State-Dependent Mass Corrections to Hyperfine Structure in Hydrogenic Atoms*

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The $\alpha^2 m/M$ corrections to the ratio of the hyperfine structure of the 1s and 2s states of hydrogenic atoms have been evaluated using a Foldy-Wouthuysen reduction of the Dirac Hamiltonian for the electron plus additional nuclear motion terms. The covariant two-fermion Bethe-Salpeter equation gives the same result, as does an approximately covariant calculation based on the Breit equation, a simple nuclear model, and the correspondence principle. In units of 10^{-6}, the $\alpha^2 m/M$ corrections to $R=(8\nu_2/\nu_1)-1$ total -0.115, -0.029, and -0.101 for H, D, and T, respectively. The corresponding theoretical R values are 34.45 ± 0.02, 34.53 ± 0.02, and 34.46 ± 0.02. These agree with the available experimental values which are 34.495 ± 0.060 and 34.2 ± 0.6 for H and D, respectively.

I. INTRODUCTION

We have calculated the $\alpha^2 m/M$ corrections to the ratio of the hyperfine structure (hfs) of the 1s and 2s states in hydrogenic atoms, where α is the fine structure constant, and m/M is the electron to proton mass ratio. The results are in agreement with the experimental values[1,2] for hydrogen and deuterium, which are known to accuracies of several parts in 10^9 and 10^8, respectively.

It should be noted that the theoretical ground-state hfs in hydrogen[3] is apparently not in agreement with the measured frequency. This calculation depends upon the structure of the proton and is very laborious for terms smaller than α^2 (hfs) and $\alpha(m/M)$ (hfs). Recent calculations[4] of the $\alpha^3(\ln\alpha)^2$ and $\alpha^3(\ln\alpha)$ parts of the α^3 correction have increased this discrepancy.

The ratio is much simpler to evaluate, and is less sensitive to nuclear structure effects. The hfs for an ns state in a hydrogenic atom can be expressed in the form

$$E_n=E_n^F[\mathfrak{M}/(m+\mathfrak{M})]^3[1+(\alpha/2\pi)+a\alpha^2 +b\alpha(m/\mathfrak{M})+c_n(Z\alpha)^2+d_n\alpha(Z\alpha)^2 +e_n\alpha^2(m/M)+\cdots]. \quad (1.1)$$

Here E_n^F is the Fermi energy[5]; in natural units $\hbar=c=1$,

$$E_n^F=2\pi\alpha g\langle\boldsymbol{\sigma}\cdot\mathbf{I}\rangle(3mM)^{-1}|u_n(0)|^2, \quad (1.2)$$

where $u_n(0)$ is the Schrödinger wave function evaluated at the nucleus, gI is the nuclear magnetic moment in nuclear magnetons, and $\boldsymbol{\sigma}$ is the electron spin operator.

The second factor in Eq. (1.1) is the nonrelativistic reduced mass correction due to motion of the nucleus; it is rigorously correct to lowest order in α. Including it as a multiplicative rather than an additive factor leads to the conventional definition of b.[6,7] The α and α^2 radiative corrections[8] and the $\alpha m/\mathfrak{M}$ mass[6,7,9] (nucleon motion) and structure[3,10] corrections are proportional to $|u_n(0)|^2$ or "state independent." The Breit corrections[11] of order $(Z\alpha)^2$ arise from the use of Dirac wave functions; $c_1=3/2$ and $c_2=17/8$.

The residual R is defined by

$$1+R=8\nu_2(\text{hfs})/\nu_1(\text{hfs}). \quad (1.3)$$

Thus, since $|u_1(0)|^2=8|u_2(0)|^2$,

$$R=(8\nu_2-\nu_1)/\nu_1 =[(c_2-c_1)(Z\alpha)^2+(d_2-d_1)\alpha(Z\alpha)^2 +(e_2-e_1)\alpha^2(m/M)][1+\alpha/2\pi+\cdots]^{-1}. \quad (1.4)$$

Therefore, only the *differences* of the α^3 and of the $\alpha^2 m/M$ coefficients must be calculated to obtain R to these orders. This greatly reduces the number of terms which contribute, and simplifies those which do. The α^3 part has been evaluated[12,13] and is in good agreement with the experimental data. Also, a portion of the $\alpha^2 m/M$ term has been computed by a nonrelativistic method.[14]

The actual calculation of the $\alpha^2 m/M$ contributions to R is discussed in Sec. II. It is based on a Foldy-Wouthuysen[15] reduction of the usual Dirac Hamiltonian for the electron plus additional terms which account for the motion of the nucleus. A comparison with the experimental values is also given here.

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[1] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. **120**, 1279 (1960). This paper gives $\nu_1(D)$. F. M. Pipkin and R. H. Lambert, Phys. Rev. **127**, 787 (1962); this gives $\nu_1(H)$ and $\nu_1(T)$.

[2] J. Gruenebaum and P. Kusch, Columbia Radiation Laboratory Quarterly Report, September 15, 1960 (unpublished); their result is $\nu_2(\text{H})=177\ 556.842\pm0.010$ kc/sec. H. A. Reich, J. W. Heberle, and P. Kusch, Phys. Rev. **104**, 1585 (1956); this gives $\nu_2(D)$.

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

[4] D. E. Zwanziger, Bull. Am. Phys. Soc. **6**, 514 (1961); A. J. Layzer, *ibid.* **6**, 514 (1961).

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

[6] W. A. Newcomb and E. E. Salpeter, Phys. Rev. **97**, 1146 (1955). Our notation in Sec. III will follow that of this paper as closely as possible.

[7] W. A. Newcomb, thesis, Cornell University, (unpublished).

[8] N. M. Kroll and F. Pollock, Phys. Rev. **86**, 876 (1952).

[9] R. Arnowitt, Phys. Rev. **92**, 1002 (1953).

[10] A. C. Zemach, Phys. Rev. **104**, 1721 (1956); D. A. Greenberg and H. M. Foley, *ibid.* **120**, 1684 (1960). See the latter paper for earlier references.

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

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

[13] D. E. Zwanziger, Phys. Rev. **121**, 1128 (1961).

[14] C. Schwartz, Ann. Phys. (N.Y.) **2**, 156 (1959).

[15] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

In Sec. III we show that the covariant two-fermion equation of motion, the Bethe-Salpeter equation,[16,17] reduces to the modified Dirac equation of Sec. II. We treat the proton as a point Fermi-Dirac particle with an anomalous Pauli moment. Momentum integrals enter which contain two Pauli interactions and consequently diverge logarithmically, requiring either an arbitrary cutoff or a proton form factor for their evaluation. However, since the high momentum portions of these integrals are state independent, these structure effects do not contribute to R to the order of interest. [Structure effects yield R contributions of order $\langle r^2\rangle_{\text{nuc}} u^{11}(0)/u(0) \approx d^2/a_0^2 \approx (10^{-13}/10^{-8})^2 \approx 10^{-10}$ for hydrogen.]

The Coulomb gauge is a convenient choice in this calculation. We use

$$\gamma_\nu{}^a\gamma_\nu{}^b/k_\mu{}^2 = -\gamma_4{}^a\gamma_4{}^b(1/k^2+\boldsymbol{\alpha}_\perp{}^2\cdot\boldsymbol{\alpha}_\perp{}^b/k_\mu{}^2), \qquad (1.5)$$

where $\boldsymbol{\alpha}_\perp\cdot\mathbf{k}\equiv 0$. Equation (1.5) is not a rigorous identity, but it is correct for the relevant matrix elements. It separates the instantaneous Coulomb interaction from the transverse part, resulting in a tractable zeroth order problem plus perturbations.[17]

Finally, in Sec. IV we use an approximately covariant calculation principle based on the Breit equation, a simple nuclear model, and the correspondence principle to obtain the modified Dirac equation for an arbitrary hydrogenic atom.

II. MODIFIED DIRAC EQUATION

In this section we will begin by reviewing the Foldy-Wouthuysen[15] reduction of the Dirac equation. We will then include additional terms needed to account for the motion of the nucleus and proceed to calculate R, reserving for the following sections the problem of justifying the various assumptions made.

The motion of an electron in an external field is given by the Dirac Hamiltonian

$$\mathcal{H} = \beta m + \boldsymbol{\alpha}\cdot(\mathbf{p}+e\mathbf{A}) - e\varphi. \qquad (2.1)$$

The "odd" term $\mathcal{O}$, which here is $\boldsymbol{\alpha}\cdot(\mathbf{p}+e\mathbf{A})$, may be eliminated to arbitrary order in m^{-1} by successive Foldy-Wouthuysen transformations. Each is of the form

$$\mathcal{H} \to e^{iS}\mathcal{H}e^{-iS} = \mathcal{H} + i[S,\mathcal{H}] + (i^2/2!)[S,[S,\mathcal{H}]] + \cdots,$$
$$S = (-i\beta/2m)\mathcal{O},$$

and reduces the order of the remaining odd term by m^{-1}. To order m^{-3}, $\mathcal{H}$ becomes

$$\mathcal{H}' = \beta m - e\varphi + (\beta/2m)[\boldsymbol{\alpha}\cdot(\mathbf{p}+e\mathbf{A})]^2 - (ie/8m^2)[\boldsymbol{\sigma}\cdot\mathbf{E},\, \boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})] - (\beta/8m^3)[\boldsymbol{\alpha}\cdot(\mathbf{p}+e\mathbf{A})]^4. \qquad (2.2)$$

For an electron bound to a fixed nucleus with charge Ze, spin $\mathbf{I}$, and magnetic moment $\boldsymbol{\mu}$, the potentials are

$$\varphi_0 = Ze/r, \quad \mathbf{A}_0 = -\boldsymbol{\mu}\times\boldsymbol{\nabla}r^{-1}, \qquad (2.3a)$$

where

$$\boldsymbol{\mu} = g(e/2M)\mathbf{I}. \qquad (2.3b)$$

For positive energy states, Eq. (2.2) now becomes

$$\mathcal{H}_0' = \left[m + \frac{p^2}{2m} - e\varphi_0\right] + \left[\frac{e}{8m^2}\boldsymbol{\nabla}\cdot\mathbf{E}_0 - \frac{p^4}{8m^3}\right] + \left[\frac{e}{2m}\boldsymbol{\sigma}\cdot\mathbf{H}_0\right] + \left[\frac{e}{8m^2}\boldsymbol{\sigma}\cdot(\mathbf{E}_0\times\mathbf{p} - \mathbf{p}\times\mathbf{E}_0) + \frac{e}{m}\mathbf{p}\cdot\mathbf{A}_0 - \frac{e}{4m^3}(p^2\mathbf{p}\cdot\mathbf{A}_0 + \mathbf{p}\cdot\mathbf{A}_0p^2)\right] + \left[\frac{e}{2m}\boldsymbol{\sigma}\cdot\left(-\frac{p^2}{4m^2}\mathbf{H}_0 - \mathbf{H}_0\frac{p^2}{4m^2} + \frac{e}{2m}\mathbf{E}_0\times\mathbf{A}_0\right)\right] + \left[\frac{e^2}{2m}A^2 + \cdots\right] + \cdots$$
$$\equiv \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \cdots + \mathcal{H}^{(5)} + \cdots. \qquad (2.4)$$

Here we have dropped terms involving $[A_i, A_j]$.[18]

We will treat all terms but the Schrödinger approximation, $\mathcal{H}^{(0)}$, as perturbations. Thus $\mathcal{H}^{(1)}$ gives relativistic corrections smaller by α^2, and $\mathcal{H}^{(2)}$ gives the lowest order hfs for s states:

$$\langle\mathcal{H}^{(2)}\rangle = (e/2m)\langle\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}\times(-\boldsymbol{\mu}\times\boldsymbol{\nabla}r^{-1})\rangle$$
$$= (e/2m)\langle\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}\boldsymbol{\mu}\cdot\boldsymbol{\nabla}r^{-1} - \boldsymbol{\sigma}\cdot\boldsymbol{\mu}\nabla^2r^{-1}\rangle$$
$$= (e/2m)\left\langle(-2/3)\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\nabla^2\frac{1}{r}\right\rangle$$
$$= (4\pi e/3m)\langle\sigma\cdot\mu\rangle|u(0)|^2. \qquad (2.5)$$

$\mathcal{H}^{(3)}$ is the spin-orbit interaction plus the convection current coupling to the magnetic field; it is proportional to $\boldsymbol{\sigma}\cdot\mathbf{L}$ and vanishes for s states.

