



Studies on Atomic Spectroscopic Terms and Term Symbols for Non-equivalent Electrons of $d^2s^1p^1$ Configuration Using Russell- Saunders Coupling Scheme

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Abstract

Russell-Saunders (R-S) coupling scheme is an important coupling scheme to determine the terms and to assign the term symbols to the terms to the valence electrons of free atoms. The atomic term symbols provide the information about the energy of atomic valence electrons, total spin, total orbital angular momentum, total angular momentum, spectral and magnetic properties of atom. In this proposed work computation is done to determine all the possible terms for the non-equivalent valence electrons of $d^2s^1p^1$ configuration manually and the term symbols are assigned to the terms using Russell-Saunders coupling scheme. The possible microstates calculated for the non-equivalent electrons of $d^2s^1p^1$ configuration are 540 and the total numbers of atomic spectroscopic terms determined from these microstates are 38 (17 types), 6 are quintets (5 types), 17 are triplets (6 types) and 13 are singlets (6 types). The ground state term for the non-equivalent electrons of $d^2s^1p^1$ configuration is quintet G (5G) and the ground state is quintet G two (5G_2).

Keywords: Term symbol, microstate, quintet, triplet and singlet.

Introduction

Non-equivalent electrons are those which have different values of either n or l such as $3p^1 3d^1$, $4f^1 5d^1$ or $4f^2 5d^1$ configuration. The coupling of angular momentum of non equivalent electrons is straight forward than for equivalent electrons¹. There are three types of interactions between the electrons viz. spin-spin coupling, orbit-orbit coupling and spin-orbit coupling. It is assumed that: spin-spin coupling > orbit-orbit coupling > spin-orbit coupling and two principle coupling schemes Russell-Saunders coupling and $j-j$ coupling adopted for arising or splitting of state in free atom and it is found that the Russell Saunders scheme gives a good approximation for the first row transition series elements where spin-orbit ($j-j$) coupling scheme 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 used²⁻⁴. However, for heavier atoms it is still convenient to use Russell-Saunders scheme⁵. These interactions (coupling) produced by the electron's orbital and spin angular momentum give rise to a series of energy levels or states which are characterized by energy, orbital angular momentum, spin angular momentum and total angular momentum and expressed by proper term symbols and defined by new quantum numbers L , M_L , M_S and S and for multi electron systems these are obtained 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 and it is characterized the

different possible combination of orbital and spin which individual electron can acquired may be called microstate⁶.

Total number of microstates increases with the increase the number of electrons in orbital and for the non equivalent electronic system the microstates are much greater than the similar equivalent electronic system. The formulation of hole 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 are vacancies in the various orbital's rather than larger number of electrons actually present. By considering holes the terms which arise for pair 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 the identical terms⁷. The term is applied for energy associated with the state of an atom involved in a transition and term symbols are abbreviated description of the energy, angular momentum and spin multiplicity of an atom in particular state and a complete term symbol is represented by $(^{2S+1})L_J^{1,5,7,8,9}$.

For a particular electronic configuration of an 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 forces¹⁰. The term splits up into singlet, doublet, triplet, quartet, quintet, sextet etc. due to 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 ¹¹. The ground state term and order of stability of other terms (excited states or terms) can be determine by applying Hund's rule^{1, 5,7,9,10,12}.

Methodology

Calculation of Total number of Microstates for Non-equivalent Electrons of $d^2s^1p^1$ Configuration: 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. 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 expression¹³.

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

$n = 2(2l+1)$ or two wise of the Total No. of orbital's, $x =$ Total No. of electron in sub Shell

For $d^2 p^1 s^1$ system $n = 10, 6$ & 2 and $x = 2$ and 1 , So,

$$N = \frac{10!}{2!(10-2)!} \times \frac{6!}{1!(6-1)!} \times \frac{2!}{1!(2-1)!}$$

$$N = \frac{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1} \times \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{1 \times 5 \times 4 \times 3 \times 2 \times 1} \times \frac{2 \times 1}{1 \times 1}$$

$$N = 45 \times 6 \times 2 = 540 \text{ Microstates}$$

Possible Spin States for the Non-equivalent Electrons of $d^2s^1p^1$ Configuration that Allowed by the Pauli Principle: Possible spin states with total number of microstates can be determined by arranging the electrons in orbital's according to Pauli principle and all possible spin states for the equivalent or

non-equivalent electrons of a particular configuration can be arranged systematically with their total spin and total number of microstates. For non equivalent electrons of $d^2 s^1 p^1$ configuration possible spin states are arranged in table-1.

