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Review of Term Symbols Computation from Multi-Electron Systems for Chemistry Students

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Abstract

We have computed the term symbols resulting from the coupling of angular momenta of both spin and orbital from the ground state electron configuration. Configurations of equivalent electrons present challenges and were handled by the group theoretical methods. Terms are the combined values of L and S while the combined values of L, S and J defines the level.

Key Words: Terms, Term Symbols, Spectroscopic term symbols, State, Level, Sub-level, Equivalent electrons, Non-equivalent electrons, Orbital angular momentum, Spin angular momentum, Spin-Orbital angular momentum, Russell-Saunders Coupling, LS coupling, j-j coupling and multiplicity.

Introduction

Spectroscopic term symbols are very important in classifying the electronic states of atoms and molecules particularly in physical and inorganic chemistry [1-4]. There is a vast amount of information on the topic of term symbols and techniques for obtaining these terms in the literature. Many authors gave credit to such textbooks as Cotton and Wilkinson [5] as well as Douglas and McDaniel [6] for the treatment of the topics and the application to transition metal complexes in the advent of the crystal and ligand field theories. Cautionary measure must be used as pointed out by Phillips and Williams [7] in the use of the terminologies: "terms", "state", "level" and "microstate". Meena et. al. [8] presented their work on the generating term symbols of electrons in f-orbitals of transition metal ions. Hyde [9] gave comparative methods for obtaining terms that include the configuration of d- and f-orbitals. Tuttle [10] introduced repetitive rules that must be adopted in order to obtain the terms of interest. Gorman [11] gave the rules for writing the Russel-Saunders terms in the ground state. McDaniel [12] introduced spin factoring technique for obtaining terms in atoms and molecules. The alternative mathematical technique of Xu and Dai [13] although gave correct terms it is just as complicated. Most of these techniques are very useful but some are rather cumbersome and not user friendly for chemistry students. In this review we take the students through the familiar route starting from the basic electron configuration that they have mastered. The caveat here is the algebra and we present the necessary algebraic series to ease the calculations.

The potential energy plot for a stable atom has negative total energy. An electron in a given quantum state and in the presence of strong magnetic field is described completely by a set of four quantum numbers (n, l, m_l, m_s). The first three quantum numbers in the set describes the spatial distribution and the last describes the spin state of the electron. n is the principal quantum number and it describes the size or the energy level of the shell (or atom). l is the azimuthal or angular momentum quantum number and it describes the shape of the orbital or the subshell. m_l is the magnetic quantum number and it describes the spatial orientation or direction of the orbital. The fourth quantum number m_s is the spin quantum number and it describes the spin orientation of the electron (symbolically represented by +1/2 or -1/2). Finally, "Pauli Exclusion Principle" established that no two electrons in a many electron atom could have the same set of the four quantum numbers.

Theory provides that for a massive nucleus with many electron elements we normally write the Hamiltonian operator as:

$$H = -\frac{h^2}{8\pi^2 m_e}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{(4\pi\epsilon_0)r_i} + \sum_{j>i}\frac{e^2}{(4\pi\epsilon_0)r_{ij}} + \sum_i \xi(r_i)\boldsymbol{L}\cdot\boldsymbol{S} - (\boldsymbol{\mu}_L + \boldsymbol{\mu}_S)\cdot\boldsymbol{B} \quad (1)$$

This Hamiltonian considers a neutral atom and therefore the atomic number Z is equal to the number of electrons N. The first term is the kinetic energy of the N electrons and the summation is over the ith electron (i =1 to N). The mathematical symbol ∇ is the Laplacian. The second term is the pairwise attractive potential energy between the nucleus having charge Ze and the electrons in the atom. r_i is the distance between the nucleus and electron i. The factor ($4\pi\varepsilon_0$) is used to express the energy in the appropriate SI unit. $\boldsymbol{\varepsilon_0}$ is a constant called permittivity

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of vacuum. The summation is over all the electrons. The third term is the pairwise potential energy for the inter-electron repulsions. The pairwise summation avoids double counting by eliminating the r_{ji}, r_{ii} and r_{jj} terms. $\mathbf{r_{ij}}$ is the inter-electron pair distance. The fourth term is the interaction between the electronic orbital angular momentum L and the electronic spin angular momentum **S**. ξ is the spin-orbit parameter. This fourth term is referred to as the spin-orbit interaction and it is explained in more details later in this section. In fact, the third term in the Hamiltonian which is the Coulomb repulsion between pairwise electrons and the fourth term is given special consideration in many books and review articles [1-3]. The fifth term is the application of external magnetic field called Zeeman Effect. In Zeeman Effect both orbital and spin moments are considered and therefore we use the magnetic field perturbation to split the individual levels into states.

L-S or Russell Saunders Coupling and j-j Coupling

The first two terms (alone) in the Hamiltonian are degenerate for all the atomic states that have the same electron configuration. If we consider the first three terms then the degeneracy between the states with different L or different S or both are lifted. If we add the fourth term the J levels (resulting from the L-S coupling) are further split into different J values. The addition of the fifth term will split each J level into M_J sublevels. This fifth term splitting will result in (2J+1) sublevels. The scheme that we just presented is the case where the third term in the Hamiltonian is stronger or larger than the Spin-Orbit interaction fourth term. In the case of L-S coupling that will be given extensive treatment in this review paper we add the orbital angular momentum of each electron to form the total orbital angular momentum L. In a similar manner we add the spin angular momentum of each electron to form the total spin angular momentum **S**. Next, we combine the L and the S to form total (coupled) spin-orbital angular momentum J. This is the Russell-Saunders Coupling (or L-S Coupling). L-S coupling involves elements having low atomic number, Z. For these elements, the individual orbital angular momentum vectors l_i's are strongly coupled together and are gyrating or precessing very fast around the total orbital angular momentum L.

