

Hyperfine and Zeeman Studies of Low-Lying Atomic Levels of La¹³⁹ and the Nuclear Electric-Quadrupole Moment*

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The atomic-beam magnetic-resonance technique has been used to determine the hyperfine-interaction constants A , B , and C and electron g values g_J for all previously unstudied atomic levels of La¹³⁹ below 9000 cm⁻¹. The results are analyzed in detail in terms of a set of eigenvectors spanning the three configurations $5d6s^2$, $5d^26s$, and $5d^3$. Corrections for hyperfine and Zeeman interactions between all low-lying states are carried out in intermediate coupling. The value deduced from the observed hyperfine structure for Q , the La¹³⁹ nuclear ground-state electric-quadrupole moment, is influenced strongly by taking account of (a) the large recently found configuration mixing between $5d6s^2$, $5d^26s$, and $5d^3$ and (b) the rather substantial Sternheimer shielding effects. The effects (a) and (b), though both about 30%, are in opposite directions and partially cancel. The value obtained is $Q = (+0.22 \pm 0.03)b$. Although the order of consistency between the experimental results and theory is encouraging, a number of problems remain.

I. INTRODUCTION

The neutral lanthanum atom, coming just before the $4f$ shell in the Periodic Table, has interested a number of authors over the years for various reasons. The $(5d+6s)^3$ electron scheme, while providing a number of low-lying closely spaced levels which interact strongly with each other, is still sufficiently simple to be susceptible to theoretical attack. In addition to investigations of the atomic structure, both optical and atomic-beam magnetic-resonance studies have been made¹⁻³ to determine the electric-quadrupole moment of the La¹³⁹ nuclear ground state.

While the presence of closely packed interacting levels may be regarded as a complication, it may also be considered as a challenge to make use of the interactions to understand the atomic structure. The hyperfine structure (hfs) of the $5d6s^2 \ ^2D_{3/2,5/2}$ ground doublet has been studied in detail by Ting.³ The present study extends his experimental work to all levels up to about 9000 cm⁻¹. Eigenvectors that span the three configurations $5d6s^2$, $5d^26s$, and $5d^3$ in intermediate coupling have been developed by Wilson⁴ by computer fitting of observed term values. The eigenvectors, in addition to satisfying the known excitation energies, should also be consistent with the electron g factors g_J and the hyperfine-interaction constants A and B of all the low levels examined. Effective operator Hamiltonians are used for analysis of the hfs interactions. While

the over-all consistency is good, a number of problems remain.

II. THEORY UNDERLYING METHOD

The atomic-beam magnetic-resonance technique devised by Rabi, Zacharias, Millman, and Kusch,⁵ and modified by Zacharias⁶ is now so classic as to require a minimum of description. Atoms of the material under investigation effuse individually through a thin slit in the source and pass in turn through three magnetic fields. The first and third fields are strong and inhomogeneous, with their gradients in the same direction, and the central field is variable and homogeneous. Individual atoms of the atomic beam are deflected away from the detector (if they have a magnetic moment) unless a suitable change of state occurs between the two deflecting magnets. The atomic-beam apparatus is normally adjusted so that the required transition causes the atom to have opposite effective magnetic moments in the two deflecting fields, and results in a resonant refocusing of the beam to a detector. For an energy difference $h\nu$ between the two atomic levels involved, this "flop" is induced by an rf field of frequency ν superimposed on the homogeneous central magnetic field.

If one limits his attention to a single fine-structure state $|\alpha SLJ\rangle$, the appropriate Hamiltonian for analyzing the hyperfine and Zeeman energies is⁷

$$\mathcal{H} = hA\vec{I} \cdot \vec{J} + hB \frac{\frac{3}{2}\vec{I} \cdot \vec{J}(2\vec{I} \cdot \vec{J} + 1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)} + hC \frac{5}{4} \{8(\vec{I} \cdot \vec{J})^3 + 16(\vec{I} \cdot \vec{J})^2 + \frac{3}{2}(\vec{I} \cdot \vec{J})[-3I(I+1)J(J+1) + I(I+1) + J(J+1) + 3] - 4I(I+1)J(J+1)\} [I(I-1)(2I-1)J(J-1)(2J-1)]^{-1} + \mu_B H(g_J J_z + g_I I_z), \quad (1)$$

TABLE I. Excitation energies and relative Boltzmann factors of the lower levels of La I. The Boltzmann factors are calculated for the approximate oven temperature of 1927 °C, for which the vapor pressure is about 0.1 Torr. The relative intensities of the rf transitions seen are roughly proportional to the Boltzmann factors.

Electron configuration	State	Excitation energy (cm ⁻¹)	Relative Boltzmann factor
5d6s ²	² D _{3/2}	0	1.000
5d6s ²	² D _{5/2}	1053	0.502
5d ² 6s	⁴ F _{3/2}	2668	0.175
5d ² 6s	⁴ F _{5/2}	3010	0.140
5d ² 6s	⁴ F _{7/2}	3495	0.102
5d ² 6s	⁴ F _{9/2}	4122	0.068
5d ² 6s	² F _{5/2}	7012	0.010
5d ² 6s	⁴ P _{1/2}	7231	0.0088
5d ² 6s	⁴ P _{3/2}	7490	0.0075
5d ² 6s	⁴ P _{5/2}	7680	0.0066
5d ² 6s	² F _{7/2}	8052	0.0052
5d ² 6s	² D _{3/2}	8446	0.0040
5d ² 6s	² P _{1/2}	9044	0.0027
5d ² 6s	² D _{5/2}	9184	0.0025
5d ² 6s	² P _{3/2}	9719	0.0017
5d ² 6s	² G _{9/2}	9919	0.0015
5d ² 6s	² G _{7/2}	9961	0.0015

where A, B , and C are the magnetic-dipole, electric-quadrupole, and magnetic-octupole hyperfine-interaction constants, respectively, \vec{I} and \vec{J} are the nuclear and electronic angular momentum operators, μ_B and h are the Bohr magneton and Planck's constant, H is the magnetic field, and g_J and g_I are the electron and nuclear g factors, respectively.

Two computer programs based on Eq. (1) are used repeatedly; the first simply calculates the required transition frequencies ν as functions of H , and the second accepts an ensemble of observations of ν and H , and varies the quantities A, B, C, g_J , and g_I to make a least-squares fit to the observed values of ν .

III. APPARATUS

The atomic-beam machine used for the experiment has been described before⁸ and no essential changes have been made. Lanthanum metal was cleaved and kept in kerosene until just before use. After washing it in benzene, it was placed in a sharp-lipped tantalum crucible to limit creeping, and the crucible was placed inside a Ta oven which was heated by electron bombardment to produce the beam. Considerable difficulty was caused by La activation of the bombardment filaments, and it was necessary to keep them as far from the front of the oven as possible. The problem was reduced by regulating the total power to the oven rather than the emission current from the heater filaments. Whenever the emission current attempted to change, the high voltage applied was altered such that the

total power used to heat the oven was kept constant.

The homogeneous magnetic field was set to the desired value by observing a suitable transition in a K³⁹ beam effusing from a separate oven. The radio frequency used for La was repeatedly swept in small steps (usually 10 kHz) through the frequency span of interest. The detector is described in Ref. 8, and the multichannel scaler, data-handling techniques, and digital noise filter used have also been described.^{9,10}

Radio frequencies below 50 MHz were produced directly; those between 50 MHz and 1 GHz were obtained by multiplication of lower crystal-stabilized frequencies and those between 1 and 8 GHz by phase-locked magnetrons and backward-wave oscillators with appropriate microwave amplifiers.

