# Inorganic Chemistry with Doc M. Group: ____________________

# Fall Semester, 2008 Names: ____________________

# Day 9. Molecular orbital theory IV. Beyond Diatomics continued.

**Introduction.**

We have already learned to create MO diagrams by first considering the B-groups all together when they are identical by symmetry. These groups we called Symmetry adapted linear combinations, or SALCs. The atomic orbitals on the central atom, A, were then overlapped with the symmetry-appropriate SALCs to create molecular orbitals. We used a ten-step process as summarized here.

## 10-step approach to making MO diagrams via symmetry considerations.

Step 1. Sketch the B groups *only* for the molecule/ion in question. This will form the SALC set.

Step 2. Determine the point group symmetry of the molecule/ion and look up its character table.

Step 3. Perform each of symmetry operations one at a time and give a “1” for *each* orbital that remains unchanged from its original position (it did not move.) If it moves, it gets a “0”. Ignore the central element “A” when doing this — only look at the “B” elements. This set of numbers is the *reducible representation*, usually called Γ.

Step 4. Determine the irreducible representation.

Step 5. Sketch the SALCs with appropriate symmetry labels, such as $a_1$, $b_2$, etc. Write in the signs or shade the SALC sets.

Step 6. List ***all*** of the central atoms valence orbitals. In some cases you will need to include empty valence orbitals such as the d-orbitals. This will always be true whenever the octet on the central atom is expanded. Form MOs between the atomic orbitals and the same-symmetry SALC sets. Sketch the MO orbital drawing.

Step 7. Create a MO energy diagram

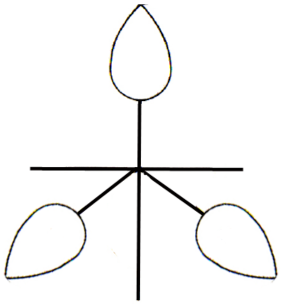
Step 8. Somehow correlate the sketches from Step 6 with the energy diagram from Step 7.

Step 9. Double check to see if you have conserved orbitals and electrons and then populate the MO diagram.

Step 10. Calculate the bond order.

## Other considerations: What if the B groups use p-orbitals for σ-bonding?

All of our examples so far have used hydrogen’s 1s orbital for SALC formation. In a molecule such as $BF_3$, the fluorine atoms form their SALCs from their 2p-orbitals. Considering σ-bonding only, the p-orbitals on the three fluorine atoms that engage in s-bonding are all directed towards the boron. Sketch this arrangement here. It is common to only draw the half of the p-orbital directed inward. This gives it a teardrop appearance.



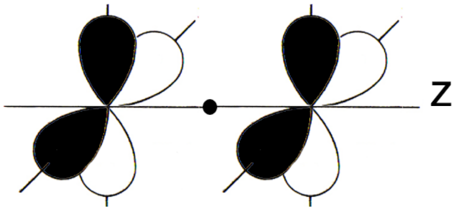
Sketch the atomic orbitals that you would use to form the SALC set for $SF_6$.

When we were focusing on the central atom, A, we had to consider all potential overlaps. So s and $p_z$ would both interact with a SALC if all three had the same symmetry ($a_1$, for example). When it comes to the B-groups, one generally considers only one orbital on the B groups for purposes of σ-bonding. It is either an s-orbital or a p-orbital.

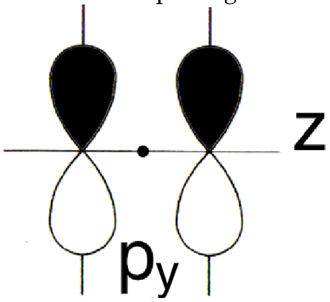
## What if there are double bonds between A and B groups such as in carbon dioxide?

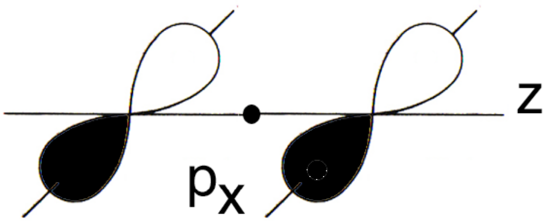
When there are double bonds, you may need two SALC sets. One SALC set will always cover the σ-MOs and another SALC set will cover the π-MOs. The π-set is needed if the double bonds involve more than one of the B groups. For example, for carbon dioxide, we will have a σ-SALC set and a π-SALC set. The latter will involve both the $p_x$ and $p_y$ orbitals on the oxygen atoms. Use the 10-step approach to create a σ-MO diagram for $CO_2$.

Now, let's repeat it for the π-SALC set. The p-orbitals on the oxygen atoms involved in SALC formation are the $p_x$ and $p_y$ because z is the principle axis. Together they look like:



We can do all four at once, but it is simpler to do the $p_x$ and $p_y$ separately. They behave exactly the same way and they do not interact in any way. So, here is just one of the two. For perspective, the paper is the yz plane and the x-axis is poking out at us.





