HW Set 1

1. Certain metals have low solubilities at physiological pH, which would make them bio-unavailable. Ligand chelation of a metal can increase the solubility of the metal by forming a metal-ligand complex that is stable and prevents direct interaction of the metal and solvent in the biological fluids.

Chapter 2

1. a. Shape: l
   b. Energy: $n \rightarrow$ H type atom
   $n+l \rightarrow$ Polyelectronic atoms

   c. Orientation: m_l

   d. size of orbitals: n

2. $n = 4$
   s, p, d, f $\rightarrow$ 16 orbitals
   1 3 5 7

3. $n = 5$ $\qquad$ $5s^2 5p^6 5d^{10} 5f^{14} 5g^{18} = 50$
   $l = 0, 1, 2, 3, 4$
   $m_l: -4, -3, -2, -1, 0, 1, 2, 3, 4$
   $m_s = \pm \frac{1}{2}$

   $n = 5$, $l: 4$, $m_l - 4$, $m_s = +\frac{1}{2}$ possible quantum #

4. p^3

$\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$

+1 0 -1

$S = 1.5$

Multiplicity $= 2S + 1 = 4$

a. $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\downarrow}$ Need to flip spin
Exchange energy penalty

b. $\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\ }$ coulombic energy penalty

c. $\underline{\uparrow\uparrow}$ $\underline{\uparrow}$ $\underline{\ }$ impossible

d. $x = 3$

$l = 1$

$N_l = 2[2(1) + 1] = 6$

# of microstates $= \frac{6!}{3!\,3!} = \frac{6 \cdot 5 \cdot 4 \cdot \cancel{3 \cdot 2 \cdot 1}}{\cancel{3!}\, 3 \cdot 2 \cdot 1} = 20$

M_L	2	2	1	1	1	1	-1	-1	1	1	-2	-2	0	0	0	0	0	0	0	0
m_ℓ +1	↑↓	↑↓	↑↓	↑↓	↑	↓			↑	↓			↑	↑	↑	↑	↓	↓	↓	↓
0	↑	↓			↑↓	↑↓	↑↓	↑↓			↑	↓	↑	↓	↑	↓	↑	↓	↑	↓
-1			↑	↓			↑	↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↓	↓	↑	↑	↓	↓
M_S	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$

M_L \ M_S	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
2		⊗	⊗	
1		☒⊗	☒⊗	
0	X	X☒⊗	X☒⊗	X
-1		☒⊗	☒⊗	
-2		⊗	⊗	

○ $^2D \longrightarrow {^2D_{3/2}}, \; {^2D_{5/2}}$

$L = 2$ $\quad J = L+S, \ldots L-S$

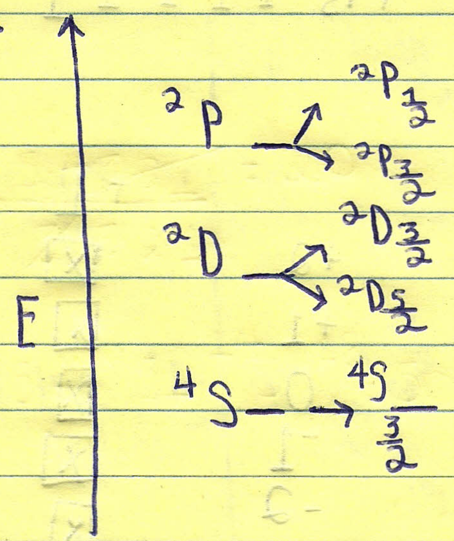
$S = \frac{1}{2}$ $\quad$ Multiplicity $= 2S+1 = 2$

□ $L = 1$ $\quad {^2P} \rightarrow {^2P_{\frac{1}{2}}}, {^2P_{\frac{3}{2}}}$

$S = \frac{1}{2}$

△ $L = 0$ $\quad {^4S} \rightarrow {^4S_{\frac{3}{2}}}$

$S = \frac{3}{2}$



5. Sc^+ $[Ar]4s^1 3d^1$

$s^1 d^1$

↑		↑				
0		+2	+1	0	-1	-2

# of microstates $= \underbrace{\frac{2!}{1!\,1!}}_{s} \times \underbrace{\frac{10!}{1!\,9!}}_{d} = 20$

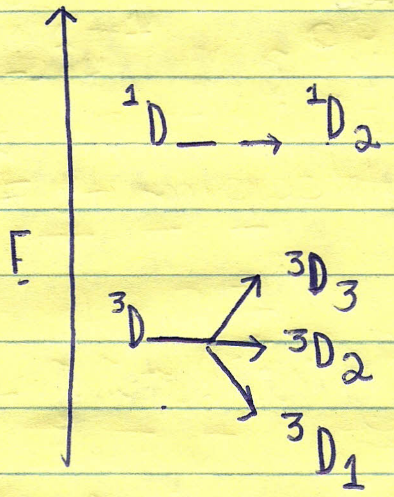
M_L	2	1	0	-1	-2	2	1	0	-1	-2	2	1	0	-1	-2	2	1	0	-1	-2
m_l 0	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
2	↑					↓					↑					↓				
1		↑					↓					↑					↓			
m_l 0			↑					↓					↑					↓		
-1				↑					↓					↑					↓	
-2					↑					↓					↑					↓
M_s	1	1	1	1	1	0	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1

