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Effect of Nuclear Motion on the Fine Structure of Hydrogen

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The problem is re-examined from the point of view of the Hamiltonian applicable to two charged particles and accounting for effects of order v^2/c^2, where v is the velocity. The work differs from that of Bechert and Meixner in that the energy of the Dirac's electron in a central field is taken as the reference point. The solution is carried out in terms of an eight-component rather than a four-component approximation to the 16-component wave function. The result is the same for practical purposes as that of Darwin for the prequantum-mechanical problem and of Bechert and Meixner for the four-component approximation. The energy formula is affected only by the original Bohr reduced mass correction to the term value and also by a term which is independent of the particular fine structure component and depends only on the principal quantum number. Bethe's electrodynamic shift is, therefore, not obscured to within terms of relative order $\alpha^2(m/M)$ by effect of nuclear motion.

I. INTRODUCTION

The effect of nuclear mass motion on the fine structure of hydrogen has been calculated by Bechert and Meixner.[1] Related considerations have been made by Lowen.[2] The increased importance of the fine structure as a test of views on quantum electrodynamics[3] has made it desirable to re-examine the question. The work of Bechert and Meixner leaves one with a partial feeling of dissatisfaction because it employs the four-component approximation to the 16-component two-particle wave equation. It is not clear without further proof that this approximation is adequate for the present problem. While it is true that for a single particle the reduction from 4 to 2 components yields results for the energy which are correct to relative order α^2, it does not follow without further proof that the perturbing effect of the mass correction can be treated by an extension of the same method. One might be especially doubtful about the meaning of such a calculation if one recalls that the Dirac and Schroedinger wave functions are represented by different powers of the distance r at the origin.

The calculation of Bechert and Meixner amounts to the carrying out of the following two steps: (a) such a rearrangement of terms in the four-component wave equation that the explicit introduction of the reduced mass becomes possible and the non-relativistic Schroedinger equation with reduced mass can be used as the zeroth-order approximation to the problem; (b) the evaluation of the expectation value of the difference between the two-particle Hamiltonian and the zeroth approximation. The relative order of the difference is $(m/M)\alpha^2$, and the first-order perturbation theory suffices. The general scheme is doubtless beyond criticism. It is clear, however, that the application of first-order perturbation theory can have only a formal significance if the wave function is strongly affected by the difference between the actual and the approximate Hamiltonian. Since the Schroedinger function is a poor approximation to the Dirac function at short distances the question arises as to whether the application of first-order theory in the arrangement of terms chosen by Bechert and Meixner has more than a formal meaning, whether the perturbation method converges, and if it converges whether the convergence is rapid enough to make the result significant. A certain degree of optimism is, of course, necessary regarding absence of mathematical difficulties, and the questions raised above would probably be out of order if it were not for the fact that it is

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

[2] I. S. Lowen, Phys. Rev. **51**, 190 (1937). Lowen's results are closely related to those of the present paper. This is especially true of his Eq. (14a). Lowen did not carry the calculation far enough to make it possible to make comparisons with experiment except for the 1*s* term.

[3] H. A. Bethe, Phys. Rev. **72**, 339 (1947); Julian Schwinger, Phys. Rev. **73**, 415 (1948); Willis E. Lamb, Jr. and Robert C. Retherford, Phys. Rev. **72**, 241 (1947); J. E. Mack and N. Austern, Phys. Rev. **73**, 1233 (A) (1948).

known that for small r the probability of finding an electron per unit volume behaves very differently with distance according to the Dirac and the Schroedinger equations and if the assumption of being able to expand the Dirac functions in terms of their non-relativistic approximations were not a part of the usual development of first-order perturbation theory. It is not clear that the large values of the ratio of Dirac electron density to the Schroedinger density can be accounted for by a series with a reasonably small number of terms or that the difference between the actual and the zero-order wave functions has a negligible effect on the final estimate of the mass correction. Some of these questions are still unclear, but it is believed that the matter is somewhat more soundly understood as a result of the present work.

