Abdelhafid Boussouf University Centre of Mila

Institute of Natural and Life Sciences,

Common Core Department

Abdelhafid Boussouf University Centre of Mila

General Chemistry

Course Support

Chapter N° 6
Chemical Bonding and Molecular Geometry

(Update : 23/10/2023)

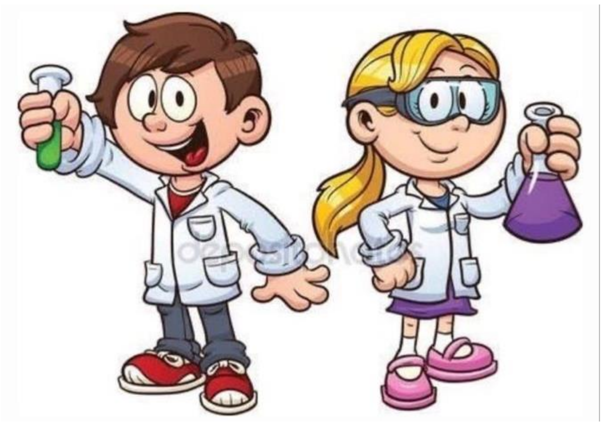


Table des matières

VI. Chemical Bonding and Molecular Geometry

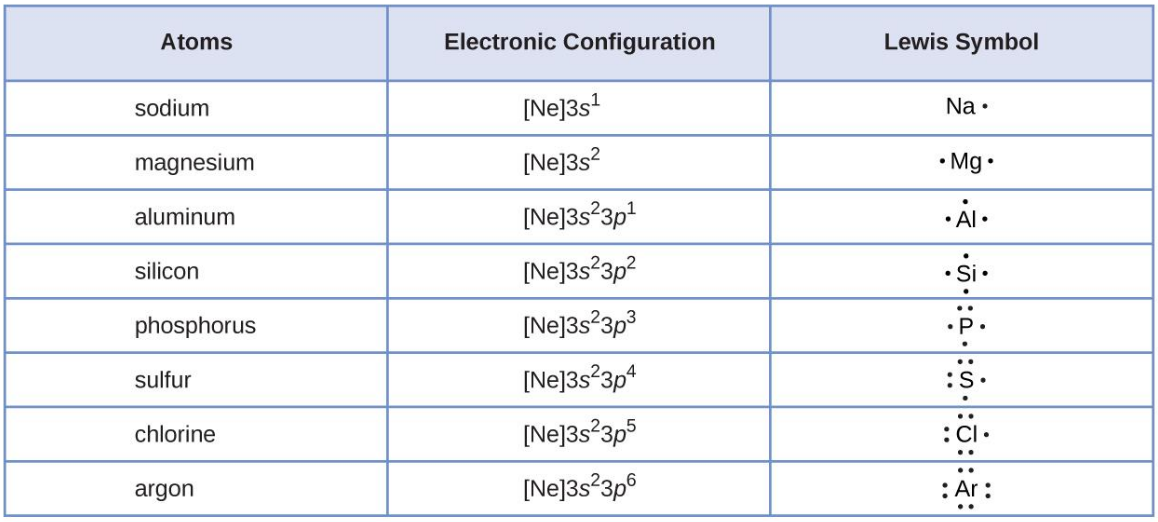
In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

VI.1 Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A **Lewis symbol** consists of an elemental symbol surrounded by one dot for each of its valence electrons:

•Ca•

Figure 6.1 shows the Lewis symbols for the elements of the third period of the periodic table.



Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na •
magnesium	$[Ne]3s^2$	• Mg •
aluminum	$[Ne]3s^23p^1$	• Al •
silicon	$[Ne]3s^23p^2$	• Si •
phosphorus	$[Ne]3s^23p^3$	• P •
sulfur	$[Ne]3s^23p^4$	: S •
chlorine	$[Ne]3s^23p^5$	: Cl •
argon	$[Ne]3s^23p^6$	: Ar :

Figure 6.1 Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium

Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:

Figure 6.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

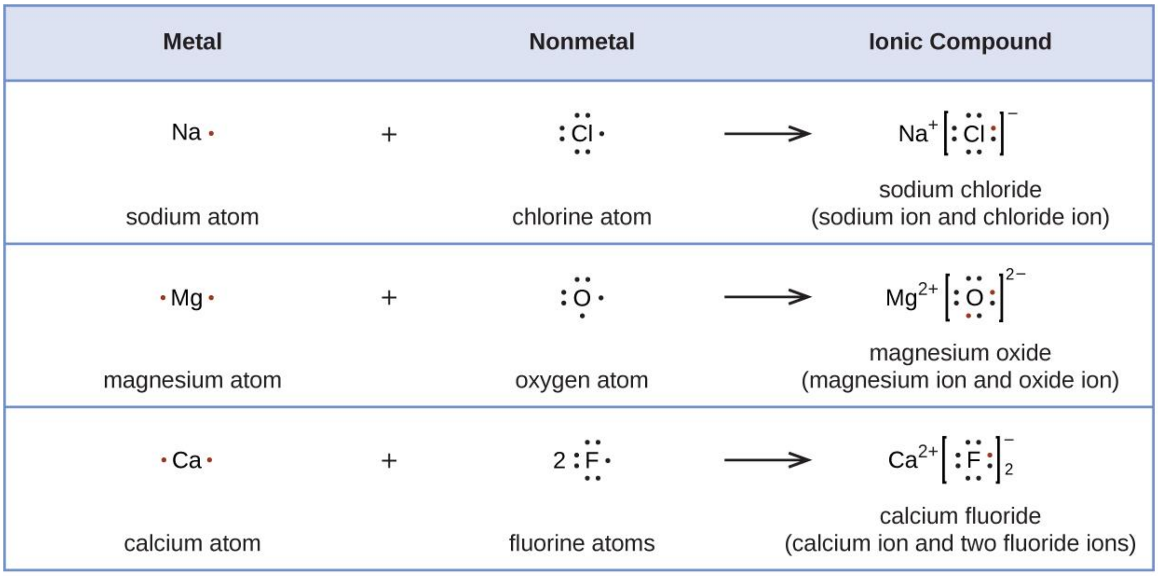
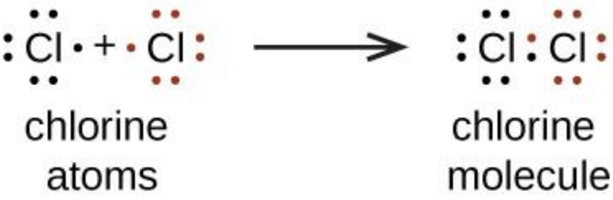


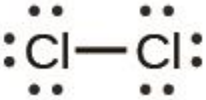
Figure 6.2 Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

VI.2 Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

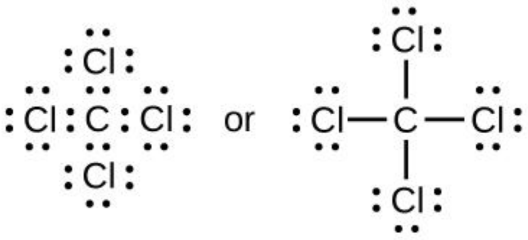


A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

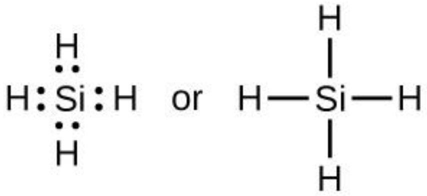
VI.3 The Octet Rule

The other halogen molecules (F2, Br2, I2, and At2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule.**

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:

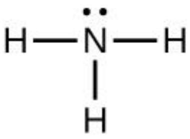


carbon tetrachloride

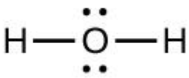


silane

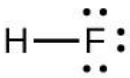
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia



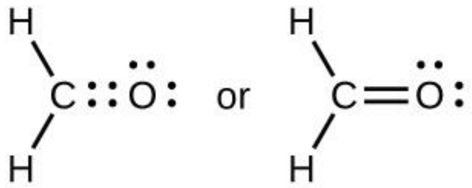
Water



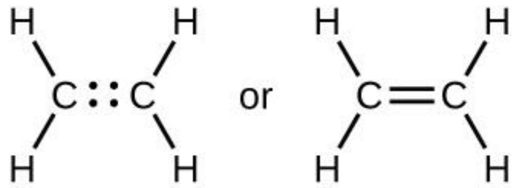
hydrogen fluoride

VI.3.1 Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

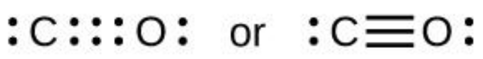


formaldehyde

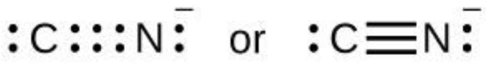


ethylene

A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN–):



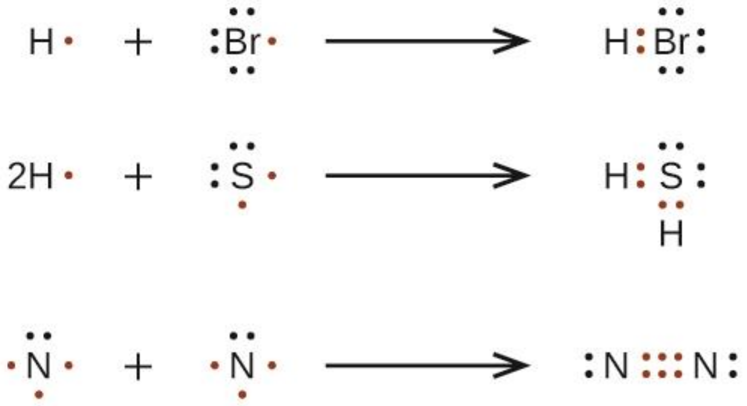
carbon monoxide



cyanide ion

VI.3.2 Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.

