6.4: Molecular Orbital Theory: Electron Delocalization

Valence bond theory can account for much of what we observe in chemical bonding—such as the rigidity of a double bond—but it also has limitations. In valence bond theory, we treat electrons as if they reside in the quantum-mechanical orbitals that we calculated *for atoms*. This is a significant oversimplification that we partially compensate for by hybridization. Nevertheless, we can do better.

In Chapter 2, we learned that the mathematical derivation of energies and orbitals for electrons *in atoms* comes from solving the Schrödinger equation for the atom of interest. For a molecule, we can theoretically do the same thing. The resulting orbitals would be the actual **molecular orbitals (MOs)** of the molecule as a whole. This is in contrast to valence bond theory, in which the orbitals are the atomic orbitals (AOs) of individual atoms. As it turns out, however, solving the Schrödinger equation exactly for even the simplest molecules is impossible without making some approximations.

In **molecular orbital (MO) theory**, we do not actually solve the Schrödinger equation for a molecule directly. Instead, we use a trial function, an "educated guess" as to what the solution might be. In other words, rather than mathematically solving the Schrödinger equation, which would give us a mathematical function describing an orbital, we start with a trial mathematical function for the orbital. We then test the trial function to see how well it "works."

> Molecular orbital theory is a specific application of a more general quantum-mechanical approximation technique called the variational principle. In this technique, the energy of a trial function within the Schrödinger equation is minimized.

We can understand this process by analogy to solving an algebraic equation. Suppose we want to know what x is in the equation $4x + 5 = 70$ without actually solving the equation. For an easy equation like this one, we might first estimate that $x = 16$. We can then determine how well our estimate works by substituting $x = 16$ into the equation. If the estimate does not work, we can try again until we find the right value of x. (In this case, we can quickly see that x must be a little more than 16.)

In molecular orbital theory, the estimating procedure is analogous. However, we need one more concept to get at the heart of molecular orbital theory. In order to determine how well a trial function for an orbital "works" in molecular orbital theory, we calculate its energy. No matter how good our trial function, *we can never do better than nature at minimizing the energy of the orbital*. The best possible orbital is the one with the minimum energy.

> We calculate the energy of an estimated orbital by substituting it into the Schrödinger equation and solving for the energy.

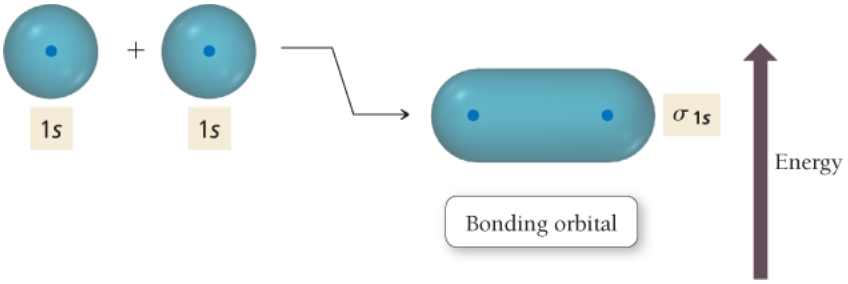
In other words, to find the orbital that "works," we must find the orbital with the lowest energy. To do this, we can devise any trial function for an orbital in a molecule and calculate its energy. The energy we calculate for the devised orbital then must always be greater than or (at best) equal to the energy of the actual orbital. In modern molecular orbital theory, computer programs are designed to try many different variations of a guessed orbital and compare the energies of each one. The variation with the lowest energy is the best approximation for the actual molecular orbital.

Linear Combination of Atomic Orbitals (LCAO)

The simplest trial functions that work reasonably well in molecular orbital theory turn out to be linear combinations of atomic orbitals, or LCAOs. An LCAO molecular orbital is a *weighted linear sum—analogous to a* *weighted average—of the valence atomic orbitals* of the atoms in the molecule. At first glance, this concept might seem similar to that of hybridization in valence bond theory. However, in valence bond theory, hybrid orbitals are weighted linear sums of the valence atomic orbitals of a *particular atom*, and the hybrid orbitals remain *localized* on that atom. In molecular orbital theory, the molecular orbitals are weighted linear sums of the valence atomic orbitals of *all the atoms* in a molecule, and many of the molecular orbitals are *delocalized* over the entire molecule.

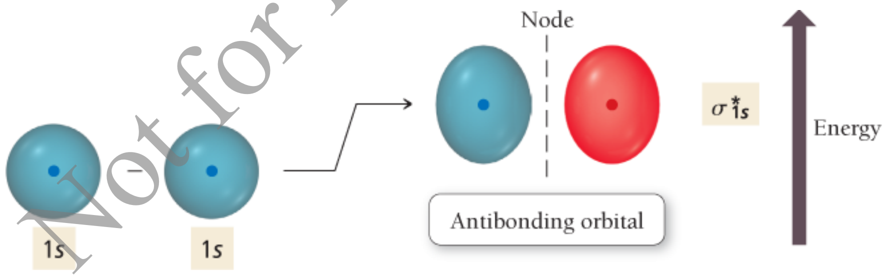
> When molecular orbitals are calculated mathematically, it is actually the *wave functions* corresponding to the orbitals that are combined.

Consider the H_2 molecule. One of the molecular orbitals for H_2 is an equally weighted sum of the 1*s* orbital from one atom and the 1*s* orbital from the other. We can represent this pictorially and energetically as follows:



The name of this molecular orbital is σ_{1s}. The σ comes from the shape of the orbital, which looks like a σ bond in valence bond theory, and the 1*s* comes from its formation by a linear sum of 1*s* orbitals. The σ_{1s} orbital is lower in energy than either of the two 1*s* atomic orbitals from which it was formed. For this reason, we call this orbital a **bonding orbital**. When electrons occupy bonding molecular orbitals, the energy of the electrons is lower than it would be if they were occupying atomic orbitals.

