

and

$$G_{mn}(\tau) = \frac{1}{2} J^2 \sum_{i \neq j} \langle \delta_{ij}(t) \delta_{ij}(t+\tau) \rangle_{av} |\langle m | \mathbf{I}^i \cdot \mathbf{I}^j | n \rangle|^2.$$

In order to calculate τ_c' , we may as well calculate the correlation time of

$$K(\tau) = \sum_i \langle \delta_{ij}(t) \delta_{ij}(t+\tau) \rangle_{av}$$

which we shall define by the condition that

$$S(\omega) \sim (2/\omega^2 \tau_c') K(0) \quad \text{for } \omega \tau_c' \gg 1,$$

where

$$S(\omega) = \int_{-\infty}^{+\infty} K(\tau) e^{-i\omega\tau} d\tau.$$

Then

$$T_{\text{EL}}^{-1} = \frac{K(0)}{z\tau_c'} = (2z)^{-1} \lim_{\omega \rightarrow \infty} [\omega^2 S(\omega)]. \quad (\text{B9})$$

This can be computed using the theory of random flights, in the same way as Torrey used it to treat the nuclear spin relaxation by translational diffusion.¹⁶ It is easily found that for a hexagonal close-packed lattice (β -phase He³), in the limit $\omega \rightarrow \infty$, $S(\omega) \sim (32/\omega^2 \tau_c)$, which gives for the exchange-lattice relaxation time

$$T_{\text{EL}} = \frac{3}{4} \tau_c. \quad (\text{B10})$$

Approximately the same result will hold for any lattice.

Second-Order Hyperfine Structure in Hydrogenic Atoms*

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A calculation of the hyperfine splittings in the $1s$ and $2s$ levels of hydrogenic atoms is made. Second-order terms in the nuclear magnetic dipole moment and terms of comparable magnitude arising from nuclear structure effects are calculated. Also included is a term derived by the use of "uncrossed" and "crossed" photon diagrams; this term is necessary because the one-electron Dirac Hamiltonian which is used evidently does not properly take certain quantum electrodynamic effects into account. In order to compare with experiment the ratio of the hyperfine splitting in the $2s$ state to the splitting in the $1s$ state is taken and evaluated for the case of the hydrogen atom; this result is combined with a previous result and the final theoretical value of $\frac{1}{3}(1.00003445 \pm 0.00000002)$ is in agreement with the experimental value of $\frac{1}{3}(1.000034495 \pm 0.000000060)$. Complete agreement has not yet been reached with respect to the splittings themselves. The calculation consists in solving the separated radial equations arising from the Dirac Hamiltonian in which the nuclear magnetic moment and the finite size of the nucleus are considered as perturbations. An iteration scheme is devised which uses certain properties of the unperturbed solution; this method may well have applications elsewhere.

I. INTRODUCTION

THE present paper is concerned with an attempt at a relativistic calculation of contributions to the shift and splitting of energy levels in the s states of hydrogenic atoms arising from hyperfine structure (hfs) interaction in second order. The consideration of this problem was prompted originally by the existence of two apparent discrepancies between experiment¹ and

first-order hfs calculation.^{2,3} More recent experimental values⁴ do not remove the discrepancies. The first was in respect to the ratio of hfs splittings in the $2s$ and $1s$ states of hydrogen. Since that time some errors in the original calculations have been uncovered by Zwanziger⁵ and their correction has eliminated the discrepancy. A recent calculation by Sternheim⁶ gives additional terms to the ratio; the agreement between theory and experi-

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¹ P. Kusch, Phys. Rev. **100**, 1188 (1955); and J. W. Heberle, H. A. Reich, and P. Kusch, Phys. Rev. **101**, 612 (1956).

² M. Mittleman, Phys. Rev. **107**, 1170 (1957).

³ For a review of the subject see G. W. Series, *Spectrum of Atomic Hydrogen* (Oxford University Press, London, 1957), especially Chap. XI.

⁴ F. M. Pipkin and R. H. Lambert, Phys. Rev. **127**, 787 (1962). J. Gruenebaum and P. Kusch, Columbia Radiation Laboratory Quarterly Report, 14 September 1960 (unpublished); their result is $\Delta\nu(2s) = 177\,556.842 \pm 0.010$ kc/sec for H^1 .

⁵ D. E. Zwanziger, Phys. Rev. **121**, 1128 (1961).

⁶ M. M. Sternheim, Phys. Rev. **130**, 211 (1963).

ment is retained. The second discrepancy is in the absolute hfs splitting of the $1s$ state of hydrogen. Calculations by Zemach⁷ and by Iddings and Platzman⁸ to determine the effect of the finite electric and magnetic radii of the proton on this splitting suggested that there was a discordance between the observed value and that calculated using the values for the radii determined by Hofstadter⁹ in high-energy electron scattering experiments. This discrepancy apparently still exists.

The effect of second-order hfs interaction on the ratio of hfs splittings in the $1s$ and $2s$ states of hydrogen has previously been calculated nonrelativistically by Schwartz.¹⁰ A further (partial) calculation on the basis of the Dirac equation has been carried out by Mittleman (whose results are in agreement with the more complete calculations of the present authors, where they overlap) but these results are not in agreement with those of Schwartz. Recently Sternheim,¹¹ after a suggestion by Kroll, has traced the source of the discordance to the fact that the calculations on the basis of the Dirac equation do not properly take into account the "crossed-photon" term in the second-order interaction, and has demonstrated that when this term is taken into account the result agrees with that of Schwartz and thus leaves little doubt that Schwartz's result is correct.

While the methods of Schwartz and Sternheim are adequate to deal with the problem of the *ratio* of the hfs splittings, they do not yield results for the second-order contributions to the splittings themselves. The present paper introduces what we believe to be a novel method of dealing with the second-order problem which, insofar as the crossed-photon term is neglected, does yield results for the individual splittings themselves. It therefore has some methodological interest in spite of the fact that it, as yet, cannot yield a definitive answer for the second-order contributions to the splittings with the crossed-photon term included.

To detail the source of the difficulties involved in these calculations, we remark first that while the smallness of the hfs interaction (in first order) might suggest that straightforward second-order perturbation theory be applied to the problem, a severe difficulty is nevertheless encountered. If the nucleus is represented in its magnetic effect by a point dipole then the interaction between the electron and nucleus contains a term proportional to a Dirac delta function in their separation. While such a perturbation can be treated straightforwardly in first order, it yields divergences in second order since such a singular interaction allows no acceptable solutions of the Schrödinger or Dirac equations. Solutions can exist if the nuclear magneti-

zation is spread over a spatial region of finite extent. In principle, under these circumstances, a second-order perturbation theory would suffice to carry out the calculation. However, the hfs interaction has actually a large magnitude though it is spread only over a small spatial region and this means that the interaction will have substantial matrix elements connecting the states under consideration with many states very distant in energy, and a sum over these many virtual intermediate states is required. This problem is solved in the method presented here by employing an iteration scheme for calculating the perturbation of the wave function by the perturbing potential. Actually what is calculated is not the wave function itself but the ratios of radial wave functions of the Dirac equation. These ratios have simpler analytic forms and satisfy nonlinear first-order differential equations which can be solved by iteration in a relatively straightforward way.

The specific problem which is solved in the present paper is that of a Dirac electron moving in the electric and magnetic fields produced by an infinitely heavy nucleus with extended charge and current distributions. The latter is "attached" to the Pauli spin operator of the spin $\frac{1}{2}$ nucleus. The fields are thus considered as "external fields" except that since the vector potential involves the nuclear spin operator explicitly, its different components do not commute. It is for this circumstance that Sternheim has shown that in second order in the magnetic interaction a spurious term arises proportional to these commutators which has no counterpart in the proper field-theoretical treatment of the interaction. In fact, the "crossed-photon" term, which is obviously not properly taken into account in the present treatment leads to cancellation of the commutator contribution arising in the field theoretical treatment from the "uncrossed-photon" term alone. Sternheim then shows that this spurious term can be removed from the original problem by adding a term to the Hamiltonian of the system which cancels the contribution. Unfortunately, the evaluation of the term is simple only when one can replace energy denominators for transitions to intermediate negative energy states by $-2mc^2$ and Sternheim's correction term is indeed derived in this way. Such a treatment is valid however only if the perturbing magnetic field has small Fourier components associated with momenta transfers greater than mc ; this is not the case for the hfs interaction under consideration because of the smallness of the radius of the nuclear current distribution. In the ratio of the splittings in the $1s$ and $2s$ states the terms involving the nuclear radius cancel to terms of the order under consideration and therefore one can assume for the purpose of this particular calculation that the radius is sufficiently large that Sternheim's approximation is valid. Such an assumption is not valid with respect to the calculation of the individual splittings. In fact if one calculates the contribution of Sternheim's correction term to the individual splittings one finds enormous contributions

⁷ A. E. Zemach, Phys. Rev. **104**, 1771 (1956).

