ON THE HYPERFINE STRUCTURE OF HEAVY ELEMENTS

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Abstract

The ordinary theory of hfs splitting is incomplete for two reasons in the case of heavy elements. (1) When the electron is close to the nucleus its velocity is high. Nonrelativistic approximations to Dirac's equation become meaningless. (2) The probability of the electron being sufficiently close to the nucleus to interact with it at all may be appreciably different for different components of the same multiplet. General relativistic formulas (12), (12″) are derived for single electron spectra. Quantitative estimates are made for the specific case of the Tl lowest p term. The nonrelativistic approximations with the same $\overline{r^{-3}}$ for $p_{1/2}$ and $p_{3/2}$ are found to give values of $(\Delta\nu)p_{1/2}/(\Delta\nu)p_{3/2}$ which are too small by a factor of about $3.4=2\times1.7$. The factor 2 is attributable to relativistic corrections. The estimated factor 1.7 is due to the higher energy of the $p_{3/2}$ level which decreases the chance of the electron to be close enough to the nucleus to interact with it. Comparison with the observations of John Wulff on Tl I shows that even the corrected value of $(\Delta\nu)p_{1/2}/(\Delta\nu)p_{3/2}$ is too small by a factor of 2. A qualitatively similar disagreement exists for Bi I. The observed hfs of these elements is therefore not accounted for by the theory of a nuclear magnetic moment.

ACCORDING to the recent theoretical analysis of Goudsmit[1] the hyperfine structure of Bi and Tl is in disagreement with simple theoretical expectations. The outstanding final result is that the hfs splitting of a $p_{3/2}$ single electron state is anomalously small in comparison with the hfs splitting of a $p_{1/2}$ state. There are two omissions in the simple theory used by Goudsmit: (1) the electron is treated nonrelativistically, and (2) the difference in energy of the two p states is neglected i.e. the spin orbit coupling giving rise to doublet structure is supposed to be small. For heavy atoms both omissions may be expected to be of importance. The approximations involved in the nonrelativistic treatment amount to a neglect of higher powers of αZ where α is the fine structure constant and Z is the atomic number. For Tl $\alpha Z=81/137.3$ and is not small. As a result the $p_{1/2}$ state is somewhat similar to an s state and is subject to a large splitting. The difference in energy of $p_{3/2}$ and $p_{1/2}$ is also large being of the order of 0.9 volt. The necessity of considering these effects has been pointed out in a recent letter to the Physical Review.[2] In the present note a quantitative estimate of their influence is made for the case of Tl.

The splitting ratio $(\Delta\nu)p_{1/2}/(\Delta\nu)p_{3/2}$ as given by the simple nonrelativistic theory is found to be too small. The relativistic corrections close to the nucleus increase the ratio by a factor of 2. In addition there is a further increase of the ratio by a factor of approximately 1.7. This is due to the higher energy

[1] S. Goudsmit Phys. Rev. **37**, 663 (1931).
[2] Breit, Phys. Rev. **37**, 1182 (1931).

of $p_{3/2}$ which makes it easier for the valence electron to escape from the inner shell. The proper function is depressed by approximately $(1.7)^{1/2}$ in the region of its first four half waves. Both effects owe their origin to the same cause: the large value of αZ. The first effect is due to an essential difference in the radial distribution of "current density" of the two p states at distances of the order of 0.02 to .005 of a Bohr radius (0.528A). The second is due to differences in radial distribution on the periphery of the atom, which affects the magnitude of electron currents close to the nucleus without affecting their distribution.

The simple nonrelativistic theory gives therefore a too small value of $(\Delta\nu)p_{1/2}/(\Delta\nu)p_{3/2}$ by a factor of about 3.4. A deliberately wrong way of treating the proper function in the neighborhood of its last and most important maximum gives about 4.4 for the same factor. This deliberately wrong calculation affects the nuclear g factor by a factor of about 5. It is believed therefore that the results are fairly independent of possible inexactness in the computation of the proper functions as long as one is primarily interested in the comparison of the $p_{1/2}$ and $p_{3/2}$ splittings.

