

# 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  $34.45 \pm 0.02$ ,  $34.53 \pm 0.02$ , and  $34.46 \pm 0.02$ . These agree with the available experimental values which are  $34.495 \pm 0.060$  and  $34.2 \pm 0.6$  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  $\alpha$  is the fine structure constant, and  $m/M$  is the electron to proton mass ratio. The results are in agreement with the experimental values<sup>1,2</sup> 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<sup>3</sup> 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  $\alpha^2$  (hfs) and  $\alpha(m/M)$  (hfs). Recent calculations<sup>4</sup> of the  $\alpha^3(\ln\alpha)^2$  and  $\alpha^3(\ln\alpha)$  parts of the  $\alpha^3$  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

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

Here  $E_n^F$  is the Fermi energy<sup>5</sup>; in natural units  $\hbar = c = 1$ ,

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

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

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<sup>1</sup> 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  $\nu_1(T)$ .

<sup>2</sup> J. Gruenebaum and P. Kusch, Columbia Radiation Laboratory Quarterly Report, September 15, 1960 (unpublished); their result is  $\nu_2(H) = 177\,556.842 \pm 0.010$  kc/sec. H. A. Reich, J. W. Heberle, and P. Kusch, Phys. Rev. **104**, 1585 (1956); this gives  $\nu_2(D)$ .

<sup>3</sup> C. K. Iddings and P. M. Platzman, Phys. Rev. **113**, 192 (1959); **115**, 919 (1959).

<sup>4</sup> D. E. Zwanziger, Bull. Am. Phys. Soc. **6**, 514 (1961); A. J. Layzer, *ibid.* **6**, 514 (1961).

<sup>5</sup> E. Fermi, Z. Physik **60**, 320 (1930).

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  $\alpha$ . Including it as a multiplicative rather than an additive factor leads to the conventional definition of  $b$ .<sup>6,7</sup> The  $\alpha$  and  $\alpha^2$  radiative corrections<sup>8</sup> and the  $\alpha m/\mathfrak{M}$  mass<sup>6,7,9</sup> (nucleon motion) and structure<sup>3,10</sup> corrections are proportional to  $|u_n(0)|^2$  or "state independent." The Breit corrections<sup>11</sup> 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  $|u_1(0)|^2 = 8|u_2(0)|^2$ ,

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

Therefore, only the differences of the  $\alpha^3$  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  $\alpha^3$  part has been evaluated<sup>12,13</sup> 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.<sup>14</sup>

The actual calculation of the  $\alpha^2 m/M$  contributions to  $R$  is discussed in Sec. II. It is based on a Foldy-Wouthuysen<sup>15</sup> 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.

<sup>6</sup> 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.

<sup>7</sup> W. A. Newcomb, thesis, Cornell University, (unpublished).

<sup>8</sup> N. M. Kroll and F. Pollock, Phys. Rev. **86**, 876 (1952).

<sup>9</sup> R. Arnowitt, Phys. Rev. **92**, 1002 (1953).

<sup>10</sup> 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.

<sup>11</sup> G. Breit, Phys. Rev. **35**, 1447 (1930).

<sup>12</sup> M. H. Mittleman, Phys. Rev. **107**, 1170 (1957).

<sup>13</sup> D. E. Zwanziger, Phys. Rev. **121**, 1128 (1961).

<sup>14</sup> C. Schwartz, Ann. Phys. (N.Y.) **2**, 156 (1959).

<sup>15</sup> 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,<sup>16,17</sup> 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

$$\gamma_\nu^a \gamma_\nu^b / k_\mu^2 = -\gamma_4^a \gamma_4^b (1/k^2 + \alpha_1^2 \cdot \alpha_1^b / k_\mu^2), \quad (1.5)$$

where  $\alpha_1 \cdot \mathbf{k} \equiv 0$ . 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.<sup>17</sup>

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<sup>15</sup> 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

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

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

$$\begin{aligned} \mathcal{H} &\rightarrow e^{iS} \mathcal{H} e^{-iS} = \mathcal{H} + i[S, \mathcal{H}] \\ &\quad + (i^2/2!) [S, [S, \mathcal{H}]] + \dots, \\ S &= (-i\beta/2m)\mathcal{O}, \end{aligned}$$

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

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

<sup>16</sup> E. E. Salpeter and H. A. Bethe, Phys. Rev. **84**, 1232 (1951); M. Gell-Mann and F. Low, *ibid.* **84**, 350 (1951).

