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Simple Rules for Deducing the Ground Term of a Configuration containing Equivalent Electrons (l^q)

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Recently, during the development of the Inclined W theory [1–7] for the f-ions and the d-ions, it was found [6, 7] that the ground terms of the free ions containing equivalent f or d electrons exhibit periodicity and generate rhythmics. Well developed rhythmic in the periodicity of the ground term L-values (total orbital angular momentum) of the free atoms has been observed [6]. By rhythmic we mean [6] the unity of a whole, consisting of parts that are coordinated internally among themselves and arranged in orderly fashion showing periodicity. Thus, the ground term L-values are found to vary [6, 7] rhythmically with the number of electrons (q) in a partly filled shell (l^q) with q varying from 0 to N, where N = q_{max}, the maximum number of electrons that can be accommodated in the configuration under question.

For f^q-configuration [6, 7]:

$$L = -0.5q(q - 7) \text{ where } 0 \leqslant q \leqslant 7 \quad (1)$$

and

$$L = -0.5(q - 7)(q - 14) \text{ where } 8 \leqslant q \leqslant 14 \quad (2)$$

For d^q-configuration [6, 7]:

$$L = -0.5q(q - 5) \text{ where } 0 \leqslant q \leqslant 5 \quad (3)$$

and

$$L = -0.5(q - 5)(q - 10) \text{ where } 6 \leqslant q \leqslant 10 \quad (4)$$

Configurations Containing One Partly Filled Shell (l^q)

Inspection of eqns. (1) to (4) reveals interesting property of the ground term L with respect to the half-filled and the completely filled shell. This realization lead to the investigation of the general validity of the variation of L with q for any configuration containing equivalent electrons. By equivalent electrons we refer here to any two or more electrons having the same values of the principal (n) and the orbital angular (l) quantum numbers. The generalized forms of the above equations for direct calculation of the ground state L-values can be expressed as follows:

$$L = -0.5q(q - N/2) \text{ where } 0 \leqslant q \leqslant N/2 \quad (5)$$

and

$$L = -0.5(q - N/2)(q - N) \text{ where } (N/2 + 1) \leqslant q \leqslant N \quad (6)$$

Calculations using eqns. (5) and (6) for pure s^q, p^q, d^q and f^q ($q \rightarrow N$) configurations faithfully reproduced (Table I) the ground state L-values as experimentally observed [8, 9] for these free ion systems.

TABLE I. Calculation of the Ground Terms of Configurations Containing Equivalent s^q, p^q, d^q and f^q Electrons from eqns. (5) and (6).

l	q	L	$^{2S+1}$L	l	q	L	$^{2S+1}$L
s	1	0	^{2}S	f	1	3	^{2}F
	2	0	^{1}S		2	5	^{3}H
p	1	1	^{2}P		3	6	^{4}I
	2	1	^{3}P		4	6	^{5}I
	3	0	^{4}S		5	5	^{6}H
	4	1	^{3}P		6	3	^{7}F
	5	1	^{2}P		7	0	^{8}S
	6	0	^{1}S		8	3	^{2}F
d	1	2	^{2}D		9	5	^{3}H
	2	3	^{3}F		10	6	^{4}I
	3	3	^{4}F		11	6	^{4}I
	4	2	^{5}D		12	5	^{3}H
	5	0	^{6}S		13	3	^{2}F
	6	2	^{5}D		14	0	^{1}S
	7	3	^{4}F				
	8	3	^{3}F				
	9	2	^{2}D				
	10	0	^{1}S				

Keeping in mind the rule of maximum multiplicity by Hund [10] and the formal equivalence of electrons and holes, it is then an easy task to write down the ground state terms ($^{2S+1}$L) for the free ions of any configuration containing equivalent electrons (Table I).

Using eqns. (5) and (6) we have attempted to calculate the ground state terms for the higher configurations, *e.g.*, electrons in the partly filled g and h shells. These are presented in Table II.

It is believed [11] that in the superheavy elements (superactinides) with Z = 121–154, the 5g and 6f electrons will be filled. However, in the 5g elements early occurrence of 7d and or 8p electrons may complicate the picture. A 5g electron probably does not appear [12] before the element 125. But in their ionic states of 3+ or most probably 4+ having ground state $5g^q$ ($q \rightarrow 0$–18) structure (Table II) the systematics may follow the Inclined W theory closely.

The periodicity and rhythmics of the L-values (eqns. 5, 6) with the number of electrons (q) in the

TABLE II. Predicted Ground Terms of Configurations Containing Equivalent g^q and h^q Electrons (eqns. 5, 6).

