to reduce the positronium amplitude (from the Born result) but that the major reduction comes from the "centrifugal" term $-2p_f^2/r^2$. This term arose from the choice of coordinates [Eq. (6a)] and the requirements on the wave function at $r\to\infty$. However, the continuation to small r is certainly not unique. For instance, the modification of the basic form (6a) discussed with reference to (6b) would modify the potential in question with the resulting form $-2(p_f^2/r^2)\beta^2(r)$. The asymptotic requirement $\beta(\infty)=1$ ensures the correct asymptotic form for Ψ, but setting $\beta(0)=0$ would turn off this term at short distances. We have chosen the form

$$\beta=1-e^{-ar} \tag{27}$$

and have rerun the problem with several values of the parameter a. For $a\geq 2$ there are essentially no changes from the results quoted here. This indicates that our results do not depend critically upon the continuation of long-range effects into the origin. For small values of a, we drastically modify the short-range terms and the results are changed. The parameter a could be interpreted as a variational parameter, and optimized. This requires further calculation which we hope to report on soon.

No experimental evidence is available for comparison here. However, there are some data on positron-helium scattering.[13] This is a swarm experiment, and its analysis[14] depends upon some assumptions concerning positronium formation. One assumption in particular is that positronium will be formed rapidly when it is energetically possible. If the results of this paper are to be relied upon and if they can be extrapolated to helium, then this assumption will have to be reexamined. For this reason, and for the additional reason that direct positron scattering experiments on helium are now contemplated,[15] we propose to apply the method used here to that problem.

Note added in proof. B. Bransden and Z. Jundt have reported on a similar calculation at the Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, USSR, 1967 (unpublished), in which they solved the equations associated with our Eq. (1). Their positronium-formation results are drastically different from ours. In particular they show a pronounced peak in the s-wave results near threshold. The reason for the discrepancy is not clear.

[13] S. Marder, V. W. Hughes, C. S. Wu, and W. Bennett, Phys. Rev. **103**, 1258 (1956).
[14] W. B. Teutsch and V. W. Hughes, Phys. Rev. **103**, 1266 (1956); R. Drachman, *ibid.* **138**, A1582 (1965).
[15] W. McGowan (private communication).

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Precise Theory of the Zeeman Spectrum for Atomic Hydrogen and Deuterium and the Lamb Shift*

STANLEY J. BRODSKY AND RONALD G. PARSONS†
Stanford Linear Accelerator Center, Stanford University, Stanford, California
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In this paper we give a complete and straightforward analysis of the $n=2$ Zeeman structure which is intrinsically accurate to 1 ppm for determining the Lamb shift from present experiments. This analysis takes into account the current experimental and theoretical knowledge of the atomic Hamiltonian. It is shown that the magnetic part of this Hamiltonian can be taken as that of a free electron and a free nucleus. Radiative corrections to this assumption are shown to be negligible. The total Hamiltonian can then be diagonalized in the $|F, j, l, m_F>$ representation. Matrix representations of the Hamiltonian are given for all $n=2$ states of hydrogen and deuterium. We give theoretical predictions for the $l=1$ hyperfine intervals in hydrogen and deuterium which are accurate to 10 ppm. Values of the Lamb shift calculated from the recent Zeeman level crossings of Robiscoe and Cosens are tabulated.

I. INTRODUCTION

THE $n=2$ Zeeman structure of atomic hydrogen and deuterium has served as a precise testing ground of quantum electrodynamics. Our knowledge of the Lamb shift, the $2P_{1/2}$-$2S_{1/2}$ interval, and the fine structure separation, the $2P_{3/2}$-$2P_{1/2}$ interval, has been determined from an extrapolation to zero field of experimental measurements of the atomic spectrum in a nonzero magnetic field. In this paper we calculate in detail an accurate extrapolation of the Zeeman levels. This seems especially important now in view of the discrepancy of the measured and predicted Lamb shift.

The first comprehensive analysis of the precise Zeeman structure theory required to interpret the experimental spectrum was given by Lamb in conjunction with the pioneering experiments performed by

* Work supported by the U. S. Atomic Energy Commission.
† Present address: Department of Physics, Northeastern University, Boston, Massachusetts.

Lamb and his co-workers.[1] The same type of analysis was also applied by Robiscoe and Cosens[2] to their recent measurements of level crossings. A precise analysis of the dependence of atomic levels on a magnetic field is also necessary in order to interpret the results of experiments involving the new technique of resonance fluorescence.[3]

The analysis given by Lamb and Robiscoe involves a complicated perturbation theoretic treatment of the Zeeman spectra. Many contributions which individually could have affected the determination of the Lamb shift at the order of 0.01 MHz were not included; the intrinsic accuracy of their analysis is thus not certain.

In this paper we give a complete and hopefully straightforward analysis of the $n=2$ Zeeman structure which is intrinsically accurate to 1 ppm for determining the Lamb shift from present experiments.

The method used here is essentially a diagonalization of the total Hamiltonian of the hydrogen or deuterium atom at rest in a uniform magnetic field. It is shown that, to sufficient accuracy,[4] this Hamiltonian may be written as the sum of two parts:

(1) A magnetic Hamiltonian appropriate for the interaction of a *free* electron and a *free* nucleus with a uniform magnetic field. (See Appendix A.)

(2) The Hamiltonian of the atom with no external field applied.

All that is required for the specification of the latter part of the Hamiltonian is the eigenfunctions and eigenvalues for $n=2$. Our philosophy is to take the accurately known experimental numbers for this spectrum whenever possible. For example, the $2S$ hyperfine separation has been accurately measured, and is used in the analysis.

The P-state hyperfine levels must be calculated from theory, but to the accuracy required (≈ 100 ppm), this can readily be done without considering corrections from quantum electrodynamics. The derivation is given in Appendix B.

The Lamb shift and fine structure interval can be considered as parameters which may be adjusted to fit the observed Zeeman spectrum, and then compared to theory.

An order of magnitude estimate is given of all uncomputed contributions. In particular, the analysis of Appendix A shows that there are no important radiative corrections to the Zeeman structure which have not been taken into account.

In this paper we do not consider the complications due to asymmetry of the line shape, but confine ourselves to the magnetic field dependence of the energy levels (line centers) of a stationary atom in a uniform magnetic field. The line shapes which occur in the experimental measurements depend critically on the experimental details. A complete discussion of how line asymmetry corrections have been treated in the experiments of Ref. 2 will be published shortly.[5] Most of the symbols in this paper are defined in Table I.

TABLE I. Glossary of symbols.

m	mass of electron
M_P	mass of proton
M_D	mass of deuteron
m_H	reduced mass of electron-proton system
m_D	reduced mass of electron-deuteron system
g_s	measured electron gyromagnetic ratio
g_L	electron orbital gyromagnetic ratio
g_{IH}	Landé factor for the proton $\approx 5.58m/M_P$
g_{ID}	Landé factor for the deuteron $\approx 0.86m/M_P$
$\mathbf{S}$	electron spin vector
$\mathbf{L}$	orbital electron angular-momentum vector
$\mathbf{I}$	nucleus spin vector
$\mathbf{J}$	total electron angular momentum $=\mathbf{L}+\mathbf{S}$
$\mathbf{F}$	total atomic angular momentum $=\mathbf{J}+\mathbf{I}$
Ry_∞	Rydberg for infinite mass
ΔE_H	fine structure interval $(2P_{3/2}-2P_{1/2})$ for hydrogen
ΔE_D	fine structure interval $(2P_{3/2}-2P_{1/2})$ for deuterium
κ_P	anomalous magnetic moment of the proton $(1+\kappa_P\approx 2.79)$
κ_D	anomalous magnetic moment of the deuteron $(1+\kappa_D \approx 0.86(M_D/M_P))$
μ_P	magnetic moment of proton $\approx 2.79(e/2M_P)$
μ_D	magnetic moment of deuteron $\approx 0.86(e/2M_P)$
μ_0	electron Bohr magneton
ν_c	corrected center NMR (proton in water) frequency

II. THEORY

A. The Total Hamiltonian

We write the Hamiltonian for a hydrogenlike atom in a constant external magnetic field $\mathbf{H}$ as $\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2+\mathcal{H}_3$. $\mathcal{H}_1$ is the magnetic Hamiltonian for the electron (subscript 1) in the external potential $\mathbf{A}_1=\frac{1}{2}\mathbf{r}_1\times\mathbf{H}$ and includes a term for the anomalous magnetic moment of the electron:

$$\mathcal{H}_1=-\boldsymbol{\alpha}_1\cdot|e|\mathbf{A}_1+(g_s-2)\frac{|e|}{2m}\mathbf{S}\cdot\mathbf{H}. \tag{1}$$

Similarly, $\mathcal{H}_2$ is the magnetic Hamiltonian for the nucleus and includes a term for its magnetic moment. We write, for hydrogen,

$$\mathcal{H}_2=\boldsymbol{\alpha}_2\cdot|e|\mathbf{A}_2-(2\kappa_P)\frac{|e|}{2M_P}\mathbf{I}\cdot\mathbf{H}, \tag{2}$$

[1] W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. **79**, 549 (1950); **81**, 222 (1951); W. E. Lamb, Jr., *ibid.* **85**, 259 (1952); W. E. Lamb, Jr., and R. C. Retherford, *ibid.* **86**, 1014 (1952); S. Triebwasser, E. S. Dayhoff and W. E. Lamb, Jr., *ibid.* **89**, 98 (1953); E. S. Dayhoff, S. Triebwasser, and W. E. Lamb, Jr., *ibid.* **89**, 106 (1953). The analysis of the Zeeman structure is given in the third paper.