We can think of a molecular orbital in a molecule in much the same way that we think about an atomic orbital in an atom. Electrons seek the lowest energy molecular orbital available, but just as an atom has more than one atomic orbital (and some may be empty), a molecule has more than one molecular orbital (and some may be empty). The next molecular orbital of H_2 is approximated by summing the 1*s* orbital on one hydrogen atom with the *negative* (opposite phase) of the 1*s* orbital on the other hydrogen atom:

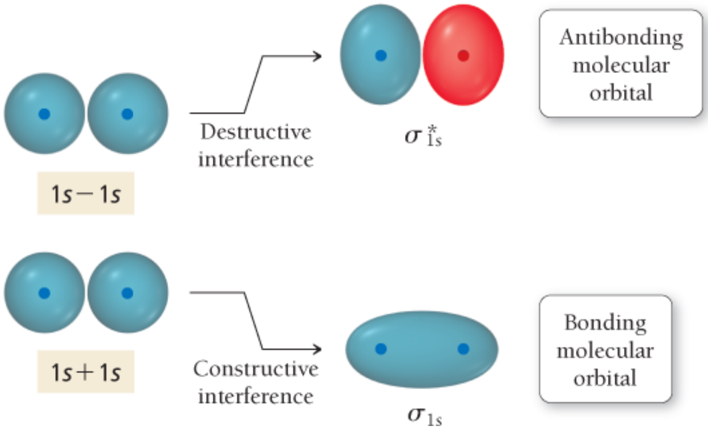


The different phases of the orbitals result in *destructive* interference between them. The resulting molecular orbital therefore has a node between the two atoms. The different colors (red and blue) on either side of the node represent the different phases of the orbital (see Section 2.6). The name of this molecular orbital is σ^*_{1s}. The star indicates that this orbital is an **antibonding orbital**. Electrons in antibonding orbitals have higher energies than they had in their respective atomic orbitals and therefore tend to raise the energy of the system (relative to the unbonded atoms).

In general, when two atomic orbitals are added together to form molecular orbitals, one of the resultant molecular orbitals will be lower in energy (the bonding orbital) than the atomic orbitals and the other will be higher in energy (the antibonding orbital). Remember that electrons in orbitals behave like waves. The bonding molecular orbital arises out of constructive interference between the atomic orbitals because both orbitals have the same phase. The antibonding orbital arises out of destructive interference between the atomic orbitals because *subtracting* one from the other means the two interacting orbitals have opposite phases (Figure 6.9).

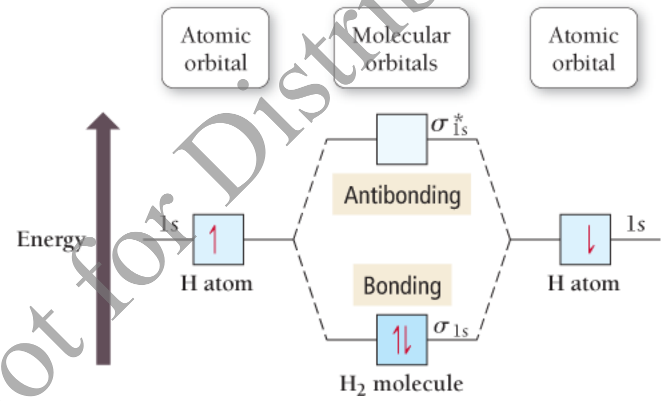
Figure 6.9 Formation of Bonding and Antibonding Orbitals

Constructive interference between two atomic orbitals gives rise to a molecular orbital that is lower in energy than the atomic orbitals. This is the bonding orbital. Destructive interference between two atomic orbitals gives rise to a molecular orbital that is higher in energy than the atomic orbitals. This is the antibonding orbital.


Antibonding molecular orbital
Destructive interference
σ^*_{1s}
1s − 1s
Bonding molecular orbital
1s + 1s
Constructive interference
σ_{1s}

For this reason, the bonding orbital has an *increased* electron density in the internuclear region, while the antibonding orbital has a *node* in the internuclear region. The greater electron density in the internuclear region for a bonding orbital *lowers its energy* compared to the orbitals in nonbonded atoms. The diminished electron density in the internuclear region for an antibonding orbital (due to the node) *increases its energy* compared to the orbitals of nonbonded atoms.

We put all of this together in the molecular orbital (MO) diagram for H_2:


Atomic orbital
Molecular orbitals
Atomic orbital
σ^*_{1s}
Antibonding
Energy
1s
H atom
Bonding
σ_{1s}
1s
H atom
H_2 molecule

The **molecular orbital (MO) diagram** shows the atomic orbitals of the atoms, the molecular orbitals of the molecule, and their relative energies (higher on the diagram corresponds to higher energy). Notice that two hydrogen atoms can lower their overall energy by forming H_2 because the electrons can move from higher-energy atomic orbitals into the lower-energy σ_{1s} bonding molecular orbital.

In molecular orbital theory, we define the **bond order** of a diatomic molecule such as H_2 as follows:

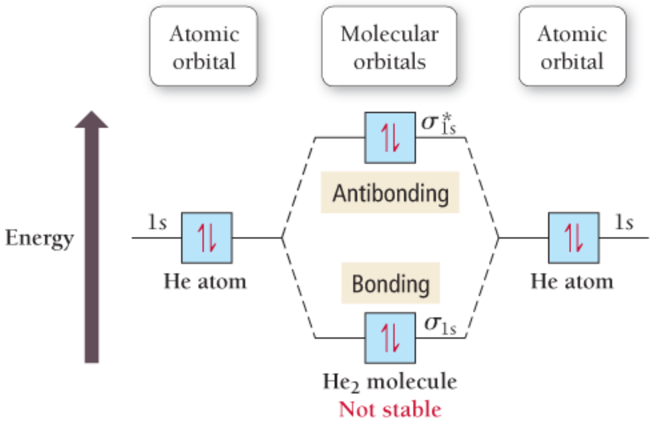
$$\text{bond order} = \frac{(\text{number of electrons in bonding MOs}) - (\text{number of electrons in antibonding MOs})}{2}$$

For H_2, the bond order is 1.

$$H_2 \text{ bond order} = \frac{2-0}{2} = 1$$

A positive bond order means that there are more electrons in bonding molecular orbitals than in antibonding molecular orbitals. The electrons therefore have lower energy than they had in the orbitals of the isolated atoms, and a chemical bond forms. In general, the higher the bond order, the stronger the bond. A negative or zero bond order indicates that a bond will *not* form between the atoms.

