Effective Potential Model for Calculating Nuclear Corrections to the Energy Levels of Hydrogen*

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The present work is an attempt to re-evaluate the nuclear corrections to the energy levels of hydrogen by using an effective potential approach. The basic idea is to infer from electron–proton scattering a potential which may then be applied to the bound-state problem. In lowest order, the potential is chosen from the first-order Feynman diagram for the scattering. With this choice the Breit equation is obtained. It is then solved in an approximate way, in the nonrelativistic limit of the proton, to obtain wave functions which are accurate enough for use in evaluating the effects of perturbations of the potential. The reduced mass corrections to the fine structure and the hyperfine structure levels are readily found. The effect on the hyperfine splitting of the distribution of the proton charge and magnetic moment is obtained by correcting the lowest-order potential to include the proton form factors. A further modification is needed in evaluating additional recoil corrections, of relative order $\alpha m/M$, to the fs and the hfs. This additional term accounts for the failure of the iteration of the lowest-order potential to reproduce the scattering obtained from the second-order Feynman diagrams. The $\alpha^2 m/M$ contribution to the state-dependent mass corrections to the hfs is also analyzed within the context of this approach. All the corrections found are in complete agreement with previous results obtained by the Bethe–Salpeter (BS) equation, but the present method has the virtue of conceptual simplicity.

CONTENTS

I. INTRODUCTION

During the past few years, discrepancies between theory and experiment on the hyperfine splitting (hfs)[1,2] and the Lamb shift[3–6] of atomic hydrogen have led to renewed interest in the nuclear corrections to the energy levels.

Previous calculations of nuclear corrections have been carried out mainly within the framework of a completely relativistic formalism such as that provided by the Bethe–Salpeter (BS) equation.[7,8] Although the need for a rigorous covariant formulation of the two-body problem is clear, it is equally clear that the BS approach is extremely complicated. Therefore, it seemed worthwhile to recalculate the corrections by using a straightforward semirelativistic approach rather than the more formal methods of the BS equation.

A re-evaluation of the nuclear corrections serves two useful purposes. First, it provides a substantial check of previous work. This is particularly important in the case of the hfs of hydrogen, where a discrepancy of 45 ppm[9] (parts per million) has provided a serious challenge to theorists for some time.[10] Second, it attempts to present a self-contained unified treatment in a single article. A systematic, simple presentation of these corrections is not currently available in the literature.

Our approach is basically an "effective potential model," in which the system is described by a modified Dirac equation with a potential inferred from scattering theory. It should be stressed at the start that this work should be understood as a model rather than a rigorous development from first principles.

In Sec. II the lowest-order potential is handled. Most of the contents of this section are a repetition of previous work recently published by us.[11] In Sec. III we present a treatment of the nuclear corrections to the hyperfine splitting of hydrogen within the context of the effective potential approach. The results are in agreement with those obtained by fully covariant techniques. Section IV contains an evaluation of the recoil corrections to the fine structure of hydrogen; confirmation of previous results is obtained. Finally, in Sec. V we discuss the recent status of the nuclear corrections and the latest situation with regard to the discrepancies previously mentioned.

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II. EFFECTIVE POTENTIAL MODEL

A. Method

In relativistic physics the problem of defining a meaningful Schrödinger-type equation for two interacting particles is a nontrivial matter. In fact, a realistic analog of the Dirac equation to describe the two-body problem does not exist. One usually resorts to a covariant field-theoretic description of the system in order to provide a rigorous foundation.

Our approach is an attempt to use a Schrödinger-type equation in which the potential is inferred from scattering theory. Logunov and Tavkhelidze[12] have done some work along similar lines. In addition, a paper by Faustov[13] on the hyperfine splitting of hydrogen treats the problem in a similar way.

Let us assume, at first, that the electron–proton scattering may be approximately predicted by using a local potential $V(\mathbf{x}_e-\mathbf{x}_p)$ which "effectively" replaces the interactions between the particles via the quantized radiation field. We use as a starting point the equation*

$$[E-H(\mathbf{x}_e)-H_p(\mathbf{x}_p)]\psi(\mathbf{x}_e,\mathbf{x}_p) = V(\mathbf{x}_e-\mathbf{x}_p)\psi(\mathbf{x}_e,\mathbf{x}_p). \quad (2.1)$$

Using the Lippmann–Schwinger equations,[14] one may obtain the scattering predicted by Eq. (2.1). The S matrix becomes $(f\neq i)$

$$-2\pi i\delta(E_1+E_2-E_3-E_4)\langle\phi_f\,|\,V\,|\,\psi_i^+\rangle, \quad (2.2)$$

where E_1 and E_2 are the incoming energies of the electron and proton, respectively, and E_3 and E_4 are the corresponding outgoing energies. An eigenstate of the free Hamiltonian representing an outgoing state is given by $\langle\phi_f\,|$, whereas $|\,\psi_i^+\rangle$ is an eigenstate of the full Hamiltonian having incoming plane waves $|\,\phi_i\rangle$ and outgoing scattered waves. We have

$$|\,\phi_i\rangle+[1/(E_i-H_{\text{free}}+i0)]V\,|\,\psi_i^+\rangle, \quad (2.3)$$

where the $+i0$ indicates that the denominator has a very small positive imaginary part. In the first Born approximation, the scattering amplitude in momentum space is

$$-(2\pi)^4 i\delta_4(p_1+p_2-p_3-p_4) \times (m^2M^2/E_1E_2E_3E_4)^{1/2}u^\dagger(p_3,s_3)u_p^\dagger(p_4,s_4) \times V(\mathbf{p}_1-\mathbf{p}_3)u(p_1,s_1)u_p(p_2,s_2), \quad (2.4)$$

where $u(p_i,s_i)$ is the Dirac spinor for a particle of momentum p_i and spin projection s_i, and δ_4 is a four-dimensional δ function for energy and momentum conservation. This may now be compared to the lowest-order amplitude, given in Fig. 1(a), for the relativistic scattering in the center-of-mass system of an electron and a proton. The amplitude is*

$$ie^2(2\pi)^4\delta_4(p_1+p_2-p_3-p_4) \times (m^2M^2/E_1E_2E_3E_4)^{1/2}u^\dagger(p_3,s_3)u_p^\dagger(p_4,s_4) \times [1/(\mathbf{p}_1-\mathbf{p}_3)^2](1-\boldsymbol{\alpha}_\perp\cdot\boldsymbol{\alpha}_p)u(p_1,s_1)u_p(p_2,s_2). \quad (2.5)$$

A comparison of (2.4) and (2.5) indicates that the lowest-order potential may be defined as

$$V(\mathbf{p}_1-\mathbf{p}_3)\equiv-[e^2/(\mathbf{p}_1-\mathbf{p}_3)^2](1-\boldsymbol{\alpha}_\perp\cdot\boldsymbol{\alpha}_p). \quad (2.6)$$

The potential of (2.6) is the sum of the Coulomb and Breit potentials. With the use of (2.6) as the potential, Eq. (2.1) is known as the Breit equation.[15]

There are a number of corrections to (2.6) which must be made to obtain a more realistic potential. First of all, the proton is not a point Dirac particle like the electron, and therefore its finite size must be accounted for. Second, the anomalous magnetic moment of the proton, which is presumably due to its pion cloud, makes it necessary to include a Pauli interaction. Third, the potential in (2.6) was chosen from the scattering amplitude on the energy shell. Although there is no unique way of describing the departure from the energy shell, we will find it convenient to choose the off-the-energy-shell behavior in such a way as to minimize the importance of further corrections to the potential. This brings us to the fourth correction, one which is chosen so as to rectify the failure of the iteration of the lowest-order potential to match the two-photon exchange. All these corrections will be discussed in detail in due course.

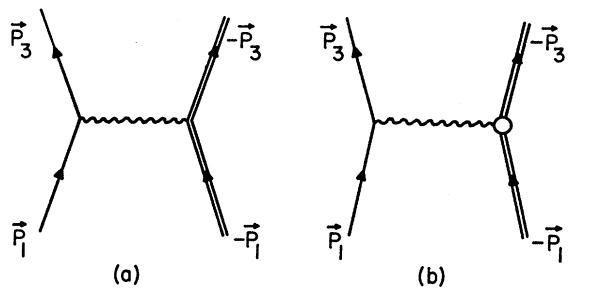

FIG. 1. One-photon-exchange amplitude for e–p scattering. (a) Point proton. (b) Finite-size proton with an anomalous moment.

B. Lowest Order and the Modified Dirac Equation

The fine structure and the hyperfine structure are relativistic corrections to the atomic binding, and therefore the electron should be treated as a relativistic particle. However, the nuclear corrections in

* Variables referring to the proton will usually contain a subscript p, whereas variables which involve the electron will either have a subscript e or no subscript at all. The free Hamiltonian for the electron is $\boldsymbol{\alpha}\cdot\mathbf{p}_e+\beta m$, whereas for the proton it is $\boldsymbol{\alpha}_p\cdot\mathbf{p}_p+\beta M$.

* We are using the Coulomb gauge. Therefore many vectors will be transverse to the photon's momentum. The symbol $\perp$ is used to denote transversality. For example, in (2.5) $\boldsymbol{\alpha}_\perp=\boldsymbol{\alpha}-(\boldsymbol{\alpha}\cdot\mathbf{k}\mathbf{k})/\mathbf{k}^2$, with $\mathbf{k}=\mathbf{p}_1-\mathbf{p}_3$.

lowest order may be obtained by treating the proton nonrelativistically, since the characteristic momenta involved are much smaller than the proton mass. Therefore, instead of using Eq. (2.1) as a starting point, we will use the nonrelativistic reduction of (2.1) for the proton variables.

In the center-of-mass system, the free Hamiltonian is

$$H_{\text{free}}=\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m+(\mathbf{p}^2/2M). \tag{2.7}$$

If the interaction between the electron and the proton is expressed by Eq. (2.6), the evaluation of this potential to order M^{-1} between free proton spinors gives

$$V_{\text{eff}}^{(2)}+\Delta V_{\text{eff}}^{(2)}=-\frac{e^2}{\mathbf{q}^2}\left[1+\boldsymbol{\alpha}_\perp\cdot\left(\frac{\mathbf{p}_1+\mathbf{p}_3}{2M}\right)\right]-\frac{i}{2M}\frac{e^2}{\mathbf{q}^2}\boldsymbol{\alpha}\cdot(\mathbf{q}\times\boldsymbol{\delta}_p), \tag{2.8}$$

where $\mathbf{q}$ stands for the momentum transfer $(\mathbf{p}_1-\mathbf{p}_3)$ from the electron to the proton; $\boldsymbol{\delta}_p$ is the (2×2) Pauli spinor of the proton. For the time being, we will use (2.8) as the lowest-order potential; corrections will be added later in order that the potential correspond to Fig. 1(b) rather than Fig. 1(a).

Equation (2.8) is the momentum-space representation of the potential which will be used in a modified Dirac equation to describe a wave function which depends on the relative coordinate of the electron and proton. This wave function is a four-component spinor for the electron and a two-component constant spinor for the proton.

It should be recognized that on the energy shell, the scattering amplitude is not changed by replacing $\boldsymbol{\alpha}_\perp$ in (2.8) by $\boldsymbol{\alpha}$; the difference vanishes in the center-of-mass frame. This illustrates a general ambiguity inherent in the effective potential approach; one may add to the effective potential terms whose matrix elements vanish for real scattering. Such terms will not vanish in higher order nor will they vanish for bound states. This ambiguity suggests that the selection of the potential should be made in such a way as to minimize the importance of corrections to the potential. In other words, our choice should be governed by a desire to obtain as much as possible of the scattering from the initial choice of the potential. The use of $\boldsymbol{\alpha}_\perp$ rather than $\boldsymbol{\alpha}$ seems to be an optimum one from this point of view. Furthermore, it is not difficult to show that had we omitted the transversality condition, the usual Dirac degeneracy in hydrogen would be split by an amount of order (m/M) fs rather than $(\alpha m/M)$ fs. This would have to be corrected later.

The proton spin-dependent part of the potential $(\Delta V_{\text{eff}}^{(2)})$ of (2.8) will at first be discarded; it will be handled later by perturbation theory. In position space the potential $V_{\text{eff}}^{(2)}$ is readily found to be

$$V+\{\boldsymbol{\alpha}\cdot\mathbf{p}/2M,\,V\}+(1/4M)[\boldsymbol{\alpha}\cdot\mathbf{p},[\mathbf{p}^2,W]], \tag{2.9}$$

where $V=-\alpha/r$ and $W=-\alpha r$.

Using the free Hamiltonian of (2.7) and the effective potential of (2.9) we arrive at a modified Dirac equation

$$\left(\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m+\frac{\mathbf{p}^2}{2M}+V+\left\{\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{2M},V\right\}+(4M)^{-1}[\boldsymbol{\alpha}\cdot\mathbf{p},[\mathbf{p}^2,W]]\right)\psi(\mathbf{r})=E\psi(\mathbf{r}). \tag{2.10}$$

Note that in the limit $M\to\infty$, this reduces to the ordinary Dirac equation with a Coulomb potential. The corresponding BS equation does not have this property since a positive energy projection operator occurs to the left of V; this difference is of course compensated by higher terms in the BS equation.

C. Solutions of the Modified Dirac Equation

We notice that some of the terms appearing in Eq. (2.10) are contained in the square of $\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m+V$. For example, the square would have a $\mathbf{p}^2$ and an $\{\boldsymbol{\alpha}\cdot\mathbf{p},V\}$; these terms appear in (2.10) but divided by $2M$. This suggests a rearrangement of (2.10) in terms of a simpler Hamiltonian whose solutions may readily be found.

The rearrangement is governed *a posteriori* by our desire to obtain the exact reduced mass correction to the nonrelativistic binding. For relativistic corrections to the energy it suffices to obtain mass corrections in terms of a power series in m/M; actually only one power is usually needed.

We find that the Hamiltonian may be rewritten as

$$H=H_1+\frac{H_1^2-m^2}{2M}+(4M)^{-1}[H_1,[\mathbf{p}^2,W]]+\frac{m}{2(M^2-m^2)}\left\{\boldsymbol{\alpha}\cdot\mathbf{p},V\beta\left(1-\beta\frac{m}{M}\right)\right\}+\frac{m\beta V^2}{2M^2}\frac{[1-\beta(m/M)]^2}{[1-(m^2/M^2)]^2}, \tag{2.11}$$

where

$$H_1=\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m+V\left(\frac{1-\beta(m/M)}{1-(m^2/M^2)}\right). \tag{2.12}$$

In obtaining (2.11) we have made use of the following identities:

$$\{\boldsymbol{\alpha},\boldsymbol{\beta}\}=0;\quad \mathbf{p}^2/2M=(1/2M)(\boldsymbol{\alpha}\cdot\mathbf{p})^2;$$
$$(1/2M)(V^2+\tfrac{1}{2}[V,[\mathbf{p}^2,W]])=0.$$

The term involving W in the last relation arises from the difference between $\boldsymbol{\alpha}_\perp$ and $\boldsymbol{\alpha}$ in (2.6); if it were not there, the Dirac degeneracy in hydrogen would be removed to order (m/M) fs.

At this point, H may be approximated by

$$H_1+[(H_1^2-m^2)/2M]+(1/4M)[H_1,[\mathbf{p}^2,W]]. \quad (2.13)$$

The error in the energy introduced by this approximation is negligible $\{\mathbf{O}[(m/M)^2\alpha^4]\}$, and the error in the wave function is also too small to be of any consequence.

If the solutions of $H_1\psi_1=E_1\psi_1$ can be determined, then the solutions of $H\psi=E\psi$ are easily seen to be approximately

$$\psi=N\{1-(1/4M)[\mathbf{p}^2,W]\}\psi_1, \quad (2.14)$$

where N is a normalization constant. The wave function ψ is correct to order M^{-1} in the relativistic corrections to it.

For ψ_1 we have the equation

$$\left[\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m+V\left(\frac{1-\beta(m/M)}{1-(m^2/M^2)}\right)\right]\psi_1=E_1\psi_1. \quad (2.15)$$

Let $\psi_1=(1+\beta\lambda)\psi_0$, where λ is a constant to be chosen in such a way that the equation for ψ_0 will not contain a term βV. Substituting ψ_1 into Eq. (2.15), multiplying on the left by $1+\beta\lambda$, and dividing by $1-\lambda^2$, we obtain, with $\lambda=(M/m)\{1-[1-(m/M)^2]^{1/2}\}$,

$$\left[\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m\left(\frac{1-(E_1/M)}{[1-(m^2/M^2)]^{1/2}}\right)+\frac{V}{[1-(m^2/M^2)]^{1/2}}\right]\psi_0 = \frac{E_1[1-(m^2/E_1M)]}{[1-(m^2/M^2)]^{1/2}}\psi_0. \quad (2.16)$$

The above equation is a Dirac equation for a particle of mass

$$m'\equiv m\left[\frac{1-(E_1/M)}{[1-(m^2/M^2)]^{1/2}}\right]$$

in the field of a Coulomb potential

$$-\frac{\alpha'}{r}\equiv-\frac{\alpha}{r}\frac{1}{[1-(m^2/M^2)]^{1/2}}.$$

Since $E_1=m+\mathbf{O}(m\alpha^2)$, we find that

$$m'\approx m\left(\frac{1-(m/M)}{1+(m/M)}\right)^{1/2}.$$

Using this value of m' in Eq. (2.16) we obtain an equation whose solutions are well-known Dirac wave functions $\psi_{0nl,jm}(m'\alpha'\mathbf{r},\alpha')$.[16] Furthermore, with the approximate value of m', we have

$$m'\alpha'=\frac{m\alpha}{1+(m/M)}=m_{\text{red}}\alpha.$$

If the wave function ψ_0 is normalized to unity, the normalization condition on ψ leads to a value of N equal to $(1+\lambda)^{-1}$ with an error of order $(m/M)\alpha^2$. The contribution to ψ from the term $(1/4M)[\mathbf{p}^2,W]\psi_1$ [see (2.14)] is ignored since it is roughly $\mathbf{O}[(m/M)\alpha^2]\psi_1$ for values of r near the Bohr radius. It should be pointed out that this term, if retained, would lead to a logarithmic divergence in the hyperfine splitting. If structure is included, as it must be, this contribution is finite and is not important.

