Dr. Ranjana
Assistant Professor, Physics
HarPrasad Das Jain College
Ara, Bihar India

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MPHYCC10 – 11

example :→ (3) Nitrogen atom has the electronic configuration

$1s^2, 2s^2, 2p^3$

outer shell e^-s = optical e^-s

$2p^3$ is the outer shell e^-s

This give rise to $^2P^\circ$, $^2D^\circ$, $^4S^\circ$ states

$^4S^\circ$ = ground state

$^2D^\circ$ = next state.

Selection rules for multielectron atoms in L-S coupling

(a) Generally one e^- jumps at a time in the most of the transitions. In this case l-value changes by one unit.

$$\Delta l = \pm 1$$

(b) For two electron transitions we would have

$$\Delta l = \pm 1 \; ; \; \Delta l_2 = 0, \pm 2$$

example 3d 4d ⟶ 4s 4p there are two possibilities here 4d → 4p ($\Delta l_1 = -1$), 3d → 4s ($\Delta l_2 = -2$)
or 3d → 4p ($\Delta l_1 = -1$); 4d to 4s ($\Delta l_2 = -2$)

(c) There is no restriction on the total quantum number n of either electrons.

(d) For the atom as a whole, the quantum numbers L, S & J must changes as follows.

$\Delta L = 0, \pm 1$ (In one e^- atom $\Delta L = 0$ is not allowed)

$\Delta S = 0$

$\Delta J = 0, \pm 1$ but $J = 0 \not\longrightarrow J = 0$ is not allowed.

These above rules are valid for the atoms in which weak L-S coupling is present

These rules are valid for lighter atoms only as we go for heavy atoms, spin orbit interaction increases rapidly.

Dr. Ranjana Singh
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Then the whole concept of L-S coupling breaks down and the concept of J-J coupling arises.

J-J coupling:- In the Heavier atom, spin-orbit interaction term in the Hamiltonian predominates over the residual electrostatic interaction and the spin-spin correlation. Therefore, splitting of the unperturbed energy level due to introduction of the various perturbations takes place in the following order

(a) spin-orbit interaction.
(b) residual electrostatic interaction.
(c) spin-spin corelation.

(a):- due to strong spin-orbit interaction the orbital & the spin angular momentum vectors of each individual e^- are are strongly coupled to form resultant angular momentum vector $\vec{j}$ of magnitude $\sqrt{j(j+1)}\frac{h}{2\pi}$ where $j = l-\frac{1}{2}$ & $j = l+\frac{1}{2}$ i.e j can take half integral values.

$j = l-\frac{1}{2}$ — will be the lowest level.

(b):- As a result of residual electrostatic interaction & spin-spin corelation, the resultant angular momentum vector $\bar{j}$ of the individual electrons are less strongly coupled with one another to form the total angular momentum vector $\vec{J}$ of the atom with magnitude $\sqrt{J(J+1)}\,h/2\pi$

$J = |\bar{j}_1+\bar{j}_2+ \cdots|_{min}, |\vec{j}_1+\vec{j}_2 \cdots|_{min}+1 \; \cdots \; (j_1+j_2 \cdots)$

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Each of the above level is splitted into a number of levels characterized by different values of 'J'.

Example:- Terms of the electron configuration 4p4d under J-J coupling 4p4d

for p electron $l_1 = 1,\ s_1 = \frac{1}{2},\ J_1 = |l_1 \pm s_1| = \frac{1}{2}, \frac{3}{2}$

for d electron $l_2 = 2,\ s_2 = \frac{1}{2},\ J_2 = |l_2 \pm s_2| = \frac{3}{2}, \frac{5}{2}$

