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A Study on Atomic Spectroscopic Term Symbols for Non-equivalent Electrons of (n-1) $d^1s^1p^1$ Configuration Using Russell-Saunders Coupling Scheme

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ABSTRACT
Electronic and magnetic properties of the inorganic molecules and complexes can be understood very well by using the term symbols. Term symbols are a shorthand method used to describe the energy, angular momentum, and spin multiplicity of an atom / ion in any particular electronic state. The Russell-Saunders atomic term symbols provide the information about spectral and magnetic properties of an atom or ion. The atomic terms have been determined for nonequivalent electrons of $(n-1)d^1s^1p^1$ configuration using Russell-Saunders coupling scheme. The total number of microstates computed for the non-equivalent electrons of $(n-1)d^1s^1p^1$ configuration are found to be 120. Among the microstates, two types of atomic terms have been determined namely, quartet (3-types) and doublet (6-types). The ground state term found for this configuration is quartet ^4F with the lower energy state as $^4F_2$.
Keywords: Term symbol, Russell-Saunders coupling, $(n-1)d^1s^1p^1$ configuration, Microstates, Quartet and doublet.

I. INTRODUCTION

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterise the electronic states of atoms. An orbiting electronic charge produces magnetic field perpendicular to the plane of the orbit. Hence the orbital angular momentum and spin angular momentum have corresponding magnetic vectors. As a result, both of these momenta couple magnetically to give rise to total orbital angular momentum. Russell Saunders coupling [1] involve coupling between the spin of one electron with the orbital angular momentum of a different electron[2].

In the Russell-Saunders coupling scheme, term symbols are in the form of $^{2S+1}L_J$, where *S* represents the total spin angular momentum, *L* specifies the total orbital angular momentum, and *J* refers to the total angular momentum. In a term symbol, *L* is always an upper-case from the sequence "s, p, d, f, g, h, i, k...", wherein the first four letters stand for sharp, principal, diffuse and fundamental, and the rest follow in an alphabetical pattern. Note that the letter j is omitted. In the Russell Saunders scheme it is assumed that spin-spin coupling > orbit-orbit coupling > spin-orbit coupling. This is found to give a good

approximation for first row transition series where J coupling is ignored, however for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme [3-5] is used. The overall spin S arises from adding the individual m_s together and is as a result of coupling of spin quantum numbers for the separate electrons. The resultant spin quantum number (S) for a system of electrons is as given below,

$$S = (s_1 + s_2), (s_1 + s_2 - 1), \dots \dots (s_1 - s_2) \quad (1)$$

where s is the azimuthal quantum number.
For two electrons, S=0 when spins are coupled opposite (↑↓) or S=1 (↑↑) when spins are coupled parallel. For three electrons: coupling of the type ↑↑↑ results in S=3/2
coupling of the type ↑↑↓ results in S=1/2
The spin multiplicity [6] is given by (2S+1). Hence, If n is the number of unpaired electrons, spin multiplicity is given by n + 1. Spin multiplicity value depends on the arrangement of electrons, that is, whether they are paired or not. S= 0→"Singlet" S= ½→"Doublet" S= 1→"Triplet" S= 1½→"Quartet".
The resultant orbital angular momentum quantum number (L) defines the energy state for a system of electrons. The allowed values of L are given below:

$$L = (l_1 + l_2), (l_1 + l_2 - 1), \dots 0 \dots (l_1 - l_2) \quad (2)$$

where l is the azimuthal quantum number. Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J the

totalangular momentum quantum number. The resultant S and L couple to give a total angular momentum, J. The possible values of J quantum number are given as

$$J = (L+S), (L+S-1), (L+S-2) \ldots \ldots |L-S|$$
(3)

The symbol | | indicates that the absolute value of (L – S) is employed, i.e., no regard is paid to ± sign. Thus for L = 2 and S = 1, the possible J states are 3, 2 and 1 in units of h/2π. This scheme of coupling is known as spin-orbit coupling or j -j coupling. Among elements beyond Z = 30, spin orbit coupling becomes significant [7] and therefore with heavy elements j-j coupling is used.

