



A COMPARATIVE STUDY OF THE ATOMIC TERM SYMBOLS OF f³ AND f¹¹ CONFIGURATION

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(Received : 13.10.2011; Revised : 30.10.2011; Accepted : 31.10.2011)

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 a f sub-shell with azimuthal quantum number 3. The determination of terms and term symbols for f^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 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 ⁴L.

Key words: Term symbol, Russell-Saunders coupling, Azimuthal quantum number, Microstate, f³ and f¹¹ 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 2p, 3p, 3d, 4d and 4f 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) j - j coupling.

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Acta Chim. Pharm. Indica: 2(1), 2012

This is found that the Russell-Saunders scheme gives a good approximation for first row transition series where spin-orbit (j-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 j-j coupling scheme is used¹⁻³. However, for heavier atoms it is still convenient to use Russell-Saunders scheme⁴. 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 momentum⁴.

Arising of states which are called spectroscopic states or microstates or multiplets expressed by proper term symbols and are defined by new quantum numbers- L, M_L , M_S , 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 (2L + 1) and spin degeneracy (2S + 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 forces⁷.

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 terms⁸. In the f³ and f¹¹, there are three holes which have same possible arrangement as f³.

A complete term symbol is $(2S + 1) L_J^{4,8,9}$. 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 L + S to L - S. This can be specified a post subscript to the L. L = Resultant orbital quantum number, S = Resultant spin quantum number, 2S + 1= Multiplicity. J = L - S state is lower in energy than the J = L + 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 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 m_s values are different. Thus each box is described by m_l 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 2r). The answer is given by the expression¹².

Number of ways of filling electrons N = $\frac{n!}{x!(n!x!)}$

N = 2(2l + 1) or two wise of the total No. of orbital's, x = Total No. of electron in sub-shell

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

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.

S. No.	Pos	sible spin	states	Total spin (S)	Total microstates
1	≜	▲	A	+3/2	35
2	↑	≜	¥	+1/2	105
3	↑	¥	¥	-1/2	105
4	¥	¥	¥	-3/2	35
5	≜ ↓	≜		+1/2	42
6	Â↓	¥		-1/2	42
	Tot	al Micros	tates		364

 Table 1: (For f³ system)

 Table 2: (For f¹¹ System)

S. No.		Po	ssibl	e spi	n sta	tes		Total spin (S)	Total microstates
1	↑ ↓	↑ ↓	1↓	↑ ↓	↑	↑	↑	+3/2	35
2	↑ ↓	↑ ↓	≜ ↓	↑ ↓	▲	▲	¥	+1/2	105
3	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑	↓	¥	-1/2	105
4	↑ ↓	↑ ↓	1↓	↑ ↓	¥	¥	¥	-3/2	35

S. No.		Po	ssibl	e spi	n sta	tes	Total spin (S)	Total microstates
5	↑ ↓	↑ ↓	↑ ↓	≜ ↓	↑ ↓	ł	+1/2	42
6	≬ ↓	≬ ↓	≬ ↓	≬ ↓	≬ ↓	¥	-1/2	42
Total Microstates					ostate		364	

Microstate Charts for f³ & f¹¹Configurations (system)

Table 3: Total No. of microstates for f³ and f¹¹

			N	Is		
		+3/2	+1/2	-1/2	-3/2	
	8		1	1		2
	7		2	2		4
	6	1	4	4	1	10
	5	1	6	6	1	14
	4	2	9	9	2	22
	3	3	12	12	3	30
	2	4	15	15	4	38
$M_{\rm L}$	1	4	16	16	4	40
IVIL	0	5	17	17	5	44
	-1	4	16	16	4	40
	-2	4	15	15	4	38
	-3	3	12	12	3	30
	-4	2	9	9	2	22
	-5	1	6	6	1	14
	-6	1	4	4	1	10
	-7		2	2		4
	-8		1	1		2
	Total	35	147	147	35	364

Determination of orbital angular momentum quantum number (L), l-l coupling

It is a vector sum of all the (l) 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 'l' 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. $L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2), ..., |(l_1 - l_2)|^{4,8,9,13}$. These states or term letters are represented in Table 5.