Statistics of Microstates: Statistically the microstates for the equivalent or non-equivalent electrons of a particular configuration can be represented numerically and symbolically. For the non equivalent electrons of $d^2 s^1 p^1$ configuration the microstates are represented statistically numerically table-2 and symbolically table-3.

Determination of Orbital Angular Momentum Quantum Number (L), l-l Coupling: It is a vector sum of all the l values of all electrons. The coupling of orbital momentum of equivalent or non-equivalent electrons is referred as l-l coupling, it gives a resultant L of magnitude $[L(L+1)]^{1/2} h/2\pi = L * h/2\pi$. It 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. The orientations of $l_1, l_2, l_3, \dots, l_n$ which they can take up are governed by values that the quantum number L can take. L is associated with the total orbital angular momentum for the four electrons of $d^2 s^1 p^1$ configuration and restricted to the values $L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2), \dots, |(l_1 - l_2)|$ ^{1,5,7,10,12}. The space quantization of L produces $2L+1$ components with $M_L = L, L-1, \dots, -L$ analogous of l. In the present case $L = 5, 4, 3, 2, 1, 0$ and magnitudes of L are $30^{1/2} h/2\pi, 20^{1/2} h/2\pi, 12^{1/2} h/2\pi, 6^{1/2} h/2\pi, 2^{1/2} h/2\pi$ and 0 respectively. The spectroscopic terms of the atom are labeled S, P, D, F, G, H, corresponding to $L = 5, 4, 3, 2, 1$ and 0 respectively. It follows that the $d^2 s^1 p^1$ configuration gives rise to S, P, D, F, G, and H terms.

Table-1
Statistics of microstates (numerically) of non-equivalent electrons of $d^2 s^1 p^1$ configuration

S.N.	Total spin	Spin orientation of electrons in orbital's				Microstates	Total microstates
1	+2	↑	↑	↑	↑	30	165
2	+1	↑	↑	↓	↑	30	
3		↑	↑	↑	↓	30	
4		↑	↑	↑	↓	30	
5		↑	↓	↑	↑	60	
6		↑↓	↑	↑	↑	15	
7	-1	↑↓	↓	↓	↓	15	75
8		↓	↓	↓	↑	30	
9		↓	↓	↑	↓	30	
10	-2	↓	↓	↓	↓	30	240
11	0	↓	↓	↑	↑	30	
12		↑	↓	↓	↑	60	
13		↑	↓	↑	↓	60	
14		↑	↓	↑	↑	60	
15		↑↓	↑	↑	↓	15	
16	↑↓	↓	↓	↑	15		
Total number of microstates-540							

Determination of Total Spin Angular Momentum Quantum Number (S) s-s Coupling: It represents the total spin of atom, while the 's' represents spin state of an electron and the coupling between the spin momentum is referred as s-s coupling. The vector for each electron is always of magnitude of $3/4^{1/2} h/2\pi$ according to $[s(s+1)]^{1/2} h/2\pi = s^* h/2\pi$. The vector can only take up orientations relative to each other such that the magnitude of s-s coupling can as follow $[S(S+1)]^{1/2} h/2\pi = S^*h/2\pi$. $S = (s_1+s_2), (s_1+s_2-1), (s_1+s_2-2), \dots, |(s_1+s_2)|$ ^{1,5,7,10,12}. In the present case of $d^2 s^1 p^1$ configuration for the four electrons the values of S = 2, 1 or 0 and the vector sums giving resultant S vectors of magnitude $6^{1/2} h/2\pi, 2^{1/2} h/2\pi$ and zero.

Determination of M_L and M_S : $M_L = \sum m_l$ = the component of the total angular momentum along a given axis and total values of are $M_L = 2L+1, M_L = +L \dots 0 \dots -L$. Total possible values of M_L for $d^2 s^1 p^1$ configuration are $2x5+1 = 11$ which are ranged from +5 to -5. $M_S = \sum m_s$, It defines spin state for given 'S' value and it is equal to (2S+1). $M_S = +S, \dots 0 \dots -S$. Total M_S values for the non equivalent electrons of $d^2 s^1 p^1$ configuration are $2x2+1=5$ which are ranged from +2 to -2.

Determination of (J) l-s Coupling: It is a resultant of the orbital angular momentum vector and the electron spin angular momentum vector. The coupling between L and S is due to spin-orbit interaction caused by the positive charge Ze on the nucleus and is proportional to (Z^4) ¹. This coupling gives total angular momentum vector J $[J(J+1)]^{1/2} h/2\pi = J^*h/2\pi$, where J are restricted to the values $J = L+S, L+S-1, \dots, L-S$, from which it follows that if $L \geq S$ the 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^{1,7,9,14}. The vector sum can be made only in certain ways and the values of 'J' may be either $1+1/2$ or $1-1/2$. $1-1/2$ is of lower energy state since in $1-1/2$ state the orbital and spin are opposed^{8,14}.

