α^3 Corrections to Hyperfine Structure in Hydrogenic Atoms*

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The α^3 term in the ratio of the hyperfine splitting in the $2S$ state of the one-electron atom to the hyperfine splitting in the $1S$ state is recalculated, and a new theoretical value for this ratio is obtained which is in agreement with the experimental value, thereby eliminating a previously reported discrepancy. The calculation consists in the evaluation of the low-momentum parts, of order α^3 hfs, of the expression for the lowest order radiative level shift in the bound interaction representation with external Coulomb and magnetic dipole fields. By rearranging the terms so as to display the gauge invariance of the matrix elements with respect to the external potentials, considerable simplicity is achieved, and the formulas are easily interpreted as a generalization of the expression for the lowest order Lamb shift. The contribution from soft photon intermediate states is obtained by an extension of the method developed by Schwartz and Tiemann for evaluating the Bethe logarithm, and an appendix contains a tabulation of twelve analogous integrals which were integrated numerically, and which may be of use elsewhere. The calculated value of the ratio is $\frac{1}{8}(1.000\ 034\ 5\pm0.000\ 000\ 2)$ which agrees with the experimental values for hydrogen: $\frac{1}{8}(1.000\ 034\ 6\pm0.000\ 000\ 3)$, and deuterium: $\frac{1}{8}(1.000\ 034\ 2\pm0.000\ 000\ 6)$.

1. INTRODUCTION

VERY precise measurements of the hyperfine structure separations of the $1S$ and $2S$ states of hydrogen and deuterium have made possible the determination of the deviation of the ratio of the $2S$ to $1S$ separations from the value, one eighth, given by the Fermi formula.[1] While the bulk of this deviation is accounted for by the Breit correction,[2] arising from the use of Dirac wave functions, a residual discrepancy, amounting to about one part per million, has remained. This discrepancy has been discussed by Mittleman,[3] who has pointed out that quantum electrodynamics contributes to this ratio in lowest order $\alpha(Z\alpha)^2$ (where α is the fine structure constant and Z the nuclear charge), which is just of the order of the observed discrepancy, and has calculated the effect. His result, while of the observed sign and order of magnitude, disagrees significantly with the experimental result. Such a discrepancy would seem to imply a failure of quantum electrodynamics at a distance of order as large as the electron Compton wavelength. In view of the difficulty of reconciling such a conclusion with the well-known successes of the theory, it appeared essential to re-examine the quantum electrodynamic correction, with the objective of either removing the discrepancy or establishing it more firmly.

We present here a new calculation[4] of the quantum electrodynamic effect, and results in agreement with the experimental observations. Notable calculational simplicity is achieved by separating the numerous gauge variant terms, which ultimately cancel each other out, from the manifestly gauge invariant terms which contribute. These latter are easily understood physically as a generalization to the case of scalar and vector potential of the expression for the lowest order Lamb shift. In addition, an improved method, due to Schwartz and Tiemann,[5] for evaluating the bound nonrelativistic propagator is used. It is also of interest to note that the arguments of Mittleman, showing that there is no contribution to the required order from nuclear structure effects, have been verified in the interim by the explicit calculations of Iddings and Platzman[6] for the case in which the nucleus is a single proton.

Before proceeding to evaluate the radiative corrections of interest here, we will briefly review the various terms which contribute to the hyperfine splitting. All of them may be obtained from the fully covariant Bethe-Salpeter equation for the two body problem. However, it turns out to be more convenient to separate out the various terms according as they may be obtained from (1) the Dirac equation for the electron in the point Coulomb and magnetic dipole fields of the nucleus, (2) quantum electrodynamics for the one-electron state with external Coulomb and magnetic dipole fields, and (3) considerations involving the dynamic properties of the nucleus such as recoil, form factor, etc.

Restricting ourselves to nS states ($n=1$, 2 here), we can express all terms as multiples of the Fermi energy,[1] $E_n{}^M=(e/3m)\langle\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\rangle\psi_n{}^2(0)$, where $\boldsymbol{\sigma}$ is the electron spin operator, $\boldsymbol{\mu}$ the nuclear magnetic moment operator, ψ_n the nonrelativistic Schrödinger wave function for the nS state, and where rationalized natural units are chosen so that $\hbar=c=1$ and $\alpha=e^2/4\pi\hbar c\approx1/137$. Under heading (1) one obtains the term

$$E_n{}^M[1+a_n(Z\alpha)^2+b_n\alpha(Z\alpha)m/M+O(\alpha^4)]. \quad (1.1)$$

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[1] E. Fermi, Z. Physik **60**, 320 (1930).

[2] G. Breit, Phys. Rev. **35**, 1447 (1930).

[3] M. Mittleman, Phys. Rev. **107**, 1170 (1957).

[4] This calculation, while similar to Mittleman's in a general way, differs sufficiently in detail to have discouraged a detailed correction of Mittleman's work. Some errors in this work have, however, been located explicitly.

[5] C. Schwartz, Ann. Phys. **6**, 156 (1959); C. Schwartz and J. Tiemann, Ann. Phys. **6**, 178 (1959); I wish to thank Dr. Schwartz for preprints of the articles cited here.

[6] C. Iddings and P. Platzman, Phys. Rev. **113**, 192 (1959); and Phys. Rev. **115**, 919 (1959).

The a_n arise from the use of Dirac instead of Schrödinger wave functions and are known as the Breit[2] corrections. The difference b_2-b_1 which contributes to $\Delta\nu_{2S}/\Delta\nu_{1S}$ has been evaluated by Schwartz[5] and is obtained by treating the dipole potential in second order perturbation theory. (The b_n individually are divergent for a point dipole.) Under heading (2) one obtains

$$E_n{}^M[\alpha/(2\pi)+(-0.328)\alpha^2/\pi^2-(5/2-\ln 2)\alpha(Z\alpha) +c_n\alpha^3+O(\alpha^4)]. \quad (1.2)$$

The first two terms are the well known radiative corrections to the static moment of the free electron.[7] The third is obtained when binding is taken into account.[8] The terms of order α^3 will be discussed below. Under heading (3) one obtains

$$E_n{}^M[-3m/M+6(m/M)^2-8.7\alpha m/M +O(\alpha^2 m/M)]. \quad (1.3)$$

The first two terms are the reduced mass corrections. The third is the result of recoil[9] and finite size[6] corrections.

The quantity which will be calculated and compared with its value, as determined by experiment, is R, the ratio of the hyperfine splitting in the $2S$ state to the hyperfine splitting in the $1S$ state. We have from (1.1), (1.2), and (1.3),

$$R=\tfrac{1}{8}[1+(5/8)(Z\alpha)^2-(5/16\pi)\alpha(Z\alpha)^2 +(c_2-c_1)\alpha^3+O(\alpha^2 m/M)]. \quad (1.4)$$

We call those terms "state independent" which are proportional to $E_n{}^M$ and hence cancel in this ratio. The radiative corrections of order α and α^2, and the reduced mass corrections fall into this category.

Let us now concentrate our attention on the terms of the form $c_n\alpha^3$ appearing in Eqs. (1.2) and (1.4). They are of three kinds which we may write as α^3, $\alpha^2(Z\alpha)$, and $\alpha(Z\alpha)^2$. By this notation we distinguish the order of the radiative correction, which is the power of α, from the effect of binding on the hfs, which is expressible as a power series in $Z\alpha$ (and as we shall see, $\ln Z\alpha$). The α^3 term is the unevaluated third order correction to the static magnetic moment of the electron. It gives a contribution proportional to the Fermi energy and so is state independent and need not be considered further. The unevaluated $\alpha^2(Z\alpha)$ term is analogous to the $\alpha(Z\alpha)$ term which by explicit calculation[8] is state independent. That both terms are state independent may be seen roughly as follows. When intermediate electron momenta are scaled $\mathbf{p}\rightarrow Z\alpha\mathbf{p}$ and the integrands are expanded about $\mathbf{p}=0$, one obtains an estimate for binding corrections of order $(Z\alpha)^2$. However, the relevant integrals in this expansion diverge at high momentum, indicating the presence of the lower order terms linear in $Z\alpha$. However, the momentum space wave functions are state independent at high momentum so that these terms are also.

This leaves only the $\alpha(Z\alpha)^2$ terms for consideration. Denoting by I_1 and I_2, respectively, the coefficients of $\alpha(Z\alpha)^2E_1{}^M$ and $\alpha(Z\alpha)^2E_2{}^M$ in the expressions for the level shifts of the $1S$ and $2S$ states, the $(c_2-c_1)\alpha^3$ term in the ratio R takes the form $(I_2-I_1)\alpha(Z\alpha)^2$. It will be the principle concern of this paper to evaluate the difference $\Delta I\equiv I_2-I_1$. As will be seen below, it is considerably easier to evaluate their difference than to evaluate I_1 or I_2 separately. The method will be to obtain the difference of the two integrals which represent the level shifts in the two states, by taking the difference of the integrands. We now proceed to the calculation itself.

2. POLARIZATION ENERGY

Kroll and Pollack[8] have given finite expressions for radiative level shifts correct to first order in α and all orders in $Z\alpha$. We will consider first the level shift due to vacuum polarization, leaving for later treatment the fluctuation energy diagram. Vacuum polarization[10] causes a change in energy given by KP Eq. (21)[11]:

$$\Delta E_P=\frac{\alpha}{\pi}\int\langle\bar{n}|\mathbf{p}_2\rangle\langle\mathbf{p}_2|ieA|\mathbf{p}_1\rangle\int_0^1\frac{dv\,v^2}{(1-v^2)} \times\frac{(1-\frac{1}{3}v^2)|\mathbf{p}_2-\mathbf{p}_1|^2}{[4m^2/(1-v^2)+|\mathbf{p}_2-\mathbf{p}_1|^2]}\langle\mathbf{p}_1|n\rangle d\mathbf{p}_1 d\mathbf{p}_2 -\langle\bar{n}|ie\delta A^P|n\rangle. \quad (2.1)$$

δA^P has a leading term in which the external potential acts three times. It is of order $\alpha(Z\alpha)^3E^m$ and will be neglected.

A contribution to hfs may arise in ΔE_P either by the explicit appearance of a magnetic potential, or by a

[7] J. Schwinger, Phys. Rev. **73**, 416 (1948); A. Petermann, Helv. Phys. Acta **30**, 407 (1957); C. Sommerfield, Phys. Rev. **107**, 328 (1957).

[8] N. Kroll and F. Pollack, Phys. Rev. **84**, 597 (1951); R. Karplus, A. Klein, and J. Schwinger, Phys. Rev. **84**, 597 (1951). We will make use of results given by N. Kroll and F. Pollack, Phys. Rev. **86**, 876 (1952), hereafter referred to as KP.

[9] R. Arnowitt, Phys. Rev. **92**, 1002 (1953); and W. Newcomb and E. Salpeter, Phys. Rev. **97**, 1146 (1955) have evaluated the recoil correction of order $\alpha m/M$ for a point nucleus. The finite-size correction was evaluated nonrelativistically by A. Zemach, Phys. Rev. **104**, 1771 (1956) and relativistically by Iddings and Platzman (see reference 6). The recoil and finite size corrections are cutoff dependent when taken separately, but their sum is well defined. It is expressed above, somewhat arbitrarily, as a multiple of $\alpha(m/M)$hfs.

[10] R. Serber, Phys. Rev. 48, 49 (1935); E. Uehling, Phys. Rev. 48, 55 (1935).