Breit's α^2 corrections to R arise in this treatment from $\mathcal{H}^{(4)}$ in first order perturbation theory, and from $\mathcal{H}^{(1)}$ together with $\mathcal{H}^{(2)}$ in second order. This will be shown explicitly below.

Corrections of order $\alpha^2 m/M$ to R arise from terms quadratic in $\mathbf{A}$, i.e., $\mathcal{H}^{(2)}$ in second-order perturbation theory. [$\mathcal{H}^{(5)}$ gives no s state hfs.] They also arise from the effects of nuclear motion, which are omitted in $\mathcal{H}_0$ and $\mathcal{H}_0'$. For a nucleus of mass $\mathfrak{M}$, terms containing both $\boldsymbol{\sigma}$ and $\boldsymbol{\mu}$ must be included to order $\mathfrak{M}^{-2}$, and other terms to order $\mathfrak{M}^{-1}$. Thus this motion is adequately

[16] E. E. Salpeter and H. A. Bethe, Phys. Rev. **84**, 1232 (1951); M. Gell-Mann and F. Low, *ibid.* **84**, 350 (1951).
[17] E. E. Salpeter, Phys. Rev. **87**, 328 (1952).
[18] M. M. Sternheim, Phys. Rev. **128**, 676 (1962); see also Sec. IIIC of the present paper.

described by the Hamiltonian

$$\mathcal{H}_{\mathfrak{M}}=\mathcal{H}_0+\mathfrak{M}+(p^2/2\mathfrak{M})+e\boldsymbol{\alpha}\cdot\delta\mathbf{A}-e\delta\varphi, \tag{2.6a}$$

$$\delta\mathbf{A}=-\frac{Ze}{2\mathfrak{M}r}\left(\mathbf{p}+\frac{\mathbf{r}}{r}\frac{\mathbf{r}}{r}\cdot\mathbf{p}\right), \tag{2.6b}$$

$$\delta\varphi=-\left(\boldsymbol{\mu}-\frac{Ze}{2\mathfrak{M}}\mathbf{I}\right)\times\frac{\mathbf{p}}{\mathfrak{M}}\cdot\boldsymbol{\nabla}\frac{1}{r}. \tag{2.6c}$$

In (2.6), $\mathbf{p}$ and $\mathbf{r}$ are now the relative momentum and position. $\delta\mathbf{A}$ is the vector potential of a moving charge Ze. $\delta\varphi$ is the scalar potential of a moving magnetic dipole; it will be discussed later in more detail.

Applying the Foldy-Wouthuysen procedure to Eq. (2.6) with $\mathbf{A}=\mathbf{A}_0+\delta\mathbf{A}$, $\varphi=\varphi_0+\delta\varphi$, we replace Eq. (2.2) by

$$\mathcal{H}_{\mathfrak{M}}'=\mathcal{H}'+\mathfrak{M}+\frac{p^2}{2\mathfrak{M}}-\frac{ie}{16m^2\mathfrak{M}}[\boldsymbol{\sigma}\cdot\mathbf{p}\times\mathbf{A}_0-\boldsymbol{\sigma}\cdot\mathbf{A}_0\times\mathbf{p},\, p^2]. \tag{2.7}$$

With $\beta=+1$,

$$\mathcal{H}'=\mathcal{H}_0'+\frac{e}{m}\mathbf{p}\cdot\delta\mathbf{A}-\frac{ie}{8m^2}[\boldsymbol{\sigma}\cdot\delta\mathbf{E},\,\boldsymbol{\sigma}\cdot\mathbf{p}]-e\delta\varphi+\frac{e}{2m}[\boldsymbol{\sigma}\cdot\delta\mathbf{H}],$$

and, with $\mu^{-1}=m^{-1}+\mathfrak{M}^{-1}$,

$$\begin{aligned}\mathcal{H}_{\mathfrak{M}}'=&\left[m+\mathfrak{M}+\frac{p^2}{2\mu}-e\varphi_0\right]+\left[\frac{e}{8m^2}\boldsymbol{\nabla}\cdot\mathbf{E}_0-\frac{p^4}{8m^3}\right.\\&+\left.\frac{e}{m}\mathbf{p}\cdot\delta\mathbf{A}\right]+\left[\frac{e}{2m}\boldsymbol{\sigma}\cdot\mathbf{H}_0\right]+\frac{e}{2m}\boldsymbol{\sigma}\cdot\left[-\frac{p^2}{4m^2}\mathbf{H}_0\right.\\&-\mathbf{H}_0\frac{p^2}{4m^2}+\frac{e}{2m}\mathbf{E}_0\times\mathbf{A}_0+\frac{1}{4m}(\delta\mathbf{E}\times\mathbf{p}-\mathbf{p}\times\delta\mathbf{E})\\&\left.-\frac{i}{8m\mathfrak{M}}[(\mathbf{p}\times\mathbf{A}_0-\mathbf{A}_0\times\mathbf{p}),\,p^2]\right]\\=&\,\mathcal{H}_{\mathfrak{M}}^{(0)}+\cdots+\mathcal{H}_{\mathfrak{M}}^{(3)}.\end{aligned} \tag{2.8}$$

Here we have omitted the terms which vanish exactly for s state, e.g., $\mathcal{H}^{(3)}$ and $(e/2m)\boldsymbol{\sigma}\cdot\delta\mathbf{H}$, as well as those not contributing to the hfs to the order of interest, e.g., $\mathcal{H}^{(5)}$ and $-e\delta\varphi$. Note that $\mathcal{H}_{\mathfrak{M}}^{(0)}$ is the Schrödinger approximation for a particle with reduced mass μ.

The state-dependent hfs terms are contained in

$$\begin{aligned}\Delta E_n=&\langle n|H_{\mathfrak{M}}^{(3)}|n\rangle+{\textstyle\sum_i}'\langle n|2H_{\mathfrak{M}}^{(1)}+H_{\mathfrak{M}}^{(2)}|i\rangle\\&\times\langle i|H_{\mathfrak{M}}^{(2)}|n\rangle(W_n-W_i)^{-1}\\\equiv&\,\Delta E^{(3)}+\Delta E^{(1,2)}+\Delta E^{(2,2)}.\end{aligned} \tag{2.9}$$

With the Schrödinger approximation, $p^2|n\rangle=2\mu(W_n+Ze^2/r)|n\rangle$,

$$\begin{aligned}\Delta E_n^{(3)}=&\left\langle n\left|-\frac{e\mu}{2m^3}\boldsymbol{\sigma}\cdot\mathbf{H}_0\left(W_n+\frac{Ze^2}{r}\right)+\frac{Ze^3}{4m^2}\boldsymbol{\sigma}\cdot\frac{\mathbf{r}}{r^3}\right.\right.\\&\times\left(\boldsymbol{\mu}\times\frac{\mathbf{r}}{r^3}\right)+\frac{e}{4m^2}(\boldsymbol{\sigma}\times\mathbf{p})_i\left[\left(\boldsymbol{\mu}-\frac{Ze}{2\mathfrak{M}}\mathbf{I}\right)\times\frac{\mathbf{p}}{\mathfrak{M}}\right]_j\\&\left.\left.\times\nabla_i\nabla_j\frac{1}{r}-\frac{Ze^3i\mu}{4m^2\mathfrak{M}}\left[\boldsymbol{\sigma}\cdot\mathbf{p}\times\left(\boldsymbol{\mu}\times\frac{\mathbf{r}}{r^3}\right),\frac{1}{r}\right]\right|n\right\rangle\\\equiv&\,\Delta E_n^{(3a)}+\Delta E_n^{(3b)}+\Delta E_n^{(3c)}+\Delta E_n^{(3d)}.\end{aligned} \tag{2.10}$$

Equations (2.9) and (2.10) contain integrals which diverge at $r=0$, e.g., $\langle r^{-4}\rangle$. Since

$$u_1(r)=N_1\exp(-\beta r),$$
$$u_2(r)=N_2(1-\beta r/2)\exp(-\beta r/2),$$

where

$$N_n=(\beta^3/n^3\pi)^{1/2},\quad \beta=Z\alpha\mu, \tag{2.11}$$

it follows that

$$8|u_{2s}|^2-|u_{1s}|^2\sim(\text{const})r^2|u_{1s}|^2\quad\text{for}\quad r\ll\beta.$$

Thus, if we cut off the integrals at r_0, evaluate R, and then let r_0 go to zero, finite results are obtained.

To illustrate the procedure, we will compute $R^{(3b)}$. Averaging over angles gives

$$\Delta E_n^{(3b)}=[Ze^3(\boldsymbol{\sigma}\cdot\boldsymbol{\mu})/6m^2]\langle n|r^{-4}|n\rangle.$$

Now

$$\begin{aligned}\langle 1s|r^{-4}|1s\rangle=&(\beta^3/\pi)\int_{r_0}^{\infty}r^{-2}\exp(-2\beta r)drd\Omega\\=&\,4\beta^4(1-2\beta r_0)/\beta r_0+8\beta^4\ln\beta r_0+8\beta^4\ln 2\gamma,\end{aligned}$$

where two partial integrations have been performed, and

$$\ln\gamma=-\int_0^{\infty}\ln x\exp(-x)dx.$$

γ is the Euler constant; its value is not needed, since it cancels out in the final results. Similarly,

$$8\langle 2s|r^{-4}|2s\rangle=4\beta^4(1-2\beta r_0)/\beta r_0+8\beta^4\ln\beta r_0+5\beta^4+8\ln\gamma.$$

Thus,

$$\begin{aligned}R^{(3b)}=&[8\Delta E_2^{(3b)}-\Delta E_1^{(3b)}]/[(4e/3m)\langle\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\rangle\beta^3]\\=&[(5/8)-\ln 2]Z^2\alpha^2\mu/m\\=&[(5/8)-\ln 2]Z^2\alpha^2(1-m/\mathfrak{M}).\end{aligned} \tag{2.12b}$$