The Russell Saunders term symbol that results from these considerations is given by:
$^{(2S+1)}$L. As an example, for a d^1 configuration, L=2 and S = ½, the Russell Saunders Ground Term is written as ^{2}D.R-S term symbol representing any spectroscopic state has many microstates. The number of microstates that a given term possesses can be calculated by using simple formula;

Number of microstates, $N = \frac{n!}{r!(n-r)!}$ (4)

Where n is the twice the number of orbitals, r is the number of electrons and !is the factorial.
For d^2 configuration, the number of microstates is given by

$$N = \frac{10!}{2!(10-2)!} = 45$$ (5)

The number of microstate[8] increase with increase in the number of electrons in orbital but in the nonequivalent electronic system the number of microstates are much greater than the similar equivalent electronic system and the coupling of angular momentum of nonequivalent electrons is straight forward than for equivalent electrons [9].

The equivalent electrons are those which have same values of l such as np^2, nd^4, nf^2, etc. In the present work, the atomic terms have been determined for nonequivalent electrons [10]of (n-1)$d^1s^1p^1$configuration.

II. METHODOLOGY
2.1. Determination of total number of microstates

The number of microstates (N) of a system corresponds to the total number of distinct arrangements for "r" number of electrons to be placed in "n" number of possible orbital positions. The number of microstates that a given term possesses can be calculated by using simple formula as given in equation (4).

So in case of $d^1s^1p^1$ Configuration, n = 10 and r = 1 for d - orbital, n = 6 and r = 1for p- orbital and n = 2 and r = 1for s- orbital, therefore, the number of microstates is,

$N = \frac{10!}{1!(10-1)!} = 10$ for d^1 electron, (6)

$N = \frac{6!}{1!(6-1)!} = 6$ for p^1 electron and (7)

$N = \frac{2!}{1!(2-1)!} = 2$ for s^1 electron (8)

Hence the total number of microstates for $d^1s^1p^1$ configuration is,

$$N = 10 \times 6 \times 2 = 120$$ (9)

Table 1: The possible spin states, spin orientations and total number ofmicrostatesfor non-equivalent electrons of $d^1s^1p^1$ configuration.

Sl. No.	Total Spin	Spin Orientations			Microstates	Total Microstates
		d	s	p		
1	+3/2	↑	↑	↑	15	15
		↑	↑	↓	15	45
2	+1/2	↑	↓	↑	15	
		↓	↑	↑	15	
	-1/2	↓	↓	↑	15	45
3		↓	↑	↓	15	
		↑	↓	↓	15	
4	-3/2	↓	↓	↓	15	15
Total number of microstates for $d^1s^1p^1$ configuration						120

The total number of possible microstates [11]for (n-1)$d^1s^1p^1$configuration is found to be 120. The presence of 120 microstates can be verified by assigning possible spin states in accordance with Pauli's principle. The possible spin states, spin orientations and total number of microstates are given in table 1.

2.2. Determination of total orbital angular momentum quantum number (L), total spin quantum number (S), M_L, M_S and J values

All the three non-equivalent electrons in (n-1)$d^1s^1p^1$configuration, are not independent of each other and their orbital angular momenta (m_l values) and spin angular momenta (m_s values) interact in a way called Russell-Saunders coupling. These interactions produce states called microstates

that can be described by the new quantum numbers M_L and M_S [12]. The energy of a multi electron species and its orbital angular momentum is determined by a resultant orbital angular momentum quantum number L which is the sum of the values of l for individual electrons.

$$orbital\ angular\ momentum = \sqrt{l(l+1)}\frac{□}{2\pi}$$
(10)

The resultant orbital angular momentum is given by:

$$orbital\ angular\ momentum\ for\ multi\ electron\ species = \sqrt{L(L+1)}\frac{□}{2\pi}$$
(11)

The resultant orbital angular momentum L assume the values 0, 1, 2, 3, 4…. which are referred to as S, P, D, F G,…terms respectively in units of h/2π. Since the orbital angular momentum has magnitude and $(2l+1)$ number of spatial orientations (M_l values), vectorial summation of individual l values is necessary [13].

