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# A COMPARATIVE STUDY OF THE ATOMIC TERM SYMBOLS OF $\mathbf{f}^{3}$ AND $f^{11}$ CONFIGURATION 

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#### Abstract

The term is a particular energy state and term symbol is a label to energy state. The importance of these term symbols has been emphasized in connection with the spectral and magnetic properties of complexes and metal free ions and also provide information about the energy of atomic electrons in orbital's and total spin, total orbital and grand total momenta of whole atom and electronic configuration. Russell-Saunders (L-S) coupling and j-j coupling schemes are important schemes for determination of terms and term symbols of the atoms and ions of inner transition elements in which electrons are filled in af sub-shell with azimuthal quantum number 3 . The determination of terms and term symbols for $\mathrm{f}^{\mathrm{n}}$ configuration is very difficult work since there are seven orbital's in f-sub shell which give large number of microstates. In this proposed work computation is done for calculating all possible terms and term symbols regarding for $f^{3}$ and $f^{11}$ configurations without any long tabulation with mental exercise and a comparative study was carried out between the $f^{3}$ and $f^{11}$ terms and term symbols. The possible microstates and spectroscopic terms calculated for $f^{3}$ and $f^{11}$ configuration (ions $\mathrm{M}^{+3}$ ) are 364 and 17. These terms are split up into quartets (5) and doublets (12). The ground state term for $f^{3} \& f^{11}$ is ${ }^{4}$ I.


Key words: Term symbol, Russell-Saunders coupling, Azimuthal quantum number, Microstate, $\mathrm{f}^{3}$ and $\mathrm{f}^{11}$ configuration.

## INTRODUCTION

The term is applied for energy associated with the state of an atom involved in a transition. Term symbols are abbreviated for description of the energy, angular momentum and spin multiplicity of an atom in particular state. When only one electron is present in a degenerate energy level or sub shell such as $2 \mathrm{p}, 3 \mathrm{p}$, $3 \mathrm{~d}, 4 \mathrm{~d}$ and 4 f etc. the energy depends on ' $l$ ' the orbital quantum number but more than one electron then they interact to each other and result in the formation of a ground state and one or more excited states for the atom or ion. Due to different possibilities for relative orbital and spin orientations among the valence electrons in atoms or ions in same energy level may have slightly different energy contents.

The interactions between the electrons are of three types. (i) spin-spin coupling (ii) orbit-orbit coupling (iii) spin-orbit coupling. It is assumed that: spin-spin coupling > orbit-orbit coupling $>$ spin-orbit coupling. The energy states obtained due to above three types of coupling or interaction depend upon the result of the orbital angular quantum number of each electron. This is a resultant of all the $l$ values and denoted by a new quantum number $L$ which defines the energy state for the atom. There are two principle coupling schemes adopted for arising or splitting of state (i) Russell-Saunders (or L-S) coupling and (ii) jj coupling.

[^0]This is found that the Russell-Saunders scheme gives a good approximation for first row transition series where spin-orbit ( $\mathrm{j}-\mathrm{j}$ ) coupling can generally be ignored, however for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant due to higher nuclear charge and the $\mathrm{j}-\mathrm{j}$ coupling scheme is used ${ }^{1-3}$. However, for heavier atoms it is still convenient to use Russell-Saunders scheme ${ }^{4}$. Such interactions (coupling) produced by the electrons orbital and spin angular momenta give rise to a series of energy levels or states or terms. These states are characterized by energy, orbital angular momentum, spin angular momentum and total angular momentum ${ }^{4}$.

Arising of states which are called spectroscopic states or microstates or multiplets expressed by proper term symbols and are defined by new quantum numbers- $\mathrm{L}, \mathrm{M}_{\mathrm{L}}, \mathrm{M}_{\mathrm{S}}, \mathrm{S}$. These quantum numbers for multi electron systems are obtained by summing vectorially the quantum numbers for the individual electrons. The terms have orbital degeneracy $(2 L+1)$ and spin degeneracy $(2 S+1)$ so that the total degeneracy is equal to multiplication of above two. This total degeneracy number is characterized the different possible combination of orbital and spin which individual electron can acquired may be called microstate ${ }^{5,6}$.

For a particular electronic configuration of an ion or atom the energy states which are degenerate when the ion is free of perturbing influences must be break up into two or more non equivalent states when the ion or atom is introduced into a lattice. These splitting are by purely electrostatic forces ${ }^{7}$.

Total number of microstates increase with the increase in the number of electron in orbital. The hole formulation can be used for the sub-shell that is more than half full. When a sub-shell is more than half full, it is simpler and more convenient to work out the terms by considering the holes that is vacancies in the various orbital's rather than larger number of electrons actually present. By considering holes the terms which arise for pairs of atoms with $p^{n}$ and $p^{6-n}$ arrangements $d^{n}$ and $d^{10-n}$ and also $f^{n}$ and $f^{14-n}$ give rise to identical terms ${ }^{8}$. In the $f^{3}$ and $f^{11}$, there are three holes which have same possible arrangement as $f^{3}$.

