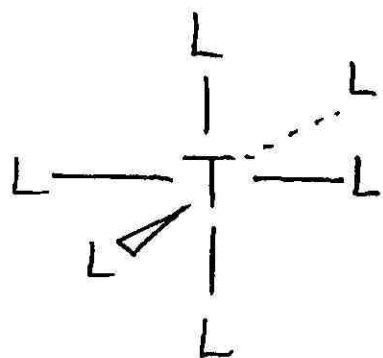


Lecture 35 Transition metals (skipped lecture 35) (See Zumdahl Chapter 20)

① A typical transition metal compound has lots of bonds. The most typical number with  $:NH_3$ ,  $CN^-$  or  $C \equiv O$  is 6.



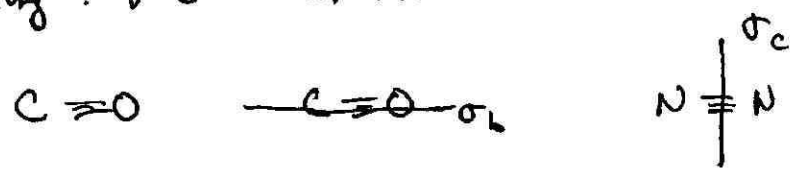
L =  $:NH_3$ ,  $:CN^-$  or  $:C \equiv O$   
 T = transition metal element

② The L part is often functioning as a Lewis base. We therefore consider the HOMO's of  $:NH_3$  and  $:C \equiv O$

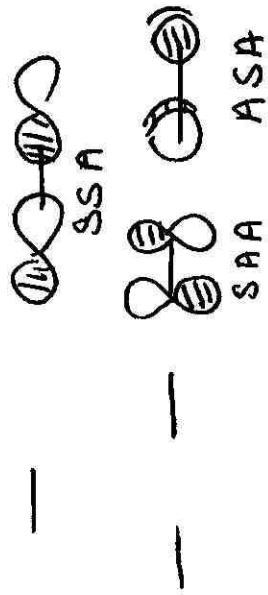
For  $NH_3$  we already know the HOMO:



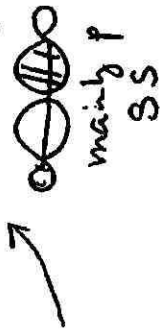
③ Let's derive the MO diagram for  $C \equiv O$ , now including s-p mixing. We concentrate on the HOMO's & LOMO's.



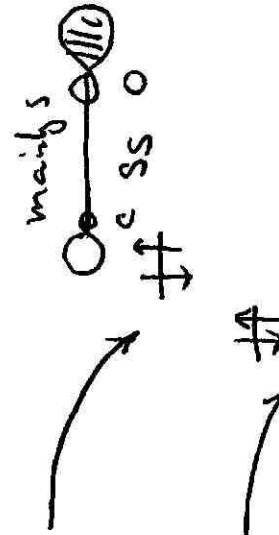
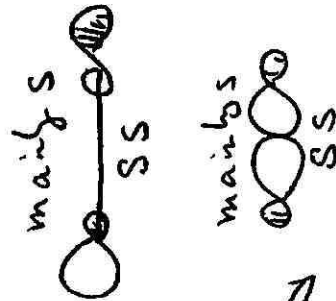
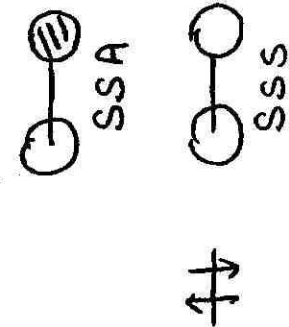
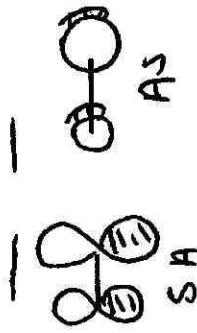
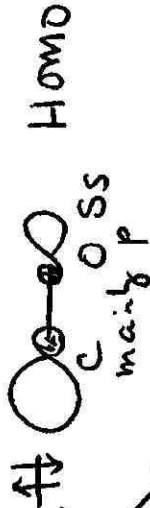
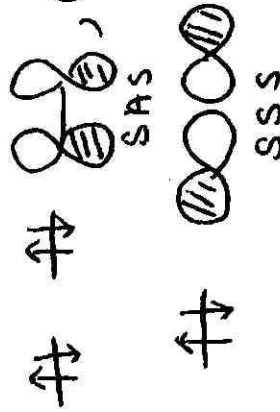
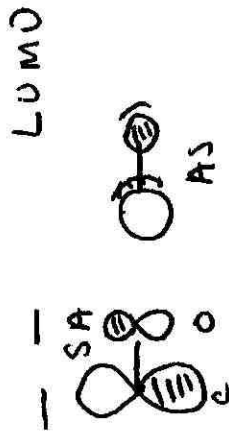
④ N<sub>2</sub> w/o sp mixing