The m_l value for any electron denotes the component of the resultant orbital angular momentum along the z-axis, m_l (h/2 π). The resultant orbital magnetic quantum number M_L can have $(2L+1)$ values L, (L-1)…..0….-(L-1), -L. For multi-electron system (n-1)$d^1s^1p^1$ configuration, all the possible values of L can be determined as shown in table 2.

Table 2: The possible values of L for non-equivalent electrons of $d^1s^1p^1$ configuration.

Sl. No	Electronic Configuration									
	d^1					p^1			s^1	
	2	1	0	-1	-2	1	0	-1	0	
	↑					↑			↑	
	Total orbital angular momentum, L values									
1	L = 3					L = 2			L = 1	
2	L = 2					L = 1			L = 0	
3	L = 1					L = 0			L = -1	
4	L = 0					L = -1			L = -2	
5	L = -1					L = -2			L = -3	
	L = ± 3 (2 times), ± 2 (4 times), ± 1 (6 times), 0 (3 times)									

Similarly the resultant spin quantum number is determined by;

$$spin\ angular\ momentum\ for\ multi\ electron\ species = \sqrt{s(s+1)}\frac{□}{2\pi}$$
(12)

M_S is obtained by algebraic summation of the m_s values for individual electrons. The value of spin, $s = \frac{1}{2}$ will have $Ms = +\frac{1}{2}$ or $-\frac{1}{2}$. In general, for any value of S, there can be $(2S+1)$ values of M_S: S, (S-1)….0….-(S-1), -S [14]. The quantity $(2S+1)$ is the multiplicity of the term where S is the total spin quantum number. Terms with values for multiplicity $(2S+1)$ = 1, 2, 3, 4, etc. correspond to the values of spin S = 0, ½, 1, 3/2 etc. meaning singlets, doublets, triplets, quartets, respectively [15].

The possible M_L and M_S values for (n-1)$d^1s^1p^1$ configuration are presented in the table 3.

Finally, we have the total angular momentum quantum number J, which is given as:

$$total\ angular\ momentum\ for\ multi\ electron\ species = \sqrt{J(J+1)}\frac{□}{2\pi}$$
(13)

Where quantum number J can take values between (L+S) and (L-S).

For a condition S < L, J can have $(2S+1)$ possible values and for L < S, J can have $(2L+1)$ values.

Table 3: The possible M_L and M_S values for non-equivalent electrons of $d^1s^1p^1$ configuration.

M_L	M_s				
	+3/2	+1/2	-1/2	-3/2	Total
3	1	3	3	1	8
2	2	6	6	2	16
1	3	9	9	3	24
0	3	9	9	3	24
1	3	9	9	3	24
2	2	6	6	2	16
3	1	3	3	1	8
Total	15	45	45	15	120

The possible J values for (n-1)$d^1s^1p^1$ configuration are presented in the table 4.

Table 4: The possible J values and terms for non-equivalent electrons of $d^1s^1p^1$ configuration.

L	S	(2S+1)	J	Terms	(2S+1)(2L+1)	Microstates
3	3/2	4	4	^{4}F	4 x 7	28
L > S	1/2	2	2	^{2}F (2)	2 x 7	14 x 2 = 28
2	3/2	4	4	^{4}D	4 x 5	20
L > S	1/2	2	2	^{2}D (2)	2 x 5	10 x 2 = 20
1	3/2	4	3	^{4}P	4 x 3	12
L < S	1/2	2	2	^{2}P (2)	2 x 3	6 x 2 = 12
			Total			120

The chart of microstates for (n-1)d $^1s^1p^1$ configuration depicting the array of M_L versus M_S for non-equivalent electrons of (n-1)d $^1s^1p^1$ configuration is given in table 5.