IV. EXPERIMENTAL PROCEDURE

Since the metastable atomic states were populated thermally in our apparatus, the intensities observed were strongly correlated with excitation energy, and were approximately proportional to the relative Boltzmann factors. These are summarized in Table I for 1927 °C, for which the vapor pressure of La is approximately 0.1 Torr. Thus, the expected intensity for transitions in the 5d²6s ²D_{5/2} state at 9184 cm⁻¹, for example, was only 1/400 of that for the ground state. To avoid confusing poorly refocused or nearly forbidden transitions in the well-populated states with normal transitions in highly excited states, the stronger states were investigated first. Figures 1 and 2 illustrate the relative intensities typically observed for two pairs of states. The signal-to-noise ratio can be improved almost arbitrarily for any state by lengthening the time of data collection. Thus, Fig. 2 was obtained while collecting data for the ²F_{5/2} state; the signal-to-noise ratio for the ²D_{3/2} state could have been improved by a longer count.

Since the zero-field hyperfine intervals of the 5d6s²²D levels of the ground term had been accurately measured by Ting,³ it was only necessary to make observations at reasonably strong values of H to determine the values of g_J .

No previous measurements of atomic-beam accuracy had been made on any levels of the 5d²6s configuration, however, and the procedure followed was virtually the same for each state. It can be shown from Eq. (1) that at small values of H (such as 10 G) the $\Delta F = 0$ transition frequencies are almost independent of the hyperfine-interaction constants A, B , and C , and can be predicted closely for any state from the known¹¹ optical value of g_J . As such $\Delta F = 0$, $\Delta M_F = \pm 1$ transitions are followed to higher fields their dependence on the hyperfine-interaction constants increases rapidly. At each step, the computer programs produced best-fit values of the parameters and predicted the transi-

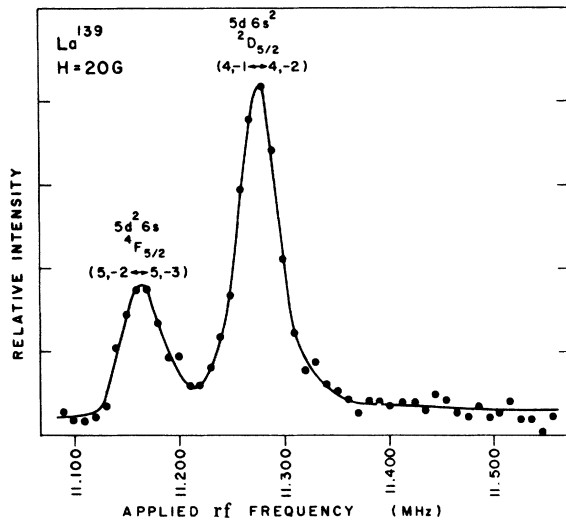


FIG. 1. Appearance of rf transitions in the $5d^2 6s^2 2D_{5/2}$ and $5d^2 6s^2 4F_{5/2}$ states of La^{139} at 20 G. The difference in intensity between the two peaks is due primarily to the fact that the two levels lie at different excitation energies and consequently have different thermal populations. A much longer data collection would have revealed a transition in the much less populated $5d^2 6s^2 D_{5/2}$ state (9184 cm^{-1}) at about 11.5 MHz.

tion frequencies for still higher fields. When the uncertainties in the values of A and B were sufficiently small that the zero-field $\Delta F = \pm 1$ intervals could be predicted with little error, these "direct" transitions were searched for. Figure 3 shows the appearance of several components of the $F = 3 \rightarrow 4$ transition in the $4F_{3/2}$ state as observed at 1 G. As the degree of excitation increased, intensity became the limiting consideration, and the procedure outlined was of necessity carried out with less completeness.

For some states, experimental difficulties were encountered because the computer programs described above were unable to produce acceptably good fits to the observed data or to make valid predictions of resonance frequencies for as yet unobserved transitions. It is shown below that when interactions with nearby atomic states are properly taken into account, such difficulties are resolved. For this purpose it is necessary to generalize Eq. (1) as discussed in Sec. VE. Certain new parameters which occur play an important role in determining the transition frequencies at high field, and, conversely, high-field observations can be very helpful in evaluating the new parameters.

Because the central field in our atomic-beam apparatus is not as homogeneous as might be desired, it was found that above 400 G the observed linewidth is proportional to H , and hence little could be gained by observing field-dependent tran-

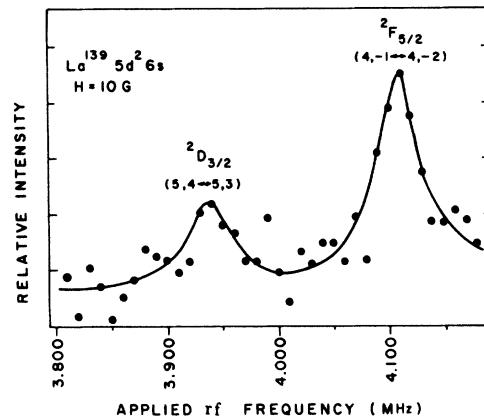


FIG. 2. Transitions in the $2F_{5/2}$ and $2D_{3/2}$ levels of the $5d^2 6s$ configuration at 10 G. The curve was obtained to determine the resonance frequency of the $2F_{5/2}$ transition and required about 30 min of data collection; still longer collections were required to yield an adequate signal-to-noise ratio for the very weakly populated $2D_{3/2}$ state.

sitions at higher fields. Calculations showed, however, that many of the $\Delta F = \pm 1$ transition frequencies have extrema (mostly minima) at certain values of H , and in these regions $\partial\nu/\partial H$ is 0 to within a few kHz over a range of several G. A number of these transitions were observed at the appropriate values of H , and these data were useful in reducing the uncertainties on certain of the hfs parameters discussed below. For these almost field-independent observations, the field was set by means of a rotating-coil gaussmeter rather than by K^{39} res-

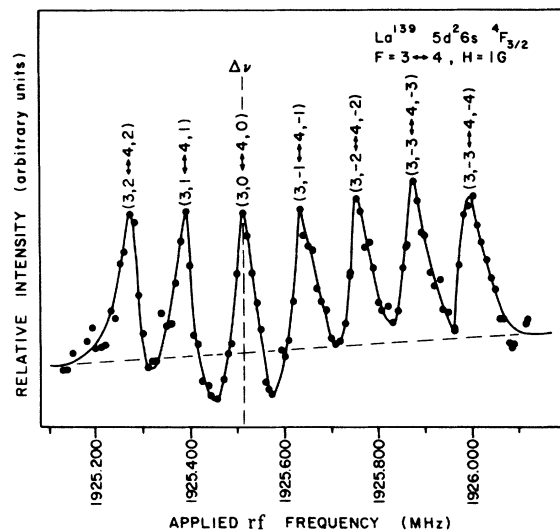


FIG. 3. Seven components of the $F = 4$ to $F = 3$ transition in the $4F_{3/2}$ state at 1 G. The vertical dashed line indicates the frequency that corresponds to the zero-field hyperfine interval $\Delta\nu$.

onances, but the gaussmeter was cross calibrated against the K^{39} transition frequency to within ± 1.5 G at several fields up to 3000 G.

