Ch. 11 HW: #1, 2, 7-10, 11b-c, 13, 14a-b, 17, 19, 20, 26, 27

1. ~~#~~ 27 a) p^3 $m_\ell = 1 \ 0 \ -1$

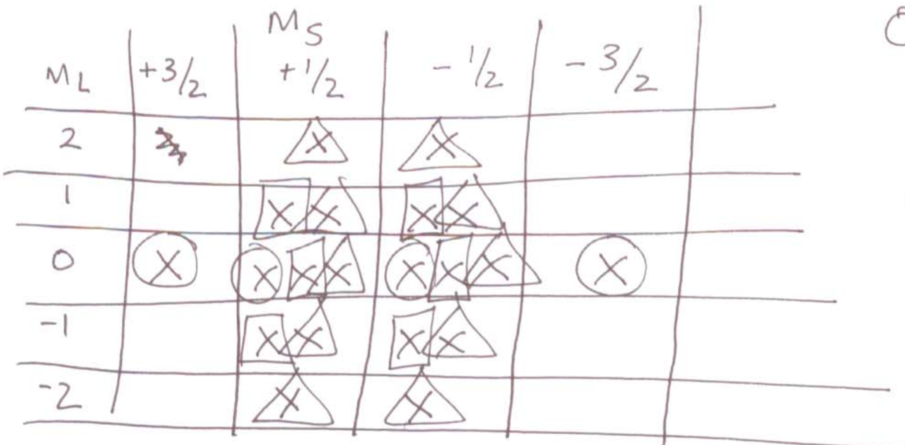
$M_L = 2, 1, 0, -1, -2$ $M_S = +3/2, +1/2, -1/2, -3/2$

$M_L = \pm 2$ $M_S = +\frac{1}{2}, -\frac{1}{2}$

$M_L = \pm 1$ $M_S = +1/2, +1/2, -1/2, -1/2$

$M_L = 0$

$M_S = +3/2, +1/2, +1/2, +1/2, -1/2, -1/2, -1/2, -3/2$



○ Max $M_L = 0$ $M_S = +3/2$ ^4S

△ Max $M_L = L = 2$ MAX $M_S = S = \frac{1}{2}$ ^2D

□ : Max $M_L = 1 = L$ MAX $M_S = \frac{1}{2} = S$ ^2P

Ground Term = $^4S \rightarrow {}^4S_{3/2}$

b) $p^1 d^1$ $1 \ 0 \ -1$ $2 \ 1 \ 0 \ -1 \ -2$ $M_L = 3, 2, 1, 0, -1, -2, -3$ $M_S = 1, 0, -1$

$M_L = \pm 3$ $M_S = 1, 0, 0, -1$

$M_L = \pm 2$ $M_S = 1, 1, 0, 0, 0, 0, -1, -1$

$M_L = \pm 1$ $M_S = 1, 1, 1, 0, 0, 0, 0, 0, 0, -1, -1, -1$

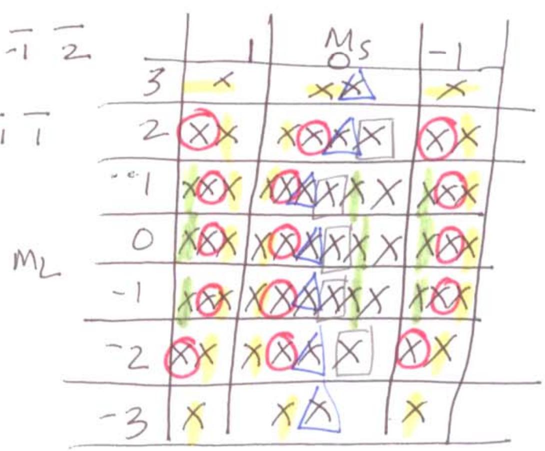
$M_L = 0$ $M_S = 1, 1, 1, 0, 0, 0, 0, 0, 0, 0, -1, -1, -1$

