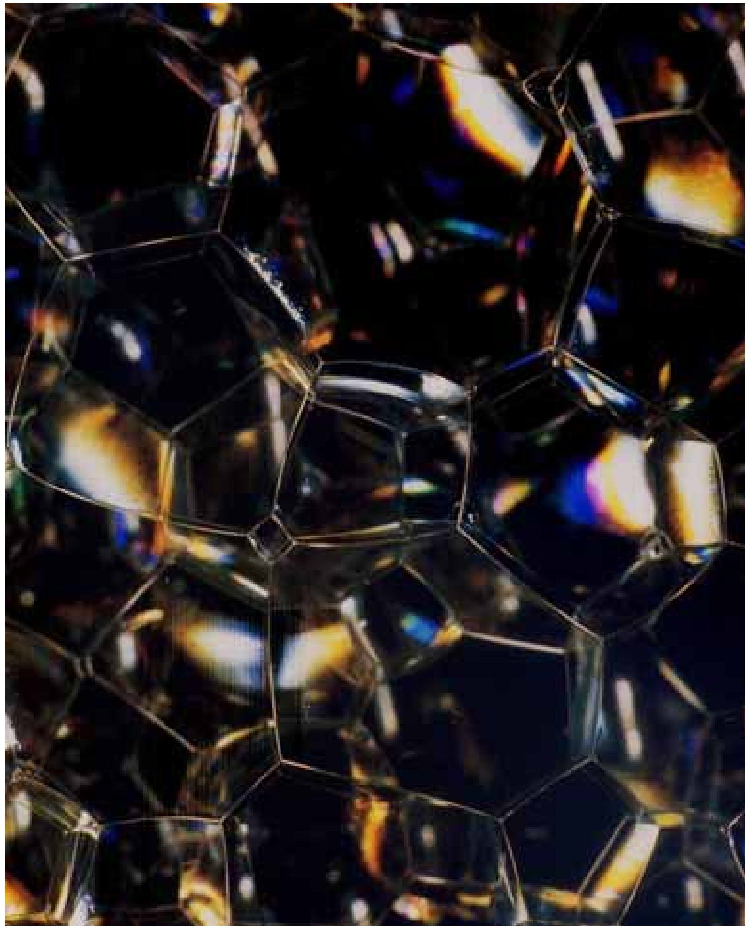
Chemistry

Zumdahl, 7th edition

歐亞書局

CH9 Covalent Bonding: Orbitals



A close-up soap bubbles reveals their geometric shapes.

Contents

Introduction

- Simple model for covalent bonding: the localized electron model.

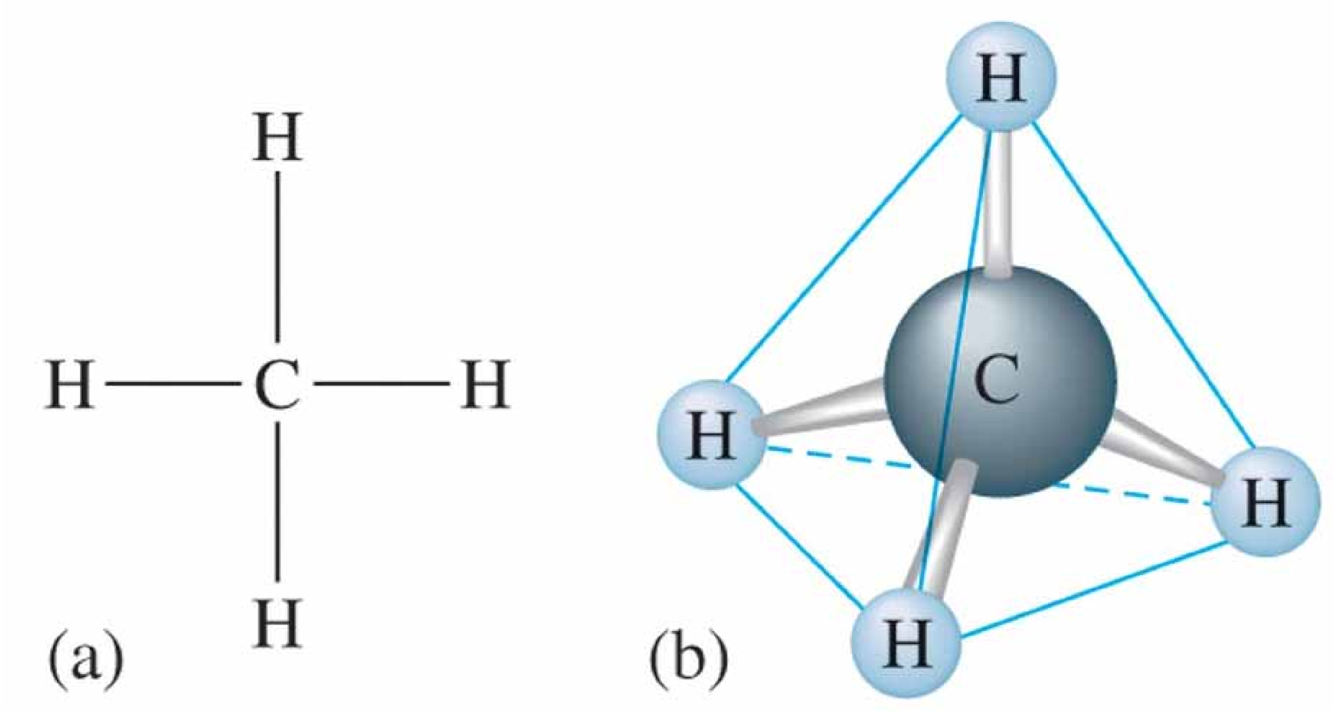
9.1 Hybridization and the Localized Electron Model

- The arrangement of valence electrons is represented by the Lewis structure, and the molecular geometry can be predicted from the VSEPR model.

sp^3 Hybridization

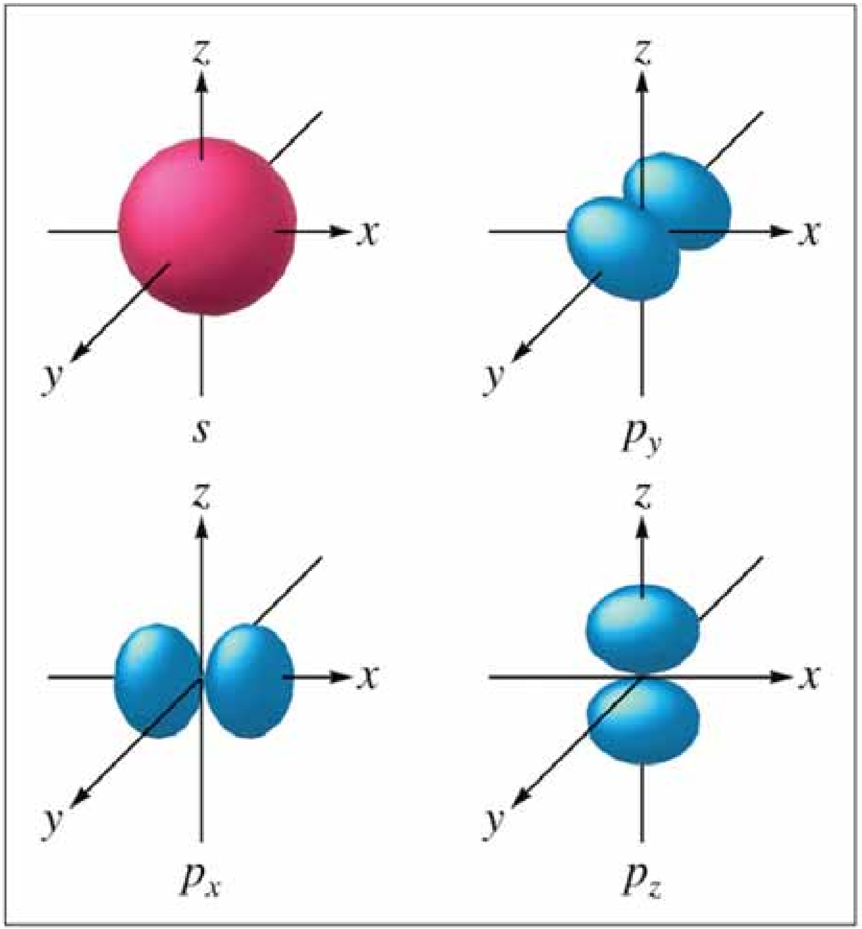
- **methane**: has the Lewis structure and molecular geometry shown in Fig. 9.1.
- The valence orbitals of a carbon atom are the 2*s* and 2*p* orbitals shown in Fig. 9.2.
- The methane molecule is known by experiment to be tetrahedral with bond angles of 109.5 degrees.

Figure 9.1



(a) The Lewis structure of the methane molecule. (b) The tetrahedral molecular geometry of the methane molecule.

Figure 9.2



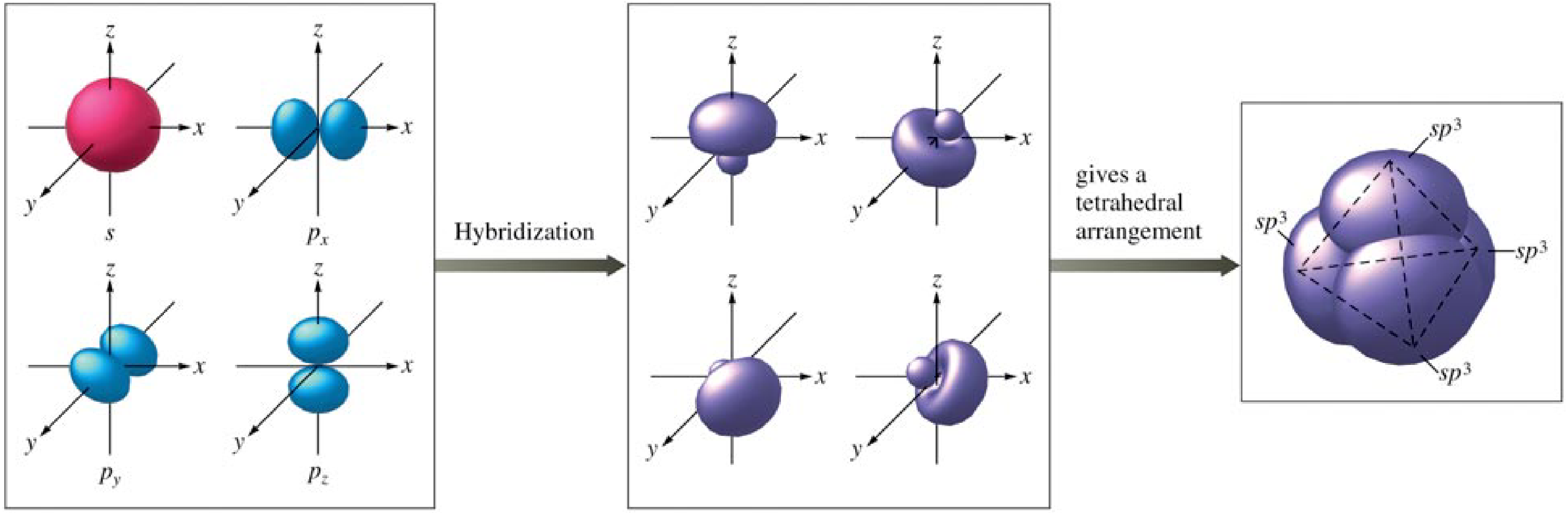
The valence orbitals on a free carbon atom: 2*s*, $2p_x$, $2p_y$, and $2p_z$.

- Two conclusions:

1. Either the simple localized electron model is wrong or carbon adopts a set of atomic orbitals other than its “native” 2*s* and 2*p* orbitals to bond to the hydrogen atoms in forming the methane molecule.
2. The 2*s* and 2*p* orbitals present on an *isolated* carbon atom may not be the best set of orbitals for bonding; a new set of atomic orbitals might better serve the carbon atom in forming molecules.

- Such a set of orbitals can be obtained quite readily by combining the carbon 2*s* and 2*p* orbitals, as shown schematically in Fig. 9.3.
- This mixing of the native atomic orbitals to form special orbitals for bonding is called **hybridization**.
- The four new orbitals are called sp^3 orbitals because they are formed from one 2*s* and three 2*p* orbitals (s^1p^3).

Figure 9.3



The “native” 2*s* and three 2*p* atomic orbitals characteristic of a free carbon atom are combined to form a new set of four sp^3 orbitals. The small lobes of the orbitals are usually omitted from diagrams for clarity.

- We say that the carbon atom undergoes ***sp*^{3} hybridization** or is ***sp*^{3} hybridized**.
- The four *sp*^{3} orbitals are identical in shape, each one having a large lobe and a small lobe (see Fig. 9.4).
- The hybridization of the carbon 2*s* and 2*p* orbitals also can be represented by an orbital energy-level diagram, as shown in Fig.9.5.

Figure 9.4

Cross section of an sp^3 orbital. This shows a “slice” of the electron density of the sp^3 orbitals illustrated in the center diagram of Fig. 9.3.

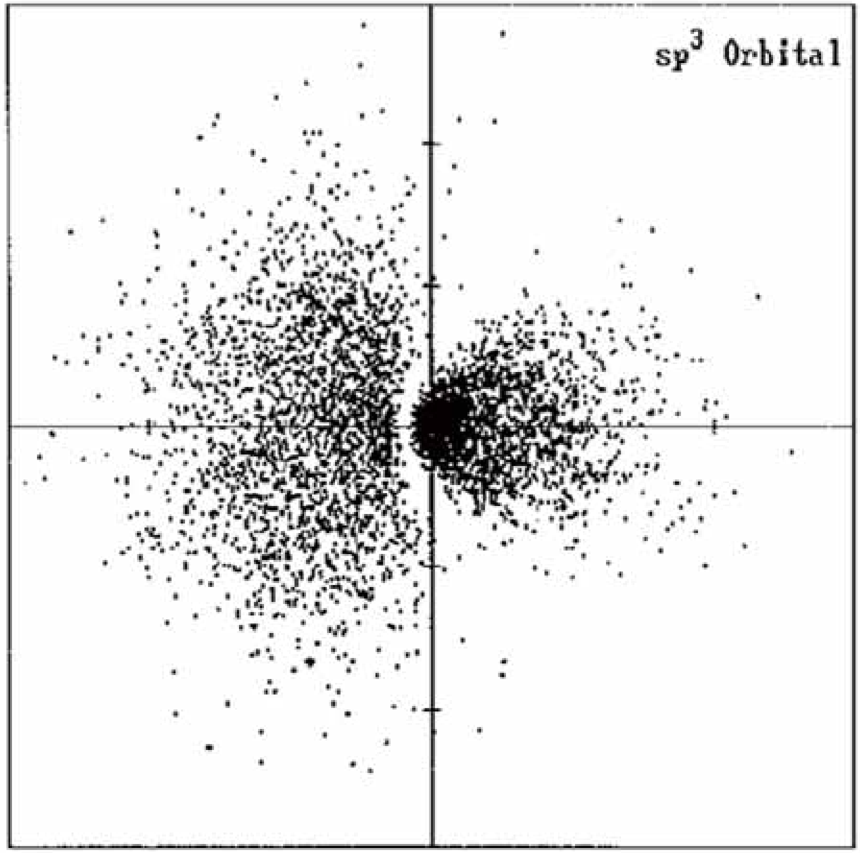
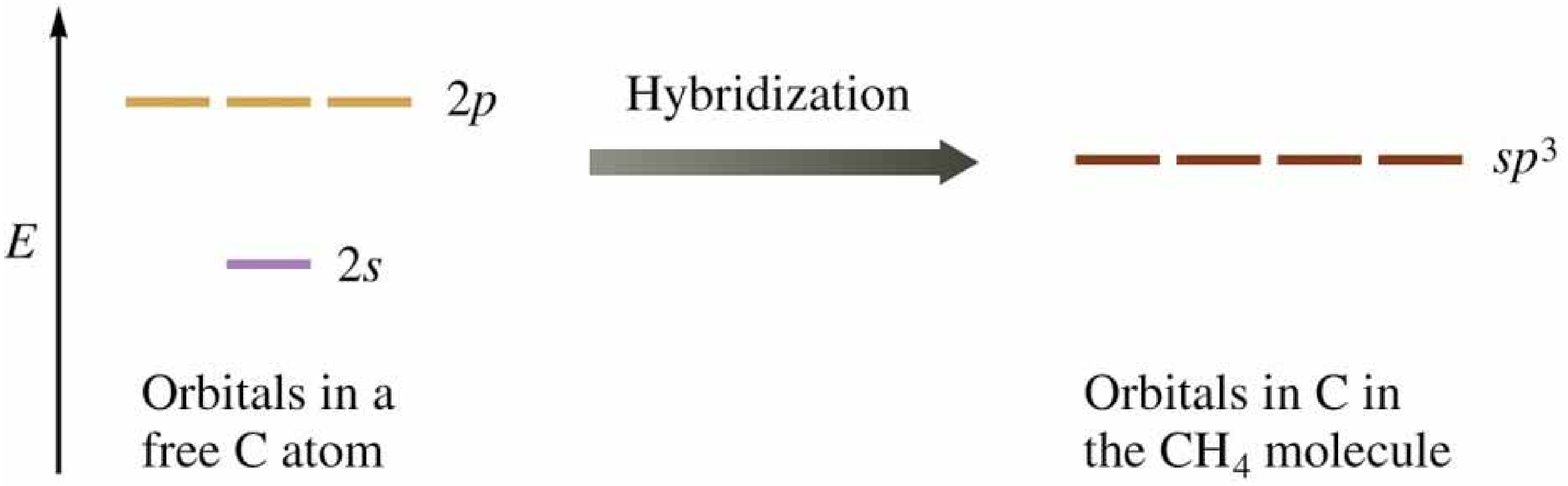


Figure 9.5

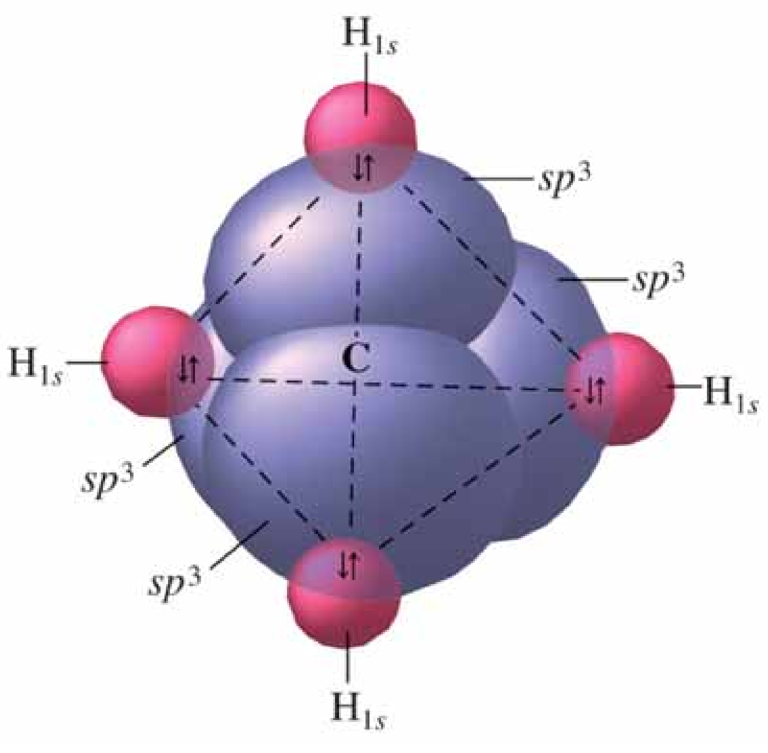


An energy-level diagram showing the formation of four *sp*^{3} orbitals.

- The new sp^3 atomic orbitals on carbon are used to share electron pairs with the 1s orbitals from the four hydrogen atoms, as shown in Fig. 9.6.

Figure 9.6

The tetrahedral set of four sp^3 orbitals of the carbon atom are used to share electron pairs with the four 1*s* orbitals of the hydrogen atoms to form the four equivalent C—H bonds. This accounts for the known tetrahedral structure of the CH_4 molecule.



- The bonding in the methane molecule: The experimentally known structure of this molecule can be explained if we assume that the carbon atom adopts a special set of atomic orbitals.
- These new orbitals are obtained by combining the 2*s* and the three 2*p* orbitals of the carbon atom to produce four identically shaped orbitals that are oriented toward the corners of a tetrahedron and are used to bond to the hydrogen atoms.

- Thus the four *sp*^{3} orbitals on carbon in methane are postulated to account for its known structure.
- **principle**: *Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, this model assumes that the atom adopts a set of sp*^{3} *orbitals; the atom becomes sp3 hybridized*.
- An atom in a molecule might adopt a different set of atomic orbitals (called **hybrid orbitals**) from those it has in the free state.

Sample Exercise 9.1

The Localized Electron Model I

Describe the bonding in the ammonia molecule using the localized electron model.

