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SEPARATIONS IN HYPERFINE STRUCTURE

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ABSTRACT

The quantum mechanics conception of a spinning electron in an s state makes it probable that its interaction energy with a nuclear moment i is simply proportional to the average of $is\cos(is)$. Expressions for this average cosine have been obtained and applied to different examples. In more complicated cases it can only be said that the interaction energy is proportional to $ij\cos(ij)$, which makes the interval rule hold for hyperfine structure.

THE existence of hyperfine structure has been accounted for by the introduction of a new quantum number[1] i, together with the quantum numbers s, l, and j associated with resultant spin moment, resultant orbital moment, and total moment respectively. The new quantum number is associated with the nucleus intrinsically in the same way that s is associated with the electron, and because of its similar properties might be interpreted as a nuclear spin moment. The i causes a single state of the multiplet to be split up into several states ($2i+1$ or $2j+1$ depending on which is smaller) each of which is denoted by a particular value of the new total quantum number f. In the hyperfine structure those transitions occur for which f changes by ± 1 or 0, except that the transition $0\rightarrow 0$ is forbidden, similar to the selection rules for j. The separations in hyperfine structure are then due to the interaction energy between the nuclear moment and the total extranuclear moment. Similar to ordinary multiplets, the hyperfine structure separations usually follow the interval rule, i. e. the separation of two adjacent states is proportional to the largest j of the two states. A discussion of hyperfine structure separations involves knowing whether the coupling which exists between the extranuclear moments is the Russell-Saunders type which gives rise to multiplets, or whether it is the (j, j) coupling which is found most frequently in the heavy elements.[2]

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[1] E. Back and S. Goudsmit, Zeits. f. Physik **43**, 321 (1927); **47**, 174 (1928).

[2] For a discussion of ordinary multiplet separations and the different vector couplings see S. Goudsmit, Phys. Rev. **31**, 946 (1928); S. Goudsmit and C. J. Humphreys, Phys. Rev. **31**, 960 (1928).

The interaction energy between the nuclear magnetic moment and the extranuclear electrons has not yet been treated in a satisfactory way. A treatment based on the classical vector model has been given by Pauling and Goudsmit.[3] Hargreaves[4] gave a quantum mechanical treatment in which however he neglected the interaction between the nucleus and the electron spin, which for small l is of the same order as the interaction with the orbital moment. Finally the calculations of Casimir,[5] which take into account both interactions, can be applied only in the simple case of a single outer electron. The common result of all the calculations is that the interaction energy will be of the form

$$Aij \cos(ij) \tag{1}$$

which might be stated as the interval rule. Using the quantum mechanics expressions for the cosines (1) becomes

$$Aij\left[\frac{f(f+1)-i(i+1)-j(j+1)}{2ij}\right].$$

The separation between states $f+1$ and f is therefore

$$A\left[\frac{(f+1)(f+2)-f(f+1)}{2}\right]=A(f+1). \tag{1'}$$

The separation is proportional to the largest f of the two states. As an example, let us consider the unassigned bismuth term 49461 with $j=1\frac{1}{2}$, $i=4\frac{1}{2}$ and f consequently 6, 5, 4, 3, with separations respectively 0.563, 0.473, 0.379 cm^{-1}. That these separations are proportional to the larger f may be seen by dividing respectively by it to obtain the interval unit A = 0.094, 0.095, 0.095. As another example consider the bismuth term $6p^3\ {}^2P_{1/2}$ with $j=1/2$, and $i=4\frac{1}{2}$ giving two states with $f=5$, 4. The measured separation is 1.875 cm^{-1} giving an interval unit of 0.375 cm^{-1}.

As the results of Casimir show, the interaction energy between the electron spin and the nucleus for the case of an electron in an s state, where l is 0, is proportional to the cosine between i and s, i.e.

$$ais \cos(is). \tag{2}$$

This expression does not hold for other states. In quantum mechanics an s state differs considerably from the orbital picture of the atom. One must consider for an s state that the charge distribution representing the electron, surrounds the nucleus completely whereas in the classical picture the nucleus and the electron are separated. This explains the fact that for an s state, the results obtained by Casimir on the basis of the quantum mechanics show that the most stable state for the nucleus is with its magnetic moment in the same

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[3] L. Pauling and S. Goudsmit, "The Structure of Line Spectra," McGraw-Hill, now being published.