Therefore, to the desired accuracy, the solution of Eq. (2.10) is

$$\psi=[(1+\beta\lambda)/(1+\lambda)]\psi_0,$$

where ψ_0 is the Dirac wave function for an electron of mass m' acted upon by a Coulomb potential whose strength is determined by α'.

D. Some Corrections to the Potential of Eq. (2.8)

As previously mentioned, the potential of Eq. (2.8) was selected on the basis of Fig. 1(a). However, the scattering is determined from Fig. 1(b), which includes the proton form factor and the anomalous moment, rather than from Fig. 1(a). Therefore Eq. (2.8) must be corrected.

The proton vertex (γ_μ) is replaced by

$$\Gamma_\mu=F_1(-q^2)\gamma_\mu+F_2(-q^2)(i\mu/2M)\sigma_{\mu\nu}q^\nu, \quad (2.17)$$

where F_1 and F_2 are the Dirac and Pauli form factors, and μ is the anomalous moment of the proton; and $\sigma_{\mu\nu}\equiv\frac{1}{2}i[\gamma_\mu,\gamma_\nu]$. The form factors F_1 and F_2 are related to the experimentally determined electric and magnetic form factors G_E and G_M.* In the region of momentum transfer of interest to us ($|q^2|\ll 4M^2$), F_1 and F_2 are approximately equal to G_E, where[17]

$$G_E(-q^2)=[\Lambda^2/(\Lambda^2-q^2)]^2, \quad \Lambda=0.91\,M.$$

Therefore, we replace Eq. (2.6) by $V^{(s)}(\mathbf{p}_1-\mathbf{p}_3)$, where

$$V^{(s)}(\mathbf{p}_1-\mathbf{p}_3)\equiv-(e^2/\mathbf{q}^2)(\gamma_0\Gamma_0) +(e^2/\mathbf{q}^2)\,\boldsymbol{\alpha}_\perp\cdot(\gamma_0\boldsymbol{\Gamma}). \quad (2.18)$$

Here Γ_0 and $\boldsymbol{\Gamma}$ are, respectively, the time and spatial parts of Γ_μ. For simplicity, we will call G_E above F. If (2.18) is evaluated between free proton spinors to order M^{-1}, we obtain the replacement for (2.8),

$$V_{\text{eff}}^{(s)(2)}+\Delta V_{\text{eff}}^{(s)(2)} =-\frac{e^2}{\mathbf{q}^2}F(\mathbf{q}^2)-\frac{e^2}{\mathbf{q}^2}\boldsymbol{\alpha}_\perp\cdot\left(\frac{\mathbf{p}_1+\mathbf{p}_3}{2M}\right)F(\mathbf{q}^2) -\frac{e^2}{\mathbf{q}^2}\frac{i}{2M}(1+\mu)\,\boldsymbol{\alpha}\cdot(\mathbf{q}\times\boldsymbol{\delta}_p)F(\mathbf{q}^2). \quad (2.19)$$

In obtaining (2.19) from (2.18) we have rejected all terms explicitly containing more than one inverse power of the proton mass. It may be shown that such terms do not contribute to the desired order of $(\alpha m/M)$ hfs and $(\alpha m/M)$ fs.

Equation (2.19) does not contain contributions from q_0 different from zero since we have assumed

* $G_E=F_1-(q^2/4M^2)\mu F_2$, $G_M=F_1+\mu F_2$.

thus far that off-the-energy-shell effects can be ignored. However, in the next section we will correct (2.19) by including some dependence off the energy shell. This correction will be chosen so as to minimize further corrections which arise from the failure of the iteration to match the two-photon exchange amplitude.

III. THE HYPERFINE STRUCTURE OF HYDROGEN

The hyperfine splitting of the ground state of hydrogen has been measured by Crampton, Kleppner, and Ramsey[2] to be

$$\nu_{\text{exptl}}=1420.405751800\pm 28\times 10^{-9}\ \text{MHz}$$

by constructing a hydrogen maser which operates between the levels of interest. Theorists can hardly hope to compete with the precision of the above results, but they have, over the years, refined the calculations so that the level of uncertainty of the known contributions is believed to be only a few parts per million relative to the Fermi splitting. Unfortunately, there are additional contributions from the internal dynamics of the proton which have not yet been reliably calculated; it would be surprising if these contributions turned out to be more than 10 ppm.

The theoretical splitting between the triplet and singlet states of the ground state of hydrogen is conveniently written in the form

$$\begin{aligned}\nu_{\text{theoret}}=&\frac{16}{3}Ry\,c\left(\frac{\mu_p}{\mu_e}\right)\left(\frac{\mu_e}{\mu_0}\right)^2\left(\frac{M}{m+M}\right)^3\\&\times\alpha^2\{1+\tfrac{3}{2}\alpha^2-\alpha^2(\tfrac{5}{2}-\ln 2)\\&+\frac{\alpha^3}{\pi}(a_0\ln^2\alpha+a_1\ln\alpha+a_2)-c_0 m\alpha R_{\text{pr}}\\&-c_1\left(\frac{m\alpha}{M}\right)-\frac{m\alpha}{M}X_{\text{pol}}\}.\end{aligned}\tag{3.1}$$

The constants factored outside the braces ({ }) are arranged in such a way as to make optimum use of the best-known fundamental constants. The first two terms in braces contain the Fermi splitting[18] and the Breit relativistic correction[19] as well as the reduced mass correction to the hfs. The additional corrections of order α^2 and α^3 are those residual radiative corrections which do not alter the magnetic moment of the electron. The coefficient $\frac{5}{2}-\ln 2$ was evaluated by Kroll and Pollock[20] and by Karplus, Klein, and Schwinger.[21] The quantities a_0 and a_1 were obtained by Layzer[22] and by Zwanziger[23] and were also verified in a recent article by Brodsky and Erickson[24] on radiative level shifts. In the latter article the authors also estimate the value of a_2.

The last three terms of Eq. (3.1) represent nuclear corrections. The calculation of these terms [we refer to them as the nonrelativistic (NR) size correction which depends on the electromagnetic radius of the proton (R_{pr}), the recoil correction given by c_1, and the proton polarization correction given by X_{pol}] requires specific knowledge of proton form factors and dynamical structure. The NR size term was derived by Zemach,[25] whereas the recoil plus size correction (not separated into two contributions) was first obtained by Iddings and Platzman.[1] It is the proton polarization correction which has only been estimated with various models.

In this section we will rederive (3.1) except for the radiative corrections. We divide the section into four parts:

A. Hyperfine splitting and reduced mass corrections;
B. Nonrelativistic size contribution;
C. Additional recoil terms;
D. Discussion.

A. Hyperfine Splitting and Reduced Mass Corrections

The interaction $V_{\text{eff}}^{(2)}$ [Eq. (2.8)] was previously put aside in Sec. II. B. This part of the potential gives rise to the hyperfine splitting, which we now proceed to calculate by first-order perturbation theory.

If we include the anomalous magnetic moment of the proton, then in the momentum representation the perturbing potential is given by

$$\Delta V_{\text{eff}}^{(2)}=-(i/2M)\mu_p[e^2/(\mathbf{p}_1-\mathbf{p}_3)^2]\,\boldsymbol{\alpha}\cdot[(\mathbf{p}_1-\mathbf{p}_3)\times\boldsymbol{\delta}_p].\tag{3.2}$$

In position space it may be written as

$$\Delta V_{\text{eff}}^{(2)}=(i/2M)\mu_p[\boldsymbol{\alpha}\times\mathbf{p},\,\alpha/r]\cdot\boldsymbol{\delta}_p.\tag{3.3}$$

For the first part of the calculation, it will be convenient to work in position space where the wave function is approximately given by

$$\psi(\mathbf{r})=[(1+\beta\lambda)/(1+\lambda)]\psi_0(\mathbf{r}).\tag{3.4}$$

Using (3.4) and the value of λ given above, we find that the large and small components of the wave function are, respectively,

$$\psi_L(\mathbf{r})=\psi_{0L}(\mathbf{r})\ \text{ and }\ \psi_S(\mathbf{r})=\left(\frac{1-(m/M)}{1+(m/M)}\right)^{1/2}\psi_{0S}(\mathbf{r}).\tag{3.5}$$

Since the interaction couples the large and small components of the wave function, the energy change may be calculated as

$$\frac{i\mu_p\alpha}{2M}\left(\frac{1-(m/M)}{1+(m/M)}\right)^{1/2}\int d^3r\psi_0^{\dagger}(\mathbf{r})[\boldsymbol{\alpha}\times\mathbf{p},\,1/r]\cdot\boldsymbol{\delta}_p\psi_0(\mathbf{r}),\tag{3.6}$$

where we have used the wave function ψ_0 rather than ψ. If the proton had infinite mass, the above

integral would be[19]

$$-\tfrac{1}{3}i(m\alpha)^2 4\alpha(1+\tfrac{3}{2}\alpha^2)\langle\delta_e\cdot\delta_p\rangle, \quad (3.7)$$

but our wave functions depend on $m_{\rm red}\alpha$ and on α' rather than $m\alpha$ and α, respectively; the result for finite mass must therefore be

$$-\tfrac{1}{3}i(m_{\rm red}\alpha)^2 4\frac{\alpha}{[1-(m^2/M^2)]^{1/2}} \times\left(1+\tfrac{3}{2}\frac{\alpha^2}{1-(m^2/M^2)}\right)\langle\delta_e\cdot\delta_p\rangle. \quad (3.8)$$

When (3.8) is combined with the numerical factors appearing in front of the integral sign in (3.6), the result obtained is

$$\frac{2\pi\alpha\mu_p}{3mM}\frac{(m_{\rm red}\alpha)^3}{\pi}\left(1+\tfrac{3}{2}\frac{\alpha^2}{1-(m^2/M^2)}\right)\langle\delta_e\cdot\delta_p\rangle. \quad (3.9)$$

We see, therefore, that the Fermi splitting E_F between the triplet and singlet states is modified to

$$E_f'=E_F\left(\frac{M}{m+M}\right)^3\left(1+\tfrac{3}{2}\frac{\alpha^2}{1-(m^2/M^2)}\right). \quad (3.10)$$

In this simple way we have obtained the reduced mass correction to the Fermi formula. The modification of the Breit correction ($\frac{3}{2}\alpha^2$) due to mass corrections should be ignored since terms of comparable magnitude were also considered to be too small.

B. Nonrelativistic Size Correction

The first estimate of the contribution to the hyperfine splitting due to the finite size of the proton was made in 1949 by Brown and Arfken,[26] who assumed for simplicity that the proton consists of a shell of charge. Although this assumption is crude, it does give a rough estimate of the correction.

A more sophisticated calculation for an arbitrary distribution of the proton charge and magnetic moment was done by Zemach in 1956.[25] This calculation, in which the nonrelativistic approximation to the wave function was used, has withstood the test of time and gives the bulk of the proton structure correction.

It is by no means obvious that the nonrelativistic approximation to the wave function suffices to obtain the major part of the structure correction. In fact, for the electron to see the proton structure it must interact with the proton in such a way as to exchange high enough momentum for the form factors to be appreciably different from unity. The occurrence of these high-momentum processes indicates that the electron will be relativistic.

In spite of the fact that the electron will be relativistic, the use of the nonrelativistic wave function can be justified.[27] A detailed examination of the integrals shows that the large components of the wave function are needed only for relatively small momenta ($p\approx m\alpha$), where the nonrelativistic approximation is valid for them. Even though the small components are needed for rather large values of momentum ($M>p\gg m$), it turns out (surprisingly) that they are very well approximated there by the corresponding NR ones (see Appendix B).

In this paper, when we say that a particular approximation is valid or that a term is negligible, we have specifically estimated the term by obtaining its order of magnitude in terms of such small quantities as α or m/M. The reader is referred to the paper of Erickson and Yennie[3] for a discussion of "rules of order" in estimating integrals.

The correction which we obtain in this section involves the ratio of a nuclear radius to the Bohr radius ($m\alpha R_{\rm pr}$). Since this is already quite small, we may evaluate it in the limit of infinite proton mass. The wave functions are therefore Coulomb wave functions, except that a two-component spinor for the proton is included. Let us denote the Coulomb wave function by ψ_c in coordinate space and by ϕ_c in momentum space. The distribution of the proton charge will modify these to $\psi_c^{(s)}$ and $\phi_c^{(s)}$, where the superscript (s) is used to indicate that structure is included.

The modification of the potential due to the proton structure is indicated in Eq. (2.19). In addition to the change of the wave function brought about by the distribution of electric charge, we must also consider the modification of the perturbation due to the distribution of the magnetic moment. Although we have previously assumed that the form factors will be denoted by F, it is convenient in what follows to distinguish between G_E and G_M, even though these are both equal to F (i.e., for $|q^2|\ll 4M^2$). The correction to the hfs due to size effects is therefore

$$\Delta E^{(s)}=\int\phi_c^{\dagger(s)}(\mathbf{p}_3)\left(\frac{-i\mu_p}{2M}\right)\frac{e^2}{(\mathbf{p}_1-\mathbf{p}_3)^2}\,\boldsymbol{\alpha}\cdot(\mathbf{p}_1-\mathbf{p}_3) \times\delta_p G_M[(\mathbf{p}_1-\mathbf{p}_3)^2]\phi_c^{(s)}(\mathbf{p}_1)\,d^3p_1d^3p_3 -\int\phi_c^{\dagger}(\mathbf{p}_3)\left(\frac{-i\mu_p}{2M}\right)\frac{e^2}{(\mathbf{p}_1-\mathbf{p}_3)^2}\,\boldsymbol{\alpha}\cdot(\mathbf{p}_1-\mathbf{p}_3) \times\delta_p\phi_c(\mathbf{p}_1)\,d^3p_1d^3p_3. \quad (3.11)$$

As mentioned previously, we will evaluate (3.11) by using the NR approximation to the wave function. To denote the NR approximation of a function ϕ, we use $\tilde{\phi}$; to indicate the usual spin-independent factor in the NR wave function, we use $\hat{\phi}$. Therefore, the wave functions are written

$$\tilde{\phi}_c(\mathbf{p}_1)=\hat{\phi}_c(\mathbf{p}_1)\chi_p\begin{pmatrix}\chi_e\\(\boldsymbol{\delta}\cdot\mathbf{p}_1/2m)\chi_e\end{pmatrix}$$

and

$$\tilde{\phi}_c^{(s)}(\mathbf{p}_1)=\hat{\phi}_c^{(s)}(\mathbf{p}_1)\chi_p\begin{pmatrix}\chi_e\\(\boldsymbol{\delta}\cdot\mathbf{p}_1/2m)\chi_e\end{pmatrix}, \quad (3.12)$$

where χ_e and χ_p are two-component spinors for the electron and proton;

$$\hat{\phi}_c(\mathbf{p}_1) = -[\epsilon-(\mathbf{p}_1^2/2m)]^{-1}\int\frac{d^3p'}{(2\pi)^3}\frac{e^2}{(\mathbf{p}_1-\mathbf{p}')^2}\hat{\phi}_c(\mathbf{p}') \tag{3.13}$$

and, to a sufficiently good approximation,

$$\hat{\phi}_c^{(s)}(\mathbf{p}_1)\approx\hat{\phi}_c(\mathbf{p}_1)-[\epsilon-(\mathbf{p}_1^2/2m)]^{-1}\int\frac{d^3p'}{(2\pi)^3}\frac{e^2}{(\mathbf{p}_1-\mathbf{p}')^2}\times\{G_E[(\mathbf{p}_1-\mathbf{p}')^2]-1\}\hat{\phi}_c(\mathbf{p}'), \tag{3.14}$$

where ϵ is the NR binding energy.

Using (3.11) and (3.12) we obtain a contribution to the hyperfine structure given by

$$\frac{e^2}{6mM}\langle\boldsymbol{\sigma}_e\cdot\boldsymbol{\sigma}_p\rangle\left[\int\hat{\phi}_c^{\dagger(s)}(\mathbf{p}_3)G_M[(\mathbf{p}_1-\mathbf{p}_3)^2]\times\hat{\phi}_c^{(s)}(\mathbf{p}_1)d^3p_1d^3p_3-\int\hat{\phi}_c^{\dagger}(\mathbf{p}_3)\hat{\phi}_c(\mathbf{p}_1)d^3p_1d^3p_3\right]. \tag{3.15}$$

In coordinate space, (3.15) may be written as

$$\frac{e^2}{6mM}\langle\boldsymbol{\sigma}_e\cdot\boldsymbol{\sigma}_p\rangle\left[\int\hat{\psi}_c^{\dagger(s)}(\mathbf{r})\rho_M(\mathbf{r})\hat{\psi}_c^{(s)}(\mathbf{r})d^3r-|\hat{\psi}_c(0)|^2\right], \tag{3.16}$$

where

$$\rho_M(\mathbf{r})=\int\frac{d^3q}{(2\pi)^3}\exp(i\mathbf{q}\cdot\mathbf{r})G_M(\mathbf{q}^2).$$

From (3.16) it is clear that we need a good approximation for $\hat{\psi}_c^{(s)}(\mathbf{r})$ only for small values of r. This permits us to make some simplifying approximations in the following paragraph.