V. DATA ANALYSIS AND COMPARISON WITH THEORY

A. Introduction

As pointed out in Sec. IV, the observed resonance frequencies may be computer analyzed with the aid of Eq. (1), the traditional Hamiltonian for atomic-beam studies. The computer, while constraining g_I to be consistent with the NMR value,¹² varies A, B, C and g_J for each state independently to produce a best least-squares fit to the observed resonance frequencies. The first of the two columns of residuals in Table II gives the differences between the observed and the calculated resonance frequencies according to this procedure. It is clear that the residual is very much larger than the experimental uncertainty for many observations, particularly for those at large H . The best-fit values of the quantities A, B, C , and g_J for these fits are listed in the fourth column of Table III, together with the χ^2 found. The large values of χ^2 found for the fits to the ${}^4F_{3/2}$, ${}^4P_{1/2}$, and ${}^4F_{5/2}$ data illustrate the same point.

It is clear that the resonance frequencies calculated on the basis of Eq. (1) are not in agreement

with experiment, particularly at large H . The source of the trouble is that Eq. (1) ignores hfs and Zeeman interactions with neighboring atomic levels. Equation (1) also fails to tell us anything of the way in which the hyperfine-interaction constants may be expected to vary from state to state. Clearly, the theoretical treatment must be refined.

B. Eigenvectors and g_J Values

Figure 4 shows the low even-parity energy levels of the neutral lanthanum atom, including the recently observed¹³ $5d^3$ 4F term. It can immediately be seen that the departure from the LS limit¹⁴ is important; in fact, the spin-orbit interaction has caused substantial intermingling of terms in the $5d^26s$ configuration. In addition to this complication, the three low even configurations are close in energy, and some configuration interaction can be expected between like terms. Coulomb interaction with higher configurations and smaller magnetic effects might also be important. In 1966 Stein¹³ made a least-squares fit to all the known levels of the $5d6s^2$, $5d^26s$, and $5d^3$ configurations; all the levels but one were fitted to within 100 cm^{-1} .

Wilson⁴ has recently determined the phases and approximate values of the required R^k integrals by Hartree-Fock calculations. With this information, and with several sets of assumptions to keep the number of free parameters reasonably small, he has also fitted the known levels of the three configurations simultaneously. Of these LS eigenvector sets, the set that gives the smallest mean difference between observed and calculated term values (set A of Ref. 4) is the one this paper consistently uses in the analysis.

The Wilson eigenvectors show that although the 4F term of $5d^26s$ is rather pure, the higher more closely packed states of $5d^26s$ are considerably mixed. The $5d6s^2$ 2D ground term contains a large admixture of $5d^26s$ 2D . The g_J values predicted from the eigenvectors for the low-lying $5d6s^2$ 2D and $5d^26s$ 4F terms are in very good agreement with the experimental values. The agreement is less satisfactory for the higher $J = \frac{3}{2}, \frac{5}{2}$ states of $5d^26s$ which can mix with $5d6s^2$ 2D . Details of the development of the eigenvectors and the theoretical values of g_J are given in Ref. 4.

Judd and Lindgren¹⁵ have given an expression which the g_J values of an LS multiplet should obey. The expression, in addition to satisfying the Landé formula with the Schwinger correction, also takes account of spin-orbit mixing through second order and of relativistic and diamagnetic corrections to the g factors. Although it disregards the effects of configuration interaction, such effects are normally small since in lowest order the states mixed by the Coulomb interaction have the same S, L , and J and consequently the same g_J . The relation is

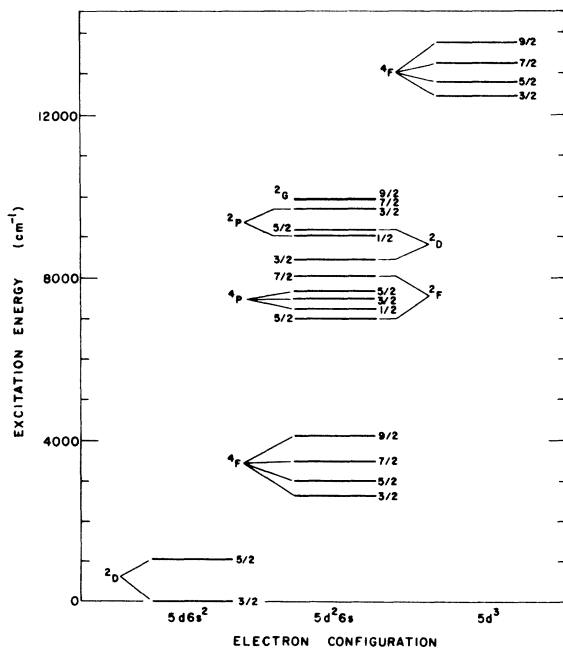


FIG. 4. Scale drawing of the low even-parity atomic energy levels of the neutral La atom. All the levels of the $5d6s^2$, $5d^26s$, and $5d^3$ configuration that have been observed are shown. The intermingling of multiplets of $5d^26s$ is apparent.

TABLE II. Resonance frequencies observed in low-lying levels of La^{139} . Two columns of residuals (differences between observed and calculated resonance frequencies) are given at the right of the table, both in kHz. The calculated frequencies used for the first column are from Eq. (1); i. e., they presuppose the atomic state to be completely pure and isolated. Those used for calculating the residuals of the second column are corrected for hyperfine and Zeeman interactions with all neighboring levels. The parameters used for the correction are those of the upper right-hand section of Table VIII, except that the value of $a_3^{10}(5d^26s)$ was very slightly altered for the ${}^4P_{1/2}$ and ${}^4F_{3/2}$ states to be consistent with Eqs. (17) and (18), respectively. The corrections calculated for $5d6s^2{}^2D_{3/2,5/2}$ and $5d^26s^2{}^2D_{3/2,5/2}$ are so small that the residuals for the corrected and uncorrected cases are the same. Values of H given without a decimal point in the table were precisely set by using the K^{39} calibration resonance. Those marked by an asterisk were set to within ± 1.5 G by a rotating-coil gaussmeter. As discussed in the text, the value of $\partial\nu/\partial H$ is very nearly zero in the vicinity of those values of H marked by asterisks.