[11] A word on notation is appropriate. We denote the charge on the electron by $-e$. $p\cdot q\equiv\mathbf{p}\cdot\mathbf{q}+p^4q^4\equiv\mathbf{p}\cdot\mathbf{q}-p^0q^0$; $\not{p}\equiv p\cdot\gamma$; $\sigma_{\mu\nu}\equiv[\gamma_\mu,\gamma_\nu]/2i$; $|n\rangle$ represents the electronic state nS, with $\langle n|n\rangle\equiv 1$, $\langle\bar{n}|\equiv\langle n|\beta$, $\boldsymbol{\gamma}\equiv-i\beta\boldsymbol{\alpha}$. All electromagnetic potentials are external potentials, $A\equiv(\mathbf{A},A^0)\equiv(\boldsymbol{\mu}\times\mathbf{r}/4\pi r^3, Ze/4\pi r)$, in rationalized units. $\hbar=c=1$. [KP use a normalization $\varphi_n(\mathbf{p})=(2\pi)^{-\frac{3}{2}}\langle\mathbf{p}|n\rangle$ and denote the charge on the electron by e.]

dependence of the wave function on the hyperfine state. We denote the two cases by a and b, respectively, and consider case a first. Since

$$\langle \mathbf{p}_2|A^M|\mathbf{p}_1\rangle=\left\langle \mathbf{p}_2\left|\frac{1}{4\pi}\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}\frac{1}{r}\times\boldsymbol{\mu}\right|\mathbf{p}_1\right\rangle$$
$$=\frac{i}{4\pi}\boldsymbol{\gamma}\cdot(\mathbf{p}_2-\mathbf{p}_1)\times\boldsymbol{\mu}\left\langle \mathbf{p}_2\left|\frac{1}{r}\right|\mathbf{p}_1\right\rangle, \quad (2.2)$$

we find

$$\Delta E_{Pa}=\frac{-\alpha}{\pi}\int_0^1 dv\, v^2\frac{(1-\frac{1}{3}v^2)}{(1-v^2)}$$
$$\times\int\langle\bar{n}|\mathbf{p}_2\rangle\frac{e}{4\pi}\boldsymbol{\gamma}\cdot(\mathbf{p}_2-\mathbf{p}_1)\times\boldsymbol{\mu}$$
$$\times\left\langle \mathbf{p}_2\left|\frac{1}{r}\exp\left(\frac{-2mr}{(1-v^2)^{\frac{1}{2}}}\right)\right|\mathbf{p}_1\right\rangle\langle\mathbf{p}_1|n\rangle d\mathbf{p}_1 d\mathbf{p}_2, \quad (2.3)$$

$$\Delta E_{Pa}=\frac{-\alpha}{\pi}\int_0^1 dv\, v^2\frac{(1-\frac{1}{3}v^2)}{(1-v^2)}$$
$$\times\left\langle\bar{n}\left|\frac{ie}{4\pi}\boldsymbol{\gamma}\cdot\boldsymbol{\mu}\times\boldsymbol{\nabla}\left[\frac{1}{r}\exp\left(\frac{-2mr}{(1-v^2)^{\frac{1}{2}}}\right)\right]\right|n\right\rangle. \quad (2.4)$$

This expression is easily interpreted as the expectation value of the interaction energy of the Dirac electron with the induced magnetic polarization potential. Since we are interested only in terms linear in the nuclear magnetic moment, we take the wave functions to be Coulomb wave functions. Furthermore their nonrelativistic form suffices to the required order. Performing the Dirac algebra, we find

$$\Delta E_{Pa}=\frac{-\alpha}{\pi}\int_0^1 dv\, v^2\frac{(1-\frac{1}{3}v^2)}{(1-v^2)}\frac{e}{3m}\langle\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\rangle$$
$$\times\frac{i}{4\pi}\left\langle n\left|\left\{\mathbf{p}\cdot,\boldsymbol{\nabla}\left[\frac{1}{r}\exp\left(\frac{-2mr}{(1-v^2)^{\frac{1}{2}}}\right)\right]\right\}\right|n\right\rangle, \quad (2.5)$$

where $|n\rangle$ is now the Schrödinger electronic state. Taking a position representation,

$$\Delta E_{Pa}=\frac{\alpha}{\pi}\int_0^1 dv\, v^2\frac{(1-\frac{1}{3}v^2)}{(1-v^2)}E_n{}^M\frac{1}{\psi_n{}^2(0)}$$
$$\times\int_0^\infty\frac{d}{dr}\left[\frac{1}{r}\exp\left(\frac{-2mr}{(1-v^2)^{\frac{1}{2}}}\right)\right]\frac{d}{dr}[\psi_n{}^2(r)]r^2dr. \quad (2.6)$$

Writing $\Delta E_{Pa}=\alpha(Z\alpha)^2E_n{}^M(I_n)_{Pa}$, the quantity we seek $\Delta I=I_2-I_1$, is given by

$$\Delta I_{Pa}=\frac{-1}{(Z\alpha)^2\pi}\int_0^1 dv\, v^2\frac{(1-\frac{1}{3}v^2)}{1-v^2}$$
$$\times\int_0^\infty\left[\exp\left(\frac{-2mr}{(1-v^2)^{\frac{1}{2}}}\right)\right]\left[\frac{1}{r^2}+\frac{2m}{(1-v^2)^{\frac{1}{2}}r}\right]\frac{d}{dr}$$
$$\times\left[\frac{\psi_2{}^2(r)}{\psi_2{}^2(0)}-\frac{\psi_1{}^2(r)}{\psi_1{}^2(0)}\right]r^2dr. \quad (2.7)$$

We expand $[\psi_2{}^2(r)/\psi_2{}^2(0)-\psi_1{}^2(r)/\psi_1{}^2(0)]$ in a power series in r and retain only the first nonvanishing term. Then

$$\Delta I_{Pa}=\frac{3}{8\pi}\int_0^1 dv\, v^2(1-\tfrac{1}{3}v^2)=\frac{1}{10\pi}. \quad (2.8)$$

We now take up case b in which a contribution to hfs arises from a dependence of the wave function on the hyperfine state. To obtain this dependence, the nuclear magnetic dipole field is treated as a perturbation of the nS Coulomb state of the electron. The change in the wave function is treated nonrelativistically and to first order in the perturbation. We therefore write $|n\rangle=|C\rangle+|M\rangle$, where $|C\rangle$ is the Coulomb nS state and $|M\rangle$ is linear in the nuclear magnetic moment. (See Appendix A for the perturbing Hamiltonian and the magnetic wave functions.) Elementary considerations indicate that for a nucleus of arbitrary spin, $|M\rangle$ is a superposition of $S_{\frac{1}{2}}$, $D_{\frac{3}{2}}$, and $D_{\frac{5}{2}}$ states. The energy level shift which we seek is proportional to $\langle\bar{C}|A^P|M\rangle$, where A^P is the polarization potential. Since we seek only terms linear in the nuclear moment, in this expression A^P is the polarization potential due to an external Coulomb field only. Since it is spherically symmetric the $D_{\frac{3}{2}}$ and $D_{\frac{5}{2}}$ part of the magnetic wave functions can give no contribution to the level shift. A similar argument holds for the fluctuation energy. Consequently, in all expressions we will retain only the $S_{\frac{1}{2}}$ part of the magnetic wave function. It is given by Eqs. (A.4) and (A.5).

We now return to Eq. (2.1) to evaluate ΔE_{Pb}. Either of the states may be magnetic and they contribute equally, so we let one be magnetic and double:

$$\Delta E_{Pb}=-\frac{2\alpha}{\pi}\int\langle\bar{C}|\mathbf{p}_2\rangle\left\langle \mathbf{p}_2\left|\frac{Z\alpha}{r}\gamma_4\right|\mathbf{p}_1\right\rangle$$
$$\times\int_0^1 dv\, v^2\frac{(1-\frac{1}{3}v^2)}{1-v^2}$$
$$\times\frac{|\mathbf{p}_2-\mathbf{p}_1|^2}{[4m^2/(1-v^2)+|\mathbf{p}_2-\mathbf{p}_1|^2]}\langle\mathbf{p}_1|M\rangle d\mathbf{p}_1 d\mathbf{p}_2, \quad (2.9)$$

$$\Delta E_{Pb}=-\frac{2\alpha}{\pi}\int_0^1 dv\, v^2\frac{(1-\frac{1}{3}v^2)}{1-v^2}$$
$$\times\left\langle C\left|\frac{Z\alpha}{r}\exp\left(\frac{-2mr}{(1-v^2)^{\frac{1}{2}}}\right)\right|M\right\rangle. \quad (2.10)$$

We follow the same procedure for ΔE_{Pa}, choosing a position space representation in the nonrelativistic limit. Writing $\langle \mathbf{x}|M\rangle=(E^M/\mathrm{ry})u(r)$, we obtain

$$\Delta I_{Pb}=\frac{-2}{\pi Z\alpha\,\mathrm{ry}}\int_0^1 dv\,v^2\frac{(1-\frac{1}{3}v^2)}{1-v^2}\times\int\frac{1}{r}\exp\left[\frac{-2mr}{(1-v^2)^{\frac{1}{2}}}\right](\psi_2u_2-\psi_1u_1)d\mathbf{x}. \quad (2.11)$$

As before, we expand $\Delta\psi u=\psi_2u_2-\psi_1u_1$ as a power series in r, retain the first nonvanishing term, and obtain

$$\Delta I_{Pb}=\frac{2\ln 2-3}{\pi}\int_0^1 dv\,v^2(1-\tfrac{1}{3}v^2)=\frac{-4}{15\pi}(3-2\ln 2). \quad (2.12)$$

The net contribution from the polarization diagram is thus

$$\Delta I_P=\Delta I_{Pa}+\Delta I_{Pb}=\frac{-1}{10\pi}\left(7-\frac{16}{3}\ln 2\right). \quad (2.13)$$

It will be observed that a position space representation of the polarization energy makes all integrals trivial, and that one can easily obtain the level shift as a power series in $Z\alpha$ by expanding the wave functions in powers of r. Alternatively, we could have obtained ΔI_P by neglecting $(\mathbf{p}_2-\mathbf{p}_1)^2$ in the denominator of Eq. (2.1) and evaluated

$$\Delta E_P=\frac{-\alpha}{4\pi m^2}\langle\bar{n}|ie\nabla^2A|n\rangle\int_0^1 dv\,v^2(1-\tfrac{1}{3}v^2)=\frac{-\alpha}{15\pi m^2}\langle\bar{n}|ie\nabla^2A|n\rangle. \quad (2.14)$$

This is actually a divergent expression for ΔE_P but $\Delta I_P\equiv[(\Delta E_P)_{2S}/E_2{}^M-(\Delta E_P)_{1S}/E_1{}^M]/\alpha(Z\alpha)^2$ remains well defined. We will make use of this second method of evaluation when calculating the contribution of the fluctuation energy to ΔI.