The experiments of Wulff[3] indicate that the disagreement with the nonrelativistic formulas is by a factor of about 7. On making a correction for the effects discussed here there remains a discrepancy between theory and experiment by a factor of $7/3.4=2$. The splitting of the $p_{1/2}$ level is twice as large in comparison with that of $p_{3/2}$ as it should be according to the theory of a fixed magnetic moment of the nucleus. In order to account for Wulff's results it seems necessary to consider other types of interaction. Of the two states the $p_{1/2}$ is the more penetrating. Qualitatively the anomaly is such as though at close distances from the nucleus the interaction between the nucleus and the electron became greater than it should be on the hypothesis of a nuclear magnetic moment.

General Relativistic Treatment

We suppose for the present purpose that the nucleus is a rigid point charge of electrostatic charge Ze and magnetic moment

$$g\mu_0 \boldsymbol{I}$$

where $\mu_0=eh/4\pi mc$ is the Bohr magneton. The angular momentum is $\boldsymbol{I}$ in units $h/2\pi$. The factor g is a pure number which may be called the Landé g-factor for the nucleus. The magnetic moment $\boldsymbol{I}$ may be represented by a matrix. The maximum proper value of a component of $\boldsymbol{I}$ is denoted by i. The interaction energy of the electron with the nucleus is

$$+\frac{e}{c}\boldsymbol{\alpha}\cdot g\mu_0 r^{-3}[\boldsymbol{r}\times\boldsymbol{I}]. \tag{1}$$

Here $\boldsymbol{\alpha}=(\alpha_1, \alpha_2, \alpha_3)$ is the vector composed of the first three of Dirac's α's.

[3] John Wulff, Zeits. f. Physik **69**, 70 (1931).

The charge of the electron is taken to be $(-e)$. The angular momentum of nucleus and electron together is

$$F = J + I \tag{2}$$

where J is the angular momentum of the electron alone. In the usual notation the maximum proper values of components of F and J are written f, j. The interaction energy (1) is of the form

$$A \cdot I \tag{1'}$$

with A involving only the electron variables. The first order perturbation in the energy is

$$\Delta w = (AJ)_j[f(f+1) - i(i+1) - j(j+1)]/[2j(j+1)]. \tag{3}$$

Here $(AJ)_j$ is the value of any diagonal element in the matrix AJ in that part of it which belongs to the quantum number j. We have

$$A = (ge\mu_0/c)r^{-3}[\alpha \times r]. \tag{4}$$

In order that (3) should hold it is sufficient that the commutation relations

$$[J_z, A_z] = 0, \quad [J_x, A_y] = iA_z \text{ etc.}$$

be satisfied. This is the case. The substitution of Landé's cosine into the classical precession formula made in (3) is therefore justified whenever the hfs splitting is small in comparison with the multiplet structure.

Nonrelativistically

$$(AJ)_j = 2g\mu^2{}_0 l(l+1)\overline{(r^3)} \tag{5}[4]$$

where l is the azimuthal quantum number. The relativistic value of $(AJ)_j$ can be obtained by direct calculation. It is much simpler however to avoid such rather complicated calculations by determining only the form of $(AJ)_j$ and then fixing the factor by comparison with (5).

The separation of angles from the radial distance for Dirac's equation in a central field has been made by Dirac and Darwin. We find it convenient to use the radial functions denoted by Gordon as ψ_1, ψ_2. In order to distinguish them from the components of the wave-function $\Psi = (\psi_1, \psi_2, \psi_3, \psi_4)$ we call them ϕ_1, ϕ_2. The ψ_μ in terms of the ϕ_1, ϕ_2 may be written as

$$= \frac{1}{r}(i\phi_1\rho_3,\ i\phi_1\rho_4,\ \phi_2\tau_3,\ \phi_2\tau_4) \tag{6}$$

where $\rho_3 = \rho_1 - \tau_1$, $\rho_4 = \rho_2 - \tau_2$, $\tau_3 = \rho_1 + \tau_1$, $\tau_4 = \rho_2 + \tau_2$ and ρ_1, ρ_2, τ_1, τ_2 are angular functions used by Weyl. The important thing for us is not the form of the functions ρ, τ but the fact that they enter Ψ as shown in (6). The differential equations satisfied by ϕ_1, ϕ_2 may be mentioned at this point for future reference. They are