⁸ C. K. Iddings and P. M. Platzman, Phys. Rev. **113**, 102 (1959); **115**, 919 (1959).

⁹ R. Hofstadter, F. Bumiller, and M. R. Yearian, Rev. Mod. Phys. **30**, 482 (1958).

¹⁰ C. Schwartz, Ann. Phys. (Paris) **2**, 156 (1959).

¹¹ M. M. Sternheim, Phys. Rev. **128**, 676 (1962).

which are certainly spurious. In order to overcome this difficulty we have introduced the *ad hoc* assumption that the Compton wavelength of the electron is to be used instead of the nuclear radius as the distance at which the potentials depart from their values for point charges. This gives the electron a finite size as well as the nucleus; this assumption is used only in evaluating the terms which would otherwise give difficulty. This point is discussed further in Appendix I.

The question as to whether the discrepancy noted by Zemach is real must await a reliable way of dealing with the second-order hfs contributions to level splittings. If the procedure were practical, the Bethe-Salpeter equation could be solved to give hfs terms of order $(\alpha^2 m/M)$.

II. HAMILTONIAN

The Hamiltonian will now be obtained for a Dirac electron moving in the electromagnetic field of an infinitely heavy nucleus of spin $\frac{1}{2}$ and charge Ze situated at the origin. The field is produced by an extended nuclear charge and current distribution which will be taken to have a radius $r_c \approx 10^{-13}$ cm. The charge distribution is spherically symmetric and is characterized by a form factor $f_e(r)$ which satisfies the conditions

$$4\pi \int_0^\infty f_e(r)r^2 dr = 1 \quad \text{and} \quad f_e(r) = 0 \quad \text{for} \quad r > r_c.$$

The associated scalar potential is given by

$$\varphi_e(r) = Ze \int \frac{f_e(r')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = Ze v_e(r). \quad (1)$$

The function $v_e(r)$ is then equal to $1/r$ for $r > r_c$, while for $r < r_c$ its exact form depends on the details of the charge distribution. We do not require precise knowledge of it, however, and it is sufficient to know that for $r < r_c$, $v_e(r) \approx 1/r_c$.

The current distribution in the nucleus is related to its spin angular momentum \mathbf{i} and can be assumed derivable from a magnetization $\mathbf{M}(r)$ through

$$\mathbf{j}(r) = \text{curl } \mathbf{M}(r). \quad (2)$$

The magnetization can then be written

$$\mathbf{M}(r) = \mu \mathbf{i} f_m(r), \quad (3)$$

where μ is the magnetic moment of the nucleus ($\mu = ge/2M$, where g is the moment in nuclear magnetons, M is the mass of the proton). Here and throughout we use units in which $\hbar = c = 1$. The factor $f_m(r)$ is a magnetic form factor which satisfies the same conditions as $f_e(r)$.

$$4\pi \int_0^\infty f_m(r)r^2 dr = 1 \quad \text{and} \quad f_m(r) = 0 \quad \text{for} \quad r > r_c.$$

The same r_c has been used for both f_e and f_m for con-

venience in the calculation; however, r_c does not appear explicitly in the result. The unretarded vector potential associated with the current distribution (2) is then given by

$$\mathbf{A}(r) = -(ge/2M)(\mathbf{i} \times \mathbf{r}) dv_m/r dr, \quad (4)$$

where $v_m(r)$ is given by

$$v_m(r) = \int \frac{f_m(r')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \quad (5)$$

The function $v_m(r) = 1/r$ and $dv_m(r)/dr = -1/r^2$ for $r > r_c$. For $r < r_c$ it is assumed that $dv_m/dr \approx -1/r_c^2$; note that in this respect v_m differs from v_e for $r < r_c$.

Since the nuclear spin \mathbf{i} is varying with time, the vector potential (4) should actually be retarded. We have shown, however, that the effects of retardation vanish to order g^2 if we take the retarded time to be $t-r$ and compute $d\mathbf{i}/dt$ with the Hamiltonian derived below [Eq. (7)] neglecting retardation.

With the above expressions for the potentials, the Dirac equation for the electron takes the form

$$i\partial\psi(\mathbf{r},t)/\partial t = \mathcal{H}\psi(\mathbf{r},t), \quad (6)$$

with

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' + \mathcal{H}'', \quad (7)$$

$$\mathcal{H}_0 = \beta m + \boldsymbol{\alpha} \cdot \mathbf{p} - Ze^2 v_e(r), \quad (8)$$

$$\mathcal{H}' = -(ge^2/2Mr) dv_m(r)/dr (\boldsymbol{\alpha} \cdot \mathbf{i} \times \mathbf{r}), \quad (9)$$

and

$$\mathcal{H}'' = (g^2 \alpha^2 / 4mM^2 r^2) (dv_m/dr)^2 (\mathbf{s} \cdot \mathbf{r})(\mathbf{i} \cdot \mathbf{r}), \quad (10)$$

where s is the spin of the electron.

\mathcal{H}'' is the term which Sternheim added to the Dirac equation in order to obtain agreement with a proper quantum electrodynamic treatment of the electron-nuclear interaction. This has been mentioned earlier and is further discussed in Appendix I.

It should be noted that the wave function ψ has eight components since the space in which we are working is the direct product of the two-dimensional Pauli spin space of the nucleus and the four-dimensional spin space of the Dirac matrices.

III. THE RADIAL EQUATIONS

Our next problem is to reduce the eigenvalue equation

$$\mathcal{H}\psi = E\psi, \quad (11)$$

with \mathcal{H} given by (7), (8), (9), and (10) to equations for radial functions. In general there will be four equations for four radial functions which can be seen as follows: Letting F represent the total angular momentum quantum number of the atom, and J and L the total angular momentum quantum number and orbital angular momentum quantum number of the electron, we have for given F , the possibilities $J = F \pm \frac{1}{2}$, and for each J , the possibilities $L = J \pm \frac{1}{2}$. For each value of F , J , and L , there are two eigenvalues possible for the Dirac matrix β , but since the parity of a state is deter-

mined by both B , the eigenvalue of β and L , there is only one value of B allowed for each L when the parity of the state is given. Thus, there are four spin-angular dependences possible for an eigenstate of \mathcal{H} and therefore four radial functions. An exception occurs for $F=0$, in which case only $J=\frac{1}{2}$, $L=0, 1$ are possible.

We shall not derive the radial equations for arbitrary F values, but only for $F=0$ and $F=1$ which are the possibilities for nonrelativistic s states of the atom. For the Dirac electron in a central field it is common to employ the eigenvalues k of the operator¹² k defined below in Eq. (15) to label the angular momentum states of the electron. The nonrelativistic ${}^2S_{1/2}$ states correspond to the eigenvalue $K=-1$. While, in the absence of the hyperfine structure (hfs) interaction $\mathcal{H}' + \mathcal{H}''$, k is a constant of the motion, the hfs interaction couples states with $K=2$ to states with $K=-1$, except when $F=0$ and even in this latter case the radial equations are, of course, modified by the hfs interaction terms in the Hamiltonian.