A complete term symbol is $(2 \mathrm{~S}+1) \mathrm{L}_{\mathrm{J}}{ }^{4,8,9} . \mathrm{J}=$ Total angular quantum number, it is a vector sum of orbital angular momentum and spin angular momentum and useful in accounting for the energy of state and can have values $\mathrm{L}+\mathrm{S}$ to $\mathrm{L}-\mathrm{S}$. This can be specified a post subscript to the $\mathrm{L} . \mathrm{L}=$ Resultant orbital quantum number, $\mathrm{S}=$ Resultant spin quantum number, $2 \mathrm{~S}+1=$ Multiplicity. $\mathrm{J}=\mathrm{L}-\mathrm{S}$ state is lower in energy than the $\mathrm{J}=\mathrm{L}+\mathrm{S}$ state since in former state the orbital and spin moments are opposed ${ }^{10,11}$. The number of different values of ' J ' is called the multiplicity of the atom. For the S term $\mathrm{J}=1 / 2$ only but for other terms it split up into multiplets.

## Methodology

## Calculation of total number of microstates

Each arrangement of electrons in a set of orbital's has a slightly different energy and called a microstate. When placing electrons in orbital's there is usually more than one way to accomplish this, particularly when the electrons are going into a degenerate set of orbital's. The orbital's can be considered to be boxes, two boxes per orbital corresponding to the two different values of the electron spin. This is just another way of saying that each orbital can "hold" two electrons as long as their $\mathrm{m}_{\mathrm{s}}$ values are different. Thus each box is described by $m_{1}$ and $m_{s}$. The question of arranging $x$ electrons in a degenerate set of ' $r$ ' orbital's is equivalent to asking how many ways are there to distribute n indistinguishable objects among n boxes (where n would equal 2 r ). The answer is given by the expression ${ }^{12}$.

Number of ways of filling electrons $N=\frac{n!}{x!(n!x!)}$
$\mathrm{N}=2(21+1)$ or two wise of the total No. of orbital's, $\mathrm{x}=$ Total No. of electron in sub-shell

$$
\begin{aligned}
& \text { For } f^{3} \text { system } n=14 \text { and } \times 3 \text {, so, } N=\frac{14!}{3!(14!-3!)} \\
& N=\frac{13 \times 12 \times 11 \times 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{3 \times 2 \times 1 \times 11 \times 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1} \\
& N=364 \text { Microstates } \\
& \text { For } \mathrm{f}^{11} \text { system } \mathrm{n}=14 \text { and } \times=11, \text { so, } \mathrm{N}=\frac{14!}{11!(14!-11!)} \\
& \mathrm{N}=\frac{14 \times 13 \times 12 \times 11 \times 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{11 \times 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1 \times 3 \times 2 \times 1} \\
& N=364 \text { Microstates }
\end{aligned}
$$

Determination of electronic configuration that allowed by the Pauli Principle or Possible spin conditions for $f^{3}$ and $f^{11}$ system

It is determined by arranging the possible spin states of electrons in orbitals. Total microstates with possible spin states are given in Table 1 and 2.

Table 1: (For f ${ }^{3}$ system)

| S. No. | Possible spin states |  | Total spin (S) | Total microstates |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $+3 / 2$ | 35 |
| $\mathbf{2}$ | $\uparrow$ | $\uparrow$ | $\downarrow$ | $+1 / 2$ | 105 |
| $\mathbf{3}$ | $\uparrow$ | $\downarrow$ | $\downarrow$ | $-1 / 2$ | 105 |
| $\mathbf{4}$ | $\downarrow$ | $\downarrow$ | $\downarrow$ | $-3 / 2$ | 35 |
| $\mathbf{5}$ | $\uparrow \downarrow$ | $\uparrow$ |  | $+1 / 2$ | 42 |
| $\mathbf{6}$ | $\uparrow \downarrow$ | $\downarrow$ | $-1 / 2$ | 42 |  |
|  | Total Microstates |  | 364 |  |  |

Table 2: (For $\mathbf{f}^{11}$ System)


| S. No. | Possible spin states |  |  |  |  |  |  | Total spin (S) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 5 Total microstates |  |  |  |  |  |  |  |  |
|  | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow$ | $+1 / 2$ | 42 |
| 6 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\downarrow$ | $-1 / 2$ | 42 |
| Total Microstates |  |  |  |  |  |  | 364 |  |

Microstate Charts for $f^{3} \& f^{11}$ Configurations (system)
Table 3: Total No. of microstates for $f^{\mathbf{3}}$ and $\mathbf{f}^{\mathbf{1 1}}$


Determination of orbital angular momentum quantum number ( L ), l-l coupling
It is a vector sum of all the (1) value i.e. orbital angular momentum quantum number of all electrons coupling together electrostatically gives (L). It defines the state of free atom /ion as a whole while ' 1 ' defines the state of the electron only, L is always an integer including zero, it is quantized so the only permissible arrangements are those where the resultant is whole number of quanta. $L=\left(1_{1}+1_{2}\right),\left(1_{1}+1_{2}-1\right),\left(l_{1}+1_{2}-2\right), \ldots$, $\left|\left(1_{1}-l_{2}\right)\right|^{4,8,9,13}$. These states or term letters are represented in Table 5.

