

## Relativistic Contributions to the Magnetic Moment of ${}^3S_1$ Helium

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Some relativistic contributions of order  $\alpha^2 \sim (137)^{-2}$  to the magnetic moment of helium in the lowest-energy triplet state  ${}^3S_1$  have been calculated. These contributions arise from the effect of the electrostatic and Breit interactions in a relativistic wave equation. The purpose of the calculation was to isolate to order  $\alpha^2$  the quantum-electrodynamic radiative contributions to the magnetic moment of a bound two-electron system for comparison with experiment. The method of calculation was to evaluate the sixteen-component form of the matrix element of magnetic interaction energy in terms of nonrelativistic wave functions in Pauli approximation and to use the angular and spin symmetry properties of the  ${}^3S_1$  state. This procedure was possible because Russell-Saunders coupling in the Pauli approximation could be shown to hold rigorously to order  $\alpha^2$ . The result derived was that

the  $g$  value for two interacting electrons bound in a  ${}^3S_1$  state is  $2(1 - \frac{1}{3}\langle T \rangle - \frac{1}{6}\langle e^2/r_{12} \rangle)$  where  $\langle T \rangle$  is the expectation value of total kinetic energy and  $\langle e^2/r_{12} \rangle$  of electrostatic interaction in the  ${}^3S_1$  state, in units  $mc^2$ . The contribution  $-\frac{1}{3}\langle T \rangle$  corresponds to the Breit-Margenau result for one electron and  $-\frac{1}{6}\langle e^2/r_{12} \rangle$  arises from the Breit interaction. For  ${}^3S_1$  helium the preceding  $g$  value was evaluated numerically as  $2[1 - (38.7 + 2.3) \times 10^{-6}]$ . Comparison of theory and experiment tends to substantiate the nonradiative contribution  $-\frac{1}{3}\langle T \rangle$  and the additivity properties of radiative and nonradiative contributions to the magnetic moment of  ${}^3S_1$  helium. The fourth-order radiative contribution is not contradicted. The Breit interaction contribution is too small to be noticed, with the present experimental error.

### INTRODUCTION

THE present perturbation theory of quantum-electrodynamics yields finite and unambiguous equations of motion for electrons and positrons interacting with electromagnetic fields. The resulting relativistic theoretical predictions of energy levels in various arrangements of electric and magnetic fields have been experimentally investigated for a single bound electron<sup>1</sup> and for the bound electron-positron system of positronium.<sup>2</sup> In this paper a bound two-electron system is studied. Specifically, some relativistic contributions to the magnetic moment of  ${}^3S_1$  helium will be calculated and, combined with the existing radiative contributions to the intrinsic magnetic moment of the electron, will be compared with experiment.

The experiment, described in detail in the preceding paper,<sup>3</sup> yielded the ratio of the  $g$  value of helium in the metastable  ${}^3S_1$  state to the  $g$  value of hydrogen in the ground  ${}^2S_{1/2}$  state. The essential quantities measured were the transition frequency between the magnetic levels  $M = \pm 1 \leftrightarrow 0$  of  ${}^3S_1$  helium and the transition frequency between the levels  $(F, m_F) = (1, 0) \leftrightarrow (1, -1)$  of  ${}^2S_{1/2}$  hydrogen, both in the same uniform magnetic field. The magnetic moment of  ${}^3S_1$  helium is about two Bohr magnetons. The experimental ratio was determined to an accuracy of  $\pm 16 \times 10^{-6}$ . Inasmuch as the theoretical fourth-order radiative contribution to the

intrinsic magnetic moment of the electron is  $16 \times 10^{-6}$  Bohr magnetons,<sup>4</sup> an approximate test of fourth-order radiative corrections to the magnetic moment of the two interacting electrons in  ${}^3S_1$  helium appears possible.

To make this test, or rather as part of the over-all comparison of theory and experiment, it is necessary to calculate that part of the magnetic moment of the system yielded by the Dirac equation without internal radiation field but with the Coulomb and Breit interactions. This part is of the same order,  $\alpha^2$ , as the fourth-order contribution of the radiation field. For hydrogen-like atoms this well-known calculation has been made rigorously by Breit and by Margenau.<sup>5</sup> The main purpose of this paper is to make the corresponding calculation for helium-like atoms in the  ${}^3S_1$  state.

### THE WAVE EQUATION

The wave equation for the stationary states  $\Psi$  of the system of two electrons in a given external electromagnetic field is taken as

$$\begin{aligned} 0 &= (E - \mathcal{H})\Psi \\ &= \{E + \sum_{i=1,2} [e\phi_i + mc^2\beta_i + \alpha_i \cdot (c\mathbf{p}_i + e\mathbf{A}_i)] \\ &\quad + \sum_{n \geq 1} \alpha^n [\Omega_1^{(n)} + \Omega_2^{(n)} + \Omega_{12}^{(n)}]\} \Psi, \quad (1) \end{aligned}$$

in which  $E$  is the energy eigenvalue including the rest energy  $2mc^2$  of the two electrons,  $-e = -|e|$  the observed charge on the electron,  $m$  the observed mass of the electron,  $\phi$  and  $\mathbf{A}$  the given scalar and vector potentials of the external field,  $\beta$  and  $\alpha$  the usual Dirac variables,  $\mathbf{p}$  the momentum operator,  $\alpha \approx 1/137.037$

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<sup>1</sup> W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. **79**, 549 (1950); **81**, 222 (1951); and **85**, 259 (1952); J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948); A. G. Prodell and P. Kusch, Phys. Rev. **79**, 1009 (1950); P. Kusch and H. M. Foley, Phys. Rev. **74**, 250 (1948); Koenig, Prodell, and Kusch, Phys. Rev. **83**, 687 (1951).

<sup>2</sup> M. Deutsch and S. C. Brown, Phys. Rev. **85**, 1047 (1952); R. Karplus and A. Klein, Phys. Rev. **87**, 848 (1952).

<sup>3</sup> Hughes, Tucker, Rhoderick, and Weinreich, preceding paper [Phys. Rev. **91**, 828 (1953)].

<sup>4</sup> R. Karplus and N. M. Kroll, Phys. Rev. **77**, 536 (1950).

<sup>5</sup> G. Breit, Nature **122**, 649 (1928); H. Margenau, Phys. Rev. **57**, 383 (1940); N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition; p. 72.

the fine structure constant, and the subscripts 1, 2, 12 denote dependence respectively on electron 1 with spatial coordinate variable  $\mathbf{r}_1$ , electron 2 with spatial coordinate variable  $\mathbf{r}_2$  and  $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$ . The external field is taken as the nuclear Coulomb field and a constant uniform magnetic field  $\mathbf{H}$ .

Reduced mass effects, due to a Hamiltonian for the nucleus analogous to that in (1),<sup>6</sup> are zero in order  $m/M$  ( $M$ =nuclear mass) in the present case because the nucleus has zero spin and the total electronic orbital angular momentum is zero. Higher-order reduced mass effects, apparently first occurring<sup>7</sup> in order  $\alpha^2 m/M$ , are negligible relative to the retained order  $\alpha^2$ .

The summation in (1) over the self- and mutual-energy operators  $\Omega_i^{(n)}$ ,  $\Omega_{12}^{(n)}$  represents the finite corrections yielded by quantum electrodynamics when the internal radiation field variables are eliminated by covariant perturbation theory. The operators  $\Omega^{(n)}$  are functions of the electron and external field variables  $\mathbf{r}$ ,  $\mathbf{p}$ ,  $\alpha$ ,  $\mathbf{A}$ , etc. The first two mutual energy operators in (1) are the electrostatic and the Breit interaction,<sup>8</sup>

$$\alpha\Omega_{12}^{(1)} + \alpha^2\Omega_{12}^{(2)} = -e^2/r_{12} + B_{12}, \quad (2)$$

$$B_{12} = e^2/r_{12}(\alpha_1 \cdot \alpha_2 + \alpha_1 \cdot \mathbf{r}_{12} \alpha_2 \cdot \mathbf{r}_{12}/r_{12}^2). \quad (3)$$

The self-energy operators in (1) that contribute linearly to the external magnetic interaction energy do so in the orders

$$[O(\alpha) + O(\alpha^2) + O(\alpha^3 \log \alpha) + O(\alpha^3) + \dots] \mu_0 H, \quad (4)$$

where  $\mu_0 = e\hbar/2mc$  = Bohr magneton. The  $[O(\alpha) + O(\alpha^2)] \mu_0 H$  contributions, corresponding respectively to the second<sup>9</sup> and fourth<sup>4</sup> order corrections to the magnetic moment of the electron, arise from the operator

$$\Omega_H = \mu_0(\alpha/2\pi - 2.973\alpha^2/\pi^2) \sum_{i=1,2} \sigma_i' \cdot \mathbf{H}_i, \quad (5)$$

where  $\sigma'$  is the  $4 \times 4$  Pauli spin matrix. As justified in the next section, this operator may be evaluated in the 2-electron Russell-Saunders  $^3S_1$  state, to yield the self-radiative contribution to the  $g/2$  value<sup>10</sup> of the system,

$$(\Delta g/2)_r \equiv \Delta E_{Hr}/2M\mu_0 H = \alpha/2\pi - 2.973\alpha^2/\pi^2 = 0.0011614 - 0.0000160 = 0.0011454. \quad (6)$$

This evaluation neglects  $O(\alpha^3) \mu_0 H$  contributions. The  $O(\alpha^3 \log \alpha) \mu_0 H$  term in (4), which comes from the Bethe contribution<sup>11</sup> to the Lamb shift operator, is

<sup>6</sup> W. E. Lamb, Jr., Phys. Rev. **85**, 259 (1952).

<sup>7</sup> E. E. Salpeter, Phys. Rev. **87**, 328 (1952); G. Breit and G. E. Brown, Phys. Rev. **74**, 1278 (1948); T. Ishidzu, Progr. Theoret. Phys. (Japan) **6**, 48, 154 (1951).

