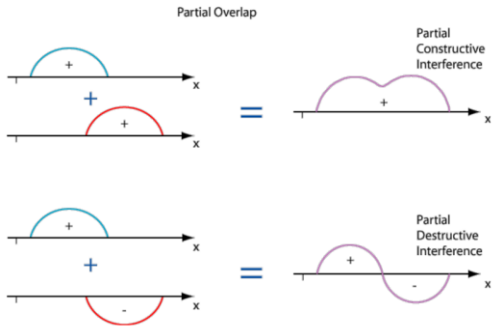
Molecular Orbital Theory

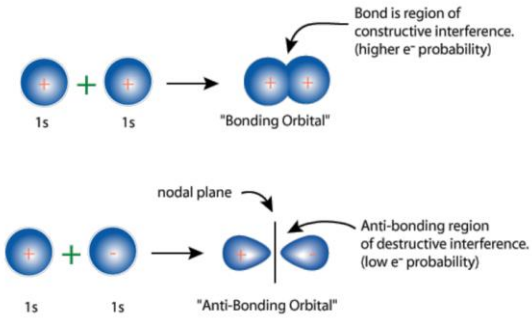
The **Lewis Structure** approach provides an extremely simple method for determining the electronic structure of many molecules. It is a bit simplistic, however, and does have trouble predicting structures for a few molecules. Nevertheless, it gives a reasonable structure for many molecules and its simplicity to use makes it a very useful tool for chemists.

A more general, but slightly more complicated approach is the **Molecular Orbital Theory**. This theory builds on the electron wave functions of Quantum Mechanics to describe chemical bonding. To understand MO Theory let's first review constructive and destructive interference of standing waves starting with the full constructive and destructive interference that occurs when standing waves overlap completely.

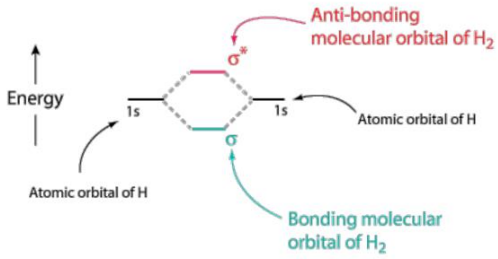
When standing waves only partially overlap we get partial constructive and destructive interference.



To see how we use these concepts in Molecular Orbital Theory, let's start with H_2, the simplest of all molecules. The 1s orbitals of the H-atom are standing waves of the electron wavefunction. In Molecular Orbital Theory we view the bonding of the two H-atoms as partial constructive interference between standing wavefunctions of the 1s orbitals.



The energy of the H_2 molecule with the two electrons in the bonding orbital is lower by 435 kJ/mole than the combined energy of the two separate H-atoms. On the other hand, the energy of the H_2 molecule with two electrons in the antibonding orbital is higher than two separate H-atoms. To show the relative energies we use diagrams like this:

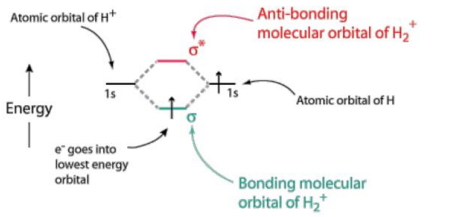


In the H_2 molecule, the bonding and anti-bonding orbitals are called **sigma** orbitals (σ).

Sigma Orbital: A bonding molecular orbital with cylindrical symmetry about an internuclear axis.

When atomic orbitals are combined to give molecular orbitals, **the number of molecular orbitals formed equals the number of atomic orbitals used**. So, the two 1s orbitals of H combine to give the σ orbitals of the H_2 molecule. A molecular orbital (like an atomic orbital) can contain no more than two electrons (Pauli Exclusion Principle), and are filled starting with the lowest energy orbital first. In general, the energy difference between a bonding and anti-bonding orbital pair becomes larger as the overlap of the atomic orbitals increase. Now let's look at some examples:

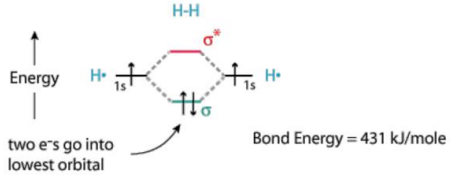
The H_2^+ molecule has only one valence electron.



