## ATOMIC MODELS

VECTOR MODEL OF ATOM

The first paradox between the quantum theory of the atom and the experimental data was observed in the hydrogen atom. Two spectral lines were observed experimentally, while a single spectral line was expected according to the Schrödinger equation in the electronic transition n=3→n=2 in the induced hydrogen atom. The second paradox was observed in the Zeeman effect. The Zeeman effect is the splitting of the orbitals with equal energies in the magnetic or electrical field into different energy levels. The quantum rule stipulates three spectral lines for the 3p→3s electronic transition. Experimental data showed that the number of lines was different.

Magnetic field
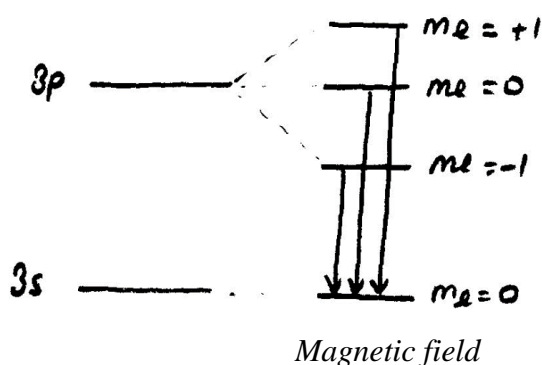
Transitions according to quantum theory

The paradox between the quantum theory of the atom and the experimental data is due to the interaction of the electron motion with the spin movement of the electron. Loaded particles in motion create a magnetic field. The electron creates a magnetic field due to both its spin movement and its movement in the orbital. The orbital angular momentum (L) and the spin angular momentum (S) resulting from these two movements interacts with each other. These new energy states of the atom are called microstates. Symbols used to specify microstates are called atomic term symbols. Since the symbols are spectroscopic symbols, these energy states are also called spectroscopic conditions.

It is assumed that angular momentums are quantized but take certain values. Orbital angular momentum l($h/2\Pi$) and spin angular quantum s($h/2\Pi$) have quantized values. l and s are orbital quantum number and angular momentum quantum number, respectively. Angular momentum vectors should be examined on an axis. This axis may be the applied external

magnetic field axis or the magnetic field axis created around the electron in the system. This axis is taken as the z axis. The projections of angular momentum vectors on the z-axis are also quantized. The z-projection of the orbital angular momentum is determined by the magnetic quantum number m_l and the spin quantum number m_s. The orbital magnetic quantum number (m_l) takes $-l,…,0,…+1$ values, while the spin magnetic quantum number (m_s) takes $\pm 1/2$ values.

In single-electron atoms, the energy levels of the atom are the same as their orbital energies. In the case of multi-electron atoms, the energy levels of the atom depend on the regulation of the atom in electronic orbitals due to the electron-electron interaction.

Total angular momentum is found in two ways:

1. *Russel-Sounders (L-S) coupling: Orbital and spin angular momentum vectors are added together and then, resultant the total spin angular momentum vectors are taken. So these vectors are added together.*

2. *J-J (spin-orbital) coupling: First, the resultant orbital angular momentum vector and spin angular momentum vector of each electron is found and then the resultant vectors for all electrons are added.*

Russel-Sounders interaction is used more in small atoms because electron-electron interactions are more common. J-J coupling gives better results on heavy atoms. In L-S coupling, the total magnetic orbital angular momentum is M_L, the total spin angular momentum is M_S and the total angular momentum is M_J.

$$M_L = \sum_{i=1}^{k} (m_l)_i$$

$$M_S = \sum_{i=1}^{k} (m_s)_i$$

$$\left. \right\} \quad M_J = M_L + M_S$$

$k=$ *number of electrons*

$m_l=$ *magnetic quantum number of each electron,* $m_s=$ *spin quantum number of each electron*

M_L *and* M_S *components according to the selected axis*

$M_L = L, L-1, L-2, ..., -L$

$M_S = S, S-1, S-2, ..., -S$

The biggest value of M_L *is* L*, the biggest value of* M_S *is* S

L*: The values of total orbital angular momentum quantum number*

M_L*: Total magnetic orbital quantum number determining z-projection of total orbital angular momentum*