In the same fashion we find

$$R^{(3a)}=-(3/8)Z^2\alpha^2(1-2m/\mathfrak{M}), \tag{2.12a}$$

$$\begin{aligned}R^{(3c)}=&[-(7/32)+(1/2)\ln 2]\\&\times[1-ZM/g\mathfrak{M}]Z^2\alpha^2m/\mathfrak{M},\end{aligned} \tag{2.12c}$$

$$R^{(3d)}=[(5/8)-\ln 2]Z^2\alpha^2m/\mathfrak{M}. \tag{2.12d}$$

To evaluate the second-order perturbation theory terms, we note that with F_n defined by[14,19]

$$[F_n,\mathcal{H}_{\mathfrak{M}}^{(2)}]|n\rangle=\mathcal{H}_{\mathfrak{M}}^{(2)}|n\rangle-\langle n|\mathcal{H}_{\mathfrak{M}}^{(2)}|n\rangle|n\rangle, \quad (2.13)$$

it follows that

$$\sum_i{}' \; |i\rangle\langle i|\mathcal{H}_{\mathfrak{M}}^{(2)}|n\rangle(W_n-W_i)^{-1} =F_n|n\rangle-\langle n|F_n|n\rangle|n\rangle. \quad (2.14a)$$

This state is a mixture of s and d wave functions. The s-state part is given by[13,14]

$$F_{1s}=(2e\mu/3m)\langle\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\rangle[r^{-1}+2\beta\ln\beta r+2\beta^2 r],$$
$$F_{2s}=(2e\mu/3m)\langle\boldsymbol{\sigma}\cdot\boldsymbol{\mu}\rangle[r^{-1}+2\beta\ln\beta r+(\beta^2 r/2) +(7\beta/2)(1-\beta r/2)^{-1}]. \quad (2.14b)$$

By Eqs. (2.8)

$$H_{\mathfrak{M}}^{(1)}=(\pi Ze^2/2m^2)\delta^3(r)-(p^4/8m^3) -(Ze^2/2m\mathfrak{M})\mathbf{p}\cdot r^{-1}(\mathbf{p}+r^{-2}\mathbf{r}\mathbf{r}\cdot\mathbf{p}) \equiv\mathcal{H}_{\mathfrak{M}}^{(1a)}+\mathcal{H}_{\mathfrak{M}}^{(1b)}+\mathcal{H}_{\mathfrak{M}}^{(1c)}. \quad (2.15)$$

Using Eqs. (2.8) and (2.14), we find

$$R^{(12a)}=[(3/2)-\ln 2]Z^2\alpha^2(1-2m/\mathfrak{M}), \quad (2.16a)$$

$$R^{(12b)}=[-(9/8)+2\ln 2]Z^2\alpha^2(1-3m/\mathfrak{M}), \quad (2.16b)$$

$$R^{(12c)}=[-(9/4)+4\ln 2]Z^2\alpha^2 m/\mathfrak{M}. \quad (2.16c)$$

The term $\Delta E^{(22)}$ involves both the s and d parts of Eq. (2.14a). Schwartz[14] has found

$$R^{(22)}=[-(145/128)+\tfrac{7}{8}\ln 2]gZ\alpha^2 m/M. \quad (2.17)$$

Adding Eqs. (2.12), (2.16), and (2.17), we obtain the Breit correction $(5/8)Z^2\alpha^2$ plus

$$R(\alpha^2 m/M)=-(9/8)Z^2\alpha^2 m/\mathfrak{M} +[-(7/32)+(1/2)\ln 2] \times[1-(ZM/g\mathfrak{M})]Z^2\alpha^2 m/\mathfrak{M} -[(145/128)-\tfrac{7}{8}\ln 2]gZ\alpha^2 m/M. \quad (2.18)$$

For the hydrogen isotopes, this gives[20]

$$R(\alpha^2 m/M,H)=-0.115\times10^{-6},$$
$$R(\alpha^2 m/M,D)=-0.029\times10^{-6}, \quad (2.19)$$
$$R(\alpha^2 m/M,T)=-0.101\times10^{-6}.$$

The complete theoretical expression for R is[13]

$$R(\mathrm{th})=(5/8)\alpha^2+[3.40\pm0.02-(5/16\pi)]\alpha^3 +R(\alpha^2 m/M)+R(\alpha^4)+\cdots,$$

where the uncertainty in the α^3 term arises from a numerical integration. Thus we have finally

$$R(\mathrm{H, theory})=(34.45\pm0.02)\times10^{-6},$$
$$R(\mathrm{D, theory})=(34.53\pm0.02)\times10^{-6},$$
$$R(\mathrm{T, theory})=(34.46\pm0.02)\times10^{-6},$$

where the uncertainty is due to the error in the α^3 term and to the uncalculated α^4 term.

The experimental values are[1,2]

$$R(\mathrm{H, exp})=(34.495\pm0.060)\times10^{-6},$$
$$R(\mathrm{D, exp})=(34.2\pm0.6)\times10^{-6},$$

which are in good agreement with (2.19).

III. BETHE-SALPETER EQUATION

We will now demonstrate that a covariant treatment of the two-body hydrogen atom problem leads to exactly the results found for R with the modified Dirac equation.

A. Instantaneous Interaction Terms

The Bethe-Salpeter equation for the hydrogen atom is[16]

$$F(p_\mu)\psi(p_\mu)=(-2\pi i)^{-1}\int G(p_\mu,p_\mu')\psi(p_\mu')d^4p', \quad (3.1)$$

where

$$F(p_\mu)=F(\mathbf{p},\epsilon)=[\eta_a E-H_a(\mathbf{p})+\epsilon] \times[\eta_b E-H_b(\mathbf{p})-\epsilon] \quad (3.2)$$

and

$$H_a(\mathbf{p})=\boldsymbol{\alpha}^a\cdot\mathbf{p}+\beta^a m, \quad H_b(\mathbf{p})=-\boldsymbol{\alpha}^b\cdot\mathbf{p}+\beta^b M, \quad (3.3a)$$

$$\eta_a=m/(m+M), \quad \eta_b=M/(m+M). \quad (3.3b)$$

$\psi(p_\mu)$ is a 16-component spinor function of the relative momentum p_μ, and E is the corresponding eigenvalue. The interaction operator G is an expansion in powers of α which may be split into a large instantaneous Coulomb interaction,

$$G_C(\mathbf{p}-\mathbf{p}')=-(e^2/2\pi^2)|\mathbf{p}-\mathbf{p}'|^{-2}, \quad (3.4)$$

plus small perturbations.

If G is approximated by G_C, Eq. (3.1) may be integrated over ϵ, giving[17]

$$[E-H_a(\mathbf{p})-H_b(\mathbf{p})]\phi(\mathbf{p}) =[\Lambda_+^a(\mathbf{p})\Lambda_+^b(\mathbf{p})-\Lambda_-^a(\mathbf{p})\Lambda_-^b(\mathbf{p})] \times\int G_C(\mathbf{p}-\mathbf{p}')\phi(\mathbf{p}')d^3p', \quad (3.5)$$

where

$$\phi(\mathbf{p})=\int\psi(p_\mu)d\epsilon, \quad (3.6)$$

$$\Lambda_\pm^a(\mathbf{p})=[E_a\pm H_a(\mathbf{p})](2E_a)^{-1}, \quad (3.7)$$

$$E_a=E_a(\mathbf{p})=(\mathbf{p}^2+m^2)^{1/2}, \quad (3.8)$$

with similar definitions for $\Lambda_\pm^b$ and E_b. The corresponding solution for $\psi(p_\mu)$ is obtained from $\phi(\mathbf{p})$ with

$$\psi(p_\mu)=[-2\pi iF(\mathbf{p},\epsilon)]^{-1}\int G_C(\mathbf{p}-\mathbf{p}')\phi(\mathbf{p}')d^3p'. \quad (3.9)$$

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[19] R. M. Sternheimer, Phys. Rev. 84, 244 (1951); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* 93, 734 (1954).

[20] J. W. DuMond and E. R. Cohen, Phys. Rev. Letters 1, 291 (1958); in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35.

Let

$$\phi_{\pm\pm}(\mathbf{p})=\Lambda_{\pm}{}^{a}(\mathbf{p})\Lambda_{\pm}{}^{b}(\mathbf{p})\phi(\mathbf{p}), \quad (3.10)$$

$$\Gamma_a(\mathbf{p})=\boldsymbol{\sigma}^a\cdot\mathbf{p}/(E_a+m), \quad \Gamma_b(\mathbf{p})=\boldsymbol{\sigma}^b\cdot\mathbf{p}/(E_b+M). \quad (3.11)$$

Then it follows from the properties of the Dirac operators that[17a]

$$\phi_{++}(\mathbf{p})=\begin{pmatrix}1\\ \Gamma_a(\mathbf{p})\end{pmatrix}\begin{pmatrix}1\\ -\Gamma_b(\mathbf{p})\end{pmatrix}\phi_{++}{}^{++}(\mathbf{p}), \quad (3.12)$$

where the "large-large" wave function $\phi_{++}{}^{++}(p)$ is a four-component spinor. Also,

$$[\Lambda_+{}^b(\mathbf{p})\phi_{++}(\mathbf{p}')]^+ = [E_b(\mathbf{p})+M+\boldsymbol{\sigma}^b\cdot\mathbf{p}\Gamma_b(\mathbf{p}')]\phi_{++}{}^+(\mathbf{p}')/2E_b(p), \quad (3.13)$$

where the single + superscript refers to the large part of the proton wave function.

Multiplying Eq. (3.5) by $\Lambda_+{}^a\Lambda_-{}^b$ and by $\Lambda_-{}^a\Lambda_+{}^b$ shows that

$$\phi_{-+}=\phi_{+-}=0. \quad (3.14)$$

Multiplying by $\Lambda_+{}^a\Lambda_+{}^b$ gives, with $k_\mu=(\mathbf{k},\omega)=p_\mu'-p_\mu$,

$$(E-E_a-E_b)\phi_{++}{}^+(\mathbf{p})=\Lambda_+{}^a(\mathbf{p})\left(\frac{-e^2}{2\pi^2}\right)\times\int[E_b+M+\boldsymbol{\sigma}^b\cdot\mathbf{p}\Gamma_b(\mathbf{p}')]\phi_{++}{}^+(\mathbf{p}')\times d^3p'/2E_bk^2, \quad (3.15)$$

neglecting ϕ_{--} on the right-hand side. Expanding in p/M gives

$$[E-M-E_a-(p^2/2M)]\phi_{++}{}^+=\Lambda_+{}^a(-e^2/2\pi^2)\times\int\left(1+\frac{\boldsymbol{\sigma}^b\cdot\mathbf{p}\boldsymbol{\sigma}^b\cdot\mathbf{k}}{4M^2}\right)\frac{\phi_{++}{}^+(\mathbf{p}')d^3p'}{k^2}. \quad (3.16)$$

Let us compare this with the modified Dirac equation (2.6). For $\mathbf{A}_0=\delta\mathbf{A}=0$, Eq. (2.6) gives for the Dirac wave function $\bar{\phi}$ with this notation

$$(E-H_a-p^2/2M)\bar{\phi}=-e(\varphi_0+\delta\varphi)\bar{\phi}. \quad (3.17)$$

Writing this in momentum space, multiplying by $\Lambda_+{}^a(\mathbf{p})$ and using $(ge/2M)\mathbf{I}=(1+\mu_A)(e/2M)\boldsymbol{\sigma}^b$, we find

$$[E-E_a-(p^2/2M)]\bar{\phi}_+=\Lambda_+{}^a(-e^2/2\pi^2)\times\int\left(1+\frac{(1+2\mu_A)\boldsymbol{\sigma}^b\cdot\mathbf{p}\boldsymbol{\sigma}^b\cdot\mathbf{k}}{4M^2}\right)\frac{\bar{\phi}_+(\mathbf{p})d^3p'}{k^2}, \quad (3.18)$$

neglecting $\bar{\phi}_-$ and $(e^2/4M^2)\mathbf{p}\cdot\nabla r^{-1}$ on the right-hand side. Thus, if we neglect the proton's Pauli moment μ_A [which is omitted in Eq. (3.15)], we see that

$$\phi_{++}{}^+=\bar{\phi}_+. \quad (3.19)$$

Note, however, that $\bar{\phi}_-$ does not vanish; by Eq. (3.17), a good approximation for $\bar{\phi}_-$ is

$$\bar{\phi}_-(\mathbf{p})=[E+E_a-(p^2/2M)]^{-1}\Lambda_-{}^a(\mathbf{p})(-e^2/2\pi^2)\times\int\frac{\bar{\phi}_+(\mathbf{p}')d^3p'}{k^2}. \quad (3.19a)$$

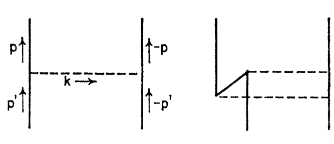

FIG. 1. Instantaneous interaction diagrams G_C and G_{CC}. The solid line on the left denotes the electron which has corresponding to p a momentum four-vector $(\mathbf{p}, \epsilon+\eta_aE)$, where $\eta_a=m/(m+M)$ and E is the total energy of the atom. The solid line on the right similarly denotes the proton. It has corresponding to $-p$ a momentum four-vector $(-\mathbf{p}, -\epsilon+\eta_bE)$, where $\eta_b=M/(m+M)$. Dashed lines represent Coulomb interactions.

