

Chemical Bonding – Part II

Molecular Orbital Theory

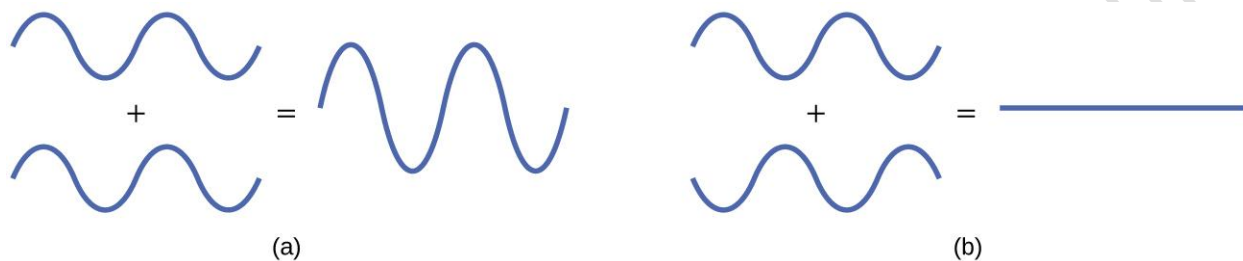
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Molecular orbital theory (MO theory) provides the bonding in a number of molecules, such as violations of the octet rule and more molecules with more complicated bonding that are difficult to describe with Lewis structures. Additionally, it provides 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 given below, summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Valence Bond Theory	Molecular Orbital Theory
1. Considers bonds as localized between one pair of atoms	1. Considers electrons delocalized throughout the entire molecule
2. Creates bonds from overlap of atomic orbitals (<i>s</i> , <i>p</i> , <i>d</i> ...) and hybrid orbitals (<i>sp</i> , <i>sp</i> ² , <i>sp</i> ³ ...)	2. Combines atomic orbitals to form molecular orbitals (σ , σ^* , π , π^*)
3. Forms σ or π bonds	3. Creates bonding and antibonding interactions based on which orbitals are filled
4. Predicts molecular shape based on the number of regions of electron density	4. Predicts the arrangement of electrons in molecules

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 (given below). 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.

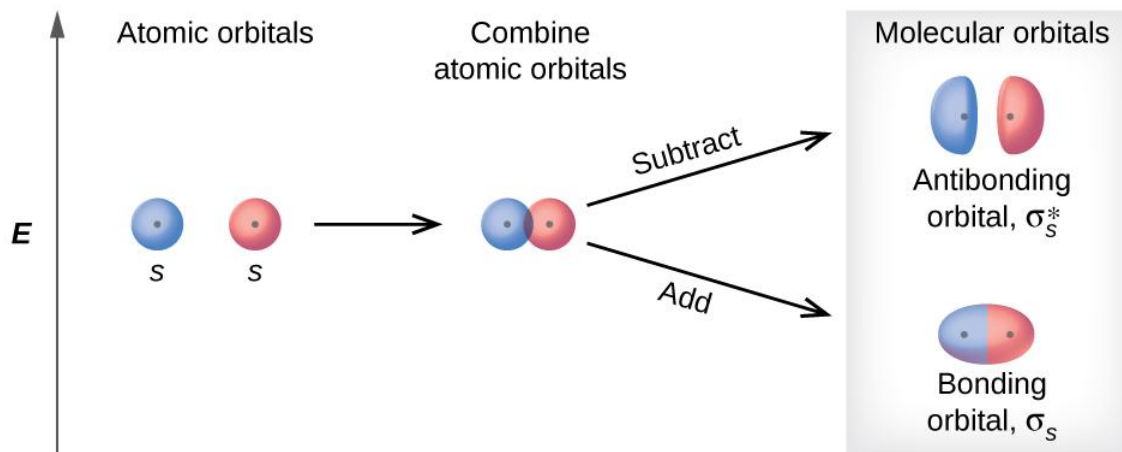


(a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

In the similar pattern, two types of molecular orbitals can be formed from the overlap of two atomic s orbitals on adjacent atoms (given below).

1. The in-phase combination produces a lower energy σ_s **molecular orbital** (read as “sigma-s”) in which most of the electron density is directly between the nuclei.
2. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy σ_s^* **molecular orbital** (read as “sigma-s-star”) molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital.

