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ON THE CALCULATION OF THE SPECTROSCOPIC TERMS DERIVED FROM EQUIVALENT ELECTRONS

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ABSTRACT

The calculation of the spectroscopic terms which result from an atomic configuration containing several equivalent electrons, in which Pauli's restriction is operative, can be made very simply by the extension of a notation due to Breit. The results are in agreement with those previously given by Hund for *p* and *d* electrons and those of Gibbs, Wilber and White for *f* electrons. Some minor alterations in notation are suggested.

IT IS now well established that the spectroscopic terms belonging to an atom in a given state of ionization depend upon the combined influence of all the electrons outside the complete "shells." When these electrons are unlike (differing in either their total or azimuthal quantum numbers) the determination of the terms produced by any configuration is very simple; but when they are equivalent in these respects, the restriction stated by Pauli becomes operative, according to which no two electrons in the same atom can have the same values for all four of the quantum numbers which define their state. The following method permits a rapid analysis of the effects of this limitation.

The notation is substantially that of Hund's book.[1] The *state of a single electron* in an atom is completely defined by five quantum numbers, s, l, n, m_s and m_l. Of these, s defines the "spin" and is always $\frac{1}{2}$ (in the usual units of $h/2\pi$), l is less by a unit than Bohr's azimuthal quantum number, and n is equal to Bohr's total quantum number. The quantities m_s and m_l are magnetic quantum numbers, giving the orientations of the spin-axis and the orbit plane in a (hypothetical) magnetic field strong enough to break down all couplings between individual orbital or spin vectors; m_s has the value $\pm\frac{1}{2}$, while m_l runs from l to $-l$ by steps of a unit. Pauli's restriction then demands that no two electrons in the same atom have the same values of n, l, m_s and m_l. The small letters, $s, p, d, f, \cdots$, are used to describe electrons for which $l=0, 1, 2, 3, \cdots$; so that, for example, $2s$, $4p$, $3d$, have exactly the same meanings as Bohr's 2_1, 4_2, 3_3.

States of an atom (which correspond to the separate magnetic levels into which a component of a multiple term is divided) may be defined by the numbers S, L, m_S and m_L.[2] Of these, S represents the vector sum of the s's

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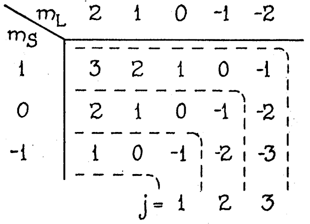
[1] Hund, Linienspektra und periodisches System der Elemente. Berlin, 1927. (Julius Springer).

[2] Hund uses l_i for the electron and l for the atom; but if both are to be used as subscripts, as is described here, the capital letter appears preferable. The use of s (and S) to denote both spin-vectors and orbits (or terms) is not likely to lead to any misunderstanding, and it is not worth while to change the notation already adopted by several active workers to avoid this formal objection.

and defines the multiplicity, being 0, $\frac{1}{2}$, 1, · · · , for singlets, doublets, triplets, · · · ; L is the vector sum of the l's and is 0, 1, 2, 3, · · · , for S, P, D, F, · · · , terms. The magnetic quantum numbers, as ordinarily defined, are in weak fields $m = m_L + m_S$, and in strong fields $m' = m_L + 2m_S$.

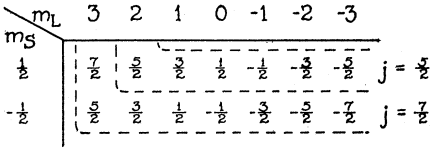
When only one electron is active (as in Na I, Ca II, etc), the quantities denoted by small and large letters become identical. In this case a total quantum number n can be assigned to the atomic state. When more than one electron is active, no such assignment is possible, and a complete description of the situation demands the specification of n and l for each electron. For example, the lowest energy-state of Ti I is $(3d)^2$ $(4s)^2$, ${}^3F_2$; two of the four active electrons being in $3d$ orbits, and the other two in $4s$ orbits.



m_S \ m_L	2	1	0	-1	-2
1	3	2	1	0	-1
0	2	1	0	-1	-2
-1	1	0	-1	-2	-3
		j = 1		2	3

Fig. 1. Relation between m_S, m_L and the inner quantum number j, for a regular ${}^3D$ term.

