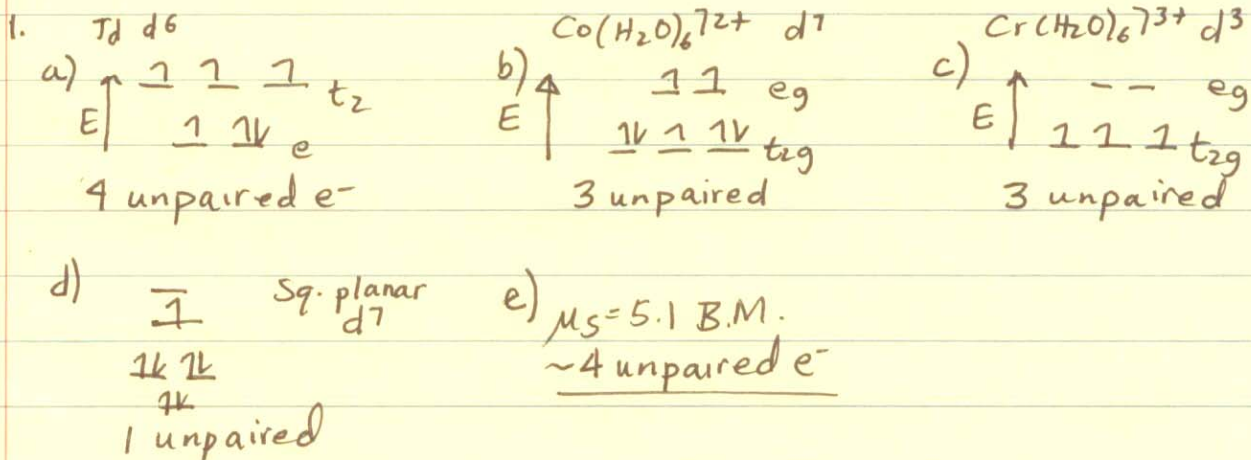
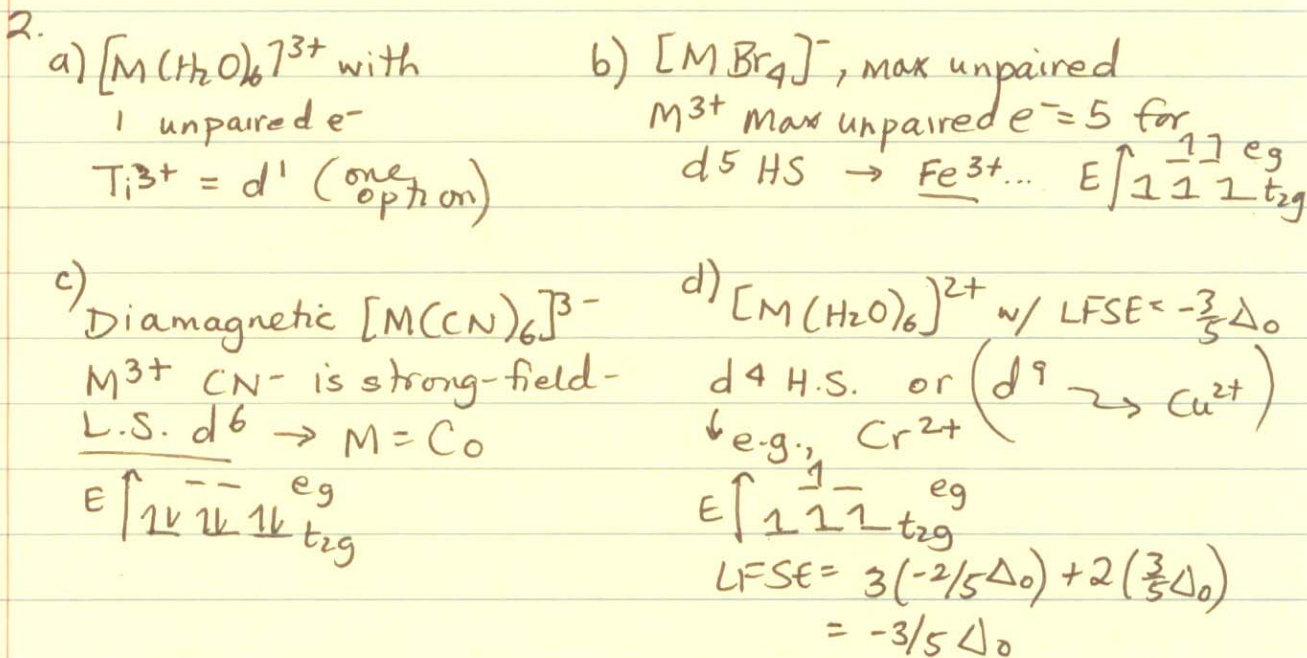


