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THEORY OF HYPERFINE STRUCTURE SEPARATIONS*

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Abstract

Expressions are derived for the hyperfine structure separations of the levels of complicated electron configurations in different types of coupling. The few available experimental data are in distinct disagreement with the theoretical calculations. This undoubtedly means that our present knowledge of the interaction with nuclear spin is incomplete. The expressions in this article are derived by the well-known method of the invariance of energy sums.

1. Description of Method

FORMULAE for the interaction energy of a nuclear magnetic moment with a single electron outside of closed electron groups have been given by Fermi,¹ Casimir,² Hargreaves,³ and Breit.⁴ If more than one electron is present besides complete groups the formulae are only known for a special case. They have been derived when only *s*-electrons interact appreciably with the nuclear magnetism and the interaction of other electrons may be neglected.⁵ This paper is a first attempt to treat the general case of the interaction of several electrons with the nuclear magnetic moment.

The method followed in this paper is very analogous to the one used to derive expressions for multiplet separations.⁶ It therefore is the well-known method of the energy sums, which originally goes back to work of Pauli⁷ and which found its representation in modern quantum mechanics in an important article by Slater.⁸ We will follow closely Slater's procedure, as it shows especially clearly the restrictions of the validity of the results to be obtained.

* The problem studied in this paper was started in the spring of 1927 at Copenhagen in cooperation with L. Pauling, with whom I later corresponded occasionally about the questions involved and to whom I owe many valuable suggestions.

¹ E. Fermi, Zeits. f. Physik **60**, 320 (1930).

² H. Casimir, quoted in Pauling and Goudsmit, Structure of Line Spectra, page 225. Also Phys. Rev. in preparation.

³ Hargreaves, Proc. Roy. Soc. A127, 141 (1930).

⁴ G. Breit, Phys. Rev. 37, 51 (1931).

⁵ S. Goudsmit and R. F. Bacher, Phys. Rev. 34, 1501 (1929).

⁶ S. Goudsmit, Phys. Rev. 31, 946 (1928).

⁷ W. Pauli, Zeits. f. Physik 16, 155 (1923).

⁸ J. C. Slater, Phys. Rev. 34, 1293 (1929).

The application of the method of sums goes as follows. One thinks the interaction between the electrons to be removed, in order that each electron can be treated as independent of the others. For certain purposes one may also imagine the interaction between the spin of each electron and its own orbit to be absent. One can think this done by the introduction of a fictitious very strong magnetic field, which should break all couplings between the electrons or their quantum vectors. One now calculates under these circumstances the perturbation energy in which one is interested for each electron separately.⁹

Each state of the complete atom is now characterized by a large set of quantum numbers, each of which can be said to refer to a particular electron.¹⁰ For this state one finds the total perturbation energy by simply adding together the perturbations of the individual electrons. If one next considers the *sum* of the perturbation energies for *all* states having the same total projection of angular momentum M (in units $h/2\pi$) on the direction of the proper interactions, which were at the start thought to be absent (or, which is the same, after one reduces the applied strong fictitious magnetic field to a weak one).

This last sentence contains the fundamental principle of the sum rules, as it can be derived from quantum mechanics. It holds only for first order perturbations and moreover as it stands it does not give much information, because the sums are to be taken over all states of the atom. In order to get further results out of this sum rule one must make, according to Slater, certain approximations. It is assumed then that the above stated sum rule will hold if one takes the sum only over the states belonging to one electron configuration.¹¹ This may become quite incorrect when the levels arising from the configuration considered intermix with those of other configurations. This, for instance, is one of the reasons why the relations derived by Slater are not fulfilled very well in the actual spectroscopic data.¹² For special perturbations one can sometimes even go one step further with approximations. Slater, in his above quoted paper, purposely neglects the spin-orbit interaction of each electron. This causes the spins to be independent of the orbital angular momenta. Instead of considering the sum of the perturbation energies for a fixed value of the total projection M, he may consider the sum for the states which

⁹ In the above quoted paper of Pauli this was the interaction energy with an external magnetic field, giving rise to the *g*-sum rule. In the paper on multiplet separations by the present author the spin-orbit interaction was considered, resulting in the Γ -sum rule. Slater treated the interaction between the electrons and it is clearly seen from his paper that his results are obtained by first calculating this interaction for each pair as if it did not disturb the approximate independence of the different electrons. The sum rules finally gave the generally valid relations between multiplet distances.

 10 In the case of a nuclear moment $Ih/2\pi$ the nuclear quantum numbers I and m_I must be added also to this set.

¹¹ One calls a configuration the assembly of states for which each electron has the quantum numbers n and l fixed. Two states for which one of the electrons has a different n or l are said to belong to different configurations.

¹² Compare on this point a recent paper by E. U. Condon, Phys. Rev. 36, 1121 (1930).

have a fixed value of both M_s and M_L , the total projection of all spins and all orbits respectively. Each of these sums, which are a part of the total sum for a fixed M, will be invariant. This approximation holds only when the spin-orbit interaction is indeed negligibly small compared to the interaction between different electrons, the case in which Slater is interested. This means that one expects to obtain extreme Russell-Saunders coupling.¹³

In order to make use of the method described here it is obviously necessary to know the effect of the perturbation on one single electron considered as independent of the others.¹⁴ This will be considered in the following section.

In most cases the hyperfine structure is smaller than any other one of the interactions present in the atom. It is possible to apply a magnetic field which will just decouple the nuclear spin from the rest of the atom, giving each an independent projection on the field direction, M_I and M_J . From the theory of the Zeeman effect of hyperfine structure¹⁵ one knows that the interaction between the nucleus and the electron core under those circumstances is given by

$$W = A(J) \cdot M_I M_J. \tag{1}$$

The constant A in front is exactly the one which will govern the magnitude of the hyperfine multiplet of that particular level after one removes the magnetic field. That is, the levels of the hyperfine multiplet are given by

 $W_J = A(J)IJ \cos(I, J) = \frac{1}{2}A(J) \left\{ F(F+1) - I(I+1) - J(J+1) \right\}$ (2)

Here F denotes as usual the resultant of I and J.

As we are finally interested in the magnitude of just that factor A, we may all the time think that there is such a field present which causes M_I and the total projection of the core to be independent. This simplifies our calculation very much. We do not need to calculate the sums for all states with the same total $M_F = M_I + M_J$. According to Slater the sum rules will also be valid for the smaller group of states which have a fixed value for both M_I and M_J . We take therefore in the following procedure a particular value of M_I in our mind and extend the sums over levels with a fixed value of M_J .

It has to be kept in mind that the independence of M_I and M_J can only be used in case their interaction is indeed very much smaller than any of the other interactions which are to be taken into account. One can not use it, for instance, in the case of ionized Lithium. Here the hyperfine structure happens to be of the same order of magnitude as the multiplet splitting.¹⁶

2. Interaction between a Single Electron and a Nuclear Magnetic Moment

The interaction of a magnetic nucleus and an electron in an *s*-state has been treated in detail before. The energy happens to be simply proportional

¹³ If one needs information about the interaction between electrons in a case of (j, j) coupling one has to alter the procedure followed by Slater somewhat.

