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Hyperfine Structure in Intermediate Coupling*

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The theory is extended to intermediate coupling and to cosine laws of force between nucleus and electron varying with different powers of their distance apart. In addition to Goudsmit's constants a', a'', there appears a third coupling constant a''' for each electron, which gives energy matrix elements for the same l and different j. The theory is in approximate agreement with observation. The gross structure is used to determine the parameters of the theory of intermediate coupling and hence $\overline{(1/r^3)}$. This together with a'' gives nuclear magnetic moments having roughly the same value for different configurations and stages of ionization. The variation of $1/r^3$ as determined from gross structure shows changes in screening agreeing with those supposed to exist for $(6s)^2$ of Pb I, Tl I in order to explain the isotope shift as due to differences in nuclear radii. The discrepancies between gross structure and theory are shown to be connected with similar discrepancies in hfs and the discrepancies of the ratios a''/a' are reasonably explained by perturbations due to other configurations.

1. Introduction

Goudsmit[1] had some success in explaining the magnitude of the observed hyperfine structure separations by considering the coupling of an electronic configuration to the nucleus as the resultant effect of the coupling of the individual electrons. At the same time he also found discrepancies of observations with the theory. These have to do with relative amounts of coupling of individual electrons in $np_{1/2}$ $np_{3/2}$ states, i.e., electrons having the same principal and azimuthal but different inner quantum numbers. The above divergences between theory and experiment have nothing to do with the validity of the hypothesis of nuclear spin and of the cosine law of interaction. They may be traced to the way in which the interaction energy between the electron and the nucleus depends on their distance apart.

These discrepancies, if real, indicate that the nucleus does not behave as a little magnet in its action on the extranuclear electrons. Instead, it would be necessary to suppose the existence of some other type of interaction satisfying the cosine law but depending on the distance between the electron and the nucleus in some other and as yet unknown way. The existence of such a force would be of great interest. The present paper contains a critical examination of the meaning of the apparent discrepancies between experiment and the picture of the nucleus as a little magnet. The conclusion is that most of the experimental material is in as good agreement with this picture as may be expected when one considers the approximate nature of calculations with many electrons. It will be recalled that Goudsmit's formulas involve sums of hyperfine splittings for levels having the same j (inner quantum number). By applying his sum relations to experimental data, one obtains a formal answer for the magnitude of coupling of individual electrons to the nucleus. The main advance of the present paper consists in dealing with the levels individually, rather than with all levels of the same j at once. It then becomes apparent that Goudsmit's "coupling constants" for individual electrons are really coupling variables; that their values, as derived from sum relations, may therefore be incorrect by considerable amounts and that the gross multiplet structure disagrees with the usual theory of intermediate coupling by amounts sufficient to account for the apparent variability of the hyperfine structure coupling constants. In order to explain the work we first discuss briefly Goudsmit's theory from a point of view which allows of further extension.

It is well known that if the nuclear spin operator is **I** and if **B** is any matrix vector involving

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[1] S. Goudsmit, Phys. Rev. **37**, 663 (1931).

only electron variables, then an interaction energy of the type

$$H' = (\mathbf{BI}) \tag{1}$$

gives rise to energy differences given by

$$\Delta w = (A/2)[f(f+1) - j(j+1) - i(i+1)], \tag{2}$$

where f, j, i are the fine structure, inner and nuclear spin quantum numbers, respectively. Here

$$A = (\mathbf{BJ})_j / j(j+1) \tag{3}$$

and $\mathbf{J}$ is the operator representing the total electronic angular momentum, while the suffix j indicates that one takes the diagonal matrix element of the matrix product of $\mathbf{B}$ and $\mathbf{J}$ in that part of it which corresponds to $\mathbf{J}^2 = j(j+1)$ when $\mathbf{J}^2$ is made diagonal. It is well known that if J_z is also made diagonal and if its matrix elements are m, then the matrix elements of B_z are given by

$$(j, m|B_z|j, m) = mA. \tag{3'}$$

So far use has been made only of the supposition that the law of interaction is a cosine law in the sense of Eq. (1) and of the smallness of the perturbation as expressed by the use of Eq. (2). It is next supposed that the spectroscopic term dealt with can be assigned to a definite electronic configuration and, in order to justify Goudsmit's procedure, it is necessary to suppose that the eigenfunctions representing all the terms of the configuration may be approximated sufficiently well by linear combinations of products of the same single electron eigenfunctions. The validity of this supposition will be examined in more detail later. For the present it will be assumed to hold. The operator B_z is a sum of parts belonging to individual electrons

$$B_z = \sum_i B_z(i). \tag{4}$$

Goudsmit's relations between the values of the interval factors A of the configurations and the single electron coupling constants may be understood in the following way.

According to Eq. (3′) it is sufficient to know the diagonal matrix elements of B_z referred to eigenfunctions describing states of definite total angular momentum and of definite projection of this momentum along z. It should be remembered however that a given electronic configuration gives, in general, several ways of obtaining the same total angular momentum. Thus, for example, the configuration sp in Russell-Saunders coupling gives the states $^3P_1$ and $^1P_1$ each of which has the angular momentum 1.

Let us start with three electrons and neglect, for the present, the symmetry due to their identity. The wave function for any spectral term of the configuration is then some linear combination of products of single electron functions and each of these functions is supposed to be the solution of a single electron problem in a proper self-consistent central field. These single electron functions are further supposed to be characterized by values of the principal and azimuthal quantum numbers which are used to designate the configuration. Each electron has $2(2l+1)$ linearly independent eigenfunctions. It is most convenient in the discussion of hyperfine structure to use the functions which correspond to definite total angular momenta of individual electrons. Thus, for each electron we have two sets of functions $u_m^{n,\,j}(j = l \pm \frac{1}{2})$. We consider the matrix for (4) with respect to products

$$u_{m_1}^{n_1,\,l_1\pm\frac{1}{2}}(1)\; u_{m_2}^{n_2,\,l_2\pm\frac{1}{2}}(2)\; u_{m_3}^{n_3,\,l_3\pm\frac{1}{2}}(3).$$

Each of the operators $B_z(i)$ operates on the i^{th} factor in the above product. We consider some value of the resultant angular momentum j and a special value of the projection of this angular momentum on the z axis. The eigenfunction for such a state is a linear combination of the above products. If there are several possible states with the same j there are several linearly independent linear combinations of these products which may be chosen so as to be orthogonal to each other and so as to correspond to the observed states. These states may be denoted by j to indicate the total angular momentum, by $m(j)$ to indicate its z component and by $n(j)$ to distinguish between different coupling possibilities in obtaining the same j. Thus, for example, $n(j)$ should have different values for the $^3P_1$, $^1P_1$ states of the sp configuration. The coupled state is described by the wave function

$$v_{m(j)}^{n(j)j}(1,\,2,\,3)=\sum c_{j_1m(j_1);\; j_2m(j_2);\; j_3m(j_3)}^{n(j),\;m(j)} \times u_{m(j_1)}^{n_1j_1}(1)\;u_{m(j_2)}^{n_2j_2}(2)\;u_{m(j_3)}^{n_3j_3}(3)\cdots \quad (5)$$

where j may take either of the values $l\pm\frac{1}{2}$ and

$$m(j_1)+m(j_2)+m(j_3)=m(j). \quad (5')$$

It is usually convenient to choose some simple set of functions (5) such as, for example, the functions corresponding to (jj) or to Russell-Saunders coupling. The energy matrix is not necessarily diagonal when referred to these functions. Nevertheless, conservation of angular momentum causes it to be diagonal in j, $m(j)$ and the secular equation for the energy breaks up into sets of equations, each set containing coefficients distinguished only by different values of $n(j)$. The matrix for B_z behaves similarly. No matter what set of functions v is used the sum of the diagonal elements of B_z is therefore the same for fixed j, $m(j)$, because the submatrices of B_z transform themselves canonically as one set of v's is transformed into another. This establishes sum relations between the interval factors A in different types of coupling.

Consider, in particular, the functions v for jj coupling. The summation in Eq. (5) is performed with fixed j_1, j_2, j_3 and the only quantities varied are the $m(j_i)$. Since, according to Eq. (4), B_z is a sum of terms referring to each electron separately, the terms in the summation (5) contribute to the diagonal elements separately.

$$\left(v_{m(j)}^{n(j)j}\,\middle|\,B_z\,\middle|\,v_{m(j)}^{n(j)j}\right)$$

has the form of a sum of terms, each term being the product of the square of the absolute value of one of the c's in Eq. (5) by the matrix element of some $B_z(i)$ of the type

$$\left(u_{m(j_i)}^{n_ij_i}(i)\,\middle|\,B_z(i)\,\middle|\,u_{m(j_i)}^{n_ij_i}(i)\right)=m(j_i)a(n_ij_i). \quad (6)$$

These matrix elements are diagonal elements for the single electron i and according to Eqs. (1), (2), (3′) they determine the interval factor A for a single electron in the state n_i, l_i, j_i by

$$A=a(n_ij_i).$$

In order to derive the interval factor A, Goudsmit considers a fixed set j_1, j_2, j_3. The complete set of Eqs. (5) for fixed j_1, j_2, j_3 may be regarded as a unitary transformation between the products of single electron functions

$$u_{m(j_1)}^{n_1j_1}(1)\;u_{m(j_2)}^{n_2j_2}(2)\;u_{m(j_3)}^{n_3j_3}(3) \quad (7)$$

and the functions v. By Eq. (5′) the transformation equations connect only such products for which the sum of m's is equal to the m of v. A canonical transformation connects the matrices for B_z referred to (7) and to v and the sum of their diagonal elements is therefore the same. For each m, linear relations between single electron interval factors and the many electron interval factors are thus established by means of Eqs. (6) and (3′) and the use of the coefficients c of Eq. (5) is avoided.

The representation of the coupled states v by a simple sum of products as written in (5) is not valid on account of the *exclusion principle.* Instead of (7) one should use determinants

$$(3!)^{-\frac{1}{2}}\left|u_{m(j_1)}^{n_1j_1},\; u_{m(j_2)}^{n_2j_2},\; u_{m(j_3)}^{n_3j_3}\right|. \quad (7')$$

This change affects the discussion only inasmuch as some of the determinants (7′) vanish and some values of j are impossible. The diagonal matrix elements of B_z with respect to (7′) are still given by the same expressions as if (7) were used provided (7′) does not vanish. It is thus only necessary to drop, in discussing sum relations, those combinations of $n_1j_1m(j_1)$, $n_2j_2m(j_2)$, $n_3j_3m(j_3)$ in which two or more sets of quantum numbers are equal.

Comparison of the theoretical formulas obtained in this manner with the experimental material leads to the conclusion that the coupling constants a for a single electron are not in agreement with expectation. Relativity was not taken into account in these considerations and corrections for its influence showed that part of the discrepancy could be explained. These corrections were made[2, 3, 4] by means of Dirac's equation for a single electron. It will be remembered that, according to this equation, there are two radial functions for an electron in a central field and that, for the same l and different j, these func-

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[2] G. Breit, Phys. Rev. **35**, 1447 (1930); **38**, 463 (1931).

[3] G. Racah, Il Nuovo Cimento **8**, 178 (1931).

[4] G. Racah, Zeits. f. Physik **71**, 431 (1931).

tions satisfy different equations. Their behavior at the origin is also different, the value of j having more to do with the nature of the singularity at the origin than the value of l. It is thus clear that any attempt at treating the hyperfine structure in intermediate coupling with due regard for relativity must be made *via jj* coupling.

In the calculations given below we suppose that many electron states may be represented by Eq. (5) but we modify the functions to mean the single electron functions of Dirac. The arguments of any u are now the three cartesian coordinates and the four-valued spin variable. The result of this change is to give a function which corresponds to nearly the same state of coupling as before the change was made because the difference between the Dirac and the Schroedinger equation with spin (Pauli's equation) is appreciable only in the small region close to the nucleus. By Dirac's equation, the interaction energy between two particles can be represented with sufficient accuracy as an electrostatic interaction e^2/r as long as one neglects the spin-spin interactions and the interactions between the spin of one electron with the orbit of another. This may be seen by inspecting the derivation[5] of the magnetic interactions in Pauli's equation from Dirac's equation. The electrostatic energy integrals, Slater's F and G integrals, will not be materially affected because contributions to them are made by regions not in the immediate vicinity of the nucleus. The magnetic terms usually attributed to the interaction of the electron spin with its own orbit will not be given quite correctly by $[\mathcal{E}_1\times\mathbf{p}_1]\boldsymbol{\sigma}_1$ for heavy nuclei. This is not important however for the applications which we shall make. For, in discussing the state of coupling, we shall not try to calculate the absolute values of the coupling parameters but will determine them from experiment.

