α^3 Corrections to the Hyperfine Structure of the 1S and 2S States of Hydrogen*

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Recent precision measurements of the hyperfine splitting in the 1S and 2S states in hydrogen would make possible the observation of α^3 corrections. A calculation of these corrections would be difficult because of the many processes that can contribute to this order and because of the uncertainty of the nuclear structure effects that can contribute in this numerical order. For these reasons only the ratio of the hyperfine structure in the 2S state to that in the 1S state is calculated here. It is shown that the formation of the ratio eliminates the contribution of most of the α^3 corrections and totally eliminates the nuclear structure effects. The coefficient, $B-A$, of the α^3 terms in the ratio is calculated as $(B-A)=5.28$. This compares with the experimental value, $(B-A)_{\rm exp}=3.4\pm0.8$.

I. INTRODUCTION

CALCULATIONS of the corrections to the Fermi formula[1] for the hyperfine structure (hfs) in S states of hydrogen have been done[2–4] to relative order α, $\alpha(Z\alpha)$, $\alpha\kappa/M$, and $(Z\alpha)^2$. Recent precision measurements[5] of hfs would make possible the observation of deviations of order α^3 from these calculated values in the 1S and 2S states of hydrogen. The calculation of the radiative corrections to hfs to order α^3 is a prohibitively difficult task because of the many electrodynamic processes that can occur in this order and the nuclear structure effects that would contribute in the same order of magnitude. However, since the radiative corrections are basically a high-energy, short-range effect, it will be shown (Sec. III) that the bulk of these processes exhibit dependence upon the state of the hydrogen atom only through an over-all scale factor of the square of the wave function evaluated at the origin. Furthermore it will be shown (Sec. IV) that the effect of the distributed nature of the proton will have the same state dependence in this order. These facts make the calculation of the ratio of hfs in the 2S to that in the 1S state a reasonable task.

In evaluating this ratio the contributions may be divided into two classes. In the first, the relativistic properties of the electron are important and the electron may be treated as free in its intermediate states. In the second, the relativistic effects do not contribute but the properties of the electron in a Coulomb field become important in the intermediate states.

In Secs. II and III the finite mass of the proton and its distributed nature will be neglected. These effects will be treated in Sec. IV, where their contribution to the ratio will be discussed.

II. FORMULATION OF THE PROBLEM

When one neglects the finite mass of the proton and its distributed nature, the hfs in the first two S states of hydrogen can be written

$$\Delta\nu_{1s}=E_1\left[1+\frac{3}{2}(Z\alpha)^2\right]\left(1+\frac{\alpha}{2\pi}-aZ\alpha^2-b\alpha^2+A\alpha^3\right),\quad(1a)$$

$$\Delta\nu_{2s}=E_2\left[1+\frac{17}{8}(Z\alpha)^2\right]\left(1+\frac{\alpha}{2\pi}-aZ\alpha^2-b\alpha^2+B\alpha^3\right),\quad(1b)$$

where the first bracket in each of these arises from the Breit[4] relativistic correction to the wave function. Here

$$E_n=-\tfrac{2}{3}(e/2\kappa)\langle\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\rangle|\psi_n{}^0(0)|^2\quad(2)$$

is the Fermi[1] energy where $|\psi_n{}^0(0)|^2$ is the square of the Schrödinger wave function for the nS state evaluated at the origin and a and b are numerical constants independent of the state.[6] The ratio of the hfs in the 2S state to that in the 1S state to order α^3 can be written

$$\frac{\Delta\nu_{2s}}{\Delta\nu_{1s}}=\frac{1}{8}\left[1+\left(\frac{17}{8}-\frac{3}{2}\right)(Z\alpha)^2+(B-A)\alpha^3\right].\quad(3)$$

The factor $\frac{1}{8}$ arises from the ratio of the wave functions occurring in the Fermi energy. The major portion of this paper will be devoted to the calculation of the difference, $(B-A)$.

III. α^3 TERMS

Radiative corrections of order α^3 can arise in three different ways, as α^3, $\alpha^2(Z\alpha)$, and $\alpha(Z\alpha)^2$. The α^3 corrections come from the sixth-order electrodynamic corrections to the magnetic moment of the electron. These are localized around the origin so that their contributions to hfs are proportional to the square of the

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[1] E. Fermi, Z. Physik **60**, 320 (1930).
[2] N. M. Kroll and F. Pollock, Phys. Rev. **84**, 594 (1951); and Karplus, Klein, and Schwinger, Phys. Rev. **84**, 597 (1951) for the α and $\alpha(Z\alpha)$ corrections. Here α is the fine structure constant and Z is the number of elementary charges on the nucleus. $Z=1$, but Z will be retained to indicate the origin of the term.
[3] R. Arnowitt, Phys. Rev. **92**, 1002 (1953), and W. A. Newcomb and E. E. Salpeter, Phys. Rev. **97**, 1146 (1955) for the $\alpha\kappa/M$ terms. Here κ is the electron mass and M the proton mass.
[4] G. Breit, Phys. Rev. **35**, 1447 (1930) for the $(Z\alpha)^2$ terms.
[5] Heberle, Reich, and Kusch, Phys. Rev. **101**, 612 (1956) for the 2S state and J. P. Wittke and R. H. Dicke, Phys. Rev. **96**, 530 (1954) and P. Kusch, Phys. Rev. **100**, 1188 (1955) for the 1S state.
[6] R. Karplus and A. Klein, Phys. Rev. **85**, 972 (1952) and the first paper cited in reference 2.

wave function of the origin. Hence they are state independent[7] in the sense that they do not contribute to the difference, $(B-A)$. The $\alpha^2(Z\alpha)$ corrections arise from the distributed nature of the fourth-order electrodynamic radiative corrections. These will depend upon the first and higher order spatial derivatives of the wave functions evaluated at the origin. Each derivative will introduce a power of $Z\alpha$ so that only the first derivative can contribute. However, using the Schrödinger equation with an external Coulomb field, the derivative of the wave function at the origin is easily shown to be proportional to the wave function at the origin, $\psi_n^{0\prime}(0)=-\kappa Z\alpha\psi_n^0(0)$, so that $\alpha^2(Z\alpha)$ contributions will not contribute to the difference, $(B-A)$. This argument has been substantiated by an explicit calculation of some of the $\alpha^2(Z\alpha)$ terms. The $\alpha(Z\alpha)^2$ terms will contribute and must be evaluated explicitly. Kroll and Pollock[2,8] have developed renormalized expressions for the energy shift of an electron due to the electrodynamic field to first order in α, and all orders in $Z\alpha$. Their results will be used here. It should be pointed out that renormalization is not necessary in this problem[9] since the high-energy, short-range effects will cancel out in the difference, $(B-A)$; however, the renormalization facilitates the splitting of relativistic and nonrelativistic effects, the importance of which will become evident below.

For reference we list here the definitions of the functions that are used in the calculation. The electron propagators satisfy the equations of motion,[10]

$$(i\gamma p_2+\kappa)S_F{}^e(p_2,p_1)=\int ie\gamma A^e(\mathbf{p}_2-\mathbf{p}_3)S_F{}^e(p_3,p_1)d^3p_3+\frac{2i}{(2\pi)^4}\delta(\mathbf{p}_2-\mathbf{p}_1), \quad (4a)$$

$$S_F{}^e(p_2,p_1)(i\gamma p_1+\kappa)=\int S_F{}^e(p_2,p_3)ie\gamma A^e(\mathbf{p}_3-\mathbf{p}_1)d^3p_3+\frac{2i}{(2\pi)^4}\delta(\mathbf{p}_2-\mathbf{p}_1), \quad (4b)$$

where the fourth component of the momentum vectors is the energy of the nS state. The wave functions,[11] $\bar{\phi}(p_2)$, $\phi(p_1)$, satisfy the homogeneous equations. The external field is

$$ie\gamma A^e(\mathbf{q})=\frac{Z\alpha}{2\pi^2}\left(\frac{\gamma_0}{\mathbf{q}^2}\right)+\frac{e}{(2\pi)^3}\left(\frac{\gamma\cdot(\boldsymbol{\mu}\times\mathbf{q})}{\mathbf{q}^2}\right), \quad (5)$$

where $\boldsymbol{\mu}$ is the nuclear magnetic moment operator. The free propagator $S_F(p)$ satisfies Eq. (4) with the potential term missing.

