

## Molecular Orbital Theory - LCAO-MO

Robert S. Mulliken realized that a Linear Combination of Atomic Orbitals (LCAO) could be used to make a set of new Molecular Orbitals (MO). The energies of these new molecular orbitals could be calculated and then filled with valence electrons.



Robert S. Mulliken  
1896-1986

Mulliken received the 1966 Nobel Prize for his work.

In MO theory, molecular orbitals are derived by taking linear combinations of atomic orbitals. Linear combinations implies addition AND subtraction.

**Example 1:**

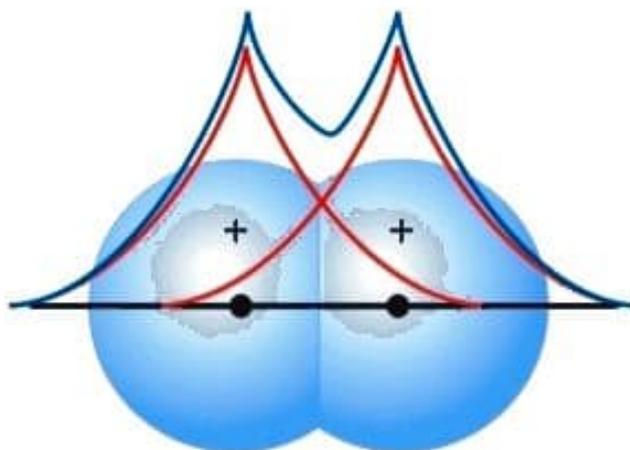
Consider the LCAO orbitals of an  $H_2$  molecule, which is comprised of two Hydrogen atoms, A and B:

$$\sigma_s = \psi_{1s_A} + \psi_{1s_B}$$

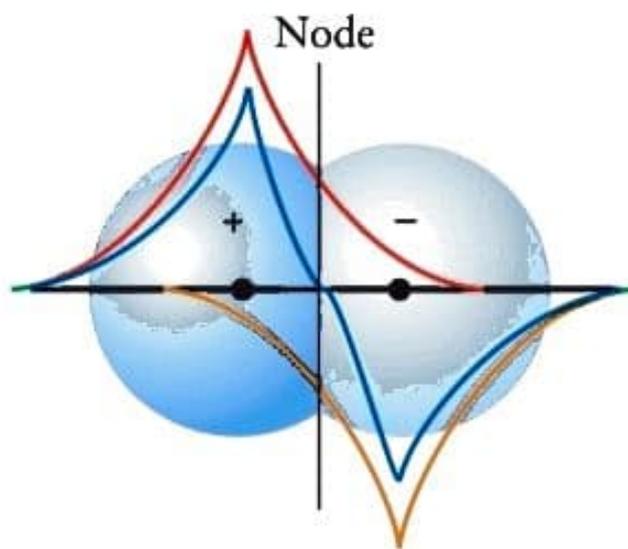
$$\sigma_s^* = \psi_{1s_A} - \psi_{1s_B}$$

The  $\sigma$  molecular orbital has a constructive interference between the two H atom wavefunctions; the  $\sigma^*$  molecular orbital exhibits a destructive interference.