3. ISOLATION OF GAUGE-INVARIANT TERMS IN THE FLUCTUATION ENERGY

We now proceed to the more difficult task of evaluating the contribution of the fluctuation energy diagram. It is given by[12]

$$\Delta E_F=\frac{\alpha}{4\pi}\int\langle\bar{n}|\mathbf{p}_2\rangle(-ie)A_\mu(\mathbf{p}_2-\mathbf{p}_1)\times K_\mu(p_2,p_1)\langle\mathbf{p}_1|n\rangle d\mathbf{p}_1d\mathbf{p}_2+\frac{3\alpha}{4\pi}\times\left\langle\bar{n}\left|(-ie)A\int_0^1\frac{-2ipy-m(1-2y)}{m^2+(p^2+m^2)y}dy(-ie)A\right|n\right\rangle+L_D+Q, \quad (3.1)$$

where

$$K_\mu=\int_0^1\frac{dz}{[p_2(1-z)+p_1z]^2}\{\tfrac{1}{2}(3-8z+8z^2)\times(p_2-p_1)^2\gamma_\mu+m(p_2-p_1)_\nu\sigma_{\nu\mu}-(ip_2+m)[(1-z)(ip_1-m)+m]\gamma_\mu-\gamma_\mu[z(ip_2-m)+m](ip_1+m)+\tfrac{3}{2}(1-2z)(p_2{}^2-p_1{}^2)\gamma_\mu+(ip_2+m)\gamma_\mu(ip_1+m)\}, \quad (3.2)$$

$$L_D=\frac{8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\frac{p_\mu}{k^2-2p\cdot k}\left[\frac{p_\mu}{k^2-2p\cdot k},ieA\right]\right|n\right\rangle\times\frac{d^4k}{k^2+\lambda^2}, \quad (3.3)$$

$$Q=\frac{-2i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\left[ieA,\frac{2ip_\mu-i\gamma_\mu k}{k^2-2p\cdot k}\right]\frac{1}{ip-ik+ieA+m}\times\left[\frac{2ip_\mu-ik\gamma_\mu}{k^2-2p\cdot k},ieA\right]\right|n\right\rangle\frac{d^4k}{k^2+\lambda^2}. \quad (3.4)$$

The general procedure we shall adopt for evaluating ΔE_F is as follows. The first two terms of K_μ are recognized as charge and magnetic moment parts of the vertex function. That part of Q which contains no powers of k in the numerator is divergent in the infrared, but will give a finite result when combined with the similarly divergent L_D. To the order of interest this will yield the remainder of the charge vertex function and an analog of the sum-over-states of the lowest order Lamb shift. All other terms will be shown to be gauge variant to the order of interest, and hence when summed give no net contribution.

In all expressions for the fluctuation energy in which 4-vector notation is used, it is understood that a 4-vector representing an electron momentum has its zeroth component fixed at the energy of the state in question. One integrates only over the space part of the electron momenta. Contributions to the hyperfine

[12] See KP Eqs. (27), (33), (34), and (36). There are transcription errors in Eqs. (29) and (33). Equation (33) should read, in our notation,

$$K_\mu=\int^1\frac{dz}{[p_2(1-z)+p_1z]^2}\{(p_2-p_1)^2\gamma_\mu[2-6z(1-z)]+m(p_2-p_1)_\nu\sigma_{\nu\mu}+\tfrac{5}{2}(1-2z)(p_2{}^2-p_1{}^2)\gamma_\mu+(ip_2+m)\gamma_\mu(ip_1+m)-\tfrac{1}{2}(ip_2+m)^2\gamma_\mu-\tfrac{1}{2}\gamma_\mu(ip_1+m)^2+z(p_2-p_1)_\nu\sigma_{\mu\nu}(ip_1+m)+(1-z)(ip_2+m)(p_2-p_1)_\nu\sigma_{\mu\nu}\}+\int_0^1dz\int_0^1du\frac{-\gamma_\mu[(p_2-p_1)^2z(1-z)+z(p_2{}^2-p_1{}^2)]}{\{p_2{}^2+u[-p_2{}^2+(p_2(1-z)+p_1z)^2]\}}.$$

The integral with respect to u is easily performed. Noting that $\langle\bar{n}|\ln(-p^2/m^2)A|n\rangle=\langle\bar{n}|A\ln(-p^2/m^2)|n\rangle$ and integrating partially with respect to z, one obtains the symmetric form given above for K_μ.

splitting from the fluctuation energy can arise in three ways: by the explicit appearance of a magnetic potential, by the dependence of the wave function on the hyperfine state, and thirdly, since the energy appears explicitly in the 4-vector, by the dependence of the energy on the hyperfine state. This last case was neglected by Mittleman.[3] It contributes to the order of interest whenever the Coulomb binding energy of the state also contributes.

The quantity, $\Delta I=I_2-I_1$, which we seek is the coefficient of $\alpha(Z\alpha)^2$ hfs in the weighted difference $(8\Delta E_2-\Delta E_1)$ of the integrals which represent the level shift in the $1S$ and $2S$ states. When the difference of the integrals is written as the integral of the difference of the integrands, the new integral converges more rapidly at small r. This is a great advantage since the operator which is being evaluated is singular at small r, and approximations may be made in the integrand of ΔI which are not correct for the level shifts ΔE_1 and ΔE_2 separately. In particular we will frequently scale electron 3-momenta $\mathbf{p}\rightarrow Z\alpha\mathbf{p}$ and expand in a power series in $Z\alpha$ to the order required. We will follow this procedure whenever it leaves ΔI finite, even though the expressions for ΔE would become divergent if so treated. In the following it will often be convenient to write formal expressions for ΔE which are divergent, with the understanding that the subtracted form $(8\Delta E_2-\Delta E_1)$ is meant whenever approximations and estimates of order of magnitude are made. The fact that $\mathbf{p}$ is of order $Z\alpha m$ in the integral representing ΔI when it is of order m in the integral for the level shift, may be expressed by the statement that high-momentum contributions are state independent.

To treat the first term of Eq. (3.2) for K_μ to the required order, we may approximate the denominator by $-m^2$. This means that in the denominator we neglect electron momenta compared to m, as explained above. The auxiliary integration with respect to z is then trivial. It yields a contribution to ΔE_F, which we denote by $\Delta E_F(1)$, that according to Eq. (3.1) is given by

$$\Delta E_F(1)=\frac{-\alpha}{4\pi m^2}\frac{5}{6}\langle\bar{n}|ie\nabla^2 A|n\rangle. \tag{3.5}$$

This is part of the charge vertex function. We will evaluate this term, as well as all others, to first order in the nuclear moment.

To evaluate the second term of K_μ, Eq. (3.2), it is again sufficient to approximate the denominator by $-m^2$ when K_μ is contracted with the Coulomb potential. However when K_μ is contracted with the magnetic potential, this term contains the $(\alpha/2\pi)$ correction to the static magnetic moment which causes a level shift of $(\alpha/2\pi)$hfs. To obtain all the terms of order $\alpha(Z\alpha)^2$ hfs, the denominator may not be approximated by $-m^2$. Instead we expand it about $-m^2$ and retain the first correction term. The auxiliary integration is then trivial and yields for the second term of K_μ

$$K_\mu(2)=\frac{-1}{m}(p_2-p_1)_\nu\sigma_{\nu\mu}\times\left[1-\frac{1}{6}\frac{(p_2-p_1)^2}{m^2}+\frac{1}{2}\frac{p_2^2+m^2}{m^2}+\frac{1}{2}\frac{p_1^2+m^2}{m^2}\right]. \tag{3.6}$$

It is understood that the last three terms in this expression are to be retained only when $K_\mu(2)$ is contracted with a magnetic potential. We will treat the last two terms of (3.6) together with the remaining terms of K_μ by making use of the equations of motion to obtain terms involving more than one power of the external potential. When we substitute the first two terms of $K_\mu(2)$ into Eq. (3.1) for ΔE_F, we obtain

$$\Delta E_F(2)=\frac{\alpha}{4\pi}\left\langle\bar{n}\left|\frac{e}{m}\sigma_{\nu\mu}\left(1+\frac{1}{6}\frac{\nabla^2}{m^2}\right)\frac{\partial A_\mu}{\partial x_\nu}\right|n\right\rangle. \tag{3.7}$$

This is the expansion up to ∇^2/m^2 of the well known second order magnetic moment form factor of the electron.[13] We again recall that the ∇^2/m^2 contributes to the order of interest only when the external potential is magnetic.

The terms we have considered up until now involve one power of the external potential. The remaining terms of K_μ contain factors of $(i\not{p}+m)$ which operate on the wave functions and so involve more than one power of the external potential. The second term of Eq. (3.1) for ΔE_F also explicitly displays two powers of the potential. We will leave these terms for later consideration and instead proceed to treat L_D, given by Eq. (3.3) which contains only one power of the external potential. Since

$$\left[\frac{p_\mu}{k^2-2p\cdot k},(-ieA)\right]\Big|n\Big\rangle=(i\not{p}+m+ie\not{A})\frac{p_\mu}{k^2-2p\cdot k}\Big|n\Big\rangle, \tag{3.8}$$

we may write

$$L_D=\frac{-8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\left(\frac{p_\mu}{k^2-2p\cdot k}-\frac{\rho_\mu}{k^2-2\rho\cdot k}\right)\times\left[\frac{p_\mu}{k^2-2p\cdot k},(-ie)A\right]\right|n\right\rangle\frac{d^4k}{k^2+\lambda^2}, \tag{3.9}$$

where ρ is any constant vector so that $\rho/(k^2-2\rho\cdot k)$ commutes with $(i\not{p}+m+ie\not{A})$ and L_D is independent of ρ. It is convenient to choose $\rho=(0,0,0,E_n)$, so that the

[13] See for instance A. Akhiezer and V. Berestetsky, *Quantum Electrodynamics* (State Technico-Theoretical Literature Press, Moscow, 1953), Eq. (44.3). In English translation, U. S. Atomic Energy Commission, AEC-tr-2876 (unpublished).

left-hand factor in the expression for L_D does not contain any spurious lower order terms, but vanishes with $\mathbf{p}=p-\rho$. The total level shift naturally cannot depend on the convergence parameter λ and the calculation is simplified if the two λ-dependent terms are combined and λ set to 0 at an early stage. For this purpose we separate out of Q the part Q_D which is divergent as $\lambda\to 0$. A simple counting of powers of k as $k\to 0$ in Eq. (3.4) indicates that

$$Q_D=\frac{8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\left[ieA,\frac{p_\mu}{k^2-2p\cdot k}\right]\frac{1}{ip-ik+m+ieA}\right.\right.$$
$$\left.\left.\times\left[\frac{p_\mu}{k^2-2p\cdot k},ieA\right]\right|n\right\rangle\frac{d^4k}{k^2+\lambda^2}, \quad (3.10)$$

i.e., that part of Q with no powers of k in the numerator. Since

$$\left\langle\bar{n}\left|\left[(-ie)A,\frac{p_\mu}{k^2-2p\cdot k}\right]\right.\right.$$
$$\left.\left.=\left\langle\bar{n}\right|\left(\frac{p_\mu}{k^2-2p\cdot k}-\frac{\rho_\mu}{k^2-2\rho\cdot k}\right)(ip+m+ieA),\right. \quad (3.11)$$

we may write $\Delta E_F(3)\equiv Q_D+L_D$ as

$$\Delta E_F(3)=\frac{8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\left(\frac{p_\mu}{k^2-2p\cdot k}-\frac{\rho_\mu}{k^2-2\rho\cdot k}\right)\right.\right.$$
$$\left.\left.\times ik\frac{1}{ip-ik+m+ieA}\left[\frac{p_\mu}{k^2-2p\cdot k},(-ie)A\right]\right|n\right\rangle$$
$$\times\frac{d^4k}{k^2}. \quad (3.12)$$

This form is now convergent and λ has been eliminated.

We will now prove that to the required order the level shift ΔE_F is given simply by $\Delta E_F(1)+\Delta E_F(2)+\Delta E_F(3)$. Although other terms are individually of the order of interest, their sum is not. The argument invokes the gauge invariance of the matrix element with respect to the external potential. Let us look into the situation in more detail. The fluctuation energy is given by

$$\Delta E_F=\frac{-2i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\gamma_\mu\frac{1}{ip+ieA-ik+m}\gamma_\mu\right|n\right\rangle\frac{d^4k}{k^2}. \quad (3.13)$$

This matrix element is formally invariant under the substitution $A_\mu\to A_\mu+\partial\Lambda/\partial x_\mu$, $|n\rangle\to\exp(-ie\Lambda)|n\rangle$, where $\Lambda(x)$ is any real scalar. One consequence is that no charge renormalization terms are present in the fluctuation energy, since they are of the form $\langle\bar{n}|ieA|n\rangle$ and hence gauge variant. We will not make use of gauge invariance in the most general form however. The potentials are chosen to be time independent and to satisfy the subsidiary condition[14] $(\partial/\partial x_\mu)A_\mu=\nabla\cdot\mathbf{A}=0$. This restricts the function $\Lambda(x)$ to the form $\Lambda_\mu x_\mu$, where Λ_μ is an arbitrary constant 4-vector. The restricted gauge transformation is then of the form $A_\mu\to A_\mu+\Lambda_\mu$, $p_\mu\to p_\mu-e\Lambda_\mu$, corresponding to a change of the external electromagnetic potentials by a constant. The proof will consist in showing that to the order required $\Delta E_F(1)$, $\Delta E_F(2)$, and $\Delta E_F(3)$ are each invariant with respect to the restricted gauge and that all other terms are of a form which is not invariant under the transformation.

