

Hence the term value is given as

$$W_1 = W(Q) - \mu E/2.$$

(b) $M = F - 1 = J + I - 1.$

In this case there are two eigenfunctions corresponding to the two ways M can be formed, i.e.,

$$\begin{aligned} M = m_J = J + m_I = I - 1, \\ = m_J = J - 1 + m_I = I, \end{aligned}$$

$$\begin{aligned} \Psi_1 &= a_1 f_1(J, m_J = J) \Phi(I, m_I = I - 1) + a_2 f_2(J, m_J = J - 1) \Phi(I, m_I), \\ \Psi_2 &= -a_2 f_1(J, m_J = J) \Phi(I, m_I = I - 1) + a_1 f_2(J, m_J = J - 1) \Phi(I, m_I). \end{aligned}$$

The coefficients a_1 and a_2 are obtained from Condon and Shortley and are

$$a_1 = (2J/2J+3)^{1/2}, \quad a_2 = (3/2J+3)^{1/2}.$$

The determinant to be solved is

$$\begin{vmatrix} W(Q_1) + \langle \Psi_1 | H_E | \Psi_1 \rangle - W & \langle \Psi_1 | H_E | \Psi_2 \rangle \\ \langle \Psi_2 | H_E | \Psi_1 \rangle & W(Q_2) + \langle \Psi_2 | H_E | \Psi_2 \rangle - W \end{vmatrix} = 0,$$

where

$$\begin{aligned} \langle \Psi_1 | H_E | \Psi_1 \rangle &= \frac{3}{2J+3} | \langle J, m_J = J | H_E | J, m_J = J \rangle |^2 \\ &+ \frac{2J}{(2J+3)} | \langle J, m_J = J - 1 | H_E | J, m_J = J - 1 \rangle |^2 \end{aligned}$$

$$= -\mu EK \left[\frac{2J+1}{(2J+3)(J+1)} \right] = a;$$

similarly

$$\langle \Psi_2 | H_E | \Psi_2 \rangle = -\mu EK \left[\frac{3(J-1)+2J^2}{J(J+1)(2J+3)} \right] = b,$$

$$\langle \Psi_1 | H_E | \Psi_2 \rangle = -\mu EK \left[\frac{(6J)^{1/2}}{J(J+1)(2J+3)} \right] = c.$$

The solution of the determinant is given by

$$\begin{aligned} W_2 = -\frac{W(Q_1) + W(Q_2) + a + b}{2} \pm \frac{1}{2} [(W(Q_1) + W(Q_2) + a + b)^2 \\ - 4(W(Q_1)W(Q_2) + ab + aW(Q_2) + bW(Q_1)) - c^2]^{1/2}. \end{aligned}$$

In the specific case of AsF_3 ($-eqQ = -235$ Mc) introducing numbers we obtain

$$\Delta v = W_2 - W_1 = [-0.4 + (\mu E/4)] \pm [((25.3 + \mu E)/4)^2 - 2.8\mu E - (\mu E/18)^2 + 176.0]^{1/2}.$$

Figure 1 shows Δv as a function of μE in megacycles/sec.

For $M = F - 2$ the equation is a cubic and can be solved in a similar fashion.

The Effect of Nuclear Motion on the Hyperfine Structure of Hydrogen*

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The problem is considered from the point of view of a Hamiltonian which is relativistic to order v^2/c^2 . The discussion results in a clearer separation of the non-relativistic correction factor $1 - 3m/M$ from relativistic effects than in previous treatments. The Hamiltonian applies through the interior as well as the exterior of the proton. By means of it the potential energy can be rounded off at small distances without contradiction to relativity, within the order v^2/c^2 . A transformation involving a new effective charge allows the calculation of part of the effect without approximation and it becomes clear that higher order effects are not separable from the so far arbitrary assumptions concerning the proton's radius. Relativistic corrections to the fine structure are reconsidered by means of this transformation and the effect of the acceleration of the proton on the hyperfine structure is discussed.

I. INTRODUCTION

THE effect under discussion has been treated by Breit and Meyerott¹ with the conclusion that the important correction factor is $1 - 3m/M$ where the mathematical notation is explained at the end of the present section. Some of the reservations which have to be made in connection with higher order terms have been brought out by the same authors.² The present note has two main objects: (a) To simplify the considerations so as to make the conclusion less dependent on the manipulative details of the previous work, (b) to improve the logical consistency of the reasoning by employing a Hamiltonian which is relativistically invariant to order v^2/c^2 not only outside the proton

radius but through the whole range of values of the relative distance r between the particles.

