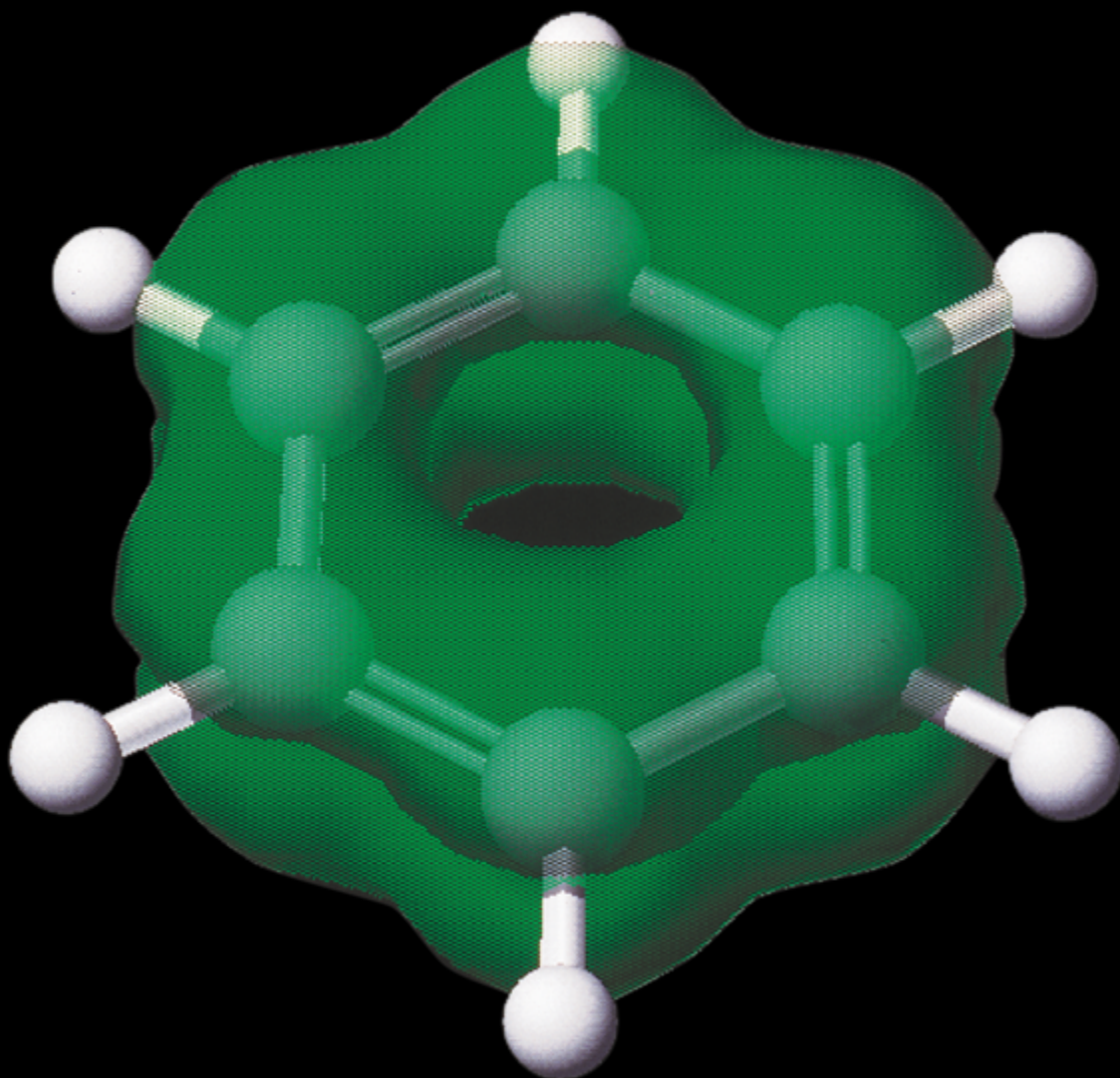


9

Molecular Orbitals in Chemical Bonding



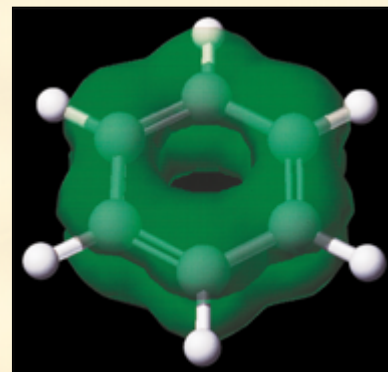
OUTLINE

- | | |
|---|---|
| 9-1 Molecular Orbitals | 9-5 Heteronuclear Diatomic Molecules |
| 9-2 Molecular Orbital Energy Level Diagrams | 9-6 Delocalization and the Shapes of Molecular Orbitals |
| 9-3 Bond Order and Bond Stability | |
| 9-4 Homonuclear Diatomic Molecules | |

OBJECTIVES

After you have finished studying this chapter, you should be able to

- Describe the basic concepts of molecular orbital theory
- Relate the shapes and overlap of atomic orbitals to the shapes and energies of the resulting molecular orbitals
- Distinguish among bonding, antibonding, and nonbonding orbitals
- Apply the Aufbau Principle to find molecular orbital descriptions for homonuclear diatomic molecules and ions
- Apply the Aufbau Principle to find molecular orbital descriptions for heteronuclear diatomic molecules and ions with small $\Delta(\text{EN})$ values
- Find the bond order in diatomic molecules and ions
- Relate bond order to bond stability
- Use the MO concept of delocalization for molecules in which valence bond theory would postulate resonance



A computer representation of one of the π molecular orbitals of benzene.

We have described bonding and molecular geometry in terms of valence bond theory. In valence bond theory, we postulate that bonds result from the sharing of electrons in overlapping orbitals of different atoms. These orbitals may be *pure atomic orbitals* or *hybridized atomic orbitals of individual atoms*. We describe electrons in overlapping orbitals of different atoms as being localized in the bonds between the two atoms involved. We then use hybridization to help account for the geometry of a molecule.

In **molecular orbital theory**, we postulate that

the combination of atomic orbitals on different atoms forms **molecular orbitals** (MOs), so that electrons in them belong to the molecule as a whole.

In some polyatomic molecules, a molecular orbital may extend over only a fraction of the molecule.

Valence bond and molecular orbital theories are alternative descriptions of chemical bonding. They have strengths and weaknesses, so they are complementary. Valence bond

Polyatomic ions such as CO_3^{2-} , SO_4^{2-} , and NH_4^+ can be described by the molecular orbital approach.



An early triumph of molecular orbital theory was its ability to account for the observed paramagnetism of oxygen, O_2 . According to earlier theories, O_2 was expected to be diamagnetic, that is, to have only paired electrons.

theory is descriptively attractive, and it lends itself well to visualization. Molecular orbital (MO) theory gives better descriptions of electron cloud distributions, bond energies, and magnetic properties, but its results are not as easy to visualize.

The valence bond picture of bonding in the O_2 molecule involves a double bond.



This shows no unpaired electrons, so it predicts that O_2 is diamagnetic. Experiments show, however, that O_2 is paramagnetic; therefore, it has unpaired electrons. Thus, the valence bond structure is inconsistent with experiment and cannot be accepted as a description of the bonding. Molecular orbital theory accounts for the fact that O_2 has two unpaired electrons. This ability of MO theory to explain the paramagnetism of O_2 gave it credibility as a major theory of bonding. We shall develop some of the ideas of MO theory and apply them to some molecules and polyatomic ions.


9-1 MOLECULAR ORBITALS

We learned in Chapter 5 that each solution to the Schrödinger equation, called a wave function, represents an atomic orbital. The mathematical pictures of hybrid orbitals in valence bond theory can be generated by combining the wave functions that describe two or more atomic orbitals on a *single* atom. Similarly, combining wave functions that describe atomic orbitals on *separate* atoms generates mathematical descriptions of molecular orbitals.

An orbital has physical meaning only when we square its wave function to describe the electron density. Thus, the overall sign on the wave function that describes an atomic orbital is not important, but when we *combine* two orbitals, the signs of the wave functions are important. When waves are combined, they may interact either constructively or destructively (Figure 9-1). Likewise, when two atomic orbitals overlap, they can be in phase (added) or out of phase (subtracted). When they overlap in phase, constructive interaction occurs in the region between the nuclei, and a **bonding orbital** is produced. The energy of the bonding orbital is always lower (more stable) than the energies of the combining orbitals. When they overlap out of phase, destructive interaction reduces the probability of finding electrons in the region between the nuclei, and an **antibonding orbital** is produced. This is higher in energy (less stable) than the original atomic orbitals. The overlap of two atomic orbitals always produces two MOs: one bonding and one antibonding.