The relation first stated by Pauli, between m_S, m_L and the inner quantum number j[3] has been simply expressed graphically by Breit.[4] The values of m_L are written above the top of a rectangle, those of m_S at the left, and the magnetic quantum numbers $m = m_S + m_L$ inside it. The magnetic levels which unite into a single component of the term in the absence of an external field, are then obtained by dividing the rectangle into L-shaped strips, as shown by the dotted lines in Fig. 1, which corresponds to a ${}^3D$ term ($S=1$, $L=2$). The three "runs" of m from 3 to -3, 2 to -2 and 1 to -1 correspond respectively to the components ${}^3D_3$, ${}^3D_2$, ${}^3D_1$. The maximum numerical value of m in each "run" gives the inner quantum number of the component, in Sommerfeld's notation.



m_S \ m_L	3	2	1	0	-1	-2	-3	
$\frac{1}{2}$	$\frac{7}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{5}{2}$	$j = \frac{5}{2}$
$-\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{5}{2}$	$-\frac{7}{2}$	$j = \frac{7}{2}$

Fig. 2. Relation between m_S, m_L and the inner quantum number j, for an inverted ${}^2F$ term.

The arrangement here given holds good in general for "regular" terms. For inverted terms, the strips are inverted as shown in Fig. 2, representing a

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[3] j is not written as a capital (a) to avoid confusion with Landé's usage, (b) because inner quantum numbers have a meaning only for atomic states, and not for the separate electron-orbits.

[4] Breit, Phys. Rev. **28**, 334 (1926).

^2F term. The same arrangement may be obtained by keeping the strips as before but changing the sign of each individual m_s and m_l.

When two unlike electrons occur in an atom, the values of L and S resulting from the combination of their individual values of l and s may be derived by the aid of Sommerfeld's form of the vector-model, or as Breit has shown, by the graphical process just illustrated. For example, Fig. 1 represents the combination of a p-electron ($l=1$) and a d-electron ($l=2$) provided that the outer vertical and horizontal rows are supposed now to represent the two sets of values of m_l and the quantities inside the rectangle the values of m_L which are obtained by adding the others in all possible conbinations. Dividing them into strips as before we obtain runs of m_L from 3 to -3, 2 to -2 and 1 to -1, which give $L=3$, 2, 1, or D, P, S, terms. If additional electrons (not equivalent to any previously considered) are to be added, the values of m_L for each term of this first resultant are to be combined independently with those of m_l for the new electron.

The s-vectors are similarly treated; thus Fig. 2 represents the addition of an additional electron ($s=\frac{1}{2}$) to a configuration giving a sextet term $S=3$, the new runs of m_S being from 7/2 to $-7/2$ and 5/2 to $-5/2$, and the new terms septets and quintets.

So long as the electrons are all dissimilar there is no restriction on these combinations. Any pair of values of m_L, m_l may be added to give a new m_L and any other pair of values of m_S, m_s to give a new m_S. It is therefore sufficient to consider the combinations of the two separately; and terms of any given type (S, P, D) will appear in both the multiplicities produced by adding the new electron.

But when the electrons are equivalent in their total and azimuthal quantum numbers, Pauli's restriction operates. All cases in which both m_l and m_s are the same for a pair of electrons must be excluded, and, what is more, cases obtainable from one another by a mere permutation of the order in which the electrons are counted correspond to the same atomic configuration, and give exactly the same energy-level.

How this works may best be seen by an illustration. In the case of two equivalent p-electrons, the diagram for m_L is as follows.

$$\begin{array}{r|ccc}
 & 1 & 0 & -1 \\
\hline
1 & [2] & 1 & 0 \\
0 & 1 & [0] & -1 \\
-1 & 0 & -1 & [-2]
\end{array}$$

When $m_S=0$, the individual values of m_s must be $+\frac{1}{2}$ and $-\frac{1}{2}$. The two electrons are dissimilar in this respect, and hence the combination of the m_l's is unrestricted, giving runs of m_L, 2 to -2, 1 to -1 and 0. But when $m_S=1$ (or -1) the two m_s's are alike, and the m_l's are restricted. The values of m_L on the diagonal, which are bracketed above must now be excluded, and the values below the diagonal become mere duplicates of those above. All that remains of m_L is the run 1 to -1.

Collecting these results we have,

$$\begin{array}{cc|c|c|c|} m_S=1 & m_L= & & 1 \text{ to } -1 & \\ 0 & & 2 \text{ to } -2, & 1 \text{ to } -1, & 0 \\ -1 & & & 1 \text{ to } -1 & \\ \hline & & {}^1D & {}^3P' & {}^1S \end{array}$$

We have evidently here exactly the sets of values of m_S and m_L which are required to form the terms indicated at the bottom.

