Learning Objectives

- To use molecular orbital theory to predict bond order
- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are not viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called orbitals, each with a particular orbital energy. Just as the positions and energies of electrons in atoms can be described in terms of atomic orbitals (AOs), the positions and energies of electrons in molecules can be described in terms of molecular orbitals (MOs) - a spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a delocalized approach to bonding.

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

### Molecular Orbitals Involving Only ns Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H$_2$, formed from two isolated hydrogen atoms, each with a 1s$^1$ electron configuration. As discussed previously, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called wave functions. The 1s atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the sum of the two H 1s wave functions, and the other produced by taking their difference:

\[
\begin{matrix}
\text{MO}(1) = & \text{AO}(\text{atom A}) & + & \text{AO}(\text{atom B}) \\
\text{MO}(1) = & \text{AO}(\text{atom A}) & - & \text{AO}(\text{atom B})
\end{matrix}
\]

The molecular orbitals created from Equation \ref{Eq1} are called linear combinations of atomic orbitals (LCAOs). Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.
Adding two atomic orbitals corresponds to constructive interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is increased. The molecular orbital corresponding to the sum of the two H 1s orbitals is called a $\sigma_{1s}$ combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure \(\PageIndex{1}\)). In a sigma (\(\sigma\)) orbital, a bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1s denotes the atomic orbitals from which the molecular orbital was derived: The \(\approx\) sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

\[ \sigma_{1s} \approx 1s(A) + 1s(B) \label{Eq2} \]

Conversely, subtracting one atomic orbital from another corresponds to destructive interference between two waves, which reduces their intensity and causes a decrease in the internuclear electron probability density (part (c) and part (d) in Figure \(\PageIndex{1}\)). The resulting pattern contains a node where the electron density is zero. The molecular orbital corresponding to the difference is called $\sigma_{1s}^*$ (“sigma one ess star”). In a sigma star (\(\sigma^*\)) orbital an antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

\[ \sigma_{1s}^* \approx 1s(A) - 1s(B) \label{Eq3} \]

A molecule must have as many molecular orbitals as there are atomic orbitals.

The electron density in the $\sigma_{1s}$ molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the $\sigma_{1s}$ orbital represents a
bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma_{1s}^\star$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma_{1s}^\star$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

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**Energy-Level Diagrams**

Because electrons in the $\sigma_{1s}$ orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the $\sigma_{1s}$ molecular orbital has a lower energy than either of the hydrogen 1s atomic orbitals. Conversely, electrons in the $\sigma_{1s}^\star$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1s atomic orbitals. Consequently, the $\sigma_{1s}^\star$ molecular orbital has a higher energy than either of the hydrogen 1s atomic orbitals. The $\sigma_{1s}$ (bonding) molecular orbital is stabilized relative to the 1s atomic orbitals, and the $\sigma_{1s}^\star$ (antibonding) molecular orbital is destabilized. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure \ref{PageIndex2}.

Figure \ref{PageIndex2}: Molecular Orbital Energy-Level Diagram for H$_2$. The two available electrons (one from each H atom) in this diagram fill the bonding $\sigma_{1s}$ molecular orbital. Because the energy of the $\sigma_{1s}$ molecular orbital is lower than that of the two H 1s atomic orbitals, the H$_2$ molecule is more stable (at a lower energy) than the two isolated H atoms.

A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).
To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H₂, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure \(\PageIndex{2}\)). We fill the orbitals according to the Pauli principle and Hund’s rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the \(\sigma_{1s}\) bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H₂ molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H₂ is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

**Bond Order in Molecular Orbital Theory**

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order \(\text{One-half the net number of bonding electrons in a molecule.}\) is defined as \(\text{one-half the net number of bonding electrons:}\)

\[\text{bond order}=\frac{\text{number of bonding electrons}-\text{number of antibonding electrons}}{2}\label{Eq4}\]

To calculate the bond order of H₂, we see from Figure \(\PageIndex{2}\) that the \(\sigma_{1s}\) (bonding) molecular orbital contains two electrons, while the \((\sigma_{1s})^\star\) (antibonding) molecular orbital is empty. The bond order of H₂ is therefore

\[\frac{2-0}{2}=1\label{Eq5}\]

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure \(\PageIndex{2}\) to describe the bonding in other pairs of atoms and ions where \(n=1\), such as the H₂⁺ ion, the He₂⁺ ion, and the He₂ molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund’s rule.

