

Lecture 27 Title: Understanding of Molecular Orbital

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In this lecture we will understand how the molecular orbitals are formed from the interaction of atomic orbitals.

We will see how the electrons occupy these molecular orbitals.

To start, we take up examples of simple diatomic homonuclear molecules and then we will discuss some heteronuclear molecules.

As the atomic orbitals are important in case of atoms, the molecular orbitals are needed to understand the structure of molecule.

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Molecular orbitals are formed from the combinations of atomic orbitals.

Since orbitals are wavefunctions, they can combine either constructively to form bonding molecular orbitals or destructively to form antibonding molecular orbitals

Why do we need Molecular Orbital theory?

Valence bond theory generally fails to explain the bonding in simple molecules. On the other hand, molecular orbital theory is better approach for the molecules those are having extended π systems.

With the help of molecular orbital one can understand the electronic transitions in molecules.

We have seen in the previous lecture that H_2^+ -ion is stable because of the bonding between the two hydrogen atoms which form a bound state with one electron.

Similar to this, if we consider two hydrogen atoms to form hydrogen molecule, we expect that the wavefunctions of two hydrogen atoms $\phi(a)$ and $\phi(b)$ will interact constructively or destructively.

If they interact constructively then the molecular wavefunction

$$\psi_+ = \frac{1}{\sqrt{2}}(\phi_{1s}(a) + \phi_{1s}(b))$$

This will form bonding orbital. And if they interact destructively, it will form antibonding orbital

$$\psi_- = \frac{1}{\sqrt{2}}(\phi_{1s}(a) - \phi_{1s}(b))$$

We have also realized that the degenerate levels of the two hydrogen atoms will be separated as the two nuclei come closer to each other.

As shown in figure 27.1, the ground state of two hydrogen atomic orbitals split into two energy levels – bonding ψ_+ and antibonding ψ_- .

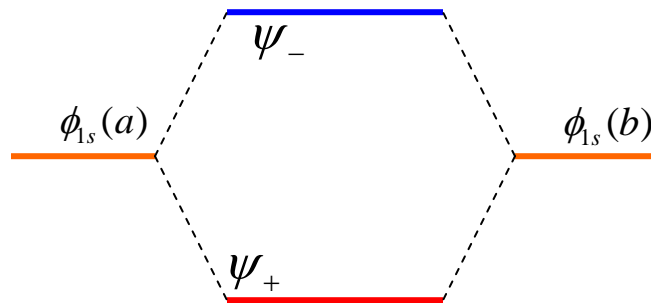


Figure-27.1

Figure-27.2 explains the energies of bonding and anti-bonding molecular orbitals for first row diatomic molecules.

Two electrons in H_2 occupy bonding molecular orbital, with anti-parallel spins. If irradiated by UV light, molecule may absorb energy and promote one electron into its anti-bonding orbital.

The filling of lower molecular orbital indicates that the molecule is stable compared to two individual atoms.

“+” and “-“ sign indicates the sign of the wavefunction.

σ_{1s} is symmetric with respect to the center of inversion (middle point of the bond), this sometimes called as symmetric or gerade and designate as $\sigma_{1s,g}$

σ_{1s}^* is not symmetric with respect to the center of inversion (middle point of the bond), this sometimes called as asymmetric or ungerade and designate as $\sigma_{1s,u}^*$

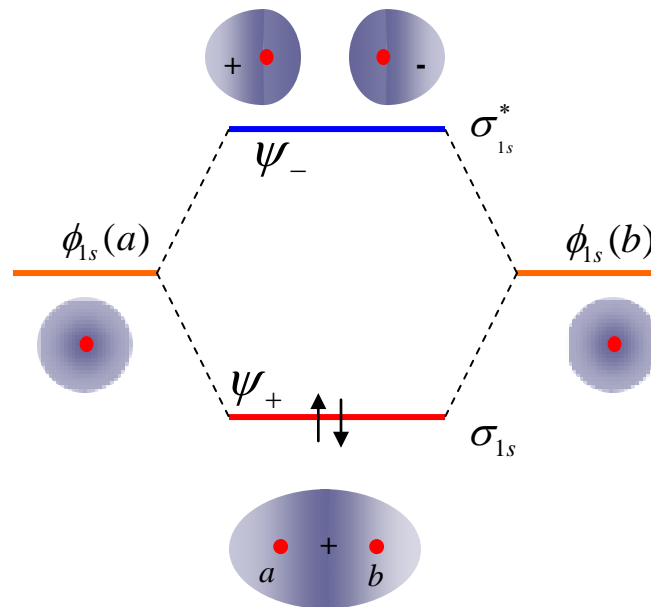


Figure-27.2

Molecular orbital form when atomic orbitals with similar energies and proper symmetry spatially overlap each other.