We can illustrate this basic principle by considering the combination of the $1s$ atomic orbitals on *two different atoms* (Figure 9-2). When these orbitals are occupied by electrons, the shapes of the orbitals are plots of electron density. These plots show the regions in molecules where the probabilities of finding electrons are the greatest.

In the bonding orbital, the two $1s$ orbitals have reinforced each other in the region between the two nuclei by in-phase overlap, or addition of their electron waves. In the antibonding orbital, they have canceled each other in this region by out-of-phase overlap, or subtraction of their electron waves. We designate both molecular orbitals as **sigma (σ) molecular orbitals** (which indicates that they are cylindrically symmetrical about the internuclear axis). We indicate with subscripts the atomic orbitals that have been combined. The star (\star) denotes an antibonding orbital. Thus, two $1s$ orbitals produce a σ_{1s} (read “sigma-1s”) bonding orbital and a σ_{1s}^{\star} (read “sigma-1s-star”) antibonding orbital. The right-hand side of Figure 9-2 shows the relative energy levels of these orbitals. All sigma

 See the Saunders Interactive General Chemistry CD-ROM, Screen 10.9, Molecular Orbital Theory.

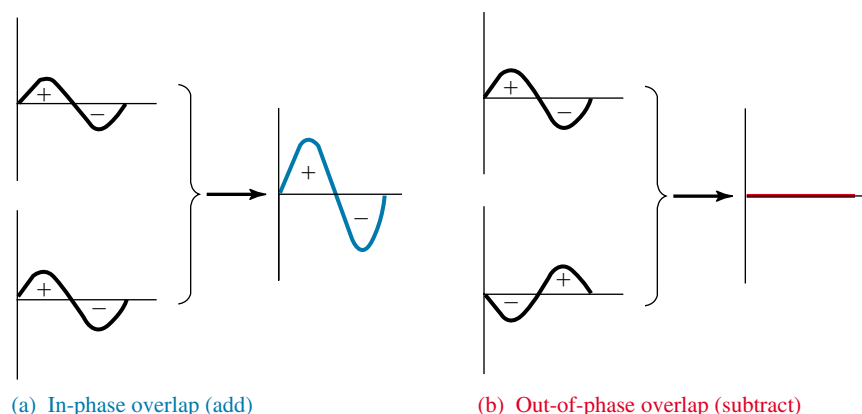


Figure 9-1 An illustration of constructive and destructive interference of waves. (a) If the two identical waves shown at the left are added, they interfere constructively to produce the more intense wave at the right. (b) Conversely, if they are subtracted, it is as if the phases (signs) of one wave were reversed and added to the first wave. This causes destructive interference, resulting in the wave at the right with zero amplitude; that is, a straight line.

antibonding orbitals have nodal planes bisecting the internuclear axis. A **node**, or **nodal plane**, is a region in which the probability of finding electrons is zero.

Another way of viewing the relative stabilities of these orbitals follows. In a bonding molecular orbital, the electron density is high *between* the two atoms, where it stabilizes the arrangement by exerting a strong attraction for both nuclei. By contrast, an antibonding orbital has a node (a region of zero electron density) between the nuclei; this allows for a strong net repulsion between the nuclei, which makes the arrangement less stable. Electrons are *more* stable (have lower energy) in bonding molecular orbitals than in the individual atoms. Placing electrons in antibonding orbitals, on the other hand, requires an increase in their energy, which makes them *less* stable than in the individual atoms.

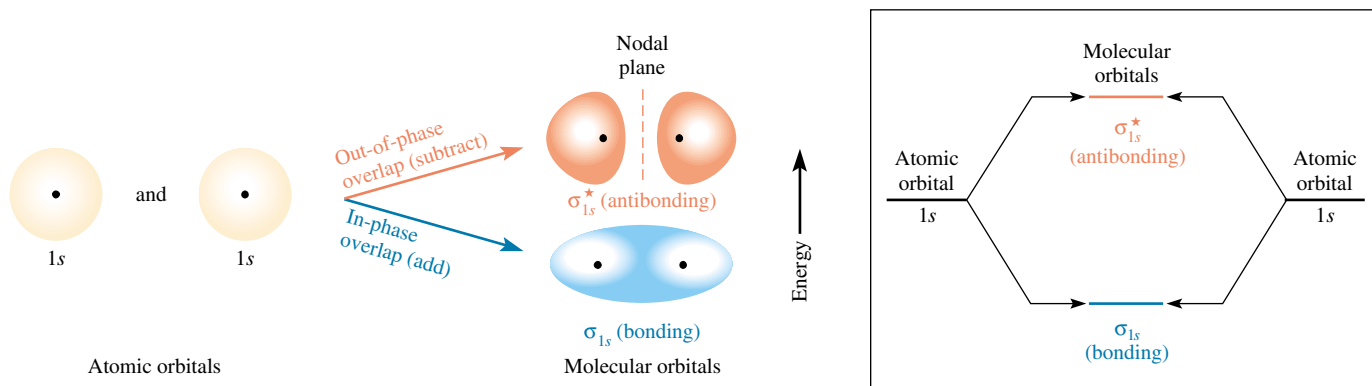


Figure 9-2 Molecular orbital (MO) diagram for the combination of the 1s atomic orbitals on two identical atoms (*at the left*) to form two MOs. One is a *bonding* orbital, σ_{1s} (*blue*), resulting from addition of the wave functions of the 1s orbitals. The other is an *antibonding* orbital, σ_{1s}^* (*red*), at higher energy resulting from subtraction of the waves that describe the combining 1s orbitals. In all σ -type MOs, the electron density is symmetrical about an imaginary line connecting the two nuclei. The terms “subtraction of waves,” “out of phase,” and “destructive interference in the region between the nuclei” all refer to the formation of an antibonding MO. Nuclei are represented by dots.

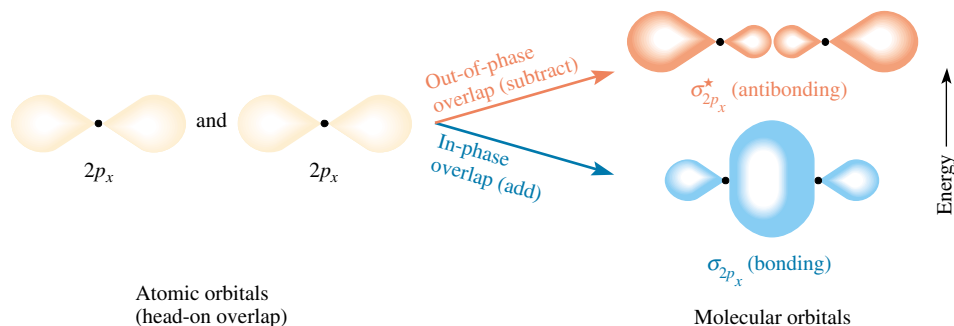


Figure 9-3 Production of σ_{2p_x} and $\sigma_{2p_x}^*$ molecular orbitals by overlap of $2p_x$ orbitals on two atoms.

How we name the axes is arbitrary. We designate the internuclear axis as the x direction.

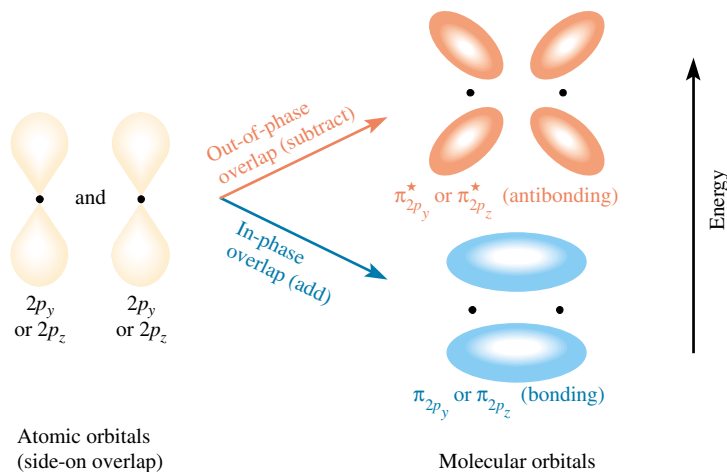
This would involve rotating Figures 9-2, 9-3, and 9-4 by 90° so that the internuclear axes are perpendicular to the plane of the pages.

