



STUDY ON THE ATOMIC TERM SYMBOLS FOR f^3 (M^{3+} FREE ION) CONFIGURATION

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ABSTRACT

In the field of inorganic chemistry, term symbols regarding to f^n configuration is to be discovered. A little work has been done in this field till now. The importance of the term symbols has been emphasized in connection with the spectral and magnetic properties of complexes, metal atoms and free ions. Russell-Saunders (L-S) coupling scheme is an important scheme 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. In this proposed work, computation is done for calculating all possible terms for f^3 configurations without any long tabulation with mental exercise. Atomic spectra have provided a wealth of information about the energy of atomic orbital to meet out the problem of distributing the electrons in them. In recent years, a great interest is developed in the field of lanthanide and actinide. The determination of terms and term symbols for f^n configuration is a very difficult work. Since there are seven orbital's in f -sub shell, which give large number of microstates. The possible combinations (microstates) of orbital and spin for f^n configuration (ions M^{3+}) are enormously large viz. 14 for f^1/f^{13} , 91 for f^2/f^{12} , 364 for f^3/f^{11} , 1001 for f^4/f^{10} , 2002 for f^5/f^9 , 3003 for f^6/f^8 and 3432 for f^7 , respectively. Due to the bulk number of microstates and cumbersome process of their derivation, it is not given attention in literature. Present work includes information and computation of terms about f^3 configuration.

Key words: Term symbol, Azimuthal quantum number, Microstate, f^3 configuration.

INTRODUCTION

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

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atom or ion. Because of different possibilities for relative orbital and spin orientations among the valence electrons in atoms or ions in same energy level, it may have slightly different energy contents. The interactions between the electrons are of three types. (i) spin-spin coupling (ii) orbit-orbit coupling and (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 principal coupling schemes adopted for arising or splitting of state (i) Russell-Saunders (or $L - S$) coupling (ii) and $j - j$ coupling. 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.

Such interactions (coupling) are produced by the electron's orbital and spin angular momenta give rise to a series of energy levels or states or terms. These states are characterized by (i) energy (ii) orbital angular momentum (iii) spin angular momentum and (iv) total angular momentum.⁴ Arising of states, which are called spectroscopic states or microstates or multiplets is 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 vectorically 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 by the different possible combinations of orbital and spin, which individual electron can acquired, may be called microstate^{4,5}.

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 and the ion or atom is introduced into a lattice. The magnitude of the splitting of the free ion or atom states may be calculated assuming the surrounding effect. These splitting are by purely electrostatic forces.⁶

Total number of microstates increases 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.⁷

A complete term symbol requires an another quantum number J that is 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. 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^{8,9}. Term symbol = (2S + 1)L_J, L = Resultant orbital quantum number, S = Resultant spin quantum number, J = Total angular orbital quantum number and 2S + 1 = Multiplicity^{7,10}

EXPERIMENTAL

Method

Calculation of total number of microstates - When placing electrons in orbitals, there is usually more than one way to accomplish this, particularly when the electrons are going into a degenerate set of orbitals. The orbitals 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 a m_l and a m_s . The question of arranging x electrons in a degenerate set of r orbitals 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 expression¹¹ -

$$\text{Number of ways of filling electrons} = \frac{n!}{x!(n-x!)} \quad \dots(1)$$

where $n = 2(2l + 1)$ or two (number of orbital in sub shell) and

$x = \text{No. of electrons in sub-shell}$

$$\begin{aligned} &= \frac{14!}{3!(14! - 3!)} \\ &= \frac{14 \times 13 \times 12 \times 11 \times 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{3 \times 2 \times 1 \times 11 \times 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1} \end{aligned}$$

$$\text{Total microstates} = 364 \quad \dots(2)$$

Determination of the electron configuration that is allowed by the Pauli principle – Possible spin conditions for f^3 system-

Table 1

S. No.	Possible spin states	Total spin (S)	Total microstates
1	↑↑↑	+3/2	35
2	↑↑↓	+1/2	105
3	↑↓↓	-1/2	105
4	↓↓↓	-3/2	35
6	↑↓↑	+1/2	42
7	↑↓↓	-1/2	42

Total of microstates = 364

Table 2: Microstate chart

		M_S				
		+3/2	+1/2	-1/2	-3/2	
M_L	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
	1	4	16	16	4	40
	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) - The total orbital angular momentum quantum number defines the energy state for a system of electrons. 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.¹² $L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \dots, l_1 - l_2$. These states or term letters are represented as follow:

