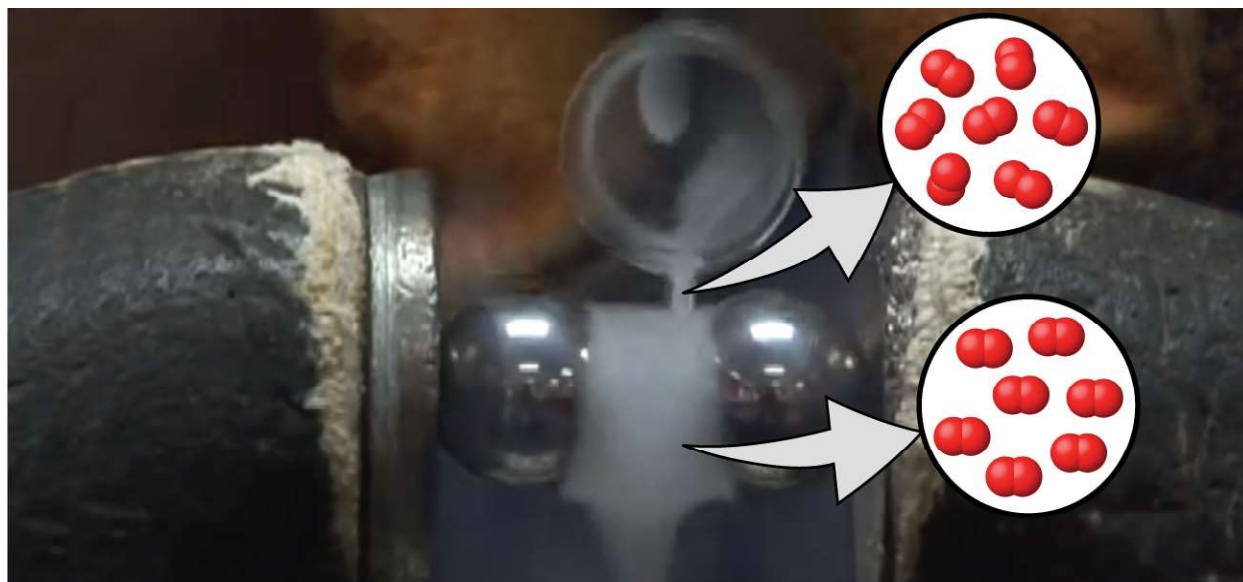# Chapter 5

Advanced Theories of Bonding

Figure 5.1   Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field is strongest. Other diatomic molecules (like N_2) flow past the magnet. The detailed explanation of bonding described in this chapter allows us to understand this phenomenon. (credit: modification of work by Jefferson Lab)

Chapter Outline

Introduction

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s, p,* and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields. Both N_2 and O_2 have fairly similar Lewis structures that contain lone pairs of electrons.

$$:N\equiv N: \qquad :\overset{..}{O}=\overset{..}{O}:$$
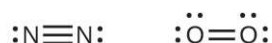
Yet oxygen demonstrates very different magnetic behavior than nitrogen. We can pour liquid nitrogen through a magnetic field with no visible interactions, while liquid oxygen (shown in **Figure 5.1**) is attracted to the magnet and floats in the magnetic field. We need to understand the additional concepts of valence bond theory, orbital hybridization, and molecular orbital theory to understand these observations.

5.1 Valence Bond Theory

By the end of this section, you will be able to:

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds

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.

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 5.2** 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 5.2**.
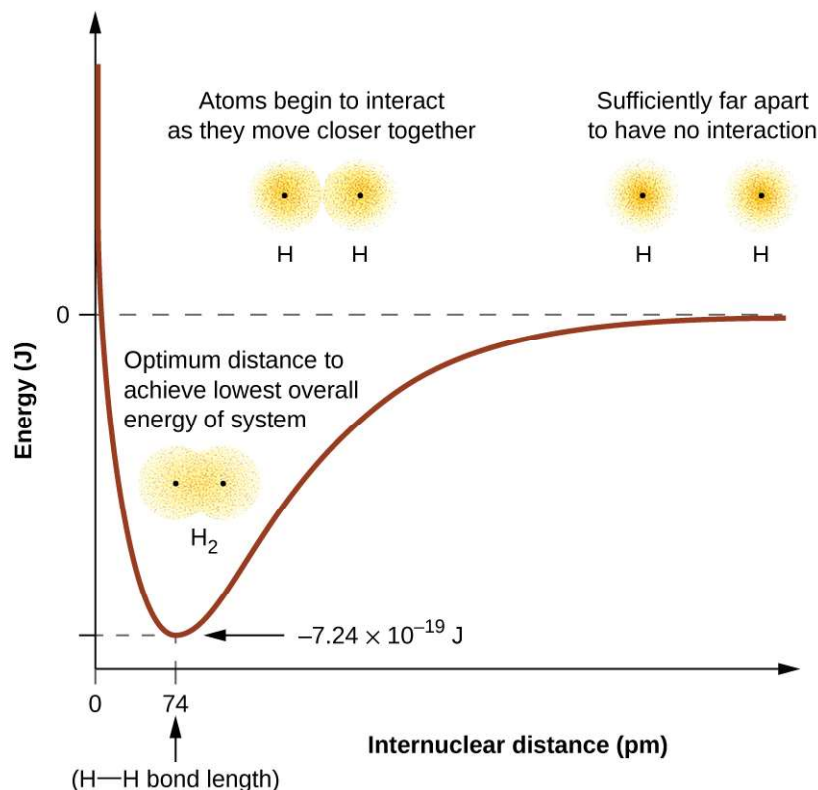
Figure 5.2   (a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

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 5.3** 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.
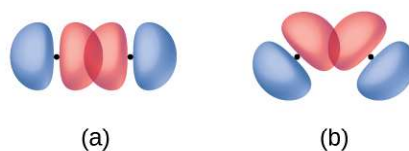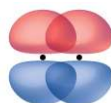

Figure 5.3   (a) The overlap of two *p* orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

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 5.4**. 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.
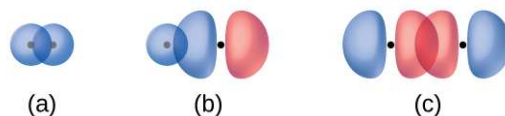
Figure 5.4 Sigma (σ) bonds form from the overlap of the following: (a) two *s* orbitals, (b) an *s* orbital and a *p* orbital, and (c) two *p* orbitals. The dots indicate the locations of the nuclei.

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 5.5**. 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.
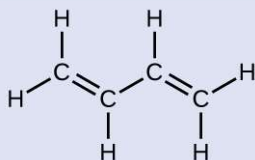

Figure 5.5 Pi (π) bonds form from the side-by-side overlap of two *p* orbitals. The dots indicate the location of the nuclei.

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.

H—C̈l:	:Ö=Ö:	:N≡N:
One σ bond	One σ bond	One σ bond
No π bonds	One π bond	Two π bonds
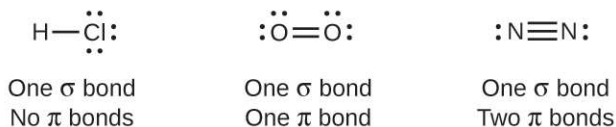
Example 5.1

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.

Check Your Learning

Identify each illustration as depicting a σ or π bond:

(a) side-by-side overlap of a 4*p* and a 2*p* orbital

(b) end-to-end overlap of a 4*p* and 4*p* orbital

(c) end-to-end overlap of a 4*p* and a 2*p* orbital

(a)   (b)   (c)
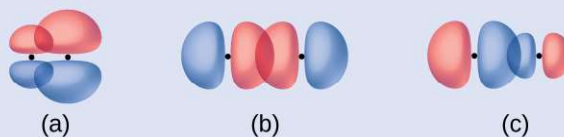
Answer: (a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

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 2*d*:

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

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.

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:

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

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.

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 5.2

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 $\left(1.60218 \times 10^{19} \text{ C}\right)\left(0.127 \times 10^{-9} \text{ m}\right)$ or $2.03 \times 10^{-29} \text{ C-m}$. Converted to D, this is $\left(2.03 \times 10^{-29} \text{ C-m}\right)\left(\frac{1 \text{Debye}}{3.336 \times 10^{-30} \text{ C-m}}\right)$ or 6.09 D. Were HCl completely ionic, this would be its molecular dipole moment. To get the partial ionic character, we divide 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.

Check Your Learning

Repeat the calculation for HI, which has a dipole moment of 0.42 D and a bond length of 0.161 nm.

Answer: Calculated 7.73, percent 5.43

What does the result suggest about the relative polarity of the HI bond vs. that of the HCl bond? Does the calculated dipole and percent ionic character reconcile with the difference in electronegativity between Cl and I?

The electron configuration of an atom or ion is key to understanding the chemical behavior of an element. The atoms that make up the element combine in various ways, ranging from the mostly ionic (NaCl) to the partially ionic (HCl) to what we will call purely covalent. At the most fundamental level, all chemical bonds involve electrons, and a significant percentage of chemical and physical properties can be explained by considering the location and separation of charge in a species. By understanding the structure of matter at the atomic level, we can begin to build an understanding of the behavior of matter at both the microscopic and macroscopic levels.

An understanding of dipoles and partial ionic character is fundamental to understanding the interactions between particles, which we will examine in the chapter on liquids and solids. These intermolecular forces become important in the liquid and solid states of matter.

5.2 Hybrid Atomic Orbitals

By the end of this section, you will be able to:

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two $2p$ orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two $2p$ orbitals with the $1s$ orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in **Figure 5.6**, because p orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.
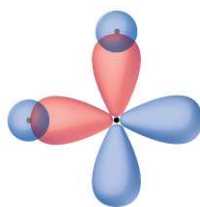

Figure 5.6   The hypothetical overlap of two of the $2p$ orbitals on an oxygen atom (red) with the $1s$ orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the $1s$ orbital of the hydrogen atoms with the $2p$ orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of

---

1. Note that orbitals may sometimes be drawn in an elongated "balloon" shape rather than in a more realistic "plump" shape in order to make the geometry easier to visualize.

electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called **hybridization** and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called **hybrid orbitals**. The valence orbitals in an *isolated* oxygen atom are a 2*s* orbital and three 2*p* orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (**Figure 5.7**). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

(a)   (b)
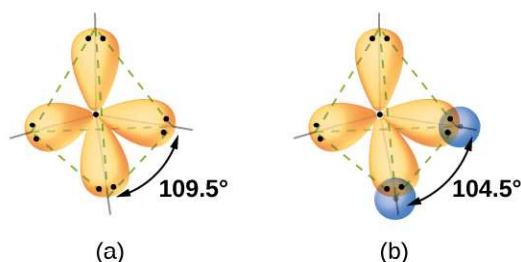
Figure 5.7   (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1*s* orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.