To exploit the radial symmetries of the Dirac equation (11) we follow the usual procedure for the Dirac equation in a central field by introducing the operators

$$\alpha_r = \boldsymbol{\alpha} \cdot \mathbf{r} / r, \quad (12)$$

$$\boldsymbol{\sigma} = -i\boldsymbol{\alpha} \times \boldsymbol{\alpha} = 2\mathbf{s}, \quad (13)$$

$$\mathbf{l} = \mathbf{r} \times \mathbf{p}, \quad (14)$$

$$k = -\beta(\boldsymbol{\sigma} \cdot \mathbf{l} + 1), \quad (15)$$

$$p_r = r^{-1}(\mathbf{r} \cdot \mathbf{p} - i), \quad (16)$$

whence

$$\boldsymbol{\alpha} \cdot \mathbf{p} = \alpha_r p_r - i r^{-1} \alpha_r \beta k. \quad (17)$$

We also introduce

$$\mathbf{j} = \mathbf{l} + \mathbf{s}, \quad (18)$$

$$\mathbf{f} = \mathbf{j} + \mathbf{i} = \mathbf{l} + \mathbf{s} + \mathbf{i}, \quad (19)$$

representing the total angular momentum of the electron and the atom, respectively. As usual

$$k^2 = j^2 + \frac{1}{4}, \quad (20)$$

so that an eigenfunction of k is an eigenfunction of j^2 but not conversely. To evaluate the hfs interaction terms it is convenient to introduce in addition the tensor operator

$$S = \sqrt{2} r^{-2} [3(\mathbf{s} \cdot \mathbf{r})(\mathbf{i} \cdot \mathbf{r}) - r^2(\mathbf{s} \cdot \mathbf{i})], \quad (21)$$

which satisfies

$$S^2 = 3/4 - S/\sqrt{2} + \mathbf{s} \cdot \mathbf{i}, \quad (22)$$

and to note that the spin dependence of the hfs interaction terms can be written

$$\boldsymbol{\alpha} \cdot \mathbf{i} \times \mathbf{r} = -i2^{-1/2} r [\alpha_r S - S\alpha_r] \quad (23)$$

and

$$(\mathbf{s} \cdot \mathbf{r})(\mathbf{i} \cdot \mathbf{r}) = r^2 S / 3\sqrt{2} + r^2(\mathbf{s} \cdot \mathbf{i}) / 3.$$

The Hamiltonian can then be written as

$$\mathcal{H}_0 = \beta m + \alpha_r p_r - i r^{-1} \alpha_r \beta k - Z e^2 v_e(r), \quad (24)$$

$$\mathcal{H}' = \frac{i g e^2}{2M} \frac{d v_m}{d r} 2^{-1/2} [\alpha_r S - S\alpha_r], \quad (25)$$

$$\mathcal{H}'' = \frac{g^2}{8mM^2} \left(\frac{d v_m}{d r} \right)^2 \frac{1}{3} [\sqrt{2} S + \boldsymbol{\sigma} \cdot \mathbf{i}], \quad (26)$$

with all angular dependences isolated in the operators α_r , k , and S . Lastly, we note that the four operators

$$f^2, \quad k, \quad \beta, \quad l^2, \quad (27)$$

mutually commute, but that of these only f^2 commutes with \mathcal{H} while k commutes with \mathcal{H}_0 but not with \mathcal{H}' or \mathcal{H}'' . We designate the eigenvalues of these four operators by $F(F+1)$, K , B , and $L(L+1)$, respectively. We are now ready to derive the radial equations for the two cases $F=0$ and $F=1$.

F=0

We introduce a normalized r -independent eight-component spinor t_1 which is a simultaneous eigenvector of the operators (27) belonging to the eigenvalues $F=0$, $K=-1$, $B=1$, and $L=0$, respectively. The spinor

$$t_2 = -i\alpha_r t_1, \quad (28)$$

is then clearly a second (normalized) eigenvector of these four operators belonging to the eigenvalues $F=0$, $K=-1$, $B=-1$, $L=1$, respectively. If we let

$$\psi_0 = r^{-1} [u_1(r)t_1 + u_2(r)t_2], \quad (29)$$

then one can verify that $\mathcal{H}\psi_0$ is also a linear combination of t_1 and t_2 with coefficients which depend only on r , so that the eigenvalue equation (11) can be satisfied by (29), provided the radial functions, u_1 and u_2 , satisfy appropriate equations. We defer writing these equations until we have discussed the case $F=1$.

F=1

Again we introduce a normalized simultaneous eigenvector t_1 of the four operators (27), but belonging to the eigenvalues $F=1$, $K=-1$, $B=1$, $L=0$. From it we may construct t_2 according to Eq. (28), which is a common eigenvector belonging to the eigenvalues $F=1$, $K=-1$, $B=-1$, $L=1$. A third normalized common eigenvector t_3 can be defined by

$$t_3 = S t_1, \quad (30)$$

and clearly belongs to the eigenvalues, $F=1$, $K=2$, $B=1$, $L=2$. Finally,

$$t_4 = -i\alpha_r t_3 = -i\alpha_r S t_1 \quad (31)$$

is a simultaneous normalized eigenvector which can be shown to belong to the eigenvalues $F=1$, $K=2$, $N=-1$,

¹² D. R. Bates, *Quantum Theory* (Academic Press Inc., New York, 1962), Vol. III, Sec. 2.8.

$L=1$. These four eigenvectors will, of course, be orthogonal since they are associated with different eigenvalues of a set of commuting operators. Now, letting

$$\psi_1 = r^{-1}[u_1(r)t_1 + u_2(r)t_2 + u_3(r)t_3 + u_4(r)t_4], \quad (32)$$

again, $\mathcal{H}\psi_1$ is a linear combination of the four t 's with coefficients, which are functions of r alone so that ψ_1 will be an eigenfunction of \mathcal{H} if the u 's satisfy appropriate equations.

To simplify the form of the radial equations, we introduce the following changes of variable and abbreviations:

$$\begin{aligned} x &= 2Zm\alpha r, \\ \lambda &= (1 - E^2/m^2)^{1/2}, \\ \Phi_e(x) &= v_e(r)/2Zm\alpha, \\ \Phi_m(x) &= v_m(r)/2Zm\alpha, \\ \alpha &= e^2 = 1/137.023, \\ \gamma(F) &= gZ\alpha^2 m/M \quad \text{for } F=0 \\ &= -gZ\alpha^2 m/3M \quad \text{for } F=1, \\ \delta(F) &= -\frac{1}{2}(gZ\alpha^2 m/M)^2 \quad \text{for } F=0 \\ &= \frac{1}{6}(gZ\alpha^2 m/M)^2 \quad \text{for } F=1. \end{aligned} \quad (33)$$

The radial functions u then satisfy the following equations in both the $F=0$ and $F=1$ cases ($u_3=u_4=0$ for $F=0$):

$$\begin{aligned} u_1' - (1/x + \gamma\Phi_m')u_1 \\ - \{[1 + (1 - \lambda^2)^{1/2}]/2Z\alpha + Z\alpha\Phi_e - Z\alpha\delta(\Phi_m')^2\}u_2 \\ + \sqrt{2}\gamma\Phi_m'u_3 + Z\alpha 2\sqrt{2}\delta(\Phi_m')^2u_4 = 0, \\ u_2' + (1/x + \gamma\Phi_m')u_2 \\ - \{[1 - (1 - \lambda^2)^{1/2}]/2Z\alpha - Z\alpha\Phi_e + Z\alpha\delta(\Phi_m')^2\}u_1 \\ - \sqrt{2}\gamma\Phi_m'u_4 - Z\alpha 2\sqrt{2}\delta(\Phi_m')^2u_3 = 0, \\ u_3' + (3/x - 2\gamma\Phi_m')u_3 \\ - \{[1 + (1 - \lambda^2)^{1/2}]/2Z\alpha + Z\alpha\Phi_e + Z\alpha\delta(\Phi_m')^2\}u_4 \\ + \sqrt{2}\gamma\Phi_m'u_1 + Z\alpha 2\sqrt{2}\delta(\Phi_m')^2u_2 = 0, \\ u_4' - (2/x + 2\gamma\Phi_m')u_4 \\ - \{[1 - (1 - \lambda^2)^{1/2}]/2Z\alpha - Z\alpha\Phi_e - Z\alpha\delta(\Phi_m')^2\}u_3 \\ - \sqrt{2}\gamma\Phi_m'u_2 - Z\alpha 2\sqrt{2}\delta(\Phi_m')^2u_1 = 0. \end{aligned} \quad (34)$$

