MULTIPLET SEPARATIONS

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Abstract

Formulas for the separations of normal multiplets, arising from general configurations, are derived by reasoning from the fundamental assumption that they are due to the interaction energy between spin and orbital magnetism of the electrons. The separations are known for multiplets arising from groups of equivalent electrons, from considerations given in the preceding paper. It is shown in this investigation, by a simple treatment of the vector model, that the interaction energy for other configurations may be found in terms of that of the equivalent group and the interaction energy of the electron or group of electrons added, provided the quantum vectors of the original configuration remain unchanged. Our treatment applies only to multiplets showing reasonably close agreement with the interval rule, and which are therefore accounted for by the Russell-Saunders coupling. Examples given for illustration are taken from data on Fe and O^+. Calculated results indicate the validity of our formulas to the extent permitted by agreement of data with the interval rule.

$\mathbf{M}$ULTIPLET separations are due to the energy of interaction between spin and orbital magnetism of the electrons. The value of this energy for a single electron is indicated by γ and is given by the formula:

$$\gamma = als \cos (ls) \tag{1}$$

In this formula, $a = R\alpha^2 Z^4 / [n^3 l(l+1/2)(l+1)]$ for a Kepler orbit, in first approximation, or $a = R\alpha^2 Z_i^2 Z_a^2 / [n^3 l(l+1/2)(l+1)]$ for a penetrating orbit. Also $s = 1/2$ and $l = 0$, 1, 2 etc., depending on the type of orbit. When only one electron is responsible for the spectrum and we thus have a doublet, the two possible values of γ give the separations of the actual levels from the position of the hypothetical level without interaction energy.

When we have multiplets due to configurations of two or more electrons, it is sufficient in most cases to consider only the interaction between the spin of each electron and its own orbit. While there is some energy due to interaction between the spin of a given electron and the orbit of another, it is proportional to a lower power of the nuclear charge, and, for purposes of this discussion, need not be considered.[1]

Suppose we have an atom in which the so-called Russell-Saunders coupling occurs. All the electronic spins s_i form a resultant s, and all orbital moments form a resultant l, while s and l combine finally to give a total resultant j. The total interaction energy between the spins and respective orbits of the electrons is then:

$$\Gamma = \sum a_i l_i s_i \overline{\cos (l_i s_i)}$$

In this ideal case it may be easily shown that

$$\overline{\cos (l_i s_i)} = \overline{\cos (l_i l)} \; \overline{\cos (ls)} \, \overline{\cos (s_i s)}$$

[1] For the interesting case of the helium triplet in which these terms must be considered, see W. Heisenberg, Zeits. f. Physik **39**, 499 (1926).

Thus the interaction energy is of the form:

$$\Gamma = Als \cos (ls), \quad \text{in which} \quad A = \sum_i (l_i/l) \cos (l_i l)(s_i/s) \cos (s_i s) \qquad (2)$$

The different levels of the same multiplet all have the same coefficient A. Γ is however determined by $\cos(ls)$ according to the formula:[2]

$$\Gamma = Als \cos (ls) = \tfrac{1}{2} A [j(j+1) - l(l+1) - s(s+1)]$$

This formula will be recognized as the familiar interval rule of Landé. If we take the energy difference between two levels of the same multiplet, one having a total moment j and the other $j-1$, we find:

$$\Gamma(j) - \Gamma(j-1) = Aj.$$

The subsequent intervals are thus proportional to the larger value of j corresponding to one of the two adjacent levels. We find the factor A for each multiplet by dividing the multiplet separations by these interval factors equal to j. If we take for instance a ^4D level, $s = 3/2$, $l = 2$, and j can have the values $7/2$, to $1/2$, as resultant of s and l. The three intervals between these four levels are proportional to $7/2$, $5/2$ and $3/2$, the proportionality factor being just A.

In a previous paper one of us[3] derived formulas for the values of Γ or A in cases where we have only a number of equivalent electrons. It was possible to express A in terms of the values of a_i for the single electrons, which of course are all equal if we take only equivalent electrons.

In this investigation we will show that it is possible to determine A for other configurations of electrons. In general the method will be to consider the addition of another electron to a group for which A is known, and to obtain a new A in terms of that of the original group and a_i of the new electron. Or the expression for A may be in terms of the values of a_i for the different electrons. Likewise the total multiplet separations may be determined in terms of the different values of a_i. The latter method is somewhat more convenient for application, as it gives at the same time an average value in cases where the interval rule does not hold strictly.

