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# PRECISE THEORY OF THE ZEEMAN SPECTRUM FOR ATOMIC HYDROGEN AND DEUTERIUM AND THE LAMB SHIFT*

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## ABSTRACT

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. 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 $|F, j, \ell, m_F>$ representation. Matrix representations of the Hamiltonian are given for all $n = 2$ states of hydrogen and deuterium. We give theoretical predictions for the $\ell = 1$ 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.

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# 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 non-zero 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 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 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 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 ($\approx$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.

## II. THEORY

### A. The Total Hamiltonian

We write the Hamiltonian for a hydrogen-like atom in a constant external magnetic field 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 $\underset{\sim}{A}_1 = \frac{1}{2}\,\underset{\sim}{r}_1 \times \underset{\sim}{H}$ and includes a term for the anomalous magnetic moment of the electron.

$$\mathcal{H}_1 = -\,\underset{\sim}{\alpha}_1 \cdot |e|\,\underset{\sim}{A}_1 + (g_s - 2)\,\frac{|e|}{2m}\,\underset{\sim}{S}\cdot\underset{\sim}{H} \qquad (1)$$

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

$$\mathcal{H}_2 = \underset{\sim}{\alpha}_2 \cdot |e|\,\underset{\sim}{A}_2 - (2\kappa_p)\,\frac{|e|}{2M_p}\,\underset{\sim}{I}\cdot\underset{\sim}{H}\,, \qquad (2)$$

and for deuterium

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

where $\underset{\sim}{A}_2 = \frac{1}{2}\,\underset{\sim}{r}_2 \times \underset{\sim}{H}$. $\mathcal{H}_3$ 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

$$\mathcal{H}_3(H) - \mathcal{H}_3(H=0) = O(\alpha^3 \mu_o H)\,. \qquad (4)$$

Thus we will take $\mathcal{H}_3$ as its H = 0 value: $\mathcal{H}_3 \rightarrow \mathcal{H}_3(H=0) = \mathcal{H}_o$. It can be specified, for our purposes, by its eigenvalues for those eigenstates with which we are concerned. Some of the eigenvalues of $\mathcal{H}_o$ can be determined accurately by experiment, for example, the $\ell = 0$ hyperfine splitting and the fine structure interval of the $n = 2$ levels. Other eigenvalues must be determined from theory such as the $\ell \neq 0$ hyperfine structure and the Lamb shift. Once the spectrum of $\mathcal{H}_o$ 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 $\ell$ 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 $\underset{\sim}{F}$ where $\underset{\sim}{F} = \underset{\sim}{J} + \underset{\sim}{I} = \underset{\sim}{L} + \underset{\sim}{S} + \underset{\sim}{I}$. The spectrum of $\mathcal{H}_0$ can thus be specified by the states[6] $|n, F, j, \ell, m_F>$. The radial dependence of the eigenfunctions is described accurately by the Dirac equation using reduced coordinates except at very small distances.[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]:

$$\begin{aligned} \mathbb{S} &= 1057.57 \pm 0.08 \text{ MHz for hydrogen} \\ \mathbb{S} &= 1058.83 \pm 0.08 \text{ MHz for deuterium .} \end{aligned} \tag{5}$$

The error in the theoretical predictions correspond to 1 s.d. error in $\alpha$ and include theoretical estimates of uncalculated terms of order $\alpha(Z\alpha)^6 mc^2$ and higher. In Section V we compare these values with $\mathbb{S}$ obtained from experiment.

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

$$\begin{aligned} \Delta\nu(2S_{1/2}, H) &= 177.55686 \pm 0.00005 \text{ MHz} \quad 1 \text{ s.d.} \\ \Delta\nu(2S_{1/2}, D) &= 40.924439 \pm 0.000020 \text{ MHz} \quad 1 \text{ s.d.} \end{aligned} \tag{6}$$

and the hyperfine levels are

$$\nu(2S_{1/2},\ H) = \Delta\nu(2S_{1/2},\ H) < \underset{\sim}{I} \cdot \underset{\sim}{J} >$$
$$\nu(2S_{1/2},\ D) = \frac{2}{3}\ \Delta\nu(2S_{1/2},\ D) < \underset{\sim}{I} \cdot \underset{\sim}{J} > \ . \tag{7}$$

The hyperfine splitting of the $\ell = 1$ 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 $\underset{\sim}{I} \cdot \underset{\sim}{J}$) we find (see Appendix B)[10]

$$\nu(2P_{1/2},\ H) = \frac{E_F(H)}{3}\left[\frac{g_s}{2} - \frac{(g_s-2)}{4} + \frac{m}{4M_p}\left(\frac{1+2\kappa_p}{1+\kappa_p}\right)\right]\left[1 + \frac{47}{24}(Z\alpha)^2\right] < \underset{\sim}{I} \cdot \underset{\sim}{J} >$$

$$\nu(2P_{3/2},\ H) = \frac{E_F(H)}{15}\left[\frac{g_s}{2} - \frac{5(g_s-2)}{8} + \frac{5m}{8M_p}\left(\frac{1+2\kappa_p}{1+\kappa_p}\right)\right]\left[1 + \frac{7}{24}(Z\alpha)^2\right] < \underset{\sim}{I} \cdot \underset{\sim}{J} > \tag{8}$$

$$\nu(2P_{1/2},\ D) = \frac{E_F(D)}{9/2}\left[\frac{g_s}{2} - \frac{(g_s-2)}{4} + \frac{m}{2M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right]\left[1 + \frac{47}{24}(Z\alpha)^2\right] < \underset{\sim}{I} \cdot \underset{\sim}{J} >$$

$$\nu(2P_{3/2},\ D) = \frac{E_F(D)}{45/2}\left[\frac{g_s}{2} - \frac{5(g_s-2)}{8} + \frac{5m}{4M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right]\left[1 + \frac{7}{24}(Z\alpha)^2\right] < \underset{\sim}{I} \cdot \underset{\sim}{J} >$$