¹⁴ In Slater's special case one needs it for each electron *pair*.

¹⁵ E. Back and S. Goudsmit, Zeits. f. Physik **47**, 174 (1928), see also Pauling and Goudsmit. reference 2, p. 215.

¹⁶ S. Goudsmit and D. R. Ingli, Phys. Rev. 37, 283 (1931).

to the Landé cosine between the spin s of the electron and the nuclear moment I. It is therefore possible to treat the cases where an s-electron is a part of a configuration, completely with the vector model. We will now consider the case of a non-s electron.

We think the spin-orbit interaction to be removed (or apply a fictitious strong magnetic field). In the classical theory the interaction energy consists of two parts. The nuclear magnetic moment is acted upon by a magnetic field caused by the orbital motion of the electron and also by a field produced by the electron spin. According to perturbation theory one must write down the instantaneous values for the interaction energy and must average this over the unperturbed motion. The expression for this interaction energy is:¹⁷

$$W_{l} + W_{s} = a \left[ll \cos(I, l) - Is \cos(I, s) + 3Is \cos(I, r) \cos(r, s) \right].$$
(3)

The factor a in front of this expression governs the absolute magnitude of the interaction energy. We are not interested in it for our problem. For a hydrogenic orbit its value is given by

$$a = \left(\frac{eh}{4\pi m_0 c}\right)^2 g(I) \left(\frac{1}{r^3}\right) = \frac{Rhc\alpha^2 Z^3}{n^3 l(l+\frac{1}{2})(l+1)} g(I) \,. \tag{4}$$

The symbols used in Eqs. (3) and (4) have the usual meaning, r denotes the radius vector combining the nucleus with the electron, g(I) stands for the Landé g value of the nucleus and as the nuclear magnetism is believed to arise from protons, one expects g(I) to be only of the order 1/1840.

We start out with the case where we neglect all interactions between the quantum vectors; these will each have independent projections on the direction of the fictitious field H. These projections we denote by M_I , m_l and m_s , the nuclear, the orbital and the spin moment respectively. The vectors I, l and s will have independent Larmor precessions about the field direction and we can therefore expand the cosines of Eq. (3) and obtain:

$$W_{l} + W_{s} = a \left[M_{I} m_{l} - M_{I} m_{s} \left\{ 1 - 3 \overline{\cos^{2} (H, r)} \right\} \right].$$
(5)

Our problem thus reduces to finding the average of $\cos^2(H, r)$. In the classical picture with a plane orbit the vector r would be at any time perpendicular to the angular momentum vector l. This, however, is no longer true in quantum mechanics. The relative probability that r makes an angle θ with the field direction is given by the square of the tesseral harmonic $P_l^{m_l}(\cos \theta)$. Thus the required average becomes

$$\overline{\cos^2(H, r)} = \int_0^{\pi} \cos^2 \theta [P_l^{m_l}]^2 \sin \theta d\theta / \int_0^{\pi} [P_l^{m_l}]^2 \sin \theta d\theta$$

$$= \frac{2(l^2 - m_l^2) + 2l - 1}{(2l - 1)(2l + 3)}.$$
(6)

¹⁷ L. Pauling and S. Goudsmit, reference 2, p. 205.

Substituting this in Eq. (5) gives finally

$$W = W_{l} + W_{s} = aM_{I} \left\{ m_{l} - m_{s} \frac{6m_{l}^{2} - 2l(l+1)}{(2l-1)(2l+3)} \right\}.$$
 (7)

One verifies easily that for large values of l Eq. (6) approaches the classical result: $\frac{1}{2} \sin^2(l, H) = (l^2 - m_l^2)/2l^2$.

Expression (7) will be the fundamental formula for all further applications. It is, however, not valid for s-electrons.

3. THE SUM RULE APPLIED TO ONE ELECTRON

The application of the sum rule and Eq. (7) to the case of a single electron provides a very simple derivation of the results obtained by Fermi, Casimir, Hargreaves and Breit. It also gives an illustration of the method before we apply it to the many electron case. A single electron gives rise to a doublet state, one level with $j_1=l+\frac{1}{2}$, the other with $j_2=l-\frac{1}{2}$. In a weak magnetic field, which just decouples the nuclear spin, the interaction with the nuclear magnetism is (compare Eq. (1)):

$$W_{j_1} = a' M_I m_{j_1}$$
 and $W_{j_2} = a'' M_I m_{j_2}$. (8)

In a very strong magnetic field this interaction is (Eq. (7)):

$$W = aM_{I} \left\{ m_{l} - m_{s} \frac{6m_{l}^{2} - 2l(l+1)}{(2l-1)(2l+3)} \right\}.$$
(9)

The sum rule says that, keeping M_I fixed, the sums of the energies for all levels with a given value of $m_i = m_s + m_l$ must come out the same, whether we use Eq. (8) or (9). We choose first $m_i = l + \frac{1}{2}$. This occurs only once; in (8) for j_1 and in (9) when $m_l = l$ and $m_s = +\frac{1}{2}$. The sum rule states

$$a'M_{I} \cdot (l + \frac{1}{2}) = aM_{I} \left\{ l - \frac{1}{2} \frac{6l^{2} - 2l(l+1)}{(2l-1)(2l+3)} \right\}.$$
 (10)

One obtains at once

$$a' = a \frac{l(l+1)}{(l+\frac{1}{2})(l+1\frac{1}{2})} = a \frac{l(l+1)}{j_1(j_1+1)}$$
(11)

Next we choose $m_j = l - \frac{1}{2}$. This occurs twice, namely in (8) both for j_1 and j_2 , and in (9) for $m_l = l$, $m_s = -\frac{1}{2}$ and $m_l = l - 1$, $m_s = +\frac{1}{2}$. Applying the sum rule gives

$$a'M_I \cdot (l - \frac{1}{2}) + a''M_I \cdot (l - \frac{1}{2})$$
(12)

$$= aM_{I}\left\{l + \frac{1}{2} \frac{6l^{2} - 2l(l+1)}{(2l-1)(2l+3)}\right\} + aM_{I}\left\{(l-1) - \frac{1}{2} \frac{6(l-1)^{2} - 2l(l+1)}{(2l-1)(2l+3)}\right\}$$

As we know a' already we can solve for a'' and find

$$a'' = a \frac{l(l+1)}{(l-\frac{1}{2})(l+\frac{1}{2})} = a \frac{l(l+1)}{j_2(j_2+1)}$$
(13)

These expressions for a' and a'' are indeed identical with the results obtained by other authors. Substituting them in Eq. (2) gives the hyperfine structure in the absence of a field. The result shows that for the two levels of a doublet the interval constant of the hyperfine structure is inversely proportional to j(j+1). The absolute magnitude can only be given when the constant a can be calculated. This would require an exact knowledge of the eigenfunctions of the state under consideration. For penetrating orbits one can make the same kind of an approximation as was applied by Landé to the calculations of doublet separations. One obtains for such cases, instead of Eq. (4), the approximate expression

$$a = \frac{Rhc\alpha^2 Z_i Z_0^2}{n_e^3 l(l+\frac{1}{2})(l+1)} g(I).$$
(14)

In this expression Z_i and Z_o stand for the effective nuclear charge in the inner and outer part of the orbit respectively, n_e represents the "effective" quantum number or Rydberg denominator.

