SALC/MO DIAGRAM EXERCISE 2

More SALC exercises! In the interest of time, I have done the first few steps for you so you can focus on figuring out what each SALC looks like and draw the MO diagram. It is up to you to make sure you can get to the same answers that I come to for the first few steps.

Note: for SALC derivation, the rule for character assignments when determining $\Gamma_{orbital}$ are: +1 if orbital stays in same place, same phase, -1 if orbitalsstays in same place, changes phase, 0 if orbital moves

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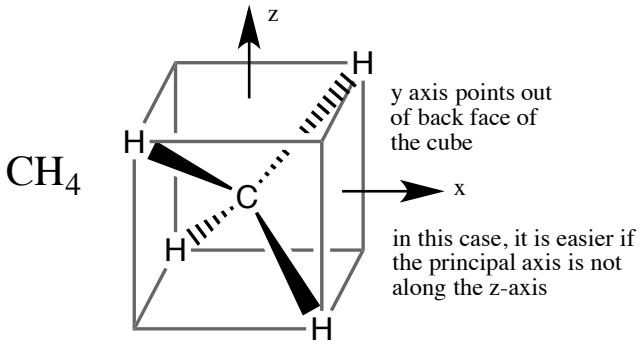
CH_4: In this example, we define the x,y,and z axes slightly differently-the z axis in this case is NOT along the principle rotation axis. If different axis orientations are required to easily complete a problem, this will be provided to you.



Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

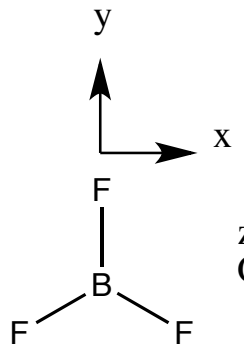
1) Identify point group: **T_d**
2) Identify relevant orbitals:
   Valence orbitals of C? **2s, 2px, 2py, 2pz**
   Valence orbitals of H? **1s**

3) Determine $\Gamma_{orbital}$ for all of the relevant valence orbitals of the H's in CH_4
In CH_4, this means we only have to do the 'gamma' for the 1s orbitals of the H's.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{1s} =	4	1	0	0	2

4) Use the reduction formula to find irreducible representations
   $\Gamma_{1s} = A_1 + T_2$

5) Using the above results, draw the 4 SALCs of the H atoms in CH_4, matching their symmetry to the symmetry of the appropriate orbitals on the central atom (as determined by the irreducible representations and character table). Draw the MO diagram on the back of this page.

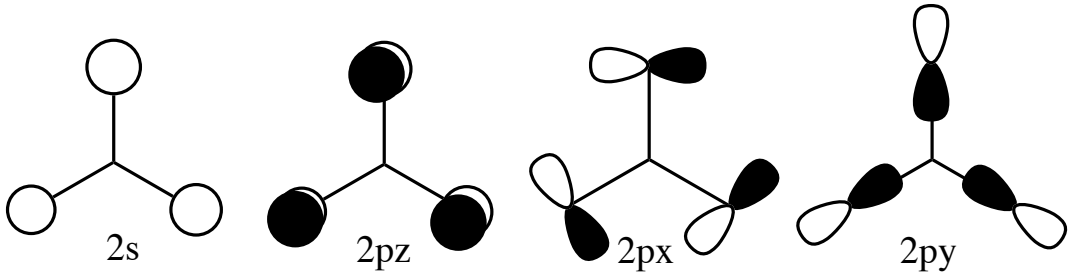


z axis along C3 axis

Character table for D_{3h} point group

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
A'_1	1	1	1	1	1	1		x^2+y^2, z^2
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

orbital orientations used for deriving reducible representations, use these as a starting point for your SALCs



BF_3: Note the orientations of the py and px orbitals.

1) Identify point group: **D_{3h}**
2) Identify relevant orbitals:
   Valence orbitals of F? **2s, 2px, 2py, 2pz**
   Valence orbitals of B? **2s, 2px, 2py, 2pz**

3) Determine $\Gamma_{orbital}$ for all of the relevant valence orbitals of the H's in CH_4
In CH_4, this means we only have to do the 'gamma' for the 1s orbitals of the H's.

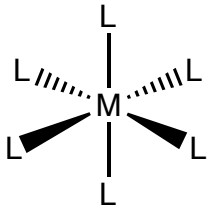
D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{2s} =	3	0	1	3	0	1
Γ_{2py} =	3	0	1	3	0	1
Γ_{2pz} =	3	0	-1	-3	0	1
Γ_{2px} =	3	0	-1	3	0	-1

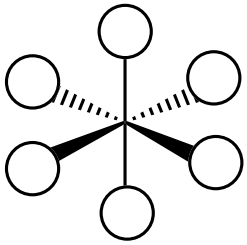
4) Use the reduction formula to find irreducible representations

$\Gamma_{2s} = A_1' + E'$ **$\Gamma_{2py} = A_1' + E'$** **$\Gamma_{2pz} = A_2'' + E''$** **$\Gamma_{2px} = A_2' + E'$**

5) Using the above results, draw the 12 SALCs of the F atoms in BF_3, matching their symmetry to the symmetry of the appropriate orbitals on the central atom (as determined by the irreducible representations and character table). Draw the MO diagram on the back of this page.

Now let's consider a generic ML_6, considering only sigma interactions between the HOMO of the ligand (we'll say these are 2s orbitals for simplicity) and the 3d, and 4s electrons on the metal center. Using the octahedral character table, derive the SALCs that I presented in class using the same steps as presented above. The x, y, and z axes are directed along the M-L bonds.





Character table for O_h point group

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		