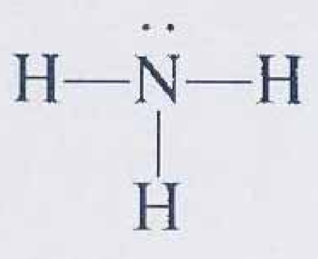
Solution

A complete description of the bonding involves three steps:

1. Writing the Lewis structure
2. Determining the arrangement of electron pairs using the VSEPR model
3. Determining the hybrid atomic orbitals needed to describe the bonding in the moleucle

Sample Exercise 9.1

The Lewis structure for NH_3 is



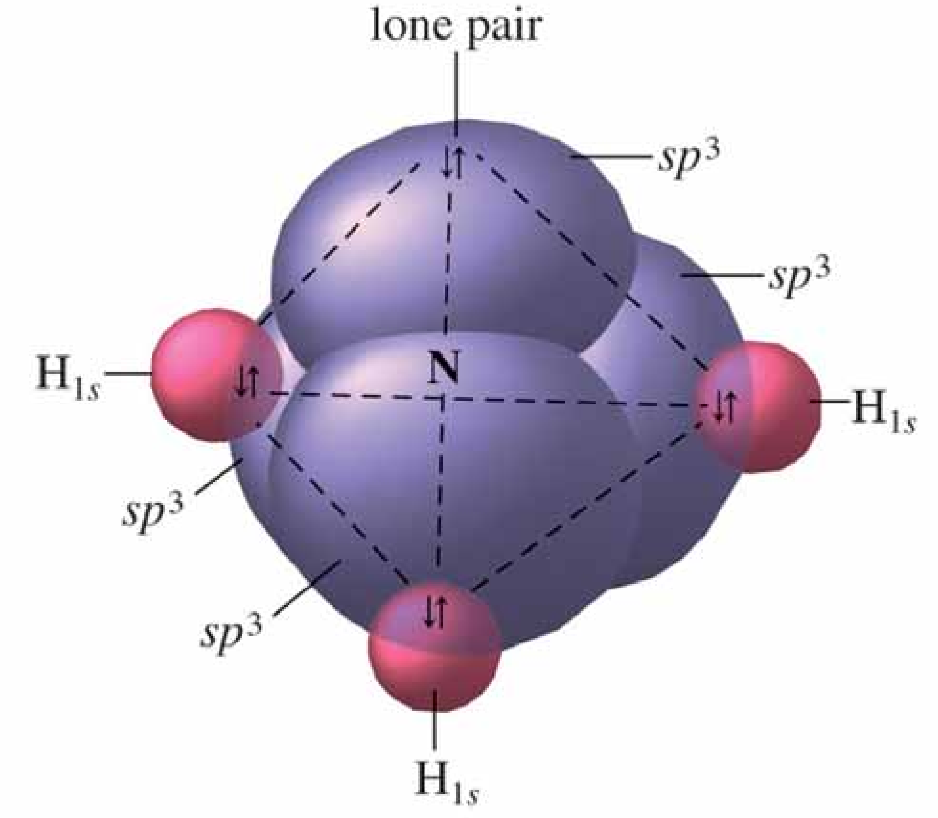
The four electron pairs around the nitrogen atom require a tetrahedral arrangement to minimize repulsions. We have seen that a tetrahedral set of sp^3 hybrid orbitals is obtained by combining the 2*s* and three 2*p* orbitals. In the NH_3 molecule three of the sp^3 orbitals are used of form

Sample Exercise 9.1

bonds to the three hydrogen atoms, and the fourth sp^3 orbital holds the lone pair, as shown in Fig. 9.7.

See Exercises 9.15.

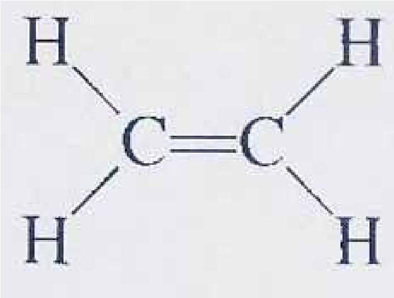
Figure 9.7



The nitrogen atom in ammonia is sp^3 hybridized.

sp^2 Hybridization

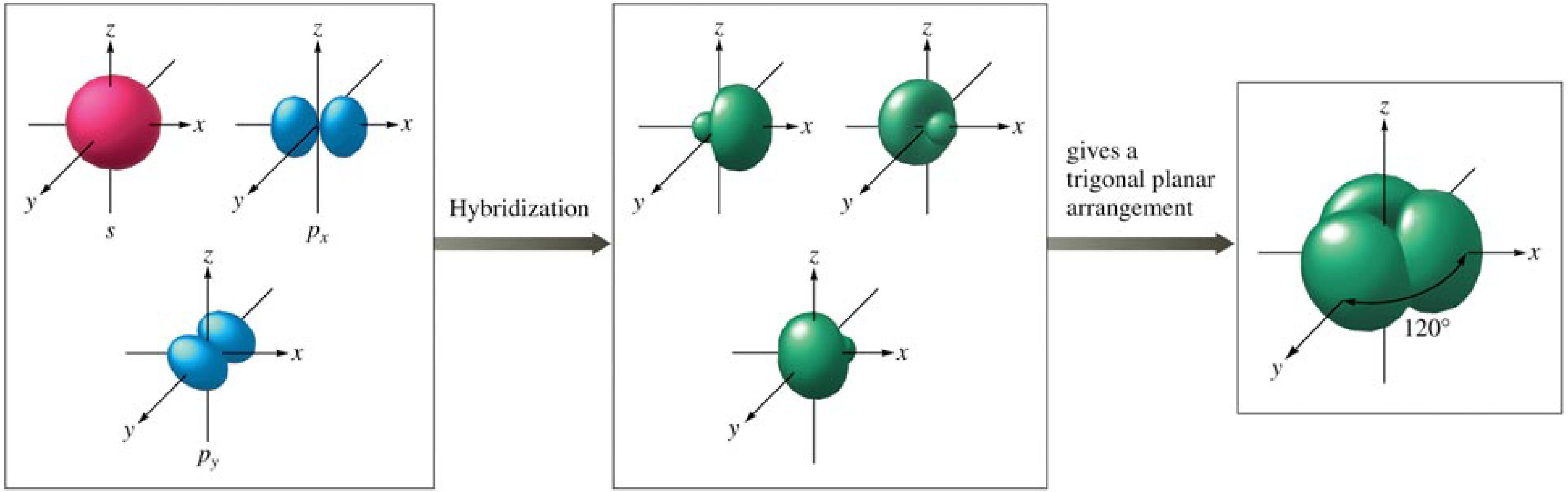
- Ethylene (C_2H_4) is an important starting material in the manufacture of plastics. The C_2H_4 molecule has 12 valence electrons and following Lewis structure:



- in the ethylene molecule each carbon is surrounded by three effective pairs. This requires a trigonal planar arrangement with bond angles of 120 degrees.

- Since the 2*s* and 2*p* valence orbitals of carbon do not have the required arrangement, we need a set of hybrid orbitals.
- The sp^3 orbitals we have just considered will not work because they are at angles of 109.5 degrees rather than the required 120 degrees.
- A set of three orbitals arranged at 120-degree angles in the same plane can be obtained by combining one *s* orbital and two *p* orbitals, as shown in Fig. 9.8.

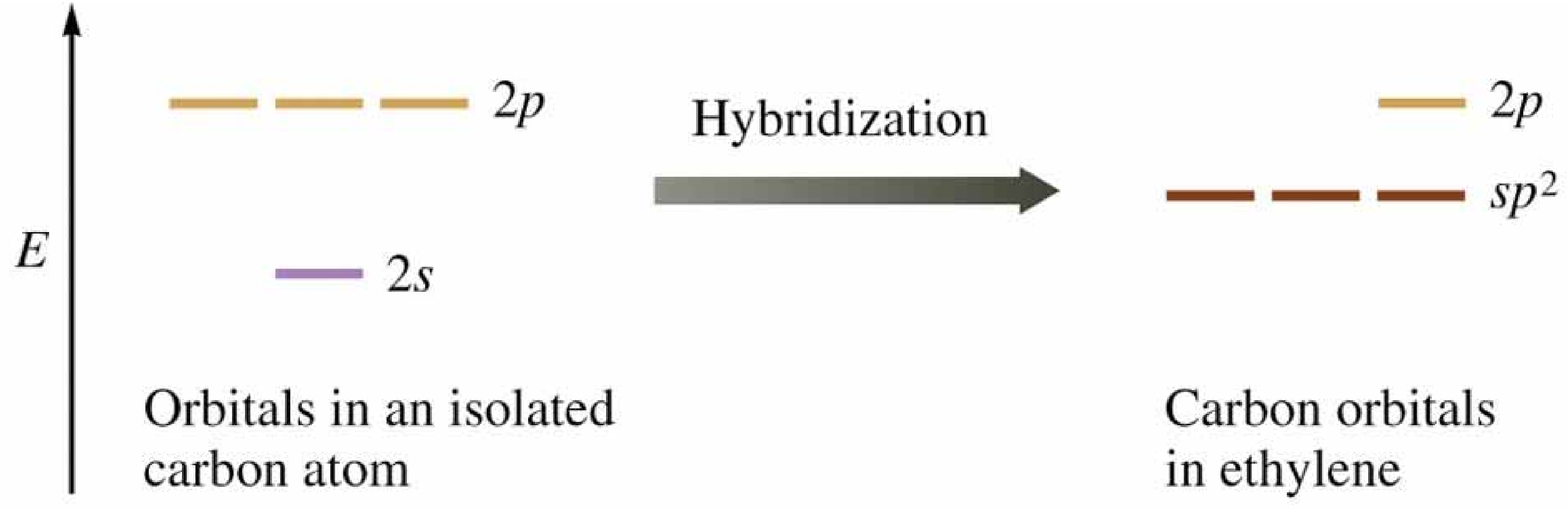
Figure 9.8



The hybridization of the *s*, p_x, and p_y atomic orbitals results in the formation of three sp^2 orbitals centered in the *xy* plane. The large lobes of the orbitals lie in the plane at angles of 120 degrees and point toward the corners of a triangle.

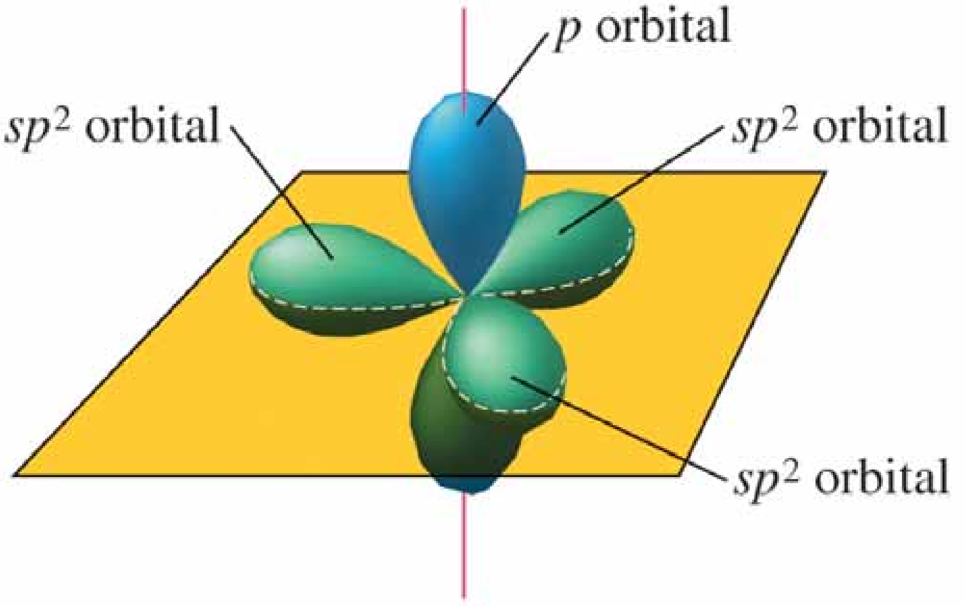
- The orbital energy-level diagram for this arrangement is shown in Fig. 9.9.
- Since one 2*s* and two 2*p* orbitals are used to form these hybrid orbitals, this is called sp^2 hybridization.
- In forming the sp^2 orbitals, one 2*p* orbital on carbon has not been used.
- This remaining *p* orbital (p_z) is oriented perpendicular to the plane of the sp^2 orbitals, as shown in Fig. 9.10.

Figure 9.9



An orbital energy-level diagram for sp^2 hybridization. Note that one p orbital remains unchanged.

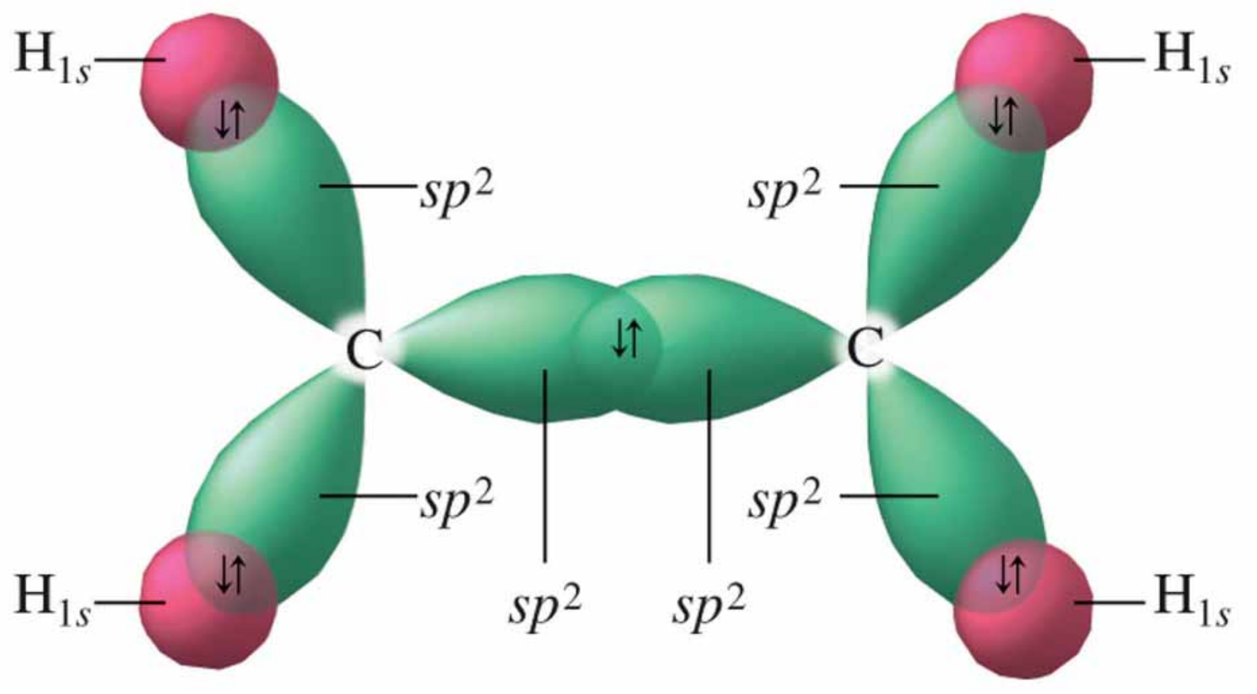
Figure 9.10



When an s and two p orbitals are mixed to form a set of three *sp*^{2} orbitals, one *p* orbital remains unchanged and is perpendicular to the plane of the hybrid orbitals. Note that in this figure and those that follow, the orbitals are drawn with narrowed lobes to show their orientations more clearly.

- The three sp^2 orbitals on each carbon can be used to share electrons, as shown in Fig. 9.11.
- In each of these bonds, the electron pair is shared in an area centered on a line running between the atoms.
- This type of covalent bond is called a **sigme (σ) bond**. In the ethylene molecule, the σ bonds are formed using sp^2 orbitals on each carbon atom and the 1s orbital on each hydrogen atom.

Figure 9.11



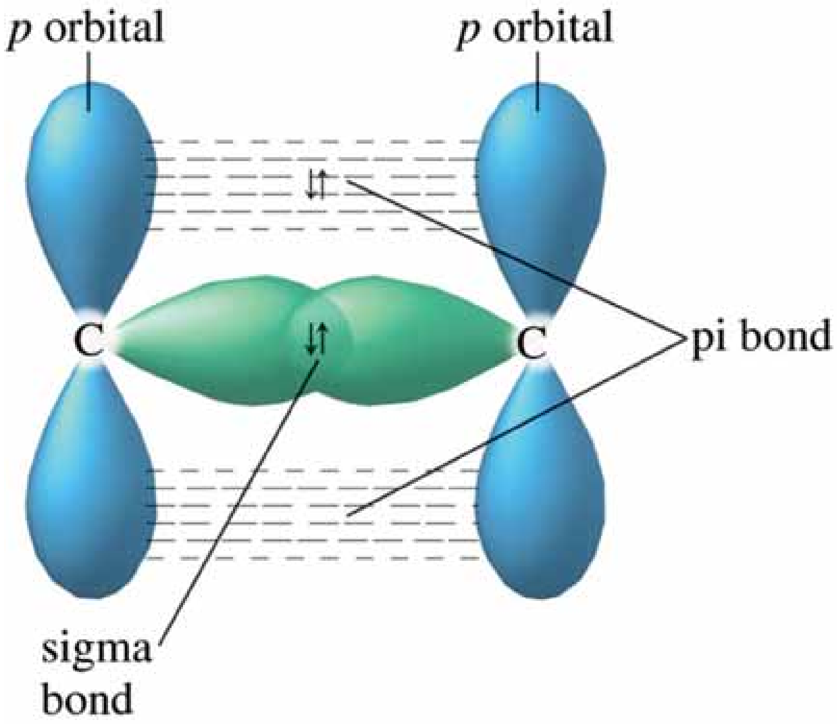
The σ bonds in ethylene. Note that for each bond the shared electron pair occupies the region directly between the atoms.

- In the σ bond the electron pair occupies the space between the carbon atoms.
- The second bond must therefore result from sharing an electron pair in the space above and below the σ bond.
- This type of bond can be formed using the 2*p* orbital perpendicular to the sp^2 hybrid orbitals on each carbon atom (refer to Fig. 9.10).

- These parallel *p* orbitals can share an electron pair, which occupies the space above and below a line joining the atoms, to form a **pi (π) bond**, as shown in Fig. 9.12.

Figure 9.12

A carbon-carbon double bond consists of a σ bond and a π bond. In the σ bond the shared electrons occpy the space directly between the atoms. The π bond is formed from the unhybridized *p* orbitals on the two carbon atoms. In a π bond the shared electron pair occupies the space above and below a line joining the atoms.

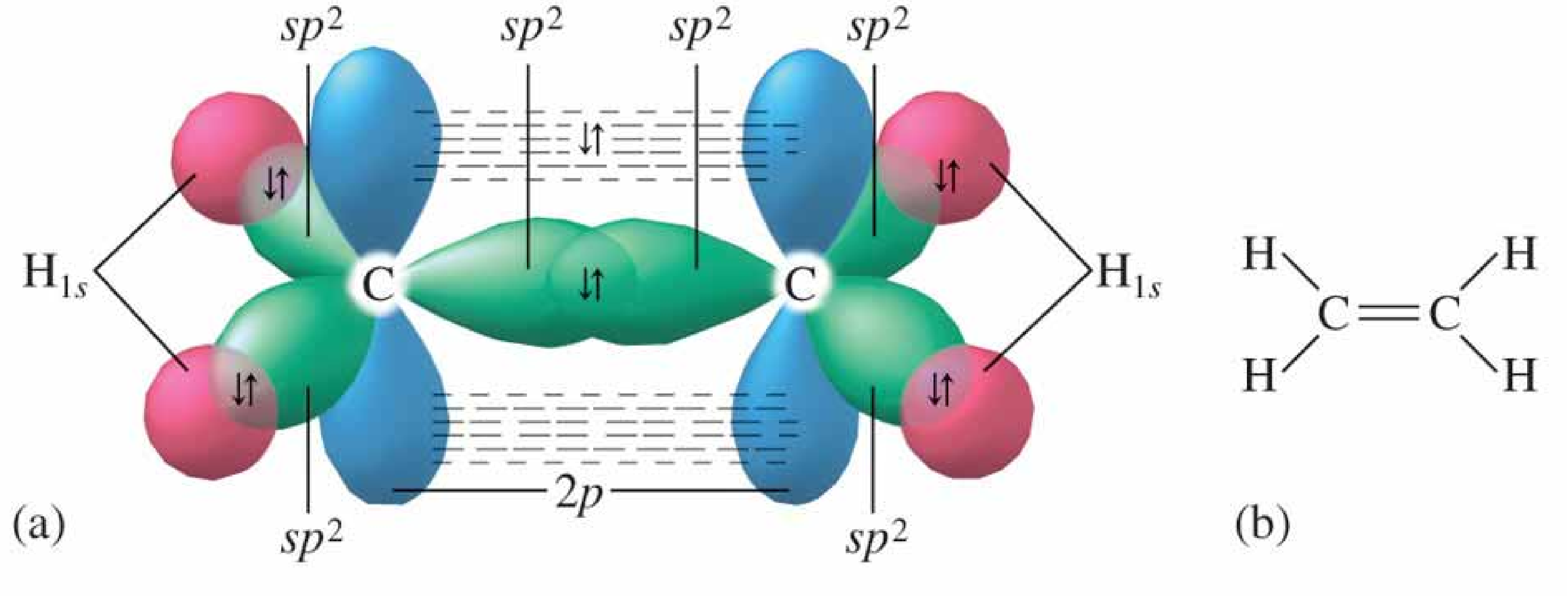


- Note that σ bonds are formed from orbitals whose lobes point toward each other, but π bonds result from parallel orbitals.
- A *double bond always consists of one σ bond, where the electron pair is located directly between the atoms,* and one π bonds, where the shared pair occpies the space above and below the σ bond.

- As shown in Fig. 9.13, the carbon atoms use *sp*^{2} hybrid orbitals to form the σ bonds to the hydrogen atoms and to each other, and they use p to form the π bond with each other.
- An important general principle of this model:

Whenever an atom is surrounded by three effective pairs, a set of sp^2 *hybrid orbitals is required.*

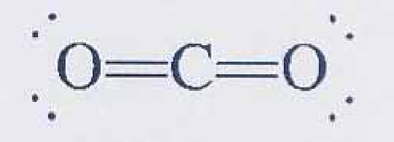
Figure 9.13



(a) The orbitals used to form the bonds in ethylene. (b) The Lewis structure for ethylene.