[2] R. T. Robiscoe, Phys. Rev. **138**, A22 (1964); R. T. Robiscoe and B. L. Cosens, Phys. Rev. Letters **17**, 69 (1966); Bull. Am. Phys. Soc. **14**, 62 (1966); B. L. Cosens, Ph. D. thesis, Yale University (unpublished).

[3] See, for example, H. Wieder and T. G. Eck, Phys. Rev. **153**, 103 (1967); F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, Phys. Rev. Letters **3**, 420 (1959).

[4] The error, which occurs due to radiative corrections, is shown in Appendix A to be of order $\alpha^3\mu_0 H$.

[5] R. T. Robiscoe (private communication).

and for deuterium

$$\mathcal{H}_2=\frac{1}{M_D}\mathbf{p}_2\cdot|e|\mathbf{A}_2-(1+\kappa_D)\frac{|e|}{2M_D}\mathbf{I}\cdot\mathbf{H}, \tag{3}$$

where $\mathbf{A}_2=\frac{1}{2}\mathbf{r}_2\times\mathbf{H}$. $\mathcal{H}_3$ is the remainder of the total Hamiltonian, and thus contains all the electron-nucleus interaction (as could be derived from the full Bethe-Salpeter equation) as well as all the self-interaction of the particles. It is shown in Appendix A that $\mathcal{H}_3$ is essentially independent of the external field, in fact

$$\mathcal{H}_3(H)-\mathcal{H}_3(H=0)=O(\alpha^3\mu_0 H). \tag{4}$$

Thus we will take $\mathcal{H}_3$ as its $H=0$ value; $\mathcal{H}_3(H=0)=\mathcal{H}_0$. It can be specified, for our purposes, by its eigenvalues for those eigenstates with which we are concerned. Some of the eigenvalues of $\mathcal{H}_0$ can be determined accurately by experiment, for example, the $l=0$ hyperfine splitting and the fine structure interval of the $n=2$ levels. Other eigenvalues must be determined from theory, for example, the $l\neq 0$ hyperfine structure and the Lamb shift. Once the spectrum of $\mathcal{H}_0$ is known, we can diagonalize the Hamiltonian and obtain a precise prediction for the Zeeman levels of the atom.

The spectrum of $\mathcal{H}_0$ in lowest order is the (n,j) spectrum of the reduced-mass Sommerfeld formula. The degeneracy with respect to l is removed by quantum electrodynamic self-energy and vacuum polarization level shift corrections as well as by relativistic reduced-mass corrections as defined by the Bethe-Salpeter equation. Finally, the hyperfine interaction removes the degeneracy with respect to the total angular momentum $\mathbf{F}$ where $\mathbf{F}=\mathbf{J}+\mathbf{I}=\mathbf{L}+\mathbf{S}+\mathbf{I}$. The spectrum of $\mathcal{H}_0$ can thus be specified by the states[6] $|n,F,j,l,m_F\rangle$. The radial dependence of the eigenfunctions is described accurately, except at very small distances, by the Dirac equation using reduced coordinates.[7]

B. The Spectrum of $\mathcal{H}_0$ for $n=2$

In this section we review the current state of knowledge of the spectrum of $\mathcal{H}_0$ for $n=2$.

The theoretical predictions for the Lamb shift $2S_{1/2}$-$2P_{1/2}$ are[8]

$$\begin{aligned}&\text{S}=1057.57\pm0.08\text{ MHz for hydrogen},\\&\text{S}=1058.83\pm0.08\text{ MHz for deuterium}.\end{aligned} \tag{5}$$

The error in each theoretical prediction corresponds to 1 standard deviation (s.d.) error in α and includes theoretical estimates of uncalculated terms of order $\alpha(Z\alpha)^6mc^2$ and higher. In Sec. V we compare these values with S obtained from experiment.

The total hyperfine splittings of the $2S_{1/2}$ state in hydrogen and deuterium have been measured[9] and found to be

$$\begin{aligned}&\Delta\nu(2S_{1/2},H)=177.55686\pm0.00005\text{ MHz}\quad 1\text{ s.d.},\\&\Delta\nu(2S_{1/2},D)=40.924439\pm0.000020\text{ MHz}\quad 1\text{ s.d.},\end{aligned} \tag{6}$$

and the hyperfine levels are

$$\begin{aligned}&\nu(2S_{1/2},H)=\Delta\nu(2S_{1/2},H)\langle\mathbf{I}\cdot\mathbf{J}\rangle,\\&\nu(2S_{1/2},D)=\tfrac{2}{3}\Delta\nu(2S_{1/2},D)\langle\mathbf{I}\cdot\mathbf{J}\rangle.\end{aligned} \tag{7}$$

The hyperfine splitting of the $l=1$ levels must be predicted from theory. One complication is that the hyperfine interaction is off-diagonal in j. For the diagonal part of the hyperfine Hamiltonian (proportional to $\mathbf{I}\cdot\mathbf{J}$) we find (see Appendix B)[10]

$$\begin{aligned}
\nu(2P_{1/2},H)&=\frac{E_F(H)}{3}\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}+\frac{m}{4M_P}\left(\frac{1+2\kappa_P}{1+\kappa_P}\right)\right]\\
&\quad\times\left[1+\frac{47}{24}(Z\alpha)^2\right]\langle\mathbf{I}\cdot\mathbf{J}\rangle,\\
\nu(2P_{3/2},H)&=\frac{E_F(H)}{15}\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}+\frac{5m}{8M_P}\left(\frac{1+2\kappa_P}{1+\kappa_P}\right)\right]\\
&\quad\times\left[1+\frac{7}{24}(Z\alpha)^2\right]\langle\mathbf{I}\cdot\mathbf{J}\rangle,\\
\nu(2P_{1/2},D)&=\frac{E_F(D)}{9/2}\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}+\frac{m}{2M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right]\\
&\quad\times\left[1+\frac{47}{24}(Z\alpha)^2\right]\langle\mathbf{I}\cdot\mathbf{J}\rangle,\\
\nu(2P_{3/2},D)&=\frac{E_F(D)}{45/2}\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}+\frac{5m}{4M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right]\\
&\quad\times\left[1+\frac{7}{24}(Z\alpha)^2\right]\langle\mathbf{I}\cdot\mathbf{J}\rangle,
\end{aligned} \tag{8}$$

[6] If $l\neq 0$, j is no longer a good quantum number due to the tensor part of the hyperfine interaction. This will be dealt with later.

[7] E. E. Salpeter, Phys. Rev. **87**, 328 (1952).

[8] G. W. Erickson and D. R. Yennie, Part I, Ann. Phys. (N. Y.) **35**, 271 (1965); Part II, Ann. Phys. (N. Y.) **35**, 447 (1965). M. F. Soto, Jr., Phys. Rev. Letters **17**, 1153 (1966). The numerical values for the Lamb shift were given by D. R. Yennie at the International Conference on Electromagnetic Interactions of Low and Intermediate Energies, Dubna, February 1967 (unpublished). He used $\alpha^{-1}=137.0359\pm0.0004$ (1 s.d.) obtained from a new value of $2e/h$ from the ac Josephson effect. See W. H. Parker, B. N. Taylor, and D. N. Langenberg, Phys. Rev. Letters **18**, 287 (1967). This new value of α changes the theoretical prediction of the Lamb shift by $+0.07$ MHz.

[9] J. W. Heberle, H. A. Reich, and P. Kusch, Phys. Rev. **101**, 612 (1956). H. A. Reich. J. W. Heberle, and P. Kusch, *ibid.* **104**, 1585 (1956).