(yellow) $L = 3$ $S = 1$ ^3F ○ $L = 2$ $S = 1$ ^3D

△ $L = 3$ $S = 0$ ^1F □ $L = 2$ $S = 0$ ^1D

(green) $L = 1$ $S = 1$ ^3P remaining: $L = 1$ $S = 0$ ^1P

Ground term: $^3F \rightarrow {}^3F_2$



#3 not assigned

3. $s^1 d^1$ ($m_\ell = 0$; $m_\ell = \pm 2, \pm 1, 0$)

		M_S
$M_L = \pm 2$	$\frac{1}{s \cdot 0}$ $\frac{1}{2}$	1, 0, 0, −1
$M_L = \pm 1$		1, 0, 0, −1
$M_L = 0$		1, 0, 0, −1

Term 1:
$L = 2$ $S = 1$ $\rightarrow$ ^3D

Term 2:
$L = 2$ $S = 0$ $\rightarrow$ ^1D

M_L \ M_S	1	0	−1
2	X	XX	X
1	X	XX	X
0	X	XX	X
−1	X	XX	X
−2	X	XX	X

Lowest energy: ^3D

7.
a) ^2D $L=2$ $M_L = -2, -1, 0, 1, 2$ $S = \frac{1}{2}$ $M_S = +\frac{1}{2}, -\frac{1}{2}$
b) ^3G $L=4$ $M_L = -4, -3, -2, -1, 0, 1, 2, 3, 4$ $S=1$ $M_S = -1, 0, 1$
c) ^4F $L=3$ $M_L = \pm 3, \pm 2, \pm 1, 0$ $M_S = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ $S = \frac{3}{2}$

8.
a) $J = 5/2,\ 3/2$ $d^3 = < \frac{1}{2}$ full $\rightarrow$ $^2D_{3/2}$
b) d^4 $J = 5, 4, 3$ $< \frac{1}{2}$ full $\rightarrow$ $^3G_3$
c) ^4F d^7 $J = \frac{9}{2}, \frac{7}{2}, 5/2, 3/2$ $> \frac{1}{2}$ full $\rightarrow$ $^4F_{9/2}$

9.
$A = \varepsilon b c$ $\varepsilon = 0.038\ M^{-1}cm^{-1}$ $A = 0.10$ $b = 1.00\ cm$

$$c = \frac{0.10}{(0.038\ M^{-1}cm^{-1})(1.00\ cm)} = 2.6\ M$$

10. a) $\frac{1}{\lambda} = 24900\ cm^{-1}$ $\lambda = 4.02 \times 10^{-5}\ cm = 402\ nm$

$$\nu = \frac{c}{\lambda} = c\bar{\nu} = (24{,}900\ cm^{-1})(2.998 \times 10^{8}\ m/s) = 7.47 \times 10^{14}\ Hz$$

b) $$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ J \cdot s)(2.988 \times 10^{8}\ m/s)}{366 \times 10^{-9}\ m} = 5.43 \times 10^{-19}\ J$$

$$\left(366\ nm\left(\frac{1\ cm}{1 \times 10^{7}\ nm}\right)\right)^{-1} = 27{,}300\ cm^{-1} = \bar{\nu}$$

#11a,d not assigned

11.

a. d^8 O_h $L = \max M_L = 2(2) + 2(1) + 2(0) + (-1) + (-2)$

$L = 3$ $S = \max M_S = 1$

e_g: ↑ ↑

t_{2g}: ↑↓ ↑↓ ↑↓

^3F $(J = 4)$

b. d^5 HS $L = 0$ $S = +5/2$ → ^6S $(J = 5/2)$

d^5 LS $L = 6$ $S = +\frac{1}{2}$ → ^2I

c. t_2: ↑ ↑ —

e: ↑ ↑

$L = 2$ $S = 2$ → ^5D $(J = 0)$

d. $L = 2$ $S = +\frac{1}{2}$ ^2D $(J = 5/2)$

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13. $[Ni(H_2O)_6]^{2+}$ Ni^{2+} d^8

Δ_o ≈ energy of lowest-energy peak in UV-vis spectrum (Fig. 11.8, p. 421)

$\Delta_o \approx 8{,}000\ cm^{-1}$

Further splitting - Don't expect Jahn-Teller distortion in the ground state (d^8 = equally occupied orbitals); however, there will be unequal occupation in the excited state (when an e^- is promoted), leading to distortion & splitting.