Before proceeding to a derivation of the expression for A it is necessary to state the conditions under which we may consider the result of adding a new electron to a given configuration. A solution of Eq. (2) must involve an evaluation of $\cos (l_i l)$ and of $\cos (s_i s)$. This makes it necessary that the quantum vectors be determined in a definite fashion. Accordingly we must impose the following restriction, which the accompanying figure will help make clear. The values of l_i and s_i of the original group combine separately, according to the Russell-Saunders scheme, to yield resultant quantum vectors which we designate by l' and s'. These vectors are not to be disturbed or

[2] This expression for the cosine of the angle between two quantum vectors was originally found as an empirical relationship by Landé, but has now been verified by the application of new mechanics.

[3] Goudsmit, Phys. Rev. **31**, 946 (1928). Preceding paper in this issue.

altered by the addition of a new electron. We then obtain the resultant vectors, l and s, of the new configuration, by combining l' with l_2 of the added electron, and s' with s_2. In making this composition we consider l' and s' as single vectors and are entirely unconcerned as to their origin. The total resultant, that is of l and s, we again call j.

This special case will not occur very often, since the resultant, l' and s', of the electrons already present will usually be disturbed by the addition of the new one, and one cannot say that the new resultant l is built up of the old l' and the added l_2 and similarly for s, which is essential for the discussion to follow. It will appear however that our formula for A is applicable in cases where the interval rule holds fairly well. Two cases may be mentioned
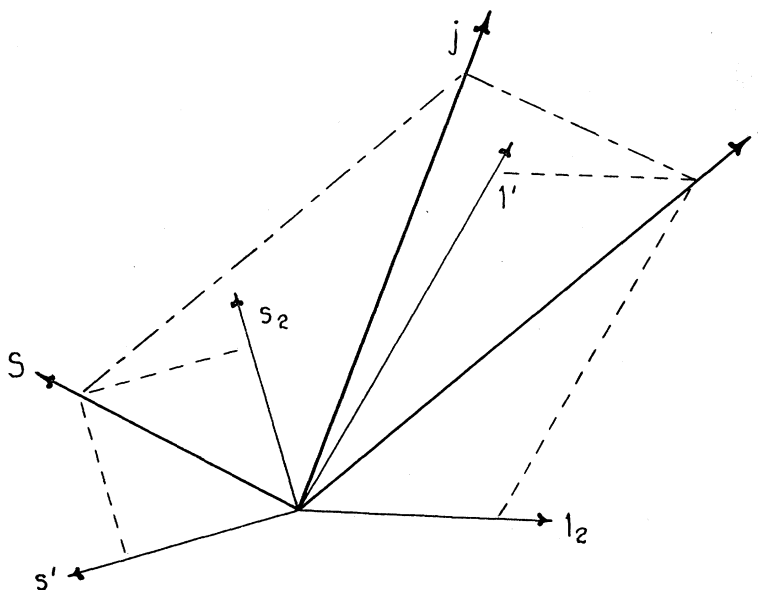

Fig. 1.

as examples in which we are quite certain that the restriction, as to the relation of the quantum vectors of the new electron with the resultant vectors of the original group, is valid.

If we have a group of equivalent electrons and add another kind of electron, the resultant quantum vectors will be formed as indicated above, since the interaction between the equivalent electrons will in general be stronger than between them and the new one.

A simpler case is to be found in the addition of a second electron to an atom having only one valence electron. Here it is certain that the new electron cannot change the quantum vectors, l_1 and s_1, of the original one. Consequently resultant l is obtained by the combination of l_1 and l_2, and resultant s from s_1 and s_2.

It must be remembered however that these results are not perfectly general. In all cases we assume that we are to get normal multiplets, to which the interval rule may be applied with reasonable success. These occur when the vectors have the so-called Russell-Saunders coupling, in which the spins always form a resultant spin moment s, while the orbital moments combine to form a resultant l.