[10] These expressions ignore possible radiative corrections of order $(\alpha/\pi)(Z\alpha)^2\ln(Z\alpha)E_F$ and relativistic recoil and nuclear size corrections of order $\alpha(m/M_p)E_F$. Note also that $\nu(2P_{3/2},D)$ does not take into account the deuteron's induced or static electric quadrupole moment.

where E_F is the Fermi splitting for the $2S_{1/2}$ state[11]

$$E_F(H)=\tfrac{2}{3}\alpha^2 cRy_\infty\frac{\mu_p}{\mu_0}\left(\frac{m_H}{m}\right)^3,$$
$$E_F(D)=\alpha^2 cRy_\infty\frac{\mu_D}{\mu_0}\left(\frac{m_D}{m}\right)^3, \tag{9}$$

and where g_s is the measured electron gyromagnetic ratio[12]

$$g_s/2=1.001159622\pm0.000000027.$$

The off-diagonal hyperfine Hamiltonian is[13]

$$\mathcal{H}_{\rm hfs}'=\frac{E_F(H)}{16}\left[2-\frac{g_s}{2}+\frac{m}{M_P}\left(\frac{1+2\kappa_P}{1+\kappa_P}\right)\right]\langle\mathbf{I}\cdot\mathbf{L}\rangle \tag{10a}$$

for hydrogen, and

$$\mathcal{H}_{\rm hfs}'=\frac{E_F(D)}{24}\left[2-\frac{g_s}{2}+\frac{2m}{M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right]\langle\mathbf{I}\cdot\mathbf{L}\rangle \tag{10b}$$

for deuterium.

The $2P_{3/2}$-$2P_{1/2}$ fine structure can be predicted from theory using the value of α from the ac Josephson effect[8,14];

$$\Delta E(H)=\tfrac{1}{16}\alpha^2 Ry_\infty c\left(\frac{m_H}{m}\right)^3\left[g_s\left(\frac{m}{m_H}\right)-1+\tfrac{5}{8}\alpha^2+\frac{\alpha^3}{\pi}\ln(\alpha^2)\right]$$
$$=10969.0542\text{ MHz},$$
$$\Delta E(D)=\tfrac{1}{16}\alpha^2 Ry_\infty c\left(\frac{m_D}{m}\right)^3\left[g_s\left(\frac{m}{m_D}\right)-1+\tfrac{5}{8}\alpha^2+\frac{\alpha^3}{\pi}\ln(\alpha^2)\right] \tag{11}$$
$$=10972.0485\text{ MHz}.$$

If we wish, the fine-structure separation and the Lamb shift can be considered as parameters which are to be adjusted to fit the observed Zeeman spectrum and then compared with the theoretical results given in Eq. (5). In our analysis we concentrate on determining the Lamb shift from the data in Ref. 2. For this purpose, we can adopt the theoretical value for ΔE since a 75 ppm change in ΔE is required to produce a 1 ppm change in the determined Lamb shift.

The spectrum of $\mathcal{H}_0$ (excepting $\mathcal{H}_{hfs}'$) for $n=2$ is thus known. The radial dependence of the eigenfunctions is not known exactly, but from perturbation theory we know that they differ from the $n=2$ Dirac wave functions only for $r\ll\hbar/mc$.[7] The eigenfunctions are then completely specified by $|F,j,l,m_F\rangle$.

C. Evaluation of the Magnetic Hamiltonian

If one performs the radial integration for the $n=2$ states, then $\mathcal{H}_1+\mathcal{H}_2$ is replaced by a general form

$$\mathcal{H}_1+\mathcal{H}_2\underset{n=2}{\longrightarrow}\mathcal{H}_{\rm mag}=[A_sS_z+\tfrac{1}{2}A_LL_z+\tfrac{1}{2}L_zA_L+A_II_z]\mu_0H$$
$$+O(e^2\mathbf{A}_1^2/m), \tag{12}$$

where S_z, L_z, and I_z are the z components of the electron spin, relative orbital angular momentum, and the nucleon spin operators, respectively. The z direction is defined as the direction of $\mathbf{H}$ and $H\equiv|\mathbf{H}|$. The coefficients A_s, A_L, and A_I are

$$\begin{aligned}A_I&=-g_{IH}\text{ for hydrogen}\\&=-g_{ID}\text{ for deuterium},\\A_s&=g_s(1+\tfrac{2}{3}W/m)\text{ for }l=0\\&=g_s(1+\tfrac{4}{5}W/m)\text{ for }l=1,\\A_L&=g_L(1+W/m-\mathbf{S}\cdot\mathbf{L}(2W/5m))\text{ for }l=1,\end{aligned} \tag{13}$$

where W is the Bohr energy of the $n=2$ state; $W=-(Z\alpha)^2m/8$. Here $g_L=(1-m/M_P)$ for hydrogen and $g_L=(1-m/M_D)$ for deuterium taking into account the magnetic interaction of the nucleon motion about the atomic center of mass.[15]

The binding corrections given here are just the first term in the expansion in $(Z\alpha)^2$ obtained from the Dirac wave functions. The error made in not using the exact eigenfunctions of $\mathcal{H}_0$ should be of the same order as if W were replaced by the actual binding energy. Such corrections are of order $(Z\alpha)^2m/M_P$. Thus the theoretical expressions given for A_s and A_L are accurate to 0.1 ppm. Note that for a uniform magnetic field $\mathbf{H}\neq\mathbf{H}(\mathbf{x})$, quantum electrodynamics affects A_s only through the static anomalous magnetic moment and does not affect A_L.

The quadratic Zeeman term $\langle\frac{1}{2}e^2\mathbf{A}_1^2\rangle$ is approximately 0.01 MHz for $H=1500$ G.[15] However all $n=2$ levels are affected similarly and the maximum change in separation of any two $n=2$ levels is 0.001 MHz for $H=1500$ G. This term can thus be ignored in our analysis, as well as the negligible $\Delta l=2$ state mixing it induces.

We have also ignored the negligible $\Delta n\neq0$ contributions of $\mathcal{H}_0$.

III. CALCULATIONS

Our task in this section is to find the eigenvalues of the total Hamiltonian $\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2$. To do this we shall

[11] $E_F(H)$ could also be obtained from $\Delta\nu(2S)$ by removing the binding corrections, radiative corrections and nuclear size effects.

$$E_F=\Delta\nu(2S)\,(2/g_s)\left[1-\frac{\alpha^2}{8}+(\tfrac{5}{2}-\ln2)\alpha^2+\frac{2}{3}\frac{\alpha^3}{\pi}\ln^2(1/\alpha^2)-\delta_{\rm nuc}\right]$$

Using $\alpha^{-1}=137.0359$ and $\delta_{\rm nuc}=-36\times10^{-6}$ the two formulas give identical results. See S. J. Brodsky and G. W. Erickson, Phys. Rev. **148**, 26 (1966).

[12] D. T. Wilkinson and H. R. Crane, Phys. Rev. **130**, 852 (1963).

[13] The binding corrections of order $(Z\alpha)^2$ can be ignored here since $\mathcal{H}_{\rm hfs}'$ is itself only a $\frac{1}{4}\%$ correction to the hyperfine energies.

[14] R. P. Feynman, in *The Quantum Theory of Fields* (Interscience Publishers, Inc., New York, 1961), p. 61. The radiative correction $(\alpha/\pi)(Z\alpha)^2\ln(Z\alpha)^2\Delta E$ was computed by A. J. Layzer, Phys. Rev. Letters **4**, 580 (1960) and confirmed by Erickson and Yennie (Ref. 8). A bound on the next term, $(\alpha/\pi)(Z\alpha)^2\Delta E\times(16/3)a$, has been given by Erickson: $|a|<1$. [G. W. Erickson (private communication).]

[15] See the third paper of Ref. 1.

require matrix representations of S_z, I_z, L_z, F_z, and $\mathbf{I}\cdot\mathbf{L}$ in the basis of eigenfunctions of the diagonal part of $\mathcal{H}_0$. In this basis, F and m_F are good quantum numbers and $F_z|F,j,l,m_F\rangle=m_F|F,j,l,m_F\rangle$. We can eliminate L_z by $L_z=F_z-I_z-S_z$. The matrix elements of S_z, I_z, and $\mathbf{I}\cdot\mathbf{L}$ are most easily calculated by the general methods of angular momentum in quantum mechanics.[16]

For $S=\frac{1}{2}$

$$\langle j',I',F',m_{F'}|S_z|j,I,F,m_F\rangle=(-1)^{l+S+I+1+2j'-m_F}\delta_{SS'}\delta_{ll'}\delta_{II'}[\tfrac{3}{2}(2F'+1)(2F+1)(2j'+1)(2j+1)]^{1/2}$$
$$\times\begin{pmatrix}F' & F & 1\\ -m_{F'} & m_F & 0\end{pmatrix}\begin{Bmatrix}F' & F & 1\\ j & j' & I\end{Bmatrix}\begin{Bmatrix}\frac{1}{2} & j' & l\\ j & \frac{1}{2} & 1\end{Bmatrix}, \quad (14)$$

$$\langle j',I',F',m_{F'}|I_z|j,I,F,m_F\rangle=(-1)^{F'+F-I-j-m_F}\delta_{ll'}\delta_{SS'}\delta_{II'}\delta_{jj'}[(2F'+1)(2F+1)(2I+1)(I+1)(I)]^{1/2}$$
$$\times\begin{pmatrix}F' & F & 1\\ -m_{F'} & m_F & 0\end{pmatrix}\begin{Bmatrix}F' & F & 1\\ I & I & j\end{Bmatrix}, \quad (15)$$

and for $l\neq 0$ and $I\neq 0$

$$\langle j',I',F',m_{F'}|\mathbf{I}\cdot\mathbf{L}|j,I,F,m_F\rangle=(-1)^{2j+l+F+I+3/2}\delta_{FF'}\delta m_F m_{F'}\delta_{ll'}\delta_{SS'}\delta_{II'}$$
$$\times[(2j+1)(2j'+1)(2I+1)(I+1)(I)(2l+1)(l+1)(l)]^{1/2}\begin{Bmatrix}F & I & j'\\ 1 & j & I\end{Bmatrix}\begin{Bmatrix}l & j' & \frac{1}{2}\\ j & l & 1\end{Bmatrix}. \quad (16)$$

