

A Simple Method for Obtaining Russell-Saunders Atomic Terms for Equivalent Electrons of nf^6 Configuration

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Abstract

Atomic terms represent the energy levels in free atom or ion and the term symbols are codes assigned to the terms. Terms are applicable in explaining the colour exhibit by complexes and their magnetic properties, and the atomic spectra. A number of methods has been developed to obtain the terms for atoms with partially filled sub shell, in these methods mainly two types of coupling schemes, one is L-S and another is j-j coupling scheme used. In this manuscript we used electronic arrangement method to obtain the Russell-Saunders terms for equivalent electrons of nf^6 configuration in which microstate are build up and the terms are resolved out from microstate array. There are 3003 microstates build up for this configuration and four types of (Singlet, Triplet, Quintet and Septet) terms were obtained from these microstates. The terms are 7F , 5L , 5K , $^5I(2)$, $^5H(2)$, $^5G(3)$, $^5F(2)$, $^5D(3)$, $^5P(5)$, 5S , 3O , 3N , $^3M(3)$, $^3L(3)$, $^3K(6)$, $^3I(6)$, $^3H(9)$, $^3G(7)$, $^3F(9)$, $^3D(5)$, $^3P(3)$, 1Q , $^1N(2)$, $^1M(4)$, $^1K(8)$, 1I , $^1H(7)$, $^1G(8)$, $^1F(4)$, $^1D(6)$, 1P and $^1S(4)$. The predicted ground state term for this configuration is septet F (7F_6) and the ground state will be septet F six (7F_6).

Key words : Quintet, Russell-Saunders term, Septet, Singlet, Term symbol, Triplet

Introduction

A number of methods have been developed to obtain the spectroscopic LS terms for equivalent as well as nonequivalent electrons via Vector model (Lande, 1921), Quantum mechanical method (Russell and Saunders, 1925).

L-S coupling gradually change to jj coupling in going from light to heavy atom due to increase nuclear charge. L-S coupling scheme assumes that angular momentums of each electron, l couple together to produce total orbital angular momentum and spin momentums, s of each electron couple together to produce total spin momentum of atom, S than L and S produce the total angular momentum for atom, J . In the spin-orbit coupling (jj coupling) the orbital angular momentum, l of each electron couples with spin angular momentum to give the electron total angular momentum, j . Then these j vectors for each electron couple to give the atom total angular momentum, J . The methods developed to obtain the LS terms are Generating functions derived via group theory method (Curl and Kilpatrik, 1960), Slater graphics (Slater, 1960). The Russell -Saunders (L-S) coupling scheme first proposed by Henry Russell and Frederick Saunders in 1923 and originally used for electrons in partially filled sub shells of the elements with lower atomic number, but

for the elements with greater atomic number spin-orbit coupling becomes more significant because higher nuclear charge (Wong, 1963). The other important methods developed are Group theoretical method (Wybourne, 1966; Judd, 1967), Ford method (Ford, 1972), Hyde method (Hyde, 1975), Spin factoring method (McDaniel, 1977), Partitioning total spin method (Guofan and Ellzey, 1987), Numerical algorithm method (Kiremire, 1987), Group representation method (Chen, 1989). The microstate building through electronic arrangement method has been used to generate the spectroscopic LS terms for equivalent electrons of f^3 and f^4 configurations (Meena *et al*, 2011 and 2011) and Partitioning technique (Olson, 2011).

Materials and Method

The current nomenclature for the various energy levels (^{2S+1}L) is based on the Russell-Saunders coupling which leads to the three vectors \vec{S} , \vec{L} and \vec{J} . \vec{L} is the vectorial sum of the orbital angular momentum vectors of the valence electrons, and the length of \vec{L} is $\sqrt{L(L+1)}\hbar$. \vec{S} is the vectorial sum of the spin angular momentum vectors of individual valence electrons, and the length of \vec{S} is $\sqrt{S(S+1)}\hbar$. \vec{J} is the vectorial sum of \vec{L} and \vec{S} and the

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length of \vec{J} is $\sqrt{J(J+1)}\hbar$. L and S coupled together to give a state of definite J and the allowed values of J range from $|L+S|$ to $|L-S|$. The nomenclature used in this article is illustrated in Table 1.

