

1.6: Day 6- Molecular Orbitals; Lewis Structures

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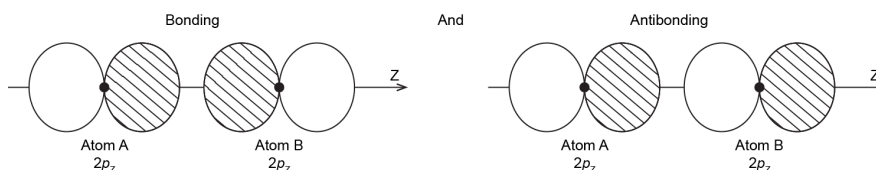
D6.1 Second-Row Diatomic Molecules

Let's consider some slightly more complex examples of molecular orbitals. F_2 , O_2 , and N_2 are diatomic molecules formed by elements from the second row of the periodic table. These molecules contain many more electrons than H_2 , and their molecular orbitals are derived from p atomic orbitals as well as s atomic orbitals.

Additional Practice

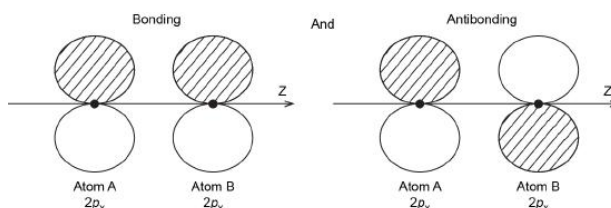
Now think about what happens when two atoms containing $2p$ atomic orbitals approach each other. Assume that the internuclear axis is the z axis. This means that the $2p_z$ atomic orbitals are aligned along the internuclear axis while the $2p_x$ and $2p_y$ atomic orbitals are oriented perpendicular to the internuclear axis.

When the two atoms approach, the bonding and antibonding overlap of the two $2p_z$ atomic orbitals occurs along the internuclear axis (z axis):



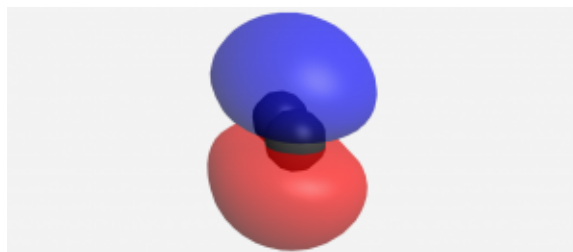
MOs derived from these two combinations are labeled σ_{2p_x} and $\sigma^*_{2p_x}$. *If you don't understand why these MOs are have the label σ , review [Section D5.5](#).*

It is also possible to make bonding and antibonding combinations from the two $2p_x$ AOs and from the two $2p_y$ AOs. Here is a diagram for the two ways the $2p_x$ AOs can overlap. Notice that the orbitals overlap side-by-side, not end-on, because the $2p_x$ AOs are aligned perpendicular to the internuclear axis (z axis).



Additional Practice

When two $2p$ AOs overlap side-by-side, the bonding MO formed is not symmetric with respect to rotation around the internuclear axis. Thus, the bond formed is not a σ bond. If you look down the internuclear (bond) axis, the “side view” of the MO looks similar to a $2p$ atomic orbital; this MO is called a π orbital.



When you look along the internuclear axis, a π MO looks like a p AO. π is the Greek letter corresponding to p , which is the reason for designating the MO as π . A π MO has one node (a horizontal plane in this case) that contains the internuclear axis.

Think about all atomic orbitals that are occupied in a fluorine atom, F: $1s$, $2s$, $2p_z$, $2p_x$, and $2p_y$. For each pair of AOs (such as $2s$ on atom A with $2s$ on atom B), overlap produces one bonding and one antibonding MO. There is σ and σ^* for $1s - 1s$, $2s - 2s$, and

$2p_z - 2p_z$ overlaps. There is π and π^* for $2p_x - 2p_x$, and $2p_y - 2p_y$ overlaps. These ideas result in the MO energy-level diagram shown here:

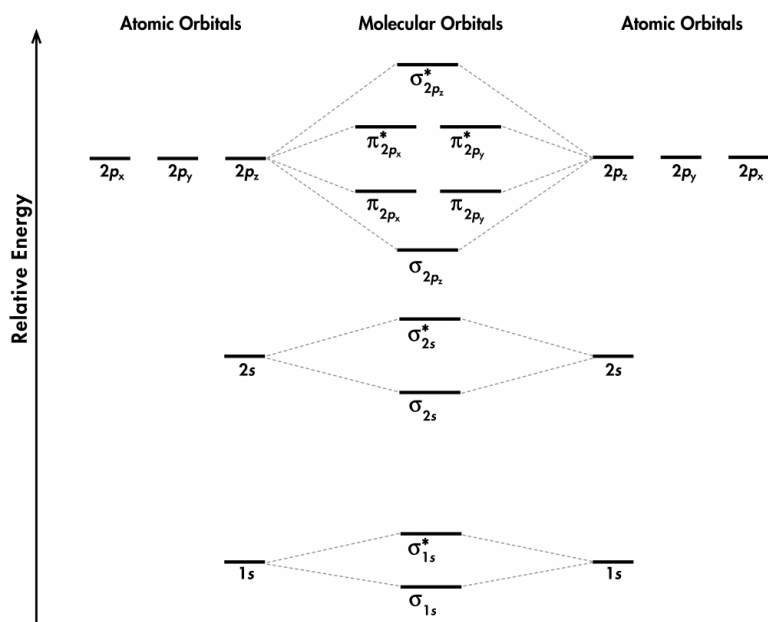


diagram for a F_2 molecule.

Figure 1. Molecular orbital energy level

From the ten AOs (five from each F atom), ten MOs are formed in F_2 . Note that whether a MO is bonding or antibonding is dependent on whether it is lower or higher in energy than the AOs from which it is derived. Hence, even though σ^*_{1s} is lower in energy than σ_{1s} , it is still an antibonding MO.

We also see in Figure 1 that the two π bonding MOs, π_{2p_x} and π_{2p_y} , are degenerate (have the same energy). This is because the side-by-side overlap of two $2p_x$ AOs is identical to the side-by-side overlap of two $2p_y$ AOs. They differ only in that π_{2p_x} and π_{2p_y} are perpendicular to each other, because the $2p_x$ AO is perpendicular to the $2p_y$ AO. Similar reasoning leads to the conclusion that the $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ MOs are also degenerate. Recognizing degenerate MOs is important when applying Hund's rule to determine molecular electron configurations.

Figure 2 shows the formation of the two perpendicular π bonds as two N atoms approach each other. (The two molecular depictions in the figure represent the same N_2 molecule: one shows the $2p_x - 2p_x$ orbital overlap and the other shows the $2p_y - 2p_y$ orbital overlap.)

Figure 2. A graph of energy versus distance between two nitrogen atoms. Boundary surface plots are shown for the two degenerate π bonding MOs formed from the in-phase overlap of the $2p_x$ AOs and the in-phase overlap of the $2p_y$ AOs. To watch the bond form, place the slider all the way to the right and then move it step-by-step toward the left.

Additional Practice

Based on the electron configuration for the F_2 molecule, the π and π^* MOs are all filled; there is no net π bond in the molecule. This is reflected in the bond order calculation: F_2 has a bond order of 1, corresponding to a single σ bond.

D6.2 Bond Length and Bond Enthalpy

Formation of a stable covalent molecule involves sharing electrons between two or more nuclei (the electrons occupy molecular orbitals that increase electron density between nuclei). The **bond length** between any two adjacent nuclei in such a covalent molecule is the *distance between the two nuclei at the minimum energy in a graph of energy versus nuclear separation*. For example, the bond length in a H_2 molecule is 74 pm, as shown in Figure 3.

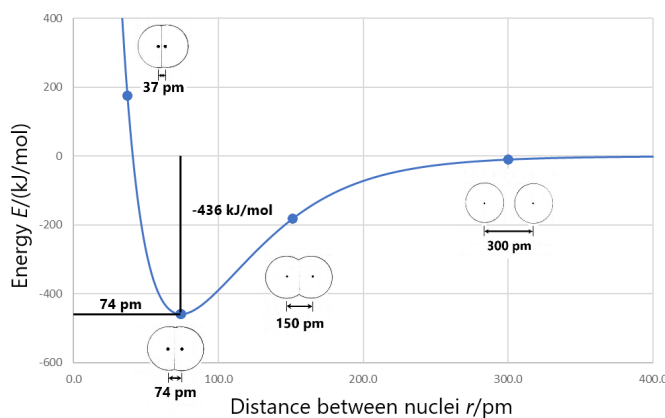


Figure 3. The bond length in a H_2 molecule is 74 pm. This is the distance between the two H-atom nuclei at the minimum in the curve of energy versus distance. Bond enthalpy is the energy required to separate two bonded atoms, which is the vertical distance from the minimum in the curve to zero on the graph, 436 kJ/mol.

