Inorganic Chemistry with Doc M.
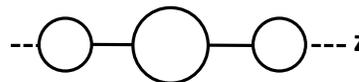
Day 8. Molecular Orbitals: Symmetry adapted linear combinations, SALCs

Topics:

1. Symmetry adapted linear combinations (SALC) of bonding group atomic orbitals
2. The 10-Step approach to making MO diagrams via symmetry considerations
3. Molecular orbital diagram for bent H_2O
4. Molecular orbital diagram for linear BeH_2
5. Molecular orbital diagram for square planer XeF_4
6. Using p-orbitals for σ-bonding: molecular orbital diagram for trigonal planer BF_3

1. 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 OH_2 (AB_2E_2) molecules, qualitatively describing the bonding is more of a challenge, not to mention, a bigger challenge to sketch! We already know that symmetry is one of the three critical factors in creating possible molecular orbitals: the contributing atomic orbitals must overlap in a way that is allowed by symmetry. For example, in the linear molecule BeH_2, the 2s orbital on beryllium can overlap with the 1s orbitals on both hydrogen atoms as shown at right.

How does this work? How are electrons shared? What do the molecular orbitals look like? How do we make an energy diagram? To answer these questions, we use symmetry and the character tables. The basic strategy is to consider the B groups collectively. If there are two B groups such as in BeH_2, they collectively form two symmetry-allowed combinations that can (usually) overlap with the atomic orbitals on the central atom. If there are three B groups such as in pyramidal NH_3 or planer SO_3, they collectively form three symmetry-allowed combinations. Four equivalent B groups (CH_4, XeF_4) form four symmetry-allowed combinations, and so on. These various symmetry-allowed combinations of B orbitals are called symmetry-adapted linear combinations or SALCs for short.
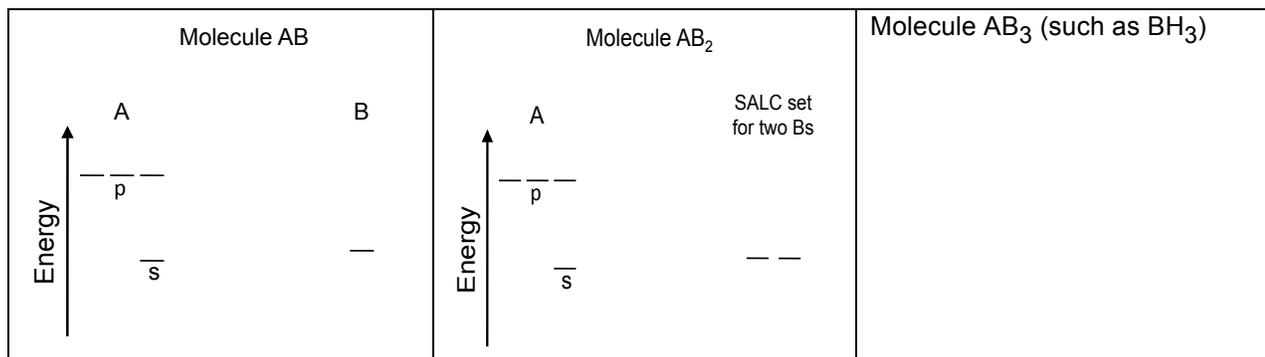
SALC sets do NOT include the central atom. For example, if we were creating a MO sketch for BeH_2, we would need to consider the hydrogen orbitals in the form of a SALC set, without the central atom, Be as shown at right. The orbitals on the central atom are added later for form the molecular orbital:

Molecular orbital(s) = SALC orbital(s) + atomic orbital(s) on central atom

To sketch the MO energy diagram, we draw orbital energy lines under the heading SALC set. At left below shows the general approach for simple heteronuclear diatomics. At right, notice that when there are two B groups, we list them both. The two lines shown under the caption "SALC set for two Bs" are SALC orbitals created from two atomic orbitals. If the atomic orbitals were both 1s orbitals, the SALC orbitals would have the same energy as the 1s orbitals did, because they are separated in space and do not overlap with each other, even though they may have the same symmetry and energy. What would the energy diagram look like if you were embarking on creating one for BH_3?