Table 1. Nomenclature used for term symbols

Nomenclature	Symbol	Quantum Number used
Configuration	n^N	n and l
Term	$(2S+1)L$	n, L, and S
Level	$(2S+1)L_J$	n, L, S and J
Microstate	$(2S+1)L_J(M_J)$	n, L, S, J and M_J

Calculation of Total Number of microstates nf^6 Configuration

The numbers of microstates increase with increasing the number of electrons in sub shells, and the number of microstates for nonequivalent electronic system are greater than the microstates for a configuration that has same number of equivalent electrons. The expression microstates for any electronic configuration is

$$N = \frac{n!}{x!(n-x)!}, n = 2(2l+1) \text{ or two wise of the total number of orbital's, } x = \text{total number of electrons in sub shell. So,}$$

for nf^6 configuration $n = 14$ and $x = 6$. $N = \frac{14!}{6!(14-6)!}$,

$$N = \frac{14 \times 13 \times 12 \times 11 \times 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{6 \times 5 \times 4 \times 3 \times 2 \times 1 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1} = 3003 \text{ Microstates.}$$

Possible Spin States and Number of Microstates for nf^6 Configuration

The number microstates for each type of spin orientation are counted by building microstate tables in which six electrons are arranged in seven f-orbital's with different values of s and l. The possible spin states for six electrons of nf^6 configuration that allowed by Pauli Exclusion Principle with their possible arrangements in seven f-orbital's is illustrated in Table 2.

Determination of values for L, S, M_L and M_S

$L = \sum l_i$ and $S = \sum s_i$ and $M_L = 2L+1$, $M_S = (2S+1)$. The M_L and M_S values are ranged from +L to -L, and +S to -S, L and S values are the highest values of L and S that obtained from the arrangement of six electrons of nf^6 configuration in seven f-orbital's. For this configuration maximum L and S values are 12 and 3. Therefore, M_L is +12 to -12 and M_S is +3 to -3. The total number of microstate according to M_L and M_S values are illustrated in Table 3 and microstate arrays in Table 4.

Table 2. The fundamental table for equivalent electrons for nf^6 configuration used in Russell Saunders coupling scheme representing possible spin states that allowed by the Pauli Principle with microstates

Spin orientation of electrons in nf-orbital's						Total spin	Micro-states
↑	↑	↑	↑	↑	↑	+3	7
↑	↑	↑	↑	↑	↓	+2	42
↑	↑	↑	↑	↓	↓	+1	105
↑	↑	↑	↓	↓	↓	0	140
↑	↑	↓	↓	↓	↓	-1	105
↑	↓	↓	↓	↓	↓	-2	42
↓	↓	↓	↓	↓	↓	-3	7
↑↓	↑	↑	↑	↑		+2	105
↑↓	↑	↑	↑	↓		+1	420
↑↓	↑	↑	↓	↓		0	630
↑↓	↑	↓	↓	↓		-1	420
↑↓	↓	↓	↓	↓		-2	105
↑↓	↑↓	↑	↑			+1	210
↑↓	↑↓	↑	↓			0	420
↑↓	↑↓	↓	↓			-1	210
↑↓	↑↓	↑↓				0	35
Total microstates for nf^6 configuration-3003							

Table 3. The fundamental table representing total number of microstate according to M_L and M_S values

M_S	+3	+2	+1	0	-1	-2	-3	Total
12				1				1
11			1	2	1			4
10			2	5	2			9
9			5	12	5			22
8		1	9	16	9	1		36
7		2	16	31	16	2		67
6		4	24	40	24	4		96
5		6	35	58	35	6		140
4		9	45	76	45	9		184
3	1	12	57	92	57	12	1	232
2	1	15	65	106	65	15	1	268
1	1	16	72	114	72	16	1	292
$\uparrow M_L 0$	1	17	73	119	73	17	1	301
-1	1	16	72	114	72	16	1	292
-2	1	15	65	106	65	15	1	268
-3	1	12	57	92	57	12	1	232
-4		9	45	76	45	9		184
-5		6	35	58	35	6		140
-6		4	24	40	24	4		96
-7		2	16	31	16	2		67
-8		1	9	16	9	1		36
-9			5	12	5			22
-10			2	5	2			9
-11			1	2	1			4
-12				1				1
Total	7	147	735	1225	735	147	7	3003