2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.

3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.

4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.

5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.

6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent ***sp* hybrid orbitals** that are oriented in a linear geometry (**Figure 5.8**). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point

180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.
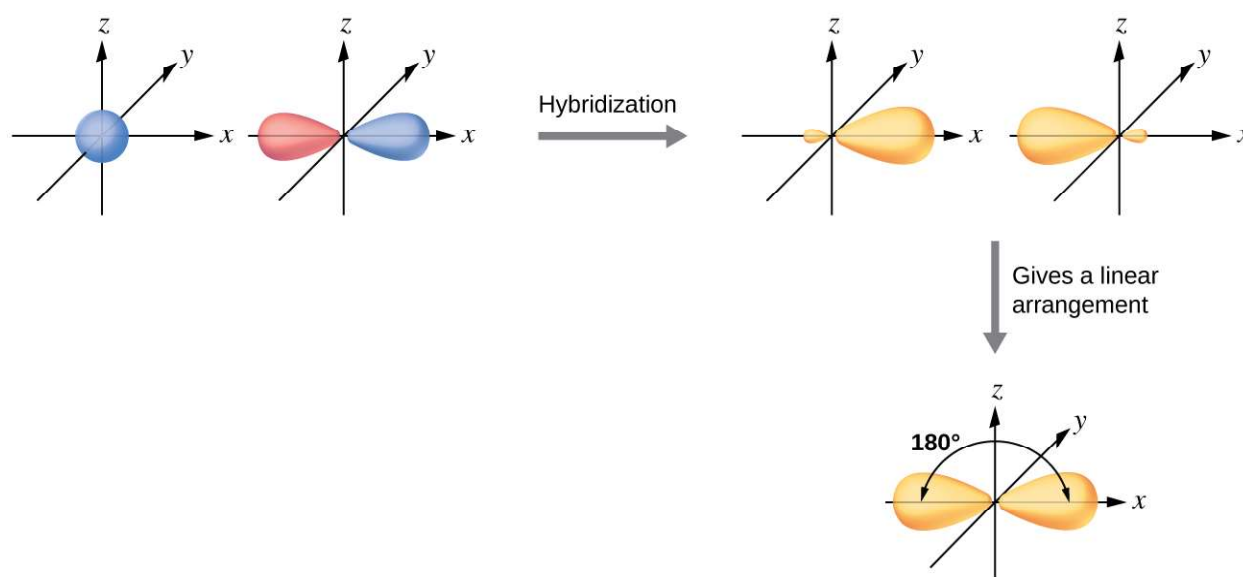
Figure 5.8 Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in **Figure 5.9**. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.
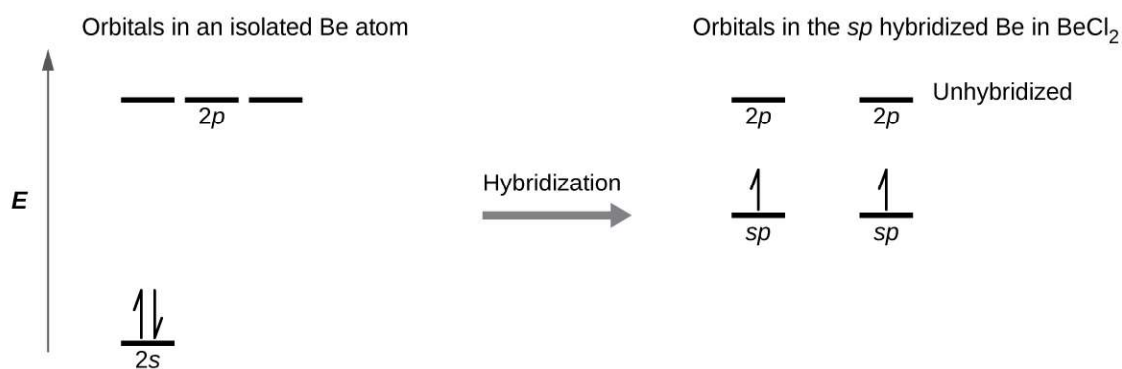
Figure 5.9 This orbital energy-level diagram shows the *sp* hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two *sp* hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3*p* orbital.

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the

unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.

Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear $HgCl_2$ molecule, the zinc atom in $Zn(CH_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2.

Link to Learning

Check out the University of Wisconsin-Oshkosh **website (http://openstaxcollege.org/l/16hybridorbital)** to learn about visualizing hybrid orbitals in three dimensions.
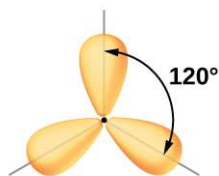
sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three **sp^2 hybrid orbitals** and one unhybridized *p* orbital. This arrangement results from sp^2 hybridization, the mixing of one *s* orbital and two *p* orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (**Figure 5.10**).
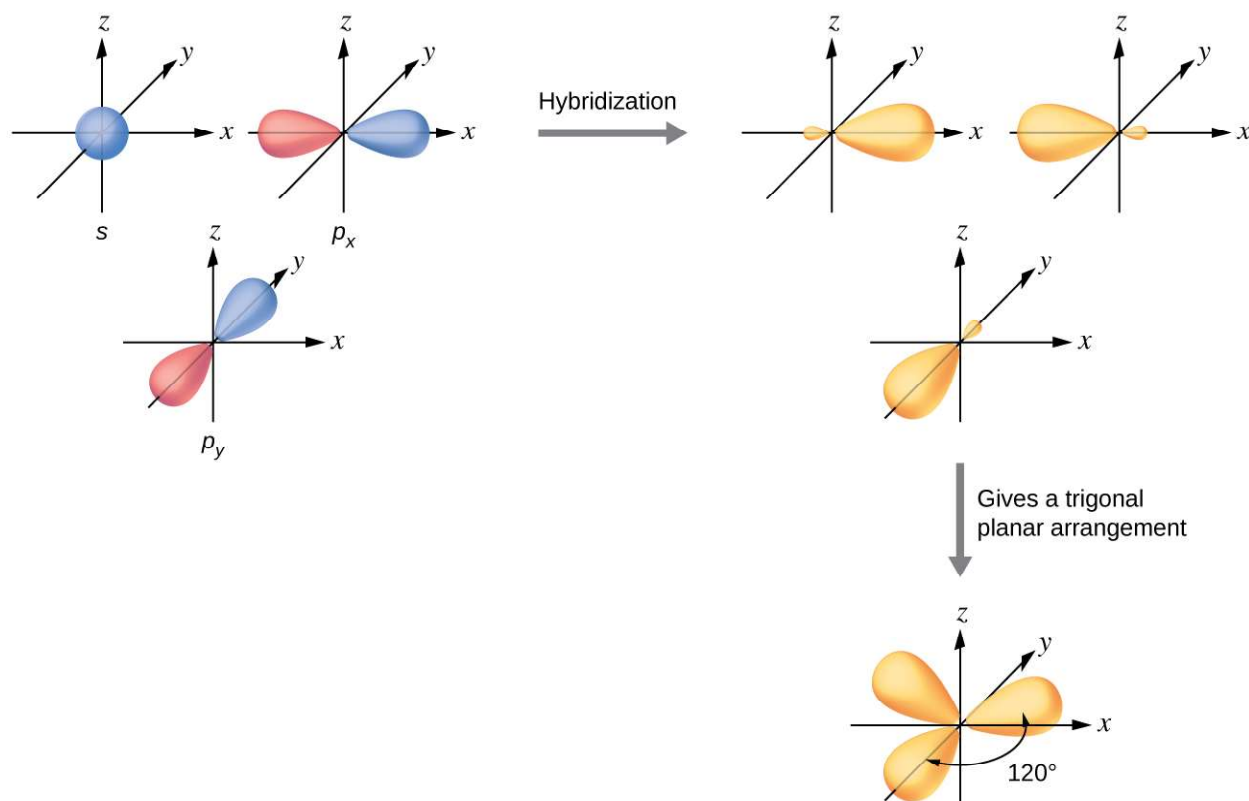
Figure 5.10 The hybridization of an *s* orbital (blue) and two *p* orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized *p* orbital is not shown here, but is located along the z axis.

Although quantum mechanics yields the "plump" orbital lobes as depicted in **Figure 5.10**, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in **Figure 5.11**, to avoid obscuring other features of a given illustration. We will use these "thinner" representations whenever the true view is too crowded to easily visualize.


