

Inorganic Chemistry with Doc M. Group: _____

Fall Semester, 2009

Names: _____

Day 8. Molecular orbital theory III. Beyond Diatomics

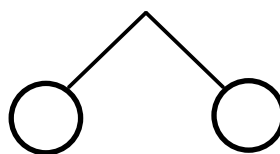
Symmetry adapted linear combinations (SALC) of bonding group atomic orbitals.

For molecules where the central atom is bonded to more than one other B group such as the BeH_2 (AB_2) and H_2O (AB_2E_2) molecules, there is a central atom with orbitals that overlap with atomic orbitals on more than one atom at a time. As the number of B groups (in the ABE designation) increases, the more important it is to have a method for dealing with them all together. (For example, in SF_6 , all of the fluorine atoms have an AO (the 2p) that can σ -overlap with the 3s on sulfur.) To do this we use symmetry and the character tables.

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

Example 1. Water.

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



for water

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

C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$	
A_1	1	1	1	1	z
A_2	1	1	-1	1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

Step 3. For purposes of orientation, the principle rotation axis is always the z-axis. Although it is a fielder's choice after that, let us suppose that the H AOs are in the yz plane. 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. Complete the table:

	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
Γ	2	0		

Step 4. The set of numbers obtained above represent a reducible representation, usually called Γ , of two irreducible representations (from the list A_1, A_2, B_1, B_2). For simple examples such as this one, one can peruse the character table and find which irreducible representations would add up to give the sums determined for the reducible representations. You should get $A_1 + B_2$. Show that they add up to give the sum obtained for the irreducible representation.

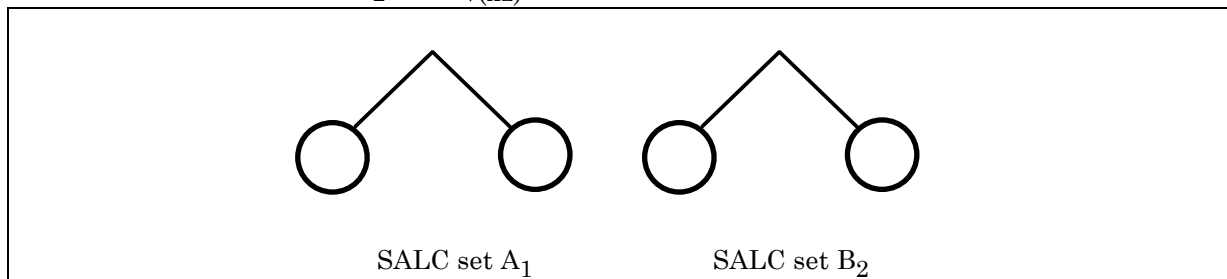
For more complicated situations, one can always get a hint by looking at the noted orbitals in the rightmost column of the character table. The top row always has all +1 values and the s-orbital always “transforms as the top row.” In this character table, it happens to be the irreducible representation “ A_1 .” The s-orbital is never listed, but it is always the top row. All the other orbitals are listed as follows: The “x” refers to the x-axis or, in our case, the p_x orbital, “y” to the p_y orbital, “xy” to the d_{xy} orbital, and so on. More on all this later. In fact, there is a mathematical equation that we will eventually introduce and start using when the examples get tougher, but for now, just looking and thinking is best.

OK, back to what we were doing before that enlightening diversion above. You filled in the box above and should look like this, depending on your handwriting:

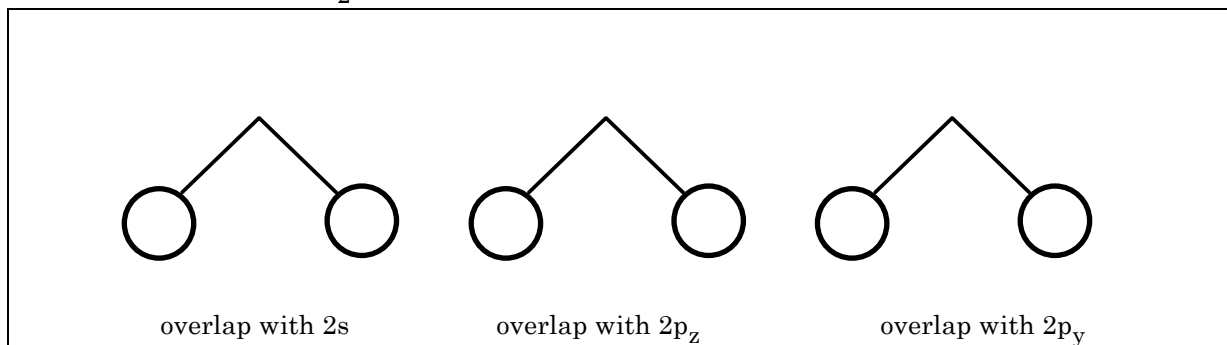
	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
A_1	1	1	1	1
B_2	1	-1	-1	1
Γ	2	0	0	2

You (hopefully) picked $A_1 + B_2$ because these two added up to the reducible representation, Γ . These ($A_1 + B_2$) will give us the *two* SALC sets that result from the *two* atomic orbitals. We will use these to form MOs with the central atom’s AOs. As usual, orbitals are conserved so n AOs will make n SALC sets.