An additional reason for undertaking it is the desirability of being able to see the answer in such a form that the exact solution of Dirac's equation for a fixed nucleus is approached as a limit for $M=\infty$. This is not the case for Bechert and Meixner's calculations, although it is the aim of Lowen's reductions. The latter are not carried, however, to the point of estimating the effects on the energy. It is obviously better to be able to carry out the development in such a way as to have the energy appear as the Dirac energy for $M=\infty$ because by doing so one is in a better position to obtain a theoretical understanding of the problem for cases of high atomic number Z. It may be mentioned that for small values of r the usual reduction of the 16-component equation to the four-component form requires modification and that for this reason the 4-component approach appears to be questionable. It derives an energy value by changing the wave equation close to $r=0$ and in a sense also the boundary condition at $r=0$.

In addition, it appears pertinent that the extra terms brought into the Hamiltonian by the nuclear motion have to be taken into account to the second order of perturbation theory. It is true that with Bechert and Meixner's arrangement of the calculation only first-order perturbation theory is used. This is the result of employing the non-relativistic Hamiltonian for reduced mass as the zeroth approximation and removing terms from the Hamiltonian which can give rise to effects of relative order m/M. The Bechert-Meixner work thus amounts to the calculation of the expectation value of the Hamiltonian employing the wave function of the non-relativistic reduced mass problem. A justification for employing this rather than another wave function is easy to give for the four-component treatment because for it effects of relative order m/M are removed from the perturbing Hamiltonian. The fact that the whole argument depends on this property of the four-component approximation and that the 16- or 8-component equations appear to require the consideration of second-order effects when one takes infinite nuclear mass as a starting point also suggested a re-examination of the problem.

NOTATION

$m=$ electronic mass
$M=$ mass of proton
$e=$ electronic charge
$Z=$ atomic number
$\hbar=$ Planck's $h/2\pi$
$c=$ velocity of light
$\alpha=e^2/\hbar c$
$E=$ energy of system in rest mass system $-Mc^2$
$r_e=(x_e, y_e, z_e)=$ coordinates of electron
$R_M=(x_M, y_M, z_M)=$ coordinates of proton
$r=r_e-R_M$
$\mathbf{p}_e=(\hbar/i)(\partial/\partial x_e, \partial/\partial y_e, \partial/\partial z_e)$
$\mathbf{p}_M=(\hbar/i)(\partial/\partial x_M, \partial/\partial y_M, \partial/\partial z_M)$
$\boldsymbol{\alpha}, \beta=$ the four matrices, α_1, α_2, α_3, α_4, of Dirac. These matrices operate on the spin coordinates of the electron; $\beta=\rho_3$
$n=$ principal quantum number
$a_{\mathrm{H}}=\hbar^2/me^2=$ Bohr radius
$T=$ non-relativistic kinetic energy
$Ry=$ absolute value of energy of ground state of hydrogen for $M=\infty$; $Ry=e^2/2a_{\mathrm{H}}$
$\psi=$ four-component wave function for Dirac's equation
$W=$ energy of single electron according to Dirac's equation
$L=$ azimuthal quantum number
$\langle A\rangle=$ expectation value of operator A.

II. THE 8-COMPONENT EQUATION

The 16-component equation is equivalent to a set of two simultaneous equations on two four-component functions. In addition one has to add to the energy the expectation value of an operator Y which represents the combined effect of the magnetic interaction and a correction for the effect of retardation on the electrostatic energy. The representation can be chosen in such a way that the equations have the form[4]

$$\begin{aligned}(\mathfrak{L}+2Mc)+(\boldsymbol{\sigma}_M\mathbf{p}_M)\Psi=0,\\ \mathfrak{L}\Psi+(\boldsymbol{\sigma}_M\mathbf{p}_M)\Phi=0,\end{aligned} \tag{1}$$