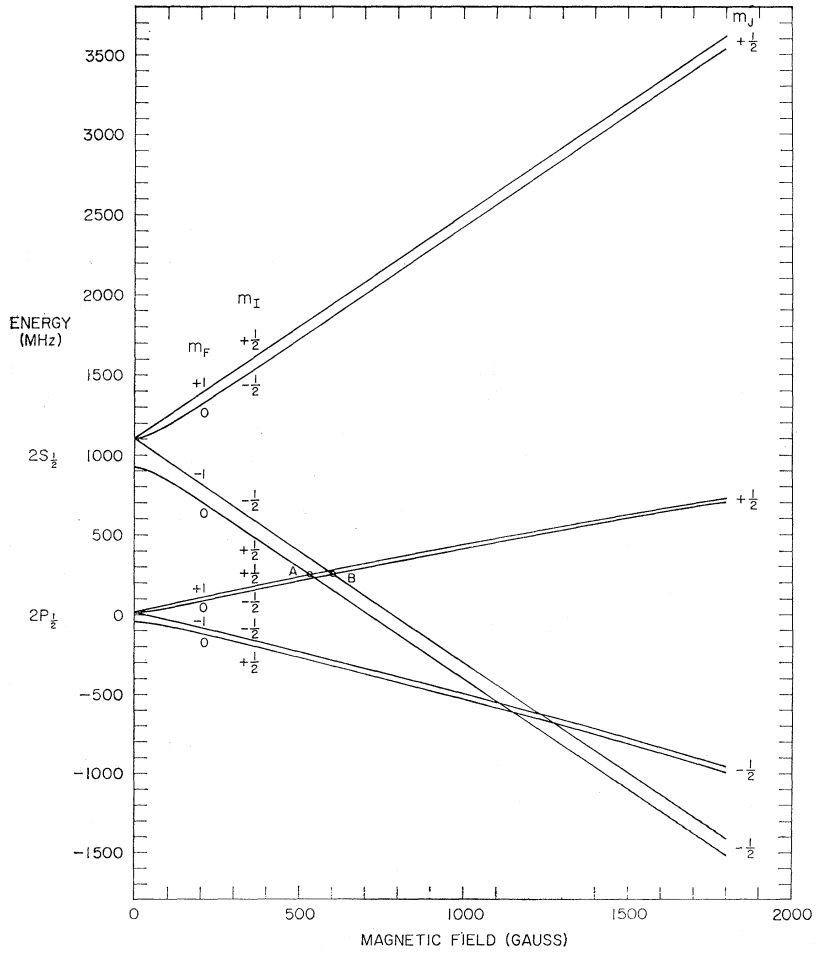

FIG. 1. Zeeman diagram of the $J=\frac{1}{2}$ levels in hydrogen, $n=2$, including hyperfine structure. Crossings marked A and B are observable transitions with $\Delta m_I=0$.

[16] See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey 1957).

TABLE II. Submatrices of the Hamiltonian for $I=\frac{1}{2}$ (hydrogen). The notation in this table is explained in Eq. (17).

$\{I=\frac{1}{2}, l=0, m_F=-1\}$

F	j	$\frac{1}{2}$
1	$\frac{1}{2}$	$\left[(-1,-\frac{1}{2},-\frac{1}{2})+\frac{\Delta\nu(2S,H)}{4}\right]$

$\{I=\frac{1}{2}, l=0, m_F=0\}$

F	j	$\frac{1}{2}$	$\frac{0}{2}$
1	$\frac{1}{2}$	$(0,0,0)+\frac{\Delta\nu(2S,H)}{4}$	$(0,\frac{1}{2},-\frac{1}{2})$
0	$\frac{1}{2}$		$(0,0,0)-\frac{3\Delta\nu(2S,H)}{4}$

$\{I=\frac{1}{2}, l=0, m_F=+1\}$

F	j	$\frac{1}{2}$
1	$\frac{1}{2}$	$\left[(1,\frac{1}{2},\frac{1}{2})+\frac{\Delta\nu(2S,H)}{4}\right]$

$\{I=\frac{1}{2}, l=1, m_F=-2\}$

F	j	$\frac{2}{3}$
2	$\frac{3}{2}$	$[(-2,-\frac{1}{2},-\frac{1}{2})+E_{11}]$

$$E_{11}=\left(\frac{E_F(H)}{15/2}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_H$$

$\{I=\frac{1}{2}, l=1, m_F=-1\}$

F	j	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{2}{3}$
1	$\frac{1}{2}$	$(-1,\frac{1}{6},-\frac{1}{2})+E_{11}$	$\left(0,\frac{-\sqrt{2}}{6},0\right)+E_{12}$	$\left(0,\frac{-1}{\sqrt{6}},0\right)$
1	$\frac{3}{2}$		$\left(-1,\frac{-5}{12},\frac{1}{4}\right)+E_{22}$	$\left(0,\frac{1}{4\sqrt{3}},\frac{-\sqrt{3}}{4}\right)$
2	$\frac{3}{2}$			$(-1,-\frac{1}{4},-\frac{1}{4})+E_{33}$

$$E_{11}=\left(\frac{E_F(H)}{3}\right)\left(\frac{1}{4}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right]$$

$$E_{22}=\left(\frac{E_F(H)}{15/2}\right)\left(\frac{-5}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_H$$

$$E_{33}=\left(\frac{E_F(H)}{15/2}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_H$$

$$E_{12}=E_F(H)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{2}}{48}\right)$$

$\{I=\frac{1}{2}, l=1, m_F=0\}$

F	j	$\frac{1}{2}$	$\frac{0}{2}$	$\frac{1}{3}$	$\frac{2}{3}$
1	$\frac{1}{2}$	$(0,0,0)+E_{11}$	$(0,-\frac{1}{6},-\frac{1}{2})$	$(0,0,0)+E_{13}$	$\left(0,\frac{-\sqrt{2}}{3},0\right)$
0	$\frac{1}{2}$		$(0,0,0)+E_{22}$	$\left(0,\frac{-\sqrt{2}}{3},0\right)$	$(0,0,0)$
1	$\frac{3}{2}$			$(0,0,0)+E_{33}$	$(0,\frac{1}{6},-\frac{1}{2})$
2	$\frac{3}{2}$				$(0,0,0)+E_{44}$

$$E_{11}=\left(\frac{E_F(H)}{3}\right)\left(\frac{1}{4}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right]$$

$$E_{22}=\left(\frac{E_F(H)}{3}\right)\left(\frac{3}{4}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right]$$

$$E_{33}=\left(\frac{E_F(H)}{15/2}\right)\left(\frac{5}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_H$$

$$E_{44}=\left(\frac{E_F(H)}{15/2}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_H$$

$$E_{13}=E_F(H)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{2}}{48}\right)$$

$\{I=\frac{1}{2}, l=1, m_F=+1\}$

F	j	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{2}{3}$
1	$\frac{1}{2}$	$(1,-\frac{1}{6},\frac{1}{2})+E_{11}$	$\left(0,\frac{\sqrt{2}}{6},0\right)+E_{12}$	$\left(0,\frac{-1}{\sqrt{6}},0\right)$
1	$\frac{3}{2}$		$\left(1,\frac{5}{12},-\frac{1}{4}\right)+E_{22}$	$\left(0,\frac{1}{4\sqrt{3}},\frac{-\sqrt{3}}{4}\right)$
2	$\frac{3}{2}$			$(1,\frac{1}{4},\frac{1}{4})+E_{33}$

$$E_{11}=\left(\frac{E_F(H)}{3}\right)\left(\frac{1}{4}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right]$$

$$E_{22}=\left(\frac{E_F(H)}{15/2}\right)\left(\frac{-5}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_H$$

$$E_{33}=\left(\frac{E_F(H)}{15/2}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_H$$

$$E_{12}=E_F(H)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{2}}{48}\right)$$

$\{I=\frac{1}{2}, l=1, m_F=+2\}$

F	j	$\frac{2}{3}$
2	$\frac{3}{2}$	$[(2,\frac{1}{2},\frac{1}{2})+E_{11}]$

$$E_{11}=\left(\frac{E_F(H)}{15/2}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_H$$

TABLE III. Submatrices of the Hamiltonian for $I=1$ (deuterium). The notation in this table is explained in Eq. (17).