In order to distinguish between primed and unprimed terms a very simple rule which is now being followed by several investigators may be deduced from Heisenberg's statement that, in any electron transition which gives rise to radiation, one electron changes its azimuthal quantum number by one unit, while at the same time one other may change by two. If then we assign to the various types of orbits 0, 1, 2, 3, for *s*, *p*, *d*, *f*, electrons respectively (which are Hund's values of l) it is evident that the sum of the l's, in any transition, must change from odd to even, or vice versa. This gives us two groups of terms,—even terms (l sums even); S, P', D, F', G, etc.: odd terms (l sums odd): S', P, D', F, G', etc.—which may be distinguished by the fact that the odd terms have an odd number of p and f electrons, taken together, in the configuration. If primed terms are defined in this way, a notation is obtained which is consistent with the accepted notation for the sodium, calcium and aluminum groups, and which may be applied without ambiguity to all cases.

In the case of three p-electrons, the sum $m_S=\pm 3/2$ may be obtained only when all three of the values of m_s are alike. The three values of m_l must then all be different; that is, they must be 1, 0 and -1, and $m_L=0$. The sum $m_S=\frac{1}{2}$ is obtained when two of the m_s's are $\frac{1}{2}$ and the other $-\frac{1}{2}$. The first two give the run 1 to -1 for m_L. Since the third electron is dissimilar (having a different value of m_s) this run combines freely with the m_l of the third electron, giving runs from M_L of 2 to -2, 1 to -1 and 0. The case where $m_s=-\frac{1}{2}$ is exactly similar.

We thus find the array

$$\begin{array}{ccccc} m_S=\pm\frac{3}{2} & m_L{}^m= & & & 0 \\ \pm\frac{1}{2} & = & 2 \text{ to } -2, & 1 \text{ to } -1, & 0 \\ \hline & & {}^2D' & {}^2P & {}^4S' \end{array}$$

Beyond this point we need not go, for, as is well known, a complete shell of six p-electrons must have $m_S=0$, $m_L=0$, giving a ${}^1S$ term. A shell of five electrons gives the same values as a single electron, and one of four the same as one of two, except that the sign of each individual m_S and m_L is changed, whence it follows that the terms are the same as those previously calculated, but are inverted.

The advantages of the present method of calculation are more apparent in the case of equivalent d-electrons. When discussing it, we will, for brevity, write (4) to denote the "run" 4 to -4, etc. The free combination of any two runs (m) and (n) (where we may suppose $m \geqq n$), then gives a set of runs $(m+n)$, $(m+n-1)$, and so on to $(m-n)$.

For two d-electrons, we have the diagram

$$\begin{array}{r|rrrrr}
 & 2 & 1 & 0 & -1 & -2 \\
\hline
2 & [4] & 3 & 2 & 1 & 0 \\
1 & 3 & [2] & 1 & 0 & -1 \\
0 & 2 & 1 & [0] & -1 & -2 \\
-1 & 1 & 0 & -1 & [-2] & -3 \\
-2 & 0 & -1 & -2 & -3 & [-4]
\end{array}$$

When $m_S=0$ combination is unrestricted, but when $m_S=\pm 1$ the diagonal values must be rejected and the quantities below the diagonal are duplicates of those above, so that we have simply the runs (3) and (1). Our array then becomes

$$\begin{array}{rccccc}
m_S=\pm 1 & m_L= & (3) & & (1) & \\
0 & =(4) & (3) & (2) & (1) & (0) \\
\hline
 & {}^1G & {}^3F' & {}^1D & {}^3P' & {}^1S
\end{array}$$

We may next note that, with five d-electrons and $m_s=\pm 5/2$, all the m_s's are of the same sign and m_L must necessarily be 0. With four electrons and $m_s=\pm 2$, only one of the five possible values of m_l is lacking in any set, so then m_L has the run (2) as in the case of a single electron. Finally, for three electrons, and $m_s=\pm 3/2$, two are lacking, and m_L has the runs (3) and (1).

