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# Magnetic and electric fine structure in helium Rydberg states

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An improved method for calculating magnetic fine structures in helium Rydberg states is developed and the results are compared with previous calculations and with existing precise experimental determinations. Agreement with experiment is markedly improved in *D* manifolds, but systematic anomalies in *F* and *G* manifolds remain unexplained. Relativistic and mass-polarization contributions to electric fine structure are evaluated and found to be significant at the same order as recently calculated radiative corrections. Agreement with experimental determinations is no better than about 1%.

The excited helium atom is a particularly simple case of an atomic Rydberg system since its core is a hydrogenlike ion whose properties are easily calculated. The fine-structure intervals of such a system are a sensitive indicator of the differences between the Rydberg system and hydrogen. Helium fine structure in high-angular-momentum manifolds ($L > 1$) has been the object of a number of theoretical calculations concerned with the breakdown of *LS* coupling,[1] its effect on excitation transfer,[2-5] and the validity of the polarization model.[6] In their turn, experimental measurements have become increasingly more precise since early optical measurements.[7] They encompass level-crossing,[8-10] electric[11] and magnetic[12,13] anticrossing, and quantum beat[14,15] techniques applied to *D* states; MacAdam and Wing[16-18] have used a microwave-optical technique to make precise measurements of a large number of intervals in *F* and *G* as well as *D* manifolds.

## I. THE HAMILTONIAN AND ITS EIGENVALUES

The Hamiltonian for a two-electron system in the field of a fixed, spinless nucleus is usually taken to be that Hamiltonian obtained from the Breit equation (in the Pauli approximation).[19-21] To include the effects of nuclear motion one must add to this Hamiltonian the relativistic single-particle Hamiltonian for a spinless nucleus of mass $M$ and charge $Ze$[22] and the retardation and spin-orbit[23,24] corrections to the electron-nucleus interaction owing to the motion of the nucleus. Then, using relative coordinates and reduced mass atomic units [$\hbar$, $e$, and $mM/(m+M)$ have magnitude 1][25] and dropping terms dependent on the center-of-mass motion or of higher order than $\alpha^3$ yields the Hamiltonian

$$H = H_0 + H_{mp} + H_{\text{spin}} + H_{\text{rel}} \,, \tag{1}$$

in which

$$H_0 = \tfrac{1}{2}(p_1^2 + p_2^2) - Z/r_1 - Z/r_2 + 1/r_{12} \,,$$

$$H_{mp} = -(\vec{p}_1 \cdot \vec{p}_2)/M \,,$$

$$\begin{aligned} H_{\text{spin}} = {} & \tfrac{1}{4} Z\alpha^2 (1 - M^{-2} + \alpha/\pi m)[\vec{H}_N^{+} \cdot \vec{S}^{+} + \vec{H}_N^{-} \cdot \vec{S}^{-}] - \tfrac{1}{2}(\alpha^2/m^2)[(\tfrac{3}{2} + \alpha/\pi)\vec{H}_e^{+} \cdot \vec{S}^{+} - \tfrac{1}{2}\vec{H}_e^{-} \cdot \vec{S}^{-}] \\ & + Z(\alpha^2/mM)(1 + \tfrac{1}{2}\alpha/\pi)[r_1^{-3}(\vec{r}_1 \times \vec{p}_2) \cdot \vec{S}_1 + r_2^{-3}(\vec{r}_2 \times \vec{p}_1) \cdot \vec{S}_2] \\ & + (\alpha^2/m^2)(1 + \alpha/\pi)\{r_{12}^{-3}[\vec{S}_1 \cdot \vec{S}_2 - 3(\vec{S}_1 \cdot \hat{r}_{12})(\vec{S}_2 \cdot \hat{r}_{12})]\}' , \end{aligned}$$

$$\vec{S}^{\pm} = \vec{S}_1 \pm \vec{S}_2 ,\ \vec{H}_N^{\pm} = \frac{\vec{L}_1}{r_1^3} \pm \frac{\vec{L}_2}{r_2^3} ,\ \vec{H}_e^{\pm} = \frac{\vec{r}_{12}}{r_{12}^3} \times (\vec{p}_1 \mp \vec{p}_2) , \quad \vec{r}_{12} = \vec{r}_1 - \vec{r}_2 \,,$$

and

$$H_{\mathrm{rel}} = -\tfrac{1}{8}(\alpha^2/m^3)(p_1^4+p_2^4) - \tfrac{1}{8}(\alpha^2/M^3)(\vec{p}_1+\vec{p}_2)^4 - \tfrac{1}{2}(\alpha^2/m^2)r_{12}^{-1}[\vec{p}_1\cdot\vec{p}_2 + \hat{r}_{12}\cdot(\hat{r}_{12}\cdot\vec{p}_1)\vec{p}_2]$$
$$-\tfrac{1}{2}Z(\alpha^2/mM)\{r_1^{-1}[\vec{p}_1+\hat{r}_1(\hat{r}_1\cdot\vec{p}_1)]\cdot(\vec{p}_1+\vec{p}_2) + r_2^{-1}[\vec{p}_2+\hat{r}_2(\hat{r}_2\cdot\vec{p}_2)]\cdot(\vec{p}_1+\vec{p}_2)\}$$
$$+\frac{i\alpha^2}{4m^2}\left[\vec{p}_1\cdot\left(Z\frac{\vec{r}_1}{r_1^3}-\frac{\vec{r}_{12}}{r_{12}^3}\right)+\vec{p}_2\cdot\left(Z\frac{\vec{r}_2}{r_2^3}+\frac{\vec{r}_{12}}{r_{12}^3}\right)\right]+2\pi(\alpha^2/m^2)(1+\alpha/\pi)\delta^{(3)}(\vec{r}_{12}) .$$

The fine structure of helium can be conceptually divided into three parts. There is an overall shift dependent only on the radial and orbital angular momentum quantum numbers (direct electric fine structure); the required symmetry of the electronic wave function splits the singlet-triplet degeneracy, contributing the exchange electric fine structure; the spin-dependent interactions that split the degeneracy in the total angular momentum quantum number contribute the magnetic fine structure. In our Hamiltonian, the magnetic fine structure is caused by $H_{\mathrm{spin}}$ and the electric fine structure by the other terms in $H$.[26]

Since $H_0$, the nonrelativistic, fixed-nucleus part of $H$, is $\alpha^{-2}$ or $M/m$ times larger than the other terms in $H$, we will compute approximate eigenvalues of $H$ by using (approximate) wave functions of $H_0$ to evaluate the expectation value of $H-H_0$. Since $H_0$ is diagonal in $L$ and $S$ it is usual and convenient to use $LS$ coupled basis states for calculating the eigenvalues of $H$, even though the operators $H_{ss}$ and $S^-$ keep $L$ and $S$ from being exact quantum numbers for $H$. We denote these basis states by $|NLSJM\rangle$, in which $N$ is some radial quantum number. The matrix elements of $H-H_0$ between states differing in $N$ or $L$ are small enough to cause no shifts greater than 1 kHz in the eigenvalues of states with $L>1$. In terms of reduced matrix elements[27] (that is, integrals of radial wave functions), the nonzero matrix elements of $H$ between basis states with the same $N$ and $L$ are

