

Inorganic Chemistry with Doc M.

Fall Semester, 2011

Day 9. Molecular Orbitals, Part 4. Beyond Diatomics, continued

Name(s):	Element:
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Introduction.

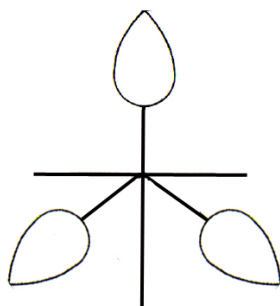
We have already learned to create MO diagrams by first considering the B-groups all together when they are identical by symmetry. These groups we called Symmetry adapted linear combinations, or SALCs. The atomic orbitals on the central atom, A, were then overlapped with the symmetry-appropriate SALCs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



Suppose you were about work up the MO diagram for octahedral SF_6 . The orbital's on fluorine that have the correct energy for bonding to sulfur are the 2p orbital's, not the 2s. In the left box below, sketch the six atomic orbital's (p-orbitals in their entirety) that you would use to form the SALC set. In the right box, sketch the abbreviated form -- either use the tear-drop shape or a circle shape -- but either one represents one lobe each F's p-orbitals.

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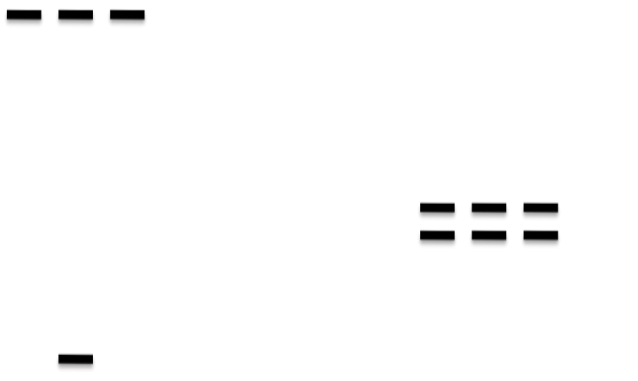
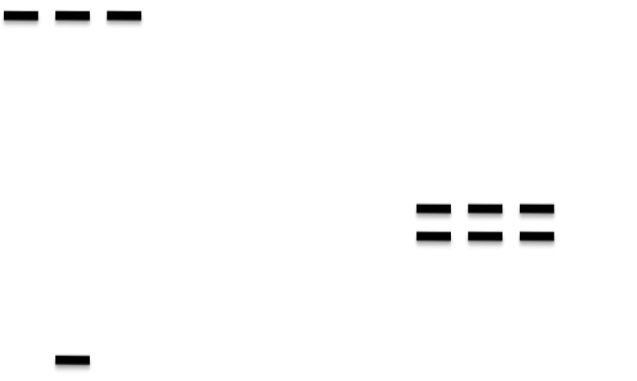
When we were focusing on the central atom, A, we had to consider all potential overlaps. So s and p_z would both interact with a SALC if all three had the same symmetry (a_1 , for example). *When it comes to the B-groups in species with more than one B group, one generally considers only one orbital on each B group 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?

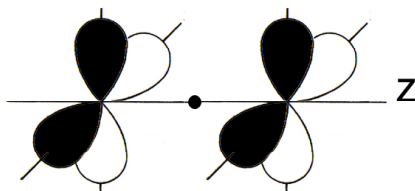
When there are double bonds, we will solve it as two problems in one. One SALC set will always cover the σ -MOs and another SALC set will cover the π -MOs. The π -set is needed if the double bonds involve more than one of the B groups. For example, for carbon dioxide, we will have a σ -SALC set and a π -SALC set. The latter will involve both the p_x and p_y orbitals on the oxygen atoms. Use Steps 1 – 6 of the 10-step approach to create a σ -MO diagram for CO_2 . **Important note:** *As per the discussion in the book, it is possible to substitute a simpler symmetry point group as long as it retains the basic symmetry of the orbitals involved. In this case we will use the D_{2h} instead of the $D_{\infty h}$ which is difficult to work with because of the infinite rotation axis. The principle rotation axis C_2 (or C_{∞}) will be the O-C-O axis, which is also the z-axis.*



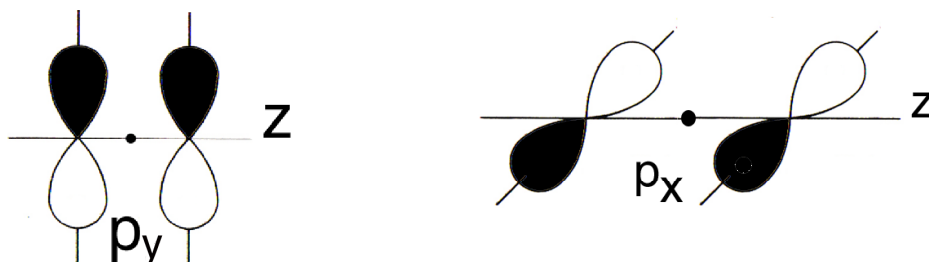
In the left box below, create a σ -only MO diagram for CO_2 (Steps 7-10). Leave the right box blank until later.