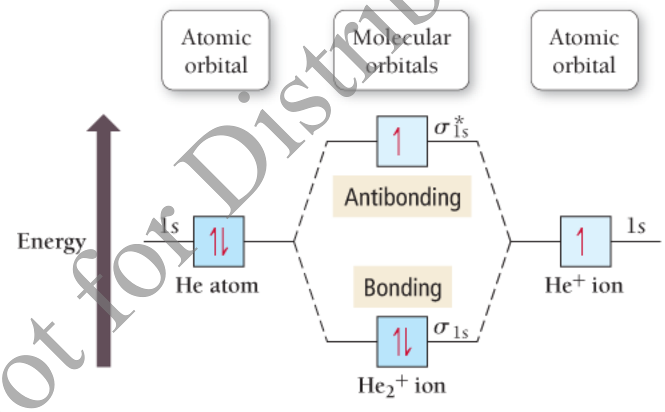
For example, consider the MO diagram for He_2:


Atomic orbital
Molecular orbitals
Atomic orbital
Energy
σ^*_{1s}
Antibonding
1s
He atom
1s
He atom
Bonding
σ_{1s}
He_2 molecule
Not stable

Notice that the two additional electrons must go into the higher-energy antibonding orbital. There is no net stabilization by joining two helium atoms to form a helium molecule, as indicated by the bond order:

$$He_2 \text{ bond order} = \frac{2-2}{2} = 0$$

So according to MO theory, He_2 should not exist as a stable molecule, and indeed it does not. Another interesting case is the helium–helium ion, $He_2{}^+$, which we can represent with the following MO diagram:


Atomic orbital
Molecular orbitals
Atomic orbital
Energy
σ^*_{1s}
Antibonding
1s
He atom
1s
He^+ ion
Bonding
σ_{1s}
$He_2{}^+$ ion

The bond order is $\frac{1}{2}$, indicating that $He_2{}^+$ should exist, and indeed it does.

Summarizing LCAO–MO Theory:

- We can approximate molecular orbitals (MOs) as a linear combination of atomic orbitals (AOs). The total number of MOs formed from a particular set of AOs always equals the number of AOs in the set.
- When two AOs combine to form two MOs, one MO is lower in energy (the bonding MO) and the other is higher in energy (the antibonding MO).
- When assigning the electrons of a molecule to MOs, we fill the lowest energy MOs first with a maximum of two spin-paired electrons per orbital.
- When assigning electrons to two MOs of the same energy, we follow Hund's rule—fill the orbitals singly first, with parallel spins, before pairing.
- The bond order in a diatomic molecule is the number of electrons in bonding MOs minus the number in antibonding MOs divided by two. Stable bonds require a positive bond order (more electrons in bonding MOs than in antibonding MOs).

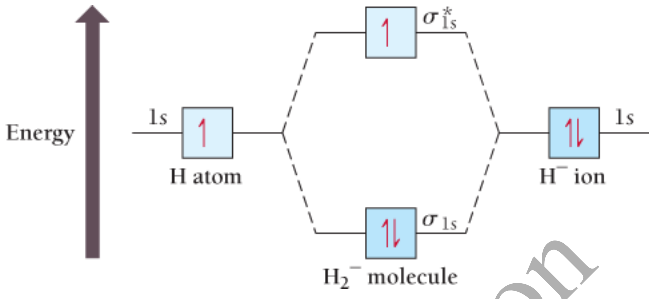
Notice the power of the molecular orbital approach. Every electron that enters a bonding molecular orbital stabilizes the molecule or polyatomic ion, and every electron that enters an antibonding molecular orbital destabilizes it. The emphasis on electron pairs has been removed. One electron in a bonding molecular orbital stabilizes half as much as two, so a bond order of one-half is not at all mysterious.

Example 6.4 Bond Order

Apply molecular orbital theory to predict the bond order in H_2^-. Is the H_2^- bond a stronger or weaker bond than the H_2 bond?

SOLUTION

The H_2^- ion has three electrons. Assign the three electrons to the molecular orbitals, filling lower-energy orbitals first and proceeding to higher-energy orbitals.



Calculate the bond order by subtracting the number of electrons in antibonding orbitals from the number in bonding orbitals and dividing the result by two.

$$H_2^- \text{ bond order} = \frac{2-1}{2} = +\frac{1}{2}$$

Since the bond order is positive, H_2^- should be stable. However, the bond order of H_2^- is lower than the bond order of H_2 (which is 1); therefore, the bond in H_2^- is weaker than in H_2.

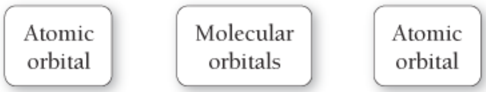
FOR PRACTICE 6.4 Apply molecular orbital theory to predict the bond order in H_2^+. Is the H_2^+ bond a stronger or weaker bond than the H_2 bond?

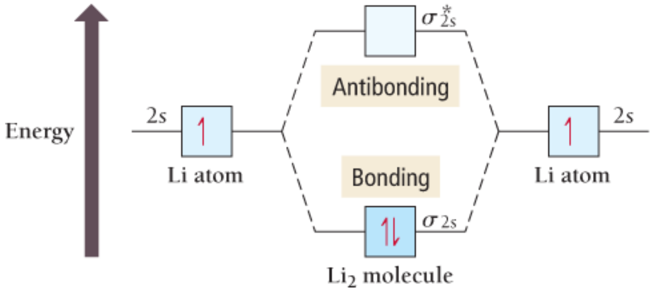
Second-Period Homonuclear Diatomic Molecules

Homonuclear diatomic molecules (molecules made up of two atoms of the same kind) formed from second-period elements that have between 2 and 16 valence electrons. To explain bonding in these molecules, we must consider the next set of higher-energy molecular orbitals, which we can approximate by linear combinations of the valence atomic orbitals of the period 2 elements.

> The core electrons can be ignored (as they are in other models for bonding) because these electrons do not contribute significantly to chemical bonding.

