JUNE, 1928 PHYSICAL REVIEW VOLUME 31

MULTIPLET SEPARATIONS FOR EQUIVALENT ELECTRONS AND THE ROENTGEN DOUBLET LAW

By S. Goudsmit

Abstract

Expressions are derived for the separation of multiplets arising from configurations of equivalent electrons. It is explained why the Roentgen doublets obey the Sommerfeld formula, although this formula was derived formerly for a single electron only. The separations of more complicated multiplets are proved to be connected also with the Sommerfeld formula. According to Landé the multiplet separations can be characterized by factors, designated by Γ, which give the displacement of each level from the centre of gravity of the whole multiple level. The properties of these Γ factors are studied in this paper. They are quite analogous to the well-known properties of the magnetic separation factors, g, introduced by Landé for the explanation of the Zeeman effect. It is pointed out that there is a Γ sum rule, corresponding to the well-known g sum rule, stating that, for given quantum numbers of the electrons, the sum of the Γ values belonging to a certain total moment j is a constant, independent of the type of coupling of the electrons. This rule is important especially because it makes it possible to obtain expressions for the multiplet separations in general cases.

IN HIS celebrated paper on the building up of electron groups, Pauli[1] has shown that the absence of a given number of electrons from an otherwise complete configuration gives rise to quantum states analogous to those which appear when only this same number of electrons is present. Pauli has developed a rule for the determination of the quantum states and quantum numbers of an electronic configuration from those of the electrons involved in the configuration, but it gives us no information as to the energy relationships of these quantum states. It is well known that a single valence electron yields a doublet spectrum, and, according to Pauli's reasoning, the energy levels in the Roentgen spectrum, in the production of which one electron is absent from a complete group, should exhibit a similar structure. It has never been clearly explained however why the doublets in the Roentgen spectra are similar in their energy relationships to optical doublets due to single electrons, and follow exactly the same doublet formula, which up to now has been derived only for a single electron.[2]

Proof of the validity of the Roentgen doublet formula will be given in the present paper and still other properties of multiplet separations for a given number of equivalent electrons will be deduced. Results are given first for cases in which the spectrum shows normal multiplets.

For a single electron the doublet separation is given by the well-known Sommerfeld formula:

---

[1] W. Pauli, Zeits. f. Physik **31**, 765 (1925).

[2] W. Heisenberg and P. Jordan, Zeits. f. Physik **37**, 263 (1926).

$$\Delta\nu=\frac{R\alpha^2Z_{\text{eff}}^4}{n^3l(l+1)}$$

or for penetrating orbits, according to Landé, approximately:[3]

$$\Delta\nu=\frac{R\alpha^2Z_i^2Z_a^2}{n_a^3l(l+1)}$$

(In these formulas R stands for the Rydberg constant, α the Sommerfeld fine-structure constant, n the principal quantum number, n_a the so-called effective principal quantum number, l the azimuthal quantum number in the notation of the new quantum mechanics, Z_a the effective nuclear charge in the outer part of the orbit, and Z_i that in the inner part).

In connection with what follows this formula for the doublet separation is written:

$$\Delta\nu=a(l+\tfrac{1}{2})$$

in which the factor a is consequently given by:

$$a=\frac{R\alpha^2Z_{\text{eff}}^4}{n^3l(l+\frac{1}{2})(l+1)}, \tag{1a}$$

or for penetrating orbits:

$$a=\frac{R\alpha^2Z_i^2Z_a^2}{n_a^3l(l+\frac{1}{2})(l+1)} \tag{1b}$$

Table I gives the values of the total multiplet separations for equivalent p and d electrons, expressed in terms of the factor a associated with one single electron. The quantum numbers of the single electron must always be introduced in the expression for this factor a, independently of those of the multiplet given by the configuration. In the case of p electrons for example, l is accordingly always made equal to 1 in the factor a, while in the case of d electrons l is always made equal to 2.

The last column gives the value of the interval factor A. The meaning of this factor, which is constant for a given multiplet, may be understood by looking ahead to the expression for the interval rule given by Eq. (4). It will be seen that A is equal to the displacement divided by the number given by the interval rule. It may also be found by the same formula by dividing the separation of two adjacent levels by the larger of the inner quantum numbers belonging respectively to these two levels.

A minus sign before the separation indicates that it is an inverted multiplet, that is that the level with the largest total impulse moment j lies lowest. As would be expected the values in this table are correct only to an approximation as close, let us say, as the interval rule of Landé, for example.

---

[3] A. Landé, Zeits. f. Physik **25**, 46 (1925).