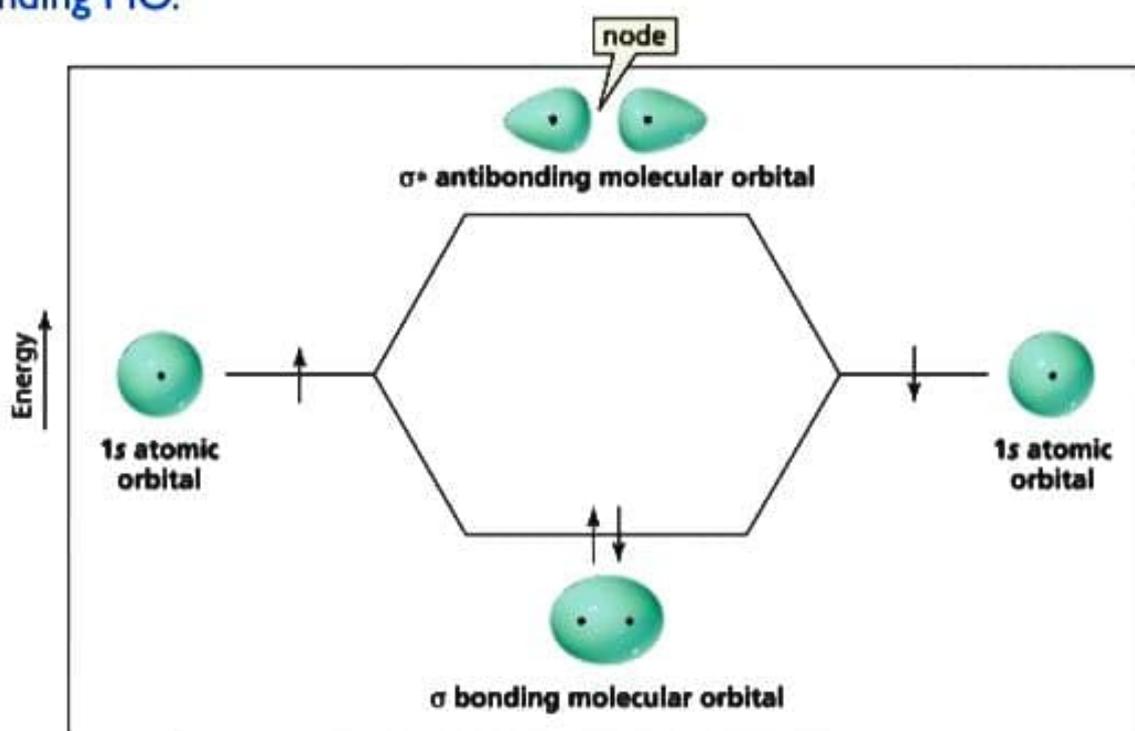
**addition:**  
constructive interference



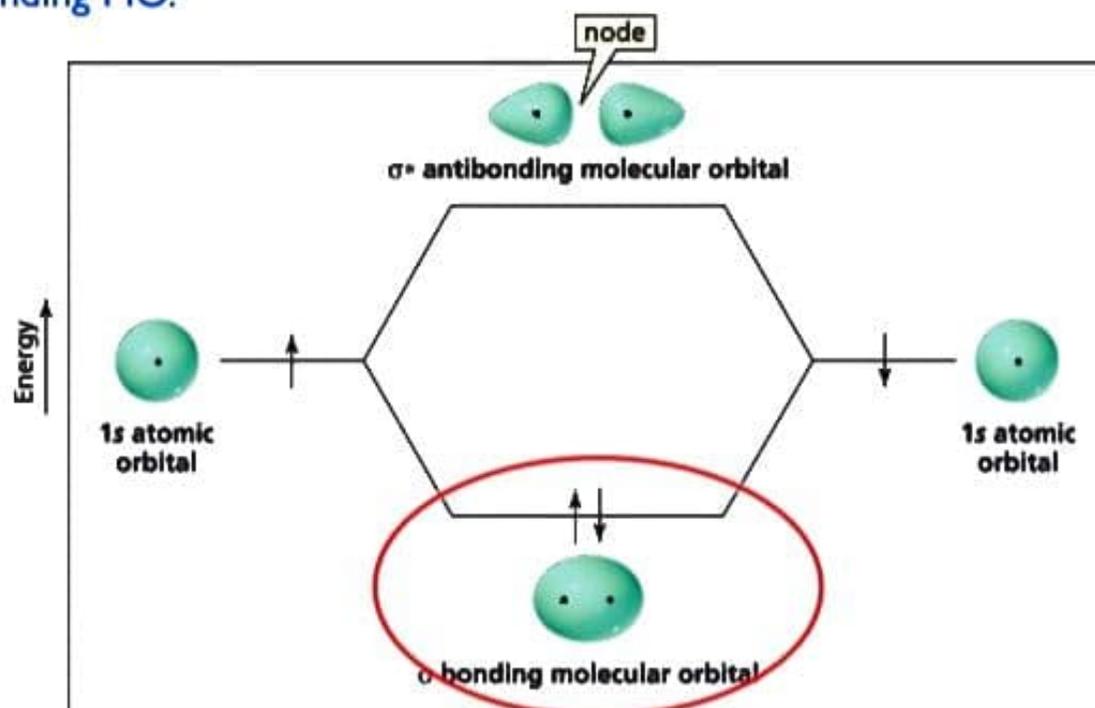
**subtraction:**  
destructive interference



We then calculate the energies of these two molecular orbitals. The  $\sigma$  bonding MO leads to a lower energy state, and the  $\sigma^*$  antibonding MO leads to a higher energy state with a node. The two electrons fill the  $\sigma$  bonding MO.

