Electronic spectra Bands

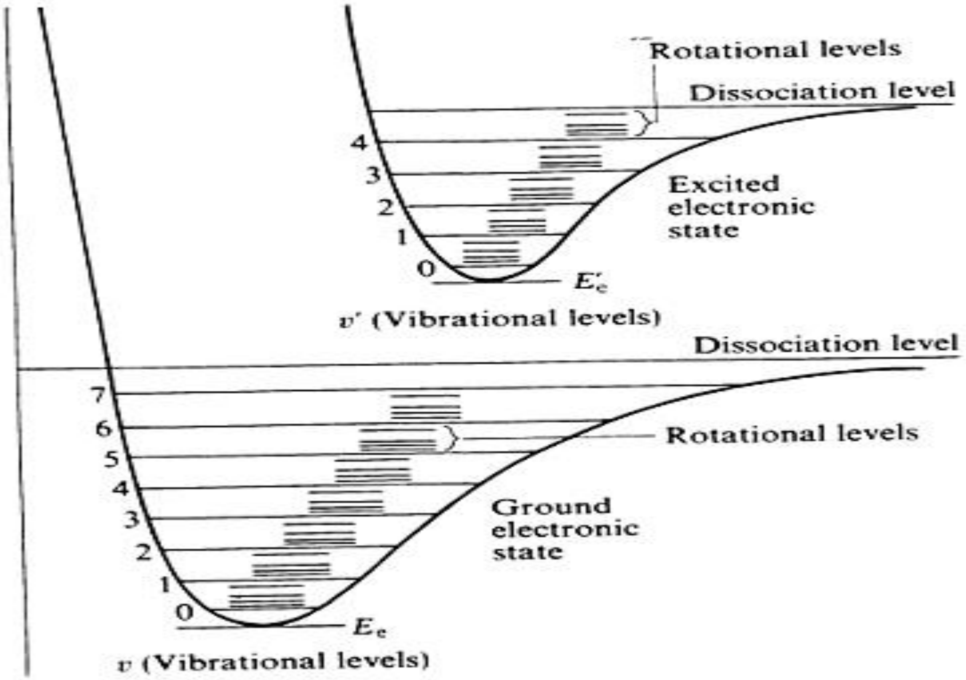
The energy states and spectra of molecules are much more complex than those of isolated atoms. In addition to the energies associated with molecular electronic states, there is kinetic energy associated with vibrational and rotational motions. The total energy, E , of a molecule can be expressed as the sum of three terms:

$$E = E_{electronic} + E_{rotational} + E_{vibrational}$$

Absorption of electromagnetic radiation by molecules occurs not only by electronic excitation of the type described for atoms, but also by changes in the vibrational and rotational energies.

The electronic energy levels are almost always much more widely spaced than any of the other types of energy levels we have discussed. Electronic energy transitions are typically observed in the ultraviolet or visible range, which corresponds to photon wavelengths of a few hundred nm, or energies in the range of 10^{-18} J.

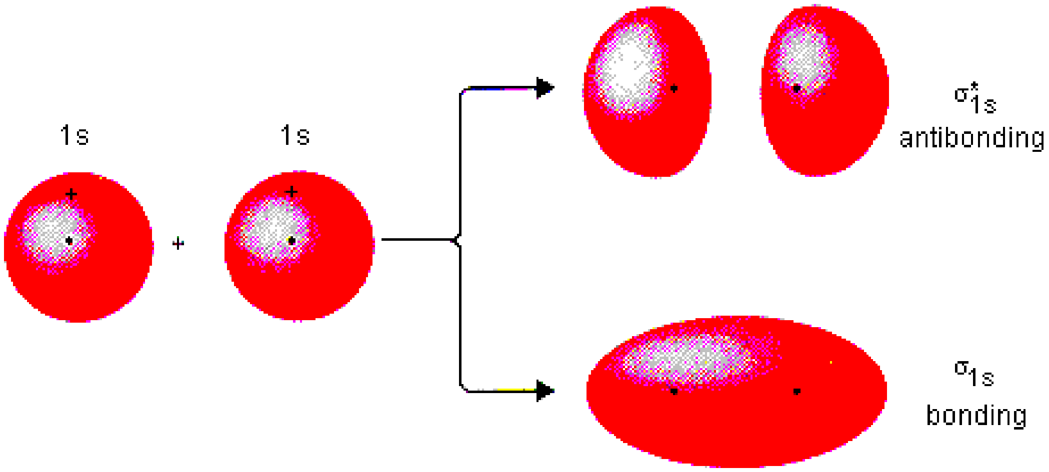
The figure below shows two different excited electronic states of a diatomic molecule (upper and lower electronic states) corresponding to each there are vibrational and rotational levels. The electronic transitions are in the visible and ultraviolet region.