19

Y

18

Х

20

Ζ

			$\mathbf{M}_{\mathbf{S}}$			
		+3/2	+1/2	-1/2	-3/2	
_	8					2
	7					4
	6					10
	5					14
	4					22
	3					30
	2					38
M_{L}	1					40
IVIL	0					44
	-1					40
	-2					38
	-3					30
	-4					22
	-5					14
	-6					10
	-7					4
	-8					2
Mici	rostates	35	147	147	35	364
Table 5	: States or 1	term letters				
Value	of L 0	1 2 3	4 5 6 7	8 9 10	11 12 1	3 14 15 16

Symbol of L S P D F G H I K L M N O Q

Table 4: Set up of a Chart of microstates for f³ and f¹¹

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

R

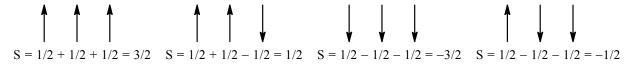
Т

U

V

W

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. $S = (s_1+s_2), (s_1+s_2-1), (s_1+s_2-2), ..., |(s_1+s_2)|^{4,8,9,13}$ $S = \sum_i s$ for f³ and f¹¹ 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 M_L and M_s: M_L = $\sum m_{l=}$ the component of the total angular momentum along a given axis. Total values of M_L = 2L + 1, M_L = + L ...0...-L, M_L = m_l + m_{l2}+.....+m_{ln.} Total possible values

of M_L for $f^3 \& f^{11}$ system are 2 x 8 + 1 = 17; $M_L = +8, +7, +6, +5, +4, +3, +2, +1, 0, -1, -2, -3, -4, -5, -6, -7, -8. <math>M_S = \sum m_s$, It define spin state for given 'S' value, it is equal to (2S + 1). $M_S = +S...0...-S$. $M_S = m_{s1} + m_{s2} + ... + m_s$. Total M_S values are 2 x 3/2 + 1 = 4 ranged from + 3/2 to -3/2.

Determination of (J); I-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 opposed¹³. j = 1 + s, $J = j_1 + j_2 + j_3 + \dots + j_n J = (L + S)$, (L + S - 1), (L + S - 2), $\dots + |(L - S)|^{8,9,13,14}$. Possible number of values of J is (2S + 1) when $L \ge S$ and (2L + 1) when $L \le S$. When L = 0 J can have only one value viz. J = S.

Resolve the chart of microstate into appropriate atomic states

An atomic state forms an array of microstate consisting 2S + 1 columns and 2L + 1 rows. Thus, ${}^{2}L$ state requires two columns or (17 x 2) array and ${}^{2}K$ state requires (15 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 term¹⁵-Table 6 (Sub-Tables 6.1 to 6.13).

Table	6.1
-------	-----

		M _s	
		+1/2	-1/2
	8		
	7		
	6		
	5		
	4		
	3		
	2		
M _L	1		
	0		
	-1		
	-2		
	-3		
	-4		
	-5		
	-6		
	-7		
	-8		
		17	17
L =		+ 1 = 2; Microst	ates = 34;
	1	$\Gamma erm = {}^{2}L$	

		Ms	
		+1/2	-1/2
	7		
	6		
	5		
	4		
	3		
	2		
	1		
M _L	0		
IVIL	-1		
	-2		
	-3		
	-4		
	-5		
	-6		
	-7		
		15	15
		= 2; Microstates	= 30
$\Gamma \text{erm} = 2$	K		

Table	6.3
-------	-----

		Ν	⁄Is		
		+3/2	+1/2	-1/2	-3/2
	6				
	5				
	4				
	3				
	2				
	1				
$\mathbf{M}_{\mathbf{L}}$	0				
	-1				
	-2				
	-3				
	-4				
	-5				
	-6				
		13	13	13	13
		$\mathbf{S}+1=4;$	Microsta	tes = 52	
Term =	⁴ I				

Table 6.4

		$\mathbf{M}_{\mathbf{S}}$	
		+1/2	-1/2
	6		
	5		
	4		
	3		
	2		
	1		
M_L	0		
	-1		
	-2		
	-3		
	-4		
	-5		
	-6		
		13	13