**Figure \(\PageIndex{3}\): Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals.**

(a) The H₂⁺ ion, (b) the He₂⁺ ion, and (c) the He₂ molecule are shown here.

Part (a) in Figure \(\PageIndex{3}\) shows the energy-level diagram for the H₂⁺ ion, which contains two protons and only one electron. The single electron occupies the \(\sigma_{1s}\) bonding molecular orbital, giving a \((\sigma_{1s})^1\) electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is \((1-0)/2=1/2\) Because the bond order is greater than zero, the H₂⁺ ion should be more stable than an isolated H atom and a proton. We can
therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H$_2^+$. With a bond order of only 1/2 the bond in H$_2^+$ should be weaker than in the H$_2$ molecule, and the H–H bond should be longer. As shown in Table \(\PageIndex{1}\), these predictions agree with the experimental data.

Part (b) in Figure \(\PageIndex{3}\) is the molecular orbital energy-level diagram for He$_2^+$. This ion has a total of three valence electrons. Because the first two electrons completely fill the $\sigma_{1s}$ molecular orbital, the Pauli principle states that the third electron must be in the $\sigma_{1s}$ antibonding orbital, giving a $\left(\sigma_{1s}\right)^2\left(\sigma_{1s}^*\right)^1$ electron configuration. This electron configuration gives a bond order of $(2-1)/2=1/2$.

As with H$_2^+$, the He$_2^+$ ion should be stable, but the He–He bond should be weaker and longer than in H$_2$. In fact, the He$_2^+$ ion can be prepared, and its properties are consistent with our predictions (Table \(\PageIndex{1}\)).

Table \(\PageIndex{1}\): Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

<table>
<thead>
<tr>
<th>Molecule or Ion</th>
<th>Electron Configuration</th>
<th>Bond Order</th>
<th>Bond Length (pm)</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2^+$</td>
<td>$\left(\sigma_{1s}\right)^1$</td>
<td>1/2</td>
<td>106</td>
<td>269</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$\left(\sigma_{1s}\right)^2$</td>
<td>1</td>
<td>74</td>
<td>436</td>
</tr>
<tr>
<td>He$_2^+$</td>
<td>$\left(\sigma_{1s}\right)^2\left(\sigma_{1s}^*\right)^1$</td>
<td>1/2</td>
<td>108</td>
<td>251</td>
</tr>
<tr>
<td>He$_2$</td>
<td>$\left(\sigma_{1s}\right)^2\left(\sigma_{1s}^*\right)^1$</td>
<td>0</td>
<td>not observed</td>
<td>not observed</td>
</tr>
</tbody>
</table>

Finally, we examine the He$_2$ molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure \(\PageIndex{3}\) is the molecular orbital energy-level diagram for He$_2$. With a total of four valence electrons, both the $\sigma_{1s}$ bonding and $\left(\sigma_{1s}\right)^2\left(\sigma_{1s}^*\right)^1$ antibonding orbitals must contain two electrons. This gives a $\left(\sigma_{1s}\right)^2\left(\sigma_{1s}^*\right)^1$ electron configuration, with a predicted bond order of $(2-2) + 2 = 0$, which indicates that the He$_2$ molecule has no net bond and is not a stable species. Experiments show that the He$_2$ molecule is actually less stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H$_2^+$ ion.

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example \(\PageIndex{1}\)
Use a molecular orbital energy-level diagram, such as those in Figure \(\PageIndex{3}\), to predict the bond order in the \(\text{He}_2^{2+}\) ion. Is this a stable species?

**Given:** chemical species

**Asked for:** molecular orbital energy-level diagram, bond order, and stability

**Strategy:**

A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.

B. Determine the total number of valence electrons in the \(\text{He}_2^{2+}\) ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund’s rule while doing so.