Where E_e is the energy of the electron at the minimum of the potential, while the change in energy that takes place during an electronic transition between the initial and final state.

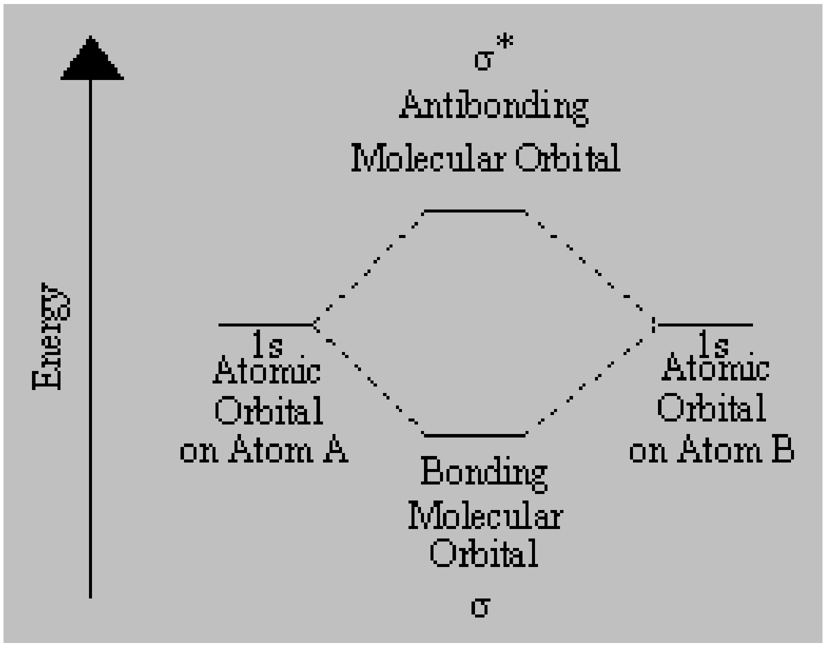
Molecular orbital

Molecular orbitals are obtained by combining the atomic orbitals on the atoms in the molecule. Consider the H_2 molecule, for example. One of the molecular orbitals in this molecule is constructed by adding the mathematical functions for the two 1*s* atomic orbitals that come together to form this molecule. Another orbital is formed by subtracting one of these functions from the other, as shown in the figure below.

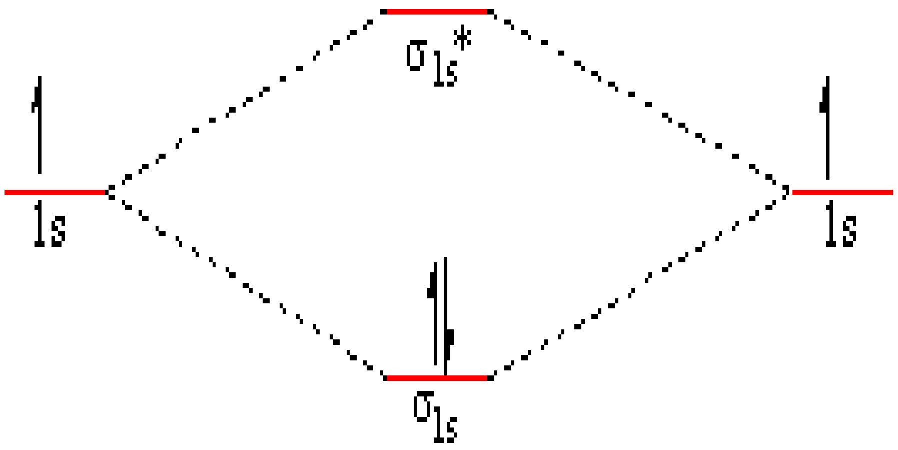


One of these orbitals is called a **bonding molecular orbital** because electrons in this orbital spend most of their time in the region directly between the two nuclei. It is called a **sigma** (σ) molecular orbital because it looks like an *s* orbital when viewed along the H-H bond. Electrons placed in the other orbital spend most of their time away from the region between the two nuclei. This orbital is therefore an **antibonding**, or *sigma star* (σ*), molecular orbital.

The σ bonding molecular orbital concentrates electrons in the region directly between the two nuclei.Placing an electron in this orbital therefore stabilizes the H_2 molecule. Since the σ* antibonding molecular orbital forces the electron to spend most of its time away from the area between the nuclei, placing an electron in this orbital makes the molecule less stable.

