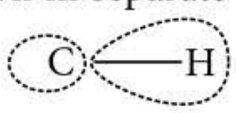
ADVANCED CHEMISTRY BLOC

(Concept of Anti-bonding Orbitals and Their Role in Explaining Chemical Phenomena)

The central theme of molecular orbital theory (MOT) is the linear combination of atomic orbitals (LCAO). Two atomic orbitals combine to produce two molecular orbitals, one of them is anti-bonding molecular orbital. It is true that MOT is relatively complex as compared to VBT but the role of anti-bonding orbital in the explanation of certain phenomena has been remarkable.

Before you begin, see the location of anti-bonding orbital. It lies on the same axis as the bonding orbital. For a C – H bond, two orbitals, bonding and anti-bonding orbitals are shown in separate diagrams.

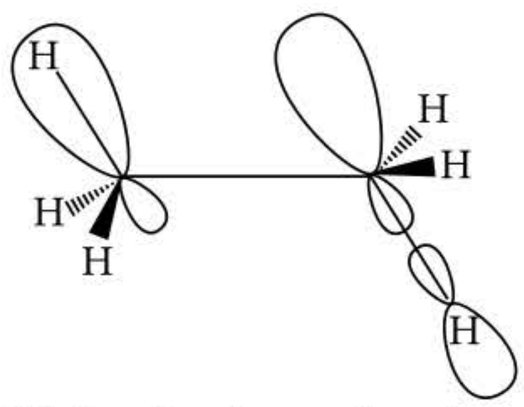


C – H σ orbital

C – H σ* orbital

We know that highest occupied molecular orbitals (HOMO) in oxygen are $(\pi^*_x)^1 = (\pi^*_y)^1$ and oxygen is paramagnetic with bond order two. When two hydrogen atoms combine with one O_2 molecule to form H_2O_2 they push electrons to these anti-bonding orbitals making them fully-filled and reducing the bond order to one. But what about O_2F_2, two fluorine atoms are a bit reluctant to give electrons to oxygen atoms. Though they bind with O_2 molecule but do not fill the anti-bonding orbitals effectively owing to their higher electronegativity. Consequently the O — O bond order in O_2 molecule is not reduced to one. In other words, the O — O bond length in O_2F_2 is smaller than that in H_2O_2.

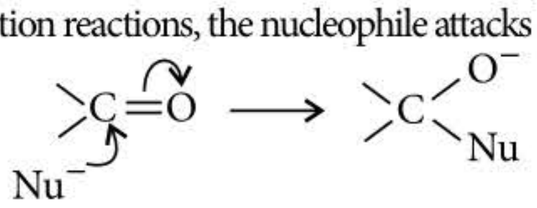
The eclipsed conformation of ethane is less stable than its staggered form. Besides the relaxation from steric factor, the stabilising interaction between the C — H σ-bonding orbital on one carbon atom with the C — H σ* anti-bonding orbital on the other carbon atom is partly responsible. This interaction is greatest when the two orbitals are exactly parallel.



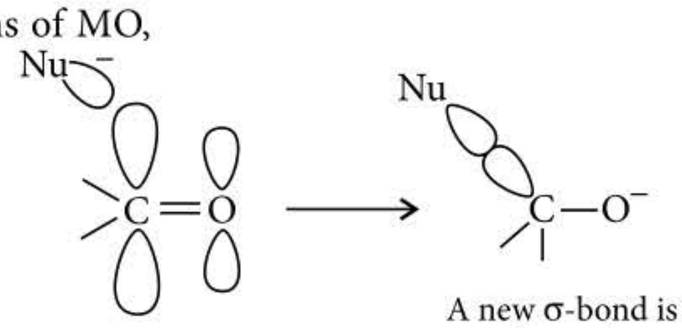
In S_N2 reaction, the incoming nucleophile approaches the leaving group (LG) exactly from opposite side. The anti-bonding orbital of C — LG bond lies on the same axis as the bonding axis.

As the nucleophile fills the anti-bonding orbital, the bond between C — LG breaks. This explains the typical backside attack behaviour of S_N2.

In the addition reactions, the nucleophile attacks $\rangle C{=}O$ group.



In terms of MO,



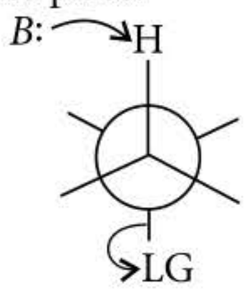
Electrons from nucleophile begin to interact with π* orbital

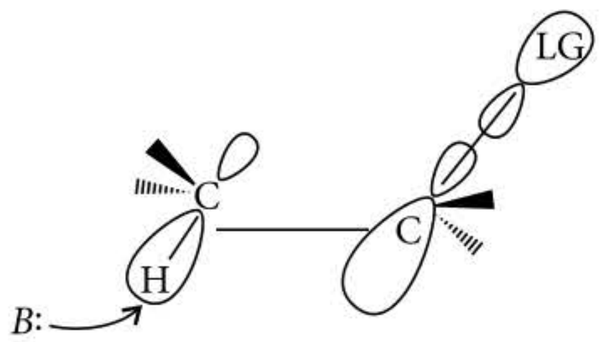
A new σ-bond is formed

As you can notice that the size of lobes on oxygen are smaller as compared to those on carbon. With higher electronegativity, oxygen contributes more to bonding orbital and less to anti-bonding orbital.

The leaving groups must have anti-periplanar arrangement in E2 reaction just before the reaction takes place.

In terms of MO, the C — H bonding electron slowly move to anti-bonding orbital of C — LG bond as the base removes the proton. This smooth transfer is most effective in anti-periplanar rearrangement.





PF_3 : A π-acid ligand accepts back donation from metal. The anti-bonding P — F sigma orbital is well positioned in space to accept the donation.

In Birch reduction, Na pushes electrons to the anti-bonding π* orbital of non-terminal alkyne, which in turn becomes a radical anion. The radical anion then accepts proton from solvent ammonia to form alkene.