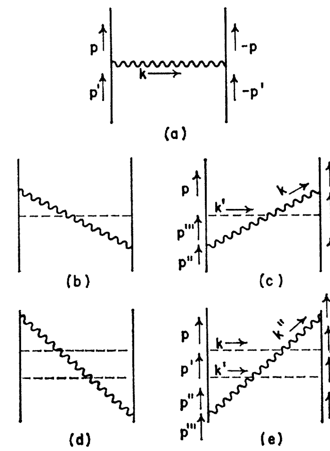

FIG. 2. One-Dirac-photon diagrams G_D, G_{CD1}, G_{CD2}, G_{CCD1}, G_{CCD2}. The wavy lines represent Dirac photons.

Both instantaneous and time-dependent perturbations are included in the full expansion for G, the interaction operator in Eq. (3.1). The instantaneous perturbations include all irreducible Feynman diagrams containing only Coulomb interactions. The largest of these is G_{CC}, shown in Fig. 1. It is easily proved that these diagrams vanish unless there is a negative-energy intermediate state. The leading energy terms are $\lesssim\alpha^5m$ and spin independent; the state-dependent hfs terms are negligibly small.

The time-dependent perturbations will now be considered.

B. One-Dirac-Photon Terms

The one-Dirac-photon diagrams contribution to R are shown in Fig. 2. ΔE_D, ΔE_{CD}, and ΔE_{CCD} are of order (hfs), α(hfs), and α^2(hfs), respectively. Together they give the hfs due to the proton's Dirac moment along with the Breit and nonrelativistic reduced mass corrections, as well as $\alpha(m/M)$(hfs) and $\alpha^2(m/M)$(hfs)

[17a] H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer-Velag, Berlin, 1957), Vol. 35.

terms. We note that

$$\Delta E_{CD1}=\Delta E_{CD2}=\tfrac{1}{2}\Delta E_{CD}$$

and

$$\Delta E_{CCD1}=\Delta E_{CCD2}=\tfrac{1}{2}\Delta E_{CCD},$$

and that the several other diagrams containing two Coulomb interactions and one Dirac photon do not contribute to R.

The first-order perturbation theory energy arising from a small G_i is

$$\Delta E_i=\int\bar{\psi}(p_\mu)G_i(p_\mu,p_\mu'')\psi(p_\mu')d^4pd^4p'', \quad (3.20)$$

where ψ is expressed in terms of ϕ by Eq. (2.9) and

$$\bar{\psi}(p_\mu)=\left[\int G_C(\mathbf{p}-\mathbf{p}')\phi^*(\mathbf{p}')d^3p'\right][-2\pi iF(\mathbf{p},\epsilon)]^{-1}. \quad (3.21)$$

From Eqs. (3.5) and (3.9), we obtain a convenient expression for ψ_{++}:

$$\psi_{++}(p_\mu)=[-2\pi iF_{++}(\mathbf{p},\epsilon)]^{-1}\times[E-E_a(\mathbf{p})-E_b(\mathbf{p})]\phi_{++}(\mathbf{p}). \quad (3.22)$$

A similar expression for $\bar{\psi}_{++}$ follows from Eqs. (3.5) and (3.21).

To sufficient accuracy, ϕ may be replaced by ϕ_{++} in Eqs. (3.9) and (3.21). Using

$$\psi=\psi_{++}+\psi_{+-}+\psi_{-+}+\psi_{--},$$

we may integrate Eq. (3.20) over the fourth components of the momenta. Only terms containing ψ_{++} or $\bar{\psi}_{++}$ or both contribute to R to order α^2m/M; terms containing ψ_{--} are negligible.

Newcomb and Salpeter[6] have calculated explicitly the $\alpha(m/M)$ (hfs) terms: ΔE_D, ΔE_{CD}, and various terms treated in later sections give such contributions, but not ΔE_{CCD}. They have found that all these terms can be cast into the form

$$\Delta E_i^{\mathrm{NS}}=\left(\frac{e^2}{2\pi^2}\right)^2\int\phi_{++}^{++*}(\mathbf{p})J_i(\mathbf{p},\mathbf{p}',\mathbf{p}'')\phi_{++}^{++}(\mathbf{p}'')\times\frac{d^3pd^3p'd^3p''}{k^2k'^2}, \quad (3.23)$$

where $k_\mu'=p_\mu''-p_\mu'$. Since $\phi_{++}^{++}(\mathbf{p})$ diminishes rapidly for $p\gg p_0$, to lowest order they take $\mathbf{k}=\mathbf{k}'=\mathbf{p}'$ for $p'\gg p_0$. Thus to lowest order they find

$$\begin{aligned}\Delta E_i^{\mathrm{NS}}(k\gg p_0)&=\left(\frac{e^2}{2\pi^2}\right)^2\int\phi_{++}^{++*}(\mathbf{p})J_i(0,\mathbf{k},0)\phi_{++}^{++}(\mathbf{p}'')\times d^3pd^3kd^3p''/k^4\\&=\left(\frac{e^2}{2\pi^2}\right)^2(2\pi)^3\phi_{++}^{++*}(0)\int\frac{J_i(0,\mathbf{k},0)d^3k}{k^4}\times\phi_{++}^{++}(0), \quad (3.24)\end{aligned}$$

where $\phi_{++}^{++}(0)$ is the large-large wave function at $r=0$. This result is state-independent and is $\lesssim\alpha$(hfs) in all cases of interest. The integrands of Eqs. (3.23) and (3.24) differ in lowest order by terms of the form $(\mathbf{p}\cdot\mathbf{k}\text{ or }\mathbf{p}''\cdot\mathbf{k})/k^2$ times the integrand of Eq. (3.24). These change sign under $\mathbf{k}\to-\mathbf{k}$ and therefore integrate to zero for $k\gg p_0$. Similarly, taking into account p and/or $p''\gg p_0$ gives energy terms $\lesssim\alpha^2$(hfs) which are also state-independent. Thus, the state-dependent part of ΔE_i^{NS} is negligible unless p, p', p'' are all $\sim p_0$. Similarly, we can show that R_{CCD} is negligible unless p, p', p'', p''' are all $\sim p_0$.

When put into the form (3.22), all the integrals contribute to R only for low momentum values and can be correspondingly simplified without affecting R to the required order. For convenience we may write formal expressions for ΔE_i which diverge. They are not correct for evaluation of ΔE_i but do yield R_i correctly. Thus, terms like $[u^2(r)/r]_{r\to0}$ will appear in ΔE_i but cancel later in R_i. Alternatively we could work only with expressions for R_i, but this would be more cumbersome.

We first consider ΔE_D, using Eq. (3.22) and

$$\begin{aligned}G_D&=-(e^2/2\pi^2)\boldsymbol{\alpha}_\perp{}^a\cdot\boldsymbol{\alpha}_\perp{}^b/k_\mu{}^2,\\k_\mu{}^2&=\omega^2-k^2+i\Delta.\end{aligned} \quad (3.25)$$

Integrating over ϵ and ϵ', the term containing $\bar{\psi}_{++}$ and ψ_{++} becomes

$$\begin{aligned}\Delta E_D^{++}&=\frac{e^2}{2\pi^2}\int d^3pd^3p'\,\phi_{++}{}^*(\mathbf{p})\boldsymbol{\alpha}_\perp{}^a\cdot\boldsymbol{\alpha}_\perp{}^b\\&\quad\times\left[\frac{1}{k^2-(E_b-E_b')^2}+\frac{E-E_a-E_b}{(2k)(k+E_a+E_b'-E)(k-E_b+E_b')}+\frac{E-E_a'-E_b'}{(2k)(k+E_a'+E_b-E)(k-E_b'+E_b)}\right]\times\phi_{++}(\mathbf{p}')\\&=\Delta E_D^{++a}+\Delta E_D^{++b}+\Delta E_b^{++c}.\end{aligned} \quad (3.26)$$

These terms arise from poles at $\omega=E_b-E_b'$, $+k$, $-k$, respectively.

For p and $p'\sim p_0$, ΔE_D^{++a} gives the nonrelativistic hfs; it is the only term which must be evaluated with wave functions containing the relativistic corrections. Since ΔE^{++a} contributes to R only for p and $p'\sim p_0$, $(E_b-E_b')/k^2\sim\alpha^2m^2/M^2$ may be neglected. With Eq. (3.12), we find

$$\begin{aligned}\Delta E_D^{++a}&=\frac{-e^2}{2\pi^2}\int d^3pd^3p'\,k^{-2}\phi_{++}{}^{+*}(\mathbf{p})\boldsymbol{\alpha}_\perp{}^a\cdot[\boldsymbol{\sigma}^b\Gamma_b(\mathbf{p}')+\Gamma_b(\mathbf{p}')\boldsymbol{\sigma}^b]\phi_{++}{}^+(\mathbf{p}')\\&=\frac{-e^2}{2\pi^2}\int d^3pd^3p'\,\phi_{++}{}^{+*}(\mathbf{p})\boldsymbol{\alpha}_\perp{}^a\cdot(\mathbf{p}+\mathbf{p}'+i\boldsymbol{\sigma}\times\mathbf{k})(2Mk^2)^{-1}\phi_{++}{}^{+*}(\mathbf{p}').\end{aligned} \quad (3.27)$$

Fourier-transforming this to coordinate space, with Eq. (3.19) we find

$$\Delta E_D{}^{++a}=\int \bar{\phi}_+{}^*(\mathbf{r})\boldsymbol{\alpha}^a\cdot\mathbf{A}\bar{\phi}_+(\mathbf{r})d^3r, \qquad (3.28)$$

where $\mathbf{A}=\mathbf{A}_0+\delta\mathbf{A}$ is given by Eqs. (2.3) and (2.6a) with $Z=1$, $g=2$.