Figure 5.11   This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (**Figure 5.12**). We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in **Figure 5.13**. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.
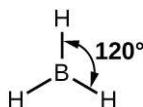

Figure 5.12 BH_3 is an electron-deficient molecule with a trigonal planar structure.
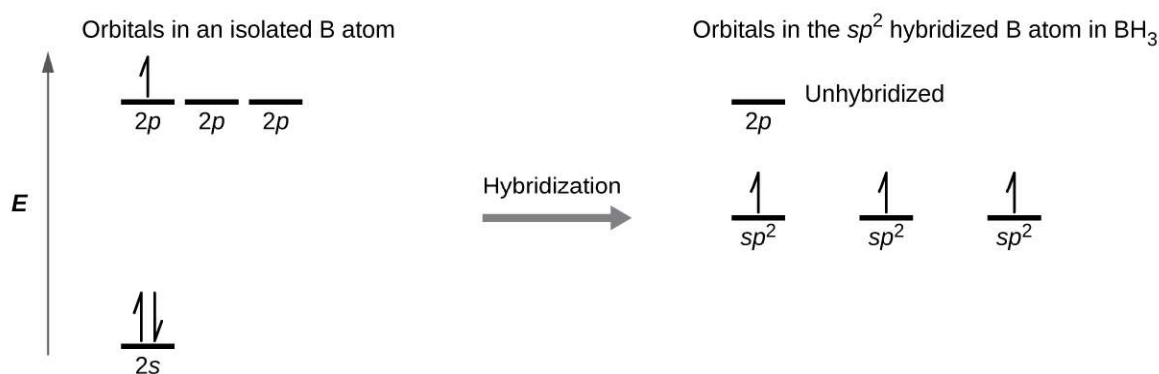
Figure 5.13   In an isolated B atom, there are one $2s$ and three $2p$ valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized $2p$ orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (**Figure 5.14**), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.
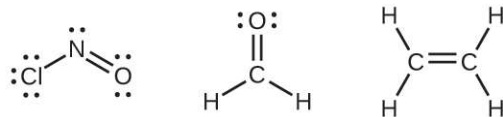
Figure 5.14   The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.
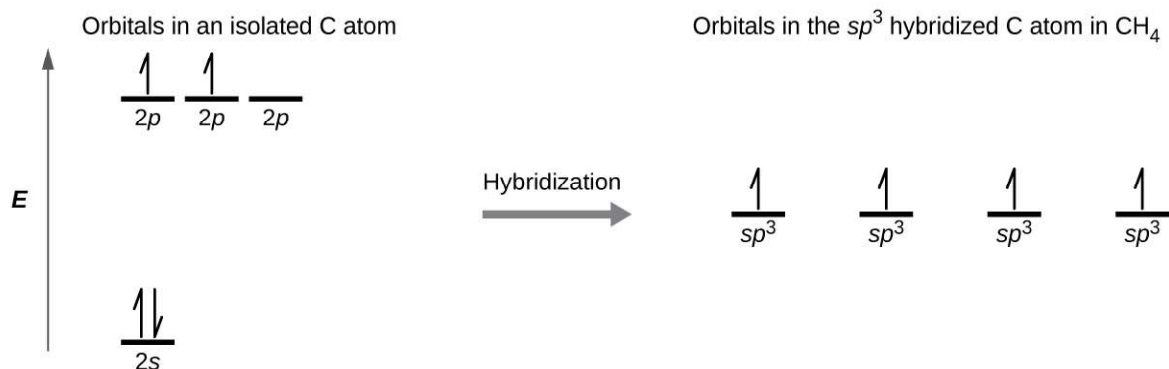
sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four sp^3 **hybrid orbitals**. The hybrids result from the mixing of one s orbital and all three p orbitals that produces four identical sp^3 hybrid orbitals (**Figure 5.15**). Each of these hybrid orbitals points toward a different corner of a tetrahedron.
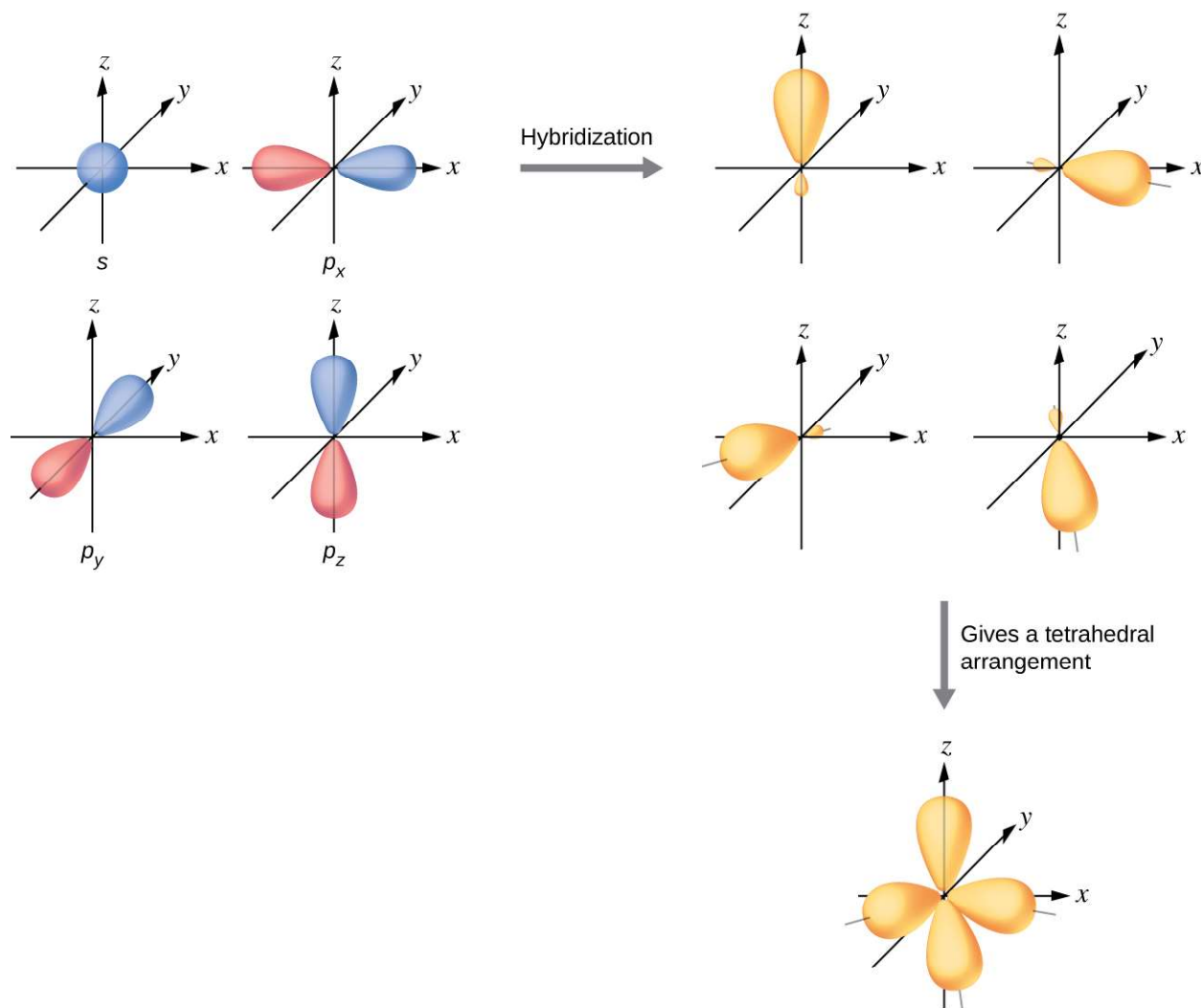
Figure 5.15 The hybridization of an *s* orbital (blue) and three *p* orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in **Figure 5.16**. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

Orbitals in an isolated C atom   Orbitals in the sp^3 hybridized C atom in CH$_4$

Figure 5.16 The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH$_4$ with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

In a methane molecule, the 1s orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH$_4$.

The structure of ethane, C$_2$H$_6$, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (**Figure 5.17**). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 hybrid orbitals overlaps with an s orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in **Figure 5.17**. The orientation of the two CH$_3$ groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

(a)   (b)
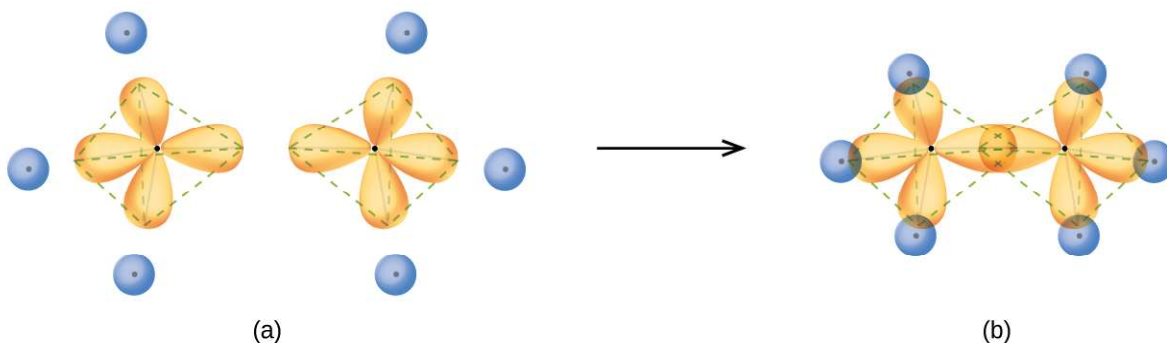
Figure 5.17 (a) In the ethane molecule, C$_2$H$_6$, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl$_4$,

PCl_3, and NCl_3.

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the s orbital, the three p orbitals, and one of the d orbitals), which gives five sp^3d **hybrid orbitals**. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the s orbital, the three p orbitals, and two of the d orbitals in its valence shell), which gives six sp^3d^2 **hybrid orbitals**. These hybridizations are only possible for atoms that have d orbitals in their valence subshells (that is, not those in the first or second period).

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the $3s$ orbital, the three $3p$ orbitals, and one of the $3d$ orbitals to form the set of five sp^3d hybrid orbitals (**Figure 5.19**) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in $ClF_4{}^+$. (The electrons on fluorine atoms are omitted for clarity.)
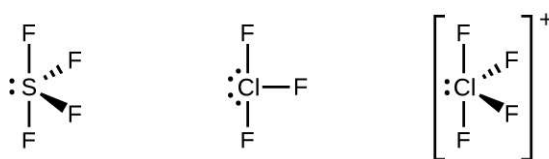
**Figure 5.18** The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and $ClF_4{}^+$ have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.
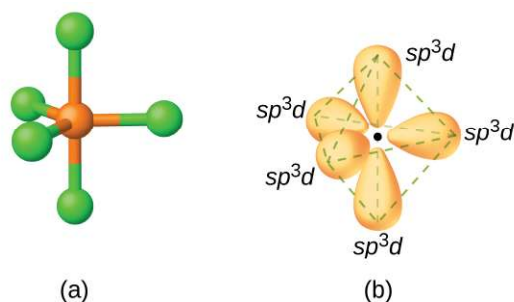
Figure 5.19 (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