<sup>17</sup> E. E. Salpeter, Phys. Rev. **87**, 328 (1952).

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

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

where

$$\mathbf{u} = g(e/2M)\mathbf{I}. \quad (2.3b)$$

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

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

Here we have dropped terms involving  $[A_i, A_j]$ .<sup>18</sup>

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

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

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

Breit's  $\alpha^2$  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  $\mathcal{M}$ , terms containing both  $\sigma$  and  $\mathbf{u}$  must be included to order  $\mathcal{M}^{-2}$ , and other terms to order  $\mathcal{M}^{-1}$ . Thus this motion is adequately

<sup>18</sup> M. M. Sternheim, Phys. Rev. **128**, 676 (1962); see also Sec. IIIC of the present paper.

described by the Hamiltonian

$$\mathcal{H}_{3\pi} = \mathcal{H}_0 + \mathcal{H}\pi + (\mathbf{p}^2/2\mathcal{M}) + e\boldsymbol{\alpha} \cdot \delta\mathbf{A} - e\delta\varphi, \quad (2.6a)$$

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

$$\delta\varphi = -\left( \mathbf{u} - \frac{Ze}{2\mathcal{M}} \mathbf{I} \right) \times \frac{\mathbf{p}}{\mathcal{M}} \cdot \frac{\nabla}{r}. \quad (2.6c)$$

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

$$\mathcal{H}_{3\pi}' = \mathcal{H}' + \mathcal{H}\pi + \frac{\mathbf{p}^2}{2\mathcal{M}} - \frac{ie}{16m^2\mathcal{M}} [\boldsymbol{\sigma} \cdot \mathbf{p} \times \mathbf{A}_0 - \boldsymbol{\sigma} \cdot \mathbf{A}_0 \times \mathbf{p}, \mathbf{p}^2]. \quad (2.7)$$

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  $\mu^{-1} = m^{-1} + \mathcal{M}^{-1}$ ,

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

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  $\mathcal{H}_{3\pi}^{(0)}$  is the Schrödinger approximation for a particle with reduced mass  $\mu$ .

The state-dependent hfs terms are contained in

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

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

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

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

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

it follows that

$$8|u_2|^2 - |u_1|^2 \sim (\text{const})r^2 |u_1|^2 \quad \text{for } r \ll \beta.$$

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

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

Now

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

where two partial integrations have been performed, and

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

$\gamma$  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,

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

In the same fashion we find

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

$$R^{(3c)} = [-(7/32) + (1/2) \ln 2] \times [1 - ZM/g\mathcal{M}] Z^2 \alpha^2 m/\mathcal{M}, \quad (2.12c)$$

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

To evaluate the second-order perturbation theory terms, we note that with  $F_n$  defined by<sup>14,19</sup>

$$[F_n, \mathcal{H}_{3\pi}^{(2)}] |n\rangle = \mathcal{H}_{3\pi}^{(2)} |n\rangle - \langle n | \mathcal{H}_{3\pi}^{(2)} |n\rangle |n\rangle, \quad (2.13)$$

it follows that

$$\sum_{i'} |i\rangle \langle i | \mathcal{H}_{3\pi}^{(2)} |n\rangle (W_n - W_i)^{-1} = F_n |n\rangle - \langle n | F_n |n\rangle |n\rangle. \quad (2.14a)$$

This state is a mixture of  $s$  and  $d$  wave functions. The  $s$ -state part is given by<sup>13,14</sup>

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

By Eqs. (2.8)

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

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<sup>14</sup> has found

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

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

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

For the hydrogen isotopes, this gives<sup>20</sup>

$$\begin{aligned} R(\alpha^2 m/M, H) &= -0.115 \times 10^{-6}, \\ R(\alpha^2 m/M, D) &= -0.029 \times 10^{-6}, \\ R(\alpha^2 m/M, T) &= -0.101 \times 10^{-6}. \end{aligned} \quad (2.19)$$

The complete theoretical expression for  $R$  is<sup>13</sup>

$$\begin{aligned} R(\text{th}) &= (5/8)\alpha^2 + [3.40 \pm 0.02 - (5/16\pi)]\alpha^3 \\ &\quad + R(\alpha^2 m/M) + R(\alpha^4) + \dots, \end{aligned}$$

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

$$\begin{aligned} R(H, \text{theory}) &= (34.45 \pm 0.02) \times 10^{-6}, \\ R(D, \text{theory}) &= (34.53 \pm 0.02) \times 10^{-6}, \\ R(T, \text{theory}) &= (34.46 \pm 0.02) \times 10^{-6}, \end{aligned}$$

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

<sup>20</sup> 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.

where the uncertainty is due to the error in the  $\alpha^3$  term and to the uncalculated  $\alpha^4$  term.