[4] Pauling and Goudsmit, McGraw Hill, 1930. p. 225. The present derivation of the relativistic result is an almost exact parallel of a short derivation of (5) given by the writer (Phys. Rev. **37**, 51 (1931). The $\overline{A}$ of the present text corresponds to $g\mu_0\overline{A}$ of the just mentioned note.

$$\frac{d\phi_1}{dr} - \frac{j'\phi_1}{r} = [(2\pi/\Lambda)(1 - E/mc^2) + V]\phi_2$$
$$\frac{d\phi_2}{dr} + \frac{j'\phi_2}{r} = [(2\pi/\Lambda)(1 + E/mc^2) - V]\phi_1 \tag{7}$$

$j' = -1, 1, -2$, etc. for s, $p_{1/2}$, $p_{3/2}$, . . . where $\Lambda = h/mc$ is the Compton wavelength, E is the energy and V is the potential energy.

In order to find $(AJ)_j$ it is sufficient to find the diagonal matrix element of A corresponding to the magnetic quantum number $m = j$. If this matrix element be called a then $(AJ)_j = (j+1)a$. To find a we must integrate $\Psi^*(\alpha_1 y - \alpha_2 x)\Psi$ over the whole configuration space. An inspection of (6) and the matrices α_1, α_2 shows that the summation over the spin variables brings in a common factor $\phi_1\phi_2/r^2$. The radius r is contained in this combination only. Besides there is also a factor involving the polar angles which gives rise on integration to a number depending on l, j but not on a. Thus $(AJ)_j$ is $C(l, j)\int^\infty_0 \phi_1\phi_2 r^{-2}dr$. The function $C(l, j)$ may be determined by comparison with (5). The radial properties of the proper function are contained in (5) only in $\overline{(r^{-3})}$. We look, therefore, for a connection between $\overline{(r^{-3})}$ and $\int^\infty_0 \phi_1\phi_2 r^{-2}dr$. This is given by the two Eqs. (7). We multiply the first by ϕ_1, the second by ϕ_2 and add, thus eliminating V. The result we divide by r^2 on both sides and obtain

$$(4\pi/\Lambda)\phi_1\phi_2/r^2 = (1/2r^2)\frac{d(\phi_1^2 + \phi_2^2)}{dr} + (j'/r^3)(\phi_2^2 - \phi_1^2).$$

By partial integration

$$(4\pi/\Lambda)\int_0^\infty (\phi_1\phi_2/r^2)dr = (4\pi/\Lambda)\int_0^{r_0} (\phi_1\phi_2/r^2)dr - (\phi_1^2 + \phi_2^2)_{r_0}/(2r_0^2)$$
$$+ \int_0^\infty [(j' + 1)\phi_2^2 - (j' - 1)\phi_1^2]r^{-3}dr \tag{8}$$

where r_0 is arbitrary. We now consider (8) for a light atom where the relativistic corrections are not important. We may then choose such a value for the so far arbitrary r_0 that the value of the first two terms on the right side of (8) is small in comparison with the last. This may be done for anything but s terms. For these the second term approaches a constant value also in the non-relativistic case and the last term vanishes because $j' = -1$ and ϕ_1 is small. In the limit $c \to \infty$ for anything but s terms the right hand side of (8) is therefore $(j'+1)\overline{(r^{-3})}$ with the normalization

$$\int_0^\infty (\phi_1^2 + \phi_2^2)dr = 1. \tag{9}$$

Since $C(l, j)$ does not involve α we may replace $\overline{(r^{-3})}$ in (5) by

$$\overline{(r^{-3})} \to [(4\pi/\Lambda)/(j' + 1)]\int_0^\infty (\phi_1\phi_2/r^2)dr. \tag{10}$$