$$\langle N L 1 L-1 M|H|N L 1 L-1 M\rangle$$
$$= E_{NL1} + Lh_{so} + [2L/(2L+3)]h_{ss} ,$$
$$\langle N L 1 L M|H|N L 1 L M\rangle E_{NL1} - h_{so} - 2h_{ss} ,$$
$$\langle N L 0 L M|H|N L 0 L M\rangle = E_{NL0}$$
$$\langle N L 1 L+1 M|H|N L 1 L+1 M\rangle$$
$$= E_{NL1} - (L+1)h_{so} + [(2L+2)/(2L-1)]h_{ss} ,$$

and

$$\langle NL1LM|H|NL0LM\rangle = \langle NL0LM|H|NL1LM\rangle$$
$$= (L(L+1))^{1/2}h_{\mathrm{off}} ,$$

in which

$$E_{NLS} = \langle NLS|H_0 + H_{mp} + H_{\mathrm{rel}}|NLS\rangle ,$$

$$h_{so} = D[\tfrac{1}{4}Z\alpha^2(1-M^{-2}+\alpha/\pi m)\langle NLS=1||\vec{H}_N^+||NLS=1\rangle$$
$$-\tfrac{1}{4}(\alpha^2/m^2)(3+2\alpha/\pi)\langle NLS=1||\vec{H}_e^+||NLS=1\rangle$$
$$-Z(\alpha^2/mM)(1+\alpha/2\pi)$$
$$\times\langle NLS=1||r_1^{-3}(\vec{r}_1\times\vec{p}_2)||NLS=1\rangle] ,$$

$$h_{\mathrm{off}} = D[\tfrac{1}{4}Z\alpha^2(1-M^{-2}+\alpha/\pi m)\langle NLS=1||\vec{H}_N^-||NLS=0\rangle$$
$$+\tfrac{1}{4}(\alpha^2/m^2)\langle NLS=1||\vec{H}_e^-||NLS=0\rangle$$
$$+Z(\alpha^2/mM)(1+\alpha/2\pi)$$
$$\times\langle NLS=1||r_1^{-3}(\vec{r}_1\times\vec{p}_2)||NLS=0\rangle] ,$$

$$h_{ss} = -\tfrac{1}{8}D[6(2L+3)(2L-1)]^{1/2}(\alpha^2/m^2)(1+\alpha/\pi)$$
$$\times\langle NLS=1||r_{12}^{-3}(2/3)^{1/2}C^{(2)}(\hat{r}_{12})||NLS=1\rangle ,$$

and

$$D = [L(L+1)(2L+1)]^{-1/2} .$$

In this $4\times4$ matrix the only off-diagonal matrix element is $h_{\mathrm{off}}$, which mixes the singlet and triplet states of the same $L$ and $J$. For states with $L>2$, this matrix element is comparable to or larger than the nonrelativistic singlet-triplet splitting; for $L>3$ the observed eigenstates are superpositions of roughly equal amounts of the pure $S=0$ and $S=1$ basis states. Since the singlet state always adiabatically connects with the mixed state of higher energy and the triplet state with the mixed state of lower energy, we will still use the terms "singlet" and "triplet" to denote the observed mixed eigenstates with higher and lower energy, respectively. The problem is now reduced to (i) finding eigenfunctions and eigenvalues of $H_0$, (ii) evaluating the radial integrals using these eigenfunctions, and (iii) diagonalizing the $4\times4$ matrix for each $N$ and $L$.

The wave functions needed to evaluate the radial integrals are the solutions of the equation

$$(H_0 - E)|NLSM_L\rangle = 0$$

having the correct symmetry and angular momentum. Since the wave function depends on $S$ only in its symmetry, we may find any solution to the differential equation

$$(H_0 - E)|NLM_L\rangle = 0 \qquad (2)$$

and impose the symmetry requirements afterwards by writing

$$\langle \vec{r}_1\vec{r}_2|NLS\,M_L\rangle$$

$$= [\langle \vec{r}_1\vec{r}_2|NLM_L\rangle + (-1)^S\langle \vec{r}_2\vec{r}_1|NLM_L\rangle]/\sqrt{2}\ .$$

For singly excited states (configuration $1snL$) a perturbation series solution of Eq. (2) is appropriate.[21,28,29] We use

$$\tilde{H}_0 = \tfrac{1}{2}p_1^2 + \tfrac{1}{2}p_2^2 - Z/r_1 - (Z-1)/r_2$$

for the unperturbed Hamiltonian and

$$V = 1/r_{12} - 1/r_2$$

for the perturbing potential; the zeroth-order wave function has electron one in the $1s$ state of a charge $Ze$ nucleus and electron two in the $nL$ state of a charge $(Z-1)e$ nucleus. Thus we write

$$\langle \vec{r}_1\vec{r}_2|NLM_L\rangle = \Psi^0(\vec{r}_1,\vec{r}_2) + \Psi^1(\vec{r}_1,\vec{r}_2) + \cdots\ ,$$

$$\Psi^0(\vec{r}_1,\vec{r}_2) = R^Z_{1S}(r_1)R^{Z-1}_{nL}(r_2)Y_{10}(\Omega_1)Y_{LM_L}(\Omega_2)$$

$$\equiv \psi^0(r_1,r_2)Y_{10}(\Omega_1)Y_{LM_L}(\Omega_2)\ ,$$

$$E = E_0 + E_1 + \cdots\ ,$$

$$E_0 = -\tfrac{1}{2}Z^2 - \tfrac{1}{2}(Z-1)^2/n^2\ ,$$

$$E_1 = \int\!\!\int \psi^0(r_1,r_2)(1/r_> - 1/r_2)\psi^0(r_1,r_2) \times r_1^2 r_2^2\,dr_1\,dr_2\ ,$$

and $\Psi^1$ satisfies

$$(\tilde{H}_0 - E_0)\Psi^1 + (V - E_1)\Psi^0 = 0\ .$$

The first-order wave function can be written as the correctly coupled partial wave expansion

$$\Psi^1(\vec{r}_1,\vec{r}_2) = \sum_{l_1 l_2} R_{l_1 l_2}(r_1,r_2)(-1)^L\left(\frac{2l_2+1}{2l_1+1}\right)^{1/2}\begin{pmatrix} l_1 & l_2 & L\\ 0 & 0 & 0\end{pmatrix} \times \sum_{m_1 m_2}(l_1 m_1 l_2 m_2|LM_L)Y_{l_1 m_1}(\Omega_1)Y_{l_2 m_2}(\Omega_2)\ .$$

Then the $R_{l_1 l_2}$ satisfy the equation

$$[\overline{H}_{1l_1} + \overline{H}_{2l_2}]R_{l_1 l_2}(r_1,r_2) = [(E_1 + 1/r_2)\delta_{l_1 0} - r_<^{l_1}/r_>^{l_1+1}]\psi^0(r_1,r_2)\ , \qquad (3)$$

in which

$$\overline{H}_{1l_1} = -\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} - \frac{l_1(l_1+1)}{r_1^2}\right) - \frac{Z}{r_1} + \frac{1}{2}Z^2$$

and

$$\overline{H}_{2l_2} = -\frac{1}{2}\left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} - \frac{l_2(l_2+1)}{r_2^2}\right) - \frac{Z-1}{r_2} + \frac{1}{2}\frac{(Z-1)^2}{n^2}\ .$$