- For a molecule, we add the number of valence electrons on each atom in the molecule:

SiH4

Si: 4 valence electrons/atom×1 atom=4
+H: 1 valence electron/atom×4 atoms=4

=8 valence electrons

- For a negative ion, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

CHO_2^-
C: 4 valence electrons/atom×1 atom=4
H: 1 valence electron/atom×1 atom=1
O: 6 valence electrons/atom×2 atoms=12
+1 additional electron=1

=18 valence electrons

- For a positive ion, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

NO^+
N: 5 valence electrons/atom×1 atom=5
O: 6 valence electron/atom×1 atom=6
+ −1 electron (positive charge) =−1

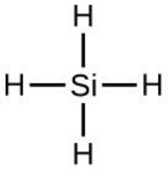
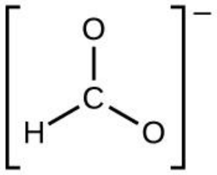
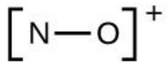
=10 valence electrons

- Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

OF_2
O: 6 valence electrons/atom×1 atom=6
+F: 7 valence electrons/atom×2 atoms=14

=20 valence electrons

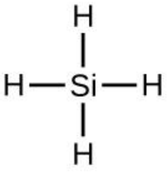
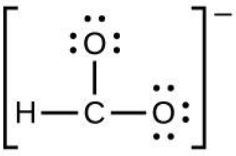
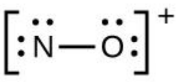
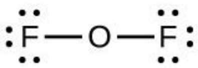
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)


When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- There are no remaining electrons on SiH4, so it is unchanged:

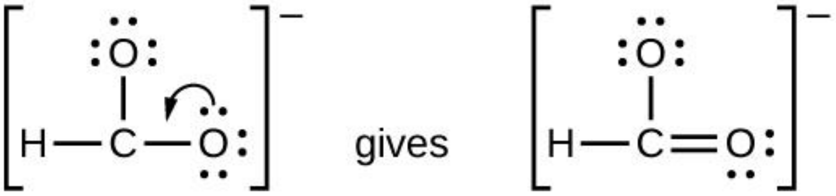





4. Place all remaining electrons on the central atom.

- For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
- For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

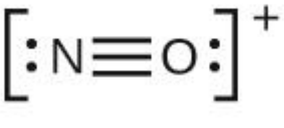
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

- SiH_4: Si already has an octet, so nothing needs to be done.
- CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:

This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

EXAMPLE 1

Writing Lewis Structures

NASA’s Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn’s moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

Step 1. Calculate the number of valence electrons.

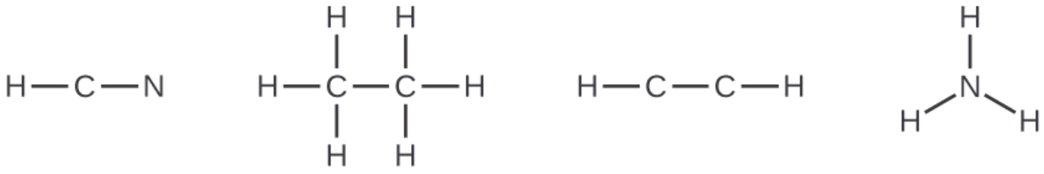
HCN: (1 × 1) + (4 ×1) + (5 ×1) = 10

H_3CH_3: (1 ×3) + (2 ×4) + (1 ×3) = 14

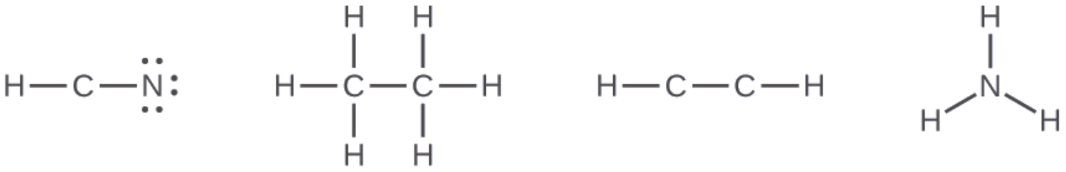
HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10

NH_3: (5 × 1) + (3 ×1) = 8

Step 2. Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:



Step 3. Where needed, distribute electrons to the terminal atoms:



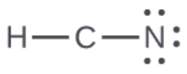
HCN: six electrons placed on N

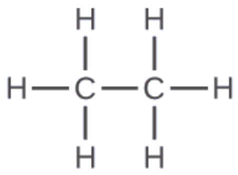
H_3CCH_3: no electrons remain

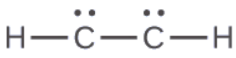
HCCH: no terminal atoms capable of accepting electrons

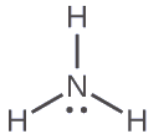
NH_3: no terminal atoms capable of accepting electrons

Step 4. Where needed, place remaining electrons on the central atom:









HCN: no electrons remain

H_3CCH_3: no electrons remain

HCCH: four electrons placed on carbon

NH_3: two electrons placed on nitrogen

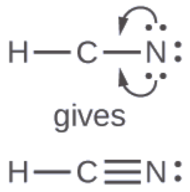
Step 5. Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

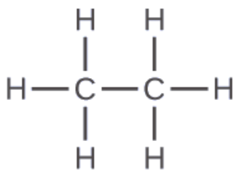
HCN: form two more C–N bonds

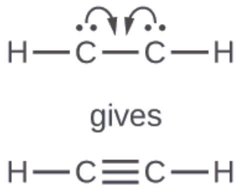
H_3CCH_3: all atoms have the correct number of electrons

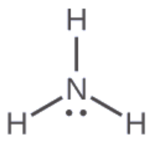
HCCH: form a triple bond between the two carbon atoms

NH_3: all atoms have the correct number of electrons









Check Your Learning

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

ANSWER:

Two Lewis structures are shown. The left shows a carbon triple bonded to an oxygen, each with a lone electron pair. The right structure shows a carbon double bonded to an oxygen on each side. Each oxygen has two lone pairs of electrons.

VI.3.3 Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

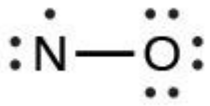
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

VI.3.4 Odd-electron Molecules

We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

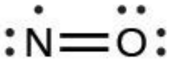
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. Determine the total number of valence (outer shell) electrons. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. Draw a skeleton structure of the molecule. We can easily draw a skeleton with an N–O single bond: N–O
3. Distribute the remaining electrons as lone pairs on the terminal atoms. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus, oxygen has the filled valence shell:



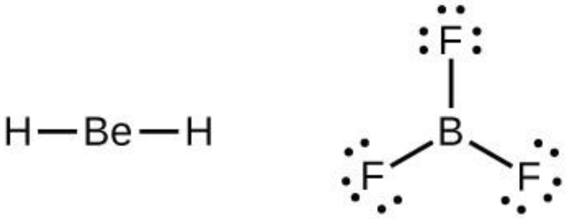
4. Place all remaining electrons on the central atom. Since there are no remaining electrons, this step does not apply.
5. Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible. We know that an odd-electron molecule cannot have

an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

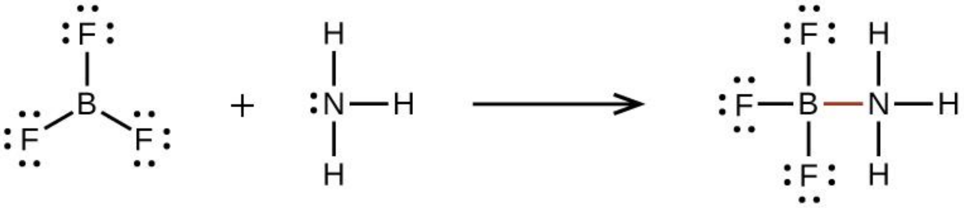


VI.3.5 Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



VI.3.6 Hypervalent Molecules

Elements in the second period of the periodic table (n = 2) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2s and three 2p orbitals). Elements in the third and higher periods (n ≥ 3) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty d orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. **Figure 6.3** shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