On the other hand there is the j-j coupling scheme. This coupling scheme involves elements with higher atomic number, typically Z greater than 40. j-j coupling is when the spin-orbit interaction is very strong. For this reason the orbital l and spin s angular momentum of individual electrons are first added to give total angular momentum of that electron $j = l + s$. Next the total angular momentum of each electron is added to give the total angular momentum $J = \sum_i j_i$ of the element. The implication of large atomic number is that it will result in increase in the average speed of the electrons. In this regime, as the ratio of the average speed of electrons to the speed of light u/c, increases then relativistic effect such as the spin-orbit interaction increases. When this happens, the spin-orbit interaction that makes up the fourth term in the Hamiltonian supersedes the third term (inter-electronic Coulomb repulsion). In addition, if the nucleus has nuclear spin say I, then that nuclear spin magnetic moment will interact further with the electronic spin and orbital magnetic moments to generate hyperfine structures. This new scheme is $F = I + J$.

Spin-Orbit coupling may be explained by recognizing that electron orbital motion generates magnetic dipole just like a spinning electron generates also magnetic dipole. These dipoles can interact with one another because each electron performs these two motions. This interaction is called the dipole-dipole interaction. The coupling of the orbital motion with the spin motion means that the fourth term in the Hamiltonian in equation (1) is problematic depending on the strength of the coupling. The solutions to the Hamiltonian operator H, which is called the wave-functions cannot be Eigen-functions of the orbital separately as well as the spin separately, instead it is the wave-function of the coupled orbital and spin. Therefore the vector sum of L and **S** called J must be considered.

L-S or Russell Saunders Coupling

We present the scheme below in addition with the overall symbolic designation for the Atomic Term Symbol (ATS) or Atomic (Spectroscopic) Term symbol for the L-S coupling:

$$\mathbf{ATS = n\ ^{2S+1}L_J} \qquad (2)$$

The quantum number ***n*** retains the same meaning and has been define earlier. The total orbital angular momentum L is written as:

$$\mathbf{L = \Sigma\, l_i = (l_1 + l_2), (l_1 + l_2 - 1) \ldots |l_1 - l_2|} \quad \textit{Clebsch-Gordan Series} \qquad (3)$$

It is important to note that L has non-negative value and it is obtained by coupling the individual orbital angular momenta using the Clebsch-Gordon mathematical series that is defined above. The maximum value of L is $(l_1 + l_2)$, this is when l_1 and l_2 are in the same direction; the absolute value $|l_1 - l_2|$ ensures that L is non-negative and it is the lowest value where l_1 and l_2 are opposed in direction. This definition gives the possible values for L as: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, etc. and the corresponding orbital designations are: S, P, D, F, G, H, I, K, L M, and N respectively. It could be noted in the ordering that the J term is omitted. This avoids the confusion with the total (coupled) angular momenta of the orbital and spin notation.

The superscript (2S+1) that precedes L is called the Spin multiplicity. The total spin angular momentum S is written as:

$$\mathbf{S = \Sigma\, S_i = (s_1 + s_2), (s_1 + s_2 - 1) \ldots |s_1 - s_2|} \qquad (4)$$

This definition gives the possible values for S as: 0, ½, 1, 3/2, 2, 5/2, 3, etc. and the corresponding spin multiplicities, (2S+1) are: singlet, doublet, triplet, quartet, quintet, sextet and septet respectively.

The subscript J in the term symbol is the total (coupled) orbital - spin angular momentum and it is sometimes called Spin-orbit coupling. J is written as:

$$\mathbf{J = \Sigma\, (L+S) = (L+S), (L+S-1) \ldots |L-S|} \qquad (5)$$

Before we can begin to write out the term symbols, we must distinguish between two different types of electron configuration namely equivalent and non-equivalent electrons.

Non-Equivalent Electrons

These are electrons that belong to different *n, l,* subgroups; that is, electrons having at least either different *n* or *l*. The *n* and *l* are the atomic principal quantum number and orbital angular momentum quantum number respectively. For example, for each electron occupying the *p, d, f,…* orbital or $2p^1$, $3p^1$, $4p^1$,… we see at least one of the *n* or the *l* values are different. For non-equivalent electrons the Pauli's Exclusion Principle is always satisfied.

Equivalent Electrons

These are electrons that belong to the same *n, l* subgroups; that is, the electrons that have the same values of *n* and *l*. Examples of equivalent electrons are np^2, np^3, np^4, … nd^2, nd^3, nd^4, nd^5, nd^6, …etc. For the electronic configuration just described, some of the states that are generated when the electrons are non-equivalent vanish due to Pauli's Exclusion Principle.

Energy Levels - Hund's Rule for The Term Symbols Arrangement

We provide below in hierarchy the arrangement of the Terms energy levels according to Hund's Rule. In addition, we provide the allowed transitions referred to as selection rules for the total spin angular momentum S, total orbital angular momentum L, and total (coupled) spin-orbital angular momentum J.

1. The state that has the highest spin multiplicity has the lowest energy.
2. If two states have the same spin multiplicity, then the state with the greater L value will be lower in energy.
3. If two or more terms are the same following rules 1 and 2 then for the orbital which is less than half filled, the state with small J value will be lower in energy, whereas if the orbital is half or more than half filled, the state with largest J value will be lower in energy.

