that an orbital, either atomic or molecular, can hold only two electrons.

The Aufbau principle states that each electron added to an atom must be placed in the lowest energy unfilled orbital.

According to the **Pauli Exclusion Principle**, each orbital contains a maximum of two electrons. These two electrons must have opposite values for the spin, which is generally indicated by showing the electrons as arrows pointing up (\uparrow) or down (\downarrow). When filled, the first shell (one $1s$ orbital) holds two electrons, the second shell (one $2s$ and three $2p$ orbitals) holds eight electrons, and the third shell (one $3s$, three $3p$ orbitals, and five $3d$ orbitals) holds eighteen electrons.

The **Aufbau Principle** (“aufbau” means “building up” in German) explains the order in which the electrons fill the various orbitals in an atom. Filling begins with the orbitals in the lowest-energy, or most stable, shells and continues through the higher-energy shells, until the appropriate number of orbitals is filled for each atom. Thus, the $1s$ orbital fills first, then the $2s$, followed by the $2p$ and the $3s$ orbitals. Figure 1.9 shows the energy relationships among the first three levels of orbitals.

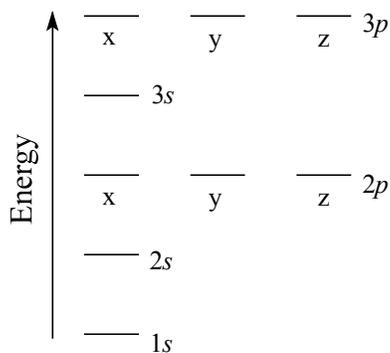


Figure 1.9. The relationship among the first three energy levels of atomic orbitals.

Hund's rule for degenerate orbitals states that each orbital must have one electron before any of them gets a second electron.

The three degenerate $2p$ orbitals require special consideration. **Hund's rule** states that each degenerate orbital, $2p_x$, $2p_y$, and $2p_z$, must first receive one electron before any of the orbitals can receive a second electron. For example, carbon has a total of six electrons. According to the Aufbau Principle, the $1s$, $2s$, and $2p$ orbitals contain

two electrons each. However, according to Hund's Rule, the electrons in the $2p$ orbitals must go into two separate orbitals—arbitrarily designated as $2p_x$ and $2p_y$. Figure 1.10 illustrates carbon's electron configuration.

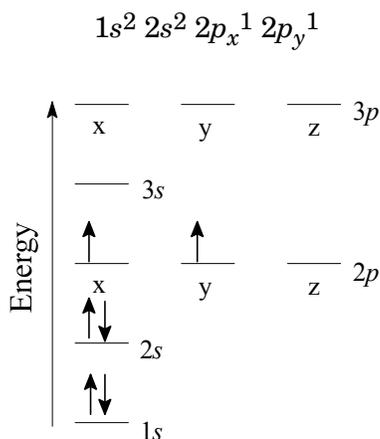


Figure 1.10. Hund's Rule applied to the filling of the atomic orbitals of carbon.

Exercise 1.1

Write a complete electron configuration for each of the eight third-row elements, Na through Ar.

This process of filling successive atomic orbital levels with electrons can be used to construct the entire periodic table. But the number of electrons in the outer shell determines the bonding that occurs between atoms. Section 1.5 looks at bonding of atoms.

1.5 Bond Formation

Bonding is the joining of at least two atoms to form a molecule. The electrons in the **valence shell** are the active portion of an atom during bonding. In 1913, G. N. Lewis proposed several theories about how atoms combine to form molecules. The essence of his theories is that an atom with a filled outer shell of electrons is more stable than an atom with a partially filled outer shell. Therefore, bonds form between atoms such that each atom attains a filled outer shell. With a filled outer shell, an atom has the electron configuration of one of the noble gases—helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). This tendency of atoms to have a full outer shell is called the **Octet Rule**.

The valence shell of an atom is the highest energy shell that contains electrons.

The Octet Rule states that an atom forms bonds that allow it to have the outer shell equivalent to the nearest noble gas.

Noble Gases

All the noble gases, except for He, have eight electrons in their outer shell. Helium has only two. Most atoms that you will encounter in organic chemistry follow the Octet Rule; that is, they form bonds that give eight electrons in their outer shells. Hydrogen is an exception to the Octet Rule, because it can only bond with two electrons. Because the elements that form organic compounds are largely located in the second row of the periodic table, the electron configuration of their atoms usually becomes that of neon. Neon has eight electrons in its outer shell.

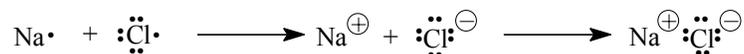
An ionic bond involves a transfer of electrons from one atom to another atom forming an electrostatic attraction between the atoms, or groups.

A covalent bond involves the sharing of electrons between two atoms to form a molecule.

Lewis structures are schematic representations of the electron configuration of atoms and molecules in which each dot represents one valence electron.

Atoms that bond to attain noble gas configurations do so by forming either **ionic**¹ or **covalent bonds**. Ionic bonding usually takes place between elements positioned on opposite sides of the periodic table because they either have only one or two electrons in their valence shell or need only one or two more electrons to fill their valence shell. Covalent bonding takes place more among the elements in the center of the periodic table, as these elements have too many electrons in their valence shells to readily transfer from one atom to another.

An example of ionic bonding occurs between sodium and chlorine. Sodium has one electron in its valence shell, and chlorine has seven in its valence shell. When they react, sodium transfers its one valence electron to the valence shell of chlorine; thus, giving both a noble gas configuration. Sodium attains the configuration of neon, and chlorine that of argon. Below is a representation of this reaction using **Lewis structures**.



By giving up its one valence electron, sodium becomes a positively charged ion. When chlorine accepts that electron, it becomes a negatively charged ion. An ion is an atom, or group of atoms, bearing a charge. Because they have opposite charges, Na^{\oplus} and Cl^{\ominus} attract each other; thus, forming an ionic bond. Such bonding is common with inorganic compounds, but seldom occurs in organic compounds.

A covalent bond involves the sharing of electrons between two atoms. For example, a hydrogen atom has a single unpaired electron.

¹Usually, the word “bond” refers to the overlap of orbitals and the electron sharing between two atoms to form a molecule. In the strictest sense, ionic bonding is an inaccurate term. A more accurate term is ionic interaction. An ionic interaction involves electrostatic interactions with little or no electron sharing—the atoms are held together by their charges. However, this book uses the term “ionic bonding,” because it allows for easier reading.

The noble gas configuration for hydrogen is that of helium, which has two electrons in the first shell (1s). When two hydrogen atoms form a bond, they share two electrons—one from each atom. Thus, both atoms, in effect, have a pair of electrons.



Covalent bonding is typically how organic compounds bond. The element of particular importance to organic chemists is carbon. In its **ground state** carbon has a total of four electrons in its valence shell (2s and 2p orbitals). The Octet Rule predicts that carbon will either give up or acquire four electrons in order to form stable compounds. Because of the great amount of energy required to transfer that many electrons, carbon forms covalent bonds by sharing its electrons.

A fundamental principle concerning electrons of atoms is that they reside in atomic orbitals. When atoms bond into molecules, **molecular orbitals** result. Molecular orbitals, regardless of the number of atoms involved, have many of the same properties of atomic orbitals. They fill with electrons beginning with the lowest energy levels, they have well-defined energy levels, and each orbital contains a maximum of two electrons. An additional characteristic of molecular orbitals is that each one may involve as few as two atoms or many atoms over a large part of the molecule.

1.6 Molecular Orbitals

When looking at the way atoms combine to form molecules, scientists use the **Linear Combination of Atomic Orbitals—Molecular Orbital** method (LCAO-MO) to describe both the shapes of the molecular orbitals and the distribution of the electron density within those orbitals. The mathematics of the LCAO-MO method is beyond the scope of this book, but the primary concepts are not. The LCAO-MO method simply states that the shape of a molecular orbital is derived from the shape of the atomic orbitals that overlap to form that molecular orbital.

As two atoms form a bond, they interact very much like waves on a lake. When two waves on a lake are traveling in the same direction and one overtakes the other, the amplitude of the new wave is greater than the amplitude of either of the two that created it. In contrast, when two waves are traveling in opposite directions, and they meet, as in the wakes of two boats, their amplitudes cancel each other. During bonding, atoms do the atomic equivalent—wave functions with the same sign overlap in an **in-phase overlap**, and wave functions of opposite signs overlap in an **out-of-phase overlap**.

The ground state of a particular atom is the lowest energy level for that atom.

A molecular orbital forms when two or more atomic orbitals overlap to form a bond.

The LCAO-MO method describes the shapes of molecular orbitals and is based on the atomic orbitals that form the molecular orbitals.

In-phase overlap is a constructive, or bonding, overlap of atomic orbitals.

Out-of-phase is a destructive, or antibonding, overlap of atomic orbitals.

In a bonding molecular orbital two or more in-phase orbitals overlap to form a bond.

With an in-phase overlap, the wave functions reinforce one another. This reinforcement increases the probability of finding the electrons in the region between the two nuclei. The molecular orbital that results from an in-phase overlap is a **bonding molecular orbital**. Figure 1.11 illustrates the formation of a bonding molecular orbital.



Figure 1.11. In-phase overlap of the 1s orbitals of two hydrogen atoms forming a bonding molecular orbital.

An antibonding molecular orbital results from the out-of-phase overlap of two or more atomic orbitals.

An out-of-phase overlap forms an **antibonding molecular orbital**. With an out-of-phase overlap, a node develops between the two nuclei. For each bonding molecular orbital that forms, an antibonding molecular orbital also forms. Figure 1.12 illustrates the formation of an antibonding molecular orbital.

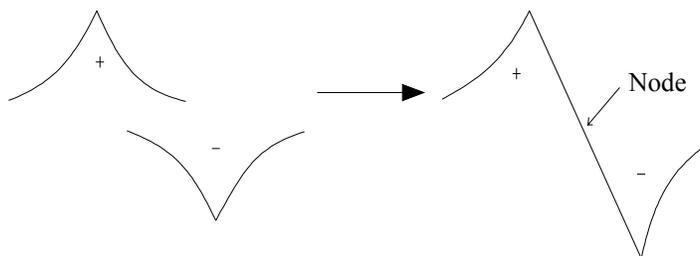


Figure 1.12. Out-of-phase overlap of the 1s orbitals of two hydrogen atoms forming an antibonding molecular orbital.

Usually, an antibonding molecular orbital contains no electrons because being occupied destabilizes the bond. However, in some systems the antibonding molecular orbitals are partially occupied. Generally, molecules at their lowest energy state have empty antibonding molecular orbitals. In most discussions of bonds, this book considers only the bonding and not the antibonding interaction.

To illustrate these concepts, examine the bond between two hydrogen atoms in a hydrogen molecule (H_2). The 1s atomic orbital of each hydrogen atom combines and generates the hydrogen—hydrogen molecular orbitals. Note in Figure 1.13 that a hydrogen molecule contains not one, but *two*, molecular orbitals.

According to the LCAO-MO method, whatever number of atomic orbitals combine to form molecular orbitals, the same number of molecular orbitals result. Therefore, orbitals are neither lost nor gained.

