Proton Structure and the Hyperfine Shift in Hydrogen*

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The effect of the electromagnetic structure of the proton upon the hyperfine splitting of s states in hydrogen is determined without recourse to any specialized model for proton interactions. The principal modification of the Fermi formula, derivable nonrelativistically, appears as a multiplicative correction $1-2a_0^{-1}\langle r\rangle_{em}$ where a_0 is the Bohr radius and $\langle r\rangle_{em}$ is the first statistical moment of a distribution which characterizes the proton structure. The absence of additional structure corrections of experimental consequence is rigorously demonstrated. The method relies on a phenomenological representation of the proton deduced from the invariance principles of quantum field theory. The size of the proton is estimated from the available bound state data and compared with the size prediction inferred from scattering experiments.

1. INTRODUCTION

A NUMBER of theoretical calculations[1–4] of the hydrogen hyperfine structure have been performed in recent years. Common to all of these has been the assumption of a simplified model for the proton; it is treated as a Dirac particle bearing an anomalous point magnetic moment. Nevertheless, the interactions of the proton with various quantum fields produce charge and current densities distributed about a finite neighborhood of its position. The existence of such an electromagnetic structure accompanying the proton necessitates a reexamination of the previous work.

The importance of these "structure effects" has been recognized earlier; however, a more exact knowledge of meson-nucleon interactions than currently available had seemed essential for their evaluation. Thus, although the doublet separation of the hydrogen ground state is presently numbered among the most accurately known physical quantities, its significance for the determination of related physical constants and for the interpretation of other phenomena has remained uncertain.[5] In the present work, we shall show how these difficulties are resolved by the introduction of a suitable phenomenological description of the proton, and how the hyperfine measurement, in conjunction with an independent measurement of the fine structure constant, provides an estimate of the spatial extension of the proton's electromagnetic structure.

The success of the phenomenological approach rests on the feasibility of describing the structure of the bound proton in terms of form factors which characterize the electromagnetic properties of a free particle. The relative errors thereby introduced are no larger, we shall find, than the ratio of the hydrogen binding energy to the proton rest energy. Since this magnitude is merely a few parts in 100 million, no limitation is imposed, as yet, upon the interpretation of experimental data. The relatively low velocity of the hydrogen nucleus implies the additional simplification that only the static parts of the form factors observably affect the hyperfine shift.

The principal correction to the hyperfine shift due to proton structure is calculated nonrelativistically in the next section. In Sec. 3, we derive the field-theoretic relations which determine the energy level shifts in the hydrogen atom and permit the introduction of a phenomenological description of the proton. The succeeding section is devoted to the elaboration of the phenomenological method. The formalism is then employed in a detailed analysis of the hyperfine separation in hydrogen s states and an estimate of the electromagnetic size of the proton is obtained.

2. NONRELATIVISTIC FORMULATION

The hyperfine splitting of atomic energy levels is caused by the magnetic interactions of orbital electrons with the nucleus. We are concerned with the hyperfine separation of the s-state energy levels of hydrogen associated with the two possible relative spin orientations of electron and proton. The leading structure correction to this separation may be deduced from a nonrelativistic calculation which represents the electromagnetic properties of the proton by rigid, spherically symmetric distributions of charge and magnetization. Placing the proton at the origin of coordinates, we write these distrbitutions as $e_2 f_e(\mathbf{r})$ and $\mu_2\boldsymbol{\sigma}_2 f_m(\mathbf{r})$, respectively, where $\boldsymbol{\sigma}_2$ is the proton spin operator.[6] The electric and magnetic form factors $f_e(\mathbf{r})$ and $f_m(\mathbf{r})$ are normalized to unity,

$$\int f_e(\mathbf{r})d\mathbf{r}=\int f_m(\mathbf{r})d\mathbf{r}=1, \tag{2.1}$$

so that e_2 and μ_2 denote the charge and total magnetic moment of the proton.

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[6] The indices 1 and 2 will be consistently affixed to electron and proton variables, respectively.

In the presence of a magnetic field $\mathbf{H}(\mathbf{r})$, an electron bound to the proton's charge distribution suffers an energy displacement (hyperfine shift) ΔE,

$$\Delta E=\mu_1\int\phi^*(\mathbf{r})\langle\boldsymbol{\sigma}_1\cdot\mathbf{H}(\mathbf{r})\rangle\phi(\mathbf{r})d\mathbf{r}, \tag{2.2}$$

where $\phi(\mathbf{r})$ is the Schrödinger wave function for an electron moving in the field of the distribution $e_2f_e(\mathbf{r})$, $\mu_1=e_1/2m_1$ denotes the electron magnetic moment, and $\boldsymbol{\sigma}_1$ is the electron spin. The bracket indicates a spin expectation value to be evaluated in the appropriate atomic spin state. If $\mathbf{H}'(\mathbf{r}-\mathbf{s})$ specifies the magnetic field at $\mathbf{r}$ due to a point magnetic dipole of strength $\mu_2\boldsymbol{\sigma}_2$ at $\mathbf{s}$, then

$$\mathbf{H}'(\mathbf{r}-\mathbf{s})=(\mu_2/4\pi)\nabla_r\times(\nabla_r\times\boldsymbol{\sigma}_2/|\mathbf{r}-\mathbf{s}|).$$

The field $\mathbf{H}(\mathbf{r})$ to be inserted into Eq. (2.2) is given by

$$\mathbf{H}(\mathbf{r})=\int\mathbf{H}'(\mathbf{r}-\mathbf{s})f_m(\mathbf{s})d\mathbf{s}.$$

The spherical symmetry of $|\phi(\mathbf{r})|^2$ for s states permits the replacement of $\mathbf{H}(\mathbf{r})$ in (2.2) by its spherical average $[\mathbf{H}(r)]_{\text{Av}}$. We find

$$\begin{aligned}[\mathbf{H}(\mathbf{r})]_{\text{Av}}&=\left[(\mu_2/4\pi)(-\nabla^2+\nabla\nabla\cdot)\int\boldsymbol{\sigma}_2f_m(\mathbf{s})/|\mathbf{r}-\mathbf{s}|\,d\mathbf{s}\right]_{\text{Av}}\\&=(\mu_2/4\pi)(-\tfrac{2}{3}\nabla^2)\int\boldsymbol{\sigma}_2f_m(\mathbf{s})/|\mathbf{r}-\mathbf{s}|\,d\mathbf{s}\\&=-\tfrac{2}{3}\mu_2\boldsymbol{\sigma}_2f_m(\mathbf{r}).\end{aligned}$$

Therefore,

$$\Delta E=-\tfrac{2}{3}\mu_1\mu_2\langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2\rangle\int|\phi(\mathbf{r})|^2f_m(\mathbf{r})d\mathbf{r}. \tag{2.3}$$

If $f_e(\mathbf{r})$ and $f_m(\mathbf{r})$ are taken to be delta-functions (point charge and point magnetic moment), $\phi(\mathbf{r})$ becomes the Coulomb wave function $\phi_C(\mathbf{r})$ and (2.3) reduces to the familiar Fermi formula:

$$\Delta E_0=-\tfrac{2}{3}\mu_1\mu_2\langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2\rangle|\phi_C(0)|^2. \tag{2.4}$$

The value of the Coulomb wave function at the origin is expressed by[7]

$$\phi_C(0)=\pi^{-\frac{1}{2}}(m_1\alpha/n)^{\frac{3}{2}},$$

where n is the total quantum number of the s state and, in our choice of units, $\alpha=|e_1e_2|/4\pi$.

The wave functions $\phi(\mathbf{r})$ and $\phi_C(\mathbf{r})$ satisfy the homogeneous integral equations

$$\phi(\mathbf{r})=-2m_1\int G_E(\mathbf{r},\mathbf{s})V(\mathbf{s})\phi(\mathbf{s})d\mathbf{s}, \tag{2.5}$$

$$\phi_C(\mathbf{r})=-2m_1\int G_{E_C}(\mathbf{r},\mathbf{s})V_C(\mathbf{s})\phi_C(\mathbf{s})d\mathbf{s}. \tag{2.6}$$

[7] We adopt the conventional system of units in which $\hbar$ and c have magnitude unity.