III. RESULT AND DISCUSSION

It is possible to identify R-S terms comprising of specific microstates from the chart of microstates. The microstate having largest M_L value is to be selected and corresponding M_S values are also noted. From the tables 5 and 6, microstates with $M_L = 3$ and $M_S = +3/2, +1/2, -1/2, -3/2$ constitutes ^{4}F term. This is the first term with (2L+1) (2S+1) = (2x3+1) (2x3/2 +1) = 7 x 4 = 28 microstates.

Table 5: Chart of microstates for non-equivalent electrons of $d^1s^1p^1$ configuration.

	L	M_s				
		+3/2	+1/2	-1/2	-3/2	Total
M_L						
	3	|	| | |	| | |	|	8
	2	| |	| | | | | |	| | | | | |	| |	16
	1	| | |	| | | | | | | | |	| | | | | | | | |	| | |	24
	0	| | |	| | | | | | | | |	| | | | | | | | |	| | |	24
	-1	| | |	| | | | | | | | |	| | | | | | | | |	| | |	24
	-2	| |	| | | | | |	| | | | | |	| |	16
	-3	|	| | |	| | |	|	8
	Total	15	45	45	15	120

After assigning all of these 28 microstates, out of 120, 92 microstates are left to be grouped accordingly. Adopting the similar method [16], the remaining microstates results in the following terms:

^{2}F (2), ^{4}D, ^{2}D (2), ^{4}P and ^{2}P (2).

It is observed that all the microstates for non-equivalent electrons of (n-1)d $^1s^1p^1$ configuration give ^{4}F, ^{2}F (2), ^{4}D, ^{2}D (2), ^{4}P and ^{2}P (2) atomic terms (Table 6). The microstates of electrons of (n-1)d $^1s^1p^1$ configuration remain conserved [17] in the number of atomic terms and verified by obtaining the microstates from the atomic terms as given in table 6.

Table 6: Microstate matrix of atomic terms for non-equivalent electrons of $d^1s^1p^1$ configuration.

Sl. No.	L	S	Multiplicity (2S+1)	Term Symbol	J	Split Term Symbols	Array	Total Microstates
1	3	3/2	4	^{4}F	4	$^4F_{9/2}, ^4F_{7/2}, ^4F_{5/2}, ^4F_{3/2}$	7 x 4	28

2	3	1/2	2	^2F (2)	2	$^2F_{7/2}$, $^2F_{5/2}$	7 x 2	14 x 2 = 28
3	2	3/2	4	^4D	4	$^4D_{7/2}$, $^4D_{5/2}$, $^4D_{3/2}$, $^4D_{1/2}$	5 x 4	20
4	2	1/2	2	^2D (2)	2	$^2D_{5/2}$, $^2D_{3/2}$	5 x 2	10 x 2 = 20
5	1	3/2	4	^4P	3	$^4P_{5/2}$, $^4P_{3/2}$, $^4P_{1/2}$	3 x 4	12
6	1	1/2	2	^2P (2)	2	$^2P_{3/2}$, $^2P_{1/2}$	3 x 2	6 x 2 = 12
Total number of microstates for $d^1s^1p^1$ configuration								120

The stability of the Russell-Saunders's terms for the non-equivalent electron of (n-1)d $^1s^1p^1$configurationis determined in accordance with Hund's rules [18-22] as given below:

(i) The ground state term should have largest spin multiplicity.

(ii) If two or more terms have same spin multiplicity, then the state with the largest value of L will be considered as ground state.

(iii) In case, if the subshell is less than half full, the lowest J corresponds to the lowest energy.

If the subshell is greater than half full, the highest J corresponds to the lowest energy.

The stability order for the terms of non-equivalent electrons of (n-1)d $^1s^1p^1$configurationis found as follows:

^4F $<^4D<$ ^4P $<^2F$ (2) $<^2D$(2) $<^2P$(2).