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

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

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

$$\frac{g_s}{2} = 1.00159622 \pm 0.00000023 \ .$$

The off-diagonal hyperfine Hamiltonian is[13]

$$\mathcal{H}'_{\text{hfs}} = \frac{E_F(H)}{16}\left[2 - \frac{g_s}{2} + \frac{m}{M_P}\left(\frac{1+2\kappa_P}{1+\kappa_P}\right)\right] < \underset{\sim}{I}\cdot\underset{\sim}{L} > \tag{10a}$$

for hydrogen, and

$$\mathcal{H}'_{\text{hfs}} = \frac{E_F(D)}{24}\left[2 - \frac{g_s}{2} + \frac{2m}{M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right] < \underset{\sim}{I}\cdot\underset{\sim}{L} > \quad . \tag{10b}$$

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

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

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 $\Delta E$ since a 75 ppm change in $\Delta E$ is required to produce a 1 ppm change in the determined Lamb shift.

The spectrum of $\mathcal{H}_o$ (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 wavefunctions only for $r \ll \frac{\hbar}{mc}$.[7] The eigenfunctions are then completely specified by $| F, j, \ell, m_F >$.

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

$$\mathcal{H}_1 + \mathcal{H}_2 \xrightarrow[n=2]{} \mathcal{H}_{mag}$$

$$= \left[ A_s S_z + \frac{1}{2} A_L L_z + \frac{1}{2} L_z A_L + A_I I_z \right] \mu_o H$$

$$+ O\left( e^2 \underset{\sim}{A}_1^2 / m \right), \tag{12}$$

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 $\underset{\sim}{H}$ and $H \equiv |\underset{\sim}{H}|$. The coefficients $A_s$, $A_L$, and $A_I$ are

$$A_I = \begin{cases} -g_{IH} & \text{for hydrogen} \\ -g_{ID} & \text{for deuterium} \end{cases}$$

$$A_s = \begin{cases} g_s \left(1 + \frac{2}{3} \ W/m\right) & \text{for } \ell = 0 \\ g_s \left(1 + \frac{4}{5} \ W/m\right) & \text{for } \ell = 1 \end{cases} \tag{13}$$

$$A_L = g_L \left( 1 + W/m - \underset{\sim}{S} \cdot \underset{\sim}{L} \ (2W/5m) \right) \text{ for } \ell = 1$$

where W is the Bohr energy of the $n = 2$ state: $W = -(Z\alpha)^2 m/8$. Here $g_L = (1 - m/M_P)$ for hydrogen and $g_L = (1 - m/M_D)$ for deuterium to take 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 wavefunctions. The error made in not using the exact eigenfunctions of $\mathcal{H}_o$ should be of the same order as if W were replaced by the actual binding energy. Such corrections are of order $(Z\alpha)^2 m/M_P$. Thus the theoretical expressions given for $A_s$ and $A_L$ are accurate to 0.1 ppm. Note that for a uniform magnetic field $\underset{\sim}{H} \neq \underset{\sim}{H}(\underset{\sim}{x})$, quantum electrodynamics affects $A_s$ only through the static anomalous magnetic moment and does not affect $A_L$.

The quadratic Zeeman term $<\frac{1}{2} e^2 \underset{\sim}{A}_1^2>$ 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 $\Delta\ell = 2$ state mixing it induces.

We have also ignored the negligible $\Delta n \neq 0$ contributions of $\mathcal{H}_o$.

## III. CALCULATIONS

Our task in this section is to find the eigenvalues of the total Hamiltonian $\mathcal{H}_o + \mathcal{H}_1 + \mathcal{H}_2$. To do this we shall require matrix representations of $S_z$, $I_z$, $L_z$, $F_z$ and $\underset{\sim}{I} \cdot \underset{\sim}{L}$ in the basis of eigenfunctions of the diagonal part of $\mathcal{H}_o$. In this basis, F and $m_F$ are good quantum numbers and $F_z |F,j,\ell,m_F> = m_F |F,j,\ell,m_F>$. We can eliminate $L_z$ by $L_z = F_z - I_z - S_z$. The matrix elements of $S_z$, $I_z$ and $\underset{\sim}{I} \cdot \underset{\sim}{L}$ are most easily calculated by the general methods of angular momentum in quantum mechanics.[16]