The sulfur atom in sulfur hexafluoride, SF_6, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the $3s$ orbital, the three $3p$ orbitals, and two of the $3d$ orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in $PCl_6{}^-$, the iodine atom in the interhalogens $IF_6{}^+$, IF_5, $ICl_4{}^-$, $IF_4{}^-$ and the xenon atom in XeF_4.
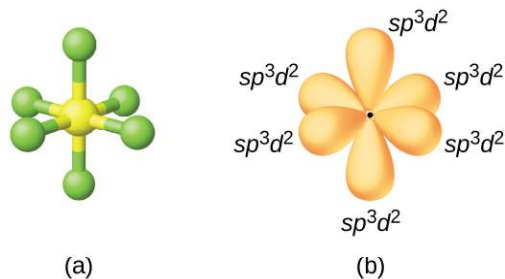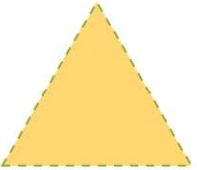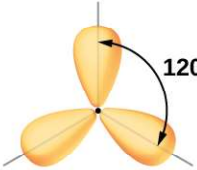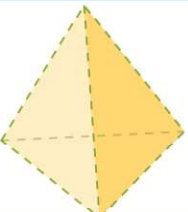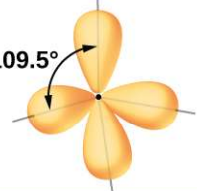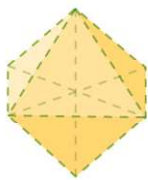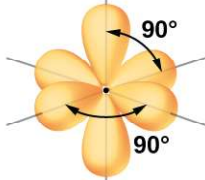
Figure 5.20   (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in **Figure 5.21**. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:
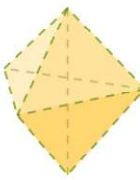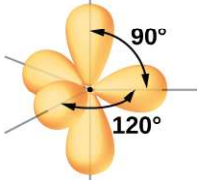
1. Determine the Lewis structure of the molecule.

2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.

3. Assign the set of hybridized orbitals from **Figure 5.21** that corresponds to this geometry.

| Regions of Electron Density	Arrangement		Hybridization	
2	- - - - - - - - - -	linear	sp	180°
3	(triangle)	trigonal planar	sp^2	120°
4	(tetrahedron)	tetrahedral	sp^3	109.5°
5	(trigonal bipyramid)	trigonal bipyramidal	sp^3d	90° 120°
6	(octahedron)	octahedral	sp^3d^2	90° 90°

Figure 5.21 The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data. For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with $2p$ orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the $5p$ orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.
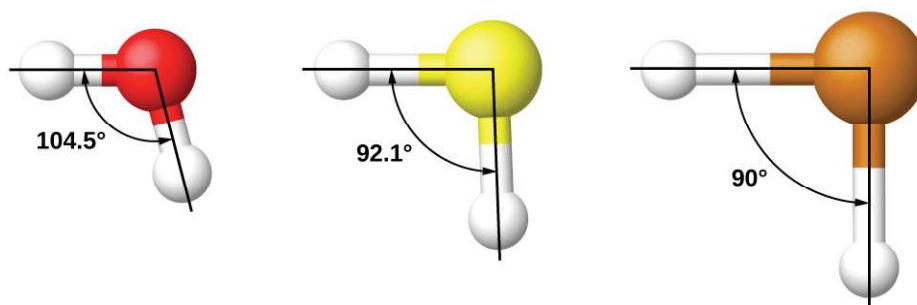
Example 5.3

Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, $SO_4{}^{2-}$?

Solution

The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp^3.
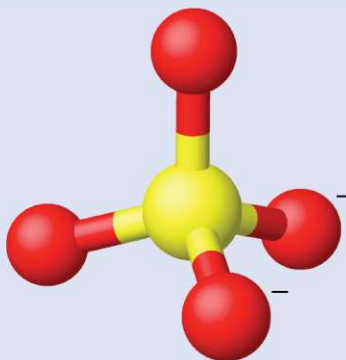
Check Your Learning

What is the hybridization of the selenium atom in SeF$_4$?

Answer: The selenium atom is sp^3d hybridized.

Example 5.4

Assigning Hybridization

Urea, NH$_2$C(O)NH$_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen and carbon atom in urea?

Solution

The Lewis structure of urea is

$$\text{H}-\overset{\displaystyle \overset{..}{\underset{..}{\text{O}}}}{\underset{\text{H}}{\overset{..}{\text{N}}}}-\overset{\|}{\text{C}}-\overset{..}{\underset{\text{H}}{\overset{..}{\text{N}}}}-\text{H}$$

The nitrogen atoms are surrounded by four regions of electron density, which arrange themselves in a tetrahedral electron-pair geometry. The hybridization in a tetrahedral arrangement is sp^3 (**Figure 5.21**). This is the hybridization of the nitrogen atoms in urea.

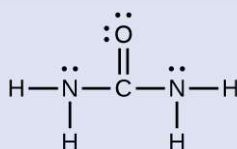The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (**Figure 5.21**), which is the hybridization of the carbon atom in urea.

Check Your Learning

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?
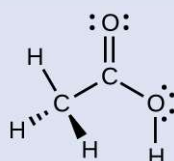
Answer: $H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

5.3 Multiple Bonds

By the end of this section, you will be able to:

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to π-bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4, shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.
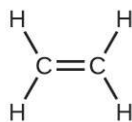
The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the $2p$ orbitals and the $2s$ orbital (**Figure 5.22**). These orbitals form the C–H single bonds and the σ bond in the $C = C$ double bond (**Figure 5.23**). The π bond in the $C = C$ double bond results from the overlap of the third (remaining) $2p$ orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in **Figure 5.23**) is perpendicular to the plane of the sp^2 hybrid orbitals. Thus the unhybridized $2p$ orbitals overlap in a side-by-side fashion, above and below the internuclear axis (**Figure 5.23**) and form a π bond.
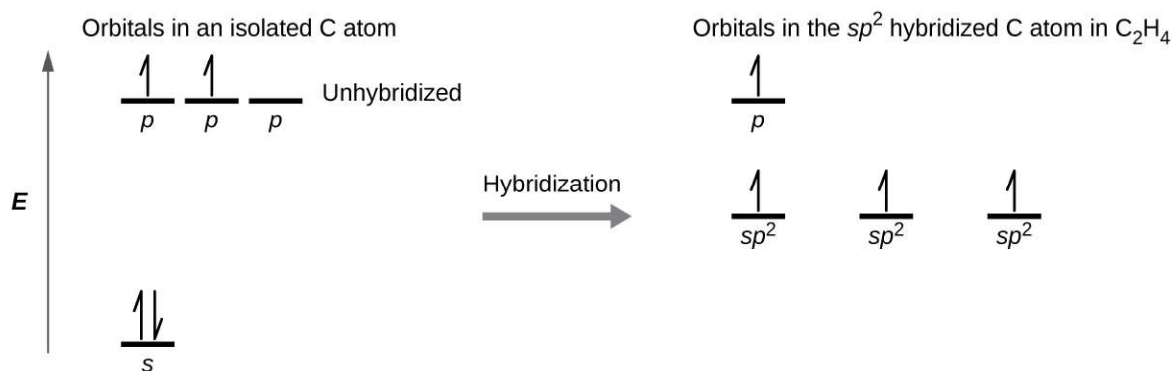
Figure 5.22 In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the p orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the p orbitals on each carbon atom overlap to form a π bond.
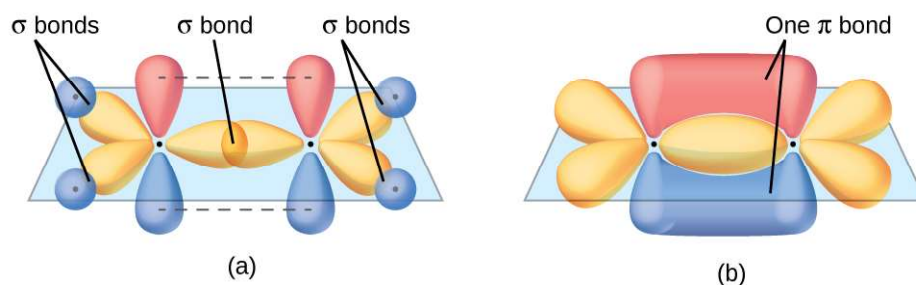
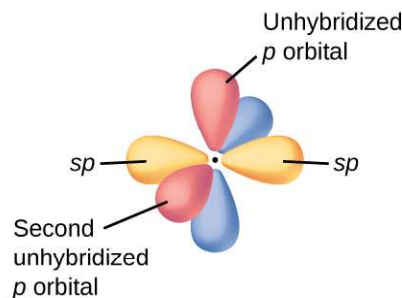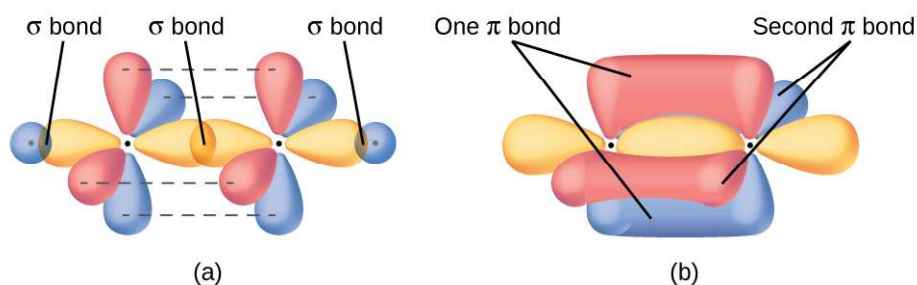**Figure 5.23** In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the p orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.

In molecules with sp hybrid orbitals, two unhybridized p orbitals remain on the atom (**Figure 5.24**). We find this situation in acetylene, $\mathrm{H-C{\equiv}C-H,}$ which is a linear molecule. The sp hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms (**Figure 5.25**). The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized p orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

Figure 5.24 Diagram of the two linear *sp* hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized *p* orbitals at perpendicular angles.

Figure 5.25 (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a $C \equiv C$ triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized *p* orbitals. (b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (**Figure 5.26**). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)
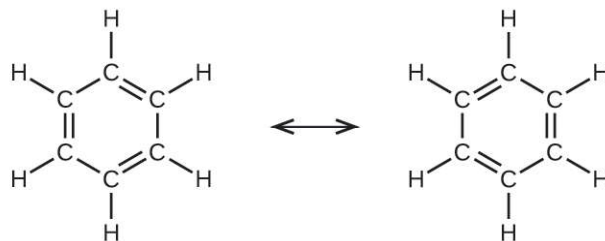
Figure 5.26 Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of *p* orbitals or the other, but rather delocalized throughout the molecule.