In order to calculate the interval factors for states in intermediate coupling, we need to know the matrix elements of the type (6) and, in addition, also matrix elements of the nondiagonal type corresponding to transitions between states having the same l but different j. The possible matrix elements between such states are considered in the next section.

2. Relativistic Matrix Elements for a Single Electron

The interaction energy (1) consists according to (4) of a sum of parts, each part being due to a single electron. We shall suppose that the nucleus produces a magnetic field and that this magnetic field acts on the electrons. If the nucleus is very small and if it produces the magnetic field as though it were a little magnet,

$$\mathbf{B}(i)=eg\mu_0 r_i^{-3}[\boldsymbol{\alpha}_i\times\mathbf{r}_i] \tag{8}$$

where e is the absolute value of the electronic charge, $\mu_0=eh/4\pi mc$ is the Bohr magneton, r is the distance of the electron from the nucleus and α_i is the vector having for components the first three of Dirac's α's. Since we are interested, in this section, in a single electron, we need not use the letter i to distinguish between different electrons. We also find it easy to make calculations for a generalization of (8)

$$\mathbf{B}=eg\mu_0 r^{-n}[\boldsymbol{\alpha}\times\mathbf{r}]. \tag{9}$$

For $n=3$ we have the interaction energy corresponding to a little magnet. For other values of n we obtain the interaction energy due to a nucleus having finite dimensions. The nucleus is thought of as being spherical; the intensity of magnetization is supposed to be parallel to $\mathbf{I}$ and uniform in concentric spherical shells. Thus, if the intensity of magnetization at a point R is $\mathbf{I}f(R)$, the interaction energy is

$$eg\mu_0\boldsymbol{\alpha}[\mathbf{X}\times\mathbf{I}] \tag{10}$$

with

$$\mathbf{X}=\int_0^\infty(\mathbf{r}-\mathbf{R})|\mathbf{r}-\mathbf{R}|^{-3}f(R)4\pi R^2dR. \tag{11}$$

Here $\mathbf{X}$ may be interpreted as the electric intensity at $\mathbf{r}$ due to a charge distribution uniform in concentric layers and having the value $f(R)$ and it may thus be taken to be $(\mathbf{r}/r^3)\int_0^r 4\pi f(R)R^2dR$. The spherical shell model gives, thus, instead of $1/r^3$ in (8), simply some function of r. By means of sums of expressions (9) multiplied by proper coefficients we can represent such a function.

We use the form of solution of Dirac's equation in a central field due to Darwin[6] in the notation of Roess.[7] We have then certain expressions for

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[5] G. Breit, Phys. Rev. **34**, 553 (1929); **39**, 616 (1932).

[6] C. G. Darwin, Proc. Roy. Soc. **A118**, 654 (1928).

[7] L. C. Roess, Phys. Rev. **37**, 532 (1931).

Dirac's wave function in terms of two radial functions which are denoted by F_l and G_l if $j=l+\frac{1}{2}$ and by F_{-l-1}, G_{-l-1} if $j=l-\frac{1}{2}$. We recall that the matrix elements of a matrix vector are given by formulas of the type

$$(j+1,\, m\pm 1|X+iY|j,\, m) = \mp\rho(j\pm m+2)^{\frac{1}{2}}(j\pm m+1)^{\frac{1}{2}} \quad (12.1)$$

$$(j,\, m\pm 1|X+iY|j,\, m) = \sigma(j\pm m+1)^{\frac{1}{2}}(j\mp m)^{\frac{1}{2}} \quad (12.2)$$

$$(j-1,\, m\pm 1|X+iY|j,\, m) = \pm\tau(j\mp m)^{\frac{1}{2}}(j\mp m-1)^{\frac{1}{2}} \quad (12.3)$$

if a suitable canonical transformation is performed on these matrices.[8] The Roess functions[7] are not necessarily such as to give matrix elements just in this form. They make, however, the Z components diagonal and thus they differ from the functions which one must use in order to obtain Eqs. (12) only by constant phase factors which are not necessarily the same for different j, l, m. Their relative values for the same j and l do not interest us because they can be properly adjusted so as to correspond to (12.2). The value of σ is then independent of the common phase factor, as is seen from the Eq. (12.2). The values of ρ, τ will be affected, however, by the choice of common phase factors for each j. This circumstance will have to be considered in applying the formulas. By means of Eqs. (12) the calculation reduces itself to the calculation of $(J,\, m|B_z|j,\, m)$ where $J=j\pm 1$, j. We are, therefore, concerned with

$$[\boldsymbol{\alpha}\times\mathbf{r}]_z = ir\sin\theta\begin{Bmatrix} 0 & 0 & 0 & e^{-i\phi} \\ 0 & 0 & -e^{i\phi} & 0 \\ 0 & e^{-i\phi} & 0 & 0 \\ -e^{i\phi} & 0 & 0 & 0 \end{Bmatrix}. \quad (13)$$

The dependence of Ψ on the azimuthal angle ϕ and on the colatitude angle θ restricts the possibilities for nonvanishing matrix elements. Performing summations over the four-valued spin variable and using Eq. (13) we obtain

$$(\Psi'^*[\boldsymbol{\alpha}\times\mathbf{r}]\Psi).$$

TABLE I. *Nonvanishing matrix elements for B_z.*

l'	j'	m'	l''	j''	m''	$(l', j', m'\|B_z\|l'', j'', m'')$
$l-1$	$l-\frac{1}{2}$	$l-\frac{1}{2}$	$l+1$	$l+\frac{1}{2}$	$l-\frac{1}{2}$	$\tau(2l)^{\frac{1}{2}}$
l	$l+\frac{1}{2}$	$l-\frac{1}{2}$	l	$l-\frac{1}{2}$	$l-\frac{1}{2}$	$\rho(2l)^{\frac{1}{2}}$
l	$l+\frac{1}{2}$	$l+\frac{1}{2}$	l	$l+\frac{1}{2}$	$l+\frac{1}{2}$	$(l+\frac{1}{2})\sigma_1$
l	$l-\frac{1}{2}$	$l-\frac{1}{2}$	l	$l-\frac{1}{2}$	$l-\frac{1}{2}$	$(l-\frac{1}{2})\sigma_2$

For the Roess form of the Dirac wave functions and (13) we find for B_z as given by Eq. (9) only the nonvanishing matrix elements shown in Table I where

$$\tau = -I/(2l+1), \quad (14.1)$$

$$\rho = I/(2l+1), \quad (14.2)$$

$$\sigma_1 = (l+1)I/j(j+1), \quad (14.3)$$

$$\sigma_2 = -lI/j(j+1) \quad (14.4)$$

and

$$I = eg\mu_0\int_0^\infty (F'^*G''+G'^*F'')r^{3-n}dr.$$

Here F', G' are radial factors in the Roess form[7] corresponding to j', l' and F'', G'' are similarly solutions corresponding to j'', l''. Eqs. (14.3), (14.4) will be applied in most cases to the calculation of diagonal elements, i.e., to the condition in which $F', G' = F'', G''$. In such cases σ is determined by the above formulas quite independently of common phase factors in F, G. The connection with $\overline{r^{-3}}$ is as in reference 2. We introduce the functions used by Gordon[9] which are related to Darwin's functions by

$$rG = \phi_2, \quad rF = -\phi_1 \quad (15)$$

and Dirac's quantum number k which has been denoted by $-j'$ in reference 2. We note that

$$k(k-1) = l(l+1) \quad (16)$$

and we may thus summarize (14.3) and (14.4) by the single formula

$$\sigma = -\frac{2keg\mu_0}{j(j+1)}\int_0^\infty \phi_1\phi_2 r^{1-n}dr = -\frac{2eg\mu_0}{k-1}\frac{l(l+1)}{j(j+1)}\int_0^\infty \phi_1\phi_2 r^{1-n}dr \quad (17)$$

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[8] B. L. van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik*, p. 78, Berlin, Julius Springer (1932).

[9] W. Gordon, Zeits. f. Physik **48**, 11 (1928).

when the principal quantum numbers are the same and the functions ϕ_1, ϕ_2 are real. This formula is equivalent to Eq. (10) of reference 2. From the nonrelativistic[10] $1/r^3$ it may be expressed as

$$l(l+1)\overline{(r^{-3})} \rightarrow -(ek/\mu_0)\int_0^\infty \phi_1\phi_2/r^2 dr. \qquad (17')$$

This gives Eq. (17) when $n=3$.

We now consider ρ as given by (14.2) for the case of the same principal quantum number in the $'$ and $''$ states. The function G is closely related to the radial factor in the solution of Schroedinger's nonrelativistic equation and is approximately equal to it except in the neighborhood of the nucleus. We standardize the choice of phase factors by requiring G to be approximately the same in two functions corresponding to $j=l\pm\frac{1}{2}$. For large r the function F is not important. The two functions of the Roess type which enter the matrix element (14.2) are:

$$\begin{aligned} &j=l+\tfrac{1}{2}, \quad m=l-\tfrac{1}{2}, \\ &\qquad \Psi = M_\theta'(\quad,\quad, 2lG'P_l{}^{l-1}, -G'P_l{}^l) \\ &j=l-\tfrac{1}{2}, \quad m=l-\tfrac{1}{2}, \\ &\qquad \Psi = M_\theta''(\quad,\quad, G''P_l{}^{l-1}, G''P_l{}^l). \end{aligned} \qquad (18)$$

These wave functions should be compared with wave functions for Pauli's equation. The third place in Ψ refers to the spin being parallel and the fourth place to the spin being antiparallel to z. The function $GP_l{}^l$ is an orbital function corresponding to $m_l=l$ while $GP_l{}^{l-1}$ similarly corresponds to $m_l=l-1$. The relative signs of these functions are not correct, however, if one wishes to obtain matrices of the form of Eqs. (12). To obtain this form for **L** and other orbital matrix vectors[11] one must use $(-)^n P_l{}^u$ as the angular factor. We see therefore that the Pauli approximation to the functions (18) may be taken to be

$$\begin{aligned} &j=l+\tfrac{1}{2}, \quad m=l-\tfrac{1}{2}, \\ &\qquad \psi=(2l+1)^{-\frac{1}{2}}[(2l)^{\frac{1}{2}}u_{l-1}s_+ + u_l s_-] \\ &j=l-\tfrac{1}{2}, \quad m=l-\tfrac{1}{2}, \\ &\qquad \psi=(2l+1)^{-\frac{1}{2}}[u_{l-1}s_+ - (2l)^{\frac{1}{2}}u_l s_-] \end{aligned} \qquad (18')$$

where u_l, u_{l-1}, are normalized orbital functions which correspond to the form of Eq. (12) and s_+, s_- are similarly chosen spin functions referring to the electron spin being parallel and antiparallel to the z axis. A common phase factor or sign in the two functions (18′) is still immaterial because it does not affect the value of ρ. Having fixed the relative phase factors of the two functions (18′) we have automatically fixed the relative phase factors between all functions corresponding to $j=l\pm\frac{1}{2}$ because the form Eq. (12) determines all functions[12] of one j when one of them is given. Such phase relations between functions of the same j we will call standard phase relations and the phase relations between all functions of the same principal and azimuthal quantum numbers which are determined by (18′) we will also call standard. The matrix elements $(j'=l+\frac{1}{2},\ l'=l,\ m'|\mathbf{s}|j''=l-\frac{1}{2},\ l''=l,\ m'')$ are given by (12.1) where the constant of proportionality ρ is

$$s_{l+\frac{1}{2},\, l-\frac{1}{2}} = 1/(2l+1), \qquad (19)$$

while the orbital angular momentum matrix elements are similarly given by (12.1), the constant of proportionality ρ having the value

$$l_{l+\frac{1}{2},\, l-\frac{1}{2}} = -1/(2l+1). \qquad (19')$$

The correctness of Eqs. (19), (19′) is readily verified by computing the z components of $\mathbf{s}$, $\boldsymbol{l}$ by using Eqs. (12), (18′).

Approximate expressions for the constants ρ, σ in Eqs. (14) may be obtained by using Darwin's approximations to F and G by means of Bessel functions in the neighborhood of $r=0$, similarly to the way in which Racah[3,4] has given approximations to σ for the case $n=3$. We use the symmetrical form[2] of the Bessel function approximations

$$\begin{aligned} &j=l+\tfrac{1}{2}, \quad k'=l+1; \quad \phi_1 = C'Z\alpha J_{2\rho'}; \\ &\qquad \phi_2 = C'[y^{\frac{1}{2}}J_{2\rho'+1} - (k'+\rho')J_{2\rho'}] \end{aligned} \qquad (20.1)$$

$$\begin{aligned} &j=l-\tfrac{1}{2}, \quad k''=-l; \quad \phi_1 = C''Z\alpha J_{2\rho''}; \\ &\qquad \phi_2 = C''[y^{\frac{1}{2}}J_{2\rho''+1} - (k''+\rho'')J_{2\rho''}] \end{aligned} \qquad (20.2)$$

where

$$y=2Zr/a_H; \quad \rho=(k^2-Z^2\alpha^2)^{\frac{1}{2}}, \quad \alpha=2\pi e^2/hc. \qquad (20')$$

Here the Bohr radius $h^2/4\pi^2 me^2$ is denoted by a_H, Z is the atomic number and the Bessel functions have the argument $2y^{\frac{1}{2}}$. For sufficiently large r, the Bessel functions can be approximated

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[10] G. Breit, Phys. Rev. **37**, 51 (1931).

