Skills to Develop

- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

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 N₂, O₂, and F₂.

Four key points to remember when drawing molecular orbital diagrams:

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.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F₂. We use the diagram in part (a) in Figure \(\PageIndex{1}\); 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 \(\langle \sigma_{2p_z} \rangle\) and the next most stable are the two degenerate orbitals, \(\langle \pi_{2p_x} \rangle\) and \(\langle \pi_{2p_y} \rangle\). 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 \(\langle \pi_{2p_z}^* \rangle\) orbital is higher in energy than either of the degenerate \(\langle \pi_{2p_x} \rangle\) and \(\langle \pi_{2p_y} \rangle\) 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 F₂ 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 \(\langle \sigma_{2p_z} \rangle\) 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 F₂ to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of \((8 - 6) ÷ 2 = 1\). Thus F₂ is predicted to have a stable F–F single bond, in agreement with experimental data.
Figure \(\PageIndex{1}\): Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules. (a) For F\(_2\), 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\(_2\), with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the \(\pi^*\) pair of orbitals. Hund’s rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O\(_2\) 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\(_2\). 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\(_2\), we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure \(\PageIndex{1}\). 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 \((8 - 4) / 2 = 2\), 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 O\(_2\). Chemists had long wondered why, unlike most other substances, liquid O\(_2\) is attracted into a magnetic field. As shown in Figure \(\PageIndex{2}\), it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for 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(2)): Liquid O₂ Suspended between the Poles of a Magnet. Because the O₂ 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?featur...&v=Lt4P6cft06Q.

The magnetic properties of O₂ 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 H₂O, CO₂, and N₂ 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 H₂O, CO₂, and N₂, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O₂ with organic compounds to give H₂O, CO₂, and N₂ would require that at least one of the electrons on O₂ 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 N₂ 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 \( \pi_{2p} \) orbitals. The difference in energy between the 2s and 2p atomic orbitals increases from Li₂ to F₂ 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 Li₂, Be₂, B₂, C₂, and N₂, the \( \sigma_{2p_z} \) orbital is higher.
in energy than the $\sigma_{3p_{z}}$ orbitals, as shown in Figure \(\PageIndex{3}\). Experimentally, it is found that the energy gap between the $ns$ and $np$ atomic orbitals increases as the nuclear charge increases (Figure \(\PageIndex{3}\)). Thus for example, the $\sigma_{2p_{z}}$ molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ 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 \(\PageIndex{3}\): Diatomic Sulfur

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 S$_2$. 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 S$_2$. 

Figure \(\PageIndex{3}\): Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li$_2$ through N$_2$, the $\sigma_{2p_{z}}$ orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the $\sigma_{2p_{z}}$ orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for O$_2$ and F$_2$ due to the increase in the energy difference between the 2s and 2p atomic orbitals as the nuclear charge increases across the row.
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]3s\(^2\)3p\(^4\) valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure \(\PageIndex{1}\) and Figure \(\PageIndex{3}\), we need to know how close in energy the 3s and 3p atomic orbitals are because their energy separation will determine whether the \(\pi_{3p_{x,y}}\) or the \(\sigma_{3p_z}\) molecular orbital is higher in energy. Because the ns–np energy gap increases as the nuclear charge increases (Figure \(\PageIndex{3}\)), the \(\sigma_{3p_z}\) molecular orbital will be lower in energy than the \(\pi_{3p_{x,y}}\) pair.

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

![Molecular Orbital Energy-Level Diagram]

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 \(\pi^*_{3p_{x}}\) and \(\pi^*_{3p_{y}}\) 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 S\(_2\) is \(\left(\sigma_{3s}\right)^2\left(\sigma^*_{3s}\right)^2\left(\sigma_{3p_z}\right)^2\left(\pi_{3p_{x,y}}\right)^4\left(\pi^*_{3p_{x,y}}\right)^2\) with 2 unpaired electrons. The bond order is \((8 - 4) ÷ 2 = 2\), so we predict an S=S double bond.

Exercise \(\PageIndex{3}\): The Peroxide Ion

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 (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 \(\PageIndex{4}\)). 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.

Figure \(\PageIndex{4}\)): 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.

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 \(\PageIndex{5}\)) shows that the general pattern is similar to that.
for the O₂ molecule (Figure \(\PageIndex{3}\)). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2p atomic orbitals, the 11th electron must occupy one of the degenerate \(\pi^*\) orbitals. The predicted bond order for NO is therefore \((8-3) ÷ 2 = 2 \frac{1}{2}\). 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 N₂ and O₂ 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.

Figure \(\PageIndex{5}\): Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the \(\left(\pi^*_{\text{2p}_x}, \pi^*_{\text{2p}_y}\right)\) pair of orbitals.

Molecular orbital theory can also tell us something about the chemistry of \(\text{NO}\). As indicated in the energy-level diagram in Figure \(\PageIndex{5}\), 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 \(\PageIndex{6}\) 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 3pₓ, can interact with the H 1s orbital. The 3pₓ and 3pᵧ 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 3pᵧ 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 \((2 - 0) \div 2 = 1\). Because the \(\sigma\) bonding molecular orbital is closer in energy to the \(\text{Cl}\ 3p_z\) than to the \(\text{H}\ 1s\) 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 \(\text{H}--\text{Cl}\) bond to give \(\text{H}^{\delta^+} \cdots \text{Cl}^{\delta^-}\).

Electrons in nonbonding molecular orbitals have no effect on bond order.

Example: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure \(\PageIndex{4}\) 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 \(\PageIndex{4}\) 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 \(\PageIndex{4}\) 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.

The resulting valence electron configuration gives a predicted bond order of $(8 - 2) / 2 = 3$, indicating that the CN$^-$ ion has a triple bond, analogous to that in N$_2$.

Exercise $\PageIndex{4}$: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl$^-\$). What is the bond order?

**Answer:**

All molecular orbitals except the highest-energy $\sigma^*$ 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 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 O$_2$ 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

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