C. Calculate the bond order and predict whether the species is stable.

**Solution:**

A. Two He \(1s\) atomic orbitals combine to give two molecular orbitals: a \(\sigma_{1s}\) bonding orbital at lower energy than the atomic orbitals and a \(\sigma_{1s}^\star\) antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:

![Molecular Orbital Diagram](image)

B. The \(\text{He}_2^{2+}\) ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view \(\text{He}_2^{2+}\) as being formed from two \(\text{He}^+\) ions, each of which has a single valence electron in the \(1s\) atomic orbital. We can now fill the molecular orbital diagram:

![Molecular Orbital Diagram](image)

The two electrons occupy the lowest-energy molecular orbital, which is the bonding \((\sigma_{1s})\) orbital, giving a \((\sigma_{1s})^2\) electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. C. So the bond order is

\[
\text{bond order} = \frac{2-0}{2} = 1
\]

\(\text{He}_2^{2+}\) is therefore predicted to contain a single He–He bond. Thus it should be a stable species.
Exercise \(\PageIndex{1}\)

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the \(\text{H}_2^{2-}\) ion. Is this a stable species?

**Answer**

\(\text{H}_2^{2-}\) has a valence electron configuration of \(\left(\sigma_{1s}\right)^2\left(\sigma_{1s}^*\right)^2\) with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (\(\text{Li}_2\) and \(\text{Cs}_2\), for example) is shown in part (a) in Figure \(\PageIndex{4}\), where \(\text{M}\) represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a \(\sigma_{ns}\) bonding molecular orbital and a \(\sigma_{ns}^*\) antibonding molecular orbital. Because each alkali metal (\(\text{M}\)) has an \(ns^1\) valence electron configuration, the \(\text{M}_2\) molecule has two valence electrons that fill the \(\sigma_{ns}\) bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (\(\text{Li}_2\), \(\text{Na}_2\), \(\text{K}_2\), \(\text{Rb}_2\), and \(\text{Cs}_2\)). The general features of these \(\text{M}_2\) diagrams are identical to the diagram for the \(\text{H}_2\) molecule in Figure \(\PageIndex{2}\).

Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as \(\text{Be}_2\)), in which each metal atom has an \(ns^2\) valence electron configuration, resemble the diagram for the \(\text{He}_2\) molecule in part (c) in Figure \(\PageIndex{3}\). As shown in part (b) in Figure \(\PageIndex{4}\), this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the \(\sigma_{ns}\) bonding orbital and the \(\sigma_{ns}^*\) antibonding orbital and give a bond order of 0. Thus \(\text{Be}_2\), \(\text{Mg}_2\), \(\text{Ca}_2\), \(\text{Sr}_2\), and \(\text{Ba}_2\) are all expected to be unstable, in agreement with experimental data. In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, \((\text{Be}_2\)) is stable.
Example (PageIndex{2})

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na\(^{2−}\) ion.

**Given:** chemical species

**Asked for:** molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

**Strategy:**

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

B. Determine the total number of valence electrons in the Na\(^{2−}\) ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund’s rule while doing so.

C. Calculate the bond order and predict whether the species is stable.

**Solution:**

A Because sodium has a [Ne]3\(^s\)\(^1\) electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1\(^s\) atomic orbitals. B The Na\(^{2−}\) ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled \(σ_{3s}\) molecular orbital, a half-filled \(σ_{3s}^*\) and a \(\left(σ_{3s}\right)^2\left(σ_{3s}^*\right)^1\) electron configuration.

C The bond order is \((2-1)+2=1/2\) With a fractional bond order, we predict that the Na\(^{2−}\) ion exists but is highly reactive.

Exercise (PageIndex{2})

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca\(^{2+}\) ion.