<sup>8</sup> G. Breit, Phys. Rev. **34**, 553 (1929); **39**, 616 (1932). This interaction has been discussed by the newer methods by G. E. Brown and D. G. Ravenhall, Proc. Roy. Soc. (London) **A208**, 552 (1951), and by E. E. Salpeter (reference 7).

<sup>9</sup> J. Schwinger, Phys. Rev. **82**, 664 (1951).

<sup>10</sup> Throughout this paper we shall use one-half the  $g$  value,  $g/2$ , which is approximately unity.

<sup>11</sup> Bethe, Brown, and Stehn, Phys. Rev. **77**, 370 (1950).

estimated to be completely negligible. Thus the first neglected order of magnitude due to self-radiative effects of various kinds is  $\alpha^3 \mu_0 H$  which, inasmuch as  $\alpha^3 = 0.39 \times 10^{-6}$ , will be considered to introduce an uncertainty of  $\pm 1 \times 10^{-6}$  in the final theoretical result.

The wave equation for the present problem is, then,

$$\{E - V + \sum_{i=1,2} [mc^2 \beta_i + \alpha_i \cdot (c\mathbf{p}_i + e\mathbf{A}_i)] + B_{12} - \Omega_H\} \Psi = 0, \quad (7)$$

where

$$V = V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \quad (8)$$

$$= -Ze^2/r_1 - Ze^2/r_2 + e^2/r_{12}. \quad (9)$$

### MAGNETIC INTERACTION ENERGY VIA PAULI APPROXIMATION

The present problem is to evaluate to order  $\alpha^2$  the external magnetic interaction contribution  $\Delta E_H$  to the energy eigenvalue  $E$ . Inasmuch as quadratically  $H$ -dependent contributions are negligible at the magnetic fields used in the experiment, first-order perturbation theory can be used. Hence, from (7),

$$\Delta E_H = \langle U | -e(\alpha_1 \cdot \mathbf{A}_1 + \alpha_2 \cdot \mathbf{A}_2) + \Omega_H | U \rangle, \quad (10)$$

where  $U$ , the 16-component wave function corresponding to the lowest-energy  $^3S_1$  state of helium, satisfies

$$(E - V + \beta_1 + \beta_2 + \alpha_1 \cdot \mathbf{p}_1 + \alpha_2 \cdot \mathbf{p}_2 + B_{12})U = 0. \quad (11)$$

In (11) energies are expressed in units  $mc^2$  and momenta in units  $mc$ . Equation (10) will be evaluated by first expressing the 16-component  $U$  in terms of four 4-component  $U$ 's, then eliminating all but the largest 4-component  $U$  by (11), to order  $\alpha^2 \mu_0 H$ , and finally evaluating the result by means of the nonrelativistic (Pauli approximation) properties of the largest 4-component  $U$ .

Thus, consider  $U$  as a 4-component column matrix with components  $|kl\rangle$ , each value of  $k=1, 2$  and  $l=1, 2$  representing two<sub>2</sub> Pauli spinor components of  $U$ . Write

$$\alpha_i \cdot \mathbf{A}_i = \sigma_i \cdot \mathbf{A}_i \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_i = A_i \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_i, \quad i=1, 2, \quad (12)$$

where  $\sigma_i$  is the 2-component Pauli spin variable for electron  $i$ . For  $i=1$ , denoting electron 1, the matrix in (12) operates on the first subscript  $k$  of  $|kl\rangle$  keeping the second subscript  $l$  fixed (a unit matrix for electron 2 can be understood as operating to keep subscript  $l$  fixed). Similarly for  $l=2$ . Then the  $\alpha \cdot \mathbf{A}$  terms in (10) become

$$\begin{aligned} \Delta E_A &= -e \langle U | \alpha_1 \cdot \mathbf{A}_1 + \alpha_2 \cdot \mathbf{A}_2 | U \rangle \\ &= -e \{ \langle 11 | A_1 | 21 \rangle + \langle 21 | A_1 | 11 \rangle + \langle 12 | A_1 | 22 \rangle \\ &\quad + \langle 22 | A_1 | 12 \rangle + \langle 11 | A_2 | 12 \rangle + \langle 12 | A_2 | 11 \rangle \\ &\quad + \langle 21 | A_2 | 22 \rangle + \langle 22 | A_2 | 21 \rangle \}. \end{aligned} \quad (13)$$

Define

$$E = 2 + W, \quad (14)$$

$$\sigma_i \cdot \mathbf{p}_i = P_i, \quad i=1, 2. \quad (15)$$

Carrying out the matrix operations in (11) yields four relations among the  $|kl\rangle$ ,

$$\left. \begin{aligned} (4+W-V)|11\rangle+P_1|21\rangle+P_2|12\rangle+M_{12}|22\rangle &= 0, & (a) \\ (2+W-V)|21\rangle+P_1|11\rangle+P_2|22\rangle+M_{12}|12\rangle &= 0, & (b) \\ (2+W-V)|12\rangle+P_1|22\rangle+P_2|11\rangle+M_{12}|21\rangle &= 0, & (c) \\ (W-V)|22\rangle+P_1|12\rangle+P_2|21\rangle+M_{12}|11\rangle &= 0, & (d) \end{aligned} \right\} (16)$$

where

$$M_{12} = (e^2/r_{12})(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_1 \cdot \mathbf{r}_{12} \boldsymbol{\sigma}_2 \cdot \mathbf{r}_{12}/r_{12}^2). \quad (17)$$

In the positive energy state here considered,  $W$ , the eigenvalue minus the rest energy of the two electrons, is of order  $\gamma^2 = \alpha^2 Z^2 = (2/137)^2$ . Also  $V$ ,  $M_{12} \sim \gamma^2$  and  $P_1, P_2 \sim \gamma$ . Hence from (16), the largest component wave function is  $|22\rangle$  and

$$|11\rangle \sim \gamma^2 |22\rangle, \quad |12\rangle \sim |21\rangle \sim (\gamma + \gamma^3) |22\rangle. \quad (18)$$

Higher orders (which go up in powers of  $\gamma^2$ ) than

$$\left. \begin{aligned} |11\rangle &= \frac{1}{4}[P_1 P_2 - M_{12}] |22\rangle, & (a) \\ |21\rangle &= -\left[\frac{1}{2}P_2 + \frac{1}{4}(V-W)P_2 + \frac{1}{8}P_2 P_1^2 - \frac{1}{8}(P_1 M_{12} + 2M_{12} P_1)\right] |22\rangle, & (b) \\ |12\rangle &= -\left[\frac{1}{2}P_1 + \frac{1}{4}(V-W)P_1 + \frac{1}{8}P_1 P_2^2 - \frac{1}{8}(P_2 M_{12} + 2M_{12} P_2)\right] |22\rangle. & (c) \end{aligned} \right\} (20)$$

The two-electron Schrödinger-Pauli approximation equation given by Breit<sup>8,12</sup> can be obtained by substituting (20) into (16d). This equation will not be needed here explicitly.<sup>13</sup> Substitution of (20) into (13) yields for  $\Delta E_A$  in terms of the largest component wave function

$$\begin{aligned} \Delta E_A &= \frac{1}{4}e\langle 22 | 2(P_1 A_1 + A_1 P_1 + P_2 A_2 + A_2 P_2) \\ &\quad + [P_1(V-W)A_1 + A_1(V-W)P_1 \\ &\quad + P_2(V-W)A_2 + A_2(V-W)P_2] \\ &\quad + [(P_1 A_1 + A_1 P_1)P_2^2 + (P_2 A_2 + A_2 P_2)P_1^2] \\ &\quad - [M_{12}(A_1 P_2 + A_2 P_1) + (A_1 P_2 + A_2 P_1)M_{12} \\ &\quad + A_1 M_{12} P_2 + P_1 M_{12} A_2 \\ &\quad + A_2 M_{12} P_1 + P_2 M_{12} A_1] | 22 \rangle, \end{aligned} \quad (21)$$

in which the commutation of subscript 1 variables with subscript 2 variables has been used. The terms in (21) involving  $M_{12}$  arise from the Breit interaction  $B_{12}$ . Although derived via (20) apparently without regard for Breit's prescription that  $B_{12}$  be used only in a first order perturbation expectation value, these terms do actually conform with this prescription. For, the same terms result from the linearly  $A$ -dependent part of  $-\langle U' | B_{12} | U' \rangle$ , where  $U'$  satisfies, instead of (11),

$$[E' - V + \beta_1 + \beta_2 + \boldsymbol{\alpha}_1 \cdot (\mathbf{p}_1 + e\mathbf{A}_1) + \boldsymbol{\alpha}_2 \cdot (\mathbf{p}_2 + e\mathbf{A}_2)] U' = 0. \quad (22)$$

The same terms also occur in the Schrödinger-Pauli approximation Hamiltonian derivable from (7) to order  $\alpha^2 \mu_0 H$ .<sup>13</sup>

<sup>12</sup> H. Bethe, *Handbuch der Physik* (Verlag. Julius Springer, Berlin, 1933), second edition, Vol. 24/1, p. 354.

<sup>13</sup> W. Perl, following paper [Phys. Rev. **91**, 852 (1953)].

indicated in (18) will not be needed. Explicit expressions for the wave function components can therefore be obtained by first solving (16b, c) for components  $|21\rangle$  and  $|12\rangle$  respectively to  $\sim \gamma |22\rangle$ , substituting these in (16a) to get the first of (18), which is then put back into (16b, c) to give the second and third of (18). In this way, and expanding

$$(2+W-V)^{-1} = \frac{1}{2} + \frac{1}{4}(V-W) \quad (19)$$

to the order needed, we obtain

#### RELATIVITY-SPIN CONTRIBUTION

Equation (21) contains the usual non-relativistic magnetic energy  $\Delta E_{A0}$ , of order  $\mu_0 H$ , an order  $\alpha^2 \mu_0 H$  contribution  $\Delta E_{A3}$  due to the terms containing  $M_{12}$  arising from the Breit interaction (not to be confused with the Breit-Margenau effect), and the remaining order  $\alpha^2 \mu_0 H$  contribution which will be expressed in two parts as  $\Delta E_{A1} + \Delta E_{A2}$ .