This expansion is an infinite series in $l_1$, but for fixed $l_1$ the summand is nonzero for only $l_1+1$ values of $l_2$. Equation (3) is a partial differential equation with no simple solution. But since the kinetic energy of the outer electron is much smaller, by a factor of about $1/n^2$, than the kinetic energy of the inner electron, we expect the operator $\overline{H}_{2l_2}$ to be small compared to $\overline{H}_{1l_1}$ and the following, formally exact, series expansion to be convergent:

$$R_{l_1 l_2} = \sum_{m=0}^{\infty} R^m_{l_1 l_2} \qquad (4)$$

$$l_1 = 0:\ \overline{H}_{2L}R^0_{0L} = [E_1 - \tilde{E}_1(r_2)]\psi^0$$

$$\overline{H}_{1l_1}R^1_{0L} = (\tilde{E}_1 - 1/r_> + 1/r_2)\psi^0$$

$$\overline{H}_{1l_1}R^m_{0L} = -\overline{H}_{2L}R^{m-1}_{0L},\quad m>1$$

$$\tilde{E}_1(r_2) = \int R^Z_{1S}(r_1)\left(\frac{1}{r_>} - \frac{1}{r_2}\right)R^Z_{1S}(r_1)r_1^2\,dr_1$$

$$l_1 \neq 0:\ R^0_{l_1 l_2} = 0$$

$$\overline{H}_{1l_1}R^1_{l_1 l_2} = -(r_<^{l_1}/r_>^{l_1+1})\psi_0$$

$$\overline{H}_{1l_1}R^m_{l_1 l_2} = -\overline{H}_{2l_2}R^{m-1}_{l_1 l_2},\quad m>1$$

The quantities $\tilde{E}_1$ and $R^0_{0L}$ are introduced to avoid solutions for $R_{0L}$ which are ill behaved at the origin. The differential equations for the $R^m_{l_1 l_2}$ can be solved analytically by standard methods, though the solutions have lengthy functional forms. We have developed procedures which give all the $R^m_{l_1 l_2}$ and have evaluated those with $m<2$ for all $l_1$ and $m=2$ for $l_1=1$. The non-Coulombic potential near the origin causes the outer electron's wave function to be somewhat nonhydrogenic; this is the $m=0$ contribution to the first-order wave function. The terms with $m=1$ represent the $2^{l_1}$-pole polarization of the inner electron in the field of the outer electron, with the inner electron's wave function adapting instantaneously to changes in the position of the outer electron. Keeping only the $m=0$ and $m=1$ terms yields the adiabatic approximation to the wave function.[30] The kinetic energy of the electrons is altered by the adiabatic corrections to the wave function; this interaction energy causes the $m=2$ contributions to the wave function. The terms with larger $m$ contain other interactions of the motion of the outer electron with the polarized core.

If only the zero-order wave function $\psi^0$ is used to evaluate the matrix elements of $H - H_0$, as in Refs. 1 and 10, we obtain the hydrogenic approximation of the magnetic fine structure. If in addition the first-order matrix elements $(\langle\psi^1|H|\psi^0\rangle$ and $\langle\psi^0|H|\psi^1\rangle)$ are included but terms with $m>1$ in $R_{l_1 l_2}$ are dropped, we have the adiabatic approximation. If we use only the $m=1$, $l_1 = 0, 1$ terms we have the procedure of Araki[31] and Parish and Mires.[30] In this paper we evaluate the first-order matrix elements with $m=0$, 1, and 2 (extended adiabatic approximation).

The contributions to $h_{so}$, $h_{\text{off}}$, and $h_{ss}$ for the $n=3$–12, $L=2$–4 manifolds are detailed in Table I. The first line in each group gives the zeroth-order integrals (hydrogenic approximation) and line two the $m=0$ portion of the first-order integrals. The $m=1$ integral has contributions from all $l_1$, but the terms decrease in size as $l_1$ increases. For example, Table II shows the contributions to $h_{so}$ from individual $l_1$ for the 5$D$, 5$F$, and 5$G$ manifolds. The values listed in line three of Table I include all terms greater than 0.01 MHz (through $l_1 = 8$) for $D$ manifolds and all terms greater than 0.001 MHz (through $l_1 = 4$) for $F$ and $G$ manifolds. As noted by Parish and Mires,[30] the dipole portion (line 4) constitutes nearly all of the polarization, though this is partly because other terms have opposite signs.

Line five of Table I gives the $m=2$ dipole contribution; it is surprising to see that this is nearly as large as the adiabatic term. This would at first seem to cast doubt on the convergence of the series in Eq. (4) and prompts us to estimate the relative size of the contributions to the reduced matrix elements. For this we use the following procedure. The reduced matrix elements contained in $h_{so}$, $h_{ss}$, and $h_{\text{off}}$ can be written as expectation values of pseudopotentials in the $(nL)$ state. The leading terms in the pseudopotentials for the direct (i.e., spin-independent) matrix elements are inverse powers of $r_2$. The other terms in the pseudopotentials insure that the matrix elements do not diverge for small $L$. We can estimate the size of the radial integrals by evaluating the expectation value of these leading terms; however, since the remaining terms are not small compared to the leading terms, we can only obtain order of magnitude results.

In terms of the radial wave functions the direct part of the first-order reduced matrix element of $H_e^\pm$, for example, is

$$
\begin{aligned}
Y = {} & (2L+1)^{1/2} \sum_{m l_1 l_2} \frac{[l_1(l_1+1)]^{1/2}}{2l_1+1}(2l_2+1)\begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & L \\ 1 & 0 & -1 \end{pmatrix} \\
& \times \int\int R^m_{l_1 l_2}(r_1, r_2)\frac{r_<^{l_1}}{r_>^{l_1+1}}\left[\left(\pm\frac{1}{r_2^2} \pm \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{1}{r_1}\frac{\partial}{\partial r_1}\right)\psi^0(r_1, r_2)\right] r_1^2 r_2^2\, dr_1\, dr_2 \qquad (5) \\
& \mp [L(L+1)(2L+1)]^{1/2} \sum_{m l_1 l_2} \frac{2l_2+1}{2l_1+1}\begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2 \int\int R^m_{l_1 l_2}(r_1, r_2)\left[\frac{1}{r_2}\frac{\partial}{\partial r_2}\frac{r_<^{l_1}}{r_>^{l_1+1}}\right]\psi^0(r_1, r_2) r_1^2 r_2^2\, dr_1\, dr_2\,.
\end{aligned}
$$

Most of the contribution to the integrals comes from the region $r_1 < r_2$. In this region and for $l_1 \neq 0$ and $m \neq 0$, we have, approximately,

$$R^m_{l_1 l_2} \sim P^m_{l_1}(r_1) Q^m_{l_1 l_2}(r_2);$$

by Eq. (4), the $P$'s and $Q$'s satisfy

$$\overline{H}_{1 l_1} P^1_{l_1} = r_1^l R^Z_{1s}(r_1), \quad \overline{H}_{1 l_1} P^m_{l_1} = P^{m-1}_{l_1}\ ,$$

$$Q^1_{l_1 l_2} = r_2^{-l_1-1} R^{Z-1}_{nL}(r_2), \quad Q^m_{l_1 l_2} = -\overline{H}_{2 l_2} Q^{m-1}_{l_1 l_2}\ .$$