Table 4: Set up of a Chart of microstates for $f^{\mathbf{3}}$ and $f^{11}$

| $\mathrm{M}_{\text {S }}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | +3/2 | +1/2 | -1/2 | -3/2 |  |
| 8 |  | \| | \| |  | 2 |
| 7 |  | \|| | \|| |  | 4 |
| 6 | \| | \|||| | \|||| | \| | 10 |
| 5 | \| | \|||||| | \|||||| | \| | 14 |
| 4 | \|| | \||||||||| | \||||||||| | \|| | 22 |
| 3 | \||| | \|||||||||||| | \|||||||||||| | \||| | 30 |
| 2 | \|||| | \||||||||||||||| | \||||||||||||||| | \|||| | 38 |
| L | \|||| | \|||||||||||||||| | \|||||||||||||||| | \|||| | 40 |
| $\mathrm{M}_{\mathrm{L}}$ | \|||| | \|||||||||||||||| | \|||||||||||||||| | \||||| | 44 |
| -1 | \|||| | \||||||||||||||| | \||||||||||||||| | \|||| | 40 |
| -2 | \|||| | \||||||||||||||| | \||||||||||||||| | \|||| | 38 |
| -3 | \||| | \|||||||||||| | \|||||||||||| | \||| | 30 |
| -4 | \|| | \||||||||| | \||||||||| | 1 | 22 |
| -5 | \| | \|||||| | \|||||| | \| | 14 |
| -6 | \| | \|||| | \|||| | \| | 10 |
| -7 |  | 1 | 1 |  | 4 |
| -8 |  | \| | \| |  | 2 |
| Microstates | 35 | 147 | 147 | 35 | 364 |

Table 5: States or term letters

| Value of L | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Symbol of L | S | P | D | F | G | H | I | K | L | M | N | O | Q | R | T | U | V | W | X | Y | Z |

For the $\mathrm{f}^{3}$ and $\mathrm{f}^{11}$ configuration the maximum and minimum value of L obtained are +8 and 0 , Therefore L is ranged from 0 to +8 and $\mathrm{L}=0,1,2,3,4,5,6,7,8$. The Term labels for L are $\mathrm{S}, \mathrm{P}, \mathrm{D}, \mathrm{F}, \mathrm{G}, \mathrm{H}$, I, K, L.

Determination of total spin angular momentum quantum number ( S ); s-s coupling: It represents total spin of atom while' $s$ ' states for spin of an electron. $S=\left(s_{1}+s_{2}\right),\left(s_{1}+s_{2}-1\right),\left(s_{1}+s_{2}-2\right) \ldots \ldots$, $\left|\left(s_{1}+s_{2}\right)\right|^{4,8,9,13}$. $S=\sum_{i} s$ for $f^{3}$ and $f^{11}$ system maximum value of $S$ is $+3 / 2$ when all the electrons are unpaired and other values are $+3 / 2,+1 / 2,-1 / 2,-3 / 2$.


Determination of $\mathbf{M}_{\mathbf{L}}$ and $\mathbf{M}_{\mathbf{S}}: \mathbf{M}_{\mathbf{L}}=\sum \mathrm{m}_{1}=$ the component of the total angular momentum along a given axis. Total values of $\mathrm{M}_{\mathrm{L}}=2 \mathrm{~L}+1, \mathrm{M}_{\mathrm{L}}=+\mathrm{L} \ldots 0 \ldots-\mathrm{L}, \mathrm{M}_{\mathrm{L}}=\mathrm{m}_{1}+\mathrm{m}_{12}+\ldots \ldots+\mathrm{m}_{\text {In.. }}$ Total possible values
of $M_{L}$ for $f^{3} \& f^{11}$ system are $2 \times 8+1=17 ; \mathrm{M}_{\mathrm{L}}=+8,+7,+6,+5,+4,+3,+2,+1,0,-1,-2,-3,-4,-5,-6,-7$, $-8 . \mathrm{M}_{\mathrm{S}}=\sum \mathrm{m}_{\mathrm{s}}$, It define spin state for given ' S ' value, it is equal to ( $2 \mathrm{~S}+1$ ). $\mathrm{M}_{\mathrm{S}}=+\mathrm{S} \ldots 0 \ldots-\mathrm{S} . \mathrm{M}_{\mathrm{S}}=\mathrm{m}_{\mathrm{s} 1}+$ $\mathrm{m}_{\mathrm{s} 2}+\ldots+\mathrm{m}_{\mathrm{s}}$. Total $\mathrm{M}_{\mathrm{s}}$ values are $2 \times 3 / 2+1=4$ ranged from $+3 / 2$ to $-3 / 2$.