For any two sets of p orbitals on two different atoms, corresponding orbitals such as p_x orbitals can overlap *head-on*. This gives σ_p and σ_p^* orbitals, as shown in Figure 9-3 for the head-on overlap of $2p_x$ orbitals on the two atoms. If the remaining p orbitals overlap (p_y with p_y and p_z with p_z), they must do so sideways, or *side-on*, forming *pi* (π) *molecular orbitals*. Depending on whether all p orbitals overlap, there can be as many as two π_p and two π_p^* orbitals. Figure 9-4 illustrates the overlap of two corresponding $2p$ orbitals on two atoms to form π_{2p} and π_{2p}^* molecular orbitals. There is a nodal plane along the internuclear axis for all pi molecular orbitals. If one views a sigma molecular orbital along the internuclear axis, it appears to be symmetrical around the axis like a pure s atomic orbital. A similar cross-sectional view of a pi molecular orbital looks like a pure p atomic orbital, with a node along the internuclear axis.

The number of molecular orbitals (MOs) formed is equal to the number of atomic orbitals that are combined. When two atomic orbitals are combined, one of the resulting MOs is at a *lower* energy than the original atomic orbitals; this is a *bonding* orbital. The other MO is at a *higher* energy than the original atomic orbitals; this is an *antibonding* orbital.

If we had chosen the z axis as the axis of head-on overlap of the $2p$ orbitals in Figure 9-3, side-on overlap of the $2p_x-2p_x$ and $2p_y-2p_y$ orbitals would form the π -type molecular orbitals.

Figure 9-4 The π_{2p} and π_{2p}^* molecular orbitals from overlap of one pair of $2p$ atomic orbitals (for instance, $2p_y$ orbitals). There can be an identical pair of molecular orbitals at right angles to these, formed by another pair of p orbitals on the same two atoms (in this case, $2p_z$ orbitals).



9-2 MOLECULAR ORBITAL ENERGY LEVEL DIAGRAMS

Figure 9-5 shows molecular orbital energy level diagrams for homonuclear diatomic molecules of elements in the first and second periods. Each diagram is an extension of the right-hand diagram in Figure 9-2, to which we have added the molecular orbitals formed from $2s$ and $2p$ atomic orbitals.

For the diatomic species shown in Figure 9-5a, the two π_{2p} orbitals are lower in energy than the σ_{2p} orbital. Molecular orbital calculations indicate, however, that for O_2 , F_2 , and hypothetical Ne_2 molecules, the σ_{2p} orbital is lower in energy than the π_{2p} orbitals (see Figure 9-5b).

“Homonuclear” means consisting only of atoms of the same element.

“Diatomic” means consisting of two atoms.

Spectroscopic data support these orders.

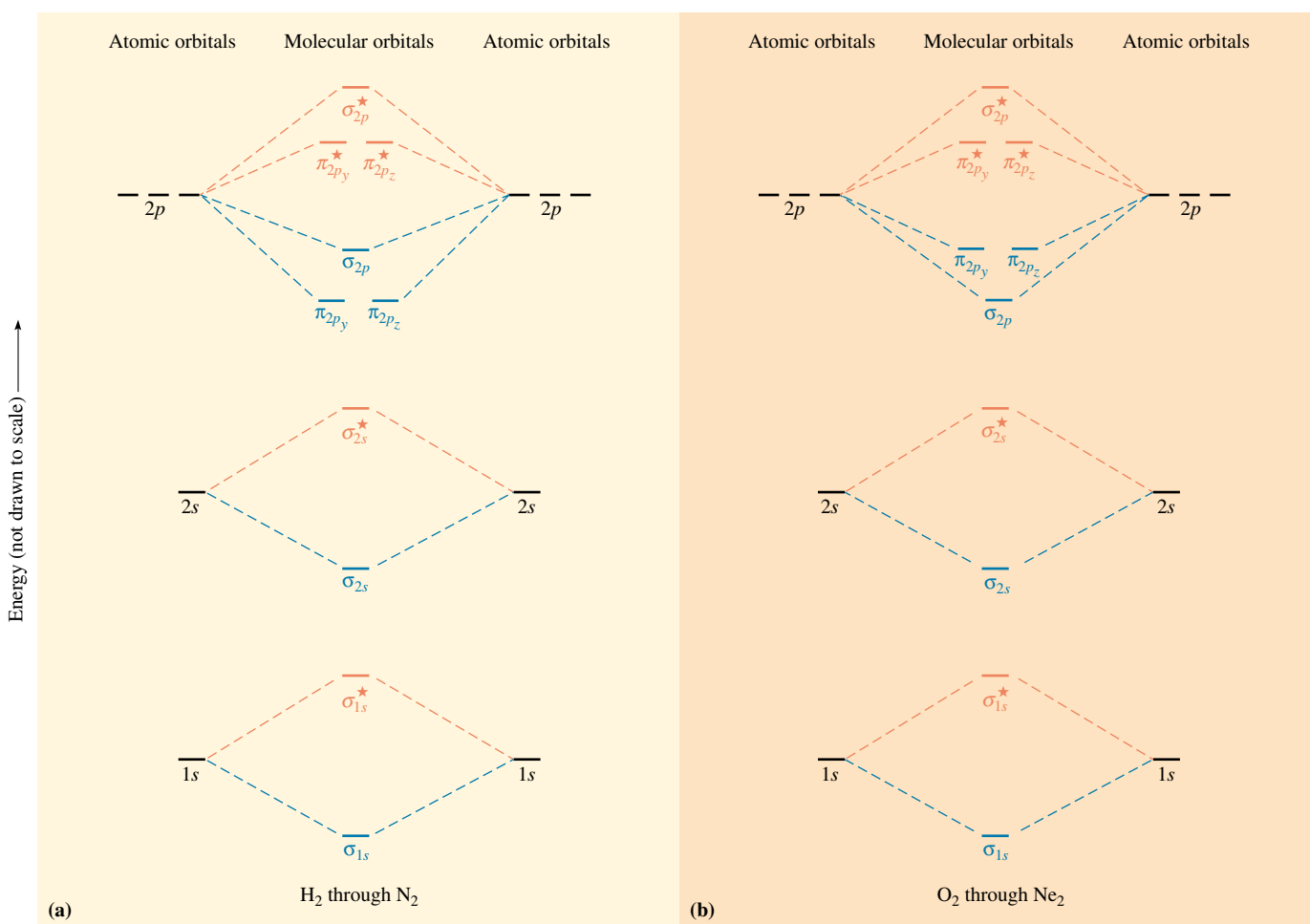



Figure 9-5 Energy level diagrams for first- and second-period homonuclear diatomic molecules and ions (not drawn to scale). The solid lines represent the relative energies of the indicated atomic and molecular orbitals. (a) The diagram for H_2 , He_2 , Li_2 , Be_2 , B_2 , C_2 , and N_2 molecules and their ions. (b) The diagram for O_2 , F_2 and Ne_2 molecules and their ions.

Diagrams such as these are used to describe the bonding in a molecule in MO terms. Electrons occupy MOs according to the same rules developed for atomic orbitals; they follow the Aufbau Principle, the Pauli Exclusion Principle, and Hund's Rule. (See Section 5-17.) To obtain the molecular orbital description of the bonding in a molecule or ion, follow these steps:

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 10.10, Molecular Electron Configurations.

1. Draw (or select) the appropriate molecular orbital energy level diagram.
2. Determine the *total* number of electrons in the molecule. Note that in applying MO theory, we will account for *all* electrons. This includes both the inner-shell electrons and the valence electrons.
3. Add these electrons to the energy level diagram, putting each electron into the lowest energy level available.
 - a. A maximum of *two* electrons can occupy any given molecular orbital, and then only if they have opposite spin (Pauli Exclusion Principle).
 - b. Electrons must occupy all the orbitals of the same energy singly before pairing begins. These unpaired electrons must have parallel spins (Hund's Rule).

9-3 BOND ORDER AND BOND STABILITY

Now we need a way to judge the stability of a molecule once its energy level diagram has been filled with the appropriate number of electrons. This criterion is the **bond order** (bo):

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

Electrons in bonding orbitals are often called **bonding electrons**, and electrons in antibonding orbitals are called **antibonding electrons**.

Usually the bond order corresponds to the number of bonds described by the valence bond theory. Fractional bond orders exist in species that contain an odd number of electrons, such as the nitrogen oxide molecule, NO (15 electrons) and the superoxide ion, O_2^- (17 electrons).

A bond order *equal to zero* means that the molecule has equal numbers of electrons in bonding MOs (more stable than in separate atoms) and in antibonding MOs (less stable than in separate atoms). Such a molecule would be no more stable than separate atoms, so it would not exist. A bond order *greater than zero* means that more electrons occupy bonding MOs (stabilizing) than antibonding MOs (destabilizing). Such a molecule would be more stable than the separate atoms, and we predict that its existence is possible. But such a molecule could be quite reactive.

The greater the bond order of a diatomic molecule or ion, the more stable we predict it to be. Likewise, for a bond between two given atoms, the greater the bond order, the shorter is the bond length and the greater is the bond energy.