	M_s +1	0	-1
+2	☒	☒ ⊗	☒
+1	☒	☒ ⊗	☒
0	☒	☒ ⊗	☒
-1	☒	☒ ⊗	☒
-2	☒	☒ ⊗	☒

□ $L = 2$ $\quad {}^3D \rightarrow {}^3D_3,\ {}^3D_2,\ {}^3D_1$

$S = 1$

O $L=2$ ${}^1D \rightarrow {}^1D_2$
$S=0$



Ti $4s^2 3d^2$

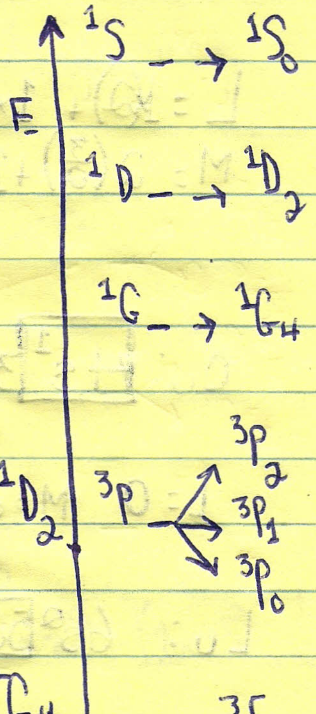
$\uparrow$ $\uparrow$ — — —
$+2$ $+1$ 0 -1 -2

$x = 2$
$\ell = 2$
$N_e : 2[2(2)+1] = 10$
# of microstates : $\frac{10!}{2!\,8!} = \frac{10 \cdot 9}{2} = 45$

^3P $L=1$, $S=1$ — $^3P_2$, $^3P_1$, $^3P_0$
^1D $L=2$, $S=0$ — $^1D_2$

^3F $L=3$, $S=1$ — $^3F_4$, $^3F_3$, $^3F_2$
^1G $L=4$, $S=0$ — $^1G_4$

^1S $L=0, S=0$ — $^1S_0$



6. B : $1s^2\ 2s^2\ \boxed{2p^1}$

m_ℓ $\underset{+1}{\uparrow}$ $\underset{0}{\_\_}$ $\underset{-1}{\_\_}$ 1 unpaired

$L = 1$

$M = 2(\frac{1}{2}) + 1 = 2$ $\underbrace{{}^2P}$

Ground state

V: $4s^2\ \boxed{3d^3}$

m_ℓ $\underset{+2}{\uparrow}$ $\underset{+1}{\uparrow}$ $\underset{0}{\uparrow}$ $\underset{-1}{\_\_}$ $\underset{-2}{\_\_}$ 3 unpaired

$L = 1(2) + 1\times(1) = 3$

$M = 2(\frac{3}{2}) + 1 = 4$ $\underbrace{{}^4F}$

Ground state

Cu: $\boxed{4s^1}\ 3d^{10}$ m_ℓ $\underset{0}{\uparrow}$ 1 unpaired

$L = 0$ $M = 2(\frac{1}{2}) + 1 = 2$ ${}^2S \rightarrow$ Ground state

Lu: $6s^2\ \boxed{5d^1}\ 4f^{14}$ m_ℓ $\underset{+2}{\uparrow}$ $\underset{+1}{\_\_}$ $\underset{0}{\_\_}$ $\underset{-1}{\_\_}$ $\underset{-2}{\_\_}$ 1 unpaired

$L = 2$ $M = 2(\frac{1}{2}) + 1 = 2$ ${}^2D \rightarrow$ Ground state

7. Ti^{3+}: $3d^1$ $\quad m_\ell$ $\quad \underline{\uparrow}\ \underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }$ $\rightarrow$ 1 unpaired

$\qquad\qquad\qquad +2\ \ +1\ \ 0\ \ -1\ \ -2$

$L = 2 \rightarrow {}^2D$

$M = 2(\frac{1}{2}) + 1 = 2$

Mn^{2+} $3d^5$ $\quad m_\ell$ $\quad \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$ $\rightarrow$ 5 unpaired

$\qquad\qquad\qquad +2\ \ +1\ \ 0\ \ -1\ \ -2$

$L = \cancel{(1\times 2)} + \cancel{(1\times +1)} + (1\times 0) + \cancel{(1\times -1)} + \cancel{(1\times -2)} = 0$