The main step in the simplification consists in a transformation which appears under Eqs. (7.6), (7.6') below. The equations which are being transformed are those listed in Eq. (7.3) with neglect of the terms in $(\hbar/2Mc)$ which are present in Eq. (7.5). The latter can be taken account of by a perturbation calculation. The transformation brings the equations back to the form of radial equations for a Dirac electron in a Coulomb field. It involves changes in the linear scale, the charge and the ratio of the radial functions. The effect of the transformation is to change the hyperfine structure in the ratio given by Eq. (9.6) and contains all the terms of interest for comparison with experiment.

Improvement in logical consistency is obtained by employing one of the relativistically invariant forms of the Hamiltonian outside the proton radius. This form

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¹ G. Breit and R. E. Meyerott, Phys. Rev. **72**, 1023 (1947).

² G. Breit and R. E. Meyerott, Phys. Rev. **75**, 1447 (1948).

agrees with the equation which follows from quantum electrodynamics for two charged particles.³ Inside the proton radius the Coulomb potential is replaced by the function J . In order to avoid a logical failure of this scheme care must be taken to have J reasonably small inside the proton radius so as to keep the electron from moving too fast. This feature of the present note is admittedly arbitrary in its quantitative aspects for the numerical value of the proton radius and regarding the way in which the function J is rounded off. Qualitatively, however, there would appear to be little doubt concerning the inapplicability of the Coulomb potential e^2/r inside the proton radius. The Hamiltonian used here is believed therefore to approximate reality better than a Coulomb potential and the logical consistency is improved by the inclusion of correction terms for the relative velocity which appear in terms of the function J and its derivatives.

The conclusion reached is in agreement with previous work:¹ the correction to the hyperfine structure caused by the finiteness of the proton's mass is represented by the factor $1 - 3m/M$ within terms which do not involve the products $\alpha^2 m/M$. The effect of the part of the proton's magnetic moment which is not a consequence of Dirac's equation is not explicitly treated in this note. The considerations mentioned toward the end of reference 1 apply to this contribution and the changes in the radial functions which are discussed here bring about uncertainties of relative order $\alpha^2 m/M$.

The transformation with changed charge is also made use of to present the effects of order $\alpha^2 m/M$ on the fine structure in a way different from that of Breit and Brown.⁴ Effects on the hyperfine structure which arise from the effect of the acceleration of the proton are discussed by means of Eqs. (6.2)–(6.4). These are analogous to the Thomas terms for ordinary spectroscopic fine structure. They disappear for s terms. For p terms they are so small as to make their experimental detection very improbable.

The following notation is used except where stated:

- α = fine structure constant.
- v = relative velocity.
- r = distance between proton and electron.
- m = electronic mass.
- M = mass of proton.
- e = charge of proton.
- c = velocity of light.
- \hbar = Planck's h divided by 2π .
- $\mathbf{p}_e = (\hbar/i)(\partial/\partial x_e, \partial/\partial y_e, \partial/\partial z_e)$.
- $\mathbf{p}_M = (\hbar/i)(\partial/\partial x_M, \partial/\partial y_M, \partial/\partial z_M)$.
- $p_0 = -\hbar\partial/ic\partial t + e^2/cr$.
- α_e, β = the four matrices, $\alpha_1, \alpha_2, \alpha_3, \alpha_4$, of Dirac. These matrices operate on the spin coordinates of the electron; $\beta = \rho_3$.

α_M, β_M = the four matrices of Dirac which operate on the proton spin coordinates; conventions followed for α_M are similar to those for α_e .

$a_H = \hbar^2/mc^2$ = Bohr radius.

R_y = absolute value of energy of ground state of hydrogen for $M = \infty$; $R_y = e^2/2a_H$.

$\langle A \rangle$ = expectation value of operator A .