where

$$\mathfrak{L}=p_0+\boldsymbol{\alpha}\mathbf{p}_e+\beta mc, \tag{1.1}$$

with

$$p_0=(E+e^2/r)/c. \tag{1.2}$$

In order to simplify the formulas the nuclear charge is taken to be e. In order to change results to a nuclear charge Ze, the quantities e^2, α should be replaced, respectively, by Ze^2, $Z\alpha$. The subscript M refers to the nucleus. The vector matrix $\boldsymbol{\sigma}_M$ has components having the form of Pauli's three spin matrices. The functions Ψ, Φ have two indices, the first of which is the Dirac four-valued spin index for the electron and the second of which is the two-valued spin index of the proton. The matrices $\boldsymbol{\alpha}$, β operate on the first index; σ_M operates on the second. The operator Y is

$$Y=(e^2/2r)[(\boldsymbol{\alpha}\boldsymbol{\alpha}_M)+(\boldsymbol{\alpha}\mathbf{r})(\boldsymbol{\alpha}_M\mathbf{r})/r^2] \tag{1.3}$$

in the original 16-component representation. In the notation used in the present paper $\boldsymbol{\alpha}_M$ converts Φ into Ψ, Ψ into Φ, and after this operates like $\boldsymbol{\sigma}_M$. The calculation will be carried out with an attempt at not making the assumption that the velocity of the electron is small until the final stage of the calculation. The operator $\boldsymbol{\alpha}$ will be left, therefore, in Y and will be considered accurately. It is realized that Y is only accurate to order v^2/c^2 and that at this point the gain in accuracy is questionable. The contribution of Y is of the last highest order of quantities considered here and its effect vanishes for $M=\infty$. For hydrogen it does not matter whether the effect of Y is evaluated accurately or not. Since it turned out to be just as easy to calculate the expectation value accurately as approximately, the accurate evaluation will be used almost up to the end of this paper. The replacement of Y by something better requires a more thorough investigation. One of the objects here is to provide accurate forms of the answer for the approximate theory so as to make it easier to see in what way the physical effects that are approximately represented by Y can be treated more satisfactorily.

From the first of the two Eqs. (1) one finds

$$\Phi=-[1-(\mathfrak{L}/2Mc)+\cdots](\boldsymbol{\sigma}_M\mathbf{p}_M)\Psi/(2Mc). \tag{1.4}$$

The condition

$$(\mathbf{p}_e+\mathbf{p}_M)\Psi=(\mathbf{p}_e+\mathbf{p}_M)\Phi=0 \tag{1.5}$$

will be imposed on the wave function so as to have the total momentum equal to zero. The partial differential equations thus obtained show that each of the 16 components depends only on the relative coordinates $\mathbf{r}$. The operator $\mathbf{p}_e$ is the same for this wave function as the operator

$$\mathbf{p}=(\hbar/i)(\partial/\partial x,\ \partial/\partial y,\ \partial/\partial z). \tag{1.6}$$

Substitution of Eq. (1.4) into the second of the two Eqs. (1) gives the following equation on linearizing in $\boldsymbol{\sigma}_M$ and omitting terms in $\boldsymbol{\sigma}_M$ which contribute only to the hyperfine structure,

$$[\mathfrak{L}-p^2/2Mc+\mathfrak{L}_1]\Psi=0, \tag{1.7}$$

where

$$\mathfrak{L}_1=\mathbf{p}\,\mathfrak{L}\mathbf{p}/4M^2c^2. \tag{1.8}$$

One has

$$\mathfrak{L}_1\Psi=p^2\mathfrak{L}\Psi/4M^2c^2+\mathfrak{L}_2\Psi \tag{1.81}$$

where

$$\mathfrak{L}_2=he^2(\mathbf{p}\mathbf{r})/(4iM^2c^3r^3). \tag{1.82}$$

The first two terms of Eq. (1.7) give an approximate wave equation which corrects the energy for the kinetic energy of the nucleus and includes, therefore, effects on the energy of the system to the first order of m/M. If the equation were exact then the first part of $\mathfrak{L}_1$ in Eq. (1.81) would be equivalent to an addition to the energy operator of