The part  $\Delta E_{A012} = \Delta E_{A0} + \Delta E_{A1} + \Delta E_{A2}$  of (21) is evaluated as follows. Using

$$\boldsymbol{\sigma} \cdot \mathbf{A} \boldsymbol{\sigma} \cdot \mathbf{B} = \mathbf{A} \cdot \mathbf{B} + i\boldsymbol{\sigma} \cdot \mathbf{A} \times \mathbf{B}, \quad (23)$$

and, in a Schrödinger representation,

$$\mathbf{p}V = V\mathbf{p} - i\hbar\nabla V, \quad (24)$$

and also

$$P_i A_i + A_i P_i = \hbar(\mathbf{L}_i + \boldsymbol{\sigma}_i) \cdot \mathbf{H}, \quad (25)$$

where

$$\begin{aligned} \hbar\mathbf{L}_i &= \mathbf{r}_i \times \mathbf{p}_i, & \mathbf{A}_i &= \frac{1}{2}\mathbf{H} \times \mathbf{r}_i, \\ \mathbf{H} &= \text{curl}_i \mathbf{A}_i, & \text{div}_i \mathbf{A}_i &= 0, \end{aligned} \quad (26)$$

yields

$$\begin{aligned} \Delta E_{A012} &= \frac{1}{2}\mu_0 \langle 22 | 2(\mathbf{L}_1 + \mathbf{L}_2 + \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2) \cdot \mathbf{H} \\ &\quad + p_1^2(\mathbf{L}_2 + \boldsymbol{\sigma}_2) \cdot \mathbf{H} + p_2^2(\mathbf{L}_1 + \boldsymbol{\sigma}_1) \cdot \mathbf{H} \\ &\quad + (V-W)(\mathbf{L}_1 + \mathbf{L}_2 + \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2) \cdot \mathbf{H} \\ &\quad + \boldsymbol{\sigma}_1 \cdot \nabla_1 V \times \mathbf{A}_1 + \boldsymbol{\sigma}_2 \cdot \nabla_2 V \times \mathbf{A}_2 | 22 \rangle, \end{aligned} \quad (27)$$

in which has also been used

$$\begin{aligned} \nabla_1 V \cdot \mathbf{A}_1 + \nabla_2 V \cdot \mathbf{A}_2 &= \nabla_i [V_1(\mathbf{r}_1) + V_{12}(\mathbf{r}_{12})] \cdot \mathbf{H} \times \mathbf{r}_1/2 \\ &\quad + \nabla_2 [V_2(\mathbf{r}_2) + V_{12}(\mathbf{r}_{12})] \cdot \mathbf{H} \times \mathbf{r}_2/2 = 0. \end{aligned} \quad (28)$$

The wave function  $|22\rangle$  has the Russell-Saunders angular dependence  ${}^3S_1$ , to the order required in evaluating Eq. (27). The reason is that it satisfies a

Schrödinger-Pauli equation (the equation not written down above) in which the perturbing terms, of the spin-orbit and spin-spin type,<sup>8,12</sup> are of order  $\alpha^2$  Ry. Hence the wave function  $|22\rangle$  can be expressed as

$$|22\rangle = \Psi_0(^3S_1) + \alpha^2 \sum_m c_m \Psi_m(^1,^3L_1), \quad (29)$$

where the  $\Psi_m$  are Russell-Saunders eigenfunctions of the nonrelativistic 2-electron Schrödinger equation

$$(W_m - V - T)\Psi_m = 0, \quad (30)$$

with

$$T = \frac{1}{2}(\mathbf{p}_1^2 + \mathbf{p}_2^2). \quad (31)$$

Specifically, only  $^1P$ ,  $^3P$  and  $^3D$  are included in the summation in (29).<sup>14</sup> The numerical order of magnitude of  $c_m$  in (29) is much less than one because of the necessity of combining electrostatic interaction to configurations like  $2p\ 3p$ ,  $3d\ 4d$ , with spin-orbit type interaction, to mix in the  $\Psi_m$  (see, for example, Appendix A). Let the magnetic field be in the  $z$  direction,  $\mathbf{H} = (0, 0, H)$ . The first term in (27) evaluated for the state (29) has the diagonal contribution from the  $^3S_1$  eigenstate,

$$\begin{aligned} \Delta E_{A0} + \Delta E_{A1} &= \mu_0 H \langle ^3S_1 | (L_1 + L_2 + \sigma_1 + \sigma_2)_z | ^3S_1 \rangle \\ &= 2N\mu_0 H, \end{aligned} \quad (32)$$

where  $N$  is a normalization constant. Additional diagonal contributions from  $^1,^3L_1$ , of order  $\alpha^4\mu_0 H$  are negligible. There are no cross-product contributions between  $^3S_1$  and  $^1,^3L_1$ . The remaining terms in (27) have diagonal contributions of order  $\alpha^2\mu_0 H$  in the  $^3S_1$  state, which will be evaluated, and cross-product contributions between  $^3S_1$  and  $^1,^3L_1$  of order  $\alpha^4\mu_0 H$ , hence negligible. Thus, to order  $\alpha^2\mu_0 H$ , the wave function  $|22\rangle$  in Eq. (27) may be considered a Russell-Saunders  $^3S_1$  eigenstate of Eq. (30).<sup>15</sup> The normalization constant  $N$  is necessary in (32) because normalization to unity has already been assumed for the 16-component  $U$  in (10). Thus by (20),

$$\begin{aligned} 1 = \langle U | U \rangle &= \langle 11 | 11 \rangle + \langle 21 | 21 \rangle + \langle 12 | 12 \rangle + \langle 22 | 22 \rangle \\ &= O(\alpha^4) + \frac{1}{4} \langle 22 | \mathbf{p}_1^2 + \mathbf{p}_2^2 | 22 \rangle + \langle 22 | 22 \rangle, \end{aligned} \quad (33)$$

or, to order  $\alpha^2$ ,

$$\langle 22 | 22 \rangle = 1 - \frac{1}{4} \langle \Psi_0 | \mathbf{p}_1^2 + \mathbf{p}_2^2 | \Psi_0 \rangle = 1 - \frac{1}{2} \langle T \rangle, \quad (34)$$

where now  $\Psi_0(^3S_1)$ , the usual Russell-Saunders  $^3S_1$  eigenfunction of (30) normalized to unity may be used on the right in (34) and also with the remaining terms in (27). Substituting (34) for  $N$  in (32) yields for the contribution of the first term in (27)

$$\Delta E_{A0} + \Delta E_{A1} = 2\mu_0 H - \mu_0 H \langle T \rangle. \quad (35)$$

<sup>14</sup> G. Breit and E. Teller, *Astrophys. J.* **91**, 215 (1940).

<sup>15</sup> More detailed analogous arguments for the heavier atoms have been given by M. Phillips, *Phys. Rev.* **88**, 202 (1952), who finds non-negligible configuration mixing contributions, despite the order  $\alpha^4$  involved.

Because of the symmetrical dependence of a 2-electron  $^3S_1$  eigenfunction on the spin and orbital angular momentum variables of the two electrons, the second and third terms of (27) cancel, by (30), the fourth term [the  $O(\alpha^2)$  differences between  $|22\rangle$  and  $\Psi_0$  and between  $W$  and  $W_0$  are immaterial for this purpose].

The last two terms  $\Delta E_{A2}$  in (27) can be evaluated as follows:

$$\begin{aligned} \Delta E_{A2} &= \frac{1}{2} \mu_0 \langle \sigma_1 \cdot \nabla_1 V \times \mathbf{A}_1 + \sigma_2 \cdot \nabla_2 V \times \mathbf{A}_2 \rangle \\ &= \frac{\mu_0}{4} \left\langle \sigma_1 \cdot \left( \frac{\partial V_1}{r_1 \partial r_1} \mathbf{r}_1 + \frac{\partial V_{12}}{r_{12} \partial r_{12}} \mathbf{r}_{12} \right) \times (\mathbf{H} \times \mathbf{r}_1) \right. \\ &\quad \left. + \sigma_2 \cdot \left( \frac{\partial V_2}{r_2 \partial r_2} \mathbf{r}_2 + \frac{\partial V_{12}}{r_{12} \partial r_{12}} \mathbf{r}_{21} \right) \times (\mathbf{H} \times \mathbf{r}_2) \right\rangle. \end{aligned} \quad (36)$$

The two-electron eigenfunction  $\Psi_0(^3S_1)$  is the product of a triplet spin function and an  $L=0$  orbital function. Hence

$$\langle \sigma_{1x} \rangle = \langle \sigma_{2x} \rangle = \langle \sigma_{1y} \rangle = \langle \sigma_{2y} \rangle = 0, \quad (37)$$

$$\langle \sigma_{1z} \rangle = \langle \sigma_{2z} \rangle = 1, \quad (38)$$

and (36) becomes

$$\begin{aligned} \Delta E_{A2} &= \frac{\mu_0 H}{4} \left\langle r_1 \frac{\partial V_1}{\partial r_1} \left( 1 - \frac{z_1^2}{r_1^2} \right) + r_2 \frac{\partial V_2}{\partial r_2} \left( 1 - \frac{z_2^2}{r_2^2} \right) \right. \\ &\quad \left. + r_{12} \frac{\partial V_{12}}{\partial r_{12}} \left( 1 - \frac{z_{12}^2}{r_{12}^2} \right) \right\rangle. \end{aligned} \quad (39)$$