This form for the $R^m_{l_1 l_2}$ leaves out an additional term which is a homogenous solution of Eq. (4); this term is necessary in the exact form to insure continuity where $r_1 = r_2$, but explicit calculation shows that its contribution to the integrals under consideration is small. By using the above form for $R^m_{l_1 l_2}$ and extending the integrals to all $r_1$ and $r_2$, we can separate the double integral into a product of two single integrals and rewrite the $r_2$ integral in the form $\int R_{nL} r_2^{-k} R_{nL} r_2^2\, dr_2$, as desired. Now the $Q^m_{l_1 l_2}$ have the following leading terms:

$$\begin{aligned}
m=1:&\quad Q^{m}_{l_1 l_2}\sim r_2^{-l_1-1}R_{nL}\quad(\text{coeff. independent of } l_2)\,,\\
m=2:&\quad Q^{m}_{l_1 l_2}\sim r_2^{-l_1-2}R'_{nL}\quad(\text{coeff. independent of } l_2)\,,\\
&\qquad\sim r_2^{-l_1-3}R_{nL}\quad(\text{coeff. dependent on } l_2)\,,\\
m\geqslant 3,\ \text{odd}:&\quad Q^{m}_{l_1 l_2}\sim r_2^{-l_1-m}R_{nL}\quad(\text{coeff. independent of } l_2)\,,\\
&\qquad\sim r_2^{-l_1-m-1}R'_{nL},\, r_2^{-l_1-m-2}R_{nL}\quad(\text{coeff. dependent on } l_2)\,,\\
m\geqslant 3,\ \text{even}:&\quad Q^{m}_{l_1 l_2}\sim r_2^{-l_1-m}R'_{nL}\quad(\text{coeff. independent of } l_2)\\
&\qquad\sim r_2^{-l_1-m-1}R_{nL},\, r_2^{-l_1-m-2}R'_{nl}\quad(\text{coeff. dependent on } l_2)\,.
\end{aligned}$$

By inserting these expressions in Eq. (5) and noting that the first term vanishes if the integral is independent of $l_2$, we find that for $l_1 \neq 0$ and $m \neq 0$, the leading term in the pseudopotential is $r_2^{-2l_1-m-3}$ for odd $m$ and $r_2^{-2l_1-m-2}$ for even $m$. Thus the overall leading terms are $r_2^{-6}$ (as opposed to $r_2^{-3}$ for the hydrogenic expectation values) and occur in the $m=1$ and $m=2$ dipole terms. Solving for the $P^{m}_{l_1}$ and computing the coefficients of these terms shows that the coefficient of the $m=2$ term is half that of the $m=1$. The operators $H^{\pm}_{N}$ contribute only monopole terms; the leading terms of $H_{ss}$ are $r_2^{-2l_1-m-3}$ for odd $m$ and $r_2^{-2l_1-m-4}$ for even $m$. The $l_1=0$ terms are not covered by the above analysis, but explicit calculations show that they are comparable to the $l_1=2$ terms. We would expect then that the $m=1$ and 2 dipole terms are the most important and are comparable in magnitude; terms decrease in size as $l_1$ increases and roughly half as fast as $m$ increases. This is consistent with the exact results given in Tables I and II.

Thus the size of the $m=2$ dipole term does not indicate that the expansion in Eq. (4) is invalid but that the approximation which truncates the series after $m=1$ is not a good approximation for fine-structure calculations for any $n$ and $L$. The leading terms omitted by a calculation including $R^0$, $R^1$, and $R^2$ are proportional to $\langle r_2^{-8}\rangle$ and should be comparable to the quadrupole $m=1$ and 2 terms, whose magnitudes are about 20%, 10%, and 1% of the adiabatic first-order contributions for the $D$, $F$, and $G$ states, respectively. Hence we expect that the contributions to $h_{so}$, $h_{\text{off}}$, and $h_{ss}$ from uncalculated terms in the first-order wave function are about 1.5% for $D$ states, 0.1% for $F$ states, and 0.001% for $G$ states. The improvement in the relative precision of the calculations with increasing $L$ is obvious. Since the dipole terms give the largest contributions (within 10% of the total), we have not computed the full $m=2$ contribution, but have included in the extended adiabatic approximation the hydrogenic and adiabatic terms and an estimate of the $m=2$ terms obtained by multiplying the $m=2$ dipole term by the quotient of the full $m=1$ contribution and the $m=1$ dipole contribution.

The cutoff in $m$ in the calculation of the first-order term is solely because of loss of numerical precision in the computation of the radial integrals. When this problem is remedied, we expect to be able to extend the calculation so that this truncation error is less than the errors resulting from the limitations of our general procedure. We also expect to calculate the electric fine structure and thereby to reproduce the results of Poe and Chang.[29] Our general procedure follows perturbation theory and hence its accuracy is limited by the truncation of the perturbation series; it gives the energy to second-order in $(1/r_{12}-1/r_2)$ and to first order in $(H-H_0)$. We estimate that terms that are third order in $(1/r_{12}-1/r_2)$ contribute about 0.2%, 0.004%, and 0.0003% to the magnetic fine structure of the $D$, $F$, and $G$ states, respectively. Terms that are second order in $H-H_0$ (i.e., $\alpha^4$ terms) contribute about 0.005%.

## II. COMPARISON WITH MAGNETIC FINE-STRUCTURE MEASUREMENTS

The splittings between the four fine-structure states of the same $n$ and $L$ depend on $h_{so}$, $h_{\text{off}}$, $h_{ss}$, and the singlet-triplet splitting in the absence of $H_{\text{spin}}$. But to estimate the nonrelativistic singlet-triplet splitting to an accuracy comparable to the errors in the other parameters requires a better wave function. So to separate the nonrelativistic problem from the magnetic fine-structure problem, we have adopted the following procedure. We determine that value of $X$, the electric exchange (equal to half the singlet-triplet splitting in the absence of $H_{\text{spin}}$), which, with the calculated matrix elements of $H_{\text{spin}}$, gives the best fit to the experimental data in the least-squares sense, using quoted standard deviations. The goodness of the fit is taken to be the indicator of the correctness of the theoretical calculations. This procedure puts each theory in the most favorable light, since

TABLE I. Radial integrals for magnetic fine structure.