$\Delta E_D{}^{++b}$ and $\Delta E_D{}^{++c}$ are equal and of order α(hfs). Using Eq. (3.5)

$$\Delta E_D{}^{++bc}=-\left(\frac{e^2}{2\pi^2}\right)^2\int d^3p d^3p'\ \phi_{++}{}^*(\mathbf{p})\alpha_\perp{}^a \cdot\alpha_\perp{}^b\Lambda_+{}^a(\mathbf{p}')\Lambda_+{}^b(\mathbf{p}')\phi_{++}(\mathbf{p}'') \times[k(k+E_a'+E_b-E)(k-E_b'+E_b)]^{-1}.$$

For p, p', $p''\sim p_0$, this gives

$$J_D{}^{++b,c}=\frac{-(\boldsymbol{\sigma}^a\times\mathbf{k})\cdot(\boldsymbol{\sigma}^b\times\mathbf{k})}{4mMk}\times\left[1+\frac{1}{k}\left(W-\frac{p^2}{M}-\frac{p'^2}{2m}+\frac{p'^2}{2M}\right)\right], \qquad (3.29)$$

where J is defined by Eq. (3.23). Equation (3.29) is correct for $\alpha^2m\ll k\ll m$, the k range contributing to R. Its leading contribution is of order α but will be cancelled by a similar term from $J_{CD}{}^{++}$.

The other ΔE_D terms of the required order are those containing $\bar{\psi}_{++}$ and ψ_{-+} or ψ_{+-}, and the complex conjugates of such terms. Integrating over the fourth components of the momenta, we obtain the low-momentum approximations

$$J_D{}^{-+}=-(\boldsymbol{\sigma}^a\times\mathbf{k}')\cdot(\boldsymbol{\sigma}^b\times\mathbf{k})/8m^2M, \qquad (3.30)$$

$$J_D{}^{+-}=-(\boldsymbol{\sigma}^a\times\mathbf{k})\cdot(\boldsymbol{\sigma}^b\times\mathbf{k}')/8mM^2. \qquad (3.31)$$

Since $\mathbf{k}$ and $\mathbf{k}'$ may be interchanged in Eq. (3.30) without affecting $\Delta E_D{}^{+-}$, the sum of Eqs. (3.30) and (3.31) is

$$J_D{}^{-+}+J_D{}^{+-}=-(\boldsymbol{\sigma}^a\times\mathbf{k})\cdot(\boldsymbol{\sigma}^b\times\mathbf{k}')/8m\mu M \qquad (3.32)$$

which gives an α^2 contribution to R.

We now treat ΔE_{CD} similarly. With Eq. (3.20),

$$\Delta E_{CD}=\frac{i}{\pi}\left(\frac{-e^2}{2\pi^2}\right)^2\int d^4pd^4p'd^4p''\ [k'^2(\omega^2-k^2+i\Delta)]^{-1} \times\sum\bar{\psi}(p_\mu)\alpha_i{}^b[\eta_aE-H_a(\mathbf{p}''')+\epsilon''-\omega]^{-1} \times[\eta_bE-H_b(\mathbf{p}')-\epsilon-\omega]^{-1}\alpha_i{}^a\psi(p_\mu''), \qquad (3.33)$$

where i is summed over directions perpendicular to k. To remove the Dirac operators from the denominators we insert into the integrand the factor

$$1=[\Lambda_+{}^a(\mathbf{p}''')+\Lambda_-{}^a(\mathbf{p}''')][\Lambda_+{}^b(\mathbf{p}')+\Lambda_-{}^b(\mathbf{p}')]. \qquad (3.34)$$

To sufficient accuracy we may use here

$$\psi=\psi_{++},\quad \bar{\psi}=\bar{\psi}_{++}. \qquad (3.35)$$

Labeling energy terms by the projection operators, we find three terms contribute to R: $\Delta E_{CD}{}^{++}$, $\Delta E_{CD}{}^{-+}$, $\Delta E_{CD}{}^{+-}$. After integrating over the fourth components of the momenta we find

$$J_{CD}{}^{++}=\frac{(\boldsymbol{\sigma}^a\times\mathbf{k})\cdot(\boldsymbol{\sigma}^b\times\mathbf{k})}{4mMk}\times\left[1+\frac{1}{k}\left(2W-\frac{p'''^2}{2m}-\frac{p^2}{2m}-\frac{p''^2}{2M}-\frac{p'^2}{2M}\right)\right], \qquad (3.36)$$

$$J_{CD}{}^{-+}+J_{CD}{}^{+-}=-(\boldsymbol{\sigma}^a\times\mathbf{k})\cdot(\boldsymbol{\sigma}^b\times\mathbf{k}')/8mM\mu. \qquad (3.37)$$

Thus, the leading term of $J_{CD}{}^{++}$ cancels that of $J_D{}^{++bc}$, and $J_{CD}{}^{-+}+J_{CD}{}^{+-}=J_D{}^{-+}+J_D{}^{+-}$.

The last one-Dirac-photon term to be considered is

$$\Delta E_{CCD}=\frac{-1}{2\pi^2}\left(\frac{-e^2}{2\pi^2}\right)^3\int d^4pd^4p'd^4p''d^4p''' \times[k^2k'^2(\omega''^2-k''^2+i\Delta)]^{-1} \times\sum\bar{\psi}(p_\mu)\alpha_l{}^b[\eta_aE-H_a(\mathbf{p}')+\epsilon']^{-1} \times[\eta_aE-H_a(\mathbf{p}'')+\epsilon'']^{-1} \times[\eta_bE-H_b(\mathbf{p}^{\mathrm{V}})-\epsilon+\epsilon'''-\epsilon'']^{-1} \times[\eta_bE-H_b(\mathbf{p}^{\mathrm{IV}})-\epsilon'-\epsilon''-\epsilon]^{-1} \times\alpha_l{}^a\psi(p_\mu'''), \qquad (3.38)$$

where l is summed over directions perpendicular to $k_\mu''=p_\mu'''-p_\mu''$. Again we use Eq. (3.35) and insert suitable projection operators. Only the term corresponding to positive energies in all intermediate states is of the required order, and it contributes to R only if p, p', p'', p''' all $\sim p_0$. It reduces to

$$\Delta E_{CCD}{}^{++}=\left(\frac{e^2}{2\pi^2}\right)^3(1/4mM)\int d^3pd^3p'd^3p''d^3p''' \times\phi_{++}{}^{++*}(\mathbf{p})(\boldsymbol{\sigma}^a\times\mathbf{k}'')\cdot(\boldsymbol{\sigma}^b\times\mathbf{k}'')\phi_{++}{}^{++}(\mathbf{p}''') \times(k^2k'^2k''^4)^{-1}. \qquad (3.39)$$

Averaging over angles and using the Schrödinger approximation for ϕ_{++}, we find

$$J_{CCD}{}^{++}=-(\boldsymbol{\sigma}^a\times\mathbf{k})\cdot(\boldsymbol{\sigma}^b\times\mathbf{k})(4mMk^2)^{-1}\times(W-p''^2/2\mu). \qquad (3.40)$$

Note that $J_{CCD}{}^{++}$ cancels the α^2(hfs) terms from $J_D{}^{++bc}+J_{CD}{}^{++}$.

Defining $J_D{}^-$ as the sum of the J's in Eq. (3.29), (3.32), (3.36), (3.37), and (3.40), discarding terms leading to vanishing integrals, and averaging over

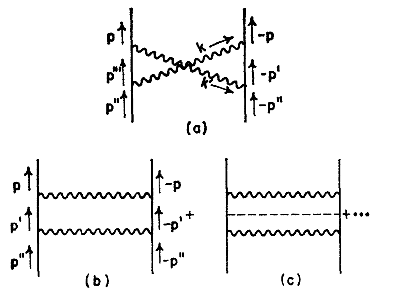

FIG. 3. The irreducible two-Dirac-photon diagram $G_{DD}{}^X$ and the first two terms of $G_{DD}{}^0$, which gives the second-order perturbation theory contribution for G_D.

angles, we obtain

$$J_D{}^- = -(\sigma^a\cdot\sigma^b)\mathbf{k}\cdot\mathbf{k}'/6m^2M. \quad (3.41)$$

Transforming to coordinate space, this gives

$$\Delta E_D{}^- = \frac{e^4}{6m^2M}\int \phi_{++}{}^{++*}(\mathbf{r})\sigma^a\cdot\sigma^b(\nabla r^{-1})^2 \times\phi_{++}{}^{++*}(\mathbf{r})d^3r$$
$$=\int[\bar\phi_+{}^*\alpha^a\cdot\mathbf{A}\bar\phi_- + \bar\phi_-{}^*\alpha^a\cdot\mathbf{A}\bar\phi_+]d^3r, \quad (3.42)$$

using Eq. (3.19a); **A** is defined as in Eq. (3.28). Combining Eqs. (3.28) and (3.42),

$$\Delta E_{CD} = \Delta E_D{}^{++a} + \Delta E_D{}^-$$
$$=\int\bar\phi\alpha\cdot\mathbf{A}\bar\phi d^3r, \quad (3.43)$$

neglecting the small term involving $\bar\phi_-{}^*\bar\phi_-$.

Thus, we see that the low-momentum parts of the various Bethe-Salpeter one-Dirac-photon diagrams sum to the simple expression (3.43), i.e., to the result obtained with the modified Dirac equation for $Z=1$, $g=2$, to first order in A.

C. Two-Dirac-Photon Diagrams

The two-Dirac-photon diagrams shown in Fig. 3 include the irreducible diagram $G_{DD}{}^X$ and the second-order perturbation theory term $G_{DD}{}^0$ arising from G_D. We shall show that together they contribute to R the nonrelativistic second-order perturbation theory term.

We first consider

$$\Delta E_{DD}{}^X = \frac{i}{2\pi}\left(\frac{e^2}{2\pi^2}\right)^2\int d^4p d^4p' d^4p''\ (\omega^2-k^2+i\Delta)^{-1}$$
$$\times(\omega'^2-k'^2+i\Delta')^{-1}\psi(p_\mu)\textstyle\sum_{i,j}\alpha_j{}^a\alpha_i{}^b$$
$$\times[\eta_aE-H_a(\mathbf{p}''')+\epsilon''-\omega]^{-1}$$
$$\times[\eta_bE-H_b(\mathbf{p}')-\epsilon-\omega]^{-1}\alpha_i{}^a\alpha_j{}^b\psi(p_\mu''), \quad (3.44)$$

where i and j are summed over directions perpendicular to **k** and **k'**, respectively. Inserting projection operators and using the approximation (3.35), upon integrating over the fourth components of the momenta we obtain the low-momentum expressions

$$J_{DD}{}^{X-+} = \sigma^a\cdot(\sigma^b\times\mathbf{k})\sigma^a\cdot(\sigma^b\times\mathbf{k}')/16mM^2,$$
$$J_{DD}{}^{X+-} = (\sigma^a\times\mathbf{k})\cdot\sigma^b(\sigma^a\times\mathbf{k}')\cdot\sigma^b/16m^2M, \quad (3.45)$$
$$J_{DD}{}^{X--} = \sigma_\perp{}^a\cdot\sigma_\perp{}^b\sigma_{\perp'}{}^a\cdot\sigma_{\perp'}{}^b kk'/8(k+k')mM.$$

The contributions $R_D{}^{X-+}$, $R_{DD}{}^{X+-}$, and $R_{DD}{}^{X--}$ are of order α^2m/M, α^2, and α, respectively; $R_{DD}{}^{X++}$ is negligible.