N<sub>2</sub> w/ sp mixing

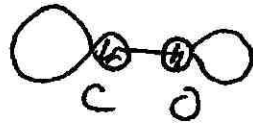


CO w/ sp mixing

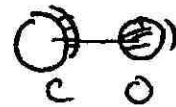
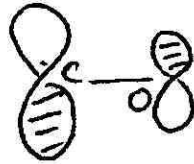


⑤ CO

HOMO

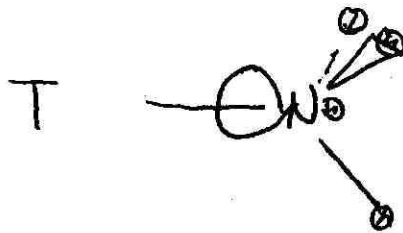
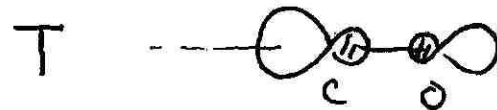


LUMO



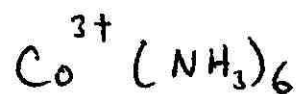
⑥ Considering (for now) L as a Lewis base, look at HOMO.

geometry expected:

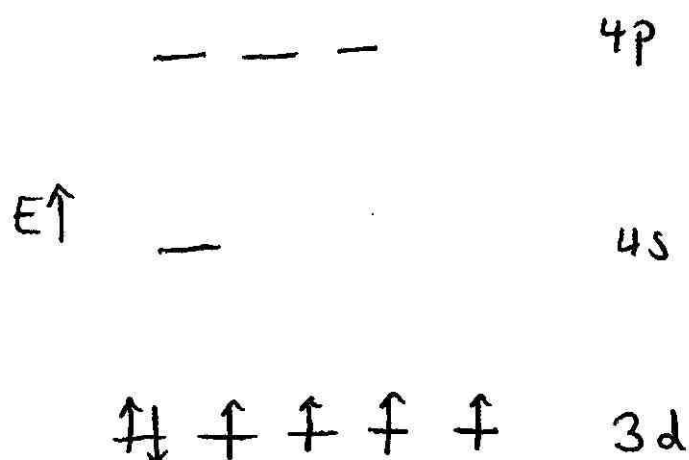


These geometries are essentially always the observed ones.