| | | $L=2$ | | | $L=3$ | | | $L=4$ | |
|---|---|---|---|---|---|---|---|---|---|
| | $h_{so}$ | $h_{\text{off}}$ | $h_{ss}$ | $h_{so}$ | $h_{\text{off}}$ | $h_{ss}$ | $h_{so}$ | $h_{\text{off}}$ | $h_{ss}$ |
| $N=3$ | | | | | | | | | |
| $HYD$ | −221.067 | −648.642 | 215.633 | | | | | | |
| $M=0$ | −0.297 | −0.799 | 0.239 | | | | | | |
| $M=1$ | 10.614 | 2.770 | −4.135 | | | | | | |
| $M=1, l_1=1$ | 10.674 | 2.173 | −3.316 | | | | | | |
| $M=2, l_1=1$ | −7.118 | 1.463 | 1.985 | | | | | | |
| $N=4$ | | | | | | | | | |
| $HYD$ | −94.048 | −273.464 | 90.788 | −32.564 | −97.889 | 32.648 | | | |
| $M=0$ | −0.134 | −0.351 | 0.101 | −0.000 | −0.001 | 0.000 | | | |
| $M=1$ | 5.991 | 1.540 | −2.280 | 0.121 | 0.030 | −0.060 | | | |
| $M=1, l_1=1$ | 5.971 | 1.195 | −1.811 | 0.124 | 0.027 | −0.054 | | | |
| $M=2, l_1=1$ | −3.952 | 0.881 | 1.145 | −0.066 | 0.019 | 0.010 | | | |
| $N=5$ | | | | | | | | | |
| $HYD$ | −48.342 | −139.969 | 46.438 | −16.676 | −50.119 | 16.715 | −7.779 | −23.389 | 7.801 |
| $M=0$ | −0.061 | −0.156 | 0.043 | −0.000 | −0.001 | 0.000 | 0.000 | 0.000 | 0.000 |
| $M=1$ | 3.434 | 0.875 | −1.293 | 0.086 | 0.024 | −0.044 | 0.006 | −0.001 | −0.002 |
| $M=1, l_1=1$ | 3.406 | 0.676 | −1.023 | 0.089 | 0.022 | −0.039 | 0.006 | −0.001 | −0.002 |
| $M=2, l_1=1$ | −2.216 | 0.546 | 0.660 | −0.049 | 0.015 | 0.008 | −0.002 | 0.001 | 0.000 |
| $N=6$ | | | | | | | | | |
| $HYD$ | −28.035 | −80.986 | 26.859 | −9.651 | −29.004 | 9.673 | −4.502 | −13.535 | 4.514 |
| $M=0$ | −0.030 | −0.074 | 0.019 | −0.000 | −0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $M=1$ | 2.105 | 0.534 | −0.787 | 0.058 | 0.017 | −0.030 | 0.005 | −0.000 | −0.002 |
| $M=1, l_1=1$ | 2.080 | 0.412 | −0.622 | 0.060 | 0.015 | −0.027 | 0.005 | −0.000 | −0.002 |
| $M=2, l_1=1$ | −1.326 | 0.364 | 0.406 | −0.032 | 0.011 | 0.006 | −0.002 | 0.001 | 0.000 |
| $N=7$ | | | | | | | | | |
| $HYD$ | −17.678 | −50.994 | 16.909 | −6.078 | −18.265 | 6.091 | −2.835 | −8.524 | 2.843 |
| $M=0$ | −0.015 | −0.036 | 0.008 | −0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $M=1$ | 1.371 | 0.346 | −0.510 | 0.040 | 0.012 | −0.021 | 0.003 | 0.000 | −0.001 |
| $M=1, l_1=1$ | 1.352 | 0.267 | −0.403 | 0.041 | 0.010 | −0.018 | 0.003 | 0.000 | −0.001 |
| $M=2, l_1=1$ | −0.840 | 0.258 | 0.264 | −0.022 | 0.008 | 0.004 | −0.001 | 0.000 | 0.000 |
| $N=8$ | | | | | | | | | |
| $HYD$ | −11.853 | −34.160 | 11.325 | −4.072 | −12.236 | 4.081 | −1.899 | −5.710 | 1.905 |
| $M=0$ | −0.008 | −0.018 | 0.003 | −0.000 | −0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $M=1$ | 0.938 | 0.237 | −0.348 | 0.028 | 0.008 | −0.014 | 0.002 | 0.000 | −0.001 |
| $M=1, l_1=1$ | 0.924 | 0.182 | −0.275 | 0.029 | 0.007 | −0.013 | 0.002 | 0.000 | −0.001 |
| $M=2, l_1=1$ | −0.558 | 0.193 | 0.181 | −0.015 | 0.006 | 0.003 | −0.001 | 0.000 | 0.000 |
| $N=9$ | | | | | | | | | |
| $HYD$ | −8.329 | −23.990 | 7.953 | −2.860 | −8.594 | 2.866 | −1.334 | −4.011 | 1.338 |
| $M=0$ | −0.004 | −0.008 | 0.001 | −0.000 | −0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $M=1$ | 0.668 | 0.168 | −0.248 | 0.020 | 0.006 | −0.011 | 0.002 | 0.000 | −0.001 |
| $M=1, l_1=1$ | 0.657 | 0.129 | −0.195 | 0.021 | 0.005 | −0.009 | 0.002 | 0.000 | −0.001 |
| $M=2, l_1=1$ | −0.385 | 0.149 | 0.129 | −0.011 | 0.005 | 0.002 | −0.001 | 0.000 | 0.000 |
| $N=10$ | | | | | | | | | |
| $HYD$ | −6.075 | −17.488 | 5.797 | −2.085 | −6.265 | 2.089 | −0.972 | −2.924 | 0.975 |
| $M=0$ | −0.002 | −0.003 | −0.000 | −0.000 | −0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $M=1$ | 0.492 | 0.124 | −0.182 | 0.015 | 0.005 | −0.008 | 0.001 | 0.000 | −0.001 |
| $M=1, l_1=1$ | 0.484 | 0.095 | −0.144 | 0.016 | 0.004 | −0.007 | 0.001 | 0.000 | −0.001 |
| $M=2, l_1=1$ | −0.274 | 0.120 | 0.095 | −0.008 | 0.004 | 0.002 | −0.001 | 0.000 | 0.000 |
| $N=11$ | | | | | | | | | |
| $HYD$ | −4.565 | −13.139 | 4.355 | −1.567 | −4.707 | 1.570 | −0.731 | −2.197 | 0.733 |
| $M=0$ | −0.001 | −0.001 | −0.001 | −0.000 | −0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $M=1$ | 0.373 | 0.094 | −0.138 | 0.011 | 0.003 | −0.006 | 0.001 | 0.000 | −0.000 |
| $M=1, l_1=1$ | 0.366 | 0.072 | −0.109 | 0.012 | 0.003 | −0.005 | 0.001 | 0.000 | −0.000 |
| $M=2, l_1=1$ | −0.200 | 0.098 | 0.072 | −0.006 | 0.003 | 0.001 | −0.000 | 0.000 | 0.000 |

TABLE I. *(Continued).*

| | $L=2$ | | | $L=3$ | | | $L=4$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $h_{so}$ | $h_{\text{off}}$ | $h_{ss}$ | $h_{so}$ | $h_{\text{off}}$ | $h_{ss}$ | $h_{so}$ | $h_{\text{off}}$ | $h_{ss}$ |
| $N=12$ | | | | | | | | | |
| *HYD* | −3.517 | −10.120 | 3.354 | −1.207 | −3.625 | 1.209 | −0.563 | −1.692 | 0.564 |
| $M=0$ | −0.000 | 0.001 | −0.001 | −0.000 | −0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $M=1$ | 0.288 | 0.072 | −0.107 | 0.009 | 0.003 | −0.005 | 0.001 | 0.000 | −0.000 |
| $M=1, l_1=1$ | 0.283 | 0.056 | −0.084 | 0.009 | 0.002 | −0.004 | 0.001 | 0.000 | −0.000 |
| $M=2, l_1=1$ | −0.148 | 0.082 | 0.056 | −0.004 | 0.003 | 0.001 | −0.000 | 0.000 | 0.000 |

the agreement with experiment could not be better no matter what other value of $X$ is assumed. The results of such fits are displayed in Table III for those $n$ and $L$ for which there exists a complete set of three measurements of magnetic fine-structure intervals. The table lists the experimental data and, for the hydrogenic, adiabatic, and extended adiabatic approximations in turn, the differences between the measurements and the theoretical fit, the value of $\chi^2$ for the fit, and the fitted value of $X$. (For two degrees of freedom the 5% and 1% significance levels for $\chi^2$ are 6.0 and 9.2.)

There is a complete set of data for $D$ manifolds through $n=10$ except for the $8D$ manifold. Table III shows that the results of this work give markedly superior predictions of the magnetic fine structure compared to the naive hydrogenic approximation. In contrast, the adiabatic approximation yields consistently poorer agreement with experiment than the hydrogenic approximation despite its supposedly better wave function. Furthermore the residual discrepancies between experiment and the predictions of the extended adiabatic approximation are comparable to the estimated theoretical errors (1.5%).