Selection Rules:

Selection rules are very important when considering certain transitions. The rules governing these transitions are as follow:

$$\Delta S = 0 \tag{6}$$

$$\Delta L = 0, \pm 1;\ \text{however, } L = 0 \not\longleftrightarrow L = 0 \text{ (i.e., not allowed)} \tag{7}$$

$$\Delta J = 0, \pm 1;\ \text{however, } J = 0 \not\longleftrightarrow J = 0 \text{ (i.e., not allowed)} \tag{8}$$

$$\Delta l = \pm 1 \text{ and } \Delta n \text{ is any value (no restriction)} \tag{9}$$

The sign $\not\longleftrightarrow$ indicates a forbidden transition

Terms from Non-Equivalent and Equivalent Electrons Using L-S Coupling

We now provide few examples to illustrate the terms resulting from L-S coupling of one, two and three electrons. We give one-electron example to represent atoms having the electron configurations ns^1, np^1, nd^1, etc., two-electron example to represent atoms with the electron configurations ns^1np^1, np^1nd^1, nd^1nf^1, etc. where *n* takes any value and np^2, nd^2, nf^2, etc., and three-electron example to represent atoms with the electron configurations $ns^1np^1nd^1$, $np^1nd^1\ nf^1$, etc. where *n* takes any value and $(n-1)p^1np^1nd^1$, $(n-1)d^1nd^1nf^1$, etc. All the examples provided are for the non-equivalent electrons except the np^2, nd^2, nf^2, etc. We are confident that there is no confusion in following these examples.

Calculations Involving Non-Equivalent Electrons

Example #I: Calculate the **L, S,** and **J** values for the configuration: $1s^22s^22p^63s^13p^1$. (Note that this configuration is an excited state of a magnesium atom). The electrons of interest here are in the: $3s^13p^1$

Answer:

This is a problem of interaction of one electron in the s-orbital and one electron in the p-orbital. Let the s-orbital electron be #1 and the p-orbital electron is #2. Therefore:

Electron #1: $n_1 = 3$, $l_1 = 0$, and $s_1 = ½$

Electron #2: $n_2 = 3$, $l_2 = 0$, and $s_2 = ½$

$$S = (s_1 + s_2), (s_1 + s_2 - 1) \ldots |s_1 - s_2| \tag{I-1a}$$
$$= (½ + ½), \ldots\ |½ - ½| \tag{I-1b}$$
$$= 1, \qquad 0 \tag{I-1c}$$

$$2S+1 = 2(1) + 1 \qquad 2(0) + 1 \tag{I-2a}$$
$$= 3 \text{ (Triplet)} \qquad 1 \text{ (Singlet)} \tag{I-2b}$$

$$L = (l_1 + l_2), (l_1 + l_2 - 1) \ldots |l_1 - l_2| \tag{I-3a}$$

$$= (0 + 1), \qquad |0 - 1| \tag{I-3b}$$
$$= 1 \text{ (this corresponds to a } \mathbf{P} \text{ - term state)} \tag{I-3c}$$

$$J = (L+S), (L+S-1) \ldots |L+S| \tag{I-4a}$$

$$= (1 + 1), (1 + 1 - 1), \ldots |1 - 1| \qquad \text{(}\underline{\textbf{Case\#1} \ L=1, S = 1}\text{)} \tag{I-4b}$$
$$= 2, \qquad 1, \qquad 0 \tag{I-4c}$$

$$= (1 + 0), (1 + 1 - 0), \ldots |1 - 0| \qquad \text{(}\underline{\textbf{Case\#2} \ L=1, S = 0}\text{)} \tag{I-4d}$$
$$= 1 \tag{I-4e}$$

The Term Symbols are: $\mathbf{^3P_{2,1,0}}$ **and** $\mathbf{^1P_1}$ or written detail: $\mathbf{^3P_2}$, $\mathbf{^3P_1}$, $\mathbf{^3P_0}$ **and** $\mathbf{^1P_1}$

Example #II: Find the Term symbols for the interaction of one electron in a d-orbital and one electron in an f-orbital.

Answer:

Electron #1: $l_1 = 2$, and $s_1 = ½$

Electron #2: $l_2 = 3$, and $s_2 = ½$

$$S = (s_1 + s_2), (s_1 + s_2 - 1) \ldots |s_1 - s_2| \tag{II-1a}$$

$$= (½ + ½), \qquad \ldots\ |½ - ½| \tag{II-1b}$$
$$= 1, \qquad 0 \tag{II-1c}$$

$$2S+1 = 2(1) + 1 \qquad 2(0) + 1 \tag{II-2a}$$
$$= 3 \text{ (Triplet)} \qquad 1 \text{ (Singlet)} \tag{II-2b}$$

$$L = (l_1 + l_2), (l_1 + l_2 - 1) \ldots |l_1 - l_2| \tag{II-3a}$$

$$= (2 + 3), (2 + 3 - 1), (2 + 3 - 2), \ldots \quad |2 - 3| \tag{II-3b}$$
$$= 5, \qquad 4, \qquad 3, \qquad 2, \qquad 1 \tag{II-3c}$$
$$\mathrm{H} \qquad \mathrm{G} \qquad \mathrm{F} \qquad \mathrm{D} \qquad \mathrm{P} \rightarrow \underline{\textit{(L states)}} \tag{II-3d}$$

$$J = (L+S), (L+S-1) \ldots |L-S| \tag{II-4a}$$

$$= (5 + 1), (5 + 1 - 1), \ldots |5 - 1| \qquad \text{(}\underline{\textbf{Case\#1} \ L = 5, S = 1}\text{)} \tag{II-4b}$$
$$= 6, \qquad 5, \qquad 4 \tag{II-4c}$$

$= (4 + 1), (4 + 1 - 1), \ldots |4 - 1|$ *(Case#1 L = 4, S = 1)* (*II-4d*)
$= 5, \quad 4, \quad 3$ (*II-4e*)

$= (3 + 1), (3 + 1 - 1), \ldots |3 - 1|$ *(Case#1 L = 3, S = 1)* (*II-4f*)
$= 4, \quad 3, \quad 2$ (*II-4g*)

$= (2 + 1), (2 + 1 - 1), \ldots |2 - 1|$ *(Case#1 L = 2, S = 1)* (*II-4h*)
$= 3, \quad 2, \quad 1$ (*II-4i*)