$$-(cp^4/8M^3c^3) \tag{1.83}$$

which for small Z is of relative order

$$\frac{1}{4}\left(\frac{m}{M}\right)^3\frac{\alpha^2}{n^2} \tag{1.84}$$

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[4] The arrangement of the calculation is similar to that in G. Breit and R. E. Meyerott, Phys. Rev. **72**, 1023 (1947) and G. Breit, Phys. Rev. **39**, 616 (1932). Equation (1) of the present paper does not include magnetic interaction and retardation effects. The expectation value of an operator called Y is used later in order to take into account these interaction effects, in accordance with the view that this is the proper way of employing the 16-component equation. A justification of this view is given in the (1932) paper quoted in this footnote.

and is negligible. The first-order effect of $\mathfrak{L}_2$ on the energy is obtained by taking the expectation value of $-c\mathfrak{L}_2$. For light nuclei this is

$$\begin{aligned}\langle -c\mathfrak{L}_2\rangle &\cong (\hbar^2e^2/4M^2c^2)\int_r^\infty \Psi_S(d\Psi_S/dr)4\pi dr \\ &\cong -\hbar^2e^2\Psi_S{}^2(0+)/2M^2c^2 \\ &= -Ry(m/M)^2\alpha^2/n^3.\end{aligned} \tag{1.85}$$

Here the subscript S on Ψ indicates the nonrelativistic Schroedinger approximation, the lower limit of integration is designated by r, and the notation $0+$ indicates that Ψ_S is evaluated for the small value r. The reason for putting the matter in terms of this notation should now be explained. The operator $\mathfrak{L}_2$ arose in the step between Eq. (1.8) and Eq. (1.81) as the result of interchanging the positions of $\mathfrak{L}$ and $\mathbf{p}$. The whole term $\mathfrak{L}$ came in as a consequence of the presence of $-\mathfrak{L}/2Mc$ in the brackets of Eq. (1.4). At distances of the order e^2/Mc^2 it is no longer satisfactory to stop with the second term in the brackets of Eq. (1.4) because then the potential energy and Mc^2 are of the same order. Carrying out the integration from $r=0$ to ∞ would not have much meaning, therefore. A second reason for employing the notation $0+$ is the convenience of not having to bring in the difference represented essentially by the factor $\exp[-(\alpha^2/2)\log r]$ between the larger of the two Dirac functions and the Schroedinger function Ψ_S. The small value of α does not make the integral diverge and the factor $\exp[-(\alpha^2/2)\log r]$ changes by $\sim$0.3 percent when r changes by a factor e. It changes, therefore, by roughly 2 percent between e^2/mc^2 and e^2/Mc^2 and is thus practically constant between the point at which the two terms of Eq. (1.4) are sufficient and the point at which the approximation of the larger Dirac radial function by the corresponding Schroedinger function becomes good up to values of r considerably greater than the Bohr radius. The right side of Eq. (1.85), while larger than the expression in Eq. (1.84), is, nevertheless, negligible.

It remains to consider the effect of the term in p^2 which enters Eq. (1.7). To the first order it brings in a correction of the order (m/M) of the term value. It gives besides effects of order $(m/M)^2$, $(m/M)\alpha^2$ and higher order terms. Effects of order $(m/M)^2\alpha^2$ and those of higher order will be neglected. Corrections of order $(m/M)^2$ cannot differ from the $(m/M)^2$ effects for the Schroedinger equation and are therefore taken care of by the second term in the Taylor expansion of the factor $[1+(m/M)]^{-1}$ in the original Bohr reduced mass correction. It is further seen that there are no correction terms of order $(m/M)^2\alpha$. In fact the process of expansion of the eigenvalue of Eq. (1.7) into a Taylor series in (m/M) is equivalent to the employment of the Rayleigh-Schroedinger perturbation method with $p^2/2M$ as the perturbing term in the Hamiltonian. The power $(m/M)^2$ is obtained in the second-order perturbation energy which is given by the standard expression

