Skills to Develop

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule \( \text{O}_2 \), presents a problem with respect to its Lewis structure. We would write the following Lewis structure for \( \text{O}_2 \):

\[ \text{O}==\text{O} \]

This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, \( \text{O}_2 \) is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called paramagnetism, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of \( \text{O}_2 \) indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure \( \PageIndex{1} \)), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

Experiments show that each \( \text{O}_2 \) molecule has two unpaired electrons. The Lewis-structure model does not predict the
presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

Video \(\PageIndex{1}\): Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more (https://www.youtube.com/watch?v=A1vyB-O5i6E)

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table \(\PageIndex{1}\) summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.
**Table \((\text{PageIndex}1)\): Comparison of Bonding Theories**

<table>
<thead>
<tr>
<th>Valence Bond Theory</th>
<th>Molecular Orbital Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>considers bonds as localized between one pair of atoms</td>
<td>considers electrons delocalized throughout the entire molecule</td>
</tr>
<tr>
<td>creates bonds from overlap of atomic orbitals ((s, p, d\ldots)) and hybrid orbitals ((sp, sp^2, sp^3\ldots))</td>
<td>combines atomic orbitals to form molecular orbitals ((\sigma, \sigma^<em>, \pi, \pi^</em>))</td>
</tr>
<tr>
<td>forms (\sigma) or (\pi) bonds</td>
<td>creates bonding and antibonding interactions based on which orbitals are filled</td>
</tr>
<tr>
<td>predicts molecular shape based on the number of regions of electron density</td>
<td>predicts the arrangement of electrons in molecules</td>
</tr>
<tr>
<td>needs multiple structures to describe resonance</td>
<td></td>
</tr>
</tbody>
</table>

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, \(\Psi\), analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital \(\langle \Psi^2 \rangle\). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (\(\text{H}_2\) or \(\text{Cl}_2\), for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the linear combination of atomic orbitals (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (Figure \((\text{PageIndex}2)\)). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

![Figure \((\text{PageIndex}2)\): (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.](image)

There are two types of molecular orbitals that can form from the overlap of two atomic \(s\) orbitals on adjacent atoms. The two types are illustrated in Figure 8.4.3. The in-phase combination produces a lower energy \(\sigma_s\) molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also
be thought of as subtracting the wave functions) produces a higher energy \(\langle \sigma^*-s \rangle\) molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a \(\sigma_s\) orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the \(\langle \sigma^*-s \rangle\) orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

**Figure \(\PageIndex{3}\):** Sigma (\(\sigma\)) and sigma-star (\(\sigma^*\)) molecular orbitals are formed by the combination of two \(s\) atomic orbitals. The plus (+) signs indicate the locations of nuclei.

In \(p\) orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When \(p\) orbitals overlap end to end, they create \(\sigma\) and \(\sigma^*\) orbitals (Figure \(\PageIndex{4}\)). If two atoms are located along the \(x\)-axis in a Cartesian coordinate system, the two \(p_x\) orbitals overlap end to end and form \(\sigma_{px}\) (bonding) and \(\langle \sigma^*-p_x \rangle\) (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with \(s\)-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

**Figure \(\PageIndex{4}\):** Combining wave functions of two \(p\) atomic orbitals along the internuclear axis creates two molecular orbitals, \(\sigma_p\) and \(\langle \sigma^*-p \rangle\).

The side-by-side overlap of two \(p\) orbitals gives rise to a \(\pi\) (\(\pi\)) bonding molecular orbital and a \(\pi^*\) antibonding molecular orbital, as shown in Figure \(\PageIndex{5}\). In valence bond theory, we describe \(\pi\) bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the \(p\) orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the \(\pi\) orbital by this same shape, and a \(\pi\) bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.
In the molecular orbitals of diatomic molecules, each atom also has two sets of \( p \) orbitals oriented side by side (\( p_y \) and \( p_z \)), so these four atomic orbitals combine pairwise to create two \( \pi \) orbitals and two \( \pi^* \) orbitals. The \( \pi_{py} \) and \( \langle \pi^* \_\{py\}\rangle \) orbitals are oriented at right angles to the \( \pi_{pz} \) and \( \langle \pi^* \_\{pz\}\rangle \) orbitals. Except for their orientation, the \( \pi_{py} \) and \( \pi_{pz} \) orbitals are identical and have the same energy; they are degenerate orbitals. The \( \langle \pi^* \_\{py\}\rangle \) and \( \langle \pi^* \_\{pz\}\rangle \) antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic \( p \) orbitals in two atoms: \( \sigma_{px} \) and \( \langle \sigma^* \_\{px\}\rangle \), \( \pi_{py} \) and \( \langle \pi^* \_\{py\}\rangle \), \( \pi_{pz} \) and \( \langle \pi^* \_\{pz\}\rangle \).