$= (1 + 1), (1 + 1 - 1), \ldots |1 - 1|$ *(Case#1 L = 1, S = 1)* (*II-4j*)
$= 2, \quad 1, \quad 0$ (*II-4k*)

$= (5 + 0), (5 + 0 - 1), \ldots |5 - 0|$ *(Case#2 L = 5, S = 0)* (*II-4l*)
$= 5$ (*II-4m*)

$= (4 + 0), (4 + 0 - 1), \ldots |4 - 0|$ *(Case#2 L = 4, S = 0)* (*II-4n*)
$= 4$

$= (3 + 0), (3 + 0 - 1), \ldots |3 - 0|$ *(Case#2 L = 3, S = 0)* (*II-4o*)
$= 3$ (*II-4p*)

$= (2 + 0), (2 + 0 - 1), \ldots |2 - 0|$ *(Case#2 L = 2, S = 0)* (*II-4q*)
$= 2$ (*II-4r*)

$= (1 + 0), (1 + 0 - 1), \ldots |1 - 0|$ *(Case#2 L = 1, S = 0)* (*II-4s*)
$= 1$ (*II-4t*)

The Term symbols are: $\mathbf{^3H_{6,5,4}}$; $\mathbf{^3G_{5,4,3}}$; $\mathbf{^3F_{4,3,2}}$; $\mathbf{^3D_{3,2,1}}$; $\mathbf{^3P_{2,1,0}}$; $\mathbf{^1H_5}$; $\mathbf{^1G_4}$; $\mathbf{^1F_3}$; $\mathbf{^1D_2}$; $\mathbf{^1P_1}$

Example #III: Calculate the L, S, and J for the ground state of sodium atom.

Answer:

Here there is only one electron. It is therefore trivial. This example will apply to all the group IA elements of the periodic table. The only difference among these elements is the principal quantum number n that does not play any part in the computation. The electron configuration for sodium atom is: $[1s^2 2s2^2 p^6] 3s^1$.

Electron#1: $l_1 = 0$, $s_1 = ½$

$S = s_1 = ½$ (*III-1*)

$2S+1 = 2(½) + 1 = 2$ (doublet) (*III-2*)

$L = l_1 = 0 = S$ (*III-3*)

$J = L + S = (0 + ½), \ldots | 0 - ½| = ½$ (*III-4*)

Therefore, the Term Symbol is: $\mathbf{^2S_{1/2}}$

Example #IV

Calculate the spectroscopic term symbol for the electronic configuration $2p^1 3p^1 4d^1$ system.

Answer:

Electron #1: $n_1 = 2$, $l_1 = 1$, and $s_1 = 1/2$
Electron #2: $n_2 = 3$, $l_2 = 1$, and $s_2 = 1/2$
Electron #3: $n_3 = 4$, $l_3 = 2$, and $s_3 = 1/2$

We couple electron #1 and electron #2 first and we couple the resulting states with electron #3 accordingly.

Step #1: Coupling electron #1 and electron #2

$S = (s_1 + s_2), (s_1 + s_2 - 1) \ldots |s_1 - s_2|$ (*IV-1a*)

$= (½ + ½), \ldots |½ - ½|$ (*IV-1b*)
$= 1, \quad 0$ (*IV-1c*)

$2S+1 = 2(1)+1 \quad 2(0)+1$ (*IV-2a*)
=3 (Triplet) 1 (Singlet) (*IV-2b*)

$L = (l_1 + l_2), (l_1 + l_2 - 1) \ldots |l_1 - l_2|$ (*IV-3a*)

$= 2, \quad 1, \quad 0$ (*IV-3b*)
D P S →*(L states)* (*IV-3c*)

From this coupling we obtain the states: $\mathbf{^3D}$; $\mathbf{^3P}$; $\mathbf{^3S}$; **and** $\mathbf{^1D}$; $\mathbf{^1P}$; $\mathbf{^1S}$.
The reader is left to compute J values for each of the computed terms as exercise.

Step #2: Coupling each of the six states with electron #3

Next we couple each of the six states with the $4d^1$ electron (i.e. electron #3) as follow:

^3D ($l = 2$, $s = 1$) and $4d^1$ ($l_3 = 2$, and $s_3 = ½$)

$S = (s + s_3), (s + s_3 - 1) \ldots |s - s_3|$ (*IV-4a*)

$= (1 + ½), \ldots |½ - ½|$ (*IV-4b*)
$= 3/2, \quad ½$ (*IV-4c*)

$2S+1 = 2(3/2)+1 \quad 2(½)+1$ (*IV-5a*)
= 4 (quartet) 2 (doublet) (*IV-5b*)

$L = (l + l_3), (l + l_3 - 1), (l + l_3 - 2) \ldots |l - l_3|$ (*IV-6a*)

$= 4, \quad 3, \quad 2, \quad 1, \quad 0$ (*IV-6b*)
G F D P S →*(L states)* (*IV-6c*)

From this coupling we obtain the states: $\mathbf{^4G}$; $\mathbf{^4F}$; $\mathbf{^4D}$; $\mathbf{^4P}$; $\mathbf{^4S}$; $\mathbf{^2G}$; $\mathbf{^2F}$; $\mathbf{^2D}$; $\mathbf{^2P}$; $\mathbf{^2S}$.
The reader is left to compute J values for each of the computed terms as exercise.

Similarly, we couple ^3P ($l = 1$, $s = 1$) and $4d^1$ ($l_3 = 2$, and $s_3 = ½$) will give:

$\mathbf{^4F}$; $\mathbf{^4D}$; $\mathbf{^4P}$; **and** $\mathbf{^2F}$; $\mathbf{^2D}$; $\mathbf{^2P}$ (*IV-7*)

Coupling ^3S ($l = 0$, $s = 1$) and $4d^1$ ($l_3 = 2$, and $s_3 = ½$) will give:

$\mathbf{^4D}$ **and** $\mathbf{^2D}$ (*IV-8*)

Similarly, we obtain the following results by coupling the singlet states with the $4d^1$.