We will first show that all other terms are gauge variant to the order of interest. These are the remaining terms of K_μ, the second term of Eq. (3.1) and $Q_C=Q-Q_D$, the part of Q which is convergent. We consider them in turn. The last term of K_μ [Eq. (3.2)] contains three powers of the external potential, when one makes use of the equations of motion. It vanishes to the order of interest. The next to the last term vanishes by the auxiliary integration when the denominator is set equal to $-m^2$. The third and fourth terms of Eq. (3.2) contain zero or one power of p in the numerator and factors of $(ip+m)$ which operate on wave functions. To the order of interest, these two-potential terms yield the forms $(e\alpha/m^2)\langle\bar{C}|(Z\alpha/r)\boldsymbol{\sigma}\cdot\mathbf{B}|C\rangle$, $(e^2\alpha/m^2)\langle\bar{C}|\boldsymbol{\sigma}\cdot\mathbf{A}\times\mathbf{E}|C\rangle$ and $(\alpha/m)\langle\bar{C}|(Z\alpha/r)^2|M\rangle$.[I] [The form $(\alpha/m)\langle\bar{C}|(Z\alpha/r)\boldsymbol{\gamma}\cdot ie\mathbf{A}|C\rangle$ also appears, but can be reduced to the others by using the equations of motion and dropping terms trilinear in the potential.] The last two terms of $K_\mu(2)$ [Eq. (3.6)] and the second term of ΔE_F [Eq. (3.1)] also contain two powers of the potential and give rise to the same gauge-variant forms.

We next examine $Q_C=Q-Q_D$, that part of Q which is convergent in the infrared. We first note that it is sufficient to replace the bound propagator by the free propagator, because the main contribution comes from the region $k\approx m$. In fact, when this substitution has been made, Q_C is evaluated by scaling $k\to mk$, $\mathbf{p}\to mZ\alpha\mathbf{p}$, and expanding about $\mathbf{p}=0$. When both potentials are electric, only the term independent of $\mathbf{p}$ contributes to the order of interest. When one potential is magnetic, terms linear in $\mathbf{p}$ must also be retained. Since Q_C contains two powers of the potential, it yields the same gauge-variant forms as have been found previously.

We have now examined all terms besides $\Delta E_F(1)$, $\Delta E_F(2)$, and $\Delta E_F(3)$, and found only the gauge-variant forms

$$(e\alpha/m^2)\langle\bar{C}|(Z\alpha/r)\boldsymbol{\sigma}\cdot\mathbf{B}|C\rangle,$$
$$(e^2\alpha/m^2)\langle\bar{C}|\boldsymbol{\sigma}\cdot\mathbf{A}\times\mathbf{E}|C\rangle$$

and

$$(\alpha/m)\langle\bar{C}|(Z\alpha/r)^2|M\rangle.$$

It is clear that no nonvanishing sum of such terms is gauge invariant.[I] We will complete the proof by showing

[14] See KP, footnote 19.

that $\Delta E_F(1)$, $\Delta E_F(2)$, and $\Delta E_F(3)$ contain only gauge-invariant terms, so that the others sum to zero. The cancellation of the gauge-variant terms has actually been verified by explicit calculation.

$\Delta E_F(1)$ and $\Delta E_F(2)$ are manifestly invariant, as may be verified by inspection of Eqs. (3.5) and (3.7). To prove the invariance of $\Delta E_F(3)$ we will carry out the k integration and thereby reduce it to a manifestly invariant form. This term contains the complete bound propagator. It will be found that an expansion of the propagator in powers of the external potential is not an expansion in powers of $Z\alpha$, so that the whole series must be summed. Furthermore the first term in this series will be found to yield a contribution to ΔI containing $\ln(Z\alpha)\approx -5$ as a factor. These two effects account for the bulk of ΔI. We make use of the operator identity

$$\frac{1}{ip-ik+m+ieA}=\frac{1}{ip-ik+m}\left[1-ieA\frac{1}{ip-ik+m+ieA}\right], \quad (3.14)$$

to write $\Delta E_F(3)$ of Eq. (3.12) in the form

$$\Delta E_F(3)=\frac{-8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\left(\frac{p_\mu}{k^2-2p\cdot k}-\frac{\rho_\mu}{k^2-2\rho\cdot k}\right)\right.\right. \times ik\frac{(-ip+ik+m)}{(k-p)^2+m^2}\left[1-ieA\frac{1}{ip-ik+m+ieA}\right] \times\left.\left[\frac{p_\mu}{k^2-2p\cdot k},ieA\right]\right|n\left.\right\rangle\frac{d^4k}{k^2}. \quad (3.15)$$

We now simplify the Dirac structure, making use of the equations of motion:

$$\left\langle\bar{n}\left|\left(\frac{p_\mu}{k^2-2p\cdot k}-\frac{\rho_\mu}{k^2-2\rho\cdot k}\right)ik(-ip+ik+m)\right.\right. =-\left\langle\bar{n}\left|\left(\mathbf{p}+\frac{2\mathbf{p}\cdot k\rho_\mu}{k^2-2\rho\cdot k}\right)\right.\right. +\left\langle\bar{n}\left|(-ie)Aik\left(\frac{p_\mu}{k^2-2p\cdot k}-\frac{\rho_\mu}{k^2-2\rho\cdot k}\right)\right.\right., \quad (3.16)$$

since $p_\mu=\mathbf{p}+\rho_\mu$. The right-hand term in the last expression contains an extra power of the external potential. Although it is of order $\alpha(Z\alpha)$ hfs, it does not contribute to the order of interest in the ratio, as indicated by a low energy ($\mathbf{p}\approx mZ\alpha$) estimate of this term. $\Delta E_F(3)$ now takes the form

$$\Delta E_F(3)=\frac{8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\frac{\mathbf{p}+2\mathbf{p}\cdot k\rho/(k^2-2\rho\cdot k)}{(k-p)^2+m^2}\right.\right. \cdot\left(1-ieA\frac{1}{ip-ik+m+ieA}\right) \times\left.\left[\frac{p_\mu}{k^2-2p\cdot k}-\frac{\rho_\mu}{k^2-2\rho\cdot k},ieA\right]\right|n\left.\right\rangle\frac{d^4k}{k^2}. \quad (3.17)$$

It is convenient to treat separately the two terms of the central parentheses, writing $\Delta E_F(3)=L'+Q'$, where L' is the result of retaining the first term:

$$L'=\frac{8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\left(\mathbf{p}+\frac{2\mathbf{p}\cdot k\rho}{k^2-2\rho\cdot k}\right)\cdot\frac{1}{(k-p)^2+m^2}\right.\right. \times\left.\left[\frac{1}{k^2-2p\cdot k}\left(\mathbf{p}+\frac{2\mathbf{p}\cdot k\rho}{k^2-2\rho\cdot k}\right),ieA\right]\right|n\left.\right\rangle\frac{d^4k}{k^2}. \quad (3.18)$$

Comparing Eqs. (3.9) and (3.18), we note that L' differs from L_D in that a factor of $1/(k^2-2p\cdot k)$ is replaced by $1/(k^2-2p\cdot k+p^2+m^2)$, which makes L' convergent. If we attempt the usual scaling $k\rightarrow mk$, $\mathbf{p}\rightarrow mZ\alpha\mathbf{p}$, and neglect all $Z\alpha$ compared to 1, L' becomes divergent. However to evaluate L' to lowest order, we may omit all terms which would be negligible under this scaling except the convergence parameter p^2+m^2. Then

$$L'=\frac{8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\frac{1}{(k^2-2\rho\cdot k+p^2+m^2)}\frac{1}{(k^2-2\rho\cdot k)}\right.\right. \times\left(\mathbf{p}+\frac{2\mathbf{p}\cdot k\rho}{k^2-2\rho\cdot k}\right)\cdot\left.\left[\mathbf{p}+\frac{2\mathbf{p}\cdot k\rho}{k^2-2\rho\cdot k},ieA\right]\right|n\left.\right\rangle\frac{d^4k}{k^2}. \quad (3.19)$$

It is now a trivial matter to carry out the k integration to obtain to lowest order in p^2+m^2,

$$L'=\frac{-\alpha}{\pi m^2}\left\langle\bar{n}\left|\left(\frac{2}{3}\ln\frac{m^2}{p^2+m^2}+\frac{13}{18}\right)\mathbf{p}\cdot[\mathbf{p},ieA]\right|n\right\rangle, \quad (3.20)$$

$$L'=\frac{\alpha}{4\pi m^2}\left(\frac{4}{3}\ln\frac{m}{2\,\mathrm{ry}}+\frac{13}{9}\right)\langle\bar{n}\,|\,ie\nabla^2A\,|\,n\rangle +\frac{\alpha}{\pi m^2}\left\langle n\left|\frac{2}{3}\ln\left(\frac{2m\,\mathrm{ry}}{p^2+m^2}\right)\mathbf{p}\cdot(H-E)\mathbf{p}\right|n\right\rangle, \quad (3.21)$$

where H and E may be taken to be the nonrelativistic Hamiltonian and energy. The entire expression is independent of ry, which we have arbitrarily chosen to be the rydberg energy [$=\frac{1}{2}m(Z\alpha)^2$]. The first term is manifestly gauge invariant and will later be combined with $\Delta E_F(1)$ which has the same form. The second term has been written in nonrelativistic form,

and will be combined with the remainder of $\Delta E_F(3)$ which we will evaluate next.

