Calculation of atomic spectroscopic terms for f^2 and f^{12} orbital configurations, assigning the term symbols and comparative study

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A term is a particular energy state and term symbol is a label to an energy state. Russell-Saunders (L-S) coupling and j-j coupling schemes are important schemes to determine the terms and to assign the term symbols. In this proposed work computation is done to calculate all possible microstates and atomic spectroscopic terms for f^2 and f^{12} configuration without any long tabulation with mental exercise and a comparative study was carried out between the atomic spectroscopic terms for f^2 and f^{12} orbital configuration. The possible microstates and atomic spectroscopic terms calculated for f^2 and f^{12} orbital configuration are 91 and 7 for each. These terms are triplets (3) and singlet's (4).The ground state term for f^2 and f^{12} configuration is triplet H (^3H) and the ground state for f^2 is $^3H_4$ and for f^{12} is $^3H_6$.

Key words: Term symbol, Russell-Saunders coupling, microstate, singlet, triplet.

1. INTRODUCTION

The term refers to the energy associated with the state of an atom involved in a transition. Term symbols are abbreviated descriptions of the energy, angular momentum and spin multiplicity of an atom in a particular state. When only one electron is present at a degenerate energy level or sub shell such as 2p, 3d, 4f, etc., the energy depends on 'l' - the orbital quantum number but when more than one electron is present, they interact with one another with the formation of a ground state and one or more excited states for the atom or ion.

It is found that the Russell-Saunders scheme gives a good approximation for the 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 the higher nuclear charge and the j-j coupling scheme is used [1-3]. However, for heavier atoms it is still convenient to use the Russell-Saunders scheme [4].

The microstates are 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 vectorial summing of the quantum numbers for the individual electrons [5].

The total number of microstates increases with the increase in the number of electrons in the orbital. The formulation of a hole can be used for a 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 are vacancies in the various orbital's rather than the larger number of electrons actually present. By considering the holes, the terms which arise for pairs of atoms with p^n and p^{6-n}, d^n and d^{10-n} and f^n and f^{14-n} arrangements give rise to identical terms [6]. In the f^{12} configuration there are two holes which have the same possible arrangements as the electrons in f^2 configuration. A complete term symbol is $^{(2S+1)}L_J$[4,6,7].

2. EXPERIMENTAL

2.1. Calculation of the total number of microstates

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 expression [8]:

Number of ways of filling electrons

$$N= \frac{2(2l+1)!}{x!\,(2(2l+1)!-x!)} \text{ or } \frac{n!}{x!\,(n!-x!)}$$

n= 2(2l+1) or two wise of the total number of orbital's,

x = Total number of electrons in sub shell.

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So, for f² configuration n= 14 and x= 2

$$N = \frac{14!}{2!(14!-2!)},$$

$$N = \frac{14 \, x13x12x11x10x9x8x7x6x5x4x3x2x1}{12x11x10x9x8x7x6x5x4x3x2x1x2x1},$$

N = 91 Microstates

For f¹² configuration n= 14 and x=12

$$N = \frac{14!}{12!(14!-12!)},$$

$$N = \frac{14x13x12x11x10x9x8x7x6x5x4x3x2x1}{12x11x10x9x8x7x6x5x4x3x2x1x2x1},$$

N = 91 Microstates

2.2. Determination of the electronic configuration allowed by the Pauli principle or possible spin conditions for f² and f¹² configuration

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

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

The coupling of orbital momentums of non-equivalent electrons referred to as *l-l* coupling gives a resultant L of magnitude $[L(L+1)]^{1/2}$ h/2π =L*h/2π. The orientations of l_1 and l_2 for f² configuration, which can be taken, are governed by the values that the quantum number L can take. L is associated with the total orbital angular momentum for the two electrons of the f² and the twelve electrons of the f¹² configuration and is restricted to the values L= (l_1+l_2), (l_1+l_2-1), (l_1+l_2-2)…| (l_1-l_2) | [4, 6, 7, 9]. The space quantization of L produces 2L+1 components with M_L = L, L-1,… -L analogous of *l*. In the present case L= 6,5,4,3,2,1,0 and the magnitudes of L are $42^{1/2}$ h/2π, $30^{1/2}$ h/2π, $20^{1/2}$ h/2π, $12^{1/2}$ h/2π, $6^{1/2}$ h/2π, $2^{1/2}$ h/2π and 0, respectively, which can be drawn by vector diagrams. Some of them are shown in Fig.1, Fig.2 and Fig.1. It follows that the f² and f¹² configurations give rise to S, P, D, F, G, H and I terms corresponding to L= 0,1,2,3,4,5 and 6 respectively.