^1D ($l = 2$, $s = ½$) and $4d^1$ ($l_3 = 2$, and $s_3 = ½$) will give:
$\mathbf{^2G}$, $\mathbf{^2F}$, $\mathbf{^2D}$, $\mathbf{^2P}$, $\mathbf{^2S}$ (*IV-9*)

^1P ($l = 1$, $s = ½$) and $4d^1$ ($l_3 = 2$, and $s_3 = ½$) will give:
$\mathbf{^2F}$, $\mathbf{^2D}$, $\mathbf{^2P}$ (*IV-10*)

^1S ($l = 0$, $s = ½$) and $4d^1$ ($l_3 = 2$, and $s_3 = ½$) will give: $\mathbf{^2D}$ (*IV-11*)

The sum total of the $2p^1 3p^1 4d^1$ coupling gives the terms:

$\mathbf{^4G}$; $\mathbf{2\,^4F}$; $\mathbf{3\,^4D}$; $\mathbf{2\,^4P}$; $\mathbf{^4S}$; $\mathbf{2\,^2G}$; $\mathbf{4\,^2F}$; $\mathbf{6\,^2D}$; $\mathbf{4\,^2P}$; $\mathbf{2\,^2S}$ (*IV-12*)

The numbers before the terms indicate the number of times the particular state is formed by different combinations.

Calculations Involving Equivalent Electrons

Let us treat the case of two equivalent interacting electrons.

Example #V

Calculate the terms resulting from ground state electron configuration of carbon or oxygen.

Answer

The electronic configuration is $1s^2 2s^2 2p^2$ for carbon and $1s^2 2s^2 2p^4$ for oxygen.

Step #1

Make a table of m_l values of one electron as row and the m_l of the second electron as column.

Step #2

Calculate the elements of the square table by adding the two m_l values. $M_L = m_{l1} + m_{l2}$

Step #3

Elements lying on the diagonal of the table are the singlets and those occurring on the off-diagonal are the triplets.

Step #4

Use of only the M_L values of one side of the diagonal elements (zero being the mid-point). The element(s) on the side are mirror images. Similarly, make use of only the M_L values of one side of the off-diagonal elements (the diagonal elements represent the mid-line).

Electron #1: $n_1 = 2$, $l_1 = 1$, $m_{l1} = (-1, 0, \text{or } 1)$ and $s_1 = ½$

Electron #2: $n_2 = 2$, $l_2 = 1$, $m_{l2} = (-1, 0, \text{or } 1)$ and $s_2 = ½$

$m_{l2}\backslash m_{l1}$	-1	0	1
-1	**$\underline{-2}$**	**-1**	**0**
		• •	•
0	**-1**	**$\underline{0}$**	**•1**
			•
1	**0**	**1**	**$\underline{2}$**

The absolute values of the diagonal elements are L = 2 and 0 and they correspond to the singlet states ^{1}**D** and ^{1}**S** respectively. The off-diagonal elements: **-1, 0, 1** belongs to L =1 will be the triplet state, that is: ^{3}**P**.

The total angular momentum quantum number, J can be calculated accordingly as:

For ^{1}**D**: L = 2, S = 0 (singlet), then J = 2: The term symbol is $^1\mathbf{D}_2$

For ^{1}**S**: L = 0, S = 0 (singlet), then J = 0: The term symbol is $^1\mathbf{S}_0$

For ^{3}**P**: L = 1, S = 1 (triplet), then J = 2, 1, 0: The term symbol is $^3\mathbf{P}_{2,1,0}$

Calculations of Terms Involving Equivalent Electrons from a generating Formula of Curl and Kilpatrick [4]

Calculating terms resulting from more than two equivalent electrons are very complicated. There are many articles written on computation of term symbols of equivalent electrons [4-7]. We will adopt the group theoretical methods of Curl and Kilpatrick [4] for this treatment without further proof. We reproduce below the generating formula that was presented in section III of their paper, highlight the prescribed recipes and we appeal to the readers to refer to the paper for details.

$$J_s(q) = -\frac{1-q}{q^{\gamma}} * \frac{P_1(q)*P_2(q)}{D_1(q)*D_2(q)} = \sum\nolimits_{L=0} n_{LS}\left(q^{L} - q^{-L-1}\right) \qquad (10)$$

$J_S(q)$ is always a polynomial with positive coefficients for all positive powers of q. For example: $q^0 = 1 = S$; $q^1 = P$; $q^2 = D$; $q^3 = F$; $q^4 = G$; $q^5 = H$; $q^6 = I$; etc.

N = number of electrons

l = angular momentum (or azimuthal) quantum number of each electron

$\upsilon = 2l + 1$

S = spin quantum number of the desired terms

$\alpha = N/2 - S$, (this is the number of electron pairs)

$\beta = 2S$, (this is the number of unpaired electrons)

$\gamma = (Nl + 1) - [N(N-2) + 4S^2]/4$

(2S + 1) = the multiplicity of the spin under consideration

The coefficients of the non-negative powers of q are of interest in the generating formula. We disregard the negative powers. The generating function $J_S(q)$ consists of the product of the factor - $(1-q)/q^{\gamma}$ and the ratio P and D. P is itself a product of two series of terms namely: $P_1(q)$ and $P_2(q)$. D is also a product of $D_1(q)$ and $D_2(q)$ series. $P_1(q)$ series of terms (referred to as the *α* sequence) has power of q ranging from $(\upsilon + 1)$ to $(\upsilon + 1 - \alpha)$. There are a sum total of $(\alpha + 1)$ terms; exception is if $(\alpha = 0)$, then the sequence is omitted. The first term and the last term in $P_1(q)$ occurs once and every term in between occurs twice. $P_2(q)$ series of terms (referred to as the β sequence) has power of q ranging from $(\upsilon - \alpha)$ to $(\upsilon + 1 - \alpha - \beta)$. There are a sum total of β terms, each term occurs once and if $(\beta = 0)$, then the sequence is omitted. We reproduce below the four series: $P_1(q)$, $P_2(q)$ $D_1(q)$ and $D_2(q)$.