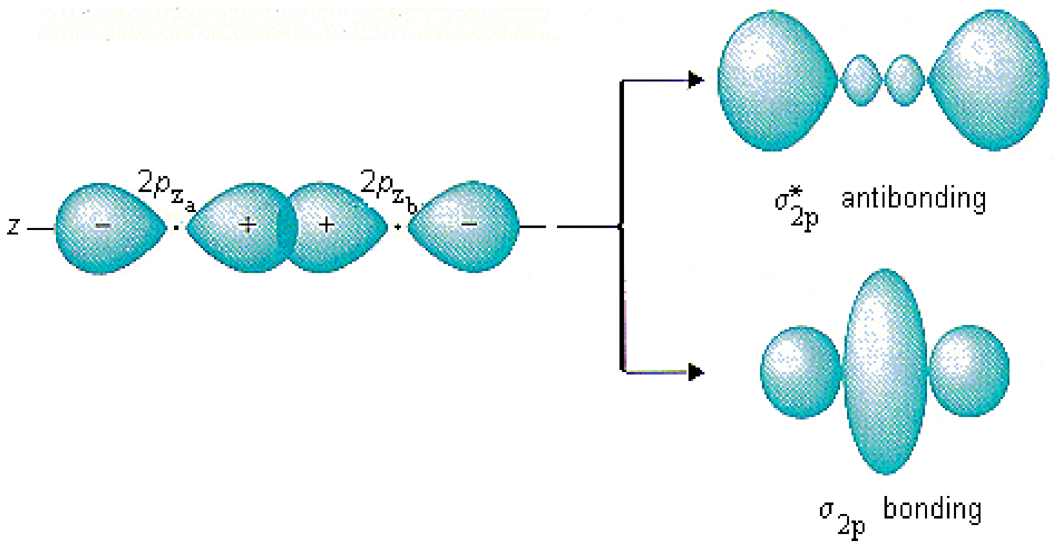


Electrons are added to molecular orbitals, one at a time, starting with the lowest energy molecular orbital. The two electrons associated with a pair of hydrogen atoms are placed in the lowest energy, or σ bonding, molecular orbital, as shown in the figure below. This diagram suggests that the energy of an H_2 molecule is lower than that of a pair of isolated atoms. As a result, the H_2 molecule is more stable than a pair of isolated atoms.



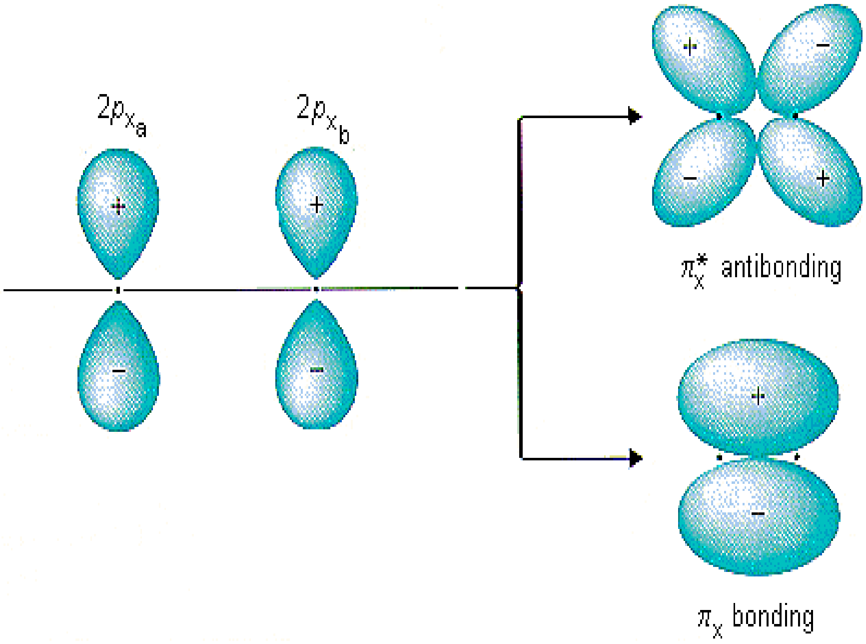
Molecular Orbitals of the Second Energy Level

The 2*s* orbitals on one atom combine with the 2*s* orbitals on another to form a σ_{2s} bonding and a σ_{2s}^* antibonding molecular orbital, just like the σ_{1s} and σ_{1s}^* orbitals formed from the 1*s* atomic orbitals. If we define the *Z* axis of the coordinate system for the O_2 molecule as the axis along which the bond forms, the $2p_z$ orbitals on the adjacent atoms will meet head-on to form a σ_{2p} bonding and a σ_{2p}^* antibonding molecular orbital, as shown in the figure below. These are called sigma orbitals because they look like *s* orbitals when viewed along the oxygen-oxygen bond.