The fits for the $F$ and $G$ manifolds, where the data are more sparse, show no significant difference between the hydrogenic and the extended adiabatic (or even the adiabatic) approximations. That this should be expected is clear from the small size (< 0.2 MHz) of the corrections which the first-order wave function introduces. However, the fits are unacceptable wherever relatively precise (< 2%) data are available, i.e., in the $7F$, $9F$, and $7G$ manifolds. The residual discrepancies are up to five times the quoted standard deviations of the measurements and an order of magnitude more than the expected theoretical errors. It would be interesting to have additional data to determine whether these anomalies are also present in other $F$ and $G$ manifolds.

TABLE II. First-order $m=1$ contributions to $h_{so}$ (in MHz).

| | $5D$ | $5F$ | $5G$ |
|---|---|---|---|
| $l=0$ | −0.800 84 | −0.012 99 | −0.000 07 |
| 1 | 3.405 65 | 0.089 09 | 0.006 15 |
| 2 | 0.653 58 | 0.007 53 | 0.000 07 |
| 3 | 0.104 17 | 0.001 91 | 0.000 01 |
| 4 | 0.037 26 | 0.000 47 | 0.000 00 |
| 5 | 0.016 42 | 0.000 19 | |
| 6 | 0.008 35 | 0.000 10 | |
| 7 | 0.004 71 | | |
| 8 | 0.004 28 | | |

Table IV lists the experimental data for those $D$, $F$, and $G$ manifolds for which not all the fine-structure intervals have been measured. From each of these we have extracted a value for $X$; since the fit is no longer overdetermined, this value for $X$ reproduces the data exactly.

## III. COMPARISON WITH ELECTRIC FINE STRUCTURE MEASUREMENTS

By subtracting the magnetic and exchange electric contributions, as determined in the previous section, from experimental values for the intervals between states of different $L$, we obtain a semiexperimental "spinless" value which can be compared directly with calculations of the direct electric fine structure. In Table VI we give the experimental values for those intervals which have been measured directly and the spinless values obtained from them using the extended adiabatic approximation. The superscript $M$ indicates that the average of the singlet and triplet values of the same $J$ has been used.

The most extensive calculation of these energy differences in $D$, $F$, and $G$ manifolds is that of Poe and Chang.[29] Their diagrammatic calculation is in principle equivalent to a computation of the zero- and first-order matrix elements of $(1/r_{12} - 1/r_2)$ using the complete first-order wave func-

TABLE III. Magnetic fine structure (values in MHz).

| Interval | | Ref. | Measured value | Experiment–theory | | |
|---|---|---|---|---|---|---|
| | | | | Hydrogenic | Adiabatic | Extended adiabatic |
| $3^1D_2-{}^3D_2$ | | 13 | 102 360.00(200.0) | 1 448.85 | −2 123.19 | 400.94 |
| ${}^3D_1-{}^3D_3$ | | 10 | 1 400.67 (0.29) | −12.71 | 44.44 | 5.52 |
| ${}^3D_2-{}^3D_3$ | | 10 | 75.97 (0.23) | −7.72 | 12.21 | −2.21 |
| | $\chi^2$: | | | 3 101.0 | 26 416.0 | 459.0 |
| | $x$: | | | 50 325.0 | 52 111.0 | 50 850.0 |
| $4^1D_2-{}^3D_2$ | | 13 | 59 140.00 (80.0) | 60.80 | −73.59 | 19.88 |
| ${}^3D_1-{}^3D_3$ | | 10 | 591.25 (0.14) | −8.69 | 23.71 | 1.83 |
| ${}^3D_1-{}^3D_2$ | | 15 | 553.00 (0.70) | −5.84 | 14.67 | 1.03 |
| ${}^3D_2-{}^3D_3$ | | 10 | 36.15 (0.24) | −4.94 | 6.94 | −1.30 |
| | $\chi^2$: | | | 4 343.0 | 29 965.0 | 202.0 |
| | $x$: | | | 29 488.0 | 29 555.0 | 29 509.0 |
| $5^1D_2-{}^3D_2$ | | 13 | 34 125.00 (45.00) | 3.23 | −5.62 | 0.34 |
| ${}^3D_1-{}^3D_2$ | | 15 | 284.10 (0.60) | −1.78 | 10.00 | 2.23 |
| ${}^3D_2-{}^3D_3$ | | 9 | 20.30 (0.30) | −1.87 | 5.00 | 0.41 |
| | $\chi^2$: | | | 47.5 | 556.0 | 15.6 |
| | $x$: | | | 17 035.0 | 17 039.0 | 17 037.0 |
| $6^1D_2-{}^3D_2$ | | 13 | 20 946.00 (30.00) | 0.76 | −2.42 | −0.37 |
| ${}^3D_1-{}^3D_2$ | | 15 | 165.30 (1.0) | −0.09 | 7.16 | 2.44 |
| ${}^3D_2-{}^3D_3$ | | 9 | 12.30 (0.3) | −0.88 | 3.37 | 0.64 |
| | $\chi^2$: | | | 8.22 | 177.0 | 10.6 |
| | $x$: | | | 10 458.0 | 10 459.0 | 10 458.0 |
| $7^1D_2-{}^3D_2$ | | 32 | 13 657.66 (0.26) | 0.00 | 0.00 | 0.00 |
| ${}^3D_1-{}^3D_3$ | | 32 | 109.15 (0.29) | −3.39 | 4.10 | −0.63 |
| ${}^3D_2-{}^3D_3$ | | 32 | 6.35 (0.19) | −2.06 | 0.70 | −1.01 |
| | $\chi^2$: | | | 254.0 | 220.0 | 31.8 |
| | $x$: | | | 6 815.0 | 6 817.0 | 6 816.0 |
| $9^1D_2-{}^3D_3$ | | 32 | 6 662.00 (0.09) | 0.00 | 0.00 | 0.00 |
| ${}^3D_1-{}^3D_3$ | | 32 | 52.18 (0.15) | −0.83 | 2.84 | 0.65 |
| ${}^3D_2-{}^3D_3$ | | 32 | 3.79 (0.11) | −0.23 | 1.12 | 0.36 |
| | $\chi^2$: | | | 33.0 | 438.0 | 27.9 |
| | $x$: | | | 3 325.0 | 3 325.0 | 3 325.0 |
| $10^1D_2-{}^3D_2$ | | 12 | 4 889.00 (30.0) | 0.51 | −0.25 | 0.15 |
| ${}^3D_1-{}^3D_3$ | | 18 | 37.59 (0.52) | −1.06 | 1.65 | 0.08 |
| ${}^3D_2-{}^3D_3$ | | 18 | 2.28 (0.30) | −0.66 | 0.33 | −0.20 |
| | $\chi^2$: | | | 9.1 | 11.3 | 0.46 |
| | $x$: | | | 2 441.0 | 2 441.0 | 2 441.0 |
| $7^1F_3-{}^3F_3$ | | 16 | 146.30 (0.30) | −0.18 | −0.19 | −0.14 |
| ${}^3F_2-{}^3F_3$ | | 16 | 69.10 (1.3) | −7.41 | −7.15 | −7.20 |
| ${}^3F_4-{}^3F_3$ | | 16 | 28.30 (0.30) | 0.02 | −0.01 | −0.09 |
| | $\chi^2$: | | | 32.9 | 30.6 | 31.0 |
| | $x$: | | | 33.84 | 33.92 | 33.93 |
| $9^1F_3-{}^3F_3$ | | 32 | 71.06 (0.06) | 0.08 | 0.10 | 0.10 |
| ${}^3F_2-{}^3F_3$ | | 32 | 35.51 (0.10) | 0.44 | 0.56 | 0.55 |
| ${}^3F_4-{}^3F_3$ | | 32 | 12.47 (0.11) | 0.10 | 0.07 | 0.13 |
| | $\chi^2$: | | | 22.0 | 34.7 | 34.3 |
| | $x$: | | | 17.89 | 17.90 | 17.93 |
| $12^1F_3-{}^3F_3$ | | 18 | 30.17 (0.65) | −0.34 | −0.33 | −0.32 |
| ${}^3F_2-{}^3F_3$ | | 18 | 13.97 (0.69) | −0.60 | −0.54 | −0.55 |
| ${}^3F_4-{}^3F_3$ | | 18 | 4.68 (0.60) | −0.31 | −0.33 | −0.30 |
| | $\chi^2$: | | | 1.30 | 1.18 | 1.13 |
| | $x$: | | | 8.06 | 8.06 | 8.07 |
| $7^1G_4-{}^3G_4$ | | 32 | 76.47 (0.24) | 0.15 | 0.15 | 0.15 |
| ${}^3G_3-{}^3G_4$ | | 32 | 57.09 (0.15) | −0.32 | −0.31 | −0.31 |
| ${}^3G_5-{}^3G_4$ | | 32 | 30.49 (0.20) | 0.59 | 0.57 | 0.58 |
| | $\chi^2$: | | | 13.7 | 12.9 | 13.2 |
| | $x$: | | | 0.415 | 0.407 | 0.406 |

