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Methods for Obtaining Russell-Saunders Term Symbols from Electronic Configurations

A thorough understanding of the concepts of energy terms, levels, and microstates is paramount for students engaging in the study of quantum mechanics, spectroscopy, and the crystal or ligand field theories of bonding in transition metal complexes. In teaching courses of physical or inorganic chemistry to our undergraduate students we have found that few texts present a scheme that may be used to derive the appropriate energy level diagram for configurations more complex than the p^2 case. Most of the available texts recommend forming all possible arrangements of electrons in the available orbitals and discarding those which violate either the Pauli principle or are identical with one another by the indistinguishability of electrons. The problem of equivalent or nonequivalent electrons only adds to the confusion. The case illustrated is most often p^2 but we believe that this is one of the few multielectron cases that can be handled by the above technique without extreme confusion and tedium. The purpose of this article is to illustrate and comment on several other procedures that are available and may be used for the more complex electron configurations.

Of the techniques described in current texts the method advocated by Douglas and McDaniel *(1)* leads to a maximum of understanding and a minimum of frustration. Surprisingly, this method has not appeared in any of the more recent inorganic *(2-4)* or physical texts. When this method has been thoroughly explained, our students have been capable of generating the correct energy levels for electron configurations as complex as d^4, d^5, f^2, f^3 and mixed configurations such as d^2s^1 and d^1f^2. The application of this method is described under the heading Method I. It should be noted that while the original ideas for this method were presented by Douglas and McDaniel *(1)*, the treatment offered here is fuller and in more detail.

Another procedure illustrated by E. R. Tuttle *(5)* for obtaining terms for configurations involving equivalent electrons is about as convenient as that of Douglas and McDaniel's but its weakness lies in the fact that a set of rules (the origin of these rules is not immediately obvious to the beginning student) must be adopted and a process of repetitively applying these rules leads to the proper terms for the configuration of interest. A detailed description of this treatment may be obtained by writing this author.

A third technique involving generating functions derived via group theory has been developed by Curl and Kilpatrick *(6)*. The main disadvantage lies in an excess of algebraic manipulations. Without a knowledge of group theory the origin of the generating functions and their relation to the problem at hand cannot be demonstrated. To obtain the proper term symbols from a given configuration, group theory is not required. A fuller treatment of this procedure may also be obtained from this author.

As Phillips and Williams *(7)* point out, additional confusion exists over what is meant by the use of the words term, state, level, and microstate. We advocate the use of the terminology given in Table 1, when the Russell-Saunders coupling scheme is applicable. In order to alleviate a confusing situation, it is strongly recommended that this terminology be adopted by all who use these descriptions.

As a means of illustrating the application of the previously described method we chose the nd^3 case as an example. For three d electrons the total degeneracy of microstates is given by

$$T.D. = \frac{(4l + 2)!}{(4l + 2 - N)!N!}$$

where N is the number of electrons in the configuration and l is the secondary quantum number. For nd^3 we have $l = 2$ for a d electron, $N = 3$, and $T.D. = 10!/(7! \times 3!) = 120$. There are 120 ways of arranging three d electrons in the five degenerate d orbitals. The problem is to sort out the energy terms contained within these 120 arrangements.

Table 1. Terminology Used in the Generation of Energy Levels for Multielectron Atoms

Nomenclature	Quantum numbers specified[a]	Symbol
Configuration	n and l (the number of electrons N is also specified)	nl^N
Term	n, L, and S	$2S + 1L$
Level	n, L, S, and J	$2S + 1L_J$
Microstate	n, L, S, J, and M_J	$2S + 1L_{J(M_J)}$

[a]The usual convention of lower case letters representing single electron quantum numbers and upper case letters representing those for a multielectron atom has been used.

Table 2. Possible M_S Values for Groupings of Arrangements with Zero to Seven Unpaired Electrons[a]

Number of unpaired electrons in group (β).	M_S[b] values for group	2^{β}[c]
0	0	1
1	+1/2, −1/2	2
2	1, 0(2), −1	4
3	+3/2, +1/2(3), −1/2(3), −3/2	8
4	2, 1(4), 0(6), −1(4), −2	16
5	+5/2, +3/2(5), +1/2(10), −1/2(10), −3/2(5), −5/2	32
6	+3, 2(6), 1(15), 0(20), −1(15), −2(6), −3	64
7	+7/2, +5/2(7), 3/2(21), 1/2(35) −1/2(35), −3/2(21), −5/2(7), −1/2	128

[a]The table can be generated by adding $\pm 1/2$ to the possible M_S values for an arrangement with β unpaired electrons to give the possible M_S values for grouping with $\beta + 1$ unpaired electrons.
[b]The number in parentheses indicates the number of times that particular M_S value will appear for a configuration having the specified β unpaired electrons.
[c]The quantity 2^{β} represents the total number of arrangements or M_S values that can be written for β unpaired electrons.