Here, $G_{E_C}(\mathbf{r},\mathbf{s})$ and $G_E(\mathbf{r},\mathbf{s})$ are the free-particle Green's functions for the energies $E_C=\frac{1}{2}m_1(\alpha/n)^2$ and $E\approx E_C$ of the appropriate bound states, and

$$V_C(\mathbf{s})=-\alpha/\mathrm{s},\quad V(\mathbf{s})=-\alpha\int f_e(\mathbf{u})/|\mathbf{s}-\mathbf{u}|\,d\mathbf{u}.$$

As will shortly become clear, the evaluation of (2.3) requires a knowledge of $\phi(\mathbf{r})$ accurate only to first order in α. For any realistic estimate of the size of the proton charge distribution, a simple perturbation argument demonstrates that $(E-E_C)$ is much smaller than α^2E_C. Accordingly, $G_E(\mathbf{r},\mathbf{s})$ may be equated to $G_{E_C}(\mathbf{r},\mathbf{s})$. The subtraction of (2.6) from (2.5) then yields

$$\phi(\mathbf{r})=\phi_C(\mathbf{r})-2m_1\int G_{E_C}(\mathbf{r},\mathbf{s})[V(\mathbf{s})\phi(\mathbf{s})-V_C(\mathbf{s})\phi_C(\mathbf{s})]d\mathbf{s}. \tag{2.7}$$

Because the second term on the right of Eq. (2.7) is explicitly an order in α higher than the first, the Green's function for zero energy, $G_0(\mathbf{r},\mathbf{s})=(4\pi|\mathbf{r}-\mathbf{s}|)^{-1}$, may be substituted for $G_{E_C}(\mathbf{r},\mathbf{s})$, and $\phi(\mathbf{s})$, $\phi_C(\mathbf{s})$ both replaced by $\phi_C(0)$. Then

$$\phi(\mathbf{r})=\phi_C(\mathbf{r})+\frac{m_1\alpha}{2\pi}\phi_C(0)\times\int\int\frac{1}{|\mathbf{r}-\mathbf{s}|}\left(\frac{1}{|\mathbf{s}-\mathbf{u}|}-\frac{1}{s}\right)f_e(\mathbf{u})d\mathbf{s}d\mathbf{u}.$$

Approximating $\phi_C(\mathbf{r})$ by $\phi_C(0)(1-m_1\alpha r)$ and noting the identity

$$\frac{1}{2\pi}\int\frac{1}{|\mathbf{r}-\mathbf{s}|}\left(\frac{1}{|\mathbf{s}-\mathbf{u}|}-\frac{1}{s}\right)d\mathbf{s}=r-|\mathbf{u}-\mathbf{r}|,$$

we find, correct to first order in α,

$$\phi(\mathbf{r})=\phi_C(0)\left(1-m_1\alpha\int f_e(\mathbf{u})|\mathbf{u}-\mathbf{r}|\,d\mathbf{u}\right).$$

To this order, the dependence of $\phi_C(\mathbf{r})$, and hence of $\phi(\mathbf{r})$, on the total quantum number appears solely in the factor $\phi_C(0)$. We now obtain, by (2.3),

$$\Delta E=\Delta E_0\left(1-2m_1\alpha\int f_e(\mathbf{u})|\mathbf{u}-\mathbf{r}|f_m(\mathbf{r})d\mathbf{r}\right). \tag{2.8}$$

The last equation is simplified by the introduction of a new electromagnetic distribution function $f_{em}(\mathbf{r})$, defined to be the convolution of the electric and magnetic distributions:

$$f_{em}(\mathbf{r})=\int f_e(\mathbf{r}-\mathbf{s})f_m(\mathbf{s})d\mathbf{s}. \tag{2.9}$$

The conditions (2.1) imply that $f_{em}(\mathbf{r})$ is likewise

normalized to unity:

$$\int f_{em}(\mathbf{r})d\mathbf{r}=\int f_e(\mathbf{r}-\mathbf{s})f_m(\mathbf{s})d\mathbf{s}d\mathbf{r}=1.$$

Performing successively upon the integral in (2.8) the transformations $\mathbf{r}\rightarrow\mathbf{r}+\mathbf{u}$, $\mathbf{u}\rightarrow\mathbf{s}-\mathbf{r}$, we learn that[8]

$$\Delta E=\Delta E_0(1-2m_1\alpha\langle r\rangle_{em}), \tag{2.10}$$

where

$$\langle r\rangle_{em}=\int r f_{em}(\mathbf{r})d\mathbf{r}$$

is the first statistical moment of $f_{em}(\mathbf{r})$.

The structure term of (2.10) is seen to depend on the ratio of $\langle r\rangle_{em}$ to the Bohr radius $a_0=(m_1\alpha)^{-1}$. Under the reasonable assumption that $\langle r\rangle_{em}$ lies between the proton and meson Compton wavelengths, a correction to ΔE_0 of several parts in 10^5 may result from the consideration of proton structure nonrelativistically. The fact that this is the sole structure correction of experimental interest will emerge from the arguments of the work to follow.

We observe that, according to (2.10), the ratio of the doublet separations of two different s states is independent of structure.

3. PERTURBATION THEORY FOR THE HYDROGEN ATOM

An initial approximation to hydrogenic energy levels is defined by the electrostatic interaction of electron and proton. In this section, we develop a perturbation procedure for obtaining corrections in these levels, to fourth order in the electronic charge,[9] which does not presuppose any specific knowledge of the proton's coupling to other fields. The electron, however, is assumed to interact directly only with the electromagnetic field. Direct couplings of proton to electron, as in the very weak Fermi interactions, are thereby excluded. The theory employed makes use of the Green's functions or propagators for the fields of interest, and the operational calculus developed for their study.[10]

In the presence of an external current source, the electron propagator G_1 satisfies the equation

$$[\gamma_1(p_1-e_1A)+m_1+M_1(A)]G_1=1. \tag{3.1}$$

Here, M_1 is the electron's mass operator (exclusive of rest mass) and A represents the vacuum expectation value of the electromagnetic field excited by the external current. In terms of the photon propagator D, the mass operator is characterized by

$$M_1G_1=ie_1\gamma_1D(\delta/\delta A)G_1.$$

The methods of reference 10 may be utilized to show that the proton propagator G_2 obeys an equation identical in form to (3.1). The precise nature of the mass operator M_2 for the proton depends upon the unspecified fields to which the proton is coupled and need not concern us. If $\tilde{M}_2$ and $\tilde{G}_2$ are the operators to which M_2 and G_2 reduce in the absence of electromagnetic interactions, and $M_2=\tilde{M}_2+M_2'$, we have the further relations

$$[\gamma_2(p_2-e_2A)+m_2+\tilde{M}_2]\tilde{G}_2=1, \tag{3.2}$$

$$[\tilde{G}_2^{-1}+M_2']G_2=1. \tag{3.3}$$

The behavior of the interacting electron-proton system is prescribed by the two-body propagator G_{12} which obeys

$$G_2^{-1}\mathfrak{F}_1G_{12}=1, \tag{3.4}$$

in which $\mathfrak{F}_1$ is the operator

$$\mathfrak{F}_1=\gamma_1(p_1-e_1A)+m_1+ie_1\gamma_1D(\delta/\delta A).$$

The alternative equation,

$$(G_2^{-1}G_1^{-1}-I)G_{12}=1, \tag{3.5}$$

defines the interaction operator I.

A term I_0 may be separated from I and used to define an approximate bound state eigenfunction. The remainder, $(I-I_0)$, is then treated as a perturbation interaction. The static Coulomb potential is customarily selected as the primary cause of binding. In the present instance, a more natural choice for I_0 is the electrostatic potential which takes into account the proton's finite distribution of charge. The bound state wave function is then determined from the wave equation

$$(G_2^{(0)-1}G_1^{(0)-1}-I_0)\psi=0, \tag{3.6}$$

where $G_1^{(0)}=(\gamma_1p_1+m_1)^{-1}$, $G_2^{(0)}=(\gamma_2p_2+m_2)^{-1}$ are the free-particle propagators. The corresponding propagator $G_{12}^{(0)}$ is defined by the inhomogeneous equation

$$(G_2^{(0)-1}G_1^{(0)-1}-I_0)G_{12}^{(0)}=1. \tag{3.7}$$

If all electromagnetic interactions but I_0 are placed equal to zero, G_{12} reduces not to $G_{12}^{(0)}$, but to $\tilde{G}_{12}$ which is the solution of

$$[G_2^{(0)-1}G_1^{(0)-1}-I_0+\tilde{M}_2G_1^{(0)-1}]\tilde{G}_{12}=1. \tag{3.8}$$

By (3.5), together with (3.1), (3.3), and (3.8), we have

$$(\tilde{G}_{12}^{-1}-J)G_{12}=1,$$

in which

$$J=I-I_0-M_1\tilde{G}_2^{-1}-M_2'G_1^{(0)-1}.$$

If $\tilde{\psi}$ is an eigenfunction of total energy defined by

$$\tilde{G}_{12}^{-1}\tilde{\psi}=(\tilde{G}_2^{-1}G_1^{(0)-1}-I_0)\tilde{\psi}=0, \tag{3.9}$$

then the displacement in energy due to J is expressed

[8] A similar formula, not including the effect of the proton's charge distribution, was derived by W. Moellering, Ph.D. thesis, Indiana University, 1954 (unpublished).