The combination which occurrs in (5) is

$$l(l+1)\overline{(r^{-3})} \rightarrow (4\pi j'/\Lambda)\int_0^\infty (\phi_1\phi_2/r^2)dr. \tag{11}$$

The replacement (10) has no meaning for s terms ($l=j'+1=0$). Formula (5) with the substitution (11) is correct however also in this case.[5]

Combining (3), (4), (11) we have

$$\Delta w = 4\pi j' g\mu_0{}^2[f(f+1)-j(j+1)-i(i+1)]\int_0^\infty \phi_1\phi_2 r^{-2}dr/[\Lambda j(j+1)] \tag{12}$$

with the radial function normalizing condition (9). For practical applications it is convenient to express all lengths in terms of

$$a_H = h^2/(4\pi^2 me^2). \tag{13}$$

We then have on letting $\mu_0{}^2/a_H{}^3 = R_\infty\alpha^2/2 = 2.909\ \text{cm}^{-1}$

$$\Delta w = 2.909g\frac{l(l+1)}{j(j+1)}[f(f+1)-j(j+1)-i(i+1)]\overline{\left(\frac{a_H}{r}\right)^3} \tag{12'}$$

nonrelativistically. On the other hand if in formula (12) and the normalizing condition (9) we use a_H as the unit length the factor

$$4\pi g\mu_0{}^2/\Lambda \rightarrow R_\infty a g = 799g\text{cm}^{-1} = 0.434(1840g)\ \text{cm}^{-1}. \tag{12''}$$

Numerical Calculations

To start with the central field of Thomas and Fermi[6] was used. On trying it we find that it must be modified somewhat to bring about agreement with the experimentally known energies. The field is changed so as to agree with the term value of $p_{1/2}$ and it then is found by numerical trial to agree also with the energy of $p_{3/2}$. We first explain the method of calculation for a given field.

The same units as those used by Fermi[7] are employed.

$$r = (h^2/8\pi^2 me^2)x = a_H x/2$$
$$-\eta = (h^2/8\pi^2 me^4)E = E/(4R_\infty).$$

The unit of length is 1/2 of the Bohr radius and the unit of energy is 4 times the Rydberg constant. Here E is the term value energy. The total energy is

$$mc^2 - 4R_\infty\eta.$$

In these units in terms of the central field function denoted by Fermi as ϕ the Eqs. (7) become

[5] This may be found by means of (8) remembering that nonrelativistically $(r^{-3}(l+1)=2\pi\psi^2(0)$ where ψ is Schroedinger's function normalized so as to have $\int_0^\infty 4\pi\psi^2(r)r^2dr=1$.

[6] L. H. Thomas, Proc. Cambridge Phil. Soc. **23,** 542 (1927); Fermi, Zeit. f. Physik **48,** 73 (1928).

[7] Fermi, Zeit. f. Physik **49,** 550 (1928).

$$\frac{d\phi_1}{dx} - \frac{j'\phi_1}{x} = \alpha[\eta - (1/x)\{1 + (Z-1)\Phi(\gamma x)]\phi_2$$
$$\frac{d\phi_2}{dx} + \frac{j'\phi_2}{x} = (1/\alpha)[1 - \alpha^2\eta + (\alpha^2/x)\{1 + (Z-1)\Phi(\gamma x)\}] \tag{14}$$

where $\gamma = (16(Z-1)/9\pi^2)^{1/3}$, Z is the atomic number and $\alpha = 2\pi e^2/hc$. For small values of the argument $\gamma x (\gamma x < 0.3)\Phi$ may be approximated by

$$\Phi(\gamma x) = 1 - \gamma x$$

In this region it is convenient to use the variable

$$y = Zx \tag{15'}$$

in terms of which (14) becomes

$$\frac{d\phi_1}{dy} - \frac{j'\phi_1}{y} = \left(b - \frac{a}{y}\right)\phi_2$$
$$\frac{d\phi_2}{dy} + \frac{j'\phi_2}{y} = \left(c + \frac{a}{y}\right)\phi_1 \tag{15}$$