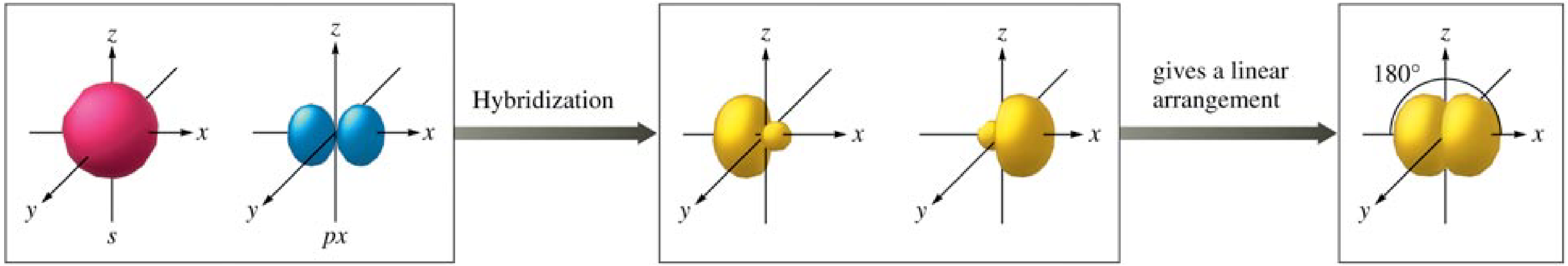
sp Hybridization

- Another type of hybridization occurs in carbon dioxide, which has the following Lewis structure:



- In the CO_2 molecule the carbon atom has two effective pairs that will be arranged at an angle of 180 degrees.
- To obtain two hybrid orbitals arranged at 180 degrees requires ***sp* hybridization**, involving one s orbital and one p orbital, as shown in Fig. 9.14.

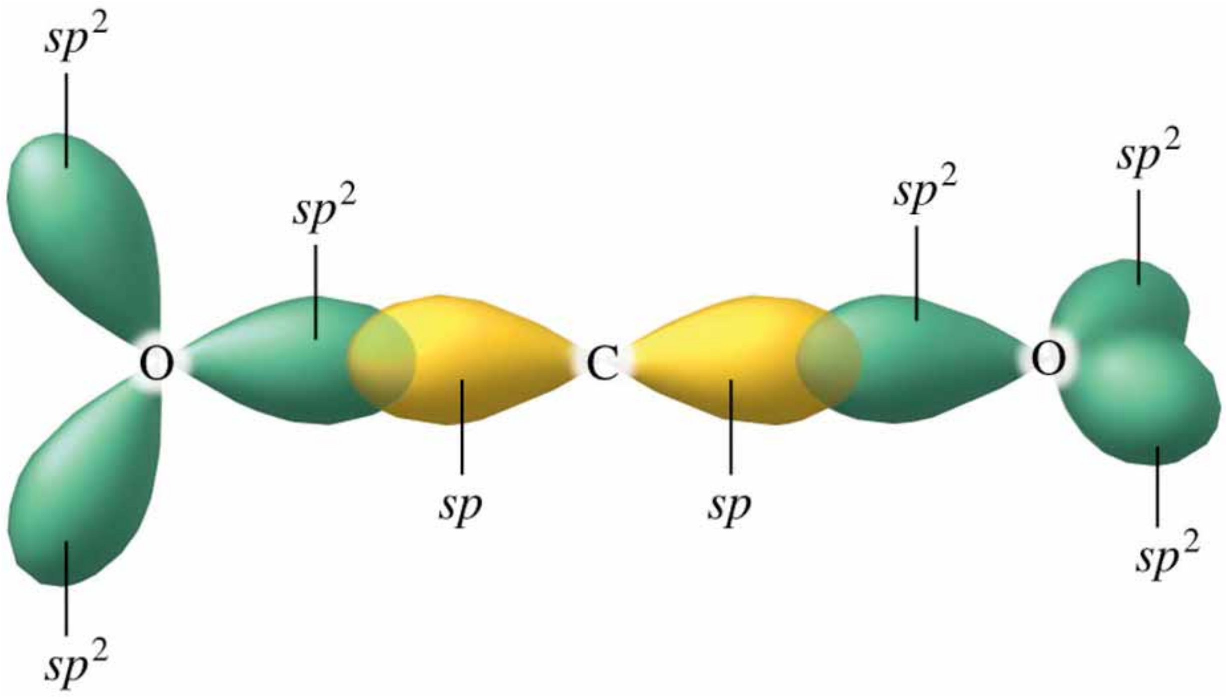
Figure 9.14



When one *s* orbital and one *p* orbital are hybridized, a set of two *sp* orbitals oriented at 180 degrees results.

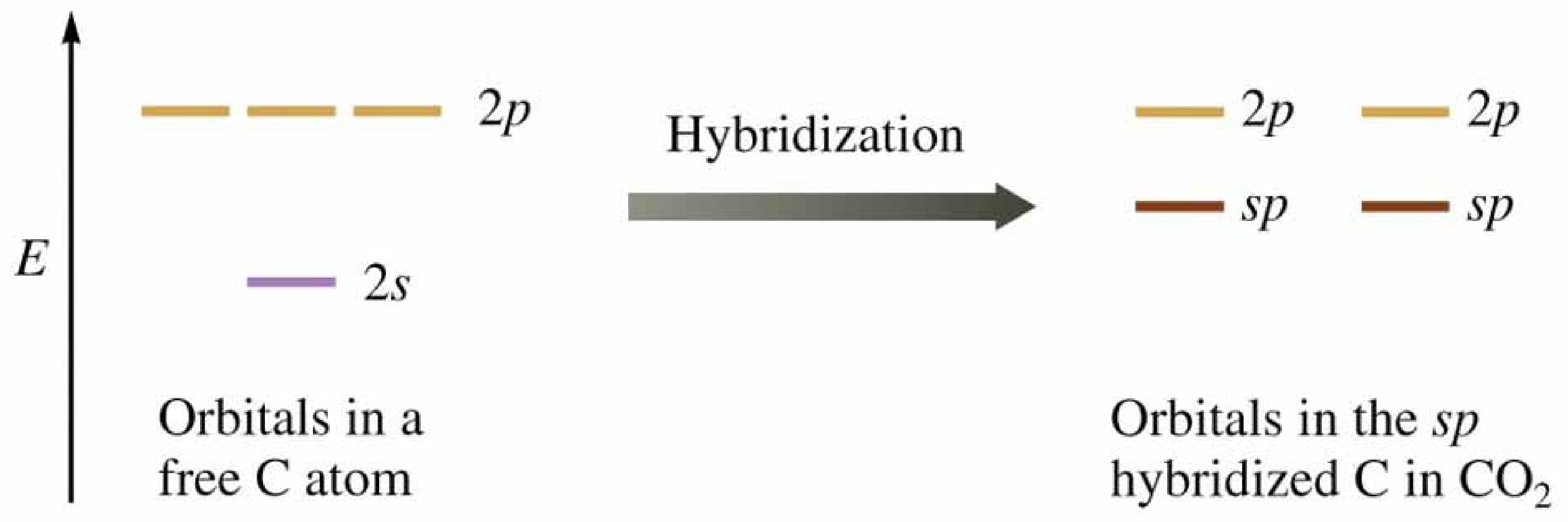
- In terms of this model, two effective pairs around on atom will always require sp hybridization of that atom.
- The *sp* orbitals of carbon in carbon dioxide can be seen in Fig. 9.15, and the corresponding orbital energy-level diagram for their formation is given in Fig. 9.16.
- The bonding in carbon dioxide.
- The *sp* orbitals on carbon form σ bonds with the sp^2 orbitals on the two oxygen atoms (Fig. 9.15).

Figure 9.15



The hybrid orbitals in the CO_2 molecule.

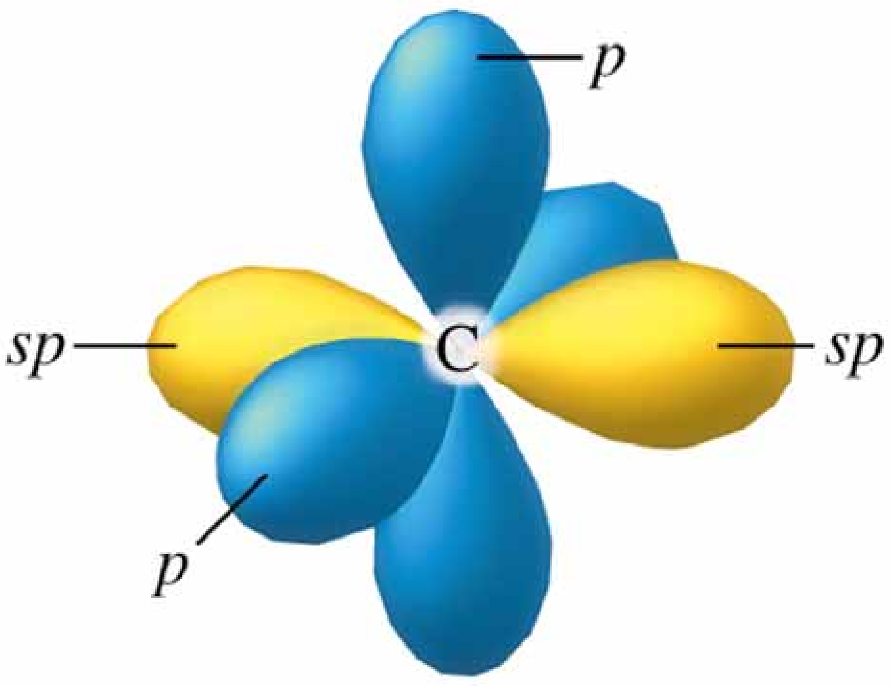
Figure 9.16



The orbital energy-level diagram for the formation of *sp* hybrid orbitals on carbon.

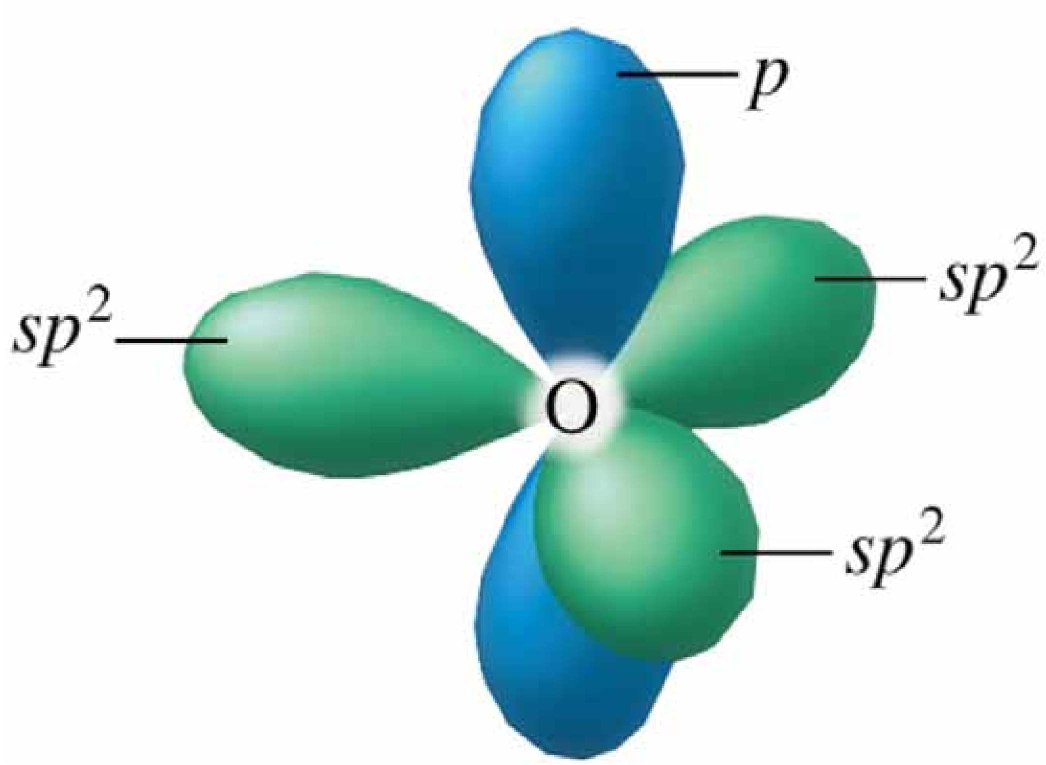
- The remaining sp^2 orbitals on the oxygen atoms hold lone pairs.
- The π bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel 2*p* orbitals.
- The *sp* hybridized carbon atom has two unhybridized *p* orbitals, pictured in Fig. 9.17.
- Each of these *p* orbitals is used to form a π bond with an oxygen atom (see Fig. 9.18).

Figure 9.17



The orbitals of an sp hybridized carbon atom.

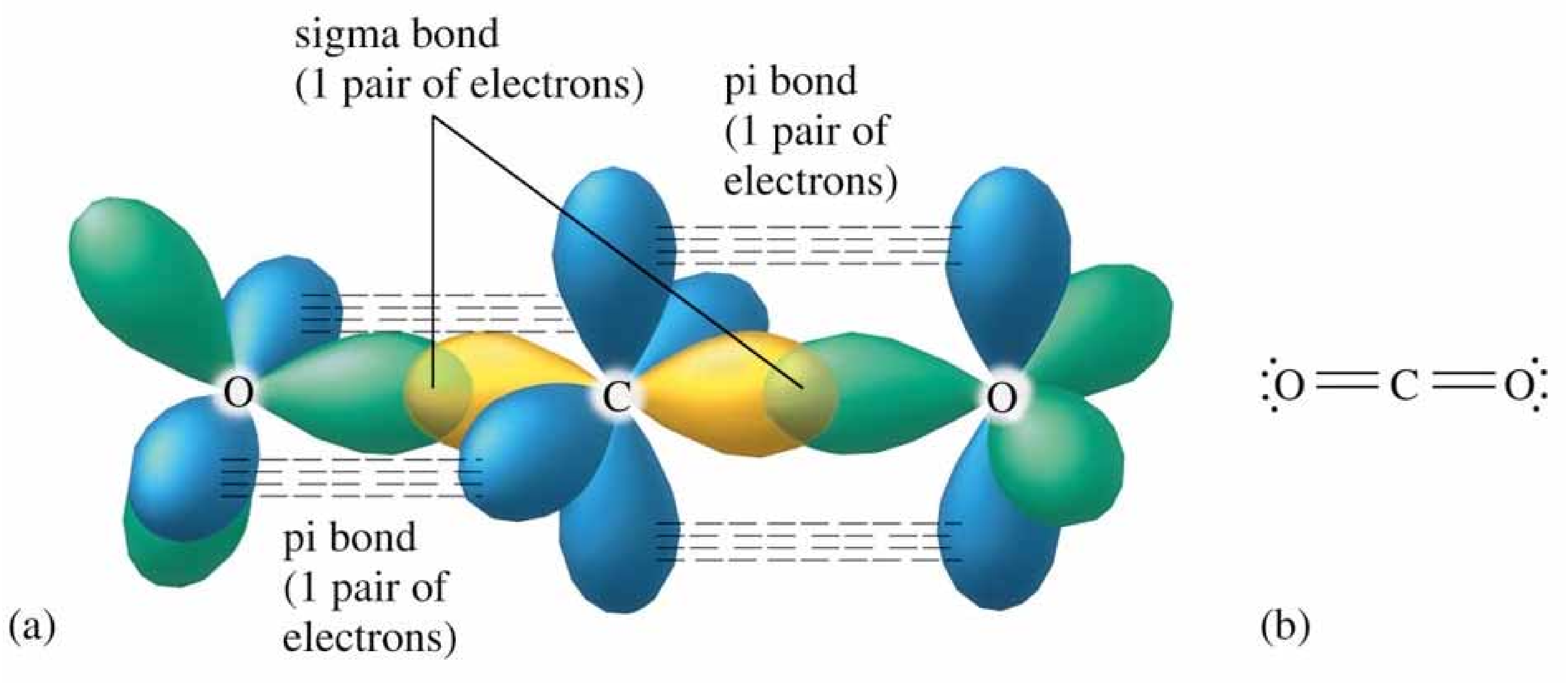
Figure 9.18



The orbital arrangement for an *sp*^{2} hybridized oxygen atom.

- The total bonding picture for the CO_2 molecule is shown in Fig. 9.19.
- Note that this picture of the bonding neatly explains the arrangement of electrons predicted by the Lewis structure.

Figure 9.19



(a) The orbitals used to form the bonds in carbon dioxide. Note that the carbon-oxygen double bonds each consist of one σ bond and one π bond. (b) The Lewis structure for carbon dioxide.

Sample Exercise 9.2

The Localized Electron Model II

Describe the bonding in the N_2 molecule.

Solution

The Lewis structure for the nitrogen molecule is

$$:N \equiv N:$$

where each nitrogen atom is surrounded by two effective pairs. (Remermber that a multiple bond counts as one effective pair.) This gives a linear arrangement (180 degrees) requiring a pair of oppositely directed orbitals. This situation requires sp hybridization. Each nitrogen

Sample Exercise 9.2

atom in the nitrogen molecule has two *sp* hybrid orbitals and two unchanged *p* orbitals, as shown in Fig. 9.20(a). The sp orbitals are used to form the σ bond between the nitrogen atoms and to hold lone pairs, as shown in Fig. 9.20(b). The p orbitals are used to form the two π bonds [see Fig. 9.20(c)]; each pair of overapping parallel *p* orbitals holds one electron pair. Such bonding accounts for the electron arrangement given by the Lewis structure. The triple bond consist of a σ bond (overlap of two *sp*

Sample Exercise 9.2

orbitals) and two π bonds (each one from an overlap of two *p* orbitals). In addition, a lone pair occupies an *sp* orbital on each nitrogen atom.

See Exercises 9.17 and 9.18.

Figure 9.20

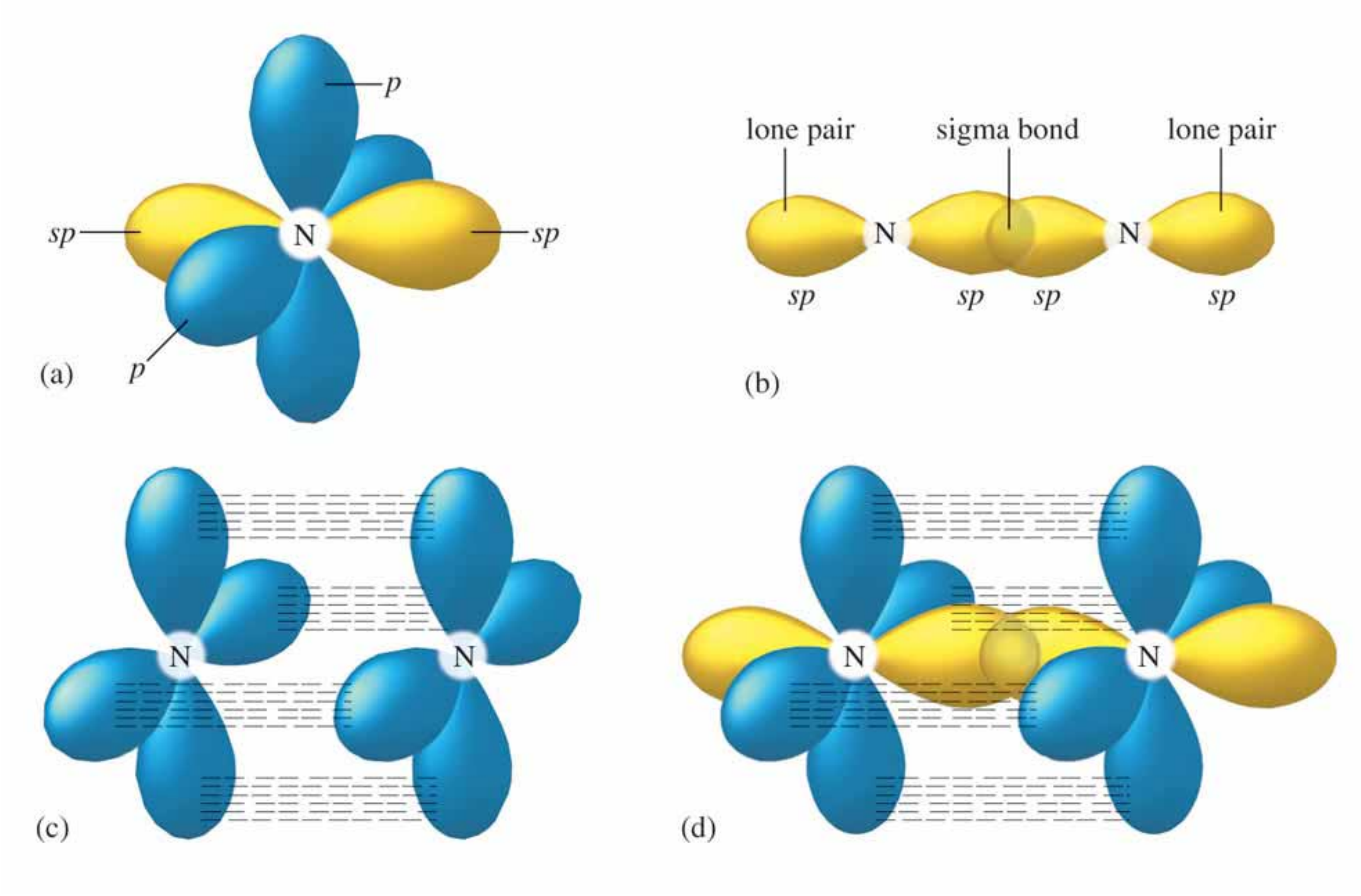
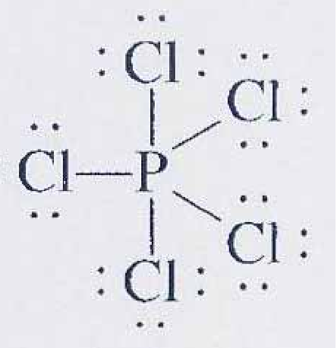

p
sp
N
sp
p
(a)
lone pair
sigma bond
lone pair
N
N
sp
sp
sp
sp
(b)
N
N
(c)
N
N
(d)

Figure 9.20

(a) An *sp* hybridized nitrogen atom. There are two *sp* hybrid orbitals and two unhybridized *p* orbitals. (b) The σ bond in the N_2 molecule. (c) The two π bonds in N_2 are formed when electron pairs are shared between two sets of parallel *p* orbitals. (d) The total bonding picture for N_2.

dsp^3 Hybridization

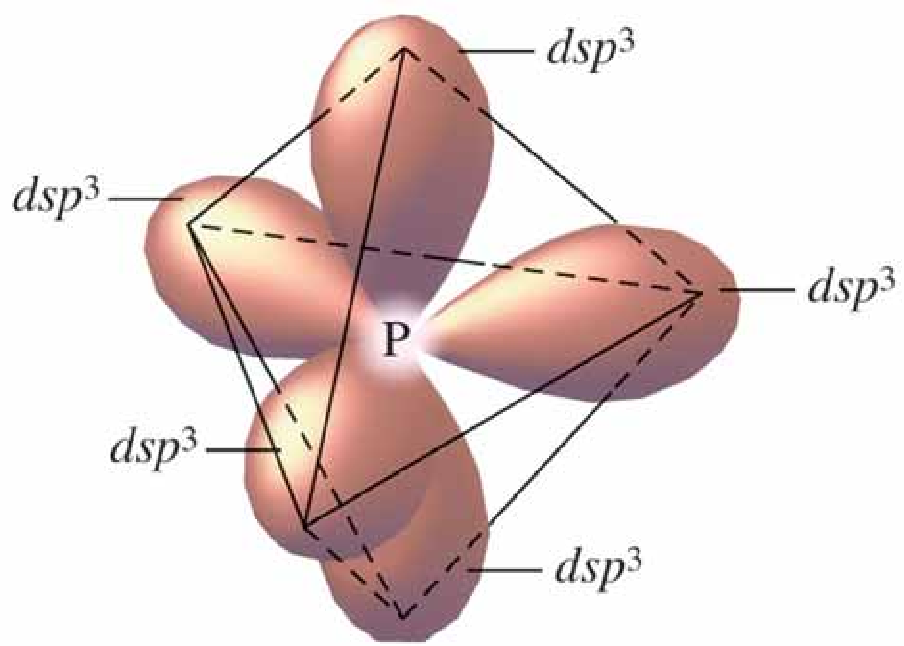
- phosphorus pentachloride molecule (PCl_5). The Lewis structure



- shows that the phosphorus atom is surrounded by five electron pairs.