Very little further calculation is now necessary. For three electrons and $m_S=\frac{1}{2}$, we have two with $m_s=+\frac{1}{2}$, giving runs (3) and (1), and one with $m_s=-\frac{1}{2}$, giving the run (2). These runs combine without restriction, giving, in the first case, runs of (1), (2), (3), (4) and (5), and in the second (1), (2) and (3). Here we have

$$\begin{array}{rcccccccc}
m_S=\pm\frac{3}{2} & m_L=(1) & (2) & (3) & (4) & (5) & (1) & (2) & (3) \\
\pm\frac{1}{2} & & & & & & (1) & & (3) \\
\hline
 & {}^2P' & {}^2D & {}^4F' & {}^2G & {}^2H' & {}^4P' & {}^2D & {}^2F'
\end{array}$$

For four electrons, $m_S=\pm 1$ can be obtained from three electrons from which m_s has one sign and $m_L=(3)$ or (1), and one of the other sign, giving the same combinations as before, while when $m_S=0$, $m_s=+\frac{1}{2}$ for two and $-\frac{1}{2}$ for the other two, giving runs of (3) and (1) to be combined freely with another (3) and (1).

In writing the resulting array, we may record simply the number of runs of m_L of each length found for any given value of m_S, as is done below. The number of terms of the highest multiplicity and of any given sort (S, P, D) is then equal to the number of runs listed under the corresponding value of m_L and in the row headed by the highest value of m_S. The numbers of terms of any lower multiplicity are found by subtracting, from the numbers in the row headed by the corresponding value of m_S, the numbers in the row next above these.

The results for four and five equivalent d-electrons are shown in Table I. In the latter case, $m_S = \pm 5/2$ gives the single run (0), $m_S = \pm 3/2$ the resultant of runs of (2) for the four similar electrons, and (2) for the other one and $m_S = \pm\frac{1}{2}$ that of (1) and (3) for the group of three electrons and (1) and (3) again for the group of two.

TABLE I

The array for four and five equivalent d electrons.

	m_L	(0)	(1)	(2)	(3)	(4)	(5)	(6)
Four electrons	$m_S = \pm 2$			1				
	± 1		2	2	2	1	1	
	0	2	2	4	3	3	1	1
Five	$m_S = \pm 5/2$	1						
	$\pm 3/2$	1	1	1	1	1		
	$\pm 1/2$	2	2	4	3	3	1	1
Terms		S	P'	D	F'	G	H'	I
Four electrons	Quintets			1				
	Triplets		2	1	2	1	1	
	Singlets	2		2	1	2		1
Five electrons	Sextets	1						
	Quartets		1	1	1	1		
	Doublets	1	1	3	2	2	1	1

Our analysis is now complete. The resulting terms may be arranged in the form shown in Table II.

TABLE II

Resulting terms for equivalent d electrons

d^{10}	${}^1S$		
d, d^9	${}^2D$		
d^2, d^8	${}^3P', {}^3F'$	${}^1S$; ${}^1D$ ${}^1G$	
d^3, d^7	${}^4P', {}^4F'$	${}^2D$; ${}^2P', {}^2D, {}^2F', {}^2G, {}^2H'$	
d^4, d^6	${}^5D$	${}^3P', {}^3F'$; ${}^3P', {}^3D, {}^3F', {}^3G, {}^3H'$	${}^1S$ ${}^1D$ ${}^1G$; ${}^1S, {}^1D, {}^1F', {}^1G, {}^1I$
d^5	${}^6S$	${}^4P', {}^4F'$; ${}^4D$ ${}^4G$	${}^2D$; ${}^2P', {}^2D, {}^2F', {}^2G, {}^2H'$; ${}^2S, {}^2D, {}^2F', {}^2G, {}^2I$

This is identical, in content, with Hund's table[5] but brings out the noteworthy regularities in arrangement in a somewhat different manner. The terms of lowest energy level are found in the second column and the other terms of practical importance in the third.

The case of equivalent f electrons demands a little more reckoning. Two such electrons may be treated in the same fashion as two d-electrons, giving

$$\begin{array}{rlccccccc} m_S = \pm 1 & m_L = & & (1) & & (3) & & (5) & \\ 0 & \quad = & (0) & (1) & (2) & (3) & (4) & (5) & (6) \\ \hline & & {}^1S & {}^3P' & {}^1D & {}^3F' & {}^1G & {}^3H' & {}^1I \end{array}$$

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[5] Hund, *Linienspektra*, p. 119. The table in his original paper, lacks a ${}^3G$ term for d^4 and a ${}^1S$ for d^5.

With three electrons, and $m_S = \pm 3/2$, the actual cases must once more be counted, and care must be taken not to count the same combination twice. This may be assured by combining the first two electrons as above and adding a third only when its value of m_L is less than for either of the other two. In this way each permutation will evidently be counted once and only once.