TABLE I. *Values of the total multiplet separations for the equivalent p and d electrons.*

Configuration	Multiplet	Total separation	Separation factor A	Configuration	Configuration	Multiplet	Total separation	Separation factor A	Configuration
p	^2P	$3a_i/2$	a_i	$-p^5$	d^3	$^2F'$	$-7a_i/12$	$-a_i/6$	$-d^7$
p^2	$^3P'$	$3a_i/2$	$a_i/2$	$-p^4$		^2D	$5a_i/6$	$a_i/3$	
p^3	$^2D'$	0	0	$-p^3$		^2D			
	^2P	0	0			$^2P'$	a_i	$a_i/3$	
					d^4	^5D	$5a_i/12$	$a_i/4$	$-d^6$
d	^2D	$5a_i/2$	a_i	$-d^9$		$^3H'$	$11a_i/10$	$a_i/10$	
d^2	$^3F'$	$7a_i/2$	$a_i/2$	$-d^8$		^3G	$27a_i/20$	$3a_i/20$	
	$^3P'$	$3a_i/2$	$a_i/2$			$^3F'$	$7a_i/12$	$a_i/12$	
d^3	$^4F'$	$7a_i/2$	$a_i/3$	$-d^7$		$^3F'$			
	$^4P'$	$4a_i/10$	$a_i/3$			^3D	$-5a_i/12$	$-a_i/12$	
	$^2H'$	$11a_i/10$	$a_i/5$			$^3P'$	$3a_i/2$	$a_i/2$	
	^2G	$27a_i/20$	$3a_i/10$			$^3P'$			
					d^5	all	0	0	$-d^5$

EXAMPLES

The spark spectrum of titanium[4] is the only spectrum in which an interesting group of levels arising from equivalent electrons is almost completely known. In the other spectra only one or two of the many expected multiplets have been found. In the case of the d^3 configuration in Ti II one of the two expected ^2D levels is still unknown. In this example however, the interval rule does not hold at all for the ^4P state, and it is of course impossible to decide whether it is valid or not for the doublets. Table II gives the observed and calculated multiplet separations, the latter being given in italics. The constant a_i was taken from the ^2H separation. The agreement is very good in most cases. Note especially the inverted ^2F term. It is very

TABLE II. *Observed and calculated multiplet separations in Ti II.*

Term notation (Russell)	Ti II d^3 configurations Multiplet separations				
b^4F'	obs. *calc.*	128.37 *133.2*	103.41 *103.6*	75.84 *74.1*	
a^4P'				122.29 *74.1*	32.05 *44.4*
a^2H'	97.82 (*97.8*)				
a^2G		120.46 *120.0*			
b^2F'			−59.89 *−51.8*		
b^2D $-^2D$				129.38 — Σ*74.1*	
a^2P'					125.02 *88.9*
j=11/2	9/2	7/2	5/2	3/2	1/2

---

[4] H. N. Russell, Astrophys. J. **66**, 283 (1927).

probable that the poor agreement for the separations between the levels with low values of j is due to the large deviations from the ordinary interval rule.

Another way to illustrate the formulas given here is to show that the constant a_i for different elements is represented by Eq. (1). Substituting Eq. (1) in Table I for the cases of equivalent d electrons, one finds that the total separation of the D level of highest multiplicity [if there is one] is just given by the well-known relativistic doublet law of Sommerfeld:

$$\Delta\nu=\frac{R\alpha^2(Z-\sigma)^4}{n^3l(l+1)}\cdot$$

In the cases d^2, d^3, d^7 and d^8 one finds that 5/7 of the total separation of the F term of highest multiplicity occurring obeys the same formula. For the D separation this has actually been found independently from the observed data by Dr. O. Laporte.[5] The fact that he communicated these results to me gave rise to this investigation. It could also easily be shown that the formula also holds for 5/7 of the total F separations. Table III gives the total separations of those terms in the scandium row of the periodic table. The constant a_i is calculated and also the screening constant σ by applying the relativistic doublet formula for non-penetrating orbits. Of course this will be only an approximation, but nevertheless σ appears to be near to the screening constant of the corresponding Roentgen doublet M_{33}-M_{32}.

TABLE III. *Total separations for the elements in the scandium row.*

Element	Configuration	Multiplet	Total separation	a_i	Screening constants
21 Sc	d	^2D	168.5	67	12.72
22 Ti	d^2	$^3F'$	386.7	111	12.64
23 V	d^3	$^4F'$	552.7	158	12.76
24 Cr	d^4	^5D	557.0	223	12.94
25 Mn	d^5	^6S	—	—	—
26 Fe	d^6	^5D	−978.1	−391	13.16
27 Co	d^7	$^4F'$	−1809.3	−517	13.24
28 Ni	d^8	$^3F'$	−2216.5	−632	13.53
29 Cu	d^9	^2D	−2042.9	−817	13.57
30 Zn	d^{10}	^1S	—	—	—

Roentgen doublet $M_{33}-M_{32}$, d^9 ^2D:13.0

THE Γ FACTORS

The multiplet separations are due to the interaction between the spin and the orbital motion of the electrons. In the case of a single electron this interaction energy is given by:*

$$\gamma_i=a_il_is_i\cos\,(l_is_i) \tag{2a}$$

---

* In this expression and in those which follow we indicate by a subscript i those quantities which belong only to a single electron.