σ -only MO diagram for CO_2	π -only MO diagram for CO_2
<p data-bbox="203 966 251 1039">C</p> <p data-bbox="535 945 771 1060">two O atoms: p-orbitals only</p> 	<p data-bbox="876 966 925 1039">C</p> <p data-bbox="1209 945 1445 1060">two O atoms: p-orbitals only</p> 

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.



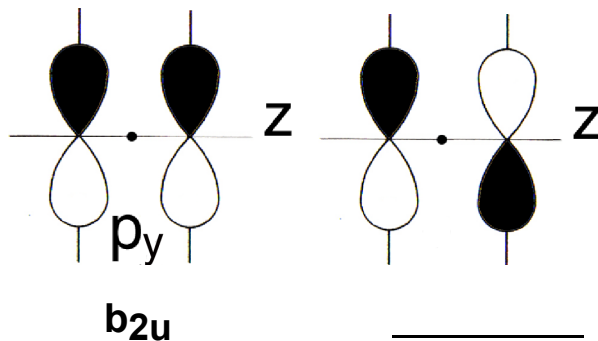
Using the D_{2h} character table, we first apply the symmetry operations on the pair of p_y orbitals:

	E	C_2	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{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	σ_{xy}	σ_{xz}	σ_{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 one at right.

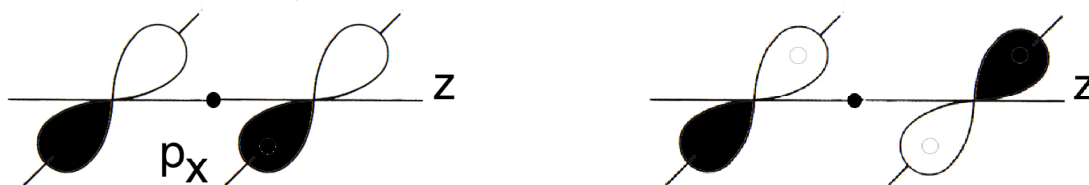


Repeat the entire process for the p_x orbitals:

	E	C_2	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{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.

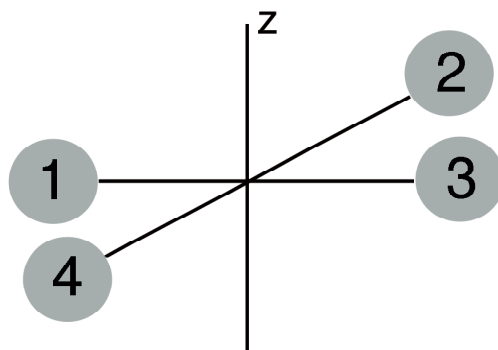
	E	C_2	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}	
Γ									



Now go back two pages and add the π -manifold of bonding to the MO diagram. Add orbital sketches for the MOs 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 as many 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 probability) from the Ψ equation for the SALC.



In the box below, performs Steps 2 – 6 using the diagram above for the square planer compound, AB₄E₂:

Before we sketch the MO diagram, we should complete the following table, designed to keep track of how each atomic orbital (1 – 4 in the picture above) is used to create the SALC set. The first SALC is done for you. Notice how each AO contributes a fraction that add up to 1.

	AO #1	AO #2	AO #3	AO #4	Total:
SALC (a_{1g})	1/4	1/4	1/4	1/4	=1
SALC ()					=1
SALC ()					=1
SALC ()					=1
Total:	=1	=1	=1	=1	

Suppose the central atom has d-orbitals available to it (as would be the case for any expanded octet species). If the central atom is P, S, or Cl, the valence orbitals would be the 3s², 3p³⁻⁵, 4s⁰ and 3d⁰ in that order of increasing energy. The 3s² would be too low in energy to make bonds. If the central element is a first row transition metal such as Mn⁺² or Cu⁺² the valence orbitals, in increasing energy, are 4s⁰(recall why), 3d⁰⁻¹⁰, and 4p⁰. For this problem, let's assume the former, such as would occur for BrF₄. The bromine orbitals are 4p⁵, 5s⁰ and 4d⁰ as placed in the box below. Complete the MO diagram, including the sketching of the orbitals for each molecular orbital.

Br

four F atoms: p-orbitals only

4d — — — — —

5s —



4p — — —

One more! 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 π -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 the 10 step approach twice – once for the σ -manifold and once for the π -manifold.

Steps 1 – 6 for the σ -manifold for BF_3 :

Steps 1 – 6 for the π -manifold for BF_3 :

σ -only MO diagram for BF_3

B

Three F atoms: p-orbitals only

2p — — —

— — —
— — —
— — —

2s —

π -only MO diagram for BF_3

B

Three F atoms: p-orbitals only

2p — — —

— — —
— — —
— — —

2s —