To evaluate the angular factors in (39), the orbital function in  $\Psi_0$  is expressed in terms of the "Hylleraas" variables<sup>12</sup> specifying the spatial location of the two electrons. These variables are the polar coordinates  $r_1, \theta_1, \phi_1$  of one radius vector,  $\mathbf{r}_1$ , say, with respect to an arbitrary polar axis  $\mathbf{r}_0$  and the polar coordinates  $r_2, \theta_2, \psi_2$  of the other radius vector  $\mathbf{r}_2$  with respect to  $\mathbf{r}_1$  as polar axis. The variable  $r_{12}$  may replace  $\theta$  in accordance with

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta. \quad (40)$$

Because of the spherical symmetry of an  $S$  state, the orbital part of  $\Psi_0(^3S_1)$  must be independent of the orientation of the polar axis  $\mathbf{r}_0$ ; i.e., must depend only on the relative dimensions of the triangle formed by  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , not on the orientation relative to  $\mathbf{r}_0$  of this triangle regarded as a rigid body. Hence the wave function is independent of  $\theta_1$ ,  $\phi_1$ , and  $\psi_2$  and, letting  $\langle \rangle_0$  represent averaging over these variables,

$$\begin{aligned} \left\langle \frac{z_1^2}{r_1^2} \right\rangle_0 &= \langle \cos^2 \theta_1 \rangle_0 \\ &= \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^\pi \cos^2 \theta_1 \sin \theta_1 d\theta_1 d\phi_1 d\psi_1 = \frac{1}{3}. \end{aligned} \quad (41)$$

By a symmetry argument, or substitution of

$$\cos \theta_2 = \cos \theta \cos \theta_1 + \sin \theta \sin \theta_1 \cos \psi \quad (42)$$

in place of  $\cos\theta_1$  in (41), there results

$$\langle z_2^2/r_2^2 \rangle_0 = \langle \cos^2\theta_2 \rangle_0 = \frac{1}{3}. \quad (43)$$

Finally

$$\begin{aligned} \left\langle \frac{z_{12}^2}{r_{12}^2} \right\rangle_0 &= \frac{1}{r_{12}^2} \langle (z_1 - z_2)^2 \rangle_0 = \frac{1}{r_{12}^2} \langle (r_1 \cos\theta_1 - r_2 \cos\theta_2)^2 \rangle_0 \\ &= \frac{1}{r_{12}^2} (r_1^2 \langle \cos^2\theta_1 \rangle_0 - 2r_1 r_2 \langle \cos\theta_1 \cos\theta_2 \rangle_0 \\ &\quad + r_2^2 \langle \cos^2\theta_2 \rangle_0) = \frac{1}{3}, \quad (44) \end{aligned}$$

by use of (41) to (43). Hence (39) becomes

$$\Delta E_{A2} = \frac{1}{6}\mu_0 H (r_1 \partial V_1 / \partial r_1 + r_2 \partial V_2 / \partial r_2 + r_{12} \partial V_{12} / \partial r_{12}). \quad (45)$$

The virial theorem<sup>16</sup> states that for a discrete state satisfying the nonrelativistic Schrödinger Eq. (30).

$$\langle \sum_i r_i \partial V(\dots r_i \dots) / \partial r_i \rangle = 2\langle T \rangle = 2(W_0 - \langle V \rangle). \quad (46)$$

Hence (45) becomes

$$\Delta E_{A2} = \frac{1}{3}\mu_0 H \langle T \rangle. \quad (47)$$

The non-Breit interaction contribution to the  $g/2$  value of the system is thus by (47) and (35)

$$(g/2)_{012} = (\Delta E_{A0} + \Delta E_{A1} + \Delta E_{A2}) / 2\mu_0 H \quad (48)$$

$$= 1 - \frac{1}{2}\langle T \rangle + \frac{1}{6}\langle T \rangle \quad (49)$$

$$= 1 - \frac{1}{3}\langle T \rangle. \quad (50)$$

The result (50) holds for the  ${}^3S_1$  bound state of two electrons in a potential  $V(r_1, r_2, r_{12})$  which depends arbitrarily on the three variables  $r_1, r_2, r_{12}$ . In the special case of Coulomb interactions (50) can be evaluated exactly. In this case  $V$  is given by (9).<sup>17</sup> Hence by (46)

$$\langle V \rangle = 2W_0 = -2\langle T \rangle, \quad (51)$$

and (50) becomes

$$(\Delta g/2)_{12} = (g/2)_{012} - 1 = \frac{1}{3}W_0. \quad (52)$$

The experimental spectroscopic value of  $W_0$  is<sup>18</sup>

$$W_0 = -2\alpha^2(1.08765) = -2(1.08765)53.3 \times 10^{-6}. \quad (53)$$

(Use of the theoretical value of Hylleraas and Undheim<sup>19</sup> here would make no appreciable difference. Also  $\alpha = 1/137$  is sufficiently accurate here.) Hence (52) yields

$$(\Delta g/2)_{12} = -38.7 \times 10^{-6}. \quad (54)$$

To complete the evaluation of the  $\alpha \cdot \mathbf{A}$  terms of (10) there remains the calculation of the Breit interaction part of (21), depending on  $M_{12}$ . Also, the evaluation of

<sup>16</sup> V. Fock, *Z. Physik* **63**, 855 (1930).

<sup>17</sup> The Coulomb interactions could be independently multiplied by  $1 + O(\alpha)$ , which might arise from higher order quantum-electrodynamic interactions, without affecting the numerical result of this evaluation.

<sup>18</sup> *Atomic Energy Levels*, Natl. Bur. Standards Circ. No. 467 (Government Printing Office, Washington, D. C., 1948).

<sup>19</sup> E. A. Hylleraas and B. Undheim, *Z. Physik* **65**, 759 (1930).

the self-radiative  $\Omega_H$  term in (10) via  $\Psi_0({}^3S_1)$  to yield (6) is now seen to be justified.

### BREIT INTERACTION CONTRIBUTION

The Breit interaction part  $\Delta E_{A3}$  of (21) can be expressed in terms of commutators  $[\cdot, \cdot]$  and anti-commutators  $[\cdot, \cdot]_+$  as follows:

$$\begin{aligned} \Delta E_{A3} &= -\frac{1}{8}e \langle V_{12} \{ [[S_{12}, A_2]_+, P_1]_+ \\ &\quad + [[S_{12}, A_1]_+, P_2]_+ \} + [P_1, V_{12}][S_1, A_2]_+ \\ &\quad + [P_2, V_{12}][S_{12}, A_1]_+ \rangle, \quad (55) \end{aligned}$$

where  $V_{12} = e^2/r_{12}$  (in  $mc^2$  units) and

$$S_{12} = \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_1 \cdot \mathbf{r}_{12} \boldsymbol{\sigma}_2 \cdot \mathbf{r}_{12} / r_{12}^2. \quad (56)$$

By use of (23) and (24), the various bracket expressions in (55) can be evaluated as

$$[S_{12}, A_2]_+ = 2 \left( \boldsymbol{\sigma}_1 \cdot \mathbf{A}_2 + \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{A}_2}{r_{12}^2} \right), \quad (57)$$

$$\begin{aligned} [[S_{12}, A_2]_+, P_1]_+ &= 4 \left( \mathbf{A}_2 \cdot \mathbf{p}_1 + \frac{\mathbf{A}_2 \cdot \mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{p}_1}{r_{12}^2} \right) \\ &\quad - 4i\hbar \frac{\mathbf{r}_{12} \cdot \mathbf{A}_2}{r_{12}^2} + 2\hbar \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{A}_2 \times \mathbf{r}_{12}}{r_{12}^2}, \quad (58) \end{aligned}$$

$$[P_1, V_{12}] = i e^2 \hbar \frac{\boldsymbol{\sigma}_1 \cdot \mathbf{r}_{12}}{r_{12}^3}. \quad (59)$$

The other bracket expressions in (55) are obtained from these by interchanging subscripts 1 and 2. Substituting these bracket expressions into (55) yields, after some reduction,

$$\begin{aligned} \Delta E_B &= -\frac{e}{2} \left\langle \frac{e^2}{r_{12}} \left( \mathbf{A}_2 \cdot \mathbf{p}_1 + \mathbf{A}_1 \cdot \mathbf{p}_2 \right. \right. \\ &\quad \left. \left. + \frac{\mathbf{A}_2 \cdot \mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{p}_1}{r_{12}^2} + \frac{\mathbf{A}_1 \cdot \mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{p}_2}{r_{12}^2} \right) \right\rangle \\ &\quad + \mu_0 \left\langle \frac{e^2}{r_{12}^3} (\boldsymbol{\sigma}_1 \cdot \mathbf{r}_{12} \times \mathbf{A}_2 + \boldsymbol{\sigma}_2 \cdot \mathbf{r}_{21} \times \mathbf{A}_1) \right\rangle, \quad (60) \end{aligned}$$

which becomes, by (37), (38), and  $\mathbf{H} = (0, 0, H)$ ,

$$\begin{aligned} \Delta E_B &= -\frac{eH}{4} \left\langle \frac{e^2}{r_{12}} [(\mathbf{r}_2 \times \mathbf{p}_1)_z + (\mathbf{r}_1 \times \mathbf{p}_2)_z] \right. \\ &\quad \left. + \frac{e^2}{2r_{12}^3} (\mathbf{r}_2 \times \mathbf{r}_1)_z r_{12} \cdot (\mathbf{p}_1 - \mathbf{p}_2) \right\rangle \\ &\quad - \frac{\mu_0 H}{2} \left\langle \frac{e^2}{r_{12}} \left( 1 - \frac{z_{12}^2}{r_{12}^2} \right) \right\rangle. \quad (61) \end{aligned}$$

