Gyromagnetic Ratio in the Hyperfine Structure of Doublet States*†

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(Received March 10, 1954)

Perturbation of the hyperfine structure of an electronic $p_{1/2}$ state by the $p_{3/2}$ state is calculated using relativistic electronic functions. The main effects are a change in apparent nuclear g factor and a common lowering of all $p_{1/2}$ sublevels. Energy corrections due to the perturbation of one level of a doublet term by the other when i is $\frac{1}{2}$ and j is arbitrary are also obtained.

I. INTRODUCTION

IN the usual theory of hyperfine structure of an atom in a magnetic field, the effects of the nucleus and applied field are treated as perturbations and the part of the secular determinant arising from unperturbed levels of the same energy is considered. When either j or i is $\frac{1}{2}$, this leads to an equation of the Breit-Rabi[1] form. Inclusion in the secular determinant of matrix elements between the components of a doublet electronic term, e.g., between $p_{\frac{1}{2}}$ and $p_{\frac{3}{2}}$ components, gives second-order corrections to this equation. Foley[2] has treated the corrections for $p_{\frac{1}{2}}$ states, using nonrelativistic wave functions, and he has shown that they lead to a change in the apparent nuclear g factor. In the present work this treatment is modified by using relativistic electronic functions and the case $i=\frac{1}{2}$ is also considered. The procedure has been to compute matrix elements of the perturbing terms of the Hamiltonian between states of definite f, m_f. These are used in the secular determinant and this determinant is solved to order $1/\delta$, where δ is the doublet separation. Expressions for the energy are thus obtained which are applicable for a range of field strengths such that the perturbing terms are small compared with δ.

II. UNPERTURBED SOLUTIONS

The Dirac Hamiltonian for an electron in an electromagnetic field is

$$H=-c\boldsymbol{\alpha}\cdot(\mathbf{p}+(e\mathbf{A})/c)-eA_0-\beta mc^2, \tag{1}$$

where $-e$ is the charge on the electron and A_0 and $\mathbf{A}$ are the scalar and vector potentials, respectively. In this problem the effect of the vector potential is treated as a perturbation. The unperturbed electronic functions are solutions of the equation

$$H_0\Psi=E_0\Psi, \tag{2}$$

where

$$H_0=-c\boldsymbol{\alpha}\cdot\mathbf{p}-eA_0-\beta mc^2. \tag{3}$$

For application to a single electron outside of closed shells, A_0 is assumed to depend only on the radial distance r_e of the electron from the nucleus and the nucleus is taken to be stationary. The solutions of Eq. (2) used here are the same as those given by Darwin[3] except that a factor $\exp[\pi i(m_j-\frac{1}{2})]$ is included for $m_j>0$. This choice of phase is convenient since the operation of the electronic angular momentum $\mathbf{J}$ then takes the form

$$J_z\Psi_j(m_j)=m_j\hbar\Psi_j(m_j), \tag{4}$$

$$(J_x\pm iJ_y)\Psi_j(m_j)=\hbar[(j\mp m_j)(j\pm m_j+1)]^{\frac{1}{2}}\Psi_j(m_j\pm1). \tag{5}$$

Here $\Psi_j(m_j)$ is the solution of Eq. (2), corresponding to particular electronic quantum numbers j, m_j.

The nucleus has been treated as of negligible spatial extent and of infinite mass so that it is taken to be stationary.[4] As is well known the angular momentum operators I_x, I_y, I_z of the nucleus may be represented by noncommuting matrices and the nuclear spin functions by column vectors $N_i(m_i)$, belonging to values i and m_i of the nuclear spin quantum numbers. Wave functions of the combined system of electron plus nucleus are linear combinations of products of the type $\Psi_j(m_j)N_i(m_i)$. Combined functions belonging to particular quantum numbers f, m_f of the total angular momentum $\mathbf{F}=\mathbf{J}+\mathbf{I}$ are obtained by using the coefficients of the product functions given by Wigner.[5] These functions with definite f, m_f are the base functions used in the perturbation calculation.

III. PERTURBATIONS

The perturbing term of the vector potential is, from Eq. (1), $-e\boldsymbol{\alpha}\cdot\mathbf{A}$. The vector potential $\mathbf{A}$ has a part $[\mathfrak{H}\times\mathbf{r}_e]/2$ due to the external field $\mathfrak{H}$ and a part $[\boldsymbol{\mu}_i\times\mathbf{r}_e]/r_e^3$ due to the nuclear moment $\boldsymbol{\mu}_i$. Here $\mathbf{r}_e$ is the position vector of the electron with respect to the nucleus. An additional perturbation is the energy

* Part of a dissertation submitted for the degree of Doctor of Philosophy at Yale University.