[4] J. Hargreaves, Proc. Roy. Soc. **A124**, 568 (1929).

[5] We are greatly indebted to H. B. G. Casimir in Leiden for the use of his unpublished work on the study of the nuclear spin problem.

direction as the magnetic moment of the electron, meaning that if $i=\frac{1}{2}$, of the two states $f=0$ and 1, the former will be the lower, which is the opposite to what is expected on the classical theory. This result means that the constant a is positive.

This factor a comes out to be proportional to the ratio of the magnetic and mechanical moment of the nucleus and to Z^3/n^3 for the state under consideration. For deeply penetrating orbits

$$a \sim Z_i z^2 / n^3_{eff} \tag{3}$$

where Z_i is the nuclear charge effective for the inner part of the orbit, z is the effective nuclear charge outside the electron core, and n_{eff} is the Rydberg denominator. The actual numerical factor occurring in a is however not known with certainty.

The interaction energy between i and a p, d or f electron is of a more complicated nature as it involves an interaction with both the orbit and the spin. It is very probable that in this case the correct quantum mechanics treatment will differ considerably from the treatment with the help of the classical atomic model. It is therefore possible to consider here the hyperfine structure separations of only those configurations which involve a deeply penetrating s electron* which is supposed to contribute the main part of the hyperfine structure and we shall therefore be interested in the evaluation of $\overline{\cos (is)}$.

For two s electrons, the interaction energy may be calculated completely in terms of each of the electrons. If the subscripts denote the two electrons, the interaction energy is given by

$$a_1 i s_1 \overline{\cos (is_1)} + a_2 i s_2 \overline{\cos (is_2)}$$

remembering that s_1 and s_2 form the resultant moment j the average cosines can be worked out and one obtains

$$ij \cos (ij) \left[\frac{a_1 s_1}{j} \cos (s_1 j) + \frac{a_2 s_2}{j} \cos (s_2 j) \right]. \tag{5}$$

The expression between the brackets is thus the constant of expression (1). Substituting the quantum mechanics expressions for the cosines one obtains

$$A = a_1 \frac{j(j+1)+s_1(s_1+1)-s_2(s_2+1)}{2j(j+1)} + a_2 \frac{j(j+1)+s_2(s_2+1)-s_1(s_1+1)}{2j(j+1)} \tag{6}$$

In the case of two s electrons this reduces to

$$A = \tfrac{1}{2}a_1 + \tfrac{1}{2}a_2. \tag{7}$$

It is quite probable that this expression (6) can be applied to more complicated cases where an s electron is added to a general multiplet S-state of the preceding ion.

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* ADDED TO PROOF: In a recent letter to the Editor in Phys. Rev. H. E. White also considers the hyperfine structure in the case of a deeply penetrating s electron arriving at qualitatively the same results as obtained in this paper.

In the case of an s electron and an arbitrary other electron the evaluation of $a\, is\, \overline{\cos\,(is)}$ depends upon the type of coupling of the quantum vectors of the extranuclear electrons. For Russell-Saunders coupling

$$a_1 is_1\, \overline{\cos\,(is_1)} = a_1 is_1 \cos\,(ij)\cos\,(js)\cos\,(ss_1)\,. \tag{8}$$

It must be remembered that in this expression the interaction with the s electron alone is taken into account and the interaction with the other electrons is regarded as negligible.

$$a_1 is_1\, \overline{\cos\,(is_1)} = ij\, \cos\,(ij)\left[a_1\frac{s_1}{j}\cos\,(s_1s)\cos\,(sj)\right]. \tag{9}$$

The expression in brackets is again the constant A of (1). Substituting the quantum mechanics cosines we get

$$A = a_1\frac{s(s+1)+s_1(s_1+1)-s_2(s_2+1)}{2s(s+1)}\;\frac{j(j+1)+s(s+1)-l_2(l_2+1)}{2j(j+1)}\,. \tag{10}$$

In case of two electrons where $s_1 = s_2 = \frac{1}{2}$

$$A = a_1\frac{j(j+1)+s(s+1)-l_2(l_2+1)}{4j(j+1)}\,. \tag{11}$$

Equation (10) will also be applicable in the case where one has the s electron added to a more general configuration than a single electron, meaning that s can have values other than $\frac{1}{2}$.