l	q	L	^{2S+1}L	l	q	L	^{2S+1}L
g	1	4	^2G	h	1	5	^2H
	2	7	^3K		2	9	^3M
	3	9	^4M		3	12	^4Q
	4	10	^5N		4	14	^5T
	5	10	^6N		5	15	^6U
	6	9	^7M		6	15	^7U
	7	7	^8K		7	14	^8T
	8	4	^9G		8	12	^9Q
	9	0	^{10}S		9	9	^{10}M
	10	4	^9G		10	5	^{11}H
	11	7	^8K		11	0	^{12}S
	12	9	^7M		12	5	^{11}H
	13	10	^6N		13	9	^{10}M
	14	10	^5N		14	12	^9Q
	15	9	^4M		15	14	^8T
	16	7	^3K		16	15	^7U
	17	4	^2G		17	15	^6U
	18	0	^1S		18	14	^5T
					19	12	^4Q
					20	9	^3M
					21	5	^2H
					22	0	^1S

partly filled shell (l^q) for s, p, d, f, g, and h electrons are shown in Fig. 1. Note that all l^q configurations, excepting s^q, exhibit the so-called tetrad groupings. Within a given configuration (l^q), the values of L are found to oscillate [2] as functions of ΔL, the difference of the L-values of the terminating configuration (l^{q+1}) and the originating configuration (l^q) and the following expression holds

$$L = L_{max} - 0.5(\Delta L) - 0.5(\Delta L)^2 \quad (7)$$

where L_{max} is the maximum value of L within the configuration under consideration (L_{max} = 0, 1, 3, 6, 10, 15 for s^N, p^N, d^N, f^N, g^N and h^N configuration respectively).

Configurations Containing More Than One Partly Filled Shell ($l^q l'^m l''^n$):

Equations (5) and (6) can also be used for an electronic configuration containing more than one partly filled shell. One proceeds as before by taking each partly filled shell in turn and then summing up all values to generate the ground state L-value

$$L = L_{l^q} + L_{l'^m} + L_{l''^n} \ldots\ldots \quad (8)$$

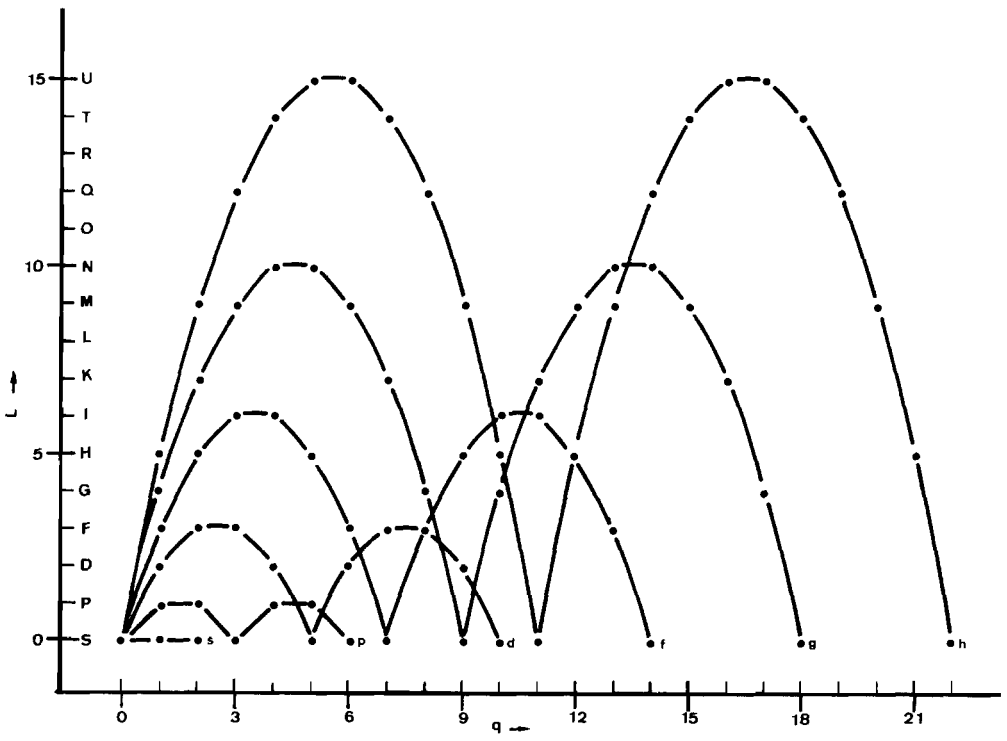

Fig. 1. Periodicity in variation of L-values of s^q, p^q, d^q, f^q, g^q and h^q electrons with q.

However, when using eqn. (8) it is absolutely necessary to make sure that Hund's rule is *strictly* obeyed by the configuration. Otherwise, discrepancies between the predicted ground terms and the experimentally observed ones may occur. This is exemplified below for the ground state (^{2S+1}L) of several configurations of CeII(Ce^{+}) and PrIII(Pr^{2+}).

For CeI			For Pr III		
Confg.	(eqn. 8)	Obs.	Confg.	(eqn. 8)	Obs.
f^3	^4I	^4I	f^3	^4I	^4I
f^2p	^4I	^4I	f^2p	^4I	$^4H^*$
f^2d	^4K	^4K	f^2d	^4K	$^2H^*$
fdp	^4I	$^2H^*$	fdp	^4I	^4I

Whereas the configurations f^2p and f^2d behave as normal for CeII, these are at variance for PrIII. The fdp configuration which does not obey Hund's rule in the case of CeII, does so for PrIII. Such deviations are observed in many electronic configurations of the lanthanides and the actinides [9].

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