† Assisted by the joint program of the U. S. Office of Naval Research and U. S. Atomic Energy Commission. The later part of the work was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

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[1] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931); Millman, Rabi, and Zacharias, Phys. Rev. **53**, 384 (1938).

[2] H. M. Foley, Phys. Rev. **80**, 288 (1950).

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

[4] For a doublet component of a particular isotope, the main effect of the finite nuclear volume is to cause a shift in energy common to all sublevels. See, e.g., J. E. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932); G. Breit, Phys. Rev. **42**, 348 (1932).

[5] E. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Vieweg und Sohn, Braunschwig, 1931).

$-\mathfrak{y}_i\cdot\mathfrak{H}$ of the nuclear moment in the external field. If $\mathfrak{H}$ is taken in the z direction, the three perturbations become

$$(e/2)\mathfrak{H}_z B_z \equiv X, \tag{6}$$

$$eg_i\mu_0(\mathbf{I}\cdot\mathbf{B})/hr_e^3 \equiv Y, \tag{7}$$

$$-g_i\mu_0\mathfrak{H}_z I_z/h \equiv Z. \tag{8}$$

Here $\mathbf{B}$ is the matrix vector $\boldsymbol{\alpha}\times\mathbf{r}_e$, μ_0 is the Bohr magneton, and the nuclear moment $\mathfrak{y}_i$ is $g_i\mu_0\mathbf{I}/h$, $\mathbf{I}$ being the nuclear angular momentum operator.

Matrix elements of matrix vectors of the type of (6), (7), and (8) have been given by Guettinger and Pauli[6] and by Johnson.[7] All the nonvanishing elements are diagonal in m_f, and f differs in the initial and final states by 0, ±1. The elements of (7) are diagonal in f while those of (8) are diagonal in j.

Matrix elements of (6) between states of different f are given in terms of the elements of (6) between electron states $\Psi_j(m_j)$. These are

$$(\Psi_j(m_j),\ X\Psi_j(m_j)) = \mu_0\mathfrak{H}_z g_j' m_j, \tag{9}$$

$$(\Psi_{l+\frac{1}{2}}(m_j),\ X\Psi_{l-\frac{1}{2}}(m_j)) = \mu_0\mathfrak{H}_z N\{(l+\tfrac{1}{2})^2-m_j^2\}^{\frac{1}{2}}/(2l+1). \tag{10}$$

The quantities g_j' and N are given by

$$g_j' = g_j\left[1-\{4k/(2k-1)\}\int_0^\infty F_j^2 dr_e\right], \tag{11}$$

$$N = \int_0^\infty G_{l+(1/2)}G_{l-(1/2)}dr_e. \tag{12}$$

Here g_j is the Lande g factor while k is the quantum number introduced by Dirac and equal to $-l-1$ for $j=l+\frac{1}{2}$ and to l for $j=l-\frac{1}{2}$. The functions F_j and G_j are solutions for particular j of Dirac's radial equations in the form used by Gordon,[8] with the normalization

$$\int_0^\infty (F_j^2+G_j^2)dr_e = 1. \tag{13}$$

The second term in the brackets of (11) is the relative correction to g_j discussed by Breit[9] and by Margenau.[10]

The matrix elements of (7) are most readily expressed in terms of coupling constants of the interaction between electron and nucleus. Between states of definite f, m the matrix elements are

$$(i,j,f,m_f|\,Y\,|i,j,f,m_f) = (a_{j,j}/2)[f(f+1)-j(j+1)-i(i+1)], \tag{14}$$

$$(i,j,f,m_f|\,Y\,|i,j-1,\ f,m_f) = \pm(b_{j,j-1}/2)[(f+j-i)\times(f+i-j+1)(f+j+i+1)(j+i-f)]^{\frac{1}{2}}. \tag{15}$$

Here $a_{j,j}$ and $b_{j,j-1}$ are the coupling constants

$$a_{j,j} = [2eg_i\mu_0 k/j(j+1)]\int_0^\infty F_jG_jr_e^{-2}dr_e, \tag{16}$$

$$b_{j,j-1} = -[eg_i\mu_0/2j]\int_0^\infty (F_{j-1}G_j+F_jG_{j-1})r_e^{-2}dr_e. \tag{17}$$

Choice of the double sign in (15) depends on the relative phases of the functions belonging to j and $j-1$. The coupling constants $a_{j,j}$ and $b_{j,j-1}$ are those of Breit and Wills' paper.[11] In their notation which was also that of Goudsmit[12] $a_{jj}=a'$ for $j=l+\frac{1}{2}$, $a_{jj}=a''$ for $j=l-\frac{1}{2}$, and $b_{j,j-1}=a'''$.