It is now possible to express the total interaction energy in terms of the coefficients A' and a_2 of the original multiplet and the added electron. If we apply Eq. (2) to this case we get:

$$A = A'(l'/l) \cos (l'l) \ (s'/s) \cos (s's) + a_2(l_2/l) \cos (l_2l) \ (s_2/s) \cos (s_2s).$$

Since s is the resultant of only two vectors, s' and s_2, we can write for the cosines involved:

$$\frac{s'}{s} \cos (s's) = \frac{s(s+1)+s'(s'+1)-s_2(s_2+1)}{2s(s+1)}$$

and

$$\frac{s_2}{s} \cos (s_2s) = \frac{s(s+1)+s_2(s_2+1)-s'(s'+1)}{2s(s+1)}.$$

In the same way

$$\frac{l'}{l} \cos (l'l) = \frac{l(l+1)+l'(l'+1)-l_2(l_2+1)}{2l(l+1)}$$

and

$$\frac{l_2}{l} \cos (l_2l) = \frac{l(l+1)+l_2(l_2+1)-l'(l'+1)}{2l(l+1)}.$$

We thus obtain the result:

$$A = A'\frac{s(s+1)+s'(s'+1)-s_2(s_2+1)}{2s(s+1)} \times \frac{l(l+1)+l'(l'+1)-l_2(l_2+1)}{2l(l+1)}$$
$$+ a_2\frac{s(s+1)+s_2(s_2+1)-s'(s'+1)}{2s(s+1)} \times \frac{l(l+1)+l_2(l_2+1)-l'(l'+1)}{2l(l+1)}.$$

(3)

This formula, applied to the triplet arising from two valence electrons, is identical with that given by Heisenberg,[4] who obtained the following equation, expressed in our notation, long before the meaning of the different quantum vectors was quite clear.

$$A = A'\frac{1}{2} \frac{l(l+1)+l_1(l_1+1)-l_2(l_2+1)}{2l(l+1)} + a_2\frac{1}{2} \frac{l(l+1)+l_2(l_2+1)-l_1(l_1+1)}{2l(l+1)}.$$

That this follows, in the case of two electrons, from Eq. (3) is clear when we remember that $s_1 = s_2 = 1/2$.

[4] W. Heisenberg, Zeits. f. Physik **32**, 841 (1925).

In order to illustrate the application of our formulas we have chosen examples from published data on the iron spectrum with sufficient material on ionized iron to show the building up of the configurations. An example is

TABLE I.