$\{I=1, l=0, m_F=-\frac{3}{2}\}$

F	$\frac{3}{2}$
j	$\frac{1}{2}$
$\frac{3}{2}$ $\frac{1}{2}$	$\left[(-\frac{3}{2}, -\frac{1}{2}, -1)+\frac{\Delta\nu(2S,D)}{3}\right]$

$\{I=1, l=0, m_F=-\frac{1}{2}\}$

F	$\frac{1}{2}$	$\frac{3}{2}$
j	$\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{2}$ $\frac{1}{2}$	$(-\frac{1}{2}, \frac{1}{6}, -\frac{2}{3})+E_{11}$	$\left(0, \frac{\sqrt{2}}{3}, \frac{-\sqrt{2}}{3}\right)$
$\frac{3}{2}$ $\frac{1}{2}$		$(-\frac{1}{2}, -\frac{1}{6}, -\frac{1}{3})+E_{22}$

$E_{11}=-\frac{2}{3}\Delta\nu(2S,D)$

$E_{22}=\frac{1}{3}\Delta\nu(2S,D)$

$\{I=1, l=0, m_F=+\frac{1}{2}\}$

F	$\frac{1}{2}$	$\frac{3}{2}$
j	$\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{2}$ $\frac{1}{2}$	$(\frac{1}{2}, -\frac{1}{6}, \frac{2}{3})+E_{11}$	$\left(0, \frac{\sqrt{2}}{3}, \frac{-\sqrt{2}}{3}\right)$
$\frac{3}{2}$ $\frac{1}{2}$		$(\frac{1}{2}, \frac{1}{6}, \frac{1}{3})+E_{22}$

$E_{11}=-\frac{2}{3}\Delta\nu(2S,D)$

$E_{22}=\frac{1}{3}\Delta\nu(2S,D)$

$\{I=1, l=0, m_F=+\frac{3}{2}\}$

F	$\frac{3}{2}$
j	$\frac{1}{2}$
$\frac{3}{2}$ $\frac{1}{2}$	$\left[(\frac{3}{2}, \frac{1}{2}, 1)+\frac{\Delta\nu(2S,D)}{3}\right]$

$\{I=1, l=1, m_F=-\frac{5}{2}\}$

F	$\frac{5}{2}$
j	$\frac{3}{2}$
$\frac{5}{2}$ $\frac{3}{2}$	$[(-\frac{5}{2}, -\frac{1}{2}, -1)+E_{11}]$

$$E_{11}=\left(\frac{E_F(D)}{45/8}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

$\{I=1, l=1, m_F=-\frac{3}{2}\}$

F	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$
j	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
$\frac{3}{2}$ $\frac{1}{2}$	$(-\frac{3}{2}, \frac{1}{6}, -1)+E_{11}$	$\left(0, -\left(\frac{2}{15}\right)^{1/2}, 0\right)$	$\left(0, \frac{-2}{3\sqrt{5}}, 0\right)+E_{13}$
$\frac{5}{2}$ $\frac{3}{2}$		$\left(-\frac{3}{2}, -\frac{3}{10}, -\frac{3}{5}\right)+E_{22}$	$\left(0, \frac{\sqrt{2}}{5\sqrt{3}}, \frac{-\sqrt{6}}{5}\right)$
$\frac{3}{2}$ $\frac{3}{2}$			$\left(-\frac{3}{2}, -\frac{11}{30}, -\frac{2}{5}\right)+E_{33}$

$$E_{11}=\left(\frac{E_F(D)}{3}\right)\left(\frac{1}{3}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right]$$

$$E_{22}=\left(\frac{E_F(D)}{45/8}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

$$E_{33}=\left(\frac{E_F(D)}{45/8}\right)\left(-\frac{1}{4}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

$$E_{13}=E_F(D)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{5}}{72}\right)$$

TABLE III. (*continued*).

$\{I=1, l=1, m_F=-\frac{1}{2}\}$

F	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
j	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
$\frac{3}{2}$ $\frac{1}{2}$	$\left(-\frac{1}{2}, \frac{1}{18}, -\frac{1}{3}\right)+E_{11}$	$\left(0, \frac{-\sqrt{2}}{9}, \frac{-\sqrt{2}}{3}\right)$	$\left(0, \frac{-1}{\sqrt{5}}, 0\right)$	$\left(0, \frac{-2}{9\sqrt{5}}, 0\right)+E_{14}$	$(0, \frac{1}{9}, 0)$
$\frac{1}{2}$ $\frac{1}{2}$		$\left(-\frac{1}{2}, -\frac{1}{18}, -\frac{2}{3}\right)+E_{22}$	$(0,0,0)$	$\left(0, \frac{-\sqrt{10}}{9}, 0\right)$	$\left(0, \frac{-2\sqrt{2}}{9}, 0\right)+E_{25}$
$\frac{5}{2}$ $\frac{3}{2}$			$\left(-\frac{1}{2}, -\frac{1}{10}, -\frac{1}{5}\right)+E_{33}$	$(0, \frac{1}{5}, -\frac{3}{5})$	$(0,0,0)$
$\frac{3}{2}$ $\frac{3}{2}$				$\left(-\frac{1}{2}, -\frac{11}{90}, -\frac{2}{15}\right)+E_{44}$	$\left(0, \frac{\sqrt{5}}{9}, \frac{-\sqrt{5}}{3}\right)$
$\frac{1}{2}$ $\frac{3}{2}$					$\left(-\frac{1}{2}, -\frac{5}{18}, \frac{1}{3}\right)+E_{55}$

$$E_{11}=\left(\frac{E_F(D)}{3}\right)\left(\frac{1}{3}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right] \qquad E_{55}=\left(\frac{E_F(D)}{45/8}\right)\left(-\frac{5}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

$$E_{22}=\left(\frac{E_F(D)}{3}\right)\left(-\frac{2}{3}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right] \qquad E_{14}=E_F(D)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{5}}{72}\right)$$

$$E_{33}=\left(\frac{E_F(D)}{45/8}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D \qquad E_{25}=E_F(D)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{2}}{72}\right)$$

$$E_{44}=\left(\frac{E_F(D)}{45/8}\right)\left(-\frac{1}{4}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

$\{I=1, l=1, m_F=+\frac{1}{2}\}$

F	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
j	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
$\frac{3}{2}$ $\frac{1}{2}$	$\left(\frac{1}{2}, -\frac{1}{18}, \frac{1}{3}\right)+E_{11}$	$\left(0, \frac{-\sqrt{2}}{9}, \frac{-\sqrt{2}}{3}\right)$	$\left(0, \frac{-1}{\sqrt{5}}, 0\right)$	$\left(0, \frac{2}{9\sqrt{5}}, 0\right)+E_{14}$	$(0, \frac{1}{9}, 0)$
$\frac{1}{2}$ $\frac{1}{2}$		$\left(\frac{1}{2}, \frac{1}{18}, \frac{2}{3}\right)+E_{22}$	$(0,0,0)$	$\left(0, \frac{-\sqrt{10}}{9}, 0\right)$	$\left(0, \frac{2\sqrt{2}}{9}, 0\right)+E_{25}$
$\frac{5}{2}$ $\frac{3}{2}$			$\left(\frac{1}{2}, \frac{1}{10}, \frac{1}{5}\right)+E_{33}$	$(0, \frac{1}{5}, -\frac{3}{5})$	$(0,0,0)$
$\frac{3}{2}$ $\frac{3}{2}$				$\left(\frac{1}{2}, \frac{11}{90}, \frac{2}{15}\right)+E_{44}$	$\left(0, \frac{\sqrt{5}}{9}, \frac{-\sqrt{5}}{3}\right)$
$\frac{1}{2}$ $\frac{3}{2}$					$\left(\frac{1}{2}, \frac{5}{18}, -\frac{1}{3}\right)+E_{55}$

$$E_{11}=\left(\frac{E_F(D)}{3}\right)\left(\frac{1}{3}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right] \qquad E_{55}=\left(\frac{E_F(D)}{45/8}\right)\left(-\frac{5}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

$$E_{22}=\left(\frac{E_F(D)}{3}\right)\left(-\frac{2}{3}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right] \qquad E_{14}=E_F(D)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{5}}{72}\right)$$

$$E_{33}=\left(\frac{E_F(D)}{45/8}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D \qquad E_{25}=E_F(D)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{2}}{72}\right)$$

$$E_{44}=\left(\frac{E_F(D)}{45/8}\right)\left(-\frac{1}{4}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

TABLE III. (*continued*).