The second-order perturbation theory energy due to G_D is[21]

$$\Delta E_{DD}{}^0 = -2\pi i(\bar\psi, \mathcal{G}_D(F-\mathcal{G}_C)^{-1}P\mathcal{G}_D\psi)$$
$$+2\pi i(\bar\psi, \mathcal{G}_D(F-\mathcal{G}_C)^{-1}P\Delta E_D \times(E-H_a-H_b)^{-1}\mathcal{G}_C\psi)$$
$$=\Delta E_{DD}{}^a + \Delta E_{DD}{}^b, \quad (3.46)$$

where

$$\mathcal{G}_i\psi(p_\mu) = -(2\pi i)^{-1}\int G_i(p_\mu,p_\mu')\psi(p_\mu')d^4p' \quad (3.47)$$

and P is a projection operator which vanishes when operating on the unperturbed state and is one otherwise; it arises from the normalization requirement. We use the expansion

$$(F-\mathcal{G}_C)^{-1} = F^{-1}+F^{-1}\mathcal{G}_CF^{-1}+\cdots. \quad (3.48)$$

Replacing $(F-\mathcal{G}_C)^{-1}$ by F^{-1} in $\Delta E_{DD}{}^a$ gives, except for the projection operator, the same result as is found by treating the diagram in Fig. 3(b) as an irreducible Feynman graph. For negative energy terms $P=1$; since the order of the $\alpha_i{}^b$ and $\alpha_j{}^b$ factors is reversed, the negative energy terms cancel those of $\Delta E_{DD}{}^X$:

$$J_{DD}{}^{a1-+} = -J_{DD}{}^{X-+},$$
$$J_{DD}{}^{a1+-} = -J_{DD}{}^{X+-}, \quad (3.49)$$
$$J_{DD}{}^{a1--} = -J_{DD}{}^{X--}.$$

Since the $++$ term here has an energy denominator smaller by α than in $\Delta E_{DD}{}^X$, we must also include

$$J_{DD}{}^{a1++} = (\sigma^a\times\mathbf{k})\cdot(\sigma^b\times\mathbf{k})P(\sigma^a\times\mathbf{k}')\cdot(\sigma^b\times\mathbf{k}') \times[16m^2M^2(W-p^2/2\mu)]^{-1}. \quad (3.50)$$

We now examine the remaining terms of $\Delta E_{DD}{}^a$. A typical one is

$$-2\pi i(\psi,\mathcal{G}_DF^{-1}\mathcal{G}_CF^{-1}\cdots\mathcal{G}_CF^{-1}P\mathcal{G}_D\psi).$$

If we insert projection operators, we find that only positive-energy states contribute to R to the required order. Integrating over the fourth components of the momenta is simple since $\mathcal{G}_C$ is instantaneous, and the first and last integrations are the same as in $\Delta E_D{}^{++}$. Thus, this term becomes

$$([\phi_{++}{}^*\alpha^a\cdot\mathbf{A}\Lambda_+{}^a]^{++}, (E-E_a-E_b)^{-1} \times(-e\varphi)(E-E_a-E_b)^{-1}\cdots(-e\varphi)(E-E_a-E_b)^{-1} \times P[\Lambda_+{}^a\alpha^a\cdot\mathbf{A}\phi_{++}]).$$

[21] This follows from Eqs. (22) and (39) of reference 17.

Thus with Eq. (3.50) we obtain

$$\Delta E_{DD}{}^{++a}=([\phi_{++}{}^*\boldsymbol{\alpha}^a\cdot\mathbf{A}\Lambda_+{}^a]^{++},\ (E-E_a-E_b-V_c)^{-1} \times P[\Lambda_+{}^a\boldsymbol{\alpha}^a\cdot\mathbf{A}\phi_{++}]^{++}). \quad (3.51)$$

A similar treatment of $\Delta E_{DD}{}^{++b}$ shows that only positive-energy states contribute, and

$$\Delta E_{DD}{}^{++b}=-([\phi_{++}{}^*\boldsymbol{\alpha}^a\cdot\mathbf{A}\Lambda_+{}^a]^{++},\ (E-E_a-E_b-V_c)^{-1} \times\Delta E_D P\phi_{++}{}^{++}). \quad (3.52)$$

Thus, for low momentum values, $\Delta E_{DD}{}^{++}=\Delta E_D{}^{++a}+\Delta E_{DD}{}^{++b}$ is identical to the result obtained by treating $e\boldsymbol{\alpha}\cdot\mathbf{A}$ in second-order perturbation theory with the modified Dirac equation, provided only positive-energy states are included in the sum. This is equivalent to dropping the terms in $\mathcal{H}$ arising from $[A_i,A_j]\neq 0$.

D. Effects of the Pauli Moment

The effects of the Pauli moment are found by replacing $\gamma_\mu{}^b$ in the Dirac terms by

$$\Gamma_\mu{}^b=(\mu_A/4M)(\gamma_\nu{}^b\gamma_\mu{}^b-\gamma_\mu{}^b\gamma_\nu{}^b)k_\nu, \quad (3.53)$$

where k_ν is the momentum absorbed by the proton.[6,7] In place of Eq. (1.5) we have the identity

$$\gamma_\nu{}^a\Gamma_\nu{}^b/k_\mu{}^2=-\gamma_4{}^a\gamma_4{}^b[A_4{}^b/k^2+\boldsymbol{\alpha}_\perp{}^a\cdot\mathbf{A}_\perp{}^b/k_\mu{}^2], \quad (3.54)$$

where

$$A_\nu{}^b=\gamma_4{}^b\Gamma_\nu{}^b, \quad (3.55a)$$

or

$$A_4{}^b=(\mu_A/2M)\beta^b\boldsymbol{\alpha}^b\cdot\mathbf{k}, \quad (3.55b)$$

$$A_i{}^b=i(\mu_A/2M)\beta^b(\boldsymbol{\sigma}^b\times\mathbf{k})_i+(\mu_A/2M)\beta^b\omega\alpha_i. \quad (3.55c)$$

Effectively the Coulomb (C) interaction is supplemented by an instantaneous "Q interaction" proportional to $A_4{}^b/k^2$, leading directly to a contribution R_Q. Replacing C by $C+Q$ in R_{CD} also gives contributions of the required order. Similarly, the Pauli (P) photons replace Dirac (D) photons to give R_{QP}, R_{PD}, and R_{PP} terms. The result is equal to that found by an extension of the simple arguments used in the preceding sections.

The inclusion of the Q interaction replaces $1/k^2$ by

$$[1+(\mu_A/2M)\beta^b\boldsymbol{\alpha}^b\cdot\mathbf{k}]/k^2 \quad (3.65)$$

in Eq. (3.5). For positive-energy states this adds to (3.5) the term involving μ_A in Eq. (3.18).

We now evaluate the one-Dirac-photon diagrams with C replaced by $C+Q$. Terms with proton positive-energy states are proportional to the proton matrix element

$$\phi_+{}^*(\mathbf{p})\alpha_i{}^b\Lambda_+{}^b(\mathbf{p}')[1+(\mu_A/2M)\beta^b\boldsymbol{\alpha}^b\cdot\mathbf{k}]\phi_+(\mathbf{p}'') =(i/2M)\phi_+{}^{+*}(\mathbf{p})(\boldsymbol{\sigma}^b\times\mathbf{k})_i \times(1+O\alpha^2m^2/M^2)\phi_+{}^+(\mathbf{p}''). \quad (3.57)$$

Thus, the change in ΔE is $\lesssim\alpha^2(m^2/M^2)$(hfs), and

$$R_{QD}{}^{-+}=R_{QD}{}^{++}=0. \quad (3.58)$$

Terms with negative-energy states contain

$$\phi_+{}^*(\mathbf{p})\alpha_i{}^b\Lambda_-{}^b(\mathbf{p}')[1+(\mu_A/2M)\beta^b\boldsymbol{\alpha}^b\cdot\mathbf{k}']\phi_+(\mathbf{p}'') =(i/2M)\phi_+{}^{+*}(\mathbf{p})(\boldsymbol{\sigma}^b\times\mathbf{k}')_i(1+\mu_A)\phi_+{}^+(\mathbf{p}''). \quad (3.59)$$

Thus, we find

$$R_{QD}{}^{+-}=\mu_A R_{CD}{}^{+-},\quad R_{QD}{}^{--}=\mu_A R_{CD}{}^{--}. \quad (3.60)$$

To evaluate the R_{CP} terms we replace $\alpha_i{}^b$ by $A_i{}^b$ in the integrals of Sec. III. For proton positive-energy states, the first term in Eq. (3.55c) gives μ_A times the Dirac photon result. The second term gives contributions smaller by ω/M, where ω must be replaced by its value at the pole. Since $\Delta E_D{}^{++a}\sim$hfs arises from $\omega=E_b-E_b'\sim\alpha^2m^2/M$ as mentioned below Eq. (3.26), $(\omega/M)\Delta E_D{}^{++a}$ is negligible. The poles in $\Delta E_D{}^{++b}$ and $\Delta E_D{}^{++c}$ are at $+k$ and $-k$, respectively, so that here the second terms are of order α^2(hfs) but cancel. Exactly the same cancellation is obtained from the diagrams contributing to $\Delta E_{CP}{}^{++}$. Finally, all other terms have poles at $|\omega/M|\lesssim k$, so that $(\omega/M)\Delta E_D\lesssim\alpha(m/M)\alpha^2$(hfs) and is negligible. Hence, we neglect the second term and conclude

$$R_{CP}{}^{++}=\mu_A R_{CD}{}^{++},\quad R_{CP}{}^{-+}=\mu_A R_{CD}{}^{-+}. \quad (3.61)$$

For proton negative-energy states, the P matrix element is $\lesssim\alpha m/M$ times the D matrix element, so that $\Delta E\lesssim\alpha(m/M)\alpha^2$(hfs), and

$$R_{CP}{}^{+-}=R_{CP}{}^{--}=0. \quad (3.62)$$

Finally, we consider the two-photon diagrams. Replacing a Dirac photon by a Pauli photon gives a factor μ_A(zero) for a positive (negative) proton energy term, so that

$$R_{PD}=R_{DP}=\mu_A R_{DD}, \quad (3.63)$$

$$R_{PP}=\mu_A{}^2R_{DD}. \quad (3.64)$$

Collecting results, we see that all the Q and P interactions are accounted for in the modified Dirac equation with $g=2(1+\mu_A)$.

IV. BREIT EQUATION

To compute the hfs of an arbitrary one-electron atom, we ideally should start from a Bethe-Salpeter equation for one electron and A nucleons. Even for deuterium this does not yet appear tractable,[22] since we do not have a covariant description of nuclear forces. Nevertheless, it may be possible to derive the modified Dirac equation (for the calculation of R) from such a Bethe-Salpeter equation by omitting nuclear excited states and utilizing the transformation properties of the electromagnetic vertex functions.[23]

[22] D. A. Greenberg and H. M. Foley, Phys. Rev. **120**, 1684 (1960).
[23] L. Durand, III, P. C. DeCelles, and R. B. Marr, Phys. Rev. **126**, 1882 (1962).

Alternatively, one may work with an approximately covariant equation of motion, the Breit equation.[24] For the hydrogen atom it leads to the modified Dirac equation if we treat the Breit and Pauli interactions as perturbations and in second order keep only positive-energy intermediate states as in the usual treatment of the Breit equation; this is equivalent to the requirement of neglecting $[A_i,A_j]$ in Sec. II.[18] We will show that with this prescription and the correspondence principle it also leads to the modified Dirac equation for $A>1$ for a simple nuclear model which neglects velocity-dependent and exchange forces.