Configuration and state	Transition ($F, M \leftrightarrow F', M'$)	H (G)	Observed resonance frequency (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$	
				Uncorrected (kHz)	Corrected (kHz)
$5d6s^2{}^2D_{3/2}$	4, -2 \leftrightarrow 4, -3	10	2.272(4)	-4	-4
	4, -2 \leftrightarrow 4, -3	20	4.646(4)	-1	-1
	5, -3 \leftrightarrow 5, -4	40	13.828(6)	3	3
	5, -3 \leftrightarrow 5, -4	100	36.282(5)	3	3
	5, -3 \leftrightarrow 5, -4	200	78.523(6)	-5	-5
	4, -2 \leftrightarrow 4, -3	200	65.215(7)	-1	-1
	5, -3 \leftrightarrow 5, -4	400	183.660(10)	5	5
$5d6s^2{}^2D_{5/2}$	6, -3 \leftrightarrow 6, -4	200	155.555(13)	1	1
	4, -1 \leftrightarrow 4, -2	200	146.317(13)	-1	-1
	5, -2 \leftrightarrow 5, -3	200	154.080(13)	11	11
	5, -2 \leftrightarrow 5, -3	400	372.878(17)	-11	-11
	6, -3 \leftrightarrow 6, -4	400	345.137(13)	1	1
$5d^26s{}^4F_{3/2}$	5, 4 \leftrightarrow 5, 3	20	3.398(5)	4	4
	4, 3 \leftrightarrow 4, 2	20	2.267(5)	1	4
	5, 4 \leftrightarrow 5, 3	40	6.804(5)	-1	-3
	4, 3 \leftrightarrow 4, 2	40	4.554(10)	-5	0
	5, 4 \leftrightarrow 5, 3	80	13.675(12)	-5	-9
	5, 4 \leftrightarrow 5, 3	100	17.151(4)	7	3
	4, 3 \leftrightarrow 4, 2	100	11.590(6)	-13	-1
	5, 4 \leftrightarrow 5, 3	200	34.727(7)	-4	-14
	4, 3 \leftrightarrow 4, 2	200	23.869(7)	-28	-4
	5, 4 \leftrightarrow 5, 3	400	71.282(10)	28	-1
	4, 3 \leftrightarrow 4, 2	400	50.553(14)	-41	-2
	5, 4 \leftrightarrow 5, 3	799.932	149.939(20)	107	17
	4, 3 \leftrightarrow 4, 2	799.932	112.640(15)	-42	9
	3, 2 \leftrightarrow 4, 2	1	1925.284(11)	-48	0
	3, 1 \leftrightarrow 4, 1	1	1925.393(14)	-52	-4
	3, 0 \leftrightarrow 4, 0	1	1925.514(11)	-44	3
	3, -1 \leftrightarrow 4, -1	1	1925.625(8)	-46	1
	3, -2 \leftrightarrow 4, -2	1	1925.744(13)	-41	7
	3, -3 \leftrightarrow 4, -3	1	1925.858(14)	-40	7
	3, -3 \leftrightarrow 4, -4	1	1925.968(14)	-42	5
	3, 2 \leftrightarrow 4, 2	6	1924.162(16)	-39	10
	3, 1 \leftrightarrow 4, 1	6	1924.826(16)	-54	-6
	3, 0 \leftrightarrow 4, 0	6	1925.508(20)	-51	-4
3, -3 \leftrightarrow 4, -3	6	1927.538(13)	-61	-16	
3, 2 \leftrightarrow 4, 2	2397.5*	1472.637(20)	124	3	
3, 1 \leftrightarrow 4, 1	1454.5*	1818.375(20)	53	-4	
3, 2 \leftrightarrow 4, 1	2190.5*	1751.014(16)	-486	-3	
4, 3 \leftrightarrow 5, 3	2873.0*	2100.162(11)	14	0	
3, 0 \leftrightarrow 4, 1	1054.0*	1850.990(14)	300	-10	
3, 1 \leftrightarrow 4, 2	1934.0*	1595.660(13)	635	7	
$5d^26s{}^4F_{5/2}$	6, -3 \leftrightarrow 6, -4	20	12.077(5)	5	7
	6, -3 \leftrightarrow 6, -4	40	24.278(10)	-8	-5
	6, -3 \leftrightarrow 6, -4	100	61.777(9)	-7	4
	6, -3 \leftrightarrow 6, -4	200	127.114(13)	-29	-3

TABLE II (continued).

Configuration and state	Transition ($F, M \leftrightarrow F', M'$)	H (G)	Observed resonance frequency (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ Uncorrected (kHz)	Corrected (kHz)
	5, -2 \leftrightarrow 5, -3	20	11.139(10)	-11	-11
	5, -2 \leftrightarrow 5, -3	40	22.517(6)	-2	-2
	4, -1 \leftrightarrow 4, -2	40	19.342(7)	2	0
	4, -1 \leftrightarrow 4, -2	100	50.612(8)	11	4
	5, -2 \leftrightarrow 5, -3	200	121.407(14)	3	5
	4, -1 \leftrightarrow 4, -2	200	108.558(9)	12	-4
	4, -1 \leftrightarrow 3, 0	1	1199.315(12)	2	-7
	4, 0 \leftrightarrow 3, 1	1	1199.487(8)	5	-4
	4, 1 \leftrightarrow 3, 2	1	1199.651(15)	0	-9
	4, 2 \leftrightarrow 3, 3	1	1199.830(20)	9	1
	4, 1 \leftrightarrow 3, 0	1	1200.262(20)	13	4
	4, 2 \leftrightarrow 3, 1	1	1200.427(10)	10	1
	4, 3 \leftrightarrow 3, 2	1	1200.602(10)	16	7
	4, 4 \leftrightarrow 3, 3	1	1200.768(13)	13	4
	5, -2 \leftrightarrow 4, -2	1	1503.028(18)	-43	0
	6, -3 \leftrightarrow 5, -3	1	1808.793(12)	0	-2
	4, -1 \leftrightarrow 3, -1	532.5*	978.915(25)	-14	-9
	6, -3 \leftrightarrow 5, -3	662.5*	1746.972(20)	26	8
	5, -2 \leftrightarrow 4, -2	622.5*	1396.259(25)	-33	3
	4, -1 \leftrightarrow 3, 0	420.5*	1001.597(16)	-49	9
	4, 0 \leftrightarrow 3, 1	231.5*	1150.437(15)	-31	2
$5d^26s\ ^4F_{7/2}$	6, -2 \leftrightarrow 6, -3	20	17.373(10)	-12	-11
	4, 0 \leftrightarrow 4, -1	20	17.373(10)	-14	-16
	7, -3 \leftrightarrow 7, -4	40	34.826(8)	-2	0
	6, -2 \leftrightarrow 6, -3	40	34.910(8)	0	0
	5, -1 \leftrightarrow 5, -2	40	34.983(10)	-6	-7
	7, -3 \leftrightarrow 7, -4	100	87.817(7)	0	5
	6, -2 \leftrightarrow 6, -3	100	88.325(10)	-5	-4
	4, 0 \leftrightarrow 4, -1	100	88.426(11)	9	3
	7, -3 \leftrightarrow 7, -4	200	178.128(14)	-3	7
	6, -2 \leftrightarrow 6, -3	200	180.208(16)	0	2
	5, -1 \leftrightarrow 5, -2	200	182.315(14)	0	-6
	4, 0 \leftrightarrow 4, -1	200	180.915(15)	9	-2
	4, -1 \leftrightarrow 3, -1	1	1847.831(12)	18	-5
	5, -1 \leftrightarrow 4, -1	1	2312.530(20)	9	-1
	6, -2 \leftrightarrow 5, -2	1	2779.047(7)	-2	0
	7, -3 \leftrightarrow 6, -3	1	3247.744(6)	0	0
	4, 0 \leftrightarrow 3, 1	469.5*	1495.801(20)	-46	-1
	4, 2 \leftrightarrow 3, 3	138.5*	1788.522(22)	8	9
	4, 1 \leftrightarrow 3, 2	272.5*	1712.095(16)	-14	5
$5d^26s\ ^4F_{9/2}$	8, -3 \leftrightarrow 8, -4	20	21.012(9)	-10	-10
	7, -2 \leftrightarrow 7, -3	20	21.693(13)	-8	-7
	6, -1 \leftrightarrow 6, -2	20	22.694(13)	-14	-15
	5, 0 \leftrightarrow 5, -1	20	24.270(15)	-20	-20
	8, -3 \leftrightarrow 8, -4	40	42.113(15)	-13	-12
	7, -2 \leftrightarrow 7, -3	40	43.505(8)	-2	-2
	6, -1 \leftrightarrow 6, -2	40	45.536(7)	-2	-2
	8, -3 \leftrightarrow 8, -4	100	105.930(12)	1	3
	7, -2 \leftrightarrow 7, -3	100	109.553(12)	-13	-13
	6, -1 \leftrightarrow 6, -2	100	114.782(15)	-5	-5
	8, -3 \leftrightarrow 8, -4	200	213.928(13)	7	12
	7, -2 \leftrightarrow 7, -3	200	221.810(15)	-39	-37
	6, -1 \leftrightarrow 6, -2	200	232.907(15)	5	5
	5, 0 \leftrightarrow 5, -1	200	248.134(15)	-18	-20
	4, 1 \leftrightarrow 4, 0	200	266.220(15)	-6	-9
	5, 0 \leftrightarrow 5, -1	399.976	515.637(15)	38	36

TABLE II (continued).