II. GENERAL REDUCTIONS

The Hamiltonian will be taken to be⁵

$$H = -c(\alpha_e \mathbf{p}_e) - c(\alpha_M \mathbf{p}_M) - \beta m c^2 - \beta_M M c^2 - J + Q \quad (1)$$

where Q is given by

$$Q = \frac{1}{2}(\alpha_e \alpha_M) J - \frac{1}{2}(\alpha_e \mathbf{r})(\alpha_M \mathbf{r}) dJ/dr. \quad (2)$$

Subscripts e, M refer to the electron and proton respectively. Elimination of "small" components for the proton leads to

$$\{\mathcal{L} - [(\boldsymbol{\sigma}_M \mathbf{p}) + Q'/c](\mathcal{L} + 2Mc)^{-1} \times [(\boldsymbol{\sigma}_M \mathbf{p}) + Q'/c]\} \Psi = 0 \quad (3)$$

where

$$Q' = \frac{1}{2}(\alpha_e \boldsymbol{\sigma}_M) J - \frac{1}{2}(\alpha_e \mathbf{r})(\boldsymbol{\sigma}_M \mathbf{r}) dJ/dr, \quad (3.1)$$

$$\mathbf{p} = \mathbf{p}_e = -\mathbf{p}_M, \quad (3.2)$$

$$\mathcal{L} = p_0 + (\alpha_e \mathbf{p}_e) + \beta m c; \quad (3.3)$$

$$p_0 = (E + J)/c. \quad (3.4)$$

The spin operator $\boldsymbol{\sigma}_M$ for the proton is a two-row square matrix. Introduction of $\Psi^{(1)}$ by⁶

$$\Psi^{(1)} = \{1 + (P^2 + i[\mathbf{P} \times \mathbf{P}] \cdot \boldsymbol{\sigma}_M)/8M^2 c^2\} \Psi \quad (3.5)$$

with

$$\mathbf{P} = \mathbf{p} + [\alpha J - \mathbf{r}(\boldsymbol{\alpha} \mathbf{r}) dJ/dr]/2c \quad (3.6)$$

yields

$$\{\mathcal{L} + \mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_3 + \mathcal{L}_4\} \Psi^{(1)} = 0 \quad (4)$$

where

$$\mathcal{L}_1 = -P^2/2Mc, \quad \mathcal{L}_2 = [\mathbf{P}, [\mathcal{L}, \mathbf{P}]]/8M^2 c^2, \quad (4.1)$$

$$\mathcal{L}_3 = -i\boldsymbol{\sigma}_M [\mathbf{P} \times \mathbf{P}]/2Mc, \quad (4.2)$$

$$\mathcal{L}_4 = i\boldsymbol{\sigma}_M ([\mathbf{P} \times [\mathcal{L}, \mathbf{P}]] - [[\mathcal{L}, \mathbf{P}] \times \mathbf{P}])/8M^2 c^2. \quad (4.3)$$

In order to obtain answers for the hyperfine structure accurate within the order of the small quantity mc^2/M it is necessary to take into account the terms in J^2 which are contained in $P^2/2M$. These terms produce effects of relative order mc^2/M on the wave function and consequently also on the hyperfine structure energy. Since these terms arise from Q and since only the expectation value $\langle Q \rangle$ can be considered as certain for any choice of Q one cannot expect⁷ Eq. (4) to be more than an ap-

⁵ Here J is a generalization of the Coulomb potential, arranged to be finite everywhere; Q corrects the non-relativistic features of J to order v^2/c^2 and is arranged to give the effects of retardation and of magnetic interaction in the limit of J approaching the Coulomb interaction. Both J and Q are discussed in Sections 1 and 2 of reference 3 for the case of two nucleons.

⁶ This reduction is analogous to Eqs. (9), (9') of the reference in footnote 3.

⁷ G. Breit, Phys. Rev. **39**, 616 (1932).

³ G. Breit, Phys. Rev. **51**, 248 (1937).

⁴ G. Breit and G. E. Brown, Phys. Rev. **74**, 1278 (1948).

proximation. The result of the reductions is given here because it makes it possible to exhibit the hyperfine structure effects contained in $\mathcal{L}_3 + \mathcal{L}_4$ and to show by comparison with an alternative calculation that the effects on hyperfine structure splitting of relative order $m\alpha^2/M$ cannot be definitely predicted and that it is probably incorrect to calculate them by means of Eq. (4).