Resolving 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, for a 3H State requires two columns or (11×3) array and 5G State requires (9×5) array^{5,7}. By removing each state from the microstate table we can draw a microstate sub table for each state¹⁵⁻¹⁸.

Drawing a Complete Matrix Table: A complete matrix table for $d^2 s^1 p^1$ configuration can be drawn table-4 that includes all terms, term symbols, total microstates, multiplicity, total J values and values taken up by J.¹⁵⁻¹⁸

Results and Discussion

The atomic spectroscopic terms determined for $d^2 s^1 p^1$ configuration are 17 types, among these 5 types are quintet, 6 types are triplet and 6 types are singlet. These terms are $^3H, ^1H, ^5G, ^3G(3\text{-Terms}), ^1G(2\text{-Terms}), ^5F, ^3F(4\text{-Terms}), ^1F(3\text{-Terms}), ^5D(2\text{-Terms}), ^3D(5\text{-Terms}), ^1D(3\text{-Terms}), ^5P, ^3P(4\text{-Terms}), ^1P(3\text{-Terms}), ^5S, ^3S(2\text{-Terms}), ^1S$ and the stability order of these atomic spectroscopic terms is $^5G > ^5F > ^5D(2) > ^5P > ^5S > ^3H > ^3G(3) > ^3F(4) > ^3D(5) > ^3P(4) > ^3S(2) > ^1H > ^1G(2) > ^1F(3) > ^1D(3) > ^1P(3) > ^1S$ and the ground state term is quintet G (5G) and ground state is quintet G two (5G_2).

Conclusion

Total atomic spectroscopic terms determined for the non equivalent electrons of $d^2 s^1 p^1$ configuration of free atom are 38 (17 types) which grouped into 17 energy states due to the s-s and l-l coupling, among these 5 are quintets, 6 are triplets and 6 are singlet, which further split up into different energy states due to spin-orbit (s-l) coupling. The splitting of terms of non equivalent electrons of $d^2 s^1 p^1$ configuration and their stability order according to Hund's rule can be drawn graphically figure-1.

Table-2
Possible spin states for the non-equivalent electrons of $d^2 s^1 p^1$ configuration

$M_L \downarrow$	M_S					Total
	+2	+1	0	-1	-2	
5		1	2	1		4
4	1	5	8	5	1	20
3	2	10	16	10	2	40
2	4	17	26	17	4	68
1	5	22	34	22	5	88
0	6	25	38	25	6	100
-1	5	22	34	22	5	88
-2	4	17	26	17	4	68
-3	2	10	16	10	2	40
-4	1	5	8	5	1	20
-5		1	2	1		4
Total	30	135	210	135	30	540

Table-3
Statistics of microstates (symbolically) of non-equivalent electrons of $d^2 s^1 p^1$ configuration

M_S						
$M_L \downarrow$	+2	+1	0	-1	-2	Total microstates
5						4
4						20
3						40
2						68
1						88
0						100
-1						88
-2						68
-3						40
-4						20
-5						4
Total number of microstates-540						

Table-4
Complete matrix table for the non-equivalent electrons of $d^2 s^1 p^1$ configuration

S.N	L	L Label	S	2S+1	Term symbol	Total values of J	Several possible states	Array	Micro states		
1	5	H	1	3	3H	J=3	$^3H_6, ^3H_5, ^3H_4$	11x3	33		
			0	1	1H	J=1		1H_5		11x1	11
2	4	G	2	5	5G	J=5	$^5G_6, ^5G_5, ^5G_4, ^5G_3, ^5G_2$	9x5	45		
			1	3	$^3G(3)$	J=3		$^3G_5, ^3G_4, ^3G_3$		(9x3)3	81
			0	1	$^1G(2)$	J=1		1G_4		(9x1)2	18
3	3	F	2	5	5F	J=5	$^5F_5, ^5F_4, ^5F_3, ^5F_2, ^5F_1$	7x5	35		
			1	3	$^3F(4)$	J=3		$^3F_4, ^3F_3, ^3F_2$		(7x3)4	84
			0	1	$^1F(3)$	J=1		3F_1		(7x1)3	21
4	2	D	2	5	$^5D(2)$	J=5	$^5D_4, ^5D_3, ^5D_2, ^5D_1, ^5D_0$	(5x5)2	50		
			1	3	$^3D(5)$	J=3		$^3D_3, ^3D_2, ^3D_1$		(5x3)5	75
			0	1	$^1D(3)$	J=1		1D_2		(5x1)3	15
5	1	P	2	5	5P	J=5	$^5P_3, ^5P_2, ^5P_1$	3x5	15		
			1	3	$^3P(4)$	J=3		$^3P_2, ^3P_1, ^3P_0$		(3x3)4	36
			0	1	$^1P(3)$	J=1		1P_0		(3x1)3	9
6	0	S	2	5	5S	J=5	5S_2	1x5	5		
			1	3	$^3S(2)$	J=3		3S_1		91x3)2	6
			0	1	1S	J=1		1S_0		1x1	1
Total number of microstates-540											