Step 5. Sooooo, one of the SALCs will transform as A_1 and the other as B_2 . The SALC sets both look alike, but each must have the same symmetry as its irreducible representation. In other words, the SALC called A_1 should transform as A_1 does (+1 with respect to all symmetry operations). The SALC set B_2 must transform as irreducible representation B_2 (the sign changes with operations C_2 and $\sigma_{v(xz)}$). Write in the signs or shade the SALC sets below:

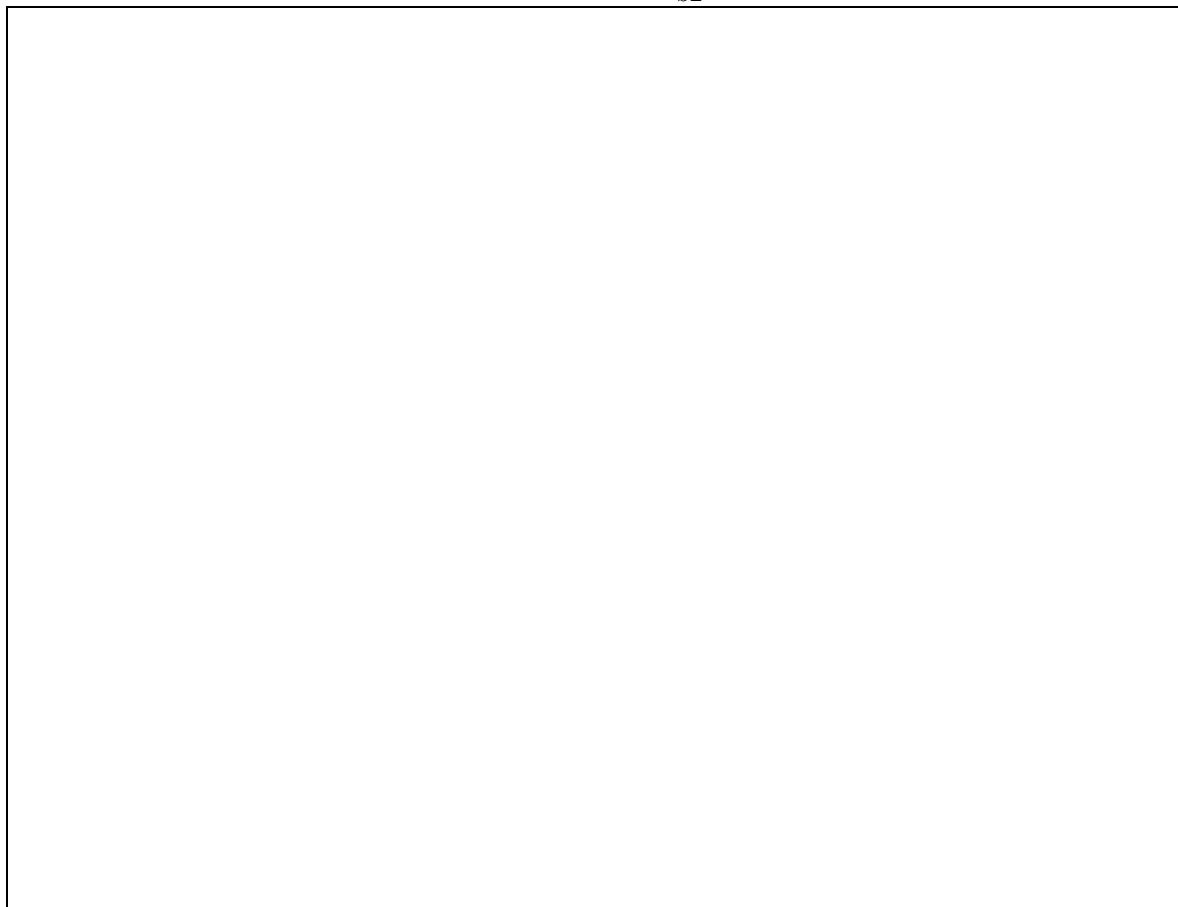


Step 6. Now it's time for the central atom, A, to debut by forming MOs with the two SALCs. We start by checking the symmetry of the atomic orbitals using the character table. The p_z transforms as A_1 (as does the s-orbital in this case), The p_x transforms as B_1 and the p_y transforms as B_2 . Thus, we expect molecular orbitals to be created between the p_y orbital on oxygen and SALC set B_2 . Sketch the MO drawing here