Example 5.5

Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2?

Solution

The resonance structures of SO_2 are

The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2.

Check Your Learning

Another acid in acid rain is nitric acid, HNO_3, which is produced by the reaction of nitrogen dioxide, NO_2, with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer: sp^2

5.4 Molecular Orbital Theory

By the end of this section, you will be able to:

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations
- Write molecular electron configurations for first- and second-row diatomic molecules
- Relate these electron configurations to the molecules' stabilities and magnetic properties

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 O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:

$$:\ddot{O}=\ddot{O}:$$
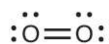
This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity, as in **Figure 5.1**. 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 5.27**), 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.
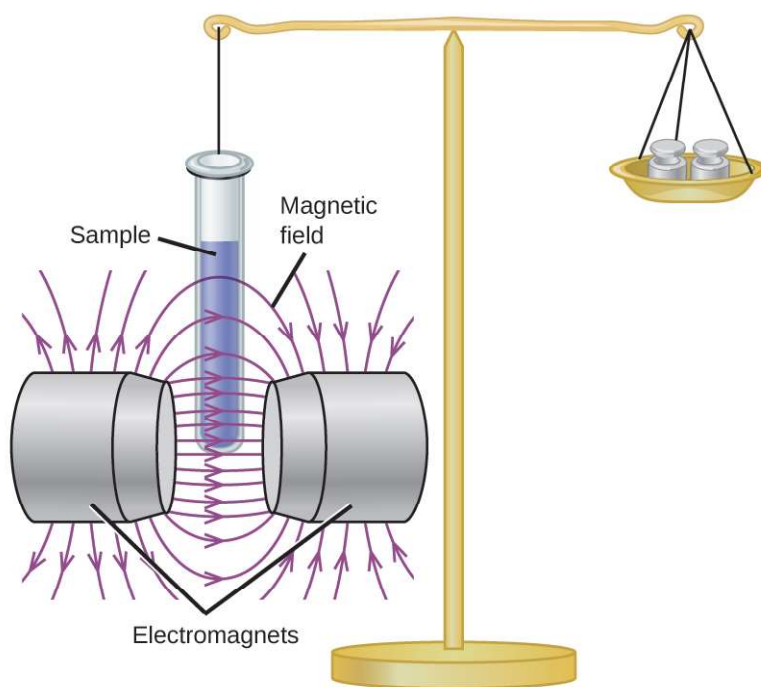
Figure 5.27 A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

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. You can see **videos (http://openstax.org/l/16diamagnetic)** of diamagnetic floating frogs, strawberries, and more.

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 5.1** summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Comparison of Bonding Theories

| 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, sp², sp³*…)	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 5.1

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 5.28**). 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.

(a)   (b)
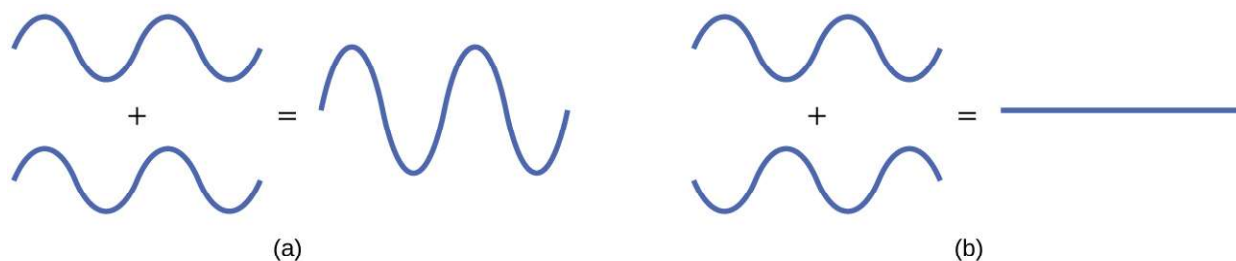
Figure 5.28 (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

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 5.29**. 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 **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 σ_s 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 σ_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.
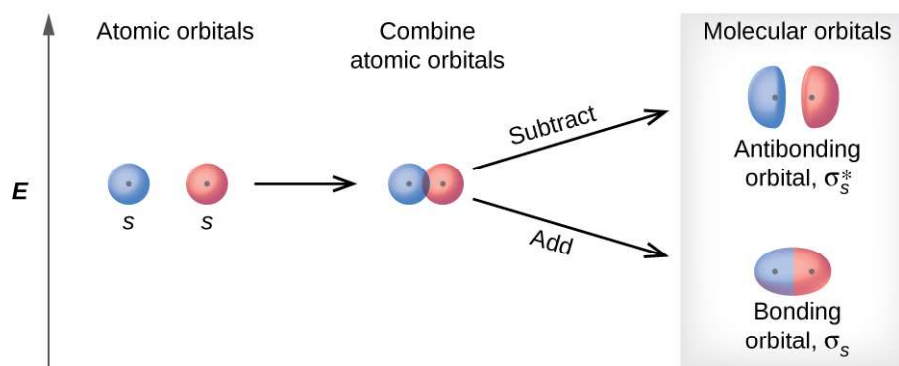


Figure 5.29 Sigma (σ) and sigma-star (σ^*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

Link to Learning

You can watch **animations (http://openstax.org/l/16molecorbital)** visualizing the calculated atomic orbitals combining to form various molecular orbitals at the Orbitron website.

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 5.30**). 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 σ_{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.
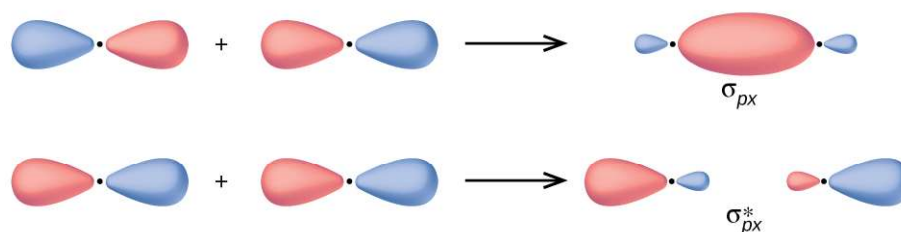
Figure 5.30   Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ_p^*.

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 5.31**. 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.
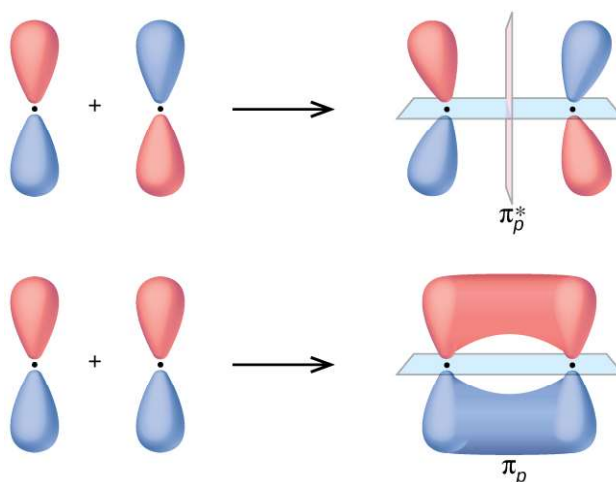
Figure 5.31   Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase 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 (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π* orbitals. The π_{py} and π^*_{py} orbitals are oriented at right angles to the π_{pz} and π^*_{pz} orbitals. Except for their orientation, the π_{py} and π_{pz} 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: σ_{px} and σ^*_{px}, π_{py} and π^*_{py}, π_{pz} and π^*_{pz}.

Example 5.6

Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.

$3p_x$ and $3p_x$ (a) $3p_x$ and $3p_y$ (b) $3p_y$ and $3p_y$ (c)
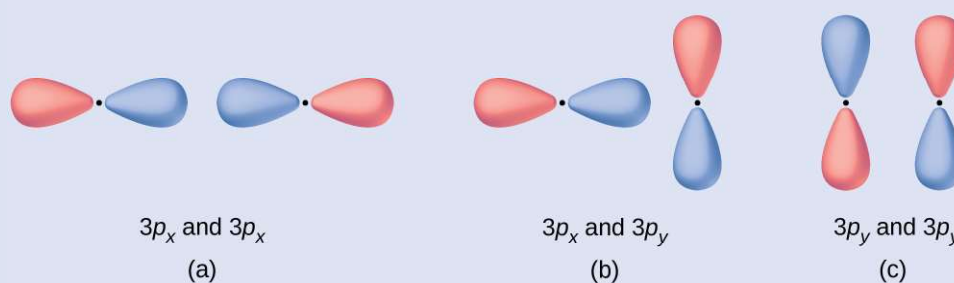
Solution

(a) is an in-phase combination, resulting in a σ_{3p} orbital

(b) will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.

(c) is an out-of-phase combination, resulting in a π^*_{3p} orbital.

Check Your Learning

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.
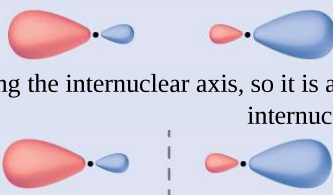
Answer: The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.

Portrait of a Chemist

Walter Kohn: Nobel Laureate

Walter Kohn (**Figure 5.32**) is a theoretical physicist who studies the electronic structure of solids. His work combines the principles of quantum mechanics with advanced mathematical techniques. This technique, called density functional theory, makes it possible to compute properties of molecular orbitals, including their shape and energies. Kohn and mathematician John Pople were awarded the Nobel Prize in Chemistry in 1998 for their contributions to our understanding of electronic structure. Kohn also made significant contributions to the

physics of semiconductors.

Figure 5.32 Walter Kohn developed methods to describe molecular orbitals. (credit: image courtesy of Walter Kohn)

Kohn's biography has been remarkable outside the realm of physical chemistry as well. He was born in Austria, and during World War II he was part of the Kindertransport program that rescued 10,000 children from the Nazi regime. His summer jobs included discovering gold deposits in Canada and helping Polaroid explain how its instant film worked. Although he is now an emeritus professor, he is still actively working on projects involving global warming and renewable energy.