$L = (l_1 + l_2 + l_3 + ...), (l_1 + l_2 + l_3 + ..., -1), (l_1 + l_2 + l_3 + ..., -2)$ *for a multi-electron atom*

$L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2), ..., |(l_1 - l_2)|$ *for an atom with two electrons*

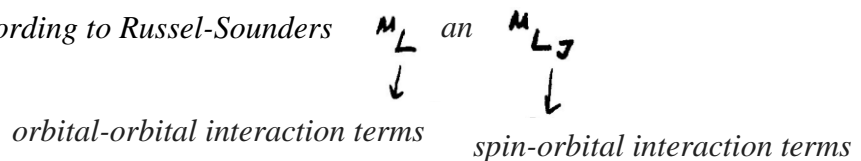$S = (s_1 + s_2 + s_3 + ...), (s_1 + s_2 + s_3 + ..., -1), (s_1 + s_2 + s_3 + ..., -2)$ *for a multi-electron atom*

$S = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), ..., |(s_1 - s_2)|$ *for an atom with two electrons*

$J = $*Total angular momentum quantum number*

$J = L+S, L+S-1, L+S-2, ..., |L-S|$

Atomic terms according to Russel-Sounders M_L *an* M_{L_J}

⬇   ⬇

orbital-orbital interaction terms   *spin-orbital interaction terms*

$M = $*Multiplicity* $M = 2S+1$

$M = 1, 2, 3, ...$ *for singlet, doublet, triplet*

for $L = 0, 1, 2, 3, 4, 5, ...$ *it is used spectroscopic symbols S, P, D, F, G*

for $L = 1$ *and* $S = 1$*, orbital-orbital interaction term is* ^3P*.*

To find the corresponding spin-orbital interaction terms,

$J = 1+1, 1+1-1, 1+1-2 = 2, 1, 0$ $^3P_2, {}^3P_1, {}^3P_0$

$^3P_2 \rightarrow$ *read in triplet P two*

The number of possible values for J *is* $2S+1$*.*

Energies of Terms (Hund's Selectivity Rule):

1. *The energy of the term with the biggest multiplicity is the lowest (Where the multiplicity is the highest, the energy is the lowest).*

2. *If the multiplicities of terms are the same, it with a big L value has a lower energy.*

3. *The energy of the term with a bigger L value among the terms with the biggest multiplicities is lower.*

4. *Among the terms which its M and its L values are the same; if the subshell is less than half-full (half filled), the energy of the term with the smaller J value is the lowest. If the subshell is more than half-full (half filled), the energy of the term with bigger J value is the lowest.*

$$^1D, \ ^3P, \ ^1S \ \Rightarrow \ ^3P < \, ^1D < \, ^1S \qquad \text{orbital-orbital interaction terms}$$

$$^3P_0 < \, ^3P_1 < \, ^3P_2 < \, ^1D_2 < \, ^1S_0 \qquad \text{spin-orbital interaction terms}$$

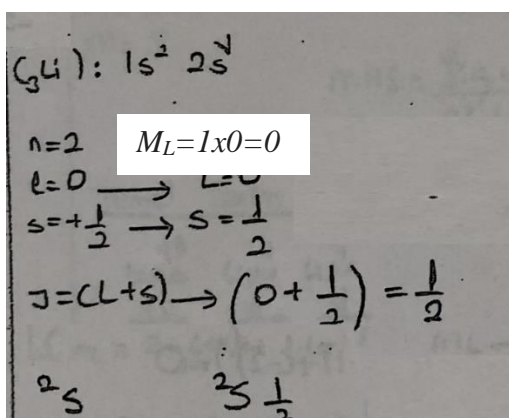|	
s^2, p^6, d^{10}	^1S
p^1 and p^5	^2P
p^2 and p^4	$^3P, \ ^1D, \ ^1S$
p^3	$^4S, \ ^2D, \ ^2P$