Matrix elements of the third perturbation, (8), may be expressed in terms of the diagonal matrix element between states $N_i(m_i)$, which is

$$(N_i(m_i),\ ZN_i(m_i)) = -g_i\mu_0\,\mathfrak{H}_z m_i. \tag{18}$$

All matrix elements of the perturbations between states of definite f, m_f are given in terms of (9), (10), (16), (17), and (18) by means of the Guettinger-Pauli formulas, and the secular determinant may thus be set up.

IV. ENERGY LEVELS OF $p_{\frac{1}{2}}$ STATES

Since the matrix elements are diagonal in m_f, the secular determinant breaks up into smaller determinants corresponding to a given m_f. For the $p_{\frac{1}{2}}$, $p_{\frac{3}{2}}$ doublet there are, in general, six values of f and the smaller determinants have six rows and columns. These may be solved in an approximation equivalent to the standard second-order perturbation approximation. The diagonal elements belonging to $p_{\frac{3}{2}}$ are approximated by δ, the doublet separation. Off-diagonal elements belonging to the $p_{\frac{3}{2}}$ state and elements between $p_{\frac{1}{2}}$ and $p_{\frac{3}{2}}$ states are eliminated to order $1/\delta$ by adding multiples of rows and columns. The determinant is thus reduced to one with two rows and columns, the elements of which contain second-order terms. This is solved for the energy E. The result is

$$E-E_0 = -\frac{\Delta\nu}{2(2i+1)} - g_i'\mu_0\mathfrak{H}_z m_f \pm \frac{\Delta\nu}{2}\left(1+\frac{4m_fx}{2i+1}+x^2\right)^{\frac{1}{2}} - \frac{2(a''')^2}{\delta}i(i+1) - \frac{2\mu_0^2\mathfrak{H}_z^2N^2}{9\delta}. \tag{19}$$

Here E_0 is the unperturbed energy and $\Delta\nu$ is the zero-field separation, given by

$$\Delta\nu = (i+\tfrac{1}{2})[a''-2(a''')^2/\delta]. \tag{20}$$

The remaining undefined quantities are

$$g_i' = g_i(1+4Na'''/3g_i\delta), \tag{21}$$

$$x = (g_j'+g_i')\mu_0\,\mathfrak{H}/\Delta\nu. \tag{22}$$

[6] P. Guettinger and W. Pauli, Z. Physik **67**, 743 (1931).
[7] M. H. Johnson, Jr., Phys. Rev. **38**, 1635 (1931).
[8] W. Gordon, Z. Physik **48**, 11 (1928). In order to avoid double double subscripts, F is here used for Gordon's ψ_1, and G for his ψ_2.
[9] G. Breit, Nature **122**, 649 (1928).
[10] H. Margenau, Phys. Rev. **57**, 383 (1940).
[11] G. Breit and L. A. Wills, Phys. Rev. **44**, 470 (1932). In terms of φ_1, φ_2 of Breit and Wills the functions used here are $F=\varphi_1$, $G=\varphi_2$; F, G of Breit and Wills differ from those here and are expressed in terms of φ_1, φ_2 by their Eq. (15).
[12] S. A. Goudsmit, Phys. Rev. **37**, 663 (1931).

TABLE I. Values of correction terms in Eq. (28) and Eq. (27).

	$-(\Delta\nu)/[6(2i+1)g_i\delta]$	$-(\Delta\nu)\chi/[6(2i+1)g_i\delta]$
Gallium	−0.0062	−0.0058
Indium	−0.0043	−0.0035

Equation (19) is seen to have the same form as the Breit-Rabi equation except for the addition of the last two terms which are the same for all sublevels of the $p_{\frac{1}{2}}$ state. Perturbation by the $p_{\frac{3}{2}}$ state also adds a small correction term to $\Delta\nu$, but the main effect is to replace g_i with g_i'.

The magnitude of this effect may be estimated by using the values of a'' and a''' obtained by Breit and Wills.[11] Near the nucleus, where the integrands of (16) and (17) are large, a Bessel function approximation may be used for the electronic functions F and G. In this way the above authors obtain

$$(a'''/a'')=-(1/16)(\mathcal{E}/\mathcal{F}). \tag{23}$$

Here $\mathcal{F}$ and $\mathcal{E}$ are relativistic correction factors given by

$$\mathcal{F}=3/[\rho''\{4(\rho'')^2-1\}], \tag{24}$$

$$\mathcal{E}=(4/\pi Z^2\alpha^2)\sin\pi(\rho''-\rho'). \tag{25}$$

The quantity $\rho'=(4-Z^2\alpha^2)^{\frac{1}{2}}$, while $\rho''=(1-Z^2\alpha^2)^{\frac{1}{2}}$, where Z is the nuclear charge and α is the fine structure constant. The ratio $\chi=\mathcal{E}/\mathcal{F}$ is