How Sciences Interconnect

Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (see **Figure 5.33**). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.
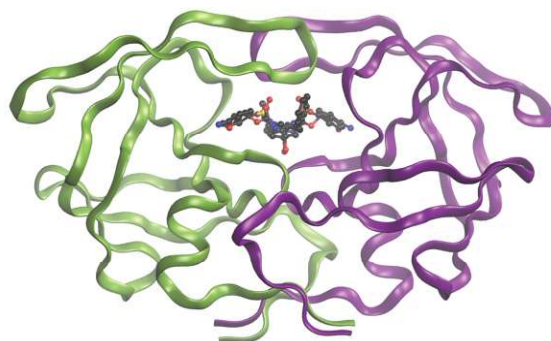
Figure 5.33   The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a **molecular orbital diagram** (**Figure 5.34**). 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 5.34**). 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.
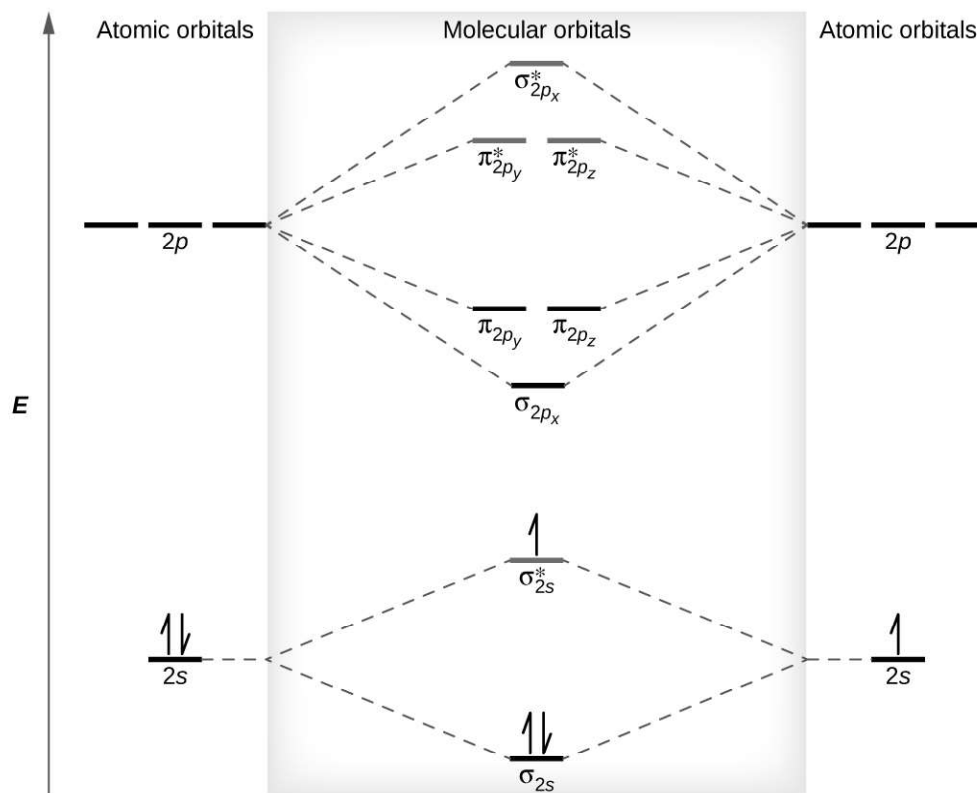
Figure 5.34 This is the molecular orbital diagram for the homonuclear diatomic $Be_2{}^+$, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

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.

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 σ_{1s} 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 σ_{1s} orbital that contains both electrons is 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 σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (**Figure 5.35**) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.
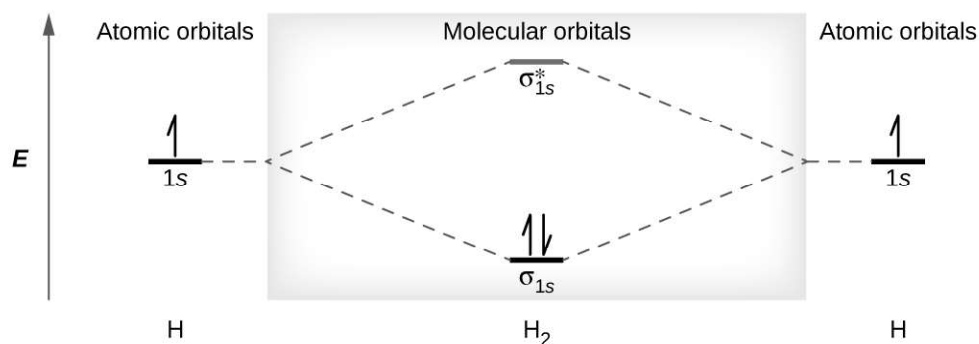
Figure 5.35   The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

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 5.36**.

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.
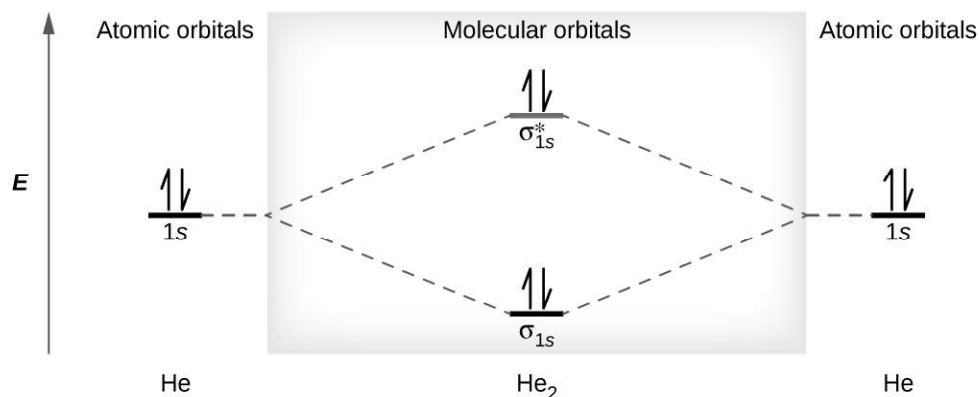
Figure 5.36   The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

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 5.2**).

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 5.37**. Looking at Ne_2 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 σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.
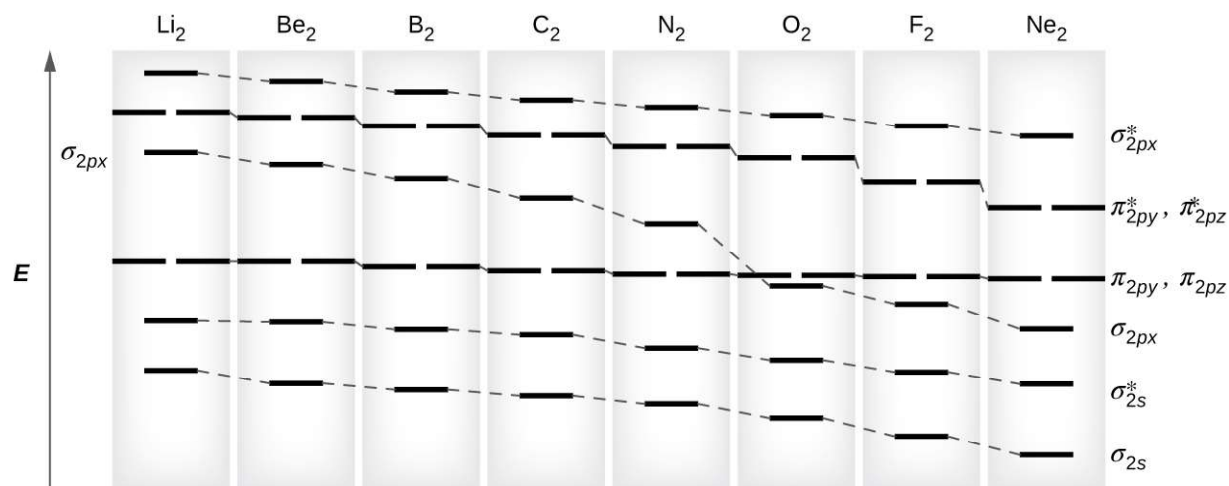
Figure 5.37 This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.

Link to Learning

You can practice labeling and filling molecular orbitals with this **interactive tutorial (http://openstax.org/l/16labelorbital)** from the University of Sydney.

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 σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (**Figure 5.38**). Similarly, the antibonding orbitals also undergo **s-p** mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.
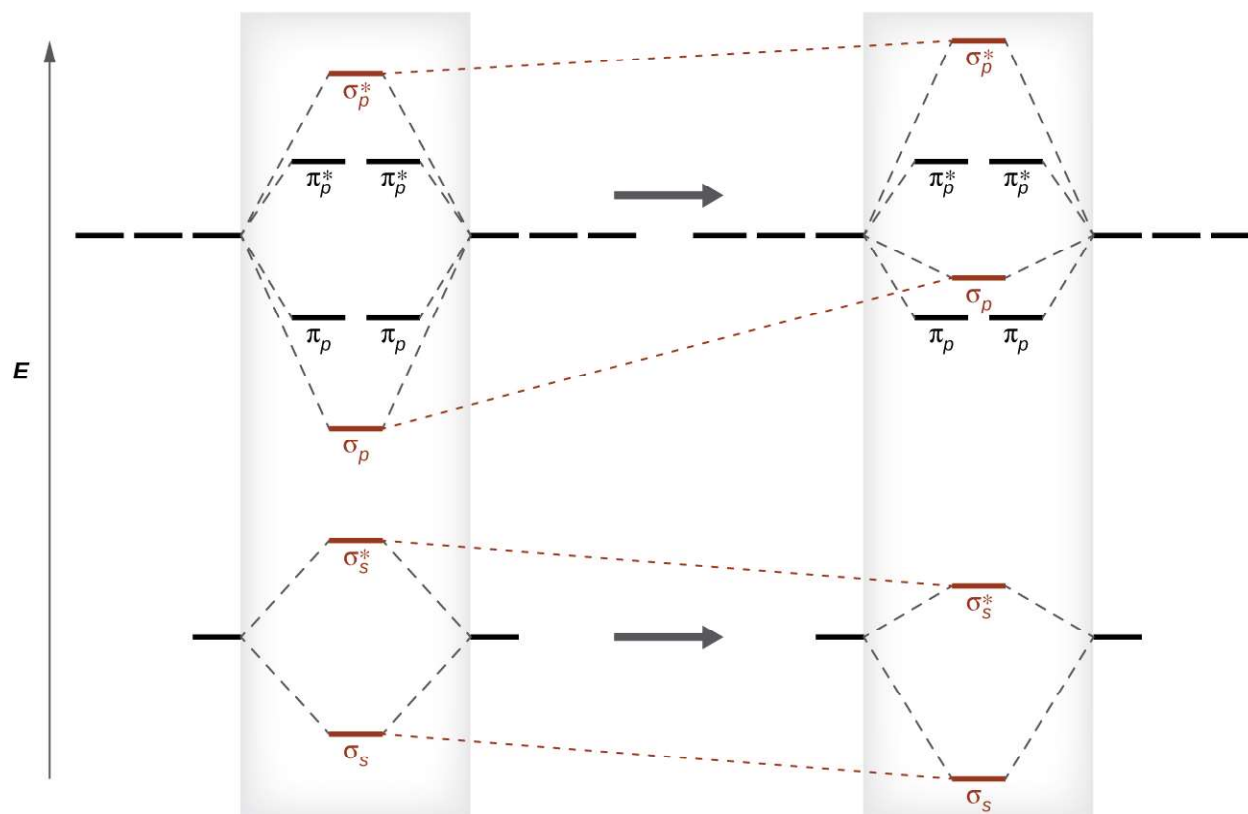
Figure 5.38 Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