Electron configuration	Equation (3)	Separation factor from adjacent levels	total separation	$\frac{A''}{d^6\,^5D}$
Fe III　　　d^6	^5D　$A=A''$			exp.>120
Fe II　　　d^6s				
$l''=2,\ s''=2,\ ^5D+s$	^6D　$A'=4A''/5$	$A'=$ 86, 81, 78,76	82	102
$l_2=0,\ s_2=1/2$	^4D　$A'=6A''/5$	$=125,115,111$	119	99
Fe I　　　d^6s^2	^5D　$A=A''$	$A=104,\ 96,\ 92,90$	98	98
d^6s,s				
$l'=2,\ s'=5/2,\ ^6D+s$	^7D　$A=2A''/3$	$A=$ 69, 68, 66,65	68	102
$l_2=0,\ s_2=1/2,\ A'=4A''/5$	^5D　$A=14A''/15$	$=$ 93, 91, 88,86	92	99
$l'=2,\ s'=3/2,\ ^4D+s$	^5D　$A=9A''/10$	$=105,\ 93,\ 82,43$	(91)	(101)
$l_2=0,\ s_2=1/2,\ A'=6A''/5$	^3D　$A=3A''/2$	$=106,160$	(128)	(86)
other coupling;		This coupling does not give right		
$l''=2,\ s''=2,\ ^5D+^1S$	^5D　$A=A''$	results for A''		
$l_2=0,\ s_2=0$ or $1,\ ^5D+^3S$	^5D　$A=5A''/6$	$\Sigma A=11A''/6$ for quintets	183	99
		independent of coupling		
d^6s,p		calc.		
$l'=2,\ s'=5/2,\ ^6D=p$	^7F　$A=4A''/9-a_2/18$	$A=$ 32, 30, 28,27,26		
		26　　28　　30		
$l_2=1\ \ s_2=1/2,\ A'=4A''/5$	$^7D'$　$=5A''/9-a_2/36$	$=$ 42, 49, 49,54　50　48		
	^7P　$=A''+a_2/12$	$=117,119$　135　118		
	^5F　$A=28A''/45+a_2/18$	$=$ 58, 57, 55,53	57	
	$^5D'$　$=7A''/9+a_2/36$	$=$ 60, 67, 70,71	65	
	^5P　$=7A''/5-a_2/12$	$=138,132$	135	
$l'=2,\ s'=3/2,\ ^4D+p$	^5F　$A=3A''/5-a_2/12$	$A=$ 69, 72, 73,73	70	
$l_2=1,\ s_2=1/2,\ A'=6A''/5$	$^5D'$　$=9A''/10-a_2/24$	$=103,\ 98,108,105$	103	
	^5P　$=27A''/20+a_2/8$	$=130,126$	129	
	^3F　$A=5A''/6+a_2/12$	$A=125,110$　119　118		
	$^3D'$　$=25A''/24+a_2/24$	$=121,126$　125　123		
	^3P　$=15A''/8-a_2/8$	$=208,193$　243　203		
Other possible coupling $d^6(sp)$:		This coupling gives no good agree-		
$^5D+^3P,\ ^5D+^1P$		ment. The following sums are		
		independent of the coupling:		
		sextets　$\Sigma A=2A''$	192	96
		quintets　$\Sigma A=113A''/120$	558	98
		triplets　$\Sigma A=15A''/4$	444	118
		F terms　$\Sigma A=5A''/2$	274	110
		D' terms　$\Sigma A=131A''/40$	339	103
		P terms　$\Sigma A=45A''/8$	580	103
		Total　$\Sigma A=57A''/5$	1194	105
		calc. $a_2/72\sim5$		
Fe II　　　d^7	$^4F'$　$A=A'$	$A=123,116,112$　　$A'd=118$		118
	$^4P'$　$A=A'$	$=$ 80,154	(108)	(108)
Fe I　　　d^7s				A'
$l'=3,\ s'=3/2,\ ^5F+s$	$^5F'$　$A=3A'/4$	$A=$ 90, 88, 86,85　4s	88	117
$l_2=0,\ s_2=1/2$		$=$ 74, 94, 94,92　5s	(87)	(117)
	$^3F'$　$A=5A'/4$	$=146,136$　4s	142	114
		$=144,134$　5s	140	112
$l'=1,\ s'=3/2,\ ^4P+s$	$^5P'$　$A=3A'/4$	$A=$ 58,100	(75)	
$l_2=0,\ s_2=1/2,$	$^3P'$　$A=5A'/4$	$=$ 54,105	(71)	
d^7p				
$l'=3,\ s'=3/2,\ ^4F+p$	$^5G'$　$A=9A'/16+a_2/16$	$A=-10,95,\ 88,82$	(56)	
$l_2=1,\ s_2=1/2$	^5F　$A=11A'/16+a_2/48$	$=$ 67, 62, 59,56	63	
	$^5D'$　$A=A'-a_2/12$	$=$ 89, 87, 87,87	87	
	$^3G'$　$A=15A'/16-a_2/16$	$A=$ 78, 78	78	
	^3F　$A=55A'/48-a_2/48$	$=119,120$	119	
	$^3D'$　$A=5A'/3+a_2/12$	$=168,159$	164	
		G' terms　$\Sigma A=3A'/2$	(134)	(89)
		F terms　$\Sigma A=11A''/6$	182	99
		D' terms　$\Sigma A=8A'/3$	251	98
		quintets　$\Sigma A=9A'/4$	(206)	(92)
		triplets　$\Sigma A=15A'/4$	363	97
		total　$\Sigma A=6A'$	(569)	(95)

also taken from the spectrum of ionized oxygen. The iron spectrum is very satisfactory for this purpose because a very complete and evidently correct analysis of it has been made, and also because it exhibits a large number of multiplets which obey the interval rule closely enough to satisfy our theory.

A very brief explanation of the tables will suffice. In the example from the iron spectrum, we begin with Fe^{++} having the configuration d^6 which yields a ^5D term. All interesting configurations of Fe^+, from which Fe is derived, are built upon this d^6 group.[5]

The values of the separation factor, determined from adjacent levels and the total separation and indicated in Column 3, are introduced to show how closely the interval rule is obeyed in a given multiplet. Equal numbers for a given multiplet would indicate perfect conformity with the interval rule. All bracketed values of the separation factor are derived from examples showing very poor agreement with the interval rule.

