SALC/MO DIAGRAM EXERCISE

This exercise will take you through how to derive SALCs for simple multinuclear molecules and derive molecular orbitals for these as well. We will walk through this using the steps detailed in the lecture slides. A SALC is a combination of orbitals from the non-central atoms of a molecule that can interact with the central atom of a molecule. Each SALC is made one type of orbital (i.e. s, pz, px, or py) from the non-central atoms

Let's begin with NH_3:

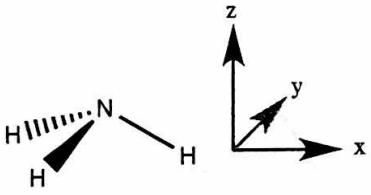
1) Identify the point group of NH_3: NH_3 is trigonal pyramidal and belongs to the C_{3v} point group

2) Identify relevant orbitals:

   What valence orbitals are present in N? 2s, 2px, 2py, 2pz

   What valence orbitals are present in H? 1s

3) Determine $\Gamma_{orbital}$ for all of the relevant valence orbitals of the H's in NH_3
   Consider the following orientation of NH_3 relative to the coordinate axes.



Character table for C_{3v} point group

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

	E	$2C_{3(z)}$	$3\sigma_v$
Γ_{1s}	3	0	1

4) Use the reduction formula to determine the irreducible representations that make up each reducible representation. Match the irreducible representations with the orbitals that have the same symmetry. These are the orbitals on the central atom that your SALCs can interact with.

$$n(A_1) = \frac{1}{6}\left((1)(1)(3) + 0 + 3(1)(1)\right) = 1$$

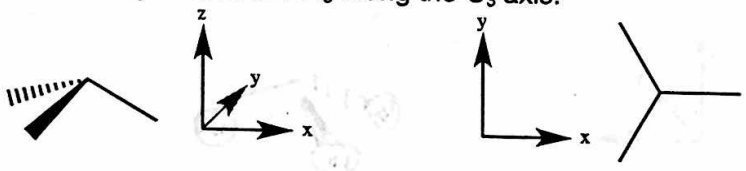
$$n(A_2) = \frac{1}{6}\left((1)(1)(3) + 0 + 3(-1)(1)\right) = 0$$

$$n(E) = \frac{1}{6}\left((1)(2)(3) + 0 + 0\right) = 1$$

$$\Gamma_{1S} = \underset{\uparrow}{A_1} + \underset{\uparrow}{E}$$

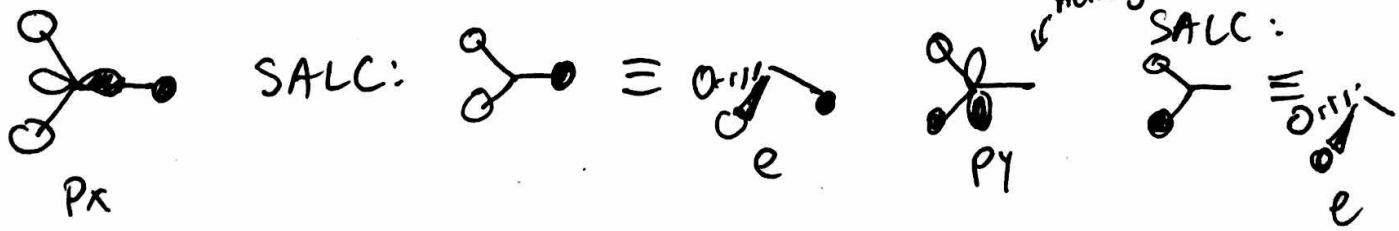
s, p_z $\quad$ p_x, p_y

5) Derive the SALCs by drawing the central atom orbitals derived above and matching the symmetry of the orbitals with orbitals from the non-central atoms. It may be easier to figure these out if you look at NH_3 along the C_3 axis.