$M = 2(\frac{5}{2}) + 1 = 6 \rightarrow {}^6S$

Cu^{2+}: $3d^9$ $\quad m_\ell$ $\quad \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}$ $\rightarrow$ 1 unpaired

$\qquad\qquad\qquad +2\ \ +1\ \ 0\ \ -1\ \ -2$

$L = (2\times 2) + \cancel{(2\times 1)} + \cancel{(2\times 0)} + \cancel{(2\times -1)} + (1\times -2)$

$= 4 - 2 = 2$

$M = 2(\frac{1}{2}) + 1 = 2 \quad {}^2D$

Gd^{3+}: $4f^8$ $\quad \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$

$\qquad\qquad +3\ \ +2\ \ +1\ \ 0\ \ -1\ \ -2\ \ -3$

$L = (3\times 2) + \cancel{(1\times 2)} + \cancel{(1\times 1)} + (1\times 0) + \cancel{(1\times -1)} + \cancel{(1\times -2)} + (1\times -3)$

$= 6 - 3 = 3$

$M = 2(\frac{6}{2}) + 1 = 7 \quad {}^7F$

8. a. P: $(1s^2)(2s^2, 2p^6)(3s^2, 3p^3)$

$S = 0.35(4) + 0.85(8) + 1(2) = 10.2 \quad Z^* = Z - S = 15 - 10.2 = 4.8$

b. Co: $(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^7)(4s^2)$

$S = (0.35)(1) + 0.85(15) + 1.00(10) = 23.10 \quad Z^* = 27 - 23.10 = 3.90$

c. Mn: $(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^5)(4s^2)$

$S = 0.35(4) + 1.00(18) = 19.40 \quad Z^* = 25 - 19.40 = 5.60$

d. Mg: $(1s^2)(2s^2, 2p^6)(3s^2)$

$S = 0.35 + 0.85(8) + 1.00(2) = 9.15 \quad Z^* = 12 - 9.15 = 2.85$

9. a. Li
b. F
c. Cu
d. Pt

10. A general trend is that I.E. increases as n increases. This is due to an increase in effective nuclear charge felt by the remaining e^- after an electron is removed because of the greater electrostatic attraction between the positive nucleus and the electrons.

A significant jump in I.E. is noticed between the values of $n=3$ + $n=4$. The e^- up to $n=3$ are those that pertain to orbitals of $n=3$, which means that they are higher in energy and it is easier for e^- to be removed from them. The remaining e^- of the plot are removed from orbitals pertaining to primary quantum # 2. It is even harder to remove e^- from orbitals in this shell.

11) a. Li
b. ~~K~~ Cl
c. Cl
d. S

Chapter 18

2) Many separation methods (i.e. ion-exchange chromatography) rely on differences in charge/size ratios. Because of the lanthanide contraction in addition to the relativistic effect, Zr^{4+} + Hf^{4+} are virtually the same size. Since they have the same charge, separation methods that rely on charge/size differences will not be able to distinguish between them.

4) a. Electron affinities increase from left to right as $\uparrow Z^*$.

But take the periodic anomalies into consideration.

b. Ionization energies increase as the value of n increases.

c. Atomic radii increase as $\uparrow$ n while $\uparrow Z^*$ slowly.

d. Atomic radii decreases from left to right because $\Delta n = 0$ and $\uparrow Z^*$ increases.

e. Skip → We did not discuss this fully.

8) C-N: N has a lower EA because

C $\underline{\uparrow}\ \underline{\uparrow}\ \underline{\ \ }$ p

N $\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$ ← adding 1 more e^- results in electrostatic repulsion

Na-Mg: Mg lower EA because extra e^- must enter a 2p orbital → higher in energy

Cu-Zn: Zn lower EA because extra e^- must enter a 4p orbital, ~~which feels~~ a Also ~~would disrupt its~~ s for Cu, Cu would obtain filled d-orbitals → very stable

9) N-O: Oxygen has a lower I.E.

N $\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$

O $\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$ → e^- repulsion; easier to remove

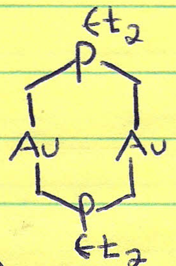
Be-B : B has lower I.E. because outer e- is in a 2p orbital → higher energy orbital.
For Be, outer e- in s orbital.

Mg-Al: Al has lower I.E. b/c its outer e- is in a 3p orbital whereas for Mg it is in a 3S.

P-S: Same as for N-O

Zn-Ga: Ga has lower IE b/c its outer e- is in a 4p orbital where for Zn it is in a 3d.

18) In the molecule



gold engages in a mostly (if not entirely) covalent bond because ΔX between Au (2.54) + C (2.55) is virtually 0. Because of the covalency of the bond, Au would not be expected to have a true formal oxidation state of +1.