According to Eq. (3.17), it is given by

$$Q'=\frac{-8i\alpha}{(2\pi)^3}\int\left\langle\bar{n}\left|\frac{\mathbf{p}+2\mathbf{p}\cdot k\rho_\mu/(k^2-2\rho\cdot k)}{(k-p)^2+m^2}ieA\right.\right.$$
$$\left.\left.\times\frac{1}{ip-ik+m+ieA}\left[\frac{p_\mu}{k^2-2p\cdot k},ieA\right]\right|n\right\rangle\frac{d^4k}{k^2}. \quad (3.22)$$

To carry out the k integration, the complete bound propagator is expanded in powers of the external potential, the Dirac structure of the denominators is rationalized, and as usual a momentum space representation is chosen, so that the term by term integrand is a rational function of k. A typical term of the series then has a denominator of the form

$$\{\prod_{i=1}^{n}[(k-q_i)^2+m^2]\}(k^2-2q\cdot k)k^2. \quad (3.23)$$

This has the poles in the k_0 plane shown in Fig. 1 for typical values of the 3-momenta. The appropriate contour for the k_0 integration is also indicated in the figure. The integration is effected by completing the contour in the lower half plane. The value of the integral is then given by the sum of the residues of the poles on the positive real axis. (The poles of $k^2-2p\cdot k$ wander over the complex k_0 plane, but the resulting integral may be obtained by analytic continuation of the integral which is obtained in the present case.) The value of the residues at $\epsilon+[m^2+(k-q_i)^2]^{\frac{1}{2}}$ and $\epsilon+[\epsilon^2+(k-q)^2-q^2]^{\frac{1}{2}}$ is estimated by scaling $(\mathbf{k},\mathbf{q},\mathbf{q}_i)\rightarrow(Z\alpha m)(\mathbf{k},\mathbf{q},\mathbf{q}_i)$ and is found to be one power of $Z\alpha$ too small. Consequently, the value of Q' is given simply by the residue at the pole $k_0=|\mathbf{k}|$, which may be obtained directly from Eq. (3.22):

$$Q'=\frac{-\alpha}{\pi^2}\int\left\langle\bar{n}\left|\left(\mathbf{p}+\frac{\mathbf{p}\cdot\mathbf{k}}{m|\mathbf{k}|}\rho_\mu\right)\cdot\frac{1}{(-ip+ik+m)}\right.\right.$$
$$\times\left(\frac{1}{ip-ik+m+ieA}-\frac{1}{ip-ik+m}\right)$$
$$\left.\left.\times\left[\frac{\mathbf{p}+(\mathbf{p}\cdot\mathbf{k}/m|\mathbf{k}|)\rho_\mu}{-2p\cdot k},ieA\right]\right|n\right\rangle\frac{d^3k}{|\mathbf{k}|}, \quad (3.24)$$

where $k=(\mathbf{k},|\mathbf{k}|)$. We rewrite the central parenthesis in the form

$$\frac{-ip+ik-ieA+m}{(p-k+eA)^2+m^2+(e/2)\sigma_{\mu\nu}F_{\mu\nu}}-\frac{-ip+ik+m}{(p-k)^2+m^2},$$

where

$$F_{\mu\nu}=\frac{\partial A_\nu}{\partial x_\mu}-\frac{\partial A_\mu}{\partial x_\nu},$$

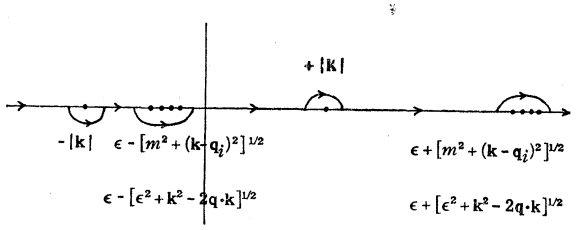

FIG. 1. The complex k_0 plane, showing the path of integration of the integral Q' (3.22) and the poles of the integrand. ϵ is the relativistic energy of the state in question.

and scale $\mathbf{k}\rightarrow(Z\alpha)^2m\mathbf{k}$, $\mathbf{p}\rightarrow(Z\alpha m)\mathbf{p}$, so that to the required order

$$Q'=\frac{-4\alpha}{3\pi m}\int_0^\infty\left\langle\bar{n}\left|\frac{\mathbf{p}\cdot}{-ip+m}\right.\right.$$
$$\times\left(\frac{1}{(\mathbf{p}+e\mathbf{A})^2+m^2+2mk+(e/2)\sigma_{\mu\nu}F_{\mu\nu}}\right.$$
$$\left.\left.-\frac{1}{p^2+m^2+2mk}\right)(-ip+m)[\mathbf{p},ieA]\right|n\right\rangle dk.$$

In the same approximation, $(-ip+m)[\mathbf{p},-ieA]|n\rangle=-2m[\mathbf{p},H]|n\rangle$, where

$$H=\frac{1}{2m}(\mathbf{p}+e\mathbf{A})^2-\frac{Z\alpha}{r}+\frac{e}{2m}\boldsymbol{\sigma}\cdot\mathbf{B},$$

the nonrelativistic Hamiltonian. As a result the numerator has an even Dirac structure, so that in the denominator we may neglect $\boldsymbol{\gamma}\cdot\mathbf{p}$ compared to m, and the spin orbit term $\boldsymbol{\alpha}\cdot\mathbf{E}$. The integral with respect to k is trivial and yields

$$Q'=-\frac{2\alpha}{3\pi m^2}\left\langle n\left|\mathbf{p}\cdot\left(\ln\frac{H-E}{\mathrm{ry}}\right.\right.\right.$$
$$\left.\left.\left.-\ln\frac{p^2+m^2}{2m\ \mathrm{ry}}\right)(H-E)\mathbf{p}\right|n\right\rangle, \quad (3.25)$$

where $|n\rangle$ is the Schrödinger eigenstate of energy E of the nonrelativistic Hamiltonian H. Adding Eqs. (3.21) and (3.25) yields $\Delta E_F(3)=L'+Q'$ in the form

$$\Delta E_F(3)=\frac{\alpha}{4\pi m^2}\left(\frac{4}{3}\ln\frac{m}{2\ \mathrm{ry}}+\frac{13}{9}\right)\langle\bar{n}|ie\nabla^2A|n\rangle$$
$$-\frac{2\alpha}{3\pi m^2}\left\langle n\left|\mathbf{p}\cdot\ln\left(\frac{H-E}{\mathrm{ry}}\right)(H-E)\mathbf{p}\right|n\right\rangle. \quad (3.26)$$

It is now easy to show that $\Delta E_F(3)$ is gauge invariant. The first term in the above expression is manifestly

invariant. In the second term, the combination $H-E$ is gauge invariant, as is $(H-E)\mathbf{p}|n\rangle=(H-E)(\mathbf{p}+\boldsymbol{\lambda})|n\rangle$ where $\boldsymbol{\lambda}$ is any constant vector. This completes the proof that to the required order $\Delta E_F=\Delta E_F(1)+\Delta E_F(2)+\Delta E_F(3)$. By Eqs. (3.5), (3.7), and (3.26)

$$\Delta E_F=\frac{\alpha}{4\pi m^2}\left[\frac{4}{3}\ln\frac{m}{2\,\mathrm{ry}}+\frac{11}{18}\right]\langle\bar{n}|ie\nabla^2\boldsymbol{A}|n\rangle$$
$$+\frac{\alpha}{4\pi}\left\langle\bar{n}\left|\frac{e}{m}\sigma_{\mu\nu}\left(1+\frac{1}{6}\frac{\nabla^2}{m^2}\right)\frac{\partial A_\nu}{\partial x_\mu}\right|n\right\rangle$$
$$-\frac{2\alpha}{3\pi m^2}\left\langle n\left|\mathbf{p}\cdot(H-E)\ln\frac{H-E}{\mathrm{ry}}\mathbf{p}\right|n\right\rangle. \quad (3.27)$$

We have observed previously that the second term in this expression is the expansion up to ∇^2/m^2 of the second order magnetic moment form factor. Similarly the first term is now recognized as the ∇^2/m^2 term in a corresponding expansion of the charge form factor, in which the fictitious photon mass, which is required in the form $\ln(\lambda)$ to make this term finite in the scattering approximation, is replaced by $\ln(2\,\mathrm{ry})-5/6$,[15] in agreement with the connection formula of French. [Equation (3.27) is independent of ry, which could be assigned any value.] When binding is properly taken into account, as it is here, the infrared divergence, characteristic of the scattering theory, disappears. The above expression is the exact analog of the formula for the lowest order Lamb shift. The external potential now includes the nuclear magnetic dipole as well as the Coulomb part, and the magnetic moment interaction is represented more accurately by the presence of the $\sigma_{\mu\nu}(\nabla^2/m^2)(\partial A_\nu/\partial x_\mu)$ term.

It must be emphasized that this expression does not correctly represent the shift in the hyperfine structure to order $\alpha(Z\alpha)^2$ hfs, but is only suited to be substituted into the formula for $\Delta I=(8\Delta E_2-\Delta E_1)/[\alpha(Z\alpha)^2\,\mathrm{hfs}]$.

Schwartz[16] has treated this problem nonrelativistically in a calculation analogous to Bethe's original nonrelativistic calculation[17] of the lowest order Lamb Shift. Independently of the present work, Schwartz has obtained the coefficient of $\ln(Z\alpha)$ and an expression equivalent to the third term of Eq. (3.27) for the low-energy part.

4. EVALUATION OF THE FLUCTUATION ENERGY

We will now evaluate the gauge-invariant terms which have been isolated in the preceding section. Let us consider the first term of Eq. (3.27) which we label ΔE_C to indicate its origin in the charge form factor.

$$\Delta E_C=\frac{-\alpha}{4\pi}\left(\frac{8}{3}\ln\frac{1}{Z\alpha}+\frac{11}{18}\right)$$
$$\times\left\{-\frac{1}{m^2}\langle\bar{C}|ie\nabla^2\boldsymbol{\gamma}\cdot\mathbf{A}^M|C\rangle+\frac{2}{m^2}\left\langle C\left|\nabla^2\frac{Z\alpha}{r}\right|M\right\rangle\right\}. \quad (4.1)$$

In this expression we have retained those terms which contribute to the hyperfine splitting. The first term takes the form

$$\Delta E_{Ca}=\frac{-\alpha}{4\pi}\left(\frac{8}{3}\ln\frac{1}{Z\alpha}+\frac{11}{18}\right)\frac{1}{m^2}\frac{e}{3m}\langle\boldsymbol{\sigma}\cdot\mathfrak{y}\rangle$$
$$\times\int\boldsymbol{\nabla}\delta(\mathbf{x})\cdot\boldsymbol{\nabla}\psi^2 d\mathbf{x}, \quad (4.2)$$

$$\Delta I_{Ca}=\frac{1}{4\pi}\left(\frac{8}{3}\ln\frac{1}{Z\alpha}+\frac{11}{18}\right)$$
$$\times\frac{1}{(mZ\alpha)^2}\nabla^2\left(\frac{\psi_2^2(r)}{\psi_2^2(0)}-\frac{\psi_1^2(r)}{\psi_1^2(0)}\right)\Bigg|_{r=0}$$
$$=\frac{-3}{8\pi}\left(\frac{8}{3}\ln\frac{1}{Z\alpha}+\frac{11}{18}\right), \quad (4.3)$$

whereas the second is given by

$$\Delta E_{Cb}=\frac{-\alpha}{4\pi}\left(\frac{8}{3}\ln\frac{1}{Z\alpha}+\frac{11}{18}\right)\frac{2}{m^2}(-4\pi Z\alpha)\langle C|\delta(\mathbf{x})|M\rangle, \quad (4.4)$$

$$\Delta I_{Cb}=\frac{-1}{\pi}(2\ln 2-3)\left(\frac{8}{3}\ln\frac{1}{Z\alpha}+\frac{11}{18}\right). \quad (4.5)$$

As a result

$$\Delta I_C=\Delta I_{Ca}+\Delta I_{Cb}=\frac{1}{\pi}\left(7-\frac{16}{3}\ln 2\right)\left(\ln\frac{1}{Z\alpha}+\frac{11}{48}\right). \quad (4.6)$$

A comparison of Eqs. (2.13), (2.14), (4.1), and (4.6) justifies the remarks immediately preceding and following Eq. (2.14) by proving the equivalence of the two methods.

We correspondingly label the second term of Eq. (3.27) ΔE_M, since it originates in the magnetic moment form factor. Recalling that the ∇^2/m^2 in this term contributes only when the potential is magnetic, we rewrite it as

$$\Delta E_M=\alpha/4\pi\left[\left\langle\bar{C}\left|\frac{e}{m}(1+\tfrac{1}{6}\nabla^2/m^2)\boldsymbol{\sigma}\cdot\mathbf{B}\right|C\right\rangle\right.$$
$$\left.+\frac{1}{m}\langle\bar{C}|i\gamma_4\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}eA_4|M\rangle+\frac{1}{m}\langle\bar{M}|i\gamma_4\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}eA_4|C\rangle\right]. \quad (4.7)$$

[15] J. French and V. Weisskopf, Phys. Rev. **75**, 1240 (1949).
[16] C. Schwartz, Bull. Am. Phys. Soc. **3**, 404 (1958). I wish to thank C. Schwartz for communicating his results.
[17] H. Bethe, Phys. Rev. **72**, 339 (1947).