- Since five pairs require a trigonal bipyramidal arrangement, we needed a trigonal bipyramidal set of atomic orbitals on phosphorus.
- Such a set of orbitals in formed by ***dsp*^3^ hybridization** of one *d* orbital, one *s* orbital, and three *p* orbitals, as shown in Fig. 9.21.

Figure 9.21



A set of *dsp*^{3} hybrid orbitals on a phosphorus atom. Note that the set of five *dsp*^{3} orbitals has a trigonal bipyramidal arrangement. (Each *dsp*^{3} orbitals also has a small lobe that is not shown in this diagram.)

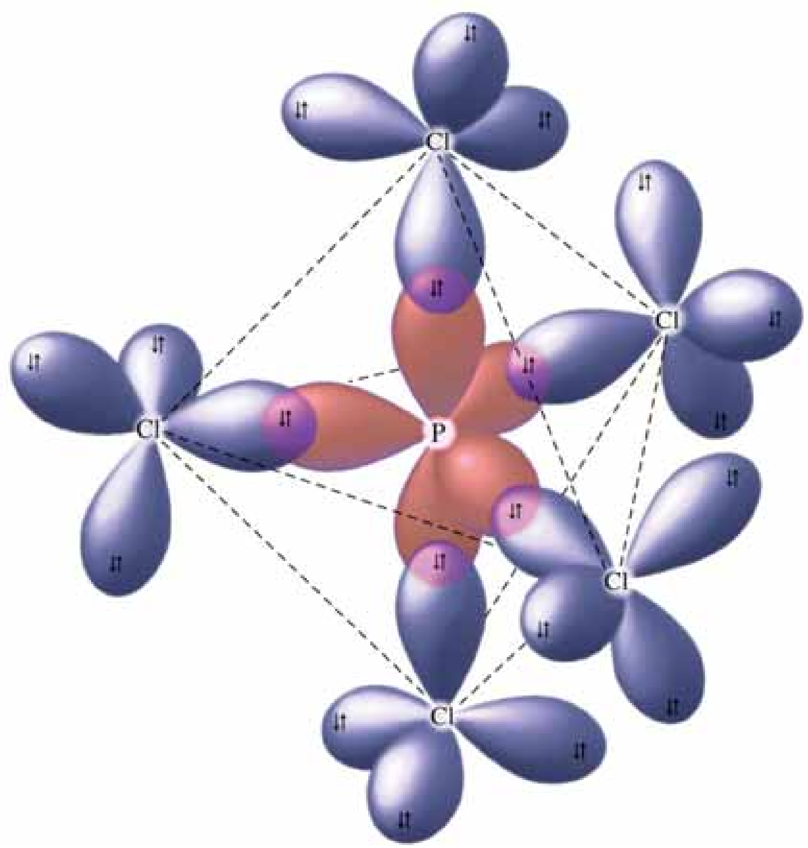
- The *dsp*^{3} hybridized phosphorus atom in the PCl_5 molecule uses its five *dsp*^{3} orbitals to share electrons with the five chlorine atoms.
- *Note that a set of five effective pairs around a given atom always requires a trigonal bipyramidal arrangement, which in turn requires dsp*^{3} *hybridization of that atom.*

- the bonding in the PCl_5 molecule: The five P—Cl σ bonds are formed by sharing electrons between a dsp^3 orbital on the phosphorus atom and an sp^3 orbital on each chlorine.
- The other sp^3 orbitals on each chlorine hold lone pairs. This is shown in Fig. 9.22.

Figure 9.22

(a) The structure of the PCl_5 molecule.

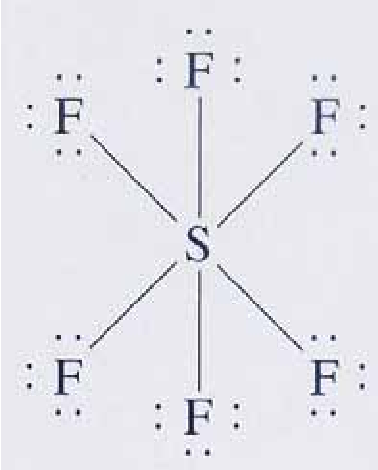
Figure 9.22



(b) The orbitals used to form the bonds in PCl_5. The phosphorus uses a set of five dsp^3 orbitals to share electron pairs with sp^3 orbitals on the five chlorine atoms. The other sp^3 orbitals on each chlorine atom hold lone pairs.

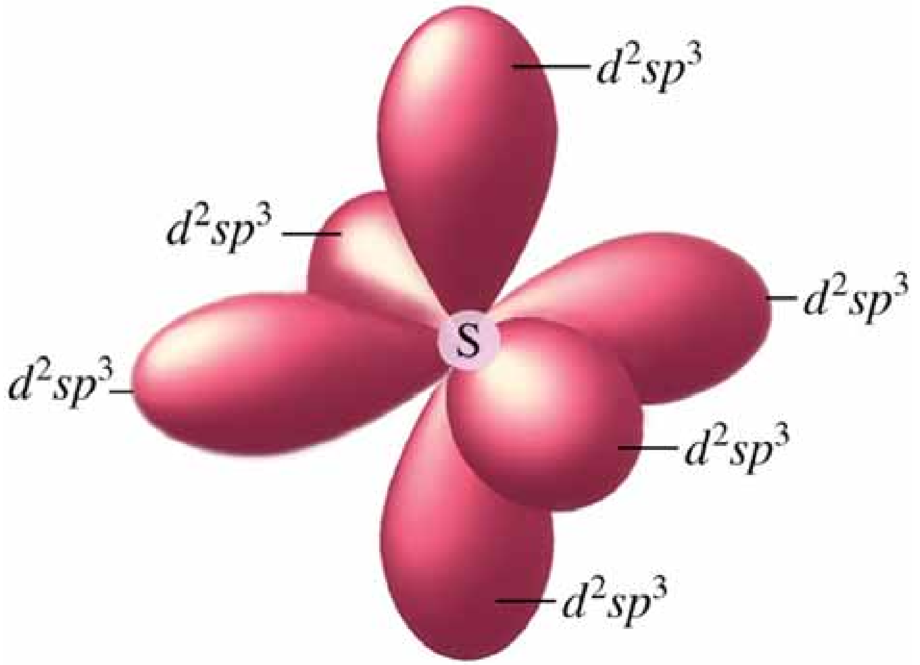
d^2sp^3 Hybridization

- sulfur hexafluoride (SF_6), has the Lewis structure



- This requires an octahedral arrangement of pairs and in turn an octahedral set of six hybrid orbitals, or ***d^2sp^3* hybridization**, in which two d orbitals, one s orbital, and three p orbitals are combined (Fig. 9.23).

Figure 9.23



An octahedral set of d^2sp^3 orbitals on a sulfur atom. The small lobe of each hybrid orbital has been omitted for clarity.

- Note that *six electron pairs around an atom are always arranged octahedrally and require* d^2sp^3 *hybridization of the atom.*

The Localized Electron Model: A Summary

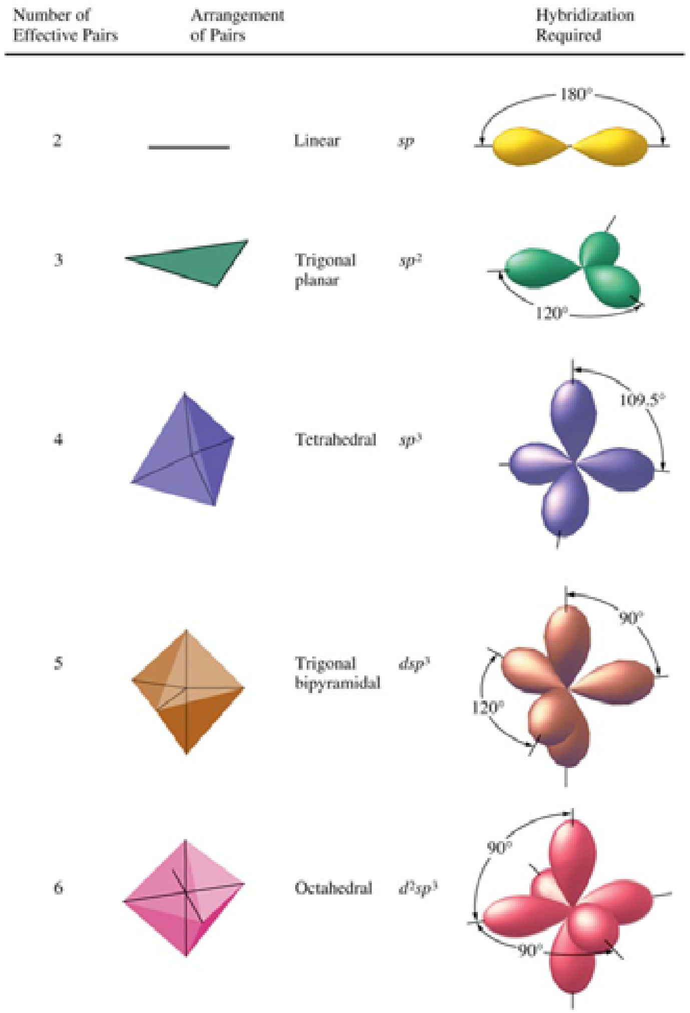
- The description of a molecule using the localized electron model involves three distinct steps.

Localized Electron Model

1. Draw the Lewis structure(s).
2. Determine the arrangement of electron pairs using the VSEPR model.
3. Specify the hybrid orbitals needed to accommodate the electron pairs.

- The various types of hybridization are summarized in Fig. 9.24.

Figure 9.24



Number of Effective Pairs	Arrangement of Pairs	Hybridization Required
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	dsp^3
6	Octahedral	d^2sp^3

The relationship of the number of effective pairs, their spatial arrangement, and the hybrid orbital set required.

Sample Exercise 9.5

The Localized Electron Model V

For each of the following molecules or ions, predict the hybridization of each atom, and describe the molecular structure.

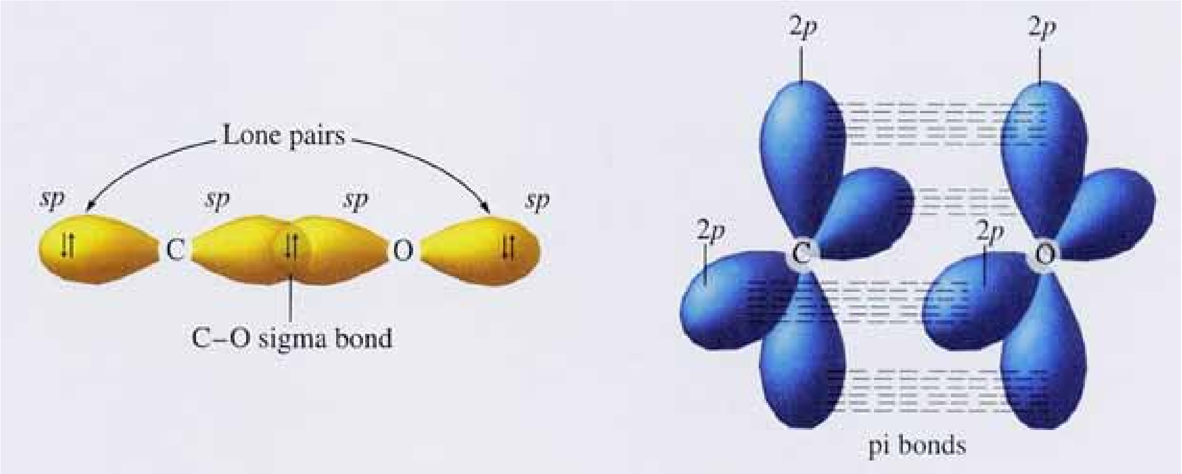
a. CO **b.** BF_4^- **c.** XeF_2

Solution

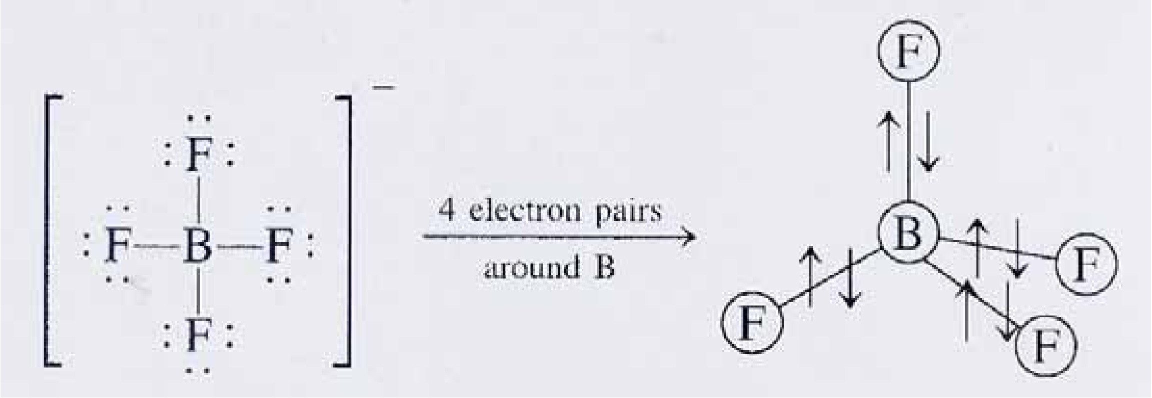
a. The CO molecule has 10 valence electrons,

$$:C\equiv O:$$

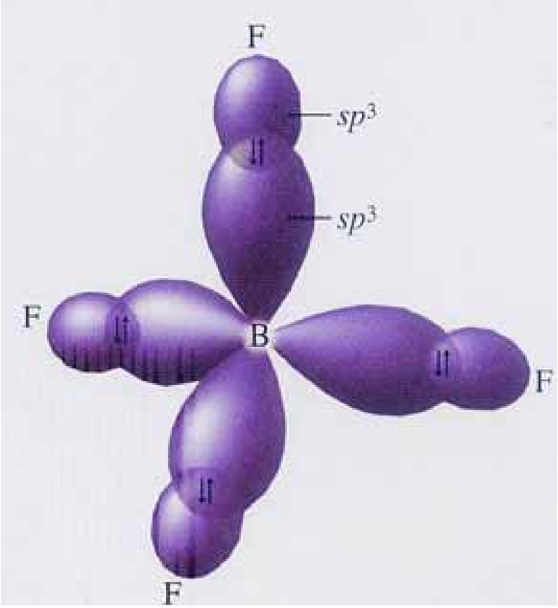
Sample Exercise 9.5



b. The BF_4^- ion has 32 valences.

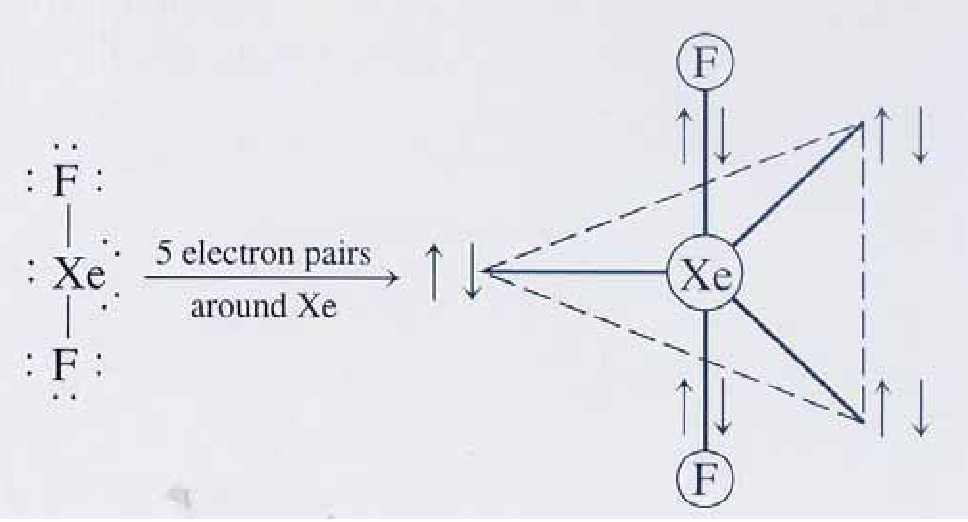


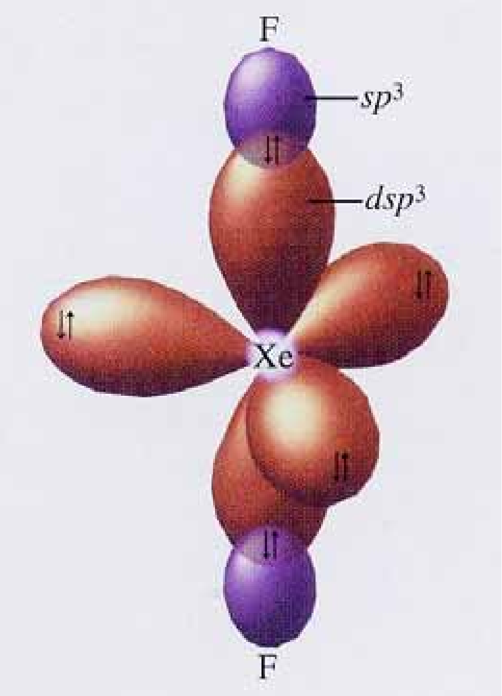
Sample Exercise 9.5



c. The XeF_2 molecule has 22 valence electrons.

Sample Exercise 9.5





See Exercises 9.27 and 9.28.

9.2 The Molecular Orbital Model

- Another model often used to describe bonding is the **molecular orbital model**.
- Just as atomic orbitals are solution to the quantum mechanical treatment of atoms, **molecular orbitals (MOs)** are solution to the molecular problem.
- Have many of the same characteristics as atomic orbitals.

- Two of the most important are: 1. they can hold two electrons with opposite spins. 2. the square of the molecular orbital wave function indicates electron probability.
- When the quantum mechanical equations for the hydrogen molecule are solved, two molecular orbitals result, which can be represented as

$$\mathrm{MO}_1 = 1s_\mathrm{A} + 1s_\mathrm{B}$$

$$\mathrm{MO}_2 = 1s_\mathrm{A} - 1s_\mathrm{B}$$

- where $1s_A$ and $1s_B$ represent the 1*s* orbitals from the two separated hydrogen atoms.
- This process is shown schematically in Fig. 9.25.
- The orbital properties of most interest are size, shape (described by the electron probability distribution), and energy.
- These properties for the hydrogen molecular orbitals are represented in Fig. 9.26.