The experimental values are<sup>1,2</sup>

$$R(H, \text{exp}) = (34.495 \pm 0.060) \times 10^{-6},$$

$$R(D, \text{exp}) = (34.2 \pm 0.6) \times 10^{-6},$$

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<sup>16</sup>

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

where

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

and

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

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

$\psi(p_\mu)$  is a 16-component spinor function of the relative momentum  $p_\mu$ , and  $E$  is the corresponding eigenvalue. The interaction operator  $G$  is an expansion in powers of  $\alpha$  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  $\epsilon$ , giving<sup>17</sup>

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

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

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

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<sup>17a</sup>

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

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

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

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  $k_\mu = (\mathbf{k}, \omega) = p'_\mu - p_\mu$ ,

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

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

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

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

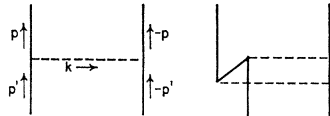


FIG. 1. Instantaneous interaction diagrams  $G_C$  and  $G_{CC}$ . The solid line on the left denotes the electron which has corresponding to  $p$  a momentum four-vector  $(\mathbf{p}, \epsilon + \eta_a E)$ , where  $\eta_a = m/(m+M)$  and  $E$  is the total energy of the atom. The solid line on the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

<sup>17a</sup> H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35.

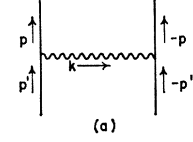
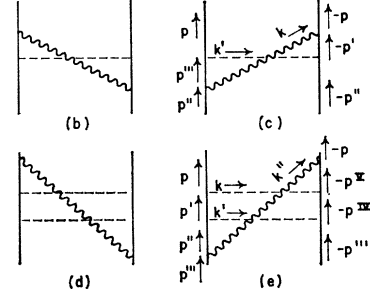


FIG. 2. One-Dirac-photon diagrams  $G_D$ ,  $G_{CD1}$ ,  $G_{CD2}$ ,  $G_{CCD1}$ ,  $G_{CCD2}$ . The wavy lines represent Dirac photons.



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

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

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  $\mu_A$  [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

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

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  $\lesssim \alpha^6 m$  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.  $\Delta E_D$ ,  $\Delta E_{CD}$ , and  $\Delta E_{CCD}$  are of order (hfs),  $\alpha$ (hfs), and  $\alpha^2$ (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)

terms. We note that

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

and

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

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

$$\Delta E_i = \int \bar{\psi}(\mathbf{p}_\mu) G_i(\mathbf{p}_\mu, \mathbf{p}'_\mu) \psi(\mathbf{p}'_\mu) d^3 \mathbf{p} d^3 \mathbf{p}', \quad (3.20)$$

where  $\psi$  is expressed in terms of  $\phi$  by Eq. (2.9) and

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

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

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

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

To sufficient accuracy,  $\phi$  may be replaced by  $\phi_{++}$  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  $\psi_{++}$  or  $\bar{\psi}_{++}$  or both contribute to  $R$  to order  $\alpha^2 m/M$ ; terms containing  $\psi_{--}$  are negligible.

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

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

where  $k_\mu' = \mathbf{p}_\mu'' - \mathbf{p}_\mu'$ . Since  $\phi_{++++}(\mathbf{p})$  diminishes rapidly for  $\mathbf{p} \gg \mathbf{p}_0$ , to lowest order they take  $\mathbf{k} = \mathbf{k}' = \mathbf{p}'$  for  $\mathbf{p}' \gg \mathbf{p}_0$ . Thus to lowest order they find