A. Polarization Energy

K. P., Eq. (21), give for the renormalized polarization energy,

$$\Delta E_p=-(2\pi)^2\alpha\int_0^1 dV\int\bar{\phi}(\mathbf{p}_2)\frac{2V^2(1-V^2/3)(\mathbf{p}_2-\mathbf{p}_1)^2}{4\kappa^2+(\mathbf{p}_2-\mathbf{p}_1)(1-V^2)}\times ie\gamma A^e(\mathbf{p}_2-\mathbf{p}_1)\phi(\mathbf{p}_1)d^3p_1d^3p_2-(2\pi)^3\int\bar{\phi}(\mathbf{p}_2)\times ie\gamma\delta A^p(\mathbf{p}_2-\mathbf{p}_1)\phi(\mathbf{p}_1)d^3p_1d^3p_2. \quad (6)$$

Examination of δA^p with the aid of Furry's theorem[12] shows that the first surviving part of δA^p is proportional to α, and three powers of A^e. If one of the A^e is a magnetic potential and the other two are Coulomb, the contribution is of the correct order in α. However, the wave functions limit the contributions to the integral to regions of momenta of the order of $Z\alpha\kappa$ so that the momenta in δA^p may be dropped relative to κ. The remaining momentum integrals can be performed. They converge and give a result proportional to $|\psi_n^0(0)|^2$ which does not contribute to the difference,[13] $(B-A)$. In the first term of Eq. (6) we are interested in extracting the hfs (terms proportional to $\boldsymbol{\sigma}\cdot\boldsymbol{\mu}$) so that either the magnetic field occurs explicitly or it is implicitly contained in a modification of the wave function. The two cases will be designated by subscripts a and b, respectively.

For ΔE_{pa} the wave functions are solutions of the Dirac equation with a Coulomb potential. These may be approximated (Appendix A) to the order of accuracy required by

$$\phi(\mathbf{p})=\begin{pmatrix}1\\ \boldsymbol{\sigma}\cdot\mathbf{p}/2\kappa\end{pmatrix}\phi^0(p), \quad (7)$$

where $\phi^0(p)$ is a solution of the Schrödinger equation with a Coulomb potential.[14] Upon using the wave function and averaging over directions in the momentum

[7] Terms that depend upon the state only through a factor of the square of the wave function at the origin will be said to be state-independent.

[8] In evaluating the $\alpha(Z\alpha)^2$ terms the notation and definitions of Kroll and Pollock, henceforth referred to as K.P., will be followed as closely as possible. It should be pointed out that certain errors in K.P. Eqs. (29) and (33) have been corrected. These mistakes do not affect the result of K.P. but will affect the results of this paper.

[9] The author wishes to thank Dr. G. Webrettiz for pointing out this fact to him.

[10] Units $\hbar=c=1$ will be used throughout. Four-vectors will be denoted by ordinary type while their space parts will be denoted in boldface, $pk=\mathbf{p}\cdot\mathbf{k}-p_0k_0$.

[11] Momentum-space Dirac-Coulomb wave functions will be denoted by ϕ, $\bar{\phi}$. The coordinate space wave functions are ψ, $\bar{\psi}$. A superscript 0 will denote the corresponding nonrelativistic Schrödinger wave function.

[12] W. Furry, Phys. Rev. **51**, 125 (1937).

[13] This may be stated in another way by noting that $\delta A^p(r)$ is a short-range potential the integral of which over all space converges.

[14] This approximation neglects terms of relative order $(Z\alpha)^2\ln(Z\alpha)$ which are too small by a factor $Z\alpha\ln(Z\alpha)$.

integral, it is found that

$$\Delta E_{pa}=-\frac{e\alpha}{2\pi}\left(\frac{\boldsymbol{\sigma}\cdot\boldsymbol{\mu}}{3\kappa}\right)\int_0^1 dv\; 2v^2(1-\tfrac{1}{3}v^2)\times\int\frac{\phi_n{}^0(\mathbf{p}_2)(\mathbf{p}_2-\mathbf{p}_1)^2\phi_n{}^0(\mathbf{p}_1)}{4\kappa^2+(\mathbf{p}_2-\mathbf{p}_1)^2(1-v^2)}d^3p_1d^3p_2. \quad (8)$$

The momenta in the denominator may be neglected relative to κ^2, and with the use of Eq. (2) this becomes

$$\Delta E_{pa}=E_n\frac{2\alpha}{15\pi\kappa^2}\int d^3p\;\mathbf{p}^2\frac{\phi_n{}^0(\mathbf{p})}{\psi_n{}^0(0)}. \quad (9)$$

The integral in Eq. (9) is logarithmically divergent at the upper end but the divergence is state independent so that when the difference, $(B-A)$, is formed the result converges.[15] The integral is evaluated in Appendix B, Eq. (B-2). The contribution to the difference is

$$(B-A)_{pa}=1/(10\pi). \quad (10)$$

To obtain ΔE_{pb}, the potential appearing explicitly is taken as Coulomb and one of the wave functions is modified by the magnetic field. One such term appears for each of the wave functions and these are identical. The modification of the wave function due to the action of the magnetic potential once can be obtained as $\phi^M\sim\int S_F ie\gamma A^M\phi$. It is tempting to expand the propagator in a Born approximation series in the Coulomb field. However, the contribution from successive terms in the series are of the same order of magnitude so that all terms of the series contribute. Thus the magnetic wave function must be obtained more exactly. Upon using the magnetic wave functions from Appendix C and transforming back to coordinate space, it is found that

$$\Delta E_{pb}=-\frac{Z\alpha^2e}{\pi}\int_0^1 dv 2v^2\frac{(1-\frac{1}{3}v^2)}{1-v^2}\int\frac{d^3r}{r}\times\psi_n(r)\psi_n{}^M(r)\exp[-2\kappa r(1-v^2)^{-\frac{1}{2}}]. \quad (11)$$

The small components of the wave functions do not contribute to the $Z^2\alpha^3$ term and the leading term in the expansion of the integral in powers of $Z\alpha$ is found to be state-independent. The contribution to the result is

$$(B-A)_{pb}=-\frac{4}{15\pi}\left(\frac{9}{2}-2\ln 2\right). \quad (12)$$

B. Fluctuation Energy: Free Intermediate States

By using methods similar to that in K. P., after renormalization the fluctuation energy can be written as

$$\Delta E_F=A+B+C+D+E+F+L_D+Q, \quad (13)$$

where the form of each will be listed as it is dealt with.

$$A=2\pi^2\alpha\int\bar{\phi}(\mathbf{p}_2)ie\gamma A^e(\mathbf{p}_2-\mathbf{q})[2\kappa(1-4x^2)+i\gamma qx(8x-1)+i\gamma p_2x]ie\gamma A^e(\mathbf{q}-\mathbf{p}_1)\phi(\mathbf{p}_1)\frac{1}{\kappa^2\Lambda^2(q,p_2)}\times d^3p_1d^3p_2d^3q dx, \quad (14)$$

where

$$\kappa^2\Lambda^2(q,p)=-[qx+p(1-x)]^2=\epsilon_n{}^2-[\mathbf{q}x+\mathbf{p}(1-x)]^2, \quad (15)$$

where ϵ_n is the energy of the nS state and the range of x is 0 to 1. In evaluating A, it is split into a and b parts as for ΔE_p. For A_a, two terms arise since either potential may be magnetic. Using Eq. (7) and performing manipulations of the Dirac algebra to extract the hfs, we find

$$A_a=\frac{Z\alpha^2e}{(2\pi)^3}(\tfrac{2}{3}\boldsymbol{\sigma}\cdot\boldsymbol{\mu})\int\frac{\phi^0(\mathbf{p}_2)\phi^0(\mathbf{p}_1)}{(\mathbf{p}_2-\mathbf{q})^2(\mathbf{p}_1-\mathbf{q})^2\kappa^2\Lambda^2(q,p_2)}\times\{-x(8x-1)[2(\mathbf{q}-\mathbf{p}_1)^2+4\mathbf{q}\cdot\mathbf{p}_1-2\mathbf{p}_1{}^2-\mathbf{q}\cdot(\mathbf{p}_1+\mathbf{p}_2)]-4x^2(\mathbf{p}_2-\mathbf{p}_1)^2-(2\mathbf{q}-\mathbf{p}_1-\mathbf{p}_2)\cdot[(1-4x^2)(\mathbf{p}_1+\mathbf{p}_2)-x\mathbf{p}_2]\}d^3p_1d^3p_2d^3q\,dx. \quad (16)$$