The terms containing  $\mathbf{p}_1, \mathbf{p}_2$  in (61) average to zero for

$\Psi_0(^3S_1)$ , as can be verified by expressing  $\Psi_0$  as a sum of products of one-electron functions and integrating over the azimuth angles. Reduction of the last term in (61) by (44) yields as the Breit interaction contribution to the  $g/2$  value of the system

$$(\Delta g/2)_3 = \Delta E_{A3}/2\mu_0 H = -\frac{1}{6}\langle\Psi_0|e^2/r_{12}|\Psi_0\rangle. \quad (62)$$

Numerical evaluation of (62) analogously to  $\langle T \rangle$  in terms of spectroscopic data cannot be made. However, a zero-order representation of  $\Psi_0$  was available (from an initial attempt to solve the entire problem in this way), as

$$\Psi_0 = \sum_n a_n \psi_n, \quad (63)$$

where  $\psi_n$ , the product of one-electron hydrogenic functions corresponding to electron configuration  $1sn_s$ , satisfies

$$[\epsilon_n + Ze^2/r_1 + Ze^2/r_2 - \frac{1}{2}(p_1^2 + p_2^2)]\psi_n = 0, \quad (64)$$

with hydrogenic eigenvalue for  $Z=2$  of

$$\epsilon_n = -2\alpha^2(1+n^{-2}). \quad (65)$$

The mixing coefficients  $a_n$  for  $n=2, 3, 4, 5, 6$  were determined by direct diagonalization of the Hamiltonian (30) using calculated values of matrix elements of  $e^2/r_{12}$  in this representation. Configurations such as  $2s3s$ ,  $2p3p$ ,  $3d4d$  were ascertained to contribute negligible mixing. Details and results are given in Appendix A and Tables II and III. With these mixing coefficients (62) was evaluated as follows: The expectation value of the Hamiltonian in (30) for  $\Psi_0(^3S_1)$  expanded as in (63) and using (9), (64) and (65), yields

$$\begin{aligned} \langle\Psi_0|e^2/r_{12}|\Psi_0\rangle &= W_0 - \sum_n a_n^2 \epsilon_n / \sum_n a_n^2 \\ &= W_0 + 2\alpha^2 [1 + (\sum_n a_n^2/n^2) / \sum_n a_n^2]. \end{aligned} \quad (66)$$

Substituting the experimental value of binding energy  $W_0$ , Eq. (53), and the  $a_n$  of Table III into (66) yields, for (62),

$$(\Delta g/2)_3 = -2.3 \times 10^{-6}. \quad (67)$$

The value in (67) as derived from (66) is not very sensitive to reasonable variations of binding energy or of mixing coefficients. Thus use of the theoretical binding energy  $W_0$ , Table III, in (66) instead of the experimental value, or use of arbitrarily altered values of  $a_n$  designed to yield the experimental value of  $W_0$  rather than the theoretical, or also a direct calculation of (62) via (63) and Tables II and III, do not change the value of (67) by more than  $\sim 0.1 \times 10^{-6}$ . It is incidentally concluded that the positive energy continuum configurations  $1sn's$ ,  $\infty > n' > 0$ , have no more than this effect on (67), if these configurations account for the difference between  $(W_0)_{\text{theor}}$  in Table III and  $(W_0)_{\text{exp}}$  in (53).

The  $g/2$ -value contributions (6), (52), (54), and (67) correspond to magnetic quantum number  $M=1$  [Eq. (38)]. By (5), (27), and (57) to (61) the linearly

$H$ -dependent magnetic energy to order  $\alpha^2$  is proportional to  $M$ .

#### BREIT-MARGENAU RESULT WITH SCREENING CONSTANTS

Breit and Margenau's result for the  $g/2$  value of a single  $s$  electron moving in a central field, obtained by evaluating  $-e\mathbf{a} \cdot \mathbf{A}$  in a Dirac eigenstate (compare Appendix B) is, to order  $\alpha^2$ ,

$$(g/2)_{BM} = \Delta E_1 / \mu_0 H = 1 - \frac{2}{3}\langle T \rangle. \quad (68)$$

Let two  $s$  electrons move independently of each other in the same binding potential  $V(r)$ . The Breit-Margenau  $g/2$  value of this hypothetical system is, by (68) (subscripts 1, 2 here denote electrons 1 and 2),

$$\begin{aligned} (g/2)_{BM} &= (\Delta E_1 + \Delta E_2) / 2\mu_0 H = \frac{1}{2}[1 - \frac{2}{3}\langle T_1 \rangle + 1 - \frac{2}{3}\langle T_2 \rangle] \\ &= 1 - \frac{1}{3}\langle T_1 + T_2 \rangle. \end{aligned} \quad (69)$$

The result (69), being a nonradiative contribution, is to be compared with the two-electron nonradiative contribution (50). This comparison shows that the simple sum of the kinetic energies of the two independent electrons in the hypothetical case is to be replaced in the

TABLE I. Breit-Margenau result with screening constants.

Case	$n_1$	$n_2$	$Z_1$	$Z_2$	$(\Delta g/2)_{BM}$
(a)	1	2	2	2	$-44.4 \times 10^{-6}$
(b)	1	2	2	1	-37.7
(c)	1	2	2.04	1.19	-40.1
(d)	1	2	2	1.19	-38.7
(e)	1	3	2	2	-39.5
(f)	1	3	2	1	-36.6

actual case by the kinetic energy of the system of two interacting electrons, which is not obviously decomposable into a sum of significant energies for each electron.

If  $V(r)$  in the hypothetical case is taken as a Coulomb potential with nuclear charge  $Z_1$  for one electron and  $Z_2$  for the other, then (69) becomes,

$$(\Delta g/2)_{BM} = (g/2)_{BM} - 1 = -\frac{1}{3}\alpha^2(Z_1^2/n_1^2 + Z_2^2/n_2^2). \quad (70)$$

Various combinations of  $Z_1$ ,  $Z_2$ ,  $n_1$  and  $n_2$  in (70) give the numerical results shown in Table I. Cases (a) to (d) assume a  $1s2s$  electron configuration. Case (a) assumes no screening of nuclear charge. Case (b) assumes complete screening by the  $1s$  core electron. Case (c) uses the screened nuclear charges derived by Hylleraas and Undheim<sup>19</sup> in connection with a variational calculation of the binding energy of  $^3S_1$  helium. In case (d)  $Z_2$  was adjusted to yield the correct value, Eq. (54). Cases (e) and (f) assume a  $1s3s$  electron configuration as possibly more representative of the superposition of  $1sn_s$  configurations making up the  $^3S_1$  eigenfunction (Appendix A), with unscreened and screened values of nuclear charge. Table I shows that reasonable values of screened nuclear charge or effective

quantum number yield results within about two parts per million of the correct value (54).

#### THE DIAMAGNETIC EFFECT

This effect<sup>20</sup> gives a negative  $\alpha^2\mu_0H$  contribution to  $g$  arising from reduction of the external magnetic field at a given electron due to the external magnetic field (diamagnetically) induced momentum in the other electrons. As might have been expected, this contribution is, for  $s$  electrons, just the spin dependent part of the Breit interaction contribution (60). This contribution can also be derived classically<sup>21</sup> as the cross-product  $\mathbf{A}_k^i \cdot \mathbf{A}_k^e$  terms of the sum of Hamiltonian contributions  $\frac{1}{2}(\mathbf{p}_k + e\mathbf{A}_k^i + e\mathbf{A}_k^e)^2$  for each electron, where  $\mathbf{A}_k^e$  is the external vector potential at electron  $k$  and  $\mathbf{A}_k^i = -\mu_0\sigma_l \times \mathbf{r}_{kl}/r_{kl}^3$  is the vector potential at electron  $k$  due to the spin magnetic moment of electron  $l$  (to be summed over  $l$ ). A more general diamagnetic interpretation is discussed in the following paper.<sup>13</sup>

#### COMPARISON OF THEORY AND EXPERIMENT

The theoretical  $g/2$  value of  $^3S_1$  helium is given to order  $\alpha^2$  by (6), (50), (54) and (67) as

$$(g/2)_{\text{He, theor}} = \Delta E_H/2\mu_0H = \Delta E_{A0} + \Delta E_{Hr} + (\Delta E_{A12} + \Delta E_{A3}) \quad (71)$$

$$= 1 + (0.0011614 - 16 \times 10^{-6}) - (38.7 + 2.3)10^{-6} \quad (72)$$

$$= 1.001104 \pm 1 \times 10^{-6}. \quad (73)$$

The indicated precision of this number,  $\pm 1 \times 10^{-6}$ , stems from the first neglected self-radiative contributions of order  $\alpha^3$  previously mentioned. The first neglected nonradiative contributions are of order  $\alpha^4 Z^4$ ,  $\alpha^2 Z^2 m/M$ , hence  $\ll 10^{-6}$ .

The experimental result<sup>3</sup> is the ratio of  $g_J$  value in  $^3S_1$  helium and in  $^2S_{\frac{1}{2}}$  hydrogen, or

$$(g_{\text{He}}/g_{\text{H}})_{\text{exp}} = 1 - (11 \pm 16)10^{-6}. \quad (74)$$

If the experiment<sup>3</sup> is considered independently of the Koenig, Prodel and Kusch (KPK) hydrogen  $g$ -value experiment,<sup>1</sup> the experimental ratio (74) is to be compared with the theoretical ratio

$$(g_{\text{He}}/g_{\text{H}})_{\text{theor}} = \frac{(1.0011454 - 41 \times 10^{-6})}{(1.0011454 - 17.8 \times 10^{-6})} \quad (75)$$

$$= 1 - (23 \pm 1)10^{-6}, \quad (76)$$

in which, for hydrogen, the same self-radiative contribution as for helium and a Breit-Margenau contribution of  $\frac{2}{3}W = -\frac{1}{3}\alpha^2$ , Eq. (68), have been used. Alternatively, assuming the theory to have been satisfactorily verified for hydrogen by the KPK experiment and hence multiplying the experimental ratio (74) by the denominator in (75) gives

$$(g/2)_{\text{He, exp}} = 1.001117 \pm 16 \times 10^{-6}, \quad (77)$$

which is to be compared with (73). (Multiplication of the ratio (74) by KPK's experimental result for  $(g/2)_{\text{H}}$  would give the same mean value as (77) but somewhat higher limits of error.)