~~$J = |J_1 \pm J_2|$ $J_1 = \frac{1}{2},\ J_2 = \frac{3}{2}$~~

~~$J = |\frac{1}{2} \pm \frac{3}{2}| =$~~

combination of possible J_1 & J_2 values are

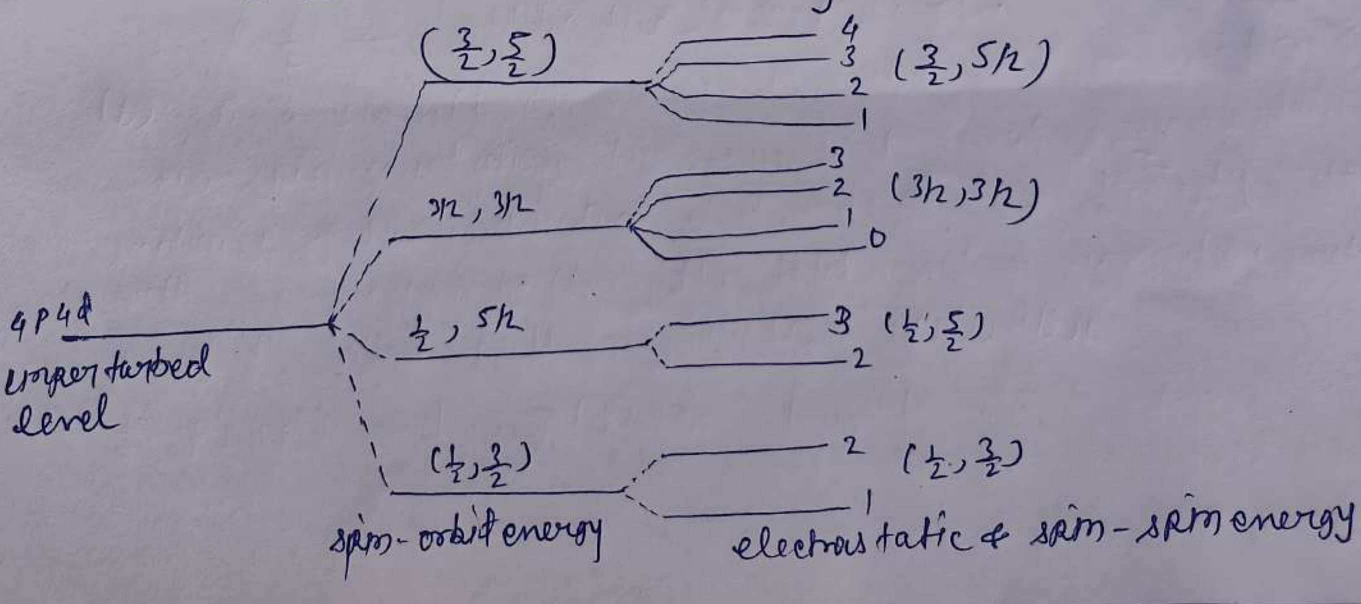
$(\frac{1}{2}, \frac{3}{2}),\ (\frac{1}{2}, \frac{5}{2}),\ (\frac{3}{2}, \frac{3}{2}),\ (\frac{3}{2}, \frac{5}{2})$

$J = (\frac{1}{2}, \frac{3}{2})$ gives $J = 1, 2$

$J = (\frac{1}{2}, \frac{5}{2})$,, $J = 2, 3$

$J = (\frac{3}{2}, \frac{3}{2})$ gives $J = 0, 1, 2, 3$

$J = (\frac{3}{2}, \frac{5}{2})$ gives $J = 1, 2, 3, 4$



Dr. Ranjana Singh
Assistant Professor Physics
Har Prasad Das Jain College
Arra, Bihar, India

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Selection rules in J-J coupling:-

(a) $\Delta l_1 = \pm 1$ for one electron atom
$\Delta l_2 = 0, \pm 2$ similar to L-S coupling

(b) $\Delta J = 0, \pm 1$ for the jumping electron
$\Delta J = 0$ for other electrons

(c) For the atom as a whole
$\Delta J = 0, \pm 1$ but $J = 0 \not\rightarrow J = 0$ not allowed.

(d) L & S are not good quantum number hence $\Delta S = 0$, $\Delta L = 0, \pm 1$ does not valid in J-J coupling.