In terms which do not contain $\mathbf{q}^2$ in the numerator, let $\kappa^2\Lambda^2\to\kappa^2$ and perform the $\mathbf{q}$ integral using

$$\int\frac{d^3q(1,\mathbf{q})}{(\mathbf{q}-\mathbf{p}_1)^2(\mathbf{q}-\mathbf{p}_2)^2}=\frac{\pi^3}{|\mathbf{p}_2-\mathbf{p}_1|}\left(1,\frac{\mathbf{p}_1+\mathbf{p}_2}{2}\right). \quad (17)$$

Then

$$A_a=\frac{Z\alpha^2}{16\kappa}E_n\int\phi_n{}^0(\mathbf{p}_2)\frac{\Delta p}{|\psi_n{}^0(0)|^2}\phi_n{}^0(\mathbf{p}_1)d^3p_1d^3p_2-\frac{2}{3}\left(\frac{Z\alpha^2e}{(2\pi)^3}\right)\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\,\psi_n{}^0(0)\times\int\frac{\phi_n{}^0(p)}{(\mathbf{p}-\mathbf{q})^2}\left(\frac{2x(8x-1)}{\epsilon_n{}^2-[\mathbf{q}x+\mathbf{p}(1-x)]^2}\right)d^3pd^3q, \quad (18)$$

where $\Delta p=\mathbf{p}_2-\mathbf{p}_1$. Upon carrying out the q integral in the second term and taking the real part, it is found that

$$\mathrm{Re}\int\frac{d^3q}{(\mathbf{q}-\mathbf{p})^2[\epsilon_n{}^2-(\mathbf{q}x+\mathbf{p}(1-x))^2]}\begin{cases}=-\pi^3/xp & \text{if } p>\epsilon_n\\ =0 & \text{if } p<\epsilon_n.\end{cases} \quad (19)$$

But ϵ_n is of the order of κ, in which region $\phi_n{}^0(p)$ is state-independent so that the second term does not contribute to the difference, $(B-A)$. The first term is divergent but gives a convergent result in the same way as ΔE_{pa}. Using Eq. (B-3), the contribution to the dif-

[15] The integral is of course convergent before the approximations of dropping $\mathbf{p}$ relative to κ are made. Convergence factors with a cut-off κ have been replaced by 1. The difference, $(B-A)$, is not affected by this method in the order of interest.

ference is

$$(B-A)_{Aa}=\frac{1}{2\pi}(\ln 2-\tfrac{5}{8}). \tag{20}$$

In evaluating A_b, the contributions from the small components of the wave functions are too small, and again $\kappa^2\Lambda^2\to\kappa^2$. Upon transforming back to coordinate space, it is found that

$$A_b=-\frac{20}{3}\left(\frac{Z^2\alpha^3}{\kappa}\right)e\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\int_0^\infty dr\psi^0(r)u^0(r). \tag{21}$$

Because of the singularity in $u(r)$ around $r=0$ arising from the singular behavior of the magnetic potential at $r=0$, this integral diverges; however, the divergence is state-independent so that the contribution to the difference is finite. Upon using Eq. (C-7), the result is

$$(B-A)_{Ab}=-\frac{10}{3\pi}(\tfrac{3}{2}-\ln 2). \tag{22}$$

The second term of Eq. (13) is

$$B=-2\pi^2\alpha\int\bar{\phi}(\mathbf{p}_2)[ie\gamma A(\mathbf{p}_2-\mathbf{q}_2)ie\gamma A(\mathbf{q}_2-\mathbf{q}_1)\times ie\gamma A(\mathbf{q}_1-\mathbf{p}_1)]\phi(\mathbf{p}_1)\frac{d^3p_1d^3p_2d^3q_1d^3q_2dx}{\kappa^2\Lambda^2(q_1,q_2)}. \tag{23}$$

Because of the explicit appearance of three potentials this term is immediately of the order required. To get its contribution, set $p_1=p_2=0$ and $\epsilon_n=\kappa$ in the square bracket. The term is then proportional to $|\psi_n^0(0)|^2$ and contains no additional state dependence. If the remaining q integrals converge, there is then no contribution to the difference. The integrals converge so that

$$(B-A)_B=0. \tag{24}$$

The third term in Eq. (13) contains the radiative correction to the magnetic moment of the electron. It can be written[16]

$$C=-2\pi^2\alpha\kappa\int\bar{\phi}(\mathbf{p}_2)(\mathbf{p}_2-\mathbf{p}_1)_\nu\sigma_{\nu\mu}A_\mu(\mathbf{p}_2-\mathbf{p}_1)\phi(\mathbf{p}_1)\times\left(\frac{1}{\kappa^2}+\frac{1-\Lambda^2}{\kappa^2\Lambda^2}\right)d^3p_1d^3p_2\,dx. \tag{25}$$

The first and second terms in the bracket are treated separately as C_1 and C_2, respectively. C_2 presents no complications. It is handled similarly to A. The result is

$$(B-A)_{C2a}=-1/(8\pi), \tag{26}$$

$$(B-A)_{C2b}=0. \tag{27}$$

For C_{1a} the exact Dirac wave functions, Eqs. (A-1), (A-2) must be used. After transforming to coordinate space and extracting the hfs, it is found that

$$C_{1a}=-\frac{\alpha e}{4\pi}\left(\frac{\boldsymbol{\sigma}\cdot\boldsymbol{\mu}}{\kappa}\right)\int\left[[|\psi(r)|^2+\tfrac{1}{3}|\eta(r)|^2]\delta(r)-\frac{1}{3\pi r^3}|\eta(r)|^2\right]d^3r. \tag{28}$$

Each of the terms in Eq. (28) is divergent because of the r^{-2} singularity in the magnetic potential. This could be avoided by postulating a distribution for the proton magnetic moment. However, this is not necessary since the divergence occurs at small r where the wave functions are state-independent so that the contribution to the difference is finite.

$$(B-A)_{C1a}=(1/4\pi)(1-\ln 2), \tag{29}$$

C_{1b} is evaluated in a straightforward way. After transforming to coordinate space, it is found that

$$C_{1b}=-6Z\alpha^2E_n\times\int_0^\infty[\psi_n^0(r)v_n^0(r)+\eta_n^0(r)u_n^0(r)]\frac{dr}{|\psi_r^0(0)|^2}. \tag{30}$$

Here the small components contribute but only in the nonrelativistic form. The integral in Eq. (30) is divergent, but again the contribution to the result is finite.

$$(B-A)_{C1b}=-(1/2\pi)[-(17/4)+4\ln 2]. \tag{31}$$

The fourth term in Eq. (13) is

$$D=-4\pi^2\alpha\int\bar{\phi}(\mathbf{p}_2)ie\gamma A(\mathbf{p}_2-\mathbf{p}_1)\phi(\mathbf{p}_1)\times\frac{(\epsilon_n^2-\kappa^2)}{\kappa^2\Lambda^2}(-2+5x-4x^2)d^3p_1d^3p_2dx. \tag{32}$$

This is proportional to the binding energy, $\sim(Z\alpha)^2$. The denominator is simplified by $\kappa^2\Lambda^2\to\kappa^2$ and the evaluation is straightforward. The result is

$$(B-A)_{Da}=5/(16\pi), \tag{33}$$

$$(B-A)_{Db}=-9/(4\pi). \tag{34}$$

The fifth term in Eq. (13),

$$E=-4\pi^2\alpha\int\bar{\phi}(\mathbf{p}_2)ie\gamma A(\mathbf{p}_2-\mathbf{p}_1)\mathbf{p}_1\cdot\mathbf{p}_2\phi(\mathbf{p}_1)\times\left(\frac{-2+5x-4x^2}{\kappa^2\Lambda^2}\right)d^3p_1d^3p_2dx, \tag{35}$$

presents no difficulty. Its contribution is

$$(B-A)_{Ea}=0, \tag{36}$$

$$(B-A)_{Eb}=-(5/3\pi)(\tfrac{9}{16}-\ln 2). \tag{37}$$

[16] The spin matrix is defined as $\sigma_{\mu\nu}=-\frac{1}{2}i[\gamma_\mu,\gamma_\nu]$.