[5] O. Laporte, Zeits. f. Physik **47**, 761, (1928).

We denote this expression by γ_i because it differs by only a factor from the γ factors introduced earlier by Landé.[6] In the case of several electrons it is permissible in general to neglect the interaction energy between the spin of one electron and the orbital magnetic field of another in comparison with the interaction with its own orbital field, as a first approximation.[7] The total interaction energy for several electrons is therefore:

$$\Gamma = \Sigma\gamma_i = \Sigma a_i l_i s_i \overline{\cos (l_i s_i)} \tag{2}$$

In general the angle between each s_i and its corresponding l_i is now no longer constant, and consequently the mean value of the cosine of the angle between the two must be introduced. In the case of normal multiplets it is known that all values of s_i combine to yield one resultant s, and likewise all values of l_i combine independently to form one resultant l. In this case it is easily shown that the mean cosine between each s_i and its corresponding l_i may be written:

$$\overline{\cos (s_i l_i)} = \overline{\cos (s_i s)} \cos (sl) \overline{\cos (l_i l)} .$$

Substituting in Eq. (2) we obtain for the total interaction energy:

$$\Gamma = ls \cos (ls) \Sigma a_i (s_i/s) \overline{\cos (s_i s)} (l_i/l) \overline{\cos (l_i l)} = Als \cos (ls) . \tag{3}$$

If the value of ls cos (ls) for a particular multiplet is substituted in this formula, we obtain:**

$$\Gamma = Als \cos (ls) = \tfrac{1}{2} A \left[j(j+1) - l(l+1) - s(s+1) \right] \tag{4}$$

The symbol j indicates the resultant of s and l as defined above. It is therefore the total impulse moment of the atom in the given state; Eq. (4) obviously gives us also the well-known interval rule of Landé. In his treatment of the Paschen-Back effect, Landé[8] has investigated the relationships which connect these Γ factors for multiplets in a weak magnetic field with their values in a strong magnetic field, without being able however to make a study of their deeper significance at that time. He found that these Γ factors obey laws similar to those governing the behavior of the magnetic separation factors, denoted by g, which have been investigated in this connection by Pauli.[9] In the celebrated article on the building up of electron groups, referred to above, Pauli has also studied the building up of the g values of an atom from those of the individual electrons. We will now give our attention to a similar investigation of the Γ values, in order to obtain in this manner the results given above.

We must however first call attention to an interesting study by Slater,[10]

** First determined half empirically by Landé and later verified by new mechanics.

[6] A. Landé, Zeits. f. Physik **19**, 112 (1923).

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

[8] A. Landé, Zeits. f. Physik **19**, 112 (1923).

[9] W. Pauli, Zeits. f. Physik **16**, 155 (1923).

[10] J. C. Slater, Phys. Rev. **28**, 291 (1926).

who has attacked this problem from the same standpoint. Slater attempted to determine the values of the cosines in Eq. (3) with the aid of the vector model of the atom. We are of the opinion however that his results are not sufficiently conclusive. For instance he assumes that the cosine between every s_i and the resultant s of all values of s_i is always equal to $+1$ or -1. It is known however that when two quantum vectors are parallel in our nomenclature, it is not at all assured that the cosine as given by the new quantum mechanics must be $+1$ or -1. In fact this is almost always not the case. His results are consequently not entirely trustworthy, and valid in part only for large quantum numbers.

THE SIGNIFICANCE OF THE Γ FACTORS IN THE SPECTRUM

We will now investigate what part the Γ factors play in the structure of a spectrum. In a doublet level the two states are separated by just the difference between their Γ values, if no external field is present. If then Γ were equal to zero, the two doublet levels would fall together. Consequently the Γ values give the displacement of the actual levels from a hypothetical level, which would be realized if the interaction energy between the spin of each electron and its orbital magnetic field were neglected.

Furthermore in the case of any normal multiplet other than a doublet, the energies of the different levels differ only by their Γ values, since only the angle between the resultant s and the resultant l is changed. Therefore when we consider the group of levels belonging to a given multiplet, a particular value of Γ gives the displacement of the corresponding level from a certain hypothetical level, which, as may be easily shown by the interval rule of Landé as given in Eq. (4) above, lies exactly at the centre of gravity of the multiplet.