Table 3

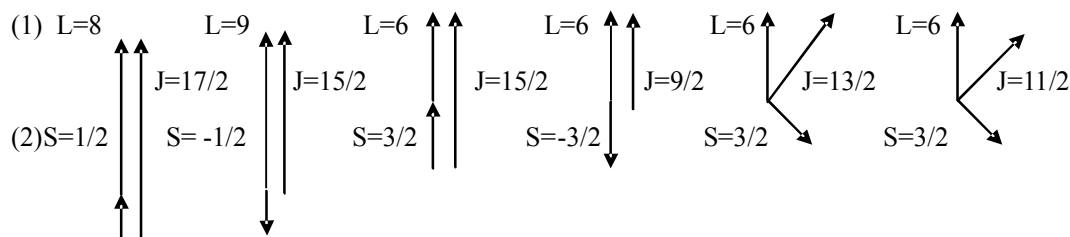
Value of L	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Symbol of L	S	P	D	F	G	H	I	K	L	M	N	O	Q	R	T	U	V	W	X	Y	Z

For the f^3 configuration, the maximum value of L is + 8 and minimum is 0, therefore L is ranged from 0 to + 8, i.e. $L = 0, 1, 2, 3, 4, 5, 6, 7, 8$. So the symbols for L are as such - S P D F G H I K L

Determination of total spin angular momentum quantum number (S) – It represent total spin of atom while ‘s’ states for spin of an electron. $S = \sum_i s_i$ For f^3 system, value maximum of S is +3/2 when all the electrons are unpaired so, $S = 1/2 + 1/2 + 1/2$ and other values of S are + 1/2, -1/2 and -3/2

Determination of M_L and M_S ¹² – $M_L = \sum m_l$ = The component of the total angular momentum along a given axis. Total values of $M_L = 2L + 1$, $M_L = +L \dots 0 \dots -L$ or $L, L-1, L-2, \dots, 0, \dots, -L$ or $M_L = m_{l1} + m_{l2} + \dots + m_{ln}$. The possible value of M_L is given by $2L + 1$, Total values of M_L for f^3 system are $2 \times 8 + 1 = 17$, $M_L = +8, +7, +6, +5, +4, +3, +2, +1, 0, -1, -2, -3, -4, -5, -6, -7, -8$. $M_S = \sum m_s$ It defines spin state for given ‘S’ value, it is equal to $(2S + 1)$ ¹². $M_S = +S \dots 0 \dots -S$ or $S, S - 1, S - 2, \dots -S$, $M_S = m_{s1} + m_{s2} + \dots + m_s$. Total M_S values are $2 \times 3/2 + 1 = 4$ ranging from +3/2 to -3/2.

Determination of J – 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 $J = l + s$, $J = j_1 + j_2 + j_3 + \dots + j_n$ or $J = L + S, L + S - 1, L + S - 2, \dots, |L - S|$. The number of J values, when $L > S$, will be equal to $(2S + 1)$ and when $S > L$, then it will be equal to $(2L + 1)$ ¹³. The coupling of L and S (L - S coupling or Russel-Saunders coupling) is as follow. Example



(1). $L > S$, $J = 2S + 1$, $L = 8$ & $S = 1/2$ so, $J = 2 \times 1/2 + 1 = 2$ (i) $8 + 1/2 = 17/2$
 (ii) $8 - 1/2 = 15/2$

(2). $L > S$, $L = 6$ & $S = 3/2$ so, $J = 2 \times 3/2 + 1 = 4$ (i) $6 + 3/2 = 15/2$ (ii) $6 - 3/2 = 9/2$
 (iii) $6 + 3/2 - 1 = 13/2$ (iv) $6 + 3/2 - 2 = 11/2$

Table 4: Set up a microstates chart¹⁴

		M_S				
		$+3/2$	$+1/2$	$-1/2$	$-3/2$	
M_L	8					2
	7					4
	6					10
	5					14
	4					22
	3					30
	2					38
	1					40
	0					44
	-1					40
	-2					38
	-3					30
	-4					22
	-5					14
	-6					10
	-7					4
	-8					2
Total microstates		35	147	147	35	364

Resolving the chart of microstate into appropriate atomic states, an atomic state forms an array of microstate consisting $2S + 1$ columns and $2L + 1$ rows¹⁴ –