In the p' integration of (3.14) only small values of p' ($p'\sim m\alpha$) are emphasized. Therefore $\hat{\phi}_c^{(s)}$ and $\hat{\phi}_c$ can differ appreciably only for large values of p_1. This means that we may neglect p' compared to p_1 in the integrand of (3.14) to obtain

$$\hat{\phi}_c^{(s)}(\mathbf{p}_1)\approx\hat{\phi}_c(\mathbf{p}_1)-[\epsilon-(\mathbf{p}_1^2/2m)]^{-1}(e^2/\mathbf{p}_1^2)\times[G_E(\mathbf{p}_1^2)-1][\hat{\psi}_c(0)/(2\pi)^3]. \tag{3.17}$$

Moreover, for large values of p_1 ($p_1\gg m\alpha$), we may certainly neglect ϵ; for small p_1 the second term of (3.17) is negligible compared to the first, and therefore it is clear that we may set $\epsilon=0$ for all p_1. With these approximations, the Fourier transform of $\hat{\phi}_c^{(s)}(\mathbf{p}_1)$ becomes

$$\hat{\psi}_c^{(s)}(\mathbf{r})\approx\hat{\psi}_c(\mathbf{r})+2m\hat{\psi}(0)\times\int\exp(-i\mathbf{p}_1\cdot\mathbf{r})\frac{e^2}{\mathbf{p}_1^4}[G_E(\mathbf{p}_1^2)-1]\frac{d^3p_1}{(2\pi)^3}$$
$$=\hat{\psi}_c(\mathbf{r})+m\alpha r\hat{\psi}_c(0)-m\alpha\hat{\psi}_c(0)\times\int|\mathbf{u}-\mathbf{r}|\rho_E(\mathbf{u})d^3u. \tag{3.18}$$

Approximating $\hat{\psi}_c(\mathbf{r})$ by $\hat{\psi}_c(0)(1-m\alpha r)$, we obtain

$$\hat{\psi}_c^{(s)}(\mathbf{r})\approx\hat{\psi}_c(0)-m\alpha\hat{\psi}_c(0)\int|\mathbf{u}-\mathbf{r}|\rho_E(\mathbf{u})d^3u. \tag{3.19}$$

When (3.19) is substituted into (3.16) and use is made of the condition

$$\int\rho_M(\mathbf{r})d^3r=1,$$

the result obtained is

$$(e^2/6mM)\langle\boldsymbol{\sigma}_e\cdot\boldsymbol{\sigma}_p\rangle|\hat{\psi}_c(0)|^2\times\left[-2m\alpha\int|\mathbf{u}-\mathbf{r}|\rho_E(\mathbf{u})\rho_M(\mathbf{r})d^3ud^3r\right]. \tag{3.20}$$

This is exactly the Zemach correction to the hfs. It is equal to

$$-2m\alpha R_{\rm pr}\times\text{hfs}, \tag{3.21}$$

where

$$R_{\rm pr}=\int|\mathbf{u}-\mathbf{r}|\rho_M(\mathbf{u})\rho_E(\mathbf{r})d^3ud^3r \tag{3.22}$$

is an appropriate proton radius. The derivation of this result for the specific case of a shell of electric charge and a point magnetic moment is presented in Appendix C using a different method.

The experimental determination of proton form factors, obtained from electron–proton scattering, indicates that the exponential fit provides a good description of both the electric and magnetic form factors.[17] We will therefore use

$$\rho_E(\mathbf{r})=\rho_M(\mathbf{r})=(\Lambda^3/8\pi)e^{-\Lambda r},$$

where $\Lambda=0.91M$. We obtain

$$R_{\rm pr}=\int|\mathbf{r}|\rho_{EM}(\mathbf{r})d^3r \tag{3.23}$$

with

$$\rho_{EM}(\mathbf{r})=\int\rho_E(\mathbf{r}-\mathbf{u})\rho_M(\mathbf{u})d^3u$$
$$=(1/64\pi)\Lambda^3e^{-\Lambda r}[1+\Lambda r+\tfrac{1}{3}(\Lambda r)^2]. \tag{3.24}$$

Evaluating (3.23) we find that

$$R_{\rm pr}=(35/8)(1/\Lambda)=1.02\text{ F}.$$

Since the relative correction is $-2m\alpha R_{\rm pr}$, we obtain a nonrelativistic size effect of

$$-38.2\text{ ppm}. \tag{3.25}$$

This simple result, obtained in terms of a suitable proton radius, represents most of the contribution due to the structure of the proton.

C. Additional Recoil Corrections

Thus far we have treated corrections to the hyperfine splitting coming from the finite size and finite

mass of the proton by considering the potential in (2.19). There are, however, further corrections of relative order $\alpha m/M$. These are not contained in the potential of (2.19), but must be found by first obtaining a suitable modification of the potential. Before going on to evaluate the effect of this modification, let us briefly review the work of others.

Some 15 to 20 years ago, Breit and his co-workers attempted an approximately relativistic treatment of nuclear motion corrections.[15,19] Although their results contained the correct reduced-mass corrections, they did not contain relative corrections of order $\alpha m/M$ for either the fine structure or the hyperfine structure. The difficulty with their approach, as discussed by Salpeter,[28] was that it corresponded to single-particle theory rather than to hole theory (so far our approach has the same flaw, but this is remedied by further corrections to the potential).

In the early 1950's Arnowitt[29] and Newcomb and Salpeter[30] independently calculated these additional recoil corrections to the hyperfine splitting by completely covariant techniques, the former based on a method developed by Karplus, Klein, and Schwinger,[31] and the latter based on the Bethe–Salpeter equation.[7,8] Unfortunately, these calculations are logarithmically divergent since they are done for a point proton with an anomalous magnetic moment; the nonrenormalizability of the Pauli interaction is responsible for the divergence.

In 1958 Iddings and Platzman[1] took into account the form factors of the proton in obtaining the corrections due to structure and recoil. Their result is not obviously separable into a part which may be attributed to a proton size [as the Zemach result in (3.25)] and a part which may be interpreted as a recoil correction. Such a separation is desirable since it clarifies the difference between the results of Iddings and Platzman and those of Zemach.

The method which we employ yields the same numerical answer as that of Iddings and Platzman, but it does make the separation referred to above.

The selection of an effective potential is made under the assumption that one which accounts for the observed electron–proton scattering will be adequate for use in the bound-state problem. Although this statement seems plausible, it is by no means obvious since the choice of a potential is not unique. Our particular choice is guided by maximum simplicity. The lowest-order potential in (2.19) predicts the first-order scattering; other choices could do just as well. However, we will modify (2.19) so as to obtain a potential which not only gives the first-order scattering but also gives a good portion of the second-order scattering. This new potential will thereby minimize the corrections which arise due to the failure of the iteration in a Lippmann–Schwinger formalism to match higher-order scattering. Let us call this new potential $V_{\text{eff}}{}'^{(2)(s)}$.

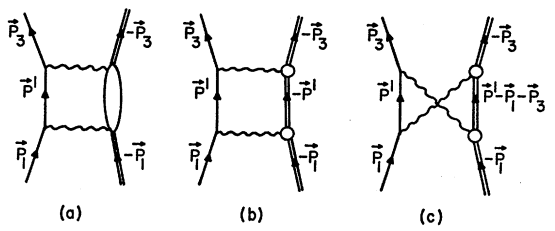

FIG. 2. Two-photon-exchange graphs. (a) Complete two-photon amplitude. (b) and (c) Approximations to (a) using on-the-mass-shell form factors and excluding excited states of the nucleon.

The second iteration of $V_{\text{eff}}{}'^{(2)(s)}$ does not correspond exactly to the scattering obtained from the graph of Fig. 2(a). This situation may be remedied by adding an additional term $(\Delta V_{\text{eff}}{}^{(4)(s)})$ which represents the difference between the two-photon exchange and the iteration. The new potential will have the property that its first and second iterations give the correct scattering to order α^2.

Although it is quite clear that $\Delta V_{\text{eff}}{}^{(4)(s)}$ is smaller by one power of α than the lowest-order potential (it is also smaller by m/M), it does not follow *a priori* that its expectation value in the bound state will be smaller by one power of α than the energy splitting induced by the lowest-order potential. The reason for this is due to the dependence of the wave functions on the fine-structure constant. Difficulties of this sort do not arise for the hyperfine structure, but are present for the fine structure.

Needless to say, the two-photon-exchange Feynman graph of Fig. 2(a) is not calculable since it involves the strong interactions. It may, however, be evaluated approximately by neglecting excited-state contributions and off-the-mass-shell, form-factor effects. By definition, these neglected contributions are called the proton polarization correction and are denoted by X_{pol} in (3.1). The diagrams actually used are shown in Figs. 2(b) and 2(c). In subtracting the iteration of the lowest-order potential, we do not include the magnetic (spin–spin) interaction of (2.19) twice. The magnetic interaction was treated only by first-order perturbation theory to obtain the hfs, and it would not be consistent to include two magnetic interactions in the iteration. Such interactions will arise from the two-photon graphs and may be handled in this way rather than from second-order perturbation theory with $\Delta V_{\text{eff}}{}^{(2)(s)}$.

In the interest of simplicity, let us first assume that the proton is a Dirac particle. We would like to demonstrate that the iteration of the lowest-order potential is contained in the two-photon graphs, but that there are residual terms which contribute to the recoil corrections. The actual calculation for a more realistic proton will be accomplished in a different way than that suggested by the work which follows.

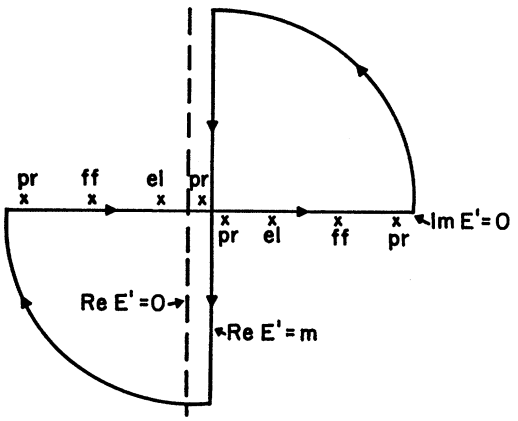

FIG. 3. The E' plane locating the poles of the integrand of (3.34a) (not drawn to scale). The symbols indicate proton (pr), electron (el), or form-factor (ff) poles.

In the Coulomb gauge, the two-photon amplitude is

$$\frac{(4\pi\alpha)^2}{(2\pi)^4}\int d^4p'\{D_{0,0}[L_{0,0}+C_{0,0}](1/\mathbf{q}_3^2)(1/\mathbf{q}_1^2)$$
$$+D_{0,\perp(1)}[L_{0,\perp(1)}+C_{\perp(1),0}]\frac{1}{\mathbf{q}_3^2}\frac{1}{q_1^2+i0}$$
$$+D_{\perp(3),0}[L_{\perp(3),0}+C_{0,\perp(3)}][1/(q_3^2+i0)](1/\mathbf{q}_1^2)$$
$$+D_{\perp(3),\perp(1)}[L_{\perp(3),\perp(1)}+C_{\perp(1),\perp(3)}]$$
$$\times(q_3^2+i0)^{-1}(q_1^2+i0)^{-1}\}, \quad (3.26)$$

where

$$\mathbf{q}_3=\mathbf{p}'-\mathbf{p}_3, \quad \mathbf{q}_1=\mathbf{p}_1-\mathbf{p}',$$
$$D_{a,b}=\bar{u}(p_3)\gamma_a[1/(\not{p}'-m+i0)]\gamma_b u(p_1), \quad (3.27a)$$
$$L_{a,b}=\bar{u}_p(p_4)\gamma_a[1/(\not{p}_2-\not{p}'+\not{p}_1+M+i0)]\gamma_b u_p(p_2), \quad (3.27b)$$

and

$$C_{a,b}=\bar{u}_p(p_4)\gamma_a[1/(\not{p}_4+\not{p}'-\not{p}_1-M+i0)]\gamma_b u_p(p_2). \quad (3.27c)$$

The notation used is rather cumbersome due to the use of the Coulomb gauge. The number in parentheses associated with the symbol $\perp$ indicates the momentum to which the gamma matrix is transverse and also serves to indicate which vectors are dotted into each other (see Appendix A on notation).

As mentioned earlier, part of the amplitude of (3.26) is predicted by the second iteration of the lowest-order potential. To see this, let us look at the term involving $D_{0,\perp(1)}L_{0,\perp(1)}$. This represents a process in which a transverse photon is exchanged, followed by a Coulomb interaction. The integral over p_0' may easily be done by contour methods, picking up the residues at the various poles. If we close the contour in the upper half of the complex p_0' plane, we obtain a contribution from the proton pole located at $E_1+E_2-(\mathbf{p}'^2+M^2)^{1/2}+i0$. We obtain

$$\frac{-(4\pi\alpha)^2 i}{(2\pi)^3}\int d^3p'\bar{u}(p_3)\gamma_0$$
$$\times[E_1+E_2-(\mathbf{p}'^2+M^2)^{1/2}-\boldsymbol{\alpha}\cdot\mathbf{p}'-\beta m]^{-1}\boldsymbol{\alpha}_{\perp(1)}u(p_1)$$
$$\times\bar{u}_p(p_4)\gamma_0\left(\frac{\gamma_0(\mathbf{p}'^2+M^2)^{1/2}+\boldsymbol{\gamma}\cdot\mathbf{p}'+M}{2(\mathbf{p}'^2+M^2)^{1/2}}\right)\boldsymbol{\gamma}_{\perp(1)}u_p(p_2)$$
$$\times\frac{1}{(\mathbf{p}'-\mathbf{p}_3)^2}\frac{1}{[E_2-(\mathbf{p}'^2+M^2)^{1/2}]^2-(\mathbf{p}_1-\mathbf{p}')^2}. \quad (3.28)$$

In the NR limit for the proton this simplifies to

$$-i\int\frac{d^3p'}{(2\pi)^3}\frac{e^2}{(\mathbf{p}'-\mathbf{p}_3)^2}\bar{u}(p_3)\gamma_0$$
$$\times[E-(\mathbf{p}'^2/2M)-\boldsymbol{\alpha}\cdot\mathbf{p}'-\beta m]^{-1}\boldsymbol{\alpha}_{\perp(1)}u(p_1)$$
$$\times\frac{e^2}{(\mathbf{p}_1-\mathbf{p}')^2-[(\mathbf{p}_1^2/2M)-(\mathbf{p}'^2/2M)]^2}\chi_4^\dagger$$
$$\times\left[\frac{\mathbf{p}'+\mathbf{p}_1}{2M}+\frac{i}{2M}(\mathbf{p}_1-\mathbf{p}')\times\boldsymbol{\delta}_p\right]\chi_2, \quad (3.29)$$

where $E=E_1+E_2-M$.

This is almost exactly the scattering predicted by part of the iteration of (2.19) (with $F=1$ and $\mu=0$); the only difference is due to the presence of some terms involving the proton kinetic energy

$$[(\mathbf{p}_1^2/2M)-(\mathbf{p}'^2/2M)]^2.$$

We note, however, that the second term in (2.18) should really have in the denominator $\mathbf{q}^2-q_0^2$ (in lowest order, $q_0=0$). Therefore we interpret this q_0 as the difference in proton energies [i.e.,

$$q_0=(\mathbf{p}_1^2+M^2)^{1/2}-(\mathbf{p}_3^2+M^2)^{1/2}].$$

We now modify (2.19) so that the new lowest-order potential is

$$V'_{\text{eff}}{}^{(2)(s)}+\Delta V'_{\text{eff}}{}^{(2)(s)}=-\frac{e^2}{\mathbf{q}^2}F(-q^2)$$
$$+\frac{e^2}{q^2}\boldsymbol{\alpha}_\perp\cdot\left(\frac{\mathbf{p}_1+\mathbf{p}_3}{2M}\right)F(-q^2)$$
$$+\frac{e^2}{q^2}\frac{i}{2M}(1+\mu)\boldsymbol{\alpha}\cdot\mathbf{q}\times\boldsymbol{\delta}_p F(-q^2). \quad (3.30)$$

Let us stress that this modification does not affect the lowest-order scattering; it does, however, affect higher-order scattering and bound states. In (3.30) we have prescribed a behavior off the energy shell. Our choice is consistent with our desire to include in the lowest-order potential as much as possible with regard to the scattering. The iteration of (3.30) (with $F=1$ and $\mu=0$) now gives exactly the same scattering as does (3.29).

It would seem that the most logical way of proceeding to the recoil corrections is as follows: (1) First evaluate the correction to the hfs due to the difference

between (3.30) and (2.19). This means that all of (3.29) has already been accounted for. (2) Obtain the corrections due to the other poles in (3.26) (e.g., electron and photon poles). However, it turns out that the most logical method is rather difficult since it does not lead us to simple integrals. In fact, when form factors are included, matters become hopelessly complicated.

It may be shown, however, that the contributions from other poles [mentioned in (2) above] can be evaluated by neglecting the external momenta in comparison to p'.[27] Furthermore, if we simply ignore the difference between (3.30) and (2.19) and instead treat the difference between (3.29) and the iteration of (2.19) as a perturbation (in the limit of ignoring external momenta), we obtain essentially the same result as if we followed prescription (1) above. These statements are not obvious, but the proof is given elsewhere.[27] The upshot of these remarks may be summarized. The two-photon-exchange contains the iteration of the lowest-order potential of (2.19), but the residual terms may all be calculated by assuming that the external momenta can be ignored compared to the internal momentum p'. Although we have only discussed the case with $F=1$ and $\mu=0$, the same conclusions apply in the more general problem. As mentioned previously, in these considerations we always bear in mind that errors can be estimated, and shown to be of higher order, in a standard way (see Ref. 3).

The method suggested above for calculating recoil corrections involves a separation into various pole terms. This procedure was used for a point proton and gave exactly the Newcomb and Salpeter correction. We will not include this calculation since we prefer to treat the more general problem of an extended proton. However, we adopt a different procedure in order to make the integrals more manageable.

We have found that after the iteration of the potential is subtracted out, it is justifiable to set the external momenta equal to zero and to ignore binding. Therefore, we may set the external momenta to zero in the two-photon amplitude and subtract the iteration, in the same approximation. The details of these approximations are discussed elsewhere.[27] All of the integrals become much simpler if this procedure is followed.