**Answer**

Ca\(^{2+}\) has a \(\left(σ_{4s}\right)^2\left(σ_{4s}^*\right)^1\) electron configurations and a bond order of 1/2 and should exist.
Molecular Orbitals Formed from $ns$ and $np$ Atomic Orbitals

Atomic orbitals other than $ns$ orbitals can also interact to form molecular orbitals. Because individual $p$, $d$, and $f$ orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each $np$ subshell, for example, there are $np_x$, $np_y$, and $np_z$ orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \label{Eq6}$$

Just as with $ns$ orbitals, we can form molecular orbitals from $np$ orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two $np_z$ atomic orbitals in part (a) in Figure 5, it is the mathematical difference of their wave functions that results in constructive interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a $\sigma_{np_z}$ bonding molecular orbital because, just as with the $\sigma$ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the $z$-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \label{Eq6a}$$

The other possible combination of the two $np_z$ orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \label{Eq7}$$

In this combination, shown in part (b) in Figure 5, the positive lobe of one $np_z$ atomic orbital overlaps the negative lobe of the other, leading to destructive interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma^*$ (antibonding) molecular orbital. Whenever orbitals combine, the bonding combination is always lower in energy (more stable) than the atomic orbitals from which it was derived, and the antibonding combination is higher in energy (less stable).

Overlap of atomic orbital lobes with the same sign produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining $p$ orbitals on each of the two atoms, $np_x$ and $np_y$, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 6, we see that we have two pairs of $np$ orbitals: the two $np_x$ orbitals lying in the plane of the page, and two $np_y$ orbitals...
perpendicular to the plane. Although these two pairs are equivalent in energy, the $np_x$ orbital on one atom can interact with only the $np_x$ orbital on the other, and the $np_y$ orbital on one atom can interact with only the $np_y$ on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of $\sigma$ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi ($\pi$) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel $np$ atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star ($\pi^*$) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel $np$ atomic orbitals, creating a nodal plane perpendicular to the internuclear axis.

$$\pi_{np_x} = np_x(A) + np_x(B)$$ \hspace{1cm} (Eq. 8)

$$\pi^*_{np_x} = np_x(A) - np_x(B)$$ \hspace{1cm} (Eq. 9)

The two $np_y$ orbitals can also combine using side-to-side interactions to produce a bonding $\pi_{np_y}$ molecular orbital and an antibonding $\pi^*_{np_y}$ molecular orbital. Because the $np_x$ and $np_y$ atomic orbitals interact in the same way (side-to-side) and have the same energy, the $\pi_{np_x}$ and $\pi_{np_y}$ molecular orbitals are a degenerate pair, as are the $\pi^*_{np_x}$ and $\pi^*_{np_y}$ molecular orbitals.

Figure (PageIndex{6}): Formation of $\pi$ Molecular Orbitals from $np_x$ and $np_y$ Atomic Orbitals on Adjacent Atoms. (a) Because the signs of the lobes of both the $np_x$ and the $np_y$ atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a $\pi$ (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a $\pi^*$ (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure (PageIndex{7}) is an energy-level diagram that can be applied to two identical interacting atoms that have three $np$ atomic orbitals each. There are six degenerate $p$ atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the $\sigma$ and $\sigma^*$ molecular orbitals is significantly greater than the difference between the two $\pi$ and $\pi^*$ sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a $\sigma$ bond than a $\pi$ bond, which means that the $\sigma$ molecular orbital is more stable (lower in energy) than the $\pi$ molecular orbitals.
The Relative Energies of the $\sigma$ and $\pi$ Molecular Orbitals Derived from $np_x$, $np_y$, and $np_z$ Orbitals on Identical Adjacent Atoms. Because the two $np_z$ orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the $\sigma$ and $\sigma^*$ molecular orbitals is greater than the energy difference between the $\pi$ and $\pi^*$ orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an $ns$ atomic orbital on one atom with an $np_z$ atomic orbital on another. As shown in Figure 8, the sum of the two atomic wave functions ($ns + np_z$) produces a $\sigma$ bonding molecular orbital. Their difference ($ns - np_z$) produces a $\sigma^*$ antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

Second Row Diatomic Molecules

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character.

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as $N_2$, $O_2$, and $F_2$.