If Q is first omitted from the Hamiltonian and if its expectation value is calculated afterward then one first obtains

$$\{\mathcal{L} - p^2/2Mc + [\mathbf{p}, [\mathcal{L}, \mathbf{p}]]/8M^2c^2 + \hbar\boldsymbol{\sigma}_M(dJ/rdr)[\mathbf{r} \times \mathbf{p}]/4M^2c^3\} \Psi^{(1)} = 0. \quad (5)$$

Here the perturbation energy Q' is given by

$$Q' = (\mathbf{u}\boldsymbol{\sigma}_M); \quad (5.1)$$

where

$$\mathbf{u} = \alpha\mathbf{J} - (\alpha\nabla)(\nabla K)/2 = \alpha\mathbf{J}/2 - (\alpha\mathbf{r})rdJ/2rdr \quad (5.2)$$

with

$$K = \int^r rJdr, \quad \alpha = \alpha_e. \quad (5.3)$$

In Eq. (5.2) the operations ∇ do not extend beyond K . The nuclear spin enters through Q' . The calculation of the expectation value of the terms containing Q' in Eq. (3) brings in the nuclear spin operator $\boldsymbol{\sigma}_M$ once more resulting in a quadratic entrance of the nuclear spin operators.

The addition to the hyperfine structure splitting is obtained by linearizing

$$(\boldsymbol{\sigma}_M\mathbf{p})(\mathcal{L} + 2Mc)^{-1}(\mathbf{u}\boldsymbol{\sigma}_M) + (\mathbf{u}\boldsymbol{\sigma}_M)(\mathcal{L} + 2Mc)^{-1}(\boldsymbol{\sigma}_M\mathbf{p})$$

in $\boldsymbol{\sigma}_M$. The difference between Ψ and $\Psi^{(1)}$ may be neglected in taking the expectation value of this operator for it introduces effects of relative order $\alpha^2(m/M)^2$ which are consistently neglected here. The spin dependent part of Q is then found to be the expectation value of Q'' where Q'' is

$$Q'' = \frac{\hbar}{2Mc} \left(1 - \frac{J}{2Mc^2} \right) \frac{dJ}{rdr} [\mathbf{r} \times \boldsymbol{\alpha}] \boldsymbol{\sigma}_M. \quad (5.4)$$

Here there is the factor differing from unity by the quantity $J/2Mc^2$ which contains correction effects of order $(m/M)\alpha^2$. Aside from this factor Eq. (5.4) is the ordinary operator for the hyperfine structure interaction. The literal application of the two-particle wave equation which is followed in the reductions leading to Eq. (4) is somewhat analogous to a similar reduction which has been tried out for two electrons.⁸ Comparison with experiment as well as theoretical considerations have indicated for two electrons that it is unjustifiable and incorrect to make literal use of the terms corresponding

to Q in the two-electron case.⁷ For this reason the discussion below is carried out along lines which have proved to be more adequate in the two-electron case. These correspond to attaching significance only to first-order effects of Q . It should be noted that this limitation makes all effects of order $\alpha^2 m/M$ somewhat uncertain. The consideration of effects of this order which follow from Eq. (1) is not pointless, however, because if the numerical coefficients with which the questionable effects appear were to be large one would have serious doubts concerning the applicability of the non-relativistic correction factor $1 - 3m/M$.

III. THE THOMAS-TYPE TERMS

The first, second and fourth terms in Eq. (5) contain effects easily describable in terms of current nomenclature. The operator \mathcal{L} corresponds to the Dirac equation in the approximation of neglecting nuclear mass motion. The second term brings in the kinetic energy of the proton. The last term corresponds to effects of the proton's acceleration on the hyperfine structure. These effects were absent in the treatment of Breit and Meyerott¹ because the latter was concerned exclusively with s terms. The effect of these terms can be found by the consideration of the matrix vector

$$\mathbf{B}^{IV} = -(\hbar/2M^2c^2)(dJ/rdr)[\mathbf{r} \times \mathbf{p}] \quad (6)$$

which combines with⁹ \mathbf{B}' to give the hyperfine structure energy as Eq. (2) of the above reference which corresponds to representing the interval factor as

$$((\mathbf{B}' + \mathbf{B}^{IV}) \cdot \mathbf{J})_j / j(j+1) \quad (6.1)$$

where \mathbf{J} is the inner quantum number operator, j the inner quantum number, and the symbol $()_j$ stands for the common value of the diagonal element of the submatrix of the operator enclosed in $()$, with both rows and columns of the submatrix labeled by the same j .