The sixth term in Eq. (13) is

$$F=-6\pi^2\alpha\int\bar{\phi}(\mathbf{p}_2)ie\gamma A(\mathbf{p}_2-\mathbf{q})\frac{[2xi\gamma q+\kappa(1-2x)]}{\kappa^2-x(q^2+\kappa^2)}\times ie\gamma A(\mathbf{q}-\mathbf{p}_1)\bar{\phi}(\mathbf{p}_1)d^3p_1d^3p_2d^3qdx. \quad (38)$$

The evaluation of the contribution introduces no new problems. After extracting the hfs it is found that

$$F_a=0, \quad (39)$$

and F_b is a multiple of A_b. Its contribution is

$$(B-A)_{F_b}=(3/\pi)(\tfrac{3}{2}-\ln 2). \quad (40)$$

The last two terms of Eq. (13) are

$$L_D=-8i\alpha\int\bar{\phi}(\mathbf{p}_2)\frac{p_{2\mu}}{k^2-2kp_2}\left(\frac{p_{2\mu}}{k^2-2kp_2}-\frac{p_{1\mu}}{k^2-2kp_1}\right)\times ie\gamma A(\mathbf{p}_2-\mathbf{p}_1)\phi(\mathbf{p}_1)\frac{d^4k}{k^2+\lambda^2}d^3p_1d^3p_2, \quad (41)$$

and

$$Q=\alpha(2\pi)^4\int\bar{\phi}(\mathbf{p}_2)\mathfrak{A}_\mu'(q_2,p_2,k)\times S_F{}^e(p_2-k-q_2,\,p_1-k+q_1)\mathfrak{A}_\mu(q_1,p_1,k)\phi(\mathbf{p}_1)\times\frac{d^4k}{k^2+\lambda^2}d^3p_1d^3p_2d^3q_1d^3q_2, \quad (42)$$

where

$$\mathfrak{A}_\mu'(q,p,k)=ie\gamma A(\mathbf{q})\left[\frac{2i(p-q)_\mu-i\gamma_\mu\gamma k}{k^2-2k(p-q)}\right]-\left[\frac{2ip_\mu-i\gamma_\mu\gamma k}{k^2-2kp}\right]ie\gamma A(\mathbf{q}), \quad (43)$$

$$\mathfrak{A}_\mu(q,p,k)=-ie\gamma A(\mathbf{q})\left[\frac{2ip_\mu-i\gamma k\gamma_\mu}{k^2-2kp}\right]+\left[\frac{2i(p+q)_\mu-i\gamma k\gamma_\mu}{k^2-2k(p+q)}\right]ie\gamma A(\mathbf{q}), \quad (44)$$

and λ is a fictitious photon mass introduced to control the infrared divergence in L_D and Q which are separately divergent. The combination L_D+Q is, however, finite in the limit $\lambda\to 0$.[17]

The term Q contains the full relativistic propagator for the electron in the presence of a Coulomb potential. It will be shown that it may be replaced by either the free function or a nonrelativistic approximation. With this in mind, Q is arbitrarily divided into three terms according to how many powers of k in the numerator come from $\mathfrak{A}_\mu'$ and $\mathfrak{A}_\mu$. The terms with two powers of k are called R. The presence of two powers of k in the numerator emphasizes the contribution from the relativistic region in the intermediate state so that it may be expected that the effect of the Coulomb field in the propagator will be unimportant up to the order of $Z\alpha$ needed. In order to substantiate this conjecture the propagator, $S_F{}^e$, is expanded in successive Born approximations and the contributions are examined. The term of $S_F{}^e$ linear in A_e contributes a term in R containing three potentials explicitly. Setting $\mathbf{p}_1=\mathbf{p}_2=0$ and $\epsilon_n=\kappa$ in all but the wave functions, it is found that the remaining integrals converge. Thus the contribution is proportional to $|\psi_n{}^0(0)|^2$ and of order of α^3. Hence the contribution to the difference is zero. It is therefore possible to replace $S_F{}^e$ by S_F in R, and drop λ^2 since there is no infrared divergence in R.

$$R=(2\pi)^4\alpha\int\bar{\phi}(\mathbf{p}_2)\left[\frac{-ie\gamma A(\mathbf{p}_2-\mathbf{q})\gamma_\mu\gamma k}{k^2-2kq}+\frac{\gamma_\mu\gamma kie\gamma A(\mathbf{p}_2-\mathbf{q})}{k^2-2kp_2}\right]S_F(q-k)\left[\frac{ie\gamma A(\mathbf{q}-\mathbf{p}_1)\gamma k\gamma_\mu}{k^2-2kp_1}-\frac{\gamma k\gamma_\mu ie\gamma A(\mathbf{q}-\mathbf{p}_1)}{k^2-2kq}\right]\phi(\mathbf{p}_1)\frac{d^4k}{k^2}d^3p_1d^3p_2d^3q. \quad (45)$$

R_a is evaluated by first performing the k integration by the standard method of combining denominators by parametric integration and then the hfs is extracted. It is found that the resultant denominators containing the momenta and the integration parameters can be simplified by dropping all momenta compared to κ. Use is then made of Eq. (17) to reduce the contribution to a simpler form. The calculation will not be reproduced here since the contribution is zero.

$$(B-A)_{R_a}=0. \quad (46)$$

In R_b the contributions of the small components of the wave functions are too small and the momenta $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{q}$ each contribute a power of $Z\alpha$, so that they may be dropped. Upon transforming back to coordinate space and eliminating the Dirac matrices, it is found that

$$R_b=\left(\frac{2iZ^2\alpha^3}{\pi^2}\right)e\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\int_0^\infty\psi_n{}^0(r)u_n{}^0(r)dr\times\int\frac{d^4k}{k^2}\frac{4k_0}{(k^2+2k_0\kappa)}(k^2-2k_0{}^2). \quad (47)$$

After performing the k integration, this becomes

$$R_b=18Z^2\alpha^3E_n\int_0^\infty dr\psi_n{}^0(r)u_n{}^0(r)/|\psi_n{}^0(0)|^2, \quad (48)$$

[17] K. P., Eq. (35).

a multiple of A_b. The contribution to the difference is

$$(B-A)_{Rb}=-(3/\pi)(\tfrac{3}{2}-\ln 2). \tag{49}$$

The contribution from $\mathcal{A}$ and $\mathcal{A}'$ linear in k is called S. This arises as two terms owing to the possibility of the k coming from $\mathcal{A}$ or $\mathcal{A}'$. These are complex conjugates of each other so twice one is taken as S. This can be treated in the same way as R and it is again found that the substitution $S_F{}^e\rightarrow S_F$ does not change the difference to the order of interest. Then

$$S=4\alpha(2\pi)^4\int\bar{\phi}(\mathbf{p}_2)\left[\frac{-ie\gamma A(\mathbf{p}_2-\mathbf{q})\gamma_\mu\gamma k}{k^2-2kq}+\frac{\gamma_\mu\gamma kie\gamma A(\mathbf{p}_2-\mathbf{q})}{k^2-2kp_2}\right]S_F(q-k)\times\left[\frac{q_\mu}{k^2-2kq}-\frac{p_{1\mu}}{k^2-2kp_1}\right]ie\gamma A(\mathbf{q}-\mathbf{p}_1)\phi(\mathbf{p}_1)\times\frac{d^4k}{k^2}d^3p_1d^3p_2d^3q. \tag{50}$$

Manipulations similar to those described for R yield

$$S_a=\frac{Z\alpha^2}{8\kappa}E_n\int\frac{\phi_n{}^0(\mathbf{p}_2)\Delta p\bar{\phi}_n{}^0(\mathbf{p}_1)}{|\psi_n{}^0(0)|^2}d^3p_1d^3p_2, \tag{51}$$

which is a multiple of A_a. The contribution to the difference is

$$(B-A)_{Sa}=(1/\pi)(\ln 2-\tfrac{5}{8}). \tag{52}$$

It is found that the various contributions to S_b cancel so that

$$(B-A)_{Sb}=0. \tag{53}$$

C. Fluctuation Energy, Bound Intermediate States

The remaining part of Q, with no powers of k in the numerator arising from $\mathcal{A}'$ and $\mathcal{A}$, is called $\bar{T}$.

$$\bar{T}=4(2\pi)^4\alpha\int\bar{\phi}(\mathbf{p}_2)\left(\frac{q_{2\mu}}{k^2-2kq_2}-\frac{p_{2\mu}}{k^2-2kp_2}\right)\times ie\gamma A(\mathbf{p}_2-\mathbf{q}_2)S_F{}^e(q_2-k,\,q_1-k)ie\gamma A(\mathbf{q}_1-\mathbf{p}_1)\times\left(\frac{q_{1\mu}}{k^2-2kq_1}-\frac{p_{1\mu}}{k^2-2kp_1}\right)\phi(\mathbf{p}_1)\frac{d^4k}{k^2+\lambda^2}\times d^3p_1d^3p_2d^3q_1d^3q_2. \tag{54}$$

The magnetic part of the potential can enter explicitly or implicitly through the wave functions or the propagator. The propagator can be expanded in powers of the magnetic potential by

$$S_F{}^e(q_2-k,\,q_1-k)=S_F{}^c(q_2-k,\,q_1-k)+\frac{(2\pi)^4}{2i}\int S_F{}^c(q_2-k,\,l_2-k)ie\gamma A^M(\mathbf{l}_2-\mathbf{l}_1)\times S_F{}^c(l_1-k,\,q_1-k)d^3l_1d^3l_2+\cdots, \tag{55}$$

where $S_F{}^c$ satisfies Eq. (4) with the external potential purely Coulomb. The contribution from the first term of Eq. (55) is called T, from the second, U.