where

$$a = \alpha Z,\ b = (\alpha/Z)[\eta + \gamma(Z-1)]$$
$$c + b = 1/a \tag{15''}$$

Eqs. (15) are exactly of the form occurring in the problem of the Coulomb field.[8] The solution of (15) may be put into the following form

$$\phi_1 = b^{1/2}(\sigma_1 - \sigma_2),\ \phi_2 = c^{1/2}(\sigma_1 + \sigma_2);$$
$$\sigma_1 = c_0^{(1)} e^{-z} z^\rho F(1 - n', 2\rho + 1, 2z);\ F(\alpha, \beta; x) = 1 + \frac{\alpha}{1!\beta}x + \frac{\alpha(\alpha+1)}{2!\beta(\beta+1)}x^2 + \cdots$$
$$\sigma_2 = c_0^{(2)} e^{-z} z^\rho F(-n', 2\rho + 1, 2z);$$
$$z = (bc)^{1/2}y,\ \rho = +(j'^2 - a^2)^{1/2} \tag{16}$$
$$n' = -B - \rho,\ A = (a/2)[(b/c)^{1/2} + (c/b)^{1/2}]$$
$$B = (a/2)[(b/c)^{1/2} - (c/b)^{1/2}]$$
$$\frac{c_0^{(1)}}{c_0^{(2)}} = \frac{j' + A}{B - \rho} = \frac{\rho + B}{-j' + A} = \frac{n'}{j' - A}.$$

It is seen from (15'') that b depends for its existence on the variation of the function Φ with distance i.e. on the rate of change of the effective charge for the potential. It is this variation that gives rise to $\gamma(Z-1)$ in the expression for b. The quantity η is negligible in comparison being of the order of 0.1 while $\gamma(Z-1) \cong 200$. Although b is not very small we obtain a rough approximation by letting $b=0$ in (15). Then we obtain simple solutions

[8] W. Gordon, Zeits. f. Physik **48**, 11 (1928); C. G. Darwin, Proc. Roy. Soc. **A118**, 654 (1928).

$$\begin{aligned}\phi_1 &= J_{2\rho}(2(acy)^{1/2}) \\ a\phi_2 &= (j' - \rho)J_{2\rho}(2(acy)^{1/2}) + (acy)^{1/2}J_{2\rho+1}(2(acy)^{1/2})\end{aligned} \tag{16'}$$

where the J_m are Bessel functions of order m.

These approximate solutions have been used[2] for a preliminary estimate of the difference between $p_{1/2}$ and $p_{3/2}$ terms. Although (16') is a sort of an approximation an examination of the numerical values makes it validity somewhat questionable. In the present case

$\gamma = 2.4334$, $a = 0.58994$, $b = 0.01751$, $c = 1.6776$
For $p_{3/2}(j' = -2)$, $\rho = 1.911$ and $n' = 0.946$
For $p_{1/2}(j' = +1)$, $\rho = 0.8074$ and $n' = 2.050$

The number $n' + \rho$ corresponds to the total quantum number of an electron moving in the field of charge Ze. In our case $n' + \rho = 2.86$. The proper function of the valence electron near the nucleus is therefore such as though there were no screening but as if the electron had an energy

$$mc^2 - \frac{RZ^2}{(2.86)^2}$$

i.e., roughly as if it were an unscreened M electron. Setting $b = 0$ amounts to letting $n' + \rho = \infty$. For this reason b was taken into account in one case by means of (16) and in another by a somewhat different but mathematically equivalent expansion. The results were checked numerically by using the expressions for $d\phi_1/dy$, $d\phi_2/dy$ which follow from the differential equations and then computing $\int d\phi_1/dydy$, $\int d\phi_2/dydy$ by Simpson's rule. The integrals $\int_0^\infty \phi_1\phi_2 r^{-2}dr$ have then been also computed by Simpson's rule. The integrand became relatively small for values smaller than those corresponding to $\gamma x < 0.3$ and of the order of $\gamma x = 0.2$.