Table 5

L	L	Multi- plicity	Array	Micro states	Term symbol	L > S or S > L & J	S	J	Different states of term
8	L	2	17 x 2	34	² L	L > S, so J = 2S + 1	1/2	J = 2	² L _{17/2} , ² L _{15/2}
7	K	2	15 x 2	30	² K	L > S, so J = 2S + 1	1/2	J = 2	² K _{15/2} , ² K _{13/2}
6	I	4	13 x 4	52	⁴ I	L > S, so J = 2S + 1	3/2	J = 3	⁴ I _{15/2} , ⁴ I _{13/2} , ⁴ I _{11/2} , ⁴ I _{9/2} ² I _{13/2} , ² I _{11/2}
		2	13 x 2	26	² I	L > S, so J = 2S + 1	1/2	J = 2	
5	H	2	11 x 2	22	² H	L > S, so J = 2S + 1	1/2	J = 2	² H _{11/2} , ² H _{9/2} ² H _{11/2} , ² H _{9/2}
		2	11 x 2	22	² H	L > S, so J = 2S + 1	1/2	J = 2	
4	G	4	9 x 4	36	⁴ G	L > S, so J = 2S + 1	3/2	J = 4	⁴ G _{11/2} , ⁴ G _{9/2} , ⁴ G _{7/2} , ⁴ G _{5/2} ² G _{9/2} , ² G _{7/2} ² G _{9/2} , ² G _{7/2}
		2	9 x 2	18	² G	L > S, so J = 2S + 1	1/2	J = 2	
		2	9 x 2	18	² G	L > S, so J = 2S + 1	1/2	J = 2	
3	F	4	7 x 4	28	⁴ F	L > S, so J = 2S + 1	3/2	J = 4	⁴ F _{9/2} , ⁴ F _{7/2} , ⁴ F _{5/2} , ⁴ F _{3/2} , ² F _{7/2} , ² F _{5/2} ² F _{7/2} , ² F _{5/2}
		2	7 x 2	14	² F	L > S, so J = 2S + 1	1/2	J = 2	
		2	7 x 2	14	² F	L > S, so J = 2S + 1	1/2	J = 2	
2	D	4	5 x 4	20	⁴ D	L > S, so J = 2S + 1	3/2	J = 4	⁴ D _{7/2} , ⁴ D _{5/2} , ⁴ D _{3/2} , ⁴ D _{1/2} ² D _{5/2} , ² D _{3/2} ² D _{5/2} , ² D _{3/2}
		2	5 x 2	10	² D	L > S, so J = 2S + 1	1/2	J = 2	
		2	5 x 2	10	² D	L > S, so J = 2S + 1	1/2	J = 1	

Cont...

L	L	Multi- plicity	Array	Micro states	Term symbol	L > S or S > L & J	S	J	Different states of term
1	P	2	3 x 2	6	² P	L > S, so J = 2S + 1	1/2	J = 2	² P _{3/2} , ² P _{1/2}
0	S	4	1 x 4	4	⁴ S	S > L, so J = 2L + 1	1/2	J = 1	⁴ S _{1/2}

The terms or energy states (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 gives different values of J.¹⁵ The ground state term and order of stability of other terms (excited states or terms) can be determined by applying Hund's rule that is as follow-(i) The most stable term is which has the highest spin multiplicity, (ii) If two or more terms have same spin multiplicity (S) than the term has higher value of (L) is more stable and (iii) If the value of (L) is similar 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 and (ii) The highest value of J for more than half filled orbital will be stable.^{7,10,11,16}

RESULTS AND DISCUSSION

(i) The f^3 system (orbital configuration) consists of 17 terms, which split up into 13 energy states due to electron-electron repulsion (spin-spin coupling and orbit-orbit coupling) in which 5 energy states are quartet and 8 are doublets, which further split up into 36 energy states because of spin-orbit coupling giving different J values. The term symbols are as follow. ⁴I, ⁴G, ⁴F, ⁴D, ⁴S, ²L, ²K, ²I, ²H, ²H, ²G, ²G, ²F, ²F, ²D, ²D, ²P and (ii) The ground state term is ⁴I, which is split up into four states. Their stability order is ${}^4I_{15/2} < {}^4I_{13/2} < {}^4I_{11/2} < {}^4I_{9/2}$. Therefore, the lowest energy state or ground state term symbol is ⁴I_{9/2}.

CONCLUSION

The stability of order of terms for f^3 system is ${}^4I > {}^4G > {}^4F > {}^4D > {}^4S > {}^2L > {}^2K > {}^2I > 2 \times {}^2H > 2 \times {}^2G > 2 \times {}^2F > 2 \times {}^2D > {}^2P$

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