When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.
The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F\textsubscript{2}. We use the diagram in part (a) in Figure \ref{fig:mo-energy-level-diagram-f2}; the \( n = 1 \) orbitals (\( \sigma_{1s} \) and \( \sigma_{1s}^* \)) are located well below those of the \( n = 2 \) level and are not shown. As illustrated in the diagram, the \( \sigma_{2s} \) and \( \sigma_{2s}^* \) molecular orbitals are much lower in energy than the molecular orbitals derived from the \( 2p \) atomic orbitals because of the large difference in energy between the \( 2s \) and \( 2p \) atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three \( 2p \) orbitals on each F is \( \sigma_{2p_{z}} \) and the next most stable are the two degenerate \( \pi_{2p_{x}} \) and \( \pi_{2p_{y}} \) orbitals, for a total of 14 electrons. The lowest-energy molecular orbital derived from the three \( 2p \) orbitals on each F is \( \sigma_{2p_{z}} \) and the next most stable are the two degenerate \( \pi_{2p_{x}} \) and \( \pi_{2p_{y}} \) orbitals. The lowest-energy molecular orbital derived from the three \( 2p \) orbitals on each F is \( \sigma_{2p_{z}} \) and the next most stable are the two degenerate \( \pi_{2p_{x}} \) and \( \pi_{2p_{y}} \) orbitals.

For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the \( \sigma_{2p_{z}} \) orbital is higher in energy than either of the degenerate \( \pi_{2p_{x}}^* \) and \( \pi_{2p_{y}}^* \) orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F\textsubscript{2} molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund’s rule. Two electrons each fill the \( \sigma_{2s} \) and \( \sigma_{2s}^* \) orbitals, 2 fill the \( \sigma_{2p_{z}} \) orbital, 4 fill the two degenerate \( \pi \) orbitals, and 4 fill the two degenerate \( \pi^* \) orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F\textsubscript{2} to have, we must calculate the bond order. According to Hund’s rule, the last 2 electrons must be placed in separate \( \pi^* \) orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of \( (8 - 6) ÷ 2 = 1 \). Thus F\textsubscript{2} is predicted to have a stable F–F single bond, in agreement with experimental data.

![Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules](image)

Figure \ref{fig:mo-energy-level-diagram-f2}: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules. (a) For F\textsubscript{2}, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, \( \sigma^*_{2p_{z}} \) are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O\textsubscript{2}, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the \( \pi^* \) orbitals, giving the O\textsubscript{2} molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O\textsubscript{2}. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O\textsubscript{2}, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure \ref{fig:mo-energy-level-diagram-o2}. We again fill the orbitals according to Hund’s rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the \( \sigma_{2s} \) and \( \sigma_{2s}^* \) orbitals, 2 more to fill the \( \sigma_{2p_{z}} \) orbital, and 4 to fill the degenerate \( \pi_{2p_{x}} \) and \( \pi_{2p_{y}} \) orbitals. According to Hund’s rule, the last 2 electrons must be placed in separate \( \pi^* \) orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of \( (8 - 6) ÷ 2 = 1 \). Thus O\textsubscript{2} is predicted to have a stable O–O single bond, in agreement with experimental data.
4) \( \frac{4}{2} = 2 \), which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in \( \text{O}_2 \). Chemists had long wondered why, unlike most other substances, liquid \( \text{O}_2 \) is attracted into a magnetic field. As shown in Figure \( \PageIndex{10} \), it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for \( \text{O}_2 \) to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.

Figure \( \PageIndex{10} \): Liquid \( \text{O}_2 \) Suspended between the Poles of a Magnet. Because the \( \text{O}_2 \) molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at https://www.youtube.com/watch?feature...&v=Lt4P6ctf06Q.