An estimate of the order of the contribution of U to the difference can be obtained by replacing the bound propagators by the free ones. Then $\mathbf{p}_1$ and $\mathbf{p}_2$ are set equal to zero and $\epsilon_n=\kappa$ everywhere but the wave functions and the hfs is extracted. The remaining integrals converge[18] and are state-independent so that U does not contribute to the difference.

In $\bar{T}$ use is made of the following identity

$$S_F{}^c(q_2-k,\,q_1-k)=[S_F{}^c(q_2-k,\,q_1-k)-S(\mathbf{q}_2,\mathbf{q}_1;\,k_0)]+S(\mathbf{q}_2,\mathbf{q}_1;\,k_0), \tag{56}$$

where

$$S(\mathbf{q}_2,\mathbf{q}_1;\,k_0)=\left(1+\frac{\boldsymbol{\alpha}\cdot\mathbf{q}_2}{2\kappa}\right)\left(\frac{1+\gamma_0}{2}\right)\left(1-\frac{\boldsymbol{\alpha}\cdot\mathbf{q}_1}{2\kappa}\right)\times G(\mathbf{q}_2,\mathbf{q}_1;\,k_0), \tag{57}$$

with the function G taken to be the nonrelativistic propagator satisfying

$$\left[\frac{\mathbf{q}_2{}^2}{2\kappa}+k_0+\frac{\beta_n{}^2}{2\kappa}\right]G(\mathbf{q}_2,\mathbf{q}_1;\,k_0)=\int d^3l V(\mathbf{q}_2-\mathbf{l})G(\mathbf{l},\mathbf{q}_1;\,k_0)+\frac{2i}{(2\pi)^4}\delta(\mathbf{q}_2-\mathbf{q}_1). \tag{58}$$

Here, $V(q)=(Z\alpha/2\pi^2)(1/\mathbf{q}^2)$ is the Coulomb potential and $\beta_n{}^2/2\kappa$ is the binding energy of the state in question. The momentum space representation that will be used in this calculation is

$$G_{k_0}(\mathbf{q}',\mathbf{q})=\frac{2i\kappa}{\pi}\sum_j\frac{\phi_j{}^0(\mathbf{q}')\phi_j{}^{0*}(\mathbf{q})}{\beta_n{}^2+2k_0\kappa-\beta_j{}^2}. \tag{59}$$

It should be pointed out that S was chosen to approximate the low-momentum behavior of $S_F{}^c$ to order v/c so that the contribution from the bracket of Eq. (56) in $\bar{T}$ should be zero since forming the difference, $B-A$, emphasizes the low-momentum contribution. Indeed, substitution of Eq. (56) into $\bar{T}$ and expansion of the bracket in a Born approximation series shows that the first two terms give no contribution so that the contribution of the bracket vanishes in the order required. Therefore the full contribution of $\bar{T}$ can be obtained by replacing $S_F{}^c$ by S.

[18] There still remains an infrared divergence in this term but it is state independent to order $Z^2\alpha^3$. The lowest order contribution of U to the difference is of order $Z^3\alpha^4\ln(Z\alpha)$ or smaller.

$\bar{T}_a$ is evaluated by using the wave function, Eq. (7), and picking out the hfs:

$$\bar{T}_a=\frac{4}{\pi}Z\alpha^2\left(\frac{e}{2\kappa}\right)(\tfrac{2}{3}\boldsymbol{\sigma}\cdot\boldsymbol{\mu})\int\frac{\phi^0(\mathbf{p}_2)\phi^0(\mathbf{p}_1)}{(\mathbf{p}_2-\mathbf{q}_2)^2(\mathbf{p}_1-\mathbf{q}_1)^2}\times G(\mathbf{q}_2,\mathbf{q}_1;k_0)\left(\frac{q_{2\mu}}{k^2-2kq}-\frac{p_{2\mu}}{k^2-2kp_2}\right)\times\left(\frac{q_{1\mu}}{k^2-2kq_1}-\frac{p_{1\mu}}{k^2-qkp_1}\right)[(\mathbf{p}_2-\mathbf{q}_2)^2+(\mathbf{p}_1-\mathbf{q}_1)^2]\times\frac{d^4k}{k^2+\lambda^2}d^3p_1d^3p_2d^3q_1d^3q_2. \quad (60)$$

In the last square bracket, terms of momentum raised to the fourth power have been dropped since their contribution to the difference is smaller than those retained by a factor of at least $(Z\alpha)^2\ln(Z\alpha)$. In addition, the two terms in the last bracket contribute identically so twice the first is retained. From the equation of motion, Eq. (58),

$$\int G(\mathbf{q}_2,\mathbf{q}_1;k_0)[f(q_1)-f(p_1)]V(\mathbf{q}_1-\mathbf{p}_1)\phi^0(\mathbf{p}_1)d^3p_1d^3q_1=-k_0\int G(\mathbf{q}_2,\mathbf{p}_1;k_0)[f(p_1)-f(\rho)]\phi^0(\mathbf{p}_1)d^3p_1+\frac{2i}{(2\pi)^4}[f(q_2)-f(\rho)], \quad (61)$$

where f is any nonmatrix function. Substitution into T results in

$$\bar{T}_a=16\pi\alpha\left(\frac{E_n}{|\psi_n{}^0(0)|^2}\right)\int\phi^0(\mathbf{p}_2)\left(\frac{q_\mu}{k^2-2kq}-\frac{p_{2\mu}}{k^2-2kp_2}\right)\times\left(\frac{p_{1\mu}}{k^2-2kp_1}-\frac{\rho_\mu}{k^2-2k\rho}\right)G(\mathbf{q}\cdot\mathbf{p}_1;k_0)\times\phi^0(\mathbf{p}_1)\frac{k_0}{k^2}d^4kd^3p_1d^3p_2d^3q+\frac{i}{\kappa}\left(\frac{\alpha e}{\pi^3}\right)(\tfrac{2}{3}\boldsymbol{\sigma}\cdot\boldsymbol{\mu})\int\phi^0(\mathbf{p})\left(\frac{q_\mu}{k^2-2kq}-\frac{p_\mu}{k^2-2kp}\right)\times\left(\frac{q_\mu}{k^2-2kq}-\frac{\rho_\mu}{k^2-2k\rho}\right)\phi(\mathbf{q})\frac{d^4k}{k^2+\lambda^2}d^3pd^3q, \quad (62)$$

where $\rho_\mu=(0\,0\,0,iE_n)$ and $k\rho=-k_0E_n$. The first term, called T_a, contains no infrared difficulties while the second, $\mathfrak{L}_a$, still contains a $\ln\lambda$ dependence and will be combined with L_D. In T_a use is now made of Eq. (59) to substitute for G and the k integration is then performed. The result is then expanded in powers of momentum, retaining only the quadratic terms as in R. Terms proportional to $\mathbf{p}_1\cdot\mathbf{p}_2$ may be dropped on symmetry considerations. Transforming to coordinate space it is found that

$$T_a=\frac{4}{3\pi}\left(\frac{\alpha}{\kappa^2}\right)E_n\sum_j\left[\ln\left(\frac{k^2}{\Delta_j}\right)+\frac{13}{12}+O\left(\frac{\Delta_j}{\kappa^2}\right)\right]\times\int d^3rd^3r'\delta(\mathbf{r}')\boldsymbol{\nabla}'\psi_j(\mathbf{r}')\cdot\psi_j{}^*(\mathbf{r})\boldsymbol{\nabla}\frac{\psi_n(r)}{\psi_0(r)}, \quad (63)$$

where j runs over all P states and $\Delta_j=\beta_n{}^2-\beta_j{}^2$. Terms of order Δ/κ^2 contribute in relative order $(Z\alpha)^2$ times an integral which diverges for the high momentum-free intermediate states. However, the divergency is state-independent so that the contribution to the difference is finite and too small. Thus only the first two terms of Eq. (63) contribute to the difference. The sum over states is now broken into a sum over bound P states and an integral over free P states. Use is made of the completeness relation,