$$E_2=\Sigma_f|H_{if}'|^2/(E_i-E_f), \tag{1.9}$$

where i, f refer to initial and final states, respectively. The difference in E_2 caused by changing from the Schroedinger to the Dirac equation consists in three effects: (a) The presence of the negative energy part of the spectrum for E_f in the Dirac case; (b) Differences in E_i-E_f for $E_f>0$; (c) Differences in the numerator of the formula for $E_f>0$. It is well known that the relativity effect on E_f can be represented by a Taylor series in even powers of α. The effect (b) is, therefore, only that of causing the appearance of α^2 rather than α. An examination of the formulas of Darwin and Gordon[5] for the wave functions shows that here too all effects are free of the first power of α and that the effect (c) is, therefore, also harmless. The only place where the first power of α has the appearance of entering explicitly in Gordon's formulas is in the ratio $C_0{}^{(1)}/C_0{}^{(2)}$. It enters, however, through

$$(\alpha E/mc^2)/[1-(E/mc^2)^2]^{\frac{1}{2}}=n'+(k^2-\alpha^2)^{\frac{1}{2}}, \tag{1.91}$$

where n' and $|k|$ are both integers. The quantity k_0 in these formulas may be thought at first sight to contain the first power of α. This quantity occurs, however, only in the combination k_0r and, since

$$k_0r=(r/a_{\mathrm{H}})\{\alpha^2+[n'+(k^2-\alpha^2)^{\frac{1}{2}}]^2\}^{-\frac{1}{2}}, \tag{1.92}$$

the effect of relativity through k_0 is describable as a change of linear scale which is free of the

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

first power of α. For E_f in the continuous positive energy spectrum one can make E_f the same for the Dirac and Schroedinger cases. The first-order radial equations,

$$\begin{cases} (p_0+mc)f-\hbar[g'+(1+k)g/r]=0, \\ (p_0-mc)g+\hbar[f'+(1-k)f/r]=0, \end{cases} \tag{1.93}$$

give the Schroedinger equation identically if one replaces the coefficient p_0+mc of f by $2mc$. For values of $|E_f-E_i|$ of the order of the ionization potential and for $r>a_H$ the effect of relativity is thus describable as a change in f/g of the order $(E-mc^2)/mc^2$ which is of the order α^2/n^2. For distances of the order e^2/mc^2 the fractional effect on f/g is of the order of 50 percent. The volume within which this is the case is of the order $(e^2/a_Hmc^2)^3=\alpha^6$, however, and this effect is negligible. For $E_f\sim mc^2$ the relativistic f/g is again appreciably (of the order of 50 percent) different from the non-relativistic value. Here, however, the final state f is practically that of a free electron for which p^2 is diagonal in the non-relativistic approximation. One expects, accordingly, the whole effect to be small. In fact the number of states f in the energy interval mc^2 for a one-dimensional problem in the interval 0 to R is $\sim(R/\pi c\hbar)mc^2$. The effect of the short wave-length of the final state is to bring in a factor of the order $(\hbar/mc)/a_H=\alpha$ into each matrix element. Besides the normalization factor for the continuum is of the order $(a_H/R)^{\frac{1}{2}}$ of what it is for the ground state. The whole contribution is therefore of the order

$$mc^2(R/\pi c\hbar)(2m/2M)(T^2/mc^2)\alpha^2(a_H/R) \sim(m/M)\alpha^3Ry, \tag{1.94}$$

where the dependence on n is not considered since the whole is negligible. The relativistic value is of the same order as that just considered and effect (c) is negligible. The consideration of effect (a) is essentially similar to that just made for the continuum, with the additional simplification of larger energy denominators and the fact that for $|E_f+mc^2|\sim Ry$ the large initial g_i pairs off with a small final g_f. This brings in an extra factor α in each matrix element which takes the place of the factor $(\hbar/mc)/a_H$, which was discussed in connection with Eq. (1.93). Effect (a) is, therefore, also negligible. No terms of order $(m/M)^2\alpha$ are seen to be present in the second-order perturbation energy, and it suffices to use the non-relativistic value $-(m/M)Ry/n^2$ for this correction. It remains, therefore, to evaluate the expectation values of $p^2/2M$ and of the part of Y which does not depend on nuclear spin orientation.