The magnetic properties of \( \text{O}_2 \) are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form \( \text{H}_2\text{O}, \text{CO}_2, \) and \( \text{N}_2 \) in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as \( \text{H}_2\text{O}, \text{CO}_2, \) and \( \text{N}_2 \), have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of \( \text{O}_2 \) with organic compounds to give \( \text{H}_2\text{O}, \text{CO}_2, \) and \( \text{N}_2 \) would require that at least one of the electrons on \( \text{O}_2 \) change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a spin barrier. Consequently, reactions of this type are usually exceedingly slow. If they were
not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N\(_2\) in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the \(\sigma_{2p_z}\) molecular orbital is slightly higher in energy than the degenerate \(\pi^\star_{np_x}\) and \(\pi^\star_{np_y}\) orbitals. The difference in energy between the 2s and 2p atomic orbitals increases from Li\(_2\) to F\(_2\) due to increasing nuclear charge and poor screening of the 2s electrons by electrons in the 2p subshell. The bonding interaction between the 2s orbital on one atom and the 2pz orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the \(\sigma_{2s}\) orbital and increases the energy of the \(\sigma_{2p_z}\) orbital. Thus for Li\(_2\), Be\(_2\), B\(_2\), C\(_2\), and N\(_2\), the \(\sigma_{2p_z}\) orbital is higher in energy than the \(\pi^\star_{2p_{x,y}}\) pair. Experimentally, it is found that the energy gap between the \(ns\) and \(np\) atomic orbitals increases as the nuclear charge increases (Figure \(\PageIndex{11}\)). Thus for example, the \(\sigma_{2p_z}\) molecular orbital is at a lower energy than the \(\pi^\star_{2p_{x,y}}\) pair.

Completing the diagram for N\(_2\) in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N\(_2\) versus 141.2 pm in F\(_2\)), and the bond energy is much greater for N\(_2\) than for F\(_2\) (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N\(_2\) bond is much shorter and stronger than the F\(_2\) bond, consistent with what we would expect when comparing a triple bond with a single bond.

Example \(\PageIndex{3}\)

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S\(_2\), a bright blue gas at high temperatures.
Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S₂. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.

B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S₂.

C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund’s rule.

D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]3s²3p⁴ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure \( \PageIndex{9} \) and Figure \( \PageIndex{11} \), we need to know how close in energy the 3s and 3p atomic orbitals are because their energy separation will determine whether the \( \pi_{3p_{x}} \) or the \( \sigma_{3p_{z}} \) molecular orbital is higher in energy. Because the ns–np energy gap increases as the nuclear charge increases (Figure \( \PageIndex{11} \)), the \( \sigma_{3p_{z}} \) molecular orbital will be lower in energy than the \( \pi_{3p_{x}} \) pair.

B The molecular orbital energy-level diagram is as follows:

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through \( \pi_{3p_{x}} \) and \( \pi_{3p_{y}} \), leaving 2 electrons to occupy the degenerate \( \pi^{\star}_{3p_{x}} \) and \( \pi^{\star}_{3p_{y}} \) pair. From Hund’s rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S₂ is \( \left( \sigma_{3s} \right)^{2} \left( \sigma^{\star}_{3s} \right)^{2} \left( \sigma_{3p_{z}} \right)^{2} \left( \pi_{3p_{x}} \right)^{4} \left( \pi^{\star}_{3p_{x}} \right)^{2} \) with 2 unpaired electrons. The bond order is \( (8 − 4) ÷ 2 = 2 \), so we predict an S=S double bond.
Exercise \(\PageIndex{3}\))

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion \(\text{O}_2^{2-}\).

**Answer**

\[
\left(\sigma_{2s}\right)^2 \left(\sigma^*_{2s}\right)^2 \left(\sigma_{2p_z}\right)^2 \left(\pi_{2p_x,y}\right)^4 \left(\pi^*_{2p_x,y}\right)^4
\]

bond order of 1;

no unpaired electrons

---

**Molecular Orbitals for Heteronuclear Diatomic Molecules**

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A \(\chi_B > \chi_A\), the net result is a “skewed” molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure \(\PageIndex{12}\)). The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

![Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where \(\chi_B > \chi_A\). The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.](image-url)
A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O\(_2\) with N\(_2\) at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O\(_2\) to produce NO\(_2\), which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure \(\PageIndex{13}\)) shows that the general pattern is similar to that for the O\(_2\) molecule (Figure \(\PageIndex{11}\)). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2\(p\) atomic orbitals, the 11th electron must occupy one of the degenerate \(\pi^*\) orbitals. The predicted bond order for NO is therefore \((8-3) + 2 = 2 1/2\). Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N\(_2\) and O\(_2\) molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

Note that electronic structure studies show the ground state configuration of \(\text{NO}\) to be \(\left(\sigma_{2s}\right)^2\left(\sigma^*_{2s}\right)^2\left(\pi_{2p_{x,y}}\right)^4\left(\sigma_{2p_z}\right)^2\left(\pi^*_{2p_{x,y}}\right)^1\) in order of increasing energy. Hence, the \(\left(\pi_{2p_{x,y}}\right)^1\) orbitals are lower in energy.
than the $\sigma_{2p_z}$ orbital. This is because the $\text{NO}$ molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure \(\PageIndex{11}\)).