$$\textstyle\sum_j\psi_j{}^0(\mathbf{r}')\psi_j{}^{0*}(\mathbf{r})=\delta(\mathbf{r}-\mathbf{r}'), \quad (64)$$

to extract the $\ln(Z\alpha)$ contribution from the first term of Eq. (63), with the result

$$T_a=3\frac{Z^2\alpha^3}{\pi}\left(\frac{2}{3}\ln(Z\alpha)-\frac{13}{36}\right)E_n+\frac{4\alpha}{3\kappa^2\pi}E_n\left[\sum_{jm}\ln\left(\frac{1}{\delta_{nj}}\right)H_{jm}I_{jmn}+\int\frac{d^3l}{(2\pi)^3}H_lI_{ln}\ln\left(\frac{1}{\delta_l}\right)\right], \quad (65)$$

where

$$\delta_{nj}=\left(\frac{1}{n^2}-\frac{1}{\beta_j{}^2}\right),\quad \delta_l=\left(\frac{1}{n^2}+\frac{l^2}{\beta_1{}^2}\right),$$

and

$$\begin{aligned}H_{jm}&=\int d^3r\delta(\mathbf{r})\boldsymbol{\nabla}\psi_{jm}(\mathbf{r}),\\ H_l&=\int d^3r\delta(\mathbf{r})\boldsymbol{\nabla}\psi_l(\mathbf{r}),\\ I_{jmn}&=\int d^3r\psi_{jm}{}^*(\mathbf{r})\boldsymbol{\nabla}\psi_n(r)/\psi_n{}^0(0),\\ I_{ln}&=\int d^3r\psi_l{}^*(\mathbf{r})\nabla\psi_n(r)/\psi_n{}^0(0).\end{aligned} \quad (66)$$

Here n represents the principal quantum numbers of the nS state, j the principal quantum number and m the magnetic quantum number of the bound intermediate P state, and $\mathbf{l}$ the momentum vector characterizing the free P state. The difference between states has already been formed in the first term of Eq. (65). The integrals I_{jmn} and H_{jm} are easily carried out using an integral representation[19] for the wave functions ψ_{jm}.

[19] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 85.

The difference, $B-A$, is then formed, resulting in a complicated infinite series. The summation has been carried out with the aid of computing machines.[20] The integrals H_l and I_{ln} can be evaluated by using an integral representation of the wave function[21] ψ_l. The remaining integral over $\mathbf{l}$ is divergent for large $\mathbf{l}$. The divergency, however, is state-independent and disappears when the difference $B-A$ is formed. The resulting numerical integral has been evaluated with the aid of computing machines.[20] The contribution to the difference is

$$(B-A)_{T_a}=\frac{3}{\pi}\left(\frac{2}{3}\ln Z\alpha-\frac{13}{36}\right)-\frac{32}{3\pi}(0.040)-\frac{16}{3\pi^2}(3.063),\quad (67)$$

where the first term has been evaluated analytically, the second results from the sum over bound states, and the third results from the integral over free states.

$\bar{T}_b$ is evaluated by substituting a magnetic wave function, Eqs. (C5, 6), for one of the ϕ's. This results in two terms which contribute identically. Twice one is taken and the hfs is extracted, the contribution from the small components of the wave functions being neglected. The result is

$$\bar{T}_b=32Z^2\alpha^3e\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\int\bar{\phi}^M(\mathbf{p}_2)\left(\frac{q_{2\mu}}{k^2-2kq_2}-\frac{p_{2\mu}}{k^2-2kp_2}\right)\times G(\mathbf{q}_2,\mathbf{q}_1;k_0)\left(\frac{q_{1\mu}}{k^2-2kq_1}-\frac{p_{1\mu}}{k^2-2kp_1}\right)\times\phi^0(\mathbf{p}_1)\frac{d^3p_1d^3p_2d^3q_1d^3q_2}{(\mathbf{p}_1-\mathbf{q}_1)^2(\mathbf{p}_2-\mathbf{q}_2)^2}\left(\frac{d^4k}{k^2+\lambda^2}\right).\quad (68)$$

Use is made of Eq. (61) to give

$$\bar{T}_b=-64\pi^2eZ\alpha^2\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\int\bar{\phi}^M(\mathbf{p}_2)\left(\frac{q_\mu}{k^2-2kq}-\frac{p_{2\mu}}{k^2-2kp_2}\right)\times G(\mathbf{q},\mathbf{p}_1;k_0)\left(\frac{p_{1\mu}}{k^2-2kp_1}-\frac{\rho_\mu}{k^2-2k\rho}\right)\phi^0(\mathbf{p}_1)\times\frac{d^3p_1d^3p_2d^3q}{(\mathbf{p}_2-\mathbf{q})^2}\left(\frac{k_0}{k^2}\right)d^4k+\frac{8i}{\pi^2}Z\alpha^2e\sigma\cdot\boldsymbol{\mu}\int\bar{\phi}^M(\mathbf{p}_2)\times\left(\frac{p_{1\mu}}{k^2-2kp_1}-\frac{p_{2\mu}}{k^2-2kp_2}\right)\left(\frac{p_{1\mu}}{k^2-2kp_1}-\frac{\rho_\mu}{k^2-2k\rho}\right)\times\phi^0(\mathbf{p}_1)\frac{d^3p_1d^3p_2}{(\mathbf{p}_1-\mathbf{p}_2)^2}\left(\frac{d^4k}{k^2+\lambda^2}\right).\quad (69)$$

The first term, T_b, contains no infrared difficulties while the second, $\mathfrak{L}_b$, still contains a $\ln\lambda$ dependence and will be combined with L_D and $\mathfrak{L}_a$. In T_b use is made of Eq. (59) to substitute for G and the same k integration as occurs in T_a is performed and expanded in powers of the momenta. As in Eq. (63) the term of order Δ/κ^2 does not contribute. The expression is transformed to coordinate space and the completeness relation, Eq. (64), is again used to extract the major contribution with the result

$$T_b=\frac{Z^2\alpha^3}{\pi}\left(5-\frac{8}{3}\ln 2\right)\left(+\frac{13}{12}-2\ln Z\alpha\right)E_n-\frac{4}{\pi}\frac{Z\alpha^2}{\kappa}E_n\left[\sum_{jm}J_{jmn}I_{jmn}\ln\left(\frac{1}{\delta_{nj}}\right)+\int\frac{d^3l}{(2\pi)^3}J_{ln}I_{ln}\ln\left(\frac{1}{\delta_l}\right)\right],\quad (70)$$

where the I's have been defined in Eq. (66) and

$$J_{jmn}=\int d^3r\nabla\left(\frac{1}{r}\right)\frac{u_n^0(r)}{\psi_n^0(0)}\psi_{jm}^0(r),\qquad J_{ln}=\int d^3r\nabla\left(\frac{1}{r}\right)\frac{u_n^0(r)}{\psi_n^0(0)}\psi_l^0(r),\quad (71)$$

and δ was defined in connection with Eq. (65). The difference between states has already been formed in the first term of Eq. (70). The integrals J_{jmn} can be evaluated in a manner similar to that used for I_{jmn}. The result is an extremely complex infinite series. The summation has been carried out with the aid of computing machines,[22] and its contribution was found to be negligible. The integral J_{ln} can be evaluated with the aid of an integral representation[23] of the P state of ψ_l. The result can be expressed in terms of hypergeometric functions of complex arguments. In extracting the real part of the result, it has been found necessary to use an integral representation of the functions. The remaining integral over $\mathbf{l}$ diverges at the upper limit but the remarks applied to the third term of Eq. (65) also apply here. The contribution of the third term of Eq. (70) to the difference is then expressed as a double integral which has been evaluated with the aid of computing machines.[20,24] The result is

$$(B-A)_{T_b}=\frac{1}{\pi}\left(5-\frac{8}{3}\ln 2\right)\left(+\frac{13}{12}-2\ln Z\alpha\right)+\frac{128}{3\pi}(-0.003)+\frac{32}{3\pi^2}(0.934),\quad (72)$$

[20] The author wishes to thank M. Ferris of the Livermore computing group for evaluating the numerical sum and integrals resulting from Eq. (65).

[21] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), pp. 48–50.

[22] The author wishes to thank R. Moore and R. Shafer of the Livermore computing group for evaluating the numerical sum resulting from Eq. (70).

[23] Reference 21, pp. 50–53.