Configuration and state	Transition ($F, M \leftrightarrow F', M'$)	H (G)	Observed resonance frequency (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$	
				Uncorrected (kHz)	Corrected (kHz)
	4, 4 \leftrightarrow 3, 3	0.897	1952.485(18)	17	8
	4, 3 \leftrightarrow 3, 2	0.897	1952.729(13)	11	2
	4, 1 \leftrightarrow 3, 1	0.950	1951.745(20)	4	-5
	4, 2 \leftrightarrow 3, 3	1	1949.847(14)	28	19
	5, 0 \leftrightarrow 4, 0	1	2442.857(22)	-22	-27
	6, -1 \leftrightarrow 5, -1	1	2935.749(10)	2	1
	7, -2 \leftrightarrow 6, -2	0.938	3430.847(13)	-3	-2
	8, -3 \leftrightarrow 7, -3	0.896	3928.625(27)	2	0
	4, 1 \leftrightarrow 3, 2	385.0*	1472.397(20)	-13	11
	4, 1 \leftrightarrow 3, 2	389.0*	1472.304(15)	-39	-14
	4, 1 \leftrightarrow 3, 2	393.0*	1472.392(20)	-44	-18
	4, 2 \leftrightarrow 3, 3	233.5*	1686.289(16)	-8	5
	4, 2 \leftrightarrow 3, 3	237.5*	1686.203(20)	-17	-3
	4, 2 \leftrightarrow 3, 3	241.5*	1686.262(15)	-30	-16
	6, -1 \leftrightarrow 5, -1	188.5*	2942.710(30)	16	14
	6, -1 \leftrightarrow 5, -1	547.5*	2933.983(23)	6	7
$5d^26s^2F_{5/2}$	6, -3 \leftrightarrow 6, -4	10	5.257(12)	8	8
	4, -1 \leftrightarrow 4, -2	10	4.111(10)	-1	-1
	6, -3 \leftrightarrow 6, -4	20	10.530(12)	6	6
	4, -1 \leftrightarrow 4, -2	20	8.280(15)	-4	-3
	6, -3 \leftrightarrow 6, -4	40	21.160(10)	5	6
	4, -1 \leftrightarrow 4, -2	40	16.805(6)	3	2
	6, -3 \leftrightarrow 6, -4	100	53.668(10)	-18	-17
	4, -1 \leftrightarrow 4, -2	100	43.711(10)	-6	-7
	6, -3 \leftrightarrow 6, -4	200	110.025(13)	-18	-18
	5, -2 \leftrightarrow 5, -3	200	104.603(13)	3	3
	4, -1 \leftrightarrow 4, -2	200	92.977(13)	-8	-11
	6, -3 \leftrightarrow 6, -4	400	230.942(17)	25	29
	4, -1 \leftrightarrow 3, 0	2	1210.262(15)	10	8
	4, 3 \leftrightarrow 3, 2	2	1212.443(20)	-30	-33
	4, 4 \leftrightarrow 3, 3	2	1212.765(15)	-4	-7
	5, -1 \leftrightarrow 4, -2	1	1523.201(15)	-5	-4
	5, -2 \leftrightarrow 4, -2	1	1522.720(22)	-5	-3
	6, -3 \leftrightarrow 5, -3	1	1840.520(15)	-20	-18
	6, -3 \leftrightarrow 5, -3	783.0*	1775.221(9)	11	9
	4, 0 \leftrightarrow 3, 1	268.0*	1161.215(17)	10	19
$5d^26s^2F_{7/2}$	6, 3 \leftrightarrow 6, 2	10	7.973(10)	1	0
	6, 3 \leftrightarrow 6, 2	15	11.969(16)	-16	-16
	6, 3 \leftrightarrow 6, 2	20	16.015(22)	1	1
	7, 4 \leftrightarrow 7, 3	30	24.040(20)	2	2
	6, 3 \leftrightarrow 6, 2	30	24.131(15)	6	5
	5, 2 \leftrightarrow 5, 1	30	24.212(18)	3	2
	7, 4 \leftrightarrow 7, 3	35	28.103(14)	15	14
	6, 3 \leftrightarrow 6, 2	35	28.214(13)	7	7
	5, 2 \leftrightarrow 5, 1	35	28.316(14)	-6	-6
	6, 3 \leftrightarrow 6, 2	50	40.572(16)	16	15
	4, 1 \leftrightarrow 4, 0	50	40.572(16)	-14	-13
	5, 2 \leftrightarrow 5, 1	50	40.804(13)	11	11
	6, 3 \leftrightarrow 6, 2	100	82.865(25)	1	0
	4, 1 \leftrightarrow 4, 0	100	83.172(13)	-6	-4
	4, 1 \leftrightarrow 4, 0	200	178.997(20)	-7	-4
	7, 4 \leftrightarrow 7, 3	200	168.814(20)	-13	-16
	6, 3 \leftrightarrow 6, 2	200	172.987(20)	-6	-7
	5, 2 \leftrightarrow 5, 1	200	177.946(17)	12	13
	3, -2 \leftrightarrow 4, -2	1	796.567(12)	-1	0
	3, -1 \leftrightarrow 4, -2	1	797.362(14)	4	4
	3, -2 \leftrightarrow 4, -1	1	795.769(20)	-6	-6
	4, 1 \leftrightarrow 5, 1	1	989.488(25)	7	6
	4, 1 \leftrightarrow 5, 1	2	989.475(20)	-4	-5

TABLE II (continued).

