A Simple Method for Obtaining Russell-Saunders Term Symbols

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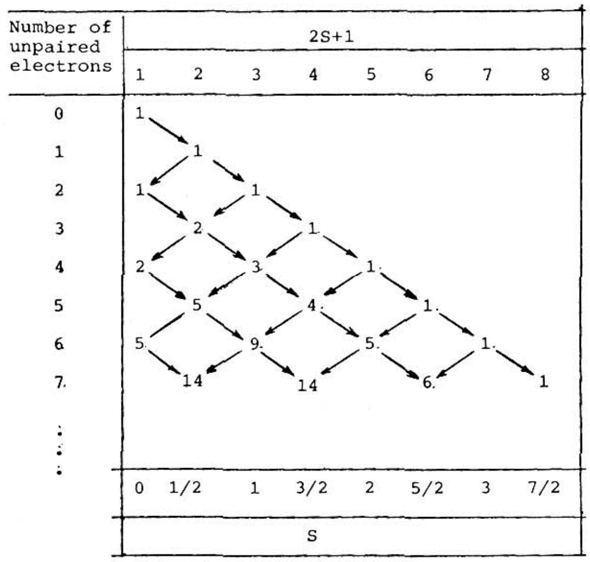
Most textbooks on inorganic chemistry (*1–3*) present the determination of spectroscopic terms obtained from a given electronic configuration by the method originally proposed by Pauli (*4*) and Goudsmit (*5*) through explicitly writing down all microstates. This procedure can be tedious when more than two electrons are considered. The technique described by Douglas and McDaniel (*6*), and very well illustrated by Hyde (*7*), reduces the number of microstates explicitly considered by ignoring the spin state of the electrons in writing the microstates. The method presented here provides further simplification by *not* tabulating all possible microstates.

Spin States

It has been shown by van Vleck and Sherman (*8*) that the spin multiplets arising from a given number of unpaired electrons depends only on the number of unpaired electrons. Their branching diagram, which indicates the number of distinct spin states of a given S (where S is the total spin quantum number) and arise from N unpaired electrons, is shown in the diagram. The diagram also indicates the spin multiplicity, $2S + 1$, of each state. The diagram is readily constructed for N electrons by considering the states produced by vector addition of spin $\frac{1}{2}$ to the previous $N - 1$ situation.

By counting multiplet states ($2S + 1$) instead of individual M_S states, the bookkeeping in the determination of spectroscopic terms may be greatly reduced. Thus, three unpaired electrons give rise to only two doublet and one quartet state for each M_L whereas the number of M_S states is, of course, 2^N or eight. Familiarity with the branching diagram itself is useful for other spectroscopies such as NMR and ESR.



Branching diagram showing the number of states of a given spin multiplicity arising from *N* unpaired electrons.

Table 1. Arrangements of Two Electron Pairs and One Unpaired Electron in the Five *d* Orbitals.

m_l																														
−2			/			/			/	X	X	X			/			/	X	X	X			/	X	X	X	X	X	X
−1		/			/		X	X	X			/		/		X	X	X			/	X	X	X			/	X	X	X
0	/			X	X	X		/			/		X	X	X		/			/		X	X	X	X	X	X			/
+1	X	X	X	/			/			/			X	X	X	X	X	X	X	X	X		/			/			/	
+2	X	X	X	X	X	X	X	X	X	X	X	X	/			/			/			/			/			/		
M_L	6	5	4	5	3	2	3	2	0	1	0	−1	4	1	0	2	0	−2	0	−2	−3	0	−1	−4	−2	−3	−5	−4	−5	−6

Table 2. Arrangements of Two Electron Pairs and One Unpaired Electron in the Five *d* Orbitals Having $M_L \geq 0$.

m_l																		
−2			/			/			/	X	X			/			X	
−1		/			/		X	X	X				/		X	X		X
0	/			X	X	X		/			/	X	X	X		/		X
+1	X	X	X	/			/			/		X	X	X	X	X	X	
+2	X	X	X	X	X	X	X	X	X	X	X	/			/		/	/
M_L	6	5	4	5	3	2	3	2	0	1	0	4	1	0	2	0	0	0
$2S + 1$			2 →															

