Ge/Ay 132
Problem Set #1 Solutions

1)

a) Rydberg constant (class notes, p. 17)

$$R_M = R_\infty / (1 + m_e/M)$$

M=mass of $12C^{5+}$ = 11.997 amu
m_e=electron mass = $5.48879\text{x}10^{-4}$ amu
R_∞=Rydberg constant for infinitely large nucleus=$109737.5152\text{cm}^{-1}$

$$==> R_M = 109732.304 \text{ cm}^{-1}$$

b) Transition frequency $\gamma_o = c_o / \lambda_o$
Wavelength in air $\lambda = \lambda_o / n$
where n = index of refraction (given in problem)

$$\nu^{\sim} = R*Z^2 * (1/2^2 - 1/n^2) = 1/\lambda_o$$

For Balmer, n=3,4,5,...
For Pfund, n=6,7,8,...
for C, Z=6

also given,

$$\lambda_{air}^{-1} = (1+n)\, \nu^{\sim}_{vac}$$

For the Balmer series,

H α line (n=3)

$\nu^{\sim}$ = 548861.5195 cm^{-1}
γ_o = $1.645\text{x}10^{16}$ Hz
n = 1 + $7.5\text{x}10^{-5}$
λ = 182.248 Å

H β line (n=4)

$\nu^{\sim}$ = 740693.0513 cm^{-1}
γ_o= $2.2205419\text{x}10^{16}$ Hz
n = 1.0000789
λ = 135.0 Å

Hγ line (n=5)

$\nu^{\sim}$ = 829576.2175 cm^{-1}
γ_o = $2.487\text{x}10^{16}$ Hz

$n = 1.000079835$
$\lambda = 120.534$ Å

$$\nu^{\sim} = R*Z^2 * (1/2^2 - 1/n^2) = 1/\lambda_o$$

For Pfund, n=6,7,8,...
for C, Z=6

Pfund α line (n=6)

$\nu^{\sim} = 48282.21372 \text{ cm}^{-1}$
$\gamma_o = 1.4474643\text{x}10^{15}$ Hz
$n = 1.0000319202$
$\lambda = 2070.495$ Å

Pfund β line (n=7)

$\nu^{\sim} = 77394.86577 \text{ cm}^{-1}$
$\gamma_o = 2.3202\text{x}10^{15}$ Hz
$n = 1.000041903$
$\lambda = 1291.534$ Å

Pfund γ line (n=8)

$\nu^{\sim} = 96290.09667 \text{ cm}^{-1}$
$\gamma_o = 2.88670\text{x}10^{15}$ Hz
$n = 1.007258$
$\lambda = 1037.7752$ Å

The first two lines with n"=100 are n= 100 → 101 and n=100→ 102

for N= 100 → 101

$\nu^{\sim} = 7.78377562 \text{ cm}^{-1}$
$\gamma_o = 2.3335172\text{x}10^{11}$ Hz
$n = 1.000272612$
$\lambda = 1.2844$mm

for N= 100 → 102

$\nu^{\sim} = 15.26380 \text{ cm}^{-1}$
$\gamma_o = 4.5769\text{x}10^{11}$ Hz
$n = 1.000272612$
$\lambda = 0.6550$mm

Classically, an = $(n^2/Z)*a_o = (100^2/6)*0.529172$ Å = 881 Å

c) From class note 1.36, For a level (n,l,j),

$$E_{nlj}^{SO} = \frac{\alpha^2 \,[j(j+1) - l(l+1) - s(s+1)]}{2(l+1)\,(l+1/2)} * \frac{Z^4}{2n^3} \quad \text{(au)}$$

For n=2; l=0,1; s=1/2 the energy levels are $2^2S_{1/2}$, $2^2P_{1/2}$, $2^2P_{3/2}$