The $2p_x$ orbitals on one atom interact with the $2p_x$ orbitals on the other to form molecular orbitals that have a different shape, as shown in the figure below. These molecular orbitals are called *pi* (π) orbitals because they look like *p* orbitals when viewed along the bond. Whereas σ and σ* orbitals concentrate the electrons along the axis on which the nuclei of the atoms lie, π and π* * orbitals concentrate the electrons either above or below this axis.

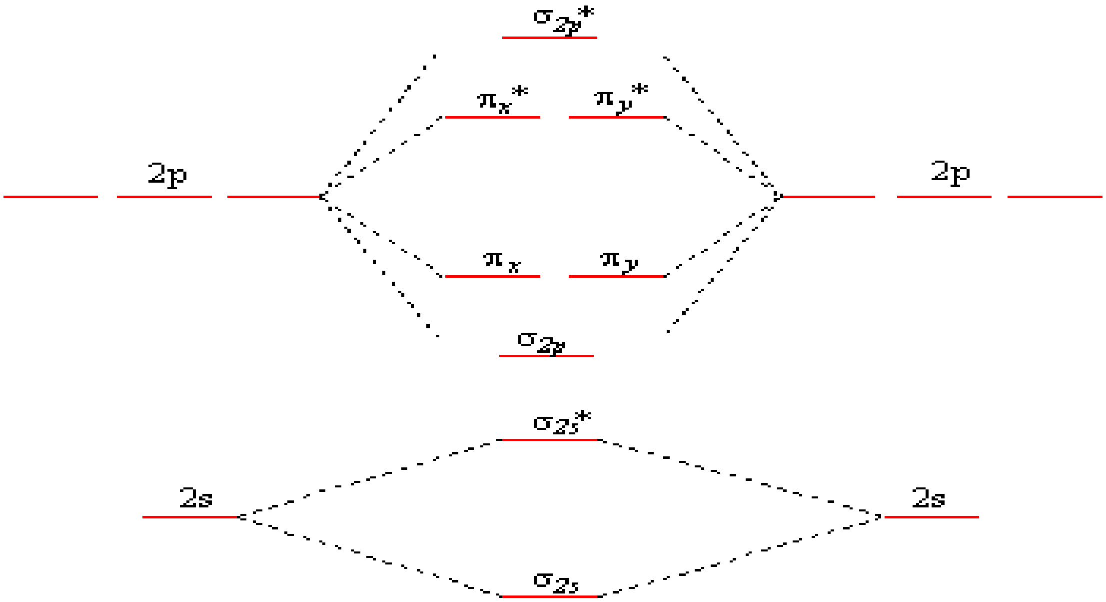
The $2p_x$ atomic orbitals combine to form a π_x bonding molecular orbital and a π_x* antibonding molecular orbital. The same thing happens when the $2p_y$ orbitals interact, only in this case we get a π_y and a π_y* antibonding molecular orbital. Because there is no difference between the energies of the 2p_x and 2p_y atomic orbitals, there is no difference between the energies of the π_x and π_y or the π_x* and π_y* molecular orbitals.



The interaction of four valence atomic orbitals on one atom (2*s*, 2p_x, 2p_y and 2p_z) with a set of four atomic orbitals on another atom leads to the formation of a total of eight molecular orbitals: σ_{2s}, σ_{2s}*, σ_{2p}, σ_{2p}*, π_x, π_y, π_x* and π_y*.

There is a significant difference between the energies of the 2*s* and 2*p* orbitals on an atom. As a result, the σ_{2s} and σ_{2s}* orbitals both lie at lower energies than the σ_{2p}, σ_{2p}*, π_x, π_y, π_x* and π_y* orbitals. To sort out the relative energies of the six molecular orbitals formed when the

2*p* atomic orbitals on a pair of atoms are combined, we need to understand the relationship between the strength of the interaction between a pair of orbitals and the relative energies of the molecular orbitals they form.
Because they meet head-on, the interaction between the $2p_z$ orbitals is stronger than the interaction between the $2p_x$ or $2p_y$ orbitals, which meet edge-on. As a result, the σ_{2p} orbital lies at a lower energy than the π_x and π_y orbitals, and the σ_{2p}* orbital lies at higher energy than the π_x* and π_y* orbitals, as shown in the figure below.