$\{I=1, l=1, m_F=+\frac{3}{2}\}$

F	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$
j	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
$\frac{3}{2}$ $\frac{1}{2}$	$(\frac{3}{2}, -\frac{1}{6}, 1)+E_{11}$	$\left(0, -\left(\frac{2}{15}\right)^{1/2}, 0\right)$	$\left(0, \frac{2}{3\sqrt{5}}, 0\right)+E_{13}$
$\frac{5}{2}$ $\frac{3}{2}$		$\left(\frac{3}{2}, \frac{3}{10}, \frac{3}{5}\right)+E_{22}$	$\left(0, \frac{\sqrt{2}}{5\sqrt{3}}, \frac{-\sqrt{6}}{5}\right)$
$\frac{3}{2}$ $\frac{3}{2}$			$\left(\frac{3}{2}, \frac{11}{30}, \frac{2}{5}\right)+E_{33}$

$$E_{11}=\left(\frac{E_F(D)}{3}\right)\left(\frac{1}{3}\right)\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}\right]$$

$$E_{22}=\left(\frac{E_F(D)}{45/8}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

$$E_{33}=\left(\frac{E_F(D)}{45/8}\right)\left(-\frac{1}{4}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

$$E_{13}=E_F(D)\left(2-\frac{g_s}{2}\right)\left(\frac{-\sqrt{5}}{72}\right)$$

$\{I=1, l=1, m_F=+\frac{5}{2}\}$

F	$\frac{5}{2}$
j	$\frac{3}{2}$
$\frac{5}{2}$ $\frac{3}{2}$	$[(\frac{5}{2}, \frac{1}{2}, 1)+E_{11}]$

$$E_{11}=\left(\frac{E_F(D)}{45/8}\right)\left(\frac{3}{8}\right)\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}\right]+\Delta E_D$$

The 3-j symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

is zero unless $m_1+m_2+m_3=0$ and the vector triplet (j_1,j_2,j_3) satisfies the triangular condition $|j_1-j_2| \leq j_3 \leq j_1+j_2$ (if $m_1=m_2=m_3=0$, $j_1+j_2+j_3$ must be odd). The 6-j symbol

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix}$$

is zero unless the triplets (j_1,j_2,j_3), (j_3,j_4,j_5), (j_1,j_5,j_6), and (j_2,j_4,j_6) satisfy the triangular condition. Thus we can easily obtain selection rules for the matrix elements of S_z, I_z, and $\mathbf{I}\cdot\mathbf{L}$. In order that $\langle S_z\rangle$, $\langle I_z\rangle$, and $\langle \mathbf{I}\cdot\mathbf{L}\rangle$ be nonzero, the triplets $(F',F,1)$ and $(j',j,1)$ must satisfy the triangular condition and we must have $m_F=m_{F'}$. In addition, if $m_F=m_{F'}=0$, then $1+F+F'$ must be odd for $\langle S_z\rangle$ and $\langle I_z\rangle$ to be nonzero.

From the selection rules, we see that the matrix representation of the magnetic Hamiltonian for a hydrogenlike atom in the $n=2$ state can be separated into submatrices of a given l and m_F. The basis states for these submatrices are then characterized by F and j. In Tables II and III, these submatrices are tabulated for $I=\frac{1}{2}$ (hydrogen) and $I=1$ (deuterium).

The notation in these tables is as follows. All matrix elements are of the form

$$\mu_0 H[F_z A_L+S_z(A_s-A_L)-I_z(A_I+A_L)]+E \equiv (F_z,S_z,I_z)+E, \quad (17)$$

where E is the matrix element of $\mathcal{H}_0$.

Since the effective values of A_s and A_L depend on l and j, the appropriate values given in Eq. (13) should be used when computing the numerical value of the matrix elements. The energy of a Zeeman line for a given magnetic field can then be found by solving for the eigenvalues of the submatrix. The submatrices are symmetric and only elements of $\langle\mathcal{H}\rangle_{ij}$ for $i\leq j$ are given. The results have been cross-checked by several methods.

IV. LAMB SHIFT

Robiscoe and Cosens[2] have recently remeasured the Lamb shift in the $n=2$ state of hydrogen and deuterium. In their experiments a magnetic field was applied to a beam of neutral metastable atoms in the $2S_{1/2}$ state and in a definite hyperfine state. The magnetic field

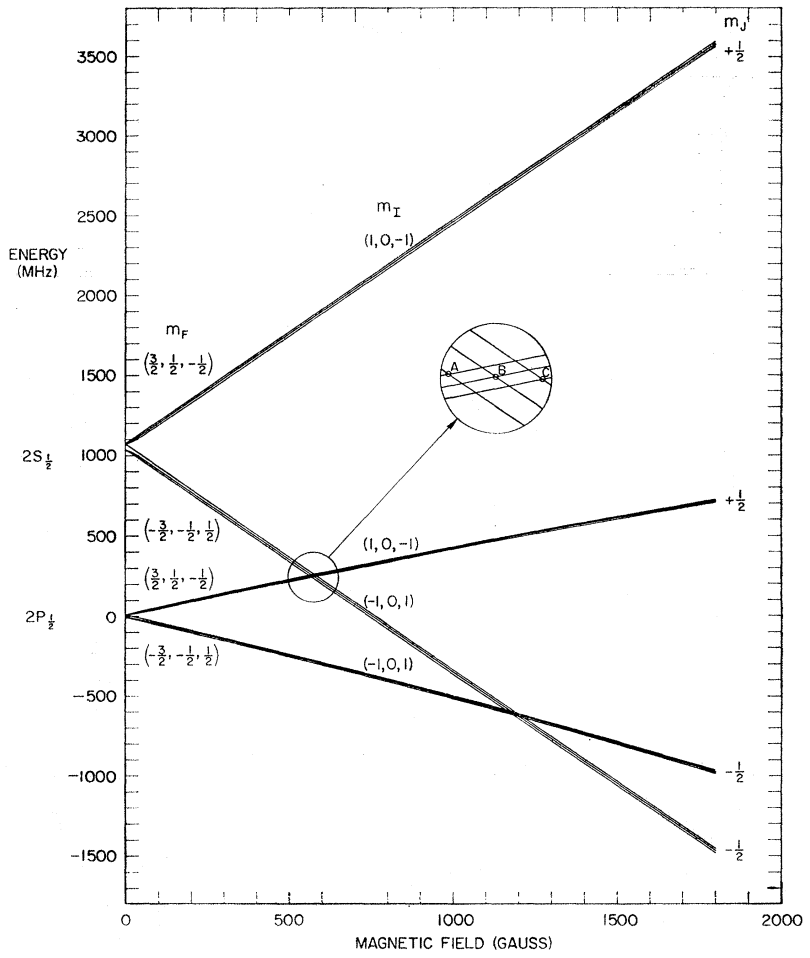

FIG. 2. Zeeman diagram of the $J=\frac{1}{2}$ levels in deuterium, $n=2$, including hyperfine structure. Crossings marked A, B, and C are observable transitions with $\Delta m_I=0$.

was adjusted so that the energy of the atom was degenerate with one of the $2P_{1/2}$ levels. The crossings which obey $\Delta m_I=0$ are observable by coupling the levels via a static electric field. These crossings are marked A and B for hydrogen in Fig. 1 and are marked A, B, and C for deuterium in Fig. 2.

By knowing the magnetic field at which these transitions occur, one can extrapolate back to zero magnetic field and determine the $2S_{1/2}$-$2P_{1/2}$ separation at $H=0$ (the Lamb shift).

In the Robiscoe and Cosens experiments, the magnetic field was measured by observing the proton NMR

TABLE IV. Lamb shift for crossing hydrogen A.

H (G)	ν_c (kHz)	S (MHz)
537.391	2288.000	1056.440
537.626	2289.000	1056.867
537.861	2290.000	1057.294
538.095	2291.000	1057.720
538.330	2292.000	1058.147
538.565	2293.000	1058.573
538.800	2294.000	1059.000
539.035	2295.000	1059.426

TABLE V. Lamb shift for crossing hydrogen B.

H (G)	ν_c (kHz)	S (MHz)
604.565	2574.000	1056.535
604.800	2575.000	1056.962
605.034	2576.000	1057.389
605.269	2577.000	1057.816
605.504	2578.000	1058.242
605.739	2579.000	1058.669
605.974	2580.000	1059.096
606.209	2581.000	1059.523

frequency ν_c in water and calculating H_c from

$$H_c=\nu_c\left(\frac{g_s}{g_p}\right)_0\frac{1}{g_s\mu_0}, \tag{18}$$

where $(g_s/g_p)_0$ is the ratio of the g factor for free electrons and the g factor for protons in water. A measurement of this ratio has been made by Lambe and reported by DuMond[17]:

$$(g_s/g_p)_0=658.22759\pm0.000022. \tag{19}$$

[17] E. R. Cohen and J. W. DuMond, Rev. Mod. Phys. **37**, 537 (1965).