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

where  $\phi_{++++}(0)$  is the large-large wave function at  $\mathbf{r} = 0$ . 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  $(\mathbf{p} \cdot \mathbf{k}$  or  $\mathbf{p}'' \cdot \mathbf{k})/k^2$  times the integrand of Eq. (3.24). These change sign under  $\mathbf{k} \rightarrow -\mathbf{k}$  and therefore integrate to zero for  $k \gg p_0$ . Similarly, taking into account  $\mathbf{p}$  and/or  $\mathbf{p}'' \gg \mathbf{p}_0$  gives energy terms  $\lesssim \alpha^2$  (hfs) which are also state-independent. Thus, the state-dependent part of  $\Delta E_i^{NS}$  is negligible unless  $\mathbf{p}$ ,  $\mathbf{p}'$ ,  $\mathbf{p}''$  are all  $\sim \mathbf{p}_0$ . Similarly, we can show that  $R_{CCD}$  is negligible unless  $\mathbf{p}$ ,  $\mathbf{p}'$ ,  $\mathbf{p}''$ ,  $\mathbf{p}'''$  are all  $\sim \mathbf{p}_0$ .

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  $\Delta E_i$  which diverge. They are not correct for evaluation of  $\Delta E_i$  but do yield  $R_i$  correctly. Thus, terms like  $[u^2(\mathbf{r})/r]_{r \rightarrow 0}$  will appear in  $\Delta E_i$  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  $\Delta E_D$ , using Eq. (3.22) and

$$\begin{aligned} G_D &= -(\epsilon^2/2\pi^2) \alpha_1^a \cdot \alpha_1^b / k_\mu^2, \\ k_\mu^2 &= \omega^2 - k^2 + i\Delta. \end{aligned} \quad (3.25)$$

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

$$\begin{aligned} \Delta E_D^{++} &= \frac{e^2}{2\pi^2} \int d^3 \mathbf{p} d^3 \mathbf{p}' \phi_{++}^*(\mathbf{p}) \alpha_1^a \cdot \alpha_1^b \\ &\quad \times \left[ \frac{1}{k^2 - (E_b - E_b')^2} \right. \\ &\quad \left. + \frac{E - E_a - E_b}{(2k)(k + E_a + E_b' - E)(k - E_b + E_b')} \right. \\ &\quad \left. + \frac{E - E_a' - E_b'}{(2k)(k + E_a' + E_b - E)(k - E_b' + E_b)} \right] \\ &\quad \times \phi_{++}(\mathbf{p}') \\ &= \Delta E_D^{++a} + \Delta E_D^{++b} + \Delta E_b^{++c}. \end{aligned} \quad (3.26)$$

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

For  $\mathbf{p}$  and  $\mathbf{p}' \sim \mathbf{p}_0$ ,  $\Delta E_D^{++a}$  gives the nonrelativistic hfs; it is the only term which must be evaluated with wave functions containing the relativistic corrections. Since  $\Delta E^{++a}$  contributes to  $R$  only for  $\mathbf{p}$  and  $\mathbf{p}' \sim \mathbf{p}_0$ ,  $(E_b - E_b')/k^2 \sim \alpha^2 m^2/M^2$  may be neglected. With Eq. (3.12), we find

$$\begin{aligned} \Delta E_D^{++a} &= \frac{-e^2}{2\pi^2} \int d^3 \mathbf{p} d^3 \mathbf{p}' k^{-2} \phi_{++++}(\mathbf{p}) \alpha_1^a \\ &\quad \cdot [\sigma^b \Gamma_b(\mathbf{p}') + \Gamma_b(\mathbf{p}') \sigma^b] \phi_{++++}(\mathbf{p}') \\ &= \frac{-e^2}{2\pi^2} \int d^3 \mathbf{p} d^3 \mathbf{p}' \phi_{++++}(\mathbf{p}) \alpha_1^a \\ &\quad \cdot (\mathbf{p} + \mathbf{p}' + i\boldsymbol{\sigma} \times \mathbf{k}) (2Mk^2)^{-1} \phi_{++++}(\mathbf{p}'). \end{aligned} \quad (3.27)$$

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

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

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  $\alpha$  (hfs). Using Eq. (3.5)

$$\begin{aligned} \Delta E_{D^{++bc}} = & - \left( \frac{e^2}{2\pi^2} \right)^2 \int d^3p d^3p' \phi_{++}^*(\mathbf{p}) \alpha_i^a \\ & \cdot \alpha_i^b \Lambda_{+^a}(\mathbf{p}') \Lambda_{+^b}(\mathbf{p}') \phi_{++}(\mathbf{p}'') \\ & \times [k(k+E_{a'}+E_b-E)(k-E_{b'}+E_b)]^{-1}. \end{aligned}$$