In (j, j) coupling a similar treatment gives

$$\begin{aligned} a_1 is_1\, \overline{\cos\,(is_1)} &= a_1 is_1 \cos\,(ij)\cos\,(js_1) \\ &= ij\, \cos\,(ij)\left[\frac{a_1s_1}{j}\cos(js_1)\right] \end{aligned}$$

$$A = a_1\frac{j(j+1)+s_1(s_1+1)-j_2(j_2+1)}{2j(j+1)}\,. \tag{12}$$

There exist relations between the values of A in the case of Russell-Saunders coupling and in the case of the (j, j) coupling which are similar to the well-known sum rule of the Landé g values. For instance, if for a given configuration a certain j value occurs for only one level the value of A for this level will be the same for all couplings. Expression (11) can easily be connected with the Landé g value. Comparison with the well-known g formula gives at once

$$A = \tfrac{1}{2}a_1(g-1). \tag{13}$$

A similar but more complicated expression can be found in the case of the (j, j) coupling.

APPLICATIONS

Cadmium I. Table I gives the $5s\ ns$ and $5s\ 5p$ configurations of Cd I[6] for

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[6] H. Shüler and H. Brück, Zeits. f. Physik **56**, 291 (1929). S. Goudsmit, Naturwiss. **17**, 805 (1929).

which the Russell-Saunders coupling holds and for which (7) or (11) can be applied.

TABLE I. *Cadmium I. Hyperfine structure.*

Configuration	$\Delta\nu$	Form. (1′)	A	a_1
$5s6s\ {}^3S_1$	0.396 cm^{-1}	$3A/2$	$a_1/2+a_2/2$	
$5s7s\ {}^3S_1$	0.369	$3A/2$	$a_1/2+a_2'/2$	
$5s8s\ {}^3S_1$	0.354	$3A/2$	$a_1/2+a_2''/2$	
Limit	0.35	$3A/2$	$a_1/2$	0.47 cm^{-1}
$5s5p\ {}^3P_2$	0.28	$5A/2$	$a_1/4$	0.44
${}^3P_1$	0.21	$3A/2$	$a_1/4$	0.55

The nuclear moment of cadmium is ½ giving rise in every case to a doublet fine structure. In the tables the first column gives the configuration and term, the second column the separation, the third the separation from (1′) or the interval rule, the fourth gives A in terms of the constant a_1 of the s electron, and the fifth gives the value of a_1 determined from the separation. As the constants a contain the factor $(1/n_{eff}^3)$ they will decrease rapidly with increasing quantum number n. This means that a_1 is expected to be much larger than a_2 and that furthermore a_2 will decrease going from $6s$ to $8s$. The values of a_1 obtained from the separations agree sufficiently well since the expressions are only approximate. This a_1 on the average is about 0.47 cm^{-1} and this value leads to the prediction of the magnitude of the fine structure of the $5s\ {}^2S_{\frac{1}{2}}$ of Cd II. This term will be split up into two levels, $f=1$ and $f=0$ with separation a_1 or 0.47 cm^{-1}.

Thallium I.[7] In this case the expressions can be applied to only the low state $7s\ {}^2S_{\frac{1}{2}}$.

TABLE II. *Thallium I. Hyperfine structure.*

Configuration	$\Delta\nu$	Form. (1′)	A	a_1
$6s^27s\ {}^2S_{1/2}$	0.40 cm^{-1}	A	a_1	0.40 cm^{-1}

Thallium II. For the $6s\ 7s\ {}^3S_1$ we can use (II). From thallium I the a for the $7s$ electron was found to be 0.40 cm^{-1}; according to (3) the a for the same electron in thallium II will be about 4 times as large, or 1.60 cm^{-1}. This value has been used for the calculation of a_1 for the $6s$ electron in Table III.