L = 6, S = 1/2, 2S + 1 = 2; Microstates = 26 Term = ²I

Table 6.5

		Ms	
		+1/2	-1/2
	5		
	4		
	3		
	2		
	1		
M_L	0		
	-1		
	-2		
	-3		
	-4		
	-5		
		22	22
		= 2; Microstates =	= 44
$Term = {}^{2}H$	H (2-Terms)		

Table	6.6
-------	-----

$\mathbf{M}_{\mathbf{S}}$								
		+3/2	+1/2	-1/2	-3/2			
-	4							
	3							
	2							
	1							
M_{L}	0							
	-1							
	-2							
	-3							
	-4							
		9	9	9	9			

L = 4, S = 3/2, 2S + 1 = 4; Microstates = 36; Term = ${}^{4}G$

Table 6.7

		M_S		
'2	-1/2	+1/2		
			4	
			3	
			2	
			1	
			0	M_L
			-1	
			-2	
			-3	
			-4	
3	18	18		
	 	 	-3	

L = 4, S = 1/2, 2S + 1 = 2; Microstates = 36;

Term = ${}^{2}G$ (2-Terms)

Table 6.8

$\mathbf{M}_{\mathbf{S}}$								
		+3/2	+1/2	-1/2	-3/2			
-	3							
	2							
	1							
$\mathbf{M}_{\mathbf{L}}$	0							
	-1							
	-2							
	-3							
		7	7	7	7			
I - 3 S	-3/2 25	$1 + 1 = 1 \cdot \mathbf{N}$	Vierostata	a - 28				

L = 3, S = 3/2, 2S + 1 = 4; Microstates = 28; Term = ${}^{4}F$

Table 6.9

		$\mathbf{M}_{\mathbf{S}}$	
		+1/2	-1/2
	3		
	2		
	1		
$\mathbf{M}_{\mathbf{L}}$	0		
	-1		
	-2		
	-3		
		14	14

L = 3, S = 1/2, 2S + 1 = 2; Microstates = 28; Term = ²F (2-Terms)

Table 6.10

Ms									
		+3/2	+1/2	-1/2	-3/2				
	2								
	1								
$\mathbf{M}_{\mathbf{L}}$	0								
	-1								
	-2								
		5	5	5	5				
I = 2 S =	= 3/2 28	$+1 = 4 \cdot N$	licrostates	x = 20					

L = 2, S = 3/2, 2S + 1 = 4; Microstates = 20; Term = ⁴D

Table	6.11
-------	------

M_S							
		+1/2	-1/2				
-	2						
	1						
$\mathbf{M}_{\mathbf{L}}$	0						
	-1						
	-2						
		10	10				

L = 2, S = 1/2, 2S + 1 = 2; Microstates = 20; Term = ²D (2-Term)

Table 6.12

		Ms	
		+1/2	-1/2
	+1		
M_L	0		
	-1		
		3	3

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

Table 6.13

M _S								
м		+3/2	+1/2	-1/2	-3/2			
M_L	0							
		1	1	1	1			
L = 0, S = $3/2$, 2S + 1 = 4; Microstates = 4; Term = ${}^{4}S$								

A complete matrix table for $f^3 \& f^{11}$ system including term, term symbol, microstate, multiplicity, total J values and possible J values¹⁵⁻¹⁷ is given in Table 7.