The agreement between (74) and (76), and between (73) and (77), is within the assigned theoretical and experimental uncertainty, of which the experimental uncertainty is greater than the theoretical by an order of magnitude. The agreement between (74) and (76) tends to substantiate the additivity properties of the radiative and nonradiative corrections in hydrogen and in helium and to some extent the magnitude of the nonradiative corrections in helium relative to hydrogen. The experimental uncertainty is too large by a factor of ten to permit any conclusion as to the mutual radiative or Breit contribution of  $-2.3 \times 10^{-6}$  to the theoretical helium  $g/2$  value. Comparison of (73) and (77) indicates that the helium experiment<sup>3</sup> in combination with either the hydrogen theory or experiment<sup>1</sup> tends to substantiate the nonradiative contribution to the theoretical helium  $g/2$  value and does not contradict the existence of the fourth-order self-radiative contribution.

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#### APPENDIX A. MATRIX ELEMENTS AND CONFIGURATION MIXING OF $e^2/r_{12}$

The nonrelativistic matrix elements of the electrostatic interaction  $e^2/r_{12}$  between nonrelativistic zero-order  $^3S_1$  states corresponding to various  $1sns$  electron configurations are<sup>22</sup>

$$\begin{aligned} \langle 1sn_1s | e^2/r_{12} | 1sn_2s \rangle &= \frac{1}{2} \langle u_1(100)u_2(n_100) - u_2(100)u_1(n_100) | (e^2/r_{12}) | \\ &\quad | u_1(100)u_2(n_200) - u_2(100)u_1(n_200) \rangle \\ &= (Ze^2/a) [R^0(10n_10, 10n_20) \\ &\quad - R^0(10n_10, n_2010)], \quad (A.1) \end{aligned}$$

where  $u_1(nlm_i)$  is the one electron nonrelativistic Coulomb eigenfunction for electron 1 with quantum numbers  $n$ ,  $l$ ,  $m_i$ , etc., and  $a = \hbar^2/me^2$ . The direct integral can be written as

$$\begin{aligned} R^0(10n_10, 10n_20) &= \int_0^\infty d\rho R_{n_10} R_{n_20} \rho \int_0^\rho R_{10}^2(\rho) \rho^2 d\rho \\ &\quad + \int_0^\infty d\rho R_{n_10} R_{n_20} \rho^2 \int_\rho^\infty R_{10}^2(\rho) \rho d\rho \quad (A.2) \end{aligned}$$

$$\equiv S(n_1, n_2) - T(n_1, n_2), \quad (A.3)$$

<sup>20</sup> W. E. Lamb, Jr., Phys. Rev. **60**, 817 (1941).

<sup>21</sup> N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

<sup>22</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 174.

where, setting  $n_1 = m, n_2 = n,$

$$S(m, n) = \int_0^\infty \rho R_{m0} R_{n0} d\rho, \quad (A.4)$$

$$T(m, n) = \int_0^\infty (\rho + \rho^2) e^{-2\rho} R_{m0} R_{n0} d\rho. \quad (A.5)$$

$R_{m0}(\rho)$  is the Coulomb radial eigenfunction with  $\rho = Zr/a$  and quantum numbers  $n = m, l = 0,$  etc. The exchange integral can be written in various ways, of which one is

$R^0(10n_10, n_2010)$

$$\begin{aligned} &= \int_0^\infty d\rho R_{10} R_{n_10} \rho^2 \int_\rho^\infty R_{10} R_{n_20} \rho d\rho \\ &+ \int_0^\infty d\rho R_{10} R_{n_20} \rho^2 \int_\rho^\infty R_{10} R_{n_10} \rho d\rho. \end{aligned} \quad (A.6)$$

$$S(m, n) = 4(m/n)^{\frac{1}{2}} \frac{1}{(n+m)^2} \frac{n!}{(n-m)!m!} \left(\frac{n-m}{n+m}\right)^{n-m} F\left[-m+1, n+1, n-m+1, \left(\frac{n-m}{n+m}\right)^2\right], \quad (A.7)$$

$$\begin{aligned} T(m, n) &= \frac{4(mn)^{\frac{1}{2}} (2mn+n-m)^{n-2} (2mn+m-n)^{m-2}}{(2mn+m+n)^{m+n}} \left\{ \left(\frac{2mn+m-n}{2mn+m+n}\right) [(2m+1)^2 n^2 - m^2 + 4m^3 n^2] \right. \\ &\quad \left. \times F\left[1-m, 1-n, 2, \frac{4mn}{4m^2 n^2 - (n-m)^2}\right] - 4(m-1)m^2 n^2 F\left[2-m, 1-n, 2, \frac{4mn}{4m^2 n^2 - (n-m)^2}\right] \right\}, \end{aligned} \quad (A.8)$$

where  $n \geq m$  and  $F$  is the hypergeometric function

$$F(\alpha, \beta, \gamma, x) = 1 + \frac{\alpha\beta}{\gamma} x + \frac{\alpha(\alpha+1)\beta(\beta+1)}{\gamma(\gamma+1)2!} x^2 + \dots \quad (A.9)$$

The formulas (A.7, 8) are for discrete states,  $n, m,$  positive integral. The formulas for one or both states in the continuum are similar but more complicated.

The direct integral (A.2) was computed by (A.7, 8) for  $2 \leq n_1, n_2 \leq 6.$  The exchange integral (A.6) was computed by direct substitution of the radial eigenfunctions in (A.6) or the equivalent, for  $2 \leq n_1, n_2 \leq 4,$  and estimated graphically by extrapolation for  $n_1, n_2 = 5, 6.$  The difference between direct and exchange integrals is by (A.1) the desired matrix element of  $e^2/r_{12},$  in units  $Ze^2/a.$  The results are shown in Table II. Also included in Table II are the matrix elements to some 2-electron-excited configurations as follows:

$$\langle 1s2s | e^2/r_{12} | 2s3s \rangle = (Ze^2/a) [R^0(1020, 2030) - R^0(1020, 3020)], \quad (A.10)$$

$$\langle 1s2s | e^2/r_{12} | 2p3p \rangle = (Ze^2/\sqrt{3}a) [-R^1(1020, 2131) + R^1(1020, 3121)], \quad (A.11)$$

TABLE II. Electrostatic interaction matrix elements (in units of  $Ze^2/a$ ).<sup>22</sup>

$1s m s, 1s n s$	$R^0(10m0, 10n0)$	$R^0(10m0, n010)$	$\mathcal{J}C'_{1sm, 1sn}$
1s2s, 1s2s	0.20988	0.02195	0.18793
2 3	0.05053	0.01122	0.03930
2 4	0.02871	0.00710	0.02161
2 5	0.01927	0.0051 <sup>a</sup>	0.0142
2 6	0.01441	0.0038 <sup>a</sup>	0.0106
3 3	0.09949	0.00577	0.09372
3 4	0.02884	0.00367	0.02517
3 5	0.01774	0.0027 <sup>a</sup>	0.0150
3 6	0.01170	0.0022 <sup>a</sup>	0.0095
4 4	0.05763	0.00234	0.05529
4 5	0.01842	0.0018 <sup>a</sup>	0.0166
4 6	0.01190	0.0016 <sup>a</sup>	0.0103
5 5	0.03752	0.0013 <sup>a</sup>	0.0362
5 6	0.01273	0.0011 <sup>a</sup>	0.0116
6 6	0.02652	0.0009 <sup>a</sup>	0.0256
1s2s, 2s3s <sup>b</sup>	0.004158	0.003936	0.000222
1s2s, 2p3p <sup>b</sup>	-0.017057	-0.004588	-0.00719
1s2s, 3d4d <sup>b</sup>	-0.002413	-0.002739	0.000146

<sup>a</sup> Estimated by graphical extrapolation.  
<sup>b</sup> See Eqs. (A.10, 11, 12).

The direct integral (A.2, 3) was evaluated by the method of Gordon<sup>23</sup> as

$$\langle 1s2s | e^2/r_{12} | 3d4d \rangle = (Ze^2/(\sqrt{5}a)) [R^2(1020, 3242) - R^2(1020, 4232)]. \quad (A.12)$$

The direct and exchange integrals for these matrix elements were computed by direct substitution of Coulomb radial eigenfunctions into formulas<sup>22</sup> equivalent to (A.2, 6).

The mixture of the configurations of Table II making up the  $^3S_1$  state was determined by solving

$$\sum_{n=2}^6 \mathcal{J}C_{mna} a_n = W' a_m, \quad m = 2, \dots, 6. \quad (A.13)$$

simultaneously for  $W', a_3, a_4, a_5, a_6$  with  $a_2 = 1$  (here  $a_m$  means  $a_{1s2s, 1sm}$ ), using for  $\mathcal{J}C$  the nonrelativistic two-electron Schrödinger Hamiltonian with Coulomb interactions. The results, after making a small allowance by extrapolation for all  $m, n > 6$  are given in Table III. The calculated binding energy  $-1.0859$  of  $^3S_1$  helium (in units of 4 Ry) may be compared with the experimental value<sup>19</sup>  $-1.08765$  and with that derived by Hylleraas and Undheim<sup>20</sup> by a variational method,  $-1.08761.$  To compare ionization energies (in units

<sup>23</sup> W. Gordon, Ann. Physik 2, 1031 (1929).



4 Ry) subtract one from each of these numbers. Probably the continuum states of type  $1sns$  account for most of the difference of about two percent between the present result for ionization energy and the experimental value.