The energy difference between (n,l,l+1/2), (n,l,l-1/2) due to spin-orbit interactions, is given by class note 1.36

$$\Delta E^{SO} = (Z^4 \alpha^2 / 2n^3) * (1/ l(l+1))$$

So the splitting between $2^2P_{1/2}$ and $2^2P_{3/2}$ is 473.5853 cm^{-1}

For n=3, the energy levels are $3^2S_{1/2}$, $3^2P_{1/2}$, $3^2P_{3/2}$, $3^2D_{3/2}$, $3^2D_{5/2}$

the splitting between $3^2P_{1/2}$ and $3^2P_{3/2}$ is 140.3216 cm^{-1}

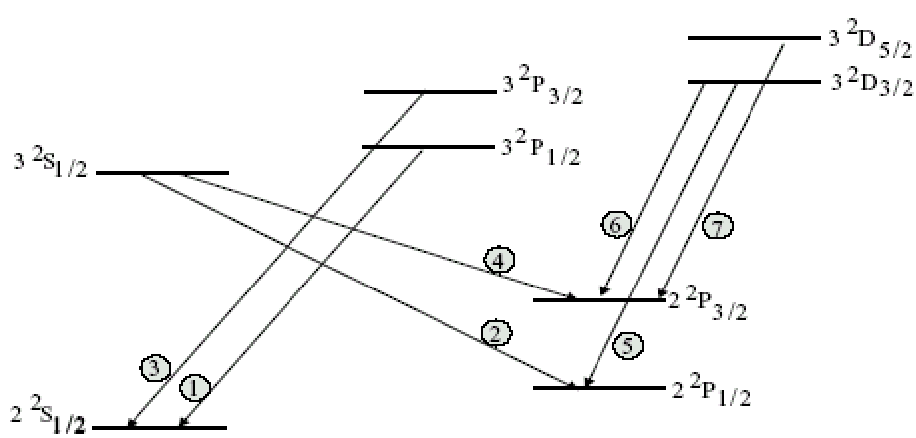
the splitting between $3^2D_{3/2}$ and $3^2D_{5/2}$ is 46.7738 cm^{-1}

so $\Delta E^{SO}_{3D} < \Delta E^{SO}_{3P}$.

d) Hα transition n=32, the energy is given by class note 1.40

$$E = \frac{-Z^2}{2n^2} - \frac{Z^4 \alpha^2}{2n^3} \left[\frac{1}{j+1/2} - \frac{3}{4n} \right]$$

So the schematic diagram is



Selection rules for electric dipole transitions in hydrogen-like atoms are

$\Delta l = \pm 1$
$\Delta j = 0, \pm 1$
$\Delta m = 0, \pm 1$ (when external B-field exists)
no restriction on Δn

This results in those 7 transitions indicated in the above diagram,

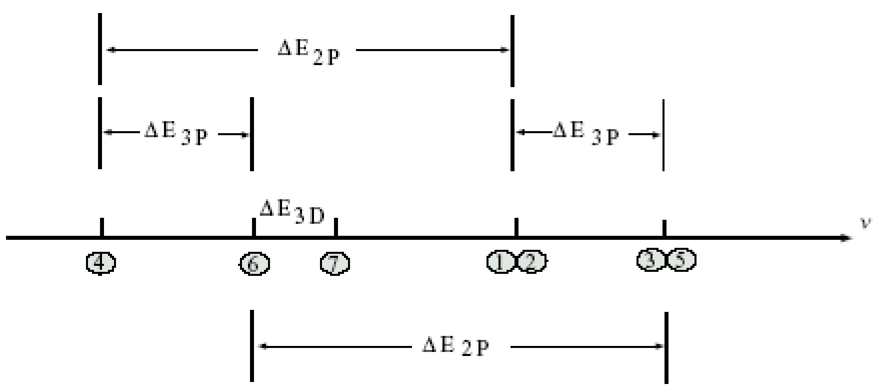
obviously $E_3 = E_5$
$E_1 = E_2$
and
$E_3 > E_1 > E_7 > E_6 > E_4$