Configuration and state	Transition ($F, M \leftrightarrow F', M'$)	H (G)	Observed resonance frequency (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$	
				Uncorrected (kHz)	Corrected (kHz)
$5d^2 6s^4 P_{1/2}$	4, -3 \leftrightarrow 4, -4	15	6.992(11)	6	7
	4, -3 \leftrightarrow 4, -4	20	9.334(10)	4	4
	4, -3 \leftrightarrow 4, -4	50	23.572(12)	13	14
	4, -3 \leftrightarrow 4, -4	100	47.919(10)	1	3
	4, -3 \leftrightarrow 4, -4	200	99.170(10)	-4	-2
	4, -3 \leftrightarrow 4, -4	400	212.917(22)	2	-5
	4, -3 \leftrightarrow 3, -2	1702.0*	7616.940(15)	430	-6
	4, -2 \leftrightarrow 3, -3	1697.0*	7614.254(15)	-214	-3
	4, -2 \leftrightarrow 3, -3	1702.0*	7614.238(15)	-212	-5
	4, -2 \leftrightarrow 3, -3	1707.0*	7614.281(15)	-196	7
4, -3 \leftrightarrow 3, -3	1987.0*	6508.968(15)	104	10	
$5d^2 6s^4 P_{3/2}$	5, -3 \leftrightarrow 5, -4	30	21.632(10)	-3	-1
	4, -2 \leftrightarrow 4, -3	60	29.743(8)	4	1
	5, -3 \leftrightarrow 5, -4	100	73.517(15)	-7	-1
	4, -2 \leftrightarrow 4, -3	100	50.858(13)	7	4
	5, -3 \leftrightarrow 5, -4	200	151.110(13)	-14	-7
	4, -2 \leftrightarrow 4, -3	200	108.226(10)	6	2
	5, -3 \leftrightarrow 5, -4	400	318.970(25)	14	6
	4, -2 \leftrightarrow 4, -3	400	243.315(17)	-4	-1
	4, 1 \leftrightarrow 3, 1	0.925	3708.290(20)	12	12
	4, 3 \leftrightarrow 3, 3	0.925	3709.167(20)	6	6
4, -1 \leftrightarrow 3, -1	0.925	3707.370(25)	-25	-25	
4, 0 \leftrightarrow 3, 0	1.500	3707.834(22)	-2	-2	
$5d^2 6s^4 P_{5/2}$	5, -2 \leftrightarrow 5, -3	10	8.101(12)	4	4
	5, -2 \leftrightarrow 5, -3	20	16.248(20)	9	9
	6, -3 \leftrightarrow 6, -4	20	17.618(8)	4	7
	6, -3 \leftrightarrow 6, -4	40	35.348(13)	6	10
	5, -2 \leftrightarrow 5, -3	40	32.657(8)	4	4
	6, -3 \leftrightarrow 6, -4	100	89.212(20)	-2	7
	5, -2 \leftrightarrow 5, -3	100	82.945(25)	-4	-4
	4, -1 \leftrightarrow 4, -2	100	71.546(12)	7	2
	6, -3 \leftrightarrow 6, -4	200	181.264(20)	-31	-21
	5, -2 \leftrightarrow 5, -3	200	170.257(18)	-24	-22
	4, -1 \leftrightarrow 4, -2	200	149.010(17)	1	-2
	6, -3 \leftrightarrow 6, -4	400	374.130(25)	11	4
	5, -2 \leftrightarrow 5, -3	400	358.263(25)	17	16
	4, 0 \leftrightarrow 3, 0	4	3216.520(20)	2	2
4, 0 \leftrightarrow 3, 0	5	3216.512(25)	-3	-3	
$5d^2 6s^2 D_{3/2}$	5, 4 \leftrightarrow 5, 3	10	3.938(13)	-1	-1
	5, 4 \leftrightarrow 5, 3	30	11.898(12)	1	1
	4, 3 \leftrightarrow 4, 2	30	8.034(5)	1	1
	5, 4 \leftrightarrow 5, 3	50	19.963(12)	3	3
	4, 3 \leftrightarrow 4, 2	50	13.602(5)	3	3
	4, 3 \leftrightarrow 4, 2	100	28.257(5)	-2	-2
	5, 4 \leftrightarrow 5, 3	100	40.584(14)	-5	-5
	5, 4 \leftrightarrow 5, 3	200	83.892(6)	0	0
	4, 3 \leftrightarrow 4, 2	200	60.837(5)	0	0
$5d^2 6s^2 D_{5/2}$	6, -3 \leftrightarrow 6, -4	20	14.663(12)	2	2
	5, -2 \leftrightarrow 5, -3	20	13.510(13)	0	0
	6, -3 \leftrightarrow 6, -4	40	29.394(7)	-1	-1
	6, -3 \leftrightarrow 6, -4	60	44.203(10)	3	3
	6, -3 \leftrightarrow 6, -4	100	74.014(15)	-14	-14
	5, -2 \leftrightarrow 5, -3	100	68.674(15)	11	11
	6, -3 \leftrightarrow 6, -4	200	149.859(15)	0	0
	5, -2 \leftrightarrow 5, -3	200	140.105(17)	4	4
	4, -1 \leftrightarrow 4, -2	200	121.802(18)	-4	-4

TABLE III. Uncorrected and corrected values of the hfs interaction constant A , B , and C , electron g_J , and χ^2 for the levels examined in La^{139} . A complete report on the hfs of the $5d6s^2D$ term is given by Ting (Ref. 3) and his results were not reexamined. Calculations of the effects of hfs interactions between the ${}^2D_{3/2}$ and ${}^2D_{5/2}$ levels indicate that they should be very small. For the $5d^26s$ configuration, the loss of precision in going from the uncorrected values to the corrected ones, which is particularly apparent for the B values, is due to uncertainties in making the corrections for hfs and Zeeman interactions between states.

Configuration	State	Quantity	Uncorrected value and experimental uncertainty	Corrected value and estimated total uncertainty
$5d6s^2$	${}^2D_{3/2}$	A
		B
		C
		g_J	0.797 55(3)	0.797 55(3)
		χ^2	2.2	2.2
	${}^2D_{5/2}$	A
		B
		C
		g_J	1.199 07(4)	1.199 07(4)
		χ^2	0.9	0.9
$5d^26s$	${}^4F_{3/2}$	A	-480.312(2)	-480.224(8)
		B	15.082(17)	14.2 ± 0.2
		C
		g_J	0.404 05(3)	0.404 46(4)
		χ^2	3 969	11.4
	${}^4F_{5/2}$	A	300.563(1)	300.631(8)
		B	10.873(25)	14.0 ± 0.3
		C	-0.008(3)	0.002(3)
		g_J	1.029 50(5)	1.029 40(5)
		χ^2	39	5.9
	${}^4F_{7/2}$	A	462.868(1)	462.889(7)
		B	17.925(24)	19.3 ± 0.2
		C	-0.005(2)	-0.002(2)
		g_J	1.237 46(4)	1.237 42(4)
		χ^2	13	4.8
	${}^4F_{9/2}$	A	489.534(1)	489.533(2)
		B	32.180(34)	31.9 ± 0.2
		C	0.001(4)	0.003(4)
		g_J	1.332 80(3)	1.332 78(3)
		χ^2	32	22
	${}^2F_{5/2}$	A	304.372(2)	304.381(4)
		B	28.091(30)	27.8 ± 0.1
		C	-0.002(3)	-0.002(3)
		g_J	0.898 32(5)	0.898 30(5)
		χ^2	14	15
	${}^2F_{7/2}$	A	-197.066(6)	-197.068(7)
		B	40.677(123)	41.4 ± 0.2
		C
		g_J	1.134 67(6)	1.134 69(6)
		χ^2	6.1	6.0
${}^4P_{1/2}$	A	2460.119(3)	2460.173(70)	
	g_J	2.651 75(18)	2.652 52(20)	
	χ^2	1338	2.7	
${}^4P_{3/2}$	A	930.0 ± 0.2	929.6 ± 0.2	
	B	42.1 ± 2.3	37.2 ± 2.5	
	C	
	g_J	1.704 27(7)	1.704 27(7)	
	χ^2	3.8	1.9	

TABLE III (continued).

Configuration	State	Quantity	Uncorrected value and experimental uncertainty	Corrected value and estimated total uncertainty
	${}^4P_{5/2}$	A	802.8 ± 0.5	801.9 ± 0.5
		B	-23.9 ± 8.0	-40 ± 8
		C
		g_J	1.505 79(8)	1.505 58(8)
		χ^2	5.2	4.3
	${}^2D_{3/2}$	A	-424.7 ± 1.4	-424.9 ± 2.0
		B	-11.3 ± 3.6	-13 ± 4
		C
		g_J	0.935 97(24)	0.936 03(30)
		χ^2	0.7	0.7
	${}^2D_{5/2}$	A	881.0 ± 5.8	881 ± 6
		B	22 ± 36	22 ± 36
		C
		g_J	1.254 49(24)	1.254 49(25)
		χ^2	1.5	1.5

$$(J+1)g_J - (J-1)g_{J-1} = eJ^2 + f, \quad (2)$$

where e and f are constants to be determined. One therefore needs the g_J values of three members of a term in order to calculate the two constants e and f required for prediction of the g 's of other members.