The Γ values of the different levels of a given multiplet may also be calculated with the aid of Eq. (4), in terms of A (which is the only unknown) if Γ is known for one of the levels. A little farther on we will show how Γ can be determined in certain cases for one of the levels of a multiplet. Two examples will illustrate the use of this formula. For a ^3P state, where $s=1$, $l=1$, $j=2, 1, 0$,

$$^3P_2,\ \Gamma=+A\quad {}^3P_1,\ \Gamma=-A\quad {}^3P_0,\ \Gamma=-2A.$$

For a ^4F state, where $s=1\frac{1}{2}$, $l=3$, and $j=4\frac{1}{2}$, $3\frac{1}{2}$, $2\frac{1}{2}$, $1\frac{1}{2}$; $^4F_{4\frac{1}{2}}$, $\Gamma=+4\frac{1}{2}$; $^4F_{3\frac{1}{2}}$, $\Gamma=0$; $^4F_{2\frac{1}{2}}$, $\Gamma=-3\frac{1}{2}A$; $^4F_{1\frac{1}{2}}$, $\Gamma=-6A$. A further consequence is that, in the case of all states consisting of a single level, that is, where either $s=0$ or $l=0$, Γ is equal to zero.

Of course all this is valid only when it is assumed that the multiplets show no more than small deviations from the Landé interval rule. In the case of a spectrum in which the levels are no longer arranged in multiplets at all, it may still be asserted however that Γ represents the separation of the levels from a hypothetical level, which would be realized if the interaction between the electron spin and the orbital motion were equal to zero.

EFFECTS OF WEAK AND STRONG MAGNETIC FIELDS UPON THE Γ FACTORS

According to the theory of the Zeeman effect, when the source of radiation is in a weak magnetic field, the vector representing the total impulse moment j of the atom has definite quantized orientations with respect to the direction of the field, while the angle between s and l remains unchanged. For a given value of j the values of Γ are consequently independent of the projection m of j upon the direction of the field and are the same as without a magnetic field.

In a strong magnetic field however, where the Paschen-Back effect occurs, the coupling between resultant s and resultant l is broken. Each has its own set of quantized orientations in the field, and each yields its own set of projections on the magnetic field, indicated respectively by m_s and m_l. In this case the angle between s and l is no longer constant and the mean cosine of this angle has now a different value from that in the weak field. It may be found easily that the mean cosine between s and l is given in this case by

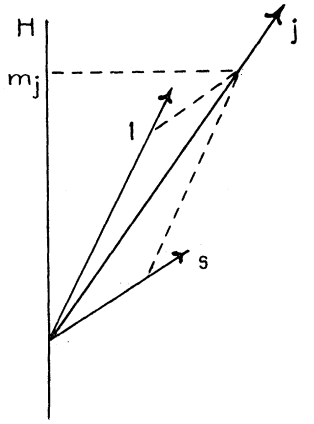

Fig. 1.

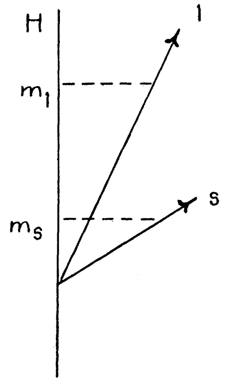

Fig. 2.

$$\overline{\cos(sl)} = \cos(sH)\cdot\cos(lH) = (m_s/s)(m_l/l)$$

In the case of a strong magnetic field the Γ values are therefore given by the formula:

$$\Gamma = Als\,\overline{\cos(ls)} = Am_s m_l. \tag{5}$$

Table IV gives the Γ values for a weak and a strong magnetic field for the simple case of a ^3D term, where $s=1$ and $l=2$. They are arranged in the table according to the values of the total projection m. In the case of a weak field m is simply the projection of j, while for the strong field it is given by $m=m_s+m_l$. The values for the weak field are therefore calculated by Eq. (4):

$\Gamma = Als\cos(ls) = \frac{1}{2}A\,[j(j+1)-l(l+1)-s(s+1)]$, where $l=2$, $s=1$, $j=3, 2, 1$.

We obtain the values of Γ for the strong field by Eq. (5):

$$\Gamma = Als\overline{\cos(ls)} = Am_sm_l, \quad \text{where } m_s = \pm 1, 0\ ;\ m_l = \pm 2, \pm 1, 0.$$

TABLE IV. Γ *values for* ^3D.