Table 3. Grouping of Arrangements with $S = {}^1/_2$

m_l = 2	1	0	−1	−2	$M_L = \Sigma m_l$	m_l = 2	1	0	−1	−2	$M_L = \Sigma m_l$
X	/				5			X	/		−1
X		/			4			X		/	−2
X			/		3		/		X		0
X				/	2			/	X		−1
/	X				4			/	X		−2
	X	/			2				X	/	−4
	X		/		1		/			X	−2
	X			/	0			/		X	−3
/		X			2			/		X	−4
	/	X			1				/	X	−5

Method I

For three d electrons there are two possible spin states, characterized by $S = 1/2$ and $S = 3/2$. Electron pairs are

indicated by a cross (X) and unpaired electrons as a slash (/). In this method each spin state is treated individually in order to obtain the various ways of orbitally arranging the X's and /'s in the five d orbitals. Each orbital arrangement of electrons gives an M_L value. The possible M_S values for each spin state are obtained from Table 2.

Grouping of Arrangements with S = 1/2 *or Only One Unpaired Electron* ($M_S = +1/2, -1/2$) *(Table 3)*

At this point it proves wise to check the total number of microstates that have been generated. The orbital degeneracy (the number of ways X and / can be arranged in the five d orbitals) is $5 \times 4 = 20$. The spin degeneracy is two since $M_S = +1/2$ and $-1/2$ (or $S = 1/2$ with $2S + 1 = 2$). The total number of microstates is the spin degeneracy times the orbital degeneracy $20 \times 2 = 40$. This implies that the remaining 80 microstates (recall d^3 configuration has 120 total) must arise from orbital arrangements consisting of three unpaired electrons.

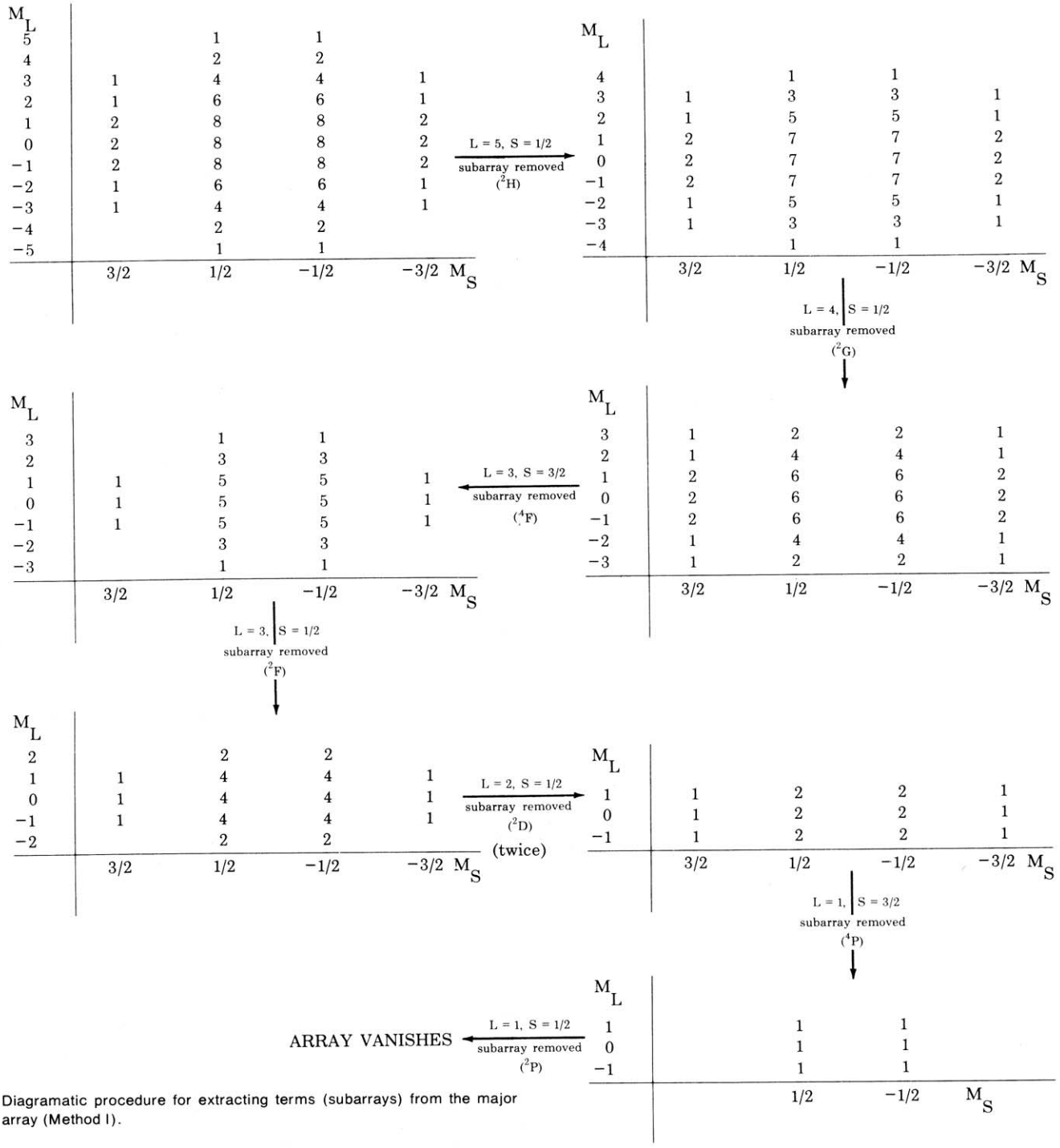
Table 4. Grouping of Arrangements with $S = {}^3/_2$