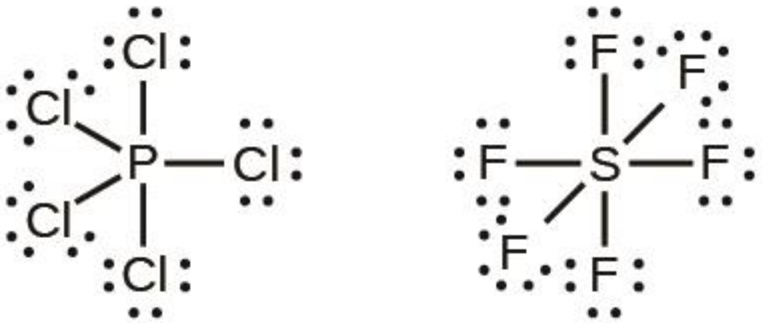
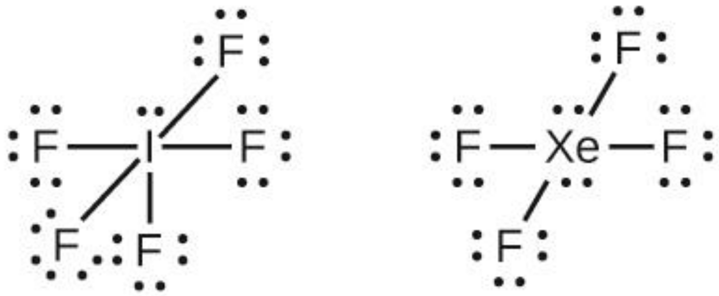


Figure 6.3 In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

EXAMPLE 2

Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

Solution

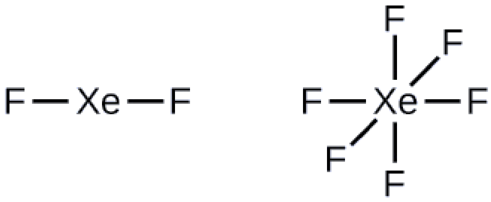
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. Calculate the number of valence electrons:

XeF_2: 8 + (2 ×7) = 22

XeF_6: 8 + (6 ×7) = 50

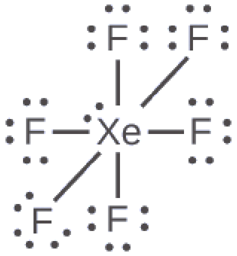
Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:



Step 3. Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell d orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:

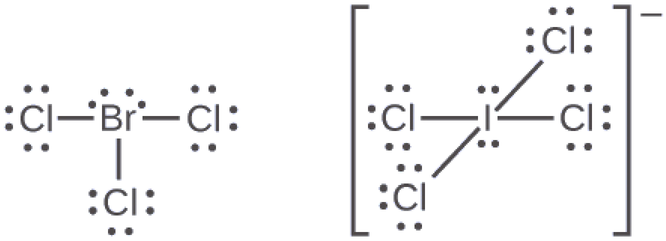
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Check Your Learning

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

ANSWER:



VI.4 Molecular Structure and Polarity

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (**Figure 6.4**). A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond distance** (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Angstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

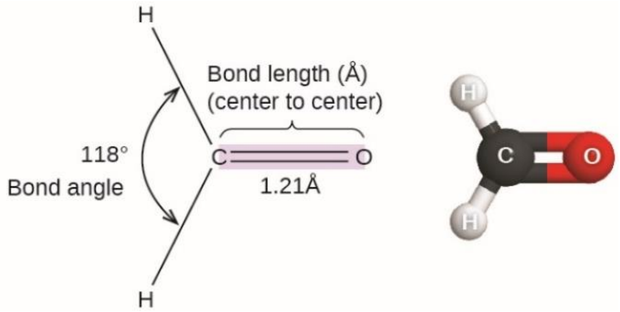


Figure 6.4 Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VI.5 VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (**Figure 6.5**) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (**Figure 6.5**).

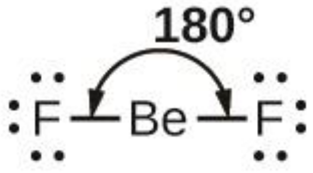


Figure 6.5 The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 6.6 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a **linear** geometry; three regions form a **trigonal planar** geometry; four regions form a **tetrahedral** geometry; five regions form a **trigonal bipyramidal** geometry; and six regions form an **octahedral** geometry.

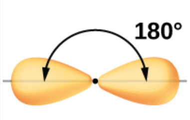
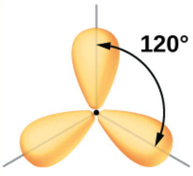
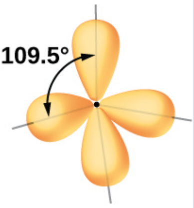
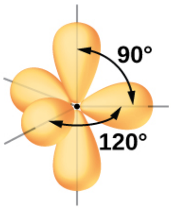
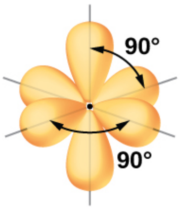
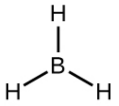
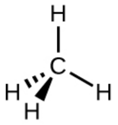
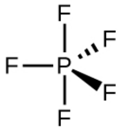
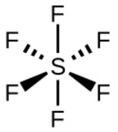
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	H—Be—H				
Electron region geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 6.6 The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

VI.5.1 Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is not the same thing as its molecular structure. The electron-pair geometries shown in **Figure 6.6** describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the atoms, not the electrons.

We differentiate between these two situations by naming the geometry that includes all electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the **molecular structures** when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (**Figure 6.7**). On the other hand, the ammonia molecule, NH3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (**Figure 6.8**).

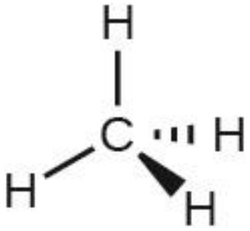


Figure 6.7 The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

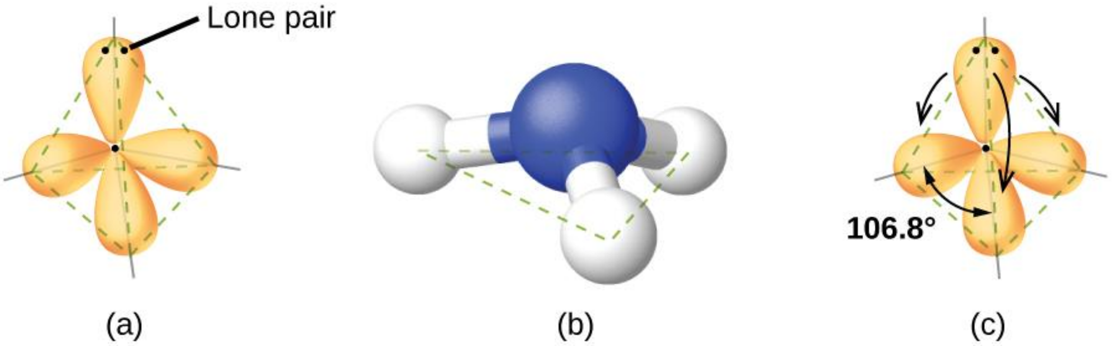


Figure 6.8 (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

As seen in **Figure 6.8**, small distortions from the ideal angles in **Figure 6.6** can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair>lone pair-bonding pair>bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

lone pair>triple bond>double bond>single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (**Figure 6.4**). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (**Figure 6.8**) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (**Figure 6.6**) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (**Figure 6.8**). **Figure 6.9** illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

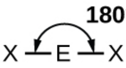
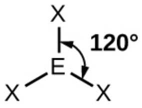
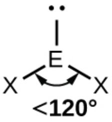
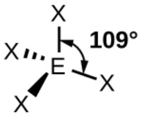
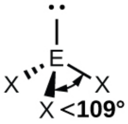
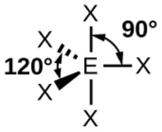
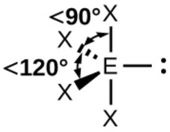
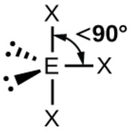
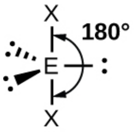
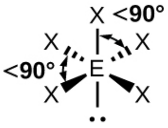
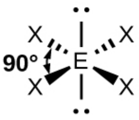
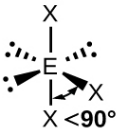
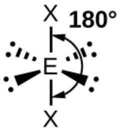
Number of electron regions	Electron region geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure 6.9 The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in **Figure 6.9**) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in **Figure 6.10**: an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in **Figure 6.9**, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (**Figure 6.10**). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

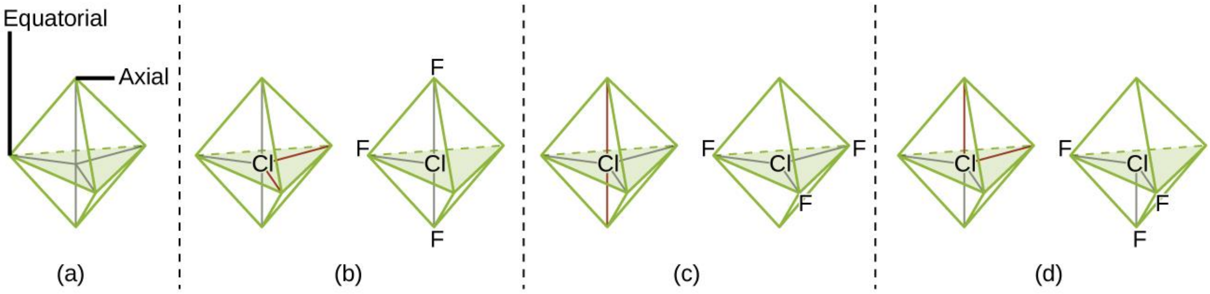


Figure 6.10 (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (**Figure 6.9**).