Bond Energy = 255 kJ/mole

$(\sigma_{1s})^1$ Molecular electronic configuration of H_2^+
(similar to atomic electron configurations)

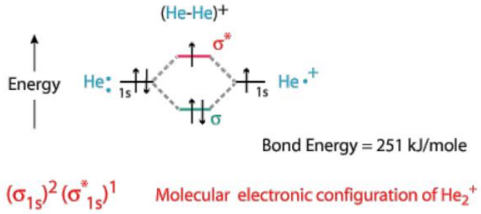
The H_2 molecule has two valence electrons.



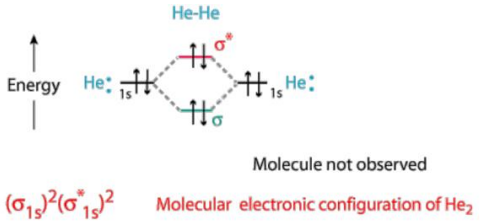
Bond Energy = 431 kJ/mole

$(\sigma_{1s})^2$ Molecular electronic configuration of H_2

The He_2^+ molecule has three valence electrons.



The He_2 molecule has four valence electrons.



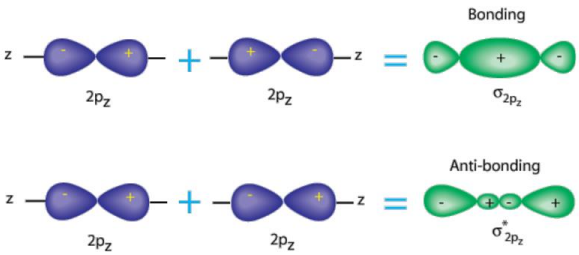
In the Lewis Structure Theory we had single, double, and triple bonds, in the Molecular Orbital Theory we similarly define the bond order.

Bond order = 1/2 (# of electrons in bonding orbitals - # of electrons in anti-bonding orbitals).

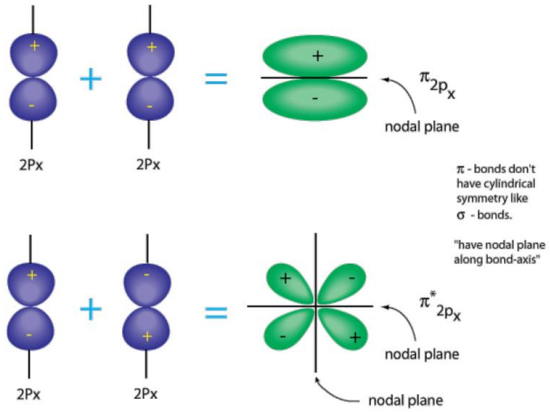
The bond order in our four examples above are given in the table below.

Bond	Bond Order
H_2^+	1/2
H_2	1
He_2^+	1/2
He_2	0

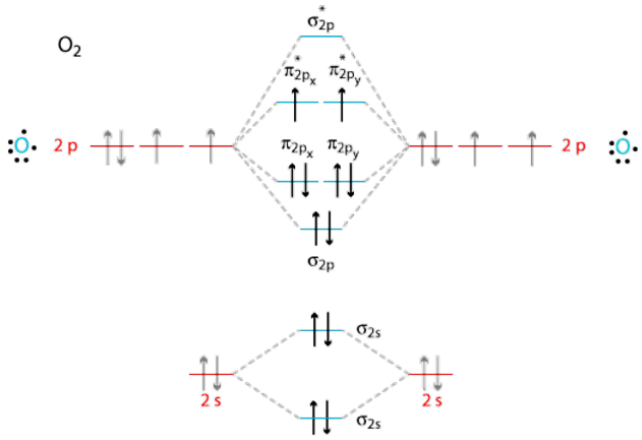
The bond order must be positive non-zero for a bond to be stable. He_2 has a bond order of zero and that is why the He_2 molecule is not observed. We can also form bonding orbitals using other atomic orbitals. To a first approximation only orbitals with similar energies can combine. For example, we can combine two p orbitals to form a sigma bond:



Using p orbitals a second type of orbital called a π orbital can also be formed.



Let's look at some examples where we have bonds forming between the s and p orbitals of two atoms bonding together. For example, e.g. O_2 has 6 + 6 = 12 valence electrons which can be placed in bonding and anti-bonding orbitals.