Molecule AB	Molecule AB_2	Molecule AB_3 (such as BH_3)

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.)

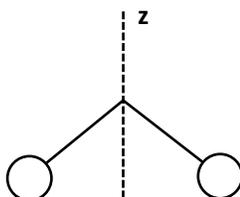## 2. The 10-step approach to making MO diagrams via symmetry considerations.

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 representations that add up to Γ.

Step 5. Sketch the SALCs (the shapes) with appropriate symmetry labels, such as a_1, b_2, etc. Write in the signs or shade the SALC sets. Start sketching the energy diagram – placing the SALCs.

Step 6. List *all* of the central atom's valence orbitals (such as 2s and $2p_x$, $2p_y$, and $2p_z$). 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 picture (with the overlapping lobes) – sketch each SALC and the symmetry-appropriate atomic orbital together – each is an individual molecular orbital.

Step 7. Finish the MO energy diagram

Step 8. 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.

3. Example 1. Water.

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

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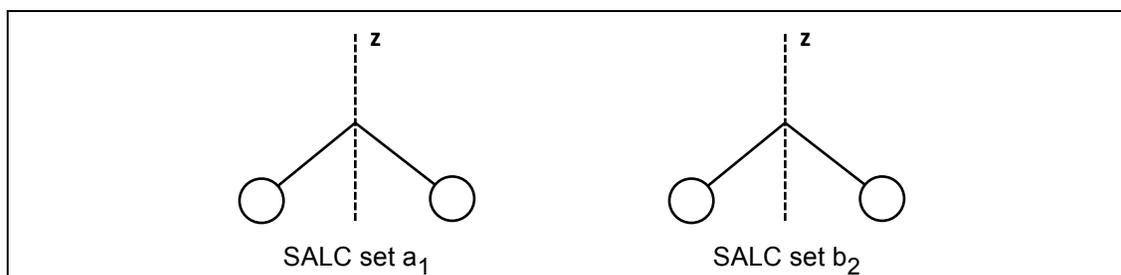
OK, back to what we were doing before that enlightening diversion above. You filled in the box above and should look like this, depending on your handwriting:

	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.
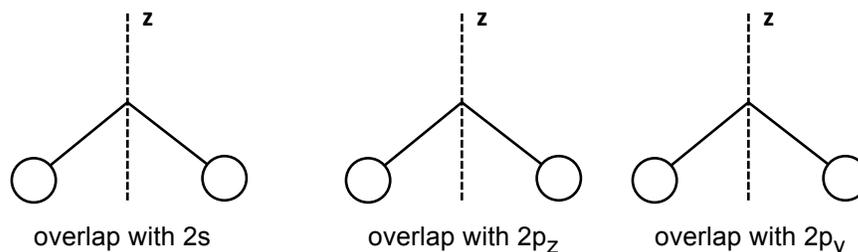
Step 5. Sooooo, one of the SALCs will transform as A_1 and the other as B_2. The SALC sets both look alike, but each must have the same symmetry as its irreducible representation. SALCs are named using the lower case version of their irreducible representation. In other words, the SALC called a_1 should 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:

SALC set a_1 SALC set b_2

Before continuing, make sure you clearly understand that each SALC is ONE orbital, home to no more than 2 electrons. The two atomic orbitals were divvied up to form two SALC orbitals. In this case, the 1s atomic orbital on each H atom was redeployed half in SALC set a_1 and SALC set b_2. Between the two SALCs, both of hydrogen's 1s atomic orbitals are accounted for. (Conservation: two B-groups get rearranged into two SALC groups that will next be used to form molecular orbitals.)