Figure 9.25

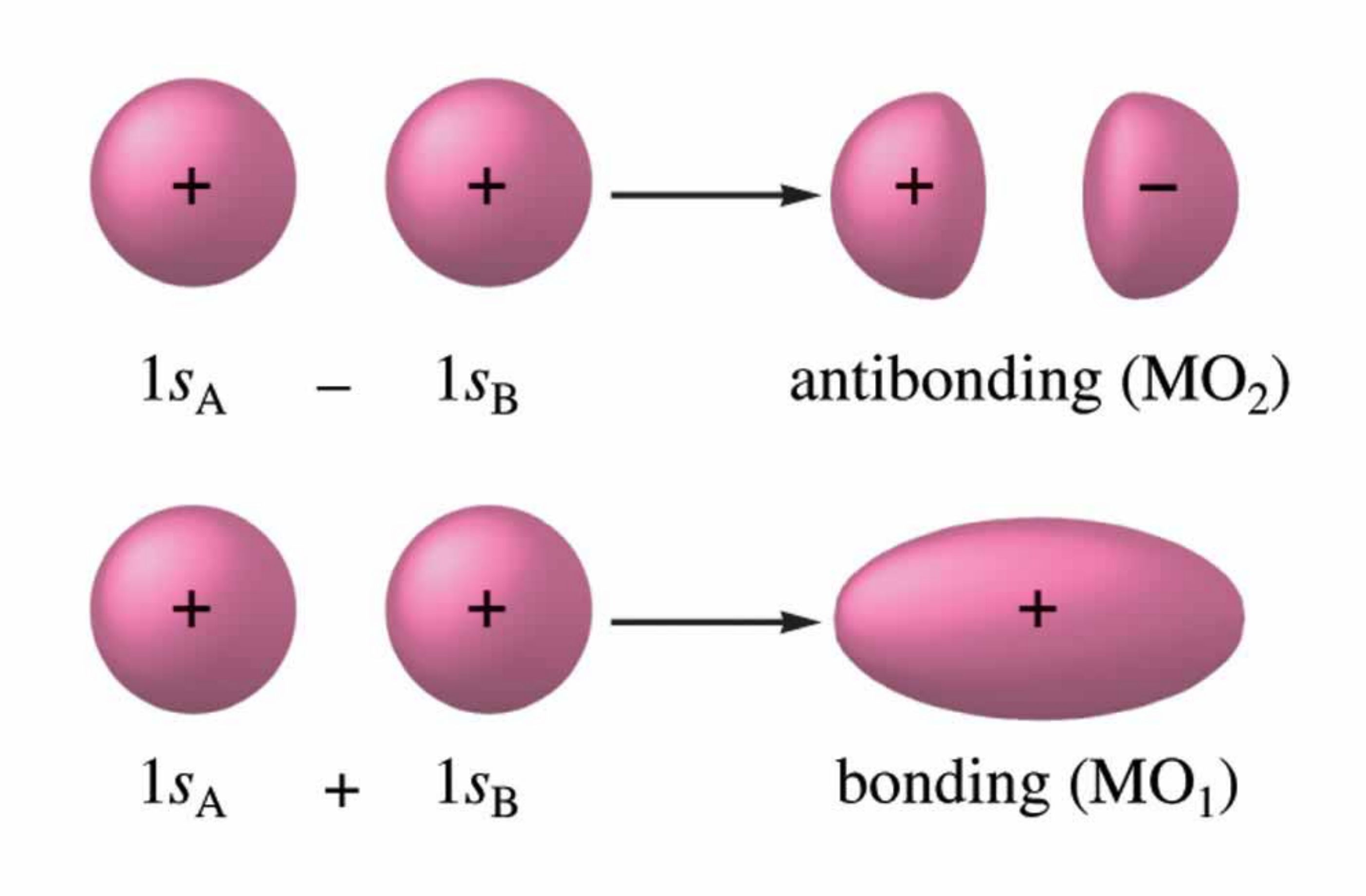
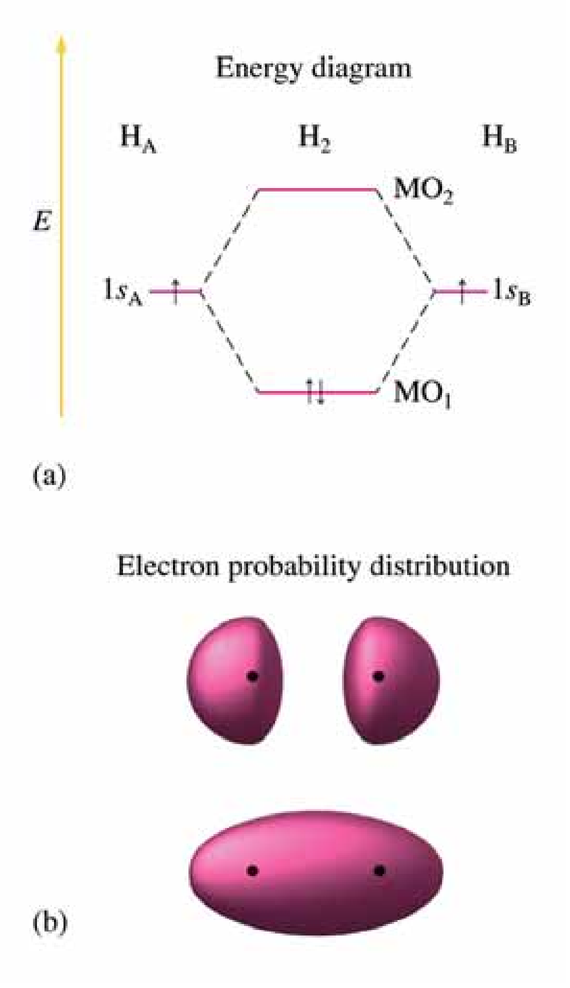


Figure 9.25

The combination of hydrogen 1*s* atomic orbitals to form Mos. The phases of the orbitals are shown by signs inside the boundary surfaces. When the orbitals are added, the matching phases produce constructive interference, which give enhanced electron probability between the nuclei. This results in a bonding molecular orbital. When one orbital is subtracted from the other, destructive interference occurs between the opposite phases, leading to a node between the nuclei. This is an antibonding MO.

Figure 9.26



(a) The MO energy-level diagram for the H_2 molecule. (b) The shapes of the MOs are obtained by squaring the wave functions for MO_1 and MO_2. The positions of the nuclei are indicated by•.

- important points:

1. The electron probability of both molecular orbitals is centered along the line passing through the two nuclei. For MO_1 the greatest electron probability is between the nuclei, and for MO_2 it is on either side of the nuclei. This type of electron distribution is described as sigma (σ), as in the localized electron model. Accordingly, we refer to MO_1 and MO_2 as sigma (σ) molecular orbitals.

2. In the molecule only the molecular orbitals are available for occupation by electrons. The 1*s* atomic orbitals of the hydrogen atoms no longer exist, because the H_2 molecule—a new entity—has its own set of new orbitals.

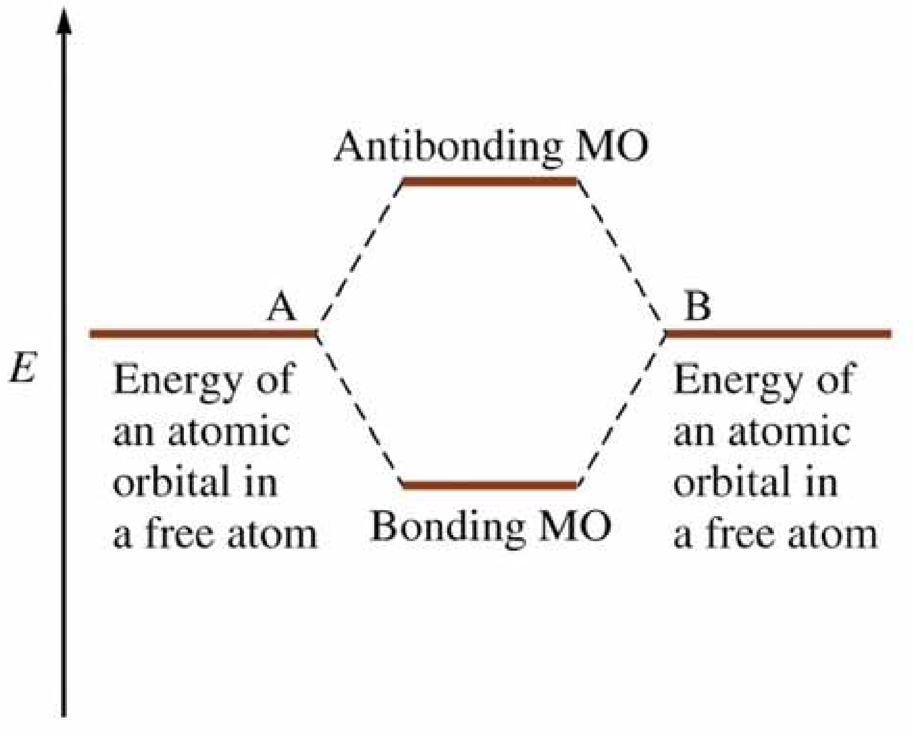
3. MO_1 is lower in energy than the 1s orbitals of free hydrogen atoms, while MO_2 is higher in energy than the 1*s* orbitals. This fact has very important implications for the stability of the H_2 molecule, since if the two electrons

(one from each hydrogen atom) occupy the lower-energy MO_1, they will have lower energy than they do in the two separate hydrogen atoms. This situation favors molecule formation, because nature tends to seek the lowest energy state. That is, the driving force for molecule formation is that the molecular orbital available to the two electrons has lower energy than the atomic orbitals these electrons occupy in the separated atoms. This situation is favorable to bonding, or *probonding*.

On the other hand, if the two electrons were forced to occupy the higher-energy MO_2, they would be definitely antibonding. In this case, these electrons would have lower energy in the separated atoms than in the molecule, and the separated state would be favored. Of course, since the lower-energy MO_1 is available, the two electrons occupy that MO and the molecule is stable.

We have seen that the molecular orbitals of the hydrogen molecule fall into two classes: bonding and antibonding. A **bonding molecular orbital** is lower in energy than the atomic orbitals of which it is composed. Electrons in this type of orbital will favor the molecule; that is, they will favor bonding. An **antibonding molecular orbital** is higher in energy than the atomic orbitals of which it is composed. Electrons in this type of orbital will favor the separated atoms (they are antibonding). Figure 9.27 illustrates these ideas.

Figure 9.27



Bonding and antibonding molecular orbitals (MOs).

4. Figure 9.26 shows that for the bonding molecular orbital in the H_2 molecule the electrons have the greatest probability of being between the nuclei. This is exactly what we would expect, since the electrons can lower their energies by being simultaneously attracted by both nuclei. On the other hand, the electron distribution for the antibonding molecular orbital is such that the electrons are mainly outside the space between the nuclei. This type of distribution is not expected to provide any

bonding force. In fact, it causes the electrons to be higher in energy than in the separated atoms. Thus the molecular orbital model produces electron distributions and energies that agree with our basic ideas of bonding. This fact reassures us that the model is physically reasonable.

5. The labels on molecular orbitals indicate their symmetry (shape), the parent atomic orbitals, and whether they are bonding or antibonding. Antibonding character is indicated by an asterisk. For the H_2 molecule,

both MOs have σ symmetry, and both are constructed from hydrogen 1s atomic orbitals. The molecular orbitals for H2 are therefore labeled as follows:

$$MO_1 = \sigma_{1s}$$

$$MO_2 = \sigma_{1s}^*$$

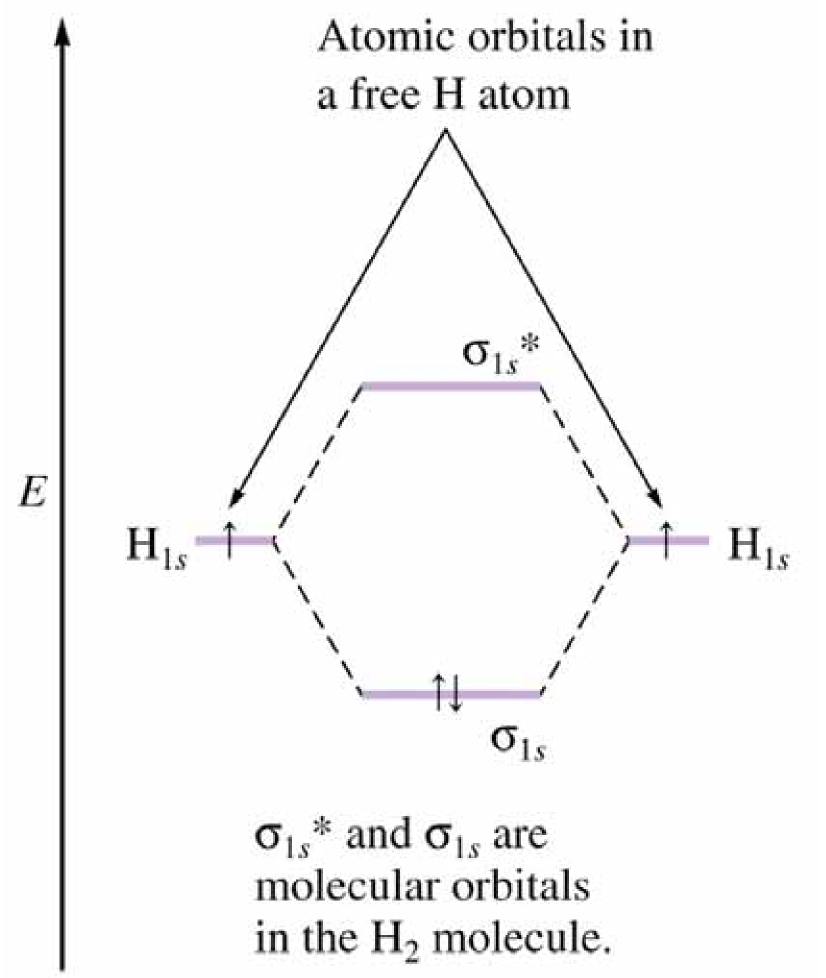
6. Molecular electron configurations can be written in much the same way as atomic (electron) configurations. Since the H2 molecule has two electrons in the σ_{1s} molecular orbital, the electron configuration is σ_{1s}^2.

7. Each molecular orbital can hold two electrons, but the spins must be opposite.

8. Orbitals are conserved. The number of molecular orbitals will always be the same as the number of atomic orbitals used to construct them.

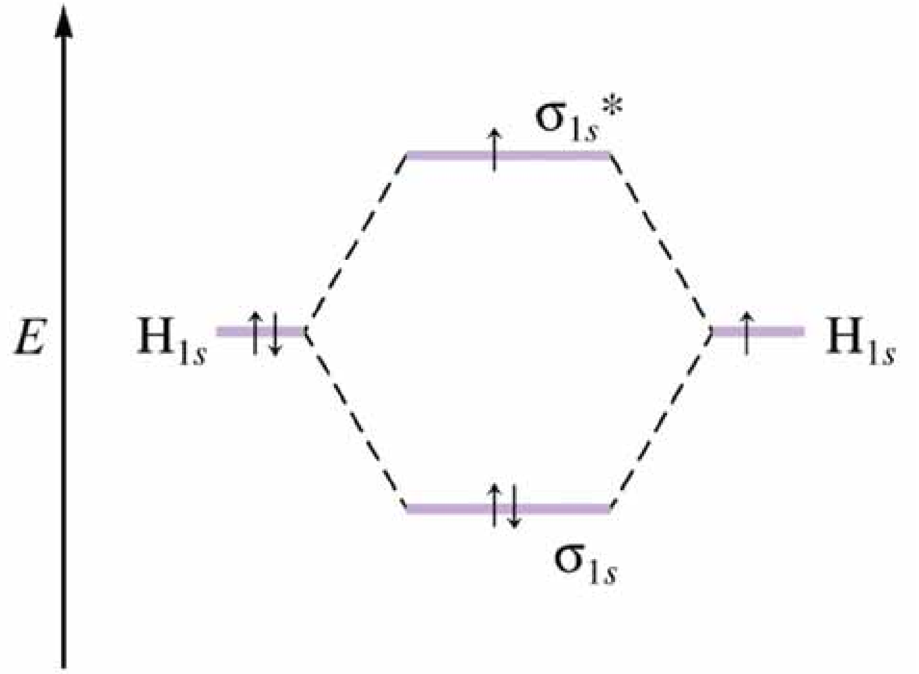
- Many of the above points are summarized in Fig. 9.28.
- Now suppose we could form the H_2^- ion from a hydride ion (H^-) and a hydrogen atom.
- Since the H^- ion has the configuration $1s^2$ and the H atom has a $1s^1$ configuration, we will use 1*s* atomic orbitals to construct the MO diagram for the H_2^- ion, as shown in Fig. 9.29. The electron configuration for H_2^- is $(\sigma_{1s})^2(\sigma_{1s}^*)^1$.

Figure 9.28



A molecular orbital energy-level diagram for the H_2 molecule.

Figure 9.29



The molecular orbital energy-level diagram for the H_2^- ion.

Bond Order

- **Bond order** is *the difference between the number of bonding electrons and the number of antibonding electrons divided by 2.*

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

- We divide by 2 because, from localized electron model, we are used to thinking of bonds in terms of *pairs* of electrons.

H^- : $$\text{Bond order} = \frac{2-0}{2} = 1$$

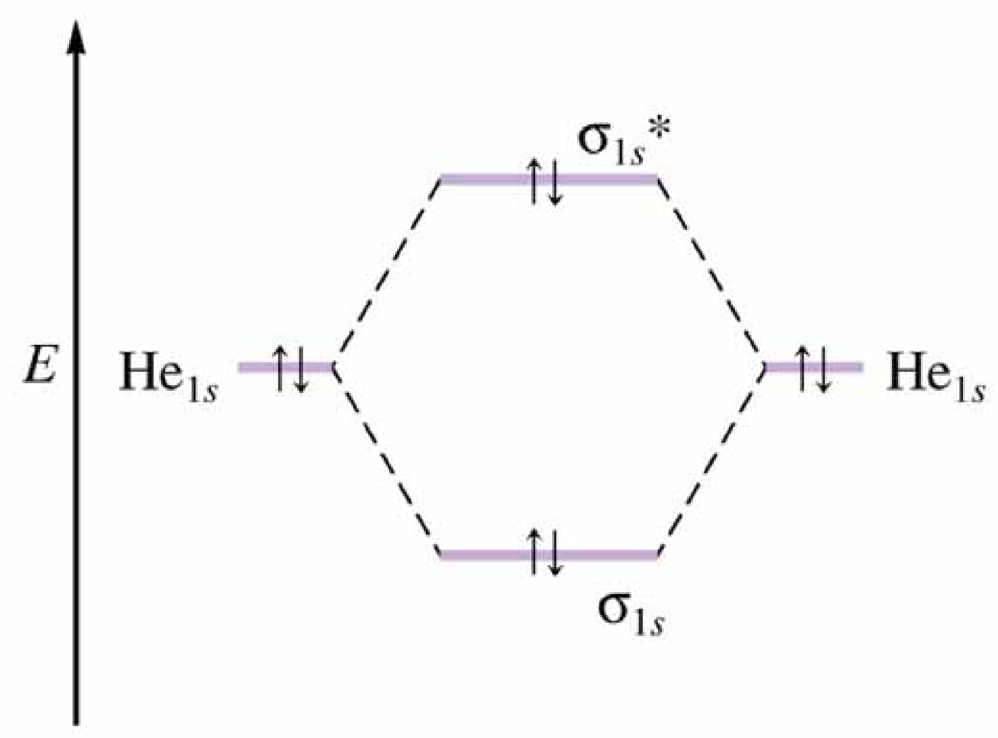
H_2^- : $$\text{Bond order} = \frac{2-1}{2} = \frac{1}{2}$$

- Larger bond order means greater bond strengh.
- Form the diagram shown in Fig. 9.30 it is apparent that two electrons are raised in energy and two are lowered in energy. Thus the bond order is zero:

$$\frac{2-2}{2} = 0$$

- This implies that the He_2 molecule is *not* stable with respect to the two free He atoms.

Figure 9.30

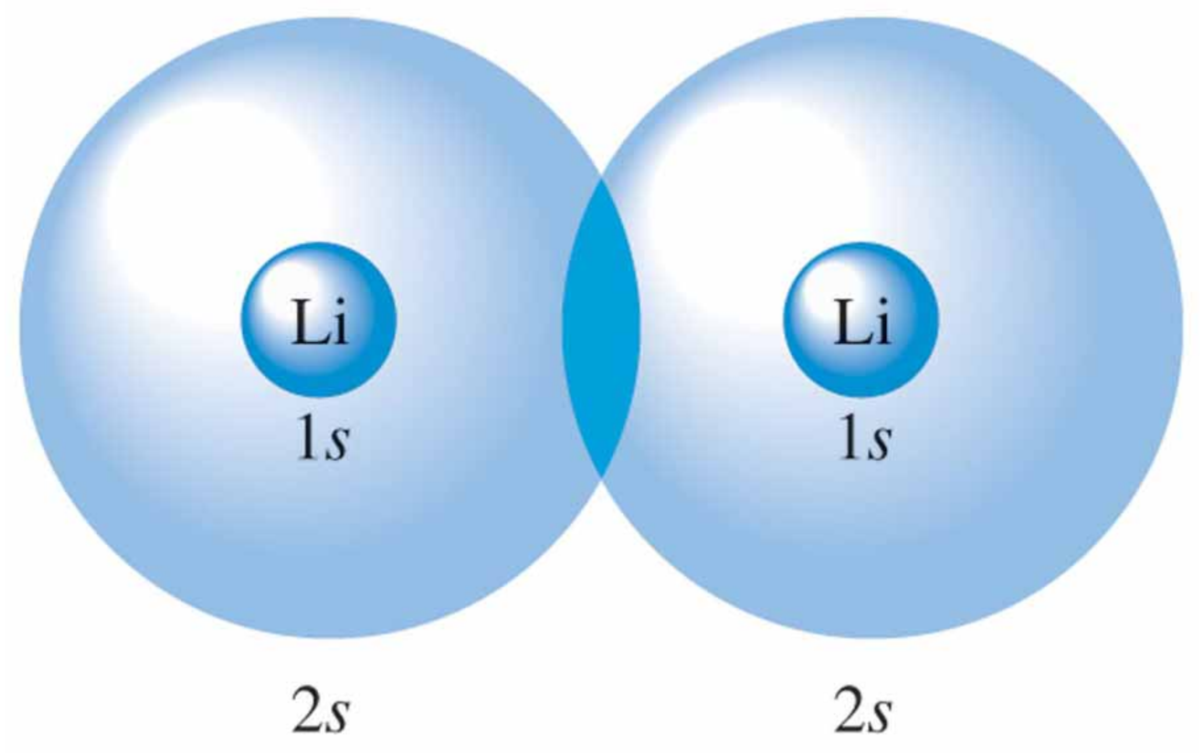


The molecular orbital energy-level diagram for the He_2 molecule.