[9] The perturbation formalism adopted here is similar to that of R. Karplus and A. Klein, Phys Rev. 87, 848 (1952) and Arnowitt, reference 3.

[10] J. Schwinger, Proc. Natl. Acad. Sci. U. S. 37, 452 (1951) and unpublished lectures, Harvard, 1955.

to fourth order in the charge, or equivalently, second order in the fine structure constant, by the formula

$$\Delta E=(-i/T)\langle\tilde{\psi}|J+J\tilde{G}_{12}J|\tilde{\psi}\rangle. \tag{3.10}$$

The quantity $J+J\tilde{G}_{12}J$ is independent of the time interval T over which the interactions are viewed so that a factor of T emerges from the expectation value to cancel the denominator. From the defining Eqs. (3.6) and (3.9) for the wave functions, we infer that, apart from a normalization constant,

$$\tilde{\psi}=\psi-G_{12}{}^{(0)}G_1{}^{(0)-1}\tilde{M}_2\psi.$$

The mass operator M_2, properly renormalized, annihilates free proton wave functions. The large mass of the proton and its weak binding in the hydrogen atom suggest that ψ describes a proton which is "nearly" free. If we anticipate the future result that $G_{12}{}^{(0)}G_1{}^{(0)-1}\times\tilde{M}_2\psi$ is ignorable relative to ψ, then the latter function can be used for $\tilde{\psi}$ in (3.10) without change of normalization. A similar consideration will later justify the neglect of terms in (3.10) containing M_1 and M_2'. The energy shift may then be written

$$\Delta E=(-i/T)\langle\psi|K|\psi\rangle, \tag{3.11}$$

where

$$K=I-I_0+(I-I_0)\tilde{G}_{12}(I-I_0).$$

A further reduction is effected by the substitution

$$\tilde{G}_{12}\rightarrow G_1{}^{(0)}\tilde{G}_2. \tag{3.12}$$

The neglect of binding in intermediate states, as expressed by (3.12), is permissable in a hyperfine calculation to this order. Its only consequence[9] is the introduction of infrared divergences which are compensated by divergences of opposite sign when the approximation is applied consistently.

The remaining task of this section is the derivation of an explicit expression for the transition operator K. We note first the definitions of the electron and proton vertex operators Γ_1 and Γ_2:

$$\Gamma_1=-(\delta/\delta e_1A)G_1{}^{-1},\quad \Gamma_2=-(\delta/\delta e_2A)G_2{}^{-1}.$$

Equation (3.4) implies that

$$G_2{}^{-1}\mathfrak{F}_1G_1G_1{}^{-1}G_{12}=1$$

whence

$$G_2{}^{-1}[1+ie_1\gamma_1G_1D(\delta/\delta A)]G_1{}^{-1}G_{12}=1.$$

Commuting $G_2{}^{-1}$ through $\delta/\delta A$, we have

$$[1+ie_1\gamma_1G_1D(\delta/\delta A)]G_2{}^{-1}G_1{}^{-1}G_{12}-ie_1\gamma_1G_1D(\delta G_2{}^{-1}/\delta A)G_1{}^{-1}G_{12}=1.$$

It follows that

$$G_2{}^{-1}G_1{}^{-1}G_{12}+[1+ie_1\gamma_1G_1D(\delta/\delta A)]^{-1}\times ie_1e_2\gamma_1G_1D\Gamma_2G_1{}^{-1}G_{12}=1. \tag{3.13}$$

Resorting temporarily to coordinate indices and the external current source J, we observe that

$$D(12)\frac{\delta}{\delta A(2)}D(34)\frac{\delta}{\delta A(4)}=\frac{\delta}{\delta J(1)}\frac{\delta}{\delta J(3)}=\frac{\delta}{\delta J(3)}\frac{\delta}{\delta J(1)}=D(34)\frac{\delta}{\delta A(4)}D(12)\frac{\delta}{\delta A(2)}.$$

Thus if $D(\delta/\delta A)$ is applied to (3.1), there results

$$-e_1\gamma_1DG_1+\mathfrak{F}_1D(\delta G_1/\delta A)=0.$$

Hence,

$$\gamma_1DG_1=\mathfrak{F}_1G_1D\Gamma_1G_1=[1+ie_1\gamma_1G_1D(\delta/\delta A)]D\Gamma_1G_1.$$

Let X be any operator. Then

$$\gamma_1DGX=[1+ie_1\gamma_1G_1D(\delta/\delta A)]D\Gamma_1G_1X-ie_1\gamma_1G_1D(\delta/\delta A)\{D\Gamma_1G_1\}X,$$

where the operators to the right of $\delta/\delta A$ which are *not* differentiated are enclosed by curly braces. Transposing the second term on the right, we obtain

$$\gamma_1DG_1[1+ie_1(\delta/\delta A)\{D\Gamma_1G_1\}]X=[1+ie_1\gamma_1G_1D(\delta/\delta A)]D\Gamma_1G_1X. \tag{3.14}$$

Applying $[1+ie_1\gamma_1G_1D(\delta/\delta A)]^{-1}$ to the right of the members of Eq. (3.14) and setting

$$[1+ie_1(\delta/\delta A)\{D\Gamma_1G_1\}]X=\Gamma_2G_2{}^{-1}G_{12},$$

we infer that

$$[1+ie_1\gamma_1G_1D(\delta/\delta A)]^{-1}\gamma_1DG_1\Gamma_2G_1{}^{-1}G_{12}=D\Gamma_1G_1[1+ie_1(\delta/\delta A)\{D\Gamma_1G_1\}]^{-1}\Gamma_2G_1{}^{-1}G_{12}. \tag{3.15}$$

A comparison of (3.15) with (3.13) and (3.5) reveals that

$$IG_{12}=-ie_1e_2\Gamma_1DG_1[1+ie_1(\delta/\delta A)\{D\Gamma_1G_1\}]^{-1}\times\Gamma_2G_1{}^{-1}G_{12}. \tag{3.16}$$

The expansion of (3.16) to order $(e_1e_2)^2$ yields, when G_{12} is replaced by $G_1{}^{(0)}\tilde{G}_2$ in the higher order term,

$$I=-ie_1e_2\Gamma_1D\Gamma_2-(e_1e_2)^2\gamma_1G_1{}^{(0)}D\times[(\delta/\delta e_2A)\Gamma_2\tilde{G}_2]D\gamma_1\tilde{G}_2{}^{-1}.$$

The transition operator, to this order, becomes

$$K=K_A+K_B+K_C, \tag{3.17}$$

$$K_A=-ie_1e_2\Gamma_1D\Gamma_2-I_0,$$

$$K_B=-(e_1e_2)^2\gamma_1G_1{}^{(0)}D[(\delta/\delta e_2A)\Gamma_2\tilde{G}_2]D\gamma_1\tilde{G}_2{}^{-1}-(e_1e_2)^2\gamma_1D\Gamma_2G_1{}^{(0)}\tilde{G}_2\gamma_1D\Gamma_2, \tag{3.18}$$

$$K_C=ie_1e_2\gamma_1D\Gamma_2G_1{}^{(0)}\tilde{G}_2I_0+ie_1e_2I_0G_1{}^{(0)}\tilde{G}_2\gamma_1D\Gamma_2+I_0G_1{}^{(0)}\tilde{G}_2I_0. \tag{3.19}$$

One understands that upon extraction of the variational derivatives, the external current and A have fulfilled their function and are set equal to zero. The presence

of K_C simply corrects for the inclusion of I_0 in the interaction $-ie_1e_2\gamma_1 D\Gamma_2$ which stands in K_B. The latter operator has the combined form

$$K_B=-(e_1e_2)^2\gamma_1 DG_1^{(0)}\Lambda_2 D\gamma_1, \tag{3.20}$$

with

$$\Lambda_2=[(\delta/\delta e_2 A)\Gamma_2 G_2]_{A=0}\tilde{G}_2^{-1}+\Gamma_2\tilde{G}_2\Gamma_2$$
$$=\tilde{G}_2^{-1}[\delta^2 G_2/\delta e_2 A\delta e_2 A]_{A=0}\tilde{G}_2^{-1}.$$

For reasons already suggested and subject to future verification, $G_2^{(0)-1}$ may be used in place of $\tilde{G}_2^{-1}$. Then Λ_2 is given by

$$\Lambda_2=G_2^{(0)-1}[\delta^2 G_2/\delta e_2 A\delta e_2 A]_{A=0}G_2^{(0)-1}. \tag{3.21}$$

When (3.17) is substituted into (3.11), a form for the energy shift is displayed in which all the radiative effects of proton propagation are implicitly contained in Γ_2 and Λ_2. It is through these operators that the interactions of the proton with one and two photons, respectively, are described. The renormalization of K is accomplished by the use of the renormalized expressions for Γ_1 and D, to appropriate order in $(e_1)^2$, and the phenomenological forms of the renormalized Γ_2 and Λ_2 to be derived in the next section.