$$\chi=1-1.396Z^2\alpha^2-0.121Z^4\alpha^4+\cdots. \tag{26}$$

Since the term $(a''')^2/\delta$ in $\Delta\nu$ is small compared with a'', one has, approximately,

$$a''\approx(2\Delta\nu)/(2i+1).$$

With these approximations the apparent nuclear g factor is

$$g_i'=g_i[1-(\Delta\nu)N\chi/\{6(2i+1)g_i\delta\}]. \tag{27}$$

V. APPLICATION TO GALLIUM AND INDIUM

Using nonrelativistic wave functions for the electron, Foley[2] found that

$$g_i'=g_i\{1-(\Delta\nu)/[6(2i+1)g_i\delta]\}. \tag{28}$$

Equation (27) is seen to be identical with this except for the factor $N\chi$ in the correction term. Taking N to be approximately unity, the effect of χ in the cases of gallium ($Z=31$) and indium ($Z=49$) is shown in Table I.

The change in apparent nuclear g factor appears experimentally in a difference in values of the g factor obtained from atomic beam experiments and those measured by magnetic resonance methods. Existence of such discrepancies has been pointed out by Kusch.[13] Using experimental values of the nuclear moments quoted by him, the ratio of the apparent moment from atomic beam work to that from magnetic resonance work is $1-0.0079\pm0.0023$ for Ga^{69} and $1-0.0077\pm0.0017$ for Ga^{71}. The theoretical values, both the nonrelativistic -0.0062 and the relativistic -0.0058 are seen to differ from the experimental ones by an amount about equal to the assigned experimental error. This difference may be due, as Foley has suggested,[2] to configuration interaction in the $p_{\frac{3}{2}}$ state.

[13] P. Kusch, Phys. Rev. **78**, 615 (1950).

VI. ENERGY LEVELS FOR $i=1/2$

When $i=\frac{1}{2}$, there are just four values of f belonging to a doublet term, and the secular determinant breaks down into smaller determinants having four rows and columns. Solution of these may be carried out along the same lines as in IV. The energy E of a doublet component is

$$E-E_0=-\frac{\Delta\nu}{2(2j+1)}+g_j'\mu_0\mathcal{H}_z m_f \pm\frac{\Delta\nu}{2}\left[1-\frac{4m_f x}{2j+1}+x^2+\Gamma\right]^{\frac{1}{2}}+\Delta. \tag{29}$$

Here E_0 is the energy of the unperturbed level. The quantities Γ and Δ are second-order corrections given by

$$\Gamma=(4/\delta)\{-m_f a'''y\pm[y^2(\Delta\nu)/(j+\tfrac{1}{2}) -xya'''(l(l+1)-m_f^2)-xy^2m_f(\Delta\nu)]\}, \tag{30}$$

$$\Delta=(1/\delta)\{-(k+1)(2l+1)(a''')^2/4 \pm[a'''(\Delta\nu)y+y^2(\Delta\nu)^2(l(l+1)-m_f^2)]\}. \tag{31}$$

The upper signs in (30) and (31) apply to $j=l+\frac{1}{2}$ and the lower signs to $j=l-\frac{1}{2}$. The parameter x is $(g_j'+g_i)\mu_0\mathcal{H}_z/(\Delta\nu)$ and y is $\mu_0\mathcal{H}_z N(2l+1)(\Delta\nu)$, where $\Delta\nu$ is the zero-field separation given by

$$\Delta\nu=(j+\tfrac{1}{2})\{a''-|k+1|(a''')^2/\delta\}. \tag{32}$$

Unlike the case when $j=\frac{1}{2}$, the second-order perturbation does not take the form of a change in apparent nuclear g factor, but can only be expressed by means of the more complex correction terms Γ and Δ.

VII. SUMMARY AND CONCLUSION

The perturbation of an atomic $p_{\frac{1}{2}}$ state by the $p_{\frac{3}{2}}$ state leads to second-order corrections to the Breit-Rabi equation. The main effects of the correction terms are: 1) to change the apparent nuclear g factor, and 2) to add a term which lowers all the sublevels of the $p_{\frac{1}{2}}$ state equally. Perturbation of one component of a doublet by the other when neither j is $\frac{1}{2}$ but $i=\frac{1}{2}$ leads to the correction terms (30) and (31) to the energy equation.

The author takes pleasure in expressing his gratitude to Professor G. Breit for suggesting this problem and for valuable discussions during the course of the work.