TABLE VI. Lamb shift for crossing deuterium A.

H (G)	ν_c (kHz)	$\mathcal{S}$ (MHz)
563.227	2398.000	1057.655
563.462	2399.000	1058.084
563.697	2400.000	1058.512
563.932	2401.000	1058.940
564.166	2402.000	1059.368
564.401	2403.000	1059.797
564.636	2404.000	1060.225
564.871	2405.000	1060.653

TABLE VII. Lamb shift for crossing deuterium B.

H (G)	ν_c (kHz)	$\mathcal{S}$ (MHz)
573.092	2440.000	1057.484
573.327	2441.000	1057.912
573.561	2442.000	1058.340
573.796	2443.000	1058.768
574.031	2444.000	1059.196
574.266	2445.000	1059.624
574.501	2446.000	1060.052
574.736	2447.000	1060.480

TABLE VIII. Lamb shift for crossing deuterium C.

H (G)	ν_c (kHz)	$\mathcal{S}$ (MHz)
583.191	2483.000	1057.421
583.426	2484.000	1057.849
583.661	2485.000	1058.277
583.896	2486.000	1058.705
584.131	2487.000	1059.133
584.366	2488.000	1059.561
584.600	2489.000	1059.989
584.835	2490.000	1060.417

TABLE IX. Experimental values of the Lamb shift. The errors given here correspond to a one-standard-deviation experimental error.[a]

Crossing	ν_c	$\mathcal{S}$
Hydrogen A	2291.627 kHz ($\pm$50 ppm)	1057.983$\pm$0.05 MHz
Hydrogen B	2577.570 kHz ($\pm$50 ppm)	1058.059$\pm$0.05 MHz
Deuterium B	2444.354 kHz ($\pm$38 ppm)	1059.348$\pm$0.04 MHz
Deuterium C	2487.261 kHz ($\pm$51 ppm)	1059.245$\pm$0.05 MHz

[a] See note added in proof after Sec. V.

The relevant eigenvalues for the Robiscoe and Cosens experiments have been calculated. The apparent value of the Lamb shift has been determined for several assumed values of the magnetic field for a zero-frequency crossing. These values are tabulated in Tables IV–VIII. These predictions for the Lamb shift are accurate to 1 ppm. If the parameters g_L, g_s, $(g_s/g_p)_0$, α, ΔE, κ, and $\Delta\nu$ are altered from their nominal value by 1 s.d. in the case of experimental numbers and by an order of magnitude estimate of error in the case of theoretical numbers, the resultant error in the Lamb shift is less than 1 ppm.

V. CONCLUSION

In this paper, we have presented a method of calculating the energy levels of a hydrogenlike atom in a magnetic field. We have applied this method to the level-crossing experiments of Robiscoe and Cosens. Their recent results for the corrected center NMR (proton in water) frequencies[2] along with the value of the Lamb shift calculated by our method are shown in Table IX.

The difference between the theoretical prediction for the Lamb shift and the averages of the results listed in Table IX are

$$\mathcal{S}_{\rm exp}-\mathcal{S}_{\rm th}=0.45\pm0.13 \text{ for hydrogen}$$
$$=0.47\pm0.13 \text{ for deuterium}.$$

The error interval given here is obtained by adding the one standard deviation experimental error to the estimated accuracy of the theoretical prediction.

The perturbation theoretic treatment given by Robiscoe for the B crossing of hydrogen can be derived by keeping the leading terms of our result.

Our results disagree with those obtained by Robiscoe and Cosens[2] by less than 0.06 MHz. The differences are understandable since their perturbation treatment ignored several terms of order 0.01 MHz. The largest correction is attributable to radiative corrections and finite mass contributions to the hyperfine splittings of the $2P_{1/2}$ state.

Note added in proof. Since this paper was written, Robiscoe (private communication) has discovered a systematic error in the Robiscoe and Cosens experimental results.[2] This error, due to a previously ignored effect of a motional electric field, reduces the experimental value of the hydrogen Lamb shift by $\approx$0.15 MHz and the value of the deuterium Lamb shift by $\approx$0.10 MHz. This effect reduces the discrepancy between theory and experiment and brings the Lamb experiments and the Robiscoe-Cosens experiments into agreement within the experimental errors.

APPENDIX A

We analyze here the extent of any residual magnetic field dependence in the total Hamiltonian beyond that already exhibited in $\mathcal{H}_1+\mathcal{H}_2$ in Sec. II-A. $\mathcal{H}_1+\mathcal{H}_2$ gives the entire interaction of free particles with a constant magnetic field. This form is also clearly correct when the electron and nucleus interact through a potential with no momentum dependence; e.g., the potential from one photon exchange. It is not true, however, that $\mathcal{H}_1+\mathcal{H}_2$ gives the entire magnetic field dependence when self-energy interactions or the full Bethe-Salpeter interaction is taken into account. The type of correction we are seeking thus involves a computation of the dependence of the quantum electrodynamic level shifts on H.

Following the approach of Erickson and Yennie,[8,18] one finds that the order α self-energy correction to the energy E_n of an electron in a static electromagnetic

[18] See, for example, Ref. 11, Eqs. (2.6) and (2.7).

field A^μ may be written in the form

$$\Delta E_n = \Delta E_n(L) + \Delta E_n(M) + \Delta E_n(R), \tag{A1}$$

where

$$\Delta E_n(L) = -\frac{2\alpha}{3\pi m^2}\langle \bar{n}|\mathbf{p}\left(\ln\frac{m}{2H_{NR}}+\frac{11}{24}\right)\cdot[\mathbf{p},e\mathbf{A}]|n\rangle, \tag{A2}$$

$$\Delta E_n(M) = \frac{\alpha}{2\pi}\left(-\frac{e}{2m}\right)\langle \bar{n}|\tfrac{1}{2}\sigma_{\mu\nu}F^{\mu\nu}|n\rangle. \tag{A3}$$

$\Delta E_n(R)$ contains terms explicitly quadratic in $F^{\mu\nu}$ and terms which modify the operators in L and M at small distances, $r<\hbar/mc$. Our notation is the same as Ref. 8 with

$$\Pi^\mu = p^\mu - eA^\mu.$$

$$2mH_{NR} = 2m\left[\frac{\mathbf{p}^2}{2m}+eA_0+\epsilon_n\right] - e\sigma_{\mu\nu}F^{\mu\nu} - \mathbf{p}\cdot e\mathbf{A} - e\mathbf{A}\cdot\mathbf{p},$$

$$\langle \bar{n}|(\gamma\cdot\Pi - m) = (\gamma\cdot\Pi - m)|n\rangle = 0, \tag{A4}$$

$$e = -|e|,$$

$$p_0 = E_n = m - \epsilon_n.$$

We are interested in the dependence of ΔE_n on the external magnetic field. When the part of $F^{\mu\nu}$ corresponding to $\mathbf{H}$ is inserted in $\Delta E_n(M)$ we obtain the contribution of the anomalous moment of the electron to order α. This is already accounted for in $\mathcal{H}_1$. To evaluate $\Delta E_n(L)$ we follow the usual Bethe sum-over-states procedure. If we use a nonrelativistic approximation, then[8]

$$\Delta E_n(L) = -\frac{2\alpha}{3\pi m^2}\sum_{n'}\left|\langle n|\frac{\mathbf{p}}{m}|n'\rangle^{NR}\right|^2(\epsilon_n{}^{NR}-\epsilon_{n'}{}^{NR}) \times\left\{\ln\left[\frac{m}{2|\epsilon_n{}^{NR}-\epsilon_{n'}{}^{NR}|}\right]+\frac{11}{24}\right\}. \tag{A5}$$

This is the major contribution to the Lamb shift $\mathcal{S}$ where $|n\rangle$ corresponds to the $2S_{1/2}$ state. The addition of an external magnetic field is reflected in $\Delta E_n(L)$ through the change in the binding energies $\epsilon_{n'}{}^{NR}$. We thus find that the change in the Lamb shift is of order

$$\mathcal{S}(H)-\mathcal{S}(0) = O(\mu_0 H/Ry)\mathcal{S}.$$

We also note that terms quadratic in the field strength in $\Delta E_n(R)$ yield corrections only of order $(\mu_0 H/m)\mathcal{S}$. The external magnetic field changes the spin dependence of the wave function $|n\rangle$. This affects $\Delta E_n(M)$ and one finds a correction of order $\alpha(Z\alpha)^2\mu_0 H$.

The vacuum polarization level shift contribution is unchanged to first order in $\mu_0 H$. The modifications due to recoil and nucleon structure corrections as obtained through the Bethe-Salpeter equation are of order $\alpha(m/M)\mathcal{S}$. The change in the contribution due to an external magnetic field thus can be no larger than order $(\mu_0 H/Ry)\alpha(m/M)\mathcal{S}$.