For homonuclear molecule such as H_2 , N_2 , ...e.t.c

s -orbitals combine with s -orbitals and p -orbitals combine with p -orbitals. In figure 27.2 we have seen the interaction of s orbital with another s orbital.

For p - orbitals :

There are three p_x , p_y and p_z orbitals. If we consider X-axis coincides with internuclear axis then for p_x orbitals, there will be end-on-end overlap along the bond axis as shown in figure 27.3. It forms σ bonding and nonbonding orbitals.

For σ bonding orbital, it is symmetric about the center of inversion and thus it is $\sigma_{2p,g}$

For σ antibonding orbital, it is asymmetric about the center of inversion and thus it is

$$\sigma_{2p,u}^*$$

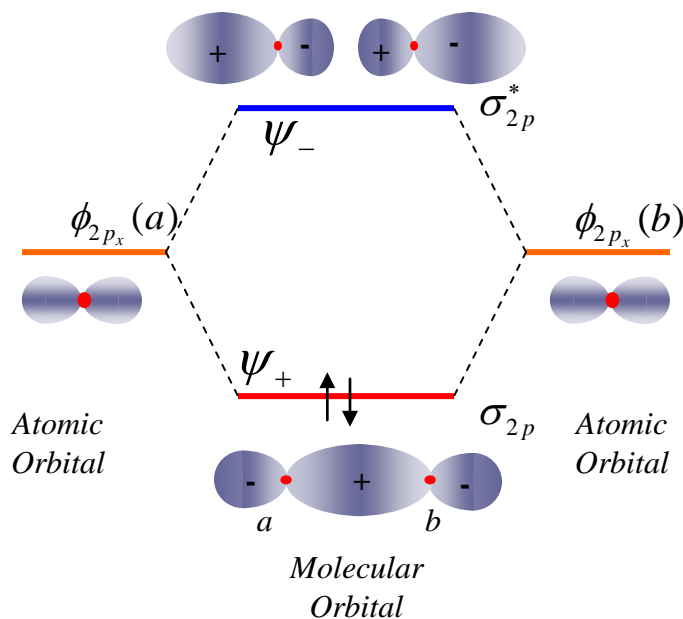


Figure-27.3

The other p_x , and p_y orbitals overlap side-by-side. This is known as π -bonding. This overlap is less than the overlap along the bond axis.

Note that, the overlap is more \rightarrow it will be more stable and thus energy will be lower.

Thus, the π -bonding orbital will be higher in energy than that of the σ -orbital.

π -orbitals are asymmetric with respect to the bond axis as shown in figure-27.4. No electron density surrounding the bond axis. It has node along the internuclear axis.

π_{2p} is asymmetric about the center of inversion, and thus $\pi_{2p,u}$

π_{2p}^* is symmetric about the center of inversion, and thus $\pi_{2p,g}^*$

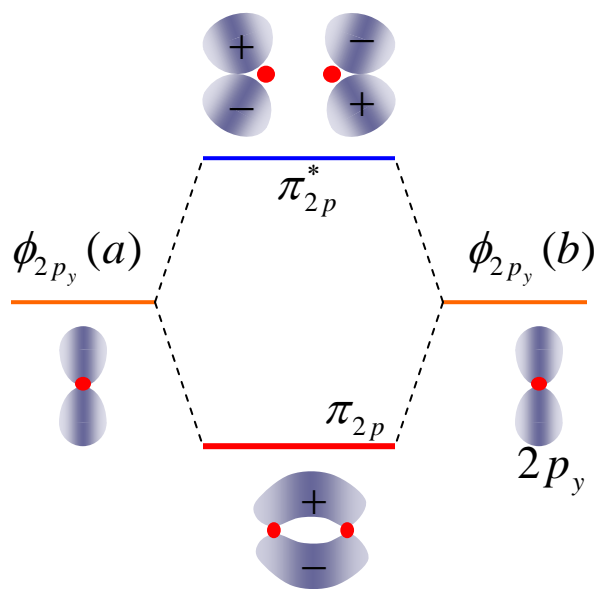


Figure-27.4

Figure-27.5 shows the total energy level diagram for p-orbitals interaction.

Note that σ -orbital is the lowest in energy due to maximum overlap.

