1. a) Les couches fermés ont $L=0$ et $S=0$, donc il suffit de considérer les e^- externes : $3s^2$

$3s^2$: $\ell_1=0,\ \ell_2=0 \Rightarrow L=0$

$s_1=1/2,\ s_2=1/2 \Rightarrow S=0,1$

e^- equivalents, donc L+S pair, $L=0, S=0$: $^1S_0$

$3s4s$: $\ell_1=0,\ \ell_2=0 \Rightarrow L=0$

$s_1=1/2,\ s_2=1/2 \Rightarrow S=0,1$

e^- non equivalents : $^1S_0,\ ^3S_1$

$3s3p$: $\ell_1=0,\ \ell_2=1 \Rightarrow L=1$

$s_1=1/2\ \ s_2=1/2 \Rightarrow S=0,1$

e^- non equivalents : $^1P_1\ \ ^3P_0,\ \ ^3P_1\ \ ^3P_2$

1 b) la base couplé : $|L,S,J,M_J\rangle$, $H_{SF} = \frac{A}{2}(J^2 - L^2 - S^2)$

$$E(3s^2, {}^1S_0) = E(3s^2) + \frac{A}{2}\langle L=0, S=0, J=0 | J^2 - L^2 - S^2 | L=0, S=0, J=0\rangle = E(3s^2)$$

$$E(4s, {}^1S_0) = E(3s\,4s)$$

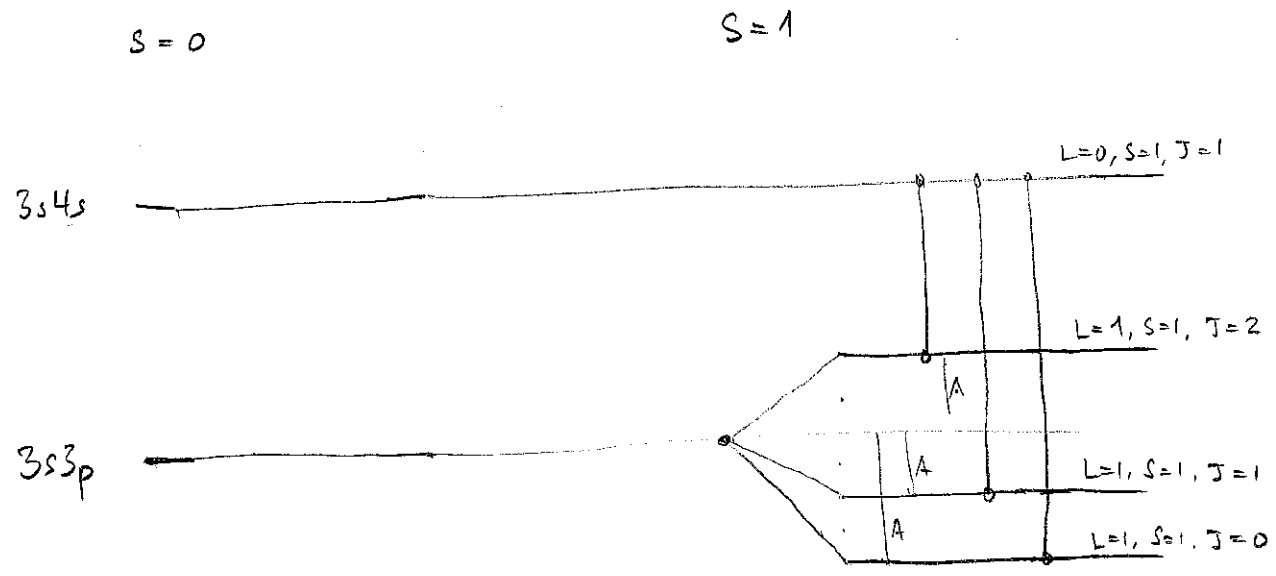
$$E(4s, {}^3S_1) = E(3s\,4s) + \frac{A}{2}\langle L=0, S=1\ J=1 | J^2 - L^2 - S^2 | L=0, S=0\ J=1\rangle = E(3s\,4s)$$

$$E(3s3p, {}^1P_1) = E(3s3p) + \frac{A}{2}\langle L=1, S=0, J=1 | J^2 - L^2 - S^2 | L=1, S=0, J=1\rangle = E(3s3p)$$

$$E(3s3p, {}^3P_0) = E(3s3p) + \frac{A}{2}\langle L=1, S=1, J=0 | J^2 - L^2 - S^2 | L=1, S=1, J=0\rangle = E(3s3p) + \frac{A}{2}(-4) \quad -2A$$

$$E(3s3p, {}^3P_1) = E(3s3p) + \frac{A}{2}\langle L=1, S=1, J=1 | J^2 - L^2 - S^2 | L=1, S=1, J=1\rangle = E(3s3p) + \frac{A}{2}(-2) \quad -A$$

$$E(3s3p\ {}^3P_2) = E(3s3p) + \frac{A}{2}\langle L=1, S=1, J=2 | J^2 - L^2 - S^2 | L=1, S=1, J=2\rangle = E(3s3p) + \frac{A}{2}(2) \quad +A$$