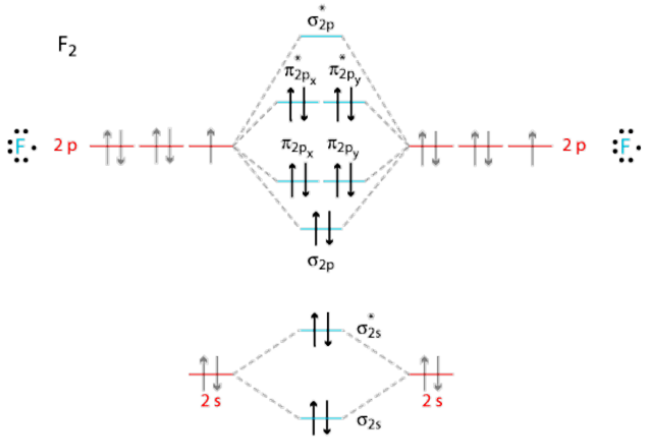


Electron Configuration: $(\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\sigma_{2p})^2\ (\pi_{2p})^4\ (\pi_{2p}^*)^2$

Bond Order $= \frac{1}{2}(2 - 2 + 2 + 4 - 2) = 2$ Double Bond

Notice that Molecular Orbital Theory predicts that O_2 has unpaired electrons, so it will be **paramagnetic**. Paramagnetic compounds (and atoms) are attracted to magnetic fields while diamagnetic compounds (and atoms) are repelled from magnetic fields. Paramagnetic compounds have unpaired electrons while in diamagnetic compounds the electrons all have paired spins. Very few individual atoms are paramagnetic since this requires having a half-filled Molecular Orbital. In contrast, nearly all molecules are diamagnetic (O_2 is a notable exception). Therefore, a simple rule of thumb is used in chemistry to determine whether a particle (atom, ion, or molecule) is paramagnetic or diamagnetic: If all electrons in the particle are paired, then the substance made of this particle is diamagnetic; If it has unpaired electrons, then the substance is paramagnetic.

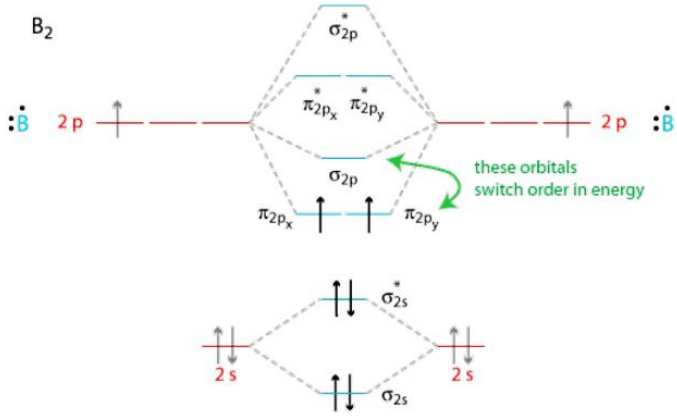
Another example is F_2. It has 14 electrons which are placed in the bonding and anti-bonding orbitals starting with the lowest energy orbital first.



Electron Configuration: $(\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\sigma_{2p})^2\ (\pi_{2p})^4\ (\pi_{2p}^*)^4$

Bond Order $= \frac{1}{2}(2 - 2 + 2 + 4 - 4) = 1$ Single Bond

In the case of B_2, C_2, and N_2 there is a slightly different ordering in orbital energies. For example, B_2 has 3 + 3 = 6 valence electrons.



Electron Configuration: $(\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\pi_{2p})^2$

Bond Order $= \frac{1}{2}(2 - 2 + 2) = 1$ Single Bond

Source: https://www.grandinetti.org/molecular-orbital-theory

Προτεινόμενες ασκήσεις: Σ. Τραχανά, Κβαντομηχανική Ι, ΠΕΚ, 2005, Αυτοεξέταση πολλαπλής επιλογής (Κεφάλαιο 12), Σελ. 575 – 576: 1 έως 8. **Απαντήσεις:** 1. (α), 2.(γ), 3.(δ), 4.(γ), 5.(β), 6.(β), 7.(γ), 8.(β)
Προσοχή: Θα πρέπει να μπορείτε να δικαιολογήσετε σύντομα την κάθε απάντηση που δίνετε.