The two-photon-exchange amplitude, including form factors and the Pauli interaction, is

$$\frac{(4\pi\alpha)^2}{(2\pi)^4}\int d^4p'\{D_{0,0}[L'_{0,0}+C'_{0,0}][1/(\mathbf{p}'-\mathbf{p}_3)^2][1/(\mathbf{p}_1-\mathbf{p}')^2]$$
$$+D_{0,\perp(1)}[L'_{0,\perp(1)}+C'_{\perp(1),0}][1/(\mathbf{p}'-\mathbf{p}_3)^2][(p_1-p')^2+i0]^{-1}$$
$$+D_{\perp(3),0}[L'_{\perp(3),0}+C'_{0,\perp(3)}][(p'-p_3)^2+i0]^{-1}[1/(\mathbf{p}_1-\mathbf{p}')^2]$$
$$+D_{\perp(3),\perp(1)}[L'_{\perp(3),\perp(1)}+C'_{\perp(1),\perp(3)}][(p'-p_3)^2+i0]^{-1}[(p_1-p')^2+i0]^{-1}\}, \quad (3.31)$$

where $D_{a,b}$ is given in (3.27a) and $L'_{a,b}$, $C'_{a,b}$ are given by replacing γ_a and γ_b of (3.27b) and (3.27c) by Γ_a and Γ_b, where

$$\Gamma_{\mu(1)}=[\gamma_\mu+(i\mu/2M)\sigma_{\mu\nu}q_1{}^\nu]F(-q_1{}^2). \quad (3.32)$$

From (3.31) and the iteration of the lowest order potential of (2.19) we may infer a correction to the potential equal to

$$\Delta V_{\text{eff}}{}^{(4)(8)}=B_1+B_\mu+B_{11}+B_{1\mu}+B_{\mu\mu}-I_1-I_\mu, \quad (3.33)$$

where p_1, p_3 are neglected compared to p'. The expressions for the B's are obtained from (3.31). The first two correspond to contributions to the hfs in which one magnetic interaction has occurred, either with the Dirac or the anomalous moment of the proton. The next three involve double magnetic interactions of various types. Finally the terms I_1 and I_μ correspond to the iteration of the lowest-order potential and are therefore subtracted. We find

$$B_1=\frac{(4\pi\alpha)^2}{(2\pi)^4}\frac{8}{3}i\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\int d^4p'\,\frac{F^2[\mathbf{p}'^2-(E'-m)^2]}{\{(E'-m)^2+2m(E'-m)-\mathbf{p}'^2+i0\}}\,\frac{1}{\{[(E'-m)^2-\mathbf{p}'^2+i0]^2-4M^2(E'-m)^2\}}, \quad (3.34a)$$

$$B_\mu=\mu B_1+\frac{8}{3}\mu\frac{(4\pi\alpha)^2}{(2\pi)^4}i\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\int d^4p'(E'-m)^2$$
$$\times\frac{F^2[\mathbf{p}'^2-(E'-m)^2]}{\{[(E'-m)^2-\mathbf{p}'^2+i0]^2-4m^2(E'-m)^2\}\{[(E'-m)^2-\mathbf{p}'^2+i0]^2-4M^2(E'-m)^2\}}, \quad (3.34b)$$

$$B_{11}=\frac{(4\pi\alpha)^2}{(2\pi)^4}\frac{4}{3}i\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\int d^4p'\,\frac{(E'-m)^2F^2[\mathbf{p}'^2-(E'-m)^2]}{\{[(E'-m)^2-\mathbf{p}'^2+i0]^2-4m^2(E'-m)^2\}}\,\frac{1}{\{[(E'-m)^2-\mathbf{p}'^2+i0]^2-4M^2(E'-m)^2\}}, \quad (3.34c)$$

$$B_{1\mu}=2\mu B_{11}, \quad (3.34d)$$

and

$$B_{\mu\mu}=2\left(\frac{\mu}{2M}\right)^2\frac{(4\pi\alpha)^2}{(2\pi)^4}i\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\int d^4p'\,\frac{F^2[\mathbf{p}'^2-(E'-m)^2]}{(E'-m)^2-\mathbf{p}'^2+i0}$$
$$\times\frac{-\frac{8}{3}M^2\mathbf{p}'^2(E'-m)^2+2[(E'-m)^2-\mathbf{p}'^2]^3+\frac{2}{3}\mathbf{p}'^2[(E'-m)^2-\mathbf{p}'^2]^2}{\{[(E'-m)^2-\mathbf{p}'^2+i0]^2-4m^2(E'-m)^2\}\{[(E'-m)^2-\mathbf{p}'^2+i0]^2-4M^2(E'-m)^2\}}. \quad (3.34e)$$

The I's turn out to be*

$$I_1=\frac{4}{3}\frac{(4\pi\alpha)^2}{(2\pi)^3}\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\int d^3p'\,\frac{F^2(\mathbf{p}'^2)}{2(m+M)\mathbf{p}'^4} \quad (3.35a)$$

and

$$I_\mu=\mu I_1. \quad (3.35b)$$

The evaluation of $\Delta V_{\text{eff}}^{(4)(s)}$ is a straightforward but arduous task. It should be noted that B_1, B_μ, I_1, and I_μ are all divergent quantities but that the divergences cancel in B_1-I_1 and $B_\mu-I_\mu$. We shall not discuss at great length the integrations of (3.34) and (3.35) but shall merely indicate the method.

The poles in the E' plane for the integral of B_1 are located as shown in Fig. 3. The contour which we have drawn does not enclose any poles of the integrand, regardless of the value of p'. Therefore, using Cauchy's theorem, we obtain[32,33]

$$\int_{-\infty}^{\infty}f(E'-m)\,dE'=i\int_{-\infty}^{\infty}f[-i(E'-m)]\,dE', \quad (3.36)$$

where f is the integrand; f could also be any other function of $E'-m$ which confines its poles as in Fig. 3 and which vanishes fast enough at infinity.

Using (3.36) and replacing $E'-m$ by E' (change of variable of integration), we find that

$$B_1=\frac{8}{3}\frac{(4\pi\alpha)^2}{(2\pi)^4}\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\int d^4p'\,\frac{(E'^2+\mathbf{p}'^2)F^2(E'^2+\mathbf{p}'^2)}{\{(E'^2+\mathbf{p}'^2)^2+4m^2E'^2\}\{(E'^2+\mathbf{p}'^2)^2+4M^2E'^2\}}. \quad (3.37)$$

In obtaining (3.37) we have discarded a term which is odd in E' and would therefore integrate to zero. The advantage achieved in transforming (3.34a) to (3.37) is that we may now work in a four-dimensional, Euclidean space. As previously mentioned, (3.37) has a divergence at small values of p' which will be canceled by a corresponding divergence in I_1. Let us therefore impose a small cutoff λ on the p' integrals of (3.37) and (3.35a). Later we may let $\lambda\to0$.

If we now transform to coordinates K and ψ as determined by

$$E'^2=K^2\cos^2\psi \quad\text{and}\quad \mathbf{p}'^2=K^2\sin^2\psi, \quad (3.38)$$

B_1 becomes

$$B_1=\frac{32\pi}{3}\frac{(4\pi\alpha)^2}{(2\pi)^4}\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\int_\lambda^\infty\int_{\sin^{-1}(\lambda/K)}^{\pi}\frac{\sin^2\psi\,d\psi K\,dK F^2(K^2)}{(K^2+4m^2\cos^2\psi)(K^2+4M^2\cos^2\psi)}, \quad (3.39)$$

and (3.35a) becomes (here $K=p'$)

$$I_1=\tfrac{8}{3}\pi\frac{(4\pi\alpha)^2}{(2\pi)^3}\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\int_\lambda^\infty\frac{dK}{K^2}\frac{F^2(K^2)}{m+M}. \quad (3.40)$$

It is a straightforward exercise to show that the integral on ψ may be extended to zero without obtaining an

---

* The iteration of the potential is

$$\int\frac{d^3p'}{(2\pi)^3}\frac{-e^2}{(\mathbf{p}'-\mathbf{p}_3)^2}F[(\mathbf{p}'-\mathbf{p}_3)^2]\left[1+\boldsymbol{\alpha}_{\perp(3)}\cdot\left(\frac{\mathbf{p}'+\mathbf{p}_3}{2M}\right)\right][E-(\mathbf{p}'^2/2M)-\boldsymbol{\alpha}\cdot\mathbf{p}'-\beta m]^{-1}\left(\frac{-i}{2M}\right)\mu_p\frac{e^2}{(\mathbf{p}_1-\mathbf{p}')^2}$$
$$\times F[(\mathbf{p}_1-\mathbf{p}')^2]\boldsymbol{\alpha}\cdot(\mathbf{p}_1-\mathbf{p}')\times\boldsymbol{\delta}_p+\text{reverse ordering}. \quad (a)$$

If we take its expectation value using the wave functions ϕ of Sec. II, we find that it is the same as the expectation value of

$$\int\frac{d^3p'}{(2\pi)^3}\left(\frac{1-\beta\lambda}{1-\lambda}\right)\frac{-e^2}{(\mathbf{p}'-\mathbf{p}_3)^2}\frac{F[(\mathbf{p}'-\mathbf{p}_3)^2]}{(1-m^2/M^2)^{1/2}}(E_r-\boldsymbol{\alpha}\cdot\mathbf{p}'-\beta m')^{-1}\left(\frac{1+\beta\lambda}{1+\lambda}\right)\left\{\frac{-i}{2M}\mu_p\frac{e^2}{(\mathbf{p}_1-\mathbf{p}')^2}F[(\mathbf{p}_1-\mathbf{p}')^2]\boldsymbol{\alpha}\cdot(\mathbf{p}_1-\mathbf{p}')\times\boldsymbol{\delta}_p\right\}$$
$$+\text{reverse ordering}, \quad (b)$$

where $E_r=m'-\frac{1}{2}m_{\text{red}}\alpha^2$. This latter expression gives I_1 and I_μ in the appropriate limit. The former (a) is difficult to work with because of a spurious pole in the propagator occurring at high momentum.

additional contribution in the limit $\lambda\to 0$. The integral over ψ in (3.39) may readily be done, thus giving

$$B_1=\tfrac{16}{3}\pi^2\frac{(4\pi\alpha)^2}{(2\pi)^4}\int_\lambda^\infty\frac{dK}{K^2}F^2(K^2)\left[M\left(1+\frac{K^2}{4M^2}\right)^{1/2}-m\left(1+\frac{K^2}{4m^2}\right)^{1/2}\right]. \tag{3.41}$$

The difference B_1-I_1 is quite well behaved in the limit $\lambda\to 0$. The integrals in (3.40) and (3.41) may readily be evaluated with the help of standard integral tables.

The result is

$$B_1-I_1=\frac{4}{3}\frac{(4\pi\alpha)^2}{(2\pi)^2}\boldsymbol{\sigma}_e\cdot\boldsymbol{\sigma}_p\frac{Op(\Lambda^2)}{M^2-m^2}\left\{\tfrac{1}{2}\pi\left(\frac{M-m}{\Lambda}\right)-\left(\frac{1}{4}-\frac{m^2}{\Lambda^2}\right)^{1/2}\ln\left[\frac{\Lambda}{2m}+\left(\frac{\Lambda^2}{4m^2}-1\right)^{1/2}\right]\right.$$
$$\left.-\left(\frac{M^2}{\Lambda^2}-\frac{1}{4}\right)^{1/2}\sin^{-1}\left(1-\frac{\Lambda^2}{4M^2}\right)^{1/2}\right\}, \tag{3.42}$$

where $Op(\Lambda^2)g(\Lambda^2)=-\frac{1}{6}\Lambda^8[\partial^3/\partial(\Lambda^2)^3](1/\Lambda^2)g(\Lambda^2)$ for any function g. This expression applies for $4m^2<\Lambda^2<4M^2$, but in going to the limit $\Lambda\to\infty$ we must make the replacement

$$\left(\frac{M^2}{\Lambda^2}-\frac{1}{4}\right)^{1/2}\sin^{-1}\left(1-\frac{\Lambda^2}{4M^2}\right)^{1/2}\to-\left(\frac{1}{4}-\frac{M^2}{\Lambda^2}\right)\ln\left[\frac{\Lambda}{2M}+\left(\frac{\Lambda^2}{4M^2}-1\right)^{1/2}\right].$$

All of the integrals may be evaluated in a similar way. The complete results are

$$B_1-I_1+B_{11}=\frac{(4\pi\alpha)^2}{(2\pi)^2}\frac{4}{3}\frac{\boldsymbol{\sigma}_e\cdot\boldsymbol{\sigma}_p}{M^2-m^2}Op(\Lambda^2)\left[\left\{\tfrac{1}{2}\pi\left(\frac{M-m}{\Lambda}\right)-\left(\frac{1}{4}-\frac{m^2}{\Lambda^2}\right)^{1/2}\ln\left[\frac{\Lambda}{2m}+\left(\frac{\Lambda^2}{4m^2}-1\right)^{1/2}\right]\right.\right.$$
$$\left.-\left(\frac{M^2}{\Lambda^2}-\frac{1}{4}\right)^{1/2}\sin^{-1}\left(1-\frac{\Lambda^2}{4M^2}\right)^{1/2}\right\}-\frac{\Lambda^2}{16M^2}\left(\left[\ln\frac{\Lambda}{M}-\left(\frac{4M^2}{\Lambda^2}-1\right)^{1/2}\sin^{-1}\left(1-\frac{\Lambda^2}{4M^2}\right)^{1/2}\right]\right.$$
$$\left.\left.-\frac{M^2}{m^2}\left\{\ln\frac{\Lambda}{m}-\left(1-\frac{4m^2}{\Lambda^2}\right)^{1/2}\ln\left[\frac{\Lambda}{2m}+\left(\frac{\Lambda^2}{4m^2}-1\right)^{1/2}\right]\right\}\right)\right], \tag{3.43a}$$

$$B_\mu-I_\mu+B_{1\mu}=\mu\frac{(4\pi\alpha)^2}{(2\pi)^2}\frac{4}{3}\frac{\boldsymbol{\sigma}_e\cdot\boldsymbol{\sigma}_p}{M^2-m^2}Op(\Lambda^2)\left[\left\{\tfrac{1}{2}\pi\left(\frac{M-m}{\Lambda}\right)-\left(\frac{1}{4}-\frac{m^2}{\Lambda^2}\right)^{1/2}\ln\left[\frac{\Lambda}{2m}+\left(\frac{\Lambda^2}{4m^2}-1\right)^{1/2}\right]\right.\right.$$
$$\left.-\left(\frac{M^2}{\Lambda^2}-\frac{1}{4}\right)^{1/2}\sin^{-1}\left(1-\frac{\Lambda^2}{4M^2}\right)^{1/2}\right\}-\frac{\Lambda^2}{4M^2}\left(\left[\ln\frac{\Lambda}{M}-\left(\frac{4M^2}{\Lambda^2}-1\right)^{1/2}\sin^{-1}\left(1-\frac{\Lambda^2}{4M^2}\right)^{1/2}\right]\right.$$
$$\left.\left.-\frac{M^2}{m^2}\left\{\ln\frac{\Lambda}{m}-\left(1-\frac{4m^2}{\Lambda^2}\right)^{1/2}\ln\left[\frac{\Lambda}{2m}+\left(\frac{\Lambda^2}{4m^2}-1\right)^{1/2}\right]\right\}\right)\right], \tag{3.43b}$$

and

$$B_{\mu\mu}=\mu^2\frac{(4\pi\alpha)^2}{(2\pi)^2}\frac{1}{24}\frac{\boldsymbol{\sigma}_e\cdot\boldsymbol{\sigma}_p}{M^2-m^2}Op(\Lambda^2)\left(\frac{-6\Lambda^2}{M^2}\left[\ln\frac{\Lambda}{M}+\left(\frac{4M^2}{\Lambda^2}-1\right)^{1/2}\sin^{-1}\left(1-\frac{\Lambda^2}{4M^2}\right)^{1/2}\right]\right.$$
$$+\frac{2\Lambda^2}{M^2}\left(\frac{M^2}{m^2}+2\right)\left\{\ln\frac{\Lambda}{m}-\left(1-\frac{4m^2}{\Lambda^2}\right)^{1/2}\ln\left[\frac{\Lambda}{2m}+\left(\frac{\Lambda^2}{4m^2}-1\right)^{1/2}\right]\right\}+\frac{\Lambda^2(M^2-m^2)}{2m^4M^2}$$
$$\left.\times\left\{m^2+2m^2\ln\frac{\Lambda}{m}-\Lambda^2\ln\frac{\Lambda}{m}+\Lambda^2\left(1-\frac{4m^2}{\Lambda^2}\right)^{1/2}\ln\left[\frac{\Lambda}{2m}+\left(\frac{\Lambda^2}{4m^2}-1\right)^{1/2}\right]\right\}\right). \tag{3.43c}$$

The correction to the potential therefore leads to an energy change of $|\hat{\psi}_e(0)|^2\langle\Delta V_{\text{eff}}^{(4)(s)}\rangle$, where the expectation value is over the appropriate spin states. The evaluation of this leads to a relative correction of

$$3.6\text{ ppm} \tag{3.44}$$

for the hfs of hydrogen. This may be interpreted as a recoil correction [$O(m\alpha/M$ hfs)] suitably modified by the proton form factors. When this correction is added to the much larger nonrelativistic size correction of (3.25) (−38.2 ppm), we obtain a total of

$$-34.6\text{ ppm}. \tag{3.45}$$

This is in complete agreement with the correction obtained by Iddings and Platzman.[1]

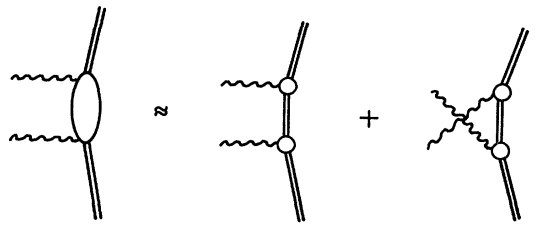

FIG. 4. Approximation of virtual Compton scattering off a proton.