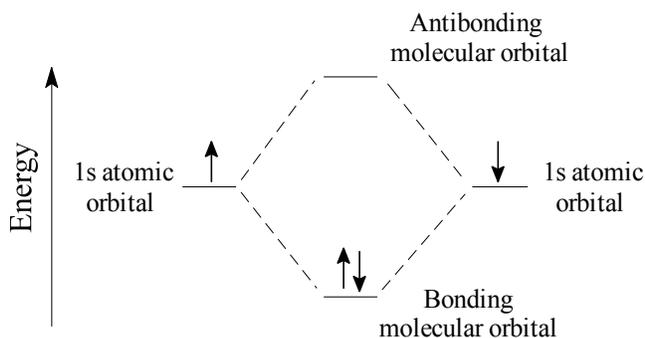


Figure 1.13. The two molecular orbitals of hydrogen generated by combining two 1s atomic orbitals. One of the molecular orbitals is bonding and lower in energy. The other is antibonding and higher in energy. The arrows represent the electrons involved in forming the bonding molecular orbital.

Why He₂ Does Not Form

A look at helium will help you see why antibonding molecular orbitals do not usually fill with electrons. Helium has a filled valence shell. In order for two helium atoms to bond, both the bonding and antibonding molecular orbitals would have to fill. This does not occur because there is no energy gain for He₂ as compared with He. Thus, He₂ does not form.

A bond possessing rotational symmetry has a circular cross section perpendicular to the bond.

Both the bonding and antibonding orbitals of hydrogen molecules have **rotational symmetry** about their internuclear axis. Chemists call orbitals with this type of symmetry σ (sigma) molecular orbitals. This symmetry is shown in Figure 1.14.

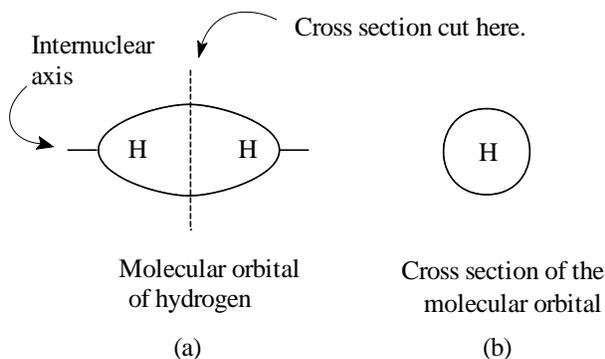


Figure 1.14. (a) A hydrogen molecule showing the σ molecular orbital. (b) A cross section of the σ molecular orbital perpendicular to the internuclear axis.

To differentiate the antibonding from the bonding orbital, chemists add an asterisk to the σ , giving σ^* (sigma star).

A σ molecular orbital results from overlap of atomic orbitals along the internuclear axis.

Electrons prefer to occupy the orbital with the lowest possible energy state. For example, consider the electrons in the hydrogen molecule. The 1s atomic orbitals of two hydrogen atoms overlap and form the **σ molecular orbital** of the H_2 molecule. The σ orbital is lower in energy than the 1s orbitals of the hydrogen atoms. The antibonding molecular orbital, the σ^* orbital, is higher in energy than either the 1s orbitals or the σ orbital. Because the σ orbital has the lowest energy, both electrons in the hydrogen molecule reside there.

Bond length is the minimum distance between two nuclei connected by a molecular orbital.

As two atoms move closer together, the energy between them at first decreases. At the point of minimum energy between the nuclei of the two atoms, the molecular orbital forms, and the system releases energy. The distance of minimum energy between the two nuclei is the **bond length**. If the nuclei continue getting closer, the energy increases. Figure 1.15 shows how the energy between two atoms decreases until the atoms reach their state of minimum energy. Once two nuclei are bonded, they require energy to move apart again.

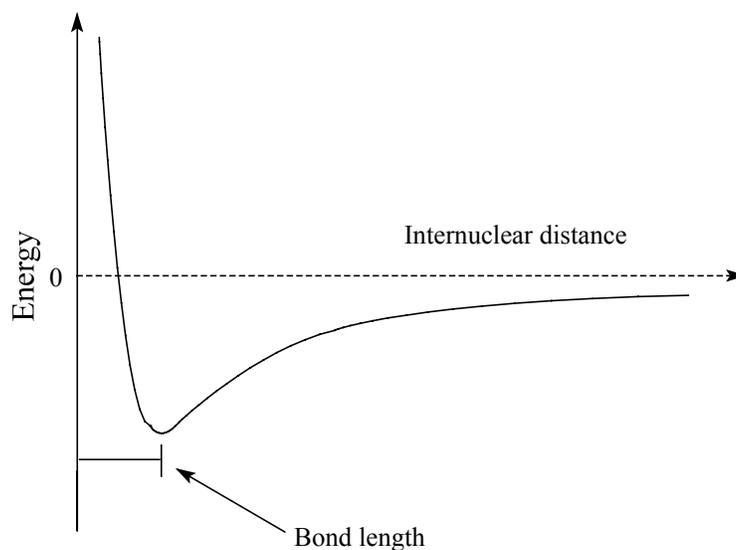


Figure 1.15. When two hydrogen atoms move into close proximity, they experience a change in energy. At the distance of the bond length, they achieve minimum energy. As the nuclei move apart, the energy of the interaction rapidly approaches zero, which it reaches at infinity.

Orbital overlap is how much an atomic orbital from one atom would extend over an atomic orbital from another atom, if the two atoms did not bond to form a molecular orbital.

For H_2 , the distance between the two nuclei (the bond length) is 74 pm. At distances greater than this, the bond weakens because of reduced **overlap** between the 1s orbitals. At distances less than 74 pm, the repulsion between the two positively charged hydrogen nuclei increases substantially.

Exercise 1.2

Describe how Figure 1.15 would change in appearance a) for a weaker bond than H₂ and b) for a stronger bond.

Figure 1.15 shows that energy is released during the formation of the bond in a hydrogen molecule. Conversely, breaking that bond to reform hydrogen atoms requires an input of energy because the energy level of the hydrogen molecule is lower than the energy level of the two hydrogen atoms. Before hydrogen can bond with another element, such as carbon, the hydrogen—hydrogen bond in the hydrogen molecule must be broken. The **bond dissociation energy** for hydrogen is 104 kcal/mole².

Chemists use the bond dissociation energies of different bond types as a measure of the reactivity of those bonds. The higher the amount of energy required to break a bond, the stronger the bond is. A stronger bond reacts less readily than a weaker bond. Table 1.1 shows some representative bond dissociation energies. These bond dissociation energies are for the **homolytic** bond dissociation process.

The bond dissociation energy is the amount of energy required to break a bond.

In a homolytic bond dissociation, a bond breaks and each of the two atoms leaves with one of the two electrons from the bond.

Bond	Dissociation Energy, kcal/mole	Bond	Dissociation Energy, kcal/mole
H—H	104	H—F	136
F—F	37	H—Cl	102
Cl—Cl	57	H—Br	87.5
Br—Br	46	H—I	71.3
I—I	36	CH ₃ —H	103
C—F	108	CH ₃ CH ₂ —H	98
C—Cl	81	(CH ₃) ₂ CH—H	94.5
C—Br	68	(CH ₃) ₃ C—H	91
C—I	55.5	C=C—H	102
C—O	90	C≡C—H	125
C=O	257	C—C	88
O—H	105	C=C	163
		C≡C	200

Table 1.1. Some representative bond dissociation energies.

1.7 Orbital Hybridization

² In your General Chemistry course, you learned to use energy units in kilojoules. Organic chemists have not universally adopted the kilojoule unit. Thus, we have chosen to use the kilocalorie energy unit.

Vitalism is discussed in Section 0.1, page 000.

The development of the modern theory of organic chemistry began in the middle of the nineteenth century. At that time, the concept that all organic compounds contained carbon started replacing the theory of vitalism. Essential to the growth of organic chemistry was the work that determined the atomic structure of the carbon atom and how it bonded with other atoms.

When chemists learned that carbon frequently bonds with four other atoms, they thought the resulting molecule was square planar. That is, they thought all five atoms resided in a square plane with carbon in the center and the other four elements at the four corners. The discovery of methylene chloride (CH_2Cl_2) forced them to reevaluate this theory. Chemists had expected to see two different structures, or **isomers**, for methylene chloride, but they found only one. Figure 1.16 shows the two possible square planar isomers of methylene chloride.

Molecules that are isomers have the same number of each type of atom, but they are arranged differently.

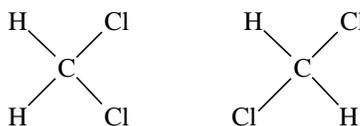


Figure 1.16. The two square planar isomers of methylene chloride.

Having only one structure meant the methylene chloride molecule was not square planar. In 1874, Jacobus H. van't Hoff and Joseph A. Le Bel proposed a three-dimensional tetrahedral structure for carbon compounds such as methylene chloride as shown in Figure 1.17. Initially, chemists scoffed at this theory. But gradually, through much discussion, they accepted it, even though no one proved it until the 1920s.

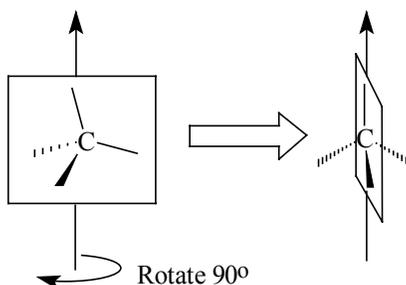


Figure 1.17. The tetrahedral structure of carbon. The wedge shaped line () indicates a bond projecting in front of the page. The dashed line () is a bond behind the page.

It was the development of the electron diffraction technique that allowed chemists to prove the tetrahedral structure of carbon. Electron diffraction measures the bond lengths and bond angles of compounds. As you may recall, bond length is the distance between two bonded nuclei. Bond angle, on the other hand, is the angle formed by the intersection of two covalent bonds at the atom common to them both. While using electron diffraction to study methane (CH_4), chemists discovered that the bond lengths and bond angles for all four C—H bond angles are identical. The bond angles measured 109.5° , instead of 90° , as was expected from the square planar theory. This measurement showed that methane was tetrahedral in shape. It also confirmed the tetrahedral shape suggested years before for methylene chloride. Figure 1.18 illustrates the actual structure of methylene chloride.

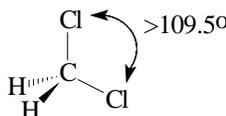


Figure 1.18. The actual structure of methylene chloride. Because the chlorines are larger than the hydrogens, they repel one another and the Cl—C—Cl bond angle is more than 109.5° .

Another problem challenging chemists at this time was how were carbon's electrons arranged? They knew that when an orbital contains only one electron, then bonding can occur with the electron in that orbital. The problem with carbon was that it had only two orbitals with one electron each, but yet carbon bonds with four atoms. The ground state of carbon has four valence electrons—two paired electrons and two unpaired electrons. These electrons are distributed among three different orbitals—two electrons in the $2s$ orbital and one electron each in the $2p_x$ and $2p_y$ orbitals. To resolve this problem, Linus Pauling pulled together all the ideas proposed by the various chemists and developed the concept of **orbital hybridization**. His concept of orbital hybridization also explained how carbon formed the measured bond angles of 109.5° rather than the expected 90° .

The theory of orbital hybridization allows the wave functions of two atomic orbitals in the valence shell of an atom to “mix” and form new orbitals called **hybrid orbitals**. This book looks at the mixing of the s and p orbitals of carbon. Hybrid orbitals have a blend of the properties, shapes, and energy levels of both orbitals. There are two important benefits of orbital hybridization. Hybridized atoms form more bonds than do unhybridized atoms. Plus, bonds formed from hybridized orbitals are stronger and more stable than bonds formed by unhybridized orbitals. The hybrid orbitals of carbon combine the

Orbital hybridization is a mathematical operation based on quantum mechanics that explains the geometry of a molecule.