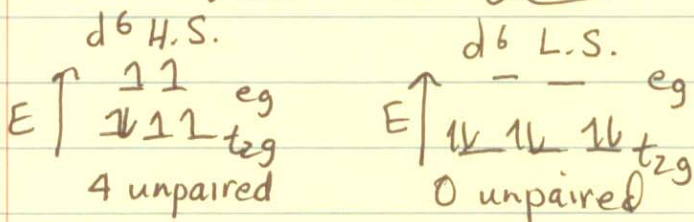
Ch. 10 HW: #1, 7-9, 19, 21a, 22, 23, 26a



#2 not assigned for 2017



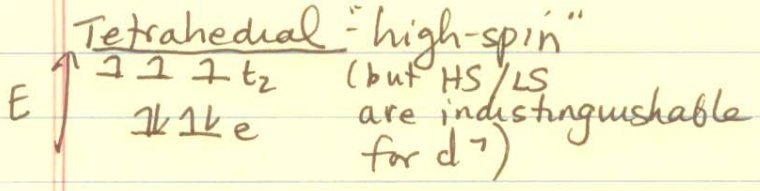
7. There are actually 3  $Fe^{2+}$  ions. The "molecular" formula is  $[Fe(H_2O)_6]_2 [Fe(CN)_6]$ .



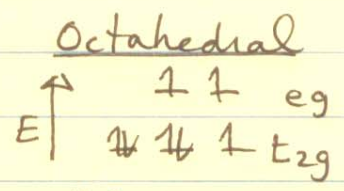
average # unpaired =

$$\frac{2(4) + 0}{3} = \frac{8}{3} = 2\frac{2}{3}$$

8.  $\text{Co}^{2+} d^7$



3 unpaired  $e^- \rightarrow 3.9 \text{ BM} = \mu_s$



H.S.  $\rightarrow 3.9 \text{ BM} = \mu_s$

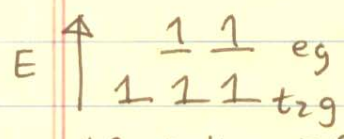
L.S.  $\rightarrow 1.7 \text{ BM} = \mu_s$

Square Planar

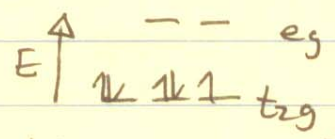
1 unpaired (see #1d)

1.7  $\text{BM} = \mu_s$

9.  $\text{Fe(III)} = d^5$  - May be either High-Spin or Low-Spin...



H.S.  $\rightarrow \mu_s \sim 5.9 \text{ BM}$



L.S.  $\rightarrow \mu_s \sim 1.7 \text{ BM}$

Red color and larger  $\mu_s$  values ( $> 5.3 \text{ BM}$ ) at high temp; orange color and smaller  $\mu_s$  values (as low as  $3.6 - 4 \text{ BM}$ ) at low temp...

- Average  $\Delta$  is decreasing with decreasing  $T$ . At low temp, there is a mixture ( $\rightleftharpoons$ ) of high-spin and low-spin species, giving an average  $\mu_s$  intermediate between  $5.9$  and  $1.7 \text{ BM}$ .

- With larger R groups, the complex is apparently locked into a high-spin configuration, resulting in  $\mu_s > 5.3 \text{ BM}$

Note:  $\text{B.M.} \equiv \mu_B \equiv \text{Bohr magnetons}$

19.

L	:	F <sup>-</sup>	Cl <sup>-</sup>	H <sub>2</sub> O	NH <sub>3</sub>	en	CN <sup>-</sup>
$\Delta_o$ (cm <sup>-1</sup> )	:	15,200	13,200	17,400	21,600	21,900	33,500

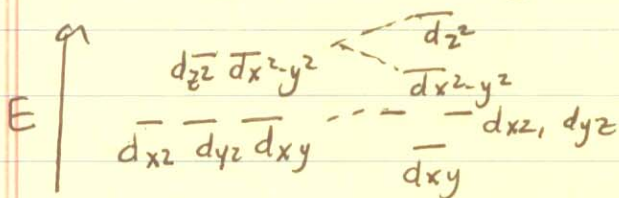
- F<sup>-</sup> and Cl<sup>-</sup> are  $\pi$ -donors. Cl<sup>-</sup> is better, resulting in the smallest  $\Delta_o$ . (Could also explain F<sup>-</sup> > Cl<sup>-</sup> because F<sup>-</sup> is a better  $\sigma$  donor.)
- H<sub>2</sub>O is a very poor  $\pi$  donor.
- NH<sub>3</sub> + H<sub>2</sub>N-NH<sub>2</sub> (en) are  $\sigma$  donors only. Of the two, en is the better base and better  $\sigma$  donor.
- CN<sup>-</sup> is a good  $\pi$ -acceptor, which increases  $\Delta$ .
- \* Review  $\pi$ -donor + -acceptor interactions with M t<sub>2g</sub> orbitals - In notes from Thurs., 4/7/11. \*