For S = 1/2

$$<j', I', F', m_{F'}, |S_z| j, I, F, m_F>$$

$$= (-1)^{\ell + S + I + 1 + 2j' - m_F} \delta_{SS'} \delta_{\ell\ell'} \delta_{II'}$$

$$\times \left[\frac{3}{2} (2F' + 1) (2F + 1) (2j' + 1) (2j + 1)\right]^{1/2} \qquad (14)$$

$$\times \begin{pmatrix} F' & F & 1 \\ -m_{F'} & m_F & 0 \end{pmatrix} \begin{Bmatrix} F' & F & 1 \\ j & j' & I \end{Bmatrix} \begin{Bmatrix} 1/2 & j' & \ell \\ j & 1/2 & 1 \end{Bmatrix},$$

$$\langle j', I', F', m_{F'} | I_z | j, I, F, m_F \rangle$$

$$= (-1)^{F' + F - I - j - m_F} \delta_{\ell\ell'} \delta_{SS'} \delta_{II'} \delta_{jj'} \qquad (15)$$

$$\times \left[(2F' + 1) (2F + 1) (2I + 1) (I + 1) (I)\right]^{1/2}$$

$$\times \begin{pmatrix} F' & F & 1 \\ -m_{F'} & m_F & 0 \end{pmatrix} \begin{Bmatrix} F' & F & 1 \\ I & I & j \end{Bmatrix},$$

and for $\ell \neq 0$ and $I \neq 0$

$$\langle j', I', F', m_{F'} | \underset{\sim}{I} \cdot \underset{\sim}{L} | j, I, F, m_F \rangle$$

$$= (-1)^{2j + \ell + F + I + 3/2} \delta_{FF'} \delta_{m_F m_{F'}} \delta_{\ell\ell'} \delta_{SS'} \delta_{II'} \qquad (16)$$

$$\times \left[(2j + 1) (2j' + 1) (2I + 1) (I + 1) (I) (2\ell + 1) (\ell + 1) (\ell)\right]^{1/2}$$

$$\times \begin{Bmatrix} F & I & j' \\ 1 & j & I \end{Bmatrix} \begin{Bmatrix} \ell & j' & 1/2 \\ j & \ell & 1 \end{Bmatrix}.$$

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 $\underset{\sim}{I} \cdot \underset{\sim}{L}$. In order that $\langle S_z \rangle$, $\langle I_z \rangle$ and $\langle \underset{\sim}{I} \cdot \underset{\sim}{L} \rangle$ be non-zero, 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 non-zero.

From the selection rules, we see that the matrix representation of the magnetic Hamiltonian for a hydrogen-like atom in the $n = 2$ state can be separated into submatrices of a given $\ell$ 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

$$\mu_o H \left[ F_z A_L + S_z (A_s - A_L) - I_z (A_I + A_L) \right] + E \equiv \left( F_z, S_z, I_z \right) + E , \tag{17}$$

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

Since the effective values of $A_s$ and $A_L$ depend on $\ell$ 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 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 in hydrogen in Fig. 1 and are marked A, B, and C in 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 frequency $\nu_c$ in water and calculating $H_c$ from

$$H_c = \nu_c \left(\frac{g_s}{g_p}\right)_o \quad \frac{1}{g_s \mu_o} \tag{18}$$

where $\left(\frac{g_s}{g_p}\right)_o$ 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 E. B. D. Lambe and reported by DuMond[17]:

$$\left(\frac{g_s}{g_p}\right)_o = 658.22759 \pm 0.000022 \tag{19}$$

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 $g_L$, $g_s$, $\left(g_s/g_p\right)_o$, $\alpha$, $\Delta E$, $\kappa$, 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 hydrogen-like 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 results listed in Table IX is

$$\mathcal{S}_{exp} - \mathcal{S}_{th} = \begin{cases} 0.45 \pm 0.13 & \text{for hydrogen} \\ 0.53 \pm 0.13 & \text{for deuterium} \end{cases} .$$

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.

## 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 Section 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 $\alpha$ self-energy correction to the energy $E_n$ of an electron in a static electromagnetic field $A^\mu$ may be written in the form

$$\Delta E_n = \Delta E_n(L) + \Delta E_n(M) + \Delta E_n(R) \tag{A.1}$$

where

$$\Delta E_n(L) = -\frac{2\alpha}{3\pi m^2} < \bar{n} \left| \underset{\sim}{p} \left( \log \frac{m}{2H_{NR}} + \frac{11}{24} \right) \cdot [\underset{\sim}{p}, e\not{A}] \right| n > \tag{A.2}$$

$$\Delta E_n(M) = \frac{\alpha}{2\pi} \left( -\frac{e}{2m} \right) < \bar{n} \left| \frac{1}{2} \sigma_{\mu\nu} F^{\mu\nu} \right| n > . \tag{A.3}$$

$\Delta E_n(R)$ 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

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

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

$$\left.\begin{aligned} &\langle \bar{n} \,|\, (\not{\Pi} - m) = (\not{\Pi} - m) \,|\, n \rangle = 0 \\ &e = -|e| \\ &p_o = E_n = m - \epsilon_n \end{aligned}\right\} \qquad (A.4)$$

We are interested in the dependence of $\Delta E_n$ on the external magnetic field. When the part of $F^{\mu\nu}$ corresponding to $\underset{\sim}{H}$ is inserted in $\Delta E_n(M)$ we obtain the contribution of the anomalous moment of the electron to order $\alpha$. 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]

$$\Delta E_n(L) = -\frac{2\alpha}{3\pi m^2}\sum_{n'}\left|\langle n\left|\frac{\underset{\sim}{p}}{m}\right|n'\rangle^{NR}\right|^2\left(\epsilon_n^{NR} - \epsilon_{n'}^{NR}\right)$$

$$\times\left\{\log\left[\frac{m}{2\left|\epsilon_n^{NR} - \epsilon_{n'}^{NR}\right|}\right] + \frac{11}{24}\right\} . \qquad (A.5)$$

This is the major contribution to the Lamb shift $\mathbb{S}$ 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 the change in the Lamb shift is of order

$$\mathbb{S}(H) - \mathbb{S}(0) = O\left(\frac{\mu_o H}{Ry}\right)\mathbb{S}$$

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

The vacuum polarization level shift contribution is unchanged to first order in $\mu_o H$. The modification 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 $(\mu_o H/Ry)\;\alpha\,(m/M)\,\mathcal{S}$.