For the two electrons the exhibit of the permissible values of m_l and m_L forms a triangle, as follows.

$$
\begin{array}{rrrrrr|r}
m_l=2 & 1 & 0 & -1 & -2 & -3 & \\
\hline
m_L=5 & 4 & 3 & 2 & 1 & 0 & 3 \\
 & 3 & 2 & 1 & 0 & -1 & 2 \\
 & & 1 & 0 & -1 & -2 & 1 \\
 & & & -1 & -2 & -3 & 0 \\
 & & & & -3 & -4 & -1 \\
 & & & & & -5 & -2
\end{array}
$$

We may begin by combining $M_L = 5$ in the first column of the triangle with the values of m_l in subsequent columns and in the outer row above, then the values $M_L = 4$, 3, in the next column with the numbers in the *following* columns of the outer row and so on. Thus we get the series of numbers

$$
\begin{array}{lllll}
6,\ 5,\ 4,\ 3,\ 2\ ; & 4,\ 3,\ 2,\ 1\ ; & 2,\ \ 1,\ \ 0\ ; & 0,\ -1\ ; & -2 \\
 & 3,\ 2,\ 1,\ 0\ ; & 1,\ \ 0,\ -1\ ; & -1,\ -2\ ; & -3 \\
 & & 0,\ -1,\ -2\ ; & -2,\ -3\ ; & -4 \\
 & & & -3,\ -4\ ; & -5 \\
 & & & & -6
\end{array}
$$

which may be immediately rearranged into the runs (6), (4), (3), (2), (0).

For $m_S = \pm\frac{1}{2}$ we have two electrons with m_s of like sign, giving the runs (1), (3), (5), and one of opposite sign with the run (3). The final array may then be written as follows.

m_L	(0)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$m_S = \pm\frac{3}{2}$	1		1	1	1		1		
$= \pm\frac{1}{2}$	1	1	3	3	3	2	2	1	1
Terms	S'	P	D'	F	G'	H	I'	K	L'
Quartets	1		1	1	1		1		
Doublets		1	2	2	2	2	1	1	1

The remaining computations are now straightforward. Four electrons with m_s alike give again the runs (0), (2), (3), (4), (6), five give (1), (3), (5), six give (3) and seven give (0).

The results were worked out independently by Messrs. Gibbs, Wilber and White, and may be found in their paper, (which immediately follows this).

(By mutual agreement, the theory has been presented by one author, and the numerical results, so far as they are new, by the others.)

A word may be said about the notation of the terms corresponding to high values of L. The letter J has been omitted by Hund in accordance with German usage. P and S are preoccupied. The list of letters then becomes

$L=$	0	1	2	3	4	5	6	7	8	9	10
	S	P	D	F	G	H	I	K	L	M	N
$L=$	11	12	13	14	15	16	17	18	19	20	
	O	Q	R	T	U	V	W	X	Y	Z	

Even this extension is barely adequate to include what may be anticipated among the rare earths. The highest multiplicity to be expected is 11, which, as Hund points out[6] should occur in Gd only, and give a term ^{11}F arising from the configuration f^7d^2s, which must be either the normal state or a very low metastable one. The highest value of L among the "middle terms" with one excited electron should occur in the same spectrum, arising from the configuration $(4f)^7\,(5d)^2\,(6p)$, which should give a term for which $m_L=16$, of type ^4V. Similar terms originating in the configuration f^6d^2p or f^8d^2p should occur in Eu and Tb. Still greater values of L could be reached in highly excited states; for example the configuration $(4f)^7\cdot(5f)\cdot(5d)\cdot(6d)\cdot(6p)$ representing an atom of Tb with three excited electrons, should give a maximum value $L=20$, and a term which would demand the notation ^6Z.

Among the multitude of levels given by this configuration would also be some derived from the ^8S term of origin f^7, which would be of multiplicity 12, and all types from ^{12}S to ^{12}L. These terms however would be very unlikely to give lines strong enough to be observable.

In conclusion, reference may be made to the beautiful manner in which Breit's graphical process[4] solves the problem of the limits of series in complex atoms, and shows which components of a given term in the arc spectrum (for example) go to given components of the limiting term in the spark spectrum. The results are naturally in accordance with those given by Hund in Fig. 34 at the end of his book.

Princeton University,
Observatory,
April 4, 1927.

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[6] Hund, *Linienspektra*, p. 177.