The **bond energy** is the amount of energy necessary to break a mole of bonds (Section 15-9); therefore, bond energy is a measure of bond strength.

Problem-Solving Tip: Working with MO Theory

MO theory is often the best model to predict the bond order, bond stability, or magnetic properties of a molecule or ion. The procedure is as follows:

1. Draw (or select) the appropriate MO energy level diagram.
2. Count the total number of electrons in the molecule or ion.
3. Follow the Pauli Exclusion Principle and Hund's Rule to add the electrons to the MO diagram.
4. Calculate the bond order: $\text{Bond order} = \left(\frac{\text{bonding } e\text{'s} - \text{antibonding } e\text{'s}}{2} \right)$.
5. Use the bond order to evaluate stability.
6. Look for the presence of unpaired electrons to determine if a species is paramagnetic.

See the Saunders Interactive General Chemistry CD-ROM, Screen 10.11, Homonuclear Diatomic Molecules.

9-4 HOMONUCLEAR DIATOMIC MOLECULES

The electron distributions for the homonuclear diatomic molecules of the first and second periods are shown in Table 9-1 together with their bond orders, bond lengths, and bond energies.

The Hydrogen Molecule, H₂

The overlap of the 1s orbitals of two hydrogen atoms produces σ_{1s} and σ_{1s}^* molecular orbitals. The two electrons of the molecule occupy the lower energy σ_{1s} orbital (Figure 9-6a).

Because the two electrons in an H₂ molecule are in a bonding orbital, the bond order is one. We conclude that the H₂ molecule would be stable, and we know it is. The energy associated with two electrons in the H₂ molecule is lower than that associated with the same two electrons in separate 1s atomic orbitals. The lower the energy of a system, the more stable it is. As the energy of a system decreases, its stability increases.

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

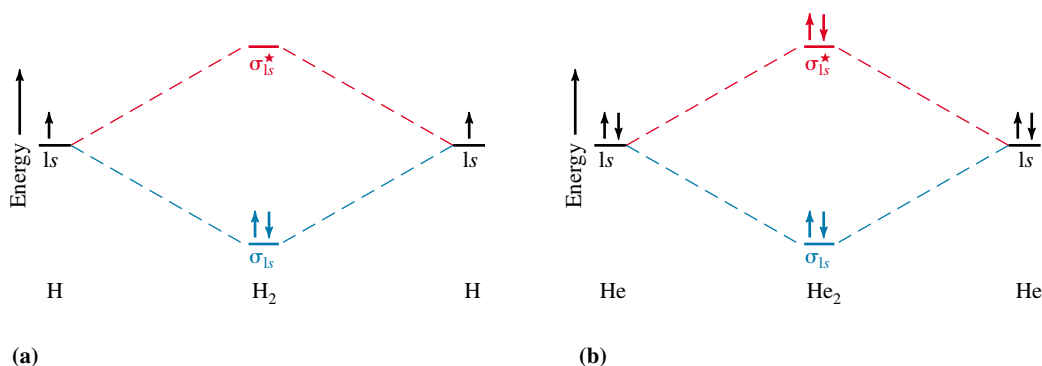


Figure 9-6 Molecular orbital diagrams for (a) H₂ and (b) He₂.

The Helium Molecule (Hypothetical), He₂

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

The energy level diagram for He₂ is similar to that for H₂ except that it has two more electrons. These occupy the antibonding σ_{1s}^* orbital (see Figures 9-5a and 9-6b and Table 9-1), giving He₂ a bond order of zero. That is, the two electrons in the bonding orbital of He₂ would be *more stable* than in the separate atoms. But the two electrons in the antibonding orbital would be *less stable* than in the separate atoms. These effects cancel, so the molecule would be no more stable than the separate atoms. The bond order is zero, and the molecule would not exist. In fact, He₂ is unknown.

The Boron Molecule, B₂

$$\text{B}_2 \text{ bond order} = \frac{6 - 4}{2} = 1$$

Orbitals of equal energy are called *degenerate* orbitals. Hund's Rule for filling degenerate orbitals was discussed in Section 5-17.

The boron atom has the configuration $1s^2 2s^2 2p^1$. Here p electrons participate in the bonding. Figure 9-5a and Table 9-1 show that the π_{p_y} and π_{p_z} molecular orbitals are lower in energy than the σ_{2p} for B₂. Thus, the electron configuration is



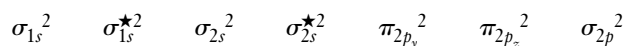
The unpaired electrons are consistent with the observed paramagnetism of B₂. Here we illustrate Hund's Rule in molecular orbital theory. The π_{2p_y} and π_{2p_z} orbitals are equal in energy and contain a total of two electrons. Accordingly, one electron occupies each orbital. The bond order is one. Experiments verify that B₂ molecules exist in the vapor state.

The Nitrogen Molecule, N₂

$$\text{N}_2 \text{ bond order} = \frac{10 - 4}{2} = 3$$

In the valence bond representation, N₂ is shown as :N≡N:, with a triple bond.

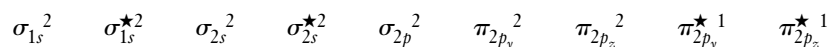
Experimental thermodynamic data show that the N₂ molecule is stable, is diamagnetic, and has a very high bond energy, 946 kJ/mol. This is consistent with molecular orbital theory. Each nitrogen atom has seven electrons, so the diamagnetic N₂ molecule has 14 electrons.



Six more electrons occur in bonding orbitals than in antibonding orbitals, so the bond order is three. We see (Table 9-1) that N₂ has a very short bond length, only 1.09 Å, the shortest of any diatomic species except H₂.

The Oxygen Molecule, O₂

Among the homonuclear diatomic molecules, only N₂ and the very small H₂ have shorter bond lengths than O₂, 1.21 Å. Recall that VB theory predicts that O₂ is diamagnetic. Experiments show, however, that it is paramagnetic, with two unpaired electrons. MO theory predicts a structure consistent with this observation. For O₂, the σ_{2p} orbital is lower in energy than the π_{2p_y} and π_{2p_z} orbitals. Each oxygen atom has eight electrons, so the O₂ molecule has 16 electrons.



The two unpaired electrons reside in the *degenerate* antibonding orbitals, $\pi_{2p_y}^*$ and $\pi_{2p_z}^*$. Because there are four more electrons in bonding orbitals than in antibonding orbitals, the bond order is two (see Figure 9-5b and Table 9-1). We see why the molecule is much more stable than two free O atoms.

$$\text{O}_2 \text{ bond order} = \frac{10 - 6}{2} = 2$$

TABLE 9-1 Molecular Orbitals for First- and Second-Period (Row) Diatomic Molecules^a

	H ₂	He ₂ ^c	Li ₂ ^b	Be ₂ ^c	B ₂ ^b	C ₂ ^b	N ₂		O ₂	F ₂	Ne ₂ ^c	
Increasing energy (not to scale)	σ_{2p}^*	—	—	—	—	—	—	$\pi_{2p_y}^*, \pi_{2p_z}^*$ σ_{2p}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
	$\pi_{2p_y}^*, \pi_{2p_z}^*$	—	—	—	—	—	—		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
	σ_{2p}	—	—	—	—	$\uparrow\uparrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
	π_{2p_y}, π_{2p_z}	—	—	—	—	$\uparrow\uparrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
	σ_{2s}^*	—	—	—	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
	σ_{2s}	—	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
	σ_{1s}^*	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
	σ_{1s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
Paramagnetic?	no	no	no	no	yes	no	no		yes	no	no	
Bond order	1	0	1	0	1	2	3		2	1	0	
Observed bond length (Å)	0.74	—	2.67	—	1.59	1.31	1.09		1.21	1.43	—	
Observed bond energy (kJ/mol)	436	—	110	9	≈270	602	945		498	155	—	

^aElectron distribution in molecular orbitals, bond order, bond length, and bond energy of homonuclear diatomic molecules of the first- and second-period elements. Note that nitrogen molecules, N₂, have the highest bond energies listed; they have a bond order of three. The species C₂ and O₂, with a bond order of two, have the next highest bond energies.

^bExists only in the vapor state at elevated temperatures.

^cUnknown species.

Similarly, MO theory can be used to predict the structures and stabilities of ions, as Example 9-1 shows.

EXAMPLE 9-1 Predicting Stabilities and Bond Orders

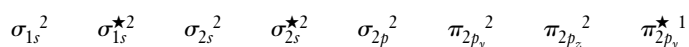
Predict the stabilities and bond orders of the ions (a) O₂⁺ and (b) O₂⁻.

Plan

(a) The O₂⁺ ion is formed by removing one electron from the O₂ molecule. The electrons that are withdrawn most easily are those in the highest energy orbitals. (b) The superoxide ion, O₂⁻, results from adding an electron to the O₂ molecule.