Table 3. Arrangements of One Electron Pair and Three Unpaired Electrons in the Five *d* Orbitals Having $M_L \geq 0$.

m_l										
−2		/	/	/		/	/		/	
−1	/		/	/	/		/	/		X
0	/	/		/	/	/		X	X	/
+1	/	/	/		X	X	X	/	/	/
+2	X	X	X	X	/	/	/	/	/	/
M_L	4	3	2	1	3	2	1	2	1	1
	2 →									
$2S + 1$	2 →									
	4 →									

Examples

In the examples that follow we use the procedure of Douglas and McDaniel in writing down "microstates" that omit the spin designation for unpaired electrons. Instead of assigning all possible M_S values for each of the "microstates," we assign the possible values of $2S + 1$, the spin multiplicities, to each, using the diagram as a guide to these assignments. We construct an array of the number of states of given M_L and $2S + 1$ values. Each column of a given $2S + 1$ in the array leads to a spectroscopic term having a spin multiplicity of $2S + 1$ and an L quantum number equal to the maximum M_L value of the column.

In order to illustrate the method we shall choose the d^5 configuration.

For five d electrons there are three different possibilities of grouping based on the number of unpaired electrons. Those having one, three, or five unpaired electrons. Let's consider the first possibility. Two electron pairs (X) and one unpaired electron (/) can be arranged in the five d orbitals (orbital degeneracy) in 30 different ways as shown in Table 1 where values of M_L are also calculated.

It is easy to see that all arrangements with $M_L \neq 0$ are symmetrical by couples (e.g., the first and the last ones). As it has been previously noted (*9*), this fact allows the simplification of considering only the arrangements with $M_L \geq 0$, and Table 1 is reduced to Table 2 with only 18 "microstates" carrying unique information about the L value. From the diagram we note that for each of these M_L values there will be one state of spin multiplicity 2.

Using the same method for the second way of grouping the five electrons, one electron pair and three unpaired electrons, we obtain in Table 3 ten "microstates." For each of these M_L values there will be two states with $2S + 1 = 2$ and one with $2S + 1 = 4$. (See diagram.)

With five unpaired electrons there is only one possible arrangement with $M_L = 0$. This has $2S + 1$ values of 2 (5 states), 4 (4 states), and 6 (1 state). (See diagram.) With these data and Tables 2 and 3 we construct the array shown in Table 4 by marking one tally for each unique M_L and $2S + 1$ value.

The array may readily be decomposed into the L and $2S + 1$ values of the spectroscopic terms. Since we have removed all the $M_L < 0$ values, L will be obtained by taking values from $M_L = L$ through $M_L = 0$. Thus, each column in the array will yield a term with an L value equal to the maximum M_L value in the column. Thus, we find in Table 4 that there are 11 doublet terms, having L values of 6, 5, 4, 4, 3, 3, 2, 2, 2, 1, and 0, giving us the terms ^{2}I, ^{2}H, ^{2}G(2), ^{2}F(2), ^{2}D(3), ^{2}P, and ^{2}S. There are four quartet terms, having L values of 4, 3, 2, and 1, giving us the terms ^{4}G, ^{4}F, ^{4}D, and ^{4}P. There is only a sextet with $L = 0$, giving us the term ^{6}S.

Table 4. The M_L Versus $2S + 1$ Array for a d^5 Configuration.

		$2S + 1$: 2	4	6		
	6	|			I	
	5	||			H	
	4	||||	|		G	
M_L↑	3	||||||	||		F	L↑
	2	|||||||||	|||		D	
	1	||||||||||	||||		P	
	0	|||||||||||	||||	|	S	

With some experience, the step of constructing the array of M_L and $2S + 1$ values may be omitted and the terms found directly from tabulations such as Tables 2 and 3.

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