4. PROTON SCATTERING BY AN ELECTROMAGNETIC FIELD

The relation of Γ_2 and Λ_2 to the formalism for scattering of a proton in an external electromagnetic field provides a correlation of the structure effects within the hydrogen atom to those observed in scattering experiments. As a consequence of the free-particle nature of the initial and final scattering states, the separation of effects into those characteristic of a free proton and those which reflect its behavior "off the energy shell" affords a special simplification here.

The scattering amplitude for the transition of a proton from a state of four-momentum p', spin u' to a (different) state of four-momentum p'', spin u'' is expressible as the spin matrix element $\langle u''|S(p'',p')|u'\rangle$ of the spin and momentum dependent function $S(p'',p')$,

$$S(p'',p')=\langle p''|G^{(0)-1}G(A)G^{(0)-1}|p'\rangle. \tag{4.1}$$

The identification of proton operators by the subscript 2 will be omitted, in this section only, for brevity. The operators $G^{(0)-1}=\gamma p+m$ in (4.1) annihilate the free particle states to which they are adjacent unless canceled by corresponding factors of $(\gamma p+m)^{-1}$ in $G(A)$. It follows that only parts of $G(A)$ possessing singularities of this type contribute to free particle matrix elements.

We investigate the scattering to second order in the external field. Expanding the propagator,

$$G(A)=G^{(0)}+A[\delta G/\delta A]_{A=0}+\tfrac{1}{2}AA[\delta^2 G/\delta A\delta A]_{A=0},$$

we have

$$G^{(0)-1}G(A)G^{(0)-1}=G^{(0)-1}+eA\Gamma+\tfrac{1}{2}e^2AA\Lambda.$$

It is convenient to introduce the momentum representations

$$A_\mu(k)=(2\pi)^{-4}\int e^{-ikx'}A_\mu(x')dx', \tag{4.2}$$

$$\delta(p''-p'-k)\Gamma_\mu(p'',p')=\langle p''|-\delta G^{-1}/\delta eA_\mu(k)|p'\rangle_{A=0}, \tag{4.3}$$

$$\delta(p''-p'-k-k')\Lambda_{\mu\nu}(p'',p',k,k')=\langle p''|G^{(0)-1}[\delta^2 G/\delta eA_\mu(k)\delta eA_\nu(k')]G^{(0)-1}|p'\rangle_{A=0}. \tag{4.4}$$

The amplitude $S(p'',p')$ then assumes the form

$$S(p'',p')=eA_\mu(p''-p')\Gamma_\mu(p'',p')+\tfrac{1}{2}e^2\int A_\mu(k)\times A_\nu(p''-p'-k)\Lambda_{\mu\nu}(p'',p',p''-p'-k)dk. \tag{4.5}$$

The desired phenomenological forms for Γ and Λ follow immediately from a suitable representation of the proton propagator. The constraints imposed by the principles of Lorentz, gauge, and charge invariance supply the key to the construction of $G(A)$. When no field is present, the inverse of the (renormalized) propagator may be written

$$G^{-1}(A=0)=\gamma p+m+(\gamma p+m)R_1(\gamma p+m).$$

The symbol R_1 which appears in the renormalized mass operator denotes a function of γ and p whose precise nature is unimportant. In order to exhibit a formula for $G(A)$, we first introduce an operator $\bar{G}$,

$$\bar{G}=[\gamma_\mu p_\mu+m-ef'(-\Box^2)\gamma_\mu A_\mu-\tfrac{1}{2}\mu_A f''(-\Box^2)\sigma_{\mu\nu}F_{\mu\nu}]^{-1}, \tag{4.6}$$

which will prove to be the only part of $G(A)$ that is effective (to first order in A) in free particle scattering. In this equation, $f'(-\Box^2)$ and $f''(-\Box^2)$ are arbitrary functions of the D'Alembertian, and μ_A is a constant of dimensions (e/m) chosen so that $f''(0)=1$. Gauge invariance implies that $f'(0)$ is likewise unity. The field potential A is to be expressed in a Lorentz gauge.

We now assert that the inverse of the proton propagator, correct to linear terms in the field, and subject to the trio of invariance requirements, is given by the expression

$$G^{-1}(A)=\bar{G}^{-1}+\bar{G}^{-1}R_1\bar{G}^{-1}+\bar{G}^{-1}R_2(F)+R_3(F)\bar{G}^{-1}, \tag{4.7}$$

in which the unspecified operators R_2 and R_3, in addition to their dependence on γ and p, are linear in the electromagnetic field strengths, vanishing when $F=0$. A derivation of (4.6) and (4.7) is given in the appendix.[11]

An application of the functional derivative $\delta/\delta A_\mu(k)$ to the equation

$$A_\lambda(x')=\int e^{ikx'}A_\lambda(k)dk$$

[11] Similar techniques have been used by A. Klein to derive the low-energy theorems of field theory [Phys. Rev. 99, 998 (1955)].

shows that

$$\delta A_\lambda(x')/\delta A_\mu(k)=e^{ikx'}\delta_{\lambda\mu},$$

which implies the *operator* relations

$$\delta A_\lambda/\delta A_\mu(k)=\delta_{\lambda\mu}e^{ikx},$$
$$\delta F_{\lambda\mu}/\delta A_\mu(k)=(\delta_{\nu\mu}\partial_\lambda-\delta_{\mu\lambda}\partial_\nu)e^{ikx}=i(k_\lambda\delta_{\nu\mu}-k_\nu\delta_{\mu\lambda})e^{ikx}.$$

We note that e^{ikx} has the property

$$e^{ikx}|p\rangle=|p+k\rangle.$$

The momentum representative of the vertex operator is now easily determined. We have, from (4.6),

$$\delta\bar{G}^{-1}/\delta A_\mu(k)=[-ef'(k^2)\gamma_\mu-i\mu_A f''(k^2)k_\lambda\sigma_{\lambda\mu}]e^{ikx}.$$

Then (4.3) yields, if (p',u') and (p'',u'') refer to free particle states,

$$\Gamma_\mu(p'',p')=f'(k^2)\gamma_\mu+i(\mu_A/e)f''(k^2)k_\lambda\sigma_{\lambda\mu},\qquad k=p''-p'. \quad (4.8)$$

After the functional derivatives have been performed, and the fields set equal to zero, the residual terms, $\bar{G}^{-1}R_1\bar{G}^{-1}$, etc. of (4.7) are found to have factors of $(\gamma p+m)$ either to the extreme right or left. It is then clear that these terms cannot contribute to free particle matrix elements of Γ.

Defining the transforms

$$f'(x)=(2\pi)^{-4}\int e^{ikx}f'(k^2)dk,$$

$$f''(x)=(2\pi)^{-4}\int e^{ikx}f''(k^2)dk,$$

of the functions which appear in $\Gamma_\mu(p'',p')$, we may construct a modified Dirac equation for a quantum mechanical particle in an electromagnetic field:

$$\Big[\gamma_\mu p_\mu+m-e\gamma_\mu\int f'(x-y)A_\mu(y)dy$$
$$-\tfrac{1}{2}\mu_A\sigma_{\mu\nu}\int f''(x-y)F_{\mu\nu}(y)dy\Big]\psi(x)=0. \quad (4.9)$$

We observe that the first order term of formula (4.5) is precisely the Born approximation amplitude for scattering by a particle whose wave function satisfies (4.9). This remark identifies μ_A as the anomalous magnetic moment of the proton and motivates the interpretation of $f'(x)$ and $f''(x)$ as form factors for charge and anomalous magnetization densities which surround the proton. The form factor $f'''(x)$ for the total intensity of magnetization about the proton is a weighted average of its intrinsic and anomalous parts, i.e.,

$$f'''(x)=\frac{(e/2m)f'(x)+\mu_A f''(x)}{(e/2m)+\mu_A}.$$

If we take seriously the view that these densities are due to the presence of virtual quanta which are continually emitted and reabsorbed by the proton, a physical interpretation may be given to the form factors which treats their space and time dependence symmetrically. They are simply probability distributions that describe, statistically, how far the individual quanta travel and how long they live.