The term containing $(\nabla^2/m^2)\boldsymbol{\sigma}\cdot\mathbf{B}$ is easily treated; only large components are retained and $\boldsymbol{\sigma}\cdot\mathbf{B}$ is replaced by its S-wave part$=\frac{2}{3}\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\delta(\mathbf{x})$. Comparison with Eqs. (4.2) and (4.3) above indicates that this term contributes $-1/(8\pi)$ to ΔI. To evaluate the term $(e/m)\langle\bar{C}|\boldsymbol{\sigma}\cdot\mathbf{B}|C\rangle$, we express the matrix elements in terms of large and small components. For the small components the nonrelativistic expression suffices, but the Dirac form, ψ_L, correct to order $(Z\alpha)^2$ is required for the large components:

$$\frac{\alpha}{4\pi}\left\langle\bar{C}\left|\frac{e}{m}\boldsymbol{\sigma}\cdot\mathbf{B}\right|C\right\rangle=\frac{\alpha}{4\pi}\int\psi_L^{\dagger}\frac{e}{m}\boldsymbol{\sigma}\cdot\mathbf{B}\psi_L d\mathbf{x}$$
$$-\frac{\alpha}{4\pi}\int\left(\frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2m}\psi\right)^{\dagger}\frac{e}{m}\boldsymbol{\sigma}\cdot\mathbf{B}\left(\frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2m}\psi\right)d\mathbf{x}. \quad (4.8)$$

The first term of this expression contributes $(1/2\pi)\times(3/16+\ln 2)$ to ΔI, and the second $(1/4\pi)(7/16-\ln 2)$. The net contribution from the first term of Eq. (4.7) is thus

$$\Delta I_{Ma}=(1/4\pi)(5/16+\ln 2). \quad (4.9)$$

After the Dirac algebra has been performed, the last two terms of Eq. (4.7) take the form

$$\Delta E_{Mb}=\frac{\alpha}{4\pi}\left[\frac{1}{m^2}\int\psi\boldsymbol{\sigma}\cdot e\mathbf{A}^M\times\nabla\frac{Z\alpha}{r}\psi d\mathbf{x}\right.$$
$$\left.-\frac{1}{m^2}\int\psi\nabla^2\frac{Z\alpha}{r}\psi^M d\mathbf{x}\right]. \quad (4.10)$$

Comparison with Eqs. (4.1) and (4.5) reveals that the second term of this expression contributes $(1/2\pi)\times(3-2\ln 2)$ to ΔI, whereas the first yields $(1/8\pi)\times(5-8\ln 2)$, for a net contribution given by

$$\Delta I_{Mb}=(1/8\pi)(17-16\ln 2). \quad (4.11)$$

The total

$$\Delta I_M=\Delta I_{Ma}+\Delta I_{Mb}$$
$$=(1/4\pi)[8+(13/16)-7\ln 2]. \quad (4.12)$$

The only term which remains to be evaluated is the last one of Eq. (3.27). It represents the contribution due to the presence of a soft photon in the intermediate state and will be denoted by ΔE_S.

$$\Delta E_S=\frac{-2\alpha}{3\pi m^2}\left\langle n\left|\mathbf{p}\cdot(H-E)\ln\left(\frac{H-E}{\mathrm{ry}}\right)\mathbf{p}\right|n\right\rangle. \quad (4.13)$$

Expressions of this sort are usually evaluated by inserting a resolution of the identity belonging to H. In the present case, where H is the Hamiltonian for a hydrogen atom, the resulting sum-over-states involves a sum over the discrete bound states of the atom, and an integral over the continuum ionized states. However, Schwartz and Tiemann[5] have recently obtained an integral representation of the corresponding term in the lowest order Lamb shift, and we will apply their method here. The derivation will be presented in some detail, as an illustration of the method, and because certain integrals appear that are of interest for other calculations, and which are evaluated numerically.

We rewrite Eq. (4.13) in the form

$$\Delta E_S=\frac{2\alpha}{3\pi m^2}\lim_{K\to\infty}\left\{-\int_0^K dk\,k\left\langle n\left|\mathbf{p}\cdot\frac{1}{H-E+k}\mathbf{p}\right|n\right\rangle\right.$$
$$\left.+K\langle n|\mathbf{p}^2|n\rangle+\frac{1}{2}\ln\frac{K}{\mathrm{ry}}\langle n|[\mathbf{p}\cdot,[\mathbf{p},H]]|n\rangle\right\}. \quad (4.14)$$

Quantities which vanish as $K\to\infty$ are dropped. As usual we will retain only those terms which are linear in the nuclear moment. Since

$$|n\rangle=|C\rangle+|M\rangle,\quad H=H^C+H^M,\quad E=E^C+E^M,$$
$$\left\langle n\left|\mathbf{p}\cdot\frac{1}{H-E+k}\mathbf{p}\right|n\right\rangle\to 2\left\langle C\left|\mathbf{p}\cdot\frac{1}{H^C-E^C+k}\mathbf{p}\right|M\right\rangle$$
$$-\left\langle C\left|\mathbf{p}\cdot\frac{1}{H^C-E^C+k}(H^M-E^M)\right.\right.$$
$$\left.\left.\times\frac{1}{H^C-E^C+k}\mathbf{p}\right|C\right\rangle. \quad (4.15)$$

The term involving H^M vanishes. This may be seen by taking a momentum representation where it has the form

$$\int f^*(\mathbf{q}_2^2)\mathbf{q}_2\cdot\left[\frac{2}{3}\boldsymbol{\sigma}\cdot\boldsymbol{\mu}-\sigma_i\left(\frac{(\mathbf{q}_2-\mathbf{q}_1)_i(\mathbf{q}_2-\mathbf{q}_1)_j}{|\mathbf{q}_2-\mathbf{q}_1|^2}\right.\right.$$
$$\left.\left.-\frac{1}{3}\delta_{ij}\right)\mu_j\right]\mathbf{q}_1 f(\mathbf{q}_1^2)d\mathbf{q}_1 d\mathbf{q}_2,$$

which vanishes upon angular integration. We may therefore rewrite Eq. (4.14) in the form

$$\Delta E_S=\frac{2\alpha}{3\pi m^2}\lim_{K\to\infty}$$
$$\times\left\{-2\int_0^K\left\langle C\left|\mathbf{p}\cdot\frac{1}{H^C-E^C+k}\mathbf{p}\right|M\right\rangle k dk\right.$$
$$-E^M\int_0^K\left\langle C\left|\mathbf{p}\cdot\frac{1}{(H^C-E^C+k)^2}\mathbf{p}\right|C\right\rangle k dk$$
$$\left.+K\langle n|\mathbf{p}^2|n\rangle+\frac{1}{2}\ln\frac{K}{\mathrm{ry}}\langle\bar{n}|[\mathbf{p}\cdot,[\mathbf{p},ieA]]|n\rangle\right\}. \quad (4.16)$$

The last term has been written in relativistic notation, since in this form the contribution of the matrix element to ΔI was evaluated for ΔI_C [Eq. (4.1)].

It is convenient to transform the second term on the right-hand side of Eq. (4.16) to put it in a form similar to the first term. For this purpose we note that

$$\lim\left\langle C\left|\mathbf{p}\cdot\int_0^K\frac{kdk\,\mathbf{p}|C\rangle}{(H^C-E^C+k)^2}\right.\right.$$
$$=\lim\left\{-\int_0^K\left\langle C\left|\mathbf{p}\cdot\frac{1}{H^C-E^C+k}im\mathbf{x}\right|C\right\rangle kdk\right.$$
$$\left.+K\langle C|\mathbf{p}\cdot im\mathbf{x}|C\rangle-\langle C|\mathbf{p}^2|C\rangle\right\},\quad(4.17)$$

since $\mathbf{p}=im[H,\mathbf{x}]$. Therefore

$$\Delta E_S=\frac{2\alpha}{3\pi m^2}\lim_{K\to\infty}\left\{-\left\langle C\left|\mathbf{p}\cdot\int_0^K\frac{kdk}{H^C-E^C+k}\right.\right.\right.$$
$$\times(2\mathbf{p}|M\rangle-im\mathbf{x}E^M|C\rangle)$$
$$+K(\langle n|\mathbf{p}^2|n\rangle-E^M\langle C|\mathbf{p}\cdot im\mathbf{x}|C\rangle)$$
$$\left.+\frac{1}{2}\ln\frac{K}{\mathrm{ry}}\langle\bar{n}|(-ie)\nabla^2A|n\rangle+E^M\langle C|\mathbf{p}^2|C\rangle\right\}.\quad(4.18)$$

To obtain ΔI_S we note that the coefficient of K is state independent. This is easily proven by applying the virial theorem to $\langle n|\mathbf{p}^2|n\rangle$ and retaining terms linear in the nuclear moment (i.e., evaluating

$$\langle n|[H,\mathbf{p}\cdot\mathbf{x}]|n\rangle=0)$$

and by noting that $E^M\langle C|\mathbf{p}\cdot im\mathbf{x}|C\rangle=\frac{1}{2}mE^M\langle C|\nabla\cdot\mathbf{x}|C\rangle=\frac{3}{2}mE^M$. The coefficient of $\ln(K/\mathrm{ry})$ is obtained from Eqs. (4.1), (4.3), and (4.5). Also $\langle C|\mathbf{p}^2|C\rangle=(mZ\alpha)^2/n^2$. Writing $|M\rangle=(E^M/\mathrm{ry})|u\rangle$, we therefore obtain

$$\Delta I_S=\frac{-2}{3\pi(mZ\alpha)^2}\lim_{K\to\infty}\Delta\left\langle C\left|\mathbf{p}\cdot\int_0^K\frac{kdk}{H^C-E^C+k}\right.\right.$$
$$\left.\times\left(\frac{2\mathbf{p}}{\mathrm{ry}}\middle|u\right\rangle-im\mathbf{x}|C\rangle\right)$$
$$-\frac{1}{2\pi}\left[7-\frac{16}{3}\ln2\right]\ln\frac{K}{\mathrm{ry}}-\frac{1}{2\pi},\quad(4.19)$$

where $\Delta(\ )\equiv(\ )_{2S}-(\ )_{1S}$.

The integration over k has been introduced as a device for evaluating ΔE_S given by Eq. (4.13). However one easily recognizes that the first term of Eq. (4.14) is the expression for the level shift which one obtains from the nonrelativistic theory. The term proportional to $\ln(K/\mathrm{ry})$, which appears subtracted off, correctly yields the contribution to ΔI proportional to $\ln(Z\alpha)$, if one sets $K=m$. The term linear in K, which is also subtracted off, is of order αE^M, if one sets $K=m$. As is characteristic of lower order terms, it is state independent.