In summary, we find that there are external magnetic field corrections to the Lamb shift $\mathcal{S}$, but these corrections are of negligible order: $(\mu_0 H/Ry)\mathcal{S}$. To this accuracy the magnetic interaction of the atom is given by the Hamiltonian corresponding to a free electron and nucleus.

We, of course, ignore in our analysis the interaction of the electric quadrupole moment of the deuteron with the external magnetic field which is due to the motion of the deuteron about the atomic center of mass.

A discussion of the radiative corrections to the line shapes which are measured in electromagnetic transitions has been given by Low.[19]

APPENDIX B

The one-photon-exchange interaction of the electron and nucleus can be written as[20]

$$V = 4\pi e^2\bar{u}(p')\gamma_\mu u(p)A^\mu, \tag{B1}$$

where

$$A^\mu = \frac{1}{q^2}\bar{u}(P')\left[\frac{(P+P')^\mu}{2M_P}+(1+\kappa_P)\frac{i\sigma^{\mu\nu}q_\nu}{2M_P}\right]u(P) \tag{B2}$$

for hydrogen, and

$$A^\mu = \frac{-1}{q^2}\epsilon_\beta{}^*(P')\left[\frac{(P+P')^\mu g^{\beta\alpha}}{2M_D} - (1+\kappa_D)\frac{g^{\beta\mu}q^\alpha - g^{\alpha\mu}q^\beta}{2M_D}\right]\epsilon_\alpha(P) \tag{B3}$$

for deuterium. The plane-wave solutions of the spin-one nucleus satisfy the subsidiary conditions

$$P^\alpha\epsilon_\alpha(P) = \epsilon_\beta{}^*(P')P'^\beta = 0, \tag{B4}$$

which can be used to eliminate the zeroth component of the nuclear polarization vector ϵ_α.

We have not included in Eq. (B3) a term which, added to the deuteron current, yields the measured static electric quadrupole moment. We will discuss its contribution at the end of this appendix.

We are interested in the part of V which yields a potential dependent on the nuclear spin,

$$\mathbf{I} = \tfrac{1}{2}\boldsymbol{\sigma} \text{ for hydrogen},$$

$$(I_k)_{ij} = -i\epsilon_{ijk} \text{ for deuterium}.$$

In the center-of-mass system, $q_0=0$ and the spin-

[19] F. Low, Phys. Rev. 88, 53 (1952).

[20] We use $e^2=\alpha$. Otherwise the notation is that of J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1964). The momentum transferred to the nucleus is $q=p-p'=P'-P$.

dependent vector part of A^μ is

$$\mathbf{A}(\mathbf{q})=-i\frac{1+\kappa}{I}\frac{1}{2M}(\mathbf{I}\times\mathbf{q})\frac{1}{\mathbf{q}^2} \tag{B5}$$

for $\mathrm{H}(I=\frac{1}{2})$ and $\mathrm{D}(I=1)$. If we assume the electron is nonrelativistic and add in the electron's anomalous magnetic moment we get

$$V\approx 4\pi e^2\left[A^0-\frac{\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}'}{2m}+i\frac{g_s}{2}\frac{\boldsymbol{\sigma}\times\mathbf{q}\cdot\mathbf{A}}{2m}\right]. \tag{B6}$$

The vector potential $\mathbf{A}(\mathbf{q})$ yields the usual hfs potential in the electron's position space.[21]

$$V_{\mathrm{hfs}}(\mathbf{r})=\frac{-e}{2m}\frac{e}{2M}\frac{1+\kappa}{I}\left[-\frac{8\pi}{3}\delta^3(\mathbf{r})g_s\mathbf{S}\cdot\mathbf{I}+g_s\frac{1}{r^3}(\mathbf{S}\cdot\mathbf{I}-3\mathbf{S}\cdot\hat{r}\mathbf{I}\cdot\hat{r})-\frac{2}{r^3}(\mathbf{I}\cdot\mathbf{L})\right]. \tag{B7}$$

The leading terms in Eqs. (8) and (10) are calculated from Eq. (B7). We must also consider the spin-dependent part of A^0.

For hydrogen,

$$\begin{aligned}A^0&=\frac{-1}{\mathbf{q}^2}\bar{u}(P')\left[\frac{E}{M_P}+(1+\kappa_P)\frac{\boldsymbol{\alpha}\cdot\mathbf{q}}{2M_P}\right]u(P)\\&\approx\frac{2}{\mathbf{q}^2}\chi^\dagger(P')\left[\frac{i\mathbf{I}\cdot(\mathbf{P}'\times\mathbf{P})}{4M_P{}^2}-(1+\kappa_P)\frac{i\mathbf{I}\cdot\mathbf{q}\times(\mathbf{P}+\mathbf{P}')}{4M_P{}^2}\right]\chi(P)\\&=\frac{-1}{\mathbf{q}^2}\chi^\dagger(P')\left[\frac{(1+2\kappa_P)}{4M_P{}^2}i\mathbf{I}\cdot\mathbf{q}\times(\mathbf{P}+\mathbf{P}')\right]\chi(P).\end{aligned} \tag{B8}$$

In the second line, we have kept only spin-dependent terms and have discarded terms of order $M_P{}^{-3}$. We thus obtain an additional contribution to V_{hfs}[22]:

$$+\frac{e^2}{2M_P{}^2}(1+2\kappa_P)\frac{\mathbf{I}\cdot\mathbf{L}}{r^3}.$$

[21] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 22. $\mathbf{q}\equiv-i\boldsymbol{\nabla}$.

[22] This agrees with the result of W. A. Barker and F. N. Glover, Phys. Rev. **99**, 317 (1955). They made use of a Foldy-Wouthuysen transformation for the two-body problem.

The contribution of this term is included in Eqs. (8) and (10).

For deuterium,

$$\begin{aligned}A^0&=\frac{1}{\mathbf{q}^2}\epsilon_\beta{}^*(P')\left[\frac{E}{M_D}g^{\beta\alpha}+(1+\kappa_D)\frac{g^{\alpha0}q^\beta-g^{\beta0}q^\alpha}{2M_D}\right]\epsilon_\alpha(P)\\&\approx\frac{1}{\mathbf{q}^2}\epsilon_j{}^*(P')\left[\frac{P_j'P_k}{M_D{}^2}-(1+\kappa_D)\frac{P_kq_j-P_j'q_k}{2M_D{}^2}\right]\epsilon_k(P)\\&\qquad j,k=1,2,3.\end{aligned} \tag{B9}$$

We have made use of the subsidiary conditions, discarded a spin-independent term, and dropped corrections of higher order in $1/M_D$. We then rewrite A^0 as

$$\begin{aligned}A^0&=\frac{1}{\mathbf{q}^2}\epsilon_j{}^*(P')\left[\frac{P_j'P_k+P_k'P_j}{2M_D{}^2}+\frac{(1+\kappa_D)(q_jq_k)}{2M_D{}^2}+\frac{[1-(1+\kappa_D)][q_j(P+P')_k-q_k(P+P')_j]}{4M_D{}^2}\right]\epsilon_k(P)\\&\approx\frac{-1}{\mathbf{q}^2}\epsilon_j{}^*(P')\left[\frac{\mathbf{I}\cdot\mathbf{q}\mathbf{I}\cdot\mathbf{q}}{2M_D{}^2}\kappa_D+\frac{\mathbf{I}\cdot\mathbf{P}\mathbf{I}\cdot\mathbf{P}+\mathbf{I}\cdot\mathbf{P}'\mathbf{I}\cdot\mathbf{P}'}{2M_D{}^2}+\frac{i\mathbf{I}\cdot\mathbf{q}\times(\mathbf{P}+\mathbf{P}')}{4M_D{}^2}\kappa_D\right]_{jk}\epsilon_k(P),\end{aligned} \tag{B10}$$

again keeping only terms dependent on nuclear spin. The last term is an induced dipole moment for the deuteron and gives the position-space potential

$$+\frac{e^2}{2M_D{}^2}\kappa_D\frac{\mathbf{I}\cdot\mathbf{L}}{r^3}.$$

The contribution of this term is included in Eqs. (8) and (10). The spin-dependent remainder of A_0 corresponds to an induced quadrupole moment. The term proportional to κ_D is a contribution to the static electric quadrupole moment which necessarily accompanies the deuteron's anomalous magnetic moment. We note, however, that the electric quadrupole moment can only affect the atomic $2P_{3/2}$ level. The additional energy of this level is of order 0.006 MHz,[23] and may be neglected in determining the Lamb shift. The hyperfine-splitting formulas in Eq. (8) include the lowest-order binding corrections as given by Rose.[24]

[23] See the third paper of Ref. 1, Appendix VI.

[24] M. E. Rose, *Relativistic Electron Theory* (John Wiley & Sons, Inc., New York, 1961).