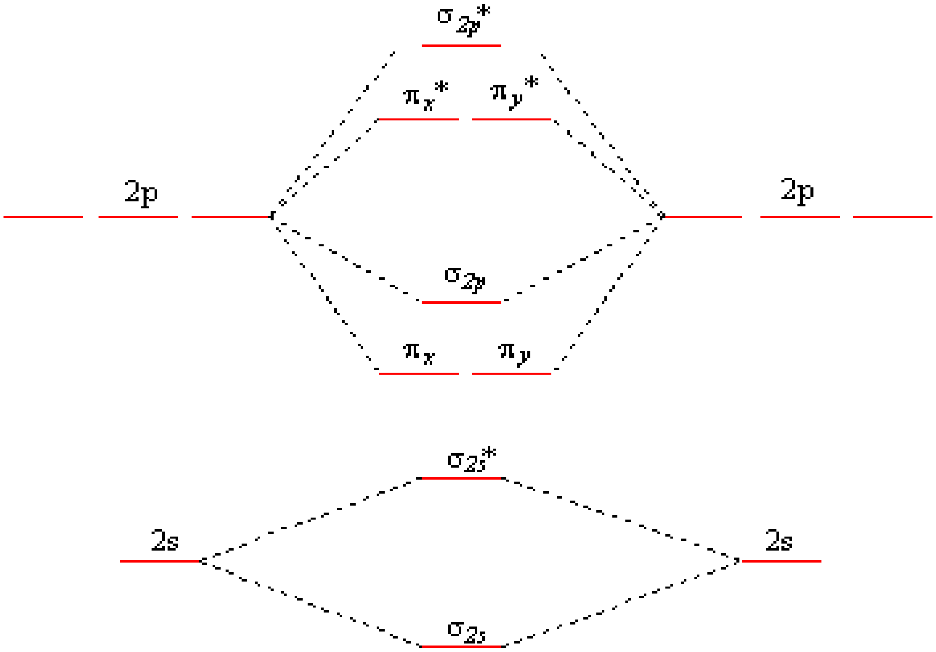


A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).

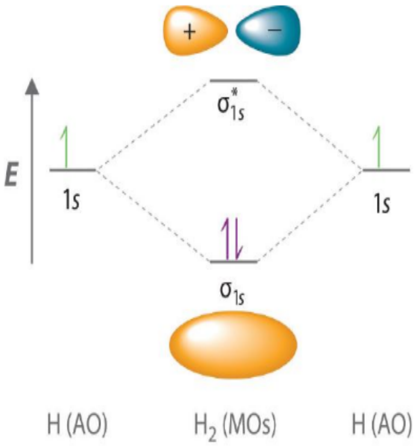
The first molecular orbitals may be arranged in order of energy as follow:

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2P_x) = \pi(2P_y) < \sigma(2P_z) < \pi^*(2P_x) = \pi^*(2P_y) < \pi^*(2P_z)$$

Unfortunately an interaction is missing from this model. It is possible for the 2*s* orbital on one atom to interact with the $2p_z$ orbital on the other. This interaction introduces an element of *s*-*p* mixing, or hybridization, into the molecular orbital theory. The result is a slight change in the relative energies of the molecular orbitals, to give the diagram shown in the figure below. Experiments have shown that O_2 and F_2 are best described by the model in the figure above, but B_2, C_2, and N_2 are best described by a model that includes hybridization, as shown in the figure below.



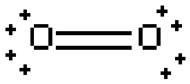
To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram. We fill the orbitals according to the Pauli principle and **Hund’s rule**: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei.



Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

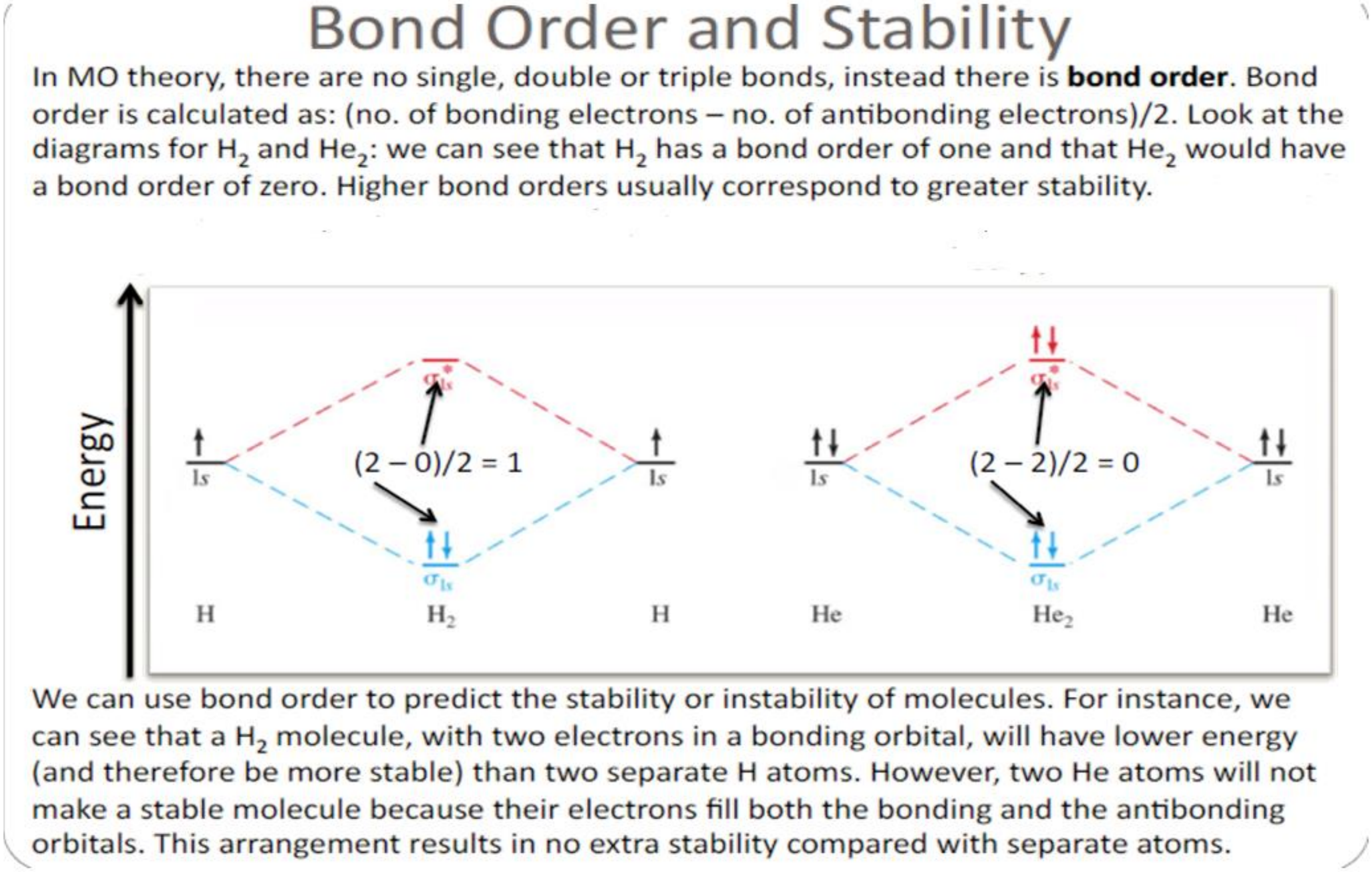
Bond Order

The number of bonds between a pair of atoms is called the **bond order**. Bond orders can be calculated from Lewis structures, which are the heart of the valence-bond model. Oxygen, for example, has a bond order of two.



In molecular orbital theory, we calculate bond orders by assuming that two electrons in a bonding molecular orbital contribute one net bond and that two electrons in an antibonding molecular orbital cancel the effect of one bond. For a molecule, we can calculate the bond order to characterize the bonding in the molecule. The bond order is equal to half of the sum of the number of electrons in bonding orbitals minus the number of electrons in anti-bonding orbitals. For diatomics, the bond order will tell us if we have single, double, or triple bonds.

$$\text{Bond order} = \frac{\text{bonding electrons} - \text{antibonding electrons}}{2} = \frac{8 - 4}{2} = 2$$



Bond Order and Stability

In MO theory, there are no single, double or triple bonds, instead there is **bond order**. Bond order is calculated as: (no. of bonding electrons – no. of antibonding electrons)/2. Look at the diagrams for H_2 and He_2: we can see that H_2 has a bond order of one and that He_2 would have a bond order of zero. Higher bond orders usually correspond to greater stability.