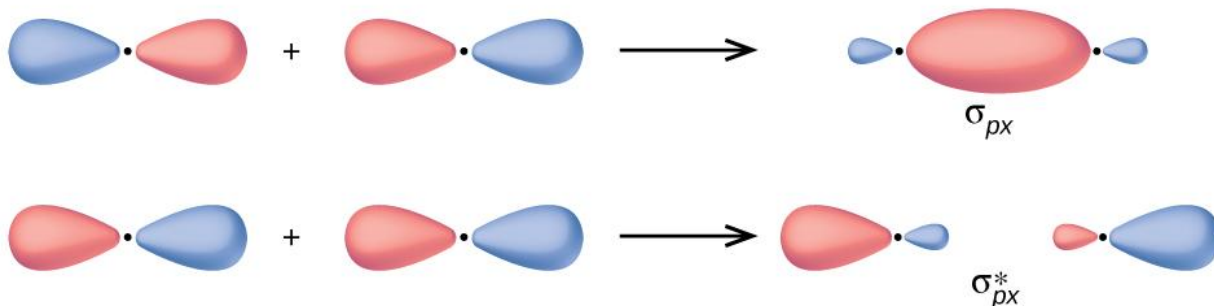
Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals **bonding orbitals**. Electrons in the σ_s^* 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.



Sigma (σ) and sigma-star (σ^*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

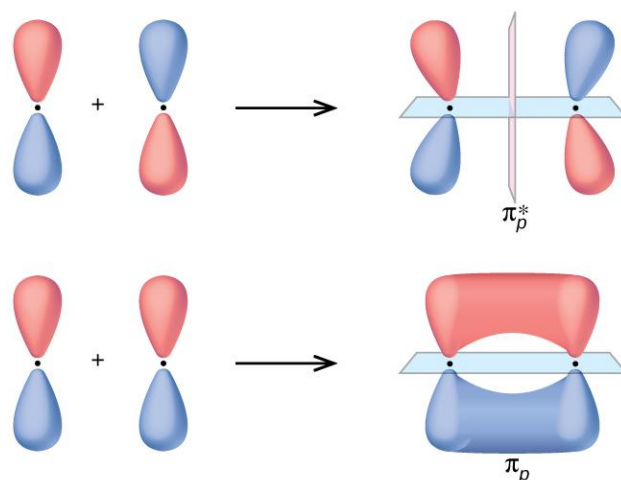
Similarly in p orbitals, combination can be understood as follows:

1. When p orbitals overlap end to end, they create σ and σ^* orbitals (Figure 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 σ_{px} (bonding) and σ_{px}^* (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.



Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p (bonding molecular orbital) and σ_p^* (antibonding molecular orbital).

2. The side-by-side overlap of rest two p orbitals (y and z axes here) gives rise to a **π bonding molecular orbital** and a **π^* antibonding molecular orbital**, as shown below:



Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

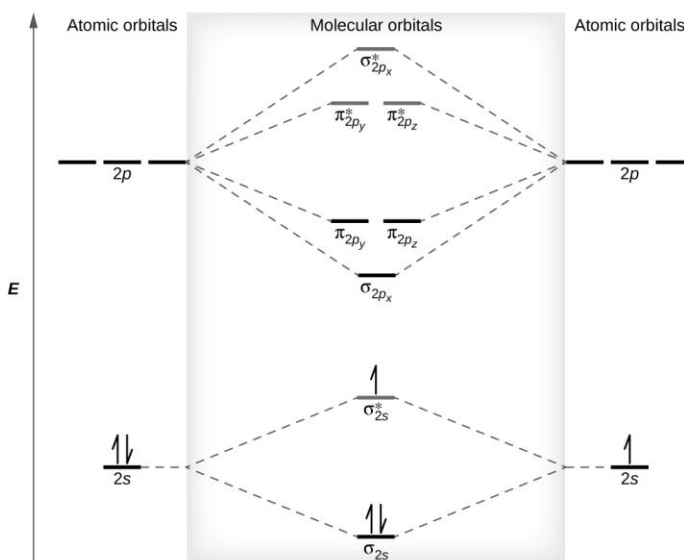
Important note: In the molecular orbitals of diatomic molecules, each atom also has two sets of p orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π^* orbitals. The π_{p_y} and $\pi_{p_y}^*$ orbitals are oriented at right angles to the π_{p_z} and $\pi_{p_z}^*$ orbitals. Except for their orientation, the π_{p_y} and π_{p_z} orbitals are identical and have the same energy; they are **degenerate orbitals** and hence, $\pi_{p_y}^*$ and $\pi_{p_z}^*$ 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: σ_{p_x} and $\sigma_{p_x}^*$, π_{p_y} and $\pi_{p_y}^*$, π_{p_z} and $\pi_{p_z}^*$ (here x-axis is assumed to be molecular axis).