[11] H. C. Brinkman, Dissertation, Utrecht, 1932.

[12] Gray and Wills, Phys. Rev. **38**, 248 (1931)

by their asymptotic expansions.[13] The important function is ϕ_2 because for large r it becomes approximately the Schroedinger radial function multiplied by r. We select values of r sufficiently small to have Eqs. (20) valid and sufficiently large to make it possible to approximate Eqs. (20) by asymptotic expansions of the Bessel functions. For such r both (20.1) and (20.2) are approximately

$$\phi_2 \cong C\pi^{-\frac{1}{2}}y^{-\frac{1}{4}}\left[y^{\frac{1}{2}}\sin\left(2y^{\frac{1}{2}}-\pi\rho-\tfrac{1}{4}\pi\right)-\left(\rho^2-k+3/16\right)\cos\left(2y^{\frac{1}{2}}-\pi\rho-\tfrac{1}{4}\pi\right)\right] \quad (21)$$

and here

$$\rho^2-k+3/16=l(l+1)+3/16-Z^2\alpha^2$$

is the same for $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$. According to (21) the two states with the same l and different j can be described as slowly oscillating functions having the same amplitude factor and phases differing by a constant amount $(\rho'-\rho'')\pi$. This may be taken to indicate that C' and C'' are approximately equal to each other essentially because the values of r for which Eq. (21) applies are sufficiently large to make the differential equations, satisfied by ϕ_2 for $j=l+\frac{1}{2}$ and ϕ_2 for $j=l-\frac{1}{2}$, differ very little from each other. Thus, under these conditions, the Schroedinger radial functions for the two states $j=l\pm\frac{1}{2}$ are obtained from the Schroedinger radial equation by continuing the two solutions (21) towards larger r. The process of continuation may be thought of as being approximated by the method of Wentzel-Kramers-Brillouin. As r increases the two solutions for $j=l\pm\frac{1}{2}$ will approach each other also in their phase because the initial phase difference $(\rho'-\rho'')\pi$ will be gradually compensated by the phase difference in the usual $\int fdx$ arising from the energy difference of the two states. The energy difference makes itself felt only for values of r comparable with a_H while the values of r dealt with in Eq. (21) are of the order of a_H/Z. As long as the above assumptions can be made consistently the W.K.B. approximation to the radial functions will approach each other in the oscillating region for large r. The normalization integral is approximately determined by this region and the region beyond the turning point of classical motion which is represented by the exponential branch of the W.K.B. solution. The absolute values of C', C'' are expected therefore to be approximately equal, provided there exists a region for r which satisfies all the above requirements, provided the W.K.B. approximation is good enough and provided the turning points which correspond to the largest possible classical distances of the electron from the nucleus are approximately in the same region. Under these conditions we may connect the constants C', C'' with the corresponding constant for the nonrelativistic approximations to (20.1), (20.2):

$$j=l+\tfrac{1}{2}, \quad \phi_2=-C'y^{\frac{1}{2}}J_{2l+1}; \quad (21.1)$$

$$j=l-\tfrac{1}{2}, \quad \phi_2=C''y^{\frac{1}{2}}J_{2l+1} \quad (21.2)$$

which is obtained from the above equations by letting $\rho=|k|$. For $j=l+\frac{1}{2}$ the difference between ρ and $|k|$ is relatively insignificant because $|k|\geqq 2$ as long as we do not deal with s states for which these considerations are not necessary. The solutions (20.1) and (21.1) thus approach each other as they are continued towards large r on account of the gradual compensation of their phase difference and similarly for (21.1) (21.2). Thus if we wish to start with radial eigenfunctions for $j=l\pm\frac{1}{2}$ which are approximately equal to each other for large r we must make

$$C'=-C''. \quad (22)$$

This relation is essential for the identification of the two functions G', G'' in Eq. (18). The additional corrections to C', C'' can be found by considering the solutions for ϕ_2 more accurately and will be called normalization corrections. They may be ascertained by numerical solutions as has been done for instance in reference 2.

We now calculate (14.2), (14.3), (14.4). We have[14]

$$(p,q,s)=\int_0^\infty J_p(t)J_q(t)t^{-s}dt=\frac{\Gamma(s)\Gamma[(p+q-s+1)/2]}{2^s\Gamma[(1+p-q+s)/2]\Gamma[(1+q-p+s)/2]\Gamma[(1+q+p+s)/2]}. \quad (s>0) \quad (23)$$

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[13] This argument is essentially Racah's.[3] We discuss the degree of approximation somewhat differently and in more detail.

[14] Whittaker and Watson, *Modern Analysis*, p. 385, Problem 50, Cambridge University Press, 1920. We let $z\rightarrow 1$ in this formula.

Hence for $s=3$

$$(p,\,q,\,3)=\frac{4\sin\tfrac{1}{2}\pi(p-q)}{\pi(p^2-q^2)[(p+q)^2-4][4-(p-q)^2]},\tag{23.1}$$

and as special cases of this

$$(2\rho+1,\,2\rho+1,\,3)=1/[16\rho(\rho+1)(2\rho+1)],\tag{23.2}$$

$$(2\rho,\,2\rho+2,\,3)=1/[32\rho(\rho+1)(2\rho+1)],\tag{23.3}$$

$$(2\rho-1,\,2\rho,\,2)=1/[8\rho(2\rho-1)],\tag{23.4}$$

$$(2\rho',\,2\rho'',\,3)=\sin\pi(\rho'-\rho'')/[16\pi Z^2\alpha^2(2l+1)],\tag{23.5}$$

$$\lim_{\alpha\to 0}(2\rho',\,2\rho'',\,3)=1/[32l(l+1)(2l+1)].\tag{23.6}$$

For $n=3$ we perform in Eq. (17) the integration over r with the aid of (23.4), (23.2). We have

$$\int_0^\infty \phi_1\phi_2 r^{-2}dr=-(2k+1)C^2Z^2\alpha/\rho(4\rho^2-1)a_H\tag{24}$$

and hence

$$\sigma=[2g\mu_0{}^2 l(l+1)/j(j+1)]\overline{(r^{-3})}F,\tag{25}$$

where

$$F=\frac{k(2k+1)(2l+1)}{\rho(2\rho-1)(2\rho+1)}\tag{25'}$$

and

$$\overline{(r^{-3})}=\left(\int_0^\infty \phi_2{}^2 r^{-3}dr\right)_{\alpha\to 0}$$

$$=2C^2Z^2/a_H{}^2 l(l+1)(2l+1)\tag{26}$$

is the nonrelativistic average of $1/r^3$. The factor F represents the relativistic correction to Eq. (17′) essentially in Racah's form. It is equivalent to (17″) as long as Eq. (20) applies and as long as the conditions necessary for the validity of Eq. (22) are fulfilled.

The constant ρ of Eq. (14.2) is obtained by substituting Eq. (20) by making use of Eq. (21) and the first Eq. (20′). We have then

$$\rho=-\frac{(-C'C'')}{C^2}\,\frac{g\mu_0{}^2}{2l+1}\overline{\left(\frac{1}{r^3}\right)}G,\tag{27.1}$$

where

$$G=[2l(l+1)/\pi Z^2\alpha^2]\sin\pi(\rho''-\rho')\tag{27.2}$$

is the relativity correction factor to the approximate form

$$\rho\cong -g\mu_0{}^2\overline{(r^{-3})}/(2l+1).\tag{27.3}$$

By Eq. (22) the factor $(-C'C''/C^2)$ in Eq. (27.1) is approximately $=1$. More accurately, we should apply it as a normalization correction. Its form shows that it is approximately equal to the geometric mean of the normalization corrections which must be applied to Eq. (25).

We need also the connection of $\overline{(1/r^3)}$ or C^2 with the magnitude of the doublet splitting for a single electron. According to Racah[3] this is given approximately by

$$\delta=(2l+1)HZ\mu_0{}^2\overline{(r^{-3})},\tag{28}$$

where

$$H=2(\rho'-1-\rho'')l(l+1)/Z^2\alpha^2\tag{28.1}$$

represents the relativity correction factor obtained formula. If by means of Sommerfeld's doublet the spin orbit interaction is represented by $\tilde{a}(\mathbf{ls})$ then $\delta=(l+\tfrac{1}{2})\tilde{a}$ so that

$$\tilde{a}=2HZ\mu_0{}^2\overline{(r^{-3})}.\tag{28.2}$$

It should be noted that the use of Eqs. (28) implies, in addition to the simplifying assumptions made in discussing ρ, σ, also the supposition that the region responsible for the magnetic interaction is so close to the nucleus that the screening of the nucleus by closed shells may be neglected. The assumption is satisfied for heavy elements if l is not too great. Under all conditions, however, we expect that instead of Z one should use in (28.2) some number smaller than Z.

We have given the matrix elements ρ, σ only for $n=3$, i.e., for a nucleus forming a magnetic doublet. Eq. (23) enables one to compute these matrix elements by direct substitution for any n as long as the integrals converge. The two values of σ which correspond to $j=l+\tfrac{1}{2}$ and $j=l-\tfrac{1}{2}$

will be written a', a'' respectively, this notation being in agreement with Goudsmit's. We thus have

$$\frac{2g\mu_0{}^2 l(l+1)}{j(j+1)}\overline{\left(\frac{1}{r^3}\right)}F \cong \begin{cases} a'(j=l+\frac{1}{2}), \\ a''(j=l-\frac{1}{2}, \end{cases} \tag{29.1}$$

$$-[g\mu_0{}^2\overline{(r^{-3})}/(2l+1)]G \cong a''', \tag{29.2}$$

and these coefficients give matrix elements of single electron states for the vector **B** by means of Eqs. (12.2), (12.1), respectively; to obtain these matrix elements we substitute a' or a'' for σ and a''' for ρ.

3. Two Electron Configurations

According to the view of Section 1 we represent the wave functions of a two electron configuration as a linear antisymmetric combination of products of wave functions describing the two single electron states. If the two electrons are not equivalent, we need not consider the antisymmetric property of the wave functions. How this comes about for the magnetic interaction has been shown by Johnson[15] by means of quantized amplitudes.

According to Güttinger and Pauli[16] the matrix elements of (**BJ**) are given by

$$\begin{aligned}(j_1, j_2|\mathbf{BJ}|j_1j_2) &= Q_{12}a_1+Q_{21}a_2, \\ (j_1, j_2|\mathbf{BJ}|j_1-1, j_2) &= P_{12}a_{j_1, j_1-1},\end{aligned} \tag{30}$$

where

$$Q_{12}=(1/2)[j(j+1)+j_1(j_1+1)-j_2(j_2+1)],$$

$$P_{12}=(1/2)[(j+j_1-j_2)(j-j_1+j_2+1) \times(j+j_1+j_2+1)(j_1+j_2-j)]^{\frac{1}{2}}.$$

Here a_1, a_2 are the constants of proportionality, denoted by σ in Eq. (12.2), which are supposed to be used for the calculation of the single electron operator **B**. The constant a_{j_1, j_1-1} is similarly the constant of proportionality ρ of Eq. (12.1). The discussion of Güttinger and Pauli does not determine the sign of the second Eq. (30). It may be shown [for example by the symbolic method[17]] that the signs of the eigenfunctions may be consistently chosen so that

$$a_{j_1, j_1-1}=a'''(n_1, l_1), \tag{31}$$

where a''' is given by (29.2). This applies not only to **B** but to any other vector. In particular

$$(j_1, j_2|\mathbf{JS}|j_1, j_2)=(g_{j_1}-1)Q_{12}+(g_{j_2}-1)Q_{21}, \tag{32.1}$$

$$(j_1, j_2|\mathbf{JS}|j_1-1, j_2)=S_{j_1, j_1-1}P_{12}, \tag{32.2}$$

$$(j_1, j_2|\mathbf{JS}|j_1, j_2-1)=S_{j_2, j_2-1}P_{21}, \tag{32.3}$$

where

$$g_{j_1}=1+\frac{j_1(j+1)+s_1(s_1+1)-l_1(l_1+1)}{2j_1(j_1+1)} \tag{32.4}$$

is the Landé g factor and $S_{j, j-1}$ is given by Eq. (19). By means of Eqs. (32) we can find simultaneously the secular equations for the coefficients of eigenfunctions and formulas for the hfs coupling constants A by means of Eq. (2). The care which must be exercised as to signs of the functions makes it dangerous to use the existing discussions of intermediate coupling without some additional considerations. We use these discussions to check our calculations.