Molecular orbital theory can also tell us something about the chemistry of $\text{NO}$. As indicated in the energy-level diagram in Figure \(\PageIndex{13}\), NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, \(\text{NO}\) is easily oxidized to the $\text{NO}^+$ cation, which is isoelectronic with \(\text{N}_2\) and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure \(\PageIndex{14}\) that the 1s orbital of atomic hydrogen is closest in energy to the 3p orbitals of chlorine. Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3p orbitals. Of the three p orbitals, only one, designated as 3pz, can interact with the H 1s orbital. The 3px and 3py atomic orbitals have no net overlap with the 1s orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3s, 3px, and 3py orbitals do not change when HCl forms, they are called nonbonding molecular orbitals. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is $(2 - 0) / 2 = 1$. Because the $\sigma$ bonding molecular orbital is closer in energy to the Cl 3pz than to the H 1s atomic orbital, the electrons in the $\sigma$ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $\text{H}^\delta+ -- \text{Cl}^\delta-$.

![Figure \(\PageIndex{14}\): Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the 3pz orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding $\sigma$ orbital is occupied by electrons, giving a bond order of 1.](image)
Electrons in nonbonding molecular orbitals have no effect on bond order.

Example \( \PageIndex{4} \)

Use a “skewed” molecular orbital energy-level diagram like the one in Figure \( \PageIndex{12} \) to describe the bonding in the cyanide ion \( \text{CN}^- \). What is the bond order?

**Given:** chemical species

**Asked for:** “skewed” molecular orbital energy-level diagram, bonding description, and bond order

**Strategy:**

A. Calculate the total number of valence electrons in \( \text{CN}^- \). Then place these electrons in a molecular orbital energy-level diagram like Figure \( \PageIndex{12} \) in order of increasing energy. Be sure to obey the Pauli principle and Hund’s rule while doing so.

B. Calculate the bond order and describe the bonding in \( \text{CN}^- \).

**Solution:**

A The \( \text{CN}^- \) ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the \(-1\) charge. Placing these electrons in an energy-level diagram like Figure \( \PageIndex{12} \) fills the five lowest-energy orbitals, as shown here:

Because \( \chi_N > \chi_C \), the atomic orbitals of N (on the right) are lower in energy than those of C. B The resulting valence electron configuration gives a predicted bond order of \((8 - 2) ÷ 2 = 3\), indicating that the \( \text{CN}^- \) ion has a triple bond, analogous to that in \( \text{N}_2 \).

**Exercise \( \PageIndex{4} \)**

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion \( \text{OCl}^- \). What is the bond order?
Answer: All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

Summary

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

A molecular orbital (MO) is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the molecular orbital theory of bonding is a delocalized approach. Molecular orbitals are constructed using linear combinations of atomic orbitals (LCAOs), which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of constructive reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are bonding molecular orbitals, and they are always lower in energy than the parent atomic orbitals.

2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of destructive interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called antibonding molecular orbitals, and they are always higher in energy than the parent atomic orbitals.

3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are nonbonding molecular orbitals, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely antibonding molecular orbital contains at least one node perpendicular to the internuclear axis. A sigma (σ) orbital (bonding) or a sigma star (σ*) orbital (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a pi (π) orbital (bonding) and a pi star (π*) orbital (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an energy-level diagram. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is,
placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the bond order, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered homonuclear diatomic molecules, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O₂ molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called heteronuclear diatomic molecules, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

Contributors and Attributions

• Modified by Joshua Halpern (Howard University)