In summary, we find that there are external magnetic field corrections to the Lamb shift $\mathcal{S}$, but these corrections are of negligible order: $(\mu_o H/Ry)\,\mathcal{S}$. 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 occurs 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 F. Low.[19]

## APPENDIX B

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

$$V = 4\pi e^2 \, \bar{u}(p') \, \gamma_\mu \, u(p) \, A^\mu \tag{B.1}$$

where

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

for hydrogen and

$$A^\mu = \frac{-1}{q^2} \, \epsilon^*_\beta(P') \left[ \frac{(P + P')^\mu \, g^{\beta\alpha}}{2M_D} - (1 + \kappa_D) \frac{g^{\beta\mu} q^\alpha - g^{\alpha\mu} q^\beta}{2M_D} \right] \epsilon_\alpha(P) \tag{B.3}$$

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

$$P^\alpha \, \epsilon_\alpha(P) = \epsilon^*_\beta(P') \, P'^\beta = 0 \tag{B.4}$$

which can be used to eliminate the zero-th component of the nuclear polarization vector $\epsilon_\alpha$.

We have not included in Eq. (B.3) 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,

$$\underset{\sim}{I} = \frac{1}{2} \underset{\sim}{\sigma} \qquad \text{for hydrogen,}$$

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

In the center-of-mass system, $q_o = 0$ and the spin dependent vector part of $A^\mu$ is

$$\underset{\sim}{A}(\underset{\sim}{q}) = -i \frac{1+\kappa}{I} \frac{1}{2M} (\underset{\sim}{I} \times \underset{\sim}{q}) \frac{1}{\underset{\sim}{q}^2} \tag{B.5}$$

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

$$V \approx 4\pi e^2 \left[ A^o - \frac{\underset{\sim}{p} \cdot \underset{\sim}{A} + \underset{\sim}{A} \cdot \underset{\sim}{p}'}{2m} + i \frac{g_s}{2} \frac{\underset{\sim}{\sigma} \times \underset{\sim}{q} \cdot \underset{\sim}{A}}{2m} \right] . \tag{B.6}$$

The vector potential $\underset{\sim}{A}(\underset{\sim}{q})$ yields the usual hfs potential in the electron's position space.

$$V_{hfs}(\underset{\sim}{r}) = \frac{-e}{2m} \frac{e}{2M} \frac{1+\kappa}{I} \left[ -\frac{8\pi}{3} \delta^3(\underset{\sim}{r})\, g_s\, \underset{\sim}{S} \cdot \underset{\sim}{I} + g_s \frac{1}{r^3} \left( \underset{\sim}{S} \cdot \underset{\sim}{I} - 3 \underset{\sim}{S} \cdot \hat{\underset{\sim}{r}}\, \underset{\sim}{I} \cdot \hat{\underset{\sim}{r}} \right) - \frac{2}{r^3} \left( \underset{\sim}{I} \cdot \underset{\sim}{L} \right) \right] \tag{B.7}$$

The leading terms in Eqs. (8) and (10) are calculated from Eq. (B.7). We must also consider the spin-dependent part of $A^o$.

For hydrogen,

$$A^o = \frac{-1}{\underset{\sim}{q}^2} \bar{u}(P') \left[ \frac{E}{M_P} + (1+\kappa_P) \frac{\underset{\sim}{\alpha} \cdot \underset{\sim}{q}}{2M_P} \right] u(P)$$

$$\approx \frac{2}{\underset{\sim}{q}^2} \chi^\dagger(P') \left[ \frac{i \underset{\sim}{I} \cdot (\underset{\sim}{P}' \times \underset{\sim}{P})}{4M_P^2} - (1+\kappa_P) \frac{i \underset{\sim}{I} \cdot \underset{\sim}{q} \times (\underset{\sim}{P} + \underset{\sim}{P}')}{4M_P^2} \right] \chi(P)$$

$$= \frac{-1}{\underset{\sim}{q}^2} \chi^\dagger(P') \left[ \frac{(1+2\kappa_P)}{4M_P^2} i \underset{\sim}{I} \cdot \underset{\sim}{q} \times (\underset{\sim}{P} + \underset{\sim}{P}') \right] \chi(P) . \tag{B.8}$$

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]