A prime denotes differentiation with respect to x . In Sec. II, v_e and v_m were defined by Eqs. (1) and (5) and their behavior as a function of r was given. For $\Phi_e(x)$ and $\Phi_m(x)$ one then has

$$\begin{aligned} \Phi_e(x) &= 1/x \quad \text{for } x > x_c \\ &= 1/x_c \quad \text{for } x < x_c, \\ \Phi_m'(x) &= -1/x^2 \quad \text{for } x > x_c, \\ \Phi_m'(x) &\approx -1/x_c^2 \quad \text{for } x < x_c, \end{aligned} \quad (35)$$

where

$$x_c = 2Zm\alpha r_c \approx 10^{-5}. \quad (36)$$

The unperturbed equations are defined as the equations which result when one sets $\Phi_e = 1/x$, $\gamma(F) = 0$,

and $\delta(F) = 0$ in Eqs. (34). The resulting solutions are then the unperturbed solutions and are well known.¹³

One could attempt to solve Eqs. (34) by straightforward perturbation theory starting with the unperturbed equations. However, this leads to computational difficulties if one wishes to go to second order in γ , since the perturbation $\gamma\Phi_m'$ assumes large values $\approx 10^9$ for $x < x_c$ and leads to substantial admixtures of unperturbed functions lying distant in energy from the unperturbed state under consideration. The unperturbed eigenfunctions are themselves quite complicated so that calculating matrix elements and summing over all intermediate states becomes quite difficult.

An alternate approach based on an iteration scheme on nonlinear equations derived from Eqs. (34) was therefore devised and represents a significant methodological contribution of this paper. We describe this method, which may also be applicable to other similar problems, in the following sections and apply it to the problem at hand.

IV. DISCUSSION OF SOLUTION

The problem is now to determine λ from Eqs. (34). To this end properties of both the unperturbed and perturbed solutions will be investigated. Use will thus be made of the unperturbed solutions which are well known¹⁰ even though, as was pointed out at the conclusion of the last section, second-order perturbation theory will not be applied to Eqs. (34). Three nonlinear equations will then be obtained; approximate solutions to two of these will be found immediately to the necessary order, and in the following section the other equation will be solved by an iteration process.

First, certain properties of the unperturbed solutions (i.e., $\Phi_e = 1/x$, $\gamma = \delta = 0$) are noted. In particular the solutions have $u_3 = u_4 = 0$, and (for bound states of principal quantum number n) u_1 and u_2 each contain a factor which is a polynomial of degree $n-1$ in x , and which is expressible in terms of confluent hypergeometric functions. We do not require the precise form of these solutions, but need concern ourselves only with certain of their properties, in particular, the ratio $u_2(x)/u_1(x)$ can be written

$$u_2(x)/u_1(x) = c(n) \prod_{i=1}^{n-1} (x - a_i) / \prod_{i=1}^{n-1} (x - b_i), \quad (37)$$

where the a_i are the nodes of u_2 and the b_i are the nodes of u_1 (apart from the nodes at $x=0$ and $x=\infty$). For $n=1$, u_2/u_1 is simply a constant. One effect of the perturbation will consist in shifting these nodes without changing their number, an observation which will be exploited in what follows. We note also that for the two lowest s states, the unperturbed values associated

¹³ H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 14.

with Eq. (37) are

$$\begin{aligned} n=1 & \quad \lambda = Z\alpha, \\ n=2 & \quad \lambda = Z\alpha/N, \quad N = (1+Z\alpha)^{1/2} + (1-Z\alpha)^{1/2}, \\ & \quad a_1 = N(N-1)(N+2), \\ & \quad b_1 = N^2(N-1). \end{aligned} \quad (38)$$

Turning now to the case where the perturbations are present, one can determine the asymptotic behavior of the ratios of the u 's. First, under the assumption [which follows from Eq. (39) but is not as restrictive] that

$$x\Phi_e(x) \rightarrow 0 \quad \text{as } x \rightarrow 0, \quad (40)$$

one readily finds that u_2/u_1 , u_3/u_1 , and u_4/u_1 all approach zero as $x \rightarrow 0$. Secondly as $x \rightarrow \infty$, one finds that

$$\begin{aligned} u_2/u_1 & \rightarrow -\lambda/[1+(1-\lambda^2)^{1/2}], \\ u_3/u_1 & \rightarrow \Lambda, \\ u_4/u_1 & \rightarrow -\Lambda\lambda/[1+(1-\lambda^2)^{1/2}], \end{aligned} \quad (41)$$

where Λ is a constant (independent of x) which is here undetermined, but which we shall see later plays no essential role in the calculation.

Our procedure now consists in introducing three new functions of x through the following relations:

$$\begin{aligned} w_1 & = -\{[1+(1-\lambda^2)^{1/2}]/\lambda\}u_2/u_1, \\ w_2 & = u_3/u_1, \\ w_3 & = -\{[1+(1-\lambda^2)^{1/2}]/\lambda\}u_4/u_1. \end{aligned} \quad (42)$$

These functions must then satisfy the boundary conditions that they all vanish as $x \rightarrow 0$, and they take on the values 1, Λ , Λ , respectively, as $x \rightarrow \infty$. Differentiation of w_1 , w_2 , and w_3 and use of the Eqs. (34) for the u 's then yields the following nonlinear first-order differential equations for the w 's:

$$\begin{aligned} w_1' + (2/x + 2\gamma\Phi_m')w_1 & + \{\lambda/2Z\alpha - Z\alpha\lambda[\Phi_e - \delta(\Phi_m')^2]/[1-(1-\lambda^2)^{1/2}]\} \\ & - \{\lambda/2Z\alpha + Z\alpha\lambda[\Phi_e - \delta(\Phi_m')^2]/[1+(1-\lambda^2)^{1/2}]\}w_1^2 \\ & - \sqrt{2}\gamma\Phi_m'(w_1w_2 + w_3) + Z\alpha 2\sqrt{2}\delta(\Phi_m')^2 \\ & \times \{[1+(1-\lambda^2)^{1/2}]\lambda^{-1}w_2 + \lambda[1+(1-\lambda^2)^{1/2}]^{-1}w_1w_3\} = 0, \\ w_2' + (3/x - \gamma\Phi_m')w_2 & + \{\lambda/2Z\alpha + Z\alpha\lambda\Phi_e/[1+(1-\lambda^2)^{1/2}]\} \\ & \times (W_3 - w_1w_2) + \sqrt{2}\gamma\Phi_m'(1-w_2^2) = 0, \\ w_3' - (1/x - 3\gamma\Phi_m')w_3 & + \{\lambda/2Z\alpha - Z\alpha\lambda\Phi_e/[1-(1-\lambda^2)^{1/2}]\}w_2 \\ & - \{\lambda/2Z\alpha + Z\alpha\lambda\Phi_e/[1+(1-\lambda^2)^{1/2}]\}w_1w_3 \\ & - \sqrt{2}\gamma\Phi_m'(w_1 + w_2w_3) = 0. \end{aligned} \quad (43)$$

It is clear from Eqs. (43) that w_2 and w_3 are of first order in g relative to w_1 , and since they enter the equation for w_1 multiplied by another factor of g , their

contribution to the equation for w_1 is of second order in g . We have dropped all terms containing δ which appear in the second and third of Eqs. (43) since these terms could contribute at most to order g^3 in the equation for w_1 . Since we are only interested in the order g^2 , we may integrate the latter two equations for w_2 and w_3 ; the first-order result is shown in Appendix II to be

$$\left. \begin{aligned} w_2 & = \sqrt{2}\gamma(1/12n^2 + w_1/2nx - x_c^2/2x^3), \\ w_3 & = \sqrt{2}\gamma(w_1/12n^2 + nx_c^2/4x^3), \\ w_2 & = 0, \\ w_3 & = \sqrt{2}\gamma nx/4x_c^2. \end{aligned} \right\} \begin{array}{l} \text{for } x > x_c \\ \text{for } x < x_c \end{array} \quad (44)$$

V. THE $n=1$, $F=0$ STATE

The set of equations (43) which hold for arbitrary n values will now be solved for four specific cases: $n=1$ and $n=2$, and for each n value $F=0$ and $F=1$. The $n=1$, $F=0$ case will be solved in detail in this section by the iteration method to be introduced here. In the following sections the method will be applied to the remaining cases which differ somewhat in detail.