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

$$\begin{aligned} J_{D^{++bc}} = & \frac{-(\boldsymbol{\sigma}^a \times \mathbf{k}) \cdot (\boldsymbol{\sigma}^b \times \mathbf{k})}{4mMk} \\ & \times \left[ 1 + \frac{1}{k} \left( W - \frac{p^2}{M} - \frac{p'^2}{2m} + \frac{p''^2}{2M} \right) \right], \quad (3.29) \end{aligned}$$

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

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

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

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

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

$$J_{D^{-+}} + J_{D^{+-}} = -(\boldsymbol{\sigma}^a \times \mathbf{k}) \cdot (\boldsymbol{\sigma}^b \times \mathbf{k}') / 8\pi\mu M \quad (3.32)$$

which gives an  $\alpha^2$  contribution to  $R$ .

We now treat  $\Delta E_{CD}$  similarly. With Eq. (3.20),

$$\begin{aligned} \Delta E_{CD} = & \frac{i}{\pi} \left( \frac{e^2}{2\pi^2} \right)^2 \int d^4p d^4p' d^4p'' [k'^2(\omega^2 - k^2 + i\Delta)]^{-1} \\ & \times \sum \bar{\psi}(\mathbf{p}_\mu) \alpha_i^b [\eta_a E - H_a(\mathbf{p}'') + \epsilon'' - \omega]^{-1} \\ & \times [\eta_b E - H_b(\mathbf{p}') - \epsilon - \omega]^{-1} \alpha_i^a \psi(\mathbf{p}_\mu''), \quad (3.33) \end{aligned}$$

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

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

To sufficient accuracy we may use here

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

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

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

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

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

$$\begin{aligned} \Delta E_{CCD} = & \frac{-1}{2\pi^2} \left( \frac{e^2}{2\pi^2} \right)^3 \int d^4p d^4p' d^4p'' d^4p''' \\ & \times [k^2 k'^2 (\omega'^2 - k'^2 + i\Delta)]^{-1} \\ & \times \sum \bar{\psi}(\mathbf{p}_\mu) \alpha_i^b [\eta_a E - H_a(\mathbf{p}') + \epsilon']^{-1} \\ & \times [\eta_a E - H_a(\mathbf{p}'') + \epsilon'']^{-1} \\ & \times [\eta_b E - H_b(\mathbf{p}^V) - \epsilon + \epsilon''' - \epsilon'']^{-1} \\ & \times [\eta_b E - H_b(\mathbf{p}^{IV}) - \epsilon' - \epsilon'' - \epsilon']^{-1} \\ & \times \alpha_i^a \psi(\mathbf{p}_\mu'''), \quad (3.38) \end{aligned}$$

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

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

Averaging over angles and using the Schrödinger approximation for  $\phi_{++}$ , we find

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

Note that  $J_{CCD^{++}}$  cancels the  $\alpha^2$  (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

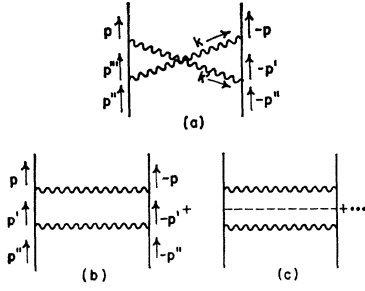


FIG. 3. The irreducible two-Dirac-photon diagram  $G_{DD}^X$  and the first two terms of  $G_{DD}^0$ , which gives the second-order perturbation theory contribution for  $G_D$ .

angles, we obtain

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

Transforming to coordinate space, this gives

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

using Eq. (3.19a);  $\mathbf{A}$  is defined as in Eq. (3.28). Combining Eqs. (3.28) and (3.42),

$$\begin{aligned} \Delta E_{CD} &= \Delta E_D^{+++} + \Delta E_D^- \\ &= \int \bar{\phi}_+ \boldsymbol{\alpha} \cdot \mathbf{A} \bar{\phi}_+ d^3 r, \end{aligned} \quad (3.43)$$