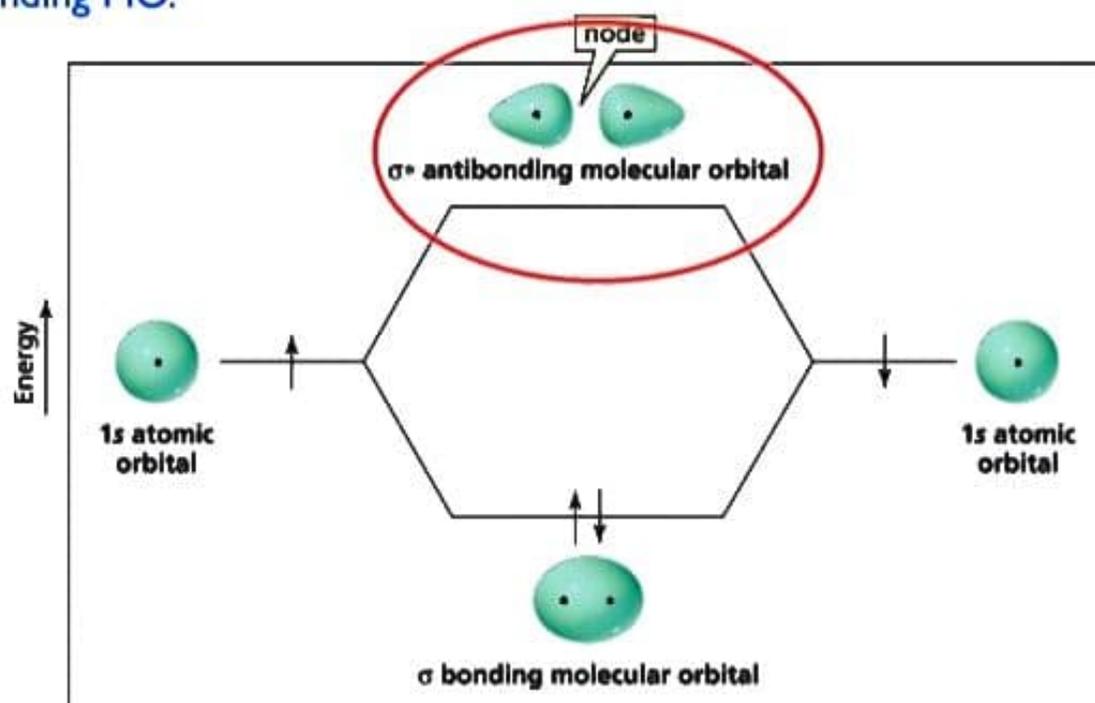


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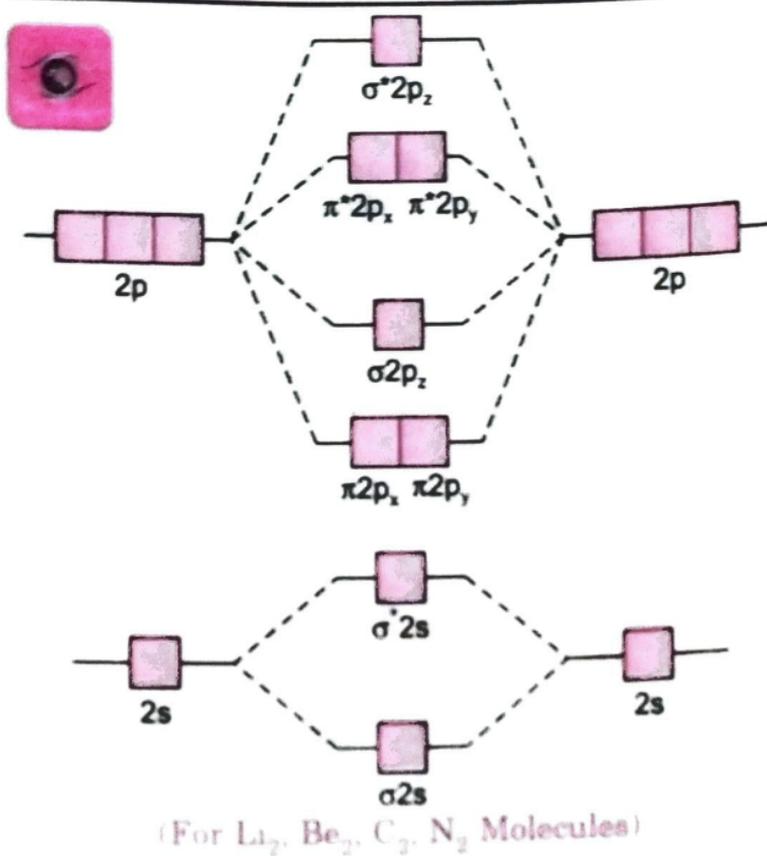
This looks like a  $\sigma$ -bond, which is what we would have predicted from VB theory.

