

Calculation of Atomic Spectroscopic Terms for Non-equivalent Electrons of $f^2 d^1$ Configuration and Assigning the Term Symbols†

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The term is a energy state, which arises from an approximation treatment of an electronic configuration and term symbol is label to that energy state. The importance of the term symbols have been emphasized in connection with the spectral and magnetic properties of complexes and metal free ions. Russell-Saunders (L-S) coupling and $J-J$ coupling schemes are important schemes for determination of terms and term symbols of the atoms and ions. In this proposed work computation is done for calculating all possible terms for non-equivalent electron of $f^2 d^1$ configuration without any long tabulation with mental exercise and term symbols are assigned the terms. The possible microstates and spectroscopic terms calculated for $f^2 d^1$ configuration are 910 and 42 respectively. These terms are quartets (13) and doublets (29). The ground state term for $f^2 d^1$ is 4K and the ground state is $^4K_{1/2}$.

Key Words: Term symbol, Azimuthal quantum number, Microstate, Quartet and doublet.

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 momenta of non equivalent electrons is straight forward than for equivalent electrons¹. 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 particular state. When only one electron is present in a degenerate energy level or sub shell such as $2p$, $3p$, $3d$, $4d$ and $4f$, etc. The energy depends on the orbital quantum number (l) but more than one electron then they interact to each other and result in the formation of a ground state and one or more excited states for the 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 may have slightly different energy contents.

The interactions between the electrons are of three types. (i) spin-spin coupling (ii) orbit-orbit coupling (iii) spin-orbit coupling. It is assumed that: spin-spin coupling > orbit-orbit coupling > spin-orbit coupling. There are two principle 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 30, 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 scheme⁴. These interactions (coupling) produced by the electron orbital and spin angular momenta give rise to a series of energy levels or states⁵. Arising of states, which are called spectroscopic states or microstates expressed by proper term symbols and are defined by new quantum numbers- L, ML, MS, S. These quantum numbers for multi electron systems are obtained by 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. This total degeneracy number is characterized the different possible combination of orbital and spin which individual electron can acquired may be called microstate^{6,7}.

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 forces⁸.

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Total number of microstates increase with the increase in the number of electron in orbital and in non equivalent electronic system the microstates are much greater than the similar equivalent electronic system. 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 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 terms⁹.

A complete term symbol is $(2S+1)L_J^{1,5,8,10}$. 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 or spin are opposed^{11,12}.

EXPERIMENTAL

Calculation of total number of microstates: 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.

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 $f^2 d^1$ system $n = 14$ and 10 and $x = 2$ and 1 ,

$$\text{So, } N = \frac{14!}{2!(14-2)!} \times \frac{10!}{1!(10-1)!}$$

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

$$N = 91 \times 10 = 910 \text{ microstates}$$

Possible spin conditions for $f^2 d^1$ configuration that allowed by the Pauli principle: It is determined by arranging the possible spin states of electrons in orbital's. Total microstates with possible spin states. Statistics of microstates of non equivalent electrons of $f^2 d^1$ configuration. Setting up a microstates chart for $f^2 d^1$ configuration.

Determination of Orbital angular momentum quantum number (L), l-l coupling: 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). The coupling of orbital momenta of non equivalent electrons referred as l-l coupling, this coupling gives a resultant L of magnitude $[L(L+1)]^{1/2} h/2\pi = L^* h/2\pi^1$. The orientations of l_1 , l_2 and l_3 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 three electrons of $f^2 d^1$ configuration and restricted to the values $L = (l_1 + l_2)$, $(l_1 + l_2 - 1)$, $(l_1 + l_2 - 2)$,, $|l_1 - l_2|$ ^{1,5,9,10,14}. The space quantization of L produces $2L + 1$

components with $M_L = L, L-1, \dots, \dots, -L$ analogous of l . In the present case $L = 8, 7, 6, 5, 4, 3, 2, 1, 0$ and magnitude of L is $7^{1/2} h/2\pi, 6^{1/2} h/2\pi, 5^{1/2} h/2\pi, 4^{1/2} h/2\pi, 3^{1/2} h/2\pi, 2^{1/2} h/2\pi, 1^{1/2} h/2\pi, 0$ respectively. The terms of the atom are labeled S, P, D, F, G, H, I, K, L. Corresponding to $L = 8, 7, 6, 5, 4, 3, 2, 1$ and 0 respectively. It follows that the $f^2 d^1$ configuration give rise to S, P, D, F, G, H, I, K, L terms.