Hybrid orbitals are the individual orbitals formed from hybridization.

strong electron attracting ability of the s orbital and more electron density along the internuclear axis characteristic of the p orbitals.

Visualizing Hybridization

Hybridization is a theoretical explanation of how carbon and similar atoms bond. Being able to visualize the process of hybridization will help you understand what happens to carbon when it bonds with other atoms. Remember, as you move through this process, that the orbitals are always there—even when they are not occupied by electrons. To begin, set aside the electrons and hybridize, or “mix,” the number of orbitals necessary to accomplish an octet; then distribute the electrons into the orbitals as needed for bonding. The rule of conservation of orbitals states that a molecule must have the same number of hybrid orbitals after hybridization and bonding as the atoms had before hybridization and bonding.

Not only does orbital hybridization enable carbon to bond to four other atoms, it also allows molecules like methane to obtain their tetrahedral shape. Because electron pairs strive to be as far apart from other electron pairs as possible, an atom bonded to four other identical atoms, as carbon is to the four hydrogens in methane, has bond angles of 109.5° . This arrangement places the four identical atoms, the hydrogens, toward the corners of a regular tetrahedron with the atom they are bonded to, the carbon, in the center. The bonding of carbon with four atoms that are not identical does change the angles somewhat, but the basic shape remains the same. The theory designed to explain the fact that electron pairs arrange themselves a maximum distance apart is called the **Valence Shell Electron Pair Repulsion (VSEPR) model**. VSEPR can be used to explain the shapes of the three hybridized orbitals.

The three types of orbital hybridization considered important in organic chemistry are called sp , sp^2 , and sp^3 . These labels tell the number and the names of the orbitals involved in the hybridization. In sp hybridization two orbitals are involved, one s and one p . In sp^2 hybridization three orbitals are involved, one s and two p orbitals. And in sp^3 hybridization four orbitals are involved, one s and three p orbitals. Because hybridization blends all the characteristics of the s and p orbitals, the name of the new orbital indicates what proportion of each orbital is like an s orbital and what portion is like a p orbital. Each sp hybridized orbital has an equal blend of the characteristics of both the s and p orbitals. With sp^2 hybridization, each hybrid orbital bears $1/3$ of the s orbital's characteristics and $2/3$ of the p orbital's characteristics. Likewise, each orbital of an sp^3 hybridization has $1/4$ of the characteristics of the s orbital and $3/4$ of the characteristics of the p orbitals.

The VSEPR model predicts the geometry of a molecule by arranging all orbitals at maximum distance from each other.

Another consideration with hybridization is the shape of the hybridized orbitals. The four hybrid sp^3 orbitals have a shape that is a combination of the s and p orbital shapes, as illustrated in Figure 1.19. Like the p orbitals, each sp^3 orbital has two lobes, but unlike the lobes of a p orbital, the two lobes are of unequal size. (The signs on the orbital lobes in Figure 1.19 and subsequent figures are the signs of the ψ wave function for those orbitals.) Therefore, for each orbital there is a greater electron density on one side of the nucleus than on the other. This unsymmetrical electron density allows for greater overlap—thus the formation of stronger bonds—than is possible with an unhybridized orbital. When the sp^3 orbitals participate in bond formation, it is the larger lobe that overlaps the orbital of the other atom. In the formation of methane, the overlap of the sp^3 orbital of carbon with the s orbital of hydrogen forms a σ bond very similar to the σ bond between two hydrogens. This type of bond is much more stable than that from the overlap of the p orbitals of an unhybridized carbon because of the greater overlap of the sp^3 orbitals as compared to the p or s orbitals.

Figure 1.20 shows the transformation of the orbital energy levels. Note that the four new hybrid orbitals all have the same energy level. This model explains why carbon forms four bonds to four other atoms and why these atoms are oriented in a tetrahedral fashion around carbon.

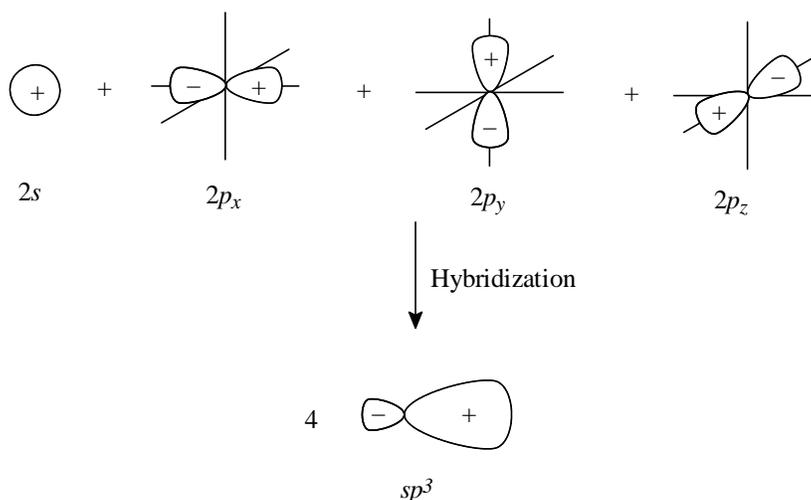


Figure 1.19. Mixing, or hybridization, of one s orbital with three p orbitals produces four sp^3 orbitals. Each of the sp^3 orbitals has 25% s character and 75% p character.

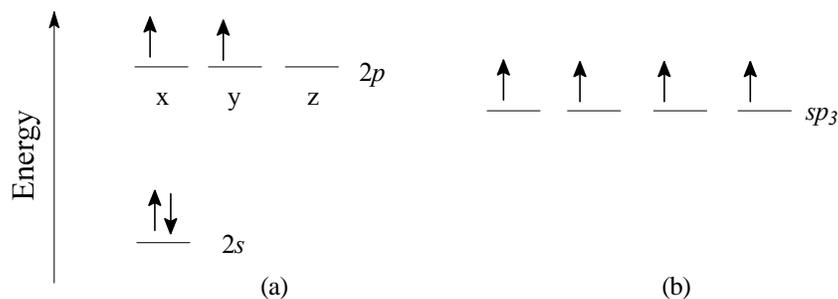


Figure 1.20. Electron configuration of carbon (a) before and (b) after hybridization. Note that the energy level of the hybrid orbitals is between that of the 2s and that of the 2p orbitals. The sum of the energies of the hybrid orbitals is equal to the sum of the energies of the unhybridized orbitals.

Thus, with methane (CH_4), each of the hydrogens is at one of the vertices of the tetrahedron and carbon is at the center.

Figure 1.21 illustrates the sp^3 hybrid orbitals. For clarity the figure shows only the large lobes of the hybrid orbitals. This arrangement allows the electrons in the orbitals to be as far apart as possible, as is called for by the VSEPR model. The tetrahedral structure allows the maximum possible distance between adjacent orbitals. The H—C—H bond angle in methane is 109.5° . This tetrahedral orientation is characteristic of an sp^3 hybridized carbon.

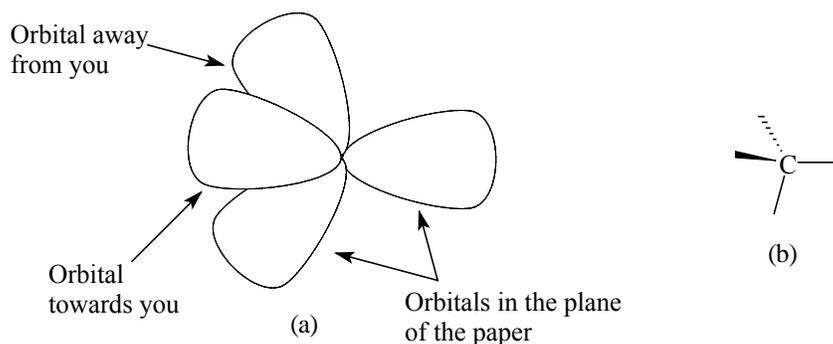


Figure 1.21. (a) Orbital hybridization arranges the sp^3 hybrid orbitals in a tetrahedron around the carbon enabling it to form four bonds with other atoms. The figure shows only the larger lobe of each sp^3 orbital. (b) The shorthand notation for an sp^3 hybridized carbon.

The overlapping of the four sp^3 hybrid orbitals of a carbon atom with the 1s orbitals of four hydrogen atoms forms the four carbon—hydrogen bonds of methane. Sigma bonds are the types of bond generated by the sp^3 -s orbital overlap. A sigma bond has rotational symmetry about the internuclear axis.

Exercise 1.3

Consider an excited state of carbon in which one of the 2s electrons is promoted to the vacant 2p orbital. How would this state of carbon fail to account for the structure of methane?

Exercise 1.4

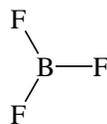
Ignoring any orbitals not in the valence shell how many orbitals are in each of the following molecules? How many are bonding, nonbonding, and antibonding? How many orbitals are occupied?

- a) NH₃ b) H₂S c) HCl
d) CO₂ e) CH₃OH f) CH₃CH₃

Sample Solution

a) A molecule of ammonia (NH₃) consists of one nitrogen and three hydrogens. Each hydrogen has a 1s orbital in its valence shell, which they contribute to the bond. Nitrogen has one 2s and three 2p orbitals in its valence shell, which it contributes to the bond. The total number of atomic orbitals in the valence shells of these atoms is seven. The formation of ammonia allows nitrogen to follow the Octet Rule because the bonded nitrogen has eight electrons in its valence shell. Thus, four of the orbitals are filled—three as bonding molecular orbitals and one orbital with a lone pair of electrons. The other three orbitals are unfilled antibonding orbitals.

Boron trifluoride (BF₃) illustrates the second type of hybridization, *sp*² hybridization. Structural studies indicate that boron has a triangular (trigonal planar) shape with three equivalent B—F bonds.



Boron trifluoride

Figure 1.22 shows the ground-state electron configuration of boron. This configuration does not account for the trivalent and trigonally bonded boron of BF₃. The best explanation is orbital hybridization. With hybridization, the 2s orbital combines with two of the 2p orbitals to give three equivalent *sp*² hybridized orbitals, as shown in Figure 1.23. The VSEPR model explains why a set of *sp*² hybrid orbitals

adopts a planar trigonal shape with the orbitals pointed to the corners of an equilateral triangle and with angles of 120° between the orbitals. Figure 1.24 shows how the electron configuration of boron changes during hybridization.

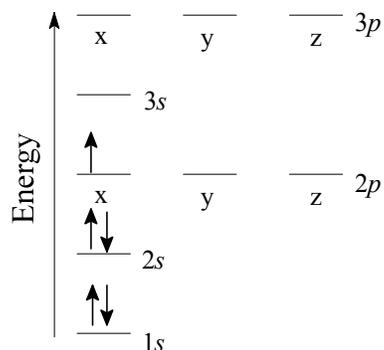


Figure 1.22. Orbital energy diagram for boron.

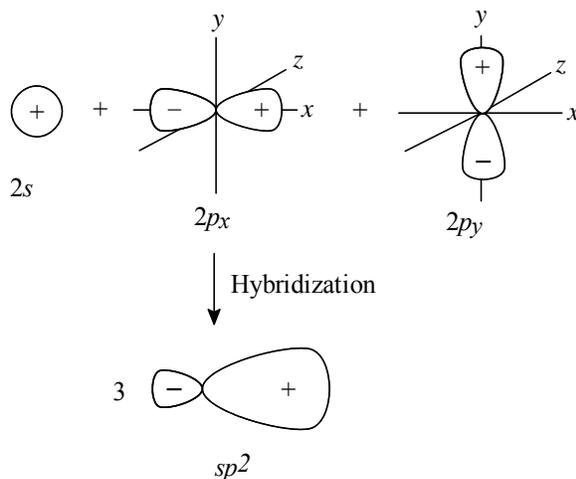


Figure 1.23. Mixing one s orbital with two p orbitals produces three sp^2 hybrid orbitals. Each orbital has 33.3% s and 66.7% p character.