The Breit equation for A nucleons and one electron is

$$[E-\sum H_\nu(\mathbf{p}^\nu)-H_a(\mathbf{p}^a)]\phi=(\sum V_\nu+V_N')\phi. \quad (4.1)$$

Here ν is summed over all nucleons, and

$$H_a(\mathbf{p}^a)=\boldsymbol{\alpha}^a\cdot\mathbf{p}^a+\beta^a m,\quad H_\nu(p^\nu)=\boldsymbol{\alpha}^\nu\cdot\mathbf{p}^\nu+\beta^\nu M. \quad (4.2)$$

V_N' is the nuclear interaction. V_ν is the interaction of the electron and the νth electron. It is composed of Coulomb, Breit, and Pauli interactions ($V_{C\nu}$, $V_{B\nu}$, and $V_{P\nu}$, respectively) for protons, and Pauli interaction for neutrons. In momentum space,

$$(V_{C\nu}+V_{B\nu})\phi(\mathbf{p}^a,\mathbf{p}^\nu,\cdots)=\left(\frac{-e^2}{2\pi^2}\right)\int[1-\boldsymbol{\alpha}_\perp{}^a\cdot\boldsymbol{\alpha}_\perp{}^\nu]\times\phi(\mathbf{p}^a+\mathbf{k},\,\mathbf{p}^\nu-\mathbf{k},\,\cdots)\frac{d^3k}{k^2}. \quad (4.3)$$

$V_{P\nu}$ is found by replacing $(1-\boldsymbol{\alpha}_\perp{}^a\cdot\boldsymbol{\alpha}_\perp{}^\nu)$ with $(A_4{}^\nu-\boldsymbol{\alpha}_\perp{}^a\cdot\mathbf{A}_\perp{}^\nu)$, where A_4 and A_i are given by Eqs. (3.55) with $\omega=0$ and $\mu_A\to\mu_A{}^\nu$.

Multiplying Eq. (4.1) by $\prod\Lambda_+{}^\nu(p^\nu)$, we obtain an approximate equation for $\chi=(\Lambda_+{}^1\Lambda_+{}^2\cdots\Lambda_+{}^A\phi)^{++\cdots}$, a 4×2^A-component spinor in the approximation $\Lambda_-{}^\nu\phi\ll\Lambda_+{}^\nu\phi$:

$$[E-\sum E_\nu(\mathbf{p}^\nu)-H_a(\mathbf{p}^a)]\chi=V_N\chi+[\prod\Lambda_+{}^\nu\sum V_\mu\phi_{++\ldots}]^{++\cdots}, \quad (4.4)$$

where V_N is defined by

$$V_N\chi=[\Lambda_+{}^a\Lambda_+{}^1\cdots\Lambda_+{}^A V_N'\phi_{++\ldots}]^{++\cdots}. \quad (4.5)$$

In general, V_N will contain spin operators even if V_N' does not.

In the frame where the total momentum of the atom vanishes, we define new variables by

$$\mathbf{p}=\mathbf{p}^a,\qquad \boldsymbol{\pi}^\nu=\mathbf{p}^\nu+\mathbf{p}/A,$$
$$\mathbf{r}=\mathbf{r}^a-\mathbf{R},\quad \boldsymbol{\varrho}^\nu=\mathbf{r}^\nu-\mathbf{R}, \quad (4.6)$$

with

$$\mathbf{p}=-\sum\mathbf{p}^\nu,\quad \mathbf{R}=\sum\mathbf{r}^\nu \quad (4.7)$$

or

$$\sum\boldsymbol{\pi}^\nu=0,\quad \sum\boldsymbol{\varrho}^\nu=0. \quad (4.8)$$

The constraints (2.8) imply that $\boldsymbol{\varrho}^\nu$ and $\boldsymbol{\pi}^\nu$ are not canonically related, but

$$[\rho_i{}^\nu,\pi_j{}^\mu]=i\delta_{ij}(\delta^{\mu\nu}-1/A). \quad (4.9)$$

Introducing these variables into Eq. (4.1), we obtain

$$E\chi(\mathbf{p},\boldsymbol{\pi}^\nu)=[\sum E_\nu(\boldsymbol{\pi}^\nu-\mathbf{p}/A)+V_N(\boldsymbol{\varrho}^\nu,\,\boldsymbol{\pi}^\nu-\mathbf{p}/A,\,\boldsymbol{\sigma}^\nu)+H_a(\mathbf{p})]\chi(\mathbf{p},\boldsymbol{\pi}^\nu)$$
$$-(e^2/2\pi^2)\int d^3k\,\{\textstyle\sum_p[I_{++}{}^\nu(\boldsymbol{\pi}^\nu-\mathbf{p}/A,\,\boldsymbol{\pi}^\nu-\mathbf{p}/A-\mathbf{k})-\boldsymbol{\alpha}_\perp{}^a\cdot\boldsymbol{\alpha}_{\perp++}{}^\nu(\boldsymbol{\pi}^\nu-\mathbf{p}/A,\,\boldsymbol{\pi}^\nu-\mathbf{p}/A-\mathbf{k})]$$
$$+\sum(\mu_A{}^\nu/2M)[\mathbf{k}\cdot(\beta^\nu\boldsymbol{\alpha}^\nu)_{++}(\boldsymbol{\pi}^\nu-\mathbf{p}/A,\,\boldsymbol{\pi}^\nu-\mathbf{p}/A-\mathbf{k})-i\boldsymbol{\alpha}^a\cdot\boldsymbol{\sigma}_{++}{}^\nu(\boldsymbol{\pi}^\nu-\mathbf{p}/A,\,\boldsymbol{\pi}^\nu-\mathbf{p}/A-\mathbf{k})\times\mathbf{k}]\}$$
$$\times k^{-2}\chi(\mathbf{p}+\mathbf{k},\,\boldsymbol{\pi}_1,\,\cdots,\,\boldsymbol{\pi}_\nu-k,\,\cdots), \quad (4.10a)$$

where $\sum_p$ means sum over all protons, and

$$I_{++}{}^\nu(p,p')=1+\frac{\boldsymbol{\sigma}^\nu\cdot\mathbf{p}\boldsymbol{\sigma}^\nu\cdot(\mathbf{p}'-\mathbf{p})+(E_\nu-M)(E_\nu-E_\nu')}{2E_\nu(E_\nu'+M)}, \quad (4.10b)$$

$$\boldsymbol{\alpha}_{++}{}^\nu(\mathbf{p},\mathbf{p}')=\frac{1}{2E_\nu}\left[\mathbf{p}-i\mathbf{p}\times\boldsymbol{\sigma}^\nu+\frac{E_\nu+M}{E_\nu'+M}(\mathbf{p}'+i\mathbf{p}'\times\boldsymbol{\sigma}^\nu)\right], \quad (4.10c)$$

$$\boldsymbol{\sigma}_{++}{}^\nu(\mathbf{p},\mathbf{p}')=\boldsymbol{\sigma}^\nu-\left(\frac{E_\nu-M}{2E_\nu}\right)\boldsymbol{\sigma}^\nu+\frac{\boldsymbol{\sigma}^\nu\cdot\mathbf{p}}{2E_\nu}\boldsymbol{\sigma}\frac{\boldsymbol{\sigma}^\nu\cdot\mathbf{p}'}{E_\nu'+M}, \quad (4.10d)$$

$$(\beta^\nu\boldsymbol{\alpha}^\nu)_{++}(\mathbf{p},\mathbf{p}')=\frac{1}{2E_\nu}\left[\frac{E_\nu+M}{E_\nu'+M}\boldsymbol{\sigma}\boldsymbol{\sigma}\cdot\mathbf{p}'-\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\right], \quad (4.10e)$$

$$E_\nu=(p^2+M^2)^{1/2},\quad E_\nu'=(p'^2+M^2)^{1/2}.$$

This can be written in the form

$$\mathcal{H}\chi=(\mathcal{H}_{\rm nuc}+\mathcal{H}_{\rm atom}+\mathcal{H}_{\rm mix})\chi=E\chi. \quad (4.10f)$$

$\mathcal{H}_{\rm nuc}$ contains only internal nuclear variables $\boldsymbol{\pi}^\nu$, $\boldsymbol{\varrho}^\nu$, and $\boldsymbol{\sigma}^\nu$; $\mathcal{H}_{\rm atom}$ contains only $\mathbf{p}$, $\mathbf{r}$, and $\boldsymbol{\sigma}^a$; $\mathcal{H}_{\rm mix}$ contains both sets of variables. Explicitly, we expand in p/M, $\boldsymbol{\pi}^\nu/M$, and ρ^ν/r, keeping terms proportional to $\lambda\equiv(p/M)$ and

[24] G. Breit, Phys. Rev. **34**, 553 (1929); **36**, 383 (1930); **39**, 616 (1932).

λ^2 which contribute to R in first order, and terms linear in λ which contribute only in second order. We may also drop all terms with more than one power of ρ^ν/r to the accuracy required. Thus,

$$\mathcal{H}_{\text{nuc}}=\sum(\pi^\nu)^2/2M-\sum(\pi^\nu)^4/8M^3+\cdots+V_N^{(0)}, \quad (4.11a)$$

$$\mathcal{H}_{\text{atom}}=AM+p^2/2AM+H_a(\mathbf{p})-e\varphi_0+e\boldsymbol{\alpha}\cdot\delta\mathbf{A}, \quad (4.11b)$$

$$\begin{aligned}\mathcal{H}_{\text{mix}}=\boldsymbol{\alpha}_\perp{}^a\cdot&[(1/4)\sum g^\nu\boldsymbol{\sigma}^\nu\times\boldsymbol{\nabla}+\sum_p\boldsymbol{\pi}^\nu]\\&\times(-e^2/M)(1-\boldsymbol{\varrho}^\nu\cdot\boldsymbol{\nabla})r^{-1}\\&-\sum(\mu_A{}^\nu/2AM^2)\boldsymbol{\sigma}^\nu\cdot\mathbf{p}\times\boldsymbol{\nabla}(-e^2/r)\\&+\sum_p\{[1-(1/4AM^2)\boldsymbol{\sigma}^\nu\cdot\mathbf{p}\times\boldsymbol{\nabla}]\\&\quad\times[1-\boldsymbol{\varrho}^\nu\cdot\boldsymbol{\nabla}]-1\}(-e^2/r)\\&+[\sum\boldsymbol{\pi}^\nu\cdot\mathbf{p}(\pi^\nu)^2/2AM^3+V_N^{(1)}]+\cdots.\end{aligned} \quad (4.11c)$$

Here φ_0 is defined as in Eq. (2.3a), $\delta\mathbf{A}$ as in Eq. (2.6b) with $\mathfrak{M}\to AM$, $g^\nu=(1+\mu_A{}^\nu)(e/2AM)$ for protons and $\mu_A{}^\nu(e/2M)$ for neutrons,

$$\mu^{-1}=m^{-1}+(AM)^{-1},$$

and V_N, which, in general, depends upon $\mathbf{p}$ but not $\mathbf{R}$, is expanded in powers of (p/M):

$$V_N=V_N^{(0)}+V_N^{(1)}+\cdots. \quad (4.12)$$

Note that the $I_{++}{}^\nu$ (Coulomb) terms in Eq. (4.10a) contribute $-e\varphi_0$ in $\mathcal{H}_{\text{atom}}$ plus the third term of $\mathcal{H}_{\text{mix}}$. The $\boldsymbol{\alpha}^a\cdot\boldsymbol{\alpha}_{++}{}^\nu$ (Breit) terms contribute $e\boldsymbol{\alpha}^a\cdot\delta\mathbf{A}$ and part of the terms containing $\boldsymbol{\alpha}^a$ in $\mathcal{H}_{\text{mix}}$. The $\boldsymbol{\alpha}^a\cdot\boldsymbol{\sigma}_{++}{}^\nu$ (Pauli) terms yield the remaining terms linear in $\boldsymbol{\alpha}^a$, and the $\mathbf{k}\cdot\boldsymbol{\alpha}_{++}{}^\nu$ (Pauli) terms give the second term in $\mathcal{H}_{\text{mix}}$.