9.3 Bonding in Homonuclear Diatomic Molecules

- *homonuclear diatomic molecules.*
- The 1*s* orbitals on the lithium atoms are much smaller than the 2*s* orbitals and therefore do not overlap in space to any appreciable extent (see Fig. 9.31).
- Thus the two electrons in each 1s orbital can be assumed to be localized and not to participate in the bonding.
- *To participate in molecular orbitals, atomic orbitals must overlap in space.*

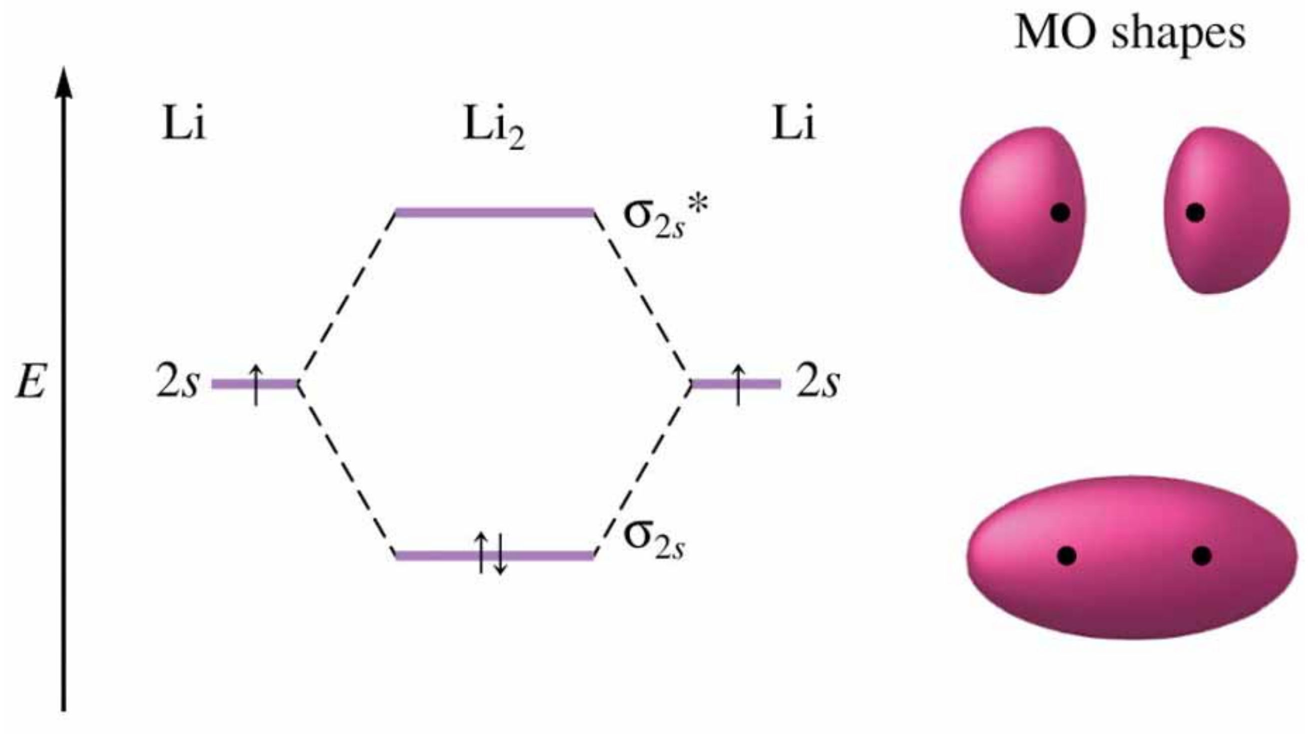
Figure 9.31



The relative sizes of the lithium 1*s* and 2*s* atomic orbitals.

- Only the valence orbitals of the atoms contribute significantly to the molecular orbitals of a particular molecule.
- The molecular orbital diagram of the Li_2 molecule and the shapes of its bonding and antibonding MOs are shown in Fig. 9.32.

Figure 9.32



The molecular orbital energy-level diagram for the Li$_2$ molecule.

- The electron configuration for Li_2 (valence electrons only) is σ_{2s}^2, and the bond order is

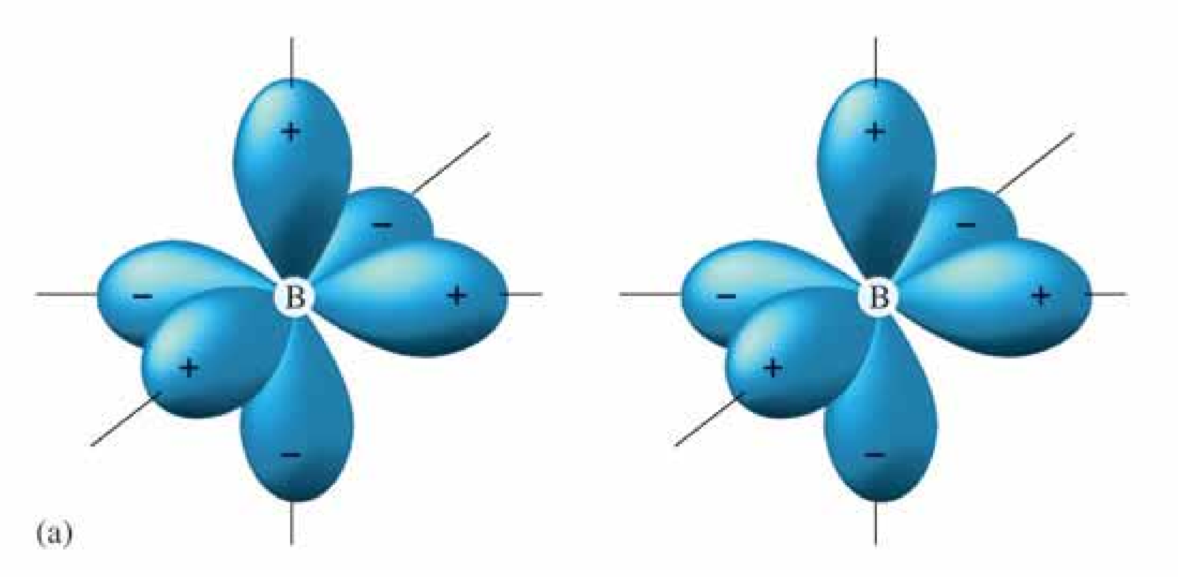
$$\frac{2-0}{2}=1$$

- For the beryllium molecule (Be_2) the bonding and antibonding orbitals both contain two electrons.
- The bond order is $(2 - 2)/2 = 0$.

Beryllium metal.

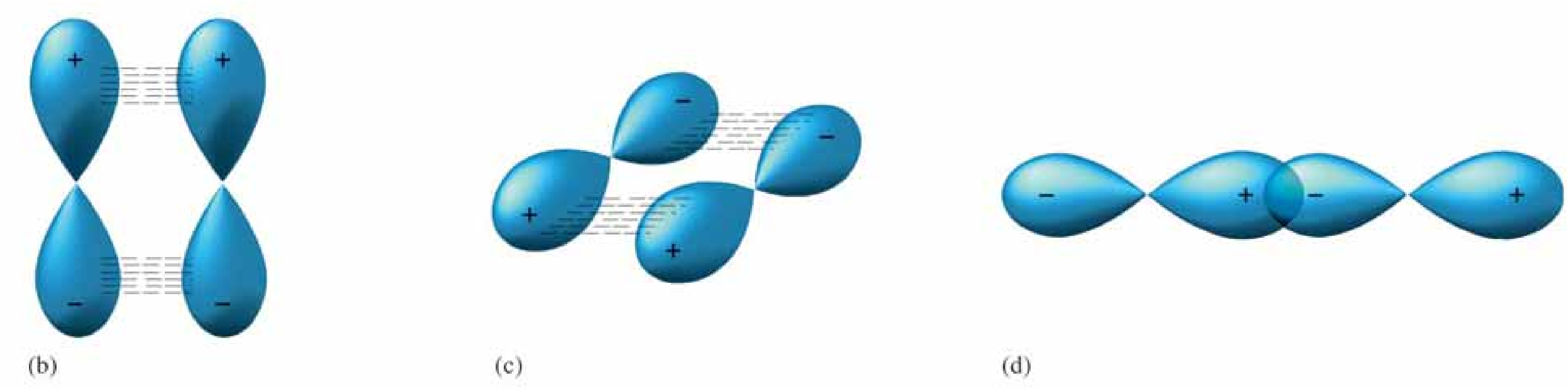
- Since the boron atom has a $1s^2 2s^2 2p^1$ configuration, we describe the B_2 molecule by considering how *p* atomic orbitals combine to form molecular orbitals.
- Recall that *p* orbitals have two lobes and that they occur in sets of three mutually perpendicular orbitals [see Fig. 9.33(a)].
- When two B atoms approach each other, two pairs of *p* orbitals can overlap in a parallel fashion [Fig. 9.33(b) and (c)] and one pair can overlap head-on [Fig. 9.33(d)].

Figure 9.33



(a) The three mutually perpendicular 2*p* orbitals on two adjacent boron atoms. The signs indicate the orbital phases.

Figure 9.33



Two pairs of parallel *p* orbitals can overlap, as shown in (b) and (c), and the third pair can overlap head-on, as shown in (d).

- The molecular orbitals from the head-on overlap, as shown in Fig. 9.34(a).
- The p orbitals that overlap in a parallel fashion also produce bonding and antibonding orbitals [Fig. 9.34(b)].
- Since the electron probability lies above and below the line between the nuclei, both the orbitals are **pi (π) molecular orbitals**.
- They are designated as π 2*p* for the bonding MO and π 2*p** for the antibonding MO.

Figure 9.34

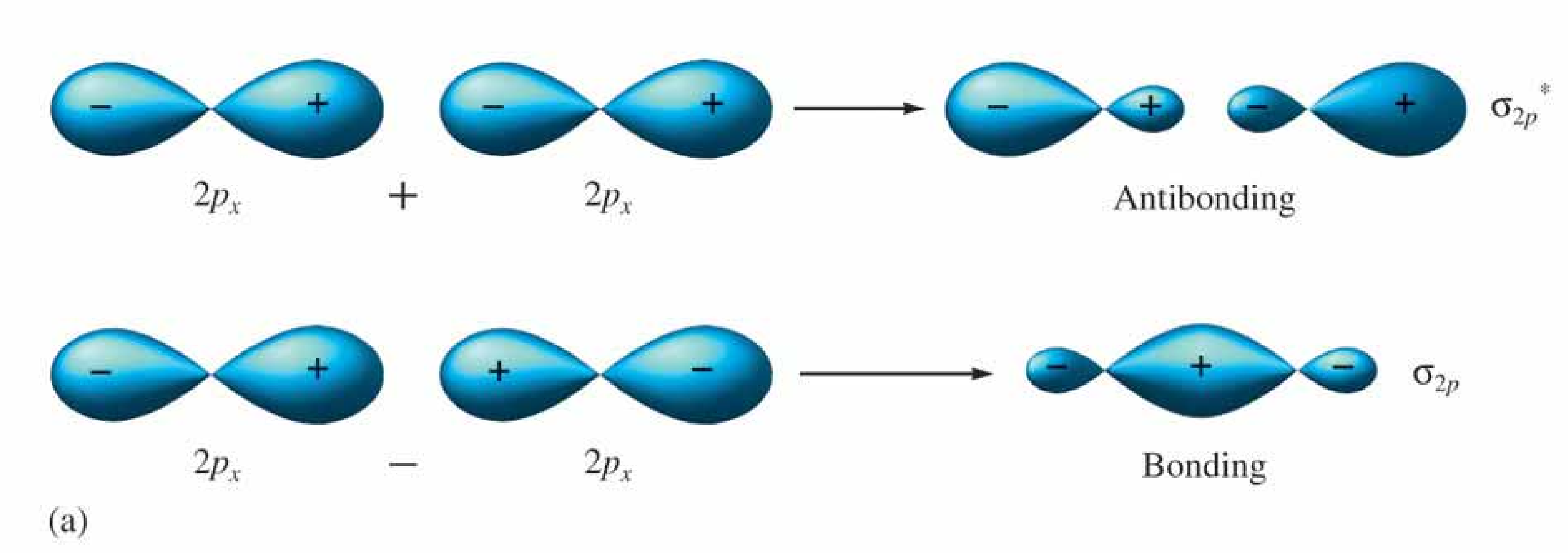


Figure 9.34

(a) The two p orbitals on the boron atoms that overlap head-on combine to form σ bonding and antibonding orbitals. The bonding orbital is formed by reversing the sign of the right orbital so the positive phases of both orbitals match between the nuclei to produce constructive interference. This leads to enhanced electron probability between the nuclei. The antibonding orbital is formed by the direct combination of the orbitals, which gives destructive interference of the positive phase of one orbital with the negative phase of the second orbital. This produces a node between the nuclei, which gives decreased electron probability.

Figure 9.34

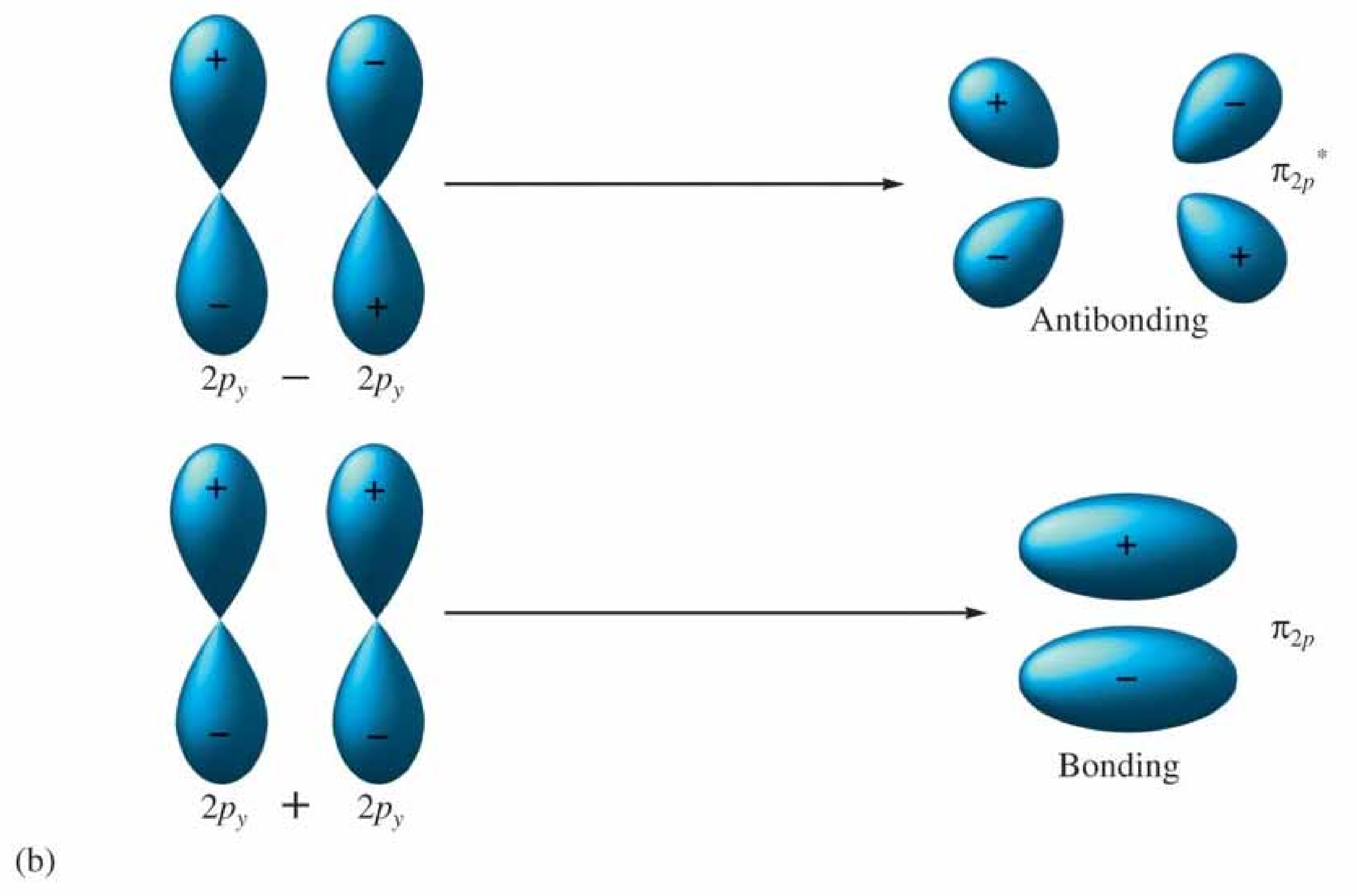
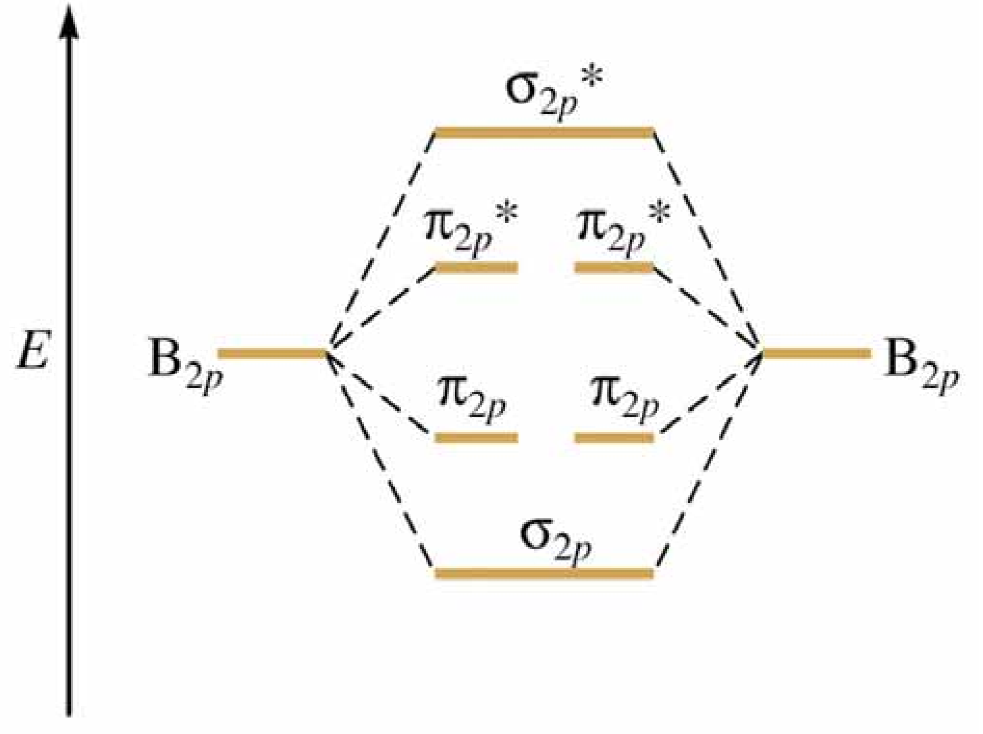


Figure 9.34

(b) When the parallel *p* orbitals are combined with the positive and negative phases matched, constructive interference occurs, giving a bonding π orbital. When the orbitals have opposite phases (the signs of one orbital are reversed), destructive interference occurs, resulting in an antibonding π orbital.

- Figure 9.35 gives the molecular orbital energy-level diagram expected when the two sets of 2*p* orbitals on the boron atoms combine to form molecular orbitals.
- Note that there are two π bonding orbitals at the same energy (degenerate orbitals) formed from the two pairs of parallel *p* orbitals, and there are two degenerate π antibonding orbitals.