The ground State Term Symbols

1. *The electron configuration of the partially filled subshell is written.*
2. *Orbitals of a subshell are arranged so that the m_l values decrease from left to right.*

$$M_\rho = \quad +2 \quad +1 \quad 0 \quad -1 \quad -2$$
$$\underline{\quad} \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad}$$

3. *According to the Hund rule, electrons are placed in orbitals starting from high m_l.*
4. *M_L, L, S and multiplicity [M=2S+1] are calculated.*
5. *If the subshell is more than half full, J=L+S; if the subshell is less than half full, J=L-S; if the subshell is half full, J=1 because of L=0.*

Write the ground state term symbol of $_3$Li

$(_3Li): 1s^2 2s^1$

$n=2$
$l=0 \longrightarrow L=0$ $M_L=1x0=0$
$s=+\frac{1}{2} \longrightarrow S=\frac{1}{2}$

$J=(L+s) \longrightarrow \left(0+\frac{1}{2}\right) = \frac{1}{2}$

$^2S \qquad\qquad ^2S_{\frac{1}{2}}$

orbital-orbital interaction term symbol   spin-orbital interaction term symbol

Write the ground state term symbol of $_4$Be.

$(_4Be) = 1s^2 2s^{2\Lambda}$

$n=2$
$l=0 \longrightarrow L=0$ $M_L=2x0=0$
$s=+\frac{1}{2} + \left(-\frac{1}{2}\right) =0$

$m=(2S+1)$
$m=(2,0+1)$
$m=1$

$J=(L+s)$
$J=0+0$
$J=0$

$^1S \qquad\qquad ^1S_0$

orbital-orbital interaction term symbol   spin-orbital interaction term symbol
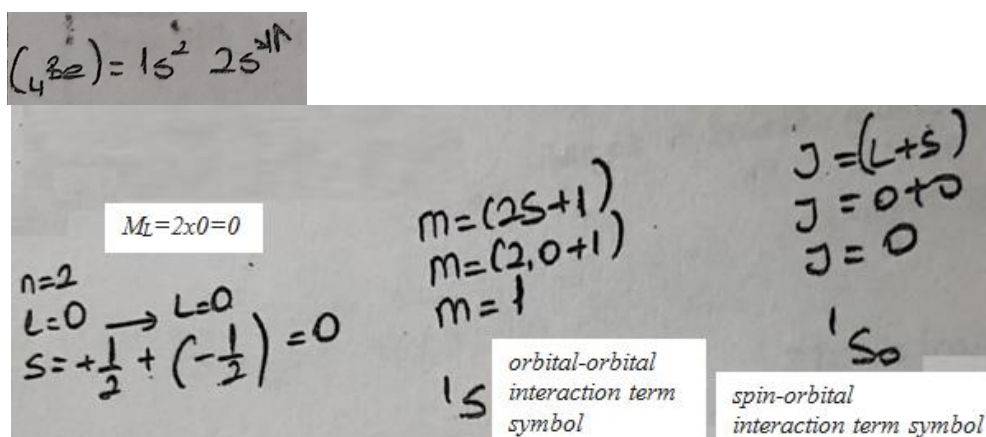
*Finding Atomic Term Symbols*

Each of the possible arrangements that give the distribution of electrons to the orbitals according to the Pauli principle is called microstate.
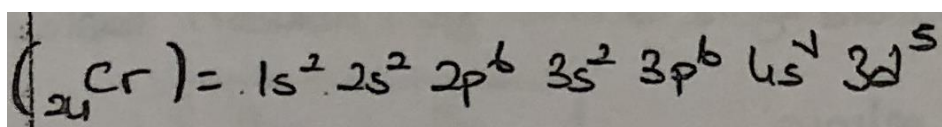
e=number of electrons

N=number of possible positions for the electron. An orbital can take up to two electrons, which is equal to twice the number of the orbital.