$m=$	-3	-2	-1	0	$+1$	$+2$	$+3$	
$j=3$	$+2A$	$+2A$	$+2A$	$+2A$	$+2A$	$+2A$	$+2A$	
$j=2$		$-A$	$-A$	$-A$	$-A$	$-A$		weak
$j=1$			$-3A$	$-3A$	$-3A$			field
$\Sigma\Gamma=$	$+2A$	$+A$	$-2A$	$-2A$	$-2A$	$+A$	$+2A$	
$m_s=-1$	$+2A$	$+A$	0	$-A$	$-2A$			
$m_s=0$		0	0	0	0	0		strong
$m_s=+1$			$-2A$	$-A$	0	$+A$	$+2A$	field

A given sum of Γ values, which is found from one vertical column, is the same for the weak as for the strong magnetic field. This is the result of the investigation of Landé.

Instead of introducing the energy of interaction between electron spin and orbital magnetic field, the magnetic energy in the external field divided by the field strength could have been substituted. It is well known that for a weak field this may be expressed by

$$m \cdot g \frac{h}{2\pi} \frac{e}{2mc}, \text{ where } g = 1 + \frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$$

while for the strong field it is

$$(m_l + 2m_s) \cdot \frac{h}{2\pi} \cdot \frac{e}{2mc}.$$

Here again the sums of corresponding vertical columns are equal for the weak and strong fields, as Pauli has pointed out.

THE ASSEMBLING OF Γ VALUES

In order to calculate Γ values for cases of configurations of several electrons, it is necessary to make use of the same method which Pauli devised for the determination of g values, especially in the somewhat altered form introduced by the author[11] in which the quantum numbers, m_l and m_s were found to be useful.

Let it now be supposed that the atom is placed in a magnetic field so strong that the magnetic energy of each electron in the field is much stronger than the interaction energy of the electrons with one another. In that case to a first approximation each electron will orient itself in the field as if the other electrons were not present. The values of l_i and s_i for each electron

---

[11] S. Goudsmit, Zeits. f. Physik **32**, 794 (1925).

are now space quantized individually, so that each electron now has its own projections m_{l_i} and m_{s_i}, upon the direction of the field, subject however to the rule of Pauli that no two electrons may have all their quantum numbers exactly alike.

The Γ values of the entire atom are as before the sums of the γ_i values of the individual electrons. That is

$$\Gamma = \Sigma\gamma_i = \Sigma a_i m_{s_i} m_{l_i}. \tag{6}$$

A table of all possible values of Γ may now again be assembled for given values of the quantum numbers of the electrons, arranged according to the values of the total projection m. The values of m are found by adding together m_{l_i} and m_{s_i} for all the electrons in the configuration. That is

$$m = \Sigma(m_{l_i} + m_{s_i}). \tag{7}$$

There are thus as many m's as there are sets of quantum numbers m_{l_i} and m_{s_i} permitted by the Pauli restriction rule. These m values are not necessarily all different.

We now assert that the sum of all Γ values belonging to a definite value of m, is independent of the strength of the field. The corresponding result was announced by Pauli for the magnetic energies in an external field, divided by the strength of the field. We have succeeded with the help of these rules in determining the Γ values in certain isolated important cases.

THE Γ SUM RULE ILLUSTRATED BY THE CASE OF TWO EQUIVALENT p ELECTRONS

We will treat as an example the case of two equivalent p electrons. Then for both electrons, $l_1 = l_2 = 1$, and $s_1 = s_2 = \frac{1}{2}$. Since we have chosen both electrons equivalent, the factor a_i is also the same for both. In the first column of Table Va is given an assembly of all possible m_{l_i} and m_{s_i} values, which are so chosen according to the Pauli restriction rule that both electrons

TABLE Va. *Two equivalent p-electrons.*

m_{s_1}	m_{l_1}	m_{s_2}	m_{l_2}	γ_1	γ_2	m_s	m_l	m	Γ
$+\frac{1}{2}$	$+1$	$+\frac{1}{2}$	0	$+\frac{1}{2}a$	0	$+1$	$+1$	$+2$	$+\frac{1}{2}a$
	$+1$		-1	$+\frac{1}{2}a$	$-\frac{1}{2}a$	$+1$	0	$+1$	0
	0		-1	0	$-\frac{1}{2}a$	$+1$	-1	0	$-\frac{1}{2}a$
$+\frac{1}{2}$	$+1$	$-\frac{1}{2}$	$+1$	$+\frac{1}{2}a$	$-\frac{1}{2}a$	0	$+2$	$+2$	0
	$+1$		0	$+\frac{1}{2}a$	0	0	$+1$	$+1$	$+\frac{1}{2}a$
	$+1$		-1	$+\frac{1}{2}a$	$+\frac{1}{2}a$	0	0	0	$+a$
	0		$+1$	0	$-\frac{1}{2}a$	0	$+1$	$+1$	$-\frac{1}{2}a$
	0		0	0	0	0	0	0	0
	0		-1	0	$+\frac{1}{2}a$	0	-1	-1	$+\frac{1}{2}a$
	-1		$+1$	$-\frac{1}{2}a$	$-\frac{1}{2}a$	0	0	0	$-a$
	-1		0	$-\frac{1}{2}a$	0	0	-1	-1	$-\frac{1}{2}a$
	-1		-1	$-\frac{1}{2}a$	$+\frac{1}{2}a$	0	-2	-2	0
$-\frac{1}{2}$	$+1$	$-\frac{1}{2}$	0	$-\frac{1}{2}a$	0	-1	$+1$	0	$-\frac{1}{2}a$
	$+1$		-1	$-\frac{1}{2}a$	$+\frac{1}{2}a$	-1	0	-1	0
	0		-1	0	$+\frac{1}{2}a$	-1	-1	-2	$+\frac{1}{2}a$