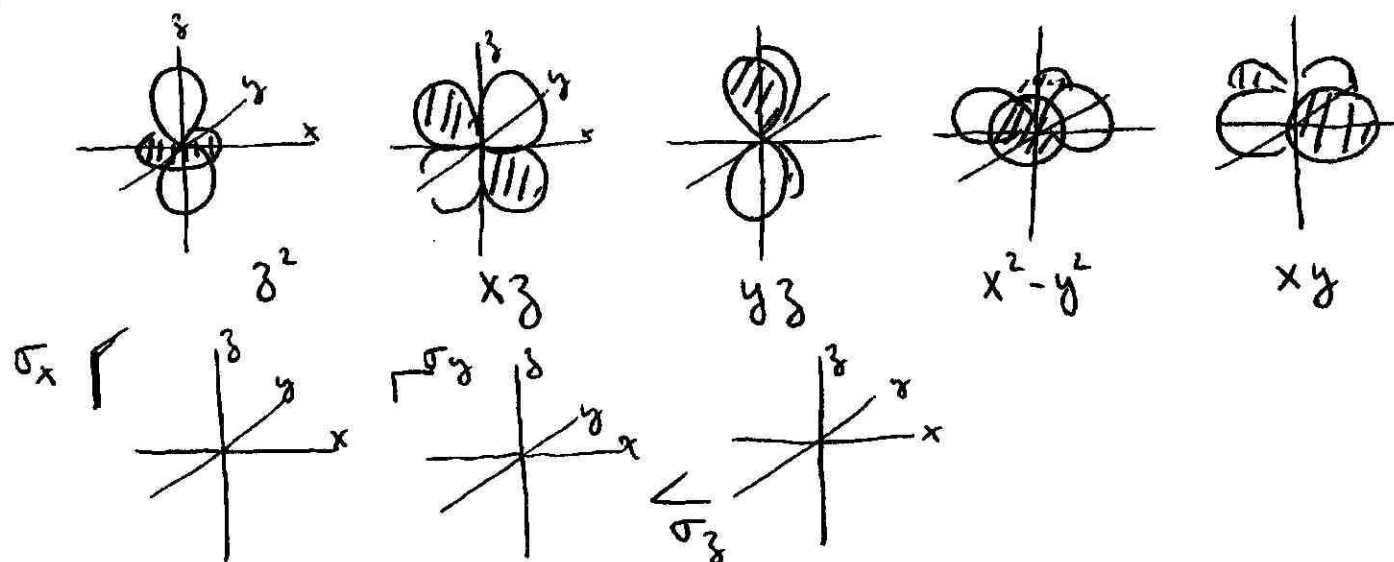
⑦ It is clear we now will have to examine the transition metal fragment orbitals. Primary attention should be on  $\pi$  LUMOs. We consider the molecule



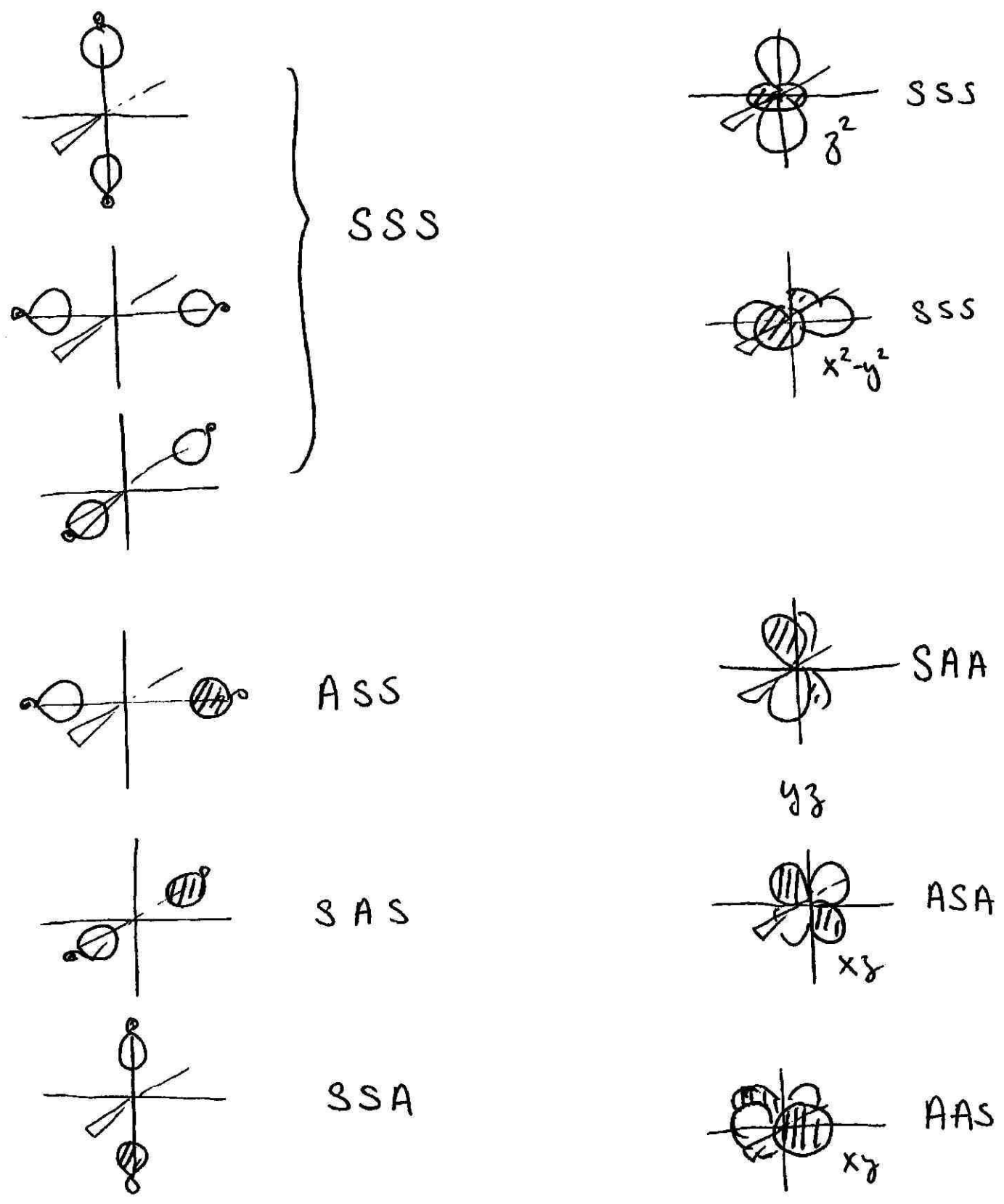
⑧ For transition metal complexes magnetic data can be used to find the number of unpaired  $e^-$ . From this data it is clear that the d-orbitals in complexes are lower in energy than the p-orbitals.