4. The Sum Rule Applied to Configurations

We will give as an illustrative example the case of three equivalent pelectrons. The first column of Table I gives the values of m_s and m_l for the individual electrons, chosen in agreement of course with the Pauli exclusion principle. The quantum numbers l and n are supposed to be the same for all three electrons and are therefore omitted from the table. We need only to consider the states which give rise to positive values of the total projection M_J , given in the second column, negative values of M_J do not give any additional information. The last column gives the interaction with the nuclear magnetism obtained by applying Eq. (9) to each electron individually and adding the result for the three together. As they are equivalent electrons they have the same constant a.

$m_{s_1} m_{l_1}$	$m_{s_2} m_{l_2} m_{s_3}$	m ₁₃ M _J	Eq. (7)	
$\frac{1}{2}$ 1	$\frac{1}{2}$ 0 $-\frac{1}{2}$	1 2 ¹ / ₂	$2\frac{2}{5} aM_{I}$	
$ \frac{\frac{1}{2}}{\frac{1}{2}} 1 \frac{1}{2} 1 \frac{1}{2} 1 \frac{1}{2} 1 $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$\begin{array}{ccc} 0 & a M_{I} \\ \frac{4}{5} & a M_{I} \\ \frac{4}{5} & a M_{I} \\ 1 \frac{3}{5} & a M_{I} \end{array}$	$\sup_{\substack{\mathfrak{3}\frac{1}{5}\ aM_{I}}}$
$\begin{array}{cccc} \frac{1}{2} & 1 \\ \frac{1}{2} & 1 \\ \frac{1}{2} & 0 \\ \frac{1}{2} & 0 \\ \frac{1}{2} & 1 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c c} -1 & & 1\\ 0 & & \\ 1 & & \\ 0 & & \\ -1 & & \\ \end{array} $	$\begin{array}{c} \frac{2}{5} \ aM_{I} \\ -\frac{2}{5} \ aM_{I} \\ \frac{3}{5} \ aM_{I} \\ \frac{1}{5} \ aM_{I} \\ 1\frac{1}{5} \ aM_{I} \end{array}$	$\sup_{\substack{2\frac{2}{5} aM_I}}$

TABLE I. Interaction for p^3 in strong field.

The states in the table are ordered according to their values of M_J . The configuration gives rise to five levels, one with $J=2\frac{1}{2}$, three with $J=1\frac{1}{2}$ and one with $J=\frac{1}{2}$. We want to know the constants A for each of these levels and shall denote them by $A(2\frac{1}{2})$, $A(1\frac{1}{2})$, $A''(1\frac{1}{2})$, $A''(1\frac{1}{2})$ and $A(\frac{1}{2})$ respectively.

The sum rule applied to the projection $M_J = 2\frac{1}{2}$, which occurs only once, gives

$$A(2\frac{1}{2}) \cdot M_I \cdot 2\frac{1}{2} = 2\frac{2}{5}aM_I. \tag{15}$$

The projection $M_J = 1\frac{1}{2}$ occurs four times, namely $J = 2\frac{1}{2}$ as well as all three levels with $J = 1\frac{1}{2}$ can give this projection on the field direction. It also occurs four times in Table I. The sum rule gives

$$\left\{A(2\frac{1}{2}) + A(1\frac{1}{2}) + A'(1\frac{1}{2}) + A''(1\frac{1}{2})\right\}M_I \cdot 1\frac{1}{2} = 3\frac{1}{3}aM_I.$$
 (16)

Finally $M_J = \frac{1}{2}$ occurs five times, giving

 $\left\{A(2\frac{1}{2}) + A(1\frac{1}{2}) + A'(1\frac{1}{2}) + A''(1\frac{1}{2}) + A(\frac{1}{2})\right\}M_{I} \cdot \frac{1}{2} = 2\frac{2}{5}aM_{I}.$ (17)

Solving these equations one obtains finally

$$\begin{array}{ccc} A(2\frac{1}{2}) &=& {}^{24}/{}_{25}a \\ A(1\frac{1}{2}) + A'(1\frac{1}{2}) + A''(1\frac{1}{2}) &=& 1{}^{13}/{}_{75}a \\ A(\frac{1}{2}) &=& 2\frac{2}{3}a \end{array} \right\}$$
(18)

Exactly as in the case of the well-known g-sum rule we are only able to obtain the sum of the A's for the levels with the same value of J. That we find the individual values for the levels with $J=2\frac{1}{2}$ and $J=\frac{1}{2}$ is because there is only one level with each of these J values.

The values of the individual A's will in general depend upon the type of coupling between the quantum vectors of the electrons, just as in the case of g-values. The method to obtain their values for extreme couplings will be described in following sections of this paper.

It is not at all difficult to make a table like Table I for any other example. When the electrons are not equivalent each has a different constant a which one has to carry along into the final result. We want to mention once more that most of the formulae used here are only valid for the interaction of a non-s electron with the nuclear magnetism. For an s electron one has to replace Eq. (7) by the simple expression

$$W = bM_I m_s. \tag{19}$$

Here follow the results for a number of configurations

TABLE II. Hyperfine structure sums.*

p and p^5	$J = 1\frac{1}{2}$	$A = \frac{8}{15}a$ $A = 2\frac{2}{3}a$	ps and p⁵s	J = 2	$A = \frac{2}{5}a + \frac{1}{4}b$ $\Sigma A = 2a + \frac{1}{4}b$
p^2 and p^4	J = 2 1 $I = 21$	$\Sigma A = 1\frac{3}{5}a$ $A = 0a$	p^2s and p^4s	$J = 2\frac{1}{2} \\ 1\frac{1}{2} \\ \frac{1}{2} $	$\begin{array}{l} \Sigma A = 1^{7/}{}_{25}a + \frac{2}{5}b \\ \Sigma A = 1^{23/}{}_{25}a - \frac{1}{15}b \\ \Sigma A = 0a + 1\frac{2}{5}b \end{array}$
P	$J = 2\frac{1}{2} \qquad A = \frac{24}{25a}$ $1\frac{1}{2} \qquad \Sigma A = 1\frac{13}{756}$ $\frac{1}{2} \qquad \Sigma A = 2\frac{2}{3}a$	$A \equiv \frac{3}{25}a$ $\Sigma A = 1^{13}/75a$ $\Sigma A = 2\frac{2}{3}a$	∲ ³ s	J = 3 2 1	$A = \frac{4}{5}a + \frac{1}{6}b$ $\Sigma A = 2a + \frac{7}{12}b$ $\Sigma A = 2\frac{4}{5}a - \frac{1}{4}b$

* The constant a refers to the p- and b to the s-electron.