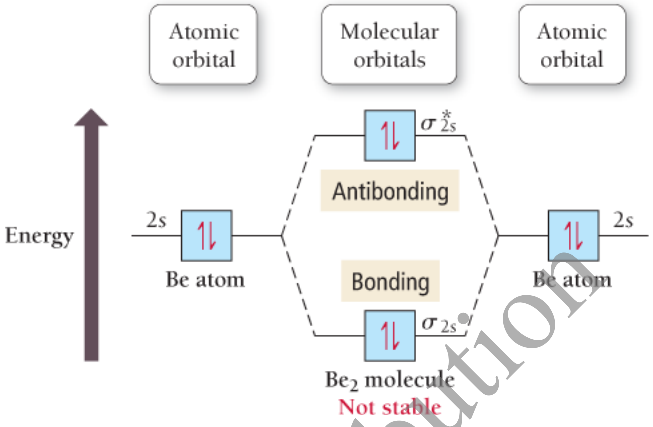
We begin with Li_2. Even though lithium is normally a metal, we can use MO theory to predict whether or not the Li_2 molecule should exist in the gas phase. We approximate the molecular orbitals in Li_2 as linear combinations of the 2*s* atomic orbitals. The resulting molecular orbitals look much like those of the H_2 molecule. The MO diagram for Li_2 therefore looks a lot like the MO diagram for H_2:




Energy
σ*2s
Antibonding
2s
Li atom
Bonding
σ2s
2s
Li atom
Li₂ molecule

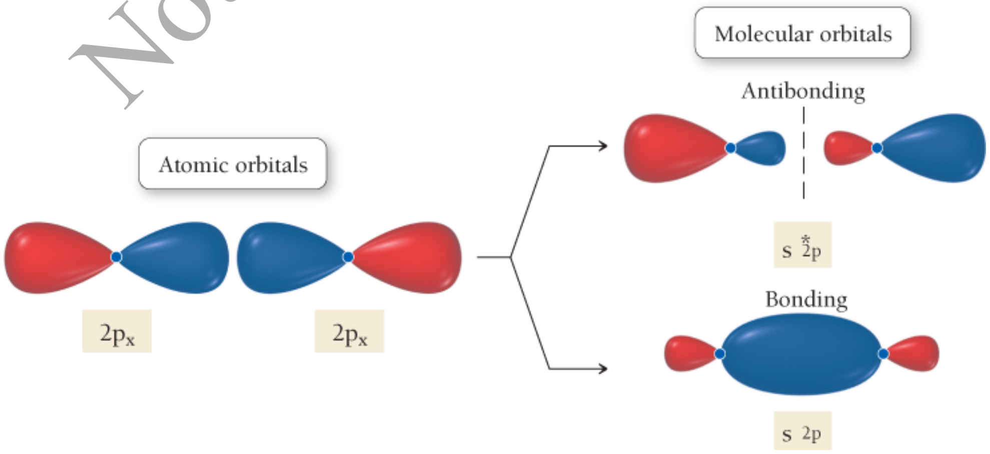
The two valence electrons of Li_2 occupy a bonding molecular orbital. We would predict that the Li_2 molecule is stable with a bond order of 1. Experiments confirm this prediction.

In contrast, consider the MO diagram for Be_2:


Atomic orbital
Molecular orbitals
Atomic orbital
Energy
σ*2s
Antibonding
2s
Be atom
Bonding
σ2s
2s
Be atom
Be₂ molecule
Not stable

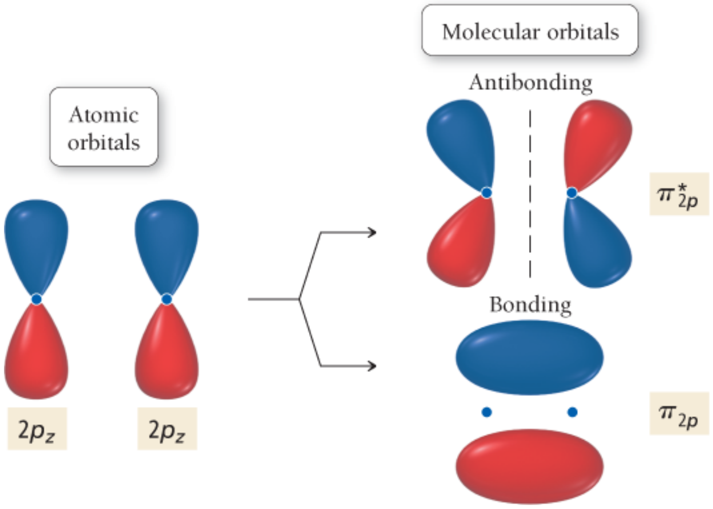
The four valence electrons of Be_2 occupy one bonding MO and one antibonding MO. The bond order is 0, and we predict that Be_2 should not be stable. This is again consistent with experimental findings.

The next homonuclear molecule composed of second-row elements is B_2, which has six total valence electrons to accommodate. We can approximate the next higher-energy molecular orbitals for B_2 and the rest of the period 2 diatomic molecules as linear combinations of the 2*p* orbitals taken in pairs. Because the three 2*p* orbitals orient along three orthogonal axes, we must assign similar axes to the molecule. In this book, we assign the internuclear axis to be the *x* direction. The LCAO–MOs that result from combining the $2p_x$ orbitals—the orbitals that lie along the internuclear axis—from each atom are represented pictorially as follows:


Molecular orbitals
Antibonding
Atomic orbitals
2px
2px
s*2p
Bonding
s 2p

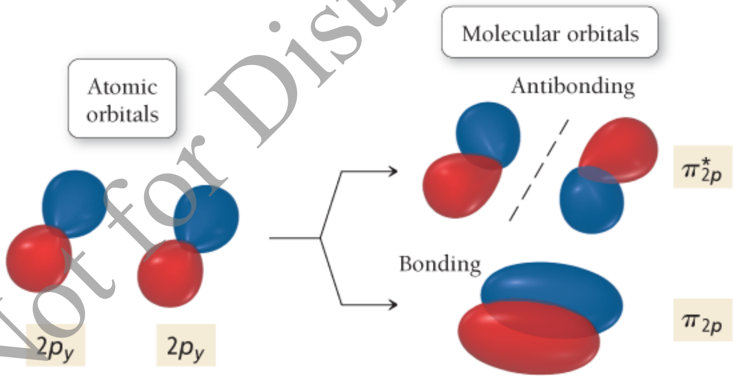
The bonding MO in this pair looks something like candy in a wrapper, with increased electron density in the internuclear region due to constructive interference between the two 2*p* atomic orbitals. It has the characteristic σ shape (it is cylindrically symmetrical about the bond axis) and is therefore called the σ_{2p} bonding orbital. The antibonding orbital, called σ^*_{2p}, has a node between the two nuclei (due to destructive interference between the two $2p$ orbitals) and is higher in energy than either of the $2p_x$ orbitals.