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 5.37**. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in **Figure 5.37**, 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 5.2**, 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

Table 5.2

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

Molecule	Electron Configuration	Bond Order
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 5.2

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 σ_{2s} 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 5.2** with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the $\left(\pi_{2py}^*,\ \pi_{2pz}^* \right)$ 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 5.40**). 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.

How Sciences Interconnect

Band Theory

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (see **Figure 5.29**). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically > 10^{23} atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When N valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, $N/2$ (filled) bonding orbitals and $N/2$ (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are *mostly* in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are *mostly* out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. **Figure 5.39** shows the bands for three important classes of materials: insulators, semiconductors, and conductors.
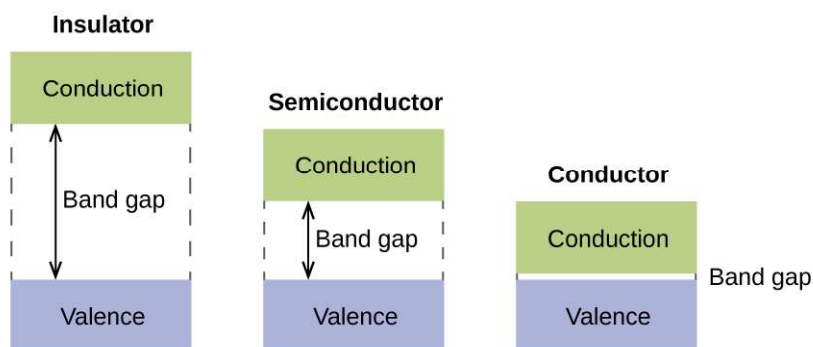
Figure 5.39 Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valance band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is "easy" to overcome, so they are good conductors of electricity. In an insulator, the band gap is so "large" that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when "moderate" amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

Example 5.7

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 5.37**. Each oxygen atom contributes six electrons, so the diagram appears as shown in **Figure 5.40**.
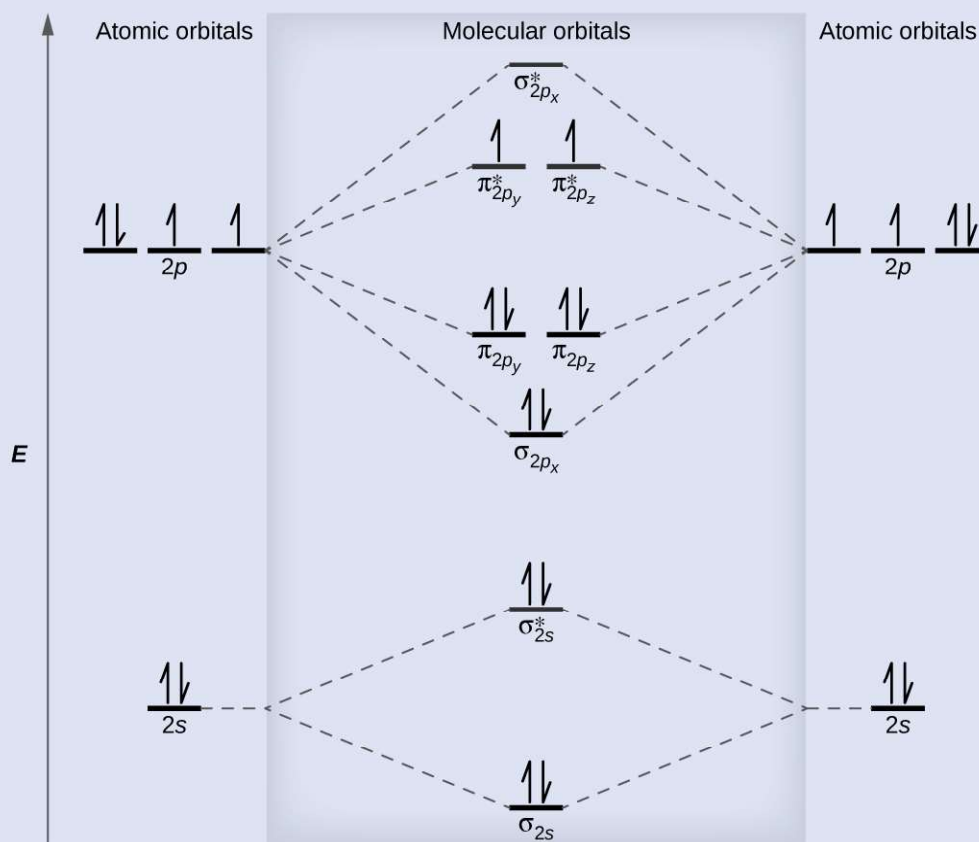
Figure 5.40   The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

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 $(\pi_{2py}, \pi_{2pz})^*$ molecular orbitals.

Check Your Learning

The main component of air is N_2. From the molecular orbital diagram of N_2, predict its bond order and whether it is diamagnetic or paramagnetic.

Answer: N_2 has a bond order of 3 and is diamagnetic.

Example 5.8

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 σ_p orbital. The valence electron configuration for C_2 is $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py}, \pi_{2pz})^4$. Adding two more electrons to

generate the $C_2{}^{2-}$ anion will give a valence electron configuration of $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2py},\ \pi_{2pz})^4 (\sigma_{2px})^2$. Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

Check Your Learning

How many unpaired electrons would be present on a $Be_2{}^{2-}$ ion? Would it be paramagnetic or diamagnetic?

Answer: two, paramagnetic

Link to Learning

Creating molecular orbital diagrams for molecules with more than two atoms relies on the same basic ideas as the diatomic examples presented here. However, with more atoms, computers are required to calculate how the atomic orbitals combine. See **three-dimensional drawings (http://openstax.org/l/ 16orbitaldiag)** of the molecular orbitals for C_6H_6.

Key Terms

antibonding orbital molecular orbital located outside of the region between two nuclei; electrons in an antibonding orbital destabilize the molecule

bond order number of pairs of electrons between two atoms; it can be found by the number of bonds in a Lewis structure or by the difference between the number of bonding and antibonding electrons divided by two

bonding orbital molecular orbital located between two nuclei; electrons in a bonding orbital stabilize a molecule

degenerate orbitals orbitals that have the same energy

diamagnetism phenomenon in which a material is not magnetic itself but is repelled by a magnetic field; it occurs when there are only paired electrons present

homonuclear diatomic molecule molecule consisting of two identical atoms

hybrid orbital orbital created by combining atomic orbitals on a central atom

hybridization model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

linear combination of atomic orbitals technique for combining atomic orbitals to create molecular orbitals

molecular orbital region of space in which an electron has a high probability of being found in a molecule

molecular orbital diagram visual representation of the relative energy levels of molecular orbitals

molecular orbital theory model that describes the behavior of electrons delocalized throughout a molecule in terms of the combination of atomic wave functions

node plane separating different lobes of orbitals, where the probability of finding an electron is zero

overlap coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

paramagnetism phenomenon in which a material is not magnetic itself but is attracted to a magnetic field; it occurs when there are unpaired electrons present

pi bond (π bond) covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

s-p mixing change that causes σ_p orbitals to be less stable than π_p orbitals due to the mixing of s and p-based molecular orbitals of similar energies.

sigma bond (σ bond) covalent bond formed by overlap of atomic orbitals along the internuclear axis

sp **hybrid orbital** one of a set of two orbitals with a linear arrangement that results from combining one s and one p orbital

sp^2 **hybrid orbital** one of a set of three orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals

sp^3 **hybrid orbital** one of a set of four orbitals with a tetrahedral arrangement that results from combining one s and three p orbitals

sp^3d **hybrid orbital** one of a set of five orbitals with a trigonal bipyramidal arrangement that results from

combining one *s*, three *p*, and one *d* orbital

sp^3d^2 hybrid orbital one of a set of six orbitals with an octahedral arrangement that results from combining one *s*, three *p*, and two *d* orbitals

valence bond theory description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

π bonding orbital molecular orbital formed by side-by-side overlap of atomic orbitals, in which the electron density is found on opposite sides of the internuclear axis

π* bonding orbital antibonding molecular orbital formed by out of phase side-by-side overlap of atomic orbitals, in which the electron density is found on both sides of the internuclear axis, and there is a node between the nuclei

σ bonding orbital molecular orbital in which the electron density is found along the axis of the bond

σ* bonding orbital antibonding molecular orbital formed by out-of-phase overlap of atomic orbital along the axis of the bond, generating a node between the nuclei

Key Equations

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

Summary

5.1 Valence Bond Theory

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond. Dipole moments can be used to determine partial separations of charges between atoms.

5.2 Hybrid Atomic Orbitals

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply *sp* hybridization; three, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (*p* or *d* orbitals).