VI.5.2 Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (**Figure 6.9**, first column).
4. Use the number of lone pairs to determine the molecular structure (**Figure 6.9**). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space

than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

EXAMPLE 3

Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

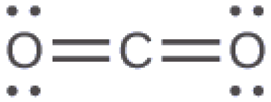
Predict the electron-pair geometry and molecular structure for each of the following:

(a) carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels

(b) boron trichloride, BCl3, an important industrial chemical

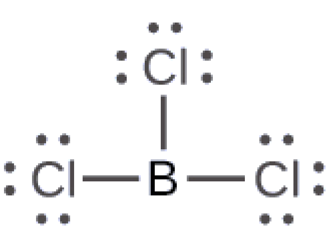
Solution

(a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus, we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure (**Figure 6.11**).

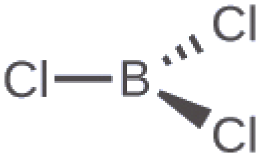


Figure 6.11

The electron-pair geometry and molecular structure of BCl3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

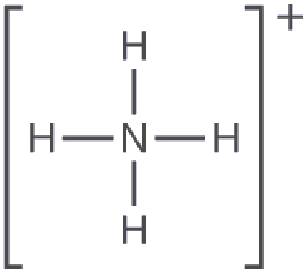
EXAMPLE 4

Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (**Figure 6.9**). Therefore, the electron pair geometry of NH_4^+ is tetrahedral, and the molecular structure is also tetrahedral (**Figure 6.12**).

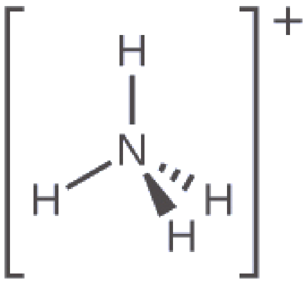


Figure 6.12 The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

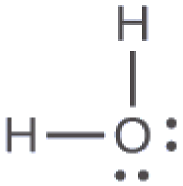
EXAMPLE 5

Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (**Figure 6.13**), as indicated in **Figure 6.9**. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

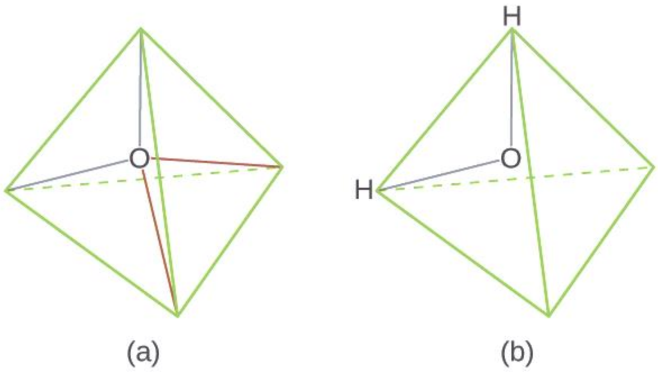


Figure 6.13 (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

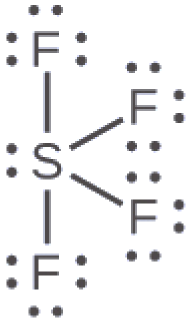
EXAMPLE 6

Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (**Figure 6.14**) is that of a seesaw (**Figure 6.9**).

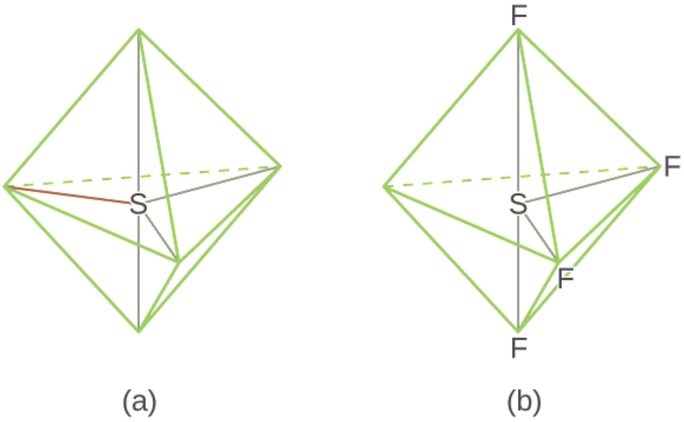


Figure 6.14 (a) SF_4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

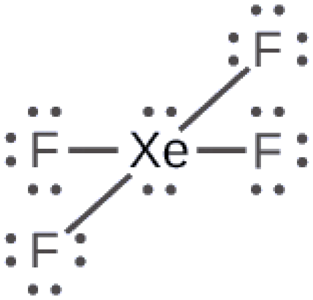
EXAMPLE 7

Predicting Electron-pair Geometry and Molecular Structure: XeF_4

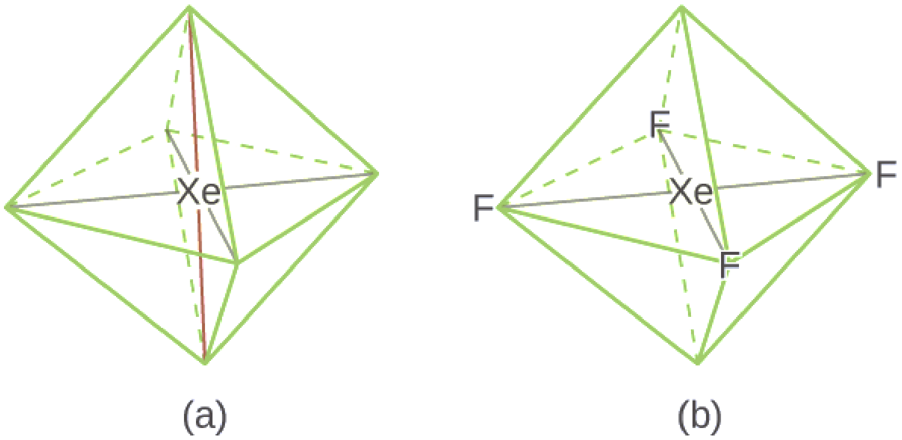
Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (**Figure 6.9**), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (**Figure 6.15**). The five atoms are all in the same plane and have a square planar molecular structure.



(a) (b)

Figure 6.15 (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

VI.6 Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond dipole moment**. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu=Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude (**Figure 6.16**). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

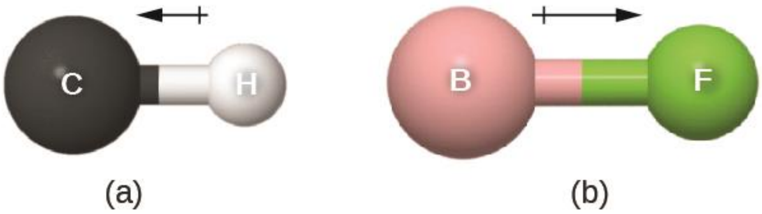


Figure 6.16 (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or dipole); otherwise, the molecule is said to be nonpolar. **The dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br2 and N2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (**Figure 6.17**). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (**Figure 6.17**), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

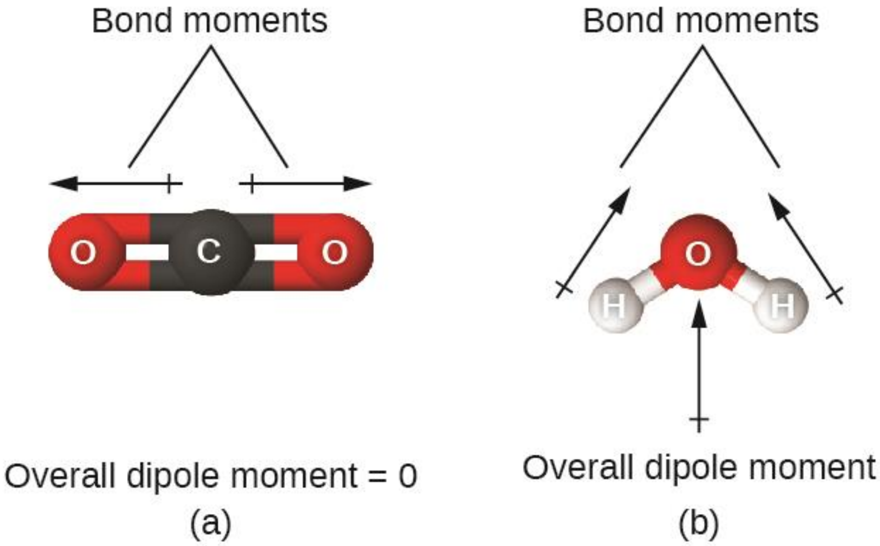
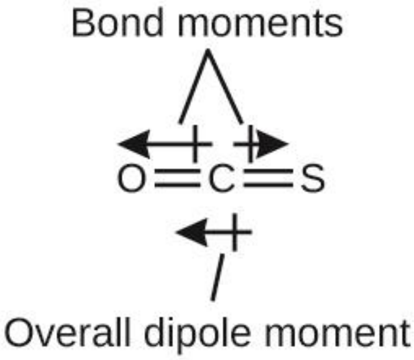