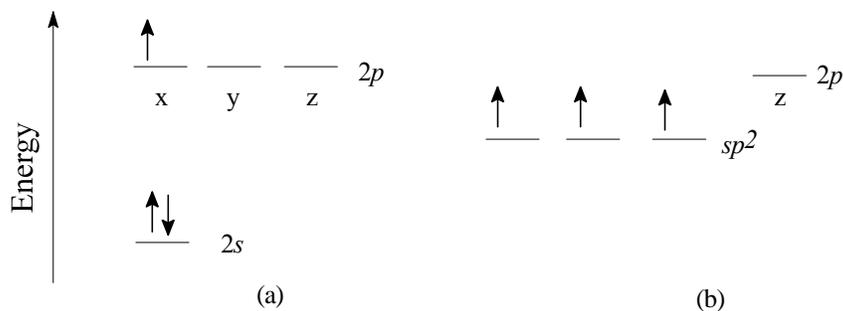


Figure 1.24. Electron configuration of boron (a) before and (b) after hybridization. Note that the energy level of the hybrid orbitals is between that of the 2s and that of the 2p orbitals.

Even after hybridization, the boron atom still has a vacant p orbital that was not involved in hybridization. This orbital orients itself at right angles to the three sp^2 orbitals. Figure 1.25 shows the orientation of the hybrid orbitals and the vacant unhybridized orbital.

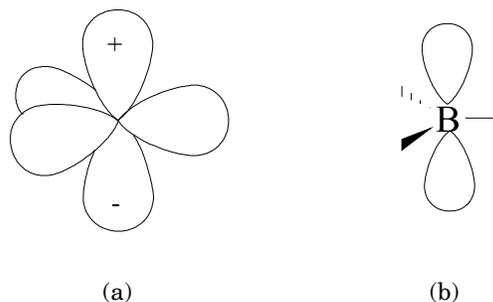


Figure 1.25. (a) The sp^2 hybrid orbitals of boron are in a planar triangle around the nucleus with an empty p orbital perpendicular to them. (b) The shorthand notation for sp^2 hybridized boron.

Exercise 1.5

What is the electron configuration of the valence electrons of a) an sp^2 hybridized carbon, b) an sp^2 hybridized nitrogen, and c) an sp^2 hybridized oxygen? For each of these, indicate the number of occupied and unoccupied orbitals and the hybridization of each orbital.

Sample solution

a) The electron configuration for an sp^2 hybridized carbon has one electron in each of three sp^2 hybrid orbitals and one electron in the $2p$ orbital.

Beryllium hydride (BeH_2) illustrates the third type of hybridization. Structural studies indicate that the H—Be—H bond angle is 180° . Thus, this molecule has a linear structure with 2 equivalent Be—H bonds. Figure 1.26 shows the ground state electron configuration for beryllium.

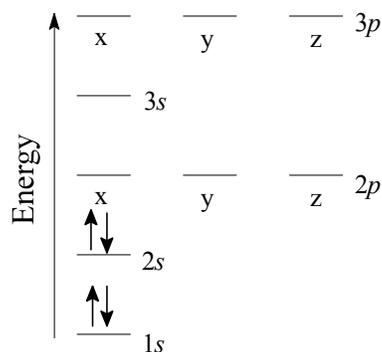


Figure 1.26. Electron configuration for the ground state of beryllium.

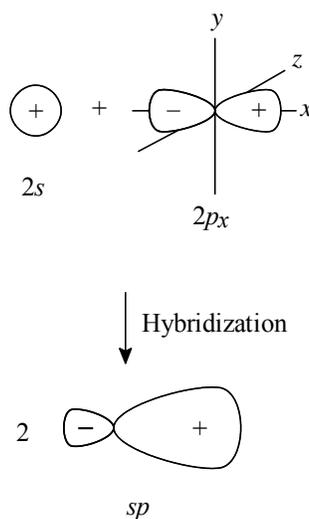


Figure 1.27. Hybridization of one s orbital with one p orbital produces two sp orbitals with 50% s character and 50% p character.

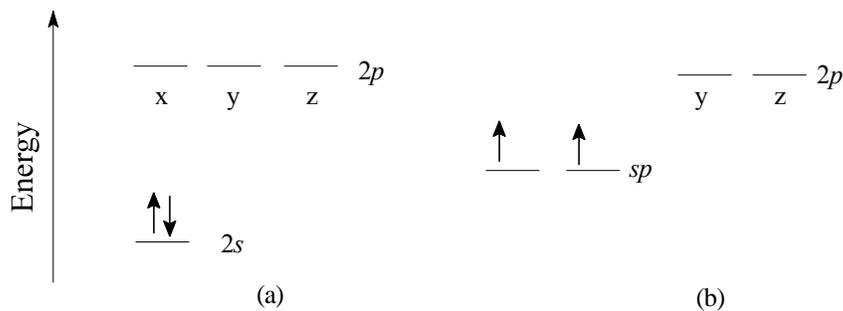


Figure 1.28. Electron configuration of beryllium (a) before and (b) after hybridization. Note that the energy level of the hybrid orbitals is between that of the $2s$ and that of the $2p$ orbitals.

To account for the structure of BeH_2 , you need the theory of orbital hybridization. Figure 1.27 shows the hybridization of beryllium. One s orbital hybridizes with only one p orbital to obtain two sp hybrid orbitals. The VSEPR model places these sp hybridized orbitals at 180° from each other. Figure 1.28 shows how the electron configuration of beryllium changes during hybridization. Figure 1.29 shows that sp hybridized Be has two vacant, unhybridized p orbitals.

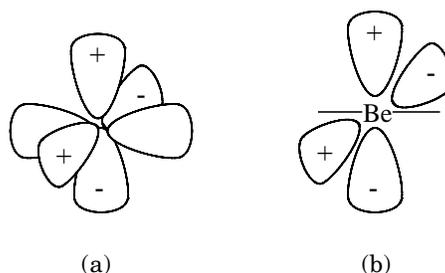


Figure 1.29. (a) The sp hybrid orbitals are on either side of the beryllium with empty p orbitals perpendicular to the sp orbitals. (b) The shorthand notation.

Remember that the drawings of the orbitals shown to this point are only schematic drawings. They are useful to help in understanding the hybridization process. In contrast, Figure 1.30 shows a contour plot of the shapes of the sp and sp^3 hybrid orbitals. Looking at these plots, you can more easily see the three-dimensional shapes of the orbitals as well as the varying size of the smaller lobe. The larger lobe is the “bonding” lobe of the orbital; the smaller one is not directly involved in bonding.

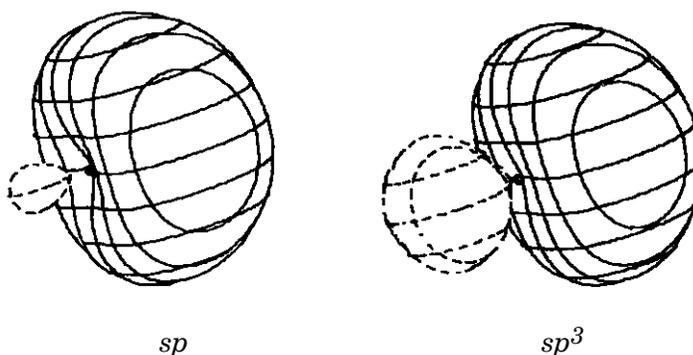
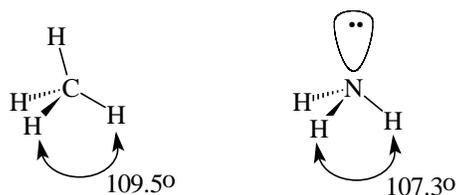


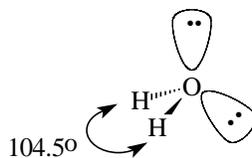
Figure 1.30. Three-dimensional perspective plots of sp and sp^3 hybrid orbitals.

So far you have learned about the spatial distribution of bonding molecular orbitals. Another factor that affects the shape of a molecule is the presence of nonbonding electron pairs. In general, a

molecule with a pair of nonbonding electrons adopts a shape similar to a molecule with a bond in place of those electrons. For example, ammonia (NH_3) has three N—H bonds and a pair of nonbonding electrons. The structure is similar to that of methane (CH_4). The difference is that the nonbonding electrons have a greater repulsive influence than a pair of bonding electrons. Thus, even though both ammonia and methane have sp^3 hybridization, the bond angles are slightly different. The H—C—H bond angle in methane is 109.5° , but the H—N—H bond angle in ammonia is 107.3° .



To predict the shape of an atom in a molecule, first determine the number of σ bonds plus the number of electron pairs in that atom. Once this is done, use the VSEPR model to predict the angles between the bonds and electron pairs. For example, the structure of water can be predicted using this approach. The oxygen of water has two σ bonds and two pairs of nonbonding electrons. The VSEPR model would predict a tetrahedral shape for water with the H—O—H bond angle about 109.5° . Because there are two nonbonding pairs of electrons, the actual angle is somewhat smaller at 104.5° .



Exercise 1.6

Predict the general shapes of the following molecules and ions. Indicate the hybridization of the central atoms.

- | | | |
|-------------------------|--------------------------|------------------------|
| a) PH_3 | b) CCl_4 | c) BH_3 |
| d) $\ominus\text{BH}_4$ | e) BeF_2 | f) $\oplus\text{CH}_3$ |
| g) SiH_4 | h) $\ominus:\text{CH}_3$ | i) $\oplus\text{NH}_4$ |

Sample Solution

d) According to the VSEPR model, the expected shape for BH_4^\ominus is tetrahedral, so the central atom (B) must be sp^3 hybridized. This shape allows for a maximum distance between the four B—H bonds.

1.8 Multiple Bonding

With each of the three types of hybridization, the carbon not only exhibits a different kind of molecular shape, it bonds with a different kind of bond. An sp^3 hybridized carbon bonds with σ , or single, bonds. That is, each hybrid orbital contains only one pair of electrons, and the compound has a tetrahedral shape. Methane is an example of a compound with sp^3 hybridization.

An sp^2 hybridized carbon forms a double bond between itself and another atom. A double bond is a combination of one σ bond and one π (pi) bond and contains two pairs of electrons. The carbon has a trigonal planar shape. Ethylene ($\text{CH}_2=\text{CH}_2$) is an example of a carbon compound with sp^2 hybridization. Both carbons in ethylene are sp^2 hybridized and bonded to each other. Structurally, ethylene is flat with all six atoms in the same plane. Experimental evidence indicates that both the H—C—H and the H—C—C bond angles are 120° . Experimental evidence also indicates that the C—H bond length in ethylene is shorter than the C—H bond length in methane.

The electron configuration of the two carbons of ethylene (see Exercise 1.5) indicates that there is a single electron in the unhybridized p orbital of each carbon. These two p atomic orbitals interact to form two new molecular orbitals, the π **molecular orbitals** (Figure 1.31). This bond, unlike the σ bond, is not oriented along the internuclear axis. Instead it is in a plane perpendicular to the plane formed by the trigonal carbons. Thus, there are two bonds between the carbons in the ethylene molecule.

A π molecular orbital results when two orbitals overlap outside the internuclear axis.