1c) $^3S_1 \longrightarrow {}^3P_{0,1,2}$

règles de selection

1d) $\Delta E = E(3s4s) - \left(E(3s3p) + A\right)$ pour $J=2$, $\lambda = 518.37\,nm$

$-\left(E(3s3p) - A\right)$ pour $J=1$ $\lambda = 517.27\,nm$

$-\left(E(3s3p) - 2A\right)$ pour $J=0$ $\lambda = 516.74nm$

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{6.62\cdot10^{-34}\ J.sec \cdot 3\cdot10^{8}\ m}{518.37\cdot10^{-9}\ m \quad sec} = 3.83\cdot10^{-19} \quad (518.37\,nm)$$

$$= 3.84\cdot10^{-19} \quad (517.27\,nm)$$

$$= 3.843\cdot10^{-19} \quad (516.74nm)$$

$$A = \frac{\Delta E_{J=2} - \Delta E_{J=1}}{2} = 4\cdot10^{-22}\ J$$

$$E(3s4s) - E(3s3p) = \frac{\Delta E_{J=2} + \Delta E_{J=1}}{2} = 3.835\cdot10^{-19}$$

1e) $\Delta E_{J=0,\,theo} = 3.835\cdot10^{-19} + 2\cdot4\cdot10^{-22} = 3.843\cdot10^{-19} \equiv exp$

règle d'intervalle très bien respecté ! LS valide

2 a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$

~~1s~~

~~2s~~ ~~2p~~

~~3s~~ 3p 3d

4s 4p 4d 4f etc..

b) $3d^2$: $l_1 = 2,\ l_2 = 2 \Rightarrow L = 0, 1, 2, 3, 4$

$s_1 = 1/2,\ s_2 = 1/2 \Rightarrow S = 0, 1$

e^- equivalent, $L+S$ = pair :

$L=0,\ S=0,\ J=0$: $^1S_0$

$L=1,\ S=1,\ J=0,1,2$: $^3P_0,\ ^3P_1\ ^3P_2$

$L=2,\ S=0,\ J=2$: $^1D_2$

$L=3,\ S=1,\ J=2,3,4$: $^3F_2,\ ^3F_3\ ^3F_4$

$L=4,\ S=0,\ J=4$: $^1G_4$

c) $^3F_2$

3. a) transitions ro-vibrationnelles

les raies fines correspondent à des transitions rotationnelles associés aux const. vibrationnelles

b) constante de rotation : $B = \frac{\hbar^2}{2\mu r^2}$

séparation entre raies rotationnelles : $\Delta E_{rot} = 2B$

branche P : $\frac{\Delta E_{rot}}{hc} \approx 15\,cm^{-1} = \frac{2B}{hc}$

$\frac{B}{hc} = 7.5\,cm^{-1}$

$B = 7.5\,cm^{-1} \cdot 6.62 \cdot 10^{-34}\,J\,sec \cdot 3 \cdot 10^{10}\,\frac{cm}{sec}$

$= 1.49 \cdot 10^{-22}\,J$

branche Q : $\frac{\Delta E_{rot}}{hc} \approx 18\,cm^{-1} = \frac{2B}{hc}$

$\frac{B}{hc} \approx 9\,cm^{-1}$

$B = 1.78 \cdot 10^{-22}\,J$

$\mu = \frac{m_H \cdot m_{Br}}{m_H + m_{Br}} = \frac{80}{81} m_H \approx m_H = 1.66 \cdot 10^{-27}\,kg$

$r = \frac{\hbar}{\sqrt{2\mu B}} = \frac{1}{2\pi} \cdot \frac{6.62 \cdot 10^{-34}\,J\,sec}{\sqrt{2 \cdot 1.66 \cdot 10^{-27}\,kg \cdot 1.49 \cdot 10^{-22}\,J}}$

$= \frac{1}{2\pi} \cdot \frac{6.62 \cdot 10^{-34} \cdot \frac{kg\,m^2}{sec^2} \cdot sec}{\sqrt{2 \cdot 1.66 \cdot 10^{-27} \cdot kg \cdot \frac{kg\,m^2}{sec^2} \cdot 1.49 \cdot 10^{-22}}}$

$= 1.4 \cdot 10^{-10} \frac{\frac{kg\,m^2}{sec}}{\frac{kg\,m}{sec}} \approx 1.4\,Å \quad (1.37\,Å)$

différence : distortion centrifuge, c-a-d

$\Delta E_{rot} \neq 2B$