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

$$\begin{aligned} \Delta E_{DD}^X &= \frac{i}{2\pi} \left( \frac{e^2}{2\pi^2} \right)^2 \int d^4 p d^4 p' d^4 p'' (\omega^2 - k^2 + i\Delta)^{-1} \\ &\quad \times (\omega'^2 - k'^2 + i\Delta')^{-1} \psi(\mathbf{p}_\mu) \sum_{i,j} \alpha_j^a \alpha_i^b \\ &\quad \times [\eta_a E - H_a(\mathbf{p}'') + \epsilon'' - \omega]^{-1} \\ &\quad \times [\eta_b E - H_b(\mathbf{p}') - \epsilon - \omega]^{-1} \alpha_i^a \alpha_j^b \psi(\mathbf{p}_\mu''), \end{aligned} \quad (3.44)$$

where  $i$  and  $j$  are summed over directions perpendicular to  $\mathbf{k}$  and  $\mathbf{k}'$ , 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

$$\begin{aligned} J_{DD}^{X-+} &= \boldsymbol{\sigma}^a \cdot (\boldsymbol{\sigma}^b \times \mathbf{k}) \boldsymbol{\sigma}^a \cdot (\boldsymbol{\sigma}^b \times \mathbf{k}') / 16m^2 M^2, \\ J_{DD}^{X+ -} &= (\boldsymbol{\sigma}^a \times \mathbf{k}) \cdot \boldsymbol{\sigma}^b (\boldsymbol{\sigma}^a \times \mathbf{k}') \cdot \boldsymbol{\sigma}^b / 16m^2 M, \\ J_{DD}^{X--} &= \boldsymbol{\sigma}_1^a \cdot \boldsymbol{\sigma}_1^b \boldsymbol{\sigma}_1^a \cdot \boldsymbol{\sigma}_1^b k k' / 8(k+k') m M. \end{aligned} \quad (3.45)$$

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

The second-order perturbation theory energy due to  $G_D$  is<sup>21</sup>

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

where

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

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

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

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  $\Delta E_{DD}^X$ :

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

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

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

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

$$-2\pi i (\psi, \mathcal{G}_D F^{-1} \mathcal{G}_C F^{-1} \dots \mathcal{G}_C F^{-1} P \mathcal{G}_D \psi).$$

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

$$\begin{aligned} &([\bar{\phi}_{++}^* \boldsymbol{\alpha}^a \cdot \mathbf{A} \Lambda_+^a]^{++}, (E - E_a - E_b)^{-1} \\ &\quad \times (-e\varphi)(E - E_a - E_b)^{-1} \dots (-e\varphi)(E - E_a - E_b)^{-1} \\ &\quad \quad \quad \times P[\Lambda_+^a \boldsymbol{\alpha}^a \cdot \mathbf{A} \phi_{++}]). \end{aligned}$$

<sup>21</sup> This follows from Eqs. (22) and (39) of reference 17.



Thus with Eq. (3.50) we obtain

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

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

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

Thus, for low momentum values,  $\Delta E_{DD}^{++} = \Delta E_D^{++} + \Delta E_{DD}^{++b}$  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  $k_\nu$  is the momentum absorbed by the proton.<sup>6,7</sup> In place of Eq. (1.5) we have the identity

$$\gamma_\nu^a \Gamma_\nu^b/k_\mu^2 = -\gamma_4^a \gamma_4^b [A_4^b/k^2 + \boldsymbol{\alpha}_1^a \cdot \mathbf{A}_1^b/k_\mu^2], \quad (3.54)$$

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  $\mu_A$  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

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

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

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

Terms with negative-energy states contain

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

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  $\mu_A$  times the Dirac photon result. The second term gives contributions smaller by  $\omega/M$ , where  $\omega$  must be replaced by its value at the pole. Since  $\Delta E_D^{++a} \sim \text{hfs}$  arises from  $\omega = E_b - E_b' \sim \alpha^2 m^2/M$  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  $\alpha^2$  (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  $\mu_A$  (zero) for a positive (negative) proton energy term, so that

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

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

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,<sup>22</sup> 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.<sup>23</sup>

<sup>22</sup> D. A. Greenberg and H. M. Foley, Phys. Rev. **120**, 1684 (1960).

<sup>23</sup> 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.<sup>24</sup> 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.<sup>18</sup> 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  $\nu$  is summed over all nucleons, and

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

$V_N'$  is the nuclear interaction.  $V_\nu$  is the interaction of the electron and the  $\nu$ th 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,

$$(V_{C\nu} + V_{B\nu})\phi(\mathbf{p}^a, \mathbf{p}^\nu, \dots) = \left( \frac{-e^2}{2\pi^2} \right) \int [1 - \alpha_1^a \cdot \alpha_1^\nu] \\ \times \phi(\mathbf{p}^a + \mathbf{k}, \mathbf{p}^\nu - \mathbf{k}, \dots) \frac{d^3 k}{k^2}. \quad (4.3)$$

$V_{P\nu}$  is found by replacing  $(1 - \alpha_1^a \cdot \alpha_1^\nu)$  with  $(A_4^a - \alpha_1^a \cdot \mathbf{A}_1^\nu)$ , where  $A_4$  and  $\mathbf{A}_4$  are given by Eqs. (3.55) with  $\omega = 0$  and  $\mu_A \rightarrow \mu_{A'}^a$ .