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

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

For deuterium,

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

$$\approx \frac{1}{\underset{\sim}{q}^2} \epsilon_j^*(P') \left[ \frac{P'_j P_k}{M_D^2} - (1 + \kappa_D) \frac{P_k q_j - P'_j q_k}{2M_D^2} \right] \epsilon_k(P) \qquad (B.9)$$

$$j, k = 1, 2, 3.$$

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 $A^o$ as

$$A^o = \frac{1}{\underset{\sim}{q}^2} \epsilon_j^*(P') \left[ \frac{P'_j P_k + P'_k P_j}{2M_D^2} + \frac{(1 + \kappa_D)(q_j q_k)}{2M_D^2} \right.$$

$$\left. + \frac{\left[1 - (1 + \kappa_D)\right]\left[q_j (P + P')_k - q_k (P + P')_j\right]}{4M_D^2} \right] \epsilon_k(P)$$

$$\approx \frac{-1}{\underset{\sim}{q}^2} \epsilon_j^*(P') \left[ \frac{\underset{\sim}{I} \cdot \underset{\sim}{q} \; \underset{\sim}{I} \cdot \underset{\sim}{q}}{2M_D^2} \kappa_D + \frac{\underset{\sim}{I} \cdot \underset{\sim}{P} \; \underset{\sim}{I} \cdot \underset{\sim}{P} + \underset{\sim}{I} \cdot \underset{\sim}{P'} \; \underset{\sim}{I} \cdot \underset{\sim}{P'}}{2M_D^2} \right.$$

$$\left. + \frac{i \, \underset{\sim}{I} \cdot \underset{\sim}{q} \times (\underset{\sim}{P} + \underset{\sim}{P'})}{4M_D^2} \kappa_D \right]_{jk} \epsilon_k(P) , \qquad (B.10)$$

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

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

The contribution of this term is included in Eqs. (8) and (10). The spin-dependent remainder of $A_o$ corresponds to an induced quadrupole moment. The term proportional to $\kappa_D$ 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 for determining the Lamb shift. The hyperfine splitting formulas in Eq. (8) include the lowest order binding corrections as given by Rose.[24]

## FOOTNOTES AND REFERENCES


1. W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. 79, 549 (1950); W. E. Lamb, Jr., and R. C. Retherford, ibid. 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); R. T. Robiscoe and B. L. Cosens, Bull. Am. Phys. Soc. 14, 62 (1966); B. L. Cosens, Ph. D. Thesis, Yale University (to be published).
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 $\alpha^3 \mu_o H$.
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6. If $\ell \neq 0$, 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).
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$\alpha^{-1} = 137.0359 \pm 0.0004$ (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 $\alpha$ changes the theoretical prediction of the Lamb shift by +0.07 MHz but does not appreciably affect the discrepancy with experiment.

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

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

11. $E_F(H)$ could also be obtained from $\Delta\nu(2S)$ by removing the binding corrections, radiative corrections and nuclear size effects.
$E_F = \Delta\nu(2S)(2/g_s)\left(1 - \frac{\alpha^2}{8} + \left(\frac{5}{2} - \ell n 2\right)\alpha^2 + \frac{2}{3}\frac{\alpha^3}{\pi}\ell n^2\left(1/\alpha^2\right) - \delta_{nuc}\right)$
Using $\alpha^{-1} = 137.0359$ and $\delta_{nuc} = -36 \times 10^{-6}$ 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 $\mathcal{H}'_{hfs}$ is itself only a 1/2 percent correction to the hyperfine energies.

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

15. See the third paper of Ref. 1.

16. See, for example, A. R. Edmonds, Angular Momentum in Quantum Mechanics, Princeton University Press, Princeton, 1957.

17. J. W. M. DuMond, Ann. Phys. (N. Y.) 7, 365 (1959).

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

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, New York, 1964. The momentum transferred to the nucleus is $q = p - p' = P' - P$.

21. H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms, Academic Press, New York, 1957, Section 22. $\underset{\sim}{q} \equiv -i\underset{\sim}{\nabla}$.

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.

23. See the third paper of Ref. 1, App. VI.

24. M. E. Rose, Relativistic Electron Theory, Wiley and Sons, New York, 1961.

## FIGURE CAPTIONS

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 $\Delta m_I = 0$.
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 $\Delta m_I = 0$.