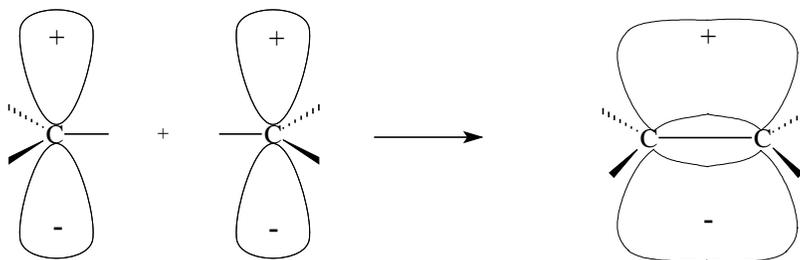


Figure 1.31. The p orbitals of two sp^2 hybridized carbons overlap to produce the π bond in ethylene.

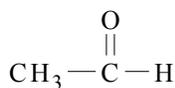
Like σ molecular orbitals, π molecular orbitals have both bonding and antibonding orbitals. If the sign of the p lobes are the same (that is, if the two p orbitals are in phase with one another), as

in Figure 1.31, the overlap forms a bonding π molecular orbital. If the two p orbitals are out of phase, then the overlap results in an antibonding π^* molecular orbital (for π^* read “pi star”).

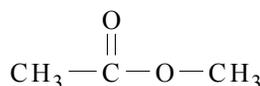
Similar to the p atomic orbitals from which it forms, a π molecular orbital has two lobes and a nodal plane through the axis between the two nuclei. The two lobes of electron density are above and below the nodal plane. The π bond, however, does not have the rotational symmetry of the σ bond.

Exercise 1.7

Double bonds can also form between carbon and oxygen. Construct a molecular orbital picture for acetaldehyde and methyl acetate. Indicate approximate bond angles and the atomic orbitals that must overlap to form the molecular orbitals.

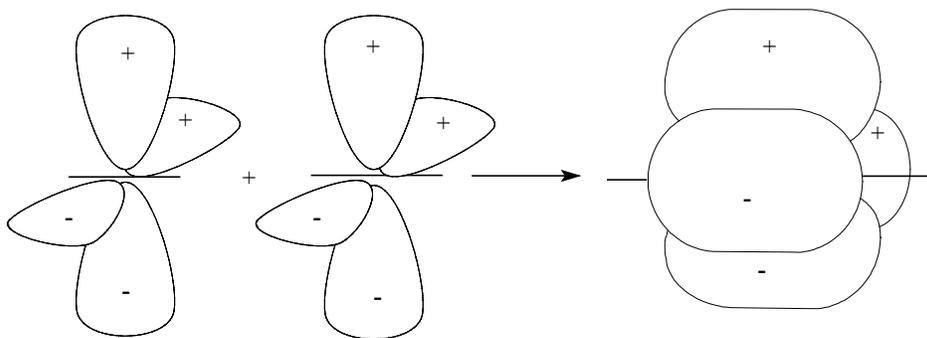


Acetaldehyde



Methyl acetate

An sp hybridized carbon forms a triple bond. A triple bond consists of three pairs of electrons shared between a carbon and another atom and is the combination of one σ and two π bonds. For example, both carbons in acetylene ($\text{CH} \equiv \text{CH}$) are sp hybridized. Experimental measurements show that the $\text{H}-\text{C}-\text{C}$ bond angle is 180° . This angle gives acetylene a linear shape. Figure 1.32 (a) shows the interaction of the unhybridized p orbitals of two sp hybridized carbon to form the π bonds of acetylene. The view from the end of the acetylene molecule in Figure 1.32 (b) shows a nodal axis that coincides with the internuclear axis. The electron cloud of the two π bonds has a toroidal (doughnut-shaped) symmetry about the internuclear axis.



(a)

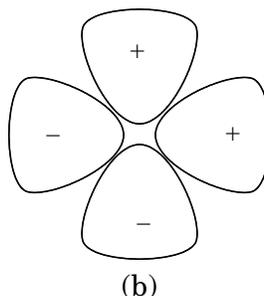
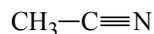


Figure 1.32. (a) The π molecular orbitals in acetylene are formed from overlap of the p orbitals of two sp hybridized carbon atoms. (b) The view of the π molecular orbitals along the internuclear axis.

Exercise 1.8

Acetonitrile has a triple bond between carbon and nitrogen. Construct a molecular orbital picture for acetonitrile. Indicate approximate bond angles and the atomic orbitals that must overlap to form the molecular orbitals.



Acetonitrile

1.9 Drawing Lewis Structures

As mentioned in Section 1.5, G. N. Lewis proposed the theory that an atom achieves its most stable electronic configuration when its valence shell is filled with electrons. Hydrogen requires two electrons. The elements in the second and third rows of the periodic table require eight electrons (the Octet Rule). Lewis proposed that during covalent bonding two atoms share one or more pairs of electrons and that each pair count as belonging individually to both atoms.

To help people visualize his theory, he developed a system that represents each electron in the valence shell of an atom by a dot (\bullet) and each pair of electrons by a pair of dots ($:$). He placed these dots around the atomic symbol of the element. For example, he drew hydrogen and chlorine atoms like this:



He represented a bonding pair of electrons by either a pair of dots ($:$) or a dash (—) placed between the two atoms. He showed hydrogen and chlorine, for example, bonded to form hydrogen chloride like this:



A Lewis structure is a schematic representation of the bonds and nonbonding electrons in an ion or molecule.

Chemists call his method of representing atoms and molecules **Lewis structures**.

When drawing Lewis structures, use only the valence electrons and strive for an octet for each atom except hydrogen. Like helium, hydrogen's valence shell has only two electrons. Remember the conservation rule for orbitals and electrons—you must end up with the same number of both as when you started. A helpful tool that makes drawing Lewis structures easier is know how many bonds each of the commonly used elements usually forms.



The single dots represent unpaired electrons available for bonding, and the paired dots represent paired electrons available for bonding. For example, nitrogen bonds to three hydrogens with the nitrogen providing one electron to each hydrogen—nitrogen bond and each of the hydrogens providing one electron to the same bonds. When nitrogen bonds with three hydrogens, the valence shells of both the nitrogen and the hydrogens are filled. However, the nitrogen could also bond with an H^{\oplus} ion by providing both electrons for the bond because the hydrogen ion has no electrons.

There are two steps to drawing a Lewis structure of a molecule. First, write the central atom of the molecule. Second, fit the other atoms around the central atom. If the molecule contains carbon, the carbon is the central atom. If the molecule contains a noncarbon other than hydrogen, the noncarbon is the central atom. If the molecule contains more than one noncarbon atom, the central atom is the first atom written in the formula, unless the first atom listed is a hydrogen. As you may remember from your course in general chemistry, a hydrogen at the start of the line structure of a non-carbon-containing molecule usually indicates a Brønsted-Lowry acid. In that case, set the hydrogen aside until the bonds for all the other atoms have been determined, then add that hydrogen at the appropriate place. When the formula for a carbon-containing molecule starts with a hydrogen, such as HCO_2H , the first hydrogen bonds to the carbon; the other hydrogen bonds to one of the oxygens.

Solved Exercise 1.1

For each of the following compounds draw a Lewis structure showing all bonding and nonbonding electrons.

a) Methane (CH_4)

Solution: First, write a carbon with its appropriate four dots representing the four valence electrons.



Then combine it with four hydrogens with each of their valence electrons to get methane.



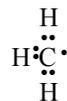
Next check the Lewis structure to make sure it contains the correct number of orbitals and electrons. Carbon has four identical valence shell orbitals, as the result of sp^3 hybridization, and each hydrogen atom has one. The carbon contributed four electrons and each hydrogen one electron, for a total of eight electrons. Methane has eight bonding electrons, and, as you see in the Lewis structure, the valence shell of each atom is full—two electrons for each hydrogen and eight for the carbon. The Lewis structure checks out.

b) Methanol, CH_3OH

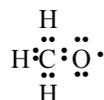
Solution: First, write a carbon with its appropriate four dots representing the four valence electrons.



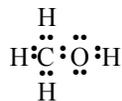
Then combine it with three hydrogens with its valence electron to get the methyl group.



Now add an oxygen with its six electrons.



Finally, add the last hydrogen to the oxygen.



Next check the Lewis structure to make sure it contains the correct number of orbitals and electrons. Carbon has four identical valence shell orbitals, as the result of sp^3 hybridization, and each hydrogen atom has one. The carbon contributed three electrons and each hydrogen one electron, for a total of six electrons. The final bond to carbon comes from the oxygen. Thus, carbon has a full octet of electrons. The oxygen has four nonbonding electrons and four bonding electrons. Each hydrogen has two bonding electrons. The Lewis structure checks out.

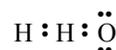
Exercise 1.9

Show all the valence electrons as you write a Lewis structure for each of the following molecules.



Sample Solution

a) Oxygen is a member of Group VI of the periodic table; thus, it has six valence electrons. Hydrogen has one. There are two possible structures for a molecule with one oxygen and two hydrogens.

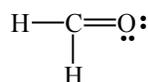


The left-hand structure is correct because it gives each atom a filled valence shell. Each hydrogen has two electrons, and the oxygen has eight. The structure on the right is incorrect because the central hydrogen has too many electrons in its valence shell (four) and the oxygen has too few (six).

Molecules with the greatest stability have all their electrons paired. Many times this requires that more than one bond form between two atoms. For example, look at formaldehyde (CH_2O). The central atom is carbon ($\cdot\dot{\text{C}}\cdot$). It combines with two hydrogens ($\text{H}\cdot$)

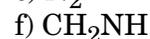
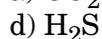
and an oxygen ($\cdot\ddot{\text{O}}\cdot$) giving $\text{H}-\overset{\cdot}{\underset{\text{H}}{\text{C}}}-\overset{\cdot}{\text{O}}\cdot$. In this case, both the carbon

and the oxygen have an unpaired electron. However, if these unpaired electrons pair, as indicated by the arrows, they form a second bond between carbon and oxygen. All four atoms now have gained their greatest stability, while maintaining the correct number of orbitals and electrons and fulfilling the Octet Rule. The completed Lewis Structure looks like this.



Exercise 1.10

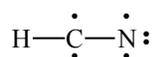
Write a Lewis structure, showing all valence electrons, for each of the following molecules.



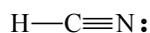
Sample Solution

b) First, write the carbon atom with its four valence electrons ($\cdot\overset{\cdot}{\text{C}}\cdot$).

Then add the hydrogen with its one electron ($\text{H}\cdot$) and the nitrogen with its five ($\cdot\overset{\cdot}{\text{N}}\cdot$). This gives the following structure:



However, this structure has four unpaired electrons—two on the carbon and two on the nitrogen. Pairing the electrons makes two additional covalent bonds and gives a Lewis structure with a carbon—nitrogen triple bond.



Now the structure satisfies all the rules for bonding.

1.10 Polar Covalent Bonds

What you have learned so far is that a bond is either ionic or covalent. With ionic bonding an electron transfers from one atom to another. When the transfer occurs, one atom becomes a positively charged ion, and the other becomes a negatively charged ion. Then the bond forms as the two ions electrostatically attract each other. An ionic bond is the most extreme type of **polar bond**. Covalent bonds do not transfer electrons. Instead, the two atoms involved in the bond share electrons to form molecular orbitals. Two atoms that share electrons equally in a covalent bond are said to have **nonpolar bonds**.