Formulas (16) contain an arbitrary factor which may be determined only by continuing the solution for larger r and determining the normalization. It is not important to continue the solution very exactly particularly where the functions are relatively small. These regions give a negligible contribution to the normalization integral and only a small one to the effective value of $\overline{r^{-3}}$. The method of Kramers-Wentzel-Brillouin[9] was used. Since in the present instance we are concerned with solving two simultaneous differential equations a slight modification of the method had to be made. Eqs. (14) are of the form

$$\frac{d\phi_1}{dx} - \frac{j'\phi_1}{x} = (b - v)\phi_2; \quad \frac{d\phi_2}{dx} + \frac{j'\phi_2}{x} = (c + v)\phi_1. \tag{17}$$

Eliminating ϕ_1 and making the substitution

$$\phi_2 = (c + v)^{1/2}\chi_2$$

[9] H. A. Kramers, Zeits. f. Physik **39**, 828 (1926); G. Wentzel, Zeits. f. Physik **38**, 518, (1926); L. Brillouin, C. R. July (1926).

we obtain the differential equation satisfied by χ_2

$$\frac{d^2\chi_2}{dx^2} + f^2\chi_2 = 0$$

$$f^2 = (v-b)(c+v) - \frac{j'(j'+1)}{x^2} - \frac{j'(dv/dx)}{x(c+v)} + \frac{(d^2v/dx^2)}{2(c+v)} - \frac{3(dv/dx)^2}{4(c+v)^2} \cdot \quad (17')$$

Here the first two terms are exactly as though we were dealing with Schroedinger's nonrelativistic equation. The third and fourth represent the main part of the interaction of the electron spin with the electric field of the nucleus. The last term is an unimportant correction. We have then in the region $f^2>0$

$$\phi_2 = [(c+v)/f]^{1/2} \cos\left\{\int f dx + \text{const.}\right\} \quad (17'')$$

a constant multiplier to be determined from normalization being understood.

The approximate solution (17'') applies in the region $f^2>0$. It has been used from somewhat beyond the first maximum of ϕ_2. It was joined to the power series (16) at the maximum of $[f/(c+v)]^{1/2}$. For the calculation of $\int_0^{r_0}\phi_1\phi_2 r^{-2}dr$ however the power series was used. The electron states in question are p states with total quantum number 6. Therefore ϕ_2 has 5 maxima and minima between $r=0$ and ∞. Solution (17'') applies reasonably well between the first and the last maximum. From there to $r=\infty$ it was joined to an exponential function by the device due to Kramers[10] which in our case consists in making

$$(c+v)^{1/2}f^{-1/2}\cos\left\{\int_r^{r_2} f dx - \pi/4\right\} (r<r_2) \quad (18')$$

join to the function

$$(\tfrac{1}{2})(c+v)^{1/2}|f|^{-1/2}\exp\left\{-\int_{r_2}^{r}|f|\,dx\right\}(r>r_2). \quad (18'')$$

Here $f=0$ at $r=r_2$

The value of $\int f dx$ from the first to the last maximum was made $(4+1/4)\pi$ in agreement with Kramers' half quantum number quantization rule. Neither (18') nor (18'') represent the transition region around $f=0$ satisfactorily. The well-known confluent hypergeometric function solution was used here. The constant factor by which it should be multiplied was determined by making it join and coincide with (18'') for large x.

Instead of using (18'), (18'') another deliberately rougher method was also tried. The phase integral was made to have the value $9\pi/2$, the limits of integration being from the first maximum to the point $f=0$. The function ϕ_2 then vanished at this point and was broken off from there on. This amounts to treating the electron classically at large distances. The ratio of the nor-

[10] See also Zwaan Utrecht Dissertation, 1929.

malization integrals was found to be roughly the same as in the more exact calculation but their values were quite different. The comparison of the two methods indicates that an absolute calculation of the g factor is more difficult than a test of its constancy.