III. EVALUATION OF EXPECTATION VALUES

Neglecting the second term in the expansion of Φ/Ψ, one obtains an equivalent operator Y' which contains $\boldsymbol{\sigma}_M$ quadratically. Linearizing in the $\boldsymbol{\sigma}_M$ and throwing away the spin dependent part, one is left with

$$Y''=(e^2/4Mc)[(\mathbf{p}\boldsymbol{\alpha})r^{-1}+r^{-1}(\boldsymbol{\alpha}\mathbf{p}) +(\mathbf{pr})(\boldsymbol{\alpha}\mathbf{r})r^{-3}+r^{-3}(\boldsymbol{\alpha}\mathbf{r})(\mathbf{rp})]. \tag{2}$$

The expectation value of this quantity and of $p^2/2M$ will be calculated. Following Dirac it is convenient to introduce the operators

$$\epsilon=(\boldsymbol{\alpha}\mathbf{r})/r,\quad k=\beta[(\mathbf{L}\boldsymbol{\sigma})+1], \tag{2.1}$$

and to recall that the meaning of Dirac's angle-dependent canonical transformation is that the application of ϵ, k, β, to the Dirac four-component wave function amounts[6] to the operation on the column matrix

$$\begin{pmatrix} f \\ g \end{pmatrix} \tag{2.2}$$

$$\epsilon=\begin{pmatrix} 0, & -i \\ i, & 0 \end{pmatrix},\quad k=k\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},\quad \beta=\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},\quad \cdots, \tag{2.3}$$

where k is used interchangeably for the operator and its eigenvalue. It follows directly from the above form for ϵ that

$$\langle(\mathbf{pr})(\boldsymbol{\alpha}\mathbf{r})r^{-3}+r^{-3}(\boldsymbol{\alpha}\mathbf{r})(\mathbf{rp})\rangle =2\hbar\int_0^\infty(gf'-fg')rdr. \tag{2.4}$$

The normalization is here such that

$$\int_0^\infty(g^2+f^2)r^2dr=1.$$

Also it follows from the wave equation that

$$\langle(\mathbf{p}\boldsymbol{\alpha})r^{-1}+r^{-1}(\boldsymbol{\alpha}\mathbf{p})\rangle=-2\langle p_0+\beta mc\rangle, \tag{2.5}$$

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[6] P. A. M. Dirac, Proc. Roy. Soc. **A117**, 611 (1928); The quantum number j of Dirac's article is called k here. His k is called L.

and hence again, by means of Eq. (2.3) as well as Eq. (2.4),

$$\langle Y''\rangle = -(e^2/2Mc)\int_0^\infty [(p_0+mc)f^2 + (p_0-mc)g^2+\hbar(fg'-gf')]rdr. \quad (2.6)$$

Multiplying the two Eqs. (1.93) by f and g, respectively, there results a relation which enables one to eliminate the derivatives and one obtains

$$\langle Y''\rangle = -(e^2/Mc)\left\{\int_0^\infty (p_0+mc)f^2 + (p_0-mc)g^2rdr - \hbar I\right\}, \quad (2.7)$$

with

$$I = k\int_0^\infty fgdr. \quad (2.8)$$

Again one has for the one-electron function ψ

$$\begin{aligned} p^2\psi = (\boldsymbol{\alpha}\mathbf{p})^2\psi &= -(\boldsymbol{\alpha}\mathbf{p})(p_0+\beta mc)\psi \\ &= -(p_0-\beta mc)(\boldsymbol{\alpha}\mathbf{p})\psi = (p_0^2-m^2c^2)\psi, \end{aligned} \quad (3)$$

and hence

$$\langle p^2/2M\rangle = (1/2M)\int_0^\infty (p_0^2-m^2c^2)(f^2+g^2)r^2dr. \quad (3.1)$$