Electronic configuration is split into terms due to inter-electronic repulsion, which is split into states by spin-orbit coupling, which is further split into microstates by magnetic field. The splitting pattern of terms associated with non-equivalent electrons of (n-1)d $^1s^1p^1$configurationis given in figure 1.
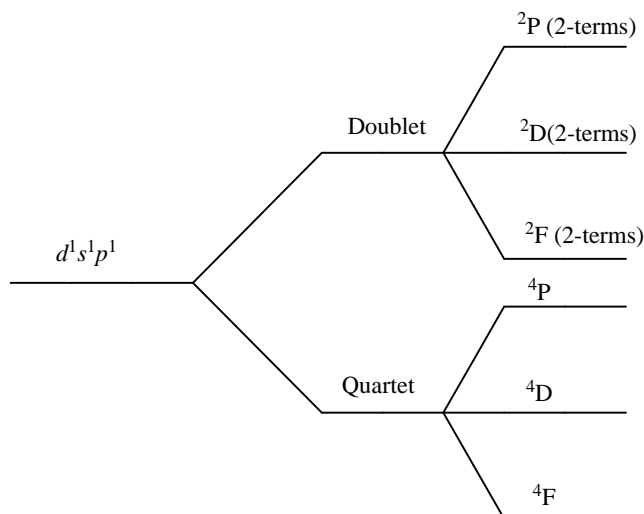

Fig. 1: The splitting pattern of R-S terms associated with non-equivalent electrons of(n-1)d $^1s^1p^1$configuration.

The microstate sub tables for each R-S term are presented in table 7:

Table 7: Sub tables for eachR-S term for non-equivalent electrons of$d^1s^1p^1$ configuration.

Table 7.1: Term ^4F

M_L	M_S	+3/2	+1/2	-1/2	-3/2
	3								
	2								
	1								
	0								
	-1								
	-2								
	-3								
L = 3, S = 3/2, 2S+1 = 4					

Table 7.2: Term ^2F

M_L	M_S	+1/2	-1/2

3		
2		
1		
0		
-1		
-2		
-3		
L = 3, S = 1/2, 2S+1 = 2		

Table 7.3: Term ^{4}D

M_L	M_S			
	+3/2	+1/2	-1/2	-3/2
2	|	|	|	|
1	|	|	|	|
0	|	|	|	|
-1	|	|	|	|
-2	|	|	|	|
L = 2, S = 3/2, 2S+1 = 4				

Table 7.4: Term ^{2}D

M_L	M_S	
	+1/2	-1/2
2	|	|
1	|	|
0	|	|
-1	|	|
-2	|	|
L = 2, S = 1/2, 2S+1 = 2		

Table 7.5: Term ^{4}P

M_L	M_S			
	+3/2	+1/2	-1/2	-3/2
1	|	|	|	|
0	|	|	|	|
-1	|	|	|	|
L = 1, S = 3/2, 2S+1 = 4				

Table 7.6: Term ^{2}P

M_L	M_S	
	+1/2	-1/2
1	|	|
0	|	|
-1	|	|
L = 1, S = 1/2, 2S+1 = 2		

IV. CONCLUSION

The application of R-S coupling scheme for non-equivalent electrons of (n-1)d $^1s^1p^1$configurationresults in the generation of 120 microstates which were grouped in to six spectroscopic terms: ^{4}F , ^{4}D, ^{4}P, ^{2}F (2), ^{2}D(2) and ^{2}P(2). The ground state term was found to be ^{4}F$_2$. The stability order for the terms of non-equivalent electrons of (n-1)d $^1s^1p^1$configurationis ^{4}F $<^4$D$<^4$P $<^2$F (2) $<^2$D(2) $<^2$P(2). The microstates of electrons of (n-1)d $^1s^1p^1$configurationremain conserved in the number of atomic terms and verified against the number of microstates from the atomic terms.

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