Bond enthalpy (also called **bond energy**) is the *enthalpy change* when a chemical bond is broken; that is, when two bonded atoms are completely separated. For example, Figure 3 shows that the bonded hydrogen atoms have energy of -436 kJ/mol relative to the separated hydrogen atoms. This means that the energy of the molecule must be increased by 436 kJ/mol to separate the atoms (break the bond). So the bond enthalpy for H_2 is 436 kJ/mol.

Lengths of single bonds can be roughly estimated by using the **covalent radii** of the bonded atoms. For example, adding the covalent radius of C (77 pm) to that of O (74 pm), estimates the length of a C—O bond to be 151 pm. This is quite close to the average C—O **bond length** of 143 pm. (Both of these values are estimates because covalent radii and bond lengths are averaged over many molecules and therefore are not exact for any specific molecule.)

In general, the bigger the atoms are, the longer the bond between them is. For example, consider the following trend in the average C-X bond lengths, where X is a halogen:

C-F	141 pm
C-Cl	176 pm
C-Br	191 pm
C-I	210 pm

Bond lengths are also dependent on bond order. For example, the C—C single bond has an average length of 154 pm, while a C=C double bond is 134 pm long, and a C≡C triple bond has an average length of 121 pm.

Comparisons of the **average bond length** and **bond enthalpy** values show a general trend: a covalent bond with a shorter bond length generally has a larger bond enthalpy.

D6.3 Bonding in Molecules with More Than Two Atoms

Molecules with three or more atoms have molecular orbitals that span the entire molecule. The MOs are derived from the overlap of AOs from all the atoms in the molecule. Both the MO wave functions and the structure of the energy-level diagram are much more complicated than for diatomic molecules, but mathematical techniques exist for calculating and displaying the electron densities that form chemical bonds. In this course we will not delve deeply into these more complicated cases except to make several general points:

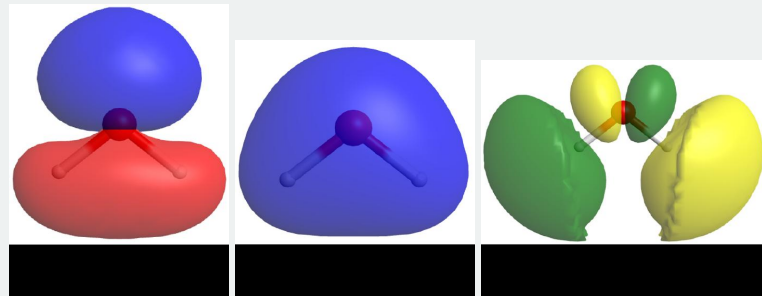
- The number of MOs for a molecule equals the number of AOs on the atoms that make up the molecule.
- The energies of the MOs increase as the number of nodes in the MO increases.
- MOs can extend over the entire molecular structure; they are not necessarily confined to pairs of atoms.

While MOs provide accurate physical information about the molecule, such as energies of the valence electrons involved in a reaction, their visualization does not always provide easy chemical understanding. It is possible to “re-combine” the MOs in such a way that the electron densities are displayed as being localized between pairs of atoms or on individual atoms; this allows us to

correlate MO derived electron densities with the more familiar Lewis structures, which represent electrons in chemical bonds as lines between pairs of atoms and electrons on a single atom as dots. We will discuss Lewis structures in more depth on Day 7.

Exercise 6: MOs for Polyatomic Molecules

Some of the molecular orbitals for a water molecule are shown here. Based only on what you know about the appearance of bonding and antibonding orbitals, rank these MOs from lowest-energy to highest-energy. (Click on each image for a rotatable 3D view of the MO.)



Activity 1: Reflection

Stop to think about molecular orbitals and bonding. Make a list of the main things you learned as you studied this topic both in today's work and the previous day's work. Your list should provide a summary you can use to review later for an exam.

D6.4 Lewis Structures for Covalent Molecules

Molecular orbitals for molecules with three or more atoms are complicated and hard to draw. Thus, although MOs would convey a more descriptive and accurate picture of electron distribution within a molecule, chemists often rely on simpler diagrams to depict the covalent bonding. It will aid your understanding of chemistry if you can connect these simpler diagrams mentally with the more complete picture given by MOs.