TABLE III. *(Continued)*.

| Interval | Ref. | Measured value | Experiment-theory Hydrogenic | Adiabatic | Extended adiabatic |
|---|---|---|---|---|---|
| $10^1G_4-{}^3G_4$ | 18 | 25.84 (0.51) | −0.34 | −0.34 | −0.34 |
| ${}^3G_3-{}^3G_4$ | 18 | 19.58 (0.53) | −0.12 | −0.11 | −0.11 |
| ${}^3G_5-{}^3G_4$ | 18 | 10.39 (0.68) | 0.13 | 0.12 | 0.12 |
| $\chi^2$: | | | 0.52 | 0.52 | 0.51 |
| $x$: | | | 0.138 | 0.135 | 0.135 |

tion [the full solution of Eq. (3)]. Table VI compares their results, for which they quote three-figure precision, with the spinless values and shows the consistent ~1.4% discrepancy noted by Poe and Chang.

The expectation values of $H_{mp}$ and $H_{\rm rel}$, which are included in Eq. (1) but not in the calculation of Poe and Chang, have the right size to account for most of this discrepancy. These operators are diagonal in $L$ and $S$ and are independent of $J$. They are expressed here in terms of their direct parts (average of the singlet and triplet expectation values) and exchange parts (half the difference between the two). In the hydrogenic approximation $H_{mp}$ has a nonzero expectation value only for $P$ states. The hydrogenic matrix elements of $H_{\rm rel}$ are listed in Table V. These are primarily the result of the relativistic correction to the kinetic energy (they do not include that part of the expectation value which is independent of both $n$ and $L$). Only $H_{mp}$ has significant first-order matrix elements; these also are given in Table V. The theoretical spinless energy of a state is then the sum of the eigenvalue of $H_0$, for which we take the value of Poe and Chang corrected for the finite mass of the nucleus, and the expectation values of $H_{mp}$ and $H_{\rm rel}$, as given in Table V. The spinless splittings found by taking differences of the appropriate energies are listed in the next to last column of Table VI.

The discrepancies are now at most 0.1% in the $D$-$F$ intervals and at most 0.25% in the $D$-$G$ intervals, a definite improvement over the simple nonrelativistic values. But there is a 2% disagreement in the $6F$-$G$ interval. Furthermore, this is not unique to $n=6$ since, if we compute the spinless and theoretical values for the 7, 9, and 10 $F$-$G$ intervals by taking differences of the values for the $D$-$G$ and $D$-$F$ intervals, we find the same 2% discrepancy. If, as we would expect, the relative accuracy of the theoretical predictions improves with larger $L$, we must conclude that the

TABLE IV. Magnetic fine-structure manifolds with insufficient data for fits (values in MHz).

| Interval | Ref. | Measured value | Exchange |
|---|---|---|---|
| $8^1D_2-{}^3D_2$ | 13 | 9345.00(35.00) | $X=4666$ |
| ${}^3D_1-{}^3D_2$ | 15 | 69.00 (3.0) | |
| $11^1D_2-{}^3D_2$ | 12 | 3696.00(30.00) | $X=1846$ |
| $6^1F_3-{}^3F_3$ | 16 | 226.64 (0.11) | $X=47.76$ |
| $8^1F_3-{}^3F_3$ | 17 | 99.90 (0.30) | $X=24.47$ |
| $10^1F_3-{}^3F_3$ | 18 | 52.38 (0.04) | $X=13.66$ |
| $11^1F_3-{}^3F_3$ | 18 | 39.55 (0.03) | $X=10.44$ |
| $9^1G_4-{}^3G_4$ | 18 | 35.97 (0.05) | $X=0.688$ |

TABLE V.

| $NL$ | Hydrogenic matrix elements of $H_{\rm rel}$ (MHz) Direct | Exchange | First-order ($M=1,2$) matrix elements of $H_{mp}$ (MHz) Direct | Exchange |
|---|---|---|---|---|
| $3D$ | −973.68 | 8.55 | −11 457.30 | 141.97 |
| $4D$ | −581.89 | 5.00 | −4 759.17 | 81.66 |
| $5D$ | −350.49 | 2.90 | −2 419.30 | 47.01 |
| $6D$ | −223.11 | 1.79 | −1 394.62 | 28.85 |
| $7D$ | −149.62 | 1.17 | −876.19 | 18.78 |
| $8D$ | −104.82 | 0.80 | −586.08 | 12.85 |
| $9D$ | −76.12 | 0.60 | −411.20 | 9.15 |
| $10D$ | −56.95 | 0.42 | −299.54 | 6.74 |
| $11D$ | −43.69 | 0.32 | −224.93 | 5.10 |
| $12D$ | −34.23 | 0.25 | −173.18 | 3.96 |
| $4F$ | −286.96 | 0.01 | −2 320.12 | 0.14 |
| $5F$ | −190.28 | 0.01 | −1 184.64 | 0.12 |
| $6F$ | −130.39 | 0.01 | −684.52 | 0.09 |
| $7F$ | −91.24 | 0.01 | −430.68 | 0.06 |
| $8F$ | −65.70 | 0.00 | −288.35 | 0.04 |
| $9F$ | −48.65 | 0.00 | −202.44 | 0.03 |
| $10F$ | −36.93 | 0.00 | −147.53 | 0.02 |
| $11F$ | −28.64 | 0.00 | −110.82 | 0.02 |
| $12F$ | −22.64 | 0.00 | −85.35 | 0.01 |
| $5G$ | −101.27 | 0.00 | −678.86 | 0.00 |
| $6G$ | −78.88 | 0.00 | −392.59 | 0.00 |
| $7G$ | −58.50 | 0.00 | −247.12 | 0.00 |
| $8G$ | −43.97 | 0.00 | −165.50 | 0.00 |
| $9G$ | −33.39 | 0.00 | −116.22 | 0.00 |
| $10G$ | −25.80 | 0.00 | −84.71 | 0.00 |
| $11G$ | −20.28 | 0.00 | −63.64 | 0.00 |
| $12G$ | −16.20 | 0.00 | −49.02 | 0.00 |

precision of these eigenvalues is only about 1% and that the agreement in the *D*-*F* and *D*-*G* intervals noted above is fortuitous. But this would be surprising in view of the quoted three figure accuracy of Poe and Chang for their calculations and the consistency of their assertion with the ~0.2% discrepancies in the *D* states.