The amplitudes for purely elastic scattering ($p_0'=p_0''$) are expressed in terms of form factors evaluated at $k_0=0$. With the use of these functions, a connection is established between the static distributions defined in Sec. 2 and their relativistic counterparts introduced on invariance grounds in the present section:

$$f_e(\mathbf{r})=\int f'(x)dt=(2\pi)^{-3}\int e^{i\mathbf{k}\cdot\mathbf{r}}f'(\mathbf{k}^2)d\mathbf{k},$$

$$f_m(\mathbf{r})=\int f'''(x)dt$$
$$=\frac{\int e^{i\mathbf{k}\cdot\mathbf{r}}[(e/2m)f'(\mathbf{k}^2)+\mu_A f''(\mathbf{k}^2)]d\mathbf{k}}{(2\pi)^3[(e/2m)+\mu_A]}.$$

The elementary relation between $f'(k^2)$ and $f'(\mathbf{k}^2)$, etc., demonstrates that at least in principle the relativistic distributions are deducible from elastic scattering experiments such as, for example, the scattering of electrons by protons.

Processes in which the proton interacts repeatedly with the electromagnetic field or, equivalently, processes involving radiation and absorption of a number of photons by the proton cannot be comprehended so simply. In addition to the distribution functions already considered, an array of parameters pertaining to the polarization of the distributions by the electromagnetic field is required. If, however, our attention is limited to small electromagnetic frequencies k, simplicity is recovered. For if the relevant wave lengths of the field are large enough to envelop the entire distributions, only the total strengths of the latter are important. Thus, it is well known[12] that the free proton matrix element $\Lambda_{\mu\nu}(p'',p',k,k')$ for photon-proton scattering depends, to first order in k and k', only upon the proton's charge and magnetic moment.

A more accurate determination of Λ requires the addition to $\bar{G}^{-1}$ of invariant terms quadratic in the field strengths. We shall see that for the hyperfine shift calculation, only the matrix elements $\Lambda_{\mu\nu}(0,0,k,-k)$ evaluated for vanishing initial and final proton momenta, are necessary. Hence, those terms which contain the momentum operator p may be discarded, although derivatives of the field strengths can still occur. We note, for later application, that as a consequence of charge invariance the remaining quadratic terms must have a spin factor either of unity, $\gamma_5\gamma_\lambda$, or γ_5.

[12] F. E. Low, Phys. Rev. **96**, 1428 (1954), M. Gell-Mann and M. L. Goldberger, Phys. Rev. **96**, 1433 (1954).

The addition of the quadratic terms to $\bar{G}^{-1}$ will alter somewhat the functional dependence of $R_2(F)$ and $R_3(F)$ without changing the canonical form (4.7). If we set

$$-\Delta=\bar{G}^{-1}R_1\bar{G}^{-1}+\bar{G}^{-1}R_2(F)+R_3(F)\bar{G}^{-1},$$

we have

$$\begin{aligned}G(A)&=(\bar{G}^{-1}-\Delta)^{-1}\\&=\bar{G}+\bar{G}\Delta\bar{G}+\bar{G}\Delta\bar{G}\Delta\bar{G}+\cdots.\end{aligned}\tag{4.10}$$

Only the first term of the expansion in (4.10) can contribute to (4.4). In the remaining terms, factors of $\bar{G}^{-1}$ from Δ cancel at least one factor of $\bar{G}$ standing to the extreme right or left. Thus, the free-particle propagators $G^{(0)-1}$ are not offset by corresponding singularities from these terms. We may then write $\Lambda_{\mu\nu}$ in the form

$$\begin{aligned}\Lambda_{\mu\nu}&=G^{(0)-1}[\delta^2\bar{G}/\delta eA_\mu\delta eA_\nu]_{A=0}G^{(0)-1}\\&=\Lambda_{\mu\nu}{}^{(a)}+\Lambda_{\mu\nu}{}^{(b)},\end{aligned}\tag{4.11}$$

with

$$\Lambda_{\mu\nu}{}^{(a)}=\Gamma_\mu G^{(0)}\Gamma_\nu+\Gamma_\nu G^{(0)}\Gamma_\mu,$$

$$\Lambda_{\mu\nu}{}^{(b)}=[\delta^2\bar{G}^{-1}/\delta eA_\mu\delta eA_\nu]_{A=0}.\tag{4.12}$$

The low-frequency approximations to (4.8) and (4.11),

$$\Gamma_\mu(p'',p')\approx\gamma_\mu+i(\mu_A/e)k_\lambda\sigma_{\lambda\mu},\tag{4.13}$$

$$\Lambda_{\mu\nu}\approx\Lambda_{\mu\nu}{}^{(a)},\tag{4.14}$$

serve to describe the electromagnetic interactions of a point proton without finite structure. In particular, (4.13) corresponds to the choice of delta functions for the coordinate representations of the form factors. It is the use of (4.13) and (4.14) rather than the more general expressions (4.8) and (4.11) which distinguishes earlier work from the present approach.

5. HYPERFINE SHIFT

The validity of the model which treats the proton as a structureless point particle may now be critically examined from the point of view developed in the present paper. Errors of relative order $\alpha^2(m_1/m_2)$ will be neglected. Because of the disparity in magnitude of the proton and electron masses, the previous calculations fell naturally into two stages. In the first stage, corrections to the Fermi formula (2.4) of relative orders α and α^2 were computed in the adiabatic limit, $(m_1/m_2)\to 0$. In this limit, the proton appears as a fixed source for the Coulomb and magnetic dipole fields. Excepting only the contribution to the electron magnetic moment, all such corrections are of order α^2. These include energy shifts due to the relativistic behavior of the electron when close to the hydrogen nucleus (Breit correction), the electron mass operator, and the polarization of the electromagnetic fields.

In the second stage, a fully relativistic two-body formalism was employed to obtain corrections of relative order $\alpha(m_1/m_2)\ln(m_1/m_2)$ and $\alpha(m_1/m_2)$. These are recoil effects resulting from the exchange between electron and proton of one or two photons. A logarithmic divergence at high photon frequency (i.e., large proton recoil) occurs in the term describing the interaction of two photons with the proton's anomalous spin current; it is rescued, however, by the imposition of a frequency cutoff.

With regard to the additions to the electron magnetic moment, proton structure plays no role. The α^2 terms computed in the adiabatic limit result from phenomena distributed over a region whose breadth is of the order of an electron Compton wavelength. Corrections to these effects caused by proton structure would then supply to the factor of α^2 already present, an additional factor of the order of (m_1/m_2). Consequently such corrections may be disregarded.

Formula (3.11) suffices for a calculation of α corrections to the hyperfine shift. In order to complete our analysis, we must (1) justify the neglect of the mass operator terms in the phenomenological expressions for Γ_2 and Λ_2, and the replacement of $\tilde{G}_2$ by $G_2{}^{(0)}$, $\tilde{\psi}$ by ψ; (2) prove that in the adiabatic limit, the only consequence of proton structure is recorded in the correction term $-2m_1\alpha\langle r\rangle_{em}$ derived in Sec. 2, (3) show that the recoil effects in single photon exchange are unmodified by structure considerations, and (4) investigate the applicability of (4.13) and (4.14) in the two-photon terms. We shall, intermittently, quote equations from Arnowitt's work without providing complete proofs, but an effort to maintain the continuity of the argument will be made.

(1) After removal of the center-of-mass dependence, the wave equation (3.6) becomes

$$\begin{aligned}&(H_1-p_0-\bar{m}E/m_2)(H_2+p_0-\bar{m}E/m_1)\psi(p)\\&\qquad=\beta_1\beta_2\int I_0(p,p')\psi(p')dp',\end{aligned}$$

where $H_1=\boldsymbol{\alpha}_1\cdot\mathbf{p}+\beta_1m_1$, $H_2=-\boldsymbol{\alpha}_2\cdot\mathbf{p}+\beta_2m_2$, $\boldsymbol{\alpha}_i$ and β_i are the usual Dirac matrices, $\bar{m}$ the reduced mass, E the bound state energy, p and p' are relative energy-momenta, and $I_0(p,p')$ is the lowest order static part of the interaction $-ie_1e_2\Gamma_1D\Gamma_2$:

$$\begin{aligned}I_0(p,p')&=-ie^2(2\pi)^{-4}\beta_1\beta_2\mathbf{k}^{-2}f'(\mathbf{k}^2),\\\mathbf{k}&=\mathbf{p}-\mathbf{p}',\quad e=|e_1|=|e_2|.\end{aligned}$$

The wave function $\psi(p)$ can be written

$$\begin{aligned}\psi(p)=&(H_1-p_0-\bar{m}E/m_2)^{-1}(H_2+p_0-\bar{m}E/m_1)^{-1}\\&\times(2\pi)^{\frac{1}{2}}\beta_1\beta_2\int I_0(p,p')\phi(\mathbf{p})d\mathbf{p}\end{aligned}$$

in terms of an "equal times" wave function $\phi(\mathbf{p})$,

$$\phi(\mathbf{p})=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}\psi(p)dp_0.$$

An adequate approximation to $\phi(\mathbf{p})$ is given by the Schrödinger equation

$$\left(\frac{\mathbf{p}^2}{2\bar{m}}+m_1+m_2-E\right)\phi(\mathbf{p})=\frac{e^2}{(2\pi)^3}\int\frac{f'((\mathbf{p}-\mathbf{p}')^2)}{(\mathbf{p}-\mathbf{p}')^2}\phi(\mathbf{p}')d\mathbf{p}'.$$

In this approximation, the equal-times wave function carries a four-component spin dependence in which the small components vanish. The energy of the eigenstate with total quantum number n is given with sufficient accuracy by

$$E=m_1+m_2-\tfrac{1}{2}\alpha^2\bar{m}^2/n^2,$$

whence

$$\psi(p)=\frac{-i}{2\bar{m}(2\pi)^{\frac{1}{2}}}\times\frac{(\mathbf{p}^2+\alpha^2\bar{m}^2/n^2)\phi(\mathbf{p})}{(H_1-p_0-\bar{m}E/m_2)(H_2+p_0-\bar{m}E/m_1)}. \quad (5.1)$$

If the distinction between the electron mass and the reduced mass is ignored, then $\phi(\mathbf{p})$, apart from its spin dependence, is simply the transform

$$(2\pi)^{-\frac{3}{2}}\int e^{-i\mathbf{p}\cdot\mathbf{r}}\phi(\mathbf{r})d\mathbf{r}$$

of the wave function $\phi(\mathbf{r})$ defined in Sec. 2.