#20 not assigned for 2017

- 20.
- NH<sub>3</sub> is NOT a  $\pi$ -donor, but H<sub>2</sub>O is. This  $\pi$ -interaction with H<sub>2</sub>O ligands raises the energy of the M t<sub>2g</sub> orbitals, decreasing the size of  $\Delta$ .
  - Also, NH<sub>3</sub> is a better base and a better  $\sigma$ -donor than H<sub>2</sub>O.

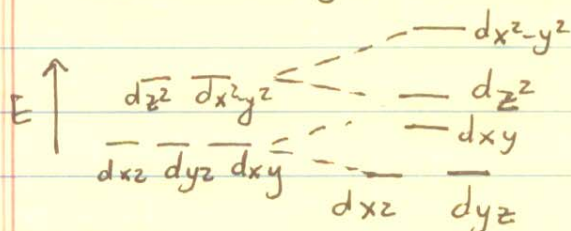
21.

a) Compression along z increases repulsion between ligands and the d<sub>z<sup>2</sup></sub>, d<sub>xz</sub> and d<sub>yz</sub> orbitals (using Crystal Field Theory - Alternately, in LFT, it causes stronger bonding/antibonding interaction with these orbitals).

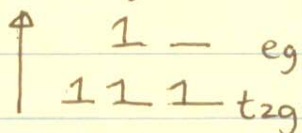
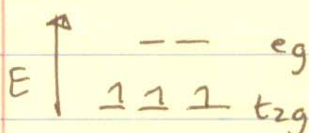
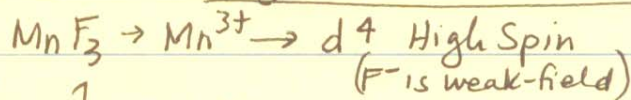
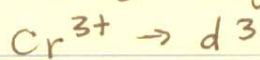


#21b not assigned for 2017

21) b) Elongation along z lowers the energies of the  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals.



22.  $\text{CrF}_3$  - regular octahedron vs.  $\text{MnF}_3$  distortion (Jahn-Teller)



$\text{Mn}^{3+}$  has unequal occupation in the eg orbitals. Jahn-Teller distortion occurs to alleviate it.

23. a)  $[\text{Co}(\text{CO})_4]^-$   $\text{Co}^-$   $4s^2 3d^8 = "d^{10}" \rightarrow 0$  unpaired;  $\text{LFSE} = 0$

$[\text{Cr}(\text{CN})_6]^{4-}$   $\text{Cr}^{2+}$   $d^4$  L.S.  $\rightarrow 2$  unpaired;  $\mu_s \sim 2.8 \text{ BM}$ ;  $\text{LFSE} = -8/5 \Delta_o$

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$   $d^5$  H.S.  $\mu_s = 5.9 \text{ BM}$   $\text{LFSE} = 0$

answer key as H.S.  $\rightarrow$   $[\text{Co}(\text{NO}_2)_6]^{4-}$   $\text{Co}^{2+}$   $d^7$  LS  $\mu_s = 1.7 \text{ BM}$   $\text{LFSE} = -9/5 \Delta_o$

if accept either.  $[\text{Co}(\text{NH}_3)_6]^{3+}$   $\text{Co}^{3+}$   $d^6$  LS  $\mu_s = 0$   $\text{LFSE} = -12/5 \Delta_o$

$[\text{MnO}_4]^-$   $\text{Mn}^{7+}$   $d^0$   $\mu_s = 0$   $\text{LFSE} = 0$

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$   $\text{Cu}^{2+}$   $d^9$   $\mu_s = 1.7 \text{ BM}$   $\text{LFSE} = -3/5 \Delta_o$

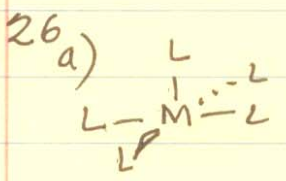
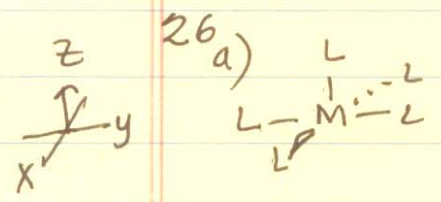
b)

The question is (really) asking why 6 or 4 ligands are preferred. We didn't discuss this, but for most of these octahedral species (except  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ) LFSE favors 6 ligands over 4 - there is more stabilization for octahedral vs. tetrahedral geom. The tetrahedral examples here have  $\text{LFSE} = 0$  in either case.

