Introduction

In general chemistry you learned about molecular orbital theory, principally with regard to homonuclear diatomic molecules such as H_2 and N_2. In order to extend a molecular orbital treatment of bonding to polyatomic molecules, we can take advantage of symmetry considerations to simplify the problem. Today's lecture covers this using the water molecule as an example.

Atomic Orbital Energies

Since molecular orbitals arise as combinations of valence atomic orbitals, it is helpful to know something about the intrinsic energies of the atomic orbitals. The term "valence orbital ionization energy" (VOIE) is the amount of energy needed to ionize an electron from a particular atomic orbital. For example, the VOIE of the hydrogen $1s$ orbital is 13.6 eV, such that an electron residing in a hydrogen 1s orbital is at -13.6 eV on the energy scale.

Oxygen is much more electronegative than hydrogen, and among the oxygen valence atomic orbitals, the $2s$ is more electronegative than the $2p$ set. The respective VOIE values are 32.3 and 15.8 eV. You can see that the oxygen $2p$ orbitals are a better energy match with the hydrogen 1s orbital than is the oxygen $2s$. Of these three valence orbital types, the oxygen $2s$ orbital is the most electronegative.

Interactions between atomic orbitals on different atoms (i.e., the formation of covalent chemical bonds and molecular orbitals) are best when the interacting atomic orbitals are close in energy and have good overlap. Ionic character arises when the interacting atoms have orbitals of greatly disparate energy; consider the LiCl molecule.

General Features of MO Diagrams

In an MO diagram, bonding orbitals are lowest in energy, followed by non-bonding orbitals (these correspond to lone pairs of electrons), while highest in energy are the virtual orbitals that include the antibonding counterparts to the bonding orbitals. The highest energy orbital that is filled with an electron pair is called the HOMO (highest occupied molecular orbital), and this orbital is generally the one that confers Lewis base character (or nucleophilic reactivity) on the molecule. On the other hand, the lowest energy unoccupied orbital (LUMO) is the one that is associated with Lewis acidic or electrophilic behavior. For example, the LUMO in BH_3 (D_{3h} symmetry) would be a pure, vacant boron p_z atomic orbital.

The MO Diagram for Water

For this problem we make reference to the C_{2v} character table. Just by consulting this character table, we can sort the oxygen valence atomic orbitals according to their symmetry types: $A_1 : s, p_z$, $B_1 : p_x$, $B_2 : p_y$. Furthermore, we can see that all the MO's for the water molecule will be singly degenerate, since all the irreducible representations for C_{2v} are singly degenerate.

By applying the operations of the point group C_{2v} to the water molecule, we can discover that the two hydrogen atoms in the molecule are *equivalent*. This means that they are interchanged upon application of some of the operations; for example, a two-fold rotation about z exchanges the hydrogens. When we have sets of symmetry-equivalent atoms/orbitals, we can treat them as one piece of the bigger molecular orbital puzzle. We will treat the two hydrogens together as a "stretched H_2" molecule. In general chemistry, you learned that the molecular orbital diagram

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for H_2 has two energy levels corresponding to the H–H σ bonding and the H–H σ^* antibonding molecular orbitals. In other words, the two hydrogen $1s$ orbitals can combine in-phase to produce a bonding MO, or out-of-phase to produce an antibonding MO that has a single inter-nuclear node perpendicular to the H–H bond axis and passing through the bond mid-point.

What are the symmetry types of the H–H bonding and antibonding molecular orbitals within the context of the C_{2v} water molecule? If we take the H–H bonding MO and apply the group operations to it we can generate the following list of characters: 1, 1, 1, 1, showing that the H–H bonding MO belongs to the totally symmetric or A_1 representation. This makes the stretched H–H bonding MO a symmetry match with the oxygen $2s$ and $2p_z$ atomic orbitals, so we will have a total of three A_1 molecular orbitals each with varying contributions from these three components. From these three components we'll generate three A_1 MO's of ascending energy representing bonding, non-bonding/weakly bonding, and anti-bonding character.

Let's find out what characters are generated when carrying out the operations of C_{2v} on the stretched H–H σ^* molecular orbital, taking the convention that the z axis coincides with our principal rotation axis, and that the water molecule resides in the yz plane. Then, here are the characters: 1, -1, -1, 1, so we find that the H–H σ^* is of B_2 symmetry and is thus a match only for the oxygen $2p_y$ orbital. Thus, we will have one bonding MO of B_2 symmetry (in-phase combination, constructive interference), and one anti-bonding MO of B_2 symmetry (out-of-phase combination, appearance of inter-nuclear nodes).

What about the oxygen $2p_x$ atomic orbital? This atomic orbital is of B_1 symmetry and finds no match among the orbitals of stretched H–H. Thus, this oxygen atomic orbital is strictly non-bonding and interacts not at all with the hydrogens upon formation of the water molecule. This atomic orbital is the HOMO in the MO digram for the water molecule.

Remember your Lewis diagram for the water molecule, with two O–H bonds and two oxygen lone pairs? Now we see that this maps onto our MO diagram. The two O–H bonds are of A_1 and B_2 symmetry, and not the same in energy, while the two "lone pairs" are also not the same energy and they're not spatially equivalent, either! Furthermore, we have virtual orbitals of A_1 and B_2 symmetry that are the anti-bonding counterparts to our O–H bonding molecular orbitals. The MO treatment yields more layers of detail to our understanding of molecular electronic structure.

More on Symmetry Equivalent Sets

In the preceding section, we took advantage of our prior knowledge of the MO's in the H_2 molecule. More generally, we could have found the correct symmetry types for our pair of equivalent hydrogen $1s$ atomic orbitals by applying the group operations to this pair together, in order to generate the following reducible representation: $\Gamma_{red} = 2\ 0\ 0\ 2$. By inspection of the character table, you can see that this reduces to $A_1 + B_2$.