Treating $\mathcal{H}_{\text{mix}}$ and $e\boldsymbol{\alpha}\cdot\delta\mathbf{A}$ as perturbations, in the lowest approximation χ is a product of an internal nuclear wave function and of an atomic wave function; the latter is the same as in Sec. II with $\mathfrak{M}\to AM$. With $[\rho_i{}^\nu,\mathcal{H}_{\text{nuc}}]=(i/M)\pi_i{}^\nu$, i.e., assuming a velocity-independent, nonexchange force, and neglecting corrections to the nonrelativistic kinetic energy, we have

$$\begin{aligned}0&=\langle[\rho_i{}^\nu\rho_j{}^\nu,\mathcal{H}_{\text{nuc}}]\rangle\\&=(i/M)\langle\pi_i{}^\nu\rho_j{}^\nu+\rho_i{}^\nu\pi_j{}^\nu\rangle\end{aligned} \quad (4.13)$$

and

$$\boldsymbol{\mu}=\langle\sum_p(e/2M)\rho^\nu\times\boldsymbol{\pi}^\nu+\tfrac{1}{2}\sum g^\nu\boldsymbol{\sigma}^\nu\rangle. \quad (4.14)$$

Thus the first term in $\mathcal{H}_{\text{mix}}$ reduces to $e\boldsymbol{\alpha}\cdot\mathbf{A}_0$, where $\mathbf{A}_0$ is given by (2.3a), when its expectation value is evaluated for the nuclear ground state. Taking the expectation value of the second and third terms gives

$$(e^2/2AM^2)\langle\sum\mu_A{}^\nu\boldsymbol{\sigma}^\nu+\sum_p\tfrac{1}{2}\boldsymbol{\sigma}^\nu\rangle\cdot\mathbf{p}\times\boldsymbol{\nabla}r^{-1} \quad (4.15)$$

which is part of $-e\delta\varphi$.

Let us now consider the fourth term of $\mathcal{H}_{\text{mix}}$, which is linear in $\mathbf{p}$ and independent of $\mathbf{r}$. Since V_N is the sum of a charge-independent nuclear potential U plus an electromagnetic interaction V_{EM}, we may write

$$V_N^{(0)}=U^{(0)}+V_{\text{EM}}^{(0)},\quad V_N^{(1)}=U^{(1)}+V_{\text{EM}}^{(1)},\cdots. \quad (4.16a)$$

The nucleon-nucleon electromagnetic interaction is, like the nucleon-electron interaction, composed of Coulomb, Breit, and Pauli terms. Thus we find

$$V_{EM}^{(0)}=e^2\sum_{p\,\mu\neq\nu}1/2\rho^{\mu\nu}+\cdots, \quad (4.16b)$$

$$V_{EM}^{(1)}=(e^2/4AM^2)\sum_{p\,\mu\neq\nu}\left[\left\{\boldsymbol{\pi}^\mu\cdot\mathbf{p},\frac{1}{\rho^{\mu\nu}}\right\}+\left\{\pi_j{}^\mu,\frac{\boldsymbol{\varrho}^{\mu\nu}\cdot\mathbf{p}\rho_j{}^{\mu\nu}}{(\rho^{\mu\nu})^3}\right\}-\boldsymbol{\sigma}^\nu\cdot\mathbf{p}\times\boldsymbol{\nabla}^\nu\frac{1}{\rho^{\mu\nu}}\right]. \quad (4.16c)$$

Note that the Pauli moments do not appear in $V_{\text{EM}}^{(1)}$; the Pauli-Coulomb (Pauli-Breit) terms contribute $+(-)\sum\mu_A{}^\nu C^{\mu\nu}$, $C^{\mu\nu}\equiv\boldsymbol{\sigma}^\nu\cdot\mathbf{p}\times\boldsymbol{\nabla}^\nu(e^2/2AM^2\rho^{\mu\nu})$. The Breit interactions contribute the spin-independent part of $V_{\text{EM}}^{(1)}$ and $-\sum C^{\mu\nu}$, and the Coulomb interactions contribute $\frac{1}{2}\sum C^{\mu\nu}$.

We may eliminate $V_{\text{EM}}^{(1)}$ and the kinetic energy term from the last part of $\mathcal{H}_{\text{mix}}$ by the transformation

$$\mathcal{H}\to e^{i\Phi}\mathcal{H}e^{-i\Phi}=\mathcal{H}+[i\Phi,\mathcal{H}]+\cdots, \quad (4.17)$$

where

$$\phi=\mathbf{p}\cdot[\sum\pi_j{}^\nu\boldsymbol{\varrho}^\nu\pi_j{}^\nu/2AM^2-\sum(\boldsymbol{\sigma}^\nu\times\boldsymbol{\pi}^\nu)/4AM^2+e^2\sum_{p\,\mu\neq\nu}\boldsymbol{\varrho}^\nu/2AM|\boldsymbol{\varrho}^\mu-\boldsymbol{\varrho}^\nu|]. \quad (4.17a)$$

The commutator of $i\Phi$ and $\mathcal{H}_{\text{nuc}}$ cancels $V_{\text{EM}}^{(1)}$ and the kinetic-energy term in $\mathcal{H}_{\text{mix}}$; $i[\Phi,\mathcal{H}_{\text{atom}}]$ is negligible and $[i\Phi,\mathcal{H}_{\text{mix}}]$ contains one term of interest:

$$\begin{aligned}i[\phi,&-\sum_p\boldsymbol{\varrho}^\mu\cdot\boldsymbol{\nabla}](-e^2/r)\\&=(e^2/2AM^2)\sum_{p\,\mu}\sum_\nu[(\rho_j{}^\nu\pi_i{}^\nu+\pi_i{}^\nu\rho_j{}^\nu)p_j\nabla_i\\&\quad+\tfrac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{p}\times\boldsymbol{\nabla}](\delta^{\mu\nu}-1/A)r^{-1}+\cdots,\end{aligned} \quad (4.18)$$

where the quadrupole term proportional to $[p_j,\nabla_i\varphi_\sigma]$ has been omitted since it does not contribute to R. The expectation value of (4.18) for the nuclear ground state is

$$\begin{aligned}(e^2/2AM^2)\langle&\sum_p(\boldsymbol{\varrho}^\nu\times\boldsymbol{\pi}^\nu+\tfrac{1}{2}\boldsymbol{\sigma}^\nu)\\&-(Z/A)\sum(\boldsymbol{\varrho}^\nu\times\boldsymbol{\pi}^\nu+\tfrac{1}{2}\boldsymbol{\sigma}^\nu)\rangle\cdot\mathbf{p}\times\boldsymbol{\nabla}r^{-1}.\end{aligned} \quad (4.19)$$

Adding (4.19) to (4.15) gives

$$\begin{aligned}(e/AM)\langle&(e/2M)(\sum_p\boldsymbol{\varrho}^\nu\times\boldsymbol{\pi}^\nu+\tfrac{1}{2}\sum g^\nu\boldsymbol{\sigma}^\nu)\\&-(Ze/2AM)\sum(\boldsymbol{\varrho}^\nu\times\boldsymbol{\pi}^\nu+\tfrac{1}{2}\boldsymbol{\sigma}^\nu)\rangle\cdot\mathbf{p}\times\boldsymbol{\nabla}r^{-1}\\&=(e/AM)[\boldsymbol{\mu}-(Ze/2AM)\mathbf{I}]\cdot\mathbf{p}\times\boldsymbol{\nabla}r^{-1}\\&=-e\delta\varphi\end{aligned} \quad (4.20)$$

by Eqs. (4.14) and (2.6b), with $\mathfrak{M}$ replaced by AM.

Equation (4.20) gives the interaction of the electric field due to the electron with the electric dipole moment arising from the motion of the nucleus. If we study a nucleus moving in a weak external potential, we obtain (4.20) again, with $(-e/r)$ replaced by that potential. As we expect from the correspondence principle, this result is identical to that obtained by Thomas[25] for a classical system using purely kinematic arguments.

Note, however, that the transformation (4.16) was constructed to cancel only the explicitly known part of $V_N^{(1)}$. If a term due to the nuclear force remains, in second-order perturbation theory together with the $\sum_p \boldsymbol{\varrho}^\mu \cdot \boldsymbol{\nabla}(e^2/r)$ term it can contribute another term of the type (constant) $\mathbf{I}\cdot\mathbf{p}\times\boldsymbol{\nabla}r^{-1}$, spoiling the agreement with the Thomas expression. Since we expect the classical limit to hold for a weak external potential, we conclude that the constant must vanish.

It may appear a bit odd that we can use $V_{\mathrm{EM}}^{(1)}$ to limit the form of $U^{(1)}$. Consider a system of interacting particles described by a Hamiltonian, $\mathcal{H}$. Thomas and Bakamjian[26] and Foldy[27] have proved that the commutation relations for the generators of the infinitesimal Lorentz group require the existence of a function Φ, such that

$$e^{i\Phi}\mathcal{H}e^{-i\Phi}=(p^2+h^2)^{1/2},$$
$$h=AM+\sum \pi_\nu^2/2M+V^{(0)}+\cdots. \quad (4.21)$$

Here, Φ is a rotationally invariant function of p and the internal variables, and h is a function of the internal variables only. The "reduced" Hamiltonian defined by (4.23) is the natural generalization of the single-particle Hamiltonian. However, in this reduced representation the coordinates and momenta do not have their usual physical interpretation.

Since $V_N^{(1)}$ is linear in $\mathbf{p}$ and the right-hand side of (4.23) is a function of p^2, $V_N^{(1)}$ arises entirely from the transformation from the reduced to the usual or "physical" representation, i.e., $V_N^{(1)}=-[i\Phi, \sum (\pi^\nu)^2/2M+V_N^{(0)}]$. Requiring a specific form for the electromagnetic part of $V_N^{(1)}$ in the physical representation therefore restricts Φ and $U^{(1)}$ substantially.

Thus, Eqs. (4.11) are equivalent to the modified Dirac equation (2.6a) if we replace AM by $\mathfrak{M}$. Since $B\equiv AM-\mathfrak{M}\lesssim 10^{-2}\mathfrak{M}$, it can be neglected. In principle, one can look at the terms quadratic in p^2 in Eq. (4.11c) and obtain the binding energy effects explicitly.

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[25] L. H. Thomas, Nature **117**, 514 (1926); Phil. Mag. **3**, 1 (1927).
[26] B. Bakamjian and L. H. Thomas, Phys. Rev. **92**, 1300 (1953).
[27] L. Foldy, Phys. Rev. **122**, 275 (1961).