5. Hyperfine Structure for Extreme (j, j) Coupling

The above described method gives only the sums of the factors which govern the hyperfine structure separations. Their individual values for each level are only determined completely in extreme couplings. The simplest case is that of extreme (j, j) coupling which we shall now discuss with the example of the p^3 configuration. We mean by extreme (j, j) coupling that the spin vector s of each electron is strongly coupled to its own orbital vector l and that therefore one can ascribe to each one of the electrons of the configuration its own resultant vector j. The spin-orbit coupling has to be considerably stronger than the interaction energy between the different electrons. It is then possible to think of an applied magnetic field which is strong enough to decouple the different electrons so as to make them independent of each other, but not yet strong enough to decouple the s and l for each of the electrons.

Under these ideal circumstances the quantum state of each electron will be characterized by the quantum numbers j and m_i , its resultant moment and the projection on the field, rather than by m_s and m_i . We now have to make again a table similar to Table I but now with the different designation for each electron. We also need to know what the interaction with the nucleus will be for each electron, when its state is characterized by j and m_i , that is when its spin and orbit are coupled. But this is just the problem solved in Section 3. Eq. (8) is the one we must use now, especially after we introduce for a' and a'' the results of Eqs. (11) and (13).

jı	m_{i_1}	$j_2 m_{i_2}$	$j_3 m_{j_3}$	M_J	Eq. (8)	
1 <u>1</u>	1 1	$1\frac{1}{2}$ $\frac{1}{2}$	$1\frac{1}{2}$ $-\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}a'M_I$	
	$1\frac{1}{2}$	$\frac{1}{2}$	1 ¹ / ₂	$\frac{1}{2}$	$\frac{1}{2}a'M_I$	
1 <u>1</u>	$1\frac{1}{2}$	$1\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	2 ¹ / ₂	$(2a' + \frac{1}{2}a'')M_I$	
	$1\frac{1}{2}$ $1\frac{1}{2}$	$-\frac{\frac{1}{2}}{\frac{1}{2}}$	$-\frac{1}{2}$ $\frac{1}{2}$	$1\frac{1}{2}$	$\begin{array}{c} (2a' - \frac{1}{2}a'')M_I \\ (a' + \frac{1}{2}a'')M_I \end{array}$	$\sup_{3a'M_I}$
	$1^{\frac{1}{2}}_{\frac{1}{2}}$	$-1\frac{1}{2} \\ -\frac{1}{2} \\ -\frac{1}{2}$		$\frac{1}{2}$	$(a' - \frac{1}{2}a''M_I) M_I (a' - \frac{1}{2}a'')M_I - \frac{1}{2}a''M_I$	$\sup_{(a'+\frac{1}{2}a'')M_I}$
$1\frac{1}{2}$	$1\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $-\frac{1}{2}$	112	$1\frac{1}{2}a'M_I$	
	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}a'M_I$	

TABLE III. Configuration p^3 in (j, j) coupling.

Table III represents the equivalent of Table I for the extreme (j, j) coupling. The example chosen is again the configuration p^3 . For reasons to be discussed later the values for a' and a'' have not been substituted.

In the ideal extreme case the electrons are quite independent of each other. Following Slater we therefore need not take the sums over all levels with a fixed value of the total M_J . The sum-rule will hold already for the levels which are designated by a special set of values of j and m_j for each of the electrons. If we choose a set of values for these quantum numbers it

happens that we find only one state in our table which possesses just this set. Thus we do not need to consider any sums at all and the third column of the table gives at once the correct value of the interaction with the nuclear spin for this extreme case.

We are, however, not yet finished. When we now gradually remove the field which decoupled the electrons, the quantum numbers m_i for the individual electrons will lose their significance and be converted together into the total M_J . In the extreme (j, j) coupling the values of j for each electron will keep their meaning. This means that for this last transition the sum rules will hold within each group of levels characterized by fixed values of the individual j, but no longer for the individual m_j . Table III has been arranged accordingly.



Fig. 1. Schematical representation of Paschen-Back effect for p^3 in extreme (j,j) coupling. (a) without field, quantum numbers: j_1 , j_2 , j_3 , J. (b) weak field, quantum numbers: j_1 , j_2 , j_3 , J, M_J . (c) strong field, quantum numbers: j_1 , j_2 , j_3 , m_{j_1} , m_{j_2} , m_{j_3} .

Figure 1 may help to understand the situation described above. At the left is shown the p^3 configuration in extreme (j, j) coupling. The highest level arises when all three electrons have maximum energy, that is when they all have $j=1\frac{1}{2}$. The next lower group occurs when one of the electrons has $j=\frac{1}{2}$. The lowest level has two electrons with $j=\frac{1}{2}$ and one with $j=1\frac{1}{2}$.¹⁸ The hyperfine structure is not included in the figure. Going to the right in Fig. 1 the effect of an applied magnetic field is represented. In a weak field each level splits into its Zeeman components. With increasing field strength each level group will undergo a Paschen-Back transition and the result is rep-

¹⁸ There exists here no lower state with all three electrons having $j = \frac{1}{2}$, because our example consists of equivalent electrons for which the Pauli principle allows only two with $j = \frac{1}{2}$. This also will be clear from considering Table III where all states are gathered which do agree with the Pauli principle. Compare Pauling and Goudsmit, l.c., page 257.

resented at the right of Fig. 1. Notice that the field does not yet break the coupling of each spin with its orbit, the three level groups are still distinctly separated. A further increase in the field would also break up this last coupling, all couplings would be broken and one would have the case represented in Table I. One sees that the right side of Fig. 1 is to be correlated with Table III. The sum rule as applied in Table III means simply that we may assume the sum rule for fixed M_J to hold within each level group separately in this extreme coupling. This gives us a means to go from the strong field to the intermediate field and to obtain our final information.

In this intermediate field, which we suppose just to decouple the nuclear spin from the rest of the atom, the interaction with the nucleus for each level will be given again by Eq. (1):

$$W = A M_I M_J.$$

Our problem is to find the value of A for each one of the many levels.

Applying the sum rule to the states which have $j_1 = j_2 = j_3 = 1\frac{1}{2}$, that is the upper level, we find at once

$$A(1\frac{1}{2}) = a'.$$

This result is found by choosing M_J either $1\frac{1}{2}$ or $\frac{1}{2}$.

For the middle group of levels, $j_1 = j_2 = 1\frac{1}{2}$, $j_3 = \frac{1}{2}$, one finds the following sums

$$\begin{split} M_J &= 2\frac{1}{2} \colon & A(2\frac{1}{2})M_I \cdot 2\frac{1}{2} = (2a' + \frac{1}{2}a'')M_I, \\ M_J &= 1\frac{1}{2} \colon & \left\{ A(2\frac{1}{2}) + A'(1\frac{1}{2}) \right\} M_I \cdot 1\frac{1}{2} = 3a'M_I, \\ M_J &= \frac{1}{2} \colon \left\{ A(2\frac{1}{2}) + A'(1\frac{1}{2}) + A(\frac{1}{2}) \right\} M_I \cdot \frac{1}{2} = (a' + \frac{1}{2}a'')M_I. \end{split}$$

From this one obtains

$$A(2\frac{1}{2}) = \frac{4}{5}a' + \frac{1}{5}a''; A'(1\frac{1}{2}) = 1\frac{1}{5}a' - \frac{1}{5}a''; A(\frac{1}{2}) = a''.$$

Finally the lowest level gives

$$A''(1\frac{1}{2}) = a'.$$

After one substitutes the values of a' and a'' from Eqs. (11) and (13) the results become

$$A(1\frac{1}{2}) = \frac{8}{15}a; \ A(2\frac{1}{2}) = \frac{24}{25}a; \ A'(1\frac{1}{2}) = \frac{8}{75}a; \ A(\frac{1}{2}) = 2\frac{2}{3}a; \ A''(1\frac{1}{2}) = \frac{8}{15}a.$$

As is to be expected the sums agree with those given in Section 4 and Table II.