Determination of (J); l-s coupling - It is a resultant of the orbital angular momentum vector and the electron spin angular momentum vector. Vector sum can be made only in certain ways and the values of ' $J$ ' may be either $1+1 / 2$ or $1-1 / 2$. $1-1 / 2$ is of lower energy state since in $1-1 / 2$ state the orbital and spin are opposed $^{13} . \mathrm{j}=1+\mathrm{s}, \mathrm{J}=\mathrm{j}_{1}+\mathrm{j}_{2}+\mathrm{j}_{3}+\ldots \ldots \ldots+\mathrm{jn} \mathrm{J}=(\mathrm{L}+\mathrm{S}),(\mathrm{L}+\mathrm{S}-1),(\mathrm{L}+\mathrm{S}-2), \ldots \ldots .|(\mathrm{L}-\mathrm{S})|^{8,9,13,14}$. Possible number of values of J is $(2 \mathrm{~S}+1)$ when $\mathrm{L} \geq \mathrm{S}$ and $(2 \mathrm{~L}+1)$ when $\mathrm{L}<\mathrm{S}$. When $\mathrm{L}=0 \mathrm{~J}$ can have only one value viz. $\mathrm{J}=\mathrm{S}$.

## Resolve the chart of microstate into appropriate atomic states

An atomic state forms an array of microstate consisting $2 \mathrm{~S}+1$ columns and $2 \mathrm{~L}+1$ rows. Thus, ${ }^{2} \mathrm{~L}$ state requires two columns or $(17 \times 2)$ array and ${ }^{2} \mathrm{~K}$ state requires $(15 \mathrm{x} 2)$ array ${ }^{4,8}$. By removing each state from the microstate table we can draw a microstate sub-table for each state as given in sub-tables of microstate for each type of term ${ }^{15}$-Table 6 (Sub-Tables 6.1 to 6.13).

Table 6.1

| Ms |  |  |  |
| :---: | :---: | :---: | :---: |
| $\mathbf{M}_{\text {L }}$ |  | +1/2 | -1/2 |
|  | 8 | \| | \| |
|  | 7 | \| | \| |
|  | 6 | \| | \| |
|  | 5 | 1 | \| |
|  | 4 | \| | \| |
|  | 3 | , | \| |
|  | 2 | \| | \| |
|  | 1 | \| | \| |
|  | 0 | 1 | \| |
|  | -1 | \| | \| |
|  | -2 | 1 | \| |
|  | -3 | , | \| |
|  | -4 | \| | \| |
|  | -5 | \| | \| |
|  | -6 | 1 | \| |
|  | -7 | 1 | \| |
|  | -8 | , | \| |
|  |  | 17 | 17 |
| $\begin{aligned} \mathrm{L}=8, \mathrm{~S}=1 / 2,2 \mathrm{~S}+1 & =2 ; \text { Microstates }=34 ; \\ \text { Term } & ={ }^{2} \mathrm{~L} \end{aligned}$ |  |  |  |

Table 6.2

| $\mathbf{M}_{\mathbf{s}}$ |  |  |  |
| :---: | :---: | :---: | :---: |
| $\mathbf{M}_{\text {L }}$ |  | $+1 / 2$ | -1/2 |
|  | 7 | \| | \| |
|  | 6 | \| | \| |
|  | 5 | - | 1 |
|  | 4 | \| | \| |
|  | 3 | \| | \| |
|  | 2 | I | \| |
|  | 1 | \| | \| |
|  | 0 | \| | \| |
|  | -1 | \| | \| |
|  | -2 | \| | 1 |
|  | -3 | , | 1 |
|  | -4 | , | \| |
|  | -5 | 1 | 1 |
|  | -6 | \| | \| |
|  | -7 |  | 1 |
|  |  | 15 | 15 |
| $\begin{aligned} & \mathrm{L}=7, \mathrm{~S}=1 / 2,2 \mathrm{~S}+1=2 \text {; Microstates }=30 \\ & \text { Term }={ }^{2} \mathrm{~K} \end{aligned}$ |  |  |  |

Table 6.3

| M |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | +3/2 | +1/2 | -1/2 | -3/2 |
|  | 6 | \| | \| | \| | \| |
|  | 5 | \| | \| | \| | \| |
|  | 4 | \| | \| | \| | \| |
|  | 3 | \| | \| | \| | \| |
|  | 2 | \| | \| | \| | \| |
|  | 1 | \| | \| | \| | \| |
| $\mathbf{M}_{\mathbf{L}}$ | 0 | \| | \| | \| | \| |
|  | -1 | \| | \| | \| | \| |
|  | -2 | \| | , | । | I |
|  | -3 | \| | \| | \| | \| |
|  | -4 | \| | \| | \| | \| |
|  | -5 | \| | \| | । | , |
|  | -6 | \| | \| | \| | \| |
|  |  | 13 | 13 | 13 | 13 |
| $\begin{aligned} & \mathrm{L}=6, \mathrm{~S}=3 / 2,2 \mathrm{~S}+1=4 ; \text { Microstates }=52 \\ & \text { Term }={ }^{4} \mathrm{I} \end{aligned}$ |  |  |  |  |  |