We represent the LCAO–MOs that result from combining the $2p_z$ orbitals from each atom as follows:



Notice that in this case the p orbitals are added together in a side-by-side orientation (in contrast to the $2p_x$ orbitals which are oriented end to end). The resultant molecular orbitals consequently have a different shape. The electron density in the bonding molecular orbital is above and below the internuclear axis with a nodal plane that includes the internuclear axis. This orbital resembles the electron density distribution of a π bond in valence bond theory. We call this orbital the π_{2p} orbital. The corresponding antibonding orbital has an additional node *between* the nuclei (perpendicular to the internuclear axis) and is called the π^*_{2p} orbital.

We represent the LCAO–MOs that result from combining the $2p_y$ orbitals from each atom as follows:

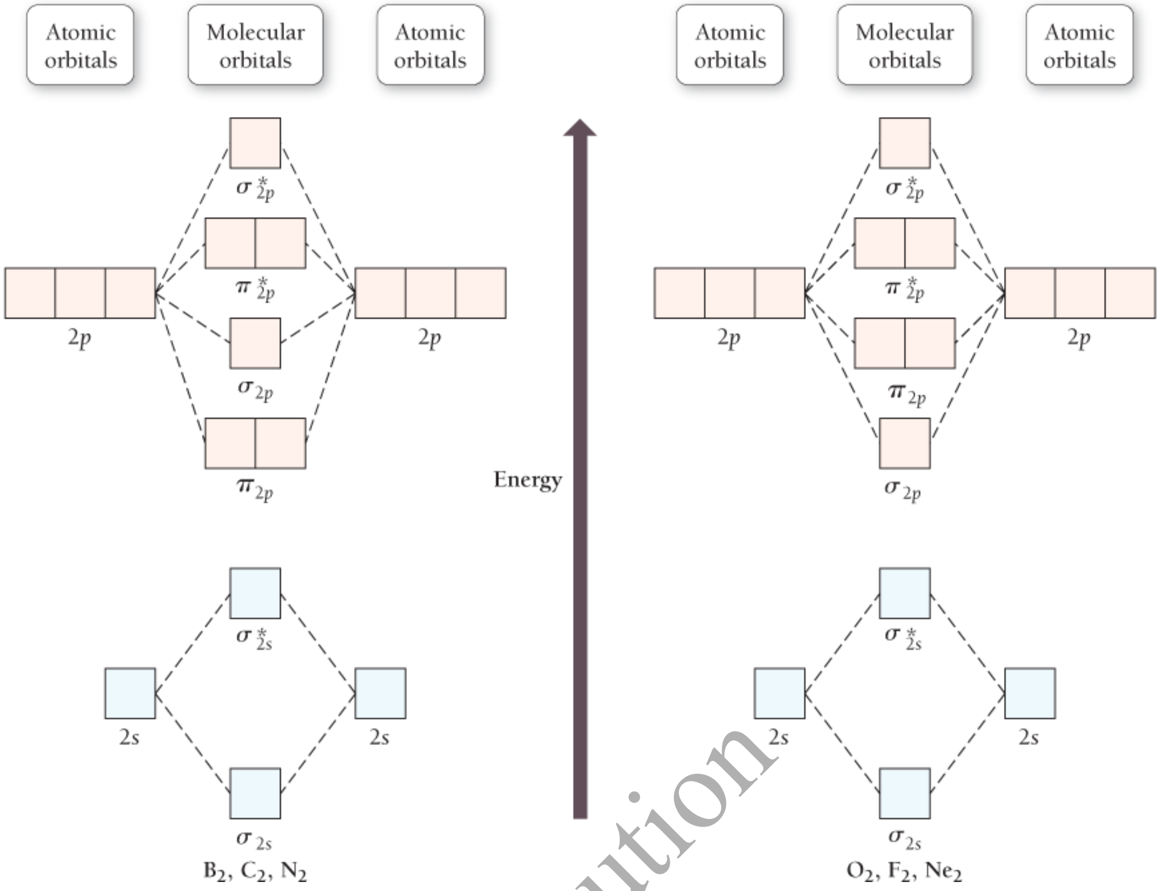


The only difference between the $2p_y$ and the $2p_z$ atomic orbitals is a 90° rotation about the internuclear axis. Consequently, the only difference between the resulting MOs is a 90° rotation about the internuclear axis. The energies and the names of the bonding and antibonding MOs obtained from the combination of the $2p_y$ AOs are identical to those obtained from the combination of the $2p_z$ AOs.

Before we can draw MO diagrams for B_2 and the other second-period diatomic molecules, we must determine the relative energy ordering of the MOs obtained from the $2p$ AO combinations. This is not a simple task. The relative ordering of MOs obtained from LCAO–MO theory is usually determined computationally. There is no single order that works for all molecules. For second-period diatomic molecules, computations reveal that the energy ordering for B_2, C_2, and N_2 is slightly different from that for O_2, F_2, and Ne_2 as shown in Figure 6.10.

Figure 6.10 Molecular Orbital Energy Ordering

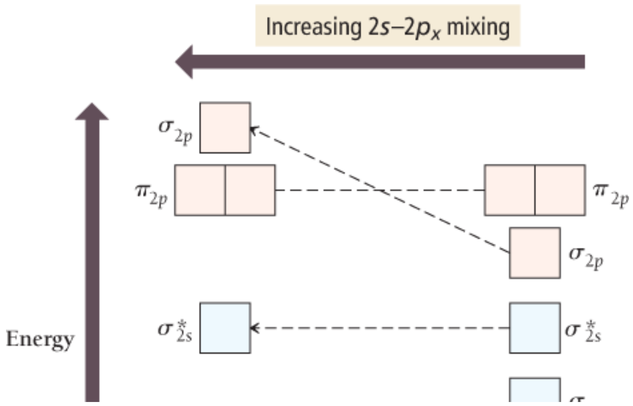
Molecular orbital energy diagrams for second-period diatomic molecules show that the energy ordering of the π_{2p} and σ_{2p} molecular orbitals can vary.