In the limit of a point proton, the correction becomes

$$\frac{m\alpha}{M}E_F[\pi(1+\mu)]^{-1}$$

$$\times\left[-3(1-\tfrac{1}{4}\mu^2)\ln\frac{M}{m}-\mu^2\left(+\frac{15}{16}+\frac{9}{4}\ln\frac{\Lambda}{M}\right)\right]. \quad (3.46)$$

This expression does not agree with the corresponding result of Newcomb and Salpeter,[30] which is

$$\frac{m\alpha}{M}E_F[\pi(1+\mu)]^{-1}$$

$$\times\left[-3(1-\tfrac{1}{4}\mu^2)\ln\frac{M}{m}-\mu^2\left(-\frac{1}{8}+\frac{9}{4}\ln\frac{2\Lambda'}{M}\right)\right], \quad (3.47)$$

where Λ' is a cutoff. As pointed out by Guerin,[33] who also obtains (3.46), the difference between (3.46) and (3.47) is due to the noncovariant introduction of a cutoff Λ', which is allowed to approach infinity whenever this would not cause a divergence.

D. Discussion

Aside from reduced mass corrections, the nuclear corrections to the hfs may be separated into three types:

(1) A size correction, first obtained by Zemach, of −38.2 ppm.

(2) A *small* recoil correction of 3.6 ppm, calculated for an extended proton. In the limit $M\to\infty$ this term vanishes, but in the limit $\Lambda\to\infty$ a logarithmic divergence appears.

(3) The proton polarization corrections, which have not yet been completely calculated.

In this paper our concern has been only with the first two terms. The separation into these two terms is useful since the difference between the results of Zemach and of Iddings and Platzman is exactly the 3.6 ppm which we have calculated. It is important to emphasize that the bulk of the correction is the −38.2 ppm above and that the calculation of this is quite simple. On the other hand, the additional small contribution of 3.6 ppm is much more difficult to obtain.

Now we should like to describe briefly the situation with respect to the remaining contributions which have been lumped together as proton polarization corrections. These have been entirely ignored in this paper but have been discussed by many authors.

First of all, there is the problem of excited-state contributions to the virtual Compton diagram. In our work, these have been avoided by approximating the diagram as illustrated in Fig. 4. Various authors have studied the excited-state contributions to the hfs and have estimated these at less than 1 ppm.[32–35] More recently, Drell and Sullivan[36] have re-examined the polarizability corrections with several nonrelativistic models and find contributions of several parts per million. They conclude that our uncertainty of proton dynamics is such that one cannot rule out the possibility of fairly sizeable corrections.

A second problem concerns the use of the usual on-the-mass-shell form factors to describe the vertex functions which arise when the intermediate state is a virtual proton. However, we have seen that most of the nuclear contribution which we have obtained comes from the nonrelativistic size term, in which the proton is on its mass shell. Therefore, we might hope that off-the-mass-shell effects will be unimportant since they would affect only the recoil correction of 3.6 ppm which is quite small already. In any case, a correct and complete calculation of the proton polarizability would include these effects.

IV. NUCLEAR MOTION CORRECTIONS TO THE FINE STRUCTURE

A. Reduced Mass Corrections

The nuclear motion corrections to the fine structure levels are of two types:

(1) Reduced mass corrections.
(2) Additional recoil terms of order $(\alpha m/M)$ fs.

The reduced mass corrections were originally computed by Breit and Brown.[15] In this section we will recalculate this correction in a different way; this calculation also appears in a recent article which we have written.[11]

From (2.13) it is easily shown that the eigenvalue E is related to E_1 by

$$E=E_1+[(E_1^2-m^2)/2M]. \quad (4.1)$$

The energy E_1 may be found by solving the equation*

$$\frac{E_1[1-(m^2/E_1M)]}{[1-(m^2/M^2)]^{1/2}}=\frac{m[1-(E_1/M)]}{[1-(m^2/M^2)]^{1/2}}f\left(n,j,\frac{\alpha}{[1-(m^2/M^2)]^{1/2}}\right).$$

* The function $f(n,j,\alpha)$ is given by

$$f(n,j,\alpha)=\{1+(\alpha/\{n-(j+\tfrac{1}{2})+[(j+\tfrac{1}{2})^2-\alpha^2]^{1/2}\})^2\}^{-1/2}.$$

This relation, obtained from Eq. (2.16), is a consequence of the fact that we are dealing with the Dirac equation for a Coulomb potential.

The value of E_1 is

$$E_1=\frac{mf+(m^2/M)}{1+(m/M)f}, \tag{4.2}$$

and therefore

$$E=m+\frac{m(f-1)\,[1-(m^2/M^2)]}{1+(m/M)f}+\frac{m^2}{2M}(f-1)^2\frac{[1-(m/M)]^2}{[1+(m/M)f]^2}. \tag{4.3}$$

Expanding in powers of $f-1$ to second order we obtain

$$E=m+\frac{m(f-1)\,[1-(m^2/M^2)]}{1+(m/M)}+\frac{m^2}{2M}(f-1)^2\frac{[1-(m/M)]\,[-1-(3m/M)]}{[1+(m/M)]^2}. \tag{4.4}$$

Using

$$f\left(n,j,\frac{\alpha}{[1-(m^2/M^2)]^{1/2}}\right)-1=-\frac{1}{2n^2}\frac{\alpha^2}{1-(m^2/M^2)}\times\left[1+n^{-1}\left(\frac{\alpha^2}{1-(m^2/M^2)}\right)\left(\frac{1}{j+\frac{1}{2}}-\frac{3}{4n}\right)+O(\alpha^4)\right],$$

we obtain

$$E=m+\frac{m}{1+(m/M)}[f(n,j,\alpha)-1]+O\left(\frac{m^2}{M}\frac{\alpha^4}{n^4}\right)+O\left(\frac{m^2}{M^2}\text{fs}\right)+O\left(\frac{m}{M}\frac{\alpha^2}{n^2}\text{fs}\right). \tag{4.5}$$

It should be mentioned that the term

$$m[1+(m/M)]^{-1}[f(n,j,\alpha)-1]$$

contains some terms of the same magnitude as those which were discarded. For practical purposes these may be discarded also, but since they are very small it does no harm to retain them. For example, terms like $(m/M)^2$ fs are still too small to measure in the hydrogen atom.

Equation (4.5) contains the fine-structure levels as well as the reduced mass correction to these levels.

B. Additional Recoil Corrections

Salpeter[28] originally derived additional recoil corrections (beyond reduced mass) by using the Bethe–Salpeter equation. As mentioned earlier, the work of Breit, Brown, and Arfken[19] did not obtain terms of the type $(\alpha m/M)$ fs; the absence of such terms is associated with use of single-particle theory rather than hole theory. The results of Salpeter were later confirmed by Fulton and Martin,[37] who employed the methods of Schwinger, of Karplus and Klein, and of Fulton and Karplus.[38–40]

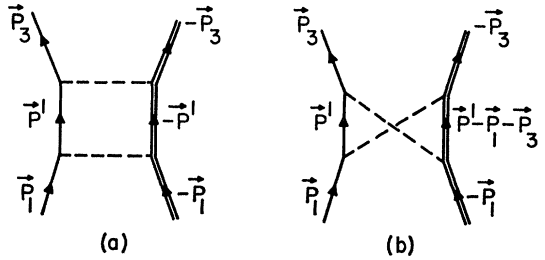

FIG. 5. Double Coulomb scattering from a nonstatic proton. (a) Ladder graph. (b) Crossed graph.

The recoil corrections referred to above are also calculable by the effective potential approach. The contributions are of three types. The first involves corrections to the exchange of two Coulomb photons. The second is obtained by considering recoil when one transverse photon is transferred. The third and last takes into account processes in which two transverse photons are present.

These three contributions will be evaluated for the $2S$ state of hydrogen. Contributions for other states may be obtained in a similar way.

1. Coulomb Correction, ΔE_{cc}

The lowest-order potential contains an instantaneous Coulomb interaction. The iteration of this part of the potential,

$$\int\frac{d^3p'}{(2\pi)^3}\frac{e^2}{(\mathbf{p}'-\mathbf{p}_3)^2}\times[E-(\mathbf{p}'^2/2M)-\boldsymbol{\alpha}\cdot\mathbf{p}'-\beta m]^{-1}[e^2/(\mathbf{p}_1-\mathbf{p}')^2], \tag{4.6}$$

describes double Coulomb interactions and should account for part of the scattering obtained from the second-order Feynman diagrams, Figs. 5(a) and 5(b). The use of slanted lines for Fig. 5(b) should not be misunderstood. In the crossed graph the interactions are really instantaneous, and if we decomposed this graph into time-ordered graphs, the lines would be horizontal. The intermediate states would involve a proton, two electrons, and a positron or an electron, two protons, and an antiproton. The dashed notation tells us to use a γ_0 at the vertices and photon propagators containing only three-momentum transfer.

The diagrams of Fig. 5(b) symbolize the amplitude

$$\frac{(4\pi\alpha)^2}{(2\pi)^4}\int d^4p'\bar{u}(p_3)\gamma_0(\not{p}'-m+i0)^{-1}\gamma_0 u(p_1)\bar{u}_p(p_4)\gamma_0\times[(p_2-p'+p_1-M+i0)^{-1}+(p_4+p'-p_1-M+i0)^{-1}]\times\gamma_0 u_p(p_2)\,[1/(\mathbf{p}_1-\mathbf{p}')^2]\,[1/(\mathbf{p}'-\mathbf{p}_3)^2]. \tag{4.7}$$

If we set E_1+E_2-M equal to E, the contribution to the ladder graph of (4.7) from the proton pole in the upper half of the complex E' plane corresponds

to the scattering predicted by (4.6), provided we treat the proton nonrelativistically. The relativistic region of the proton is unimportant in evaluating the correction. Furthermore, the proton pole of the crossed graph, which is located at $E'<-2M$, also does not contribute to order M^{-1}.

The only remaining pole in the upper-half plane comes from the electron propagator. When this pole is taken into account and the contribution evaluated to order M^{-1} and the external proton lines are assumed on the mass shell, we obtain an addition to the potential

$$\frac{-(4\pi\alpha)^2}{(2\pi)^3}\int d^3p'\left[\frac{-(\mathbf{p}'^2+m^2)^{1/2}\gamma_0-\mathbf{p}'\cdot\boldsymbol{\gamma}+m}{-2(\mathbf{p}'^2+m^2)^{1/2}}\right]\gamma_0 2M\,\frac{1}{(\mathbf{p}'-\mathbf{p}_3)^2}\,\frac{1}{(\mathbf{p}_1-\mathbf{p}')^2}$$
$$\times\left[\frac{-2\mathbf{p}'^2-2\mathbf{p}_1\cdot\mathbf{p}_3-2\mathbf{p}'\cdot(\mathbf{p}_1+\mathbf{p}_3)}{\{[m+(\mathbf{p}'^2+m^2)^{1/2}]^2+2M[m+(\mathbf{p}'^2+m^2)^{1/2}]\}\{[m+(\mathbf{p}'^2+m^2)^{1/2}]^2-2M[m+(\mathbf{p}'^2+m^2)^{1/2}]\}}\right]. \quad (4.8)$$

In obtaining (4.8) we have approximated E_1 by the mass of the electron. The bound-state wave functions will tend to emphasize values of p_1 and p_3 near the Bohr momentum when (4.8) is treated as a perturbation. The values of p' which are important are much larger, and therefore the leading contribution may be obtained by setting p_1 and p_3 equal to zero as compared to p'. With these approximations, (4.8) leads to a contribution of

$$\frac{-4\alpha^2}{M}|\hat{\psi}_{n,l}(0)|^2\int_0^\infty\frac{\mathbf{p}'^2d\mathbf{p}'}{(\mathbf{p}'^2+m^2)^{1/2}[m+(\mathbf{p}'^2+m^2)^{1/2}]^3} \quad (4.9)$$

The integral in (4.9) is easily done, and the result for the $2S$ state is

$$\Delta E_{cc}=-\tfrac{4}{3}(\alpha^2/mM)\,|\hat{\psi}_{2S}(0)|^2, \quad (4.10)$$

in complete agreement with that obtained by Fulton and Martin.[37] It should be pointed out that the result quoted in Salpeter's paper [see Eq. (3.6) of Salpeter[28]] should be multiplied by a factor of 2. This error has been noted in the past (see Footnote 1, page 102 of Bethe and Salpeter[16]).

2. *Single-Transverse-Photon-Correction, ΔE_T*

The recoil correction to the fine-structure levels involving a single transverse photon requires special treatment. Since there are contributions of order $(\alpha m/M)$ fs arising from very small values of momenta ($p\sim m\alpha$), it is not possible to ignore atomic binding in the atom; for the hfs it was possible to set the binding energy equal to zero in evaluating the small corrections, because the important values of momenta were much larger than binding effects.

This illustrates a serious problem one faces in dealing with the Feynman graphs in the bound-state problem; the expansion in terms of the fine-structure constant is often not simple since many Feynman graphs may be needed. In fact, in the present situation, the need for binding corrections suggests the necessity of considering all Coulomb exchanges occurring during the time interval between the emission and the absorption of the transverse photon. It is quite clear that one cannot easily perform the sum over all the required graphs, and therefore an alternative method is needed.

Previous calculations of this correction have been done by separating the energy of the transverse photon into a low- and a high-frequency part. Three-dimensional perturbation theory was used for the low-frequency part, whereas the high-frequency part was treated by four-dimensional methods. Actually, Salpeter also handled the high-frequency part by a three-dimensional method.

Our calculation is very similar to previous ones except that we do not invoke a separation into low- and high-frequency parts. We also use only three-dimensional perturbation theory. The perturbation Hamiltonian H' responsible for emission and absorption of transverse photons is

$$H'=e\int\frac{d^3k}{(2k)^{1/2}}$$
$$\times\{\boldsymbol{\alpha}_e\cdot[\mathbf{a}_\perp(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{x}_e)+\mathbf{a}_\perp^\dagger(\mathbf{k})\exp(-i\mathbf{k}\cdot\mathbf{x}_e)]$$
$$-\boldsymbol{\alpha}_p\cdot[\mathbf{a}_\perp(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{x}_p)+\mathbf{a}_\perp^\dagger(\mathbf{k})\exp(-i\mathbf{k}\cdot\mathbf{x}_p)]\}, \quad (4.11)$$

where $\mathbf{a}_\perp(\mathbf{k})$ and $\mathbf{a}_\perp^\dagger(\mathbf{k})$ are the usual destruction and creation operators for a transverse photon of momentum $\mathbf{k}$. The second-order perturbation of the energy corresponding to an exchanged transverse photon is therefore

$$\frac{-2e^2}{(2\pi)^3}\int\frac{d^3k}{2k}\sum_m\frac{\langle n|\,\boldsymbol{\alpha}_{e\perp}\exp(i\mathbf{k}\cdot\mathbf{x}_e)\,|m\rangle\cdot\langle m|\,\boldsymbol{\alpha}_{p\perp}\exp(-i\mathbf{k}\cdot\mathbf{x}_p)\,|n\rangle}{E_n-E_m-k}, \quad (4.12)$$

where E_m and E_n are the energies of the intermediate and initial unperturbed atomic states. The factor of 2 in front of the integral accounts for the two ways in which emission and subsequent absorption can occur.

If one makes the approximation of discarding E_n-E_m in (4.12) (corresponding to ignoring the recoil corrections of interest here), the result is simply the Breit interaction. The correction to this is therefore

$$\frac{-4\pi\alpha}{8\pi^3}\int d^3k\sum_m \frac{\langle n\mid \boldsymbol{\alpha}_{e\perp}\exp(i\mathbf{k}\cdot\mathbf{x}_e)\mid m\rangle\cdot\langle m\mid \boldsymbol{\alpha}_{p\perp}\exp(-i\mathbf{k}\cdot\mathbf{x}_p)\mid n\rangle(E_n-E_m)}{k^2(E_n-E_m-k)}. \tag{4.13}$$

We are interested in corrections of order M^{-1}. Since $\boldsymbol{\alpha}_{p\perp}$ introduces one power of M^{-1} by virtue of its coupling to the small components of the proton wave function, we replace $\boldsymbol{\alpha}_{p\perp}$ by $-\mathbf{p}_{e\perp}/M$ and thereafter use ordinary Coulomb wave functions, eigenfunctions of $\boldsymbol{\alpha}_e\cdot\mathbf{p}_e+\beta m+V$. With this approximation and the nonrelativistic approximation of replacing $\boldsymbol{\alpha}_{e\perp}$ by $\mathbf{p}_{e\perp}/m$, we obtain in the center-of-mass system

$$\frac{\alpha}{2\pi^2 mM}\int\frac{d^3k}{k^2}\times\sum_m\frac{\langle n\mid \mathbf{p}_\perp\exp(i\mathbf{k}\cdot\mathbf{r})\mid m\rangle\cdot\langle m\mid \mathbf{p}\mid n\rangle(E_n-E_m)}{E_n-E_m-k}, \tag{4.14}$$

where $\mathbf{r}=\mathbf{x}_e-\mathbf{x}_p$ and $\mathbf{p}$ is the conjugate momentum.