Table 6.4

| M |  |  |  |
| :---: | :---: | :---: | :---: |
| $\mathrm{M}_{\mathrm{L}}$ |  | +1/2 | -1/2 |
|  | 6 | 1 | \| |
|  | 5 | 1 | \| |
|  | 4 | 1 | \| |
|  | 3 | 1 | \| |
|  | 2 | 1 | \| |
|  | 1 | 1 | \| |
|  | 0 | 1 | \| |
|  | -1 | 1 | \| |
|  | -2 | 1 | \| |
|  | -3 | 1 | \| |
|  | -4 | 1 | \| |
|  | -5 | , | 1 |
|  | -6 | I | , |
|  |  | 13 | 13 |

$\mathrm{L}=6, \mathrm{~S}=1 / 2,2 \mathrm{~S}+1=2 ;$ Microstates $=26$ Term $={ }^{2} \mathrm{I}$

Table 6.5

| $\mathbf{M}_{\text {S }}$ |  |  |  |
| :---: | :---: | :---: | :---: |
|  |  | +1/2 | -1/2 |
|  | 5 | \|| | \|| |
|  | 4 | \|| | \|| |
|  | 3 | \|| | \|| |
|  | 2 | \|| | \|| |
|  | 1 | \|| | \|| |
| $\mathbf{M}_{\text {L }}$ | 0 | \|| | \|| |
|  | -1 | \|| | \|| |
|  | -2 | \|| | \|| |
|  | -3 | \|| | \|| |
|  | -4 | \|| | \|| |
|  | -5 | \|| | \|| |
|  |  | 22 | 22 |
| $\begin{aligned} & \mathrm{L}=5, \mathrm{~S}=1 / 2,2 \mathrm{~S}+1=2 ; \text { Microstates }=44 \\ & \text { Term }={ }^{2} \mathrm{H}(2 \text {-Terms }) \end{aligned}$ |  |  |  |

Table 6.6

| $\mathrm{M}_{\text {S }}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | +3/2 | +1/2 | $-1 / 2$ | -3/2 |
|  | 4 | \| | \| | \| | 1 |
|  | 3 | \| | \| | 1 | 1 |
|  | 2 | 1 | \| | \| | \| |
|  | 1 | \| | \| | \| | \| |
| $\mathbf{M}_{\text {L }}$ | 0 | \| | \| | \| | 1 |
|  | -1 | \| | \| | 1 | 1 |
|  | -2 | \| | \| | \| | \| |
|  | -3 | \| | \| | \| | 1 |
|  | -4 | 1 | \| | \| | 1 |
|  |  | 9 | 9 | 9 | 9 |
| $\begin{aligned} & \mathrm{L}=4, \mathrm{~S}=3 / 2,2 \mathrm{~S}+1=4 ; \text { Microstates }=36 ; \\ & \text { Term }={ }^{4} \mathrm{G} \end{aligned}$ |  |  |  |  |  |

Table 6.7

| $\mathbf{M}_{\text {S }}$ |  |  |  |
| :---: | :---: | :---: | :---: |
|  |  | +1/2 | -1/2 |
|  | 4 | \|| | \|| |
|  | 3 | \|| | \|| |
|  | 2 | \|| | \|| |
|  | 1 | \|| | \|| |
| $\mathbf{M}_{\text {L }}$ | 0 | \|| | 1 |
|  | -1 | \|| | 1 |
|  | -2 | \|| | \|| |
|  | -3 | \|| | \|| |
|  | -4 | \|| | \|| |
|  |  | 18 | 18 |
| $\begin{aligned} & \mathrm{L}=4, \mathrm{~S}=1 / 2,2 \mathrm{~S}+1=2 \text {; Microstates }=36 ; \\ & \text { Term }{ }^{2} \mathrm{G} \text { (2-Terms) } \end{aligned}$ |  |  |  |

Table 6.8

| $\mathbf{M}_{\text {S }}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | +3/2 | +1/2 | -1/2 | -3/2 |
|  | 3 | \| | \| | \| | \| |
|  | 2 | \| | \| | \| | \| |
|  | 1 | \| | \| | \| | \| |
| $\mathbf{M}_{\mathbf{L}}$ | 0 | \| | \| | \| | \| |
|  | -1 | \| | \| | \| | \| |
|  | -2 | \| | \| | \| | \| |
|  | -3 | \| | \| | \| | \| |
|  |  | 7 | 7 | 7 | 7 |
| $\begin{aligned} & \mathrm{L}=3, \mathrm{~S}=3 / 2,2 \mathrm{~S}+1=4 ; \text { Microstates }=28 ; \\ & \text { Term }={ }^{4} \mathrm{~F} \end{aligned}$ |  |  |  |  |  |