$P_1(q) = (1 - q^{\upsilon+1})\,(1 - q^{\upsilon})^2(1 - q^{\upsilon-1})^2 \ldots *(1 - q^{\upsilon+1-\alpha})$
if $\alpha = 0$, *then* $P_1(q) = 1$

$P_2(q) = (1 - q^{\upsilon-\alpha})\,(1 - q^{\upsilon-\alpha-1})(1 - q^{\upsilon-\alpha-2}) \ldots *(1 - q^{\upsilon+1-\alpha-\beta})$
if $\beta = 0$, *then* $P_2(q) = 1$

$D_1(q) = (1 - q)\,(1 - q^2)(1 - q^3) \ldots *(1 - q^{\alpha})$
if $\alpha = 0$, *then* $D_1(q) = 1$

$D_2(q) = (1 - q)\,(1 - q^2)(1 - q^3) \ldots *(1 - q^{\alpha+\beta+1})\,/(1 - q^{\beta+1})$

Some useful algebraic series are necessary and available for reducing the above polynomials to the final results. Few of these are presented below.

$(1 - q^n)/(1 - q) = \Sigma_i\, q^i$ *i goes from 0 to n-1*

$(1 - q^{2n})/(1 - q^2) = \Sigma_i\, q^{2i}$ *i goes from 0 to 2n-2*

$(1 - q^{3n})/(1 - q^3) = \Sigma_i\, q^{3i}$ *i goes from 0 to 3n-3*

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$(1 - q^{mn})/(1 - q^m) = \Sigma_i\, q^{mi}$ *i goes from 0 to mn-m*

$(1 - q^n) = (1 - q)\,(1 + q + q^2 + \ldots + q^{n-1})$ *here n is any positive value*

$(1 - q^n) = (1 + q)\,(1 - q + q^2 - q^3 + \ldots - q^{n-1})$ *here n = even*

$(1 + q^n) = (1 + q)\,(1 - q + q^2 - q^3 + \ldots + q^{n-1})$ *here n = odd*

Examples:

$\mathbf{(1-q^n)/(1-q) = \Sigma_i\, q^i}$ **:*i goes from 0 to n-1 and n = 1,2,3,4 …***

$(1-q^2)/(1-q) = 1 + q$

$(1-q^3)/(1-q) = 1 + q + q^2$

$(1-q^4)/(1-q) = 1 + q + q^2 + q^3$

Etc.

$(1-q^{2n})/(1-q^2) = \Sigma_i q^{2i}$: ***i goes from 0 to 2n-2 and n = 1,2,3,4 …***

$(1-q^4)/(1-q^2) = 1 + q^2$

$(1-q^6)/(1-q^2) = 1 + q^2 + q^4$

$(1-q^8)/(1-q^2) = 1 + q^2 + q^4 + q^6$

Etc.

$(1-q^{3n})/(1-q^3) = \Sigma_i q^{3i}$: ***i goes from 0 to 3n-3 and n = 1,2,3,4 …***

$(1-q^6)/(1-q^3) = 1 + q^3$

$(1-q^9)/(1-q^3) = 1 + q^3 + q^6$

$(1-q^{12})/(1-q^3) = 1 + q^3 + q^6 + q^9$

Etc.

$(1-q^{4n})/(1-q^4) = \Sigma_i q^{4i}$: ***i goes from 0 to 4n-4 and n = 1,2,3,4 …***

$(1-q^8)/(1-q^4) = 1 + q^4$

Etc.

$(1-q^{5n})/(1-q^5) = \Sigma_i q^{5i}$: ***i goes from 0 to 5n-5 and n = 1,2,3,4 …***

$(1-q^{10})/(1-q^5) = 1 + q^5$

Etc.

$(1-q^{mn})/(1-q^m) = \Sigma_i q^{mi}$: ***i goes from 0 to mn-m; n = 1,2,3,4 … n>m; m≠0***

$(1-q^{mn})/(1-q^m) = 1 + q^m + q^{2m} + q^{3m} + q^{4m} + \dots q^{mn-m}$

Etc.

We will now apply the group theoretical method to work out the term symbols of first row transition elements and beyond as they present difficulties for students.

For nd^1 and nfd^9

In each case: $N=1; S=1/2; \alpha=0; \beta=1; l=2; \upsilon=5; \gamma=3$ and $2S+1 = 2$;

$J_{1/2}(q) = [-(1-q)/q^3]*[1*(1-q^5)]/[1*(1-q)(1-q^2)/(1-q^2)] = -(1/q^3)(1-q^5) = q^2 - q^{-3}$

Since we consider only the positive powers of q then the only term is: **^{2}D**

For nf^1 and nf^{13}

In each case: $N=1; S=1/2; \alpha=0; \beta=1; l=3; \upsilon=7; \gamma=4$ and $2S+1 = 2$;

$J_{1/2}(q) = -[(1-q)/q^4]*[1*(1-q^7)]/[1*(1-q)(1-q^2)/(1-q^2)] = -(1/q^4)(1-q^7) = q^3 - q^{-4}$

Again we consider only the positive powers of q and therefore the only term is: **^{2}F**

For nd^2 and nd^8 (two electrons under consideration: the two electrons are unpaired)

In each case: $N=2; S=1; \alpha=0; \beta=2; l=2; \upsilon=5; \gamma=4$ and $2S+1 = 3$;

$J_1(q) = -[(1-q)/q^4]*[1*(1-q^5)(1-q^4)]/[1*(1-q)(1-q^2)(1-q^3)/(1-q^3)] = (q^5-1)(q^2+1)/q^4$