Configurations p·p and p²

The $p\cdot p$ configuration will be taken as a good example of the general procedure. Since the electrons are not equivalent we need not consider the exclusion principle. We denote the states by such symbols as (3/2, 1/2) meaning that the first electron state is $np_{3/2}$ and the second is $mp_{1/2}$ where $n\neq m$. This symbol in this section stands not for a product of two single electron functions but for a combination of products. The two electrons are supposed to be in states having different principal quantum numbers and the order in which the values of j are put into the symbol (j_1, j_2) is always the same with respect to the two electrons. A resultant $j=3$ can be obtained in only one way *viz.*, by vector composition of 3/2 and 3/2. The

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[15] M. H. Johnson, Jr., Phys. Rev. **43**, 627 (1933).

[16] Güttinger and Pauli, Zeits. f. Physik **37**, 743 (1931).

[17] H. A. Kramers, Proc. Amst. Academy **33**, 953 (1930); 965 (1931); H. C. Brinkman, Dissertation, Utrecht 1932; The operator which gives these matrix elements is $\left(\xi_2\frac{\partial}{\partial\xi_1}+\eta_2\frac{\partial}{\partial\eta_1}\right)\left(\frac{\partial^2}{\partial\xi_2\partial\eta_1}-\frac{\partial^2}{\partial\xi_1\partial\eta_2}\right)=\Omega$. In the notation of Kramers $\Omega(\alpha, \beta, \gamma)=\alpha\beta(\alpha+\beta+\gamma+1)(\alpha-1, \beta-1, \gamma+1)$ and $\int N(\alpha-1, \beta-1, \gamma+1)\cdot(\alpha-1, \beta-1, \gamma+1)^*\Omega N(\alpha, \beta, \gamma)\cdot(\alpha, \beta, \gamma)=[2l(2l+1)]^{\frac{1}{2}}[(l+s-j)(j+l+s+1)(j-l+s+1)(j+l-s)]^{\frac{1}{2}}$ where $N(\alpha, \beta, \gamma)$ is the normalization integral given in Brinkman's Appendix as Eq. (11).

eigenfunction is simply (3/2, 3/2) and we thus obtain $j(j+1)A=12A$ by substituting $j=3$, $j_1=j_2=3/2$ into Eq. (31). The coefficients a_1, a_2 are in this case a_1', a_2' since $j=l+1/2$ for both single electron states. Thus $A=(1/2)(a_1'+a_2')$.

The value $j=2$ can be obtained in three ways and the general eigenfunction can be written as

$$c_1(3/2,\ 3/2)+c_2(3/2,\ 1/2)+c_3(1/2,\ 3/2).$$

Hence we obtain $j(j+1)A=6A$ and find

$$A=\tfrac{1}{2}c_1{}^2(a_1'+a_2')+\tfrac{1}{4}c_2{}^2(3a_1'+a_2'')+\tfrac{1}{4}c_3{}^2(a_1''+3a_2')+c_1c_2a_2'''+c_1c_3a_1'''. \tag{33}$$

Here we must still determine c_1, c_2, c_3. It is convenient to work out the transformation from Russell-Saunders to jj coupling. This can be done easily by means of Eqs. (32.1) in which the same convention as to signs of eigenfunctions has been used as in Eqs. (30). Thus

$$\sum(\mathbf{JS})_{ik}c_k{}^\lambda=j(j+1)(g^\lambda-1)c_i{}^\lambda, \tag{34}$$

TABLE II. *g values.*

	(3/2, 3/2)	(3/2, 1/2)	(1/2, 3/2)
$^3D_2$	0	$2^{-\frac{1}{2}}$	$-2^{-\frac{1}{2}}$
$^3P_2$	$2/6^{\frac{1}{2}}$	$1/6^{\frac{1}{2}}$	$1/6^{\frac{1}{2}}$
$^1D_2$	$1/3^{\frac{1}{2}}$	$-1/3^{\frac{1}{2}}$	$-1/3^{\frac{1}{2}}$

where g^λ is the g value of the particular state in Russell-Saunders coupling. The g values are easily computed, Table II. $(\mathbf{JS})_{ik}$ involves the same quantities Q_{12}, Q_{21}, P_{12} as were used in Eq. (33). The orthogonality serves as a check. We work out the matrix for the magnetic energy $\tilde{a}_1(\mathbf{l}_1\mathbf{s}_1)+\tilde{a}_2(\mathbf{l}_2\mathbf{s}_2)$ by the formula

$$(j_1',j_2';j|\,l_1\mathbf{s}_1|\,j_1'',j_2'';j)=\delta_{j_1'j_1''}\delta_{j_2'j_2''}(1/2)\times[j_1'(j_1'+1)-s_1'(s_1'+1)-l_1'(l_1'+1)] \tag{35}$$

and obtain thus only diagonal elements. In the present case they are $(1/2)(\tilde{a}_1+\tilde{a}_2)$ for (3/2, 3/2), $(1/2)\tilde{a}_1-\tilde{a}_2$ for (3/2, 1/2), $(1/2)\tilde{a}_2-\tilde{a}_1$ for (1/2, 3/2), $-\tilde{a}_1-\tilde{a}_2$ for (1/2, 1/2) and a simple calculation shows that the magnetic energy matrix is the same as that of Johnson.[18] Similarly for $j=1$ we have the transformation matrix given in Table III and if the function is

$$c_1(3/2,\ 3/2)+c_2(3/2,\ 1/2)+c_3(1/2,\ 3/2)+c_4(1/2,\ 1/2)$$

then

$$A=\tfrac{1}{2}c_1{}^2(a_1'+a_2')+\tfrac{1}{4}c_2{}^2(5a_1'-a_2'')+\tfrac{1}{4}c_3{}^2(-a_1''+5a_2')+\tfrac{1}{2}c_4{}^2(a_1''+a_2'')+5^{\frac{1}{2}}c_1c_2a_1'''+5^{\frac{1}{2}}c_1c_3a_2'''+2^{\frac{1}{2}}c_2c_4a_1'''+2^{\frac{1}{2}}c_3c_4a_2'''. \tag{36}$$

From the results for two nonequivalent electrons we can obtain the formulas for two equivalent electrons without further calculation. We note that the only possible states for two equivalent p electrons are ^1S, ^3P, ^1D. Thus only $^3P_2$, $^1D_2$ of Table II survive because the functions (3/2, 3/2) and (3/2, 1/2)+(1/2, 3/2) are already antisymmetric. The function (3/2, 1/2)+(1/2, 3/2) must be multiplied by $1/2^{\frac{1}{2}}$ in order to make it normalized. Thus for equivalent p electrons the states with $j=2$ are represented by

$$c_1(3/2,\ 3/2)+2^{-\frac{1}{2}}c_2[(3/2,\ 1/2)+(1/2,\ 3/2)]$$

and A is obtained by substituting in Eq. (33) $2^{-\frac{1}{2}}c_2$ for both c_2 and c_3 and letting $a_1'=a_2'=a'$, $a_1''=a_2''=a''$. Thus

$$A=c_1{}^2a'+\tfrac{1}{4}c_2{}^2(3a'+a'')+2^{\frac{1}{2}}c_1c_2a'''. \tag{37}$$

For $j=1$ only the $^3P_1$ state survives. In this case (3/2, 1/2)−(1/2, 3/2) is antisymmetric while (3/2, 3/2) and (1/2, 1/2) are symmetric as is obvious from Table III. For this state A is obtained by setting $c_1=c_4=0$, $c_2=c_3=2^{-\frac{1}{2}}$ and thus $A=\frac{1}{4}(5a'-a'')$ in agreement with the formula for jj coupling as should be the case since there is only one state with $j=1$. Similarly the matrices for the electrostatic and magnetic energies for equivalent electrons can be obtained from the corresponding matrices for nonequivalent electrons. We see that by means of Eqs. (30), (32) the calculations can be made quite mechanically.

The same results can be obtained also by using antisymmetric eigenfunctions for definite j, m.

TABLE III. *Configuration pp.*

	(3/2, 3/2)	(3/2, 1/2)	(1/2, 3/2)	(1/2, 1/2)
$^3D_1$	$-2/3(6)^{\frac{1}{2}}$	$5^{\frac{1}{2}}/3(6)^{\frac{1}{2}}$	$5^{\frac{1}{2}}/3(6)^{\frac{1}{2}}$	$-2(10)^{\frac{1}{2}}/3(6)^{\frac{1}{2}}$
$^3P_1$	0	$1/2^{\frac{1}{2}}$	$-1/2^{\frac{1}{2}}$	0
$^1P_1$	$5^{\frac{1}{2}}/3$	$-1/3$	$-1/3$	$-2^{\frac{1}{2}}/3$
$^3S_1$	$2(5)^{\frac{1}{2}}/3(6)^{\frac{1}{2}}$	$4/3(6)^{\frac{1}{2}}$	$4/3(6)^{\frac{1}{2}}$	$2^{\frac{1}{2}}/3(6)^{\frac{1}{2}}$

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[18] M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931).

One must then also work out the transformation from jj to Russell-Saunders coupling in order to be able to determine the coefficients c from the empirical energy values. We have used both methods and also checked the results against nonrelativistic formulas for A in Russell-Saunders coupling derived by a third method. These formulas are

$$\frac{j(j+1)A}{2g\mu_0^2}=\overline{(r_1^{-3})}\left\{\tfrac{1}{2}[l(l+1)+l_1(l_1+1)-l_2(l_2+1)]+\frac{3Q_2(l,s,j)}{2l(l+1)(2l-1)(2l+3)}\left[\tfrac{1}{2}l_2(l_2+1)-\tfrac{1}{2}l(l+1)\right.\right.$$

$$\left.\left.-\frac{3Q_2(l_1l_2l)}{4(2l_1-1)(2l_1+3)}\right]+\frac{j(j+1)-l(l+1)-s(s+1)}{2l(l+1)}\left[\tfrac{1}{2}l_1(l_1+1)-\frac{3Q_2(l_1l_2l)}{4(2l_1-1)(2l_1+3)}\right]\right\}$$

$$+\overline{(r_2^{-3})}\{\text{symmetric term}\}, \quad (38)$$

where

$$Q_2(l,s,j)=[j(j+1)-l(l+1)-s(s+1)]^2+[j(j+1)-l(l+1)-s(s+1)]-4l(l+1)s(s+1)/3$$

$$j=l+1,\quad s=1,$$

$$\frac{j(j+1)A}{2g\mu_0^2}=\overline{\left(\frac{1}{r_1^3}\right)}\left[\alpha+\frac{\beta}{(l+1)(2l+3)}+\frac{\alpha+\beta}{l+1}\right]+\overline{\left(\frac{1}{r_2^3}\right)}[\text{symmetric term}], \quad (39.1)$$

where

$$\alpha=\tfrac{1}{2}[l(l+1)+l_1(l_1+1)-l_2(l_2+1)],$$

$$\beta=\tfrac{1}{2}[l_2(l_2+1)-l(l+1)]-\tfrac{3}{4}Q_2(l_1,l_2,l)/(2l_1-1)(2l_1+3),$$

$$\begin{cases} j=l,\quad s=1, \\ j(j+1)A=2g\mu_0^2\overline{(r_1^{-3})}\left[\alpha-\dfrac{\alpha+2\beta}{l(l+1)}\right]+2g\mu_0^2\overline{(r_2^{-3})}[\text{symmetric term}], \end{cases} \quad (39.2)$$

$$\begin{cases} j=l-1,\quad s=1, \\ j(j+1)A=2g\mu_0^2\overline{(r_1^{-3})}\left[\alpha+\dfrac{\beta}{l(2l-1)}-\dfrac{\alpha+\beta}{l}\right]+2g\mu_0^2\overline{(r_2^{-3})}\ [\text{symmetric term}], \end{cases} \quad (39.3)$$

$$\begin{cases} j=l,\quad s=0, \\ l(l+1)A=2g\mu_0^2\overline{(r_1^{-3})}\alpha+2g\mu_0^2\overline{(r_2^{-3})}[\text{symmetric term}]. \end{cases} \quad (39.4)$$

We give the results for the simpler configurations.