In all cases the value of the separation factor for the equivalent d^6 or d^7 group, for which the given configuration is derived, is calculated. The values obtained are tabulated in the last column. These should be equal except for the screening effect of the outer electrons added. In the d^6 case the values of A'' are very nearly constant, indicating that the added electrons do not change the screening due to six d electrons by a very large amount. The

TABLE II

Electron configuration	Equation (3)		Separation factor from adjacent levels	total separation	A'
O II $\quad$ s^2p^2s $l'=1,\ s'=1,\ ^3P+s$ $l_1=0,\ s_2=1/2$	$^4P'$	$A=2A'/3$	$A=\ 64,70$ $=\ 65,70$	$3s\quad 66$ $4s\quad 67$	$A'(p^2)$ 99 100
	$^2P'$	$A=4A'/3$	$=120$ $=125$	$3s\quad 120$ $4s\quad 125$	90 94
^1D+s	^2D	$A=0$	$=-0.4$ $=-0.3$	$3s\ -0.4$ $4s\ -0.3$	
p^4s ^3P+s	$^4P'$ $^2P'$	$A=2A'/3$ $A=4A'/3$	$A=-65,-55$ $=-115$	-61 -115	$A'(p^4)$ -91 -86
^1D+s	^2D	$A=0$	$=-4$	-4	
s^2p^2p ^3P+p	^4P $^4D'$ ^2P $^2D'$	$A=A'/3+a_2/6$ $=A'/3+a_2/6$ $=2A'/3-a_2/6$ $=2A'/3-a_2/6$	$A=\ 37,31$ $=\ 36,37,37$ $=\ 40$ $=\ 76$ Total $\quad \Sigma A=2A'$	34 36 40 76 186	
^1D+p	^2P $^2D'$ ^2F	$A=0-a_2/2$ $=0+a_2/6$ $=0+a_2/3$	$A=\ 31$ $=-8$ $=\ 7$	31 -8 7	93

deviations from the mean value in the A'' column are in general smaller than the deviations from the interval rule in many multiplets, and may doubtless be ascribed to this poor agreement with the interval rule, which would actually lead us to expect larger variations of A'' than are found.

In the case of configurations built upon the d^7 group, we find that an added s electron does not change the screening very much, but that it is changed considerably by the addition of a p electron. If we consider d^7s or d^7p; configurations separately we have excellent agreement in the A' values obtained from different multiplets.

[5] An almost complete term table in accordance with the classification of Laporte is given by W. F. Meggers, Astrophys. J. **60**, 60 (1924). For a discussion of the assignment of levels, see O. Laporte, Proc. Nat. Acad. Sc. **12**, 496 (1926). The lowest levels of Fe^+ are given by H. N. Russell, Astrophys. J. **64**, 194 (1926).

In the O^+ example[6] we have the interesting case discussed in the previous paper. Since six p electrons constitute a complete shell, we should obtain the same value of A' derived from p^2s as from p^4s, except that the algebraic sign would be negative in the latter case and the value should be slightly smaller because of the somewhat larger screening of four p electrons. This is actually observed, and we also find good agreement in the A' values of different multiplets if we consider p^2s and p^4s separately.

When we consider p^2p configurations of O^+ we find that both quartets, ^4P and $^4D'$, show good agreement in the values of the separation factor, but that the doublets show considerable deviation. This may be due to lack of agreement with the interval rule but this cannot be concluded definitely, because it is not possible to say whether the interval rule is obeyed or not in the case of doublets.

We expect this method to be useful in checking the assignment of configurations and terms in complicated cases. Calculations, not included in this paper, on the quintets of Ti I, and the quartets of Ti II, came out in agreement with the assignment made by Russell.[7] Also the separations in the O III[8] spectrum are in perfect agreement with the formulas given here.

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[6] For a complete term table, see H. N. Russell, Phys. Rev. **31**, 27 (1928).
[7] H. N. Russell, Astrophys. J. **66**, 283 (1927) also **66**, 347 (1927).
[8] A. Fowler, Proc. Royal Soc. January, 1928.