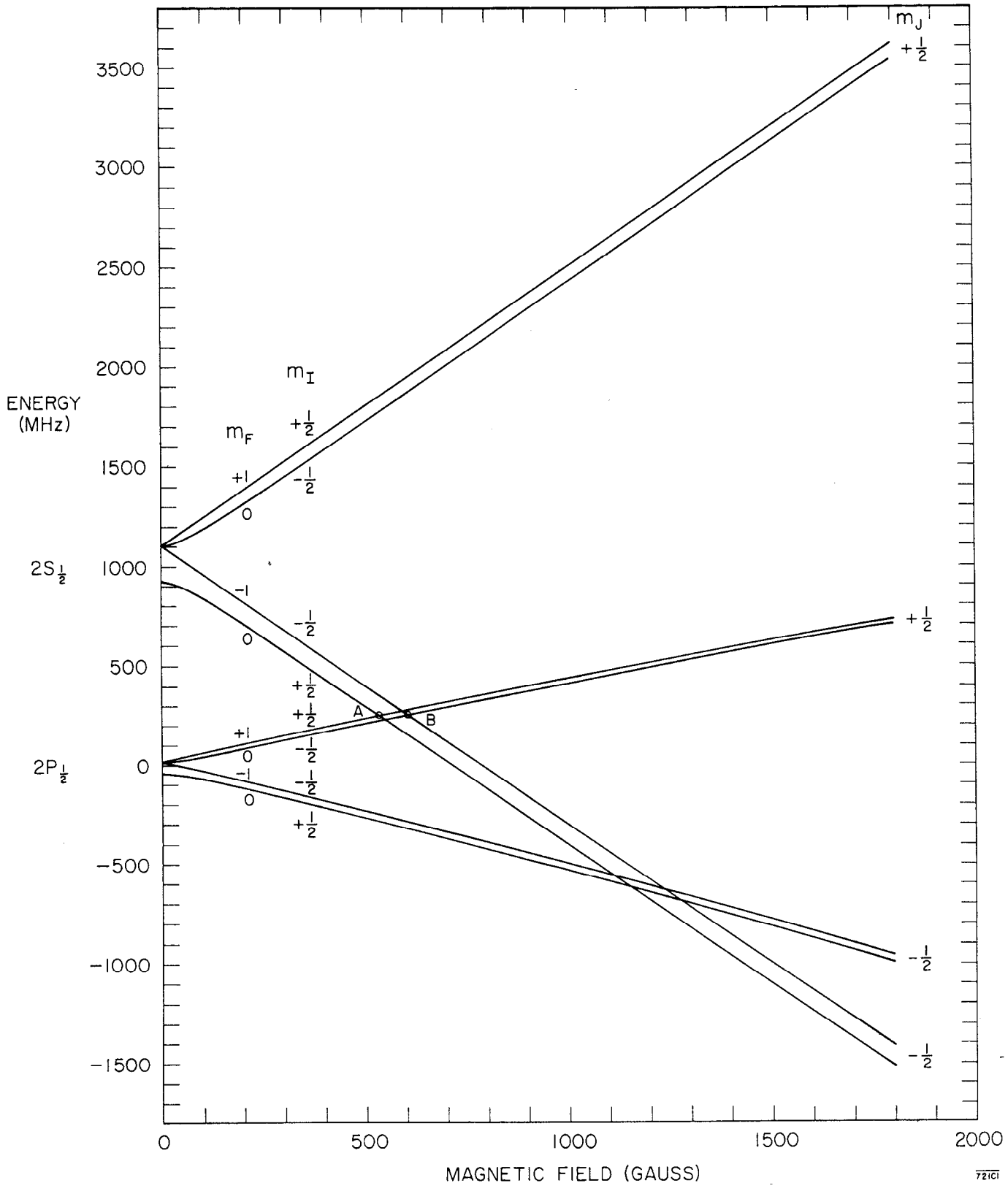
ENERGY (MHz)
3500
3000
2500
2000
1500
1000
500
0
−500
−1000
−1500
$2S_{\frac{1}{2}}$
$2P_{\frac{1}{2}}$
$m_J$
$m_I$
$m_F$
$+\frac{1}{2}$
$-\frac{1}{2}$
+1
0
−1
A
B
0
500
1000
1500
2000
MAGNETIC FIELD (GAUSS)
72ICI

FIG. 1

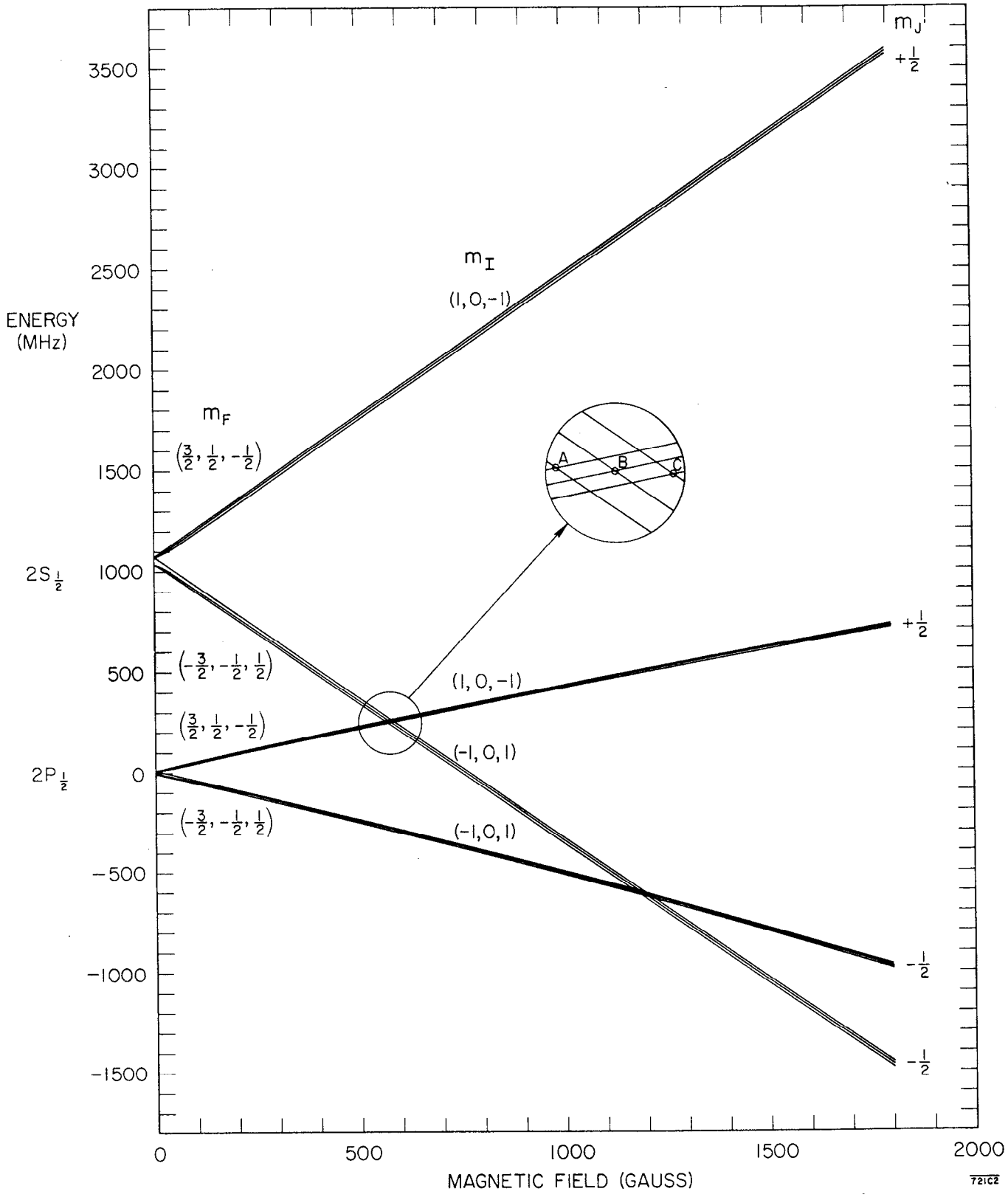
ENERGY (MHz)
3500
3000
2500
2000
1500
1000
500
0
−500
−1000
−1500
2S 1/2
2P 1/2
m_J
+1/2
m_I
(1, 0, −1)
m_F
(3/2, 1/2, −1/2)
A
B
C
+1/2
(−3/2, −1/2, 1/2)
(1, 0, −1)
(3/2, 1/2, −1/2)
(−1, 0, 1)
(−3/2, −1/2, 1/2)
(−1, 0, 1)
−1/2
−1/2
0
500
1000
1500
2000
MAGNETIC FIELD (GAUSS)
72IC2