Configurations *sp*, *sd*, *sf*

These have been already discussed by Racah.[4] Since the contributions due to p, d, f, $\cdots$ electrons are not taken into account relativistically in his work we treat this case again. The difference between his results and ours is important only for sp and perhaps sd because the coupling of f, g, $\cdots$ electrons to the nucleus is usually small. The triplet states with inner quantum numbers $l+1$, l, $l-1$ are denoted by ${}^3L_{l+1}$, ${}^3L_l$, ${}^3L_{l-1}$, respectively, and the singlet state is denoted by ${}^1L_l$. We use these symbols both in designating atomic states and as an abbreviation for the eigenfunctions. We represent the eigenfunction for a state with $j=l$ as

$$\psi=c_1(1/2,l+1/2)+c_2(1/2,l-1/2),\quad (j=l),$$

where (j_1,j_2) refers to the angular momenta of the s and l electrons, respectively. The states ${}^3L_l$, ${}^1L_l$ in Russell-Saunders coupling are special cases of the above state and correspond to certain values of c_1, c_2. As the coupling changes, the values of c_1, c_2 change also. The states obtained in this manner from ${}^3L_l$, ${}^1L_l$ will be denoted by ${}^3L_l'$, ${}^1L_l'$.

For either of these states

$$l(l+1)A=(1/2)[(l+1)c_2^2-lc_1^2]a(s)+(1/2)l(2l+3)c_1^2a'+(1/2)(l+1)(2l-1)c_2^2a''+2[l(l+1)]^{\frac{1}{2}}c_1c_2a''' \quad (j=l),$$

where a', a'', a''' are the coupling constants of the l electron. Also

$$A(^3L_{l+1})=\frac{a(s)}{2(l+1)}+\frac{2l+1}{2(l+1)}a';$$

$$A(^3L_{l-1})=-\frac{a(s)}{2l}+\frac{2l+1}{2l}a''.$$

The parameters c_1, c_2 can be represented in terms of a single parameter θ which increases from zero in Russell-Saunders to $\theta_0=\tan^{-1}(l/l+1)^{\frac{1}{2}}$ in jj coupling.

$$^1L_l':\ c_1=\cos(\theta_0-\theta),\quad c_2=-\sin(\theta_0-\theta);$$

$$^3L_l':\ c_1=\sin(\theta_0-\theta),\quad c_2=\cos(\theta_0-\theta).$$

The connection with the Landé g values is given by

$$l(l+1)[g(^1L_l')-1]=\sin^2\theta;$$

$$l(l+1)[g(^3L_l')-1]=\cos^2\theta.$$

The energy matrix with respect to states in Russel-Saunders coupling is given in Table IV. Here W_0 is expressed in terms of Slater's integral G^1 and is the energy difference between the singlet and triplet systems due to electrostatic forces. We denote the energy of a state with $j=l$ by W and let

TABLE IV. *Energy matrix in Russell-Saunders coupling.* $W_0=2G^1/3$.

	$^3L_{l+1}$	^1L_l	^3L_l	$^3L_{l-1}$
$^3L_{l+1}$	$\frac{1}{2}\tilde{a}l$	0	0	0
^1L_l	0	W_0	$\frac{1}{2}\tilde{a}[l(l+1)]^{\frac{1}{2}}$	0
^3L_l	0	$\frac{1}{2}\tilde{a}[l(l+1)]^{\frac{1}{2}}$	$-\frac{1}{2}\tilde{a}$	0
$^3L_{l-1}$	0	0	0	$-\frac{1}{2}(l+1)\tilde{a}$

$$2W/\tilde{a}=w;\quad 2W_0/\tilde{a}=w_0.$$

The secular equation is

$$w^2+(1-w_0)w-w_0-l(l+1)=0;$$

$$w(^3L_{l+1})=l;\quad w(^3L_{l-1})=-l-1.$$

Letting $w(^3L_l')=w_3$, $w(^1L_l')=w_1$ we have

$$\tan\theta=\frac{[l(l+1)]^{\frac{1}{2}}}{w_1+1}=\frac{w_1-w_0}{[l(l+1)]^{\frac{1}{2}}}=-\frac{(1+w_3)}{[l(l+1)]^{\frac{1}{2}}}=\frac{[l(l+1)]^{\frac{1}{2}}}{w_0-w_3}$$

which may be used for the calculation of θ. For the discussion of experimental material, graphs are more convenient than equations. These are computed easily by means of

$$w_1=-1-l(l+1)/(w_3+1)$$

together with $w_0=1+w_1+w_3$ giving the usual relations between energy intervals in intermediate coupling. At the same time we easily get θ, the g values and the coefficients c_1, c_2. The *sp* configuration is the most important one of this kind and we give a short table (Table V) of the necessary values.

TABLE V. *Numerical values for sp configuration.*

w_3	w_1	w_0	$(g-1)(^3P_1)$	$(g-1)(^1P_1)$	$\cos(\theta_0-\theta)$	$\sin(\theta_0-\theta)$
−2	1	0	0.334	0.167	1	0
−1.80	1.50	0.70	.378	.121	0.995	0.101
−1.666	2	1.333	.409	.088	.984	.175
−1.50	3	2.50	.445	.056	.962	.272
−1.40	4	3.60	.462	.037	.943	.334
−1.25	7	6.75	.485	.015	.904	.427

For this case $\theta_0=35.3°$ and

$$A=\tfrac{1}{4}(2c_2^2-c_1^2)a(s)+5c_1^2a'/4+\tfrac{1}{2}c_2^2a''+2^{\frac{1}{2}}c_1c_2a'''.$$

The values of Table V are shown graphically in Fig. 1.

Configuration p^2

We denote again by $'$ states in intermediate coupling. We obtain

$$A(^3P_1)=\tfrac{1}{4}(5a'-a''),$$

$$A(^1D_2')=c_1^2a'+\tfrac{1}{4}c_2^2(3a'+a'')-2^{\frac{1}{2}}c_1c_2a''',$$

$$A(^3P_2')=c_2^2a'+\tfrac{1}{4}c_1^2(3a'+a'')+2^{\frac{1}{2}}c_1c_2a''',$$

where in terms of antisymmetric wave functions denoted by [ ]

$$^1D_2'=c_1[3/2,\ 3/2]-c_2[3/2,\ 1/2);$$

$$^3P_2'=c_2[3/2,\ 3/2]+c_1[3/2,\ 1/2];$$

$$[3/2,\ 3/2]=(3/2,\ 3/2);$$

$$[3/2,\ 1/2]=2^{-\frac{1}{2}}[(3/2,\ 1/2)+(1/2,\ 3/2)],$$

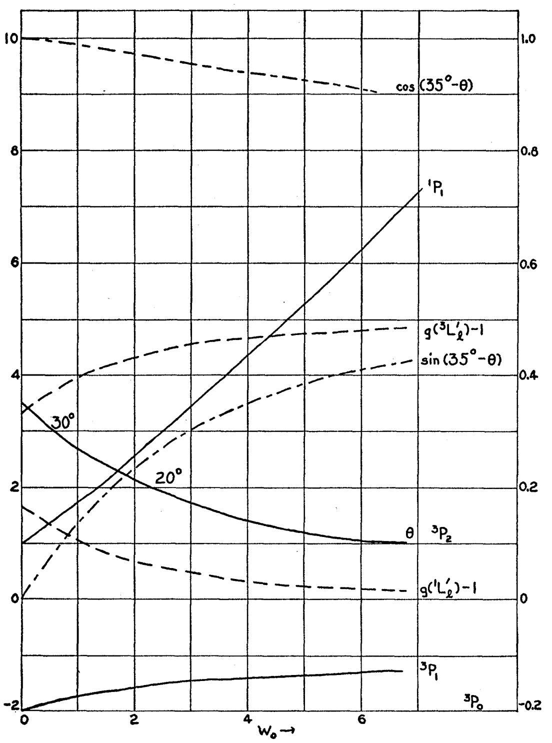

FIG. 1. Configuration *sp* in intermediate coupling. Extreme *jj* coupling is represented on the left and Russell-Saunders coupling on the right. The scale of ordinates for the broken curves is on the right; for the solid curves, with the exception of the angle θ, on the left. The scale for θ is inserted on the graph itself.

as has been shown in the explanation of the method of calculation.[19]

The numbers c_1, c_2 are obtainable from the empirical energies and g values of the configuration. The connection with the usual theory[20] of intermediate coupling is given by

$$c_1=\cos(\phi_0-\phi),\quad c_2=\sin(\phi_0-\phi),\quad \tan\phi_0=2^{\frac{1}{2}},\quad \phi_0=54.7°,$$

where ϕ is connected with Landé g values by

$$g(^1D_2')=\tfrac{1}{4}(5-\cos 2\phi),\quad g(^3P_2')=\tfrac{1}{4}(5+\cos 2\phi),$$

and with the energy values through the secular equations

$$W(^3P_1)=0;\quad X=3F^2/25;$$

$$[W=W(^1S_0'),\ W(^3P_0')],$$

$$W^2-5XW-5\tilde{a}X/2+9(\tilde{a}/2)^2=0\ ;$$

$$[W=W(^1D_2'),\ W(^3P_2')],$$

$$W^2-(3\tilde{a}/2+2X)W+2\tilde{a}X=0,$$

which give in terms of

$$w_1=2W(^1D_2')/\tilde{a},\ w_3=2W(^3P_2')/\tilde{a},$$

$$w_2=2W(^1S_0')/\tilde{a};\ w_4=2W(^3P_0')/\tilde{a},$$

the angle ϕ by

$$\tan\phi=2^{\frac{1}{2}}/(w_1-2)=(w_1-2x-1)/2^{\frac{1}{2}}$$

$$=2^{\frac{1}{2}}/(2x+1-w_3)=(2-w_3)/2^{\frac{1}{2}}$$

in terms of $x=2X/\tilde{a}$. The relations for intermediate coupling as well as ϕ are easily computed by varying w_3, w_4 in

$$w_1=(6-2w_3)/(2-w_3),$$

$$x=\tfrac{1}{4}w_1w_3=(1/2)(w_1+w_3-3),$$

$$w_2=(9+w_4)(-1-w_4),\quad x=(w_2+w_4)/5.$$

Simultaneously one computes ϕ, the g values and, from ϕ, one obtains c_1, c_2. The angle $\phi=0$ for Russell-Saunders and $\phi=\phi_0$ for *jj* coupling. The results are shown in Fig. 2.

Configuration *p.p*.

This has been discussed in connection with Eqs. (34), (37). The determination of coupling parameters is more difficult in this case on account of the larger number of coupling parameters involved. Johnson[18] worked out the secular equations. (There are some misprints in these.) Using his notation we obtain from the empirical energies the quantities

$$X_1=\beta+\delta-(3/2)(\tilde{a}_1+\tilde{a}_2),$$

$$X_2=\beta\delta-\tfrac{1}{2}(\tilde{a}_1+\tilde{a}_2)(\beta+2\delta),$$

$$X_3=\alpha+\beta-(3/2)(\tilde{a}_1+\tilde{a}_2),$$

$$X_4=\beta-\gamma/2-3(\tilde{a}_1+\tilde{a}_2)$$

as sums and products of energies.

Eliminating α, β, γ one obtains

$$\delta^2-[19X_1/9-20(X_3+X_4)/27]\delta$$
$$+(5/18)[4X_1-5(X_3+X_4)/3][X_1-(X_3+X_4)/3]$$
$$+X_2/6=0.$$

---

[19] For $m=2$ these functions are
$[3/2,\ 3/2]=2^{-\frac{1}{2}}[(p_{3/2}{}^1)_{3/2}(p_{3/2}{}^2)_{1/2}-(p_{3/2}{}^2)_{3/2}(p_{3/2}{}^1)_{1/2};$
$[3/2,\ 1/2]=2^{-\frac{1}{2}}[(p_{3/2}{}^1)_{3/2}(p_{1/2}{}^2)_{1/2}-(p_{3/2}{}^2)_{3/2}(p_{1/2}{}^1)_{1/2}]$
where the superscripts refer to electrons and the subscripts inside parentheses to j and outside parentheses to m.

[20] S. Goudsmit, Phys. Rev. **35**, 1325 (1930).

Solving this for δ one obtains also α, β, γ, $\tilde{a}_1+\tilde{a}_2$. From the equations in W for $J=1$, 2, one also obtains $\tilde{a}_1-\tilde{a}_2$. From the energy matrices given in Johnson's paper[18] on p. 1636, one obtains the coefficients of the Russell-Saunders functions and, by means of Tables II, III given here, one converts these coefficients into our coefficients c. In the applications which we have tried, this way of determining the state of coupling led to poor results because we are interested in cases approximating jj coupling. It is probable that the smaller of the two $\tilde{a}$ and α, β, γ have different values in the lower and upper groups of levels. Under these conditions it is better to write out the energy matrices in terms of states in jj coupling[21] and if the energy difference between the $(1/2, j)$ $(3/2, j)$ groups of levels is great in comparison with other energy differences the matrix elements between these groups of levels may be neglected. We obtain then the following energy matrices as well as the energy matrix shown in Table VI.