never have the same complete set of quantum numbers. The second column gives the values of both γ_i's according to Eq. (5). The fourth gives the m values according to Eq. (7), and the last of the Γ values according to Eq. (6).

In Table IV we have already illustrated the operation of the Γ sum rule. We will now prepare two tables and make use of this rule to show how the sums of the Γ values may be calculated for the case under consideration. In Table Vb the values of Γ obtained in Va are arranged in vertical columns, according to the value of m with which each is associated, and the sums are calculated. We next consider the case of a weak field and recall that there will be a value of Γ for each value of j, but, since the interaction between l and s remains unaffected by the field, these values of Γ will be independent of m. (Compare Table IV) It is well known that a configuration of two p electrons yields two quantum states with $j=2$, one with $j=1$, and two with $j=0$. We indicate the corresponding Γ values by Γ_2', Γ_2'', Γ_1, Γ_0', and Γ_0'', respectively. These are assembled, in accordance with the considerations just given, in Table Vc. A comparison of Γ sums for like values of m yields us then

$$\Gamma_2'+\Gamma_2''=a/2\ ;\qquad \Gamma_1=-a/2\ ;\qquad \Gamma_0'+\Gamma_0''=-a.$$

TABLE Vb and c.

$m=$	-2	-1	0	$+1$	$+2$	
$m_s=+1$			$-\frac{1}{2}a$	0	$+\frac{1}{2}a$	b. strong field. $m_l=m-m_s$
$m_s=0$	0	$+\frac{1}{2}a$ $-\frac{1}{2}a$	$+a$ 0 $-a$	$+\frac{1}{2}a$ $-\frac{1}{2}a$	0	
$m_s=-1$	$+\frac{1}{2}a$	0	$-\frac{1}{2}a$			
$\Sigma\Gamma=$	$+\frac{1}{2}a$	0	$-a$	0	$+\frac{1}{2}a$	
$j=2$	Γ_2'	Γ_2'	Γ_2'	Γ_2'	Γ_2'	c. weak field
$j=2$	Γ_2''	Γ_2''	Γ_2''	Γ_2''	Γ_2''	
$j=1$		Γ_1	Γ_1	Γ_1		
$j=0$			Γ_0'			
$j=0$			Γ_0''			
$\Sigma\Gamma=$	$\Gamma_2'+\Gamma_2''$	$\Gamma_2'+\Gamma_2''+\Gamma_1$	$\Gamma_2'+\Gamma_2''+\Gamma_1+\Gamma_0'+\Gamma_0''$	$\Gamma_2'+\Gamma_2''+\Gamma_1$	$\Gamma_2'+\Gamma_2''$	

This method therefore enables us to calculate the sums of the Γ *values for those levels which have equal* j*'s*, just as Pauli has been able to treat the g sums. *These* Γ *sums will remain constant for all couplings.* The individual values of Γ can be determined however only in special cases, which we will discuss in what follows.

The most important application of the Γ sum rule is to be found in the Roentgen doublets. Here we have to do with a configuration of equivalent electrons, where just one is missing out of a complete group. In this case we find a double level, the doublet separation of which will in first approximation be due only to the interaction between the spin of each electron and its orbit. If we consider a group of electrons, of which each has the same given value of l_i, the doublet levels will be found to have the j values: $j=l+\frac{1}{2}, j=l-\frac{1}{2}$. If we now make a table for this case similar to our Table V, we will find the vales of Γ to be: $\Gamma=-l_ia_i/2$ and $\Gamma=+(l_i-1)a_i/2$, for j equal to $l_i+\frac{1}{2}$ and $l_i-\frac{1}{2}$ respectively. In this case the values of Γ are completely determined. We find no Γ sums because there are no different levels with the same j. The Γ values found are therefore independent of the kind of coupling, and the doublet separations will under all circumstances be

$$\Delta\nu=\Delta\Gamma=-(l_i+\tfrac{1}{2})a_i=-\frac{R\alpha^2 Z_{\text{eff}}{}^4}{n^3 l_i(l_i+1)}$$

or the modified form of this expression given above for penetrating orbits. The coupling will in fact be very different in different cases. For inner orbits and high nuclear charge we expect the total resultant j to consist of the individual j_i of each of the electrons. For outer orbits and lower effective nuclear charge however we expect the ordinary Russell-Saunders coupling to be valid. We now know that the same doublet formula holds nevertheless for all cases. The reasoning given here is thus the proper proof of the validity of the Sommerfeld formula for Roentgen doublets.