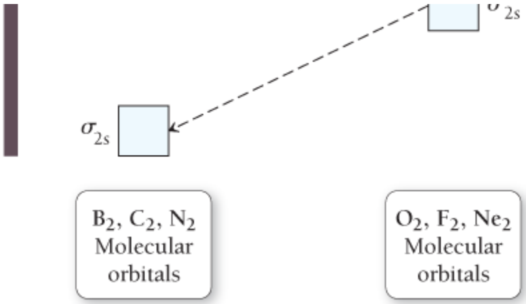

Atomic orbitals
Molecular orbitals
Atomic orbitals
σ^*_{2p}
π^*_{2p}
2p
2p
σ_{2p}
π_{2p}
σ^*_{2s}
2s
2s
σ_{2s}
B_2, C_2, N_2
Energy
Atomic orbitals
Molecular orbitals
Atomic orbitals
σ^*_{2p}
π^*_{2p}
2p
2p
π_{2p}
σ_{2p}
σ^*_{2s}
2s
2s
σ_{2s}
O_2, F_2, Ne_2

The difference in energy ordering can only be explained by going back to our LCAO–MO model. In our simplified treatment, we assumed that the MOs that result from the second-period AOs could be calculated pairwise. In other words, we took the linear combination of a 2*s* from one atom with the 2*s* from another, a $2p_x$ from one atom with a $2p_x$ from the other, and so on. In a more comprehensive treatment, the MOs are formed from linear combinations that include all of the AOs that are relatively close to each other in energy and of the correct symmetry. Specifically, in a more detailed treatment, the two 2*s* orbitals and the two $2p_x$ orbitals should all be combined to form a total of four molecular orbitals. The extent to which this type of mixing is included affects the energy levels of the corresponding MOs, as shown in Figure 6.11. The bottom line is that *s*–*p* mixing is significant in B_2, C_2, and N_2 but not in O_2, F_2, and Ne_2. The result is a different energy ordering, depending on the specific molecule.

Figure 6.11 **The Effects of 2*s*–2*p* Mixing**

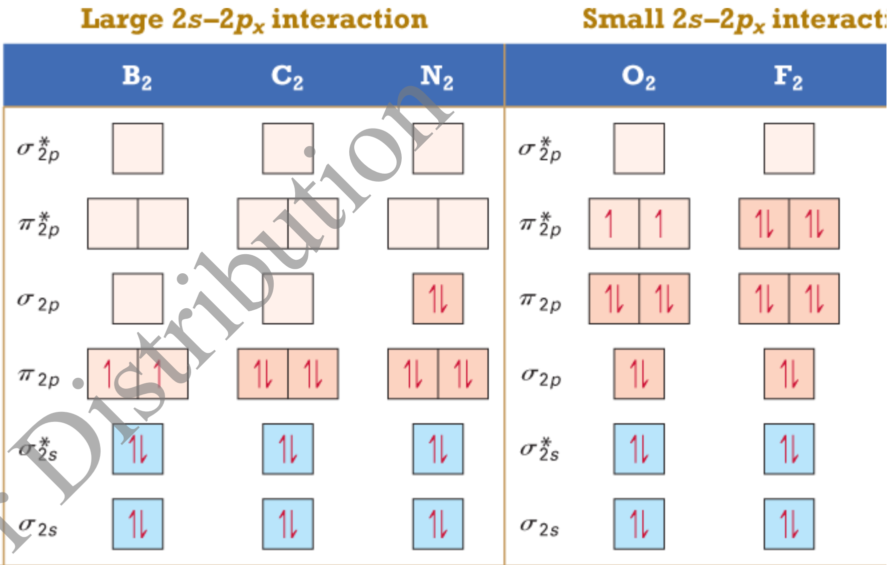
The degree of mixing between two orbitals decreases as the energy difference between them increases. The energy levels of the atomic orbitals are more closely spaced in B, C, and N than in O, F, and Ne. Therefore, mixing of the 2*s* and $2p_x$ orbitals is greater in B_2, C_2, and N_2 than in O_2, F_2, and Ne_2. This mixing produces a difference in energy ordering for the π_{2p} and σ_{2p} molecular orbitals.


Increasing $2s$–$2p_x$ mixing
σ_{2p}
π_{2p}
π_{2p}
σ_{2p}
Energy
σ^*_{2s}
σ^*_{2s}


σ_{2s}
σ_{2s}
B_2, C_2, N_2 Molecular orbitals
O_2, F_2, Ne_2 Molecular orbitals

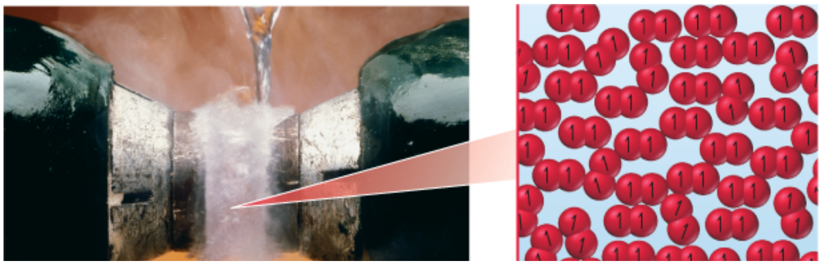
The MO energy diagrams for the rest of the second-period homonuclear diatomic molecules, as well as their bond orders, bond energies, and bond lengths, are shown in Figure 6.12. Notice that as bond order increases, the bond gets stronger (greater bond energy) and shorter (smaller bond length). For B_2, with six electrons, the bond order is 1. For C_2, the bond order is 2, and for N_2, the bond order reaches a maximum with a value of 3. Recall that the Lewis structure for N_2 has a triple bond, so both the Lewis model and molecular orbital theory predict a strong bond for N_2, which is experimentally observed.