In the unperturbed problem the function $w_1=1$; this suggests that we use

$$w_1(x) = 1 + \eta(x) \quad (45)$$

as the perturbed function. We expect η to be small, that is, proportional to γ which is $\approx 10^{-7}$. The boundary conditions on η are that $\eta(\infty)=0$ and $\eta(0)=-1$. The latter condition means that η cannot be small compared with unity for small x , but we shall find that for $x < x_c$ the magnitude of η is not critical. Here, as in all $F=0$ states, we have $w_2=w_3=0$.

We substitute (45) into (43) and obtain

$$\eta' + \eta(2/x - 1) = h_1 + h_2 \equiv h, \quad (46)$$

where the terms have been arranged so that

$$\begin{aligned} h_1 & = -2/x - 2\gamma\Phi_m' + 2Z\alpha\Phi_e/\lambda, \\ h_2 & = \eta\{-2\gamma\Phi_m' + \epsilon + 2Z\alpha\lambda\Phi_e/[1+(1-\lambda^2)^{1/2}]\} \\ & \quad + \eta^2\{\lambda/2Z\alpha + Z\alpha\lambda\Phi_e/[1+(1-\lambda^2)^{1/2}]\} \\ & \quad - 2Z\alpha\delta(\Phi_m')^2/\lambda, \end{aligned} \quad (47)$$

and

$$\epsilon = \lambda/Z\alpha - 1 \approx 10^{-7}.$$

Equation (46) has been written in such a way that the coefficient of η on the left side will yield a simple integrating factor, and the coefficient of η on the right side is a first-order quantity in g and can be neglected in the first approximation.

Since Eq. (46) is a nonlinear equation there may be spurious solutions; however, it is clear that when η is quite small and the perturbations approach zero, then $\lambda \approx Z\alpha$ and this is the desired solution. It should also be pointed out that even though λ is not the eigenvalue of any of the operators considered here, it does determine the energy eigenvalue E_1 and in fact λ will be determined

by the boundary conditions on η ; it is only for this one value of λ that Eq. (46) can be satisfied.

We now treat Eq. (46) as a first-order linear inhomogeneous differential equation for η ; we are considering h as the inhomogeneous term. We introduce the integrating factor p given by

$$p = x^2 e^{-x}. \quad (48)$$

By using the boundary conditions for η , the following equations are obtained by integrating Eq. (46):

$$\int_0^\infty p h dx = 0 \quad (49)$$

and

$$\eta(x) = -\frac{1}{p(x)} \int_0^\infty p(y) h(y) dy. \quad (50)$$

Equation (49) will be an algebraic equation for λ when the integration is carried out. In order to do this, we assume that $p h_1$ is of lower order than $p h_2$; this assumption will be verified shortly by explicit calculation. Since these functions depend on x , it is actually the relative magnitude of their integrals over x which will be compared.

We shall find it useful to use γ as a guide in defining the orders of magnitude. Relative to γ ($\approx 10^{-7}$) we shall call 1 zero order, terms between 10^{-1} and 10^{-7} inclusive first order, and terms between 10^{-8} and 10^{-14} inclusive second order. This will enable us to classify terms depending explicitly on nuclear structure (to be encountered later) as to their order. We shall drop all terms smaller than 10^{-14} . Thus we would keep γ^2 and δ , but would drop $\gamma^2 (Z\alpha)^2 \approx 10^{-8}$ and $\gamma (Z\alpha)^4 \approx 10^{-15}$.

The iteration process consists in the following. Equation (49) is solved for $\lambda^{(1)}$ (the first approximation) by neglecting $p h_2$; this $\lambda^{(1)}$ is substituted into (50) which is solved for $\eta^{(1)}$, again neglecting $p h_2$. Equation (49) is solved again with $\lambda^{(1)}$ and $\eta^{(1)}$ used in $p h_2$, and this gives $\lambda^{(2)}$ (the second approximation). Higher approximations could be obtained in this way, but the second approximation will be correct to terms of order γ^2 and this is sufficient for our purposes here.

We now proceed to carry out the iteration process explicitly. By rearranging the terms in Eq. (49) the equation for $\lambda^{(1)}$ becomes

$$\begin{aligned} \int_0^\infty p h_1 dx &= \int_0^\infty e^{-x} [2x(Z\alpha/\lambda - 1) - x^2(1/x - \Phi_e)Z\alpha/\lambda \\ &\quad - 2\gamma x^2(1/x^2 + \Phi_m') + 2\gamma] dx \\ &= 2(Z\alpha/\lambda - 1) - \langle x_e^2 \rangle Z\alpha/3\lambda + 2\gamma - 2\gamma \langle x_m \rangle = 0. \end{aligned} \quad (51)$$

The quantities $(1/x - \Phi_e)$ and $(1/x^2 + \Phi_m')$ are perturbations due to the finite size of the nucleus; they both vanish for $x > x_e$ and so contribute to the integrals only in the region $0 < x < x_e$. In Appendix III the integrals containing these perturbations are expressed

in terms of certain average quantities. For example, it is shown that

$$\int_0^\infty e^{-x} x^2 (1/x - \Phi_e) dx = \frac{1}{6} \langle x_e^2 \rangle = \frac{1}{6} (2Z\alpha m)^2 \langle r_e^2 \rangle,$$

where $\langle r_e^2 \rangle$ is the mean squared radius of the electric charge density of the nucleus. It is also shown that

$$\int_0^\infty e^{-x} x^2 (1/x^2 + \Phi_m') dx = \langle x_m \rangle = 2Z\alpha m \langle r_m \rangle,$$

where $\langle r_m \rangle$ is the mean radius of the magnetization density. This gives to terms of order 10^{-10} in $\lambda/Z\alpha$:

$$\lambda^{(1)} = Z\alpha [1 + \gamma - (\langle x_e^2 \rangle/3 + 2\gamma \langle x_m \rangle)/2]. \quad (52)$$

$\eta^{(1)}$ is then readily found from Eq. (50); for $x > x_e$

$$\eta^{(1)} = 2\gamma/x - (\langle x_e^2 \rangle/3 + 2\gamma \langle x_m \rangle)/x^2. \quad (53)$$

For $x < x_e$, we find it more convenient to expand η in a Taylor's series about $x=0$ and then match it with Eq. (53) at $x=x_e$. This gives

$$\eta^{(1)} = -1 + 2x/3x_e. \quad (54)$$

We have assumed that $x_e^2 = \langle x_e^2 \rangle$ which is reasonable. We note that the η in Eq. (54) satisfies Eq. (46) identically for any n if we let $\Phi_e = 1/x_e$ and Φ_m' is neglected for $x < x_e$.

In order to determine $\lambda^{(2)}$ we need the integral over $p h_2$ which turns out to be

$$\begin{aligned} 2\Delta &\equiv \int_0^\infty p h_2 dx = 2[\gamma(Z\alpha)^2 - 2\gamma^2 \ln \kappa x_e + 2\gamma \langle x_{em} \rangle \\ &\quad - \gamma \langle x_e \rangle + 2^{-1} (Z\alpha)^2 (\langle x_e^2 \rangle/3 + 2\gamma \langle x_m \rangle) \ln \kappa x_e \\ &\quad + \delta(-y_e^{-1} + 1 - \ln \kappa y_e)], \end{aligned} \quad (55)$$

where $y_e = 2Z\alpha \approx 10^{-2}$ as defined in Appendix I. We have used the approximation

$$\begin{aligned} \int_{x_e}^\infty x^{-1} e^{-x} dx &= -\ln(\kappa x_e) + x_e - x_e^2/2.2! + \dots \\ &\approx -\ln(\kappa x_e), \end{aligned} \quad (56)$$

where $\ln \kappa = 0.5772 \dots =$ Euler's constant. The assumption has been made that the magnitude of Φ_m' is less than 10^{10} for $x < x_e$; this means that Φ_m' can be neglected in the integrals in the region $0 < x < x_e$.