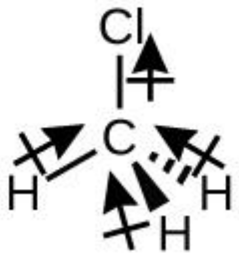
Figure 6.17 The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

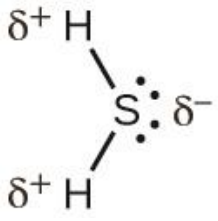


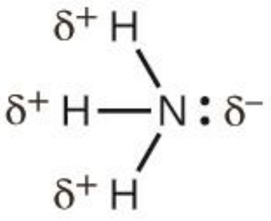
The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is H < C < Cl, and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).



For molecules of high symmetry such as BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), all the bonds are of identical polarity (same bond moment) and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of such molecules include hydrogen sulfide, H_2S (nonlinear), and ammonia, NH_3 (trigonal pyramidal).





To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

VI.6.1 Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (**Figure 6.18**). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

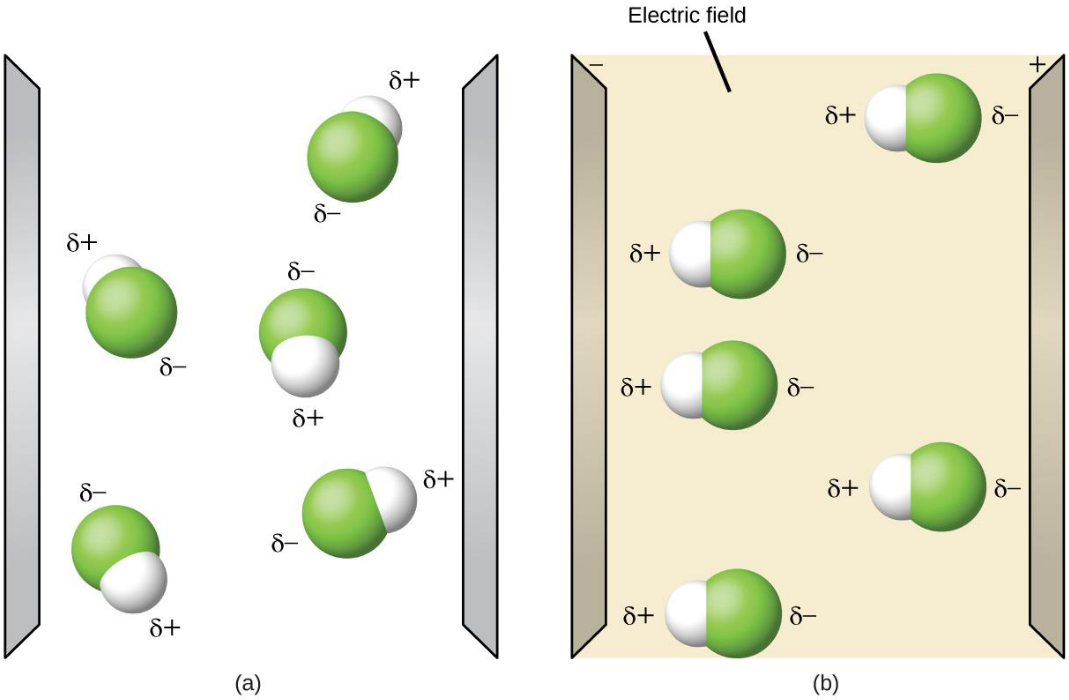


Figure 6.18 (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

VI.7 Atomic Orbital Overlap

There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an s orbital, a dumbbell shape for a p orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms **overlap** when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met: (1) an orbital on one atom overlaps an orbital on a second atom and (2) the single electrons in each orbital combine to form an electron pair. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. **Figure 6.19** illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of **Figure 6.19.**

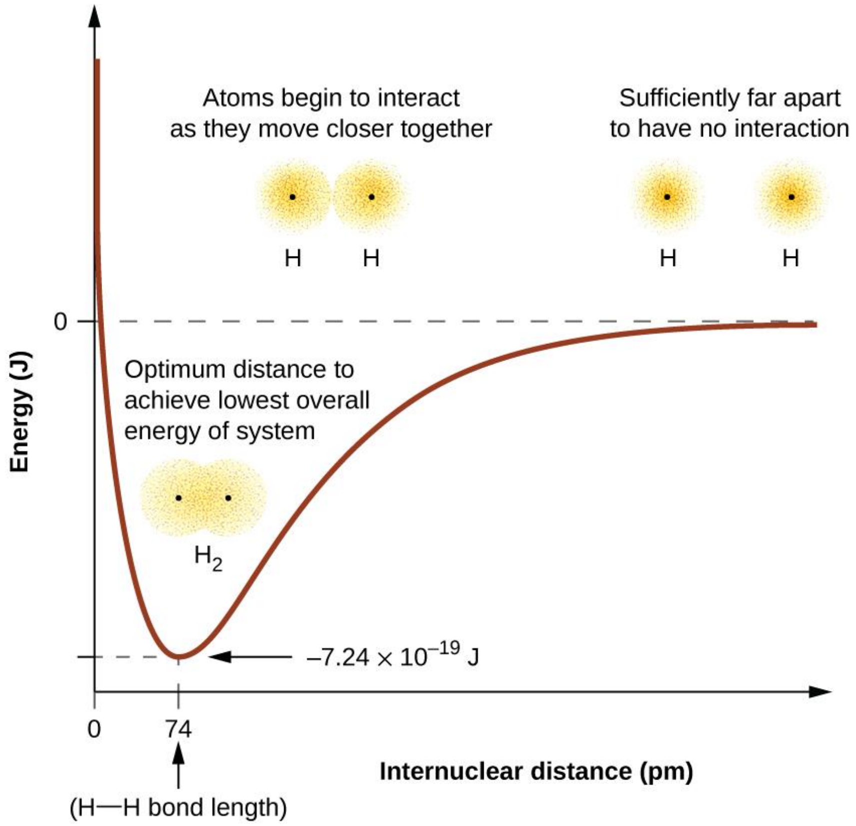


Figure 6.19 (a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interacts. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two s orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. **Figure 6.20** illustrates this for two p orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

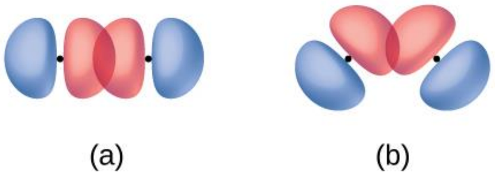


Figure 6.20 (a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two s orbitals (as in H_2), the overlap of an s orbital and a p orbital (as in HCl), and the end-to-end overlap of two p orbitals (as in Cl_2) all produce **sigma bonds (σ bonds),** as illustrated in **Figure 6.21**. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

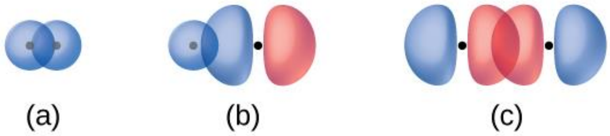


Figure 6.21 Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.

A **pi bond (π bond)** is a type of covalent bond that results from the side-by-side overlap of two p orbitals, as illustrated in **Figure 6.22**. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

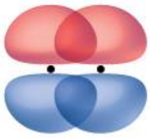
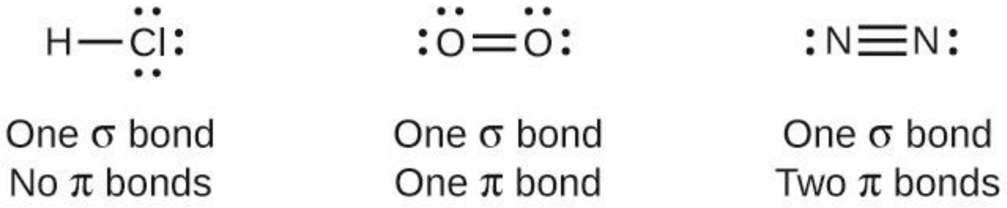


Figure 6.22 Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures below suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.