If we define $\psi(\mathbf{p},t)$ by

$$\psi(\mathbf{p},t)=(2\pi)^{-\frac{1}{2}}\int e^{-ip_0t}\psi(p)dp_0, \quad (5.2)$$

the energy shift assumes the form

$$\Delta E=-i(2\pi)^{-1}\int\psi^*(\mathbf{p},t)\beta_1\beta_2e^{-ip_0t}\times K(p,p')e^{ip_0't}\psi(\mathbf{p}',t')d\mathbf{p}d\mathbf{p}'dtdt' \quad (5.3)$$

where K is the transition operator (3.17).

We are now in a position to discuss quantitatively the approximations based on the assumption that the proton is nearly free. The equations

$$\tilde{\psi}=\psi-G_{12}^{(0)}G_1^{(0)-1}\tilde{M}_2\psi$$

and

$$\tilde{G}_2^{-1}=G_2^{(0)-1}+\tilde{M}_2$$

show that $\tilde{\psi}$ and $\tilde{G}_2$ differ from ψ and $G_2^{(0)}$ because of the presence of $\tilde{M}_2$ which can be written in the form

$$\tilde{M}_2=(\gamma_2p_2+m)R(\gamma_2p_2+m_2).$$

Further, the parts of Γ_2 and Λ_2 which were dropped in Sec. 4 had factors of $(\gamma_2p_2+m_2)$ either on the extreme right or left. It follows that all the simplifications in point amount to the neglect, in (5.3), of terms whose special characteristic is that at least one factor of $(\gamma_2p_2+m_2)$ stands immediately adjacent to a wave function. Note that terms from (3.19) containing Γ_2 such as

$$ie_1e_2\gamma_1D\Gamma_2G_1^{(0)}\tilde{G}_2I_0$$

are no exception, for by (3.6) and (3.9),

$$\langle\tilde{\psi}|\gamma_1D\Gamma_2G_1^{(0)}\tilde{G}_2I_0|\tilde{\psi}\rangle=\langle\tilde{\psi}|\gamma_1D\Gamma_2|\tilde{\psi}\rangle\approx\langle\psi|\gamma_1D\Gamma_2|\psi\rangle=\langle\psi|\gamma_1D\Gamma_2G_1^{(0)}G_2^{(0)}I_0|\psi\rangle.$$

Hence, the problem is reduced to that of showing that $[(\gamma_2p_2+m_2)/m_2]\psi$ is negligible compared to ψ. A factor of $(1/m_2)$ is inserted here for dimensional considerations. Our argument is predicated on the assumption that once the appropriate dimensional factor is introduced, the remaining coefficients are of order unity or smaller. The choice of the proton mass rather than, say, the meson mass is motivated in part by the analogy to electrodynamics. Specifically, if the masses of the quanta with which the proton interacts go to zero, one still expects finite effects from the mass operator.[13] And if these masses exceed or are comparable to the proton mass, the use of $(1/m_2)$ does not reduce the validity of the approximation. In any event, the use of the meson mass would not alter significantly the orders of magnitude in question.

Upon substitution of (5.1) into (5.2) and integration over p_0 we find

$$\psi(\mathbf{p},t)=-\left\{\frac{(m_1+E_1\epsilon(t)+\boldsymbol{\alpha}_1\cdot\mathbf{p})(E-E_1\epsilon(t)+H_2)}{4\bar{m}E_1[(E-E_1\epsilon(t))^2-E_2^2]}\times\exp\{-i[E_1\epsilon(t)-\bar{m}E/m_2]t\}+\frac{(m_2-E_2\epsilon(t)-\boldsymbol{\alpha}_2\cdot\mathbf{p})(E+E_2\epsilon(t)+H_1)}{4\bar{m}E_2[(E+E_2\epsilon(t))^2-E_1^2]}\times\exp\{-i[E_2\epsilon(t)+\bar{m}E/m_1]t\}\right\}\times(\mathbf{p}^2+\alpha^2\bar{m}^2/n^2)\phi(\mathbf{p}), \quad (5.4)$$

where

$$E_1^2=\mathbf{p}^2+m_1^2,\quad E_2^2=\mathbf{p}^2+m_2^2,\quad \epsilon(t)=t/|t|.$$

Equation (5.4) is to be compared with the expression for $\chi(\mathbf{p},t)$,

$$\chi(\mathbf{p},t)=[(\gamma_2p_2+m_2)/m_2]\psi(\mathbf{p},t)=\frac{-i}{4\pi m_2\bar{m}}\int\frac{(\mathbf{p}^2+\alpha^2\bar{m}^2)\phi(\mathbf{p})}{(H_1-p_0-\bar{m}E/m_2)}e^{-ip_0t}dp_0=-(4m_2\bar{m}E)^{-1}(H_1+E_1\epsilon(t))e^{-i[E_1\epsilon(t)-m_1]t}\times(\mathbf{p}^2+\alpha^2\bar{m}^2/n^2)\phi(\mathbf{p}). \quad (5.5)$$

Because they contain factors of the Schrödinger function $\phi(\mathbf{p})$, both ψ and χ are relatively small for momenta

[13] The infrared divergence of the renormalized mass operator in electrodynamics is logarithmic and cannot affect the dimensional arguments.

which exceed an inverse Bohr radius. Thus, the inequality $\mathbf{p}^2 \lesssim (\bar{m}\alpha)^2$ may be used in estimating their respective magnitudes. Confining our interest to the leading terms of order (m_1/m_2) and dropping corrections of relative order α^2, we obtain

$$\psi(\mathbf{p},t) \to \psi_0(\mathbf{p},t) = \left(1+\frac{\boldsymbol{\alpha}_1\cdot\mathbf{p}}{2m_1}\right)\left(1-\frac{\boldsymbol{\alpha}_2\cdot\mathbf{p}}{2m_2}\right)\phi(\mathbf{p}), \quad (5.6)$$

and correspondingly,

$$\chi(\mathbf{p},t) \sim \frac{(\mathbf{p}^2+\alpha^2 m_1^2/n^2)}{m_1 m_2}\left(1\pm 1+\frac{\boldsymbol{\alpha}_1\cdot\mathbf{p}}{m_1}\right)\phi(\mathbf{p}).$$

Hence, χ is smaller than ψ by a factor of $\alpha^2(m_1/m_2)$, i.e., the ratio of hydrogen binding energy to proton rest mass, and may be neglected in calculations to this order. The neglect, in (3.10), of the term in J containing M_1 is based on a similar consideration. The dimensional argument shows that $[(\gamma_1 p_1+m_1)/m_1]\psi$ is smaller than ψ by a factor of $m_1\alpha^2/m_1=\alpha^2$ and a third factor of α is supplied by the electrodynamic origin of M_1.