TABLE VI. *Energy matrix for $j=2$.*

	(3/2, 3/2)	(3/2, 1/2)
(3/2, 3/2)	$(\alpha+2\beta)/3$	$(\beta-\alpha)/3$
(3/2, 1/2)	$(\beta-\alpha)/3$	$\alpha/3+\beta/6$ $-3\tilde{a}_2/2$

Upper group

$$j=3,\ W=0;\quad j=0,\ W=(\beta+2\delta)/3$$

Lower group

$$j=0,\ W=-(3/2)(\tilde{a}_1+\tilde{a}_2)+(1/3)(2\beta+\delta),$$

$$j=2,\ W=-3\tilde{a}_1/2+\alpha/3+\beta/6,$$

$$j=1,\ W((1/2, 3/2))=-3\tilde{a}_1/2-\gamma/3+\tfrac{1}{2}\beta;$$

$$W((1/2, 1/2))=-3(\tilde{a}_1+\tilde{a}_2)/2+\gamma/6.$$

It will be noted that for the lower group the energy matrix is diagonal. This shows that we may treat the states of the lower group as in jj coupling even if the two states in $j=1$ are close enough to expect a perturbation between them.

4. MANY ELECTRON CONFIGURATIONS

These are usually calculated expediently by using eigenfunctions for a given magnetic quantum number.

Configuration p^3

In Russell-Saunders coupling we have the ${}^4S$, ${}^2P$, ${}^2D$ terms. There are three terms with $j=3/2$ and one each with $j=1/2$, $5/2$. The terms with $j=3/2$ can be also obtained in three ways in jj coupling, *viz.*, as (3/2, 3/2, 3/2), (3/2, 3/2, 1/2), (3/2, 1/2, 1/2) where each number gives a j for an individual electron state. In intermediate coupling the wave function is a linear combination of these three functions. In terms of their coefficients

$$A=(c_1{}^2+6c_2{}^2/5+c_3{}^2)a'-c_2{}^2a''/5$$
$$-4(2/5)^{\frac{1}{2}}c_2(c_1-c_3)a'''\quad (j=3/2).$$

Also, we add the previously derived results of Goudsmit

$$A=(4a'+a'')/5,\quad (j=5/2);\quad A=a''(j=1/2).$$

We use the results of Inglis and of Inglis and Johnson[22] and obtain the following relations between c_1, c_2, c_3 and the energy w of the terms with $j=3/2$.

$$c_1=\frac{w+3}{3(2)^{\frac{1}{2}}\beta^2}[3\beta+2(w-2)]c_4,\quad c_2=(5^{\frac{1}{2}}/w)c_4,$$

$$c_3=\frac{w+3}{3(2)^{\frac{1}{2}}\beta^2}[3\beta-2(w-2)]c_4,$$

$$c_4=[1+(1+5\beta^2/4w^2)(3+w)^2\beta^{-2}]^{\frac{1}{2}}$$

and

$$w=W/X,\quad \beta=\tilde{a}/X,\quad X=3F^2/25,\quad w({}^3P_{1/2})=2,$$
$$w({}^2D_{5/2})=0.$$

The parameter β is expressed in terms of w by $\beta^2=(4/9)w(w+3)(w-2)/(w+5/3)$. By means of this equation the graph for w against β is easily plotted. The energy reference point was chosen here so that for ${}^2P_{1/2}$, ${}^2D_{5/2}$, w has the values 2 and 0, respectively. One thus obtains X as $\frac{1}{2}[W({}^3P_{1/2})-W({}^2D_{5/2})]$. Knowing X one calculates w from the experimental W and sees at

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[21] G. H. Shortley, Proc. Am. Phys. Soc. Washington Meeting, April 28, 1933, treats in a similar way the p^5p configurations of the rare gases. The transformations from jj to Russell-Saunders coupling have been treated by Shortley similarly to the way done here in Phys. Rev. **43**, 451 (1933).

[22] D. R. Inglis, Phys. Rev. **38**, 862 (1931); D. R. Inglis and M. H. Johnson, Phys. Rev. **38**, 1642 (1931).

what part of the graph the empirical values fit, as has been done by Inglis. If the agreement is satisfactory the point at which the fit is obtained determines β and hence $\tilde{\alpha}$.

Configuration p^2s

The functions in jj coupling are conveniently thought of as arising from the coupling of the states of p^2 with an s electron. The states of p^2 are given in Table VII. The coupling of the s electron to these states can be taken into account without paying attention to symmetry. The state $j=5/2$, $m=5/2$ can be obtained as

TABLE VII. *States of p^2.*

$(j_1, j_2)=$	$(1/2, 1/2)$	$(3/2, 1/2)$		$(3/2, 3/2)$	
Resultant $j=$	0	1	2	0	2
Symbol	ψ^0	ψ^1	ψ^2	ϕ_0	ϕ_2

$$(5/2)_{5/2}=c_1s_{1/2}\phi_2{}^2+c_2s_{1/2}\psi_2{}^2.$$

Hence, by Eq. (3′)

$$A(5/2)=(4c_1{}^2+3c_2{}^2)a'/5+c_2{}^2a''/5 +4(2)^{\frac{1}{2}}c_1c_2a'''/5+a(s)/5.$$

The state $j=3/2$, $m=3/2$ may be obtained in three ways in jj coupling. The resultant states are

$$\mathrm{I}=5^{-\frac{1}{2}}(2s_{-\frac{1}{2}}\psi_2{}^2-s_{\frac{1}{2}}\psi_1{}^2);\quad \mathrm{II}=5^{-\frac{1}{2}}(2s_{-\frac{1}{2}}\phi_2{}^2-s_{\frac{1}{2}}\phi_1{}^2);$$
$$\mathrm{III}=s_{\frac{1}{2}}\psi_1{}^1,$$

and hence for

$$\psi=c_1\mathrm{II}+c_2\mathrm{I}+c_3\mathrm{III},$$

$$\begin{aligned}A=&\{(6/5)c_1{}^2+(9/10)c_2{}^2+(5/6)c_3{}^2+c_2c_3/(15)^{\frac{1}{2}}\}a'\\&+\{(3/10)c_2{}^2-(1/6)c_3{}^2-c_2c_3/(15)^{\frac{1}{2}}\}a'''\\&+\{(6/5)c_1c_2+2/(15)^{\frac{1}{2}}c_1c_3\}(2)^{\frac{1}{2}}a\\&+\{-(1/5)c_1{}^2-(1/5)c_2{}^2+(1/3)c_3{}^2\}a(s).\end{aligned}$$

The state $j=1/2$, $m=1/2$ can be obtained in three ways and in intermediate coupling may be represented by

$$\psi=c_1\mathrm{IV}+c_2s_{\frac{1}{2}}\phi_0{}^0+c_3s_{\frac{1}{2}}\psi_0{}^0;$$
$$\mathrm{IV}=3^{-\frac{1}{2}}(2^{\frac{1}{2}}s_{-\frac{1}{2}}\psi_1{}^1-s_{\frac{1}{2}}\psi_0{}^1).$$

We find

$$A(1/2)=(5/3)c_1{}^2a'-\tfrac{1}{3}c_1{}^2a''+[-4(2/3)^{\frac{1}{2}}c_1c_2 +8(1/3)^{\frac{1}{2}}c_1c_3]a'''+(-c_1{}^2/3+c_2{}^2+c_3{}^2)a(s).$$

We obtain the following connections with the functions in Russell-Saunders coupling used by Johnson.[23] The coefficients c in intermediate coupling can be obtained by using the matrices given on p. 207 in Johnson's paper to obtain the coefficients of the Russell-Saunders functions and by using the transformation matrices to jj coupling shown in Table VIII. If the coupling is nearly jj it is advisable to have the energy matrices referred to the jj functions. These may be worked out by using Table VIII. We refer the energies to the midpoint between ${}^4P_{5/2}$ and ${}^2D_{5/2}$ and obtain for the energy matrix the results shown in Table IX. Here $X=3F^2/25$ as in p^3 and G^1 is Slater's integral already used in sp. This case is somewhat too complicated for ex-

TABLE VIII.

	$s_{1/2}\phi_2{}^2$	$s_{1/2}\psi_2{}^2$	
$({}^4P_{5/2})_{5/2}$	$2^{\frac{1}{2}}$	1	$3^{-\frac{1}{2}}$
$({}^2D_{5/2})_{5/2}$	-1	$2^{\frac{1}{2}}$	

	II	I	III
$({}^2D_{3/2})_{3/2}$	$(1/3)^{\frac{1}{2}}$	$-(2/3)^{\frac{1}{2}}$	0
$({}^4P_{3/2})_{3/2}$	$1/3$	$1/3(2)^{\frac{1}{2}}$	$(5/6)^{\frac{1}{2}}$
$({}^2P_{3/2})_{3/2}$	$5^{\frac{1}{2}}/3$	$(5/2)^{\frac{1}{2}}/3$	$-1/(6)^{\frac{1}{2}}$

	IV	$(s_{1/2}\phi_0{}^0)$	$(s_{1/2}\psi_0{}^0)$
${}^4P_{1/2}$	$(3^{\frac{1}{2}}$	$-2^{\frac{1}{2}}$	$2)\times3^{-1}$
${}^2P_{1/2}$	$(6^{\frac{1}{2}}$	1	$-2^{\frac{1}{2}})\times3^{-1}$
${}^2S_{1/2}$	$(0$	$2^{\frac{1}{2}}$	$1)\times3^{-\frac{1}{2}}$

TABLE IX. *Energy matrices.*

$j=5/2$

	$s_{\frac{1}{2}}\phi_2{}^2$	$s_{\frac{1}{2}}\psi_2{}^2$
$s_{\frac{1}{2}}\phi_2{}^2$	$3a/4-X/3-G^1/18$	$-2/3(2)^{\frac{1}{2}}(X+G^1/6)$
$s_{\frac{1}{2}}\psi_2{}^2$	$-(2/3)(2)^{\frac{1}{2}}(X+G^1/6)$	$-3a/4+X/3+G^1/18$

$j=3/2$

	II	I	III
II	$3a/4-X/3+G^1/2$	$-(4X-G^1)/3(2)^{\frac{1}{2}}$	$-(1/3)(5/6)^{\frac{1}{2}}G^1$
I	$-(4X-G^1)/3(2)^{\frac{1}{2}}$	$-3a/4+X/3+G^1/3$	$-(1/6)(5/3)^{\frac{1}{2}}G^1$
III	$-(1/3)(5/6)^{\frac{1}{2}}G^1$	$-(1/6)(5/3)^{\frac{1}{2}}G^1$	$-3a/4-X$

$j=1/2$

	IV	$s_{\frac{1}{2}}\phi_0{}^0$	$s_{\frac{1}{2}}\psi_0{}^0$
IV	$-3a/4-X+G^1/2$	$(6)^{\frac{1}{2}}G^1/9$	$-2(3)^{\frac{1}{2}}G^1/9$
$s_{\frac{1}{2}}\phi_0{}^0$	$6^{\frac{1}{2}}G^1/9$	$3a/4+X/3+G^1/6$	$5(2)^{\frac{1}{2}}X/3$
$s_{\frac{1}{2}}\psi_0{}^0$	$-2(3)^{\frac{1}{2}}G^1/9$	$5(2)^{\frac{1}{2}}X/3$	$-9a/4+2X/3+G^1/6$

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[23] M. H. Johnson, Jr., Phys. Rev. **39**, 197 (1932). The functions used in this paper refer to states of lowest m while ours refer to highest m. We have adjusted the signs of our functions so as to give the same magnetic interaction energy matrices as Johnson's.

plicit formulas for the determination of the c's. They are obtained more easily from the above matrices by successive approximations to the secular equations.