Figure 9.35

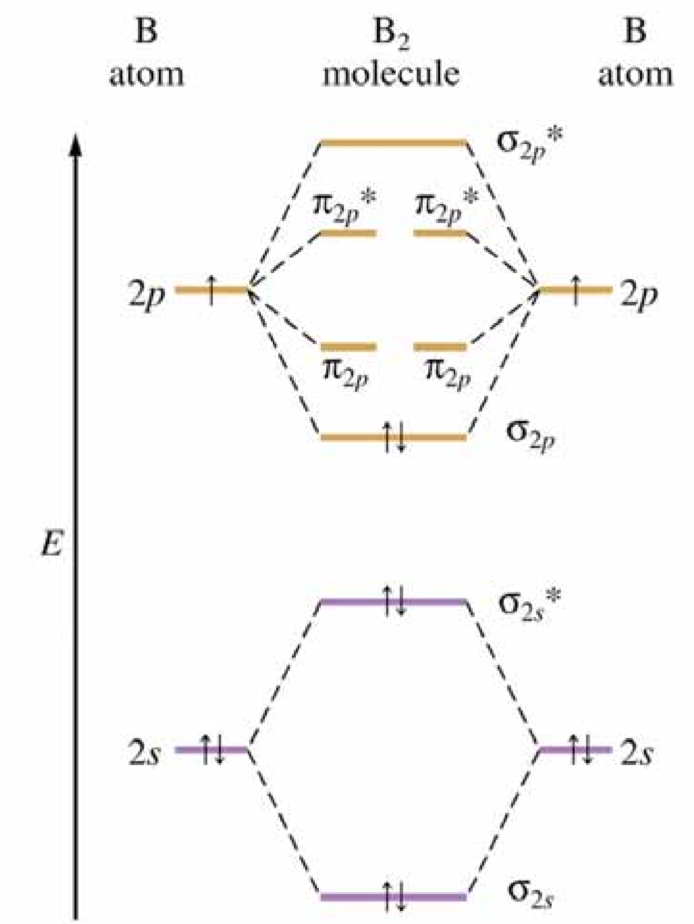


The expected molecular orbital energy-level diagram resulting from the combination of the 2*p* orbitals on two boron atoms.

- The energy of the π_{2p} orbitals is expected to be higher than that of the σ_{2p} orbital because σ interactions are generally stronger than π interactions.
- The total molecular orbital diagram for the B_2 molecule, is shown in Fig. 9.36.
- Note that B_2 has six *valence* electrons.

Figure 9.36

The expected molecular orbital energy-level diagram for the B_2 molecule.



- This diagram predicts the bond order:

$$\frac{4-2}{2}=1$$

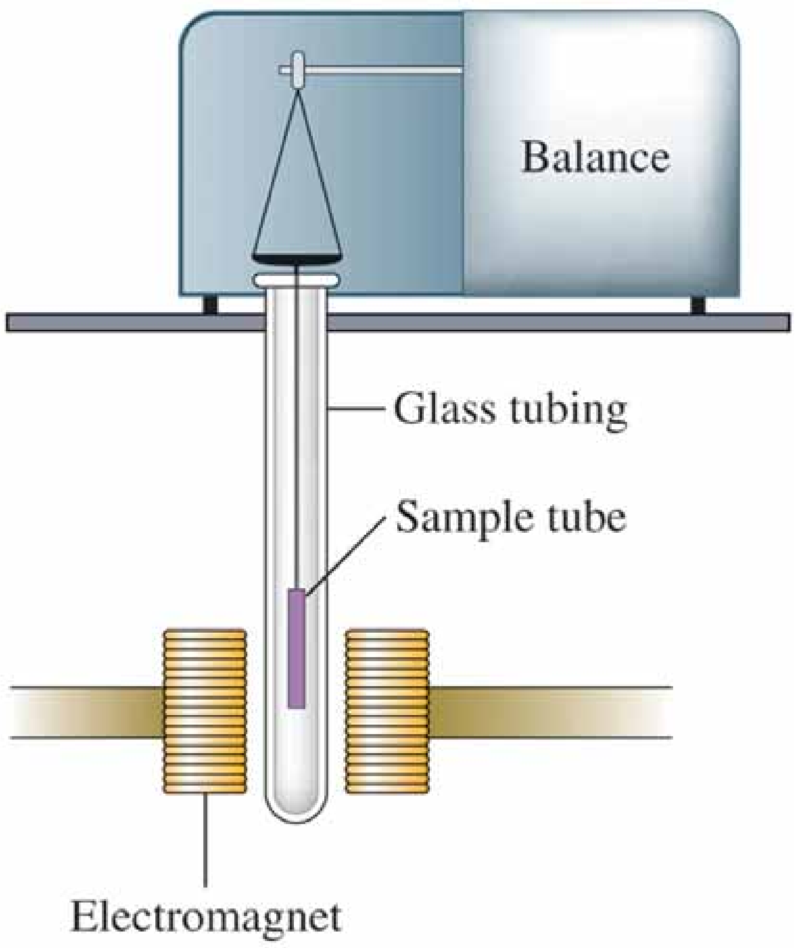
- Therefore, B_2 should be a stable molecule.

Paramagnetism

- **Paramagnetism** causes the substance to be attracted into the inducing magnetic field.
- **Diamagnetism** causes the substance to be repelled from the inducing magnetic field.
- Figure 9.37 illustrates how paramagnetism is measured.
- *Paramagnetism is associated with unpaired electrons and diamagnetism is associated with paired electrons.*

Figure 9.37

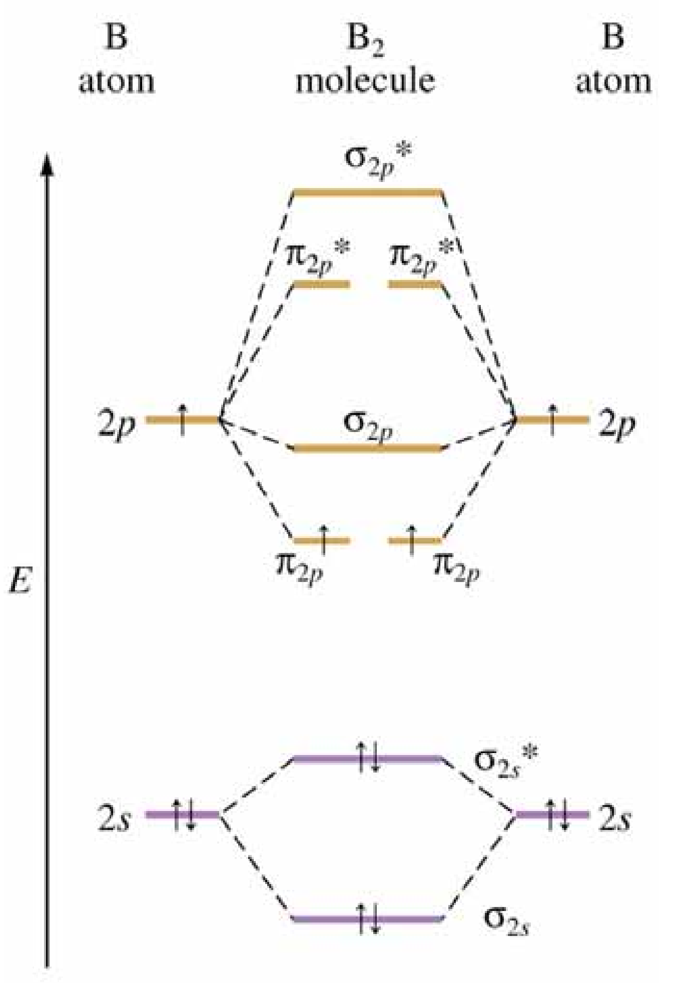
Diagram of the kind of apparatus used to measure the paramagnetism of a sample. A paramagnetic sample will appear heavier when the electromagnet is turned on because the sample is attracted into the inducing magnetic field.



- The expected molecular orbital energy-level diagram for the B_2 molecule.
- For B_2: Calculations show that when the *s* and *p* orbitals are allowed to mix in the same molecular orbital, a different energy-level diagram results (see Fig. 9.38).
- The C_2 and N_2 molecules use the same set of orbitals as for B_2 (see Fig. 9.38).

Figure 9.38

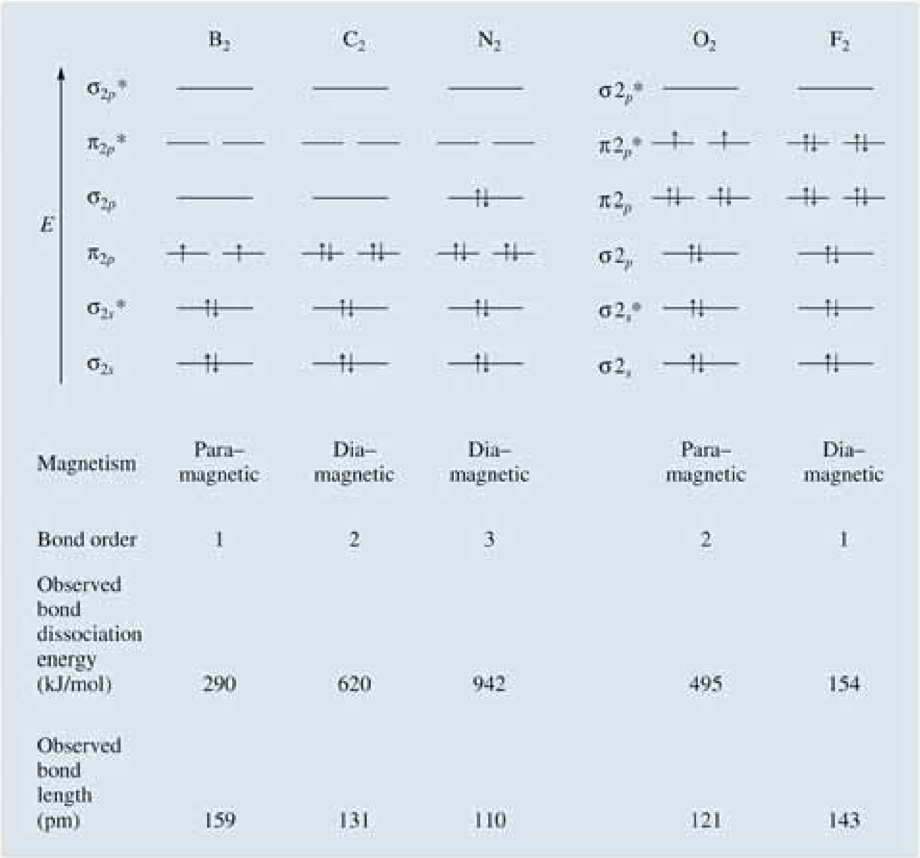
The correct molecular orbital energy-level diagram for the B_2 molecule. When *p*—*s* mixing is allowed, the energies of the σ_{2p} and π_{2p} orbitals are reversed. The two electrons from the B 2*p* orbitals now occupy separate, degenerate π_{2p} molecular orbitals and this have parallel spins. Therefore, this diagram ecplains the observed paramagnetism of B_2.



- Because the importance of 2*s*—2*p* mixing decreases across the period, the σ_{2p} and π_{2p} orbitals revert to the order expected in the absence of 2*s*—2*p* mixing for the molecules O_2 and F_2, as shown in Fig. 9.39.

Figure 9.39

The molecular orbital energy-level diagrams, bond orders, bond energies, and bond lengths for the diatomic molecules B_2 through F_2. Note that for O_2 and F_2 the σ_{2p} orbital is lower in energy than the π_{2p} orbitals.



	B_2	C_2	N_2	O_2	F_2
Magnetism	Para–magnetic	Dia–magnetic	Dia–magnetic	Para–magnetic	Dia–magnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

- Several significant points arise from the orbital diagrams, bond strengths, and bond lengths summarized in Fig. 9.39 for the Period 2 diatomics:

1. There are definite correlations between bond order, bond energy, and bond length. As the bond order predicted by the molecular orbital model increases, the bond energy increases and the bond length decreases. This is a clear indication that the bond order predicted by the model accurately reflects bond strength, and it

strongly supports the reasonableness of the MO model.

2. comparison of the bond energies of the B_2 and F_2 molecules indicates that bond order cannot automatically be associated with a particular bond energy. Although both molecules have a bond order of 1, the bond in B_2 appears to be about twice as strong as the bond in F_2. As we will see in our later discussion of the halogens, F_2 has an unusually weak single bond due to larger than usual electron-electron repulsions

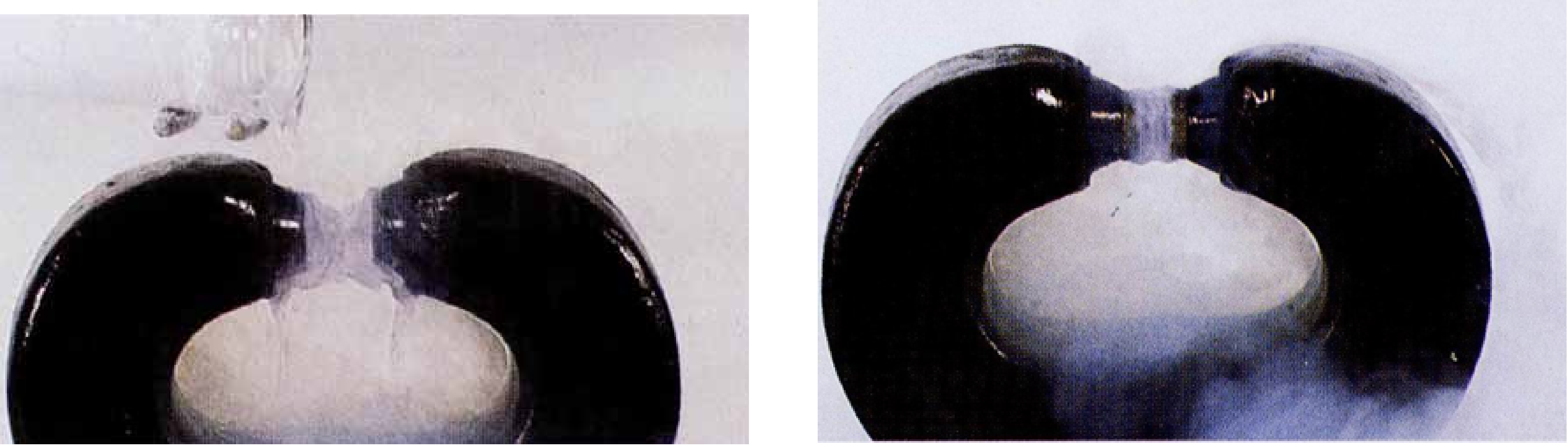
(there are 14 valence electrons on the small F_2 molecule).

3. Note the very large bond energy associated with the N_2 molecule, which the molecular orbital model predicts will have a bond order of 3, a triple bond. The very strong bond in N_2 is the principal reason that many nitrogen-containing compounds are used as high explosives. The reactions involving these explosives give the very stable N_2 molecule as a product, thus

releasing large quantities of energy.

4. The O_2 molecule is known to be paramagnetic. This can be very convincingly demonstrated by pouring liquid oxygen between the poles of a strong magnet, as shown in Fig. 9.40. The oxygen remains there until it evaporates. Significantly, the molecular orbital model correctly predicts oxygen’s paramagnetism, while the localized electron model predicts a diamagnetic molecule.

Figure 9.40



When liquid oxygen is poured into the space between the poles of a strong magnet, it remains there until it boils away. This attraction of liquid oxygen for the magnetic field demonstrates the paramagnetism of the O_2 molecule.

Sample Exercise 9.6

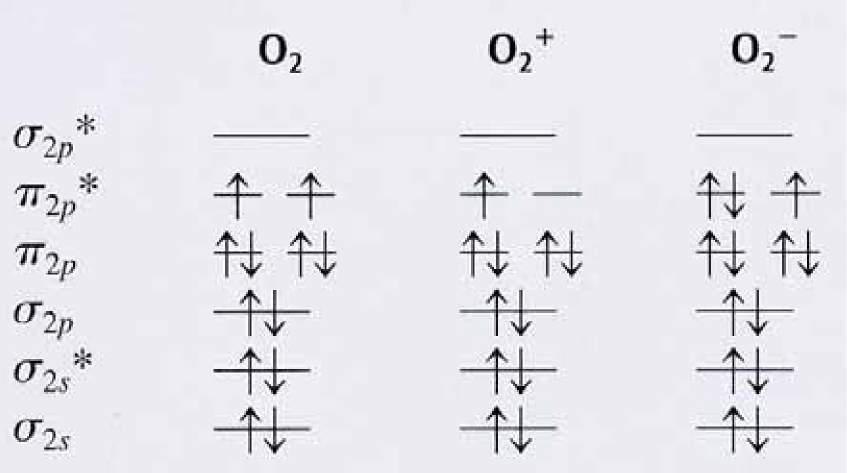
The Molecular Orbital Model I

For the species O_2, O_2^+, and O_2^-, give the electron configuration and the bond order for each. Which has the strongest bond?

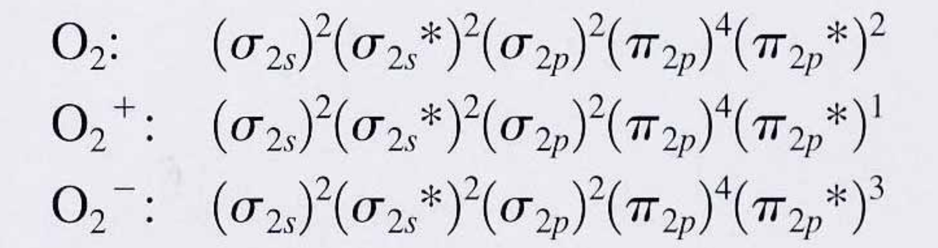
Solution

The O_2 molecule has 12 valence electrons $(6 + 6)$; O_2^+ has 11 valence electrons $(6 + 6 - 1)$; and O_2^- has 13 valence electrons $(6 + 6 + 1)$. We will assume that the ions can be treated using the same molecular orbital diagram as for the neutral diatomic molecule:

Sample Exercise 9.6



The electron configuration for each species can then be taken from the diagram:



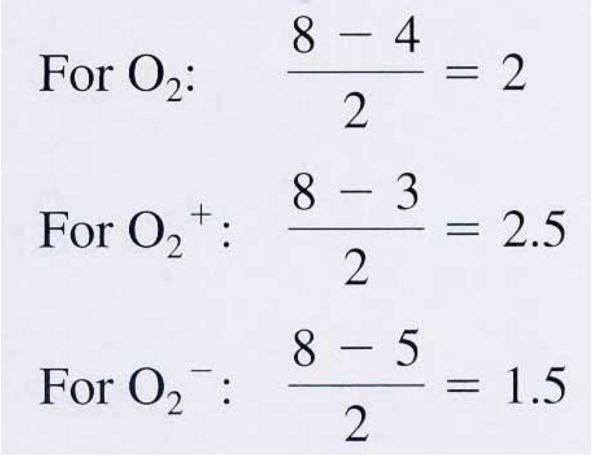
O_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$

O_2^+: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$

O_2^-: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$

Sample Exercise 9.6

The bond orders are:



$$\text{For } O_2\text{:}\quad \frac{8-4}{2} = 2$$

$$\text{For } O_2^{\,+}\text{:}\quad \frac{8-3}{2} = 2.5$$

$$\text{For } O_2^{\,-}\text{:}\quad \frac{8-5}{2} = 1.5$$

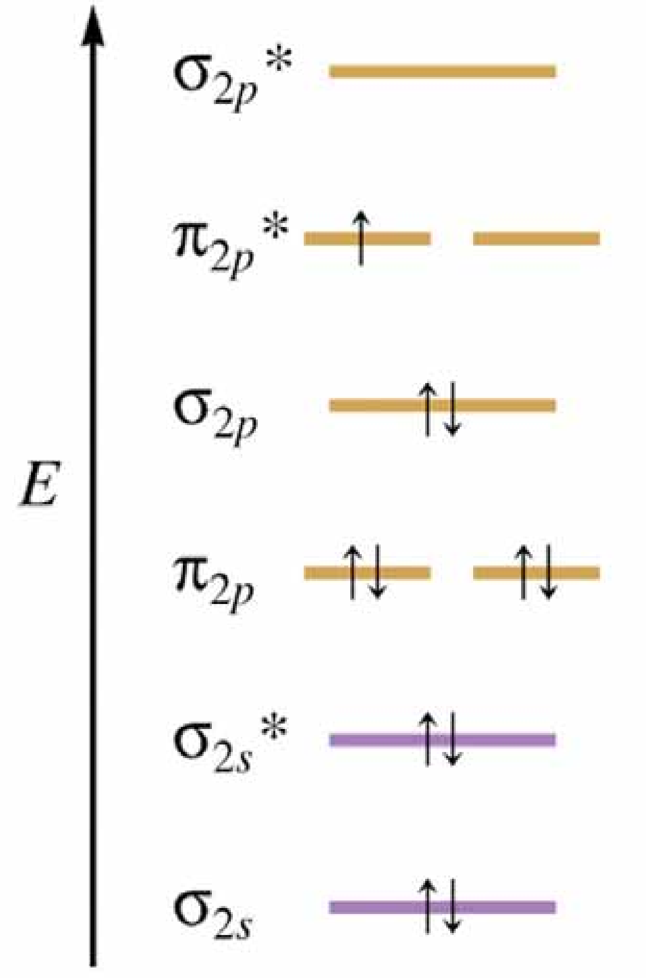
Thus $O_2^{\,+}$ is expected to have the strongest bond of the three species.

See Exercises 9.39 and 9.40.

9.4 Bonding in Heteronuclear Diatomic Molecules

- **heteronuclear** (different atoms) **diatomic molecules**.
- Since the atoms involved in such a molecule are so similar, we can use the molecular orbital diagram for homonuclear molecules.
- The bond order and magnetism of nitric oxide (NO) by placing its 11 valence electrons (5 from nitrogen and 6 from oxygen) in the molecular orbital energy-level diagram shown in Fig. 9.41.

Figure 9.41



The molecular orbital energy-level diagram for the NO molecule. We assume that orbital order is the same as that for N_2. The bond order is 2.5.

- The molecule should be paramagnetic and has a bond order of

$$\frac{8-3}{2} = 2.5$$

Sample Exercise 9.8

The Molecular Orbital Model III

Use the molecular orbital model to predict the magnetism and bond order of the NO^+ and CN^- ions.