2.4. Determination of total spin angular momentumquantum number (S) s-s coupling

It represents the total spin of an atom while 's' represents the spin state of an electron. The coupling between the spin momentums is referred to as s-s coupling. The vector for each electron is always of magnitude of $3^{1/2}$ h/2π according to $[s(s+1)]^{1/2}$ h/2π = s* h/2π. The vectors can only take orientations relative to each other such that the magnitude of the s-s coupling can be as follows: [S (S+1)]$^{1/2}$ h/2π = S*h/2π. S= (s_1+s_2), (s_1+s_2-1), (s_1+s_2-2)……., | (s_1+s_2)| [4, 6, 7, 9]. In the case of f² and f¹² configuration for the two and twelve electrons, the values of S = 1/2 or zero. The vector sums giving the resultant S vectors of magnitude $2^{1/2}$ h/2π or $1^{1/2}$ h/2π are drawn in Fig. 2.

Table 1 and 2. Possible spin arrangement of electrons with microstates according to Pauli principle for f² and f¹² configuration.

Table 1 for f² configuration

S.N	Possible spin states	Total Spin	Total M.S
1	↑ ↑	+1	21
2	↓ ↓	-1	21
3	↑ ↓	0	42
4	↑↓	0	7

Total microstates for f² configuration- 91

Table 2 for f¹² configuration

S.N	Possible spin states	Total Spin	Total M.S
1	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑	+1	21
2	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↓ ↓	-1	21
3	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑ ↓	0	42
4	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0	7

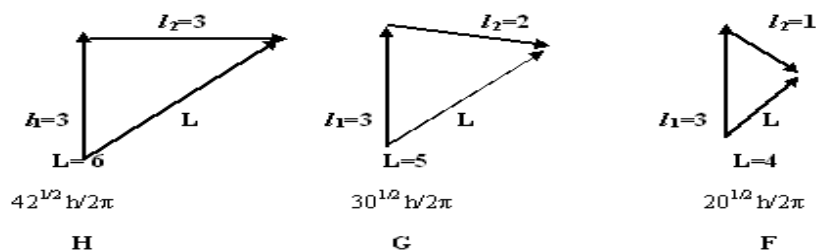Total microstates for f¹² configuration- 91

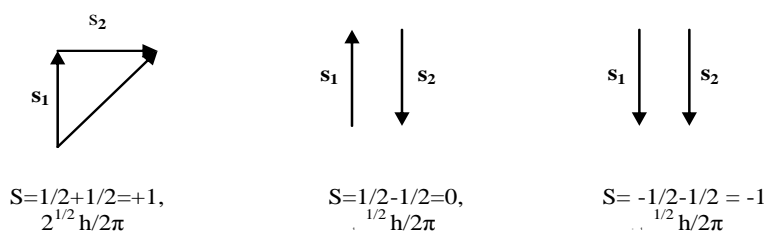**Fig.1.** *l-l* coupling (magnitude of L)

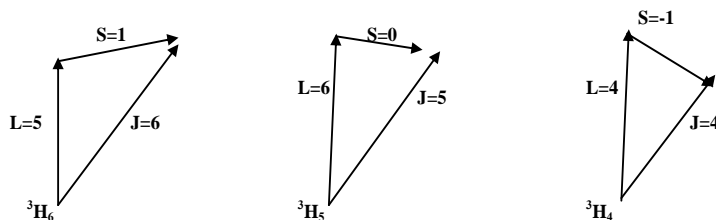**Fig.2**. s-s coupling (magnitude of S)

Fig.3. L-S coupling (Magnitude of J)

2.5. Determination of M_L and M_S

$M_L=\sum m_l$ = the components of the total angular momentum along a given axis. The total values of $M_L=2L+1$, $M_L= +L \ldots 0 \ldots -L$. The total possible values of M_L for the f^2 and f^{12} configurations are $2\times6+1=13$ $M_L=+6,+5,+4,+3,+2,+1,0,-1,-2,-3,-4,-5,-6$. $M_S=\sum m_s$. It defines the spin state for a given 'S' value, it is equal to $(2S+1)$. $M_S=+S\ldots0\ldots- S$. $M_S=m_{s1}+m_{s2}+\ldots+m_s$. Total M_S values are $2\times1+1=3$ ranging from +1 to -1.