6. Use of the Vector Model for Extreme (j, j) Coupling

When the spin and orbit of an electron are coupled the interaction with the nuclear magnetism is given by the Eq. (2)

$$W = a'Ij\cos(I, j) \quad \text{or} \quad a''Ij\cos(I, j). \tag{20}$$

The choice of a' or a'' depends on whether one considers the state with $j = l + \frac{1}{2}$ or the one with $j = l - \frac{1}{2}$. This simple expression brings it about that one often can use the vector model with advantage in extreme (j, j) coupling.

For several electrons the total interaction with the nucleus is

$$W = \sum a_k I j_k \overline{\cos(I, j_k)}.$$
(21)

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The sum has to be extended over all electrons, which we shall distinguish by the index k. As all j_k form together the resultant J one can average over their precession about this resultant and obtains

$$W = \sum a_k I j_k \cos(I, J) \overline{\cos(J, I j_k)}.$$
(22)

We may write this

$$W = AIJ \cos(I, J) \tag{23}$$

in which expression we finally want to know the value of

$$A = \sum a_k \frac{j_k}{J} \frac{1}{\cos(J, j_k)}.$$
 (24)

The problem is thus to evaluate the average cosines of each of the individual j_k with the resultant J. This can be done easily when only two j_k form the resultant J, but with more electrons it is in general impossible, unless we use again the method of sums instead of the vector model. For a restricted but interesting number of cases we can find relations between these cosines and the g values of the levels. The magnetic moment gJ of a state is given by the sum of the magnetic moments $g_k j_k$ of each electron resolved along the resultant J, thus

$$gJ = \sum g_k j_k \overline{\cos(J, j_k)}$$
 or $g = \sum g_k \frac{j_k}{J} \overline{\cos(J, j_k)}$. (25)

This defines the g value for this level. Futhermore, as J is the resultant of all j_k we have

$$J = \sum j_k \overline{\cos(J, j_k)} \quad \text{or} \quad 1 = \sum \frac{j_k}{J} \overline{\cos(J, j_k)}.$$
(26)

If we now restrict ourselves to the case of equivalent electrons the sums in expressions 24, 25 and 26 fall apart into two sums, one over the electrons with $j'=l+\frac{1}{2}$ and one over those with $j''=l-\frac{1}{2}$. We shall again denote these two kinds by a prime and a double prime. The formulae become

$$A = a' \sum_{J} \frac{j_{k'}}{J} \frac{1}{\cos(J, j_{k'})} + a'' \sum_{J} \frac{j_{k''}}{J} \frac{1}{\cos(J, j_{k''})}$$
(24a)

$$g = g' \sum \frac{j_k'}{J} \overline{\cos(\overline{J}, j_k')} + g'' \sum \frac{j_k''}{J} \overline{\cos(\overline{J}, j_k'')}$$
(25a)

$$1 = \sum \frac{j_k'}{J} \overline{\cos(J, j_k')} + \sum \frac{j_k''}{J} \overline{\cos(J, j_k'')}.$$
 (26a)

For equivalent electrons a', a'', g' and g'' can be placed before the summation, as they have the same value for each of the electrons inside any one sum.

We next can eliminate the two unknown sums between the three expressions and obtain finally

$$A = a' \frac{g - g''}{g' - g''} + a'' \frac{g - g'}{g'' - g'}$$
 (27)

The values of g' and g'' are the known g values for a single electron, the values of g to be used are those for the extreme (j, j) coupling of the configuration which we consider.¹⁹ For our standard example of the p^3 configuration the results are again:

$$g' = 1\frac{1}{3} \qquad g'' = \frac{2}{3}$$

$$J = 2\frac{1}{2} \qquad g = 1\frac{1}{5} \qquad A = \frac{4}{5}a' + \frac{1}{5}a''$$

$$J = \frac{1}{2} \qquad g = \frac{2}{3} \qquad A = a''$$

$$J = 1\frac{1}{2} \qquad g = 1\frac{1}{3} \qquad A = a' \qquad \text{upper level.}$$

$$1\frac{1}{2} \qquad g = 1^{7}/_{15} \qquad A' = 1\frac{1}{5}a' - \frac{1}{5}a'' \qquad \text{middle level.}$$

$$1\frac{1}{2} \qquad g = 1\frac{1}{3} \qquad A'' = a' \qquad \text{lower level.}$$

The addition of a single s electron to a level of which A is known can always be done with the vector model, provided the coupling is of the extreme (j, j) type. We denote with A^+ and J^+ the values for the state to which we add the s electron. The s electron itself is characterized by b and s, the resulting level finally by A and J. One obtains with the vector model

$$A = A + \frac{J^{+}}{J} \cos(J, J^{+}) + b \frac{s}{J} \cos(J, s).$$
(28)

Substituting the Landé cosines this becomes

$$A = A + \frac{J(J+1) + J^{+}(J^{+}+1) - s(s+1)}{2J(J+1)} + b \frac{J(J+1) + s(s+1) - J^{+}(J^{+}+1)}{2J(J+1)}.$$
(29)

One can simplify this formula if one considers that $s = \frac{1}{2}$ and that therefore J can only be $(J^+ + \frac{1}{2})$ or $(J^+ - \frac{1}{2})$. One can also again express A in terms of the g-values.

Table IV gives the results for a few configurations in extreme (j, j) coupling.