Straightforward calculation yields

$$((\mathbf{B}' + \mathbf{B}^{IV}) \cdot \mathbf{J})_j \cong 8\pi\mu_0\mu_N(1 - 3m/M)\Psi s^2(0) + \mu_0\mu_N \langle r^{-3} \rangle_{\delta_{L,0}'} \{ 4k(1+k)(1 - 3m/M) + (k+1)(2k-1)(m/M) \} \quad (6.2)$$

where k is the Dirac quantum number which takes on values $-1, +1, -2, +2$ for $s_{1/2}, p_{1/2}, p_{3/2}, d_{3/2}$ terms, and L is the azimuthal quantum number. The symbol δ' is 1 minus the Kronecker δ . In Eq. (6.2) there is included the ordinary mass correction effect in the first term which contains the square of the Schrödinger function Ψ_s at $r=0$ and in the first part of the second term. The last part of the second term in Eq. (6.2) represents the effect of the Thomas-type terms. This effect vanishes for s terms to the present order of approximation as has been found by Breit and Meyerott.¹ Comparison of the regular mass effect which is contained in the first term

⁸ G. Breit, Phys. Rev. **34**, 553 (1929).

⁹ G. Breit, Phys. Rev. **74**, 656 (1948).

with the special mass effect gives

$$\text{special mass effect/regular mass effect} \\ = -\delta_{L,0'}(2k-1)/12k. \quad (6.3)$$

For $L \neq 0$ this effect is seen to be of the same order of magnitude as the regular mass effect. It is nevertheless of no practical interest at this time because the experimental accuracy does not suffice for its detection in view of the much larger effect of the natural breadth of the levels from which this effect would have to be separated. In the present approximation the effect is

$$(\Delta E)_{Thom} = -\frac{\hbar^2 \delta'}{4M^2 c^2} \frac{2L(L+1)}{L+\frac{1}{2}} \left\langle \frac{dJ}{rdr} \right\rangle \\ \cong \left(\frac{m}{M} \right)^2 \frac{Ry\alpha^2 \delta'}{(L+\frac{1}{2})^2 n^3} \quad (6.4)$$

which corresponds to

$$\Delta E_T(2p_{3/2}) = 0.0029Mc/s = \Delta E_T(2p_{1/2}). \quad (6.5)$$

IV. RELATION TO FINE STRUCTURE

In the present section a transformation will be considered which enables one to understand the result of Breit and Brown⁴ for the fine structure from a different viewpoint and will also be found useful for the understanding of mass effects on hyperfine structure. The first two terms of Eq. (5) give

$$[p_0 + mc - (p_0^2 - m^2 c^2)/2Mc]f - \hbar O_+ g \\ - (\hbar/2Mc^2)(dJ/dr)g = 0, \quad (7)$$

$$[p_0 - mc - (p_0^2 - m^2 c^2)/2Mc]g + \hbar O_- f \\ + (\hbar/2Mc^2)(dJ/dr)f = 0,$$

where

$$O_+ = d/dr + (1+k)/r; \quad O_- = d/dr + (1-k)/r. \quad (7.1)$$

Introduction of Ω_+ , Ω_- , F , G by means of

$$\Omega_+ = O_+ - 1/r, \quad \Omega_- = O_- - 1/r, \quad F = rf, \quad G = rg \quad (7.2)$$

and division by $1 - J/2Mc^2$ gives

$$(W + J + mc^2)BF - \hbar\Omega_+[1 + J/2Mc^2]G = 0, \\ (W + J - mc^2)AG + \hbar\Omega_-[1 + J/2Mc^2]F = 0 \quad (7.3)$$

where

$$A = 1 - (W + mc^2)/2Mc^2, \quad B = 1 - (W - mc^2)/2Mc^2 \quad (7.4)$$

and W stands for the energy $-Mc^2$. It will be remembered, however, that in Eq. (4) the operator p^2 is replaced by P^2 . The operator \mathcal{L}_2 contains only effects of relative order $(m/M)^2$ and will, therefore, be neglected. The addition of $-(P^2 - p^2)/2M$ to the left side of Eqs. (7.3) gives

$$(W + J + mc^2)BF - \hbar\Omega_+G - (\hbar/2Mc)UG = 0, \\ (W + J - mc^2)AG + \hbar\Omega_-F + (\hbar/2Mc)UF = 0, \quad (7.5) \\ U = r\Delta J/2 + (r dJ/dr)(d/dr)$$

which is seen to contain correction terms in \hbar/Mc which do not depend on the quantum number k . It would be surprising if the correction for $P^2 - p^2$ which has just been made did not have some good quantitative meaning because, as may be seen from Eq. (3.6), it contains in it the usual effects of the vector potential caused by the electron on the momentum operator of the proton with an additional correction for retardation. There is thus a reason for believing Eq. (7.5) in preference to Eq. (7.3).