Microstate number $= \dfrac{N!}{e!(N-e)!}$

(for s orbital N=2, for p orbital N=6, for d orbital N=10, for f orbital N=14)

$$_{34}Se = (1s^2)(2s^2 \, 2p^6)(3s^2 \, 3p^6)(3d^{10}) \, 4s^2 \, 4p_z^{\uparrow\downarrow} \, 4p_y^{\uparrow} \, 4p_x^{\uparrow}$$
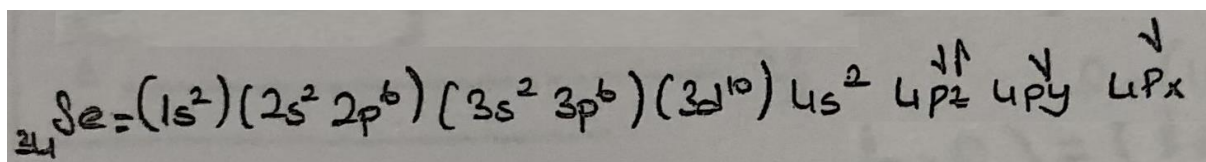
Microstate number $= \dfrac{6!}{(6-4)!\,4!} = 15$

$$(_{24}Cr) = 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 4s^{\uparrow} \, 3d^5$$

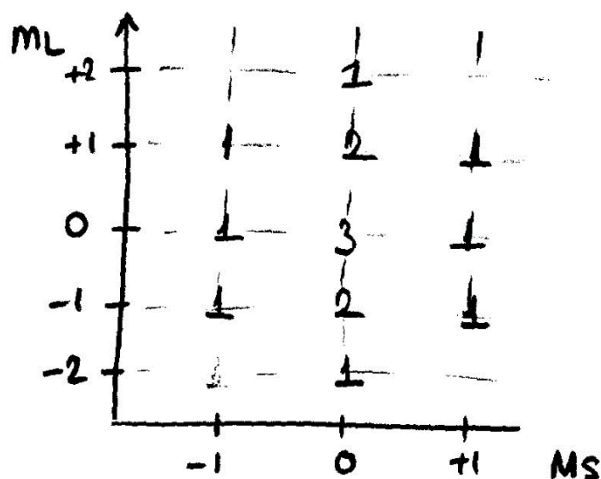Microstate number $= \dfrac{2!}{(2-1)!\,1!} \cdot \dfrac{10!}{(10-5)!\,5!} = 504$

For p^2 system

Write electron configuration, the microstate number and all term symbols of $_{14}Si$. How many spectral lines should be drawn for 3d → 3p transition?
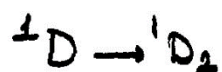
$$[_{14}Si] = ---- \, 3p^2$$
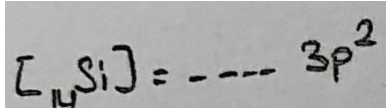
Microstate number $= \dfrac{6!}{2!(6-2)!} = \dfrac{6 \cdot 5 \cdot 4!}{2 \times 1 \times 4!} = 15$

m_ℓ			M_L	M_S
−1	0	+1		
xx			−2	0
	xx		0	0
		xx	+2	0
x	x		−1	+1, 0, 0, −1
x		x	0	+1, 0, 0, −1
	x	x	+1	+1, 0, 0, −1

$M_L = 2 \quad M_S = 0 \quad L = 2 \quad S = 0$

$$^1D \longrightarrow {}^1D_2$$

$J = (2+0), \ldots \ |2-0|$

Microstate number $= (2 \cdot 0 + 1) \cdot (2 \cdot 2 + 1) = 5$

$M_L = 1 \quad M_S = -1, 0, +1$

$L = 1 \quad S = 1$

$$^3P \rightarrow {}^3P_2, {}^3P_1, {}^3P_0$$
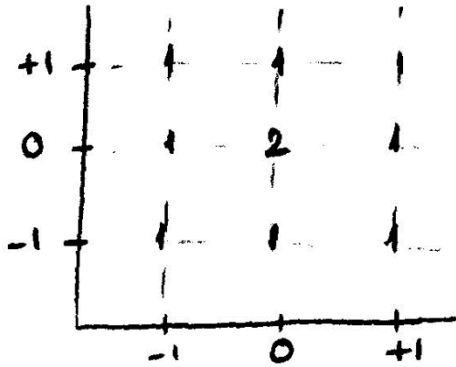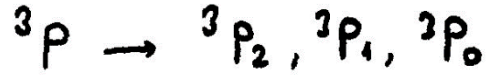
$J = |1+1|, (1+1-1) \quad |1-1|$