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 molecular orbital drawings here:

z   z   z

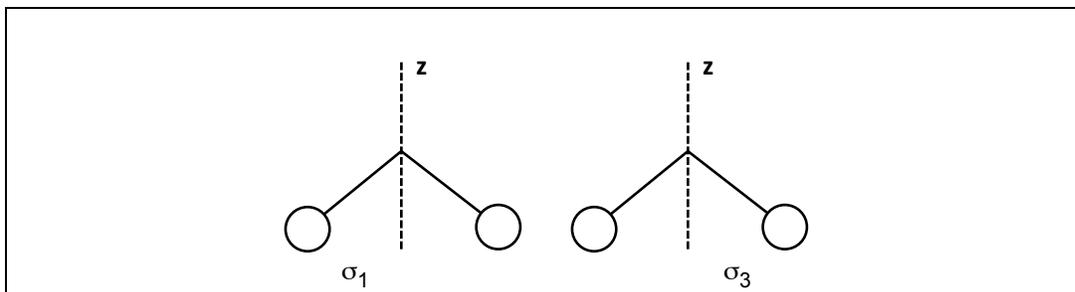overlap with 2s   overlap with $2p_z$ overlap with $2p_y$

Note to self: The SALC a_1 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.)

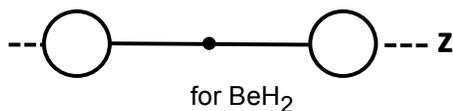z   z

σ_1 σ_3

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:

$$BO = \frac{\text{(number of bonding electrons — number of antibonding electrons)}}{\text{(2 x the number of bonds made)}}$$

4. Example 2. BeH$_2$.

This example is similar to OH$_2$, but definitely easier. Step 1. Start by sketching the B groups *only* for the molecule/ion in question. This will form the SALC set.
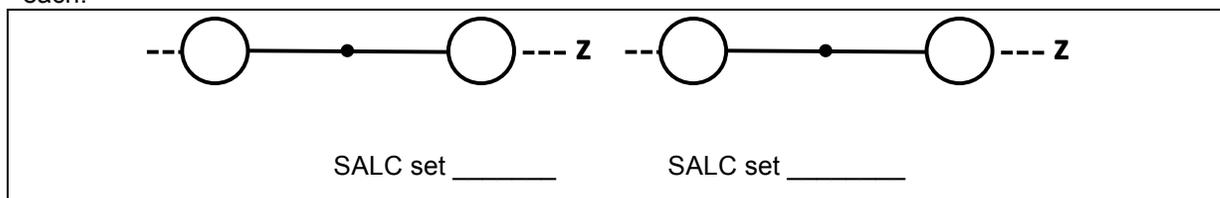

for BeH$_2$

Step 2. Determine the point group symmetry of the molecule/ion and look up its character table. Copy the character table here.
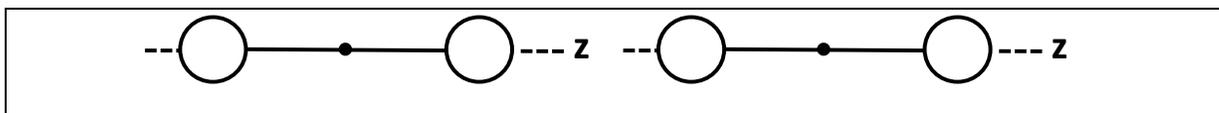
Step 3. Determine the reducible representation, Γ. Perform each of symmetry operations one at a time and give a "1" for *each* orbital that remains unchanged from its original position (it did not move.) If it moves, it gets a "0". Ignore the central element "A" when doing this — only look at the "B" elements. As before, the principle rotation axis is always the z-axis.
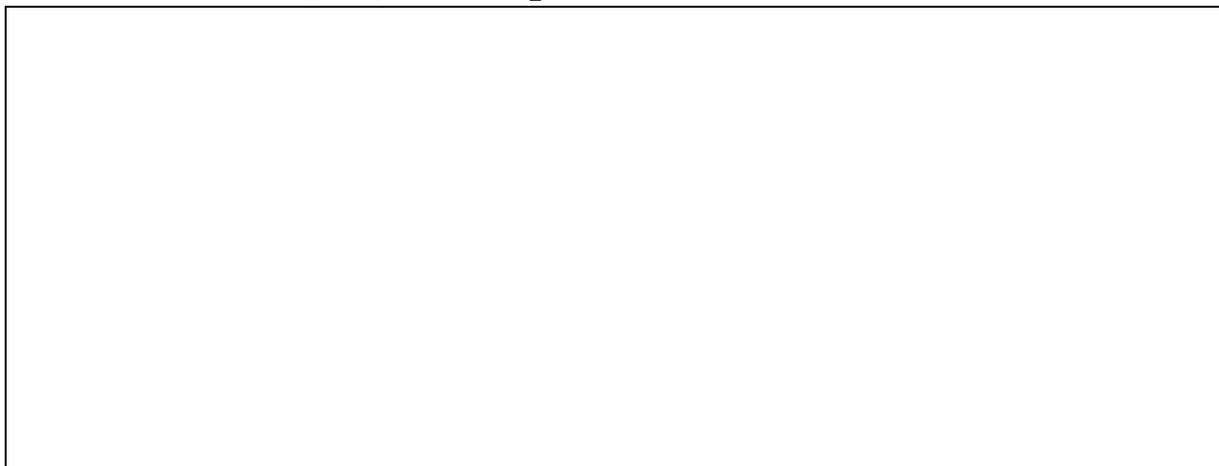
Step 4. Determine the irreducible representations.