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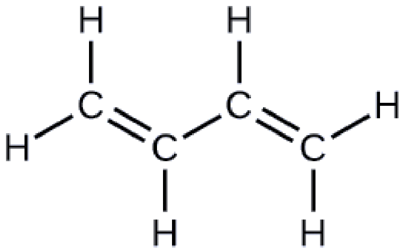
EXAMPLE 8

Counting σ and π Bonds



Butadiene, C_4H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.

Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

VI.8 Dipole Moments and Ionic Character

Now that we have seen the importance of understanding the connection between the location of electrons in atoms and the properties of elements, we can expand our understanding of the connection between atoms. This will be an introduction to more advanced aspects of the chemical bond, which is the very heart of chemistry itself. With the sole exception of the noble gases, atoms by themselves do not possess the most stable possible electron configuration. That is where the concept of chemical bonding comes into its own: atoms can attain a stable configuration by exchanging electrons with another atom, resulting in the formation of ions.

Ions, in turn, can associate by charge – simple Coulombic attraction – resulting in the formation of compounds we call ionic compounds. We will look at the ionic nature of bonds first, from a simple positive-negative attraction standpoint. Just as important is that some atoms bond by sharing rather than exchanging electrons; the sharing of electrons gives rise to the covalent bond. To add just one more dimension, some chemical species are neither completely ionic nor completely covalent; these species possess a permanent dipole, and are classified as polar.

In your introductory physics course, you will likely discuss the concept of Coulombic interactions in much more rigorous detail than we will do here. We are interested primarily in the differences in properties between species that arise from their relative covalent, ionic, or polar nature – not in a rigorous model of those properties. We are concerned with the connection between potential energy and force and the relative separation (or lack of separation) between charges. We begin by defining the electric or Coulomb force as the product of the charges divided by the square of the distance between those charges:

$$F = \frac{Q_1 Q_2}{d^2}$$

Here, Q is taken to be the fundamental constant of electron charge: one electron has a charge of 1.60218×10^{-19}C. (We will work exclusively in the SI system, so distances will be measured in meters (m)).

And as you may recall, energy is force times distance, so

$$E = \frac{Q_1 Q_2}{d}$$

To illustrate the trend in attractive force, we will consider first the attractive force between two ions of single charge separated by a distance of 2d:

$$F = \frac{(1)(-1)}{(2d)^2} = -\frac{1}{4d^2}$$

And then the attractive force between two ions of double charge separated by a distance d:

$$F = \frac{(2)(-2)}{(d)^2} = -\frac{4}{d^2}$$

The force of attraction increases with the charge and decreases with increased distance. If all matter were composed of ions that would be the end of the story, but it clearly is not. There are molecules for which the charge – either positive or negative – is permanently concentrated more on one atom than the other. Notice we say atom, because these compounds are not composed of ions but rather of atoms sharing electrons through covalent bonds.

VI.8.1 Bond Dipole Moments

The concept of a bond dipole moment allows us to examine the partial separation of charge between atoms. It is a simple model when applied to diatomic molecules, which will be more than sufficient for our purposes. The dipole moment of a bond is defined as the charge times the distance – charge once again being measured in multiples of the charge on an electron, or coulombs. The distance will always be in meters. Because we are considering very small charges and distances, and because it is the relative separation of charge rather than the actual value for it that we are interested in, we will introduce a new unit called the Debye, named after the physical chemist Peter Debye:

1 Debye(D)=3.336×10^{-30}C-m $\mu=Q\times d$

The usefulness of the Debye unit will be shown by example:

For HCl, the bond dipole moment is known to be 1.08 D

For HI, the bond dipole moment is known to be 0.44 D

Comparing the two, we can see that HI is less polar than HCl, which is what we would expect based on electronegativity values.

We have now made a transition between the concept of an ionic compound and a partially ionic one. Of course, the partially ionic compound must also by definition be partially covalent.

VI.8.2 Partial Ionic Character

The concept of the bond dipole moment helps bridge the concepts of ionic and covalent bonding. Because there is a separation of charge that is less complete than it is in an ionic bond, we can refer to polar bonds as being partially ionic in nature. In contrast to sodium chloride, hydrogen chloride shows partial charges (indicated with a delta notation) on the hydrogen and chlorine. As you would expect from the electronegativity values, hydrogen carries a partial positive charge, while chlorine carries a partial negative charge. Where do these charges come from?

It is easy to come up with the partial charges by comparing the actual dipole moments (which can be obtained experimentally, using spectroscopy) with the dipole expected in the limiting case (that is, if we were to consider the molecule ionic). The actual dipole moment is 1.03 D.

EXAMPLE 9

Finding the Partial Ionic Character

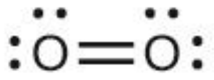
What are the partial charges of an HCl molecule, whose bond length is 0.127 nm?

Solution

The bond dipole moment is (1.60218×10^{-19}C) (0.127×10^{-9}m) or 2.03×10^{-29}C-m.

Converted to D, this is (2.03×10^{-29}C-m) (1Debye/3.336×10^{-30}C-m) or 6.09 D. Were HCl completely ionic, this would be its molecular dipole moment. To get the partial ionic character, we divide the experimentally measured bond moment by this limiting value: %ionic character=μexp/μlim×100%= (1.03D/ (6.09D) ×100%=17%. This means the bond is about 17% ionic – or, put another way, the positive charge in H is +0.17 and the partial negative charge on chlorine, –0.17.

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called **paramagnetism**, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (**Figure**

6.23), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

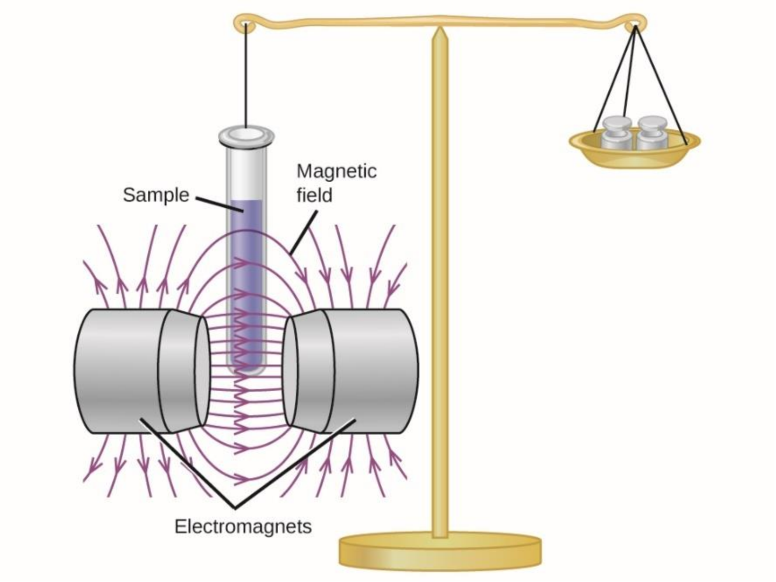


Figure 6.23 A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

LINK TO LEARNING

Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate.

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. **Table 6.1** summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Valence Bond Theory	**Molecular Orbital Theory**
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Table 6.1

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a **molecular orbital (Ψ^2).** Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called **homonuclear diatomic molecules**. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals (LCAO).** The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (**Figure 6.24**). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

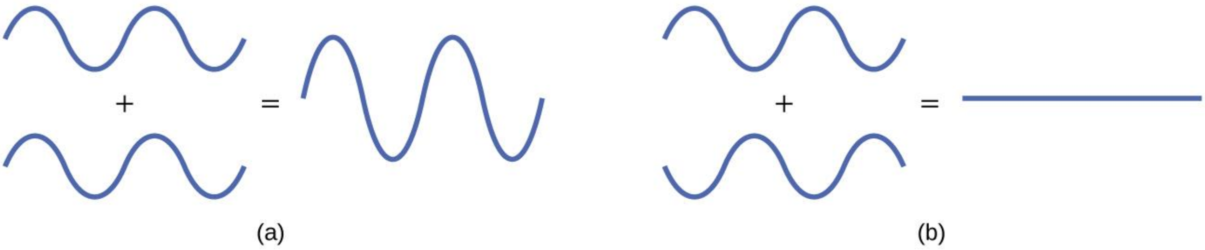


Figure 6.24 (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

There are two types of molecular orbitals that can form from the overlap of two atomic s orbitals on adjacent atoms. The two types are illustrated in **Figure 6.25**. The in-phase combination produces a lower energy **σ_s molecular orbital** (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy **$\sigma*_s$ molecular orbital** (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σs orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals **bonding orbitals**. Electrons in the $\sigma*_s$ orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called **antibonding orbitals**. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

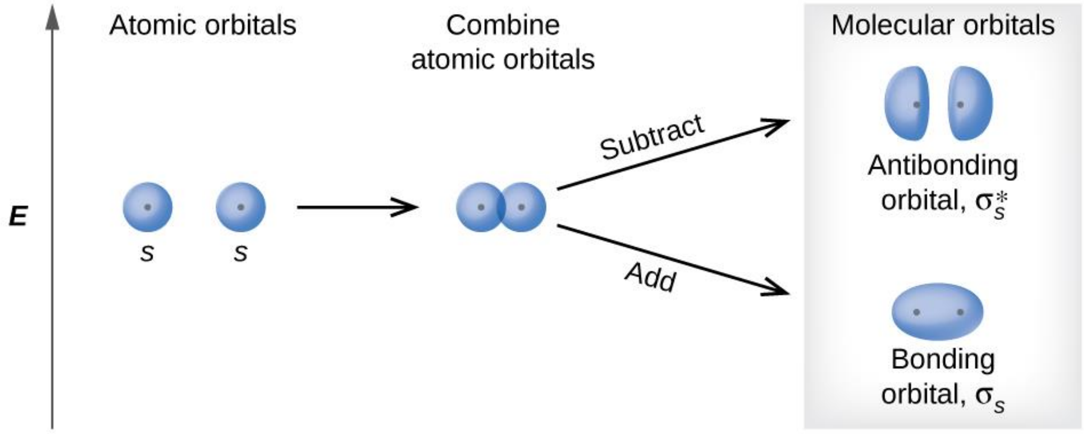


Figure 6.25 Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The dots (·) indicate the locations of nuclei.