Table 4. The fundamental table representing microstate array

M_S →	3	2	1	0
12				
11				
10				
9				
8				
7				
6				
5				
4				
3				
2				
1				
0 ↑M				

Table 5. The Array of Microstates after Removing the (25x1) Array of Microstates (1Q Term) with $M_L = 12$ and $M_S = 1/2$ for nf^6 configuration

M_S	+3	+2	+1	0	-1	-2	-3	Total
12				-				1
11			1	1	1			4
10			2	4	2			9
9			5	11	5			22
8		1	9	15	9	1		36
7		2	16	30	16	2		67
6		4	24	39	24	4		96
5		6	35	57	35	6		140
4		9	45	75	45	9		184
3	1	12	57	91	57	12	1	232
2	1	15	65	105	65	15	1	268
1	1	16	72	113	72	16	1	292
↑M _L 0	1	17	73	118	73	17	1	301
-1	1	16	72	113	72	16	1	292
-2	1	15	65	105	65	15	1	268
-3	1	12	57	91	57	12	1	232
-4		9	45	75	45	9		184
-5		6	35	57	35	6		140
-6		4	24	39	24	4		96
-7		2	16	30	16	2		67
-8		1	9	15	9	1		36
-9			5	11	5			22
-10			2	4	2			9
-11			1	1	1			4
-12				-				1
Total	7	147	735	1200	735	147	7	2978

Resolving the Microstate Chart into Appropriate Atomic States

An atomic term forms an array of microstate consisting $2S+1$ columns and $2L+1$ rows and the total degeneracy of the term is $(2S+1) \times (2L+1)$. Hence, to obtain a term all the M_L and M_S values that belong to a particular term are eliminated from microstate array arrangement table. When an array of microstate is removed from microstate array arrangement table starting from the highest M_L and M_S values it resolve out into an atomic term. When an array of microstate (25x1) with highest M_L value 12 and M_S value 0 (Zero) removed from Table 3 it resolve out into 1Q term and produce Table 5 with highest M_L value 11, removal of next microstate array (23x3) from Table 5 with highest M_L 11 and M_S value 1 produce 3O term and a Table 6 with highest M_L value 10, and the further removal of array of microstate from Table 6, and next produced Tables with highest M_L and M_S values resolve out into 3N , $^1N(2)$, $^3M(3)$, $^3M(4)$, 5L , $^3L(3)$, 5K , $^3K(6)$, $^1K(8)$, $^5I(2)$, $^3I(6)$, 1I , $^5H(2)$, $^3H(9)$, $^1H(7)$, $^5G(3)$, $^3G(7)$, $^1G(8)$, 7F , $^5F(2)$, $^3F(9)$, $^1F(4)$, $^5D(3)$, $^3D(5)$, $^1D(6)$, $^5P(5)$, $^3P(3)$, 1P , 5S and $^1S(4)$ terms for nf^6 configuration.

Table 6. The Array of Microstates after Removing the (23x3) Array of Microstates (3O Term) with $M_L = 11$ and $M_S = 1/2$ for nf^6 configuration

M_S	+3	+2	+1	0	-1	-2	-3	Total
12				-				1
11			-	-	-			4
10			1	3	1			9
9			4	10	4			22
8		1	8	14	8	1		36
7		2	15	29	15	2		67
6		4	23	38	23	4		96
5		6	34	58	34	6		140
4		9	44	74	44	9		184
3	1	12	56	90	56	12	1	232
2	1	15	64	104	64	15	1	268
1	1	16	71	112	71	16	1	292
↑M _L 0	1	17	72	117	72	17	1	301
-1	1	16	71	112	71	16	1	292
-2	1	15	64	104	64	15	1	268
-3	1	12	56	90	56	12	1	232
-4		9	44	74	44	9		184
-5		6	34	58	34	6		140
-6		4	23	38	23	4		96
-7		2	15	29	15	2		67
-8		1	8	14	8	1		36
-9			4	10	4			22
-10			1	3	1			9
-11			-	-	-			4
-12				-				1
Total	7	14	712	1177	712	147	7	2909

The pictorially illustration of L-S Atomic Term for nf^6 configuration

The R-S (L-S) atomic terms for nf^6 configuration are pictorially illustrated in Fig.1.