Solution

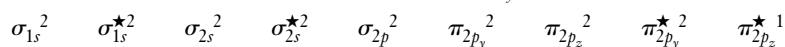
(a) We remove one of the π_{2p}^* electrons of O₂ to find the configuration of O₂⁺:



There are five more electrons in bonding orbitals than in antibonding orbitals, so the bond order is 2.5. We conclude that the ion would be reasonably stable relative to other diatomic ions, and it does exist.

In fact, the unusual ionic compound [O₂⁺][PtF₆⁻] played an important role in the discovery of the first noble gas compound, XePtF₆ (Section 24-2).

(b) We add one electron to the appropriate orbital of O₂ to find the configuration of O₂⁻. Following Hund's Rule, we add this electron into the $\pi_{2p_y}^*$ orbital to form a pair:



There are three more bonding electrons than antibonding electrons, so the bond order is 1.5. We conclude that the ion should exist but be less stable than O₂.

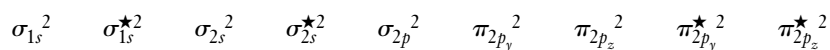
The known superoxides of the heavier Group IA elements—KO₂, RbO₂, and CsO₂—contain the superoxide ion, O₂⁻. These compounds are formed by combination of the free metals with oxygen (Section 6-8, second subsection).

You should now work Exercises 19 and 20.

The Fluorine Molecule, F₂

Each fluorine atom has 9 electrons, so there are 18 electrons in F₂.

$$\text{F}_2 \text{ bond order} = \frac{10 - 8}{2} = 1$$



The bond order is one. As you know, F₂ exists. The F—F bond distance is longer (1.43 Å) than the bond distances in O₂ (1.21 Å) or N₂ (1.09 Å) molecules. The bond order in F₂ (one) is less than that in O₂ (two) or N₂ (three). The bond energy of the F₂ molecules is lower than that of either O₂ or N₂ (see Table 9-1). As a result, F₂ molecules are the most reactive of the three.

Heavier Homonuclear Diatomic Molecules

It might appear reasonable to use the same types of molecular orbital diagrams to predict the stability or existence of homonuclear diatomic molecules of the third and subsequent periods. However, the heavier halogens, Cl₂, Br₂, and I₂, which contain only sigma (single) bonds, are the only well-characterized examples at room temperature. We would predict from both molecular orbital theory and valence bond theory that the other (nonhalogen) homonuclear diatomic molecules from below the second period would exhibit pi bonding and therefore multiple bonding.

Some heavier elements, such as S₂, exist as diatomic species in the vapor phase at elevated temperatures. These species are neither common nor very stable. The instability is related to the inability of atoms of the heavier elements to form strong pi bonds *with each other*. For larger atoms, the sigma bond length is too great to allow the atomic *p* orbitals on different atoms to overlap very effectively. The strength of pi bonding therefore decreases rapidly with increasing atomic size. For example, N₂ is *much* more stable than P₂. This is because the 3*p* orbitals on one P atom do not overlap side by side in a pi-bonding manner with corresponding 3*p* orbitals on another P atom nearly as effectively as do the corresponding 2*p* orbitals on the smaller N atoms. MO theory does not predict multiple bonding for Cl₂, Br₂, or I₂, each of which has a bond order of one.

9-5 HETERONUCLEAR DIATOMIC MOLECULES

Heteronuclear Diatomic Molecules of Second-Period Elements

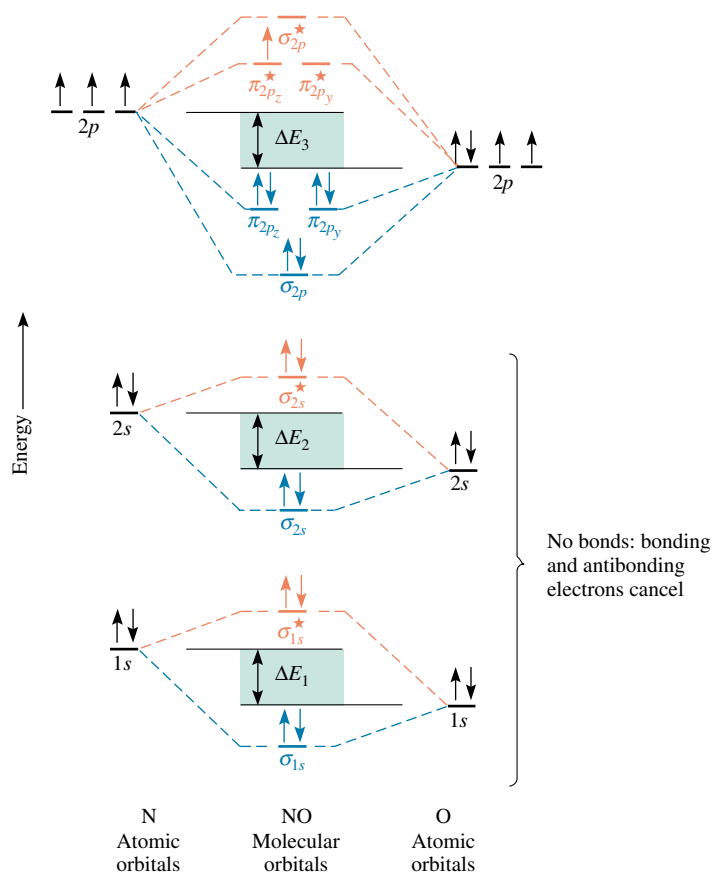
Corresponding atomic orbitals of two different elements, such as the 2*s* orbitals of nitrogen and oxygen atoms, have different energies because their nuclei have different charges and therefore different attractions for electrons. Atomic orbitals of the *more electronegative element* are *lower* in energy than the corresponding orbitals of the less electronegative

element. Accordingly, a molecular orbital diagram such as Figure 9-5 is inappropriate for *heteronuclear* diatomic molecules. If the two elements are similar (as in NO or CN molecules, for example), we can modify the diagram of Figure 9-5 by skewing it slightly. Figure 9-7 shows the energy level diagram and electron configuration for nitrogen oxide, NO, also known as nitric oxide.

The closer the energy of a molecular orbital is to the energy of one of the atomic orbitals from which it is formed, the more of the character of that atomic orbital it shows. Thus, as we see in Figure 9-7, the bonding MOs in the NO molecule have more oxygen-like atomic orbital character, and the antibonding orbitals have more nitrogen-like atomic orbital character.

In general the energy differences ΔE_1 , ΔE_2 , and ΔE_3 (green backgrounds in Figure 9-7) depend on the difference in electronegativities between the two atoms. The greater these energy differences, the more polar is the bond joining the atoms and the greater is its ionic character. On the other hand, the energy differences reflect the degree of overlap between atomic orbitals; the smaller these differences, the more the orbitals can overlap, and the greater is the covalent character of the bond.

We see that NO has a total of 15 electrons, making it isoelectronic with the N_2^- ion. The distribution of electrons is therefore the same in NO as in N_2^- , although we expect the energy levels of the MOs to be different. In accord with our predictions, nitrogen oxide is a stable molecule. It has a bond order of 2.5, a short nitrogen–oxygen bond length of 1.15 Å, a low dipole moment of 0.15 D, and a high bond energy of 891 kJ/mol.



Note: CN is a reactive molecule, not the stable cyanide ion, CN^- .

Figure 9-7 MO energy level diagram for nitrogen oxide, NO, a slightly polar heteronuclear diatomic molecule ($\mu = 0.15$ D). The atomic orbitals of oxygen, the more electronegative element, are a little lower in energy than the corresponding atomic orbitals of nitrogen, the less electronegative element. For this molecule, the energy differences ΔE_1 , ΔE_2 , and ΔE_3 are not very large; the molecule is not very polar.

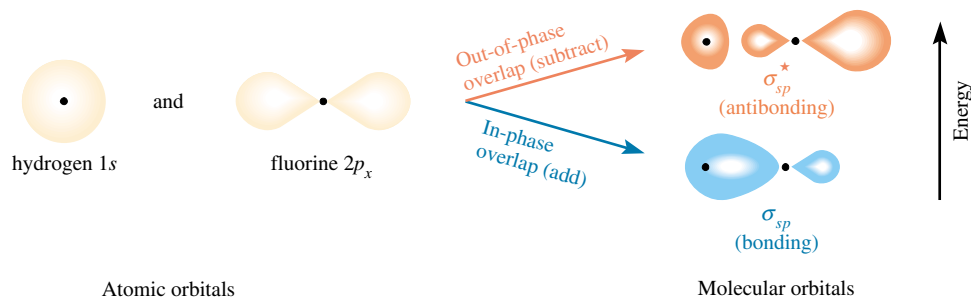


Figure 9-8 Formation of σ_{sp} and σ_{sp}^* molecular orbitals in HF by overlap of the $1s$ orbital of H with a $2p$ orbital of F.