Also, from c) we know

$$\Delta E^{SO}_{3D} < \Delta E^{SO}_{3P} < \Delta E^{SO}_{2P}$$

And, $\Delta E_{3P} = 0.000639352$ au $< \Delta E_{1,7} = 0.001305343$ au

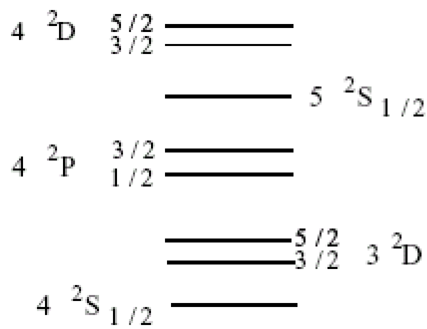
So the spectrum should look like



2. Ca II = unfilled shell 4s1, similar to alkali metal KI

a) the lowest five terms are = $4^2S_{1/2}$, $3^2D_{5/2,,3/2}$,$4^2P_{3/2,1/2}$, $5^2S_{1/2}$, $4^2D_{5/2,,3/2}$

And the schematic energy level diagram is



b) In the sharp series, nS → 4P (n=5,6,7,...)

The first doublet is $5^2S_{1/2} \rightarrow 4^2P_{1/2}$ and $5^2S_{1/2} \rightarrow 4^2P_{3/2}$

c) The spacing between the above doublet is the energy difference between

Consider the principle series = nP → 4S (n=4,5,6,...)

the spacing for the first doublet, $4^2P_{3/2} \rightarrow 4^2S_{1/2}$ and $4^2P_{1/2} \rightarrow 4^2S_{1/2}$

is also the splitting of doublet 4^2P

So the spacing of this doublet is $1/\lambda_1 - 1/\lambda_2 = 222.959\ cm^{-1}$

d) The first ionization potential corresponds to the series limit of the principal series transition from $4^2S_{1/2} \rightarrow \infty$

So $$E(4^2S_{1/2} \rightarrow \infty) = E(4^2P_{1/2} \rightarrow \infty) + E(4^2P_{1/2} \rightarrow 4^2S_{1/2})$$
$$= 95755.4\ cm^{-1} = 11.8722\ eV$$

3)LS coupling:

a) 3p4s : non equivalent electrons, simply

$L = l_1 + l_2 \, , \; . \; . \; . \; . \; , \left| \, l_1 - l_2 \, \right|$
$S = s_1 + s_2 \, , \; . \; . \; . \; . \; , \left| \, s_1 - s_2 \, \right|$
$J = L + S \, , \; . \; . \; . \; . \; , \left| \, L - S \, \right|$

parity = $\Sigma \, l_i = 1$ = odd

terms are : $^3P_{2,1,0}$, $^1P_1$

b) 4d5d : non equivalent electrons, same as a)

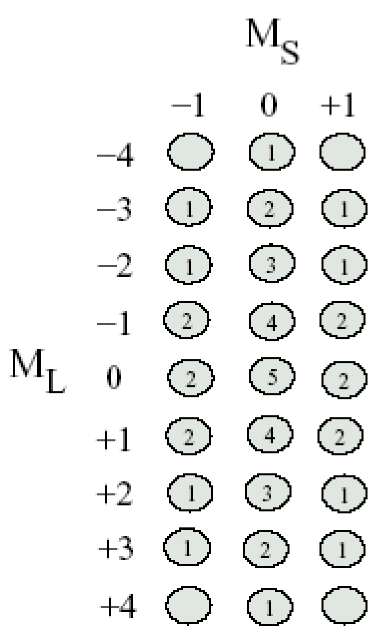
parity = $\Sigma \, l_i = 4$ = even

terms are $^3G_{5,4,3}$, $^3F_{4,3,2}$, $^3D_{3,2,1}$, $^3P_{2,1,0}$, $^3S_1$ (s=1)

$^1G_4$, $^1F_3$, $^1D_2$, $^1P_1$, $^1S_0$ (s=0)

c) $3d^2$: equivalent electrons, need to consider Pauli's Principle.