Solving Eq. (49) again for $\lambda^{(2)}$ we find, to terms of order 10^{-14} in $\lambda/Z\alpha$,

$$\lambda^{(2)} = Z\alpha [1 + \gamma - (\langle x_e^2 \rangle/3 + 2\gamma \langle x_m \rangle)/2 + \delta^2 + \Delta]. \quad (57)$$

We see that $\Delta \approx 10^{-11}$ and so is a second-order quantity as was assumed in neglecting it originally.

We see that $\gamma(Z\alpha)^2$ enters as a second-order correction; it is the Breit relativistic correction. The term $2\gamma^2 \ln \kappa x_e$ is the largest second-order term in g^2 arising

from \mathcal{H}' and would be expected to make the largest contribution to the correction to R . R is defined as the ratio of the hfs splitting in the $2s$ state to the hfs splitting in the $1s$ state in the general hydrogenic atom. However, it will turn out that no terms involving nuclear-structure effects will appear in R so that this term as well as the terms in δ due to \mathcal{H}' will make a contribution of the order of $\gamma^2 \ln 2$ to R and this is comparatively small.

We can determine whether or not the iteration process is converging by going to the next approximation in η . The order of the difference $\eta^{(2)} - \eta^{(1)}$ for $x > x_c$ is found to be (keeping only the largest term in the coefficient of each power of x)

$$\eta^{(2)} - \eta^{(1)} \approx \gamma(Z\alpha)^2/x - \gamma(Z\alpha)^2/x^2 + 2\gamma\langle x_e^2 \rangle/3x^3 - (\langle x_e^2 \rangle/3)^2(Z\alpha)^2/4x^4 - 4\gamma^2 x^{-2} e^x \times \int_0^\infty y^{-1} e^{-y} dy + 2\delta/x^3. \quad (58)$$

The first four terms are clearly less than $\eta^{(1)}$ by at least a factor of 10 for any value of x . The fifth term can be examined for $x < 1$ and $x > 1$ separately. For $x > 1$, $x^{-2} e^x \int_0^\infty y^{-1} e^{-y} dy < x^{-2}$ and this term can be neglected. For $x < 1$, $x^{-2} e^x \int_0^\infty y^{-1} e^{-y} dy < -e x^{-2} \ln x + x^{-2}$, and there is no appreciable contribution from this term for $x_c < x < 1$. The last term is to be used only for $x > y_c$ where it too is small, for $x < y_c$ it can be taken to be $\approx 2\delta y_c^{-3} \approx 10^{-8}$. For $x < x_c$, we can make no better approximation for η and so we take $\eta^{(2)} = \eta^{(1)}$. Since $\eta^{(2)} - \eta^{(1)}$ is less than $\eta^{(1)}$ for all values of x by at least a factor of 10 then the iteration process is converging up to this point. It is evident that higher approximations will introduce higher powers of quantities such as $(gZ\alpha^2 m/M)$ and $\langle x_e^2 \rangle$ and since it appears that $\eta(x)$ will never contain divergent terms in x , it is reasonable to assume that the iteration process will converge in the determination of both $\eta(x)$ and λ .

VI. THE $n=1$, $F=1$ STATE

Here the procedure is the same as in the $F=0$ state except that w_2 and w_3 are given by (44). Thus h_2 contains the additional term $2\gamma\Phi_m'(w_1 w_2 + w_3)$ which will make a second-order contribution to λ . This leads to a $\lambda^{(2)}$ which is equal to the $\lambda^{(2)}$ for the $F=0$ state plus the term $Z\alpha(2^{-1}\gamma^2 \ln \kappa x_c - \gamma^2/24)$. In evaluating the expression for λ , it must be remembered that γ and δ are functions of F .

VII. THE $n=2$ STATES

The general procedure is again the same. We now use

$$w_1(x) = \frac{x-a}{x-b} [1 + \eta(x)] \quad (59)$$

for the perturbed w_1 . This form was obtained by noting that the ratio u_2/u_1 in the unperturbed case is the

quotient of two first-degree polynomials. The factor $1 + \eta(x)$ is included to account for the perturbation. The nodes at a and b must be determined by the iteration method since they will be shifted by the perturbation.

We find it convenient to introduce the two first-order quantities ϵ_1 and ϵ_2 defined by the equations

$$(a-b)\lambda/Z\alpha = 2 - \epsilon_1$$

and

$$\lambda/Z\alpha = 1/2 + \epsilon_2.$$

ϵ_1 and ϵ_2 appear in h_2 and are determined by the first approximation of λ , a , and b .

The integrating factor is found to be

$$p = (x-a)(x-b)x^2 e^{-x/2}. \quad (60)$$

Equation (49) is now replaced by the three equations

$$\int_0^\infty p h dx = 0, \quad \int_a^\infty p h dx = 0, \quad \text{and} \quad \int_b^\infty p h dx = 0. \quad (61)$$

These three algebraic equations are used to determine the three constants λ , a , and b just as (49) was used to determine λ . Using the iteration process we obtain for $\lambda^{(2)}$

$$\lambda^{(2)} = Z\alpha [1 + \gamma/2 - (\langle x_e^2 \rangle/3 + 2\gamma\langle x_m \rangle)/4 + 11(Z\alpha)^2 \gamma/32 + 11\gamma^2/16 + (\Delta_1 + \Delta_2)/2ab] / N, \quad (62)$$

where N is given by Eq. (39) and

$$\begin{aligned} \Delta_1 = 2^{-1} \int_0^\infty p \{ & \eta [-2\gamma\Phi_m' + \epsilon_1/(x-b) + \epsilon_2 \\ & + (Z\alpha)^2(x-a)/2(x-b)] \\ & + \eta^2 [\lambda/2Z\alpha + (Z\alpha)^2\Phi_e/4] (x-a)/(x-b) \\ & - 2\delta(\Phi_m')^2(x-a)/(x-b) \} dx \\ = ab \{ & 17(Z\alpha)^2\gamma/16 + \gamma(2\langle x_{em} \rangle - \langle x_e \rangle) - 2\gamma^2 \ln \frac{1}{2} \kappa x_c \\ & + 3\gamma^2/8 + 2\delta \left[-\frac{1}{2} y_c^{-1} + \frac{7}{32} \frac{1}{2} \frac{1}{2} \ln \kappa y_c \right] \}, \end{aligned} \quad (63)$$

$$\Delta_2 = 0 \quad \text{for} \quad F=0,$$

$$\begin{aligned} \Delta_2 = \frac{1}{2} \int_0^\infty p \sqrt{2} \gamma \Phi_m'(w_1 w_2 + w_3) & [(x-b)/(x-a)] dx \\ = ab \gamma^2 (\frac{1}{2} \ln \frac{1}{2} \kappa x_c + 29/96) & \quad \text{for} \quad F=1. \end{aligned}$$

It is found that $\eta^{(1)}$ is the same for $n=2$ as for $n=1$.

VIII. STATES OF ARBITRARY n

In this section we shall outline the procedure for arbitrary n values, but no general conclusions will be drawn. We restrict our considerations to the states in which $F=0$ or 1, although an extension to other values

of the total angular momentum should be possible using the same general method.