In p orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When p orbitals overlap end to end, they create σ and σ* orbitals (**Figure 6.26**). If two atoms are located along the x-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and $\sigma*_{px}$ (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with s-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

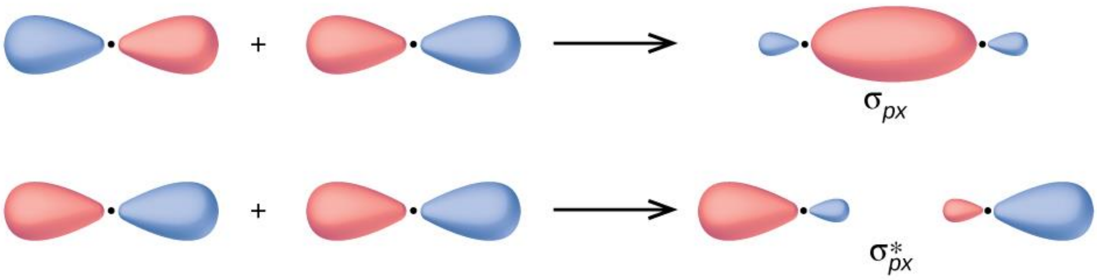


Figure 6.26 Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and $\sigma*_p$.

The side-by-side overlap of two p orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibonding molecular orbital**, as shown in **Figure 6.27**. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the p orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

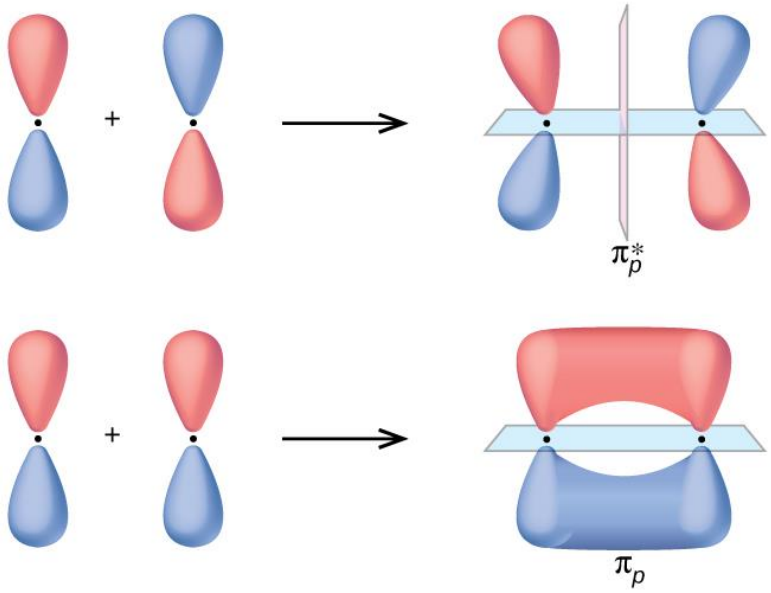


Figure 6.27 Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

In the molecular orbitals of diatomic molecules, each atom also has two sets of p orbitals-oriented side by side (py and pz), so these four atomic orbitals combine pairwise to create two π orbitals and two π* orbitals. The πpy and π∗py orbitals are oriented at right angles to the πpz and π∗pz orbitals. Except for their orientation, the πpy and πpz orbitals are identical and have the same energy; they are degenerate orbitals. The π∗py and π∗pz antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic p orbitals in two atoms: σpx and σ∗px, πpy and π∗py, πpz and π∗pz.

VI.8.3 Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a **molecular orbital diagram** (**Figure 6.28**). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus, we can see that combining the six 2p atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (**Figure 6.28**). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus, we would expect a diatomic molecule or ion containing seven electrons (such as Be_2^+)

would have the molecular electron configuration $(\sigma 1s)^2(\sigma{*}1s)^2(\sigma 2s)^2(\sigma{*}2s)^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

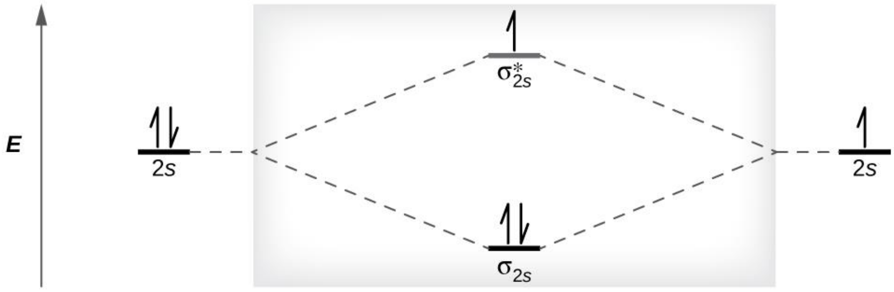


Figure 6.28 This is the molecular orbital diagram for the homonuclear diatomic Be_2^+, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

VI.8.4 Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the **bond order** that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus, a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

VI.8.5 Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the $\sigma1s$ bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms. The $\sigma1s$ orbital that contains both electrons are lower in energy than either of the two 1s atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the $\sigma1s$ bonding orbital; the electron configuration is $(\sigma1s)^2$. We represent this configuration by a molecular orbital energy diagram (**Figure 6.29**) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

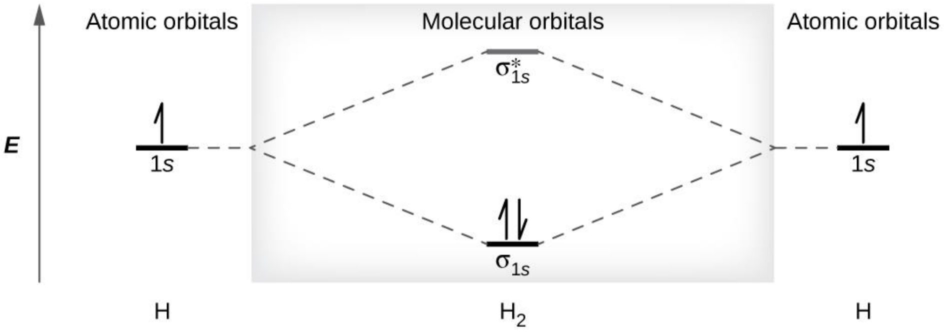


Figure 6.29 The molecular orbital energy diagram predicts that H2 will be a stable molecule with lower energy than the separated atoms.

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in H}_2 = \frac{(2-0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its 1s orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as $(\sigma 1s)^2(\sigma{*}1s)^2$ as in **Figure 6.30**. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule. In fact, helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

$$\text{bond order in He}_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

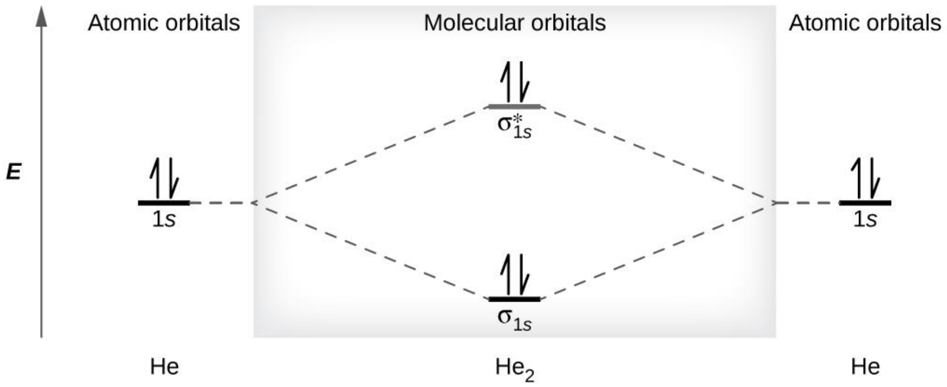


Figure 6.30 The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

VI.8.6 The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (**Table 6.2**).