Table 6.9

| $\mathbf{M}_{\text {S }}$ |  |  |  |
| :---: | :---: | :---: | :---: |
| $\mathbf{M}_{\mathbf{L}}$ |  | +1/2 | -1/2 |
|  | 3 | \|| | \|| |
|  | 2 | \|| | \|| |
|  | 1 | \|| | \|| |
|  | 0 | \|| | \|| |
|  | -1 | \|| | \|| |
|  | -2 | \|| | \|| |
|  | -3 | \|| | \|| |
|  |  | 14 | 14 |
| $\begin{aligned} & \mathrm{L}=3, \mathrm{~S}=1 / 2,2 \mathrm{~S}+1=2 ; \text { Microstates }=28 ; \\ & \text { Term }=^{2} \mathrm{~F}(2 \text {-Terms }) \end{aligned}$ |  |  |  |

Table 6.10

| Ms |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{M L}_{\text {L }}$ |  | +3/2 | +1/2 | -1/2 | -3/2 |
|  | 2 | \| | \| | \| | \| |
|  | 1 | \| | \| | \| | \| |
|  | 0 | \| | \| | \| | \| |
|  | -1 | \| | \| | \| | \| |
|  | -2 | \| | \| | \| | \| |
|  |  | 5 | 5 | 5 | 5 |
| $\begin{aligned} & \mathrm{L}=2, \mathrm{~S}=3 / 2,2 \mathrm{~S}+1=4 ; \text { Microstates }=20 ; \\ & \text { Term }={ }^{4} \mathrm{D} \end{aligned}$ |  |  |  |  |  |

Table 6.11

| $\mathbf{M s}_{\text {s }}$ |  |  |  |
| :---: | :---: | :---: | :---: |
|  |  | +1/2 | -1/2 |
|  | 2 | \|| | \|| |
|  | 1 | \|| | \|| |
| $\mathbf{M}_{\mathbf{L}}$ | 0 | \|| | \|| |
|  | -1 | \|| | \|| |
|  | -2 | \|| | \|| |
|  |  | 10 | 10 |
| $\begin{aligned} & \mathrm{L}=2, \mathrm{~S}=1 / 2,2 \mathrm{~S}+1=2 ; \text { Microstates }=20 ; \\ & \text { Term }=^{2} \mathrm{D}(2-\mathrm{Term}) \end{aligned}$ |  |  |  |

Table 6.12

| $\mathbf{M}_{\mathbf{S}}$ |  |  |  |
| :---: | :---: | :---: | :---: |
| $\mathbf{M}_{\mathbf{L}}$ | $+1 / 2$ | $-1 / 2$ |  |
|  | +1 | $\mid$ | $\mid$ |
|  | 0 | $\mid$ | $\mid$ |
|  | -1 | $\mid$ | $\mid$ |
|  |  | $\mathbf{3}$ | $\mathbf{3}$ |

$\mathrm{L}=1, \mathrm{~S}=1 / 2,2 \mathrm{~S}+1=2 ;$ Microstates $=6$;
Term $={ }^{2} \mathrm{P}$

Table 6.13

| $\mathbf{M}_{\mathbf{S}}$ |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  | $\mathbf{M}_{\mathbf{L}}$ |  | $+3 / 2$ | $+1 / 2$ | $-1 / 2$ |
|  | 0 | $\mid$ | $\mid$ | $\mid$ | $-3 / 2$ |
|  |  |  |  |  |  |
|  |  | 1 | 1 | $\mathbf{1}$ | $\mathbf{1}$ |

A complete matrix table for $\mathrm{f}^{3} \& \mathrm{f}^{11}$ system including term, term symbol, microstate, multiplicity, total J values and possible J values ${ }^{15-17}$ is given in Table 7.