FIG. 2

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 $\approx 5.58\ m/M_P$ |
| $g_{ID}$ | Landé factor for the deuteron $\approx 0.86\ m/M_P$ |
| $\underset{\sim}{S}$ | electron spin vector |
| $\underset{\sim}{L}$ | orbital electron angular momentum vector |
| $\underset{\sim}{I}$ | nucleus spin vector |
| $\underset{\sim}{J}$ | total electron angular momentum $= \underset{\sim}{L} + \underset{\sim}{S}$ |
| $\underset{\sim}{F}$ | total atomic angular momentum $= \underset{\sim}{J} + \underset{\sim}{I}$ |
| $Ry_\infty$ | Rydberg for infinite mass |
| $\Delta E_H$ | fine structure interval $(2P_{3/2} - 2P_{1/2})$ for hydrogen |
| $\Delta E_D$ | fine structure interval $(2P_{3/2} - 2P_{1/2})$ for deuterium |
| $\kappa_P$ | anomalous magnetic moment of the proton $(1 + \kappa_P \approx 2.79)$ |
| $\kappa_D$ | anomalous magnetic moment of the deuteron $\left(1 + \kappa_D \approx 0.86\ (M_D/M_P)\right)$ |
| $\mu_P$ | magnetic moment of proton $\approx 2.79\ (e/2M_P)$ |
| $\mu_D$ | magnetic moment of deuteron $\approx 0.86\ (e/2M_P)$ |
| $\mu_o$ | electron Bohr magneton |
| $\nu_c$ | corrected center nmr (proton in water) frequency |

TABLE II

Submatrices of the Hamiltonian for $I = 1/2$ (Hydrogen).

The notation in this table is explained in Eq. (17).

$$\left\{ I = \frac{1}{2},\ \ell = 0,\ m_F = -1 \right\}$$

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

---

$$\left\{ I = \frac{1}{2}, \ell = 0,\ m_F = 0 \right\}$$

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

---

$$\left\{ I = \frac{1}{2},\ \ell = 0,\ m_F = +1 \right\}$$

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

---

$$\left\{ I = \frac{1}{2},\ \ell = 1,\ m_F = -2 \right\}$$

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

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

---

$$\left\{ I = \frac{1}{2},\ \ell = 1,\ m_F = -1 \right\}$$

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

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

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

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

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

$$\left\{I = \frac{1}{2},\ \ell = 1,\ m_F = 0\right\}$$

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

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

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

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

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

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

$$\left\{ I = \frac{1}{2},\ \ell = 1,\ m_F = +1 \right\}$$

| F | | 1 | 1 | 2 |
|---|---|---|---|---|
| | j | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{3}{2}$ |

$$\begin{array}{cc} 1 & \frac{1}{2} \\ 1 & \frac{3}{2} \\ 2 & \frac{3}{2} \end{array} \begin{bmatrix} \left(1, -\frac{1}{6}, \frac{1}{2}\right) + E_{11} & \left(0, \frac{\sqrt{2}}{6}, 0\right) + E_{12} & \left(0, \frac{-1}{\sqrt{6}}, 0\right) \\ & \left(1, \frac{5}{12}, -\frac{1}{4}\right) + E_{22} & \left(0, \frac{1}{4\sqrt{3}}, \frac{-\sqrt{3}}{4}\right) \\ & & \left(1, \frac{1}{4}, \frac{1}{4}\right) + E_{33} \end{bmatrix}$$

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

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

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

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

$$\left\{ I = \frac{1}{2},\ \ell = 1,\ m_F = +2 \right\}$$

F $\quad$ 2

$\quad$ j $\quad$ $\frac{3}{2}$

2 $\quad$ $\frac{3}{2}$ $\quad$ $\left[ \left( 2, \frac{1}{2}, \frac{1}{2} \right) + E_{11} \right]$

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

TABLE III

Submatrices of the Hamiltonian for I = 1 (Deuterium).