The Hydrogen Fluoride Molecule, HF

The electronegativity difference between hydrogen (EN = 2.1) and fluorine (EN = 4.0) is very large ($\Delta(\text{EN}) = 1.9$). The hydrogen fluoride molecule contains a very polar bond ($\mu = 1.91$ D). The bond in HF involves the $1s$ electron of H and an unpaired electron from a $2p$ orbital of F. Figure 9-8 shows the overlap of the $1s$ orbital of H with a $2p$ orbital of F to form σ_{sp} and σ_{sp}^* molecular orbitals. The remaining two $2p$ orbitals of F have no net overlap with H orbitals. They are called **nonbonding** orbitals. The same is true for the F $2s$ and $1s$ orbitals. These nonbonding orbitals retain the characteristics of the F atomic orbitals from which they are formed. The MO diagram of HF is shown in Figure 9-9.

Other Diatomic Species with Large $\Delta(\text{EN})$ Values

If the energies of the atomic orbitals of the two atoms of a diatomic molecule or ion are quite different, the MO diagram may be unlike that known for any homonuclear species. Its unique MO diagram is constructed by combining the Schrödinger equations for the two atoms. Construction of the MO diagram for CO is a complex case, beyond the coverage in this textbook.

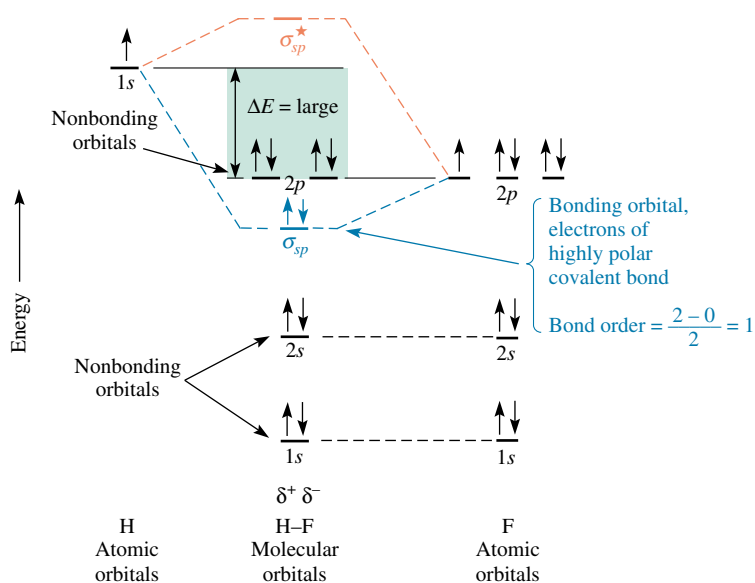


Figure 9-9 MO energy level diagram for hydrogen fluoride, HF, a very polar molecule ($\mu = 1.91$ D). ΔE is large because the electronegativity difference is large.

9-6 DELOCALIZATION AND THE SHAPES OF MOLECULAR ORBITALS

In Section 7-6 we described resonance formulas for molecules and polyatomic ions. Resonance is said to exist when two or more equivalent Lewis formulas can be written for the same species and a single such formula does not account for the properties of a substance. In molecular orbital terminology, a more appropriate description involves *delocalization* of electrons. The shapes of molecular orbitals for species in which electron delocalization occurs can be predicted by combining all the contributing atomic orbitals.

The Carbonate Ion, CO_3^{2-}

Consider the trigonal planar carbonate ion, CO_3^{2-} , as an example. All the carbon–oxygen bonds in the ion have the same bond length and the same energy, intermediate between those of typical C–O and C=O bonds. Valence bond theory describes the ion in terms of three contributing resonance structures (Figure 9-10a). No one of the three resonance forms adequately describes the bonding.

According to valence bond theory, the C atom is described as sp^2 hybridized, and it forms one sigma bond with each of the three O atoms. This leaves one unhybridized $2p$ atomic orbital on the C atom, say the $2p_z$ orbital. This orbital is capable of overlapping and mixing with the $2p_z$ orbital of any of the three O atoms. The sharing of two electrons in the resulting localized pi orbital would form a pi bond. Thus, three equivalent resonance structures can be drawn in valence bond terms (Figure 9-10b). We emphasize that there is *no evidence* for the existence of these separate resonance structures.

The MO description of the pi bonding involves the simultaneous overlap and mixing of the carbon $2p_z$ orbital with the $2p_z$ orbitals of all three oxygen atoms. This forms a delocalized bonding pi molecular orbital system extending above and below the plane of the sigma system, as well as an antibonding pi orbital system. Electrons are said to occupy the entire set of bonding pi MOs, as depicted in Figure 9-10c. The shape is obtained by averaging the contributing valence bond resonance structures. The bonding in such species as nitrate ion, NO_3^- , and ozone, O_3 , can be described similarly.

The average carbon–oxygen bond order in the CO_3^{2-} ion is $1\frac{1}{3}$.

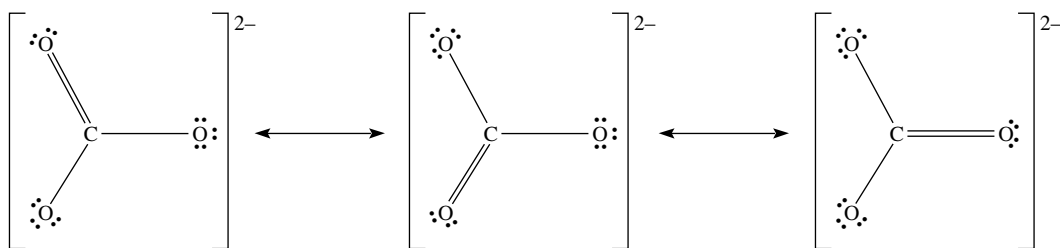
The Benzene Molecule, C_6H_6

Now let us consider the benzene molecule, C_6H_6 , whose two valence bond resonance forms are shown in Figure 9-11a. The valence bond description involves sp^2 hybridization at each C atom. Each C atom is at the center of a trigonal plane, and the entire molecule is known to be planar. There are sigma bonds from each C atom to the two adjacent C atoms and to one H atom. This leaves one unhybridized $2p_z$ orbital on each C atom and one remaining valence electron for each. According to valence bond theory, adjacent pairs of $2p_z$ orbitals and the six remaining electrons occupy the regions of overlap to form a total of three pi bonds in either of the two ways shown in Figure 9-11b.

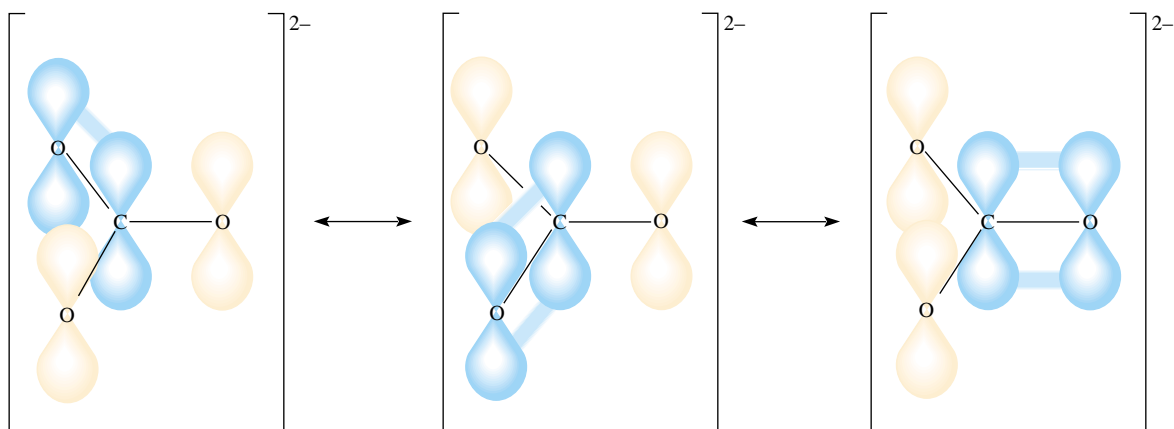
Experimental studies of the C_6H_6 structure prove that it does *not* contain alternating single and double carbon–carbon bonds. The usual C–C single bond length is 1.54 Å, and the usual C=C double bond length is 1.34 Å. All six of the carbon–carbon bonds in benzene are the same length, 1.39 Å, intermediate between those of single and double bonds.