(2) In order to rederive the result of Sec. 2 in the adiabatic limit, we observe that (5.6) already displays the adiabatic wave function to the required accuracy. The essential point is that $\psi_0(\mathbf{p},t)$ is independent of the relative time coordinate t. The portion of the transition operator which contributes to lowest order is given by

$$K^{(1)}(p,p') = ie^2(2\pi)^{-4}[\gamma_{1\mu}\gamma_{2\mu}k^{-2}f'(k^2)+\beta_1\beta_2\mathbf{k}^{-2}f'(\mathbf{k}^2)] - (\mu_A/e_2)e^2(2\pi)^{-4}\gamma_{1\mu}\sigma_{2\mu\nu}k_\nu k^{-2}f''(k^2),$$

where, again, $k=p-p'$. The higher order terms contain, in addition to the magnetic moment correction, recoil effects which disappear in the adiabatic limit. The time integrations in (5.3) introduce delta functions of p_0 and p_0'. Subsequent integration over the latter variables brings $K^{(1)}(p,p')$ into the effective form

$$K^{(1)}(p,p') \to \frac{ie^2}{(2\pi)^2}\frac{\boldsymbol{\gamma}_1\cdot\boldsymbol{\gamma}_2}{\mathbf{k}^2}f'(\mathbf{k}^2) - \left(\frac{\mu_A}{e_2}\right)\frac{e^2}{(2\pi)^2}\frac{\gamma_{1\mu}\sigma_{2\mu i}k_i}{\mathbf{k}^2}f''(\mathbf{k}^2), \quad i=1,2,3. \quad (5.7)$$

which shows how the retardation effects disappear.

The application of (5.6) and (5.7) to (5.3) leads to a hyperfine shift $\Delta E^{(1)}$,

$$\Delta E^{(1)} = -\tfrac{2}{3}(e_1/2m_1)\langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2\rangle\int\phi(\mathbf{p}) \times[(e_2/2m_2)f'(\mathbf{k}^2)+\mu_A f''(\mathbf{k}^2)]\phi(\mathbf{p}')d\mathbf{p}d\mathbf{p}', \quad (5.8)$$

which, apart from the implicit use of the reduced mass rather than the electron mass in $\phi(\mathbf{p})$, is recognized as the representation in moment space of formula (2.3).

(3) The effect of proton structure on the recoil corrections to single photon exchange is easily estimated. The presence of the Schrödinger wave functions permits a crude approximation to the integrand of (5.3) for momenta $\mathbf{p}$, $\mathbf{p}'$ larger than an inverse Bohr radius. Further, the photon propagator insures that the integrand is small unless $\mathbf{k}^2 \approx k_0^2$ But the functions $f'(k^2)$ and $f''(k^2)$ have ranges of the order of magnitude of an inverse proton Compton wavelength. They will not vary appreciably over an interval which is quite small compared to this characteristic size. Since the terms in question are already of order $\alpha(m_1/m_2)\times\ln(m_1/m_2)$ or smaller, we may reasonably put

$$f'(k^2)\approx f'(0)=1,$$
$$f''(k^2)\approx f''(0)=1,$$

when $k^2 \gtrsim (\bar{m}\alpha)^2$. We conclude that the finite proton size has no effect on these corrections.

(4). Finally, we must consider the energy shift $\Delta E^{(2)}$ produced by that portion $K^{(2)}=K_B+K_C$ of the transition operator which describes the double-photon exchange processes. Since this interaction is explicitly second order in α, the adiabatic approximation to ψ suffices, and only the low-momentum parts of $K^{(2)}$ and ψ_0 are important. Therefore

$$\Delta E^{(2)} = -2\pi i\int\psi_0^*(\mathbf{p},t)\beta_1\beta_2 K^{(2)}(0,0)\psi_0(\mathbf{p}',t')d\mathbf{p}d\mathbf{p}' = -i(2\pi)^4|\phi_C(0)|^2\langle K^{(2)}(0,0)\rangle.$$

The angular bracket enclosing $K^{(2)}$ indicates, as before, a spin expectation value. By (3.17), (3.20), and (4.11), we have

$$K^{(2)} = (ie^2\gamma_{1\mu}D\Gamma_{2\mu}-I_0)G_1^{(0)}G_2^{(0)}(ie^2\gamma_{1\mu}D\Gamma_{2\mu}-I_0) - e^4\gamma_{1\mu}D\Gamma_{2\nu}G_1^{(0)}G_2^{(0)}\gamma_{1\nu}D\Gamma_{2\nu} - e^4\gamma_{1\mu}DG_1^{(0)}\gamma_{1\nu}D\Lambda_{2\mu\nu}^{(b)}. \quad (5.9)$$

The last line of (5.9) contributes to $K^{(2)}(0,0)$ a term proportional to

$$\int dq\gamma_{1\mu}D(q^2)G_1^{(0)}(q)\gamma_{1\nu}D(q^2)\Lambda_{2\mu\nu}^{(b)}(0,0,q,-q) = \int dq\frac{\gamma_{1\mu}(m_1+q_0+\boldsymbol{\alpha}_1\cdot\mathbf{q}+\beta_1 m_1)\gamma_{1\nu}\Lambda_{2\mu\nu}^{(b)}(0,0,q,-q)}{[(m_1+q_0)^2-m_1^2-\mathbf{q}^2](\mathbf{q}^2-q_0^2)^2}. \quad (5.10)$$

We wish to argue that (5.10) cannot produce a hyperfine shift. To obtain an energy shift dependent on electron spin, we may take from the numerator of (5.10) either $\gamma_{1\mu}(m_1+q_0+\beta_1 m_1)\gamma_{1\nu}$ with μ and ν both spatial indices or $\gamma_{1\mu}(\boldsymbol{\alpha}_1\cdot\mathbf{q})\gamma_{1\nu}$ with one index spatial, the other temporal. The latter expression is an odd function of $\mathbf{q}$, while the former is even.

As we observed in the previous section,

$$\Lambda_{\mu\nu}^{(b)}(0,0,q,-q)$$

is derived from terms in the inverse proton propagator whose spin dependence is either unity, γ_5, or $\gamma_5\gamma_\lambda$. Only the last alternative, with λ a spatial index, can lead to a hyperfine shift. When the relevant part of $\Lambda_{\mu\nu}{}^{(b)}$ has been computed by functional differentiation, the spin vector will either appear contracted with q or bear one of the free indices μ, ν. The remaining one or two free indices will be carried by occurrences of q. In either case, the dependence of the expression on the vector $\mathbf{q}$ will be odd if μ and ν are both spatial, and even if only one is spatial. Thus, all spin-spin interactions in (5.10) have an odd $\mathbf{q}$ dependence in the numerator. Since the denominator is an even function of $\mathbf{q}$, the integral vanishes.

The double-photon terms in the first two lines of (5.9) were computed by both Arnowitt and Newcomb using the low-frequency approximation (4.13) to the proton vertex operator. The procedure is justified by the presence of the propagation functions for the photon and the electron in the relevant integrals. The contributing frequencies are then quite small compared to the ranges of the proton form factors. The argument breaks down for the term in which photons interact twice with the anomalous moment part of Γ_2, for the two additional factors of frequency lead to a logarithmic divergence. However, the magnitude of this already small term is satisfactorily estimated by using a frequency cutoff. A precise determination, using an assumed relativistic form factor, is possible, but would noticeably increase the labor of computation.

6. ELECTROMAGNETIC SIZE OF THE PROTON

The doublet separation $\Delta\nu_{\mathrm{H}}$ of the hydrogen ground state, including all calculated corrections, is expressed in units of frequency by

$$\Delta\nu_{\mathrm{H}}=(16/3)\alpha^2cR_\infty(\mu_2/\mu_1)(\mu_1/\mu_1{}^{(0)})^2(1+m_1/m_2)^{-3}\times[1+\tfrac{3}{2}\alpha^2-2a_0{}^{-1}\langle r\rangle_{em}+\mathcal{E}+\mathfrak{R}]$$

where $\mu_1{}^{(0)}$ represents the Bohr magneton, $(1+m_1/m_2)^{-3}$ is the reduced-mass correction to the square of the Coulomb wave function at the origin, and $\frac{3}{2}\alpha^2$ is the Breit correction. The contributions $\mathcal{E}$, due to the distributed character of electrodynamic effects, and $\mathfrak{R}$, due to proton recoil, are given by

$$\mathcal{E}=-\alpha^2(5/2-\ln 2),$$

$$\mathfrak{R}=-(\alpha m_1/\pi m_2\mu_2')\{[3-\tfrac{3}{4}(\mu_2'-1)^2]\ln(m_2/m_1)-\tfrac{1}{8}(\mu_2'-1)^2\}-(9\alpha m_1/4\pi m_2\mu_2')(\mu_2'-1)^2\ln(2\bar{k}/m_2),$$

where μ_2' is the total proton moment in nuclear magnetons, and $\bar{k}$ is the frequency cutoff.