Kelsey and Spruch[33] have proposed a radiative correction to the usual polarization potential between an electron and a polarizable core. For a hydrogenlike core, the leading term in this potential is (in our units)

$$U \sim (99/8\pi Z^4)\, m\alpha \langle r_2^{-5}\rangle \,.$$

The last column of Table VI gives the theoretical predictions when this term is included. This correction causes a 0.6% shift in the *D*-*F* and *D*-*G* interval and leaves us with ~1% discrepancies. Thus we cannot draw any conclusion on the presence or absence of this radiative correction, but in either case there remain anomalies of about 1% in these intervals.

Table VII compares the electric exchange value ($X$) extracted from the magnetic fine-structure data with the nonrelativistic value calculated by Poe and Chang and with the prediction obtained by adding the relativistic mass polarization, and finite nuclear mass terms to the result of Poe and Chang. In most *D* states the disagreement is within the relatively large experimental errors. However, the more precisely known $7D$ and $9D$ states as well as the $5D$ have significant discrepancies.

TABLE VI. Direct electric fine structure (values in MHz).

| | Ref. | Experimental value | Spinless interval | Theoretical nonrelativistic interval | Theoretical interval with relativistic and mass corrections | Theoretical interval with relativistic, mass, and radiative corrections |
|---|---|---|---|---|---|---|
| $6^1D_2 - {}^MF_3$ | 16 | 49 690.18 (0.09) | 60 155 | 59 303(−852, −1.4%) | 60 098(−57, −0.095%) | 59 728(−427, −0.71%) |
| $7^MD_2 - {}^MF_3$ | 16 | 38 310.0 (0.1) | 38 305 | 37 772(−533, −1.4%) | 38 271(−34, −0.089%) | 38 032(−273, −0.71%) |
| $8^1D_2 - {}^MF_3$ | 17 | 21 176.4 (0.2) | 25 845 | 25 477(−368, −1.4%) | 25 811(−34, −0.132%) | 25 648(−197, −0.76%) |
| $9^3D_2 - {}^MF_3$ | 17 | 21 571.7 (0.2) | 18 240 | 17 984(−256, −1.4%) | 18 218(−22, −0.121%) | 18 103(−137, −0.75%) |
| $10^1D_2 - {}^MF_3$ | 18 | 10 892.636(0.026) | 13 335 | 13 155(−180, −1.3%) | 13 325(−10, −0.075%) | 13 240 (−95, −0.71%) |
| $11^1D_2 - {}^MF_3$ | 18 | 8 195.299(0.095) | 10 042 | 9 908(−134, −1.3%) | 10 036 (−6, −0.060%) | 9 975 (−67, −0.67%) |
| $6\,D \;- G$ | | | 69 059 | 68 045(−1014, −1.5%) | 69 182(123, +0.178%) | 68 792(−267, −0.39%) |
| $7^1D_2 - {}^MG_4$ | 18 | 37 222.868(0.040) | 44 041 | 43 392(−649, −1.5%) | 44 106 (65, 0.148%) | 43 854(−187, −0.42%) |
| $9^1D_2 - {}^MG_4$ | 18 | 17 679.081(0.032) | 21 005 | 20 723(−282, −1.3%) | 21 058 (53, 0.252%) | 20 936 (−69, −0.33%) |
| $10^3D_2 - {}^MG_4$ | 18 | 17 827.23 (0.34) | 15 381 | 15 165(−216, −1.4%) | 15 409 (28, 0.182%) | 15 319 (−62, −0.40%) |
| $6^1F_3 - {}^1G_4$ | 18 | 8 854.06 (0.27) | 8 904 | 8 742(−162, −1.82%) | 9 084 (180, 2.02%) | 9 064 (160, 1.80%) |
| $7\,F \;- G$ | | | 5 736 | 5 620(−116, −2.02%) | 5 835 (99, 1.73%) | 5 822 (86, 1.50%) |
| $9\,F \;- G$ | | | 2 765 | 2 739 (−26, −0.94%) | 2 840 (75, 2.71%) | 2 833 (68, 2.46%) |
| $10\,F \;- G$ | | | 2 046 | 2 010 (−36, −1.76%) | 2 084 (38, 1.86%) | 2 079 (33, 1.61%) |

TABLE VII. Exchange electric fine structure (values in MHz).

| | Semiempirical exchange | Poe and Chang exchange | Spinless exchange |
|---|---|---|---|
| $3D$ | 50 850(100) | 50 724 | 50 868 |
| $4D$ | 29 509 (40) | 29 400 | 29 483 |
| $5D$ | 17 037 (23) | 16 924 | 16 972 |
| $6D$ | 10 458 (15) | 10 409 | 10 439 |
| $7D$ | 6 815 (<1) | 6 780 | 6 799 |
| $8D$ | 4 666 (18) | 4 634 | 4 647 |
| $9D$ | 3 325 (<1) | 3 308 | 3 318 |
| $10D$ | 2 441 (15) | 2 432 | 2 439 |
| $11D$ | 1 846 (15) | 1 844 | 1 849 |
| $4F$ | | 67.9 | 68.0 |
| $5F$ | | 59.5 | 59.6 |
| $6F$ | 47.76 | 43.2 | 43.3 |
| $7F$ | 33.93 | 30.6 | 30.7 |
| $8F$ | 24.47 | 21.9 | 21.9 |
| $9F$ | 17.93 | 16.2 | 16.2 |
| $10F$ | 13.66 | 12.2 | 12.2 |
| $11F$ | 10.44 | 9.3 | 9.3 |
| $12F$ | 8.07 | | |

For these intervals, including the relativistic and mass corrections reduces the residuals by a factor of 2, leaving discrepancies of about 0.4%. The much smaller exchange values for $F$ states have no appreciable relativistic or mass corrections, but the theoretical values are consistently 9%–11% smaller than the experimental values. Poe and Chang report that the second-order contributions to the exchange are surprisingly large, amounting to 60% of the first-order exchange; it is entirely conceivable that still higher-order contributions account for this 10%.

## IV. CONCLUSIONS

Not only does the extended adiabatic approximation developed here give better predictions of the magnetic fine structure than either the adiabatic or hydrogenic approximations, but it also explains why these approximations are not valid. The adiabatic approximation omits terms having the same order of magnitude as the corrections it introduces. Since these additional terms in part cancel the corrections introduced by the adiabatic approximation, the hydrogenic approximation gives fortuitously good results.

Theoretical calculations of direct and exchange electric fine structure and magnetic fine structure in helium Rydberg states are expected to be most accurate in high $L$ states where nonhydrogenic corrections to the wave function decrease rapidly. It may be noted that the available data do *not* confirm this expectation. In the case of magnetic fine structure, the present calculation is in acceptable agreement with all available data from $D$ manifolds, but is in marked disagreement with measurements in several $F$ and $G$ states. In the case of direct electric fine structure, agreement between theory and experiment appears to be better for intervals involving the $D$ states than in the case of higher $L$ states. Finally, in the case of exchange electric fine structure, the $D$ states confirm theoretical calculations at the acceptable level of 0.5%, while systematic discrepancies of about 10% are present in $F$ states. Experimental data for the "high $L$" $F$ and $G$ states are derived exclusively from the work of MacAdam, Wing, and Lamb. Additional data, perhaps in even higher states, would be helpful in sorting out the discrepancies which are now apparent.

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