#### APPENDIX B. MATRIX ELEMENTS OF $-e\alpha \cdot A$

As the result of initial attempts to calculate  $\alpha^2\mu_0H$  contributions by direct representation of  $U(3S_1)$  as a

$$u_{nkjm} = \begin{pmatrix} i[(j-m+1)/(2j+2)]^{1/2} f_{nk}(r) Y_{j+\frac{1}{2}, m-\frac{1}{2}}(\theta, \phi) \\ i[(j+m+1)/(2j+2)]^{1/2} f_{nk}(r) Y_{j+\frac{1}{2}, m+\frac{1}{2}}(\theta, \phi) \\ [(j+m)/2j]^{1/2} g_{nk}(r) Y_{j-\frac{1}{2}, m-\frac{1}{2}}(\theta, \phi) \\ -[(j-m)/2j]^{1/2} g_{nk}(r) Y_{j-\frac{1}{2}, m+\frac{1}{2}}(\theta, \phi) \end{pmatrix}, \quad \begin{matrix} (j=l+\frac{1}{2}) \\ (k=-l-1=-(j+\frac{1}{2})) \end{matrix} \quad (\text{B.1})$$

$$u_{nkjm} = \begin{pmatrix} i[(j+m)/2j]^{1/2} f_{nk}(r) Y_{j-\frac{1}{2}, m-\frac{1}{2}}(\theta, \phi) \\ -i[(j-m)/2j]^{1/2} f_{nk}(r) Y_{j-\frac{1}{2}, m+\frac{1}{2}}(\theta, \phi) \\ [(j-m+1)/(2j+2)]^{1/2} g_{nk}(r) Y_{j+\frac{1}{2}, m-\frac{1}{2}}(\theta, \phi) \\ [(j+m+1)/(2j+2)]^{1/2} g_{nk}(r) Y_{j+\frac{1}{2}, m+\frac{1}{2}}(\theta, \phi) \end{pmatrix}, \quad \begin{matrix} (j=l-\frac{1}{2}) \\ (k=l=j+\frac{1}{2}) \end{matrix} \quad (\text{B.2})$$

in which the angular functions  $Y_{lm}(\theta, \phi)$  are the normalized surface harmonics,

$$Y_{lm}(\theta, \phi) = (2\pi)^{-1/2} \mathcal{P}_{lm}(\theta) e^{im\phi}, \quad (\text{B.3})$$

and  $\mathcal{P}_{lm}(\theta)$  is the normalized associated Legendre polynomial. The radial functions  $f_{nk}(r)$ ,  $g_{nk}(r)$  are the regular solutions of

$$(E+1+\gamma^2/\rho)f = \gamma[dg/d\rho + (k+1)g/\rho], \quad (\text{B.4})$$

$$(E-1+\gamma^2/\rho)g = \gamma[-df/d\rho + (k-1)f/\rho], \quad (\text{B.5})$$

where  $\rho = Zr/a$ ,  $a = \hbar^2/mc^2$ ,  $\gamma = \alpha Z \simeq Z/137$ , and  $E$  is the energy eigenvalue in units  $mc^2$ ,

$$E_{nk} = 1 - \frac{\gamma^2}{2n^2} - \frac{\gamma^4}{2n^4} \left( \frac{n-3}{|k|} - \frac{3}{4} \right) + \dots \quad (\text{B.6})$$

Specialization to a Coulomb binding potential has been made in (B.4, 5). Let  $u_i, v_j, i, j=1, 2, 3, 4$  denote any two Dirac wave functions (subscripts  $i, j$  denote spinor components here). Then the matrix element to be calculated is

$$\begin{aligned} -e\langle u | \alpha \cdot A | v \rangle &= -\frac{e}{2} \langle u | \alpha \cdot \mathbf{H} \times \mathbf{r} | v \rangle \\ &= -\frac{eH}{2} \langle u | r \sin\theta (\alpha_y \cos\phi - \alpha_x \sin\phi) | v \rangle \\ &= \frac{ieH}{2} \int r \sin\theta [u_1^* e^{-i\phi} v_4 - u_2^* e^{i\phi} v_3 \\ &\quad + u_3^* e^{-i\phi} v_2 - u_4^* e^{i\phi} v_1] d\tau, \quad (\text{B.7}) \end{aligned}$$

TABLE III. Diagonalization of Schrödinger two-electron Hamiltonian.

$W'$ (unit, 4 Ry)	$a_3'$	$a_4'$	$a_6'$	$a_5'$	$a_7'$	$a_8'$	$a_9'$
-1.0859	0.523	0.090	0.052	0.049	0.00027	-0.0087	0.00014

sum of products of Dirac one-electron Coulomb wave functions, matrix elements of  $-e\alpha \cdot A$  were calculated. They are presented here for possible usefulness in this type of problem.

To be calculated to order  $\alpha^2\mu_0H$  is the matrix element of  $-e\alpha \cdot A$  between two Dirac one-electron Coulomb wave functions, where  $\mathbf{A}$  is the vector potential of a uniform magnetic field  $H$  in the  $z$  direction. The Dirac wave functions are<sup>24</sup>

where \* denotes complex conjugate and the integration is over  $r, \theta, \phi$ . Substitution of the various possible combinations of wave function (B.1, 2) into (B.7) yields (numerical subscripts now denote particular values of quantum numbers)

$$\begin{aligned} -e\langle n_1 k_2 j_1 = l_1 \pm \frac{1}{2}, m_1 | \alpha \cdot A | n_2 k_2 j_2 = l_2 \pm \frac{1}{2}, m_2 \rangle \\ = \mp \delta_{m_1 m_2} \delta_{j_1 j_2} \frac{m}{j} \left( \frac{2j+1}{2j+2} \right) \frac{eH}{2} \\ \times \int_0^\infty (f_1 g_2 + f_2 g_1) r^3 dr, \quad (\text{B.8}) \end{aligned}$$

where  $m = m_1 = m_2$ ,  $j = j_1 = j_2$ ,  $f_1 = f_{n_1 k_1}(r)$ , etc.

$$\begin{aligned} -e\langle n_1 k_1 j_1 = l_1 + \frac{1}{2}, m_1 | \alpha \cdot A | n_2 k_2 j_2 = l_2 - \frac{1}{2}, m_2 \rangle \\ = \delta_{m_1 m_2} \frac{eH}{2} \left[ \frac{(j_2^2 - m^2)^{1/2}}{2j_2} \delta_{j_2, j_1+1} \right. \\ \left. - \frac{(j_1^2 - m^2)^{1/2}}{2j_1} \delta_{j_2, j_1-1} \right] \int_0^\infty (f_1 g_2 + f_2 g_1) r^3 dr. \quad (\text{B.9}) \end{aligned}$$

The radial integrals in (B.8, 9) are next evaluated to order  $\gamma^2$  in terms of integrals of nonrelativistic hydrogenic radial functions. Thus, multiply (B.4) for  $f_1$  by  $g_2$ , (B.4) for  $f_2$  by  $g_1$ , (B.5) for  $g_1$  by  $f_2$ , (B.5) for  $g_2$  by  $f_1$  and add the four resulting equations to get

$$\begin{aligned} \left( E_1 + E_2 + \frac{2\gamma^2}{\rho} \right) (f_1 g_2 + f_2 g_1) \\ = \gamma \left[ \frac{d}{d\rho} (g_1 g_2 - f_1 f_2) + (k_1 + k_2 + 2) \frac{g_1 g_2}{\rho} \right. \\ \left. + (k_1 + k_2 - 2) \frac{f_1 f_2}{\rho} \right]. \quad (\text{B.10}) \end{aligned}$$

<sup>24</sup> Reference 12, p. 311.

The functions  $f(\rho)$  and  $g(\rho)$  are next written as power series in  $\gamma = \alpha Z$ . By (B.4, 5)  $g$  is the "large" wave function for positive energy states and starts off with the zeroth power of  $\gamma$ . By (B.4)  $f$  starts off with the first power of  $\gamma$ . Since (B.4, 5) expressed in terms of  $f/\gamma$  and  $g$  contain  $\gamma$  only as  $\gamma^2$ , there are no odd powers in the series for  $f/\gamma$  and  $g$ . Hence

$$f = \gamma(f^{(0)} + \gamma^2 f^{(2)} + \dots), \quad (\text{B.11})$$

$$g = g^{(0)} + \gamma^2 g^{(2)} + \dots \quad (\text{B.12})$$

The zero-order function  $g^{(0)}$  is the usual Schrödinger nonrelativistic hydrogenic radial function

$$g_{nk}^{(0)} = R_{nl}. \quad (\text{B.13})$$

Dividing through in (B.10) by the first factor and substitution therein of (B.6, 11, 12) yields, to order  $\gamma^2$ ,

$$\begin{aligned} \frac{2}{\gamma}(f_1 g_2 + f_2 g_1) &= \left[ \frac{d}{d\rho} + \frac{(k_1 + k_2 + 2)}{\rho} \right] g_1^{(0)} g_2^{(0)} \\ &+ \gamma^2 \left\{ \left[ \frac{d}{d\rho} + \frac{k_1 + k_2 + 2}{\rho} \right] (g_1^{(0)} g_2^{(2)} + g_1^{(2)} g_2^{(0)}) \right. \\ &- \left[ \frac{d}{d\rho} - \frac{(k_1 + k_2 - 2)}{\rho} \right] f_1^{(0)} f_2^{(0)} + \left( \frac{1}{4n_1^2} + \frac{1}{4n_2^2} - \frac{1}{\rho} \right) \\ &\left. \times \left[ \frac{d}{d\rho} + \frac{(k_1 + k_2 + 2)}{\rho} \right] g_1^{(0)} g_2^{(0)} \right\}. \quad (\text{B.14}) \end{aligned}$$