However, few bonds in organic molecules are either completely ionic or completely covalent. Most fall somewhere on a continuum between the two. The **electronegativity** of the atoms involved in a bond determines the bond's position on this continuum. Linus Pauling developed the concept of electronegativity. These values of electronegativity range from 0 to 4. The most electronegative elements are in the upper right-hand corner of the periodic table. The least electronegative elements are in the lower left-hand corner. Figure 1.33 lists the electronegativities of the elements that are most important to organic chemists.

In a polar bond the electron density of a molecular orbital is not equally distributed.

A nonpolar bond has equal electron distribution in the molecular orbital.

Pauling defined electronegativity as "the power of the atom in a molecule to attract electrons to itself" and assigned each atom a number indicative of its ability to attract electrons.

H 2.20							
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	
Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	
K 0.82	Ca 1.00					Br 2.96	
						I 2.66	

Figure 1.33. Electronegativities of the elements most important to organic chemists.

To determine where on the continuum between the completely ionic (polar) and the completely covalent (nonpolar) bonds a particular bond is, take the difference between the electronegativities of the two bonded atoms. If the difference is less than 1, that generally indicates that the bond is more covalent. If the difference is greater than 1.5, the bond is generally considered more ionic. Sodium chloride (NaCl) is a common example of a compound with a bond that is considered ionic. The electronegativity of Na is 0.93 and that of Cl is 3.16, giving a difference of 2.23. Methane is a common example of a compound whose bonds are considered covalent. The electronegativity of C is 2.55 and that of H is 2.20. The difference is 0.35.

Calling a bond covalent implies that the two bonded atoms equally share the electrons making up that bond. However, the only time that two atoms share electrons equally is when the two atoms have the same electronegativities, as do the two hydrogens in a hydrogen molecule. When two different atoms form a covalent bond, one atom attracts the electrons more strongly than the other does. This stronger attraction by one of the atoms prevents equal sharing between the atoms. It also creates a greater electron density around the atom with the higher electronegativity, giving it a partial negative charge and giving the atom with the lower electronegativity a partial positive charge. It is important to note that these partial charges are opposite and equal in magnitude. Chemists call this type of bond a **polar covalent bond**. Most bonds encountered in organic chemistry are polar covalent bonds. Hydrogen chloride (HCl) contains a covalent bond because the difference between the electronegativities of hydrogen and chlorine is 0.96. Because these are different elements and have different electronegativities, the bond is a polar covalent bond with the chlorine having the greater electron density due to its greater electronegativity. To indicate the partial charges on a polar covalent bond, chemists use δ^+ (partial positive charge) and δ^- (partial negative charge).

In a polar covalent bond the electrons in a molecular orbital are unequally distributed among the atoms of the orbital.



Bond dipole (μ) is the unit of measure that chemists use to describe the amount of polarity in a polar bond.

The **bond dipole** of a molecule is the product of the charge (e) and the distance (d) between the nuclei of the bonded atoms.

$$\mu = ed$$

The charge is the magnitude of either the positive or negative charge because, in a neutral molecule, the magnitude of both is equal. The value of the charge of an electron is 4.8×10^{-10} electrostatic units (esu), and bond lengths are typically in the range of 10^{-8} cm. Thus, molecular **dipole moments** are approximately 10^{-18} esu cm. The debye unit (D) is 1.0×10^{-18} esu cm and is named after Peter J. W. Debye, a Dutch chemist who pioneered in the study of polar molecules. Debye units simplify the reporting of dipole moments. Instead of reporting an experimentally determined dipole of 0.5×10^{-18} esu cm, using the debye unit shortens the measure to 0.5 D.

The symbol indicating the dipole moment of a molecule is $\text{+} \longrightarrow$. It is written with the Lewis structure of the molecule as follows: $\text{H}-\overset{\text{+}}{\text{C}}\text{:}$ Note that the plus end is beside the element bearing

The dipole moment of a molecule is the measure of the polarity of an entire molecule.

the partial positive charge and the arrow end beside the element bearing the partial negative charge.

Table 1.2 lists the bond dipoles of some common types of bonds found in organic molecules. For simple molecules, such as HCl, the bond dipole is the same as the dipole moment of the molecule because there is only one bond in the molecule. For other, more complex molecules, the dipole moment is the vector sum of all of the bond dipoles for the molecule. To calculate the dipole moment of such molecules, chemists must consider the three-dimensional molecular structure. Thus, obtaining a dipole moment is very complicated for large molecules. However, having an understanding of the polarity of individual bonds will be very useful to you in understanding the chemical reactions you will study in later chapters of this book.

Bond	Bond Dipole, D	Bond	Bond Dipole, D
C—F	1.53	H—F	1.82
C—Cl	1.59	H—Cl	1.08
C—Br	1.48	H—Br	0.82
C—I	1.29	H—I	0.44
C—N	0.22	H—N	1.32
C—O	0.85	H—O	1.53
C—H	0.35		

Table 1.2. Selected bond dipoles.

Exercise 1.11

Draw the Lewis structure of each of the following molecules. For each bond in the molecule, indicate the direction of polarity. Also indicate whether each bond is covalent, polar covalent, or ionic.

- a) HBr b) H₂O c) LiI
 d) BrCl e) NH₃ f) KF

Sample solution

a) The electronegativity of H is 2.20 and that of Br is 2.96, giving a difference of 0.76. The molecule has a polar covalent bond with the positive end at hydrogen.



Table 1.2 shows that the dipole of the carbon—hydrogen bond is lower than the dipole of the carbon—oxygen bond and much lower than the dipoles of the carbon—halogen bonds. The low polarity of the C—H bond is important in the chemistry of organic molecules because the greater the polarity of a bond, the more reactive, or less stable, it is.

1.11 Inductive Effects on Bond Polarity

In a molecule containing several different atoms, if one bond is polarized as a result of the high electronegativity of a constituent atom that bond increases the polarization of the other bonds adjacent to it. This is called an **inductive effect**. The inductive effect produces the strongest influence over the bonds immediately adjacent to the polarized bond and diminishes rapidly with distance. For example, the C—C bond in ethane ($\text{CH}_3\text{—CH}_3$) is completely nonpolar because it connects two equivalently bonded atoms. However, if you replace one of the hydrogens with a chlorine, forming chloroethane ($\text{CH}_3\text{—CH}_2\text{—Cl}$), the two carbon atoms are no longer equivalent. The higher electronegativity of the chlorine deprives the carbon to which it is bonded of some of its electron density; thus, creating a polarized bond. The polarized C—Cl bond effectively increases the apparent electronegativity of that carbon, and it compensates by drawing the electrons of its bond with the other carbon closer to itself. In other words, the polarized C—Cl bond of chloroethane polarizes the C—C bond through the inductive effect.

At this point it is important for you to consider a second effect, called the **field effect**. The field effect operates through space rather than through bonds like the inductive effect. The influence of this effect depends entirely on the three-dimensional structure of the molecule. Sometimes a molecule contains bonds that are separated by too many intervening atoms and bonds to interact with one another through the inductive effect. However, atoms of highly differing electronegativities can be brought close together as a result of the structure of the molecule, and the close proximity of two such atoms causes the same type of bond polarization as does the inductive effect.

Separating field effects and inductive effects experimentally is extremely difficult, as they accomplish the same result and reinforce each other. However, chemists have shown that the field effect is actually more important than the inductive effect. Because the effects have the same consequences and reinforce each other, chemists usually use the term field effect to refer to a combination of both effects.

1.12 Formal Charges

The inductive effect is the polarization of a bond by the atoms or groups of atoms attached to it.

The field effect is the polarization of a bond by atoms or groups of atoms not directly bonded to the atoms connected by the polarized bond.

The formal charge is the positive or negative charge assigned to an atom in a Lewis structure.

When studying the pathways that organic reactions follow, you will deal frequently with charged molecular intermediates, called ions. Because chemical reactions usually take place at or near the site of charged atoms, you must know which particular atom, or atoms, bears the charge. The way to determine the charge-bearing atom in a molecule is to calculate the **formal charge** on each atom in that molecule. When calculating formal charges for the atoms, use the Lewis structure of the molecule as the basis of your calculation. Treat each electron in a covalent bond as if it belongs to both atoms that the bond joins. Assume that all the electrons that reside within the molecule do so in pairs. In Chapter 21, you will study some cases of unpaired electrons, but you will be told specifically when this occurs. Both electrons in any nonbonded pair belong to the atom next to which they are drawn—following the rules for drawing Lewis structures, of course.

Use the following formula to calculate formal charge:

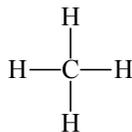
$$\begin{aligned} \text{formal charge} &= (\text{number of valence electrons}) \\ &\quad - (\text{number of nonbonding electrons}) \\ &\quad - \frac{1}{2}(\text{number of bonding electrons}) \end{aligned}$$

Solved Exercise 1.2

Locate the formal charge in each of the following structures.

a) Methane, CH₄

Solution: First, draw the Lewis structure of methane:



Because all four of the carbon–hydrogen bonds are equivalent, calculate the formal charge only once. Each hydrogen has one valence electron, no nonbonding electrons, and two bonding electrons.

$$\text{Formal charge on hydrogen} = 1 - 0 - \frac{1}{2}(2) = 0$$

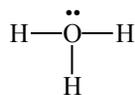
Carbon has four valence electrons and no nonbonding electrons. Because the carbon atom shares eight electrons with the four hydrogen atoms, it has eight bonding electrons.

$$\text{Formal charge on carbon} = 4 - 0 - \frac{1}{2}(8) = 0.$$

Thus, there are no formal charges in methane.

b) The hydronium ion, $\text{H}_3\text{O}^{\oplus}$

Solution: First, draw the Lewis structure of the hydronium ion:

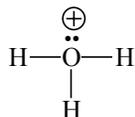


Because all three of the oxygen—hydrogen bonds are equivalent, calculate the formal charge for the hydrogens only once. Each hydrogen has one valence electron, no nonbonding electrons, and two bonding electrons.

$$\text{Formal charge on hydrogen} = 1 - 0 - \frac{1}{2}(2) = 0$$

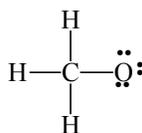
Oxygen has six valence electrons and two nonbonding electrons. Because the oxygen atom shares six electrons with the three hydrogen atoms, it has six bonding electrons.

$$\text{Formal charge on oxygen} = 6 - 2 - \frac{1}{2}(6) = +1.$$



c) The methoxide ion, $\text{CH}_3\text{O}^{\ominus}$

Solution: First, draw the Lewis structure of the methoxide ion:



Because all three of the carbon—hydrogen bonds are equivalent, calculate the formal charge for the hydrogens only once. Each hydrogen has one valence electron, no nonbonding electrons, and two bonding electrons.

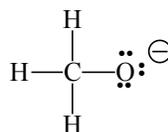
$$\text{Formal charge on hydrogen} = 1 - 0 - \frac{1}{2}(2) = 0$$

Carbon has four valence electrons and no nonbonding electrons. Because the carbon atom shares six electrons with the three hydrogen atoms and two electrons with the oxygen atom, it has eight bonding electrons.

$$\text{Formal charge on carbon} = 4 - 0 - \frac{1}{2}(8) = 0.$$

Oxygen has six valence electrons and six nonbonding electrons. Because the oxygen atom shares two electrons with one carbon atom, it has two bonding electrons.

$$\text{Formal charge on oxygen} = 6 - 6 - \frac{1}{2}(2) = -1.$$



Calculating the formal charge on a bonded atom is the same as asking whether or not it has the same number of valence electrons available to it as it did when it was unbonded. For example, oxygen normally has six valence electrons. To be uncharged in a molecule, it must have six electrons as well.