¹⁹ For equivalent electrons the g values for extreme (j, j) coupling can be obtained in general only with the help of the method of sums. This Section does therefore in reality not avoid the use of the sum rule, but it gives a connection between the hyperfine structure constants and the g values. The latter are considered to be better known and more easily derivable.

		j.		J^+	J	g	A
p^2	$1\frac{1}{2}$ $1\frac{1}{2}$	$1^{\frac{1}{2}}_{\frac{1}{2}}$			2 2 1	1 1 1 1 2	$\begin{array}{c} a' \\ \frac{3}{4}a' + \frac{1}{4}a'' \\ 1\frac{1}{4}a' - \frac{1}{4}a'' \end{array}$
₽ ³	1 <u>1</u> 1 <u>1</u> 1 <u>1</u>	$1\frac{1}{2}$ $1\frac{1}{2}$	$1\frac{1}{2}$		1 ¹ / ₂ 2 ¹ / ₂ 1 ¹ / ₂	$\begin{array}{c} 1\frac{1}{3} \\ 1\frac{1}{5} \\ 1^{7}/_{15} \\ \frac{2}{3} \end{array}$	$ \begin{array}{c} a' \\ \frac{4}{5}a' + \frac{1}{5}a'' \\ 1\frac{1}{5}a' - \frac{1}{5}a'' \\ a'' \end{array} $
	11/2	$\frac{1}{2}$	$\frac{1}{2}$		1 ¹ / ₂	1 ¹ / ₃	<i>a'</i>
ps	$1\frac{1}{2}$			112	2	1 ¹ / ₂	$\frac{\frac{3}{4}a' + \frac{1}{4}b}{1 + \frac{1}{4}a' - \frac{1}{4}b}$
	$\frac{1}{2}$			$\frac{1}{2}$	1		$\frac{1}{2}a'' + \frac{1}{2}b$
p^2s	11/2	$1\frac{1}{2}$		2	$2\frac{1}{2}$ $1\frac{1}{2}$	$1^{7/_{15}}$ $1^{\frac{1}{5}}$	$\begin{array}{c} \frac{4}{5}a' + \frac{1}{5}b\\ 1\frac{1}{5}a' - \frac{1}{5}b \end{array}$
	1 1/2	$\frac{1}{2}$			$2\frac{1}{2}$ $1\frac{1}{2}$ $1\frac{1}{2}$	$ \begin{array}{c} 2 \\ 1\frac{1}{3} \\ 1 \\ 1^{2} \end{array} $	$\begin{vmatrix} b \\ \frac{3}{5}a' + \frac{1}{5}a'' + \frac{1}{5}b \\ \frac{9}{10}a' + \frac{3}{10}a'' - \frac{1}{5}b \\ \frac{5}{5}a' + \frac{1}{5}a'' + \frac{1}{5}b \end{vmatrix}$
	1 2	$\frac{1}{2}$		0		$1\frac{3}{1}$ 2	$\begin{vmatrix} \frac{1}{6}a' & -\frac{1}{6}a' & +\frac{1}{3}b \\ \frac{5}{6}a' & -\frac{1}{6}a'' & -\frac{1}{3}b \\ b \end{vmatrix}$

TABLE IV. Hyperfine structure for (j, j) coupling.*

* The values of j_k are given for the p electrons only, the *s* electron has $j_k = \frac{1}{2}$. Levels with J = 0 are omitted. The results for the configurations p^5 , p^4 , p^5s , p^4s , are similar to the following ones in the same order p, p^2 , ps, p^2s .

7. Hyperfine Structure for Extreme Russell-Saunders Coupling

When the interaction between the different electrons of a configuration is very large compared to the interaction between the spins of the electrons and their orbital motion, one speaks of Russell-Saunders coupling. The spin vectors form together a resultant spin moment S, the orbital moments l form a resultant L and the total angular momentum vector J is the resultant of these two. To this one the nuclear spin I is again added to form the resultant F. This type of coupling yields the ordinary multiplet structure.

In the case of Russell-Saunders coupling one can imagine an applied magnetic field which is strong enough to overcome the coupling between the spins and orbits; that is, between the resultant S and the resultant L, but not yet strong enough to decouple the different electrons from each other. This situation is represented at the right of Fig. 2. The left of Fig. 2 gives the levels without magnetic field, whereas the middle shows them in an intermediate field. The strong field has caused a complete Paschen-Back effect for each of the multiplets, but the splitting up which it causes is supposed to be still small compared to the distances between the different multiplets. In this strong field each state will be characterized by the projections M_S and M_L of S and L on the field direction. As these two are supposed to have a negligible interaction under these circumstances, they will be independent and will restrict our sum rules. According to Slater's procedure the sums will now be invariant over states which have the same value of the pair of quantum numbers M_s , M_L . Table V shows the states of the example p^3 arranged in this order. This configuration yields a ${}^{4}S$, a ${}^{2}D$ and ${}^{2}P$ state. When we increase the field more

and more until it breaks the electron coupling, the total projection M_s of the resultant spin will remain invariant and can finally be interpreted as the sum



Fig. 2. Schematical representation of Paschen-Back effect for p^3 in extreme Russell-Saunders coupling. (a) without field, quantum numbers: L, S, J. (b) weak field, quantum numbers L, S, J, M_J . (c) strong field, quantum numbers L, S, M_L, M_S .

of the m_s of the electrons. In the same way M_L will be converted into the sum of m_l of the individual electrons. It is in this way that a certain pair M_s , M_L can be correlated to each of the states in Table V, simply

$$M_{S} = \sum m_{s}, \quad M_{L} = \sum m_{l}. \tag{30}$$

TABLE V. Configuration b³ in Russell-Saunders coupling

		LADL	E V. C	onjeguru		1143300	-Sunnue	rs coupung.	
m _{s1}	m_{s_2}	m _s 3	m_{l_1}	m_{l_2}	m_{l_3}	M_S	M_L	M _J	Eq. (7)
$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	1	0	1	$\frac{1}{2}$	2	2 ¹ / ₂	$2\frac{2}{5} aM_I$
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1	0	-1	$1\frac{1}{2}$	0	1 1/2	$0 a M_I$
$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	1 1	$0 \\ -1$	0 1	$\frac{1}{2}$	1	1 1/2	$\begin{array}{c} \frac{4}{5} & a M_I \\ \frac{4}{5} & a M_I \end{array}$
$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	1	0	-1	$-\frac{1}{2}$	2	$1\frac{1}{2}$	$1\frac{3}{5} aM_I$
$\frac{1}{2}$	1 <u>2</u>	$-\frac{1}{2}$	1 1 0	$ \begin{array}{c} 0 \\ -1 \\ -1 \end{array} $	$-1 \\ 0 \\ 1$	$\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{\frac{2}{5}}{\frac{4}{5}}\frac{aM_{I}}{aM_{I}}$ $-\frac{\frac{2}{5}}{\frac{2}{5}}\frac{aM_{I}}{aM_{I}}$
$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	0 1	1 1	0 -1	$-\frac{1}{2}$	1	12	$1\frac{1}{5} aM_{I}$ $1\frac{1}{5} aM_{I}$

With this table we hope to get information about the interaction with the nucleus for each multiplet if placed in a strong magnetic field. If we knew

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this we could again apply the sum rule to each multiplet separately and obtain the interaction in a weak field or without field. Table V does not help us much in this respect, however. The different states are labeled with M_s and M_L only and we do not know the values of S and L to which they belong. For instance the pair $M_s = \frac{1}{2}$ and $M_L = 0$ occurs three times. We do not know which one of these three belongs to the ${}^{4}S$, the ${}^{2}D$ or the ${}^{3}P$, which can each give this pair in a strong field. The answer to this question is that neither of the three belongs to any one of the multiplets. In the language of Slater's paper we should say that the energies entered in the last column of Table V have been calculated with eigenfunctions which do not take into account the interaction between the electrons. The correct eigenfunctions which can be associated with each multiplet are certain linear combinations of the ones which give the perturbation energies used here. The straightforward way to get further results is to use these linear combinations, which can be found in the literature,²⁰ and to use the quantum mechanics method for first order energy perturbations. In the following section we will describe a method, however, which does not involve the knowledge of the correct linear combinations of unperturbed eigenfunctions but uses certain general properties of multiplets.21

8. Hyperfine Structure of a Multiplet

The properties of a multiplet are in many respects a generalization of the properties of a doublet arising from a single electron. Darwin²² was very successful in explaining every detail of the magnetic properties of a multiplet by treating it as if it were a single electron with an orbital moment L and a spin moment S. It is obvious that not all characteristics of a multiplet state can be obtained in this way; for instance, one would find with Darwin's method that the transition $L \rightarrow L$ is forbidden, whereas in the correct theory it is not. As we are interested here in the magnetic interaction with the nucleus, it is possible that we may use again Darwin's simplification.