We write the exponential above as

$$1+[\exp(i\mathbf{k}\cdot\mathbf{r})-1]$$

and then separate the contribution ΔE_T into two terms, ΔE_{T1} and ΔE_{T2}, such that

$$\Delta E_T=\lim_{\Lambda\to\infty}(\Delta E_{T1}+\Delta E_{T2}) \tag{4.15}$$

and

$$\Delta E_{T1}=\frac{\alpha}{2\pi^2 mM}\int^\Lambda\frac{d^3k}{k^2}\times\sum_m\frac{\langle n\mid \mathbf{p}_\perp\mid m\rangle\cdot\langle m\mid \mathbf{p}\mid n\rangle(E_n-E_m)}{E_n-E_m-k}, \tag{4.16a}$$

$$\Delta E_{T2}=\frac{\alpha}{2\pi^2 mM}\int^\Lambda\frac{d^3k}{k^2}\times\sum_m\frac{\langle n\mid \mathbf{p}_\perp[\exp(i\mathbf{k}\cdot\mathbf{r})-1]\mid m\rangle\cdot\langle m\mid \mathbf{p}\mid n\rangle(E_n-E_m)}{E_n-E_m-k}. \tag{4.16b}$$

The evaluation of ΔE_{T1} is accomplished by using the Bethe logarithm.[41] After doing the k integration in (4.16a), we obtain

$$\Delta E_{T1}=(-\alpha/2\pi^2 mM)\times\sum_m\langle n\mid \mathbf{p}_\perp\mid m\rangle\cdot\langle m\mid \mathbf{p}\mid n\rangle\ln\mid\Lambda/(E_n-E_m)\mid. \tag{4.17}$$

The logarithm is a slowly varying function, and we therefore replace it by an average value

$$\ln\mid\Lambda/\langle E_n-E_m\rangle_{\mathrm{Av}}\mid.$$

The sum over states is then easily evaluated for s states, the result for $2S$ being

$$\Delta E_{T1}=\tfrac{8}{3}(\alpha^2/mM)\mid\psi_{2S}(0)\mid^2\ln\mid\Lambda/\langle E_n-E_m\rangle_{\mathrm{Av}}\mid. \tag{4.18}$$

The logarithm appearing in (4.18) has been evaluated to a high degree of accuracy for $n=2$ and also for other values of the principal quantum number.[42]

The computation of ΔE_{T2} is somewhat more complicated than that of ΔE_{T1}. However, the appearance of the factor $\exp(i\mathbf{k}\cdot\mathbf{r})-1$ in (4.16b) suggests that appreciable contributions come only from values of k which satisfy $\mathbf{k}\cdot\mathbf{r}\gg 0$. This will require $k\gg m\alpha^2$, and therefore we may ignore E_m-E_n in the denominator of (4.16b), which may then be rewritten as

$$\Delta E_{T2}\approx\frac{\alpha}{2\pi^2 mM}\int^\Lambda\frac{d^3k}{k^3}\sum_m\langle n\mid \mathbf{p}_\perp[\exp(i\mathbf{k}\cdot\mathbf{r})-1]\mid m\rangle\cdot\langle m\mid[\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m+V,\mathbf{p}]\mid n\rangle. \tag{4.19}$$

Using $[\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m+V,\mathbf{p}]=i\nabla V=\alpha\mathbf{r}/r^3$, we obtain

$$\Delta E_{T2}\approx\frac{\alpha^2 i}{2\pi^2 mM}\int^\Lambda\frac{d^3k}{k^3}\times\langle n\mid[\mathbf{p}-(\mathbf{p}\cdot\mathbf{k}\mathbf{k}/\mathbf{k}^2)]\cdot(\mathbf{r}/r^3)[\exp(i\mathbf{k}\cdot\mathbf{r})-1]\mid n\rangle \tag{4.20}$$

after summing over the intermediate states.

For $n=2$ we obtain

$$\Delta E_{T2}\approx\frac{\alpha^2(m\alpha)}{2\pi^2 mM}\frac{(m\alpha)^3}{8\pi}\times\left[1+\frac{3}{4}m\alpha\frac{d}{d(m\alpha)}+\frac{1}{8}(m\alpha)^2\frac{d^2}{d(m\alpha)^2}\right]\times\int d^3r\int^\Lambda\frac{d^3k}{k^3}\left(\hat{\mathbf{r}}-\frac{\hat{\mathbf{r}}\cdot\mathbf{k}\mathbf{k}}{\mathbf{k}^2}\right)\cdot\frac{\mathbf{r}}{r^3}[\exp(i\mathbf{k}\cdot\mathbf{r})-1]e^{-m\alpha r}. \tag{4.21}$$

The angular integral over k in (4.21) is quite straightforward and gives

$$2\pi\int_0^\Lambda\frac{dk}{k}\int d^3r e^{-m\alpha r}\frac{1}{r^2}\left[\frac{4j_1(kr)}{kr}-\frac{4}{3}\right], \tag{4.22}$$

where j_1 is a spherical Bessel function. In terms of ordinary Bessel functions, (4.22) may be written as

$$32\pi^2\int_0^\Lambda\frac{dk}{k}\int_0^\infty dr e^{-m\alpha r}\left[(\tfrac{1}{2}\pi)^{1/2}\frac{J_{3/2}(kr)}{(kr)^{3/2}}-\frac{1}{3}\right]. \tag{4.23}$$

The integral over r may be done using the aid of a good set of integral tables (e.g., Ryshik and Gradstein[43]). We obtain

$$32\pi^2\int_0^\Lambda \frac{dk}{k}(3m\alpha)^{-1}\left[F\left(\frac{1}{2},1;\frac{5}{2};\frac{-k^2}{m^2\alpha^2}\right)-1\right], \quad (4.24)$$

where F is a hypergeometric function. The remaining integration may be accomplished most readily by using an integral representation of the hypergeometric function.

The final result, after taking the indicated derivatives in (4.21), is

$$\Delta E_{T2}=(8\alpha^2/3mM)\,|\hat{\psi}_{2S}(0)|^2[\tfrac{25}{12}-\ln(\Lambda/m\alpha)]. \quad (4.25)$$

Combining (4.25) with (4.18) we obtain ΔE_T for the $2S$ state. We have

$$\Delta E_T=(8\alpha^2/3mM)\,|\hat{\psi}_{2S}(0)|^2 \times(\tfrac{25}{12}+\ln|m\alpha/\langle E_2-E_m\rangle_{\rm Av}|). \quad (4.26)$$

Note that the dependence on Λ is now gone. This result is in complete agreement with that previously obtained.[28,37]

3. *Two-Transverse-Photon Correction, ΔE_{TT}*

The recoil corrections of interest here contain only one inverse power of the proton mass. The proton pole terms arising from the diagrams in which two transverse photons are exchanged are of order M^{-2} and are therefore discarded (they also reproduce appropriate terms in the iteration).

We may therefore approximate [to $\mathbf{O}(M^{-1})$] the addition to the potential as

$$\frac{i\alpha^2}{\pi^2 M}\int d^4p'\,\frac{(E'-m)\,\boldsymbol{\delta}_{\perp(1)}\cdot\boldsymbol{\delta}_{\perp(3)}}{E'^2-\mathbf{p}'^2-m^2+i0} \times[(p'-p_3)^2+i0]^{-1}[(p_1-p')^2+i0]^{-1}. \quad (4.27)$$

In obtaining (4.27) we have evaluated the proton factors to order M^{-1} between free spinors, and we assume a coupling only to the large components of the electron wave function. It may be shown that coupling to the small components introduces additional powers of the fine-structure constant.

The addition to the potential (4.27) corresponds to the so-called "seagull graph" shown in Fig. 6. In fact, this graph is equivalent to the contact term $e^2\mathbf{A}_\perp^2/2M$ which arises from the usual "minimal" coupling, when the proton is treated nonrelativistically.

In evaluating $\boldsymbol{\delta}_{\perp(1)}\cdot\boldsymbol{\delta}_{\perp(3)}$ we retain only the part which is spin independent since we are looking for fine-structure corrections in S states. The spin-independent part is

$$1+(\mathbf{q}_1\cdot\mathbf{q}_3)^2/\mathbf{q}_1^2\mathbf{q}_3^2=1+\cos^2\theta_{q_1q_3}, \quad (4.28)$$

where $\mathbf{q}_1=\mathbf{p}_1-\mathbf{p}'$ and $\mathbf{q}_3=\mathbf{p}'-\mathbf{p}_3$. For values of p' much larger than p_1 and p_3, $\cos\theta_{q_1q_3}$ will be replaced by unity.

The integral over E' in (4.27) is most easily accomplished by contour methods. The poles in the upper half-plane arise from the vanishing of each of the three denominators. We obtain

$$\frac{-2\alpha^2}{\pi M}\int d^3p'(1+\cos^2\theta_{q_1q_3})\left[\left(\frac{m+(\mathbf{p}'^2+m^2)^{1/2}}{2(\mathbf{p}'^2+m^2)^{1/2}}\right)[2m^2+2m(\mathbf{p}'^2+m^2)^{1/2}-\mathbf{p}_1^2+2\mathbf{p}_1\cdot\mathbf{p}']^{-1}\right.$$
$$\left.\times[2m^2+2m(\mathbf{p}'^2+m^2)^{1/2}-\mathbf{p}_3^2+2\mathbf{p}_3\cdot\mathbf{p}']^{-1}+[2(q_3+q_1)]^{-1}\left(\frac{2m-q_1-q_3}{(-2mq_3+\mathbf{q}_3^2-\mathbf{p}'^2)(-2mq_1+\mathbf{q}_1^2-\mathbf{p}'^2)}\right)\right], \quad (4.29)$$

where $q_1=|\mathbf{q}_1|$ and $q_3=|\mathbf{q}_3|$. There are no factors of the external momenta in the numerator which would tend to emphasize large values of p_1 or p_3 (i.e., $\gg m\alpha$). This does not imply that we may set p_1 or p_3 equal to zero in all places since there are contributions coming from small values of p'. However, we may simplify (4.29) considerably by letting p_1 and $p_3\to 0$ in those integrals which emphasize large p'. We then have

$$\frac{-2\alpha^2}{\pi M}\int d^3p'(1+\cos^2\theta_{q_1q_3}) \times\left[\frac{1}{8m^2(\mathbf{p}'^2+m^2)^{1/2}[m+(\mathbf{p}'^2+m^2)^{1/2}]}-\frac{1}{8m^2q_1q_3} +\frac{1}{4mq_1q_3(q_1+q_3)}\right]. \quad (4.30)$$

The various terms of (4.30) are separately divergent for large p' but these divergences all cancel. At this stage it is quite clear that the first two terms of (4.30) come from values of p' much larger than the Bohr momentum, and therefore we may set

$$\cos^2\theta_{q_1q_3}=1.$$

However, the third term of (4.30) clearly has a con-

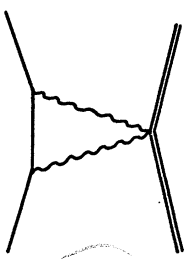

FIG. 6. Seagull graph.

tribution from small p'. Therefore (4.30) may be rewritten as $\Delta V_{TT}=\Delta V_{TT1}+\Delta V_{TT2}$, with

$$\Delta V_{TT1}=\frac{\alpha^2}{2\pi mM}\int d^3p'\,\frac{1}{\mathbf{p}'^2(\mathbf{p}'^2+m^2)^{1/2}} \quad (4.31a)$$

and

$$\Delta V_{TT2}=\frac{-\alpha^2}{2\pi mM}\int d^3p'\,\frac{(1+\cos^2\theta_{q_1q_3})}{q_1q_3(q_1+q_3)}. \quad (4.31b)$$

The correction to the energy levels is therefore

$$\Delta E_{TT}=\int d^3p_1 d^3p_3 \hat{\phi}^\dagger(\mathbf{p}_3)\Delta V_{TT}(\mathbf{p}_1,\mathbf{p}_3)\hat{\phi}(\mathbf{p}_1). \quad (4.32)$$

The evaluation of ΔE_{TT} is most readily accomplished by separating the p' integral into the regions $p'<B$ and $p'>B$, where B is much larger than $m\alpha$ and also much smaller than m. The contribution from $p'>B$ is

$$\Delta E_{TT}{}^{>B}\approx\frac{\alpha^2}{2\pi mM}\,|\,\hat{\psi}_{2S}(0)\,|^2 \times 4\pi\int_B^\infty dp'\left[\frac{1}{(\mathbf{p}'^2+m^2)^{1/2}}-\frac{1}{p'}\right] \approx\frac{2\alpha^2}{mM}\,|\,\hat{\psi}_{2S}(0)\,|^2\ln\frac{2B}{m}. \quad (4.33)$$

In obtaining (4.33) we have neglected B compared to m in certain terms which appear in the logarithms which arise.

In the region from $p'=0$ to $p'=B$ the contribution to ΔV_{TT1} is quite small. Therefore, to the desired accuracy, the contribution comes entirely from ΔV_{TT2} and is

$$\Delta E_{TT}{}^{<B}\approx\frac{-\alpha^2}{2\pi mM}\int^B d^3p_1 d^3p_3 d^3p'\hat{\phi}^\dagger(\mathbf{p}_3) \times\left[\frac{1+\cos^2\theta_{q_1q_3}}{q_1q_3(q_1+q_3)}\right]\hat{\phi}(\mathbf{p}_1). \quad (4.34)$$

This is exactly the integral which appears in (4.27) of Fulton and Martin.[37] It has been evaluated in an exact way by these authors and in an approximate way by Salpeter.[28] Therefore we merely quote the result and refer the reader to the article of Fulton and Martin for a brief discussion of the manner in which this integral may be handled. We have

$$\Delta E_{TT}{}^{<B}\approx\frac{+2\alpha^2}{mM}\,|\,\hat{\psi}_{2S}(0)\,|^2 \times\left[\ln\frac{m\alpha}{2B}+\frac{7}{4}+\frac{4}{3}(1-\ln 2)\right]. \quad (4.35)$$

When this is combined with (4.33) we obtain

$$\Delta E_{TT}=\frac{+2\alpha^2}{mM}\,|\,\hat{\psi}_{2S}(0)\,|^2\left[\ln\alpha+\frac{7}{4}+\frac{4}{3}(1-\ln 2)\right] \quad (4.36)$$

for the correction due to the exchange of two transverse photons.

When (4.36) is combined with (4.26) and (4.10) we obtain the complete recoil correction of order $(\alpha m/M)$ fs for the $2S$ state of atomic hydrogen. Our result is in total agreement with the work of Salpeter and of Fulton and Martin. The contribution of the recoil corrections to the $2P$ state has not been given here, but it may be found in a similar way. It is quite small by comparison to the $2S$ correction. Our results provide a partial confirmation of the part of the splitting $2S_{1/2}-2P_{1/2}$ due to recoil corrections to the fine structure. This correction is certainly involved in the theoretical and experimental determination of the Lamb shift.

V. DISCUSSION

The principal aim of the present work has been to provide a conceptually simple, unified treatment of the recoil and finite size corrections to the hyperfine and fine structure of hydrogen. Our results are in agreement with earlier calculations which have been based mainly on covariant perturbation theory using the Bethe–Salpeter equation. Aside from the recent work of Guerin[33] (which treats the hyperfine splitting), there has not been a complete treatment of these problems in any one paper; and it was not self-evident to the present authors that there might not be some small error due to a mismatch when the various pieces of the calculation are put together. In particular, some authors used the Coulomb gauge and others used the covariant gauge.

In any approximation scheme it is always valuable to include as much as possible in the initial part which can be treated completely. If one approximates at too early a stage, the number of small correction terms multiplies and the chance for a subtle error increases. In the present work, this has been accomplished at the expense of using a formalism which, while plausible, does not start with a correct bound-state equation. However, we can adopt the following philosophy. One can always use the solution to our equation (including finite size effects) as the starting approximation for a solution to the Bethe–Salpeter equation. This would replace the usual approach of using the solution of the Breit equation with the transverse-photon term omitted. The corrections to this initial approximation would then turn out to be very small, and one could bypass the detailed treatment of terms of intermediate size. Independently, our initial equation has been derived from the Bethe–Salpeter equation by Gross[44] using an approximation in which only the dominant pole in the contour integration over the internal energy is retained. This pole is the proton positive energy pole, so that the equation which remains after the energy integration is a Dirac equation for the electron with an effective potential.

TABLE I. Fine-structure-constant discrepancy (the nature of the uncertainty is indicated in parentheses).

Fine structure[a]	$\alpha_{fs}^{-1}=137.0388\pm0.0012$ (exptl)
Solid state[b]	$\alpha_{ss}^{-1}=137.0359\pm0.0008$ (exptl—two std. dev.)
Muonium[c]	$\alpha_{\text{muonium}}^{-1}=137.0383\pm0.0026$ (exptl)
Electron[d] $g-2$	$\alpha_{(g-2)}^{-1}=137.0382\pm0.0064$ (exptl)
Hyperfine structure[e]	$\alpha_{\text{hfs}}^{-1}=137.0358\pm0.0002$ (known theory) $\pm$ (unknown theory)

[a] Reference 50.
[b] Reference 10.
[c] W. E. Cleland, J. M. Bailey, M. E. Eckhause, V. W. Hughes, R. M. Mobley, R. Prepost, and J. E. Rothberg, Phys. Rev. Letters **13**, 202 (1964).
[d] D. T. Wilkinson and H. R. Crane, Phys. Rev. **130**, 852 (1963).
[e] Reference 2.

We should remind the reader here of the nonuniqueness of the lowest-order potential. Several different potentials (using different gauges) give the same first Born approximation to the scattering, but yield rather different results when used in a bound-state problem. Presumably these differences would be reflected in different, second-order contributions to the potential, but it is clearly advisable to include as much as possible in the effective first-order potential. Thus it turns out that the Breit potential is a better choice than one derived from a covariant gauge. For some refinements in the correct choice of the lowest-order potential, the reader is referred back to the discussion following Eq. (3.30).

Our approach to nuclear corrections, through the use of a modified Dirac equation, is similar in spirit to methods used by Barker and Glover[45] and by Sternheim.[46] The above authors have used the Foldy–Wouthuysen[47] transformation to approximate the exact two-body relativistic equation. In the Barker and Glover paper the lowest-order (in the fine-structure constant) nuclear corrections to the fine structure and hyperfine structure of hydrogen are obtained. The mass corrections are calculated up to and including terms of order $(m/M)^2$ for both the Dirac and Pauli parts of the interaction. The work of Sternheim is concerned with calculating very accurately the state-dependent mass corrections to the hfs of hydrogen and its isotopes.