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund’s rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in **Figure 6.31**. Looking at Ne2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the p orbitals (Li through N) we observe a different pattern, in which the σp orbital is higher in energy than the πp set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.

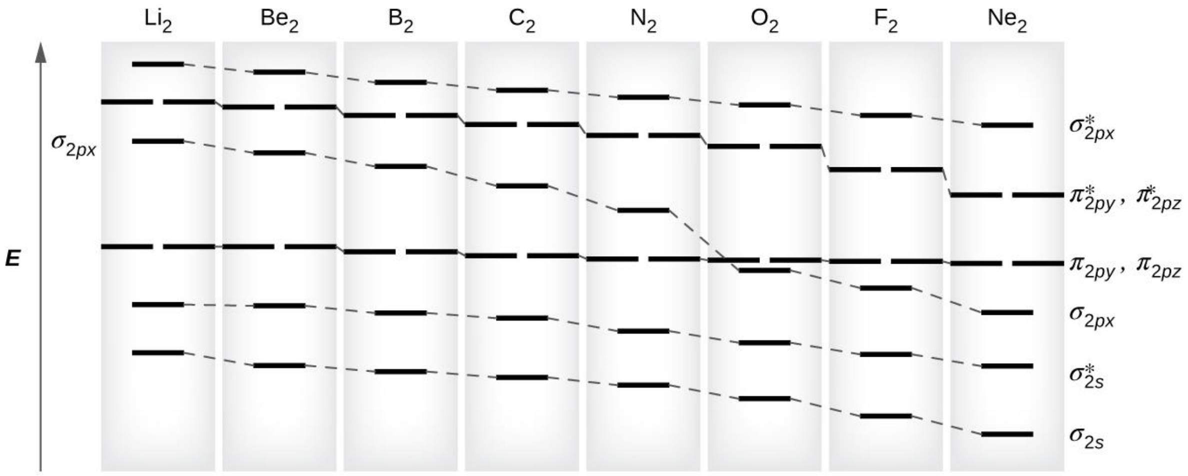


Figure 6.31 This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbital's changes.

This switch in orbital ordering occurs because of a phenomenon called s-p mixing. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σs wavefunction mathematically combines with the σp wavefunction, with the result that the σs orbital becomes more stable, and the σp orbital becomes less stable (**Figure 6.32**). Similarly, the antibonding orbitals also undergo s-p mixing, with the σs* becoming more stable and the σp* becoming less stable.

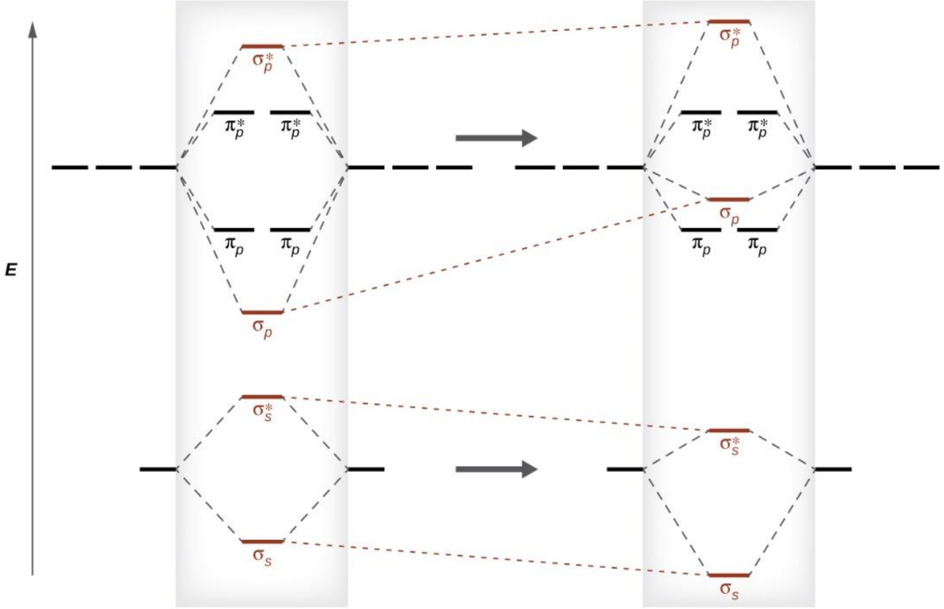


Figure 6.32 Without mixing, the MO pattern occurs as expected, with the σp orbital lower in energy than the πp orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σp orbital higher in energy than the πp orbitals.

s-p mixing occurs when the s and p orbitals have similar energies. The energy difference between 2s and 2p orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne_2 exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in **Figure 6.33**. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σp orbital is raised above the πp set.

Using the MO diagrams shown in **Figure 6.33**, we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in **Table 6.2,** Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma 2s)^2$	1
Be_2 (unstable)	$(\sigma 2s)^2(\sigma * 2s)^2$	0
B_2	$(\sigma 2s)^2(\sigma * 2s)^2(\pi 2py,\pi 2pz)^2$	1
C_2	$(\sigma 2s)^2(\sigma * 2s)^2(\pi 2py,\pi 2pz)^4$	2
N_2	$(\sigma 2s)^2(\sigma * 2s)^2(\pi 2py,\pi 2pz)^4(\sigma 2px)^2$	3
O_2	$(\sigma 2s)^2(\sigma * 2s)^2(\sigma 2px)^2(\pi 2py,\pi 2pz)^4(\pi * 2py,\pi * 2pz)^2$	2
F_2	$(\sigma 2s)^2(\sigma * 2s)^2(\sigma 2px)^2(\pi 2py,\pi 2pz)^4(\pi * 2py,\pi * 2pz)^4$	1
Ne_2 (unstable)	$(\sigma 2s)^2(\sigma * 2s)^2(\sigma 2px)^2(\pi 2py,\pi 2pz)^4(\pi * 2py,\pi * 2pz)^4(\sigma * 2px)^2$	0

Table 6.2

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence 2s orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ2s bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li_2 molecule to be stable. The molecule is, in fact, present in appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in **Table 6.2** with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the ($\pi*_{2py}$, $\pi*_{2pz}$) level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O_2 is in accord with the fact that the oxygen molecule has two unpaired electrons (**Figure 6.34**). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

EXAMPLE 10

Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2. How does this diagram account for the paramagnetism of O_2?

Solution

We draw a molecular orbital energy diagram similar to that shown in **Figure 6.33**. Each oxygen atom contributes six electrons, so the diagram appears as shown in **Figure 6.34**.

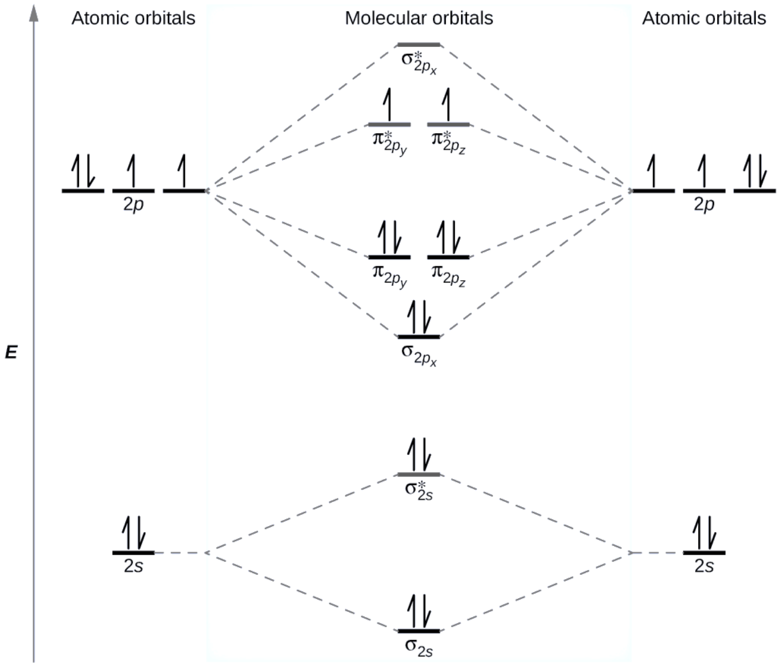


Figure 6.34 The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

$$O_2 = \frac{(8-4)}{2} = 2$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the (π_{2py}, π_{2pz})* molecular orbitals.

EXAMPLE 11

Ion Predictions with MO Diagrams

Give the molecular orbital configuration for the valence electrons in C_2^{2-}. Will this ion be stable?

Solution

Looking at the appropriate MO diagram, we see that the π orbitals are lower in energy than the σp orbital. The valence electron configuration for C_2 is $(\sigma2s)^2(\sigma{*}2s)^2(\pi2py,\ \pi2pz)^4$. Adding two more electrons to generate the C_2^{2-} anion will give a valence electron configuration of $(\sigma2s)2(\sigma{*}2s)^2(\pi2py,\ \pi2pz)^4(\sigma2px)^2$. Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.