

3.2: Background

Molecular orbital theory uses orbitals that belong to the entire molecule to house electrons and represents a more complex theory of bonding than valence bond theory. Specifically, molecular orbitals are constructed by mathematically combining atomic orbitals (s , p , d etc.) using a process known as linear combination of atomic orbitals (LCAO). This process mathematically combines atomic orbitals of similar symmetry and energy both in phase to make bonding orbitals and out of phase to create antibonding orbitals. The mathematics used in LCAO is complex, but doesn't need to be understood to successfully use M.O. theory in a sophomore-level organic chemistry class. For example, we can create a simplified molecular orbital analysis of the H-F bond of hydrogen fluoride by visually combining the sp^3 orbitals of fluorine and the s orbital of hydrogen both in phase (to create the σ bonding orbital) and out of phase (to create the σ^* antibonding orbital) as shown in Figure 1. Recall that bonding orbitals have more electron density between the two nuclei, while antibonding orbitals have more electron density outside of the bond axis. The three additional sp^3 orbitals on fluorine act as non-bonding orbitals in the molecular orbital diagram and function as lone pairs on the fluorine.

These lone pairs represent the highest occupied molecular orbital(s) (HOMO) for HF. The lowest unoccupied molecular orbital (LUMO) represents the lowest energy orbital that doesn't have any electrons in it. In this example the LUMO is the σ^* antibonding orbital. Please note that a more accurate molecular orbital picture would be generated by directly combining the s and p orbitals of fluorine with the s orbital of hydrogen, but this is more challenging to do.

The HOMO and LUMO are considered frontier molecular orbitals because they are at the frontier of where electrons are (or are not). When a molecule donates electrons, they will come from the HOMO and when a molecule accepts electrons, they will be placed in the LUMO. For example, if HF were to act as an electron pair donor (Lewis base) it would use one of the lone pairs that are acting as a HOMO. If HF were to act as an electron pair acceptor (Lewis acid) it would put a pair of electrons into the LUMO. (σ^* orbital). This would cause the corresponding H-F sigma bond to break as the LUMO is a σ antibonding orbital.

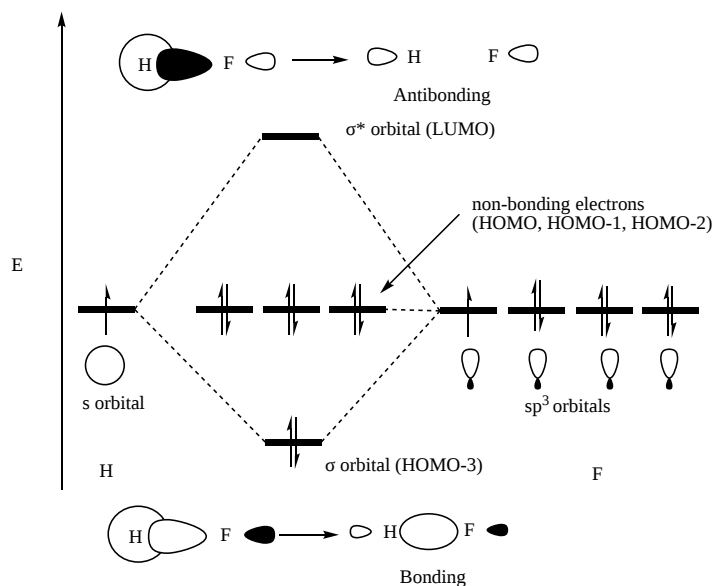


Figure 1. The simplified molecular orbital diagram of the H-F bond in hydrogen fluoride made by visually combining the sp^3 orbitals of fluorine and the s orbital of hydrogen in and out of phase.

While visually combining orbitals in and out of phase works in a qualitative sense for diatomic or selected portions of molecule (e.g., π -systems), it becomes more difficult to do this for more complex systems. Moreover, it is not possible to compute the energy values of molecular orbitals with this visual simplification. With modern computers calculating the molecular orbitals of many different small molecules is convenient and easy. Specifically, in the computational exercise that follows we will be using the quantum chemistry program Orca and a method known as density functional theory to calculate the molecular orbitals of small molecules. By working through the following tutorial, you will learn how to calculate the molecular orbitals of simple molecules using Orca.

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