[24] The author wishes to thank Dr. H. Reich and the Watson Computing Laboratory of International Business Machines Cor-

where the first term has been evaluated analytically, the second results from the sum over bound states, and the third from the integral over free states.

D. Infrared Divergent Part

The infrared divergent part of $\bar{T}$ just cancels[17] that from L_D. A check must be made for any finite contributions after the cancellation. This check could be made by adding the parts L_D, $\mathfrak{L}_a$, $\mathfrak{L}_b$, and U and explicitly evaluating them; however, a simpler method presents itself. The λ dependence in $\bar{T}$ comes entirely from T_a, T_b, and U. In the five terms arising from these,[25] use is made of

$$\int \bar{\phi}(\mathbf{p}_2)[f(q_2)-f(p_2)]ie\gamma A^c(\mathbf{p}_2-\mathbf{q}_2)S_F{}^c \times(q_2-k,\, q-k)d^3p_2d^3q_2$$
$$=\int \bar{\phi}(\mathbf{p}_2)[f(p_2)-f(\rho)]i\gamma k S_F{}^c(p_2-k,\, q-k)d^3p^2 +\frac{2i}{(2\pi)^4}\bar{\phi}(\mathbf{q})[f(q)-f(\rho)], \quad (73)$$

which is just the relativistic analogy of Eq. (61). The first term in the right-hand side of Eq. (73) contributes terms that are not λ-dependent and are dropped. The remainder is the entire λ dependence resulting from T. At this point the parts resulting from $\bar{T}_a$ are exactly what is called $\mathfrak{L}_a$, those from $\bar{T}_b$ are $\mathfrak{L}_b$. In this form the cancellation against L_D is obvious. Hence there is no contribution to the $B-A$ difference from the terms $L_D+\mathfrak{L}_a+\mathfrak{L}_b$.

IV. PROTON-STRUCTURE AND FINITE-PROTON-MASS EFFECTS

In Sec. III the nucleus was considered to be an infinitely heavy point proton. These restrictions will be relaxed here.

(a) *Proton structure.*—The effect of proton size may be accounted for roughly by modifying the external potential. Equation (5) then becomes

$$ie\gamma A^e(\mathbf{q})=\frac{Z\alpha}{2\pi^2}\left(\frac{\gamma_0}{\mathbf{q}^2}\right)\left(\frac{\Gamma_1{}^2}{\mathbf{q}^2+\Gamma_1{}^2}\right) +\frac{e}{(2\pi)^3}\left(\frac{\boldsymbol{\gamma}\cdot\boldsymbol{\mu}\times\mathbf{q}}{\mathbf{q}^2}\right)\left(\frac{\Gamma_2{}^2}{\mathbf{q}^2+\Gamma_2{}^2}\right), \quad (74)$$

where Γ_1 and Γ_2 are of the order of either the proton or the π-meson mass. In either case $\Gamma_i \gg \kappa \gg \kappa\alpha Z$. This modification can enter in one of two ways, either explicitly in the expressions for ΔE or implicitly in the wave functions. In the first case this has the effect of making the potentials effectively constant in the integrals, decreasing their contributions to $B-A$ by at least a factor of $(Z\alpha\kappa/\Gamma)^2$ which would make them much too small. In the second case the wave functions are modified by the short-range potential of the nucleus and the difference $B-A$ is insensitive to this short-range modification. It is found that the first contribution to $B-A$ from this effect is again of order $(Z\alpha\kappa/\Gamma)^2$.

(b) *Finite proton mass.*—The effects of the finite proton mass on the radiative corrections to the hfs have been calculated[3] to order $Z\alpha\kappa/M$ and have been shown to be proportional to $|\psi_n{}^0(0)|^2$. This is to be expected since these are short-range effects due to the motion of the proton. Effects of order $(Z\alpha)^2\kappa/M$ are of interest here.These arise from higher derivatives of the wave function at the origin and may be state dependent. These should be investigated further.†

V. COMPARISON WITH EXPERIMENT

As was pointed out in Sec. IV, the calculated difference, $B-A$, should completely describe the ratio $\Delta\nu_{2s}/\Delta\nu_{1s}$ in order α^3. Using[5] $\Delta\nu_{2s}=177\,556.86\pm0.05$ kc/sec, and Kusch's[5] value $\Delta\nu_{1s}=1\,420\,405.73\pm0.05$ kc/sec, one obtains

$$(B-A)_{\text{exp}}=3.4\pm0.8. \quad (75)$$

Or, using the results of Wittke and Dicke,[5]

$$\Delta\nu_{1s}=1\,420\,405.80\pm0.05 \text{ kc/sec},$$

one obtains

$$(B-A)_{\text{exp}}=3.3\pm0.8. \quad (76)$$

These are to be compared with the value calculated in Sec. III,

$$(B-A)_{\text{th}}=5.28. \quad (77)$$

This discrepancy cannot be explained by finite-proton-size effects, as was pointed out in Sec. IV. The explanation of the difference may lie in the κ/M effects, but it would be surprising if they are large enough.†

VI. ACKNOWLEDGMENTS

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poration for evaluating the integral leading to this result. The integrals and sums arising from Eqs. (65) and (70) were thought to be too lengthy to include here. The author would be happy to furnish copies of these to those who express that desire. These integrals and sums have been deposited as Document number 5226 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[25] Even though it has been shown that the infrared divergent terms of U do not contribute to the α^3 correction, it proves simpler to include them in the demonstration of the over-all cancellation.

† *Note added in proof.*—A low-energy calculation of part of this effect has been made by Dr. C. Schwartz. The contribution to the difference is small ~0.2 (private communication).

this Laboratory in general and to those individuals explicitly cited for their work in evaluating the complex numerical sums and integrals occurring in the calculation.

APPENDIX A

The Dirac wave functions for the 1S and 2S states of hydrogen can be written in the usual representation

$$\bar{\psi}_n(\mathbf{r})=\begin{pmatrix}\psi_n(r)\\(i\boldsymbol{\sigma}\cdot\mathbf{r}/r)\eta_n(r)\end{pmatrix},\tag{A-1}$$

where

$$\psi_1(r)=C_1e^{-\beta_1 r}(\beta_1 r)^s,\tag{A-2a}$$

$$\psi_2(r)=C_2e^{-\beta_2 r}(\beta_2 r)^s\left(1+\tau-\frac{2\beta_2 r}{3+2s}\right).\tag{A-2b}$$

$$\eta_1(r)=\frac{\beta_1}{(2+s)\kappa}C_1e^{-\beta_1 r}(\beta_1 r)^s,\tag{A-2c}$$

$$\eta_2(r)=\frac{\beta_2}{[1+(1+\frac{1}{2}s)^{\frac{1}{2}}]\kappa}C_2e^{-\beta_2 r}(\beta_2 r)^s\left(1-\tau-\frac{2\beta_2 r}{3+2s}\right),\tag{A-2d}$$

where

$$s=[1-(Z\alpha)^2]^{\frac{1}{2}}-1;\quad \beta_1=\kappa\alpha Z,\quad \beta_2=\kappa(-s/2)^{\frac{1}{2}},$$

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

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

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

The small components, η, are β/κ smaller than the large components, ψ. In the nonrelativistic limit $s\ll 1$,

$$\psi_1^0(r)=\psi_1^0(0)e^{-\beta_1 r};\quad \psi_2^0(r)=\psi_2^0(0)e^{-\beta_2 r}(1-\beta_2 r);$$
$$\eta_1^0(r)=\tfrac{1}{2}\beta_1\kappa^{-1}\psi_1^0(0)e^{-\beta_1 r};\tag{A-3}$$
$$\eta_2(r)=\tfrac{1}{2}\beta_2\kappa^{-1}\psi_2^0(0)e^{-\beta_2 r}(1-\tfrac{1}{2}\beta_2 r),$$

where $\beta_2\rightarrow\frac{1}{2}\kappa Z\alpha$. The nonrelativistic momentum wave function is defined by

$$\Phi_n^0(\mathbf{p})=\int\frac{d^3r}{(2\pi)^3}\psi_n^0(r)e^{-i\mathbf{p}\cdot\mathbf{r}}=\begin{pmatrix}\phi_n^0(p)\\(\boldsymbol{\sigma}\cdot\mathbf{p}/2\kappa)\chi_n^0(p)\end{pmatrix}.\tag{A-4}$$

Using (A-3) in (A-4)

$$\phi_1^0(p)=\chi_1^0(p)=\frac{\beta_1}{\pi^2}\left(\frac{\psi_1^0(0)}{(p^2+\beta_1^2)^2}\right),\tag{A-5a}$$

$$\phi_2^0(p)=\chi_2^0(p)=\frac{2\beta_2}{\pi^2}\left(\frac{p^2-\beta_2^2}{(p+\beta_2^2)^3}\right)\psi_2^0(0).\tag{A-5b}$$