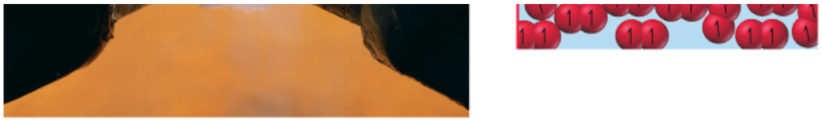
Figure 6.12 **Molecular Orbital Energy Diagrams for Second-Period *p*-Block Homonuclear Diatomic Molecules**


Large $2s$–$2p_x$ interaction
Small $2s$–$2p_x$ interact
B_2
C_2
N_2
O_2
F_2
σ^*_{2p}
π^*_{2p}
σ_{2p}
π_{2p}
σ^*_{2s}
σ_{2s}
σ^*_{2p}
π^*_{2p}
π_{2p}
σ_{2p}
σ^*_{2s}
σ_{2s}

	B_2	C_2	N_2	O_2	F_2
Bond order	1	2	3	2	1
Bond energy (kJ/mol)	290	620	946	498	159
Bond length (pm)	159	131	110	121	143

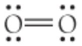
In O_2, the two additional electrons occupy antibonding orbitals and the bond order is 2. These two electrons are unpaired—they occupy the π^*_{2p} orbitals *singly with parallel spins*, as indicated by Hund's rule. The presence of unpaired electrons in the molecular orbital diagram of oxygen explains why oxygen is *paramagnetic* (see Section 6.1)—it is attracted to a magnetic field. The paramagnetism of oxygen can be demonstrated by suspending liquid oxygen between the poles of a magnet. This magnetic property is the direct result of *unpaired electrons*, whose spin and movement around the nucleus (more accurately known as orbital angular momentum) generate tiny magnetic fields.

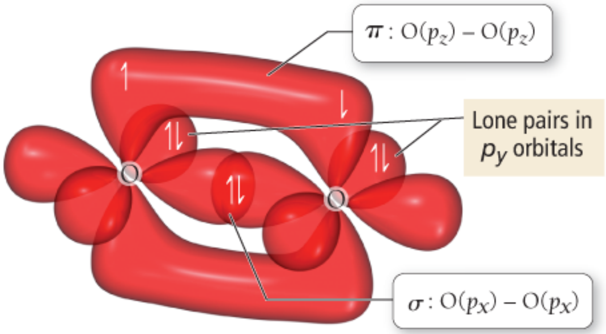




Liquid oxygen can be suspended between the poles of a magnet because it is paramagnetic. It contains unpaired electrons (depicted here in the inset) that generate tiny magnetic fields, which align with and interact with the external field.

In the Lewis structure of O_2, as well as in the valence bond model of O_2, all of the electrons seem to paired:





> The 2*s* orbital on each O atom contains two electrons, but for clarity neither the *s* orbitals nor the electrons that occupy them are shown.

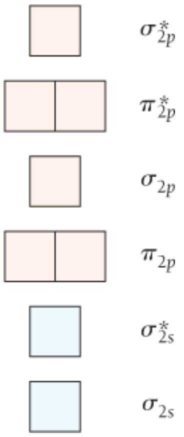
In the MO diagram for O_2, in contrast, we can account for the unpaired electrons. Molecular orbital theory is the more powerful theory in that it can account for the paramagnetism of O_2—it gives us a picture of bonding that more closely corresponds to what we see in experiments. Continuing along the second-period homonuclear diatomic molecules, we see that F_2 has a bond order of 1 and Ne_2 has a bond order of 0, again consistent with experiment since F_2 exists and Ne_2 does not.

Example 6.5 Molecular Orbital Theory

Draw an MO energy diagram and determine the bond order for the N_2^- ion. Do you expect the bond in the N_2^- ion to be stronger or weaker than the bond in the N_2 molecule? Is N_2^- diamagnetic or paramagnetic?

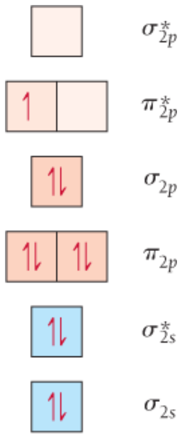
SOLUTION

Write an energy-level diagram for the molecular orbitals in N_2^-. Use the energy ordering for N_2.



The N_2^- ion has 11 valence electrons (five for each nitrogen atom plus one for the negative charge). Assign the electrons to the molecular orbitals beginning with the lowest energy orbitals and following

Hund's rule.



Calculate the bond order by subtracting the number of electrons in antibonding orbitals from the number in bonding orbitals and dividing the result by two.

$$N_2^- \text{ bond order} = \frac{8-3}{2} = +2.5$$

The bond order is 2.5, which is a lower bond order than in the N_2 molecule (bond order = 3); therefore, the N_2^- bond is weaker. The MO diagram shows that the N_2^- ion has one unpaired electron and is therefore paramagnetic.

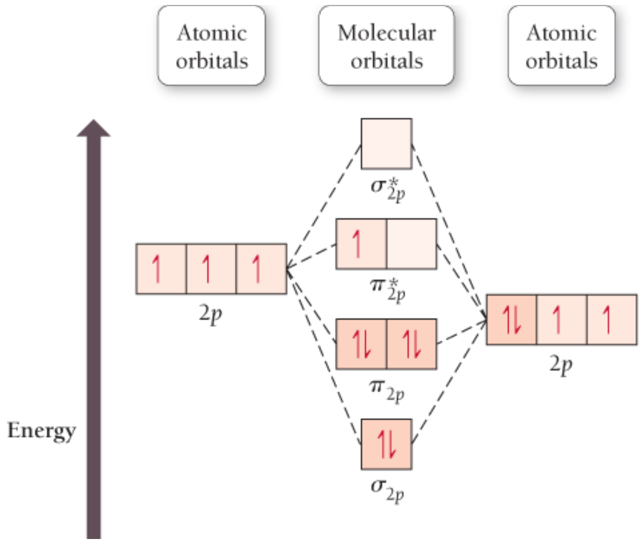
FOR PRACTICE 6.5 Draw an MO energy diagram and determine the bond order for the N_2^+ ion. Do you expect the bond in the N_2^+ ion to be stronger or weaker than the bond in the N_2 molecule? Is N_2^+ diamagnetic or paramagnetic?