2.6. Determination of (J) L-S coupling

It is a result of the orbital angular momentum vector and the electron spin angular momentum vector. This coupling gives the total angular momentum vector J $[J (J+1)]^{1/2}$ $h/2\pi$ = $J*h/2\pi$, where J is restricted to the values J = L+S , L+S-1,…..L-S, from which it follows that if L≥S, J can take 2S+1 values, but if L<S, it can take 2L+1 values. When L=0, J can take only one value, *viz.*, J=S. The vector sum can be made only in certain ways and the values of 'J' may be either 1+1/2 or 1-1/2. The 1-1/2 state is of lower energy state since the orbital and spin are opposed [6, 7, 9, 10, 11]. The L-S coupling for ^{3}H term is given in Fig. 3.

2.7. Statistical representation of microstates

All microstates for the f^2 and f^{12} orbital configuration calculated as given above can be represented statistically as given in Tables 3 and 4.

Tables 3 and 4. Microstate chart representing the total number of microstates for f^2 and f^{12} configuration (statistic chart of microstates)

Table 3

		M_S			
		+1	0	-1	
	6		1		1
	5	1	2	1	4
	4	1	3	1	5
	3	2	4	2	8
	2	2	5	2	9
	1	3	6	3	12
M_L	0	3	7	3	13
	-1	3	6	3	12
	-2	2	5	2	9
	-3	2	4	2	8
	-4	1	3	1	5
	-5	1	2	1	4
	-6		1		1
	Total	21	49	21	91

Table 4

		M_S			
		+1	0	-1	
	6		*		1
	5	*	**	*	4
	4	*	***	*	5
	3	**	****	**	8
	2	**	*****	**	9
	1	***	******	***	12
M_L	0	***	*******	***	13
	-1	***	******	***	12
	-2	**	*****	**	9
	-3	**	****	**	8
	-4	*	***	*	5
	-5	*	**	*	4
	-6		*		1
	Total	21	49	21	91

2.8. Resolving the chart of microstates into appropriate atomic spectroscopic terms

An atomic state forms an array of microstates consisting of 2S+1 columns and 2L+1 rows. Thus, a ¹I state requires one column or (13×1) array and ³H state requires (11×3) array [4, 6]. By removing each state from the microstate table (Table 4) we can draw microstate sub tables for each term [13,18]. The microstate sub tables for each atomic spectroscopic term can be drawn as given in Table 5. The term or energy state (ground and excited) splits up into singlet, doublet, triplet, etc., due to electron-electron coupling and orbit-orbit coupling, which further splits up into different states due to orbit-spin coupling that gives different values of J [19]. The ground state term and the order of stability of other terms can be determined by applying Hund's rule [4, 6, 7, 10, 11, 20].

Table 5. Sub tables representing each atomic spectroscopic term

Table 5.1

		M_S
		0
	6	|
	5	|
	4	|
	3	|
	2	|
	1	|
M_L	0	|
	-1	|
	-2	|
	-3	|
	-4	|
	-5	|
	-6	|
		13

L=6, S=0, 2S+1=1,
Microstates=13,
Term=¹I

Table 5.2

		M_S		
		+1	0	-1
	5	|	|	|
	4	|	|	|
	3	|	|	|
	2	|	|	|
	1	|	|	|
M_L	0	|	|	|
	-1	|	|	|
	-2	|	|	|
	-3	|	|	|
	-4	|	|	|
	-5	|	|	|
		11	11	11

L=5, S=1, 2S+1=3,
Microstates=33, Term=³H

Table 5.3

		M_S
		0
	4	|
	3	|
	2	|
	1	|
M_L	0	|
	-1	|
	-2	|
	-3	|
	-4	|
		9

L=4, S=0, 2S+1=1,
Microstates= 9,
Term=¹G

Table 5.4

		M_S		
		+1	0	-1
	3	|	|	|
	2	|	|	|
	1	|	|	|
M_L	0	|	|	|
	-1	|	|	|
	-2	|	|	|
	-3	|	|	|
		7	7	7

L=3, S=1, 2S+1=3,
Microstates=21, Term=¹D

Table 5.5

		M_S
		0
	2	|
	1	|
M_L	0	|
	-1	|
	-2	|
		5

L=2,S=0,2S+1=1,
Microstates=5,
Term=³P

Table 5.6

	M_S	
		0
M_L	0	|
		1

L=0, S=0, 2S+1=1,
Microstates=1,
Term=^1S

2.9. A complete matrix table for f² and f¹² orbital configuration

It can be drawn as given in Table 6 for f² and f¹² orbital configuration including atomic spectroscopic term, term symbol, microstate, multiplicity, total J values.