$Co^{3+}$  has 6 valence  $e^-$ .  $\therefore$  HOMO & LUMO are the d-orbitals.

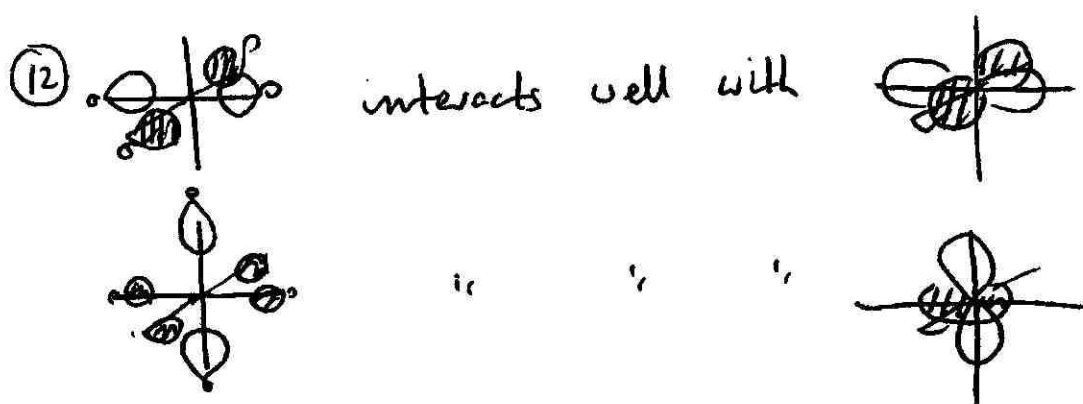
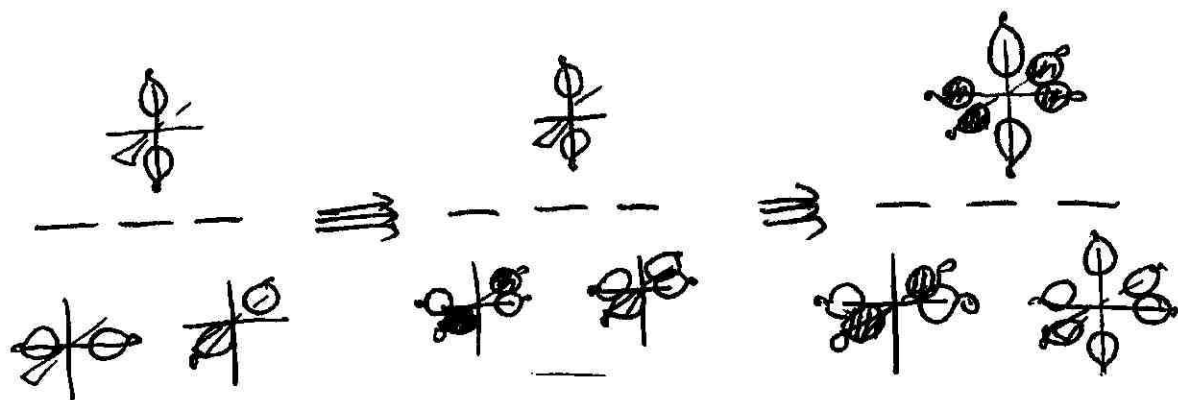