We then calculate the energies of these two molecular orbitals. The  $\sigma$  bonding MO leads to a lower energy state, and the  $\sigma^*$  antibonding MO leads to a higher energy state with a node. The two electrons fill the  $\sigma$  bonding MO.

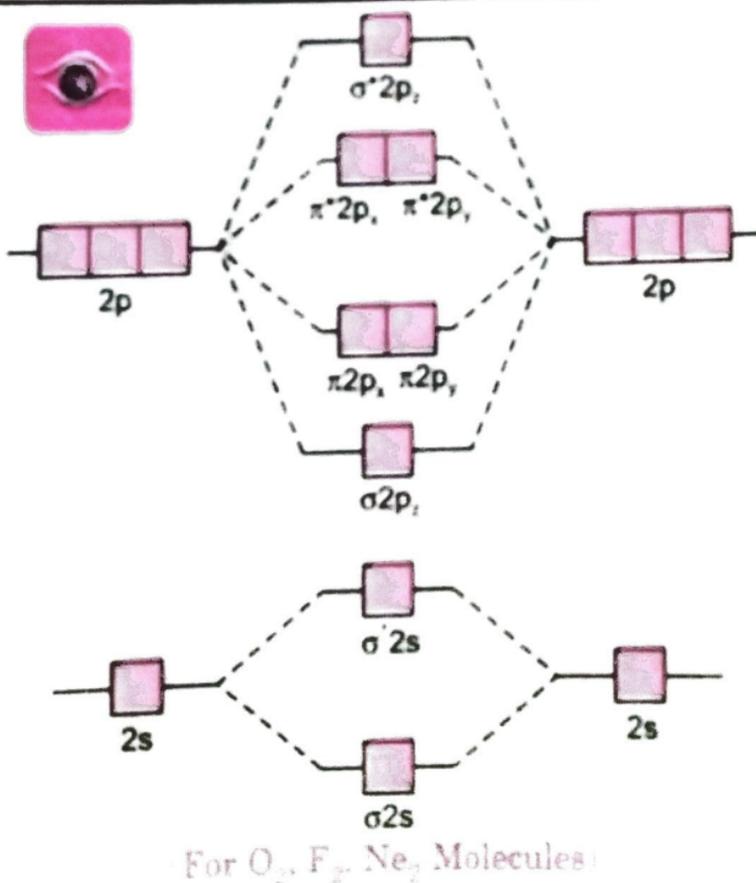


But the  $\sigma^*$  antibonding MO is new and does not come out of VB theory

The main difference between the two types of sequences is that for molecules  $O_2$ ,  $F_2$  and  $Ne_2$ , the  $\sigma_{2p}$  MO is lower in energy than  $\pi_{2p_x}$  and  $\pi_{2p_y}$  MOs while in the case of molecules  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$  and  $N_2$ ,  $\sigma_{2p}$  MO has higher energy than  $\pi_{2p_x}$  and  $\pi_{2p_y}$  MOs.



**Fig. 56. (a)** Molecular orbital energy level diagram for  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$  and  $N_2$  molecules.



**Fig. 56. (b)** Molecular orbital energy level diagram for  $O_2$ ,  $F_2$  and  $Ne_2$  molecules.

The main reason for the difference in sequences is the interaction of  $2s$  and  $2p$  AOs. For the molecules  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$  and  $N_2$ , the differences in energies of  $2s$  and  $2p$  orbitals is small and, therefore, they can interact. While the energies of  $2s$  and  $2p$  AOs for  $O_2$ ,  $F_2$  and  $Ne_2$  is large and therefore, they cannot interact. The discussion is beyond the scope of the present syllabus.