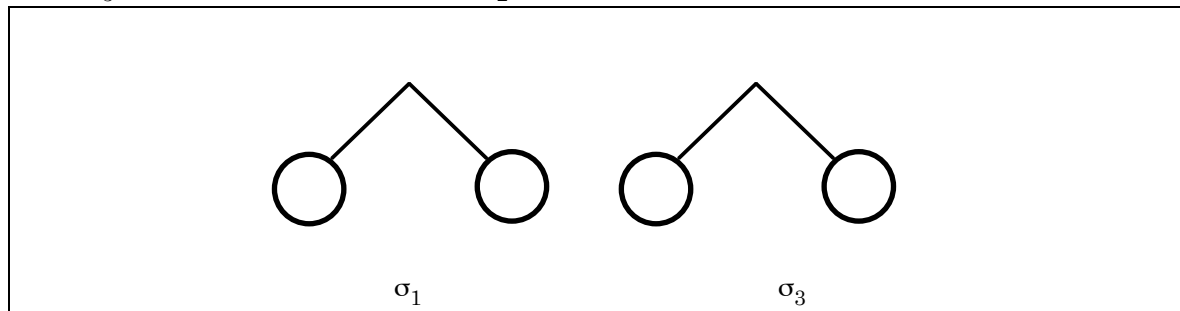
Note to self: The A_1 SALC represents ONE orbital and home to two electrons, no more. When we are showing these two overlaps with 2s and $2p_z$, we have to keep in mind that there is only one A_1 SALC, so we have to divvy it up somehow.

Step 7. Create a MO energy diagram featuring valence atomic orbitals for oxygen (on the left side) and the SALC sets on the right side. Add the MO_{b2} to the MO energy diagram.



Add the *three* MOs that could be called a_1 (two A_1 AOs from oxygen and the SALC A_1 set). Add the non-bonding orbital(s) to the diagram above.

Step 8. Sketch the most bonding a_1 MO here (call it σ_1) and the most anti-bonding a_1 MO here (call it σ_3). (The middle energy orbital, σ_2 , is non-bonding).



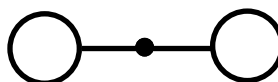
Step 9. Double check to see if you have conserved orbitals and electrons and then populate the MO diagram.

Step 10. Bond order is now:

$$BO = (\text{number of bonding electrons} - \text{number of antibonding electrons}) / (2 \times \text{the number of bonds made})$$

Example 2. BeH_2 .

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



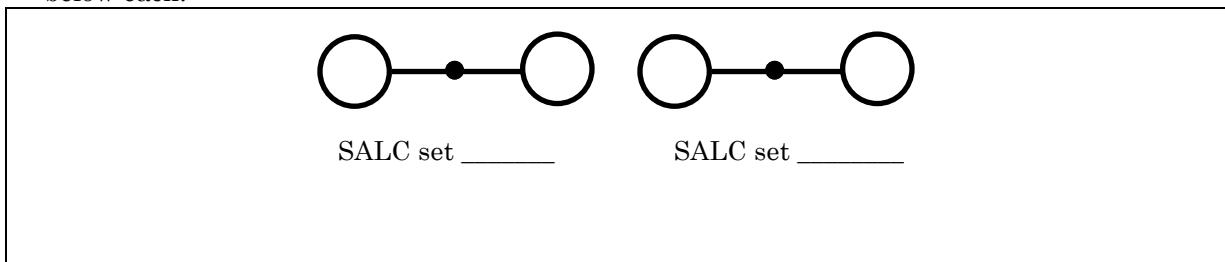
for BeH_2

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

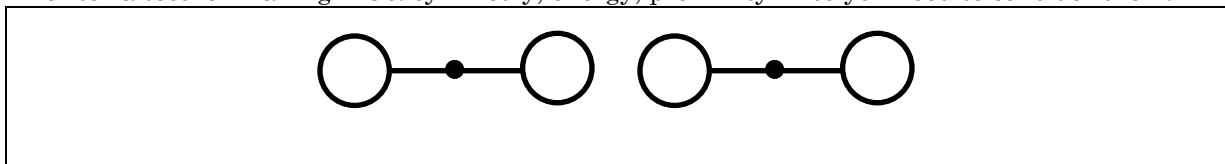
Step 3. Determine the reducible representation, Γ . Perform each of symmetry operations one at a time and give a "1" for *each* orbital that remains unchanged from its original position (it did not move.) If it moves, it gets a "0". Ignore the central element "A" when doing this — only look at the "B" elements. As before, the principle rotation axis is always the z-axis.

Step 4. Determine the irreducible representations.

Step 5. Write in the signs or shade the SALC sets below and write their symmetry designation below each:



Step 6. Add orbitals from the central atom, A, to form MOs with the SALCs. Hint: Even though beryllium does not have electrons in its 2p orbitals, they definitely qualify in terms of the 3-criteria test for making MOs: symmetry, energy, proximity — so you need to consider them.



Step 7. Create a MO energy diagram for BeH_2 .

Step 8. Sketch all of the MOs next to their energy level on the drawing above.

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

Step 10. Determine the bond order.

$$\text{BO} = (\text{number of bonding electrons} - \text{number of antibonding electrons}) / (2 \times \text{the number of bonds made})$$

Optional exercises. Are you looking forward to Day 9? What to be challenged? Repeat the process outlined above for one or more of these:

- a. square planar PdCl_4^{2-}
- b. ammonia
- c. boron trifluoride
- d. carbon dioxide
- e. octahedral SF_6