To proceed with the evaluation it is convenient to scale out all powers of $Z\alpha$ and work with dimensionless quantities. For this purpose we choose the unit of length $=(1/mZ\alpha)$, and scale $(k,H^C,E^C)\to\mathrm{ry}(k,H^C,E^C)$. All quantities are then expressed in atomic units. Since we will deal only with S states, we normalize $\psi_n(r)$ to $\int_0^\infty\psi_n^2r^2dr=1$, so that

$$\psi_{1S}=2\exp(-r);$$
$$\psi_{2S}=(1/\sqrt{2})\exp(-r/2)(1-r/2).\quad(4.20)$$

Then

$$\Delta I_S=[2/(3\pi)]\lim_{K\to\infty}\Delta J-[1/(2\pi)]$$
$$\times[7-(16/3)\ln2]\ln K-1/(2\pi),\quad(4.21)$$

where

$$J=-\int_0^K\left\langle C\left|\mathbf{p}\cdot\frac{1}{H^C-E^C+k}\right.\right.$$
$$\left.\times(2\mathbf{p}|u\rangle-\tfrac{1}{2}i\mathbf{x}|C\rangle)kdk.\quad(4.22)$$

The heart of the method is to evaluate the quantity $|v\rangle=1/(H^C-E^C+k)|w\rangle$ by considering the differential equation $(H^C-E^C+k)|v\rangle=|w\rangle$, and noting that the inner product appearing in Eq. (4.22), when expressed in a position representation, has the form of a Laplace transform. Writing

$$\hat{r}(1/r^2)f_n(r)\exp(-r/n)$$
$$=\frac{1}{H^C-E^C+k}\hat{r}\left(2\frac{du_n}{dr}+\frac{1}{2}r\psi_n\right),\quad(4.23)$$

where $\psi=\langle\mathbf{x}|C\rangle$, $u=\langle\mathbf{x}|u\rangle$, and $\hat{r}$ is the unit vector in the radial direction, we obtain

$$J_n=-\int_0^K dk\,k\int_0^\infty\frac{d\psi_n}{dr}e^{-r/n}f_n(r)dr.\quad(4.24)$$

Inserting the expressions (4.20) for ψ_n yields

$$J_1=2\int_0^K dk\,k\tilde{f}_1(2),\quad(4.25a)$$

$$J_2=2\int_0^K dk\,k2^{-3}[\tilde{f}_2(1)+\tfrac{1}{4}\tilde{f}_2'(1)],\quad(4.25b)$$

where $\tilde{f}_n(p)=\int_0^\infty\exp(-pr)f_n(r)dr$, the Laplace transform of $f_n(r)$.

The problem of evaluating ΔI_S is now reduced to the problem of obtaining the functions $\tilde{f}_n(p)$. We will show that $\tilde{f}$ satisfies a first order linear differential equation and is thus obtainable by quadrature. From Eq. (4.23)

$$(H^C-E_n{}^C+k)\hat{r}(1/r^2)f_n(r)\exp\left(-\frac{r}{n}\right)=\hat{r}\left(2\frac{du_n}{dr}+\frac{1}{2}r\psi_n\right). \quad (4.26)$$

In atomic units $E_n{}^C=-1/n^2$ and $H^C=-\nabla^2-2/r$, so that

$$rf_n''(r)-2\left(1+\frac{r}{n}\right)f_n'(r)+\left(2+\frac{2}{n}-kr\right)f_n(r)=-e^{r/n}r^3\left(2\frac{du_n}{dr}+\frac{1}{2}r\psi_n\right), \quad (4.27)$$

or

$$\left(-p^2+\frac{2p}{n}+k\right)\tilde{f}_n'(p)+2\left(\frac{2}{n}-2p+1\right)\tilde{f}_n(p)=-\int_0^\infty e^{-pr}e^{r/n}r^3\left(2\frac{du_n}{dr}+\frac{1}{2}r\psi_n\right)dr\equiv-n^{\frac{1}{2}}Q_n(p). \quad (4.28)$$

In going from (4.27) to (4.28) we have imposed the boundary condition $f_n(0)=0$. Since $Q_n(p)$ is a known function, $\tilde{f}_n(p)$ is obtainable by quadrature. Using a formula from the elementary theory of differential equations,[18] we obtain

$$\tilde{f}_n(p)=-\frac{(\lambda_n+1/n-p)^{1/\lambda_n-2}}{(\lambda_n-1/n+p)^{1/\lambda_n+2}}\times\int_{\text{const}}^{p}\frac{(\lambda_n-1/n+p')^{1/\lambda_n+1}}{(\lambda_n+1/n-p')^{1/\lambda_n-1}}n^{\frac{1}{2}}Q_n(p')dp', \quad (4.29)$$

where $\lambda_n=(k+1/n^2)^{\frac{1}{2}}$. Since $\tilde{f}_n(p)$ is a Laplace transform, it must be analytic in the right-hand half plane of the complex variable p. We therefore set const $=\lambda_n+1/n$, since $\tilde{f}_n(p)$ would be singular at the point $p=\lambda_n+1/n$ otherwise. To obtain J_n given by Eqs. (4.25) we require $\tilde{f}_n(2/n)$ and

$$k\tilde{f}_2'(1)=-2\sqrt{2}Q_2(1). \quad (4.30)$$

The latter expression is obtained directly from the differential equation (4.28) by substitution.

Inserting Eqs. (4.29) and (4.30) into Eqs. (4.25), we may write Eq. (4.21) in the form

$$\Delta I_S=\frac{4}{3\pi}\lim_{K\to\infty}\Delta\int_{1/n}^{(K+1/n^2)^{\frac{1}{2}}}\frac{d\lambda\,2\lambda}{(\lambda^2-1/n^2)}\left(\frac{\lambda-1/n}{\lambda+1/n}\right)^{1/\lambda}\times\int_{2/n}^{\lambda+1/n}\left(\frac{\lambda-1/n+p}{\lambda+1/n-p}\right)^{1/\lambda}[\lambda^2-(p-1/n)^2]\times Q_n(p)dp-\frac{1}{3\pi}Q_2(1)K-\frac{1}{2\pi}\left[7-\frac{16}{3}\ln 2\right]\times\ln K-\frac{1}{2\pi}. \quad (4.31)$$

$Q_n(p)$ is defined by Eq. (4.28). The indicated integration yields

$$Q_1(p)=\left[\frac{1}{p^2}+\frac{6}{p^3}+\frac{12\ln p/2+20}{p^4}-\frac{24}{p^5}\right], \quad (4.32a)$$

$$Q_2(p)=\left[\frac{1}{p^2}+\frac{5}{p^3}+\frac{12\ln p-4}{p^4}-\frac{12\ln p+23}{p^5}+\frac{15}{2p^6}\right], \quad (4.32b)$$

so that $Q_2(1)=-27/2$.

Due to the presence of the forms $1/p^2$, $1/p^3$, and $\ln(p)$ in Q, the analytic expression (4.31) is considerably more complicated than the corresponding expression for the Lamb shift treated by Schwartz and Tiemann.[5] As a result, it is not convenient to expand the integrand in a series, integrate term by term, and sum the series numerically, as they do. The numerical work which is required here, however, is still not very difficult.

In order to carry out the limiting process indicated in Eq. (4.31), we separate the integral over k into two parts. One part is finite as $K\to\infty$ and is evaluated numerically. The other part is integrated analytically and combined with the other K-dependent terms to yield a finite result. For this purpose we write

$$\Delta I_S=N+A-1/(2\pi), \quad (4.33)$$

where

$$N=\frac{4}{3\pi}\Delta\int_{1/n}^{\infty}d\lambda 2\lambda\int_{2/n}^{\lambda+1/n}\left\{\frac{1}{\lambda^2-1/n^2}\times\left(\frac{\lambda-1/n}{\lambda+1/n}\right)^{1/\lambda}\left[\frac{\lambda+(p-1/n)}{\lambda-(p-1/n)}\right]^{1/\lambda}-\left[\frac{1}{\lambda^2-1/n^2}+\frac{1}{\lambda^3}\ln\left(\frac{\lambda-1/n}{\lambda+1/n}\right)+\frac{1}{\lambda^3}\ln\frac{\lambda+(p-1/n)}{\lambda-(p-1/n)}\right]\right\}\times\left[\lambda^2-\left(p-\frac{1}{n}\right)^2\right]Q_n(p)dp, \quad (4.34)$$

[18] See for instance H. Phillips, *Differential Equations* (John Wiley & Sons, New York, 1934), p. 39.

and

$$A=\lim_{K\to\infty}\left\{\frac{4}{3\pi}\Delta\int_{1/n}^{(K+1/n^2)^{\frac{1}{2}}}d\lambda 2\lambda\int_{2/n}^{\lambda+1/n}dp\left\{\frac{1}{\lambda^2-1/n^2}+\frac{1}{\lambda^3}\ln\left[\left(\frac{\lambda-1/n}{\lambda+1/n}\right)\left(\frac{\lambda+(p-1/n)}{\lambda-(p-1/n)}\right)\right]\right\}\times\left[\lambda^2-\left(p-\frac{1}{n}\right)^2\right]Q_n(p)+\frac{9}{2\pi}K-\frac{1}{2\pi}\left(7-\frac{16}{3}\ln 2\right)\ln K\right\}. \quad (4.35)$$

N was evaluated on the Nevis IBM 650 computer and found to be -0.94 ± 0.02. The integration and limit process indicated to obtain term A are fairly straightforward, though somewhat lengthy. One obtains from Eqs. (4.33), (4.34), and (4.35)

$$\Delta I_S=-0.94\pm0.02+[4/(3\pi)]\times[-(58+5/32-4/9)+(75-1/2)\ln 2-10\ln^2 2+(5/6)\pi^2]-1/(2\pi). \quad (4.36)$$

5. COMPARISON WITH EXPERIMENT

Writing $\Delta I=\Delta I_P+\Delta I_C+\Delta I_M+\Delta I_S$, the respective contributions from the polarization energy, charge form factor, magnetic moment form factor, and soft photon intermediate states, we have from Eq. (2.13), (4.6), (4.12), and (4.36)

$$\Delta I=-[1/(10\pi)][7-(16/3)\ln 2]+(1/\pi)[\ln(1/Z\alpha)+11/48][7-(16/3)\ln 2]+[1/(4\pi)](8+13/16-7\ln 2)+[-0.94\pm0.02-1.126-1/(2\pi)],$$

$$\Delta I=3.40\pm0.02. \quad (5.1)$$

We now substitute the computed value of ΔI into the theoretical formula [Eq. (1.4)] for R, the ratio of the hyperfine splitting in the $2S$ state to the hyperfine splitting in the $1S$ state. Recalling the argument of Sec. 1, showing that $(c_2-c_1)\alpha^3=\Delta I\alpha(Z\alpha)^2$, we obtain

$$R_{\rm th}=\tfrac{1}{8}[1+\tfrac{5}{8}(Z\alpha)^2-[5/(16\pi)](Z\alpha)^2\alpha+(3.4\pm0.02)\alpha(Z\alpha)^2+O(\alpha^2 m/M)],$$

or

$$R_{\rm th}=\tfrac{1}{8}(1.000\,034\,5\pm0.000\,000\,2).$$

In this last expression the uncertainty is due to the $\alpha^2 m/M$ terms, estimated to be $\lesssim 0.2$ ppm. They are of three kinds. One is a cross term equal to $(15/8)(Z\alpha)^2 m/M=0.05$ ppm, which arises from the Breit correction [Eq. (1.1)] and the reduced mass correction [Eq. (1.3)] when the ratio R is formed. The second is the dipole interaction in second order perturbation theory, found by Schwartz[5] to be -0.085 ppm. The third is a recoil effect which Sternheim[19] is currently calculating by means of the Bethe-Salpeter equation.

[19] M. Sternheim (private communication).

The experimentally determined ratios for hydrogen[20] and deuterium[21] are

$$R_{\rm exp}({\rm H})=\tfrac{1}{8}(1.000\,034\,6\pm0.000\,000\,3),$$
$$R_{\rm exp}({\rm D})=\tfrac{1}{8}(1.000\,034\,2\pm0.000\,000\,6),$$

and are evidently in satisfactory agreement with the theoretical value noted above.

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APPENDIX A: WAVE FUNCTIONS

The following hydrogen atom wave functions are required.