We will now briefly compare and contrast our own work with that of Sternheim. The first point to be emphasized is that the practical aims of the two pieces of work are rather different. The present work was primarily concerned with obtaining the maximum accuracy for the $1S$ hyperfine splitting. Beyond relative order $\alpha m/M$ the calculation becomes very difficult. However, the contributions of this order come from very small distances ($\leq 1/m$) and hence turn out to give the same fractional correction to the $1S$ and $2S$ hfs; therefore they cancel in taking the ratio of the two splittings. The state-dependent corrections are of relative order $\alpha^2 m/M$ and come from larger radii ($\sim a_0$). Sternheim calculated these using nearly the same effective Hamiltonian as has been treated in this paper. In effect, he has two terms in addition to those displayed in our Eq. (2.19). The first of these (in our notation) is a correction to the time component of the potential:

$$-e\delta\phi=+(\alpha/2M^2)(\mu_p+\tfrac{1}{2})\,\boldsymbol{\delta}_p\cdot\mathbf{p}\times\boldsymbol{\nabla}(1/r). \quad (5.1)$$

It arises from the small components of the proton spinor, which we have previously ignored. The other term, whose significance will be explained shortly, is

$$-i\boldsymbol{\delta}\cdot(\mathbf{A}\times\mathbf{A})/2m, \quad (5.2)$$

where $\mathbf{A}$ is the vector potential from the proton appearing in (2.19). This term contributes whenever the components of $\mathbf{A}$ are noncommuting.

Sternheim's procedure is to make a Foldy–Wouthuysen[47] transformation of the effective Hamiltonian, keeping only those terms which contribute up to relative order $\alpha^2 m/M$. Since this is (roughly) an expansion in powers of p/m, it is valid only for distances larger than an electron Compton wavelength. It would not be adequate for a small distance contribution to a single state. This is apparent from the fact that his transformed Hamiltonian has terms with the dependence r^{-4}. He uses a small r cutoff which cancels in the contribution to the ratio of $2S$ to $1S$ hfs. Omitted terms in the expansion will be even more singular at small r, and their cutoff dependence will not cancel in the end. This implies that at some point the Foldy–Wouthuysen transformation will lead to a "false expansion,"* i.e., additional powers of p/m are of order 1 rather than of order α. Because the operators occurring in Sternheim's calculation are already singular, it is not quite obvious that higher terms in the Foldy–Wouthuysen expansion would not also contribute to the order of interest. Nevertheless, since our method of calculation yields a result in agreement with Sternheim's, this particular pathology does not actually occur.

Our calculation of the ratio is given in more detail in Appendix D and will be described here briefly. Tracing back through our calculation, it is discovered that terms of order $\alpha^2 m/M$ to the ratio can come from only five places, which are the following:

(i) A contribution of relative order $\alpha^2 m/M$ to the effective mass m' in Eq. (2.16).

(ii) A normalization correction to the wave function, which was noted in Sec. II. C to be of relative order $\alpha^2 m/M$.

(iii) The $-[\mathbf{p}^2, W]\psi_1/4M$ contribution to the wave function, which was noted in Sec. II. C to be of relative order $\alpha^2 m/M$ at a Bohr radius.

(iv) The contribution of (5.1), which comes from the small components of the electron's wave function.

* A false expansion is one in which the order in α increases less rapidly than would be estimated by assigning typical values to the momentum and coordinate operators.

(v) The residual effects of the two-photon contributions which are not already contained in our treatment of the lowest-order potential. These include a term of the form (5.2) as well as the second-order magnetic-moment interaction. The second-order magnetic-moment interaction can be split into two terms corresponding, respectively, to positive- and negative-energy intermediate electron states. The former can be evaluated nonrelativistically,[48] and the latter is canceled precisely by the term in (5.2) which is quadratic in the proton's magnetic moment.

Now let us compare these in detail with various contributions from Sternheim's treatment. The contribution from (iii) is precisely canceled by a part of the contribution from (5.2) (the cross term involving the convection and magnetic parts of **A**). Accordingly, the contributions from (i), (ii), and (iv) agree precisely with Sternheim's results from the effective Hamiltonian treated in lowest order in the proton's magnetic moment. Our calculation of (i) and (ii) is trivial, and our calculation of (iv) is identical to that of Sternheim. In toto, our calculation is therefore considerably more compact. The significance of (5.2), as shown by Sternheim,[46,49] is that the two-photon interaction of the electron does *not* contain any effective interaction of the form (5.2). This contribution is necessary to cancel a similar one from the term

$$(\beta/2m)[\boldsymbol{\alpha}\cdot(\mathbf{p}+e\mathbf{A})]^2$$

which arises in the Foldy–Wouthuysen transformation. His result is confirmed explicitly in Appendix D.

Any comparison of theory and experiment in quantum electrodynamics requires of course a knowledge of the fine-structure constant and possibly of other physical constants. At the present time there is an unresolved discrepancy between the two best determinations of α. The value accepted until recently was obtained from the measurements of the fine-structure separation in deuterium by Dayhoff, Triebwasser, and Lamb.[50] It is important to note that this was obtained by adding two experimental numbers: the Lamb shift ($2S_{1/2}-2P_{1/2}$ separation) and the high-frequency separation ($2P_{3/2}-2S_{1/2}$). Clearly, the theoretical uncertainties in the shift of the S state cancel, and those in the relative shift of the P states are small. There seems to be no obstacle in the theory toward using this experiment to determine α. More recently, an entirely different determination of α was carried out by Parker, Taylor, and Langenburg,[10] who used the ac Josephson effect. Although it may seem incredible that solid-state theory is sufficiently accurate for this purpose, it appears that it is necessary to make use of only very general features like energy conservation and gauge invariance. In any case, the internal consistency of the results using different materials and experimental conditions provides the most convincing demonstration of the interpretation.

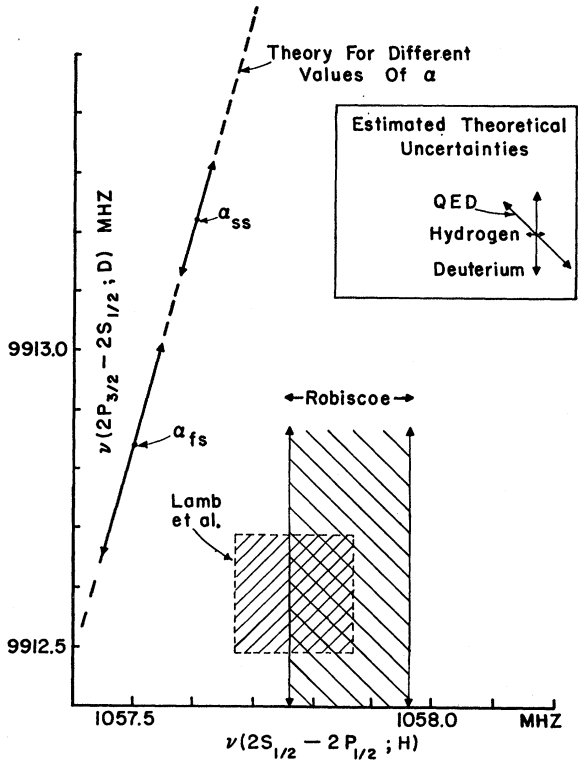

FIG. 7. Comparison of theory and experiment for the hydrogen fine structure. The shaded regions represent the experimental results. Each theoretical value has three independent uncertainties, as indicated in the box. These errors are supposed to include realistic estimates of neglected terms as well as uncertainties introduced by other experiments; they should be interpreted as a limit of error.

The situation is summarized in Table I, which includes not only the two determinations just mentioned, but also the results of other experiments expressed in terms of the value of α they would predict. Note that the indicated errors are "limits of error" which perhaps correspond to two standard deviations. With improved experimental accuracy or better theoretical understanding (as indicated), any of these experiments could resolve the discrepancy between the present two determinations. We note that if the solid-state determination is correct, a long outstanding discrepancy of about 45 ppm between theory and experiment in the hyperfine structure (hfs) would be removed. From the discussion of Sec. III. D, it would require an exceedingly large nucleon polarization effect to reconcile the hfs with the fine-structure value of α.

The disagreement between the two values of α is actually worse than is indicated by a straightforward comparison of the two values shown in Table I. This is because one value of α must predict two experimental numbers in the fine structure. The more complete situation is illustrated in Fig. 7, where we plot theoretical values of the two splittings as a function

of α together with the experimental results. The Lamb shift for H is plotted rather than that for D since it has smaller theoretical uncertainties. We see that the solid state α predicts much too large a high-frequency separation ($\sim$0.6 mHz too large), well outside the quoted error for that measurement. This seems much too large to be accounted for by any theoretical uncertainties in the Lamb shift. We can draw two conclusions from this figure: (i) The solid state α is not compatible with the fine-structure measurements. (ii) Using the fine structure α, there is a discrepancy in the Lamb shift between theory and experiment; the theory would have to be shifted about three or four times its limit of error to agree with experiment.

Before one takes the Lamb shift discrepancy too seriously, the experimental discrepancy between values of α should be resolved. If it should turn out that the high-frequency separation $(2P_{3/2}-2S_{1/2})$ should increase to yield agreement with the solid state α, the Lamb shift discrepancy would be reduced to an almost tolerable size. On the other hand, if the discrepancy persists, there are a number of possible ways it might be accounted for. One would be an error in some part of the theoretical evaluation. This seems very unlikely since all but a few very small terms have been checked by several authors.[3,4] Another would be that the contributions of the omitted terms in the perturbation expansion are unexpectedly large. Still another is that some known physical effect has been overlooked; this too seems unlikely since many competent physicists have explored a variety of possibilities. The most intriguing possibility is that some unknown physics is beginning to show up. There have been some speculations along this line.[51,52]

ACKNOWLEDGMENTS

We wish to express our thanks to our colleagues, particularly Professor H. A. Bethe, Professor F. L. Gross, Professor T. Kinoshita, and Professor E. E. Salpeter, for many helpful discussions during the course of this work.

APPENDIX A: NOTATION

The notation of Schweber's[14] book is used except as otherwise noted. We work with a metric tensor $g_{\mu\nu}=g^{\mu\nu}$ with components

$$g_{00}=-g_{11}=-g_{22}=-g_{33}=1$$

and

$$g_{\mu\nu}=0 \quad \text{for} \quad \mu\neq\nu. \tag{A.1}$$

We distinguish between covariant and contravariant vectors by using upper and lower indices. The scalar product of vectors A_μ and B^μ is

$$A_\mu B^\mu=A_0B_0-\mathbf{A}\cdot\mathbf{B}. \tag{A.2}$$

Therefore, the four-momentum p^2 is equal to $E^2-\mathbf{p}^2$. We will also use a notation defined by

$$\not{p}=p_\mu\gamma^\mu=E\gamma_0-\mathbf{p}\cdot\boldsymbol{\gamma}. \tag{A.3}$$

The symbol $\perp$ is utilized to denote transversality. In cases in which there is no ambiguity as to what momentum a vector is transverse, we will use no further indices. However, if we wish to write the components of the vector $\mathbf{A}$ perpendicular to a momentum designated as 1, we may write $\mathbf{A}_{\perp(1)}$. The number in parentheses also aids us in determining the manner in which vectors are dotted into one another. For example, vectors with the symbol (1) are multiplied by other vectors with the same symbol. For instance, the appearance of a product such as

$$\gamma_{\perp(3)}\gamma_{\perp(1)}\gamma_{p\perp(1)}\gamma_{p\perp(3)}$$

means

$$\sum_{i,j}\left(\gamma_i-\frac{\boldsymbol{\gamma}\cdot\mathbf{q}_3q_{3i}}{\mathbf{q}_3^2}\right)\left(\gamma_j-\frac{\boldsymbol{\gamma}\cdot\mathbf{q}_1q_{1j}}{\mathbf{q}_1^2}\right)\times\left(\gamma_{pj}-\frac{\boldsymbol{\gamma}_p\cdot\mathbf{q}_1q_{1j}}{\mathbf{q}_1^2}\right)\left(\gamma_{pi}-\frac{\boldsymbol{\gamma}_p\cdot\mathbf{q}_3q_{3i}}{\mathbf{q}_3^2}\right). \tag{A.4}$$

Our units are chosen such that $\hbar=c=1$ and $e^2=4\pi\alpha$. The electron mass will be denoted by m and the proton mass by M.

In various places in the text we will distinguish between proton and electron variables by using a subscript e or p. However, in most places the symbol e is dropped since it will be understood that nonsubscripted variables refer to the electron.

APPENDIX B: ASYMPTOTIC FORM OF THE HYDROGEN WAVE FUNCTION (1S)

In momentum space the Coulomb wave function satisfies the equation

$$\hat{\phi}_c(\mathbf{p})=(E-\boldsymbol{\alpha}\cdot\mathbf{p}-\beta m)^{-1}\int\frac{d^3p'}{(2\pi)^3}\frac{-e^2}{(\mathbf{p}'-\mathbf{p})^2}\hat{\phi}_c(\mathbf{p}'), \tag{B.1}$$

where E is the energy eigenvalue. We would like to obtain the asymptotic value of this wave function.

If we insert the nonrelativistic approximation to the wave function,

$$\tilde{\phi}_c(\mathbf{p}')=\frac{(2m\alpha)^{5/2}}{2\pi}\frac{1}{[\mathbf{p}'^2+(m\alpha)^2]^2}\times\begin{pmatrix}\chi_e\\ [(\boldsymbol{\sigma}\cdot\mathbf{p}')/2m]\chi_e\end{pmatrix}=\hat{\phi}_c(\mathbf{p}')\begin{pmatrix}\chi_e\\ [(\boldsymbol{\sigma}\cdot\mathbf{p})/2m]\chi_e\end{pmatrix}, \tag{B.2}$$

into the right-hand side of (B.1), we obtain on the left-hand side an excellent approximation to the wave

function for all $\mathbf{p}$. We find that

$$\phi_{cL}(\mathbf{p}) \approx \left(\frac{E+m}{2m}\right)\chi_e\hat{\phi}_c(\mathbf{p}) + \frac{e^2}{2m(-2m\epsilon+\mathbf{p}^2)}\,\boldsymbol{\sigma}\cdot\mathbf{p} \times \int \frac{d^3p'}{(2\pi)^3}\frac{\boldsymbol{\sigma}\cdot\mathbf{p}'}{(\mathbf{p}'-\mathbf{p})^2}\hat{\phi}_c(\mathbf{p}')\chi_e, \quad \text{(B.3)}$$

where E and ϵ actually contain more than just the basic binding. The integral appearing in (B.3) may be readily evaluated by contour methods.

For large values of p we obtain the result

$$[(E+m)/2m]\chi_e\hat{\phi}_c(\mathbf{p}) + \tfrac{1}{8}(\pi\alpha)(p/m)\chi_e\hat{\phi}_c(\mathbf{p}). \quad \text{(B.4)}$$

This asymptotic value is not in agreement with the asymptotic value obtained from the lowest-order treatment of the BS equation with a Coulomb kernel.

The small components of $\phi_c(p)$ are equal to

$$\phi_{cS}(\mathbf{p}) = \frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2m\epsilon-\mathbf{p}'^2}\int \frac{d^3p'}{(2\pi)^3}\frac{-e^2}{(\mathbf{p}'-\mathbf{p})^2}\chi_e\hat{\phi}_c(\mathbf{p}'), \quad \text{(B.5)}$$

but this in turn is simply

$$[(\boldsymbol{\sigma}\cdot\mathbf{p})/2m]\chi_e\hat{\phi}_c(\mathbf{p}). \quad \text{(B.6)}$$

This is exactly the same as the small components of ϕ_c. This was previously noted in Sec. III.

APPENDIX C: NONRELATIVISTIC SIZE CORRECTION—SHELL OF CHARGE

The hyperfine splitting is proportional to $|\hat{\psi}(0)|^2$, as was seen in Sec. III. If the proton consists of a shell of charge of radius R rather than a point charge, the result should change to $|\hat{\psi}^{(s)}(0)|^2$, where the superscript (s) stands for size or structure.

If we write

$$\hat{\psi}^{(s)}(\mathbf{r}) = r^{-1}\hat{\phi}^{(s)}(\mathbf{r}), \quad \text{(C.1)}$$

then for values of $r>R$ we have the equation

$$d^2\hat{\phi}^{(s)}/dr^2 + \{-\beta^2 + 2\beta(1+\eta)/r\}\hat{\phi}^{(s)} = 0, \quad \text{(C.2)}$$

where the energy is related to β by $\beta^2 = 2m|E|$ and the small quantity η is given by $\beta(1+\eta) = m\alpha$. To first order in the small quantity η, the solution of (C.2) may be shown to be

$$\hat{\phi}^{(s)} = N\{r + \eta[r\ln(\beta r) - (1/2\beta)]\}e^{-\beta r} \quad (r>R). \quad \text{(C.3)}$$

The equation for $r<R$ is

$$d^2\hat{\phi}^{(s)}/dr^2 + \{-\beta^2 + 2\beta[(1+\eta)/R]\}\hat{\phi}^{(s)} = 0. \quad \text{(C.4)}$$

Its solution is approximately given by

$$\hat{\phi}^{(s)} = Nr(1-\tfrac{1}{6}\gamma r^2 + \cdots)\hat{\psi}^{(s)}(0) \quad (r<R), \quad \text{(C.5)}$$

where

$$\gamma = -\beta^2 + [2\beta(1+\eta)/R].$$

If we match (C.3) and (C.5) at $r=R$ we obtain the relationship

$$\hat{\psi}^{(s)}(0)(1-\tfrac{1}{6}\gamma R^2) = e^{-\beta R}\{1+\eta[\ln\beta R - (1/2\beta R)]\}, \quad \text{(C.6a)}$$

and if we match derivatives we find

$$\hat{\psi}^{(s)}(0)(1-\tfrac{1}{2}\gamma R^2) = -\beta R\{1+\eta\ln\beta R - (1/2\beta R)\}e^{-\beta R} + [1+\eta(\ln\beta R+1)]e^{-\beta R}. \quad \text{(C.6b)}$$

The quotient of (C.6a) and (C.6b) may be used to obtain the value of η. The result turns out to be

$$\eta \approx \tfrac{2}{3}(m\alpha R)^2. \quad \text{(C.7)}$$

Therefore the finite size of the proton changes the binding energy to

$$E \approx \tfrac{1}{2}m\alpha^2[1-\tfrac{4}{3}(m\alpha R)^2]. \quad \text{(C.8)}$$

Using (C.6a) and the normalization of the wave function we find that

$$\hat{\psi}^{(s)}(0) \approx (1-m\alpha R)\hat{\psi}(0). \quad \text{(C.9)}$$

Therefore

$$|\hat{\psi}^{(s)}(0)|^2 \approx (1-2m\alpha R)\,|\hat{\psi}|(0)|^2, \quad \text{(C.10)}$$

and the correction due to a finite shell of charge is

$$-2m\alpha R \text{ hfs}. \quad \text{(C.11)}$$

This may be compared to the correction appearing in (3.21) of the text. It obviously agrees with the result previously obtained.