The most commonly used hand-drawn depiction is the **Lewis structure**: a diagram that represents atomic nuclei and core electrons by chemical symbols and valence electrons as dots or lines. A Lewis structure is built by combining Lewis diagrams (Section D3.4) of the constituent atoms.

Activity 2: Lewis Diagrams

Consider each element listed below. In your course notebook write the electron configuration for an atom of each element, determine the number of valence electrons, and write a Lewis diagram (Section D3.4). How are the Lewis diagrams related to the position of each element in the periodic table?

N C S As O Br F Si H

In Lewis structures, a single covalent bond is drawn as a pair of electron dots shared between two adjacent atoms, a **bond pair**. Valence electrons that are not in a bond are shown as pairs of dots associated with individual atoms, **lone pairs**. For example:



In the Cl_2 molecule, each Cl atom has three lone pairs and the two Cl atoms share one bond pair. Hence, each Cl atom in Cl_2 has formed an *octet* (is surrounded by eight valence electrons).

For simplicity and clarity, a bond pair is typically represented by a line instead of a pair of dots:



Activity 3: Lewis Structure and Electron Sharing

The Octet Rule

The **octet rule** states that *atoms of main-group elements tend to gain, lose, or share enough electrons to form an octet* (eight valence electrons). Such noble-gas electron configurations with completely filled valence shells are more stable, and therefore should correspond to how the electrons are arranged in a molecule.

The Lewis diagram for an atom can be used to predict the number of bonds the atom will form. For example, a carbon atom has four valence electrons and therefore requires four more electrons to reach an octet:

It is important to keep in mind that it is impossible to *exceed* an octet for atoms in the second period. This is particularly relevant because you will encounter numerous molecules containing the elements C, N and O.

Finally, because a hydrogen atom needs only two electrons to fill its valence shell, H is an important exception to the octet rule and forms only one bond.

Double and Triple Bonds

Two atoms may need to share more than one pair of electrons to achieve the requisite octet. In other words, the bond order is greater than 1. A **double bond** consists of *two pairs of electrons being shared between two atoms*. For example:



A **triple bond** forms when *three pairs of electron are shared between two atoms*. For example:



Activity 4: Double and Triple Bonds

Write answers to these questions in your course notebook:

Write a Lewis structure for N₂ and a Lewis structure for O₂. Describe the type of bond in each case.

Do the N atoms in N₂ and the O atoms in O₂ follow the rule for number of bonds in Exercise 7?

Use the molecular-orbital energy level diagram in Figure 1 to calculate the bond order for N₂ and for O₂. How do the bond orders relate to the Lewis structures?

D6.5 General Guidance for Drawing Lewis Structures

Often you can draw a Lewis structure based on the number of bonds formed by each kind of atom. In more complicated cases, here is a step-by-step procedure for drawing Lewis structures of molecules and polyatomic ions:

- Determine the total number of valence electrons by summing the number of valence electrons on all atoms.
 - For a polyatomic cation, subtract one electron for each positive charge.
 - For a polyatomic anion, add one electron for each negative charge.
- Choose one or more central atoms; a central atom bonds to several other atoms and is usually the atom that forms the greatest number of bonds.
 - Usually the central atom is written first in a chemical formula, such as P in PCl₃.
 - If there are two or more central atoms, connect them using single bond lines.
- Draw a skeleton structure of the molecule by arranging the other atoms (which are called terminal atoms) around the central atom or atoms.
 - Connect terminal atoms to the central atom(s) by single bond lines.
- Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
- If there are still valence electrons available, place them on the central atom(s).

6. If the number of electrons around a central atom is less than an octet, rearrange the electrons to make multiple bonds with the central atom(s) until each atom has an octet.

Let's apply these rules to a simple molecule, ammonia, NH_3 .

Here is a more complicated case: ethene (ethylene), C_2H_4 .

Exercise 8: Lewis Structures and Valence Electrons

If you were to build a Lewis structure for nitrate ion (NO_3^-), how many electrons would you need to allocate in your structure? (In other words, how many non-core electrons have to be in your structure?)

Exercise 9: Identifying Incorrect Lewis Structures

For each Lewis structure, determine whether the structure is correct. If the structure is incorrect, identify the error made in the representation.

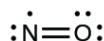
D6.6 Exceptions to the Octet Rule

Some stable covalent molecules contain one or more atoms that do not have an octet. Such molecules fall into three categories.