TABLE III. *Thallium II. Hyperfine structure.*

Configuration	$\Delta\nu$	Form. (1′)	A	a_1
$6s7s\ {}^3S_1$	5.1 cm^{-1}	$3A/2$	$a_1/2+a_2/2$	5.2 cm^{-1}
$6s6p\ {}^3P_2$	3.5	$5A/2$	$a_1/4$	5.6
${}^1P_1$	0	$3A/2$	0	—
$6s7p\ {}^3P_2$	3.4	$5A/2$	$a_1/4$	5.4
${}^3P_1$	3.9	$3A/2$	$a_1/2$	5.2
$[{}^1P_1]$	−0.6	$3A/2$	$-a_1/4$	—
$6s6d\ {}^3D_2$	1.6	$5A/2$	$a_1/12$	7.7
${}^3D_1$	−2.0	$3A/2$	$a_1/4$	5.3
${}^1D_2$	2.4	$5A/2$	0	—
$6s7d\ {}^3D_3$	3.6	$7A/2$	$a_1/6$	6.2
${}^3D_2$	0.6	$5A/2$	$a_1/12$	2.9
${}^3D_1$	−2.3	$3A/2$	$-a_1/4$	6.1
${}^1D_2$	0.3	$5A/2$	0	—

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[7] E. Back, Ann. d. Physik **70,** 333 (1923). H. Schüler and H. Brück, reference 6.

The $6s\ 7p$ configuration of thallium II is certainly much nearer to the (j, j) coupling than to Russell-Saunders coupling as can be seen from an examination of the position of the singlet and triplet terms and in this case we must use (12). The $6s\ 6d$ follows the Russell-Saunders coupling again. The values of a given in the last column agree satisfactorily particularly for those terms for which the separations are known with some certainty. The values of $\Delta\nu$ given in Table III have been recalculated with the use of proper intensity relations from the observed lines of McLennan, McLay and Crawford[8] and according to them have an error of about 0.5 cm^{-1}. For $6s\ 7p\ {}^1P_1$ a separation of -3.4 would be expected but of the two possibilities for that term both show a separation of about 0.5. The $6s\ 6d\,{}^1D_2$separation observed is much too large. Especially interesting is the inversion of the ${}^3D_1$ terms.

The values of a are somewhat irregular to show with certainty the effect of different screening with different outer electrons. The value of a for the $6s$ electron in case the second electron is removed completely will probably be about 7 or 8 cm^{-1}. This will be the doublet separation of the hyperfine structure of the $6s\ {}^2S_{\frac{1}{2}}$ state of thallium III.

Lanthanum I and II. In lanthanum only a preliminary paper by Meggers and Burns[9] has been published, the few results which are certain, are in agreement with the theory developed here. The fine structure seems to occur only in those terms involving a single $6s$ electron. Table IV gives the results of the $5d\ 6s$ configuration of lanthanum II which is an interesting intermediate case between Russell-Saunders and (j, j) coupling, and the equations derived here are valid only for the ${}^3D_1$ and ${}^3D_3$ state for which all couplings give the same. The hyperfine structure of ${}^3D_3$ makes it probable that $i=2$, however the splitting up of the $5d\ 6s\ {}^1D_2$ does not agree with expectations. The agreement of the a_1 of La I with the a_1 of La II seems to be entirely accidental.

TABLE IV. *Lanthanum. Hyperfine Structure.*

La II Configuration	$\Delta\nu$ (total)	Form. (1)	A	a_1
$5d6s\ {}^3D_3$	0.71 cm^{-1}	$14A$	$a_1/6$	0.30 cm^{-1}
${}^3D_1$	-0.375	$5A$	$-a_1/4$	0.30
La I Configuration	$\Delta\nu$	Form (1)	A	a_1
$5d^2 6s\ {}^4F_{1\frac{1}{2}}$	-0.46	$5A/2$	$-a_1/5$	0.30
${}^4F_{2\frac{1}{2}}$	[+0.04]*	$12A$	$a_1/105$	
${}^4F_{3\frac{1}{2}}$	[+0.38]*	$16A$	$5a_1/63$	
${}^4F_{4\frac{1}{2}}$	[+0.67]*	$20A$	$a_1/9$	

* Predicted values.

J C. McLennan, A. B. McLay, and M. F. Crawford, Proc. Roy. Soc. **A125, 570** (1929).

[9] W. F. Meggers and K. Burns, J.O.S.A. **14,** 449 (1927). The uncertainty in i has little effect on the results derived here.