5. Applications

$(6p)^2$ of Pb I

The experimental positions of the terms give for the energies referred to the $^3P_1$ level $W(^3P_2) = W_3 = 2830$ cm^{-1}, $W(^1D_2) = W_2 = 13{,}600$ cm^{-1}. Hence $w_3/w_1 = W_3/W_1 = 0.208$. Also $W(^3P_0) = -7820$, $W(^1S_0) = 21{,}640$ and $w_2/w_4 = -2.77$. According to Fig. 2 these values correspond to $x = 2X/\tilde{a} = 0.68$ and 0.78, respectively. The empirical g values give $x \cong 0.60$. One can also get x as $3(w_2+w_4)/[5(w_1+w_3)-2(w_2+w_4)] = 0.76$. The state of coupling is thus not determinable with complete certainty and we may determine the parameter x only within certain limits, say $0.60 < x < 0.80$, corresponding to $43° > \phi > 39°$. From sum relations and the experimental hfs material it appears probable that $a'' = 0.372$, $a' = 0.012$. The value of a''' may be obtained approximately from a' [see Eqs. (29.1), (29.2)] using the theoretical result that $a''' = [-j(j+1)/2(2l+1)l(l+1)]a' = -5a'/16$. This neglects the difference in the relativity as well as the normalization corrections to a' and a'''. The ratio of the relativity corrections to a' and a''' is very nearly 1 and the normalization correction can be estimated as the square root of that for a'' as compared with a' or ~ 1.7. In this case it does not matter much whether we use this correction to a''' or not. In Table X we use the data of Kopfermann[24] for $^3P_1$, $^3P_2$ and that of Schüler and Jones[25] for $^1D_2$. The theoretical values are close to the experimental values and the change in the theoretical values in the range of ϕ from 39° to 43° is 0.003 cm^{-1} while the difference between the theoretical and experimental values is 0.006 cm^{-1} for $\phi = 39°$. The fact that these differences are of the same order of magnitude indicates that they may be due to imperfections in the theory of intermediate coupling. This point will be discussed more fully later. The data of Rose and Granath[26] combined with that of Schüler and Jones[25] do not agree as well with the theory. We obtain, using these, $a'' = 0.381$ and $a' = 0.0096$ and for $\phi = 43°$ the formulas give $A(^1D_2) = 0.014$, $A(^3P_2) = 0.098$, while for $\phi = 39°$, $A(^1D_2) = 0.017$, $A(^3P_2) = 0.095$ against the experimental values $A(^1D_2) = 0.026$, $A(^3P_2) = 0.086$. Neither the ratio a''/a' nor the comparison of sum relations with the state of intermediate coupling is as good. The main difference between the observations of Rose and Granath and of Kopfermann is in the value of

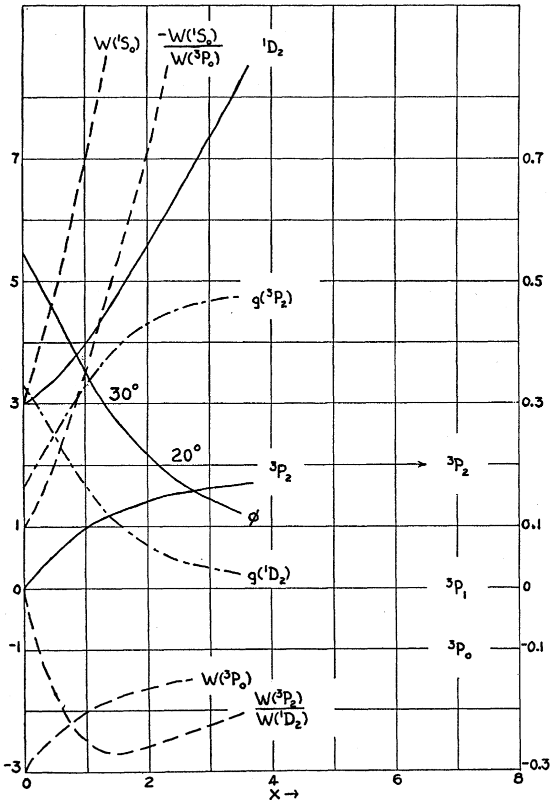

FIG. 2. Configuration p^2 in intermediate coupling. The scale of ordinates is the same as in Fig. 1.

TABLE X. *Constants for* $(6p)^2$ *of Pb I.*

x	ϕ	c_1	c_2	$A(^1D_2)$	$A(^3P_2)$
0.60	43.0	0.979	0.203	0.0167	0.097
0.80	39.0	0.963	0.271	0.0200	0.094
			Observed:	0.026	0.088
			Pure jj	0.012	

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[24] Kopfermann, Zeits. f. Physik **75**, 363 (1932).

[25] Schüler and Jones, Zeits. f. Physik **75**, 563 (1932).

[26] J. L. Rose and L. P. Granath, Phys. Rev. **40**, 760 (1932).

$A(^3P_1)$ which has, according to them, the values -0.083 and -0.078, respectively.

$(6p)^3$ of Bi I

The energies referred to $^2D_{5/2}$ and expressed in cm^{-1} are, for this configuration, $-15{,}437$, -4019, $0, 6223, 17{,}728$ for $^4S_{3/2}$, $^2D_{3/2}$, $^2D_{5/2}$, $^2P_{1/2}$, $^2P_{3/2}$ since $w=W/X$ is theoretically 2 for $^2P_{1/2}$ the values of w are empirically -4.97, -1.29, 0, 2, 5.70 and $X=3111$. From a graph such as that given by Inglis,[22] one finds that the values of w for $^4S_{3/2}$, $^2D_{3/2}$, $^2P_{3/2}$ correspond respectively to different values of $\beta(=\tilde{a}/X)$ which are approximately 3.05, 2.95, 3.30 and we may take $\beta=3.10$ as a reasonable average. The approximate values of w which correspond to the levels with $j=3/2$ are then -5.05, -1.33, 5.40 and we compute from these the constants c_1, c_2, c_3 by the formulas already given (Table XI). From the sum relations applied to $^2D_{5/2}$, $^2P_{1/2}$, Goudsmit[1] derived the values $a''=0.375$, $a'=0.007\pm0.003$. Hence we estimate $a'''=-0.00219=-0.0022$. Substituting into the formula derived for p^3, we obtain for the interval factor A of $^4S_{3/2}$, $^2D_{3/2}$, $^2P_{3/2}$ the values -0.0039, -0.055, $+0.0065$, respectively.

TABLE XI. *Constants for $(6p)^3$ of Bi I.*

	c_1	c_2	c_3
$^4S_{3/2}$	-0.188	$+0.345$	$+0.918$
$^2D_{3/2}$	$+0.0592$	-0.929	$+0.364$
$^2P_{3/2}$	$+0.980$	$+0.122$	$+0.152$

These results are affected by the contribution due to a''' and it appears that the uncertainty in a''' is of the same order as the uncertainty in the experimental values. Thus, according to Zeeman, Back and Goudsmit,[27] the total splitting of $^4S_{3/2}$ is $-0.08\ \text{cm}^{-1}$ which corresponds to $A=-0.0054$, while the tables of Bacher and Goudsmit[28] commit themselves only to the extent of giving $\Delta\nu=-0.1$ or $A=-0.0067$. The value of a''' is uncertain on account of the inaccuracy in a'. A different estimate can be made from the more accurately known a'' as $-0.375/(2\times16)$ where 2 takes care of the relativity correction. This value is -0.011 and is much larger than that obtained from a'. The discrepancy may be due to the inaccuracy of a' or else to the normalization correction. The normalization correction necessary to reconcile Goudsmit's values of a'' and a' is 5.7 which is unreasonably large. Nevertheless we correct $a'''=-0.0022$ by $(5.7)^{\frac{1}{2}}$ which gives $A(^4S_{3/2})=-0.009$. This is larger in absolute value than the possible empirical values, while without the normalization correction the theoretical value was smaller in absolute value than the experimental results. We thus see that the uncertainty in a' is quite sufficient to explain the lack of agreement between theory and experiment on account of the uncertainty which is caused in a'''. Besides a' affects $A(^4S_{3/2})$ directly and an increase in a' causes a decrease in the absolute value of $A(^4S_{3/2})$. The approximate experimental value of $A(^4S_{3/2})$ thus indicates that a' is larger than 0.007.

The theoretical value $A(^2D_{3/2})=-0.055$ is in approximate agreement with the experimental values -0.038, -0.039, -0.043 which correspond to the $f=3\rightarrow f=4$, $f=4\rightarrow f=5$, $f=5\rightarrow f=6$ intervals. The value -0.043 is presumably the better value since it is obtained from the larger interval in which the proximity effect of neighboring lines is least. An increase of a' from 0.007 to 0.018 $(=0.375/5\times2\times2)$ is just about sufficient to bring about agreement between the theoretical and experimental values.

We thus see that the hyperfine structure of the $j=3/2$ terms of the $(6p)^3$ configuration of Bi is in fair agreement with the theoretically expected interval factors. The disagreement of the values $a''=0.375$, $a'=0.007\pm0.003$ derived by Goudsmit from the $j=1/2$, $5/2$ terms may be due to experimental inaccuracies because a' is obtained from $j=5/2$ for which $A=(4a'+a'')/5$ and thus the approximately equal numbers A and $a''/5$ are subtracted from each other to obtain a'. In addition to the possible experimental errors it should be remembered that perturbations with other configurations may, in effect, change a' and a''. Thus, if a'' for $^2D_{5/2}$ is smaller than for $^2P_{3/2}$ on account of such perturbations, a' may very well be larger than 0.007. In order to discuss this more fully one will need a more complete theory of perturbations by other configurations. In addition, it must be remembered that the empirical positions of the energy levels are only in approx-

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

[28] Bacher and Goudsmit, *Atomic Energy States*, McGraw Hill (1932).

imate agreement with the theory of intermediate coupling. This indicates directly the presence of other perturbing configurations and makes one expect a certain amount of disagreement between the theoretical and experimental values.

$6p^2\ 7s$ of Bi I

The experimental values are due to Fisher and Goudsmit and they also discussed their results theoretically.[29] They treat the levels $1_{1/2}$, $5_{1/2}$, $7_{5/2}$ by formulas derived for *jj* coupling. The levels $8_{3/2}$, $4_{3/2}$ are left unused. By means of the energy matrices we have given above for this configuration, it is possible to work out the state of coupling more accurately. It is difficult to use the configuration itself to determine the parameters $\tilde{a}$, X, G^1. From $6p\ 7s$ of Bi II we obtain $G^1=2.6\times 10^3$ and also from $6p\ 7s$ of Pb I $G^1=2.6\times 10^3$. From $6p\ 7s$ itself and this G^1 we estimate approximate values $\tilde{a}=1.1\times 10^4$, $X=3.0\times 10^3$, $G^1=2.4\times 10^3$. These values do not pretend to be accurate. Only the order of magnitude is of interest in this case. (See Table XII.) The level $1_{1/2}$ is not very closely in *jj* coupling. This happens not to make much difference because c_1 is small and a'' occurs in the theoretical formula multiplied by $-c_1^2/3$ and a', a''' also occur multiplied by the small c_1. Thus $a(s)$ may be taken to be 0.166. Using the levels $5_{1/2}$, $7_{5/2}$ and supposing that $a'''=-5a'/16$ we obtain $a''=0.409=0.41$, $a'=0.028$ which is in approximate agreement with the values of Fisher and Goudsmit, 0.39, 0.026. Using these values we substitute into the formulas for $8_{3/2}$, $4_{3/2}$ and obtain 0.12(1), 0.01. These values are in approximate agreement with experiment.

TABLE XII. *Constants for $6p^2 7s$ of Bi I.*

Term symbol	W^*	(c_1, c_2, c_3)	hfs A	Obs. A
$8_{3/2}$	$-\frac{3}{4}\tilde{a}+\frac{1}{3}X+\frac{1}{3}G^1$	$(.15, .98(5), -.11)$	$.87a'+.32a''+$ $.24a'''-.194a(s)$	.094
$4_{3/2}$	$-\frac{3}{4}\tilde{a}-X$	$(.037, .11, .995)$	$.85a'-.157a''+$ $.034a'''+.328a(s)$	0
$5_{1/2}$	$-\frac{3}{4}\tilde{a}-X+\frac{1}{2}G^1$	$(1, -.03, -.07)$	$(5/3)a'-\frac{1}{3}a''-\frac{1}{3}a(s)$ $-.23a'''$	$-.142$
$1_{1/2}$	$-(9/4)\tilde{a}+\frac{2}{3}X+G^1/6$	$(.07, -.27, .98)$	$a(s)$	.166
$7_{5/2}$	$-\frac{3}{4}\tilde{a}+\frac{1}{3}X+G^1/18$	$(.22, .98)$	$.61a'+.192a''+$ $.24a'''+(1/5)a(s)$	.127

* Diagonal matrix element of energy for nearest state in *jj* coupling.

$6p\ 7p$ of Bi II

This configuration has also been discussed by Fisher and Goudsmit.[29] The upper group of levels is perturbed by $6p8p$. For the lower group we saw that the perturbation between the two levels with $j=1$ is very small even though the levels may be close together. For this reason we may use formulas for *jj* coupling, as has been done, apparently without justification by Fisher and Goudsmit. The values obtained by them are $a''(6p)=0.464$, $a'(7p)=0.012$. Here a'' compares well with other values but $a'(7p)$ seems relatively large. This may be due to perturbations by the $j=2$ levels of the upper group which is in turn perturbed by $6p\ 8p$.