For the magnetic interaction with the nucleus we assume a generalization of Eq. (7):

$$W_L + W_S = \lambda M_I M_L - \sigma M_I M_S \frac{6M_L^2 - 2L(L+1)}{(2L-1)(2L+3)}$$
(31)

Before using this expression two important remarks have to be made. This formula does not apply to the interaction between the nucleus and an unbalanced *s*-electron in the configuration. The interaction with an *s*-electron is of the simple cosine form and gives therefore

$$W_S = \beta M_I M_S. \tag{32}$$

²⁰ J. A. Gaunt, Phil. Trans. A228, 184 (1929); J. H. Bartlett, Jr., Phys. Rev. 34, 1247 (1929).

²¹ Table V, as it is now, does not give us much more information than we obtained with the general sum rule data of Table I. The only additional information one gets is by considering the state with $M_S = 1\frac{1}{2}$, $M_L = 0$. This pair can only arise from the 4S ; the table gives an interaction energy zero, thus the 4S will have A = 0 in extreme Russell-Saunders coupling. So the sum of the energies belongs to the ${}^2D_{1\frac{1}{2}}$ and the ${}^2P_{1\frac{1}{2}}$, but further separation is not possible with this method.

²⁵ C. G. Darwin. Proc. Roy. Soc. A115, 1 (1927).

If the configuration to which the multiplet belongs contains such an s-electron one must add a term like Eq. (32) to Eq. (31). The second remark concerns the factors λ and σ . For the case of one single electron these were both equal to a. For a more complicated configuration one should not expect the coefficient for the orbital part to be the same as for the spin part. As we shall see later on it is possible to obtain a relation between λ and σ in certain simple cases.

In order to find the values of A(J) for each level of the multiplet we must again consider the sums of the results of Eq. (31) for a fixed choice of $M_J = M_S + M_L$. One takes first $M_J = S + L$, which occurs only once, next $M_J = S + L - 1$, occurring twice, and so on. The procedure is exactly the same as that followed in Section 3, but of course much longer, depending upon the values of S and L. It is possible to do it for general values of S and L and one obtains finally the general formula

$$A(J) = \lambda(2-g) - \sigma \frac{6\Gamma(2-g) - 2(g-1)L(L+1)}{(2L-1)(2L+3)} + \beta(g-1).$$
(33)

The last term occurs only when there is an unbalanced *s*-electron. In this formula g is the ordinary Landé g value, and Γ stands as usual for²³

 $\Gamma = SL\cos(S, L) = \left\{ J(J+1) - L(L+1) - S(S+1) \right\} / 2.$ (34)

The derivation of this formula is elementary but too cumbersome and long to be given here, but I am willing to give personal information about it to anyone who really might need it.

In the preceding sections of this paper we have always taken together the interaction W_s with the spin and W_l with the orbital moment. It is quite simple, however, to go back to Eq. (7) and keep these two separate. If we then know these interactions for only one level of a multiplet, we can determine λ and σ and find A for all other levels of the same multiplet. The sum rule of Table I or Table V will, in practically all cases, furnish us with sufficient information to do this. We shall show this again with the p^3 example.

For p^3 the sum rule gives that for ${}^2D_{2\frac{1}{2}}A = {}^{24}/_{25}a$. If we go back to Eq. (7) via Table I we find that this is divided as follows between the interactions with spins and orbits:

with spins:
$$\frac{4}{25}a$$
, with orbits: $\frac{4}{5}a$,

Furthermore, we know that for ${}^{2}D_{2\frac{1}{2}}$: $\Gamma = +1$, $g = 1\frac{1}{5}$ and we find from Eq. (33) (omitting the last term):

$$\frac{4}{5}a = \lambda_5^4, \ \frac{4}{25}a = -\sigma \frac{4\frac{4}{5} - 2\frac{2}{5}}{21}$$

from which

$$\lambda = a, \ \sigma = -1\frac{2}{5}a.$$

²³ Γ is the deplacement of the level from the center of gravity of the multiplet.

With these values we find for the A of ${}^{2}D_{1\frac{1}{2}}$, for which $\Gamma = -1\frac{1}{2}$, $g = \frac{4}{5}$,

$$A(^{2}D_{1\frac{1}{2}}) = \lambda 1\frac{1}{5} - \sigma \frac{-10\frac{4}{5} + 2\frac{2}{5}}{21} = \frac{16}{25}a$$

It is possible to find relations between λ and σ for the different multiplets of a configuration, or for the multiplets which arise after the addition of an *s*-electron. Lack of material to test such formulae make it useless to go into more detail, also with respect to the remarks made in the following section.

For intermediate coupling one can apply to a great extent the same method as used in a previous paper.²⁴

9. SERIOUS DISCREPANCIES

The hyperfine structure is in many spectra caused by a deeply penetrating s electron, the influence of other electrons being negligibly small. For such cases the theory is simple, hyperfine structure separations can be expressed in terms of Landé cosines and the experimental data have been shown to agree with the theory.²⁵ For non-s electrons no such check has been obtained until now.

The following enumeration of data shows that there are large discrepancies between the theory and the observations for non-s electrons. Though the experimental results are very scarce and often uncertain, the reality of these discrepancies in the example of bismuth is beyond all doubt. The present material is quite insufficient, however, to give quantitative information about the deviations.

A part of the deviations will be due to higher order corrections. The method used in this paper assumes that it is sufficient to consider only first order perturbations for the interaction between the electrons and the spin orbit interactions. This means that our results are obtained by using only zeroth order eigenfunctions in the correct stabilized linear combinations. For heavy elements one must also consider the first order terms of the spin-orbit perturbation in the eigenfunctions. This will cause the hyperfine structure formulae to contain correction terms which are of exactly the same nature as those derived by Fermi²⁶ for the anomalies in the alkali doublet intensities. An estimate of the order of magnitude of these corrections shows that they are probably not large enough to account for the deviations.

Bismuth I^{27} $(I = 4\frac{1}{2})$

$$\begin{aligned} 6s^{2}6p^{3} \ ^{2}D_{2\frac{1}{2}}: \quad \frac{4}{5}a' + \frac{1}{5}a'' &= 0.081 \pm 0.002 \\ ^{2}P_{\frac{1}{2}}: \qquad a'' &= 0.375 \\ (^{2}D_{1\frac{1}{2}}: \ 1\frac{1}{5}a' - \frac{1}{5}a'' &= -0.040 \pm 0.002). \end{aligned}$$

24 S. Goudsmit, Phys. Rev. 35, 1325 (1930).

²⁵ S. Goudsmit and R. F. Bacher, Phys. Rev. 34, 1501 (1929).