APPENDIX D: CONFIRMATION OF STERNHEIM'S STATE-DEPENDENT MASS CORRECTIONS TO HYPERFINE STRUCTURE

As mentioned in Sec. V, we have obtained the same result as Sternheim for the $\alpha^2 m/M$ state-dependent mass correction to the hfs of hydrogen. Here we will work out some of the details of this calculation.

Using Eqs. (2.14) and (2.16) in the text we find that a sufficiently accurate solution of our modified Dirac equation is given by

$$\psi_{1S} = \{1/[1+\lambda-\lambda(\alpha^2/2)]\} \times \{1-(1/4M)[\mathbf{p}^2, W]\}(1+\beta\lambda)\psi_{0\,1S} \quad \text{(D.1)}$$

and

$$\psi_{2S} = \{1/[1+\lambda-\lambda(\alpha^2/8)]\} \times \{1-(1/4M)[\mathbf{p}^2, W]\}(1+\beta\lambda)\psi_{0\,2S}. \quad \text{(D.2)}$$

The state-dependent α^2 terms in the denominators arise from an evaluation of the normalization of the wave functions to the required order. The wave functions ψ_0 are solutions of Eq. (2.16) which depend on an effective mass and a modified fine-structure constant, as discussed after Eq. (2.16). The parameter λ has also been defined above Eq. (2.16). To the desired accuracy the effective masses for $1S$ and $2S$

are, respectively,

$$m'_{1S}=\frac{m[1-(m/M)+\frac{1}{2}(m/M)\alpha^2]}{[1-(m^2/M^2)]^{1/2}} \quad \text{(D.3)}$$

and

$$m'_{2S}=\frac{m[1-(m/M)+\frac{1}{8}(m/M)\alpha^2]}{[1-(m^2/M^2)]^{1/2}}. \quad \text{(D.4)}$$

The hyperfine splitting is now obtained from

$$\frac{i\mu_p\alpha}{2M}\int d^3r\psi^\dagger(\mathbf{r})[\boldsymbol{\alpha}\times\mathbf{p}, r^{-1}]\cdot\boldsymbol{\delta}_p\psi(\mathbf{r}). \quad \text{(D.5)}$$

By analogy with Eqs. (3.6)–(3.9) we obtain the following contributions from (D.5) {for the moment, we ignore the $[\mathbf{p}^2, W]$ term in (D.1) and (D.2)}:

$1S$:

$$\frac{2\alpha\mu_p}{3M}\frac{(1+\lambda)(1-\lambda)}{[1+\lambda-\lambda(\alpha^2/2)]^2}(m'_{1S}\alpha')^2\alpha'(1+\tfrac{3}{2}\alpha')\langle\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\rangle. \quad \text{(D.6)}$$

$2S$:

$$\frac{2\alpha\mu_p}{3M}\frac{(1+\lambda)(1-\lambda)}{[1+\lambda-\lambda(\alpha^2/8)]^2}(m'_{2S}\alpha')^2\alpha'(1+\tfrac{17}{8}\alpha')\langle\boldsymbol{\delta}_e\cdot\boldsymbol{\delta}_p\rangle. \quad \text{(D.7)}$$

From (D.7) and (D.6) we obtain contributions of order α^2m/M to the residual R, which is defined by

$$1+R=8\nu_2(\text{hfs})/\nu_1(\text{hfs}). \quad \text{(D.8)}$$

These contributions are

$$-\tfrac{9}{8}\alpha^2(m/M) \quad \text{(D.9)}$$

and constitute the sum of (i) and (ii) referred to in Sec. V. We see that they arise in a simple way from the normalization and the effective mass.

There is also the correction which arises from the $[\mathbf{p}^2, W]$ term of the wave functions in (D.1) and (D.2). It is

$$\frac{i\mu_p\alpha}{2M}\int d^3r\psi_0^\dagger(\mathbf{r})\left\{\frac{-\alpha i}{M}\frac{\boldsymbol{\delta}_p\times\boldsymbol{\alpha}\cdot\mathbf{r}}{r^3}\right\}\psi_0(\mathbf{r}). \quad \text{(D.10)}$$

Although it will be canceled precisely by another perturbation, this term may easily be evaluated for the $1S$ and $2S$ states (using a cutoff at small r). The resulting contribution to R is

$$(\tfrac{10}{8}-2\ln 2)\alpha^2(m/M). \quad \text{(D.11)}$$

This contribution arises in the Foldy–Wouthuysen approach from the noncommutativity of the convection and magnetic interactions. In that treatment, it is given by the interaction

$$i\boldsymbol{\delta}\cdot[(\mathbf{A}_c\times\mathbf{A}_m)+(\mathbf{A}_m\times\mathbf{A}_c)]/2m, \quad \text{(D.12)}$$

where $\mathbf{A}_m$ and $\mathbf{A}_c$ denote the magnetic and convection parts of $\mathbf{A}$. It was shown by Sternheim[49] that such effective interactions should cancel. In the present formalism, we then expect that the two-photon-exchange contributions should yield a compensating term to (D.10).

Let us consider in detail how this cancellation occurs. In momentum space the contribution due to two transverse photons of the Dirac type is

$$\frac{i(4\pi\alpha)^2}{(2\pi)^4}\int d^4p'\{\gamma_0\gamma_{\perp(3)}{}^i(\not{p}'-m+i0)^{-1}\gamma_{\perp(1)}{}^j + \gamma_0\gamma_{\perp(1)}{}^j(\not{p}_1+\not{p}_3-\not{p}'-m+i0)^{-1}\gamma_{\perp(3)}{}^i\} \times[(p'-p_3)^2+i0]^{-1}[(p_1-p')^2+i0]^{-1}\left(1\frac{-\boldsymbol{\delta}\cdot\mathbf{p}_4}{2M}\right)\gamma^i \times(\not{p}_1+\not{p}_2-\not{p}'-M+i0)^{-1}\gamma^j\begin{pmatrix}1\\ \boldsymbol{\delta}\cdot\mathbf{p}_2/2M\end{pmatrix}. \quad \text{(D.13)}$$

We are interested in terms which are explicitly $\mathbf{O}(1/M^2)$. Using a positive-energy projection operator for the proton we obtain

$$\frac{i(4\pi\alpha)^2}{(2\pi)^4}\int d^4p'[\gamma_0\gamma_{\perp(3)}{}^i(\not{p}'-m+i0)^{-1}\gamma_{\perp(1)}{}^j + \gamma_0\gamma_{\perp(1)}{}^j(\not{p}_1+\not{p}_3-\not{p}'-m+i0)^{-1}\gamma_{\perp(3)}{}^i] \times[(p'-p_3)^2+i0]^{-1}[(p_1-p')^2+i0]^{-1}(E_1-E'+i0)^{-1} \times\left[\frac{\mathbf{p}_3+\mathbf{p}'}{2M}+\frac{i}{2M}(\mathbf{p}'-\mathbf{p}_3)\times\boldsymbol{\delta}_p\right]^i \times\left[\frac{\mathbf{p}_1+\mathbf{p}'}{2M}+\frac{i}{2M}(\mathbf{p}_1-\mathbf{p}')\times\boldsymbol{\delta}_p\right]^j. \quad \text{(D.14)}$$

The E' integral of (D.14) may be done by contour methods. We will first consider the ladder graph and close the contour above the axis. The proton pole contributes

$$(4\pi\alpha)^2\int\frac{d^3p'}{(2\pi)^3}\gamma_0\gamma_{\perp(3)}{}^i(\not{p}'-m+i0)^{-1}\gamma_{\perp(1)}{}^j \times\frac{1}{(\mathbf{p}_1-\mathbf{p}')^2}\frac{1}{(\mathbf{p}'-\mathbf{p}_3)^2}\left[\frac{\mathbf{p}_3+\mathbf{p}'}{2M}+\frac{i}{2M}(\mathbf{p}'-\mathbf{p}_3)\times\boldsymbol{\delta}_p\right]^i \times\left[\frac{\mathbf{p}_1+\mathbf{p}'}{2M}+\frac{i}{2M}(\mathbf{p}_1-\mathbf{p}')\times\boldsymbol{\delta}_p\right]^j, \quad \text{(D.15)}$$

where E' in the electron propagator is equal to E_1. In the low-momentum region ($p_1, p_3, p'\sim m\alpha$) this is exactly the transverse–transverse part of the iteration of the potential.

The convection–convection and convection–magnetic terms of (D.15) have been incorporated in the effective potential treatment. Only the magnetic–magnetic term is new. Let us consider it briefly. The electron

factor may be written as

$$\alpha_{\perp(3)}{}^{i}\left[\frac{\Lambda_{+}(\mathbf{p}')}{E_1-(\mathbf{p}'^2+m^2)^{1/2}+i0}+\frac{\Lambda_{-}(\mathbf{p}')}{E_1+(\mathbf{p}'^2+m^2)^{1/2}-i0}\right]\alpha_{\perp(1)}{}^{j} \quad \text{(D.16)}$$

with Λ_+ and Λ_- the positive- and negative-energy projection operators. The positive-energy part of the propagator gives a contribution which has been evaluated by Schwartz[48] using second-order perturbation theory. (Note: In this term one should really keep all orders of the Coulomb interaction.)

Next we consider the negative-energy part of (D.15). To the desired accuracy the electron factor becomes

$$(1/2m)\sigma_{\perp(3)}{}^{i}\sigma_{\perp(1)}{}^{j}, \quad \text{(D.17)}$$

and therefore we obtain a contribution of

$$(1/2m)(\mathfrak{d}\cdot\mathbf{A}_m)^2=(1/2m)[\mathbf{A}_m\cdot\mathbf{A}_m+i\mathfrak{d}\cdot\mathbf{A}_m\times\mathbf{A}_m]. \quad \text{(D.18)}$$

Only the second term

$$(1/2m)i\mathfrak{d}\cdot\mathbf{A}_m\times\mathbf{A}_m \quad \text{(D.19)}$$

contributes to the hfs.

There are additional contributions to the ladder-graph term of (D.14). The electron pole occurs at $E'\approx -m$ and leads to photon and proton denominators which are, respectively, of order $4m^2$ and $2m$. These large denominators lead to a very high nominal order (apparent powers of α) for the resulting operator. While the true order is less, it is still higher than terms being considered and is state independent. In considering the photon pole contributions, it is convenient to separate the electron propagator into positive- and negative-energy parts. For the former, the electron denominator is of the order of the photon momentum. Since the same denominator is of the order of the binding energy in the proton pole contribution, the resulting contribution is one power of α smaller than the terms we seek.

The important contributions are those coming from the negative-energy part of the electron propagator. The electron factor becomes

$$(1/4m^2)\alpha_{\perp(3)}{}^{i}m(1-\gamma_0)\alpha_{\perp(1)}{}^{j}\longrightarrow(1/2m)\sigma_{\perp(3)}{}^{i}\sigma_{\perp(1)}{}^{j}, \quad \text{(D.20)}$$

and we obtain

$$-(4\pi\alpha)^2\int\frac{d^3p'}{(2\pi)^3}(2m)^{-1}\sigma_{\perp(3)}{}^{i}\sigma_{\perp(1)}{}^{j}\frac{1}{2}\frac{1}{(\mathbf{p}'-\mathbf{p}_3)^2}\frac{1}{(\mathbf{p}_1-\mathbf{p}')^2}\times\left[\frac{\mathbf{p}_3+\mathbf{p}'}{2M}+\frac{i}{2M}(\mathbf{p}'-\mathbf{p}_3)\times\mathfrak{d}_p\right]^{i}\times\left[\frac{\mathbf{p}_1+\mathbf{p}'}{2M}+\frac{i}{2M}(\mathbf{p}_1-\mathbf{p}')\times\mathfrak{d}_p\right]^{j}, \quad \text{(D.21)}$$

which is

$$-(1/4m)[\mathbf{A}^2+i\mathfrak{d}\cdot\mathbf{A}\times\mathbf{A}]. \quad \text{(D.22)}$$

Next we will consider the crossed graph of (D.14). Here it is convenient to close the contour in the *lower* half-plane. The electron pole is again unimportant. The photon poles are again important only for the negative-energy part, but not for the positive-energy part (the same argument as for the ladder graph). The electron factor for the negative-energy part becomes

$$(1/2m)\sigma_{\perp(1)}{}^{j}\sigma_{\perp(3)}{}^{i}, \quad \text{(D.23)}$$

and we obtain

$$+(1/4m)[\mathbf{A}^2-i\mathfrak{d}\cdot\mathbf{A}\times\mathbf{A}]. \quad \text{(D.24)}$$

The over-all sign of (D.24) differs from that of (D.22) because we have closed the contour in the lower half-plane. The relative sign of the two terms is negative due to the order of the matrices in (D.23).

Adding up the contributions (D.19), (D.22), and (D.24) we obtain

$$(1/2m)i\mathfrak{d}\cdot\mathbf{A}_m\times\mathbf{A}_m-(1/2m)i\mathfrak{d}\cdot\mathbf{A}\times\mathbf{A}. \quad \text{(D.25)}$$

We note that terms involving $\mathbf{A}_m\times\mathbf{A}_m$ cancel in (D.25), and we are left with

$$-(1/2m)i\mathfrak{d}\cdot[(\mathbf{A}_c\times\mathbf{A}_m)+(\mathbf{A}_m\times\mathbf{A}_c)]. \quad \text{(D.26)}$$

This term exactly cancels (D.12), and therefore the expression in (D.11) does not contribute to R.

We have demonstrated this cancellation only for the case of the Dirac part of the magnetic moment. The Pauli interaction will behave in the same way to the order of accuracy which we require.

Finally, the interaction of Eq. (5.1) will give a contribution to R. The interaction may be written as

$$\frac{+(\mu+\frac{1}{2})}{2M}\left(\mathfrak{d}_p\times\frac{\mathbf{p}}{M}\right)\cdot\nabla\frac{\alpha}{r}=\frac{\alpha(\mu+\frac{1}{2})}{2M^2}\frac{\mathfrak{d}_q\cdot\mathbf{L}}{r^3}. \quad \text{(D.27)}$$

The expectation value of (D.20) gives a contribution to R, connecting the small components of the Dirac wave function. We obtain

$$\int d^3r\,\psi^{\dagger}(\mathbf{r})\frac{\mathfrak{d}\cdot\mathbf{p}}{2m}\frac{\alpha(\mu+\frac{1}{2})}{2M^2}\frac{\mathfrak{d}_p\cdot\mathbf{L}}{r^3}\frac{\mathfrak{d}\cdot\mathbf{p}}{2m}\psi(\mathbf{r}). \quad \text{(D.28)}$$

Using

$$\mathfrak{d}_p\cdot\mathbf{L}=\tfrac{1}{2}(\mathfrak{d}_p\cdot\mathfrak{d}\mathfrak{d}\cdot\mathbf{L}+\mathfrak{d}\cdot\mathbf{L}\mathfrak{d}_p\cdot\mathfrak{d}) \quad \text{(D.29)}$$

and $\mathfrak{d}\cdot\mathbf{L}\mathfrak{d}\cdot\mathbf{p}\psi=-2\mathfrak{d}\cdot\mathbf{p}\psi$ (this follows from the fact that $\mathfrak{d}\cdot\mathbf{p}\psi$ is a $P_{1/2}$ state), we obtain

$$\frac{-\alpha(\mu+\frac{1}{2})}{4m^2M^2}\int d^3r\,\psi^{\dagger}(\mathbf{r})\mathfrak{d}\cdot\mathbf{p}\frac{\mathfrak{d}\cdot\mathfrak{d}_p}{r^3}\mathfrak{d}\cdot\mathbf{p}\psi(\mathbf{r}). \quad \text{(D.30)}$$

Expression (D.24) may easily be evaluated for the $1S$ and $2S$ states. We obtain a contribution to R of

$$[(\mu+\tfrac{1}{2})/\mu_p](m/M)\alpha^2(\tfrac{1}{2}\ln 2-\tfrac{7}{32}). \quad \text{(D.31)}$$

Adding (D.9), (D.31), and the term obtained by Schwartz,[48] we obtain complete agreement with Eq. (2.18) of Sternheim.[46]

In addition to the terms just discussed, we have carefully examined the two-photon contribution to the effective potential to see whether there are any further state-dependent contributions to R of order $\alpha^2 m/M$. The ladder and crossed diagrams separately have such contributions, but they are easily seen to compensate when added. We have not examined the higher-order contributions (i.e., from three or more photons) to the effective potential. In view of the cancellations in the two-photon contribution, it seems unlikely, although not impossible, that contributions arise in higher order.

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