It will now be shown how Eq. (7.5) gives results for the fine structure of hydrogen. The terms in \hbar/Mc will be treated as a perturbation and will be used only to the first order. Omitting these terms one has two simultaneous equations which agree exactly with corresponding Dirac's equations for a Coulomb field without nuclear motion provided one approximates A and B by unity. Since A , B do not contain r it is possible to transform the equations by means of

$$r' = (AB)^{1/2}r, \quad F' = (B/A)^{1/2}F, \quad G' = G, \quad e'^2 = (AB)^{1/2}e^2 \quad (7.6)$$

which gives

$$[W + mc^2 + e'^2/r']F' - \hbar\Omega_+G' = 0, \\ [W - mc^2 + e'^2/r']G' + \hbar\Omega_-F' = 0 \quad (7.6')$$

a set of two equations identical in form with the radial equations for an electron in a central field. The energy which corresponds to Eqs. (7.6') differs from that for the problem with infinite nuclear mass. For the latter

$$(1 + W/mc^2)^{1/2}/(1 - W/mc^2)^{1/2} - (1 - W/mc^2)^{1/2}/(1 + W/mc^2)^{1/2} = 2(p+s)/\alpha \quad (7.7)$$

where

$$p = (k^2 - \alpha^2)^{1/2} - 1 \quad (7.8)$$

and

$$-1 + |k| + s = \text{principal quantum number.}$$

By means of the above relation between W and α one finds the first-order effect of m/M on W to be

$$\delta W = -\left(\frac{W^2 - m^2 c^4}{2Mc^2} \right) \cdot \frac{W^2}{m^2 c^4} \left[1 + \frac{\alpha^2}{(p+1)(p+s)} \right]. \quad (7.9)$$

On the other hand the terms which have been omitted in Eq. (7.5) contribute a first-order effect to the energy which also contains the first power of m/M and amounts to

$$\Delta W = (\hbar e^2/2Mc) \int (1/r) [GdF/dr - FdG/dr] dr. \quad (7.9')$$

Evaluating the integral on the right side of this expression and adding the two energy changes one obtains

$$\delta W + \Delta W = -(W^2 - m^2 c^4)/2Mc^2. \quad (8)$$

This is identical with the quantity called E_1 by Breit and Brown⁴ as is seen by comparing with their Eq. (6) and agrees with a previous result of Bechert and Meixner.¹⁰ The meaning of the result in the present

¹⁰ K. Bechert and J. Meixner, Ann. d. Physik **22**, 525 (1935).

paper and in that of Breit and Brown is slightly different from that of Bechert and Meixner. In both of the later papers the energy correction is worked out as an addition to the exact energy of Dirac's equation while Bechert and Meixner's calculation does not consider the higher powers of α .

It has thus been verified that Eqs. (7.5) give the correction to the fine structure within terms of degree m/M in an expansion in powers of m/M within the limitations of the Hamiltonian. No approximation regarding the entrance of α has been made. For the ground term of hydrogen the integrand in Eq. (7.9') vanishes and the distortion of the wave function caused by the perturbing terms involving $1/M$ in the Eqs. (7.5) is accordingly small. It is therefore convenient to make use of Eq. (7.6') as a starting point for the calculation of the hyperfine structure effect.

V. THE MASS CORRECTION TO HYPERFINE STRUCTURE OF GROUND TERM NEGLECTING NUCLEAR VOLUME

In the present discussion quantities obtained by setting $M = \infty$ will be denoted by the subscript 0; the radial functions corresponding to F' , G' by f' , g' in the same sense as in Eq. (7.2) for f , g . One is concerned with the value of

$$-I = \int_0^\infty f g dr / \int_0^\infty (f^2 + g^2) r^2 dr \quad (9)$$

which is the most important factor in the usual formula for hyperfine splitting which depends on m/M . In terms of the primed quantities one has

$$I = -q p^{-2} \int_0^\infty f' g' dr' / \int_0^\infty (g'^2 + q^2 f'^2) r'^2 dr' \quad (9.1)$$

where

$$q = (A/B)^{1/2}, \quad p = 1/(AB)^{1/2} \quad (9.2)$$

are the factors brought in by the transformations of f and r respectively. Taking into account that for the ground term

$$f_0^2/g_0^2 \cong \alpha^2/4 \quad (9.3)$$

and that $q^2 f'^2$ is the same as f'^2 within terms of order m/M one has to a sufficient approximation

$$I = -q p^{-2} [1 - (1 - q^2)(\alpha^2/4)]^{-1} \times \int_0^\infty f' g' dr' / \int_0^\infty (f'^2 + g'^2) r'^2 dr'. \quad (9.4)$$