$J = 2, 1, 0$

Microstate number $= (2.1+1) + (2.1+1) = 9$
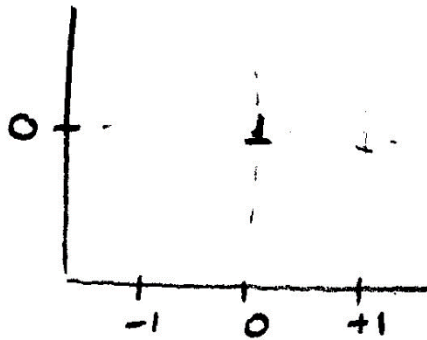
$M_L = 0 \quad M_S = 0$

$L = 0 \quad S = 0$
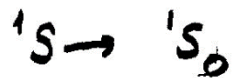
$$^1S \rightarrow {}^1S_0$$

$(2.0+1) \cdot (2.0+1) = 1$

E

$1s^2 2s^2 2p^2$

$^1S \quad \cdots \quad {}^1S_0$

$^1D \quad \quad {}^1D_2$

$^3P \quad \quad {}^3P_2$
$\quad \quad \quad {}^3P_1$
$\quad \quad \quad {}^3P_0$

J values

43
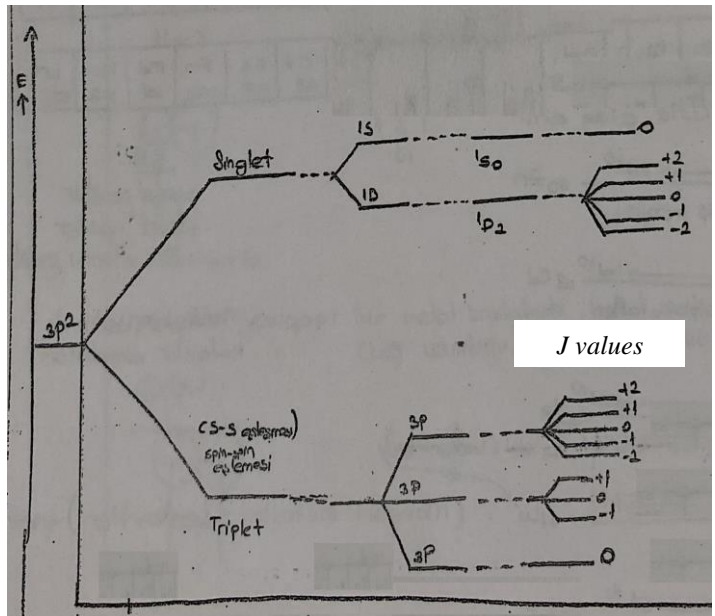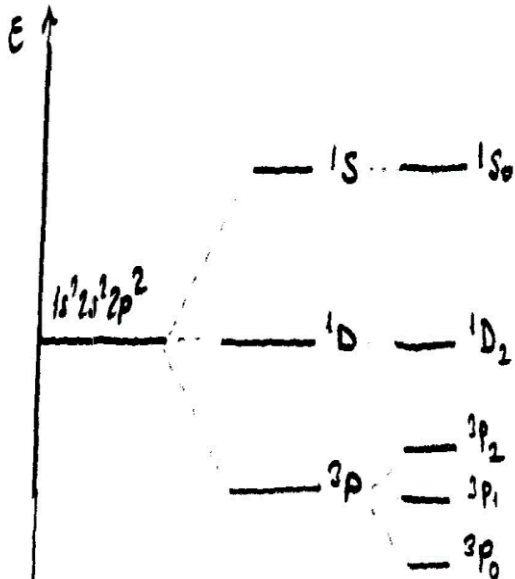
Spectroscopic Transitions