$= q^3 + q + q^{-2} - q^{-4}$; The resulting terms are: **^{3}F and ^{3}P**

For nd^2 and nd^8 (two electrons under consideration:: the two electrons are paired)

In each case: $N=2; S=0; \alpha=1; \beta=0; l=2; \upsilon=5; \gamma=5$ and $2S+1 = 1$;

$J_1(q) = -[(1-q)/q^5]*[(1-q^6)(1-q^5)*1]/[(1-q)*(1-q^2)] = (q^5-1)(1 + q^2 + q^4)/q^5$

$= q^4 + q^2 + 1 - q^{-1} - q^{-3} - q^{-5}$; The resulting terms are: **^{1}G, ^{1}D and ^{1}S**

For nd^3 and nd^7 (three electrons under consideration: the three electrons are unpaired)

In each case: $N=3; S=3/2; \alpha=0; \beta=3; l=2; \upsilon=5; \gamma=4$ and $2S+1 = 4$;

$J_{3/2}(q) = -[(1-q)/q^4]*[1*(1-q^5)(1-q^4)(1-q^3)]/[1*(1-q)(1-q^2)(1-q^3)(1-q^4)/(1-q^4)]$

$= (q^5-1)(q^2+1)/q^4 = q^3 + q + q^{-2} - q^{-4}$; The resulting terms are: **^{4}F and ^{4}P**

For nd^3 and nd^7 (three electrons under consideration: two paired and one is unpaired)

In each case: $N=3; S=1/2; \alpha=1; \beta=1; l=2; \upsilon=5; \gamma=6$ and $2S+1 = 2$;

$J_{1/2}(q) = -[(1-q)/q^6]*[(1-q^6)*(1-q^5)(1-q^4)]/[(1-q)*(1-q)(1-q^2)(1-q^3)/(1-q^2)]$

$= (q^3+1)(q^4-1)(1 + q + q^2 + q^3 + q^4)/q^6$

$= q^5 + q^4 + q^3 + 2q^2 + q - q^{-2} - 2q^{-3} - q^{-4} - q^{-5} - q^{-6}$; The terms are: **^{2}H, ^{2}G, ^{2}F, 2^{2}D and ^{2}P**

For nd^4 and nd^6 (four electrons under consideration: four unpaired electrons)

In each case: $N=4; S=2; \alpha=0; \beta=4; l=2; \upsilon=5; \gamma=3$ and $2S+1 = 5$;

$J_2(q) = -[(1-q)/q^3]*[1*(1-q^5)(1-q^4)(1-q^3)(1-q^2)]/[1*(1-q)(1-q^2)(1-q^3)(1-q^4)(1-q^5)/(1-q^5)]$

$= -(1/q^3)(1-q^5) = q^2 - q^{-3}$; **The term is: ^{5}D**

For nd^4 and nd^6 (four electrons under consideration: two unpaired and two paired)

In each case: $N=4; S=1; \alpha=1; \beta=2; l=2; \upsilon=5; \gamma=6$ and $2S+1 = 3$;

$J_1(q) = -[(1-q)/q^6]*[(1-q^6)(1-q^5)*(1-q^4)(1-q^3)]/[(1-q)*(1-q)$

$(1-q^2)(1-q^3)(1-q^4) / (1-q^3)]$

$= - (1-q^5)(1 + q + q^2)(1 + q^2 + q^4) / q^{-6}$

$= q^5 + q^4 + 2q^3 + q^2 + 2q - 2q^{-2} - q^{-3} - 2q^{-4} - q^{-5} - q^{-6}$; **^{3}H, ^{3}G, 2^{3}F, ^{3}D and 2^{3}P**

For nd^4 and *nd*^{6} (four electrons under consideration: all four electrons are paired)

In each case: N=4; S=0; α=2; β=0; *l*=2; υ=5; γ=7 and 2S+1 = 1;

$J_0(q) = -[(1-q) / q^7]*[(1-q^6)(1-q^5)^2(1-q^4) * 1] / [(1-q) (1-q^2)*(1-q) (1-q^2)(1-q^3) / (1-q)]$

$= - (1-q^5)(1 - q + q^2)(1 + q + q^2 + q^3 + q^4)(1 + q^2) / q^7$

$= q^6 + 2q^4 + q^3 + 2q^2 + 2 - 2q^{-1} - 2q^{-3} - q^{-4} - 2q^{-5} - q^{-7}$; **^{1}I, 2^{1}G, ^{1}F, 2^{1}D and 2^{1}S**

For nf^2 and *nf*^{12} (two electrons under consideration: the two electrons are unpaired)

In each case: N=2; S=1; α=0; β=2; *l*=3; υ=7; γ=6 and 2S+1 = 3;

$J_1(q) = -[(1-q) / q^6]*[1*(1-q^7)(1-q^6)] / [1*(1-q)(1-q^2)] = - (1- q^7)(1 + q^2+ q^4) /q^6$

$= q^5 + q^3 + q - q^{-2} - q^{-4} - q^{-6}$; The terms are: **^{3}H, ^{3}F and ^{3}P**

For nf^2 and *nf*^{12} (two electrons under consideration:: the two electrons are paired)

In each case: N=2; S=0; α=1; β=0; *l*=3; υ=7; γ=7 and 2S+1 = 1;

$J_1(q) = -[(1-q) / q^7]*[(1-q^8)(1-q^7)*1] / [(1-q)*(1-q^2)] = - (1 - q^7)(1 + q^2 + q^4 + q^6/) / q^7$

$= q^6 + q^4 + q^2 + 1- q^{-1} - q^{-3} - q^{-5} - q^{-7}$; The terms are: **^{1}I, ^{1}G, ^{1}D and ^{1}S**

For nf^3 and *nf*^{11} (three electrons under consideration: the three electrons are unpaired)