⑨ We take the 6 NH<sub>3</sub> HOMOs and symmetry and symmetry of the d-orbitals 365

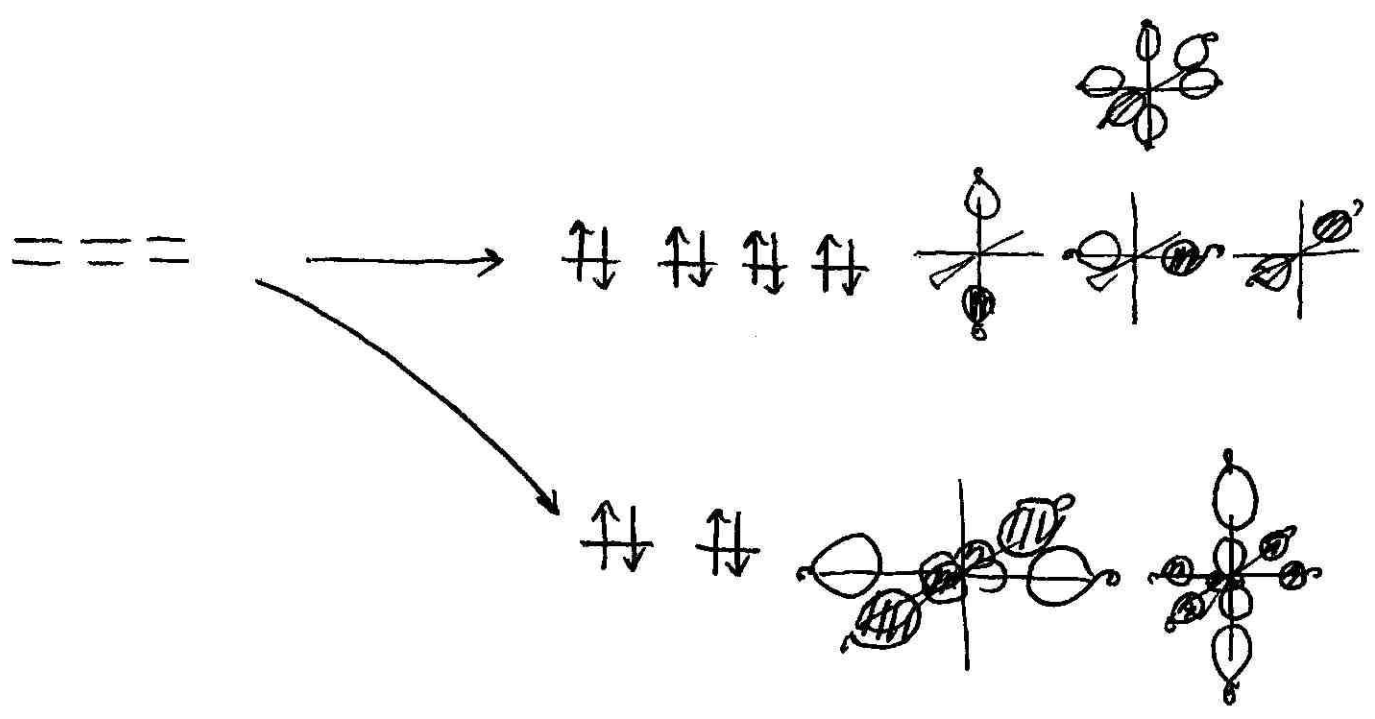
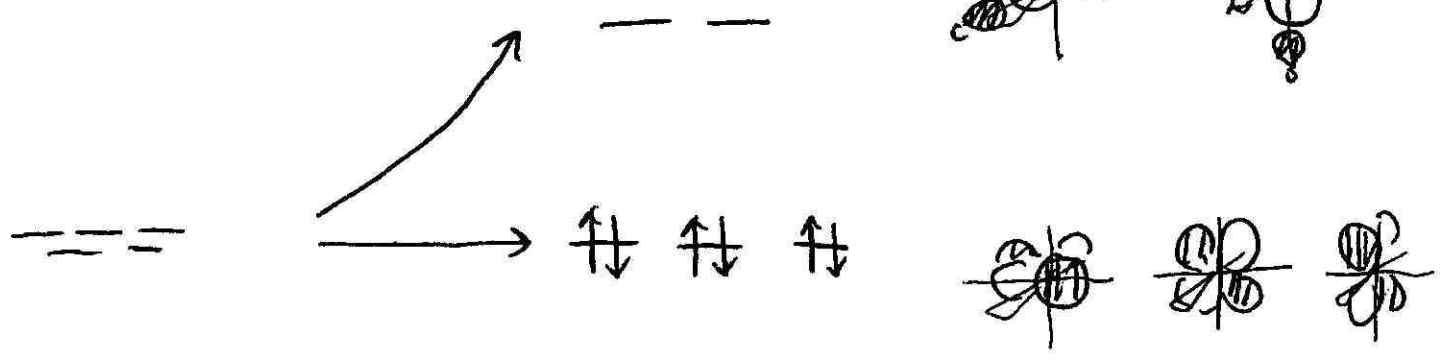
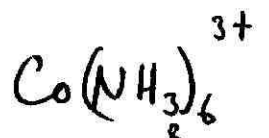