In the last formula there are three correction factors which multiply the ratio of two integrals. The latter ratio is identical in form with that for the value of I without nuclear mass motion. It differs from it, however, on account of the replacement of the unprimed quantities by primed ones. Without nuclear mass motion the

value of I is¹¹

$$I_0 = \alpha(2\rho^2 - \rho)^{-1} a_H^{-2}; \quad \rho = (1 - \alpha^2)^{1/2} \quad (9.5)$$

where a_H is the Bohr radius. Within relative order α^2 it follows that

$$I_0 = \alpha(1 + 3\alpha^2/2) a_H^{-2}. \quad (9.5')$$

Taking into account the occurrence of e in α and a_H there results from Eqs. (9.4), (9.5') together with the transformation formulas (7.6), (9.2) that

$$I/I_0 = 1 - 3m/M + 0 \cdot \alpha^2 m/M + \dots \quad (9.6)$$

At this stage of the calculation the corrections of order $\alpha^2 m/M$ have disappeared and the mass correction to the hyperfine structure for the Dirac part of the proton's moment is expressed by the factor $1 - 3m/M$.

The contribution to hyperfine structure arising from the difference between $1 - (J/2Mc^2)$ and unity in Eq. (5.4) has been neglected so far. The term in $-J/2Mc^2$ gives rise to an integral in the first-order perturbation energy which diverges as $\int \exp[(-1 - \alpha^2) \ln r] dr$ and this term cannot be treated in the usual manner. The function J should be considered, however, as being finite everywhere for otherwise the justification for Eq. (1) breaks down. It is probable, furthermore, that at distances smaller than $\sim e^2/mc^2$ the field of the proton deviates from the inverse square law and that the whole method of treatment loses meaning on account of the presence of mesons. It would be unreasonable to attach much meaning to the divergence just mentioned since it disappears if one makes J finite by rounding off the $1/r$ -type potential. The exact way in which it should be rounded off is subject to question. Speculatively it will be supposed that J has the constant value e^2/b from $r=0$ to $r=b$ and that for $r>b$ the value e^2/r applies. The ratio of the extra effect to the regular effect is

$$\text{extra effect/regular effect} \cong -(e^2/2Mc^2 a_H) \times \int_b^\infty r^{-1} \exp(-2r) dr / \int_0^\infty \exp(-2r) dr \quad (10)$$

where r is expressed in units a_H and the relativistic radial functions are replaced by their non-relativistic values with sufficient accuracy. The above ratio is expressible in terms of the Ei integral and can be approximated by

$$-(m/M)\alpha^2 [\ln(1/2b''\alpha^2) - 0.577 \dots] \quad (10.1)$$

where b'' is the value of b in units e^2/mc^2 and where terms containing additional factors α have been neglected.

Since dJ/dr vanishes in the cut off region the hyperfine structure splitting is smaller than it would be without cutting off J even if m/M is not considered. The correction factor introduced by this effect is approximately

$$\int_b^\infty e^{-2r} dr / \int_0^\infty e^{-2r} dr \cong 1 - 2b = 1 - 2b''\alpha^2$$

¹¹ G. Breit, Phys. Rev. 35, 1447 (1930).

where b is in Bohr radii. Since the mass correction corresponds approximately to multiplication by $1-3m/M$ one can expect an additional effect of approximate value $6b''\alpha^2 m/M$ which has its origin in the combined action of changes of relative order α^2 produced by a finite nuclear radius and of the mass effect. Such changes cannot be treated with certainty because the nuclear radius is not understood in a precise sense. Effects of order $(m/M)\alpha^2$ as well as that described by Eqs. (10), (10.1) are much too small to be detected with the accuracy reported in the experiments.

The Hamiltonian employed here is only approximately relativistic. The function J cannot be made too large and the introduction of a proton radius is, therefore, unavoidable in the present approach. The uncertainties in the answer which are a consequence of the arbitrariness in the value of the radius b and the shape of $J(r)$ are thus an inherent limitation of the method. Similar uncertainties arise from the fact that for a finite nuclear radius the transformation to Eqs. (7.6') can be made only in the region $r > b$. These effects can be discussed properly only if one takes into account the change in the wave function brought about by the finite rather than zero value of b . The expectation value of the hyperfine structure energy Q'' when calculated with such an improved wave function contains additional corrections of relative order $m\alpha^2/M$. These corrections are worked out in the adjoining paper¹² by G. E. Brown and G. B. Arfken.