Inserting the experimental values of $\Delta\nu_{\mathrm{H}}$[14] and of the ratio[15] (μ_2/μ_1), and all other constants from the most recent DuMond review article,[16] we obtain

$$-2a_0{}^{-1}\langle r\rangle_{em}-3.26\times10^{-6}\ln(2\bar{k}/m_2)=(3.8\pm20)\times10^{-6}. \quad (6.1)$$

The uncertainty in (6.1) is based on the "limit of error" quoted for the fine structure measurement[17] which determines the value of α^2cR_∞, rather than the less conservative "standard error" used by DuMond and Cohen. The stated error masks the inaccuracy in the treatment of the cut-off term and places an upper bound[18] on the magnitude of $\langle r\rangle_{em}$:

$$\langle r\rangle_{em}\leq 2.5(\hbar/m_2c)=0.5\times10^{-13}\text{ cm}. \quad (6.2)$$

Comparison with the electron-proton scattering results of Hofstadter and McAllister[19] is facilitated by the observation that

$$\int r^2f_{em}(\mathbf{r})d\mathbf{r}=\int f_e(\mathbf{r})(\mathbf{r}-\mathbf{s})^2f_m(\mathbf{s})d\mathbf{r}d\mathbf{s}=\int r^2f_e(\mathbf{r})d\mathbf{r}+\int r^2f_m(\mathbf{r})d\mathbf{r},$$

i.e., the second moment $\langle r^2\rangle_{em}$ with respect to $f_{em}(\mathbf{r})$ is the sum of the second moments with respect to the electric and magnetic distributions. Then the scattering experiment yields for the rms electromagnetic size,

$$\langle r^2\rangle_{em}{}^{\frac{1}{2}}=(1.0\pm0.3)\times10^{-13}\text{ cm}. \quad (6.3)$$

Although first moments are in general smaller than rms sizes, there does not appear to be complete consistency between (6.2) and (6.3). One must bear in mind that electromagnetic corrections to $\Delta\nu_{\mathrm{H}}$ of relative order $\alpha^3\ln\alpha$ have not been computed, but almost certainly are present. Their inclusion may improve the agreement between proton size predictions derived from the two different methods. A theoretical verification of the hyperfine shift must, in any case, await the calculation of $\alpha^3\ln\alpha$ terms and an improved experimental determination of α. A recalculation of the cutoff term and the other recoil corrections to two photon exchange, using form factors inferred, perhaps, from electron-proton scattering, is also necessary if accuracy to better than a few parts in a million is desired.

These considerations do not weaken the principal result of this paper. The effect of proton structure upon the hyperfine shifts of s states in hydrogen is now understood and evaluated.

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APPENDIX

We develop here the general expression for the renormalized proton propagator, through terms linear in the electromagnetic field, which proved useful in the text. It represents the maximum amount of information deducible solely from the requirements that the propagator describe a Dirac particle and be invariant under Lorentz transformations, gauge transformations, and charge conjugation.

To satisfy Lorentz invariance, it is sufficient to construct terms of $G(A)$ by multiplication and contraction of tensors of well-defined transformation properties, namely, the tensor density $\epsilon^{\lambda\eta\mu\nu}$, the spin matrices γ_μ, $\sigma_{\mu\nu}$, γ_5, $\gamma_5\gamma_\mu$, the momentum operator p_μ, and the electromagnetic potential A_μ and its derivatives. Since the enumerated spin matrices, together with the unit matrix, span the spin space, only one of them need appear in any given term. Consideration of the inhomogeneous Lorentz transformations, i.e., the space-time translations, precludes the appearance of the coordinate operator x_μ, save as an argument of the field.

The gauge requirement is obeyed by replacing p_μ with $p_\mu - eA_\mu$ and restricting further field dependence to terms containing the field strength $F_{\mu\nu}$.

In connection with the third invariance requirement, we recall that the charge conjugate of a product is the transposed product of the conjugates of the factors, and that p_μ, γ_μ, $\sigma_{\mu\nu}$, A_μ, and $F_{\mu\nu}$ reverse sign under charge conjugation while the remaining operators listed above are invariant.

We begin by attempting to write $G^{-1}(A)$ in the form

$$\begin{aligned} G^{-1}(A)=&\gamma(p-eA)+m+O(F)\\ &+[\gamma(p-eA)+m]R_1[\gamma(p-eA)+m]\\ &+(\gamma p+m)R_2(F)+R_3(F)(\gamma p+m), \end{aligned} \tag{A.1}$$

where R_1, R_2, and R_3 are as described in the text. No terms quadratic or higher in the field are considered here. We seek a canonical expression for $O(F)$ such that its member terms cannot be rearranged or reduced to other terms in $O(F)$ or to terms in the categories specified in the last two lines of (A.1).

The only charge-invariant forms containing $\epsilon^{\lambda\eta\mu\nu}$ are of the type

$$\Omega=\epsilon^{\lambda\eta\mu\nu}\gamma_5\gamma_\lambda(p_\eta F_{\mu\nu}+F_{\mu\nu}p_\eta). \tag{A.2}$$

All others are quickly seen to vanish in virtue of the anti-symmetry of $\epsilon^{\lambda\eta\mu\nu}$. Note that γ_5 and $\epsilon^{\lambda\eta\mu\nu}$ must appear together to maintain invariance under spatial reflection. With the aid of the identities[20]

$$\begin{aligned} \epsilon^{\lambda\eta\mu\nu}\gamma_5\gamma_\lambda&=-i\gamma_\eta\sigma_{\mu\nu}+\gamma_\mu\delta_{\eta\nu}-\gamma_\nu\delta_{\eta\mu}\\ &=-i\sigma_{\mu\nu}\gamma_\eta-\gamma_\mu\delta_{\eta\nu}+\gamma_\nu\delta_{\eta\mu}, \end{aligned}$$

(A.2) can be transformed into

$$\Omega=-i(\gamma p+m)\sigma F-i\sigma F(\gamma p+m)+2mi\sigma F+i\gamma_\nu\partial_\mu F_{\mu\nu}$$

which shows that in constructing $O(F)$, no additional generality results from the use of the tensor density. The same remark immediately applies to γ_5 and $\gamma_5\gamma_\mu$.

We may also dispense with explicit use of the momentum operator. Thus, occurrences of p^2 and γp are brought to the extreme right or left and transformed into multiples of $(\gamma p+m)$. A term containing $p_\lambda(-i\partial_\lambda)\times F_{\mu\nu}$ is reduced to previous cases via the relation

$$p_\lambda(i\partial_\lambda)F_{\mu\nu}=-\tfrac{1}{2}\Box^2F_{\mu\nu}+\tfrac{1}{2}(p^2F_{\mu\nu}-F_{\mu\nu}p^2).$$

Also, in the charge-symmetrized expressions

$$\begin{aligned} &\gamma_\nu p_\mu F_{\mu\nu}-\gamma_\nu F_{\mu\nu}p_\nu,\\ &i\partial_\lambda\sigma_{\lambda\nu}p_\mu F_{\mu\nu}-i\partial_\lambda\sigma_{\lambda\nu}F_{\mu\nu}p_\mu, \end{aligned}$$

the factors of p are immediately removed in favor of derivatives of the field strengths.

Contexts for the spin matrices are further restricted by the relations

$$\begin{aligned} \partial_\mu\partial_\lambda\sigma_{\nu\lambda}F_{\mu\nu}&=\tfrac{1}{2}\Box^2\sigma_{\mu\nu}F_{\mu\nu},\\ \partial_\nu\gamma_\mu F_{\mu\nu}&=-\Box^2\gamma_\mu A_\mu. \end{aligned}$$

The last equation presupposes a Lorentz gauge.

In view of all the foregoing, the operator $\bar{G}^{-1}$ defined by

$$\bar{G}^{-1}=\gamma(p-eA)+m+O(F)$$

can be expressed in complete generality as

$$\bar{G}^{-1}=\gamma p+m-g'(-\Box^2)\gamma_\mu A_\mu-g''(-\Box^2)\sigma_{\mu\nu}F_{\mu\nu},$$

where $g'(-\Box^2)$ and $g''(-\Box^2)$ are arbitrary functions of the D'Alembertian. Equation (A.1) can then be rewritten

$$G^{-1}(A)=\bar{G}^{-1}+\bar{G}^{-1}R_1\bar{G}^{-1}+\bar{G}^{-1}R_2(F)+R_3(F)\bar{G}^{-1},$$

correct to first order in the field, by a suitable alteration of $R_2(F)$ and $R_3(F)$.

The introduction of the normalized form factors $f'(-\Box^2)$ and $f''(-\Box^2)$,

$$\begin{aligned} g'(-\Box^2)&=ef'(-\Box^2),\quad f'(0)=1,\\ g''(-\Box^2)&=\tfrac{1}{2}\mu_A f''(-\Box^2),\quad f''(0)=1, \end{aligned}$$

completes the derivation of (4.6) and (4.7).

[20] Our spin matrices satisfy $\gamma_\mu\gamma_\nu+\gamma_\nu\gamma_\mu=-2\delta_{\nu\mu}$, $\sigma_{\mu\nu}=\frac{1}{2}i(\gamma_\mu\gamma_\nu-\gamma_\nu\gamma_\mu)$, $\gamma_5=\gamma_1\gamma_2\gamma_3\gamma_4$.