Table 7

| $\begin{gathered} \text { S. } \\ \text { No. } \end{gathered}$ | L | Label | S | Multiplicity $(2 S+1)$ | Term symbol | Total values of $\mathbf{J}$ | Several possible terms | Array | Micro states |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 8 | L | 1/2 | 2 | ${ }^{2} \mathrm{~L}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{~L}_{17 / 2},{ }^{2} \mathrm{~L}_{15 / 2}$ | $17 \times 2$ | 34 |
| 2 | 7 | K | 1/2 | 2 | ${ }^{2} \mathrm{~K}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{~K}_{15 / 2},{ }^{2} \mathrm{~K}_{13 / 2}$ | $15 \times 2$ | 30 |
| 3 | 6 | I | 3/2 | 4 | ${ }^{4}$ I | $\mathrm{J}=3$ | ${ }^{4} \mathrm{I}_{15 / 2},{ }^{4} \mathrm{I}_{13 / 2},{ }^{4} \mathrm{I}_{11 / 2}{ }^{4} \mathrm{I}_{9 / 2}$ | $13 \times 4$ | 52 |
|  |  |  | 1/2 | 2 | ${ }^{2} \mathrm{I}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{I}_{13 / 2},{ }^{2} \mathrm{I}_{11 / 2}$ | $13 \times 2$ | 26 |
| 4 | 5 | H | 1/2 | 2 | ${ }^{2} \mathrm{H}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{H}_{11 / 2},{ }^{2} \mathrm{H}_{9 / 2}$ | $11 \times 2$ | 22 |
|  |  |  | 1/2 | 2 | ${ }^{2} \mathrm{H}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{H}_{11 / 2}{ }^{2} \mathrm{H}_{9 / 2}$ | $11 \times 2$ | 22 |
| 5 | 4 | G | 3/2 | 4 | ${ }^{4} \mathrm{G}$ | $\mathrm{J}=4$ | ${ }^{4} \mathrm{G}_{11 / 2},{ }^{4} \mathrm{G}_{9 / 2},{ }^{4} \mathrm{G}_{7 / 2},{ }^{4} \mathrm{G}_{5 / 2}$ | $9 \times 4$ | 36 |
|  |  |  | 1/2 | 2 | ${ }^{2} \mathrm{G}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{G}_{9 / 2},{ }^{2} \mathrm{G}_{7 / 2}$ | $9 \times 2$ | 18 |
|  |  |  | 1/2 | 2 | ${ }^{2} \mathrm{G}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{G}_{9 / 2},{ }^{2} \mathrm{G}_{7 / 2}$ | $9 \times 2$ | 18 |
| 6 | 3 | F | 3/2 | 4 | ${ }^{4} \mathrm{~F}$ | $\mathrm{J}=4$ | ${ }^{4} \mathrm{~F}_{9 / 2},{ }^{4} \mathrm{~F}_{7 / 2},{ }^{4} \mathrm{~F}_{5 / 2},{ }^{4} \mathrm{~F}_{3 / 2}$ | $7 \times 4$ | 28 |
|  |  |  | 1/2 | 2 | ${ }^{2} \mathrm{~F}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{~F}_{7 / 2},{ }^{2} \mathrm{~F}_{5 / 2}$ ${ }^{2} \mathrm{~F}_{712}{ }^{2} \mathrm{~F}_{512}$ | $7 \times 2$ | 14 |
|  |  |  | 1/2 | 2 | ${ }^{2} \mathrm{~F}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{~F}_{7 / 2}, \mathrm{~F}_{5 / 2}$ | $7 \times 2$ | 14 |
| 7 | 2 | D | 3/2 | 4 | ${ }^{4} \mathrm{D}$ | $\mathrm{J}=4$ | ${ }^{4} \mathrm{D}_{7 / 2},{ }^{4} \mathrm{D}_{5 / 2},{ }^{4} \mathrm{D}_{3 / 2},{ }^{4} \mathrm{D}_{1 / 2}$ | $5 \times 4$ | 20 |
|  |  |  | 1/2 | 2 | ${ }^{2} \mathrm{D}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{D}_{5 / 2}{ }^{2} \mathrm{D}_{3 / 2}$ | $5 \times 2$ | 10 |
|  |  |  | 1/2 | 2 | ${ }^{2} \mathrm{D}$ | $\mathrm{J}=1$ | ${ }^{2} \mathrm{D}_{5 / 2},{ }^{2} \mathrm{D}_{3 / 2}$ | $5 \times 2$ | 10 |
| 8 | 1 | P | 1/2 | 2 | ${ }^{2} \mathrm{P}$ | $\mathrm{J}=2$ | ${ }^{2} \mathrm{P}_{3 / 2},{ }^{2} \mathrm{P}_{1 / 2}$ | $3 \times 2$ | 6 |
| 9 | 0 | S | 3/2 | 4 | ${ }^{4} \mathrm{~S}$ | $\mathrm{J}=1$ | ${ }^{4} \mathrm{~S}_{1 / 2}$ | $1 \times 4$ | 4 |

Total No. of microstates-364

The term or energy state (ground and excited) split up into singlet, doublet, triplet, quartet, quintet, sextet etc. due to electron-electron (spin-spin) coupling and orbit-orbit coupling which further split up into different states due to orbit-spin coupling that give different values of $\mathrm{J}^{18}$. The ground state term and order of stability of other terms (excited states or terms) can be determine by applying Hund's rule ${ }^{4,8,9,12,13,19}$ that is as follow-
(1) The most stable term is which has the highest spin multiplicity.
(2) If two or more terms have same spin multiplicity $(2 S+1)$ than the term which have higher value of $(\mathrm{L})$ is more stable.
(3) If the value of ( L ) is equal for two or more terms than the term with-
(i) The lowest value of J for half filled orbital or less than half filled will be stable.
(ii) The highest value of J for more than half filled orbital will be stable.

## RESULTS AND DISCUSSION

(i) Each $f^{3}$ and $f^{11}$ system is (orbital configuration) consist of 17 terms in which 5 terms are quartet and 12 are doublets. The term symbols are as follow -

$$
{ }^{4} \mathrm{I},{ }^{4} \mathrm{G},{ }^{4} \mathrm{~F},{ }^{4} \mathrm{D},{ }^{4} \mathrm{~S},{ }^{2} \mathrm{~L},{ }^{2} \mathrm{~K},{ }^{2} \mathrm{I},{ }^{2} \mathrm{H},{ }^{2} \mathrm{H},{ }^{2} \mathrm{G},{ }^{2} \mathrm{G},{ }^{2} \mathrm{~F},{ }^{2} \mathrm{~F},{ }^{2} \mathrm{D},{ }^{2} \mathrm{D},{ }^{2} \mathrm{P} .
$$