There is an additional effect of the terms in $(\hbar/2Mc) \times (rdJ/dr)(d/dr)$ in Eq. (7.5) which also brings in b explicitly. This effect is similar to that in Eq. (10.1). It also depends on b logarithmically and becomes infinite for zero nuclear radius. The terms in ΔJ contained in Eq. (7.5) produce in general effects of relative order $m\alpha^2/M$. For the special case of J being constant in the interval $0 < r < b$ their effect is of a higher order in α as is shown in the adjoining paper.¹² Their evaluation does not depend on the effect of the cut-off of the Coulomb potential on the wave function but it proved easier to present the matter in this order. The evaluation of the effect of terms involving dJ/dr in Eq. (7.5) will now be described. The functions F, G are represented as $(1+u)F_0, (1+v)G_0$ where F_0, G_0 are solutions of Eq. (7.5) in the absence of the terms under consideration. Substitution into Eq. (7.5) then shows that regularity of F and G at $r = \infty$ requires

$$u = v = K + (\alpha^2\beta/2)(-\rho/r - \ln r) \quad (11)$$

where $\beta = m/M$, $\rho = (1-\alpha^2)^{1/2}$ and where the unit of length is \hbar^2/mc^2 . The constant of integration remains undetermined at this stage. Since the effect of $u-K = v-K$ on F and G can be represented by the correction

factor $\exp(u-K)$ to within the relative order $\alpha^2\beta$, the effect of K amounts to employing $(1+K)F_0, (1+K)G_0$ in place of F_0, G_0 . This effect cannot be distinguished, therefore, from the determination of the normalization factor. The correction factor to the hyperfine structure is thus found to be

$$1 + \delta \quad (11.1)$$

where

$$\delta = \delta_1 + \delta_2 \quad (11.2)$$

and

$$\delta_1 = -\alpha^2\beta[\ln b - 3Ei(-2b)], \quad (11.3)$$

$$\delta_2 = \alpha^2\beta[\ln b + (5/2) - Ei(-2b)]. \quad (11.4)$$

The contributions δ_1, δ_2 arise from the inclusion of the factors $\exp(u-K)$ in the integrals of FG/r^2 and F^2+G^2 respectively. The first of these integrals arises from Q'' , the second on account of normalization. Combining the two contributions

$$\delta = \alpha^2\beta[(5/2) + 2Ei(-2b)] \\ \cong \alpha^2\beta[(5/2) - 2 \ln(1/2b\gamma)] \quad (11.5)$$

where $\ln \gamma = 0.577 \dots$. Combining with Eq. (10.1) the correction factor for both effects is

$$1 + \epsilon \quad (12)$$

where

$$\epsilon = \alpha^2\beta[(5/2) - 3 \ln(1/2b''\alpha^2\gamma)]. \quad (12.1)$$

The correctness of the argument for the elimination of K has been verified by the extension of the phase amplitude perturbation method to Dirac's equation.¹³ For $b'' = 1$ the value of ϵ is 7×10^{-7} which is negligible in comparison with experimental errors and is of the same order as the effects in $\beta^2 = (m/M)^2$ which have been neglected here.

It appears from the considerations presented that the "approximately relativistic" equation considered here gives a result which for practical purposes is the same as that of Breit and Meyerott.¹ It is desirable to emphasize again that neither treatment is free from ambiguities. There is a difference between the method of Eqs. (4), (4.1), (4.2), (4.3) and the method of Eqs. (5), (5.4) which has been adopted here. A complete treatment of the problem requires a more consistent application of electrodynamics than that attempted here.

It should also be mentioned that the transformation of Eqs. (7.6), (7.6') is not closely related to the stretching of the wave function which corresponds to the introduction of the reduced mass in the non-relativistic problem. The charge is not transformed in the latter. It is possible to employ the ordinary reduced mass transformation but the classification of effects does not appear as clearly as by means of Eq. (7.6').

¹² G. E. Brown and G. B. Arfken, Phys. Rev. **76**, 1305 (1949).

¹³ G. Breit and G. E. Brown, Phys. Rev. **76**, 1307 (1949).