Solution

The NO^+ ion has 10 valence electrons $(5 + 6 - 1)$. The CN^- ion also has 10 valence electrons $(4 + 5 + 1)$. Both ions are therefore diamagnetic and have a bond order derived from the equation

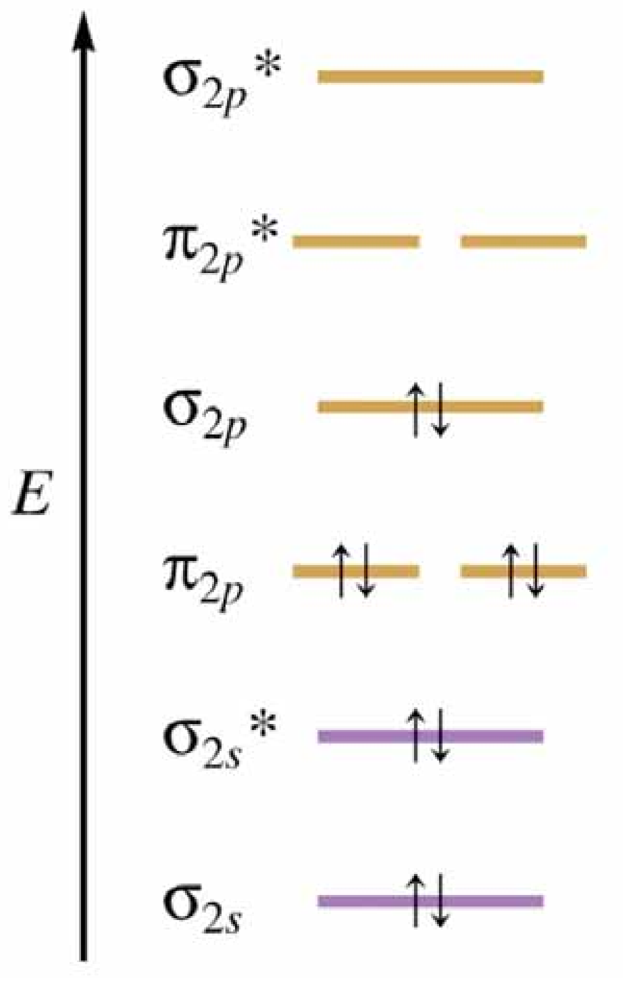
$$\frac{8-2}{2} = 3$$

Sample Exercise 9.8

The molecular orbital diagram for these two ions is the same (see Fig. 9.42).

See Exercises 9.43 and 9.44.

Figure 9.42

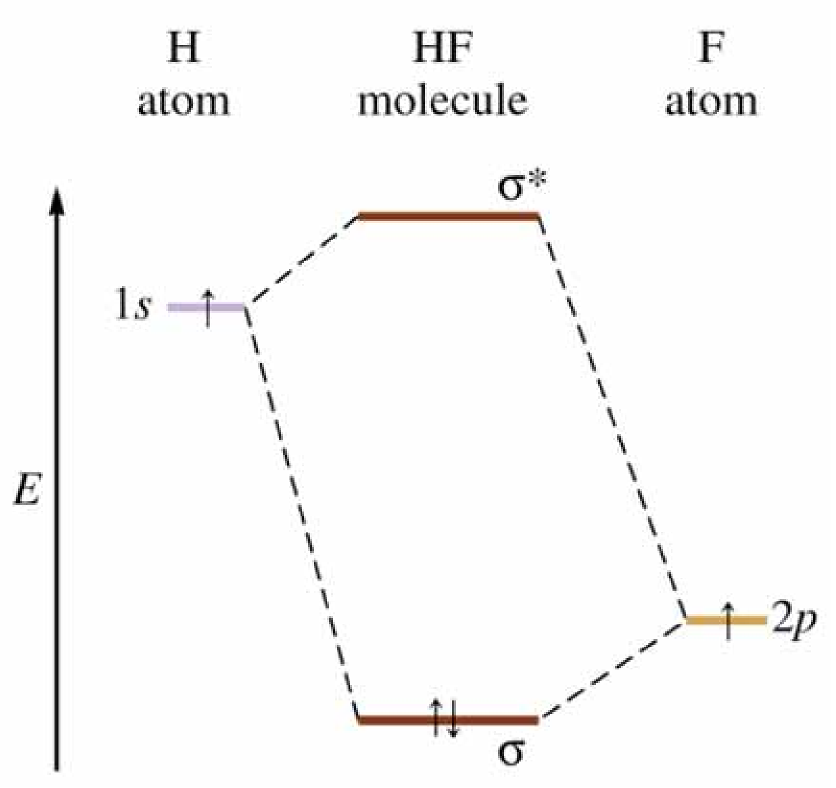


The molecular orbital energy-level diagram for both the NO^+ and CN^- ions.

- When the two atoms of a diatomic molecule are very different, the energy-level diagram for homonuclear molecules can no longer be used.
- hydrogen fluoride (HF) molecule.
- The electron configurations of the hydrogen and fluorine atoms are $1s^1$ and $1s^2 2s^2 2p^5$.
- Figure 9.43 gives the partial molecular orbital energy-level diagram for HF, focusing only on the orbitals involved in the bonding.

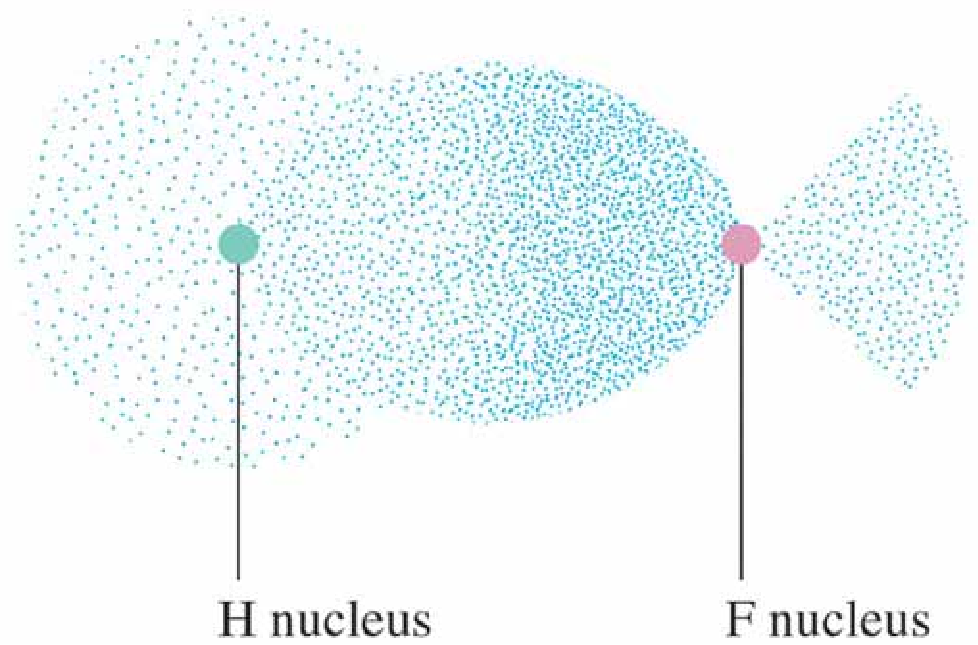
Figure 9.43

A partial molecular orbital energy-level diagram for the HF molecule.



- Because the fluorine 2*p* orbital is lower in energy than the hydrogen 1*s* orbital, the electrons prefer to be closer to the fluorine atom.
- That is, the σ molecular orbital containing the bonding electron pair shows greater electron probability close to the fluorine (see Fig 9.44).
- The electron pair is not shared equally.
- This causes the fluorine atom to have a slight excess of negative charge and leaves the hydrogen atom partially positive.

Figure 9.44

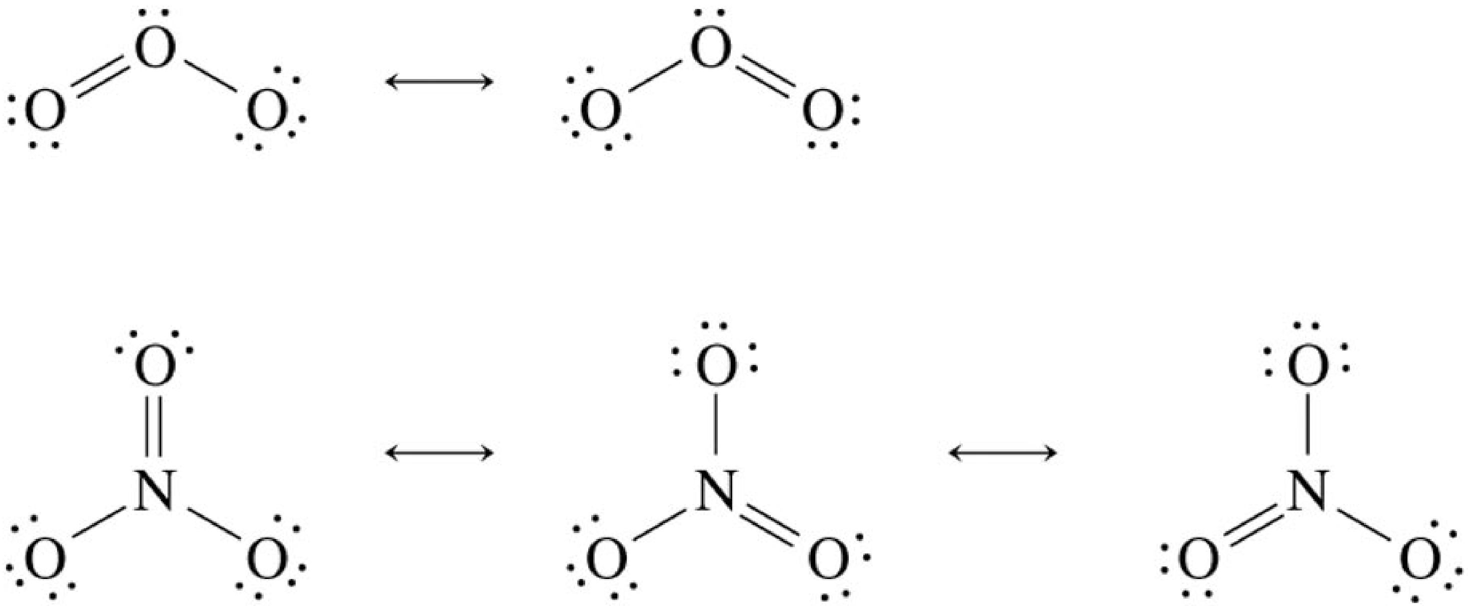


The electron probability distribution in the bonding molecular orbital of the HF molecule. Note the greater electron density close to the fluorine atom.

9.5 Combining the Localized Electron and Molecular Orbital Models

- Note that for species such as O_3 and NO_3^- the double bond changes position in the resonance structures (see Fig. 9.45).
- Since a double bond involves one σ and one π bond, there is a σ bond between all bound atoms in each resonance structure.
- It is really the π bond that has different locations in the various resonance structures.

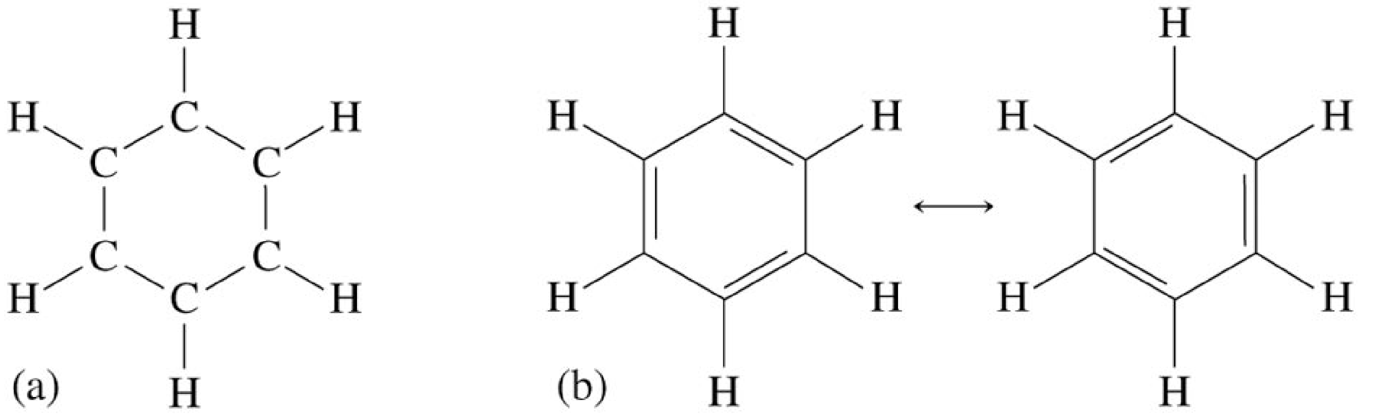
Figure 9.45



The resonance structures for O_3 and NO_3^-. Note that it is the double bond that occupies various positions in the resonance structures.

- The benzene molecule (C_6H_6) consists of a planar hexagon of carbon atoms with one hydrogen atom bound to each carbon atom, as shown in Fig. 9.46(a).
- In the molecule all six C—C bonds are known to be equivalent.
- To explain this fact, the localized electron model must invoke resonance [see Fig. 9.46(b)].

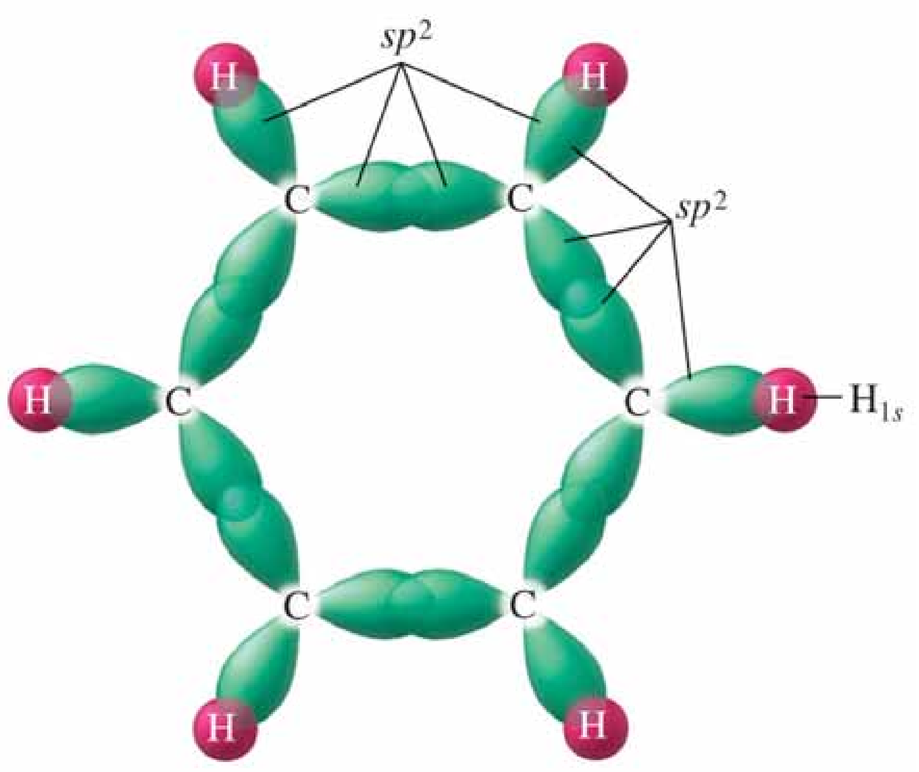
Figure 9.46



(a) The benzene molecule consists of a ring of six carbon atoms with one hydrogen atom bound to each carbon; all atoms are in the same plane. All the C—C bonds are known to be equivalent. (b) Two of the resonance structures for the benzene molecule. The localized electron model must invoke resonance to account for the six equal C—C bonds.

- Assumed that the σ bonds of carbon involve sp^2 orbitals, as shown in Fig. 9.47.
- These σ bonds are all centered in the plane of the molecule.

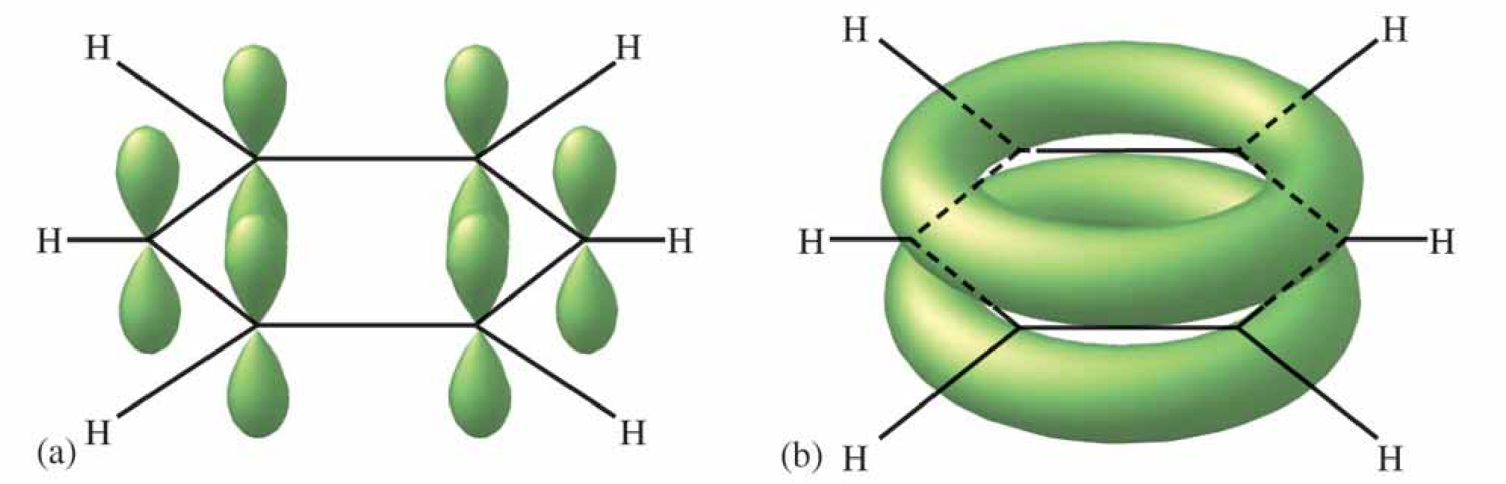
Figure 9.47



The σ bonding system in the benzene molecule.

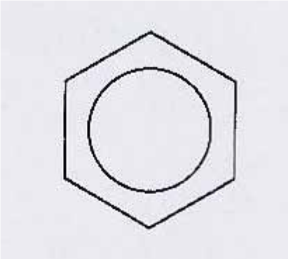
- Since each carbon atom is sp^2 hybridized, a p orbital perpendicular to the plane of the ring remains on each carbon atom.
- These six *p* orbitals can be used to form π molecular orbitals, as shown in Fig 9.48(a).
- The electrons in the resulting π molecular orbitals are delocalized above and below the plane of the ring, as shown in Fig. 9.48(b).

Figure 9.48



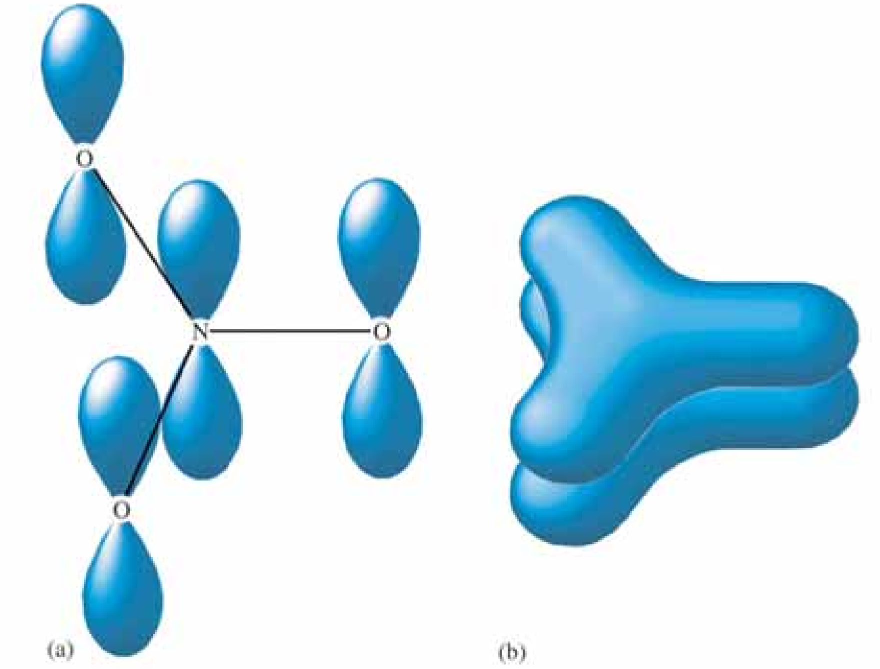
(a) The π molecular orbital system in benzene is formed by combining the six *p* orbitals from the six sp^2 hybridized carbon atoms. (b) The electrons in the resulting π molecular orbitals are delocalized over the entire ring of carbon atoms, giving six equivalent bonds. A composite of these orbitals is repesented here.

- This gives six equivalent C—C bonds, as required by the known structure of the benzene molecule.
- The benzene structure is often written as



- to indicate the **delocalized π bonding** in the molecule.
- The NO_3^- ion can be described using the π molecular orbital system shown in Fig. 9.49.

Figure 9.49



(a) The *p* orbitals used to form the π bonding system in the NO_3^- ion. (b) A representation of the delocalization of the electrons in the π molecular orbital system of the NO_3^- ion.