(ii) The stability of order of terms for $f^{3}$ and $f^{11}$ system is ${ }^{4} \mathrm{I}>{ }^{4} \mathrm{G}>{ }^{4} \mathrm{~F}>{ }^{4} \mathrm{D}>{ }^{4} \mathrm{~S}>{ }^{2} \mathrm{~L}>{ }^{2} \mathrm{~K}>{ }^{2} \mathrm{I}>2 \mathrm{x}^{2} \mathrm{H}>2 \mathrm{x}^{2} \mathrm{G}>2 \mathrm{x}{ }^{2} \mathrm{~F}>2 \mathrm{x}^{2} \mathrm{D}>{ }^{2} \mathrm{P}$.
(iii) The ground state term for $f^{3} \& f^{11}$ system is ${ }^{4} I$.
$\mathbf{f}^{3}$ System $\quad \mathbf{f}^{11}$ System


## CONCLUSION

Upon the basis of above study, we can conclude that both $f^{3}$ and $f^{11}$ system have same spectroscopic terms that are 17 in number which further split up into doublets (12) and quartets (5) due to s-s coupling and $1-1$ coupling. The ground state term for $f^{3}$ and $f^{11}$ system is ${ }^{4} I$ that split up into four states ${ }^{4} I_{15 / 2},{ }^{4} I_{13 / 2}$, ${ }^{4} \mathrm{I}_{1 / 2 / 2}$, ${ }^{4} \mathrm{I}_{9 / 2}$, due to 1 -s coupling and the stability order of these terms for $\mathrm{f}^{3}$ is ${ }^{4} \mathrm{I}_{15 / 2}<{ }^{4} \mathrm{I}_{13 / 2}<\mathrm{I}_{11 / 2}<{ }^{4} \mathrm{I}_{9 / 2}$ \& for $\mathrm{f}^{11}$ is ${ }^{4} \mathrm{I}_{15 / 2}>{ }^{4} \mathrm{I}_{13 / 2}>{ }^{4} \mathrm{I}_{11 / 2}>{ }^{4} \mathrm{I}_{9 / 2}$. This stability order of these terms can be draws as follow.

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## REFERENCES

1. J. L. Robert, W. J. Jones and T. Timberlake, Astrophysics J., 61, 38 (1925).
2. E. Y. Wopg, J. Chemical Phys., 38, 976 (1963).
3. A. B. P. Lever, J. Chem. Educ., 45, 711 (1968).
4. B. R. Puri, L. R. Sharma and M. S. Pathania, Principle of Physical Chemistry, $43^{\text {th }}$ Edition, Vishal Publishing Co. New Delhi, (2008) p. 104-107.
5. R. Goyal, M. Phil, Dissertation, MDS University, Ajmer, (2007).
6. P. K. Jain and R. Goyal, National Conference at M. L. V. PG Govt. College, Bhilwara, (Raj.) (2010).
7. H. Bethe, Splitting of Terms in Crystals, Amm. Physik, 3, 121 (1929).
8. J. D. Lee, Concise Inorganic Chemistry Fifth Edition, Chapman and Hall, London, (1996) p. 947.
9. W. U. Malik, G. D. Tuli and R. D. Madan, Selected Topics in Inorganic Chemistry, S. Chand Group New Delhi, ISBN 8121900476, (1999) p. 22-24.
10. B. E. Dougles and D. H. Mc. Daniel, Concepts of Model of Inorganic Chemistry, Oxford and IBH Publishing Company, New Delhi, (1970).
11. D. H. Mc. Daniel, J. Chem. Ed., 54(3), 147 (1977).
12. E. U. Condon and G. H. Shorttley, The Theory of Atomic Spectra, Cambidge University Press, London, (1963).
13. J. E. Huheey, E. A. Keiter and R. L. Keiter, Inorganic Chemistry, Principles of Structure and Reactivity, $4^{\text {th }}$ Reprint Edition, Harper Collins College, New York, Appendix-C, A-8-11 (2001).
14. R. S. Drago, Physical Method in Inorganic Chemistry, Reinhold, New York, (1968).
15. P. L. Meena, P. K. Jain, N. Kumar and K. S. Meena and R. Goyal, J. Chem. Bio. Phy. Sci., Vol. 1, No. 2, Sec. A, 188-203, E-ISSN - 2249-1929 (2011).
16. P. L. Meena, N. Kumar Jatav and P. K. Jain, Proceeding International Conference, AMU, Aligarh (UP) India, 122, IP-51 (2011).
17. P. L. Meena, P. K. Jain, N. K. Jatav and K. S. Meena, Int. J. Chem. Sci., 9(3), 1364-1372 (2011).
18. E. M. R. Kiremire, J. Chem. Educ., 64, 951-953 (1987).
19. D. F. Shriver and P. W. Atkins, Inorganic Chemistry $3^{\text {rd }}$ Ed., Oxford University, Press, New York, (2002) p. 441-442.

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