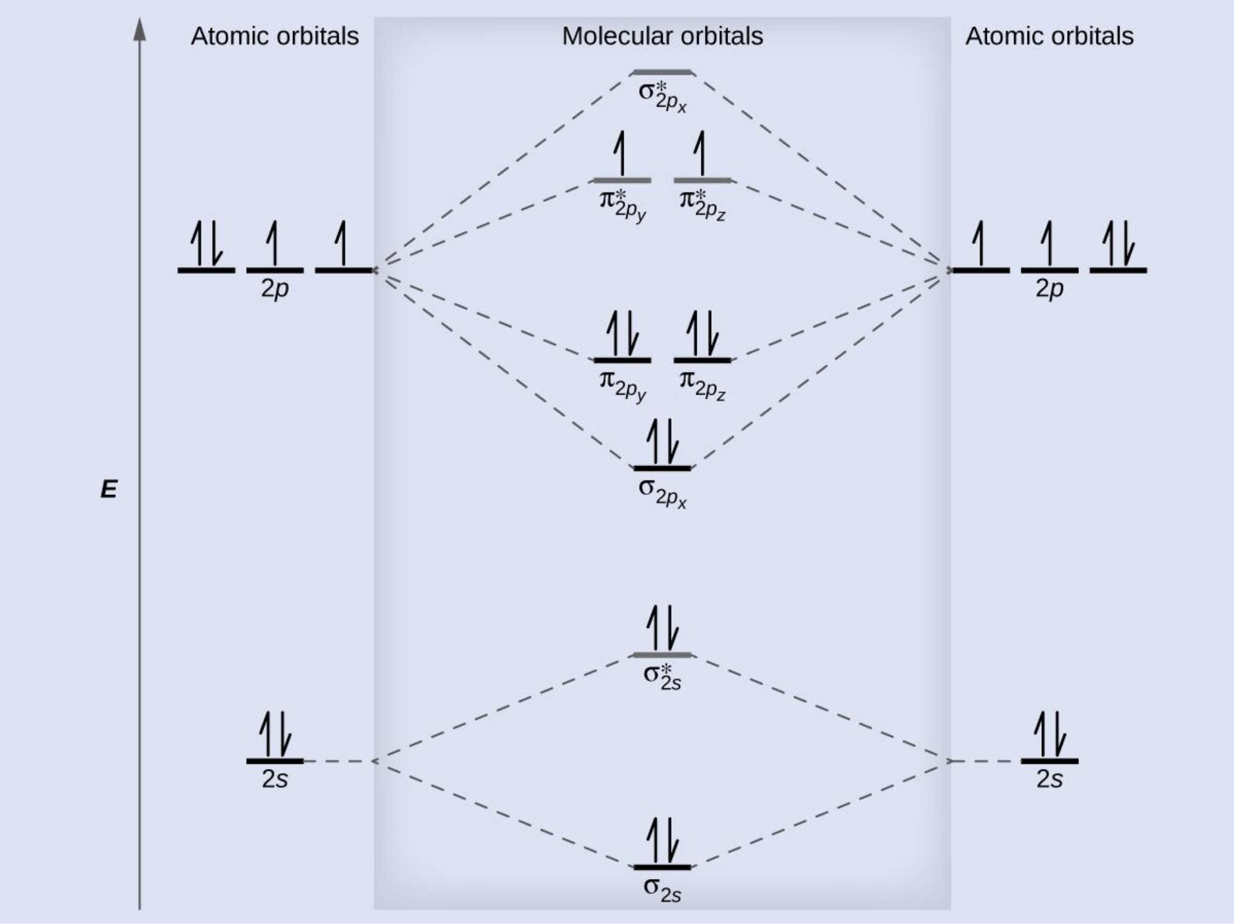
We can use bond order to predict the stability or instability of molecules. For instance, we can see that a H_2 molecule, with two electrons in a bonding orbital, will have lower energy (and therefore be more stable) than two separate H atoms. However, two He atoms will not make a stable molecule because their electrons fill both the bonding and the antibonding orbitals. This arrangement results in no extra stability compared with separate atoms.

Example 1

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2.