MOLECULAR ORBITAL ENERGY DIAGRAMS

Molecular orbital energy diagram represents relative energy levels of atomic and molecular orbitals. 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 orbitals 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^*).

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. 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 Be_2^+) would have the molecular electron configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^1$. **It is common to omit the core electrons** from molecular orbital diagrams and configurations and include only the valence electrons.



This is the molecular orbital diagram for the homonuclear diatomic Be_2^+ (7 electron system), 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

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.

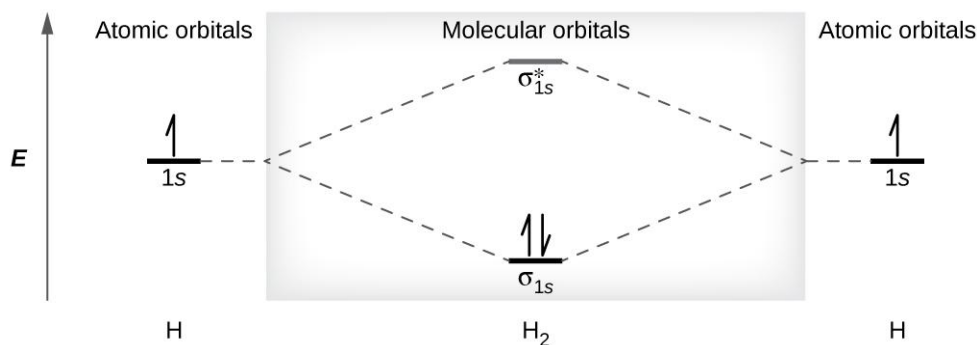
The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\begin{aligned}\text{bond order} &= [(\text{number of bonding electrons}) - (\text{number of antibonding electrons})] / 2 \\ &= (n_b - n_a) / 2,\end{aligned}$$

Note: 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.

BONDING IN DIATOMIC MOLECULES

1. **Dihydrogen molecule (H₂):** When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H₂, readily forms because the **energy of a H₂ molecule is lower than that of two H atoms**. The σ_{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 H₂ molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram, given below, in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.



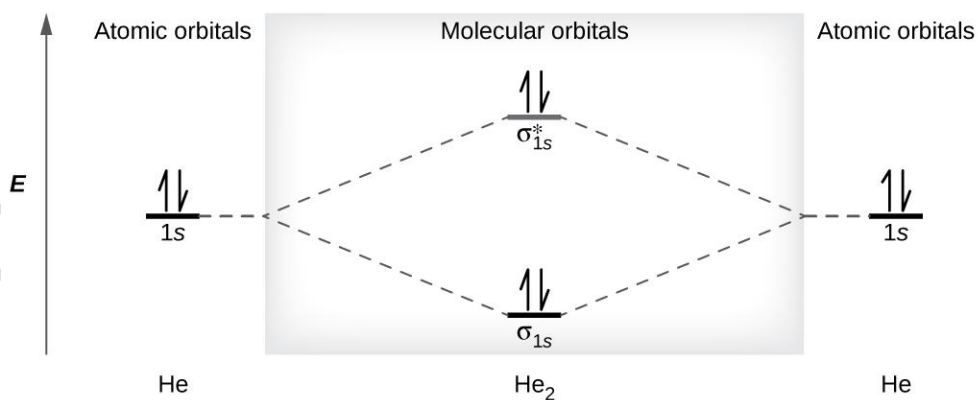
The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\begin{aligned} \text{bond order in } H_2 &= (n_b - n_a)/2 \\ &= (2-0)/2=1 \end{aligned}$$

Because the bond order for the H–H bond is equal to 1, the **bond is a single bond**.

2. **He₂ molecule:** A helium atom has two electrons, both of which are in its 1s orbital. Two helium atoms do not combine to form a dihelium molecule, He₂, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He₂ is: $(\sigma_{1s})^2(\sigma^*_{1s})^2$, as shown below:



$$\begin{aligned} \text{bond order in } He_2 &= (n_b - n_a)/2 \\ &= (2-2)/2=0 \end{aligned}$$

Because the bond order for the He–He bond is equal to 0, **hence He₂ molecule doesn't exist**.