List all posssible distinct states, then draw a Slater diagram (see class notes p. 29)



Check for the largest M_L :

for $|M_L|$ = 4 (s=0), we got 9 states $\Rightarrow$ $^1G_4$

for $|M_L|$ = 3 (s=1), we got 21 states $\Rightarrow$ $^3F_{4,3,2}$

for $|M_L|$ = 2 (s=0), we got 5 states $\Rightarrow$ $^1D_2$

for $|M_L|$ = 1 (s=1), we got 9 states $\Rightarrow$ $^3P_{2,1,0}$

for $|M_L|$ = 0 (s=0), we got 1 state $\Rightarrow$ $^1S_0$

in summary: $^1G_4$, $^3F_{4,3,2}$, $^1D_2$, $^3P_{2,1,0}$, $^1S_0$,

d) $3p^4$ 4s

Since the total spin and orbital angular momentum of a closed shell are zero, $3p^4$ 4s is the same as $3p^2$ 4s

parity = $\Sigma\, l_i$ = 4 = even

equivalent p^2 gives terms: $^1S_0$, $^3P_{2,1,0}$, $^1D_2$

i)

ii)4s coupling with p^2 are nonequivalent electrons

$L_{4s} = 0$, $S_{4s} = ½$

So the terms are $^2S_{1/2}$, $^4P_{5/2,\ 3/2,\ 1/2}$, $^2P_{3/2,\ 1/2}$, $^2D_{5/2,\ 3/2}$

e) $2p^2$ 4p :

parity = $\Sigma\, l_i = l_1 + l_2 + l_3 = 3$ = odd

same as d) first p^2 gives $^1S_0$, $^3P_{2,1,0}$, $^1D_2$

i.e. Lp = 0,1,2
Sp = 0,1,0

couple with nonequivalent 4P: $L_{4P} = 1$, $S_{4P} = 1/2$

So the terms are

$^4S_{3/2}$, $^2S_{1/2}$, $^4P_{5/2,\ 3/2,\ 1/2}$, $^2P_{3/2,\ 1/2}$, $^4D_{7/2,\ 5/2,\ 3/2,\ 1/2}$, $^2D_{5/2,\ 3/2}$, $^2F_{7/2,\ 5/2}$

f) $3p^3$:

parity = $\Sigma\, l_i = l_1 + l_2 + l_3 = 3$ = odd

from e) we rule out

^2F since all $M_L = 1$, two $M_S = ½$

^4D since two $M_L = 1$, all $M_S = ½$

^4P since two $M_L = 0$, all $M_S = ½$

^2S duplicity

so we have $^4S_{3/2}$, $^2P_{3/2,\,1/2}$, $^2D_{5/2,\;3/2}$

4)

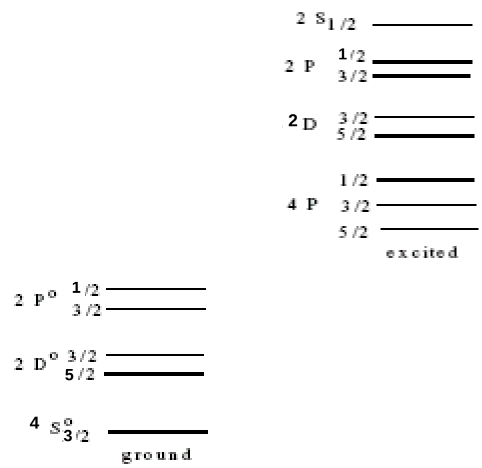
a) For the ground configuration $1s^2\ 2s^2\ 2p^3$, terms are in order of increasing energy:

$^4S_{3/2}$, $^2D_{5/2,}$ $^2D_{3/2}$, $^2P_{3/2}$, $^2P_{1/2}$

For the excited configuration $1s^2\ 2s\ 2p^4$, terms are in order of increasing energy:

$^4P_{5/2}$, $^4P_{3/2}$, $^4P_{1/2}$, $^2D_{5/2}$ $^2D_{3/2}$, $^2P_{3/2}$, $^2P_{1/2}$, $^2S_{1/2}$

So the schematic energy level diagram is:



b) Listing transitions

I) Allowed by electric dipole
The rules below apply for electric dipole transitions:

$\Delta J = 0, \pm 1$ (but $J_a = 0 \rightarrow J_b = 0$ forbidden)
$\Delta M = 0, \pm 1$
parity must change ($\Delta\ \Sigma\ l_i = 1$)

i) with strict LS coupling these additional rules apply

$\Delta M_L = 0, \pm 1$ (for sublevels)
single electron transitions only ($\Delta\ l = \pm 1$)
$\Delta L = 0, \pm 1$ (but $L_a = 0 \rightarrow L_b = 0$ forbidden)
$\Delta S = 0$

$^4P_{1/2,\ 3/2,\ 5/2} \rightarrow {}^4S_{3/2}^o$

$^2S_{1/2} \rightarrow {}^2P_{3/2}^o$, $^2P_{1/2}^o$

$^{2}P_{1/2} \rightarrow\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o}\ ,\ ^{2}D_{5/2}^{o}\ ,\ ^{2}D_{3/2}^{o}$

$^{2}P_{3/2} \rightarrow\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o}\ ,\ ^{2}D_{5/2}^{o}\ ,\ ^{2}D_{3/2}^{o}$

$^{2}D_{3/2} \rightarrow\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o}\ ,\ ^{2}D_{5/2}^{o}\ ,\ ^{2}D_{3/2}^{o}$

$^{2}D_{5/2} \rightarrow\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o},\ ^{2}D_{5/2}^{o},\ ^{2}D_{3/2}^{o}$

19 total

ii)For LS coupling including spin-orbit and configuration interaction, the rules in part i) are relaxed:

$^{4}P_{1/2} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o},\ ^{2}D_{3/2}^{o}$

$^{4}P_{3/2} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o},\ ^{2}D_{3/2}^{o}\ ,\ ^{2}D_{5/2}^{o}$

$^{4}P_{5/2} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}P_{3/2}^{o}\ ,\ ^{2}D_{3/2}^{o}\ ,\ ^{2}D_{5/2}^{o}$

$^{2}D_{3/2} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o},\ ^{2}D_{5/2}^{o},\ ^{2}D_{3/2}^{o}$

$^{2}D_{5/2} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}P_{3/2}^{o}\ ,\ ^{2}D_{5/2}^{o},\ ^{2}D_{3/2}^{o}$

$^{2}P_{1/2} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o},\ ^{2}D_{3/2}^{o}$

$^{2}P_{3/2} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o},\ ^{2}D_{5/2}^{o},\ ^{2}D_{3/2}^{o}$

$^{2}S_{1/2} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}D_{3/2}^{o}\ ,\ ^{2}P_{3/2}^{o}\ ,\ ^{2}P_{1/2}^{o}$

35 total

II) Allowed by magnetic dipole

$\Delta J = 0, \pm 1$ (but $J_a = 0 \rightarrow J_b = 0$ forbidden)
$\Delta M = 0, \pm 1$ (only important for external fields)
no parity change

ii) with strict LS coupling, these additional rules apply

$\Delta n \neq 0$
$\Delta l \neq 0$
$\Delta S \neq 0$
$\Delta L \neq 0$

$\Rightarrow$ no transitions can occur between levels of the same term,
so the allowed transitions are:

$^{2}P_{1/2}^{o} \rightarrow\ ^{4}S_{3/2}^{o}\ ,\ ^{2}D_{3/2}^{o}$

$^2P_{3/2} \rightarrow {}^4S_{3/2}^o$, $^2D_{5/2}^o$, $^2D_{3/2}^o$

$^2D_{3/2}^o \rightarrow {}^4S_{3/2}^o$

$^2D_{5/2}^o \rightarrow {}^4S_{3/2}^o$

and

$^2D_{3/2} \rightarrow {}^4P_{5/2}$, $^4P_{3/2}$, $^4P_{1/2}$

$^2D_{5/2} \rightarrow {}^4P_{5/2}$, $^4P_{3/2}$

$^2P_{1/2} \rightarrow {}^4P_{3/2}$, $^4P_{1/2}$, $^2D_{3/2}$

$^2P_{3/2} \rightarrow {}^4P_{5/2}$, $^4P_{3/2}$, $^4P_{1/2}$, $^2D_{5/2}$, $^2D_{3/2}$

$^2S_{1/2} \rightarrow {}^4P_{3/2}$, $^4P_{1/2}$, $^2D_{3/2}$, $^2P_{3/2}$, $^2P_{1/2}$

25 total

ii) LS coupling including spin-orbit and configuration interaction transitions between levels of the same term are allowed:

$^2P_{1/2}^o \rightarrow {}^4S_{3/2}^o$, $^2D_{3/2}^o$

$^2P_{3/2}^o \rightarrow {}^4S_{3/2}^o$, $^2P_{1/2}^o$, $^2D_{5/2}^o$, $^2D_{3/2}^o$

$^2D_{3/2}^o \rightarrow {}^4S_{3/2}^o$

$^2D_{5/2}^o \rightarrow {}^4S_{3/2}^o$, $^2D_{3/2}^o$

and

$^4P_{1/2} \rightarrow {}^4P_{3/2}$

$^4P_{3/2} \rightarrow {}^4P_{5/2}$

$^2D_{3/2} \rightarrow {}^4P_{5/2}$, $^4P_{3/2}$, $^4P_{1/2}$, $^2D_{5/2}$

$^2D_{5/2} \rightarrow {}^4P_{5/2}$, $^4P_{3/2}$

$^2P_{1/2} \rightarrow {}^4P_{3/2}$, $^4P_{1/2}$, $^2D_{3/2}$, $^2P_{3/2}$

$^2P_{3/2} \rightarrow {}^4P_{5/2}$, $^4P_{3/2}$, $^4P_{1/2}$, $^2D_{5/2}$, $^2D_{3/2}$

$^2S_{1/2} \rightarrow {}^4P_{3/2}$, $^4P_{1/2}$, $^2D_{3/2}$, $^2P_{3/2}$, $^2P_{1/2}$

31 total

III) Allowed by electric quadrupole:

$\Delta J = 0, \pm1, \pm2$ (with $J_a + J_b \geq 2$)
$\Delta M = 0, \pm1, \pm2$
no parity change

i) with strict LS coupling, these additional rules apply

$\Delta l \neq 0$
$\Delta S = 0$
$\Delta L = 0, \pm1, \pm2$ (with $L_a + L_b \geq 2$)
$\Delta l = 0, \pm2$ (but $l_a \rightarrow l_b$ forbidden)

so the allowed transitions are:

$^2P_{1/2}{}^o \rightarrow {}^2D_{5/2}{}^o, {}^2D_{3/2}{}^o$

$^2P_{3/2}{}^o \rightarrow {}^2P_{1/2}{}^o, {}^2D_{5/2}{}^o, {}^2D_{3/2}{}^o$

$^2D_{5/2}{}^o \rightarrow {}^2D_{3/2}{}^o$

6 total

ii) LS coupling including spin-orbit and configuration interaction

The rules listed in part i) are relaxed.

In addition to those in II)ii), the following transitions are also allowed:

$^2P_{1/2}{}^o \rightarrow {}^2D_{5/2}{}^o$

$^2P_{1/2} \rightarrow {}^4P_{5/2}, {}^2D_{5/2}$

$^4P_{1/2} \rightarrow {}^4P_{5/2}$

$^2D_{5/2} \rightarrow {}^4P_{1/2}$

$^2S_{1/2} \rightarrow {}^4P_{5/2}, {}^2D_{5/2}$

38 total