In each case: N=3; S=3/2; α=0; β=3; *l*=3; υ=7; γ=7 and 2S+1 = 4;

$J_{3/2}(q) = - [(1-q) / q^7]*[1*(1-q^7)(1-q^6) (1-q^5)] / [1*(1-q)(1-q^2)(1-q^3)(1-q^4)/(1-q^4)]$

$= - (1 - q^7)(1 - q^5)(1 + q^3) / q^7$

$= - (1 + q^2 + q^3 + q^4 + q^6 - q^7 - q^9- q^{10}- q^{11}- q^{13}) / q^7$

The terms are: **^{4}I, ^{4}G, ^{4}F, ^{4}D and ^{4}P**

For nf^3 and *nf*^{11} (three electrons under consideration: two paired and one is unpaired)

In each case: N=3; S=1/2; α=1; β=1; *l*=3; υ=7; γ=9 and 2S+1 = 2;

$J_{1/2}(q) = -[(1-q)/q^9]*[(1-q^8)(1-q^7)*(1-q^6)] / [(1-q)* (1-q)(1-q^2)(1-q^3)/(1-q^2)]$

$= - [(1 - q^6) / (1 - q^3)]*(1 - q^7)*[(1 - q^8) / (1-q)] / q^9$

$= - (1 + q + q^2 + 2q^3 + 2q^4 + 2q^5 + 2q^6 + q^7 - q^{10} - 2q^{11}- 2q^{12}- 2q^{13}- 2q^{14}- q^{15}- q^{16} - q^{17})/q^9$

$= q^8 + q^7 + q^6 + 2q^5 + 2q4 + 2q^3 + 2q^2 + q - q^{-2} - 2q^{-3} - 2q^{-4} - 2q^{-5} - 2q^{-6} - q^{-7}- q^{-8}- q^{-9}$

The terms are: **^{2}L, ^{2}K, ^{2}I, 2^{2}H, 2^{2}G,** 2^2**F, 2^{2}D and ^{2}P**; (Note that the J term is omitted as explained in the L-S Coupling section above).

For nf^4 and *nf*^{10} (four electrons under consideration: four unpaired electrons)

In each case: N=4; S=2; α=0; β=4; *l*=3; υ=7; γ=7 and 2S+1 = 5;

$J_2(q) = - [(1-q) / q^7]*[1*(1-q^7)(1-q^6)(1-q^5)(1-q^4)] / [1*(1-q)(1-q^2)(1-q^3)(1-q^4)(1-q^5)/(1-q^5)]$

$= - (1-q^7)(1 + q^2 + q^3 + q^4 + q^6) / q^{-7}$

$= q^6 + q^4 + q^3 + q^2 + 1 - q^{-1} - q^{-3} - q^{-4} - q^{-5} - q^{-7}$; The terms are: **^{5}I, ^{5}G, ^{5}F, ^{5}D and ^{5}S**

For nf^4 and *nf*^{10} (four electrons under consideration: two unpaired and two paired)

In each case: N=4; S=1; α=1; β=2; *l*=3; υ=7; γ=10 and 2S+1 = 3;

$J_1(q) = -[(1- q) / q^{10}]*[(1-q^8)(1-q^7)*(1-q^6) (1-q^5)] / [(1-q)*(1-q) (1-q^2)(1-q^3)(1-q^4) / (1-q^3)]$

$= - (1-q^7)(1 + q^4)(1 + q^2 + q^4)*(1 + q + q^2+ q^3 + q^4) / q^{-10}$

$= q^9 + q^8 + 2q^7 + 2q^6 + 4q^5 + 3q^4 + 4q^3 + 2q^2 + 3q - 3q^{-2} - 2q^{-3} - 4q^{-4} - 3q^{-5} - 4q^{-6} - 2q^{-7} - 2q^{-8} - q^{-9} - q^{-10}$;

The terms are: **^{3}M, ^{3}L,** 2^3**K, 2^{3}I, 4^{3}H, 3^{3}G, 4^{3}F, 2^{3}D and 3^{3}P**; (Note that the J term is omitted as explained in the L-S Coupling section above).

For nf^4 and *nf*^{10} (four electrons under consideration: all four electrons are paired)

In each case: N=4; S=0; α=2; β=0; *l*=3; υ=7; γ=11 and 2S+1 = 1;

$J_0(q) = - [(1-q) / q^{11}]*[(1-q^8)(1-q^7)^2(1-q^6) * 1] / [(1-q) (1-q^2)*(1-q) (1-q^2)(1-q^3) / (1-q)]$

$= - (1-q^7)(1 + q^2 + q^4 + q^6)(1 + q^2 + q^3 + q^4 + q^5 + q^6+ q^8) / q^{11}$

$= q^{10} + 2q^8 + q^7 + 3q^6 + 2q^5 + 4q^4 + q^3 + 4q^2 + 2 - 2q^{-1} - 4q^{-3} - q^{-4} - 4q^{-5} - 2q^{-6} - 3q^{-7} - q^{-8} - 2q^{-9} - q^{-11}$;

The terms are: **^{1}N, 2^{1}L, ^{1}K, 3^{1}I, 2^{1}H, 4^{1}G, ^{1}F, 4^{1}D and 2^{1}S**; (Note that the J term is omitted as explained in the L-S Coupling section above).

Conclusion

We have provided the theory of the ground state of atoms and that include the coupling of the orbital and spin angular momenta. It can be noted that by combining L and S values we obtain the term while combining the L, S and J values gives the level and J has (2J+1) microstates defined by M_J. Spectroscopic term symbols may be referred to as a formula that gives a detailed description of the electron configuration of the atoms or ions. We computed the term symbols that involve both equivalent and non-equivalent electrons using several known methods in the literature. The best method for obtaining the terms for equivalent electrons is the Curl and Kilpatrick [4]. We caution the readers to take a great care in the algebra that are involved in the computational method to avoid obvious mistakes of the terms.

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