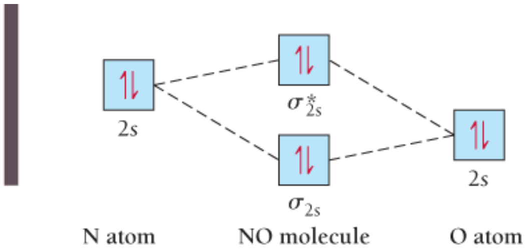
FOR MORE PRACTICE 6.5 Apply molecular orbital theory to determine the bond order of Ne_2.

Interactive Worked Example 6.5 Molecular Orbital Theory

Second-Period Heteronuclear Diatomic Molecules

We can also apply molecular orbital theory to heteronuclear diatomic molecules (molecules that include two different atoms). For example, we can draw an MO diagram for NO as follows:



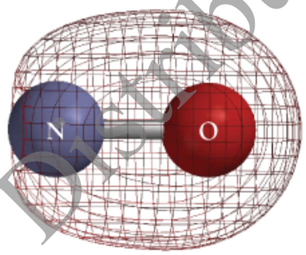


> A given orbital has lower energy in a more electronegative atom. For this reason, electronegative atoms have the ability to attract electrons to themselves.

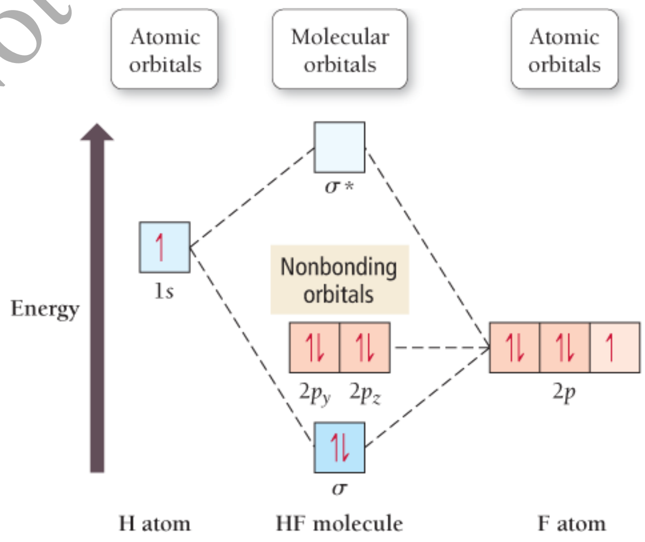
Oxygen is more electronegative than nitrogen, so its atomic orbitals are lower in energy than nitrogen's atomic orbitals. When two atomic orbitals are identical and of equal energy, the contribution of each orbital in forming a molecular orbital is identical. However, when two atomic orbitals are different, the contribution of each orbital in forming a molecular orbital may be different. More specifically, when we approximate a molecular orbital as a linear combination of atomic orbitals of different energies, the lower-energy atomic orbital makes a greater contribution to the bonding molecular orbital and the higher-energy atomic orbital makes a greater contribution to the antibonding molecular orbital. For example, notice that the σ_{2s} bonding orbital is closer in energy to the oxygen 2*s* orbital than to the nitrogen 2*s* orbital. We can also see this unequal weighting in the shape of the resultant molecular orbital, in which the electron density is concentrated on the oxygen atom, as shown in Figure 6.13.

Figure 6.13 Shape of σ_{2s} Bonding Orbital in NO

The molecular orbital shows greater electron density at the oxygen end of the molecule because the atomic orbitals of oxygen, the more electronegative element, are lower in energy than those of nitrogen. The atomic orbitals of oxygen therefore contribute more to the bonding molecular orbital than those of nitrogen.



As another example of a heteronuclear diatomic molecule, consider the MO diagram for HF:



Fluorine is so electronegative that all of its atomic orbitals are lower in energy than hydrogen's atomic orbitals.

In fact, fluorine's $2s$ orbital is so low in energy compared to hydrogen's $1s$ orbital that it does not contribute significantly to the molecular orbitals. The molecular orbitals in HF are approximated by the linear combination of the fluorine $2p_x$ orbital and the hydrogen $1s$ orbital. The other $2p$ orbitals remain localized on the fluorine and appear in the energy diagram as **nonbonding orbitals**. The electrons in these nonbonding orbitals remain localized on the fluorine atom.

Example 6.6 Molecular Orbital Theory for Heteronuclear Diatomic Molecules and Ions

Apply molecular orbital theory to determine the bond order of the CN^- ion. Is the ion paramagnetic or diamagnetic?

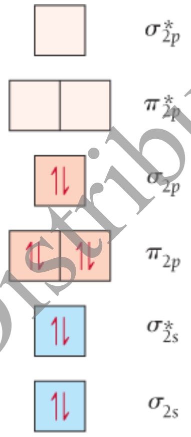
SOLUTION

Determine the number of valence electrons in the molecule or ion.

Number of valence electrons

$= 4(\text{from C}) + 5(\text{from N}) + 1(\text{from negative charge}) = 10$

Write an energy-level diagram using Figure 6.12 as a guide. Fill the orbitals beginning with the lowest energy orbital and progressing upward until you have assigned all electrons to an orbital. Remember to allow no more than two electrons (with paired spins) per orbital and to fill degenerate orbitals with single electrons (with parallel spins) before pairing.



Calculate the bond order using the formula:

$$\text{Bond order} = \frac{(\text{number of e}^- \text{ in bonding MOs}) - (\text{number of e}^- \text{ antibonding MOs})}{2}$$

$$CN^- \text{ bond order} = \frac{8-2}{2} = +3$$

If the MO energy diagram has unpaired electrons, the molecule or ion is paramagnetic. If the electrons are all paired, the molecule or ion is diamagnetic.

Since the MO diagram has no unpaired electrons, the ion is diamagnetic.

FOR PRACTICE 6.6 Apply molecular orbital theory to determine the bond order of NO. (Use the energy ordering of N_2.) Is the molecule paramagnetic or diamagnetic?