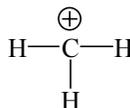
Exercise 1.12

Draw a Lewis structure for each of the following and determine whether any of the atoms bear formal charges.

- a) CH_3F b) $\text{CH}_3\text{OH}_2^{\oplus}$ c) CH_3^{\oplus} d) NH_3BF_3
 e) $^{\ominus}\text{CH}_3$ (the : indicates nonbonding electrons)
 f) $:\text{CH}_2$ g) HNO_2

Sample solution

c) According to the conventions of drawing Lewis structures, carbon is the central atom.

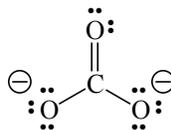


$$\text{Formal charge on hydrogen} = 1 - 0 - \frac{1}{2}(2) = 0$$

$$\text{Formal charge on carbon} = 4 - 0 - \frac{1}{2}(6) = +1$$

1.13 Resonance

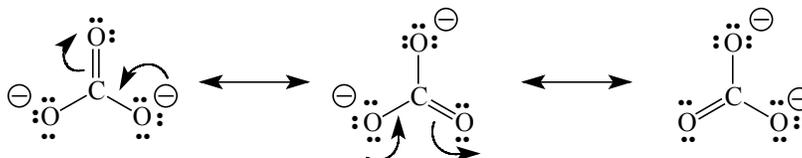
Some covalent molecules are impossible to represent satisfactorily with a single Lewis structure. The carbonate ion ($\text{CO}_3^{2\ominus}$) is an example. The following illustration seems to represent $\text{CO}_3^{2\ominus}$ accurately, according to the rules for drawing Lewis structures:



A Lewis structure also allows you to calculate the correct formal charges. Two of the oxygen atoms each bear a formal charge of -1 , giving the ion a total charge of -2 . However, experimental evidence demonstrates that this structure is not an accurate representation of the molecule. Instead, the evidence shows that the ion has three identical C—O bonds, that each O—C—O angle measures 120° , and that each of the three oxygens bears the same amount of negative charge.

What is needed is a structure that represents the electrons as being equally distributed among the three oxygen atoms. Lewis structures do not allow for this, so chemists developed another model. They call this model **resonance**. To represent a molecule in which there is resonance, as many structures as possible are drawn that differ only in the location of the pairs of electrons—for the carbonate ion there are three. In each structure, the atoms maintain the same relative positions.

With resonance, two or more Lewis structures that differ in the position of π and nonbonding electrons describe the same ion or molecule.



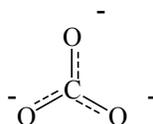
That is, the ion is not simply being rotated. The oxygen atoms are drawn in the same location in each structure, whereas the electrons are drawn showing all the possible positions that they might be in. A two-headed arrow (\longleftrightarrow) is the notation used to indicate resonance. This symbol does not mean that there is any kind of equilibrium, nor does it imply any kind of reaction.

A curved arrow indicates the direction of electron movement. The arrowhead shows the destination of the electrons.

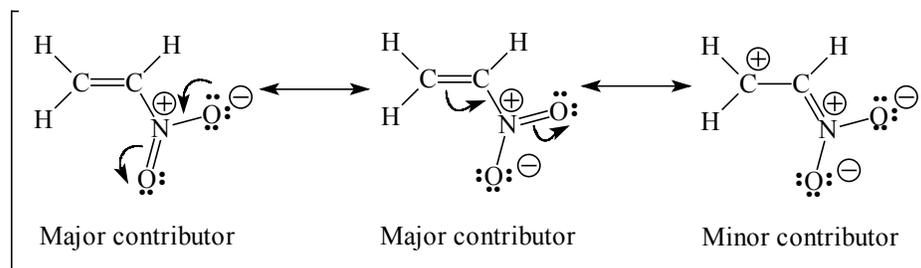
Chemists frequently use **curved arrows** () to indicate the direction of *electron movement*. In the resonance structures for the carbonate ion, the curved arrows show one pair of nonbonding electrons moving to become a new carbon—oxygen double bond, and a pair of bonding electrons from another carbon—oxygen double bond moving to become nonbonding. Understanding what curved arrows mean will help you to understand many of the reactions you will study in organic chemistry.

A resonance hybrid is the combination of the individual resonance contributors to the structure of a molecule.

Although three resonance structures are drawn for the carbonate ion, keep in mind that it has only one actual structure. That structure is a **resonance hybrid** of the three Lewis structures, which are called **resonance contributors**. None of the individual resonance contributors shown above actually exists. Also, the molecule that the resonance contributors illustrate is not a mixture of the different forms. There is only one actual molecule, and its properties are the weighted averages of the properties of the resonance contributors. With the carbonate ion, each oxygen bears $2/3$ of a negative charge, and each carbon—oxygen bond has a bond length of 129 pm. This length is longer than a typical carbon—oxygen double bond (122 pm), but shorter than a typical carbon—oxygen single bond (143 pm). A more accurate drawing of the carbonate ion shows the bonds using a combination of solid and dashed lines indicating that the bonds fall somewhere between single and double bonds.



The three resonance contributors of the carbonate ion are equivalent. That is, they all have equal energy and contribute equally to the structure of the ion. But this is not always the case. For example, nitroethene ($\text{CH}_2=\text{CHNO}_2$) has three resonance contributors, but only two of them are equivalent; the third is different.



The first two structures are equivalent contributors to the resonance hybrid. Both have a double bond between nitrogen and one oxygen and a single bond between nitrogen and the other oxygen. Both have a positive charge on nitrogen and a negative charge on the oxygen with the single bond. The first two structures are important because the structures with the largest number of covalent bonds contribute most to the characteristics of the group. All three atoms also have noble gas configurations. Thus, these two resonance structures are the major contributors to the resonance hybrid of nitroethene.

The third structure has more charges and fewer bonds than the first two structures. Plus one carbon does not have an octet. In the third structure, the carbon is positively charged, and both oxygens are negatively charged. The third contributor has a **separation of charge**. A molecule accomplishes separation of charge only with an expenditure of energy. These factors decrease the impact this structure has on the features of nitroethene, making it a minor contributor to the resonance hybrid.

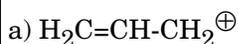
Separation of charge occurs when two adjacent atoms have a plus and a minus charge that could be eliminated by the formation of a bond.

Writing resonance contributors requires a careful analysis of the Lewis structure for a molecule or ion. To write the resonance contributors, follow these rules:

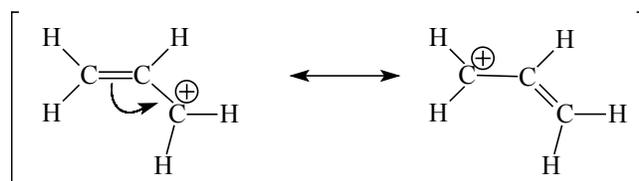
1. Only nonbonding and π bonding electrons change locations from one resonance contributor to another.
2. The atoms in the different resonance contributors remain in the same relative positions.
3. All resonance contributors must have the same number of paired and unpaired electrons.
4. Resonance contributors with atoms from the second period that have eight electrons around them are more important than those in which such atoms lack a full octet.
5. A resonance contributor with a greater number of covalent bonds is more important than one with a smaller number.
6. Because phosphorus and sulfur have empty $3d$ orbitals, you can write structures with ten or more electrons about these atoms.
7. Resonance contributors with no separation of charge are more important than those with a separation of charge.
8. When a charge is present, the more important resonance contributor is the one with a negative charge on the most electronegative atom or a positive charge on the least electronegative atom.

Solved Exercise 1.3

For each of the following compounds, draw all important resonance contributors. Decide which resonance contributor, or contributors, is more important.



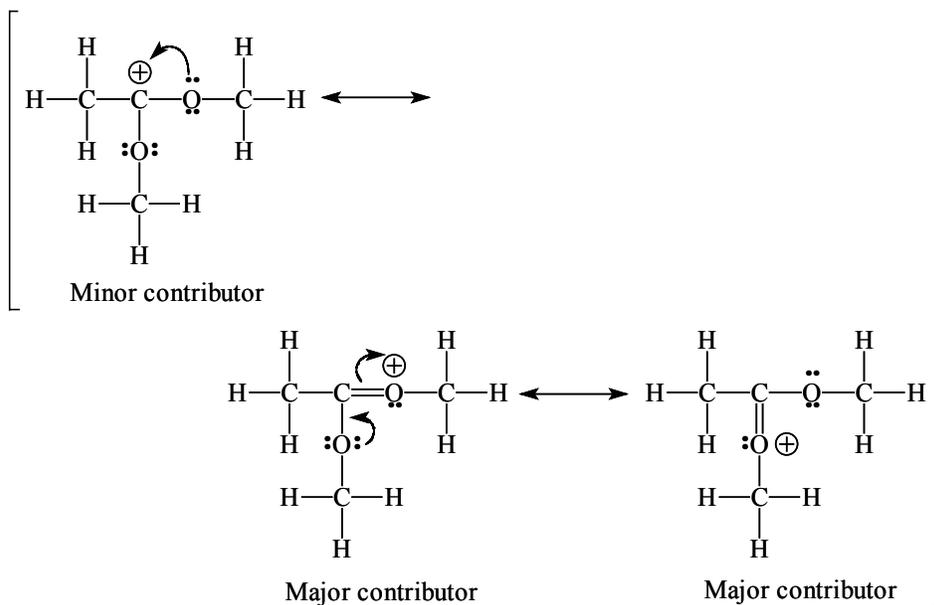
Solution: The resonance contributors are:



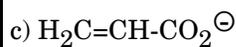
Both structures have octets on two of the carbon atoms and an incomplete octet on the third carbon atom. They have the same number of bonds and charges; thus, they are equivalent resonance structures.



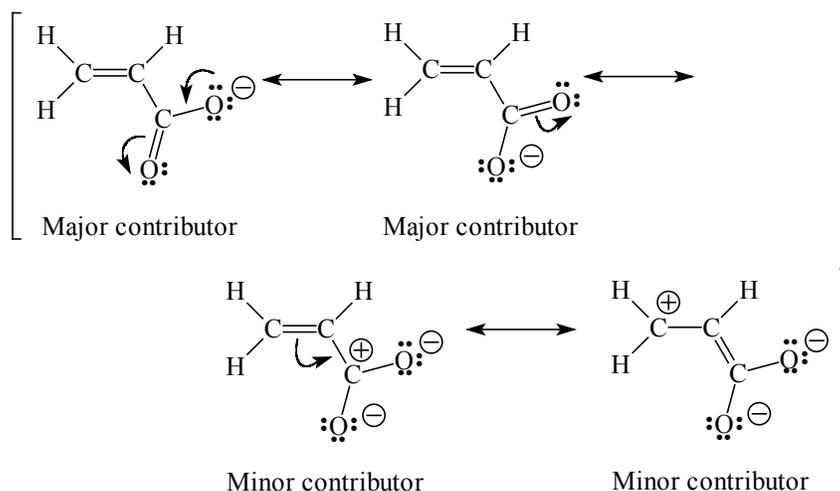
Solution: First draw the resonance structures:



In the first structure one of the carbon atoms has only three bonds making it electron deficient. Both the second and third contributors have full octets on all the atoms; thus, they are equivalent.



Solution: First draw the resonance contributors:



The first two resonance contributors have equal numbers of bonding and nonbonding electrons and equal numbers of charges. Thus, they are equivalent structures. The third and fourth structures have an increase in the number of charges giving them higher energy levels. They are minor contributors to the structure of this anion.