Integration by  $\rho^3 d\rho$  and integration by parts (assuming regularity at infinity) yields

$$\begin{aligned} \frac{2}{\gamma} \int_0^\infty (f_1 g_2 + f_2 g_1) \rho^3 d\rho &= (k_1 + k_2 - 1) \int_0^\infty g_1^{(0)} g_2^{(0)} \rho^2 d\rho \\ &+ \gamma^2 \left[ (k_1 + k_2 - 1) \int_0^\infty (g_1^{(0)} g_2^{(2)} + g_1^{(2)} g_2^{(0)}) \rho^2 d\rho \right. \\ &+ (k_1 + k_2 + 1) \int_0^\infty f_1^{(0)} f_2^{(0)} \rho^2 d\rho \\ &+ \frac{1}{4} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) (k_1 + k_2 - 1) \int_0^\infty g_1^{(0)} g_2^{(0)} \rho^2 d\rho \\ &\left. - (k_1 + k_2) \int_0^\infty g_1^{(0)} g_2^{(0)} \rho d\rho \right]. \quad (\text{B.15}) \end{aligned}$$

Further reduction can be made on the assumption  $k_1 = k_2$  as is usually the case. The orthogonality relations for  $f$  and  $g$  can now be used. Thus, from (B.4, 5) is readily derived

$$\int_0^\infty (F_1 F_2 + G_1 G_2) \rho^2 d\rho = \delta_{12}, \quad (\text{B.16})$$

where the subscripts 1, 2 now denote only  $n_1, n_2$

( $k_1 = k_2 = k$  being understood) and

$$F = (a/Z)^{3/2} f, \quad G = (a/Z)^{3/2} g, \quad (\text{B.17})$$

are nondimensional wave functions. In case both  $n_1, n_2$  belong to the continuum, the Kronecker delta in (B.16) is to be replaced by the Dirac  $\delta$  function. Expanding (B.16) to order  $\gamma^2$  yields

$$\int_0^\infty [G_1^{(0)} G_2^{(0)} + \gamma^2 (F_1^{(0)} F_2^{(0)} + G_1^{(0)} G_2^{(2)} + G_1^{(2)} G_2^{(0)})] \rho^2 d\rho = \delta_{12}. \quad (\text{B.18})$$

Substitution in (B.15) yields

$$\begin{aligned} \frac{1}{\gamma} \int_0^\infty (F_1 G_2 + F_2 G_1) \rho^3 d\rho &= (k - \frac{1}{2}) \delta_{12} \\ &+ \gamma^2 \left[ \int_0^\infty F_1^{(0)} F_2^{(0)} \rho^2 d\rho + \frac{(2k-1)}{8} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \delta_{12} \right. \\ &\left. - k \int_0^\infty G_1^{(0)} G_2^{(0)} \rho d\rho \right]. \quad (\text{B.19}) \end{aligned}$$

Further reduction of  $F_1^{(0)} F_2^{(0)}$  to  $G_1^{(0)} G_2^{(0)}$  can be made. Thus, multiply (B.4) for  $f_1$  by  $f_2$  and (B.4) for  $f_2$  by  $f_1$  and add. Multiply (B.5) for  $g_1$  by  $g_2$  and (B.5) for  $g_2$  by  $g_1$  and add. Subtract the resulting two equations from each other and integrate by  $\rho^2 d\rho$ . Integrate the right-hand side by parts. For  $k_1 = k_2$  it reduces to zero. The left-hand side equated to zero can be written

$$\begin{aligned} \int_0^\infty \left[ \frac{(E_1 + E_2)}{2} + 1 + \frac{\gamma^2}{\rho} \right] F_1 F_2 \rho^2 d\rho \\ = \int_0^\infty \left[ \frac{(E_1 + E_2)}{2} - 1 + \frac{\gamma^2}{\rho} \right] G_1 G_2 \rho^2 d\rho, \quad (\text{B.20}) \end{aligned}$$

which yields

$$\begin{aligned} \int_0^\infty F_1^{(0)} F_2^{(0)} \rho^2 d\rho &= -\frac{1}{8} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \int_0^\infty G_1^{(0)} G_2^{(0)} \rho^2 d\rho \\ &+ \frac{1}{2} \int_0^\infty G_1^{(0)} G_2^{(0)} \rho d\rho. \quad (\text{B.21}) \end{aligned}$$

Substituting (B.21) into (B.19) yields the desired radial integral to order  $\gamma^2$

$$\begin{aligned} \frac{1}{\gamma} \int_0^\infty (F_1 G_2 + F_2 G_1) \rho^3 d\rho \\ = (k - \frac{1}{2}) \delta_{12} + \gamma^2 \left[ \frac{(k-1)}{4} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \delta_{12} \right. \\ \left. + (\frac{1}{2} - k) \int_0^\infty G_1^{(0)} G_2^{(0)} \rho d\rho \right]. \quad (\text{B.22}) \end{aligned}$$

Equation (B.22) in (B.8) yields the desired matrix element for  $k_1=k_2=k$ . Note that by (B.17) and the definitions after (B.5) the dimensional radial integral in (B.8) is given in terms of the nondimensional integral (B.22) by

$$\frac{eH}{2} \int_0^\infty (f_1 g_2 + f_2 g_1) r^3 dr = \mu_0 H \frac{1}{\gamma} \int_0^\infty (F_1 G_2 + F_2 G_1) \rho^3 d\rho. \quad (\text{B.23})$$

For  $k_1 \neq k_2$ , as in (B.9), the more complicated (B.15) appears to be necessary. The Breit-Margenau result (70) for a Coulomb field is obtained by setting  $n_1=n_2$  and

$$\int_0^\infty G_1^{(0)2} \rho d\rho = (1/\rho)_{n_1 n_2} = 1/n^2 \quad (\text{B.24})$$

in (B.22). The matrix element  $(1/\rho)_{n_1 n_2}$  on the right hand side in (B.22) is given by Eqs. (A.4, 7) in Appendix A.

## Relativistic Contributions to the Magnetic Moment of $n$ -Electron Atoms

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A Schrödinger-Pauli approximation wave equation for an  $n$ -electron atom in an external magnetic field  $H$  is derived from a Dirac equation by straightforward extension of the procedure for  $n=2$ . The order  $\alpha^2$  terms in the resulting Hamiltonian contain corresponding  $\alpha^2 \mu_0 H$  and  $\alpha^2 \text{Ry}$  (fine structure) parts. The  $\alpha^2 \mu_0 H$  terms can be arranged as a sum of the existing relativistic bound state contributions due to Breit, Margenau, and Lamb, and an additional contribution. The additional contribution is analogous to the spin-orbit contribution to fine structure. In the  ${}^2S_{1/2}$  ground state of the heavier alkalis it is estimated to yield a positive contribution to the atomic  $g$  value of the order of ten times the aforementioned (negative) contributions, which may help to account for some experimental results.

### INTRODUCTION

**P**RECISION measurements of the Zeeman effect by atomic beam spectroscopy<sup>1</sup> have yielded deviations from unity of the  $g_J$  values of the heavier alkali atoms in their ground state,  ${}^2S_{1/2}$ . The relevant experimental results are:

rubidium relative to sodium,

$$(g_J)_{\text{Rb}} / (g_J)_{\text{Na}} = 1 + 5 \times 10^{-5}; \quad (1a)$$

cesium relative to sodium,

$$(g_J)_{\text{Cs}} / (g_J)_{\text{Na}} = 1 + 13.4 \times 10^{-5}, \quad (1b)$$

with a statistical probable error of approximately  $\pm 1 \times 10^{-5}$ . The  $g_J$  of lithium, sodium, and potassium were found to be identical to within  $\pm 2.5 \times 10^{-5}$ . An additional measurement is reported by Franken and Koenig:<sup>2</sup>

potassium relative to hydrogen,

$$(g_J)_{\text{K}} / (g_J)_{\text{H}} = 1 + (1.6 \pm 0.4) \times 10^{-5}. \quad (2)$$

The results (1) and (2) have so far not been quantitatively explained (i.e., to the experimental accuracy), nor will they be in this paper. A qualitative interpretation of at least part of the effects involved will however be added to the existing one.<sup>3</sup>

The deviations from unity in (1) and (2) should be attributable to relativistic effects inasmuch as non-relativistic theory predicts  $g_J = 1$  in a  ${}^2S_{1/2}$  state. Quantum-electrodynamic self-radiative effects on a single free electron, producing an altered "intrinsic" magnetic moment of the electron,<sup>4</sup> would be expected to affect similar Zeeman levels of one-electron spectra similarly and hence to yield no deviations from unity in the ratios (1) and (2). Of the various bound-state relativistic effects, i.e., effects arising from the atom obeying a relativistic rather than a nonrelativistic wave equation, those due to Breit and Margenau<sup>5</sup> and to Lamb<sup>6</sup> appear too small by a factor of the order of ten.<sup>7</sup> However effects of breakdown of Russell-Saunders coupling by a combination of electrostatic interaction and spin-orbit coupling mixing states of higher configurations into the ground state have been estimated by Phillips<sup>8</sup> to yield differing amounts to the magnetic moments of the alkalis of the right order of magnitude to account for at least part of (1) and (2).

<sup>4</sup> J. Schwinger, Phys. Rev. **82**, 664 (1951); R. Karplus and N. M. Kroll, Phys. Rev. **77**, 536 (1950).

<sup>5</sup> G. Breit, Nature **122**, 649 (1928); H. Margenau, Phys. Rev. **57**, 383 (1940); N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 72.

<sup>6</sup> W. E. Lamb, Jr., Phys. Rev. **60**, 817 (1941).

<sup>7</sup> See W. Perl and V. Hughes (preceding paper) [Phys. Rev. **91**, 842 (1953)] for an evaluation of these effects in  ${}^3S_1$  helium.

<sup>1</sup> P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

<sup>2</sup> P. Franken and S. Koenig, Phys. Rev. **88**, 199 (1952).

<sup>3</sup> M. Phillips, Phys. Rev. **88**, 202 (1952).