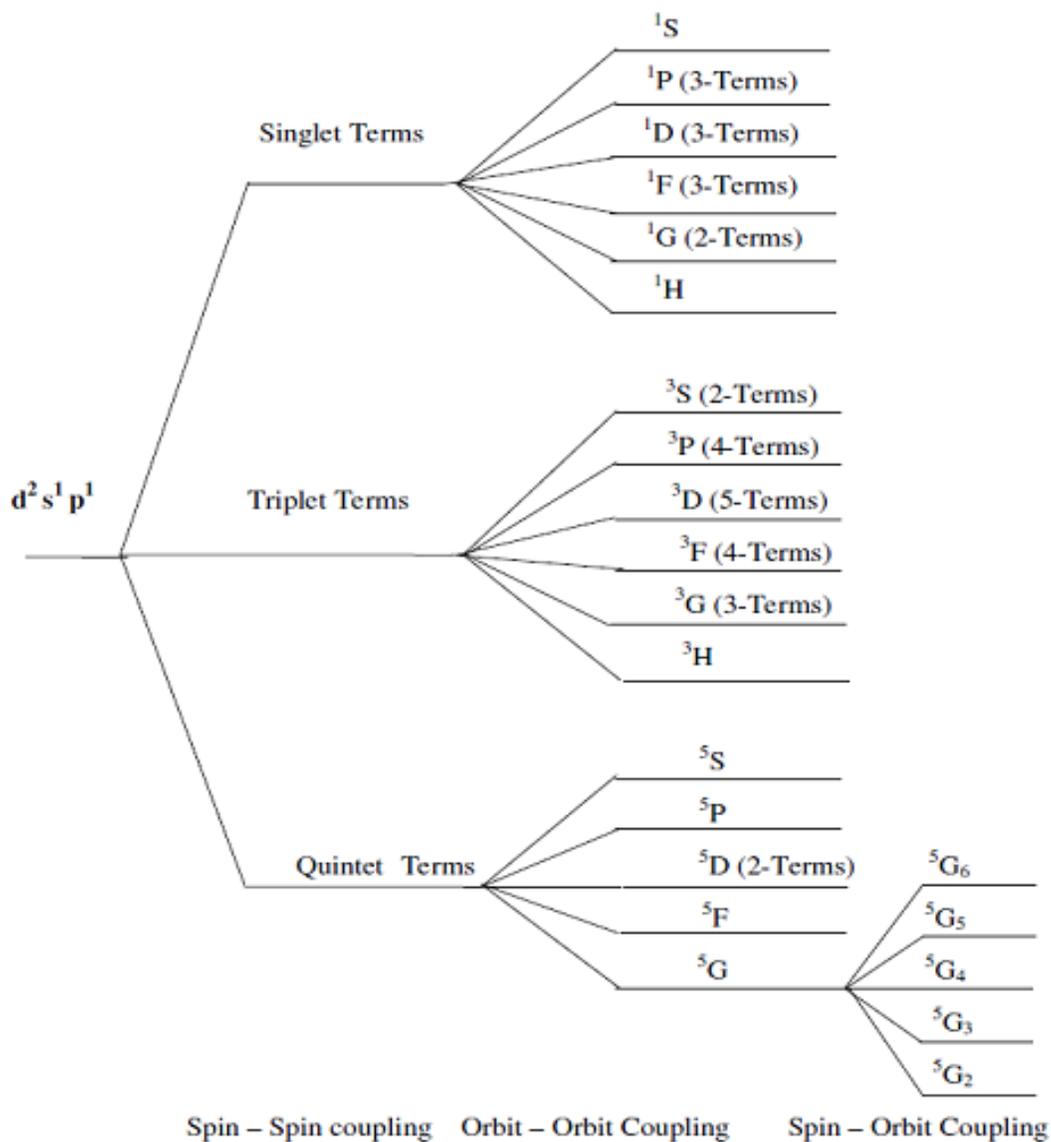


Figure-1
Splitting of the terms of the non-equivalent electrons of $d^2s^1p^1$ configuration

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