The atomic number of oxygen is 8

$1s^2\ 2s^2\ 2p^4$

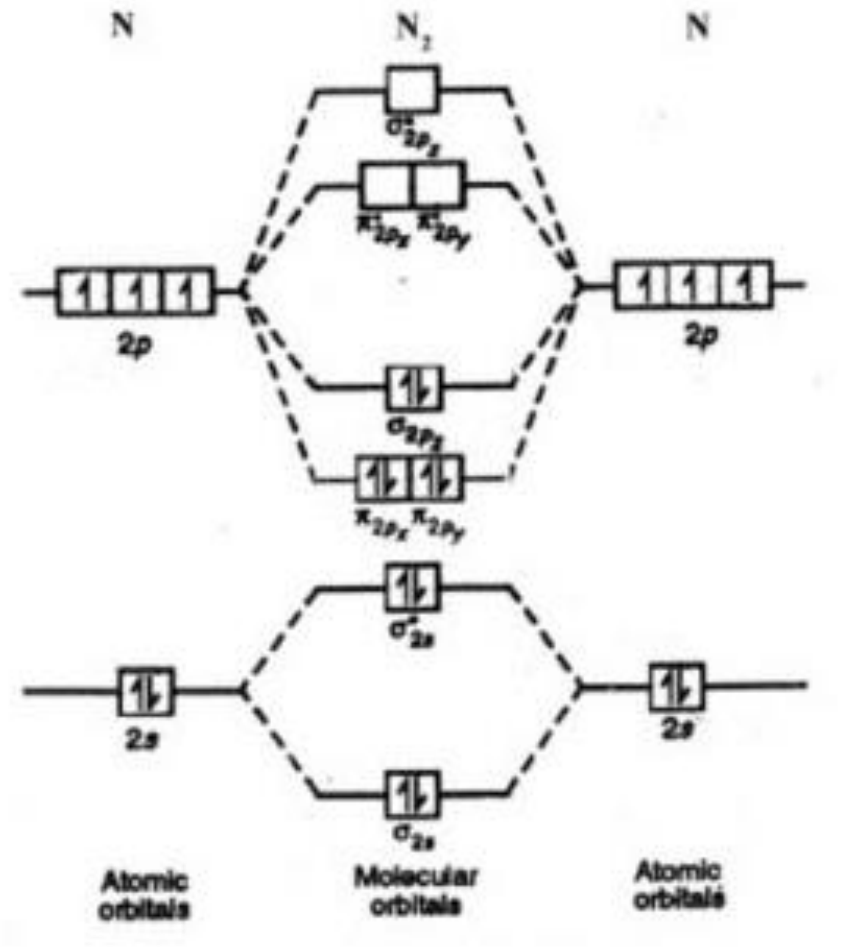


The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as →Bond order for $O_2 = \frac{8-4}{2} = 2$

Example 2

Draw the molecular orbital diagram for the Nitrogen molecule, N_2. Then, calculate the bond order for N_2.



The atomic number of nitrogen is 7

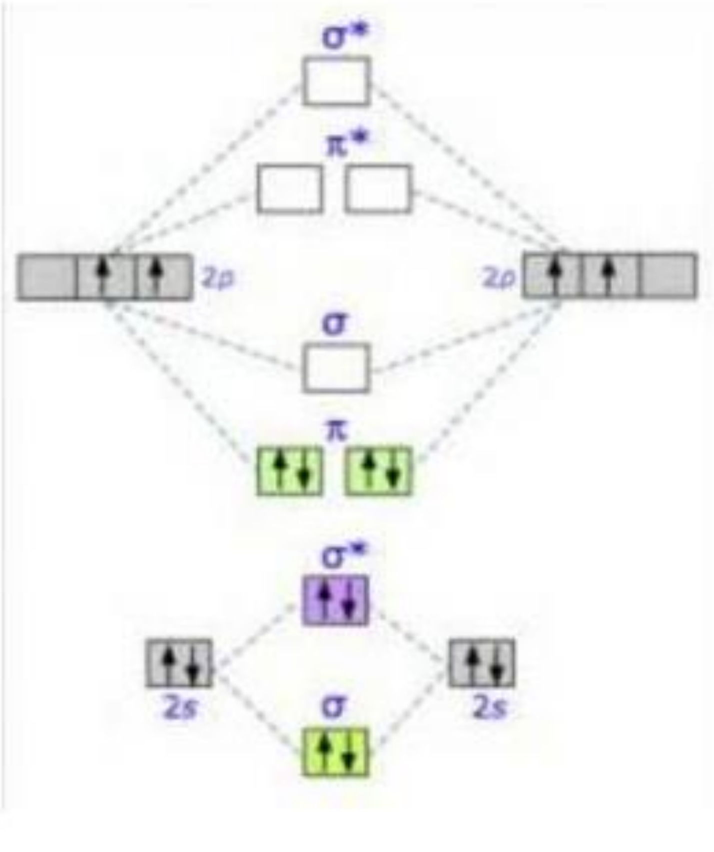
N_b=8,   Na=2

Bond order $= \frac{N_b - N_a}{2} = \frac{8-2}{2} = 3$

Example 3

Draw the molecular orbital diagram for the carbon molecule, C_2. Then, calculate the bond order for C_2.

The atomic number of carbon is 6



N_b=6, Na=2 →Bond order $= \frac{N_b - N_a}{2} = \frac{6-2}{2} = 2$