$\Delta M=0$

$\Delta L=\pm1$ *allowed transitions*

$\Delta J=0, \pm1$

$J=0 \rightarrow J=0$ *forbidden transition*

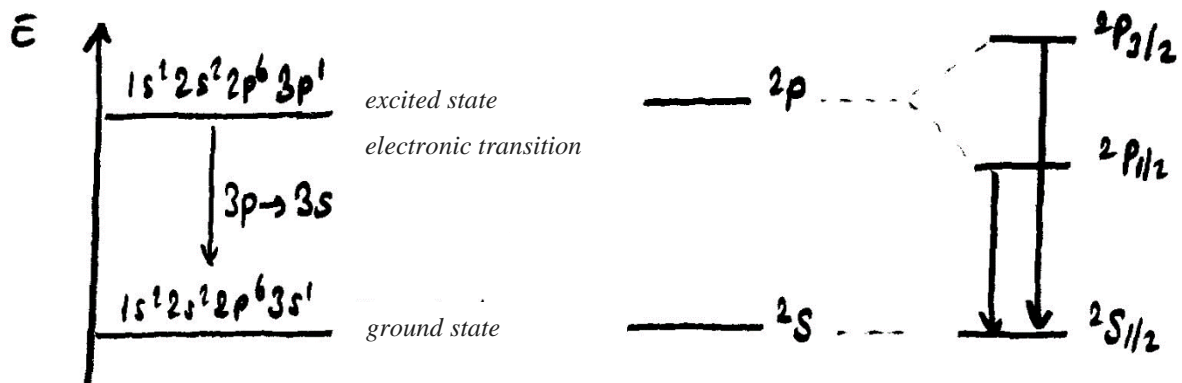*That a transition is forbidden means that the intensity is too low to be measured. Transitions that do not comply with M=0 rule are transitions with the lowest intensity. This rule is expressed in some sources.as singlet → singlet, triplet → triplet transitions are allowed transitions. In the emission spectra of atoms, each spectral line corresponds to an allowed spectroscopic transition. In other words, in the emission spectra of atoms, the number of lines are the same as the number of spectroscopic passes allowed.*

How many spectral lines are observed in the emission spectrum of the Na atom when it's electron passes (or is excited) from 3s to 3p?
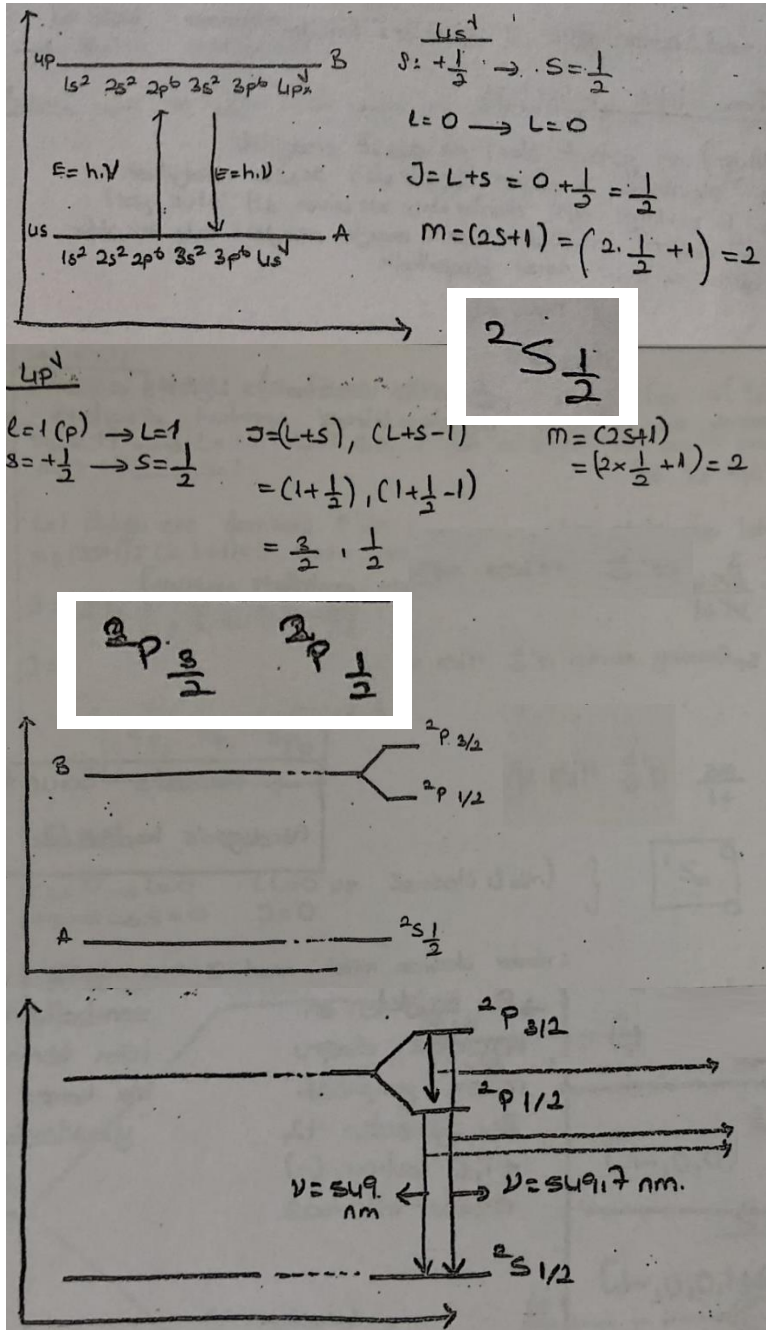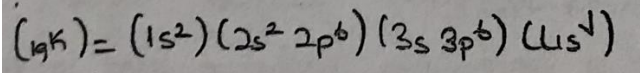
$1s^2 2s^2 2p^6 3s^1$ *ground state* $1s^2 2s^2 2p^6 3p^1$ *excited state*