²⁶ E. Fermi, Zeits. f. Physik **59**, 680 (1930). This remark about the second order terms I owe to Dr. H. Casimir, with whom I discussed the discrepancies during his stay here last summer. Phys. Rev. in preparation.

²⁷ P. Zeeman, E. Back and S. Goudsmit, Zeits. f. Physik 66, 1 (1930).

The coupling is not of the extreme (j, j) type. This does not, however, affect the validity of the formulae given for the first two levels, as they are the only ones with $J = 2\frac{1}{2}$ and $\frac{1}{2}$ in this configuration. The two first equations give

$$\begin{aligned} 6p \ J &= \frac{1}{2}; \ a'' &= 0.375 \\ 1\frac{1}{2}; \ a' &= 0.007 \pm 0.003. \end{aligned}$$

The second order corrections for this case are uncertain, a study of the levels of Bi III makes one believe that they should decrease a'' and increase a' by not more than about 5 percent. One sees that a' is much too small for the theory predicts that $a' = \frac{1}{5}a''$. Though the formula given for ${}^{2}D_{1\frac{1}{2}}$ is not strictly valid here, the negative value of its separation factor corroborates our conclusion that a' is much too small.

Bismuth II²⁸

$$\begin{array}{rcl} 6s^2 & 6p_{\frac{1}{2}}7s & 2_1{}^0 \colon \frac{1}{2}a^{\prime\prime} + \frac{1}{2}b = 0.391 \pm 0.001 \\ & 6p_{1\frac{1}{2}}7s & 9_2{}^0 \colon \frac{3}{4}a^\prime + \frac{1}{4}b = 0.109 \pm 0.007 \,. \end{array}$$

One expects the values for a'' and a' of the 6p electron in Bi II to be about the same as in Bi I. The above equations are indeed in agreement with this and give both for *b* about 0.38. If one assumed, however, that a' were really $\frac{1}{5}a''$ one would obtain an impossible negative value for *b* and a too large value for a' and a''.

Bi III

$$6s^2 \ 7p^{-2}P_{\frac{1}{2}}: \ a'' = 0.102 \pm 0.003$$
$${}^2P_{\frac{1}{2}}: \ a' = 0.021 \pm 0.004.$$

The second order corrections for the 7p electron are expected to be somewhat larger than for the 6p. They tend to increase a'' by perhaps 10% and to decrease a' by about 5%. We have here a case where indeed the theoretical ratio between a' and a'' is close to the observed one, but one has to keep in mind that a' is not known with accuracy.

*Manganese*²⁹ $(I=2\frac{1}{2})$. Most of the hyperfine structure in manganese is caused by the 4s electron. For a few levels the hyperfine structure is due to the 3d and 4p electrons, but for these levels the separations are not known with sufficient accuracy to check any formulae.

Indium.³⁰ The measurements on the principal doublet of the indium spectrum made by McLennan and Allin and by Jackson differ so entirely from each other that they are useless.³¹ This example would have been a very significant check of the theory.

²⁸ New observations on Bi II and III made by R. A. Fisher and the present author, to be published shortly. Classification and notation from J. C. McLennan, A. B. MacLay and M. F. Crawford, Proc. Roy. Soc. A. **129**, 579 (1931).

²⁹ H. E. White and R. Ritschl, Phys. Rev 35, 1146 (1930).

³⁰ J. C. McLennan and E. J. Allin, Proc. Roy. Soc. **A128**, 508 (1930). D. A. Jackson, Proc. Roy. Soc. **A129**, 208 (1930).

³¹ The fair agreement which Jackson seems to obtain between his measurements and the theory is caused by an unfortunate error in a paper by Fermi. Fermi (ref. 2) gives formulae for the hyperfine splitting of a ${}^{2}P_{1\frac{1}{2}}$ level in case $I \ge 1\frac{1}{2}$. He mentions in the text how these formulae change for a case where $I < 1\frac{1}{2}$ and just this sentence happens to be incorrect. Jackson's results again give a' too small.

Thallium I. $(I = \frac{1}{2})$. Only one of the two lines of the principal doublet of thallium has been studied in detail.³² The present data on the other line are insufficient to draw any certain conclusions, though they also seem to indicate for this case that a' is too small.

Thallium III.³³

$$7p \,{}^{2}P_{\frac{1}{2}}: a'' = 0.375$$

 ${}^{2}P_{\frac{1}{2}}: a' = 0.218.$

The second order corrections are rather large in this case, namely about 15%. They would increase a'' and decrease a'. For this example a' is much larger than the theoretical value.

CONCLUSION

Though the experimental data are scarce we come to the conclusion that the present theory of the hyperfine structure separations is incorrect or at least incomplete. The method used in this paper is not the cause, for it has been applied very successfully to many other problems, but the use of the classical Eq. (3),

 $W_{l} + W_{s} = a \left[Il \cos \left(I, l \right) - Is \cos \left(I, s \right) + 3Is \cos \left(I, r \right) \cos \left(r, s \right) \right].$

The correct quantum mechanical expression for the spin-spin interaction will perhaps contain different terms. The generalizations of the Dirac theory for the two-body problem given by Gaunt³⁴ and Breit³⁵ contain indeed extra terms for the spin-spin interaction. From a study of the helium triplet, with which one can test a part of these extra terms, Breit³⁶ concluded that their presence was in disagreement with the experimental data on the spin-spin interaction of two electrons. Perhaps such terms do have a real significance for the interaction between nuclear and electron spin³⁷.

This discussion shows the importance of the study of hyperfine structure as a guide for the further development of the quantum theory, especially for the generalization of the Dirac equation. Let us, therefore, hope that experimental physics will soon provide us with at least one doublet state for which the hyperfine structure of both levels can be given with certainty and accuracy.

Appendix

Just before sending off this paper I received a letter from Dr. John Wulff, National Research Fellow at Tübingen, in which he describes important new measurements on the hyperfine structure as well as the Zeeman effect of the principal thallium doublet. The $6p_{\frac{1}{2}}$ level has a'' = 0.708, whereas the $6p_{\frac{1}{2}}$ level is unresolvably small. The value for a' is probably of the order 0.015, thus about ten times too small.

- ³³ J. C. McLennan and E. J. Allin, Proc. Roy. Soc. A129, 43 (1930).
- ³⁴ J. A. Gaunt, Phil. Trans. 228, 151 (1929). Proc. Roy. Soc. A122, 153 (1929).
- ⁸⁵ G. Breit, Phys. Rev. 34, 553 (1929).
- ³⁶ G. Breit, Phys. Rev. 36, 383 (1930).
- ³⁷ This will be discussed in a paper by D. R. Inglis, to be published soon.

³² E. Back and J. Wulff, Zeits. f. Physik **66**, 31 (1930).