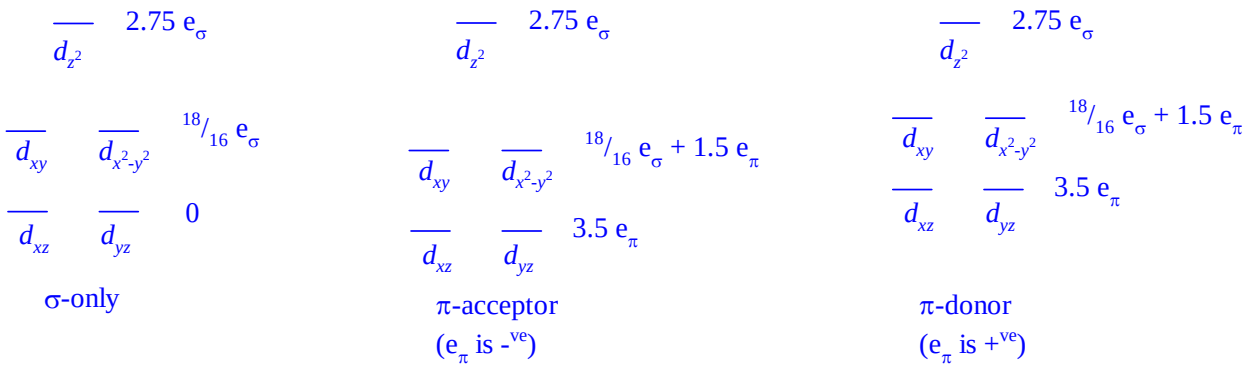
CHEM 3371 (fall 2012)

ASSIGNMENT #1

due date: Friday 5 October 2012

Using the Angular Overlap Model, develop the *d*-orbital splitting patterns for a trigonal bipyramidal structure. Do both the σ-only picture (2 points) and the σ + π picture (1 point).

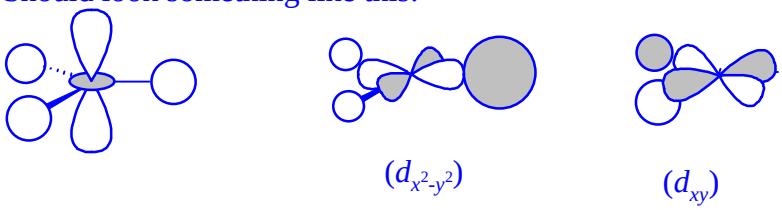
Should look something like this:



(only one of the π-pictures is necessary for full marks)

(a) Draw pictures of the orbitals for the σ-only set, using the D_{3h} SALCs from your textbook. (2 points)

Should look something like this:



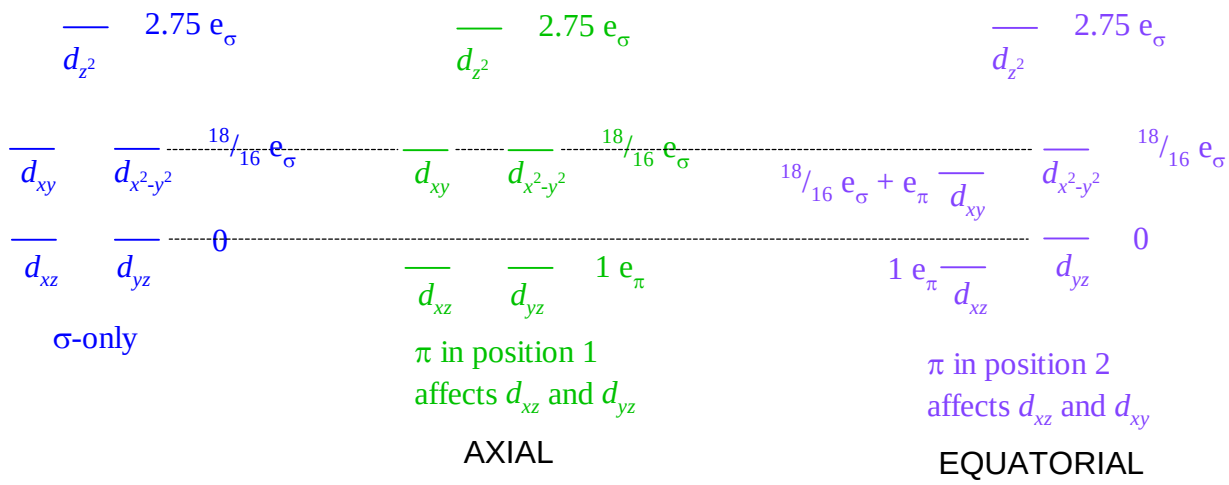
I've drawn the antibonding combinations here because these will technically be antibonding orbitals. I did not deduct marks if you drew the bonding combinations instead.

(b) In the σ-only set, what electron configurations would be susceptible to a Jahn-Teller Distortion? (Hint: for O_h, d^9, high-spin d^4, and low-spin d^7 are the only σ-only states susceptible to a JT Distortion). (2 points)

A Jahn-Teller distortion occurs with a doubly-degenerate electron-filling. This is one or three electrons in a doubly-degenerate set. Therefore, d^1 and low-spin d^3 will fit the bill for the lowest pair, and high-spin d^3, low spin d^5, and low-spin d^7 will fit the bill for the middle pair of orbitals

(c) When a strong π-acceptor ligand attaches to a trigonal bipyramidal structure, it can go in either an axial or an equatorial site. Assuming you have the structure $L_4L'M$, where L is σ-only and L' is a strong π-acceptor ligand, for what *d*-electron configurations would the π-acceptor prefer to be in the axial position? Hints: (i) assume low-spin at all times; (ii) compare the effect of adding a π-ligand at position 1 (axial) and position 2 (equatorial). (3 points = 1.5 for orbital energy level diagrams, 1.5 for correct electron configurations)

Remember to only put *one* π-acid ligand on. I would suggest putting in position 1 for axial and position 2 for equatorial (recall that the trigonal bipyramidal structure uses positions 1, 2, 6, 11, and 12 in the Angular Overlap model, and that 1 and 6 lie along *z* and position 2 lies along *x*). This would give the following pictures:



For a 1 or 2 electron count, each electron (axially-substituted and equatorially-substituted) would be stabilized by e_π in both structures. However, a three-electron count (remember everything is low spin!) would give a total stabilization (relative to the σ-only picture) of $3e_\pi$ for the axial but only $2e_\pi$ for the equatorial. This is the same argument for d^4. For d^5, we're starting to get a difference in the middle pair of orbitals. Because the stabilization is the same in each case (for both pairs of orbitals), the total stabilization for the d^5 count still favours the axial. The rest of the *d*-fillings will be the same.

To summarize, the following (low spin) *d*-counts will favour axial: 3, 4, and 5

Assignment marked out of 10, worth 5% of your final grade