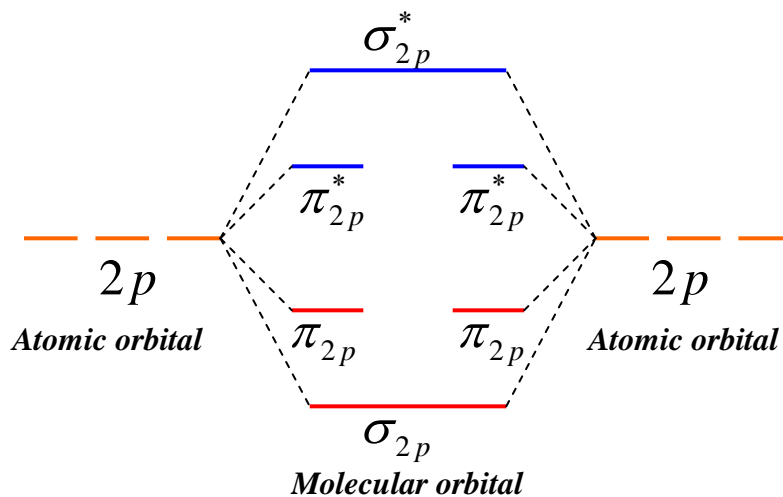


Figure-27.5

Note:

Electron can occupy molecular orbital that are lower in energy.

Molecular orbitals may be empty or contain one or two electrons.

For two electrons occupied orbitals, electrons must be spin paired due to Pauli exclusion principle.

When occupying molecular orbitals, electrons occupy separate orbitals with parallel spin before pairing.

The highest occupied molecular orbital is known as HOMO.

The lowest unoccupied molecular orbital is known as LUMO.

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Let us take an example of oxygen molecule.

Oxygen atom is having electron configuration $1s^2 2s^2 2p^4$. So the oxygen molecule is having total of 16 electrons.

$$1s^2, 1s^2 \Rightarrow \sigma_{1s} \rightarrow \sigma_g$$

$$\Rightarrow \sigma_{1s}^* \rightarrow \sigma_u^*$$

$$2s^2, 2s^2 \Rightarrow \sigma_{2s} \rightarrow \sigma_g$$

$$\Rightarrow \sigma_{2s}^* \rightarrow \sigma_u^*$$

$$2p^2, 2p^2 \Rightarrow \sigma_{2p} \rightarrow \sigma_g$$

$$\Rightarrow \pi_{2p} \rightarrow \pi_u$$

$$\Rightarrow \pi_{2p}^* \rightarrow \pi_g^*$$

$$\Rightarrow \sigma_{2p}^* \rightarrow \sigma_u^*$$

The figure-27.6 shows that for oxygen molecule, there are two unpaired electrons.

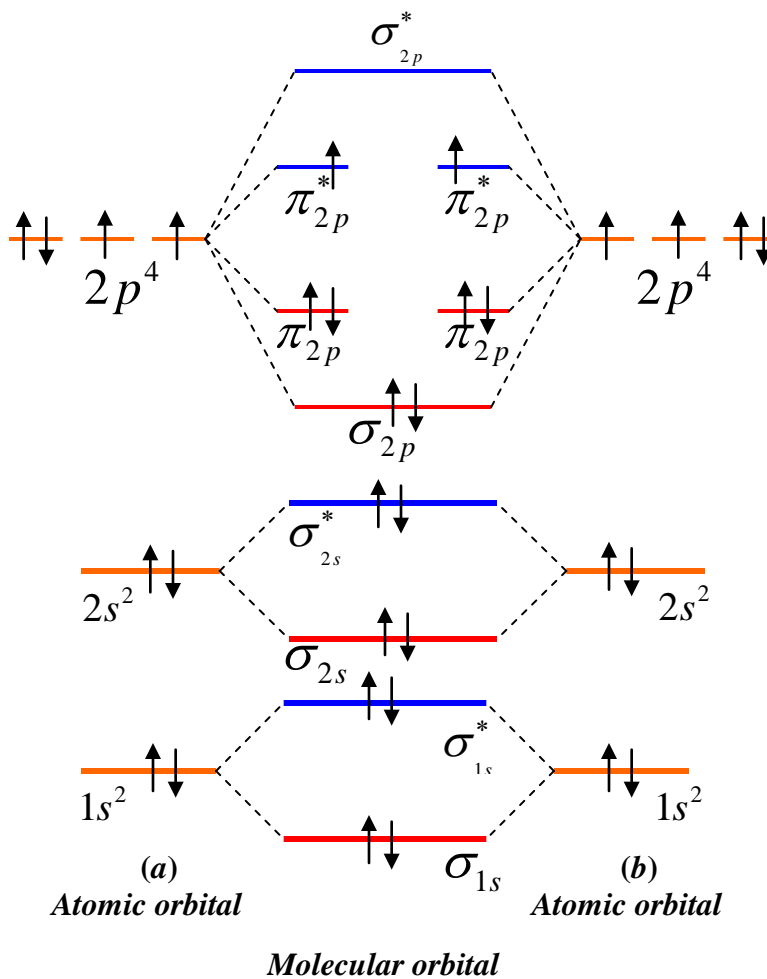


Figure-27.6

Bond order indicates the strength of a bond and is defined as

Bond order = (no. of electrons in bonding orbitals)/2

– (no. of electrons in the antibonding orbitals)/2

For oxygen, considering only the valence electrons (2p orbital)

Bond order = (8-4)/2 = 2. So the result is a double bond.