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

--○——•——○--- **z**   --○——•——○--- **z**

SALC set _____   SALC set _____

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.
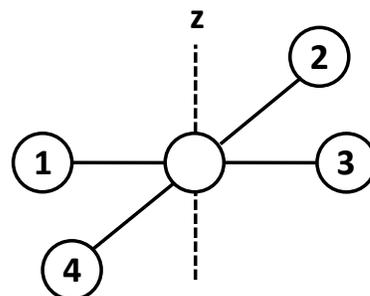
--○——•——○--- **z**   --○——•——○--- **z**

Step 7. Create a MO energy diagram for BeH_2.

Complete Steps 8 - 10.

5. Example 3. XeF_4

We have seen how atomic orbitals work together to form SALC sets that can overlap with the central atom's atomic orbitals. We can next consider how the SALC orbitals on a square planer molecule such as the one shown here can overlap with the central atom's atomic orbitals. It is easy to see how the central atom's s-orbital will overlap, but what about the p-orbitals on the central atom? Any one p-orbital can overlap with either B orbitals 1 and 3 OR 2 and 4, but not with the others. The short answer is that the two p-orbitals, p_x and p_y, together overlap with the four B atom orbitals (in a SALC set, of course). How does this work? What sort of MOs will they form?
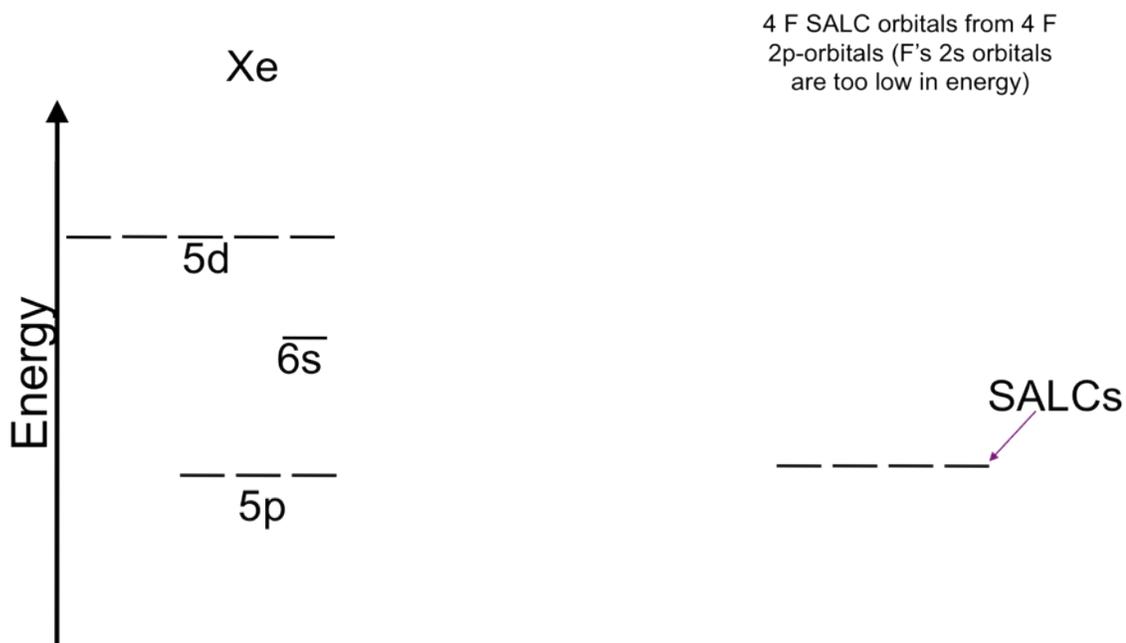
We have seen that the atomic orbitals of the B-groups that form the SALCs, get divvied up. After all is said and done, however, we have to deploy x atomic orbital to form x SALCs. We can use an accounting table to organize our work. The table will feature all of the pertinent atomic orbitals on the central 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, AB_4E_2:

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.

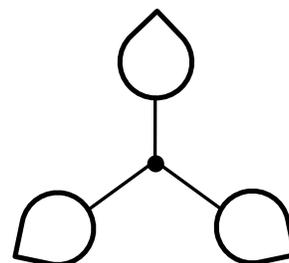|	AO #1	AO #2		AO #4	Total:
SALC (a_{1g})	¼	¼	¼	¼	=1
SALC ( )					=1
SALC ( )					=1
SALC ( )					=1
Total:	=1	=1	=1	=1	

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 $3s^2$, $3p^{3-5}$, $4s^0$ and $3d^0$ in that order of increasing energy. The $3s^2$ 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 $4s^0$(recall why), $3d^{0-10}$, and $4p^0$. For this problem, let's assume the former, such as would occur for XeF_4. The xenon orbitals are $5p^6$, $6s^0$ and $5d^0$ as shown below. We want to use the frontier orbitals – those that are partially filled, just recently filled and/or empty. Complete the MO diagram, including the sketching of the orbitals for each molecular orbital.

4 F SALC orbitals from 4 F 2p-orbitals (F's 2s orbitals are too low in energy)

Xe

Energy

5d

6s

SALCs

5p

6. Example 4. BF₃.

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. Here we will create a MO diagram using the 10 step approach twice – once for the σ-manifold and once for the π-manifold.

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 because the energy of F's 2p orbitals is similar to the energies of boron's 2s and 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 as sketched 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.

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 <u>only one</u> orbital on each B group for purposes of σ-bonding.* It is either an s-orbital or a p-orbital.
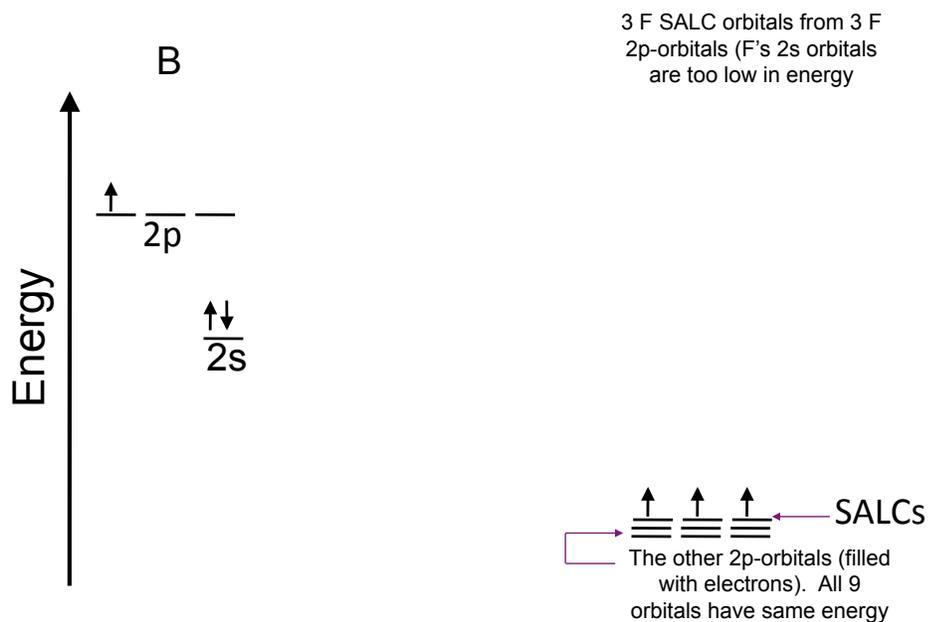