This is well explained by the MO theory, which predicts that the six $2p_z$ orbitals of the C atoms overlap and mix to form three pi-bonding and three pi-antibonding molecular

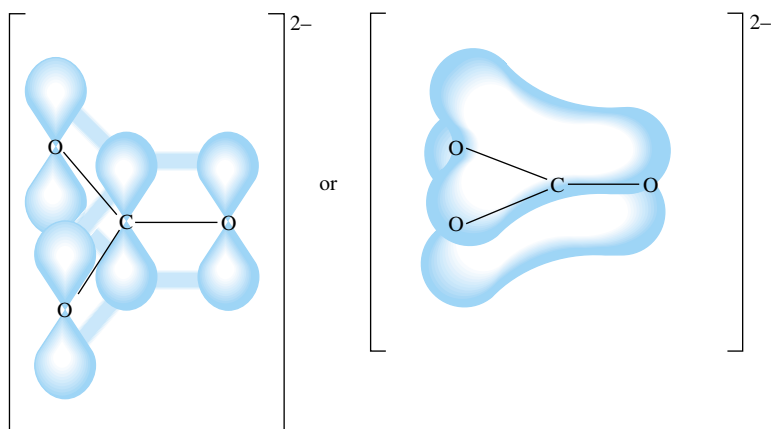
There is no evidence for the existence of either of these forms of benzene. The MO description of benzene is far better than the valence bond description.



(a) Lewis formulas for valence bond resonance structures



(b) p -Orbital overlap in valence bond resonance



(c) Delocalized MO representation

Figure 9-10 Alternative representations of the bonding in the carbonate ion, CO_3^{2-} . (a) Lewis formulas of the three valence bond resonance structures. (b) Representation of the p orbital overlap in the valence bond resonance structures. In each resonance form, the p orbitals on two atoms would overlap to form the π components of the hypothetical double bonds. Each O atom has two additional sp^2 orbitals (not shown) in the plane of the nuclei. Each of these additional sp^2 orbitals contains an oxygen unshared pair. (c) In the MO description, the electrons in the π -bonded region are spread out, or *delocalized*, over all four atoms of the CO_3^{2-} ion. This MO description is more consistent with the experimental observation of equal bond lengths and energies than are the valence bond pictures in parts (a) and (b).

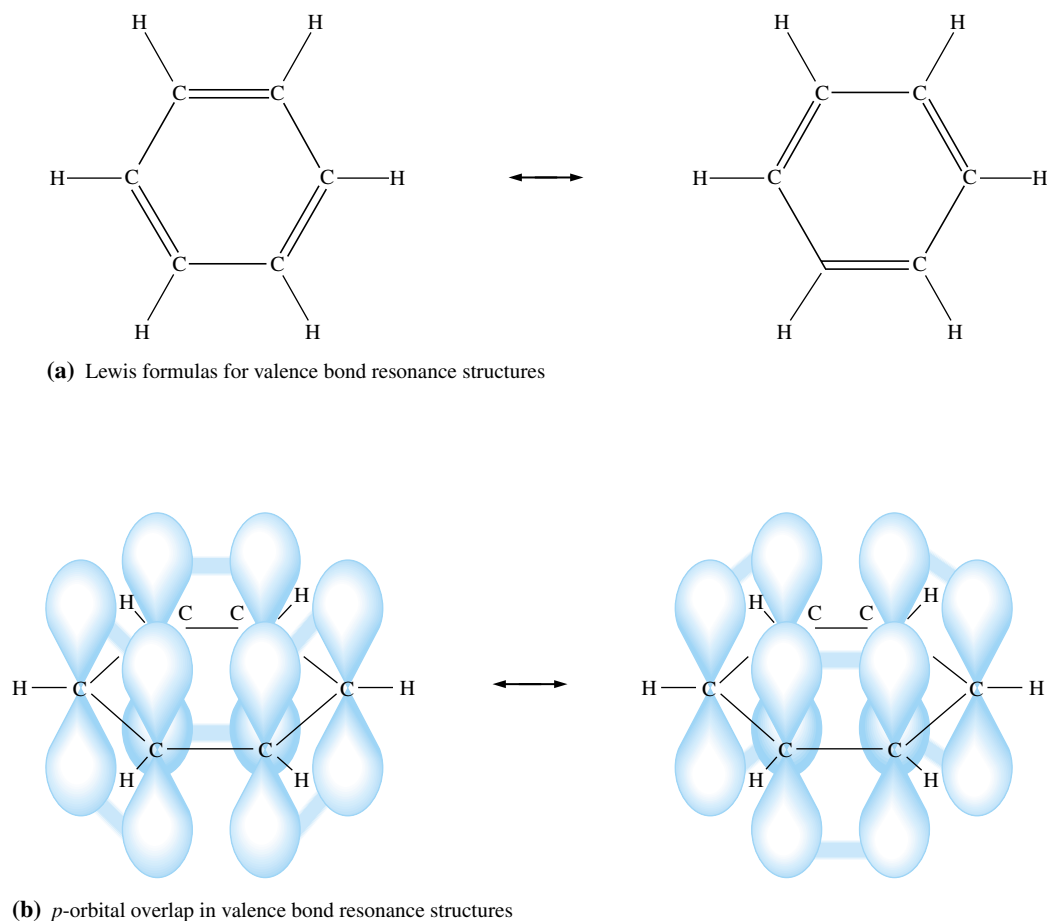


Figure 9-11 Representations of the bonding in the benzene molecule, C_6H_6 . (a) Lewis formulas of the two valence bond resonance structures. (b) The six *p* orbitals of the benzene ring, shown overlapping to form the (hypothetical) double bonds of the two resonance forms of valence bond theory. (c) In the MO description the six electrons in the pi-bonded region are *delocalized*, meaning they occupy an extended pi-bonding region above and below the plane of the six C atoms.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 10.13, Molecular Orbitals and Vision.

orbitals. For instance, the most strongly bonding pi molecular orbital in the benzene pi-MO system is that in Figure 9-11c. The six pi electrons occupy three bonding MOs of this extended (delocalized) system. Thus, they are distributed throughout the molecule as a whole, above and below the plane of the sigma-bonded framework. This results in identical character for all carbon-carbon bonds in benzene. Each carbon-carbon bond has a bond order of 1.5. The MO representation of the extended pi system is the same as that obtained by averaging the two contributing valence bond resonance structures.

Key Terms

Antibonding orbital A molecular orbital higher in energy than any of the atomic orbitals from which it is derived; when populated with electrons, lends instability to a molecule or ion. Denoted with a star (\star) superscript on its symbol.

Bond energy The amount of energy necessary to break one mole of bonds of a given kind (in the gas phase).

Bond order Half the number of electrons in bonding orbitals minus half the number of electrons in antibonding orbitals.

Bonding orbital A molecular orbital lower in energy than any of the atomic orbitals from which it is derived; when populated with electrons, lends stability to a molecule or ion.

Degenerate orbitals Orbitals of the same energy.

Delocalization The formation of a set of molecular orbitals that extend over more than two atoms; important in species that valence bond theory describes in terms of *resonance*.

Heteronuclear Consisting of different elements.

Homonuclear Consisting of only one element.

Molecular orbital (MO) An orbital resulting from overlap and mixing of atomic orbitals on different atoms. An MO belongs to the molecule as a whole.

Molecular orbital theory A theory of chemical bonding based on the postulated existence of molecular orbitals.

Nodal plane (node) A region in which the probability of finding an electron is zero.

Nonbonding orbital A molecular orbital derived only from an atomic orbital of one atom; lends neither stability nor instability to a molecule or ion when populated with electrons.

Pi (π) bond A bond resulting from electron occupation of a pi molecular orbital.

Pi (π) orbital A molecular orbital resulting from side-on overlap of atomic orbitals.

Sigma (σ) bond A bond resulting from electron occupation of a sigma molecular orbital.

Sigma (σ) orbital A molecular orbital resulting from head-on overlap of two atomic orbitals.

Exercises

MO Theory: General Concepts

- Describe the main differences between the valence bond theory and the molecular orbital theory.
- In molecular orbital theory, what is a molecular orbital? What two types of information can be obtained from molecular orbital calculations? How do we use such information to describe the bonding within a molecule?
- What is the relationship between the maximum number of electrons that can be accommodated by a set of molecular orbitals and the maximum number that can be accommodated by the atomic orbitals from which the MOs are formed? What is the maximum number of electrons that one MO can hold?
- Answer Exercise 3 after replacing “molecular orbitals” with “hybridized atomic orbitals.”
- What differences and similarities exist among (a) atomic orbitals, (b) localized hybridized atomic orbitals according to valence bond theory, and (c) molecular orbitals?
- What is the relationship between the energy of a bonding molecular orbital and the energies of the original atomic orbitals? What is the relationship between the energy of an antibonding molecular orbital and the energies of the original atomic orbitals?
- Compare and contrast the following three concepts: (a) bonding orbitals; (b) antibonding orbitals; (c) nonbonding orbitals.
- Describe the shapes, including the locations of the nuclei, of σ and σ^* orbitals.
- Describe the shapes, including the locations of the nuclei, of π and π^* orbitals.