In lanthanum, the only suitable term is $5d^26s {}^4F$ for which the g_J values are accurately known for all four J 's. If the g_J values of the ${}^4F_{7/2,5/2,3/2}$ states are used to determine e and f , one then predicts g_J (${}^4F_{9/2}$) = 1.331 66(19), which may be compared with the measured value 1.332 78(3). The difference, $g_J^{\text{obs}} - g_J^{\text{alc}} = 0.001 12(19)$, is, surprisingly, well outside experimental error. Wilson's eigenvectors show that although the $5d^26s {}^4F_{9/2,7/2}$ states contain only about 0.01% of states in $5d6s^2$ and $5d^3$, the ${}^4F_{5/2,3/2}$ states contain about 1% of $5d6s^2 {}^2D_{5/2,3/2}$. The failure of Eq. (2), which ignores configuration-interaction effects, is thus due to the fact that the g_J values of 2D_J and 4F_J are very different, and a 1% admixture of 2D into 4F produces a change in g_J much larger than the experimental error.

C. Effective Operators for the Hyperfine Interaction

Sanders and Beck¹⁶ have shown that the hyperfine interaction of order K due to an unclosed electron shell l^N may be described by suitable linear combinations of tensor operators of the form

$$\bar{T}_n^{(K)} \cdot \bar{U}^{(0,K)K}, \quad \bar{T}_n^{(K)} \cdot \bar{U}^{(1,K-1)K},$$

and

$$\bar{T}_n^{(K)} \cdot \bar{U}^{(1,K+1)K},$$

where the operator $\bar{T}_n^{(K)}$ is associated with the nucleus, and the operator $\bar{U}^{(k_s, k_l)K}$ is associated with

the electrons. The first quantity in the parentheses in the exponent of U is the rank of the operator in spin space, the second the rank in orbital space, and K is the total rank. For the magnetic-dipole hyperfine interaction, for which $K=1$, the Hamiltonian will therefore contain operators proportional to $\bar{I} \cdot \bar{L}$, $\bar{I} \cdot \bar{S}$, and $\bar{I} \cdot \sum_i [\bar{s} \times \bar{C}^{(2)}]_i^{(1)}$ for each unclosed shell. In the lanthanum system $(5d+6s)^3$ each of these terms will be required for the d electrons, but only the second will be needed for an unpaired s electron. Thus the dipole Hamiltonian when evaluated within $5d6s^2$ or $5d^3$ contains three terms, all associated with the d electrons. When evaluated in the $5d^26s$ configuration, however, an additional contact term of the form $\bar{I} \cdot \bar{s}$ is required for the $6s$ electron. Although the two contact terms are equivalent in the LS limit, they are not equivalent in intermediate coupling because they connect LS basis states differently.

Dipole hyperfine interactions between the $5d^26s$ and $5d6s^2$ or $5d^3$ configurations can arise only from the term $I \sum_i [\bar{s} \times \bar{C}^{(2)}]_i^{(1)}$, and the strength depends on $\langle 5d | r^{-3} | 6s \rangle$. Evaluation of this integral by the use of the radial wave functions derived by Herman and Skillman¹⁷ yields almost exactly zero, so such cross-configuration hfs interactions are ignored in what follows.

We may therefore write the Hamiltonian for the magnetic-dipole hyperfine interaction in the form

$$\mathcal{H}(M1) = \sum_{i=1}^N [\alpha^{01} \bar{I}_i - \sqrt{10} \alpha^{12} [\bar{s} \times \bar{C}^{(2)}]_i^{(1)} + \alpha_d^{10} \bar{s}_i] \cdot \bar{I} + \alpha_s^{10} \bar{s}_{N+1} \cdot \bar{I}, \quad (3)$$

where the last term is used for the $5d^26s$ configuration but not for $5d6s^2$ or $5d^3$. For the present it is not necessary to assume relationships between

the α 's in different configurations. Thus, we do not assume relations of the type $\alpha^{01}(5d6s^2) = \alpha^{01}(5d^26s)$, for example, though later it will be desirable to reduce the number of parameters by imposing some constraints of this type.

It follows from the considerations above that the effective operator for the electric-quadrupole hyperfine interaction will contain tensor operators of the three types:

$$\bar{T}_n^{(2)} \cdot \bar{U}^{(02)2}, \quad \bar{T}_n^{(2)} \cdot \bar{U}^{(11)2}, \quad \bar{T}_n^{(2)} \cdot \bar{U}^{(13)2}$$

for the unfilled d shell; the $6s$ electron makes no contribution. The effective Hamiltonian may then be written¹⁶

$$\mathcal{H}(E2) = \frac{r_n^2}{Q} \bar{C}_n^{(2)} \cdot \sum_{i=1}^N \left[b^{02} \left(\frac{2l(l+1)(2l+1)}{(2l-1)(2l+3)} \right)^{1/2} \bar{U}_i^{(02)2} + \sqrt{\frac{3}{10}} b^{13} \bar{U}_i^{(13)2} + \sqrt{\frac{3}{10}} b^{11} \bar{U}_i^{(11)2} \right], \quad (4)$$

where

$$er_n^2 \bar{C}_n^{(2)} = \bar{T}_n^{(2)}, \quad (5)$$

$$\langle II | \bar{T}_n^{(2)} | II \rangle \equiv \frac{1}{2} eQ. \quad (6)$$

In these expressions r_n is the nuclear charge radius and l is 2 for the d electrons here considered. The quantities b^{02} , b^{13} , and b^{11} may be regarded as independent parameters, or they may be related to the nonrelativistic parameter $b_{nl} \equiv e^2 Q \langle r^{-3} \rangle_{nl}$ if relativistic radial wave functions are known. Even without the relativistic wave functions, the relation between these quantities may be approximated by the use of Casimir factors¹⁸ according to the expressions given by Childs and Goodman.¹⁹ Taking the effective charge for the d electrons of lanthanum as $Z_{\text{eff}} = Z - 12 = 45$, it is found in this way that

$$b^{02} \approx 1.060 b_{5d}, \quad b^{13} \approx 0.235 b_{5d}, \quad (7)$$

$$b^{11} \approx -0.040 b_{5d}.$$

If these relations are put into Eq. (4), it is reduced to a one-parameter expression. It is interesting to note that the relativistic parameter b^{13} is not small, but is predicted to be about 23% as large as the nonrelativistic b_{5d} .

There is no need at this point to assume that values of the three parameters of Eq. (4) will be the same in each of the three configurations spanned by our eigenvectors. Matrix elements of the quadrupole Hamiltonian *between* the configurations considered may arise only from the $\bar{U}^{(02)2}$ term but, as in the dipole case, such terms will not be considered because of the extremely small size of the radial integral $\langle 5d | r^{-3} | 6s \rangle$.

D. Theoretical Expressions for Hyperfine-Interaction Constants A and B

The magnetic-dipole hyperfine-interaction con-

stant A of a state for which the intermediate coupling composition is known may be expressed in terms of the α 's of Eq. (3) by using the procedure given by Chan, Childs, and Goodman.²⁰ Basically, one evaluates the matrix elements of the Hamiltonian of Eq. (3) between all LS basis states that occur in the eigenvector, separates out the F -dependent part, and by use of the eigenvector arrives at the parametrized expression for A . Computer programs have been written to (i) calculate all the required matrix elements in the LS scheme and (ii) to combine them for the given eigenvectors to form the parametrized expressions for the A 's of all the states of interest. For example, the A value of the $5d^26s^4P_{5/2}$ state may be expressed as $A(5d^26s^4P'_{5/2})$

$$\begin{aligned} &= 0.4598\alpha^{01}(5d^26s) + 0.0810\alpha^{12}(5d^26s) \\ &+ 0.3276\alpha_d^{10}(5d^26s) + 0.1886\alpha_s^{10}(5d^26s) \\ &+ 0.0156\alpha^{01}(5d6s^2) - 0.0022\alpha^{12}(5d6s^2) \\ &+ 0.0039\alpha_d^{10}(5d6s^2) + 0.0042\alpha^{01}(5d^3) \\ &- 0.0007\alpha^{12}(5d^3) + 0.0003\alpha_d^{10}(5d^3), \end{aligned} \quad (8)$$

where the prime is used to distinguish the real state of the atom from an LS basis state.