For $n > 1$, the perturbed w_1 is of the form

$$w_1 = \left[\prod_{i=1}^{n-1} (x - a_i) \right] / \left[\prod_{i=1}^{n-1} (x - b_i) \right] [1 + \eta(x)]. \quad (64)$$

a_i and b_i are constants to be determined as were a and b in the $n=2$ case. w_2 and w_3 are given by Eq. (44). The w 's are still as defined in Eq. (42) and so satisfy Eq. (43). The integrating factor is now

$$p = \prod_{i=1}^{n-1} (x - a_i) \prod_{i=1}^{n-1} (x - b_i) x^2 e^{-x/n}. \quad (65)$$

When Eqs. (64) and (65) are substituted into Eq. (43) an equation of the form $(p\eta)' = p(h_1 + h_2)$ is obtained where h_1 does not depend on η . It is easy to show that

$$\int_{x_0}^{\infty} p h dx = 0, \quad (66)$$

where x_0 takes on the values 0, a_i , and b_i , and

$$\eta = -p(x)^{-1} \int_x^{\infty} p(y) h(y) dy. \quad (67)$$

Equations (66) and (67) are iterated as before. Equation (66) represents $2n-1$ equations for a_i , b_i , and λ . As an aid in writing h_2 , it can be shown that

$$\frac{\lambda}{Z\alpha} \frac{\prod_{i=1}^{n-1} (x - a_i)}{\prod_{i=1}^{n-1} (x - b_i)} = \frac{1}{n} - 2 \sum_{i=1}^{n-1} \frac{1}{x - b_i} + \sum_{i=1}^{n-1} \frac{\epsilon_i}{x - b_i} + \epsilon_n,$$

where

$$\epsilon_i = 2(Z\alpha)^2/\lambda + 2\eta(b_i) \quad \text{for } i < n, \quad \epsilon_n = \lambda/Z\alpha - 1/n.$$

Carrying out the steps sketched above involves complicated algebra, but is a straightforward task in principle.

IX. RESULTS

The results of the calculations are tabulated in this section for reference. The energy eigenvalues, correct to second order in the nuclear magnetic moment, are found from the equation $E = m\sqrt{(1 - \lambda^2)}$. The radical is expanded, using the appropriate λ , and terms of order g^2 are kept. The energy levels for the $n=1$ ($1s$) and $n=2$ ($2s$) states are given by the following expressions:

$$E_{1s} = m - \frac{1}{2}m(Z\alpha)^2 \left[1 + \frac{1}{4}(Z\alpha)^2 \right] + \frac{1}{2}m(Z\alpha)^2 \left(\frac{1}{3}\langle x_e^2 \rangle + 2\gamma\langle x_m \rangle \right) \left[1 + \frac{1}{2}(Z\alpha)^2 \right] - m(Z\alpha)^2 \gamma \left[1 + \frac{3}{2}(Z\alpha)^2 - 2\gamma \ln \kappa x_c \right] + 2\langle x_{em} \rangle - \langle x_e \rangle + \frac{3}{2}\gamma + F\gamma \left(\frac{1}{2} \ln \kappa x_c - 1/24 \right) + m(Z\alpha)^2 \delta (y_c^{-1} - 1 + \ln \kappa y_c). \quad (68)$$

$$E_{2s} = m - \frac{1}{2}m(Z\alpha)^2 N^{-2} \left[1 + \frac{1}{4}(Z\alpha)^2 N^{-2} \right] + \frac{1}{4}m(Z\alpha)^2 N^{-2} \left(\frac{1}{3}\langle x_e^2 \rangle + 2\gamma\langle x_m \rangle \right) \left[1 + \frac{1}{2}(Z\alpha)^2 N^{-2} \right] - \frac{1}{2}m(Z\alpha)^2 N^{-2} \gamma \left[1 + 15(Z\alpha)^2/8 - 2\gamma \ln \frac{1}{2} \kappa x_c \right] + 2\langle x_{em} \rangle - \langle x_e \rangle - \frac{5}{8}\gamma + F\gamma \left(\frac{1}{2} \ln \frac{1}{2} \kappa x_c + 29/96 \right) + \frac{1}{2}m(Z\alpha)^2 N^{-2} \delta (y_c^{-1} - \frac{3}{8} + \ln \frac{1}{2} \kappa y_c). \quad (69)$$

The energy splittings are given by

$$\Delta E_{1s} = E_{1s}(F=1) - E_{1s}(F=0) = \frac{4}{3}m(Z\alpha)^2 \times (gZ\alpha^2 m/M) \left[1 + \frac{3}{2}(Z\alpha)^2 + 2\langle x_{em} \rangle - \langle x_e \rangle - \frac{1}{3}(gZ\alpha^2 m/M) (33/8 \ln \kappa x_c - 145/96 - \frac{3}{2} \ln \kappa y_c - \frac{3}{2} y_c^{-1}) \right]. \quad (70)$$

$$\Delta E_{2s} = E_{2s}(F=1) - E_{2s}(F=0) = \frac{1}{5}m(Z\alpha)^2 \times (gZ\alpha^2 m/M) \left[1 + (17/8)(Z\alpha)^2 + 2\langle x_{em} \rangle - \langle x_e \rangle - \frac{1}{3}(gZ\alpha^2 m/M) ((33/8) \ln \frac{1}{2} \kappa x_c + 725/384 - \frac{3}{2} \ln \frac{1}{2} \kappa y_c - \frac{3}{2} y_c^{-1}) \right]. \quad (71)$$

This yields for R

$$R = \Delta E_{2s}/\Delta E_{1s} = \frac{1}{5} \left[1 + \frac{5}{8}(Z\alpha)^2 + (gZ\alpha^2 m/M) \left(\frac{7}{8} \ln 2 - 145/128 \right) \right]. \quad (72)$$

The result for the ordinary hydrogen atom, for which $g=5.58$, is

$$R = \frac{1}{5} \left[1 + \frac{5}{8}\alpha^2 - 0.526(g\alpha^2 m/M) \right] = \frac{1}{5} (1.00003321). \quad (73)$$

The result obtained when $\delta=0$, that is, when the crossed photon diagram is not properly taken into account is

$$R = \frac{1}{5} \left\{ 1 + \frac{5}{8}(Z\alpha)^2 + (gZ\alpha^2 m/M) \times \left[(11/8) \ln 2 - 185/128 \right] \right\}. \quad (74)$$

X. DISCUSSION

In order to make a comparison with the experimental value for R , the result of Sternheim⁵ (which includes the present result) is used. It is

$$R = \frac{1}{5} (1.00003445 \pm 0.00000002).$$

The latest experimental result is

$$R = \frac{1}{5} (1.000034495 \pm 0.000000060),$$

so that agreement between theory and experiment is retained when the present result is included in the theoretical value of R .

The other quantities of interest are the hfs splittings themselves. The present work gives the second-order corrections in the nuclear magnetic moment to the $1s$ and $2s$ splittings plus terms of comparable magnitude due to nuclear structure effects. As far as is known, the radiative corrections have not been calculated for the splittings so that a direct comparison with experiment is not possible. Indeed, the present method is the only one known which gives the energy shifts and splittings without very tedious computations.

The effect of the uncrossed and crossed photon diagrams made negligible difference in R , but did

contribute the relatively large term proportional to y_c^{-1} to the splittings. It is assumed that $y_c^{-1} \approx 10^2$, but its magnitude is uncertain. The significance of this term is not clear; a proper treatment of the problem in which the quantum electrodynamic effects are included in the original equations is necessary to obtain a meaningful result. It is not entirely satisfactory to add the term \mathcal{H}'' to the Dirac Hamiltonian, but no better method could be devised for the present work. It is true that in principle the solution of the Bethe-Salpeter equation should give a meaningful result; however, the solution cannot be effected in practice without an improvement in the mathematical technique required.

The iteration method itself is straightforward and appears to converge with no difficulties. This method may well have applications in similar problems.

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APPENDIX I

Recently Sternheim has pointed out that the Dirac equation does not give the correct result for the hfs interaction energy in the hydrogen atom when the effect of the magnetic dipole moment of the proton is taken to second order. The reason is that the quantization of the radiation field is not properly represented in the Dirac equation, which employs the "classical" potentials φ and \mathbf{A} .

Sternheim first shows that second-order perturbation theory applied to the Dirac equation for an electron in an external field leads to the second-order energy term $(e^2/2m)\langle i | A^2 + i\boldsymbol{\sigma} \cdot \mathbf{A} \times \mathbf{A} | i \rangle$. This term also occurs when the Foldy-Wouthuysen (F-W) or Pauli reductions are carried out and perturbation theory applied. The term containing $\mathbf{A} \times \mathbf{A}$ is not usually given because in most cases $\mathbf{A} \times \mathbf{A} = 0$. In fact, using the F-W transformation the Hamiltonian itself contains the term $(e^2/2m)(a^2 + i\boldsymbol{\sigma} \cdot \mathbf{A} \times \mathbf{A})$ without reference to the state $|i\rangle$ of the electron.