The notation in this table is explained in Eq. (17).

$$\left\{I = 1,\ \ell = 0,\ m_F = -\frac{3}{2}\right\}$$

| F | | $\frac{3}{2}$ |
|---|---|---|
| | j | $\frac{1}{2}$ |

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

---

$$\left\{I = 1,\ \ell = 0,\ m_F = -\frac{1}{2}\right\}$$

| F | | $\frac{1}{2}$ | $\frac{3}{2}$ |
|---|---|---|---|
| | j | $\frac{1}{2}$ | $\frac{1}{2}$ |

$$\begin{array}{cc} \frac{1}{2} & \frac{1}{2} \\ \frac{3}{2} & \frac{1}{2} \end{array}\begin{bmatrix} \left(-\frac{1}{2}, \frac{1}{6}, -\frac{2}{3}\right) + E_{11} & \left(0, \frac{\sqrt{2}}{3}, \frac{-\sqrt{2}}{3}\right) \\ & \left(-\frac{1}{2}, -\frac{1}{6}, -\frac{1}{3}\right) + E_{22} \end{bmatrix}$$

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

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

---

$$\left\{I = 1,\ \ell = 0,\ m_F = +\frac{1}{2}\right\}$$

| F | | $\frac{1}{2}$ | $\frac{3}{2}$ |
|---|---|---|---|
| | j | $\frac{1}{2}$ | $\frac{1}{2}$ |

$$\begin{array}{cc} \frac{1}{2} & \frac{1}{2} \\ \frac{3}{2} & \frac{1}{2} \end{array} \begin{bmatrix} \left(\frac{1}{2},\ -\frac{1}{6},\ \frac{2}{3}\right) + E_{11} & \left(0, \frac{\sqrt{2}}{3},\ \frac{-\sqrt{2}}{3}\right) \\ & \left(\frac{1}{2},\ \frac{1}{6},\ \frac{1}{3}\right) + E_{22} \end{bmatrix}$$

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

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

---

$$\left\{I = 1,\ \ell = 0,\ m_F = +\frac{3}{2}\right\}$$

| F | | $\frac{3}{2}$ |
|---|---|---|
| | j | $\frac{1}{2}$ |

$$\begin{array}{cc} \frac{3}{2} & \frac{1}{2} \end{array} \begin{bmatrix} \left(\frac{3}{2},\ \frac{1}{2},\ 1\right) + \frac{\Delta\nu(2S, D)}{3} \end{bmatrix}$$

---

$$\left\{I = 1,\ \ell = 1,\ m_F = -\frac{5}{2}\right\}$$

| F | $\frac{5}{2}$ |
|---|---|
| j | $\frac{3}{2}$ |

$$\frac{5}{2} \quad \frac{3}{2} \quad \left[\left(-\frac{5}{2},\ -\frac{1}{2},\ -1\right) + E_{11}\right]$$

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

---

$$\left\{I = 1,\ \ell = 1,\ m_F = -\frac{3}{2}\right\}$$

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

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

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

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

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

$$\left\{I = 1,\ \ell = 1,\ m_F = -\frac{1}{2}\right\}$$

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

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

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

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

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

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

$$E_{14} = E_F(D)\left(2 - \frac{g_s}{2}\right)\left(\frac{-\sqrt{5}}{72}\right)$$

$$E_{25} = E_F(D)\left(2 - \frac{g_s}{2}\right)\left(\frac{-\sqrt{2}}{72}\right)$$

$$\left\{I = 1,\ \ell = 1,\ m_F = +\frac{1}{2}\right\}$$

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

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

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

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

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

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

$$E_{14} = E_F(D)\left(2 - \frac{g_s}{2}\right)\left(\frac{-\sqrt{5}}{72}\right)$$

$$E_{25} = E_F(D)\left(2 - \frac{g_s}{2}\right)\left(\frac{-\sqrt{2}}{72}\right)$$

$$\left\{I = 1,\ \ell = 1,\ m_F = +\ \frac{3}{2}\right\}$$

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

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

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

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

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

$$\left\{ I = 1,\ \ell = 1,\ m_F = +\frac{5}{2} \right\}$$

| | |
|---|---|
| F | $\frac{5}{2}$ |
| j | $\frac{3}{2}$ |

$$\frac{5}{2} \quad \frac{3}{2} \qquad \left[ \left( \frac{5}{2},\ \frac{1}{2},\ 1 \right) + E_{11} \right]$$

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

---

TABLE IV

Lamb Shift for Crossing Hydrogen A

| H (Gauss) | $\nu_c$ (kHz) | $\mathbb{S}$ (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 (Gauss) | $\nu_c$ (kHz) | $\mathbb{S}$ (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 |

TABLE VI

Lamb Shift for Crossing Deuterium A

| H (Gauss) | $\nu_c$ (kHz) | $\mathbb{S}$ (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 (Gauss) | $\nu_c$ (kHz) | $\mathbb{S}$ (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 |