m_l = 2	1	0	−1	−2	$M_L = \Sigma m_l$	m_l = 2	1	0	−1	−2	$M_L = \Sigma m_l$
/	/	/			3	/			/	/	−1
/	/		/		2		/	/	/		0
/	/			/	1		/	/		/	−1
/		/	/		1		/		/	/	−2
/		/		/	0			/	/	/	−3

Grouping of Arrangements with S = 3/2 *or Three Unpaired Electrons* ($M_S = 3/2, 1/2(3), -1/2(3), -3/2$) *(Table 4)*

The spin degeneracy is eight (eight possible M_S values) and the orbital degeneracy is $5 \times (4/2) \times (3/3) = 10$ or the total number of microstates is the product $8 \times 10 = 80$.

The total number of arrangements for the two spin states indicated above is $80 + 40 = 120$ which checks with the total degeneracy calculated for the nd^3 system.



Diagramatic procedure for extracting terms (subarrays) from the major array (Method I).

The Major Array that Contains the 120 Arrangements

The array is constructed by realizing that each M_L value that occurs in arrangements with but one unpaired electron has two possible M_S values while each M_L value that occurs in arrangements with three unpaired electrons has eight M_S values.

M_L					
5		1	1		
4		2	2		
3	1	4	4	1	
2	1	6	6	1	
1	2	8	8	2	
0	2	8	8	2	
−1	2	8	8	2	
−2	1	6	6	1	
−3	1	4	4	1	
−4		2	2		
−5		1	1		
	3/2	1/2	−1/2	−3/2	M_S

Within this major array are 120 allowed arrangements of three electrons in the five d orbitals. Alternatively, we can view the major array as containing several subarrays where each subarray defines a term. Since L and S are specified for a term, each term is the equivalent of an array of M_L and M_S values that arise from the L and S values of the term. For instance, the term ^3P ($L = 1$, $S = 1$) is equivalent to the array

M_L				
1	1	1	1	
0	1	1	1	
−1	1	1	1	
	1	0	−1	M_S

The ^3P term is three-fold ($2S + 1$) spin degenerate and three-fold ($2L + 1$) orbitally degenerate and hence has a total degeneracy of nine. Nine microstates or nine arrangements of electrons exist.

The problem that exists after the construction of the major array is simply one of determining what subarrays (or terms) are contained within the major array. The simplest procedure is one of eliminating all M_L and M_S values (a subarray) that belong to a particular term, thus producing a new major array. This process is repeated until the major array vanishes.

One can always pick the term of maximum L from the major array by realizing that L for this term is given by the maximum value of M_L in the major array. This must be true since the M_L values of this term are related to L by $M_L = L, L - 1, \ldots 0 \ldots, -L$ (M_L takes all values from $+L$ through zero to $-L$). Once L or M_L(max) is established for the term the S value is given by the maximum value for M_S with this same M_L(max). This also follows since $M_S = S, S - 1, \ldots 0, \ldots -S$; hence S for the term under consideration is M_S(max).

To illustrate by use of the major array generated for the nd^3 configuration we note that M_L(max) = 5; hence $L = 5$ or an H type term is present. The maximum value in the array for M_S is $+1/2$ if M_L is still at its maximum value of five; therefore M_S(max) = $S = +1/2$. The conclusion is that the term ^2H is present in the major array.

The subarray of M_L and M_S values generated by the ^2H term is subtracted from the major array. The new major array generated contains the ^2G term, which must be removed from the new array. The procedure is repeated until the major array vanishes. The figure illustrates this procedure diagramatically. Results indicate that the nd^3 configuration contains the terms ^2H, ^2G, ^4F, ^2F, ^2D(twice), ^4P, and ^2P.

Conclusion

Herein have been presented three alternative methods for deriving the Russell-Saunders terms for any electronic configurations. The advantages and disadvantages of each have been mentioned at the beginning. When only the ground term for a configuration is desired, it can be obtained by a straightforward and simple procedure. A recent article in *this Journal (8)* illustrates the process and it will not be described here.

Acknowledgment

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