A_1 SALC needs to interact w/ s or p_z (or d_{z^2}) on central atom

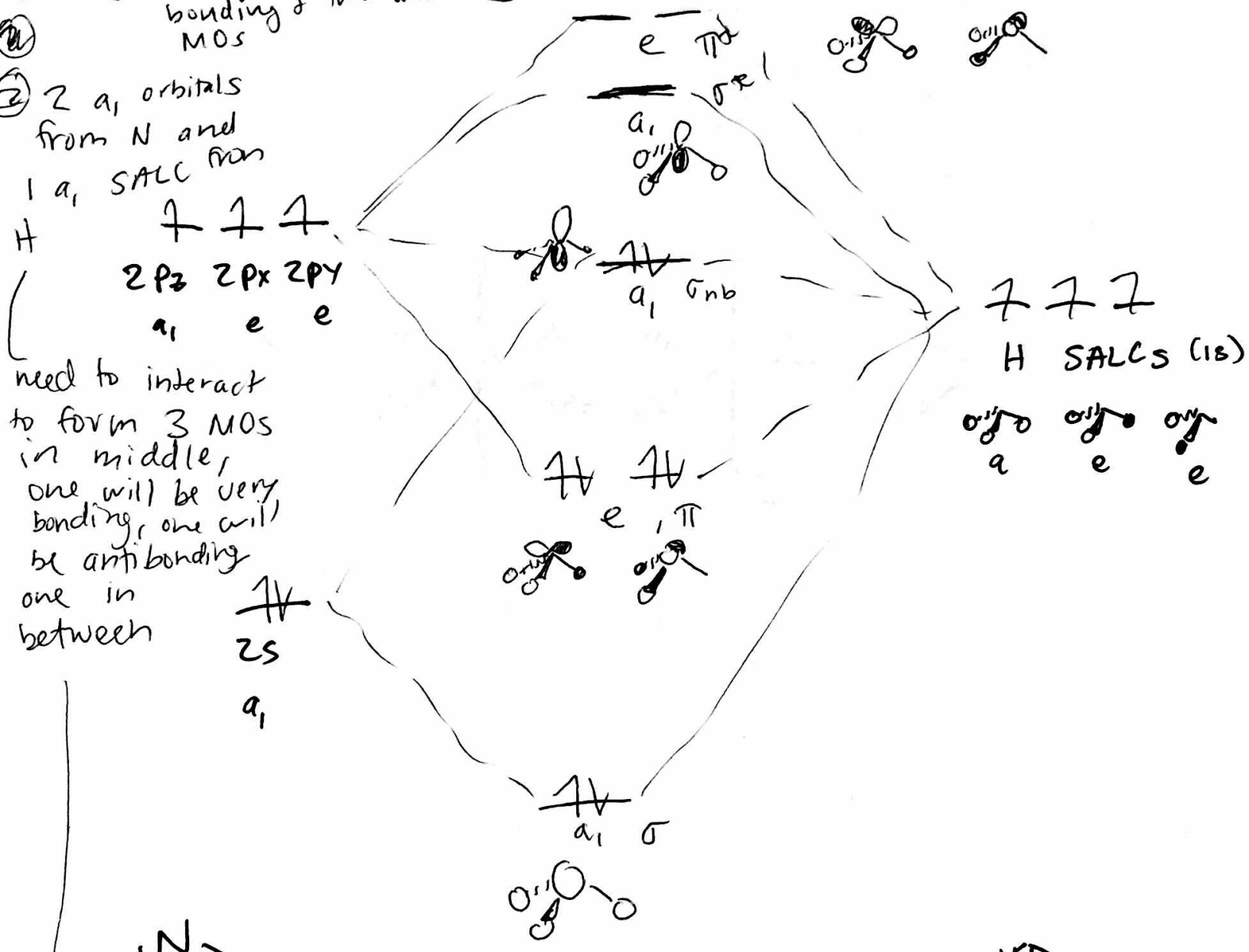
E SALCs (2 → doubly degenerate) need to look like p_x and p_y. We will use the second orientation shown above to look at this



6) Now we can draw the MO diagram!
7) What are the relative energies of the atomic valence orbitals in NH_3? Draw the atomic orbitals for N and the 3H's on either side of the MO diagram.
8) Fill in bonding, nonbonding and antibonding orbitals. If two orbitals on the central atom can interact with one SALC, this will result in three molecular orbitals in the middle.

① 2 "e" orbitals on left interact with 2 "e" SALCs on right to form two bonding & two antibonding MOs

② 2 a_1 orbitals from N and 1 a_1 SALC from H need to interact to form 3 MOs in middle, one will be very bonding, one will be antibonding one in between



on exam, if top two MOs are flipped in energy, that's ok. It's hard to know the exact order of orbitals in these diagrams