Table 7	
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S. No.	L	Label	S	Multiplicity (2S + 1)		Total values of J	Several possible terms	Array	Micro states
1	8	L	1/2	2	^{2}L	J = 2	${}^{2}L_{17/2}$, ${}^{2}L_{15/2}$	17 x 2	34
2	7	Κ	1/2	2	² K	J = 2	${}^{2}K_{15/2}$, ${}^{2}K_{13/2}$	15 x 2	30
3	6	Ι	3/2	4	^{4}I	J = 3	${}^{4}I_{15/2,} {}^{4}I_{13/2,} {}^{4}I_{11/2} {}^{4}I_{9/2}$	13 x 4	52
			1/2	2	^{2}I	J = 2	${}^{2}I_{13/2}, {}^{2}I_{11/2}$	13 x 2	26
4	5	Н	1/2	2	$^{2}\mathrm{H}$	J = 2	${}^{2}H_{11/2}{}^{2}H_{9/2}$	11 x 2	22
			1/2	2	$^{2}\mathrm{H}$	J = 2	${}^{2}H_{11/2,}{}^{2}H_{9/2}$	11 x 2	22
5	4	G	3/2	4	⁴ G	J = 4	${}^4G_{11/2,}{}^4G_{9/2,}{}^4G_{7/2,}{}^4G_{5/2}$	9 x 4	36
			1/2	2	^{2}G	J = 2	${}^{2}G_{9/2}$, ${}^{2}G_{7/2}$	9 x 2	18
			1/2	2	^{2}G	J = 2	$^{2}G_{9/2}, ^{2}G_{7/2}$	9 x 2	18
6	3	F	3/2	4	⁴ F	J = 4	${}^{4}F_{9/2}, {}^{4}F_{7/2}, {}^{4}F_{5/2}, {}^{4}F_{3/2}$	7 x 4	28
			1/2	2	^{2}F	J = 2	${}^{2}F_{7/2}, {}^{2}F_{5/2}$	7 x 2	14
			1/2	2	^{2}F	J = 2	${}^{2}\mathrm{F}_{7/2},{}^{2}\mathrm{F}_{5/2}$	7 x 2	14
7	2	D	3/2	4	⁴ D	J = 4	${}^{4}D_{7/2}$, ${}^{4}D_{5/2}$, ${}^{4}D_{3/2}$, ${}^{4}D_{1/2}$	5 x 4	20
			1/2	2	^{2}D	J = 2	${}^{2}D_{5/2,}{}^{2}D_{3/2}$	5 x 2	10
			1/2	2	² D	J = 1	${}^{2}D_{5/2}$, ${}^{2}D_{3/2}$	5 x 2	10
8	1	Р	1/2	2	^{2}P	J = 2	${}^{2}P_{3/2}$, ${}^{2}P_{1/2}$	3 x 2	6
9	0	S	3/2	4	⁴ S	J = 1	${}^{4}S_{1/2}$	1 x 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 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 (2S + 1) than the term which have higher value of (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

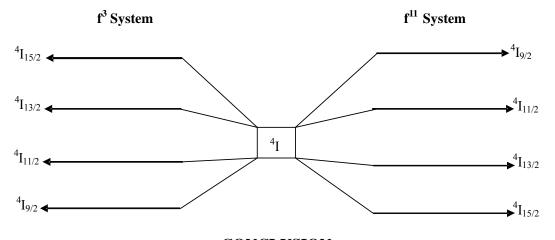
(i) Each f³ and f¹¹ system is (orbital configuration) consist of 17 terms in which 5 terms are quartet and 12 are doublets. The term symbols are as follow -

⁴I, ⁴G, ⁴F, ⁴D, ⁴S, ²L, ²K, ²I, ²H, ²H, ²G, ²G, ²F, ²F, ²D, ²D, ²P.

(ii) The stability of order of terms for f^3 and f^{11} system is –

$${}^{4}I > {}^{4}G > {}^{4}F > {}^{4}D > {}^{4}S > {}^{2}L > {}^{2}K > {}^{2}I > 2 x {}^{2}H > 2 x {}^{2}G > 2 x {}^{2}F > 2 x {}^{2}D > {}^{2}P.$$

(iii) The ground state term for $f^3 \& f^{11}$ system is ⁴I.



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 l-l coupling. The ground state term for f^3 and f^{11} system is ⁴I that split up into four states ⁴I_{15/2}, ⁴I_{13/2}, ⁴I_{11/2}, ⁴I_{9/2}, due to l-s coupling and the stability order of these terms for f^3 is ⁴I_{15/2} <⁴I_{13/2} <⁴I_{11/2} <⁴I_{9/2} & for f^{11} is ⁴I_{15/2} <⁴I_{13/2} <⁴I_{11/2} <⁴I_{9/2}. This stability order of these terms can be draws as follow.

ACKNOWLEDGEMENT

Authors are thankful to all the members of Department of Chemistry M.L.V. Govt. College, Bhilwara.

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