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

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

where  $V_N$  is defined by

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

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

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

$$\mathbf{r} = \mathbf{r}^a - \mathbf{R}, \quad \boldsymbol{\rho}^\nu = \mathbf{r}^\nu - \mathbf{R},$$

with

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

or

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

The constraints (2.8) imply that  $\boldsymbol{\rho}^\nu$  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

$$E\chi(\mathbf{p}, \boldsymbol{\pi}^\nu) = [\sum E_\nu(\boldsymbol{\pi}^\nu - \mathbf{p}/A) + V_N(\boldsymbol{\rho}^\nu, \boldsymbol{\pi}^\nu - \mathbf{p}/A, \boldsymbol{\sigma}^\nu) + H_a(\mathbf{p})]\chi(\mathbf{p}, \boldsymbol{\pi}^\nu) \\ - (e^2/2\pi^2) \int d^3 k \{ \sum_p [I_{++}^\nu(\boldsymbol{\pi}^\nu - \mathbf{p}/A, \boldsymbol{\pi}^\nu - \mathbf{p}/A - \mathbf{k}) - \alpha_1^a \cdot \alpha_{1++}^\nu(\boldsymbol{\pi}^\nu - \mathbf{p}/A, \boldsymbol{\pi}^\nu - \mathbf{p}/A - \mathbf{k})] \\ + \sum (\mu_{A'}^\nu/2M) [\mathbf{k} \cdot (\beta^\nu \boldsymbol{\alpha}^\nu)_{++}(\boldsymbol{\pi}^\nu - \mathbf{p}/A, \boldsymbol{\pi}^\nu - \mathbf{p}/A - \mathbf{k}) - i\alpha^a \cdot \boldsymbol{\sigma}_{++}^\nu(\boldsymbol{\pi}^\nu - \mathbf{p}/A, \boldsymbol{\pi}^\nu - \mathbf{p}/A - \mathbf{k}) \times \mathbf{k}] \} \\ \times k^{-2} \chi(\mathbf{p} + \mathbf{k}, \boldsymbol{\pi}_1, \dots, \boldsymbol{\pi}_\nu - \mathbf{k}, \dots), \quad (4.10a)$$

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

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

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

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

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

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

This can be written in the form

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

<sup>24</sup> G. Breit, Phys. Rev. **34**, 553 (1929); **36**, 383 (1930); **39**, 616 (1932).

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

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

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

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

$$\begin{aligned} \mathcal{H}_{\text{mix}} = & \alpha_1^a \cdot [(1/4) \sum g^v \boldsymbol{\sigma}^v \times \nabla + \sum_p \boldsymbol{\pi}^v] \\ & \times (-e^2 / M) (1 - \boldsymbol{\rho}^v \cdot \nabla) r^{-1} \\ & - \sum (\mu_A^v / 2AM^2) \boldsymbol{\sigma}^v \cdot \mathbf{p} \times \nabla (-e^2 / r) \\ & + \sum_p \{ [1 - (1/4AM^2) \boldsymbol{\sigma}^v \cdot \mathbf{p} \times \nabla] \\ & \quad \times [1 - \boldsymbol{\rho}^v \cdot \nabla] - 1 \} (-e^2 / r) \\ & + [\sum \boldsymbol{\pi}^v \cdot \mathbf{p} (\pi^v)^2 / 2AM^3 + V_N^{(1)}] + \dots \end{aligned} \quad (4.11c)$$

Here  $\varphi_0$  is defined as in Eq. (2.3a),  $\delta\mathbf{A}$  as in Eq. (2.6b) with  $\mathfrak{N} \rightarrow AM$ ,  $g^v = (1 + \mu_A^v)(e/2AM)$  for protons and  $\mu_A^v(e/2M)$  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  $(p/M)$ :