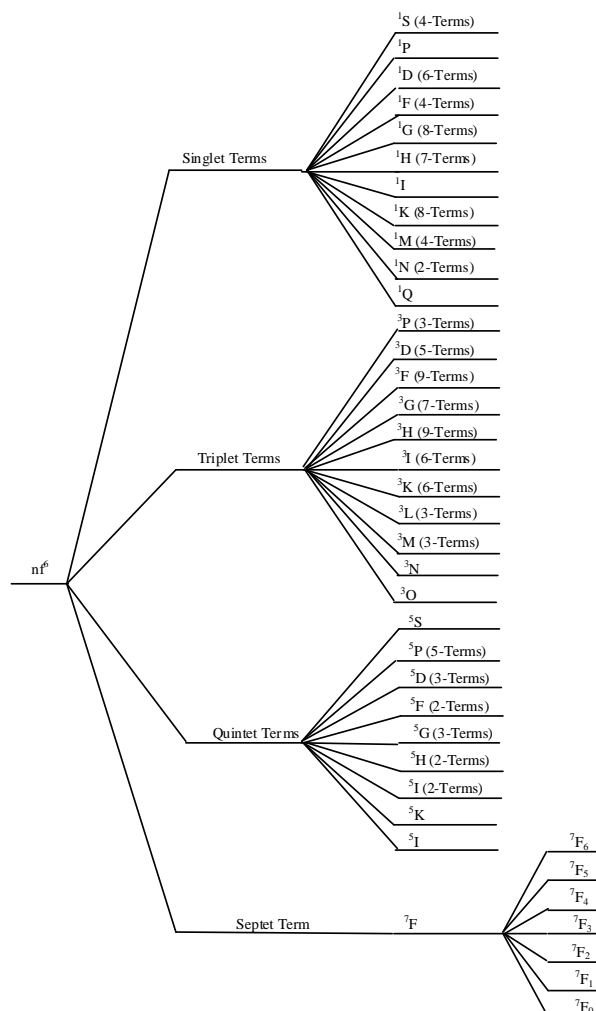


Fig.1. The pictorially illustration of Russell- Saunders (L-S) atomic term for nf^6 configuration

Results and discussion

Four types of Russell Saunders (R-S) atomic terms obtained from this method (singlet, triplet, quintet and septet) and total terms obtained are 120 (46 singlet, 53 triplet, 20 quintet and 1 septet) [$^7\{F\}$, $^5\{L, K, I(2), H(2), G(3), F(2), D(3), P(5), S\}$, $^3\{O, N, M(3), L(3), K(6), I(6), H(9), G(7), F(9), D(5), P(3)\}$, $^1\{Q, N(2), M(4), K(8), I, H(7), G(8), F(4), D(6), P, S(4)\}$]. The determined ground state term for nf^6 configuration is septet F (7F).

Conclusions

In this article we have described a simple and systematic method for derivation of Russell-Saunders atomic terms and atomic electronic states (J- levels) for equivalent electrons of f^6 configuration. The obtained L-S terms atomic terms are pictorially shown in figure 1. The determined ground state term upon the basis of Hund's rule is 7F and energy order of ground states is $^7F_6 > ^7F_5 > ^7F_4 > ^7F_3 > ^7F_2 > ^7F_1 > ^7F_0$. Hence, the ground state is septet F six (7F_6). This is believed that this procedure will be able to make L-S terms atomic terms more popular in chemistry students and chemistry text books and the students will gain a better understanding of the concept of atomic terms, and these terms will be helpful to understand and describe the atomic and electronic spectra.

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