$6p\ 7s$ of Pb I and of Bi II

The parameter $w_0=2W_0/\tilde{a}$ may be estimated for Pb I from the value of $w_1-1=3[W(^1P_1)-W(^3P_2)]/[W(^3P_2)-W(^3P_0)]=0.284$. According to Fig. 1 this corresponds to $w_0 \cong 0.4$ or $\theta=33°$. From the Landé g value $g(^1P_1)=1.131$ we obtain $w_0=.5$, $\theta=31°$ and from $g(^3P_1)=1.349$ $w_0=0.25$, $\theta=33°$. The value of $\tilde{a}$ which follows from $W(^3P_2)-W(^3P_0)$ is 8.8×10^3 and the value of G^1 which corresponds to this $\tilde{a}$ and $w_0=0.40$ is 2.6×10^3. The values of c_1, c_2 are for $^1P_1$ $(c_1, c_2)=(0.998, -0.060)$ and for $^3P_1$, $(c_1, c_2)=(0.060, 0.998)$. From the sum of $A(^1P_1)$ and

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[29] R. A. Fisher and S. Goudsmit, Phys. Rev. **37**, 1057 (1931).

$A(^3P_1)$ we obtain $a(7s)=0.220$ using $a''=0.372$ $a'=0.012$ and $A(^1P_1)=-0.040$, $A(^3P_1)=0.296$. With these values of the coupling constants we find that the coupling is sufficiently close to jj to make the difference between this and the actual condition negligible and the data are in perfect agreement with jj coupling.

For Bi II we similarly obtain $w_0\sim 0.25$ and this is even a more extreme case of jj coupling than that of Pb I. The results of Goudsmit and Fisher can thus be used with complete accuracy in this case so far as corrections for intermediate coupling are concerned. Their values are $a'=0.028$, $a''=0.430$, $a(7s)=0.352$ and the position of the levels gives $\tilde{a}=1.31\times 10^4$, $G^1=(3/4)w_0\tilde{a}=2.5\times 10^3$.

Hg^{199} I 6*s* 6*p*

This configuration is more closely in Russell-Saunders coupling than those just discussed. The ratio $[W(^1P_1)-W(^3P_2)]/[W(^3P_2)-W(^3P_0)]$ gives $w_0\cong 5.4$ while $[W(^3P_1)-W(^3P_0)]/[W(^3P_2)-W(^3P_0)]$ gives $w_0>10$. The ordinary intermediate coupling theory thus applies only poorly. The discrepancy between the values of w_0 may be qualitatively described by saying that the interval rule in the ^3P is obeyed better than one would expect from the proximity of ^1P. We do not expect therefore to be able to obtain exact results. Approximately, using $w_0=5.38$ and the separation between $^3P_2$ and $^3P_0$ the intermediate coupling theory parameters are $\tilde{a}=4.26\times 10^3$, $G^1=1.72\times 10^4$. An approximate estimate of $a(6s)$, a'', a' may be made by using sum relations only. The overall hfs splittings of $^3P_2$, $^3P_1$, $^1P_1$ are 0.758, 0.727, -0.181 and the corresponding values of A are 0.303, 0.485, -0.121. From the sum relations we obtain $a''+a'=0.122$ and, supposing that $a'=a''/15$, the approximate value $a''=0.114$ follows. This value may be compared with a more exact estimate by means of formulas for hfs in intermediate coupling. This gives us in addition to the sum relations an additional condition

$$A(^3P_1)-A(^1P_1)=[(3/4)a(s)-(5/4)a'+(1/2)a'']\cos 2(\theta_0-\theta)+2^{\frac{1}{2}}a'''\sin 2(\theta_0-\theta)$$

and $w_0=5.38$ corresponds to $\theta=11.5°$. Supposing that the approximate theoretical relation $a'''\cong 5a'/16$ is satisfied, we obtain $a'=0.016$, $a''=0.10(6)$, $a(6s)=1.16(5)$, which is in fair agreement with our first estimate. We do not examine the data for Hg^{201} separately since this obviously will give no new result.

6. CONCLUSIONS

It is seen from the above comparison between theory and experiment that the predictions of the theory of hfs for intermediate coupling are in approximate agreement with the observed patterns. The agreement is best when the electronic configuration approaches pure jj coupling. For coupling conditions intermediate between this and that of Russell-Saunders, neither the theoretical predictions for the positions of electronic energy levels and Landé g values, nor the theoretical predictions for the interval factors of hfs are accurately verified by experiment. Thus for the 6*p* 7*s* configurations of Pb I and Bi II the coupling is very nearly pure jj and the values of $a(7s)$, $a''(6p)$, $a'(6p)$ derived from sum relations of $6p^2$ Pb I fit perfectly the observed splittings of $^3P_1$, $^1P_1$ while in 6*s* 6*p* of Hg I $(6p)^3$ of Bi I, $(6p)^2$ of Pb I, the agreement is only approximate. Also, in the case of $(6p)^2$ of Pb I different ways of determining the state of coupling lead to different results and the uncertainty introduced by this is of the right order of magnitude to account for the differences between theory and experiment. The same is true qualitatively for the other intermediate coupling configurations. On the other hand, in nearly pure jj coupling, the exact state of coupling is immaterial for the comparison between the observed splittings for levels of the same j and the theoretical expressions using a', a'' as derived from sum relations. This is due to the fact that close to jj coupling, the difference between A for the actual condition and for the pure jj condition is represented by terms involving squares of small quantities multiplied by a'', a' and first order small quantities multiplied by a'''. The small numerical value of a''' makes the formulas insensitive to deviations from the pure jj condition and we have thus no decisive evidence that the theory is better when the condition of pure jj coupling is approached. It is simply more difficult to test the theory for internal consistency under these coupling conditions.

On the other hand, we regard it as significant that when the values of a'', a' are tested against experimental data in more detail than the sum relations permit, disagreements between theory and experiment are found and that these disagreements are connected with imperfections in the theory of intermediate coupling. This fact indicates the necessity of caution in the description of an electronic state by means of wave functions of a single electronic configuration and suggests that in all cases the values of a', a'' may be wrong. This applies, particularly, to the smaller numbers a'.

We have explained above the apparent agreement of theory and experiment in *jj* coupling by the lack of sensitivity of our formulas to deviations from theory and at the same time we have pointed to evidence of the importance of possible perturbations by other electronic configurations. Now, in general, a perturbation will make our formulas inapplicable and we must conclude that whatever perturbations exist in $6p\,7s$ of Pb I, Bi II they are of such a nature as to leave our equations formally correct. There is an obvious reason for such a formal correctness of the equations. The usual theory of intermediate coupling presupposes that the electronic states of all terms of a given configuration (say $6s\,7p$) can be represented sufficiently well by antisymmetric combinations of products of the $6s$ and $7p$ functions in some suitable central field. The radial parts of both the $6s$ and the $7p$ functions are supposed to be strictly the same for all the four terms of this configuration. A more exact type of consideration is that of Fock.[30] According to this, one looks for solutions of the variational problem by means of trial wave functions having the correct rotational and exchange symmetry types but having arbitrary radial factors for the $6s$, $7p$ wave functions. For the present purpose one must make a slight extension of Fock's scheme by allowing all linear combinations, rather than those belonging definitely to the singlet or triplet systems. Let us suppose, then, for simplicity, that the central field due to the inner closed shells is approximately the same for all four terms. Even so, the self-consistent fields for $6s$ and $7p$ will be different for ${}^1P_1$, ${}^3P_0$, ${}^3P_1$, ${}^3P_2$ and it is thus clear that with this refinement of the intermediate coupling theory we will obtain also a variation in the hfs coupling "constants" $a(s)$, a'', a', a''' from term to term in the same configuration. Another way of discussing the same solution is to keep the central field for each electron fixed and to allow, then, linear combinations of all antisymmetric products between functions of the type ns, mp. Perturbations between the states $nsmp$ and $6s\,7p$ are then taken into account. We expect that the perturbations which take place between all the successions of ${}^1P_1$, ${}^3P_2$ are of the same order, because close to *jj* coupling, the distance between ${}^1P_1$, ${}^3P_2$ is small compared to the distance apart of such successive pairs of levels; similarly for ${}^3P_0$ and ${}^3P_1$. There is, on the other hand, no general reason why the perturbations of the ${}^1P_1$ and ${}^3P_2$ should be equal to those of ${}^3P_0$ and ${}^3P_1$. Thus, for the upper group $[{}^1P_1, {}^3P_2]$ we may expect one set of coupling constants $a(s)$, a' and for the lower, another set $a(s)$, a''. The empirical comparison in *jj* coupling is made by using

$$A({}^1P_1) = (1/4)a(s) + (5/4)a',$$
$$A({}^3P_1) = (1/2)a(s) + (1/2)a'',$$
$$A({}^3P_2) = (1/4)a(s) + (3/4)a'.$$

The equations for ${}^1P_1$, ${}^3P_2$ just suffice for the determination of $a(s)$, a'. Using the $a(s)$ so found in the equation for ${}^3P_1$, one determines a''. By this procedure one thus does not even determine a'' correctly for ${}^3P_1$ because one supposes that $a(s)$ did not change from the upper to the lower group and the ratio of a''/a' does not necessarily have its theoretical value for a single electron in a fixed central field of force. The check between theory and experiment is made for Pb I by comparison with $6p^2$ and for this the agreement between ${}^1D_2$ and ${}^3P_2$ was not nearly as good as the one for $6p\,7s$. For $6p\,7s$ of Bi II we can make approximate comparisons with $6p^3$, $6p^2\,7s$ of Bi I, $6p\,7p$, $6p\,6d$ of Bi II. But in no case do we have exact agreement nor evidence of the exact validity of the formulas in *jj* coupling.

On account of the expected variation of the constants a', a'' within a configuration, we expect the values of a' to be quite inaccurate because a small fractional change in a'' may be responsible for an apparent change in a', as well as on account of the sensitivity of a' to experimental errors. We thus regard the conclusions from sum relations about the ratio a''/a' as questionable and we saw in the case of $6p^3$ of Bi I that there is some evi-

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[30] V. Fock, Zeits. f. Physik **81**, 195 (1933); **61**, 126 (1930).

dence in the splitting of ${}^4S_{3/2}$ for $a'>0.007$. The objections to the little magnet theory of the nucleus on the score of a''/a' being too large are thus not very strong. The only clear case seems to be that of $6p$ of Tl I and here the analysis of the experimental pattern into lines is complicated by the presence of the two isotopes. Just as from $6p^3$ of Bi I, sum relations give an anomalously high value of a''/a', the ${}^2D_{5/2}$, ${}^2P_{1/2}$ terms of Sb^{121} I give $a''=0.158$, $a'=0.035$ which corresponds to $a''/a'=4.5$ and is too low in comparison with the theoretical $5\times 1.24=6.2$. The agreement between theory and experiment for the relative positions of the levels for this configuration is not very good and we are tempted to ascribe it to the same cause as the discrepancy between the theoretical and experimental values of a''/a'.

TABLE XIII. *Typical results for p electrons.*

		$\tilde{a}$	a''	g
Tl	$7p$	3.79×10^3	0.375	2.8
	I $6p$	5.25×10^3	.73	3.9 2.9*
Bi	I $6p^3$	$9.6\ \times 10^3$	.375	1.2
	II $6p\,7s$	1.31×10^4	.430	1.0
Pb^{207}	I $6p^2$	$7.4\ \times 10^3$	.372	1.5
	I $6p\,7s$	$8.8\ \times 10^3$	.372	1.2(5)
Hg^{199}	I $6s\,6p$	4.26×10^3	.106	0.71
Sb^{121}	I $5p^3$	3.50×10^3	.158	1.3
	I $5p\,6s$	$4.0\ \times 10^3$	.191	1.3

* From numerical calculations of eigenfunctions.[2]

Magnetic moments

Even though the determination of either a'' or a' is subject to doubt we expect that a'', which is the larger of these, may be determined approximately by present data. Typical results for p electrons are given in Table XIII.

In Bi, Pb, and Sb we see that there is approximate agreement for the $6p$, $5p$ electron under different conditions. The values of g are not constant, however, but show variations of the order of 20 percent. This again supports our opinion that the numbers a', a'' are only approximately constants. The magnetic moments derivable at present we must thus also regard as only approximately correct. By averaging a large number of magnetic moment determinations for the same element, as has been done in some cases by Goudsmit,[31] the errors may cancel statistically.

Our main conclusions are thus: (1) The experimental data on hfs in intermediate coupling is in as good agreement with the little-magnet picture of the nucleus as may be expected. (2) The discrepancies in the ratio a''/a' are reasonably explained by the sensitivity of the apparent value of a' to the variations in a'', $a(s)$, etc., due to perturbations by other configurations as well as its sensitivity to experimental errors.[32]

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[31] S. Goudsmit, Phys. Rev. **43**, 636 (1933).

[32] On completing this manuscript we received a paper by Fermi and Segrè, Zeits. f. Physik **82**, 729 (1933), in which the same conclusion is reached by different methods involving explicit and accurate calculations of $\overline{(1/r^3)}$ and the calculation of the effect of perturbations by high energy levels with large hfs.