3. RESULTS AND DISCUSSION

For the f² and f¹² configuration the total number of atomic spectroscopic terms calculated are 7, out of 7, 3 are triplets and 4 are singlet's. These terms are ^3H, ^3F, ^3P, ^1I, ^1G, ^1D and ^1S. The stability order terms is $^3H > ^3F > ^3P > ^1I > ^1G > ^1D > ^1S$. The ground

state term for f² and f¹² is triplet H (^3H) which is split up into three energy states due to orbit-spin (interaction) coupling, which are $^3H_6$, $^3H_5$, $^3H_4$.

4. CONCLUSIONS

It is concluded that there are 7 atomic spectroscopic terms for the f² and f¹² configuration which split up into triplets (3) and singlet's (4) due to s-s and l-l coupling. The stability order of the ground state terms for the f² configuration is $^3H_6 < ^3H_5 < ^3H_4$ and for the f¹² configuration it is $^3H_6 > ^3H_5 > ^3H_4$, so that the ground state for f² configuration is $^3H_4$ and for f¹² configuration it is $^3H_6$. The order of energy of all terms and ground state terms can be drawn as given in fig.4 for f² and f¹² configuration.

Table 6 A complete matrix table

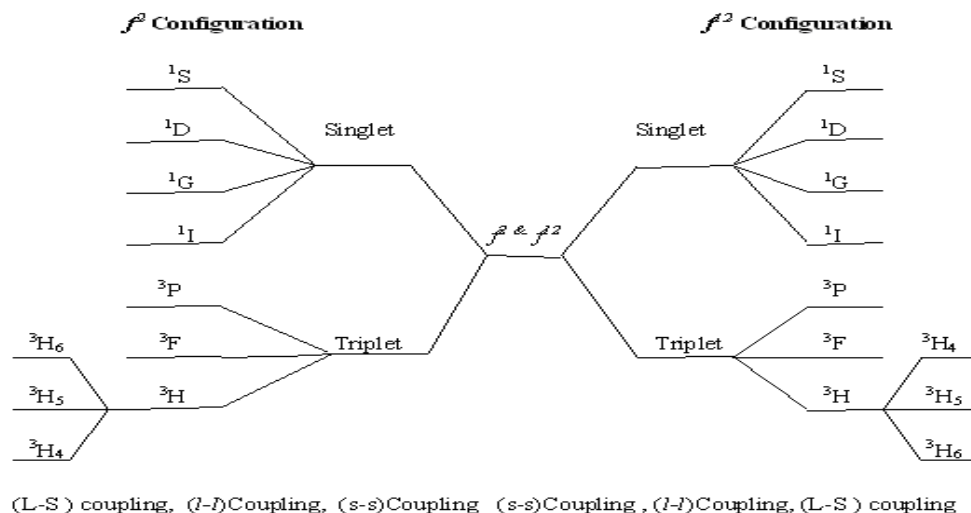| S. N	L	L Label	S	Multiplicity (2S+1)	Term symbol	Total values of J	Several Possible Terms	Array	Microstates
1	6	I	0	1	^1I	J=1	$^1I_6$	13x1	13
2	5	H	1	3	^3H	J=3	$^3H_6$,$^3H_5$,$^3H_4$	11x3	33
3	4	G	0	1	^1G	J=1	$^1G_4$	9X1	9
4	3	F	1	3	^3F	J=3	$^3F_4$,$^3F_3$,$^3F_2$	7x3	21
5	2	D	0	1	^1D	J=1	$^1D_2$	5x1	5
6	1	P	1	3	^3P	J=3	$^3P_2$,$^3P_1$,$^3P_0$	3x3	9
7	0	S	0	1	^1S	J=1	$^1S_0$	1x1	1
								Total No of Microstates-91	

Fig.4. Stability order of different atomic spectroscopic terms

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Изчисляване на атомни спектроскопски нива за f^2 и f^{12} орбитални конфигурации чрез сравнително изследване и символи на нивата

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(Резюме)

Нивото е особено енергийно състояние, а символът на нивото е означение на това състояние. Свързването по Ръсел-Саундърс (L-S) и j-j – свързването са важни схеми за определянето на нивата и за присвояването на символите към тях. В настоящата работа са изчислени всички възможни микросъстояния и атомни спектроскопски нива за f^2 и f^{12} конфигурации без никакво табулиране. Извършено е сравнително изследване за f^2 и f^{12} орбиталните конфигурации. Възможните микросъстояния и атомни спектроскопски нива, изчислени за f^2 и f^{12} орбитални конфигурации са съответно 91 и 7. Тези нива са триплети (3) и синглети (4). Нивото за основното състояние за f^2 и f^{12} –конфигурациите е триплет H (^{3}H); основното състояние за f^2 е $^3H_4$ а за f^{12} е $^3H_6$