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

Note that the  $I_{++'}$  (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  $\boldsymbol{\alpha}^a \cdot \boldsymbol{\alpha}_{++'}$  (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  $\boldsymbol{\alpha}^a \cdot \boldsymbol{\sigma}_{++'}$  (Pauli) terms yield the remaining terms linear in  $\boldsymbol{\alpha}^a$ , and the  $\mathbf{k} \cdot \boldsymbol{\alpha}_{++'}$  (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  $\chi$  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  $\mathfrak{N} \rightarrow AM$ . With  $[\rho_i^v, \mathcal{H}_{\text{nuc}}] = (i/M)\pi_i^v$ , i.e., assuming a velocity-independent, nonexchange force, and neglecting corrections to the nonrelativistic kinetic energy, we have

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

and

$$\mathbf{u} = \langle \sum_p (e/2M) \rho^v \times \boldsymbol{\pi}^v + \frac{1}{2} \sum g^v \boldsymbol{\sigma}^v \rangle. \quad (4.14)$$

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

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

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  $V_{\text{EM}}$ , we may write

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

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

$$V_{\text{EM}}^{(0)} = e^2 \sum_p 1/2\rho^{\mu\nu} + \dots, \quad (4.16b)$$

$$\begin{aligned} V_{\text{EM}}^{(1)} = & (e^2 / 4AM^2) \sum_p \left[ \left\{ \boldsymbol{\pi}^\mu \cdot \mathbf{p}, \frac{1}{\rho^{\mu\nu}} \right\} \right. \\ & \left. + \left\{ \pi_j^\mu, \frac{\boldsymbol{\rho}^{\mu\nu} \cdot \mathbf{p} \rho_j^{\mu\nu}}{(\rho^{\mu\nu})^3} \right\} - \boldsymbol{\sigma}^v \cdot \mathbf{p} \times \nabla r^{-1} \right]. \end{aligned} \quad (4.16c)$$

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

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

where

$$\begin{aligned} \Phi = & \mathbf{p} \cdot [\sum \pi_j^v \boldsymbol{\rho}^v \pi_j^v / 2AM^2 - \sum (\boldsymbol{\sigma}^v \times \boldsymbol{\pi}^v) / 4AM^2 \\ & + e^2 \sum_p \boldsymbol{\rho}^v / 2AM | \boldsymbol{\rho}^\mu - \boldsymbol{\rho}^v |]. \end{aligned} \quad (4.17a)$$

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:

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

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

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

Adding (4.19) to (4.15) gives

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

by Eqs. (4.14) and (2.6b), with  $\mathfrak{N}$  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<sup>25</sup> 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  $\sum_{\mathbf{p}} \mathbf{p}^\mu \cdot \nabla (e^2/r)$  term it can contribute another term of the type (constant)  $\mathbf{I} \cdot \mathbf{p} \times \nabla r^{-1}$ , 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  $V_{EM}^{(1)}$  to limit the form of  $U^{(1)}$ . Consider a system of interacting particles described by a Hamiltonian,  $\mathcal{H}$ . Thomas and Bakamjian<sup>26</sup> and Foldy<sup>27</sup> have proved that the commutation relations for the generators of the infinitesimal Lorentz group require the existence of a function  $\Phi$ , such that

$$e^{i\Phi} \mathcal{H} e^{-i\Phi} = (\mathbf{p}^2 + h^2)^{1/2},$$

$$h = AM + \sum \pi_r^2 / 2M + V^{(0)} + \dots \quad (4.21)$$

<sup>25</sup> L. H. Thomas, *Nature* **117**, 514 (1926); *Phil. Mag.* **3**, 1 (1927).

<sup>26</sup> B. Bakamjian and L. H. Thomas, *Phys. Rev.* **92**, 1300 (1953).

<sup>27</sup> L. Foldy, *Phys. Rev.* **122**, 275 (1961).

Here,  $\Phi$  is a rotationally invariant function of  $\mathbf{p}$  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  $\mathbf{p}^2$ ,  $V_N^{(1)}$  arises entirely from the transformation from the reduced to the usual or "physical" representation, i.e.,  $V_N^{(1)} = -[i\Phi, \sum (\pi^r)^2 / 2M + V_N^{(0)}]$ . Requiring a specific form for the electromagnetic part of  $V_N^{(1)}$  in the physical representation therefore restricts  $\Phi$  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  $\mathbf{p}^2$  in Eq. (4.11c) and obtain the binding energy effects explicitly.

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