Example (\( \PageIndex{1} \))

Molecular Orbitals Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.

Solution

a. This is an in-phase combination, resulting in a \( \sigma_{3p} \) orbital

b. This will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.

c. This is an out-of-phase combination, resulting in a \( \langle \pi^* \_\{3p\}\rangle \) orbital.
Exercise \PageIndex{1}

Label the molecular orbital shown as $\sigma$ or $\pi$, bonding or antibonding and indicate where the node occurs.

\begin{center}
\includegraphics[width=0.5\textwidth]{molecular_orbital.png}
\end{center}

**Answer**

The orbital is located along the internuclear axis, so it is a $\sigma$ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.

\begin{center}
\includegraphics[width=0.5\textwidth]{molecular_orbital.png}
\end{center}

**Application: Computational Chemistry in Drug Design**

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (Figure \PageIndex{6}). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{hiv protease.png}
\caption{The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.}
\end{figure}

**Molecular Orbital Energy Diagrams**

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure \PageIndex{7}). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic
orbits combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2p atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

**Figure \(\PageIndex{7}\):** This is the molecular orbital diagram for the homonuclear diatomic \(\ce{Be2+}\), showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund’s rule.

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure \(\PageIndex{7}\)). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as \(\ce{Be2+}\)) would have the molecular electron configuration \((σ_{1s})^2(σ^*_{1s})^2(σ_{2s})^2(σ^*_{2s})^1\). It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

**Bond Order**

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the bond order that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it
contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

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

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

**Bonding in Diatomic Molecules**

A dihydrogen molecule (H\(_2\)) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the \(\sigma_{1s}\) bonding orbital. A dihydrogen molecule, H\(_2\), readily forms because the energy of a H\(_2\) molecule is lower than that of two H atoms. The \(\sigma_{1s}\) orbital that contains both electrons is lower in energy than either of the two 1s atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H\(_2\) molecule are in the \(\sigma_{1s}\) bonding orbital; the electron configuration is \((\sigma_{1s})^2\). We represent this configuration by a molecular orbital energy diagram (Figure \(\PageIndex{8}\)) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

![Molecular Orbital Energy Diagram](image)

**Figure \(\PageIndex{8}\):** The molecular orbital energy diagram predicts that H\(_2\) will be a stable molecule with lower energy than the separated atoms.

**PREVIEW: Band Theory in Extended Systems**

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (e.g., \(\text{H}_2\)) in Figure \(\PageIndex{8}\)). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically \(> 10^{23}\) atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When \(N\) valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, \(N/2\) (filled) bonding orbitals and \(N/2\) (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are mostly in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are
mostly out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. Figure \( \PageIndex{9} \) shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

**Figure \( \PageIndex{9} \):** Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the “band gap” between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is “easy” to overcome, so they are good conductors of electricity. In an insulator, the band gap is so “large” that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when “moderate” amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

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**Key Concepts and Summary**

Molecular orbital (MO) theory describes the behavior of electrons in a molecule in terms of combinations of the atomic wave functions. The resulting molecular orbitals may extend over all the atoms in the molecule. Bonding molecular orbitals are formed by in-phase combinations of atomic wave functions, and electrons in these orbitals stabilize a molecule. Antibonding molecular orbitals result from out-of-phase combinations of atomic wave functions and electrons in these orbitals make a molecule less stable. Molecular orbitals located along an internuclear axis are called σ MOs. They can be formed from s orbitals or from p orbitals oriented in an end-to-end fashion. Molecular orbitals formed from p orbitals oriented in a side-by-side fashion have electron density on opposite sides of the internuclear axis and are called π orbitals.
We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund’s rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

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