Determination of total spin angular momentum quantum number (S) s-s coupling: It represents the total spin of atom while 's' represents spin state of an electron. The coupling between the spin momenta is referred as s-s coupling. The vector for each electron is always of magnitude of $3^{1/2} h/2\pi$ according to $[s(s+1)]^{1/2} h/2\pi = s^* h/2\pi^1$. The vector can only take up orientations relative to each other such that the magnitude of s-s coupling can as follow $[S(S+1)]^{1/2} h/2\pi = S^* h/2\pi$. $S = (s_1 + s_2)$, $(s_1 + s_2 - 1)$, $(s_1 + s_2 - 2)$,, $|s_1 + s_2|$ ^{1,5,9,10,14}. In the case of $f^2 d^1$ configuration for the three electrons the values of S = $3/2$ or $1/2$. The vector sums giving resultant S vectors of magnitude of $15/4^{1/2} h/2\pi$ or $3/4^{1/2} h/2\pi$.

Determination of M_L and M_S : $M_L = \sum m_l =$ the component of the total angular momentum along a given axis. Total values of $M_L = 2L + 1$, $M_L = +L \dots 0 \dots -L$. Total possible values of M_L for $f^2 d^1$ 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 $(2S+1)$. $M_S = +S \dots 0 \dots -S$. $M_S = m_{s1} + m_{s2} + \dots + m_s$. Total M_S values are $2 \times 3/2 + 1 = 4$ ranged from $+3/2$ to $-3/2$.

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 momenta 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 $L = S$ 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^{1,9,10,14,15}. 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^{11,12,15}.

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 2L state requires two columns or (17×2) array and 4K state requires (15×4) array^{5,9}. By removing each state from the microstate table we can draw a microstate sub table for each state¹⁶⁻²⁰. A complete matrix Table¹⁶⁻²⁰ for $f^2 d^1$ configuration including term, term symbol, microstate, multiplicity, total J values and values taken up by J. The terms split up into singlet, doublet, triplet, quartet, 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 give different values of J^{21} . The ground state term and order of stability of other terms (excited states or terms) can be determine by applying Hund's rule^{1,5,9,10,13,14,22}.

RESULTS AND DISCUSSION

For the $f^2 d^1$ configuration total number of atomic spectroscopic terms calculated are 42, among these 13(7-types) are

quartets and 29 (9-types) are doublets. 2L , 2K (2), 4K , 4I 2I (3), 4H (2), 2H (4), 4G (2) 2G (5), 4F (3), 2F (5), 4D (2), 2D (5), 4P (2), 2P (3), 2S . The stability order of atomic spectroscopic terms is $^4K > ^4I > ^4H$ (2) $> ^4G$ (2) $> ^4F$ (3) $> ^4D$ (2) $> ^4P$ (2) $> ^2L > ^2K$ (2) $> ^2I$ (3) $> ^2H$ (4) $> ^2G$ (5) $> ^2F$ (5) $> ^2P$ (3) $> ^2S$. The ground state term for $f^2 d^1$ is quartet K (4K), which is further split up into four states is $^4K_{17/2} < ^4K_{15/2} < ^4K_{13/2} < ^4K_{11/2}$.

Concussion

Upon the basis of above study we can conclude that the total number of atomic spectroscopic terms arising from the non equivalent electrons of $f^2 d^1$ configuration of free atom are 42 which split up into 16 energy states due to the s-s and l-l coupling, among these 13 are quartets and 29 are doublets, which further split up into 44 energy states due to spin-orbit (s-l) coupling. The energy order of all atomic spectroscopic terms and ground state.

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