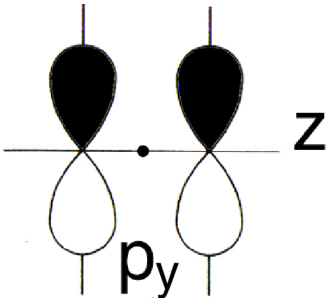
Using the $D_{2h}$ character table, we first apply the symmetry operations on the pair of $p_y$ orbitals:

| | E | $C_2$ | $C_2(y)$ | $C_2(x)$ | i | $\sigma_{xy}$ | $\sigma_{xz}$ | $\sigma_{yz}$ | |
|---|---|---|---|---|---|---|---|---|---|
| Γ | 2 | -2 | 0 | 0 | 0 | 0 | -2 | 2 | |

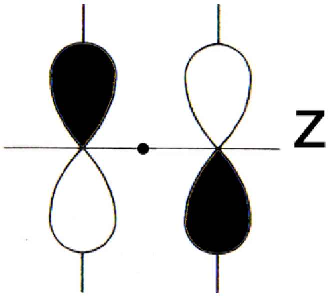
By inspection of the character table, we can solve for the two irreducible representations. Also, we know one of them must overlap with the $p_y$ orbital on carbon, so we know that one of them must be the $B_{2u}$. Determine what the other one must be, remembering that the irreducible representations must add up to Γ.

| | E | $C_2$ | $C_2(y)$ | $C_2(x)$ | i | $\sigma_{xy}$ | $\sigma_{xz}$ | $\sigma_{yz}$ | |
|---|---|---|---|---|---|---|---|---|---|
| Γ | 2 | -2 | 0 | 0 | 0 | 0 | -2 | 2 | |
| $B_{2u}$ | 1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | $p_y$ |
| | | | | | | | | | |

We know what the $B_{2u}$ SALC set must look like because it has to make a molecular orbital with carbon's $p_y$ orbital. The second one is shown at right. Once you complete the chart above, you can use some of the symmetry operations to see how each transforms. For example, i = -1 for $B_{2u}$ but will be +1 for the pne on the right.



**$b_{2u}$**



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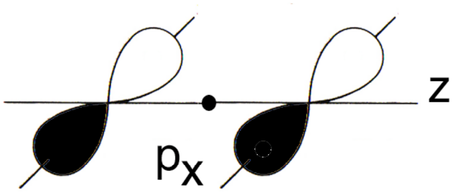
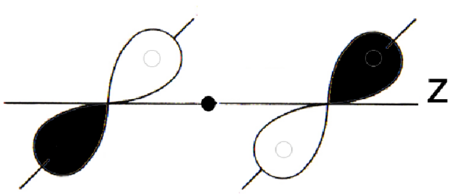
Repeat the entire process for the px orbitals:

| | E | $C_2$ | $C_2(y)$ | $C_2(x)$ | i | $\sigma_{xy}$ | $\sigma_{xz}$ | $\sigma_{yz}$ | |
|---|---|---|---|---|---|---|---|---|---|
| Γ | | | | | | | | | |

By inspection of the character table, we can solve for the two irreducible representations. Similar to the discussion above, we know one of these new combinations must overlap with the $p_x$ orbital on carbon. Determine the reducible representation and the two irreducible representations.

| | E | $C_2$ | $C_2(y)$ | $C_2(x)$ | i | $\sigma_{xy}$ | $\sigma_{xz}$ | $\sigma_{yz}$ | |
|---|---|---|---|---|---|---|---|---|---|
| Γ | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |

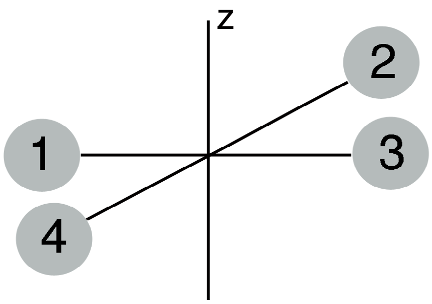




Now go back two pages and add the π-manifold of bonding to the MO diagram. Sketch the orbitals near the energy levels.

## How do doubly degenerate SALC sets work? What sort of MOs will they form?

We have seen doubly degenerate sets of SALCs already when we did ammonia in class. They had the symmetry designation of "E" and under the identity symmetry element in the character table there was a "2." (In a similar way, there will be triply degenerate sets that we will soon encounter when we get to the octahedron. They will be designated as "T" and there will be a "3" under the identity element.) It can be confusing to keep track of what is happening to each atomic orbital and how it is being used to form molecular orbitals. We can use a table to organize our work. The table will feature all of the pertinent atomic orbitals on the central atom, A, across the top (or down the side, your choice) and the SALC orbitals as the rows. The SALC orbitals are given their symmetry names. In doubly degenerate cases, two SALCs will be listed. The table should have rows as it has B-groups. The values inside the cells represent the fraction of the atomic orbital that is being used to create each SALC orbital. Basically, it is the square of the coefficient (the probablility) from the Ψ equation for the SALC.



Let's create a MO diagram for a square planer compound, $AB_4E_2$. As we do so, we will complete the table:

| | AO #1 | AO #2 | AO #3 | AO #4 | Total: |
|---|---|---|---|---|---|
| SALC ( ) | | | | | =1 |
| SALC ( ) | | | | | =1 |
| SALC ( ) | | | | | =1 |
| SALC ( ) | | | | | =1 |
| Total: | =1 | =1 | =1 | =1 | |

Complete the MO diagram for the square plane.

Question. $BF_3$ is flat and a monomer. Most other compounds of similar formula are dimers, such as $B_2H_6$ and $AlCl_3$, which is actually $Al_2Cl_6$. It is thought that $BF_3$ is a monomer because there is some $\pi$-bonding between boron's empty $p_z$ orbital and a SALC set of $p_z$ orbitals on the three fluorine atoms. Create a MO diagram using all that we have learned for $BF_3$.