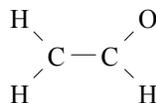
Exercise 1.13

Draw the Lewis structures of the following molecules or ions. Draw all important resonance contributors if the molecule is a resonance hybrid. Decide which contributor, or contributors, is more important.

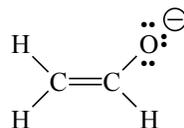
- | | | |
|-----------------------------|------------------------------------|-------------------------------|
| a) HNO_3 | b) $\text{CH}_2\text{CHO}^\ominus$ | c) CH_3NO_2 |
| d) $\text{SO}_4^{2\ominus}$ | e) CH_3NCO | f) CH_3SOCH_3 |

Sample Solution

b) First, note that there are a total of eighteen valence electrons available for the structure. The two carbons have four each, the three hydrogens have one each, the oxygen has six, and the negative charge represents one. Then, draw a Lewis structure.



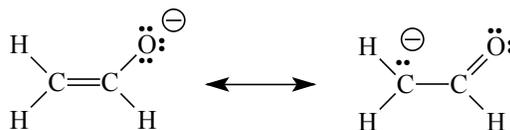
This structure accounts for ten of the eighteen valence electrons in the ion. Complete the structure, giving each atom a full valence shell of electrons.



Now confirm the formal charge on oxygen.

$$\text{Formal charge} = 6 - 6 - \frac{1}{2}(2) = -1$$

The above structure is a valid Lewis structure for the molecule. Decide whether or not there are any valid resonance contributors by exploring ways of moving nonbonding and bonding electrons. This structure has two resonance contributors.



Finally, the more important contributor (see rule 8, page 000) is the one on the left.

Key Ideas from Chapter 1

- Electrons in atoms and molecules exist only in certain allowed energy states, called orbitals. These orbitals are regions of probability for finding an electron.
- An orbital has nodes, or regions, where there is no electron density. These nodes separate the electron wave peaks from the wave troughs or other peaks.
- The distribution of electron density in a given type of orbital has a characteristic arrangement in space. All *s* orbitals are spheres; all *p* orbitals have two lobes.
- Hybrid orbitals form by mixing atomic orbitals. The VSEPR model predicts the orientation of these hybrid orbitals in space.
- Bonds form when orbitals on different atoms overlap. Overlap of the 1s orbitals of two hydrogen atoms results in the formation of two molecular orbitals—one bonding and the other antibonding.

- The Aufbau Principle, Hund's Rule, and the Pauli Exclusion Principle determine the arrangement of electrons in both the atomic and molecular orbitals.
- Chemical compounds contain two types of bonds—ionic and covalent. In ionic compounds, electrostatic attraction holds the ions together. In covalent compounds, the atoms are held together by the sharing of electrons.
- When the second-row elements form chemical compounds, they tend to follow the Octet Rule. That is, each atom surrounds itself with eight electrons.
- Drawing a Lewis structure for a molecule requires that, as far as possible, each atom have an octet of electrons and that charge separation be minimized.
- In covalent compounds, atoms sometimes share electrons unequally and may give a molecule a dipole moment. A dipole moment is the vector sum of the dipoles of individual bonds.
- The formal charge convention assigns the total charge of a given chemical species to its constituent atoms. It also determines whether an uncharged species may have equal numbers of positive and negative charges present in the molecule.
- A single Lewis structure cannot always adequately represent an ion or molecule. For some cases, draw resonance structures by shifting nonbonding and/or π bonding electrons. The actual molecule is the weighted sum of its resonance contributors.

Supplementary Exercises

1.14 For each of the following compounds, tell whether the bonds are ionic or covalent. If covalent, show the polarity by drawing an arrow

() indicating the direction of the dipole.

- | | | | |
|-------------------|-----------------|------------------|-------------------|
| a) CaF_2 | b) NaH | c) FCl | d) SiH_4 |
| e) BeF_2 | f) NaI | g) BH_3 | h) PH_3 |

1.15 Draw Lewis structures for each of the following compounds showing all bonds, any nonbonding electrons present, and any formal charges.

- | | | |
|-----------------------------|--------------------------------------|--------------------------------------|
| a) AlCl_3 | b) NF_3 | c) H_2O_2 |
| d) SO_2 | e) $\text{CH}_3\text{NH}_3\text{Cl}$ | f) $\text{CH}_3\text{CH}_2\text{OH}$ |
| g) CH_3NHOH | h) CH_3SCH_3 | |

1.16 Indicate which of the following molecules have a dipole moment. Using the geometry of orbital hybridization, draw a three-dimensional representation of the molecule and show the direction of the dipole for the molecule using an arrow ($\text{+} \longrightarrow$).

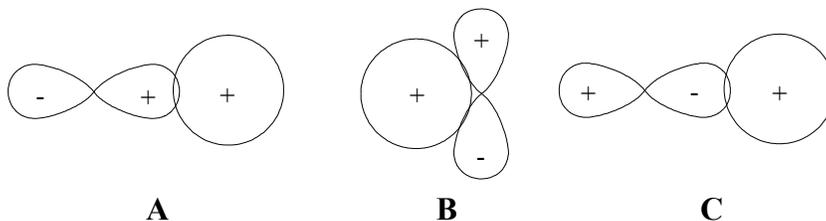
- | | | |
|---------------------------------------|---------------------------------|------------------------------|
| a) CCl_4 | b) CFBr_3 | c) CH_3NH_2 |
| d) CH_3Cl | e) $\text{CH}_2=\text{CHBr}$ | f) CH_3OCH_3 |
| g) $\text{CH}_3\text{CH}=\text{CH}_2$ | h) $\text{CH}_3\text{CHClCH}_3$ | |

1.17 The compounds ICl and FCl have dipole moments that are similar in magnitude (0.7 D and 0.9 D) but opposite in direction. Specify the direction of each dipole moment. Explain your reasoning.

1.18 Sulfur dioxide has a dipole moment of 1.6 D. Carbon dioxide has a dipole moment of zero, even though the $\text{C}=\text{O}$ bonds are more polar than the $\text{S}=\text{O}$ bonds. Explain.

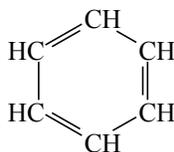
1.19 Two hydrogen atoms ($\text{H}\cdot$) prefer to share electrons and form H_2 rather than forming H^{\oplus} and H^{\ominus} by transferring an electron. Why?

1.20 Below are three types of orbital overlaps. One is bonding, one is antibonding, and one is nonbonding. Which orbital overlap corresponds to which type of interaction? Explain.

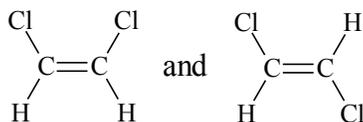


1.21 The hydrogen molecular ion, H_2^{\oplus} , is widely found in molecular clouds in interstellar space as a result of cosmic ray bombardment of H_2 . Is the dissociation of this ion into a hydrogen atom ($\text{H}\cdot$) and a hydrogen ion (H^{\oplus}) exothermic (releases energy) or endothermic (requires energy)?

1.22 Chemists took a number of years to deduce the structure of benzene. Given the experimental fact that all of the C—C bonds in benzene are equal in length, why is the structure shown below inaccurate? What is necessary to make a more accurate representation?

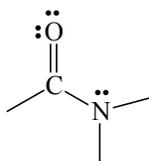


1.23 Two isomers of 1,2-dichloroethene can be differentiated by their dipole moments. One has a dipole moment $\mu = 1$ D and the other $\mu = 0$ D. Assign the dipole moments to the following structures:



Isomers of 1,2-dichloroethene

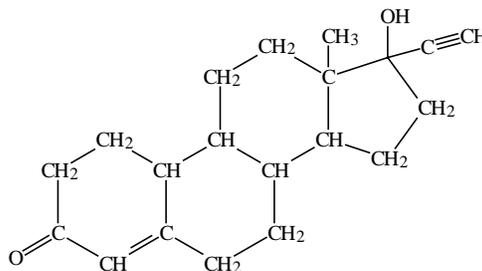
1.24 The structure of proteins depends on the amide functional group, shown below, because such groups make up the backbone of proteins. Resonance best explains the properties of the amide group. Write the three resonance contributors for the amide group. Discuss the relative stability of each contributor.



1.25 Draw the Lewis structures of isocyanic acid (HNCO) and cyanic acid (HOCN).

- These structures are not resonance structures. Explain.
- When either acid loses a proton, the same ion results. Explain.

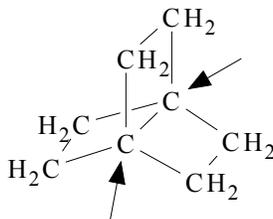
1.26 Norethindrone is an example of a molecule used in oral contraceptives. In this molecule, locate an example of each of the following types of atoms or bonds. (Ignore any bonds to hydrogen.)



Norethindrone

- A nonpolar covalent bond.
- A highly polarized covalent bond.
- An sp hybridized atom.
- An sp^2 hybridized atom.
- An sp^3 hybridized atom.
- A bond between atoms of different hybridizations.

1.27 Below is the complex molecule [2.2.2]propellane. Given the fact that the $\text{CH}_2\text{—C—CH}_2$ bond angle is 120° , what hybridization would you expect for the carbons designated by the arrows? What orbitals are involved in the bonding of those two carbons?



1.28 Imagine that the carbon atom of CH_2Cl_2 has some orbital hybridization other than sp^3 . With this other hybridization, the compound has a planar structure placing the carbon at the center and the other four atoms at the corners of a square. Using this hybridization, the compound has more than one distinct structure.

- How many structures are there? Draw them.
- Suppose you have samples of each of these compounds. How would measurement of the dipole moment help you distinguish the isomers?

1.29 The van der Waals radius of sulfur is greater than that of an oxygen atom. How might that account for the fact that the H—S—H bond angle (92.2°) is less than the H—O—H bond angle (104.5°) of water? What orbitals from sulfur are involved in the bonds?

1.30 The C—O bond dipole is large—usually greater than 1.5 D. Surprisingly, carbon monoxide (CO) has a small dipole moment of 0.1 D. This fact puzzled chemists and led to many experiments and theoretical discussions. What explanation can you give?

- Draw a Lewis structure for CO.
- There are three resonance contributors for the structure of CO. Draw and analyze them for formal charge and whether or not each atom has an octet of electrons.
- Carbon monoxide is highly toxic because it binds tightly to the iron ($\text{Fe}^{2\oplus}$) in hemoglobin and prevents oxygen transport by the hemoglobin. What does this tell you about the relative importance of the various resonance contributors for CO?

1.31 Allene has the structural formula $\text{CH}_2=\text{C}=\text{CH}_2$. What is the hybridization of each of the three carbon atoms? What orbitals are involved in the bonds of this molecule? What shape does the molecule have?

1.32 Consider the N—Br bond. Given the fact that nitrogen and bromine have nearly the same electronegativity (3.04 and 2.96), answer the following questions. Is the N—Br bond covalent, polar covalent, or ionic? Explain your answer. Is the N—Br bond a stable bond?

1.33 Account for the differences in bond length for the series of compounds in the table below:

Compound	C—Cl bond length, pm
$\text{H}_3\text{C—Cl}$	178
$\text{ClH}_2\text{C—Cl}$	177
$\text{Cl}_2\text{HC—Cl}$	176
$\text{FH}_2\text{C—Cl}$	176
$\text{Cl}_3\text{C—Cl}$	175
$\text{F}_3\text{C—Cl}$	172

1.34 Addition of an electron to a hydrogen molecule (H_2) leads to a very unstable hydrogen anion, H_2^\ominus . Why is this species unstable?