⑩ We need to carefully consider the SSS set with 5 orbitals (2 d's & 3 N lone pair fragment orbitals). Just as in the case of naphthalene, it is wisest to make combinations of one group to optimize interaction with the other set.

⑪ Keeping in mind the  $z^2$  and  $x^2 - y^2$ :



⑬ We now construct the full MO diagram (using T d orbitals & NH<sub>3</sub> HOMO's)

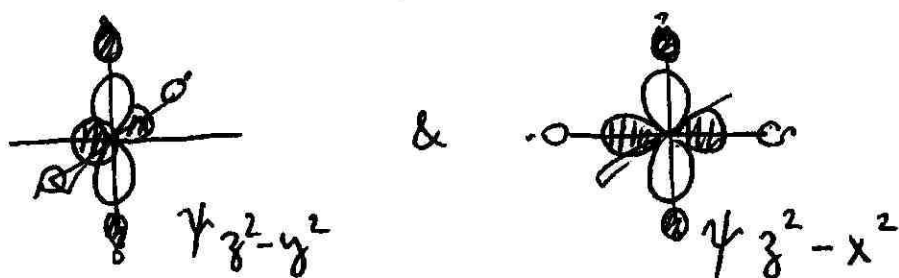


⑭

One question we have is the relative energies of:



⑮ To answer this question consider the pair of orbitals

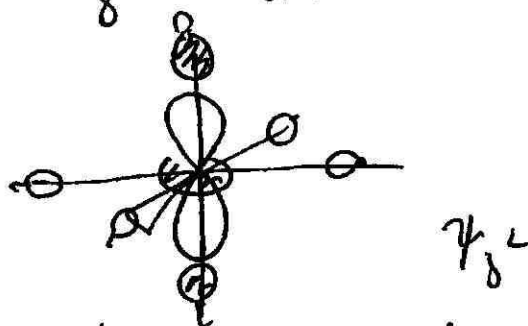


These orbitals must have the same energy as  $\psi_{x^2-y^2}$

⑯ We now add these orbitals together.

$$(z^2 - y^2) + (z^2 - x^2) = 2z^2 - x^2 - y^2$$

This is the  $z^2$  orbital:



⑰  $\therefore \psi_{x^2-y^2}$  and  $\psi_{z^2}$  are equal in energy.



⑮ Summary

— —      d-orbitals      antibonding

↑↓ ↑↓ ↑↓      d-orbitals      non-bonding

↑↓ ↑↓ ↑↓ ↑↓      :NH<sub>3</sub>      non-bonding

↑↓ ↑↓      :NH<sub>3</sub>      bonding

All bonding & non-bonding orbitals filled.  
A fairly stable system