The second part of Sternheim's paper gives the result $(e^2/4m)(A^2 + i\boldsymbol{\sigma} \cdot \mathbf{A} \times \mathbf{A})$ for the energy due to the uncrossed photon diagram and $(e^2/4m)(A^2 - i\boldsymbol{\sigma} \cdot \mathbf{A} \times \mathbf{A})$ for the energy due to the crossed-photon diagram. This gives a total energy contribution of $(e^2/2m)A^2$ with the $\mathbf{A} \times \mathbf{A}$ terms obviously canceling.

Since the Dirac equation contains the term in $\mathbf{A} \times \mathbf{A}$ implicitly we remove its effect to second order by adding the term

$$\mathcal{H}'' = -(e^2/2m)i\boldsymbol{\sigma} \cdot \mathbf{A} \times \mathbf{A}$$

to the Dirac Hamiltonian in order to obtain agreement with quantum electrodynamics.

In the use of the \mathcal{H}'' term we shall make a modification in the picture of the electron. In the original Dirac equation the electron is treated as a *point* charge and this leads to a correct result. However, in the representation resulting from the use of the F-W transformation the electron is "spread out" over a distance comparable to its Compton wavelength, $1/m$ (this is \hbar/mc , but we have let $\hbar=c=1$). The spurious term in $\mathbf{A} \times \mathbf{A}$ occurs explicitly in the representation and so in evaluating integrals over terms arising from \mathcal{H}'' we shall assume that the potential v_m as defined in Eq. (5) is equal to $1/r$ for $r > 1/m$ and is $\approx (1/m)^{-1}$ for $r < 1/m$. This removes difficulties with "enormous" (first-order) contributions to the energy splittings arising from the second-order \mathcal{H}'' which occur if v_m continues as $1/r$ down to the proton radius.

The splittings still contain spurious terms which may be large enough to contribute appreciably to second order, so that a more satisfactory method should be found to account for the quantum electrodynamic effects.

We are essentially using $1/2Z\alpha m$ as the unit of length so that the critical distance is $y_c = 2Z\alpha m(1/m) = 2Z\alpha \approx 10^{-2}$. The quantity y_c will be used as the lower limit to "cut off" the integrals arising from \mathcal{H}'' and would otherwise give rise to anomalously large terms.

APPENDIX II

Here the lowest order solutions of Eqs. (43) will be found. This will be done by making approximations in the equations themselves in order to obtain simple low-order equations. The approximations are

$$\lambda/Z\alpha \approx 1/n,$$

$$Z\alpha\lambda/[1 - (1 - \lambda^2)^{1/2}] = Z\alpha\lambda^{-1}[1 + (1 - \lambda^2)^{1/2}] \approx 2n,$$

$$Z\alpha\lambda/[1 + (1 - \lambda^2)^{1/2}] \approx \frac{1}{2}Z\alpha\lambda \approx (Z\alpha)^2/2n,$$

and the last term in $(Z\alpha)^2$ is to be neglected in comparison with unity; this corresponds to taking the nonrelativistic limit. We shall also neglect $\gamma\varphi_m'$ completely in the first equation and also in the second and third equations when multiplied by w_2 or w_3 . For $x < x_c$, φ_m' will be neglected altogether. Also we let $\delta(\varphi_m')^2 = 0$ everywhere.

The equations then become for $x > x_c$

$$w_1' + 2w_1/x + 1/2n - 2n/x - w_1^2/2n = 0, \quad (43.1)$$

$$w_2' + 3w_2/x + (w_3 - w_1w_2)/2n = \sqrt{2}\gamma/x^2, \quad (43.2)$$

$$w_3' - w_3/x + (w_2 - w_1w_3)/2n - 2nw_2/x = -\sqrt{2}\gamma w_1/x^2. \quad (43.3)$$

For $n=1$, we find immediately that $w_1=1$ is a solution of (43.1). This is obviously the only solution which makes sense physically. It is easily verified that the solutions to Eqs. (43.2) and (43.3) are

$$w_2 = \sqrt{2}\gamma(1/12 + 1/2x) + c_1(1/x^3 + 3/2x^2 + 1/4x + 1/24),$$

$$w_3 = \sqrt{2}\gamma/12 + c_1(-1/2x^3 + 3/4x^2 + 1/24).$$

The constant c_1 multiplies the homogeneous solution which is finite as x becomes infinite. For $x < x_c$ we have

$$\begin{aligned} w_2' + 3w_2/x - \frac{1}{2}(w_2 - w_3) &= 0, \\ w_3' - w_3/x + \frac{1}{2}(w_2 - w_3) - w_2/x_c &= 0. \end{aligned}$$

We expand the solutions about $x=0$ in a Taylor's series and the lowest order terms are

$$\begin{aligned} w_2 &= -c_2 x^2/10, \\ w_3 &= c_2(x + \frac{1}{2}x^2). \end{aligned}$$

The constants are found (by matching at $x=x_c$) to be $c_1 = -\frac{1}{2}\sqrt{2}\gamma x_c^2$ and $c_2 = -\sqrt{2}\gamma/x_c^2$. We note that for $x < x_c$, w_2 is of higher order than w_3 so that to lowest order $w_2=0$ and $w_3 = \sqrt{2}\gamma x/x_c^2$. By dropping the terms which will not contribute to the integral over ph_2 we have for $x > x_c$

$$\begin{aligned} w_2 &= \sqrt{2}\gamma(1/12 + 1/2x - x_c^2/2x^3), \\ w_3 &= \sqrt{2}\gamma(1/12 + x_c^2/4x^3). \end{aligned}$$

These solutions will satisfy Eqs. (43.2) and (43.3) for $n=1$ *only* to lowest order which is all we require.

For arbitrary n the solutions given by Eqs. (44) can be substituted into Eqs. (43.2) and (43.3) directly and in both cases Eq. (43.1) will result when the higher order terms in x_c^2/x^3 are dropped for $x > x_c$.

APPENDIX III

We wish to evaluate integrals of the form

$$\int_0^\infty x^n e^{-x} (1/x - \varphi_e) dx.$$

The exponential can be replaced by unity in the range $0 < x < x_c$, and since the integrand vanishes in the region

$x > x_c$ we can replace e^{-x} by 1 to obtain results to the order required. We integrate twice by parts to obtain the Laplacian of the potential, and then use the relation $-(4\pi)^{-1}\nabla^2 v_e(r) = f_e(r)$ to obtain the result

$$\begin{aligned} &\int_0^\infty x^n e^{-x} (1/x - \varphi_e) dx \\ &= -[n(n+1)]^{-1} \int x^n (4\varphi)^{-1} \nabla^2 v_e(r) d\mathbf{r} \\ &= [n(n+1)]^{-1} \int x^n f_e(r) d\mathbf{r} \\ &= [n(n+1)]^{-1} \int x^n \rho(r) d\mathbf{r} / \int \rho(r) d\mathbf{r} \\ &= \langle x_e^n \rangle / n(n+1), \quad n > 0. \end{aligned}$$

This is an average over the electric charge density $\rho(r) = Zef_e(r)$. The result

$$\int_0^\infty x^n e^{-x} (1/x^2 + \varphi_m') dx = \langle x_m^{n-1} \rangle / (n-1), \quad n > 1,$$

is obtained in the same way. We also define

$$\langle x_{em} \rangle = \int_0^\infty x^2 e^{-x} (1/x - \varphi_e) (1/x - \varphi_m) dx.$$

Some of these averages, such as $\langle x_e^2 \rangle$ can be measured experimentally; the others can be evaluated only by assuming a form for φ_e or φ_m and carrying out the integrations. None of these will appear in the final expression for R , but they would be needed to evaluate the expressions for the energy levels and splittings.