By adding an s electron to a multiplet state one can prove in exactly the same way that in certain cases the total separation of the resulting multiplet with highest multiplicity is also independent of the coupling. This is illustrated, for example, by the fact that in the neon and argon spectra the separation of the s levels with $j=2$ and $j=0$ is exactly constant through the whole series of levels and equal to the p doublet of the ion.[12]

THE INDIVIDUAL Γ VALUES

If we assume that the interaction between the spins of different electrons is much smaller than the interaction between the orbital magnetic field and the spin of each electron, then the individual Γ values for this case may be calculated in a simple manner. Moreover this special coupling affords a simpler method for the determination of Landé g sums, especially in cases of non-equivalent electrons.

With this coupling of the quantum vectors, each s_i and each l_i combine to form a resultant j_i. The γ_i value for each electron is calculated by Eq. (2a), and the sum of these values gives Γ for the whole atom. In our somewhat complicated example of two equivalent p electrons, j_i may have the value $1\frac{1}{2}$ or $\frac{1}{2}$. The corresponding γ_i values are $+\frac{1}{2}a_1$ and $-a_1$ respectively. If both electrons have $j_i=1\frac{1}{2}$, then $\Gamma=\gamma_1+\gamma_2=+a_1$. In this case the building rules of Pauli for two equivalent electrons give one state with the total impulse moment $j=0$, and one with $j=2$. If $j_i=1\frac{1}{2}$ for one electron and $j_i=\frac{1}{2}$ for the other, one state is obtained with $j=2$ and one with $j=1$, each with the Γ value, $\frac{1}{2}a_1-a_1=-\frac{1}{2}a_1$. If $j_i=\frac{1}{2}$ for each electron one state is obtained according to Pauli in which j is equal to zero, and for which Γ becomes $-2a_1$. These results may be tabulated as follows:

---

[12] S. Goudsmit and E. Back, Zeits. f. Physik **40**, 530 (1927).

$$\begin{array}{lllll}
p^2: & j_1=1\tfrac{1}{2} & j_2=1\tfrac{1}{2} & j=0 & \Gamma=\tfrac{1}{2}a_1+\tfrac{1}{2}a_1=a_1 \\
 & & & j=2 & \qquad\qquad\quad =a_1 \\
 & j_1=1\tfrac{1}{2} & j_2=\tfrac{1}{2} & j=2 & \Gamma=\tfrac{1}{2}a_1-\ a_1=-\tfrac{1}{2}a_1 \\
 & & & j=1 & \qquad\qquad\quad =-\tfrac{1}{2}a_1 \\
 & j_1=\tfrac{1}{2} & j_2=\tfrac{1}{2} & j=0 & \Gamma=-a_1-a_1=-2a_1 \\
 & & \text{For} & j=2 & \Sigma\Gamma=\tfrac{1}{2}a_1 \\
 & & \text{For} & j=1 & \Sigma\Gamma=-\tfrac{1}{2}a_1 \\
 & & \text{For} & j=0 & \Sigma\Gamma=-a_1.
\end{array}$$

In most spectra there is a different coupling of the quantum vectors, the Russell-Saunders[13] coupling, which is responsible for normal multiplets. The spin moments of the individual electrons, s_i, form one resultant s, and the orbital moments, l_i, form a single resultant l. The total resultant j is then obtained by the combination of s and l.

In the case of only two electrons the mean cosines appearing in Eq. (3) may be calculated very simply, since they are constant. This calculation may be carried out as follows:

$$\frac{s_1}{s}\cos(s_1s)=\frac{s_1(s_1+1)+s(s+1)-s_2(s_2+1)}{2s(s+1)}$$

$$\frac{l_1}{l}\cos(l_1l)=\frac{l_1(l_1+1)+l(l+1)-l_2(l_2+1)}{2l(l+1)}$$

Our example of two equivalent p electrons yields us then the following results in the case of the Russell-Saunders coupling:

$$\begin{array}{lllll}
{}^1S_0 & l=0 & s=0 & j=0 & \Gamma=0 \\
{}^1D_2 & \ =2 & \ =0 & \ =2 & \ =0 \\
{}^3P_2 & \ =1 & \ =1 & \ =2 & \ =+\tfrac{1}{2}a_1 \\
{}^3P_1 & \ =1 & \ =1 & \ =1 & \ =-\tfrac{1}{2}a_1 \\
{}^3P_0 & \ =1 & \ =1 & \ =1 & \ =-a_1.
\end{array}$$

The total separation of ${}^3P$ is therefore $+\tfrac{1}{2}a_1-(-a_1)=1\tfrac{1}{2}a_1$.