One has the helpful relations[7]

$$W = mc^2\int_0^\infty (g^2-f^2)r^2dr, \quad (4)$$

$$mc = \int_0^\infty p_0(g^2-f^2)r^2dr, \quad (4.1)$$

where the value of E for $M=\infty$ is denoted by W and $cp_0 = W+e^2/r$. It follows from these two relations that

$$\int_0^\infty (W+e^2/r)(g^2-f^2)r^2dr = mc^2, \quad (4.2)$$

and hence

$$\int_0^\infty (e^2/r)(g^2-f^2)r^2dr = (m^2c^4-W^2)/mc^2. \quad (4.3)$$

The factor e^2 and the combination $mc(f^2-g^2)$ under the integral sign of Eq. (2.7) are expressible by means of Eq. (4.3). Performing this substitution one has

$$\langle Y''\rangle = (m^2c^4-W^2)/Mc^2 + [-W\langle e^2/r\rangle - \langle e^4/r^2\rangle + e^2c\hbar I]/Mc^2. \quad (4.4)$$

Again Eq. (3.1) gives

$$\langle p^2/2M\rangle = (W^2-m^2c^4)/2Mc^2 + [W\langle e^2/r\rangle + \langle e^4/2r^2\rangle]/(Mc^2). \quad (4.5)$$

Adding the last two equations one has

$$E_1 = \langle (p^2/2M) + Y''\rangle = \{-(W^2-m^2c^4)/2 + [-\langle e^4/2r^2\rangle + e^2c\hbar I]\}/Mc^2. \quad (4.6)$$

The quantity $W\langle e^2/r\rangle$ which occurs in Eqs. (4.5), (4.6) disappeared on addition. This was arranged on purpose so as not to have to evaluate corrections of order α^2 to $\langle e^2/r\rangle$. The deviation of the relativistic wave functions from their nonrelativistic approximations is taken into account implicitly in the value of W and appears besides in the terms $\langle e^2/2r^2\rangle$ and $c\hbar I$. The latter two terms will be seen to contribute only amounts of relative order $(m/M)\alpha^2$, and it will suffice to evaluate them without correcting for higher powers of α.

For a Coulomb field it will be seen that the terms in square brackets cancel in the nonrelativistic limit of small nuclear charge. In fact the well-known hydrogenic value of $\langle r^{-2}\rangle$ gives

$$(1/Mc^2)\langle e^4/2r^2\rangle = (m/M)\alpha^2 Ry/[n^3(L+\tfrac{1}{2})]. \quad (5)$$

The integral I occurs[6] in the theory of hyperfine structure and has the value

$$I = (\hbar/2mc)\{-kg^2(0+)/2 + \langle k(1+k)/r^3\rangle\} \quad (5.1)$$

in the approximation of small nuclear charge. The notation $0+$ means that g is evaluated at $r \sim e^2/mc^2$. The first term in braces is

$$-4\pi k\Psi_S^2(0), \quad (5.2)$$

and it vanishes except for s terms. One has, besides,

$$k(k+1) = L(L+1), \quad (5.3)$$

and for a Coulomb field

$$\langle r^{-3}\rangle = 1/[a_{\mathrm{H}}^3 L(L+\tfrac{1}{2})(L+1)n^3], \quad (5.4)$$

$$\Psi_S^2(0) = 1/[\pi n^3 a_{\mathrm{H}}^3]. \quad (5.5)$$

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[7] The derivation of these equations is given in Appendix I. The object in introducing these relations is to express $\langle p^2/2M\rangle$ in terms of W and also only quantities which have to be evaluated only approximately. Equation (4) is analogous to the virial theorem. Equations (4) make it possible to express $\langle e^2/r\rangle$ in terms of W.