5.3 Multiple Bonds

Multiple bonds consist of a σ bond located along the axis between two atoms and one or two π bonds. The σ bonds are usually formed by the overlap of hybridized atomic orbitals, while the π bonds are formed by the side-by-side overlap of unhybridized orbitals. Resonance occurs when there are multiple unhybridized orbitals with the appropriate alignment to overlap, so the placement of π bonds can vary.

5.4 Molecular Orbital Theory

Molecular orbital (MO) theory describes the behavior of electrons in a molecule in terms of combinations of the atomic wave functions. The resulting molecular orbitals may extend over all the atoms in the molecule. Bonding molecular orbitals are formed by in-phase combinations of atomic wave functions, and electrons in these orbitals stabilize a molecule. Antibonding molecular orbitals result from out-of-phase combinations of atomic wave functions and electrons in these orbitals make a molecule less stable. Molecular orbitals located along an internuclear axis are called σ MOs. They can be formed from *s* orbitals or from *p* orbitals oriented in an end-to-end fashion. Molecular orbitals formed from *p* orbitals oriented in a side-by-side fashion have electron density on opposite sides of the

internuclear axis and are called π orbitals.

We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund's rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

Exercises

5.1 Valence Bond Theory

1. Explain how σ and π bonds are similar and how they are different.

2. Use valence bond theory to explain the bonding in F_2, HF, and ClBr. Sketch the overlap of the atomic orbitals involved in the bonds.

3. Use valence bond theory to explain the bonding in O_2. Sketch the overlap of the atomic orbitals involved in the bonds in O_2.

4. How many σ and π bonds are present in the molecule HCN?

5. A friend tells you N_2 has three π bonds due to overlap of the three p-orbitals on each N atom. Do you agree?

6. Draw the Lewis structures for CO_2 and CO, and predict the number of σ and π bonds for each molecule.

(a) CO_2

(b) CO

5.2 Hybrid Atomic Orbitals

7. Why is the concept of hybridization required in valence bond theory?

8. Give the shape that describes each hybrid orbital set:

(a) sp^2

(b) sp^3d

(c) sp

(d) sp^3d^2

9. Explain why a carbon atom cannot form five bonds using sp^3d hybrid orbitals.

10. What is the hybridization of the central atom in each of the following?

(a) BeH_2

(b) SF_6

(c) $PO_4{}^{3-}$

(d) PCl_5

11. A molecule with the formula AB_3 could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

12. Methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$, is an amino acid found in proteins. The Lewis structure of this compound is shown below. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?
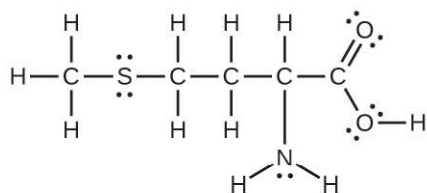

13. Sulfuric acid is manufactured by a series of reactions represented by the following equations:

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$$

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$
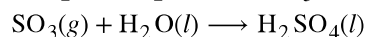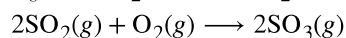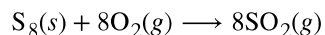
Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

(a) circular S_8 molecule

(b) SO_2 molecule

(c) SO_3 molecule

(d) H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

14. Two important industrial chemicals, ethene, C_2H_4, and propene, C_3H_6, are produced by the steam (or thermal) cracking process:

$$2C_3H_8(g) \longrightarrow C_2H_4(g) + C_3H_6(g) + CH_4(g) + H_2(g)$$
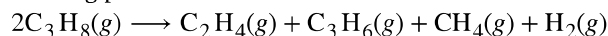
For each of the four carbon compounds, do the following:

(a) Draw a Lewis structure.

(b) Predict the geometry about the carbon atom.

(c) Determine the hybridization of each type of carbon atom.

15. Analysis of a compound indicates that it contains 77.55% Xe and 22.45% F by mass.

(a) What is the empirical formula for this compound? *(Assume this is also the molecular formula in responding to the remaining parts of this exercise).*

(b) Write a Lewis structure for the compound.

(c) Predict the shape of the molecules of the compound.

(d) What hybridization is consistent with the shape you predicted?

16. Consider nitrous acid, HNO_2 (HONO).

(a) Write a Lewis structure.

(b) What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in the HNO_2 molecule?

(c) What is the hybridization on the internal oxygen and nitrogen atoms in HNO_2?

17. Strike-anywhere matches contain a layer of $KClO_3$ and a layer of P_4S_3. The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match. $KClO_3$ contains the $ClO_3{}^-$ ion. P_4S_3 is an unusual molecule with the skeletal structure.
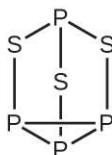
(a) Write Lewis structures for P_4S_3 and the $ClO_3{}^-$ ion.

(b) Describe the geometry about the P atoms, the S atom, and the Cl atom in these species.

(c) Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species.

(d) Determine the oxidation states and formal charge of the atoms in P_4S_3 and the $ClO_3{}^-$ ion.

18. Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.)

```
      H   H              H   H

  H   C   C   C   C   C   C   H

      H   H              H   H
```
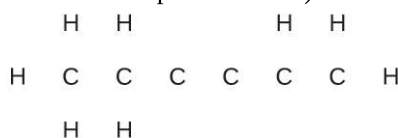
19. Write Lewis structures for NF_3 and PF_5. On the basis of hybrid orbitals, explain the fact that NF_3, PF_3, and PF_5 are stable molecules, but NF_5 does not exist.

20. In addition to NF_3, two other fluoro derivatives of nitrogen are known: N_2F_4 and N_2F_2. What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule?

5.3 Multiple Bonds

21. The bond energy of a C–C single bond averages 347 kJ mol^{-1}; that of a $C \equiv C$ triple bond averages 839 kJ mol^{-1}. Explain why the triple bond is not three times as strong as a single bond.

22. For the carbonate ion, $CO_3{}^{2-}$, draw all of the resonance structures. Identify which orbitals overlap to create each bond.

23. A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

(a) Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.

(b) Identify the hybrid orbitals used by the carbon atoms in the molecule to form σ bonds.

(c) Describe the atomic orbitals that form the π bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

24. For the molecule allene, $H_2C = C = CH_2$, give the hybridization of each carbon atom. Will the hydrogen atoms be in the same plane or perpendicular planes?

25. Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

**26.** Describe the molecular geometry and hybridization of the N, P, or S atoms in each of the following compounds.

(a) H_3PO_4, phosphoric acid, used in cola soft drinks

(b) NH_4NO_3, ammonium nitrate, a fertilizer and explosive

(c) S_2Cl_2, disulfur dichloride, used in vulcanizing rubber

(d) $K_4[O_3POPO_3]$, potassium pyrophosphate, an ingredient in some toothpastes

27. For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:
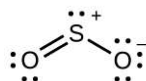
(a) ozone (O_3) central O hybridization

(b) carbon dioxide (CO_2) central C hybridization

(c) nitrogen dioxide (NO_2) central N hybridization

(d) phosphate ion (PO_4^{3-}) central P hybridization

28. For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:
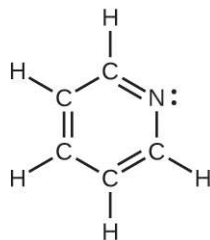
(a) Hybridization of each carbon
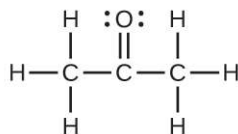
(b) Hybridization of sulfur

(c) All atoms

29. Draw the orbital diagram for carbon in CO_2 showing how many carbon atom electrons are in each orbital.

5.4 Molecular Orbital Theory

30. Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two *s* orbitals and from two *p* orbitals.

31. How are the following similar, and how do they differ?

(a) σ molecular orbitals and π molecular orbitals

(b) ψ for an atomic orbital and ψ for a molecular orbital

(c) bonding orbitals and antibonding orbitals

32. If molecular orbitals are created by combining five atomic orbitals from atom A and five atomic orbitals from atom B combine, how many molecular orbitals will result?

33. Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

34. Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

35. Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

36. Calculate the bond order for an ion with this configuration:

$$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}, \ \pi_{2pz})^4 (\pi_{2py}^*, \ \pi_{2pz}^*)^3$$
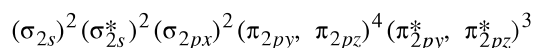
37. Explain why an electron in the bonding molecular orbital in the H_2 molecule has a lower energy than an electron in the 1*s* atomic orbital of either of the separated hydrogen atoms.

38. Predict the valence electron molecular orbital configurations for the following, and state whether they will be stable or unstable ions.

(a) $Na_2{}^{2+}$

(b) $Mg_2{}^{2+}$

(c) $Al_2{}^{2+}$

(d) $Si_2{}^{2+}$

(e) $P_2{}^{2+}$

(f) $S_2{}^{2+}$

(g) $F_2{}^{2+}$

(h) $Ar_2{}^{2+}$

39. Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

(a) H_2, $H_2{}^+$, $H_2{}^-$

(b) O_2, $O_2{}^{2+}$, $O_2{}^{2-}$

(c) Li_2, $Be_2{}^+$, Be_2

(d) F_2, $F_2{}^+$, $F_2{}^-$

(e) N_2, $N_2{}^+$, $N_2{}^-$

40. For the first ionization energy for an N_2 molecule, what molecular orbital is the electron removed from?

41. Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

(a) H and H_2

(b) N and N_2

(c) O and O_2

(d) C and C_2

(e) B and B_2

42. Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

43. A friend tells you that the 2s orbital for fluorine starts off at a much lower energy than the 2s orbital for lithium, so the resulting σ_{2s} molecular orbital in F_2 is more stable than in Li_2. Do you agree?

44. True or false: Boron contains $2s^2 2p^1$ valence electrons, so only one p orbital is needed to form molecular orbitals.

45. What charge would be needed on F_2 to generate an ion with a bond order of 2?

46. Predict whether the MO diagram for S_2 would show s-p mixing or not.

47. Explain why $N_2{}^{2+}$ is diamagnetic, while $O_2{}^{4+}$, which has the same number of valence electrons, is paramagnetic.

48. Using the MO diagrams, predict the bond order for the stronger bond in each pair:

(a) B_2 or $B_2{}^+$

(b) F_2 or $F_2{}^+$

(c) O_2 or $O_2{}^{2+}$

(d) $C_2{}^+$ or $C_2{}^-$