14. a) $[Cr(C_2O_4)_3]^{3-}$: $Cr^{3+} \Rightarrow d^3$ $\Delta_o = 17{,}400\ cm^{-1}$

b) $[Ti(NCS)_6]^{3-}$: $Ti^{3+} \Rightarrow d^1$ $\Delta_o = 18{,}400\ cm^{-1}$

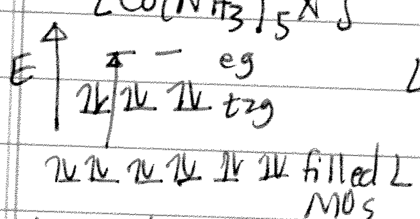
Splitting is due to Jahn-Teller distortion.

17.

M^{3+}: M =	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	(Cu	Zn)
# e^-	0	1	2	3	4	5	6	7	8	9
Jahn-Teller?	N	Y	Y	N	Y	Y (LS)	Y (HS)	Y	N	Y

(Note that some of these 3+ metal ions are not commonly observed - Ni^{3+}, Cu^{3+}, Zn^{3+}..)

19. $[Co(NH_3)_5X]^{2+}$ X = Cl, Br, I Co^{3+} d^6 low spin

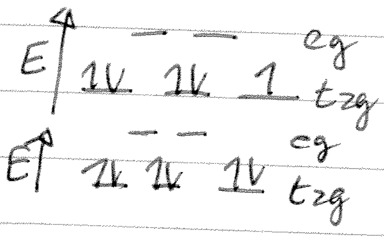


LMCT here will occur from filled L σ MOs to empty eg orbitals on Co^{3+}. The lowest energy LMCT band will occur for the ligand with orbitals closest in E to Co d orbitals. This should be I (5p orbitals vs. 4p or 3p).

20.
$[Fe(CN)_6]^{3-}$ 2 sets of CT bands -
$[Fe(CN)_6]^{4-}$ only 1 CT at high energy (UV)

$[Fe(CN)_6]^{3-}$ $Fe^{3+} \rightarrow d^5$ LS

$[Fe(CN)_6]^{4-}$ $Fe^{2+} \rightarrow d^6$ LS



For LMCT, $[Fe(CN)_6]^{3-}$ (Fe^{3+}) can accept e^- into the t_{2g} and the e_g orbitals, giving rise to 2 CT bands. In $[Fe(CN)_6]^{4-}$ (Fe^{2+}), the t_{2g} orbitals are full; the only LMCT transition possible is into the higher energy e_g set.

26.
a) CrO_4^{4-} MnO_4^{3-} FeO_4^{2-} RuO_4^{2-}
Cr^{4+} Mn^{5+} Fe^{6+} Ru^{6+}

Δ_t increases from $CrO_4^{4-} < MnO_4^{3-} < FeO_4^{2-} < RuO_4^{2-}$.
Δ_t increases with increasing charge on the metal ion and with increasing size (radial extent).

b)
Since FeO_4^{2-} has the highest charge on the metal (Fe^{6+}), it should have the strongest M-O electrostatic attraction and the shortest M-O bond distance.

c) O^{2-} is a σ-donor with no empty π^* orbitals. Therefore, MLCT is very unlikely. Thus, these are probably LMCT transitions.

27. $Ni(NO_3)_2 \equiv [Ni(H_2O)_6]^{2+}(NO_3)_2$

$[Ni(H_2O)_6]^{2+} \xrightarrow{6NH_3} [Ni(NH_3)_6]^{2+} \xrightarrow{3\,en} [Ni(en)_3]^{2+}$

	$[Ni(H_2O)_6]^{2+}$	$[Ni(NH_3)_6]^{2+}$	$[Ni(en)_3]^{2+}$
Appears:	Green	Blue	Violet
Absorbs:	Red	Orange	Yellow

The color of light absorbed changes from red → orange → yellow as the ligand goes from H_2O → NH_3 → en. The energy absorbed — and the size of Δ_o — are increasing. This is consistent with the positions of the ligands in the spectrochemical series.