Hence

$$I=(\alpha/2)\langle r^{-2}\rangle, \tag{5.6}$$

so that the square bracket in Eq. (4.6) vanishes. The cancellation is a consequence of the equality of $\langle r^{-2}\rangle$ and $a_{\mathrm{H}}L(L+1)\langle r^{-3}\rangle$ for a Coulomb field. The result is simply

$$E_1=-(W^2-m^2c^4)/(2Mc^2), \tag{6}$$

which can also be written as

$$E_1=-(m/M)(W-mc^2) -(m/4M)(\alpha^2/n^2)\,|\,W-mc^2|, \tag{6.1}$$

which is identical in form with the results of Darwin as well as Bechert and Meixner.

As has been discussed in the introduction, the meaning of the result is somewhat different from those previously obtained because it is expressed as a correction to Dirac's W rather than an approximation to it. This is only partially satisfying because Y'' is good only to order v^2/c^2 and one cannot be sure of the applicability of the second term in Eq. (6.1) for heavier nuclei.

The reasons explained in the introduction make one more certain, however, of the applicability of the answer. To within terms of order $(m/M)^2\alpha^2$ the latter may be written as

$$E-mc^2=(W-mc^2)/[1+(m/M)] -(m/4M)(\alpha^2/n^2)\,|\,W-mc^2|. \tag{7}$$

One may conclude that it is probably appropriate to apply Bethe's electrodynamic shift correction to the above formula for comparison with experimental values of the Lamb effect. It may be noted especially that there are no terms of order $(m/M)\alpha Ry/n^2$ which would be a serious effect, since $(m/M)\alpha Ry=1.3\times 10^4 mc/s$.

The considerations carried out above apply directly only to an idealized proton having a magnetic moment $e\hbar/2Mc$. The magnetic moment of the proton may be described phenomenalogically, however, by adding to the Hamiltonian terms involving the electromagnetic six vector in the manner proposed by Pauli as a mathematical possibility for uncharged particles. Attributing to the extra Pauli-like terms a physical significance only through their expectation values, one finds that nothing essential is changed in the reasoning which gave Eq. (6). It is still possible to start with Eq. (1). The terms independent of relative spin orientations of proton and electron are still represented by Eq. (2), and the remaining steps leading to Eq. (6) remain unchanged.

APPENDIX I

Some useful relations for the Dirac functions

Equations (4), (4.1) of the text do not seem to have been recorded in the literature. Equation (4) is a generalization of the virial theorem for the Schroedinger equation. To derive it one can start with the radial equations (1.93) and perform the similarity transformation

$$r=(1+\theta)r',$$

where θ is an arbitrary real number which will be made to have small positive values. The equations which result from the substitution are brought back to their original form on multiplication with $1+\theta$. Only now r' occurs everywhere in place of r and, $(1+\theta)E$, $(1+\theta)mc^2$ replace E, mc^2. Making θ small and recalling that the eigenvalue of an equation cannot depend on whether the independent variable is called r or r', one sees that the perturbation energy $mc^2\begin{pmatrix}-1 & 0\\ 0 & +1\end{pmatrix}\theta$, in the sense of Eq. (2.2), has caused a change in the eigenvalue of magnitude θE. Application of first-order perturbation theory yields Eq. (4).

One also has on multiplying the two radial equations by $-f$, g, respectively, and adding

$$(p_0-mc)g^2-(p_0+mc)f^2+\hbar d(fg)/dr+2\hbar fg/r=0.$$

Multiplying by r^2 and integrating, one obtains Eq. (4.1). Another useful relation which follows from the second-order equations is

$$\int_0^\infty (p_0^2-m^2c^2)(f^2+g^2)r^2dr =\hbar^2\int_0^\infty [(dg/dr)^2+(df/dr)^2+k(k+1)g^2/r^2 +k(k-1)f^2/r^2]r^2dr.$$

This equation is not used in the paper, but since it was helpful in some preliminary considerations it is reproduced here for possible use of other workers.