σ-bonding in BF_3

The molecule BF_3 is flat and monomer. Create a reasonable MO diagram using the approach we have learned. You can assume that you can use the p_z orbitals on the three fluorine atoms for σ-bonding and the 2s and 2p atomic orbitals on boron. Perform Steps 1 – 6 for the σ-manifold for BF_3.

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

Now you can complete Steps 7 – 10 for the σ-manifold for BF_3 using this energy diagram:

B

3 F SALC orbitals from 3 F
2p-orbitals (F's 2s orbitals
are too low in energy

Energy

↑ —— ——
2p

↑↓
2s

↑ ↑ ↑ ◄—— SALCs
⎓ ⎓ ⎓
The other 2p-orbitals (filled
with electrons). All 9
orbitals have same energy

π-bonding in BF_3 As stated above, the molecule BF_3 is flat and monomer. It is thought that BF_3 is a

monomer because there is 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 familiar approach for the π-manifold.
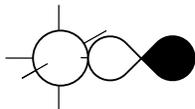
Steps 1 – 6 for the π-manifold for BF_3:

Now combine the σ-manifold and the π-manifold energy diagrams for BF$_3$ into one MO energy diagram.
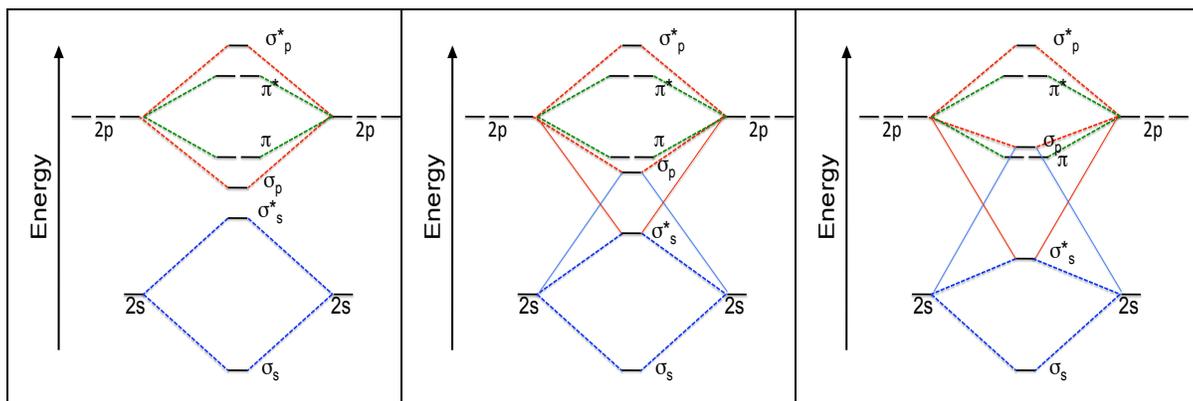
Answers to Day 7.
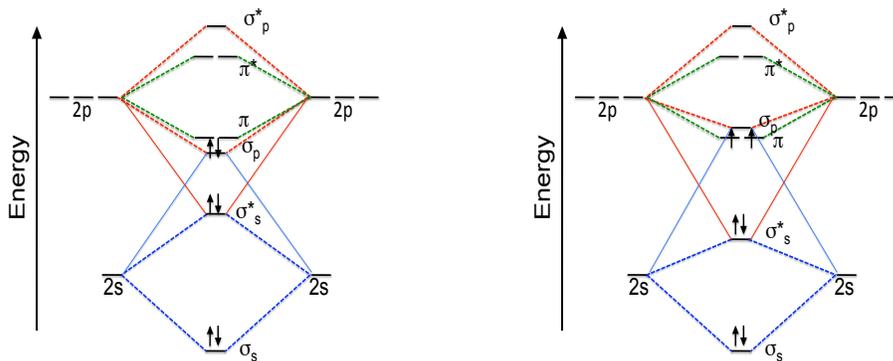
1. similar energy, allowed symmetry and proximity

1C.