$^2S_{1/2}$ $^2P_{1/2}$, $^2P_{3/2}$
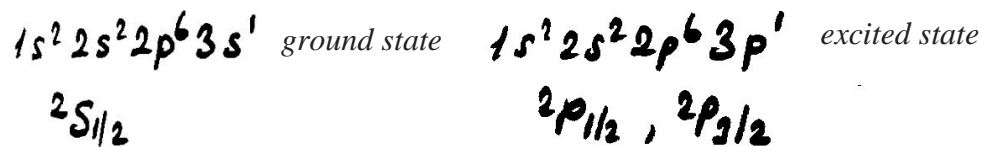
$3p \rightarrow 3s$ *How many?*

Write the electron configuration and the ground state term symbol of $_{19}K$. How many spectral lines should be drawn for 4s → 4p or 4p → 4s transition? *(The vector model of the atom was born due to this transition.)*

$$(_{19}K) = (1s^2)(2s^2\,2p^6)(3s\,3p^6)(4s^1)$$

$$4s^1$$
$$S: +\tfrac{1}{2} \rightarrow S = \tfrac{1}{2}$$
$$L = 0 \rightarrow L = 0$$
$$J = L+S = 0+\tfrac{1}{2} = \tfrac{1}{2}$$
$$m = (2S+1) = \left(2\cdot\tfrac{1}{2}+1\right) = 2$$

$$^2S_{\tfrac{1}{2}}$$

$$4p^1$$
$$\ell = 1\,(p) \rightarrow L=1 \qquad J=(L+S),\,(L+S-1) \qquad m=(2S+1)$$
$$s=+\tfrac{1}{2} \rightarrow S=\tfrac{1}{2} \qquad = (1+\tfrac{1}{2}),\,(1+\tfrac{1}{2}-1) \qquad = (2\times\tfrac{1}{2}+1)=2$$
$$= \tfrac{3}{2},\,\tfrac{1}{2}$$

$$^2P_{\tfrac{3}{2}} \qquad ^2P_{\tfrac{1}{2}}$$

The energy is too low to be observed.

$\nu = 549\,nm$ $\nu = 549,7\,nm$

K and other alkali metals show one transition, according to the quantum model and two transitions according to the vector model of the atom. There are two transitions for all alkali metals.