1. The $1S$ and $2S$ nonrelativistic Schrödinger wave functions of the electron in a Coulomb field. We denote them by $\psi_n=\langle \mathbf{x}|C\rangle$,

$$\psi_1=(\beta^3/\pi)^{\frac{1}{2}}\exp(-\beta r), \quad (A.1)$$
$$=(\beta^3/8\pi)^{\frac{1}{2}}\exp(-\beta r/2)(1-\beta r/2), \quad (A.2)$$
$$\beta=mZ\alpha.$$

They are the S-state eigenfunctions of the nonrelativistic Coulomb Hamiltonian $H^C=p^2/2m-Z\alpha/r$, with eigenvalues $E^C=m(Z\alpha)^2/2$ and $m(Z\alpha)^2/8$, respectively. It is important for this calculation that these wave functions satisfy $\psi_n'(0)=-\beta\psi_n(0)$, so that $|\psi_n'(0)|^2$ and $\psi_n(0)\psi_n'(0)$ are state independent.

2. The $1S$ and $2S$ nonrelativistic Schrödinger magnetic wave functions. They are the corrections, linear in the nuclear magnetic moment, to the ψ_n given above, due to the perturbing Hamiltonian

$$H^M\equiv\frac{e}{3m}\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\delta(\mathbf{x})+\frac{e}{8\pi m}\frac{1}{r^3}\left[\frac{3\boldsymbol{\sigma}\cdot\mathbf{x}\boldsymbol{\mu}\cdot\mathbf{x}}{r^2}-\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\right]. \quad (A.3)$$

Writing $H=H^C+H^M$, $E=E^C+E^M$, and $|n\rangle=|C\rangle+|M\rangle$, then $|M\rangle$ satisfies

$$(H^C-E^C)|M\rangle=(E^M-H^M)|C\rangle,$$

and

$$\langle C|M\rangle=0.$$

As argued in Sec. 2, we require only the S-state part, denoted by $(E_n{}^M/{\rm ry})u_n$, of the magnetic wave functions $\psi_n{}^M=\langle\mathbf{x}|M\rangle$:

$$u_1=\tfrac{1}{4}\psi_1(0)e^{-\beta r}\left(\frac{-1}{\beta r}+2\ln 2\beta r+(2\gamma-5)+2\beta r\right), \quad (A.4)$$

$$u_2=2\psi_2(0)e^{-\frac{1}{2}\beta r}\left[\frac{-1}{\beta r}+2\ln\beta r+(2\gamma-\tfrac{3}{2})-\beta r\ln\beta r-\left(\gamma-\frac{13}{4}\right)\beta r-\tfrac{1}{4}(\beta r)^2\right], \quad (A.5)$$

[20] J. W. Heberle, H. A. Reich, and P. Kusch, Phys. Rev. **101**, 612 (1956).

[21] H. A. Reich, J. W. Heberle, and P. Kusch, Phys. Rev. **104**, 1585 (1956).

where $\gamma=0.577215\cdots$. The value of γ is not needed for this calculation.

3. The $1S$ and $2S$ Dirac Coulomb wave functions. Except in the case mentioned below, they are everywhere used in the nonrelativistic limit where the large components are ψ_n and the small components are $(\boldsymbol{\sigma}\cdot\mathbf{p}/2m)\psi_n$. To evaluate the contribution to ΔI from Eq. (4.8), the large components ψ_L are required at the origin correct to order $(Z\alpha)^2$. The exact large-component wave functions are

$$\psi_{L1}=C_1e^{-\beta_1 r}(\beta_1 r)^s, \tag{A.6}$$

$$\psi_{L2}=C_2e^{-\beta_2 r}(\beta_2 r)^s\left(1+\tau-\frac{2\beta_2 r}{3+2s}\right), \tag{A.7}$$

where $\beta_1=mZ\alpha$, $\beta_2=m(-s/2)^{\frac{1}{2}}$, $s=[1-(Z\alpha)^2]^{\frac{1}{2}}-1$,

$$\tau=\frac{1-[2(s+2)]^{\frac{1}{2}}}{3+2s},$$

$$C_1^2=\frac{\beta_1^3}{\pi}\frac{2^{2s}(2+s)}{\Gamma(2s+3)},$$

$$C_2^2=\frac{\beta_2^3}{2\pi}\frac{2s+3}{\Gamma(2s+3)}\frac{1+[2(s+2)]^{\frac{1}{2}}}{2(s+2)}\left[1+\left(\frac{s+2}{2}\right)^{\frac{1}{2}}\right].$$

4. The $1S$ and $2S$ Dirac magnetic wave functions in the nonrelativistic limit. The large components are given by $\psi_n{}^M$ (only the S-state part given above is needed) and the small components by $(\boldsymbol{\sigma}\cdot\mathbf{p}/2m)\psi_n{}^M+(\boldsymbol{\sigma}\cdot e\mathbf{A}^M/2m)\psi_n$.

5. In Sec. 4, atomic units are used and wave functions are normalized to $\int_0^\infty\psi_n{}^2r^2dr=1$. To obtain the appropriate wave functions, simply set $\beta=1$ and multiply by $(4\pi)^{\frac{1}{2}}$ in the above expressions. The quantity $Q_n(p)$ is easily obtained in terms of these wave functions from its definition in Eq. (4.28),

$$Q_n(p)=n^{-\frac{3}{2}}\int_0^\infty e^{-pr}e^{r/n}r^3\left(2\frac{du_n}{dr}+\tfrac{1}{2}r\psi_n\right). \tag{A.8}$$

The result is given in Eq. (4.32).

APPENDIX B: ARRANGEMENT OF THE NUMERICAL WORK AND A TABULATION OF TWELVE INTEGRALS

The problem at hand is to evaluate the double integral N given by Eq. (4.34). The method will be to transform the integral by successive changes of variable so that the Riemann sum may be conveniently performed numerically. For this purpose we require finite limits of integration and an integrand which is finite throughout the region of integration.

We introduce the new variables $y=1/n\lambda$ and

$$u_n(p)=\frac{1}{2}\ln\left[\left(\frac{\lambda-1/n}{\lambda+1/n}\right)\left(\frac{\lambda+(p-1/n)}{\lambda-(p-1/n)}\right)\right]$$

$$=\tanh^{-1}\left(\frac{p-1/n}{\lambda}\right)-\tanh^{-1}\left(\frac{1}{n\lambda}\right),$$

so that

$$N=\frac{4}{3\pi}\Delta\frac{2}{n^3}\int_0^1\frac{dy}{y^4}(1-y^2)\times\int_0^\infty du\frac{[e^{2nyu}-1-2nyu(1-y^2)]\,\mathrm{sech}^4u}{(1+y\tanh u)^4}\times Q_n(p_n), \tag{B.1}$$

where $Q_n(p)$ is given by Eqs. (4.32) and

$$\frac{1}{p_n}=\frac{ny(1+y\tanh u)}{\tanh u+2y+y^2\tanh u}. \tag{B.2}$$

Writing $Q_n(p_n)=R_n(p_n)p_n{}^{-2}$ and $u=(1-v)/v$, we obtain

$$N=\frac{4}{3\pi}\Delta\frac{2}{n}\int_0^1\frac{dy}{y^2}(1-y^2)\int_0^1\frac{dv}{v^2}\times\frac{[e^{2nyu}-1-2nyu(1-y^2)]\,\mathrm{sech}^4u}{(1+y\tanh u)^2(\tanh u+2y+y^2\tanh u)^2}\times R_n(p_n), \tag{B.3}$$

where

$$R_1(p_1)=\left(1+\frac{6}{p_1}+\frac{12\ln(p_1/2)+20}{p_1{}^2}-\frac{24}{p_1{}^3}\right),$$

$$R_2(p_2)=\left(1+\frac{5}{p_2}+\frac{12\ln p_2-4}{p_2{}^2}-\frac{12\ln p_2+23}{p_2{}^3}+\frac{15}{2p_2{}^4}\right).$$

Setting $y=s(1+v)/(s+v)$, we obtain finally

$$N=\sum_{r=1}^{12}I_r, \tag{B.4}$$

where

$$I_r=\int_0^1 ds\int_0^1 dv\frac{[e^{2n_ryu}-1-2n_ryu(1-y^2)]\,\mathrm{sech}^4u[s(1+v)+s+v]S_r(1-s)^2}{s^2(s+v)^2(1+v)(1+y\tanh u)^2(\tanh u+2y+y^2\tanh u)^2}, \tag{B.5}$$

TABLE I. Values of the integrals I_r, defined in Eq. (B.5), obtained on an IBM 650 computer using a trapezoidal rule with successive meshes M_1 (10×10), M_2 (20×20), and M_3 (40×40).

I_r	M_1	M_2	M_3	M_2-M_1	M_3-M_2	$(M_3-M_2)/3$
1	−0.29507	−0.25004	−0.23577	+0.04502	+0.01427	+0.00476
2	−0.22373	−0.26506	−0.28173	−0.04133	−0.01667	−0.00556
3	−0.14677	−0.16035	−0.16398	−0.01358	−0.00363	−0.00121
4	+0.10713	+0.11272	+0.11406	+0.00559	+0.00134	+0.00045
5	−0.15987	−0.18377	−0.19123	−0.02390	−0.00746	−0.00249
6	+0.60672	+0.51345	+0.48331	−0.09327	−0.03014	−0.01005
7	+0.80816	+0.93612	+0.98841	+0.12796	+0.05229	+0.01743
8	−1.35946	−1.46159	−1.48915	−0.10213	−0.02756	−0.00919
9	−1.17292	−1.21873	−1.22975	−0.04581	−0.01102	−0.00367
10	+0.45511	+0.46687	+0.47018	+0.01176	+0.00331	+0.00110
11	+1.38185	+1.55795	+1.61338	+0.17610	+0.05543	+0.01848
12	−0.94981	−1.00758	−1.02095	−0.05777	−0.01337	−0.00446
N	−0.94865	−0.96001	−0.94322	−0.01136	+0.01679	+0.00556

$n_r=1$ for $r=1-5$, $n_r=2$ for $r=6-12$,
$y=s(1+v)/(s+v)$, $u=(1-v)/v$,

$$S_r=\frac{4}{3\pi}\left(-2,\frac{-12}{p},-\frac{40-24\ln 2}{p^2},\frac{48}{p^3},\frac{-24\ln p}{p^2},\right.$$
$$1,\frac{10}{p},-\frac{16+48\ln 2}{p^2},-\frac{184-96\ln 2}{p^3},\frac{120}{p^4},$$
$$\left.\frac{48\ln p}{p^2},\frac{-96\ln p}{p^3}\right),$$

and

$$\frac{1}{p}=\frac{y(1+y\tanh u)}{\tanh u+2y+y^2\tanh u}.$$

The I_r were evaluated on the Nevis IBM 650 computer using a trapezoidal rule for each variable s and v. Three successive runs were made with meshes M_1 (10×10), M_2 (20×20), and M_3 (40×40). The results are given in Table I.

The error inherent in the trapezoidal rule has the form $a(\Delta s)^2+b(\Delta v)^2$, for increments Δs and Δv. Since the increments in the three runs decrease by a factor of 2, the error is expected to decrease by a factor of 4, so that for monotonic convergence the successive differences should decrease by a factor of 3. This is in fact what is observed for each I_r. Making a rough extrapolation, we take the best estimate for I_r to be $M_3+(M_3-M_2)/3$, with an estimated error of $(1/3)\times(M_2-M_1)$. The accurately known Bethe logarithm[22] for the $1S$ and $2S$ states was expressed in terms of I_3, and I_8 and I_9, and the estimate of error for these integrals was verified. The first difference M_2-M_1 for $N=\sum I_r$ is fortuitously small. We take $N=-0.94\pm 0.02$ which generously estimates the error.

The values of I_r may be useful in other calculations involving soft-photon intermediate states. The contribution of these integrals to the $1S$ and $2S$ hyperfine splitting is

$$E_1{}^M\alpha(Z\alpha)^2(-\sum_{r=1}^{5} I_r) \quad \text{and} \quad E_2{}^M\alpha(Z\alpha)^2(\sum_{r=6}^{12} I_r),$$

respectively.

[22] J. Harriman, Phys. Rev. **101**, 594 (1956).