Bond order =1 (single bond); Bond order = 2 (double bond) e.t.c

For heteronuclear atoms, due to the small energy gap between s and p orbitals, s and p orbitals overlap is possible. Figure-27.7 shows the overlap between s and p orbital.

This interaction could be constructive or destructive.

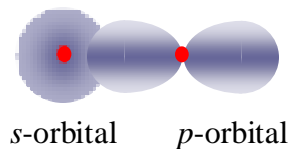


Figure-27.7

Let us take an example of HF molecule. Figure 27.8 shows the energy level diagram of the HF molecule. Hydrogen $1s$ orbital interact with $2s$ and $2p_x$ orbitals of fluorine. $2p_y$ and $2p_z$ orbitals do not have the proper symmetry to interact with $1s$ orbital. So these are nonbonding orbitals.

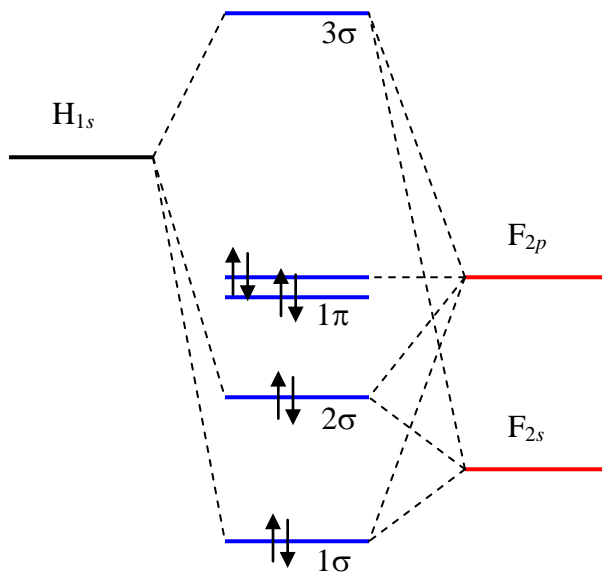


Figure 27.8

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Let us take another example of CO as shown in figure 27.9.

Generally to simplify the things, interactions of the orbitals containing valence electrons are considered to form the molecular orbitals.

The molecular orbital 2σ is the highest filled orbital and is HOMO

The molecular orbital 3σ is the lowest unfilled orbital and is LUMO.

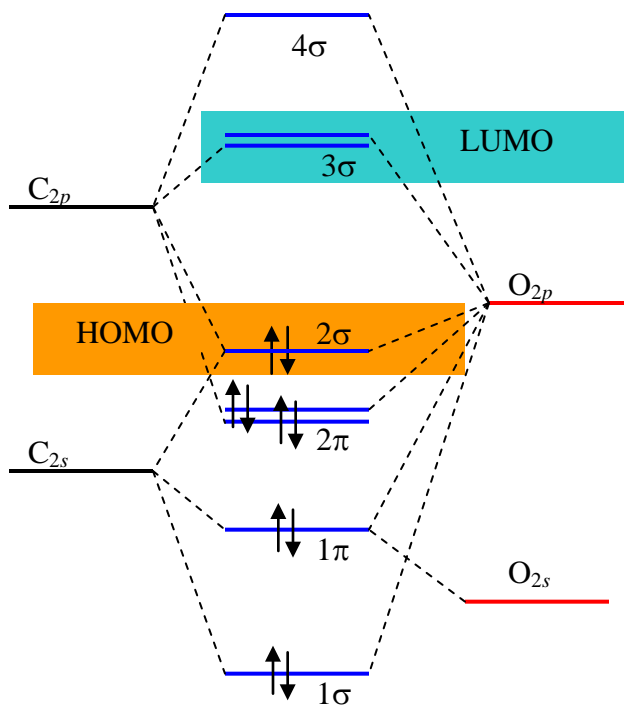


Figure 27.9

Recap

In this lecture we learnt the formation of molecular orbital from the atomic orbitals.

We also came to know about their symmetry such as gerade (g) and ungerade (u) depending on electronic distribution about the center of inversion.

This arises only for the symmetric molecules that have inversion symmetry.

We have also understood how to distribute electrons into the molecular orbitals.

We have also learnt that the overlap is more, orbital will be more stable and thus energy will be lower.

Thus, the π -bonding orbital will be higher in energy than that of the σ -orbital.

We have also learnt that for heteronuclear molecule due to the small energy gap between s and p orbitals, s and p orbital overlap is possible.