Odd-electron Molecules

A molecule that contains an odd number of electrons must have at least one electron unpaired and therefore must have an atom with fewer than eight electrons in its valence shell (typically it's seven electrons). A *molecule with at least one unpaired electron* is called a **free radical**. Nitric oxide, NO , which is produced in internal combustion engines when oxygen and nitrogen react at high temperatures, is an example.

To draw the Lewis structure for an odd-electron molecule, follow the same steps as outlined previously, but recognize that an odd-electron molecule must have less than an octet on some atom. For example, the Lewis structure for NO is:

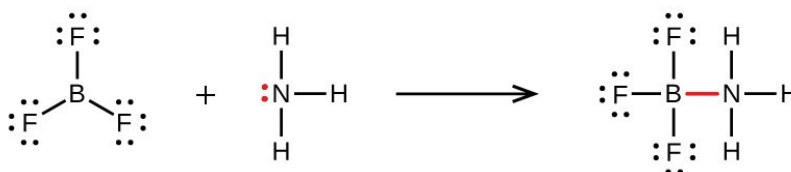


Forming a triple bond would cause either oxygen or nitrogen to exceed an octet, which is a very unlikely electron arrangement.

Molecules with an Incomplete Octet on a Central Atom

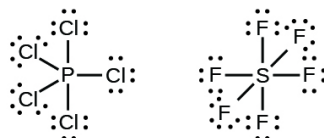
Some molecules contain a central atom that does not have a filled valence shell. Usually, these central atoms are from groups 2 (IIA) and 13 (IIIA). For example, the Lewis structure of beryllium chloride, BeCl_2 , shows beryllium with only four electrons, and that of boron trifluoride, BF_3 , shows boron with only six electrons.

It is possible to draw a structure for each of these molecules where there are double bonds to the central atom and therefore an octet. For example, BF_3 with one $\text{B}=\text{F}$ double bond would satisfy the octet rule. However, experimental evidence tells us that the bond lengths in BF_3 are closer to $\text{B}-\text{F}$ single bonds. The observed reactivity of BF_3 is also consistent with less than an octet on boron: BF_3 reacts readily with NH_3 , with the lone pair on nitrogen (red) forming a bond (red) that completes the octet on the boron atom:



Molecules with More Than an Octet on a Central Atom

Some Lewis structures show more than four pairs of electrons around the central atom. This usually happens when the central atom is in the third or a higher period ($n \geq 3$). Molecules with more than an octet around a central atom are called **hypervalent molecules**. For example, in the Lewis structure for PCl_5 , the central phosphorus atom is surrounded by five pairs of electrons. In SF_6 , sulfur has six pairs of electrons.

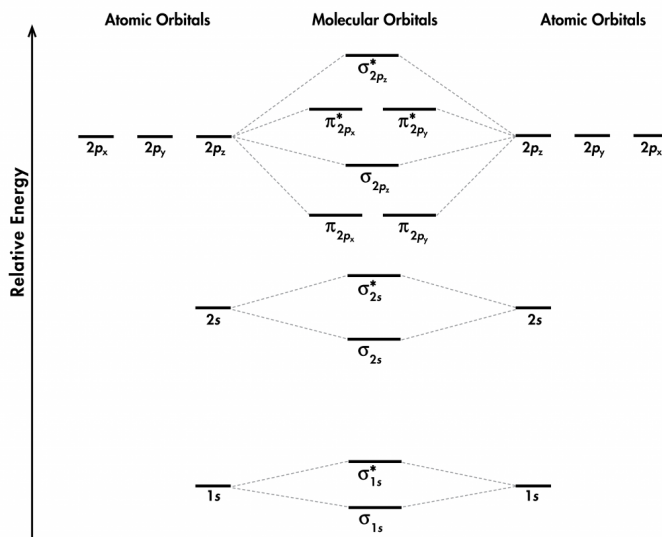


Day 6 Pre-class Podia Problem: Molecular Orbital Energy Levels

This Podia problem is based on today's pre-class material; working through that material will help you solve the problem.

The molecule C_2 is quite unstable and can only be isolated and studied experimentally in the gas phase. Molecular spectroscopy of C_2 reveals that a C_2 molecule in the ground state has no unpaired electrons.

1. Use the MO energy-level diagram in Figure 1 to predict the ground state electron configuration of C_2 . Does your result agree with the experimental observation?
2. Consider the MO diagram below. Is this a better diagram than Figure 1 for C_2 ? Use scientifically appropriate language to explain which diagram is better.



Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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