23 c) Co(II)  $d^7$  vs. Ni(II)  $d^8$

$$E \uparrow \begin{array}{c} 1 \ 1 \ 1 \\ \hline 1 \ 1 \ 1 \end{array} t_2 \quad d^7 \text{ LFSE} = -\frac{6}{5} \Delta_t \quad d^8 = -\frac{4}{5} \Delta_t$$

One can also compare LFSEs for tetrahedral vs. octahedral complexes of these 2 ions (recalling that  $\Delta_t \approx 4/9 \Delta_o$ ).



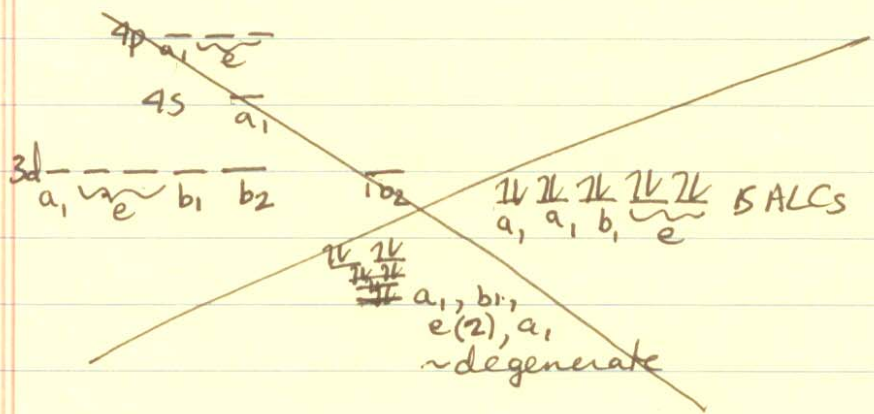
$C_{4V}$	E	$C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$	Basis set:
$\Gamma_R$	5	1	1	3	1	$\left\{ \begin{array}{l} L \\ P \end{array} \right\}$ orb. pointed toward M

Decompose  $\Gamma_R$

$\Gamma_R = 2A_1 + B_1 + E \leftarrow$  symmetries of L SALCs

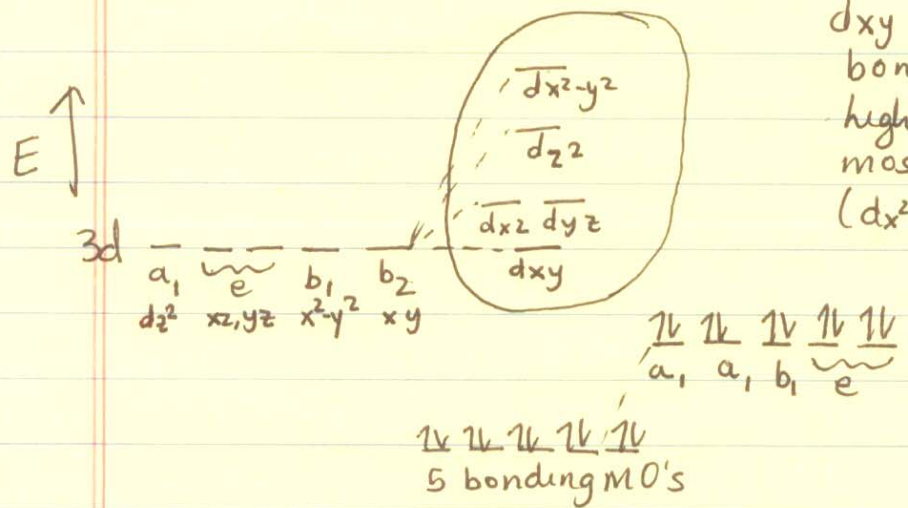
Symmetries of M orbitals (from character table):

- 4s:  $a_1$
- 3d:  $x^2-y^2: b_1$ ,  $(xz, yz): e$
- 4p:  $(x, y): e$ ,  $z: a_1$
- $z^2: a_1$ ,  $xy: b_2$



See next page - Focus only on interactions between L's and M d orbitals, keeping in mind that  $d_{x^2-y^2}$  and  $d_{z^2}$  interact most strongly with the ligands.

26a, cont.



$dxy$  is lowest in E  $\rightarrow$  non-bonding.  $dx^2-y^2$  and  $dz^2$  are highest because they interact most strongly with L's ( $dx^2-y^2$  with 4 L's,  $dz^2$  with 1 L)

M 3d

L SALCs