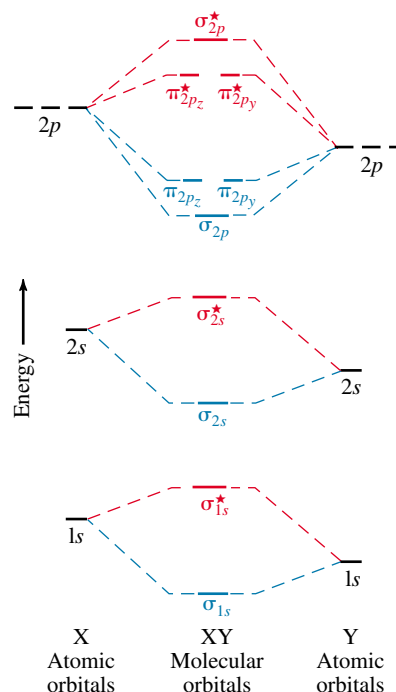
- State the three rules for placing electrons in molecular orbitals.
- What is meant by the term “bond order”? How is the value of the bond order calculated?
- Compare and illustrate the differences between (a) atomic orbitals and molecular orbitals, (b) bonding and antibonding molecular orbitals, (c) σ bonds and π bonds, and (d) localized and delocalized molecular orbitals.
- Is it possible for a molecule or polyatomic ion in its ground state to have a negative bond order? Why?

Homonuclear Diatomic Species

- What do we mean when we say that a molecule or ion is (a) homonuclear, (b) heteronuclear, or (c) diatomic?
- Use the appropriate molecular orbital energy diagram to write the electron configuration for each of the following; calculate the bond order of each, and predict which would exist. (a) H_2^+ ; (b) H_2 ; (c) H_2^- ; (d) H_2^{2-} .
- Repeat Exercise 15 for (a) He_2^+ ; (b) He_2 ; (c) He_2^{2+} .
- Repeat Exercise 15 for (a) N_2 ; (b) Ne_2 ; (c) C_2^{2-} .
- Repeat Exercise 15 for (a) Li_2 ; (b) Li_2^+ ; (c) O_2^{2-} .
- Use the appropriate molecular orbital energy diagram to write the electron configurations of the following molecules and ions: (a) Be_2 , Be_2^+ , Be_2^- ; (b) B_2 , B_2^+ , B_2^- .
- What is the bond order of each of the species in Exercise 19?
- Which of the species in Exercise 19 are diamagnetic and which are paramagnetic?
- Use MO theory to predict relative stabilities of the species in Exercise 19. Comment on the validity of these predictions. What else *must* be considered in addition to electron occupancy of MOs?
- Which homonuclear diatomic molecules or ions of the second period have the following electron distributions in MOs? In other words, identify X in each.
 - $\text{X}_2 \quad \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_y}^2 \pi_{2p_z}^2 \sigma_{2p}^2$
 - $\text{X}_2 \quad \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_z}^2 \pi_{2p_y}^{*1} \pi_{2p_z}^{*1}$
 - $\text{X}_2^- \quad \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_y}^2 \pi_{2p_z}^2 \sigma_{2p}^2 \pi_{2p_y}^{*1}$
- What is the bond order of each of the species in Exercise 23?
- (a) Give the MO designations for O_2 , O_2^- , O_2^{2-} , O_2^+ , and O_2^{2+} . (b) Give the bond order in each case. (c) Match these species with the following observed bond lengths: 1.04 Å; 1.12 Å; 1.21 Å; 1.33 Å; and 1.49 Å.
- (a) Give the MO designations for N_2 , N_2^- , and N_2^+ . (b) Give the bond order in each case. (c) Rank these three species by increasing predicted bond length.
- Assuming that the σ_{2p} MO is lower in energy than the π_{2p_y} and π_{2p_z} MOs for the following species, write out electron configurations for (a) F_2 , F_2^+ , F_2^- ; (b) C_2 , C_2^+ , C_2^- .
- (a) What is the bond order of each species in Exercise 27? (b) Are they diamagnetic or paramagnetic? (c) What would MO theory predict about the stabilities of these species?

Heteronuclear Diatomic Species

The following is a molecular orbital energy level diagram for a heteronuclear diatomic molecule, XY, in which both X and Y are from Period 2 and Y is slightly more electronegative. This diagram may be used in answering questions in this section.



- Use the preceding diagram to fill in an MO diagram for NO^- . What is the bond order of NO^- ? Is it paramagnetic? How would you assess its stability?
- Repeat Exercise 29 for NO^+ .
- Repeat Exercise 29 for CN^+ . Refer to the preceding diagram but assume that the π_{2p_y} and π_{2p_z} MOs are lower in energy than the σ_{2p} MO.
- Compare the MO descriptions for CN , CN^- , and CN^{2-} . Refer to the preceding diagram but assume that the π_{2p_y} and π_{2p_z} MOs are lower in energy than the σ_{2p} MO. Which would be most stable? Why?
- For each of the two species OF and OF^- : (a) Draw MO energy level diagrams. (b) Write out electron configurations. (c) Determine bond orders and predict relative stabilities. (d) Predict diamagnetism or paramagnetism.
- For each of the two species NF and NF^+ : (a) Draw MO energy level diagrams. (b) Write out electron configurations. (c) Determine bond orders and predict relative stabilities. (d) Predict diamagnetism or paramagnetism.

35. Considering the shapes of MO energy level diagrams for nonpolar covalent and polar covalent molecules, what would you predict about MO diagrams, and therefore about overlap of atomic orbitals, for ionic compounds?
36. To increase the strength of the bonding in the hypothetical compound BC, would you add or subtract an electron? Explain your answer with the aid of an MO electron structure.

Delocalization

37. Use Lewis formulas to depict the resonance structures of the following species from the valence bond point of view, and then sketch MOs for the delocalized π systems. (a) NO_3^- , nitrate ion; (b) HCO_3^- , hydrogen carbonate ion (H is bonded to O); (c) NO_2^- , nitrite ion.
38. Use Lewis formulas to depict the resonance structures of the following species from the valence bond point of view, and then sketch MOs for the delocalized π systems: (a) SO_2 , sulfur dioxide; (b) O_3 , ozone; (c) HCO_2^- , formate ion (H is bonded to C).

Mixed Exercises

39. Draw and label the complete MO energy level diagrams for the following species. For each, determine the bond order, predict the stability of the species, and predict whether the species will be paramagnetic or diamagnetic. (a) He_2^+ ; (b) CN; (c) HeH^+ .
40. Draw and label the complete MO energy level diagrams for the following species. For each, determine the bond order, predict the stability of the species, and predict whether the species will be paramagnetic or diamagnetic. (a) O_2^{2+} ; (b) HO^- ; (c) HF.
41. Which of these species would you expect to be paramagnetic or diamagnetic? (a) He_2^- ; (b) N_2 ; (c) NO^+ ; (d) N_2^{2+} ; (e) F_2^+ .

CONCEPTUAL EXERCISES

42. Refer to the diagrams in Figure 9-5 as needed. Can the bond order of a diatomic species having 20 or fewer electrons be greater than three? Can the bond order be a value that is not divisible by 0.5? Why?
43. As NO ionizes to form NO^+ , does the nitrogen–oxygen bond become stronger or weaker?



44. Which of the homonuclear diatomic molecules of the second row of the periodic table (Li_2 to Ne_2) are predicted by MO theory to be paramagnetic? Which ones are predicted to have a bond order of one? Which ones are predicted to have a bond order of two? Which one is predicted to have the highest bond order?

BUILDING YOUR KNOWLEDGE

45. When carbon vaporizes at extremely high temperatures, among the species present in the vapor is the diatomic molecule C_2 . Write a Lewis formula for C_2 . Does your Lewis formula of C_2 obey the octet rule? (C_2 does not contain a quadruple bond.) Does C_2 contain a single, a double, or a triple bond? Is it paramagnetic or diamagnetic? Show how molecular orbital theory can be used to predict the answers to questions left unanswered by valence bond theory.
46. Rationalize the following observations in terms of the stabilities of σ and π bonds: (a) The most common form of nitrogen is N_2 , whereas the most common form of phosphorus is P_4 (see the structure in Figure 2-3); (b) The most common forms of oxygen are O_2 and (less common) O_3 , whereas the most common form of sulfur is S_8 .