A serious limitation on the accuracy of these calculations is the lack of knowledge of the central field. The potential function $\Phi(\gamma x)$ is multiplied throughout by $Z-1=80$ which makes an accurate knowledge of Φ important. Fermi's table for Φ was tried first. The phase integral for $p_{1/2}$ was found to be $>9\pi/2$. The field was then changed so as to have it purely Coulomb and due to a single charge e from a certain point on. The amount $(Z-1)\Phi$ at this point was subtracted from the potential for smaller values of x. Recomputing the phase integral for a few such trial fields a field giving the desired value of the phase integral was found. The phase integral for $p_{3/2}$ was then computed and was found to give the same result. This indicates that the field used was not very bad for the present purpose. A summary of the main results of the calculation follows.

$\gamma=2.4334$, $\xi=\gamma x$. From $\xi=12$ field is purely Coulomb

	$p_{1/2}$	$p_{3/2}$
Experimental η	$=0.11223$	$=0.09448$
First maximum of $f^{1/2}(c+v)^{1/2}\phi_2$ at	$y=4.4$	5.2
	$\int_{y=4.4}^{\xi=2} f dx = 0.707$	$\int_{y=5.2}^{\xi=2} f dx = 0.431$
Roots $\xi \leqq$	0.30, 0.9, 2.1, 4.8	0.35, 0.98, 2.2, 5.3
$\int_0^\infty \phi_2^2 d\xi =$	31.3	53.2
$\xi_0 =$	0.2	0.3
$\frac{4\pi}{\Lambda(j'+1)}\int_0^{\xi_0} \phi_1\phi_2 r^{-2} dr =$	$28.8 a_H^{-3}$	$8.3 a_H^{-3}$
$\frac{4\pi}{\Lambda(j'+1)}\int_{\xi_0}^\infty \phi_1\phi_2 r^{-2} dr =$	$0.7 a_H^{-3}$	$0.7 a_H^{-3}$
$\frac{4\pi}{\Lambda(j'+1)}\int_0^\infty \phi_1\phi_2 r^{-2} dr =$	$29.5 a_H^{-3}$	$9.0 a_H^{-3}$.

Using Wulff's observed value of $(\Delta\nu)p_{1/2}=0.727$ cm^{-1} and $i=1/2$, 1840 $g \leqq 2.9$. From the splitting of $p_{3/2}$ however 1840 $g \leqq 1.4$.

Calculations with the phase integral adjusted to be $9\pi/2$ gave a ratio of $4\pi/\Lambda(j'+1)\int_0^\infty \phi_1\phi_2 r^{-2} dr$ for $p_{1/2}$ to $p_{3/2}$ of about 4.4. The only difference from the preceding solution is in the normalization factors which in this case give rise to a factor of roughly 2. The qualitative reason for this factor (1.7 by the more accurate calculation) if that the electron has a higher energy in the $p_{3/2}$

state so that it escapes vigorously from the inner shells of the atom. The relativistic corrections consisting in the use of $\int_0^\infty \phi_1\phi_2 r^{-2}dr$ are seen also to lead to a correction by about a factor of 2. This may be also verified analytically by the more easily handled solutions in terms of Bessell functions (16′) and leads to approximately the same result. It is felt that the above considerations are sufficiently independent of the special assumptions made about the nature of the central field. It is quite possible that the ratio of the values of $4\pi/\Lambda(j'+1)\int_0^\infty \phi_1\phi_2 r^{-2}dr$ for the two p terms is somewhere between 3 and 4 but it appears impossible that it should be as large as 7. For Bi I, according to Goudsmit[1] we would have to account for a factor of more than 10. On applying the corrections worked out here there remains a discrepancy by a factor of roughly 3. In both cases $(\Delta\nu)p_{1/2}/(\Delta\nu)p_{3/2}$ is anomalously great. This suggests that at close distances the nucleus binds the electron to the nuclear spin axis more tightly than the magnetic doublet model would lead one to suppose.

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