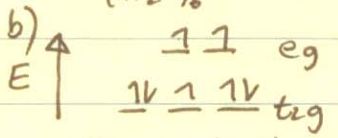
Ch. 10 HW: #1, 7-9, 19, 21a, 22, 23, 26a

PART A:
#1(b,c), 7, 9, 23(6-coord. only), 26a due by Wed., 4/3/2019

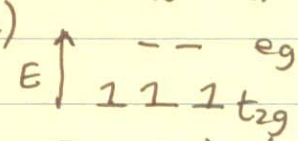
1.

b) $Co(H_2O)_6^{2+}$ d^7



3 unpaired

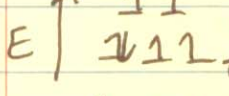
c) $Cr(H_2O)_6^{3+}$ d^3



3 unpaired

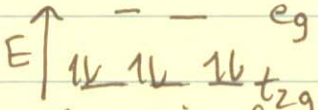
7. There are actually 3 Fe^{2+} ions. The "molecular" formula is $[Fe(H_2O)_6]_2[Fe(CN)_6]$.

d^6 H.S.



4 unpaired

d^6 L.S.

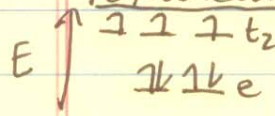


0 unpaired

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

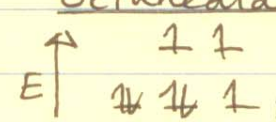
8. Co^{2+} d^7

Tetrahedral - "high-spin" (but HS/LS are indistinguishable for d^7)



3 unpaired e^- → 3.9 BM = μ_S

Octahedral



H.S. → 3.9 BM = μ_S

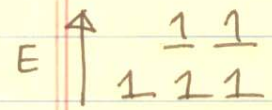
L.S. → 1.7 BM = μ_S

Square Planar

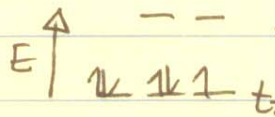
1 unpaired (See #1d)

1.7 BM = μ_S

9. Fe(III) = d^5 - May be either High-Spin or Low-Spin...



H.S. → $\mu_S \sim 5.9$ BM



L.S. → $\mu_S \sim 1.7$ BM

Red color and larger μ_S values (> 5.3 BM) at high temp; orange color and smaller μ_S values (as low as 3.6 - 4 BM) at low temp...

- Average Δ is decreasing with decreasing T. At low temp., there is a mixture ($\rightleftharpoons$) of high-spin and low-spin species, giving an average μ_S intermediate between 5.9 and 1.7 BM.
- With larger R groups, the complex is apparently locked into a high-spin configuration, resulting in $\mu_S > 5.3$ BM

Note: B.M. $\equiv \mu_B \equiv$ Bohr magnetons

23.a) $[Co(CO)_4]^-$

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

$[Fe(H_2O)_6]^{3+}$ d^5 H.S. $\mu_S = 5.9$ BM LFSE = 0

$[Co(NO_2)_6]^{4-}$ Co^{2+} d^7 LS $\mu_S = 1.7$ BM LFSE = $-9/5\Delta_o$

$[Co(NH_3)_6]^{3+}$ Co^{3+} d^6 LS $\mu_S = 0$ LFSE = $-12/5\Delta_o$

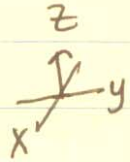
$[MnO_4]^-$

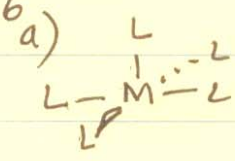
$[Cu(H_2O)_6]^{2+}$ Cu^{2+} d^9 $\mu_S = 1.7$ BM LFSE = $-3/5\Delta_o$

nswer key
as H.S.
ll accept
either.

b)

26 a)





C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	Basis set:
Γ_R	5	1	1	3	1	{L p orb. pointed toward M}

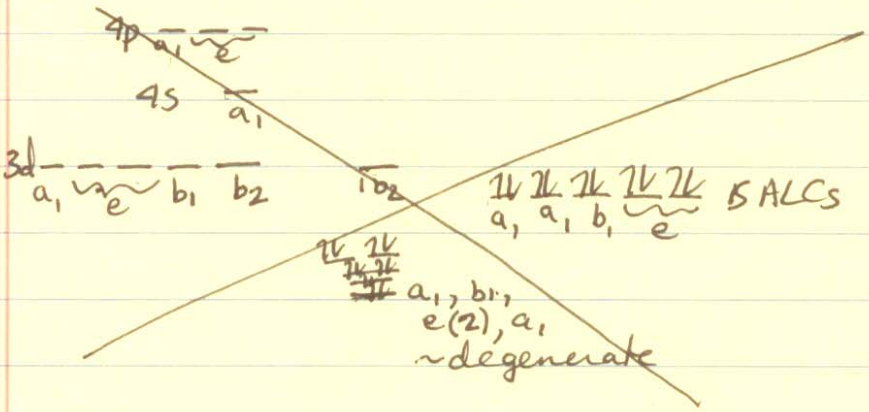
Decompose. Γ_R

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

Symmetries of M orbitals (from character table):

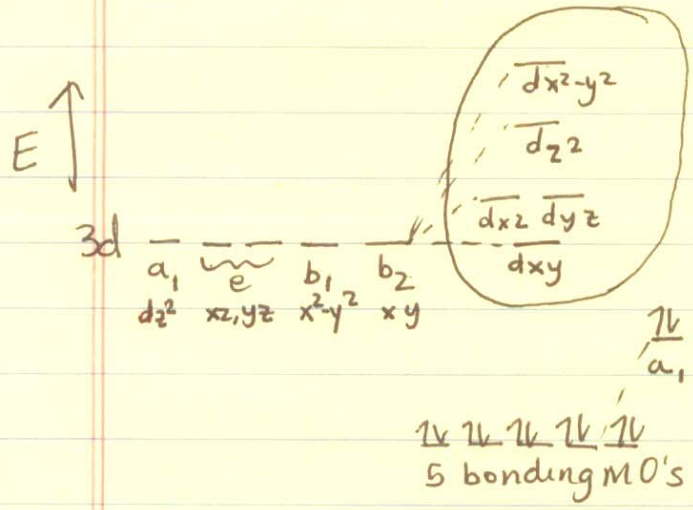
4s: a_1 3d x^2-y^2: b_1 (xz, yz): e

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.



d_{xy} is lowest in E → non-bonding. $d_{x^2-y^2}$ and d_{z^2} are highest because they interact most strongly with L's ($d_{x^2-y^2}$ with 4 L's, d_{z^2} with 1 L)

a_1 a_1 b_1 e

5 bonding MO's

M 3d L SALCs