THREE EQUIVALENT *d* ELECTRONS

As soon as one has several equivalent electrons, more complicated methods must be employed, in order to be able to determine the separate Γ values for important cases of the Russell-Saunders coupling. We give here only one example, that of three equivalent d electrons.

If complete tables are made for this example corresponding to Tables Va, Vb, and Vc, for the other example, the following results are obtained:

---

[13] H. N. Russell and F A Saunders, Astrophys. J. **61,** 38 (1925).

1 Level for which $j=5\frac{1}{2}$, $\Gamma=\frac{1}{2}a_1$
3 Levels “ “ $j=4\frac{1}{2}$, $\Sigma\Gamma=1\frac{1}{2}a_1$
3 “ “ “ $j=3\frac{1}{2}$, $\Sigma\Gamma=-a_1$
4 “ “ “ $j=2\frac{1}{2}$, $\Sigma\Gamma=0$
4 “ “ “ $j=1\frac{1}{2}$, $\Sigma\Gamma=-2\frac{1}{2}a_1$
3 “ “ “ $j=\frac{1}{2}$, $\Sigma\Gamma=-1\frac{1}{2}a_1$.

The value of Γ is thus uniquely determined only in the case of the first level, for which $j=5\frac{1}{2}$. We obtain only the sums for the other values of j.

Let us now make the special assumption however, that we have here the Russell-Saunders coupling and consequently normal multiplets. This configuration will then give the following multiplets:

$$^4F',\ ^4P',\ ^2H',\ ^2G,\ ^2F',\ ^2D,\ ^2D,\ ^2P'.$$

If we take as unknowns the single values of A corresponding to each of these normal multiplets, we can express the Γ's in terms of these A values by means of Eq. (4). We thus have eight unknowns and the determined Γ sums give us only six equations for them. Moreover these equations will be found to be not independent. For example we cannot separate the unknown A values for the two expected ^2D states. We must therefore first apply another method.

This is to make use of the fact that, if each multiplet is considered separately, the sums of the Γ values will be the same in weak and strong magnetic fields, as is also the case with the g values. We would be prepared to apply this method if we could only tell which configurations from the table, constructed for this example after the manner of Table V, would give a certain one of these multiplets. This is not possible for all configurations, but for just a sufficient number to determine the values of A for our multiplets.

If we consider for instance the ^4F level in a strong magnetic field, among the levels which arise there is one with the projections $m_l=3$ and $m_s=3/2$, giving $m=4\frac{1}{2}$. This level originates from the $^4F_{4\frac{1}{2}}$ level, that being the only one which can have $m=4\frac{1}{2}$. Now indeed our table, alluded to above, gives one configuration for which

$$m_s=\Sigma m_{s_i}=1\tfrac{1}{2},\ \text{and}\ m_l=\Sigma m_{l_i}=3,$$

viz. $m_{s_i}=m_{s_2}=m_{s_3}=+\frac{1}{2}$; and $m_{l_1}=2$, $m_{l_2}=1$, $m_{l_3}=0$.

For this configuration we find: $\Gamma=\Sigma a_1 m_{l_i} m_{s_i}=1\frac{1}{2}a_1$. As this is the only one of the ^4F levels with $m=4\frac{1}{2}$, this Γ will be the same in a weak field and it follows thus that $\Gamma=1\frac{1}{2}a_1$ for $^4F_{4\frac{1}{2}}$. If we denote the A value of this multiplet by $A\,(^4F)$, we find from Eq. (4) and the example on page 5, $A\,(^4F)=a_1/3$, and for the total separation

$$\Delta\nu=10\tfrac{1}{2}A\,(^4F)=7a_1/2$$

We use the same process once more to determine Γ for the ${}^4P_{2\frac{1}{2}}$ level. After that we can finally use the six equations given by the determined Γ sums and find the results as given in Table I. This example is the most complicated one. In the other cases the results can be obtained much more simply but by using the same methods.

The author wishes to express his thanks to Dr. Laporte for many valuable discussions which have given impetus to the present paper.

Department of Physics,
University of Michigan.
January, 1928.*

---

* Received March 14, 1928. Ed.