APPENDIX B

The difference of two divergent integrals, as in Eq. (9), is defined by

$$\Delta\int d^3p p^2\frac{\phi^0(p)}{\psi^0(0)}=\int d^3p\, p^2\left[\frac{2\beta_2}{\pi^2}\left(\frac{(p^2-\beta_2^2)}{(p^2+\beta_2^2)^3}\right)-\frac{\beta_1}{\pi^2}\left(\frac{1}{(p^2+\beta_1^2)^2}\right)\right].\tag{B-1}$$

This is finite, since $2\beta_2=\beta_1$. The result is

$$\Delta\int d^3p\, p^2\frac{\phi^0(p)}{\psi^0(0)}=\tfrac{3}{4}\beta_1^2.\tag{B-2}$$

The values of the other differences of integrals which occur are

$$\Delta\int\frac{d^3p_1d^3p_2}{|\psi^0(0)|^2}\phi^0(p_2)\Delta p\phi^2(p_1)=\frac{8}{\pi}\beta_1(\ln 2-\tfrac{5}{8}),\tag{B-3}$$

and

$$\Delta\int\frac{d^3p_1d^3p_2}{|\psi^0(0)|^2}\phi^0(p_2)\frac{\mathbf{p}_2\cdot\mathbf{p}_1\phi(p_1)}{\Delta p}=\frac{\beta_1}{4\pi}.\tag{B-4}$$

APPENDIX C

The magnetic wave function can be obtained from the Dirac equation by treating the magnetic potential as a perturbation. The action of the magnetic potential on the Coulomb S state will introduce some D state which cannot contribute to the results of this paper. Therefore only the S state part of ψ^M will be dealt with.

$$\psi_n^M(r)=e\begin{pmatrix}\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\, u_n(r)\\(i\boldsymbol{\sigma}\cdot\mathbf{r}/r)\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\, v_n(r)\end{pmatrix}.\tag{C-1}$$

Only the nonrelativistic limit of $u(r)$ and $v(r)$ is required. These are completely determined by

$$\left(\nabla^2-\beta_n^2+\frac{2\kappa Z\alpha}{r}\right)u_n^0(r)=-\tfrac{2}{3}\psi_n^0(0)\delta(\mathbf{r})+\tfrac{2}{3}|\psi_n^0(0)|^2\psi_n(r),\tag{C-2}$$

$$2\kappa v_n^0(r)=-\frac{1}{6\pi r^2}\psi_n^0(r)-\frac{d}{dr}u_n^0(r).\tag{C-3}$$

and

$$\int u_n^0(r)\psi_n^0(r)d^3r=0,\quad \int|u_n^0(r)|^2d^3r<\infty.\tag{C-4}$$

The differential equation, (C-2), is solved subject to the condition, Eq. (C-4) and substituted back into

Eq. (C-3) to get: For the ground state,

$$u_1^0(r)=-\frac{1}{6\pi}\psi_1^0(0)e^{-\beta_1 r}[-(1/r)+2\beta_1\ln(2\beta_1 r)+\beta_1(2\gamma-5)+2\beta_1^2 r],\quad \text{(C-5a)}$$

$$v_1^0(r)=-\frac{1}{6\pi}\psi_1^0(0)\frac{\beta_1}{2\kappa}e^{-\beta_1 r}[-(3/r)+2\beta_1\ln(2\beta_1 r)+\beta_1(2\gamma-7)+2\beta_1^2 r],\quad \text{(C-5b)}$$

and for the excited state

$$u_2(r)=-\frac{1}{6\pi}\psi_2^0(0)e^{-\beta_2 r}[-(1/r)+4\beta_2\ln(2\beta_2 r)+\beta_2(4\gamma-3)-4\beta_2^2 r\ln 2\beta_2 r+\beta_2^2 r(13-4\gamma)-2\beta_2^3 r^2],\quad \text{(C-6a)}$$

$$v_2(r)=-\frac{1}{6\pi}\psi_2^0(0)\frac{\beta_2}{2\kappa}e^{-\beta_2 r}[-(6/r)+8\beta_2\ln(2\beta_2 r)+\beta_2(8\gamma-12)-4\beta_2^2 r\ln 2\beta_2 r+\beta_2^2 r(17-4\gamma)-2\beta_2^3 r^2],\quad \text{(C-6b)}$$

where $\gamma=2.5777\cdots$ is Euler's constant.

The integrals involving u and v that are required are

$$\Delta\int_0^\infty \psi^0(r)u^0(r)\frac{dr}{|\psi^0(0)|^2}=-\frac{1}{6\pi}(\tfrac{3}{2}-\ln 2),\quad \text{(C-7)}$$

$$\Delta\int_0^\infty [\psi^0(r)v^0(r)+\eta^0(r)u^0(r)]\times\frac{dr}{|\psi^0(0)|^2}=\frac{Z\alpha}{3\pi}(\ln 2-17/16),\quad \text{(C-8)}$$

$$\Delta\int_0^\infty \psi^0(r)u^0(r)\frac{dr}{|\psi^0(0)|^2}=\frac{1}{8\pi\kappa Z\alpha},\quad \text{(C-9)}$$

$$\Delta\int_0^\infty u^0(r)\left(r\frac{d^2}{dr^2}+\frac{d}{dr}\right)\psi^0(r)\times\frac{dr}{|\psi^0(0)|^2}=-\frac{\kappa Z\alpha}{6\pi}(\tfrac{9}{16}-\ln 2).\quad \text{(C-10)}$$

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Convergent Schrödinger Perturbation Theory

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A formulation of Schrödinger perturbation theory is developed that gives a unified treatment of nondegenerate and degenerate cases, is unique, and has a nonzero radius of convergence under very general conditions. Two alternative procedures are given for finding perturbed eigenvectors, one of which is simpler for the nondegenerate case or for small finite degeneracy, the other simpler for infinite or large finite degeneracy. The low-order terms in the perturbation expansions of quantities used in applications are given. The perturbation theory formulated in this paper has the following advantages over the conventional Schrödinger and Brillouin-Wigner perturbation theories: (i) When the convergence criterion is satisfied, bounds on the error made in replacing an appropriate infinite perturbation series by its first n terms can be obtained. (ii) For the case of degeneracy, the conventional Schrödinger perturbation theory can break down under conditions to which the convergence of the perturbation theory developed in this paper are insensitive. (iii) There is no implicit dependence on the eigenvalue, such as appears in the Brillouin-Wigner perturbation theory. (iv) For the case of degeneracy, statistical information about the distribution of certain eigenvalues can be obtained without finding the individual eigenvalues. (v) The theory is applicable to a wider class of problems than the conventional Schrödinger and Brillouin-Wigner perturbation theories.

I. INTRODUCTION

THE conventional Schrödinger perturbation theory is concerned with finding the eigenvectors and eigenvalues in a Hilbert space of a Hermitean operator of the form $\mathbf{H}_0+\epsilon\mathbf{V}$ as a power series in the real parameter ϵ.[1] We want to go into this theory in some detail to point out the relation between it and the theory developed in this paper. The advantages of the latter will be pointed out as we go along. To avoid difficulties of a purely mathematical nature, we will assume that the Hermitean operator $\mathbf{H}_0$ possesses a complete orthonormal set of eigenvectors $\xi_0, \xi_1, \cdots, \xi_n, \cdots$ with eigenvalues $E_0, E_1, \cdots, E_n, \cdots$, respectively. We fix our attention on the eigenvalue E_0, and require that, if $E_n\neq E_0$, then in fact $|E_n-E_0|>\delta>0$ for some fixed δ. In other words, E_0 is an isolated point in the spectrum of $\mathbf{H}_0$.

Let $\mathbf{P}$ be the projection operator onto the closed linear manifold M_{E_0} of all solutions ψ_0 of the equation $\mathbf{H}_0\psi_0=E_0\psi_0$. Then $\mathbf{P}\xi_n=\xi_n$ for $E_n=E_0$, and $\mathbf{P}\xi_n=0$ for $E_n\neq E_0$, and thus $\mathbf{H}_0\mathbf{P}\xi_n=E_0\mathbf{P}\xi_n=E_n\mathbf{P}\xi_n=\mathbf{P}\mathbf{H}_0\xi_n$, so

[1] E. Schrödinger, Ann. Physik 80, 437 (1926).