H<sub>2</sub> molecule

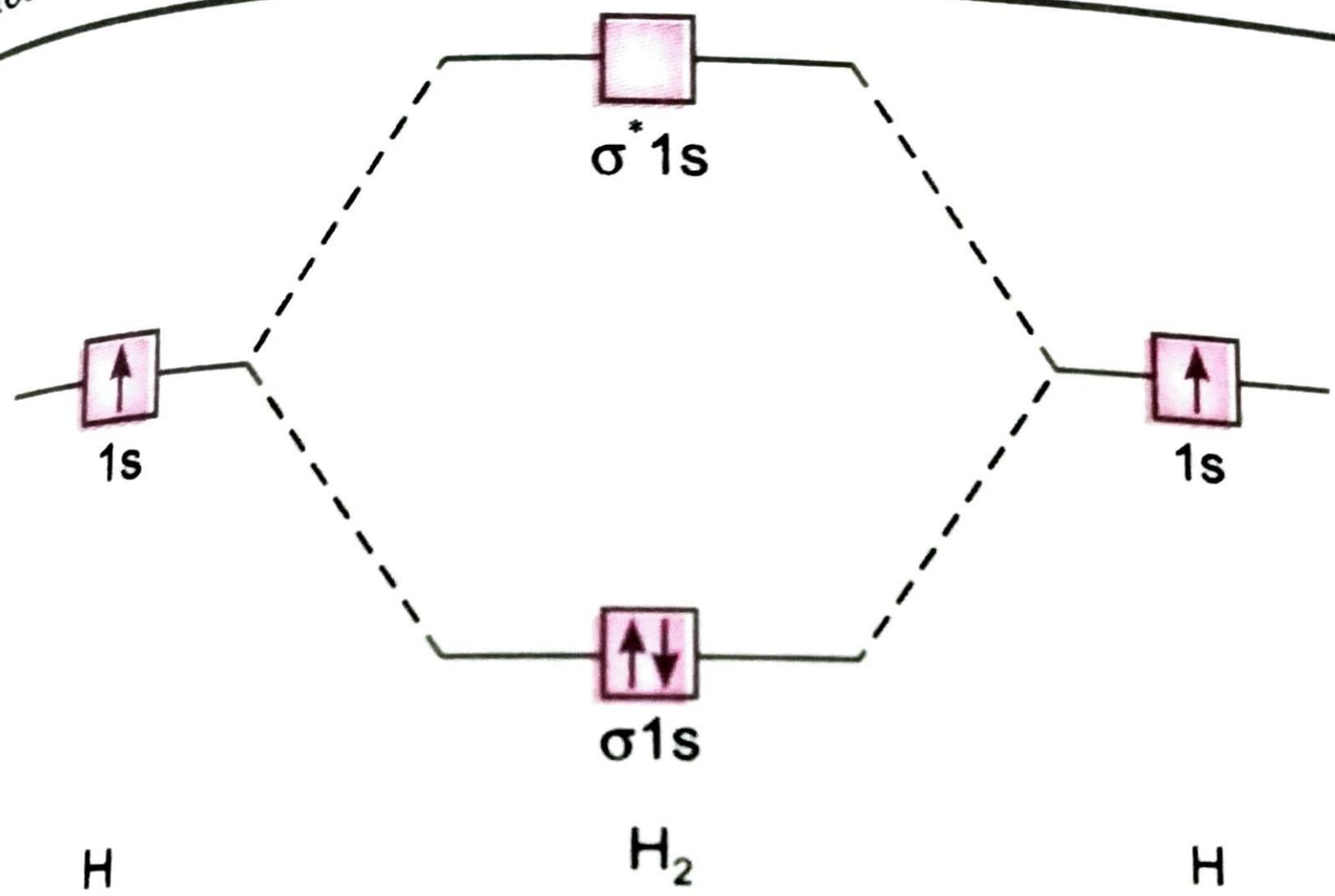
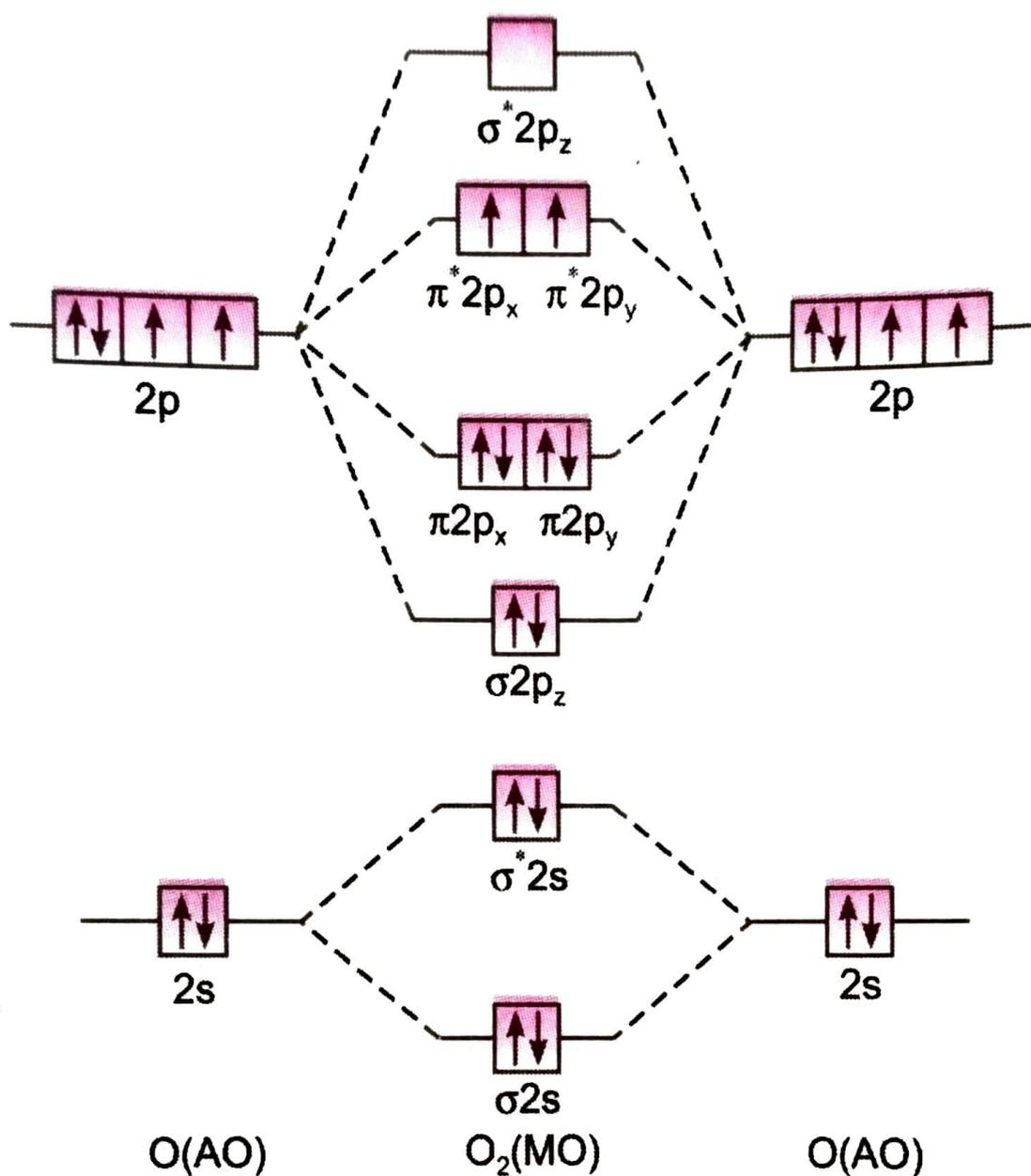


Fig. 57. Molecular orbital energy level diagram for H<sub>2</sub> molecule.

molecule.

**10. Oxygen molecule ( $O_2$ ).** The electronic configuration of oxygen atom is  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ . Therefore, oxygen molecule has 16 electrons. In the formation of molecular orbitals, the electrons in the inner shells are expressed as KK denoting  $(\sigma 1s)^2 (\sigma^* 1s)^2$ . The remaining 12 electrons are filled in molecular orbitals as shown in Fig. 61.



**Fig. 61.** Molecular orbital energy level diagram for  $O_2$  molecule.