Resketch…

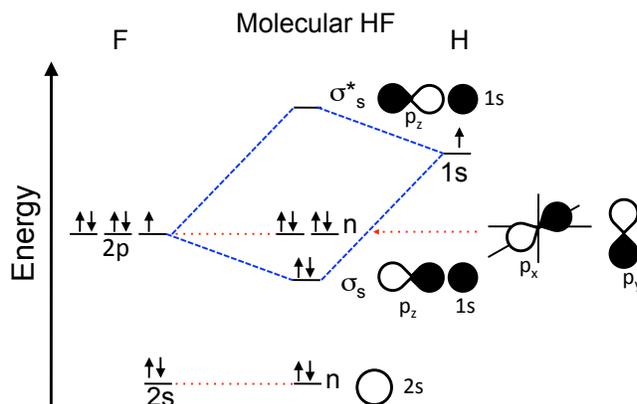2. Populate the new diagrams for B_2. The first one is diamagnetic and the second one is paramagnetic.

3. C_2 has two more electrons than B_2. That would make the left figure paramagnetic and the right figure diamagnetic.
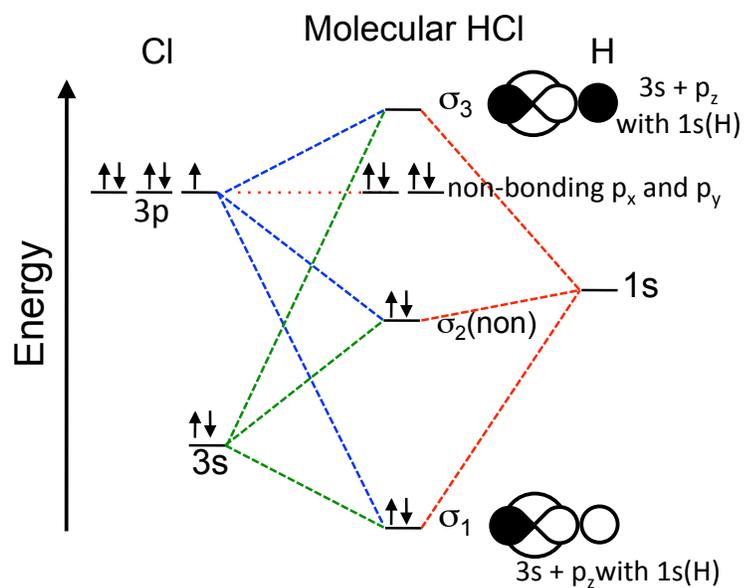
2. HF

The HF bond order is 1.0

The HOMO is more F-like, and the LUMO is more H-like.

2. HCl

Molecular HCl

Cl — 3p ↑↓ ↑↓ ↑

σ_3 3s + p_z with 1s(H)

↑↓ ↑↓ non-bonding p_x and p_y

— 1s

↑↓ σ_2(non)

3s ↑↓

↑↓ σ_1

3s + p_z with 1s(H)

Energy

3. Carbon monoxide. Bond order = 3

Molecular CO

C — 2p ↑ ↑

σ_3

π^*

2s + $2p_z$ with 2s(O)

↑↓ σ_2(non) ↑↓ ↑ ↑ 2p

↑↓ ↑↓ π

$p_{x\,or\,y}$ (C) with $p_{x\,or\,y}$ (O) (only one shown)

2s ↑↓

↑↓ σ_1

2s + $2p_z$ with 2s(O)

↑↓ ↑↓ 2s

Energy