The procedure for the electric-quadrupole hyperfine-interaction constants B is entirely analogous, and one finds in the same way for the same state

$$\begin{aligned} &B(5d^26s^4P'_{5/2}) \\ &= -0.3420b^{02}(5d^26s) + 0.0983b^{11}(5d^26s) \\ &- 0.0220b^{13}(5d^26s) + 0.0111b^{02}(5d6s^2) \\ &+ 0.0026b^{11}(5d6s^2) - 0.0007b^{13}(5d6s^2) \\ &+ 0.0020b^{02}(5d^3) + 0.0000b^{11}(5d^3) \\ &+ 0.0002b^{13}(5d^3). \end{aligned} \quad (9)$$

An expression for the required matrix elements of Eq. (4) has been published.¹⁹

E. Off-Diagonal Corrections to Calculated Transition Frequencies

As pointed out in Sec. IV, the Hamiltonian of Eq. (1) is not completely consistent with all of the observed resonance frequencies, and in some cases, particularly at large H , the discrepancies amount to many times the probable error and lead to large values of χ^2 . Eigenvalues calculated from Eq. (1) must be corrected for hyperfine and Zeeman interactions with nearby atomic states. Even at zero field where the Zeeman interaction plays no role, it is well known that hfs interactions with other states can distort the $\Delta F = \pm 1$ intervals and yield incorrect values for the hfs constants A , B , and

C even though the fit to the data is good and χ^2 is small.

Several procedures have been used^{21, 22} for making such corrections within an LS multiplet. In the present case, however, there are two complications: (a) There are a number of nearby states of different terms and the perturbing states cannot be assumed to be of the same α LS as the state being perturbed; (b) the departure of some of the states from the LS limit is so severe that it seemed necessary to take account of the individual eigenvectors and to make the corrections in intermediate coupling. By generalizing Eq. (17) of Ref. 21 it can be shown that the amount δE by which the energy of the magnetic substate \mathcal{FM} of the state Ψ is shifted by nearby states Ψ' is given very closely by

$$\delta E(\Psi, I\mathcal{FM}) = \sum_{\Psi' \neq \Psi} \sum_{F'} \frac{|\langle \Psi, I\mathcal{FM} | \mathcal{K}_{\text{hfs}} + \mathcal{K}_z | \Psi', IF'M \rangle|^2}{E(\Psi) - E(\Psi')}, \quad (10)$$

where the \mathcal{F} indicates the particular mixture of F 's required to represent the level at the field H and \mathcal{K}_{hfs} and \mathcal{K}_z are the hyperfine and the Zeeman Hamiltonians, respectively. The intermediate-coupling eigenvectors of the states Ψ and Ψ' may both be represented as linear combinations of the LS basis states. Equation (10) treats the switching on of hyperfine and Zeeman interactions between the state Ψ and other states Ψ' as a perturbation; it does not treat the magnetic field or the departure from the LS limit as perturbations, however, and these can therefore be large. In addition to the explicit summations over perturbing states Ψ' and possible values of F' in such states, three coherent sums are required to take account of the intermediate-coupling eigenvector compositions of Ψ and Ψ' , and of the proper mixture of F 's introduced into Ψ by the field H . It is important to note that the hfs and Zeeman interactions enter coherently since they may connect the same states, and in fact the energy shifts in $\Delta F = 0$ transitions at large H are frequently nearly linear in H due to the hfs-Zeeman interference term.

A computer program has been written to evaluate the shifts of Eq. (10). Calculation of the perturbation of one resonance frequency at one value of H requires about 1 min of IBM-360-75 computing time if there are about ten perturbing states Ψ' and if each state has about three components in its eigenvector.

The expressions for the matrix elements of the

magnetic-dipole hyperfine Hamiltonian (3) are given in Eq. (3) of Ref. 20. Since the last two terms in the electric-quadrupole hyperfine Hamiltonian (4) are relativistic in origin and normally much smaller than the first term, they are neglected in the computer program. The expression for the matrix elements of $\mathcal{K}(E2)$ (in which $b^{02} = b_{n1}$ in the nonrelativistic limit) is given by Eq. (A15) of Ref. 21. Matrix elements of the Zeeman interaction can be obtained from Eq. (A16) of Ref. 21.

In order to carry out the computer evaluation of shifts of Eq. (10), numerical values must be given for the a 's and for b^{02} of Eqs. (3) and (4). The procedure for obtaining the appropriate values are discussed in Secs. V H and V L. The final values will be summarized in Table VIII.

Table IV illustrates the results of a typical calculation of this type. The perturbation of the (3, 1 \rightarrow 4, 2) transition frequency in the $5d^26s^4F_{3/2}$ state is calculated both at $H = 0$ and at $H = 1934$ G, where $(\partial\nu/\partial H) \approx 0$. Perturbations due to states of $5d6s^2$ or $5d^3$ are neglected because of the extremely small size of $\langle 5d | r^{-3} | 6s \rangle$. All states of $5d^26s$ were considered explicitly in the computer calculation except $^2S_{1/2}$ for which the calculated excitation energy is more than 18000 cm^{-1} (and which has never been observed). It is seen that four states perturb the transition frequency by at least 1 kHz, but that only the $^4F_{5/2}$ perturbation is highly field dependent. For some transitions, it was found that as many as six different states produced perturbations of 1 kHz or more.

For the residuals given in the last column of Table II all the calculated resonance frequencies were corrected for perturbations in this way. It is important to notice not only that the residuals and χ^2 values drop to reasonable values after correction, but also that the best-fit values of the hfs constants A, B, C , and g_J change. The last column of Table III gives the corrected values of A, B, C , and g_J which result from the least-squares fits when the calculated frequencies are corrected for the shifts by use of Eq. (10). In some cases the changes are seen to be substantial.

In evaluating frequency shifts by Eq. (10) it was immediately evident that because a_2^{10} is much larger for the $5d^26s$ configuration in La than are any of the other a 's or b 's, all shifts are dominated by the contact part of the dipole interaction, and that quadrupole and orbital dipole contributions, while not negligible, are not important for a qualitative picture. The dipole matrix element for $\Delta J = \pm 1$ between quartet states 4L of d_s^2 may be written

$$\langle 5d^2(^3L), 6s; ^4L_J \frac{7}{2} FM | \mathcal{K}_{\text{hfs}}(M1) | 5d^2(^3L), 6s; ^4L_{J+1} \frac{7}{2} FM \rangle = (-1)^{J+F-1/2} \begin{Bmatrix} J & J+1 & 1 \\ \frac{7}{2} & \frac{7}{2} & F \end{Bmatrix} \left\{ \frac{7}{2} \right\}^{1/2} \left(\frac{(L+J+\frac{7}{2})(L+J-\frac{1}{2})(J+\frac{5}{2}-L)(\frac{3}{2}+L-J)}{(J+1)} \right)^{1/2} \cdot \Theta, \quad (11)$$

where

$$\Theta = a_s^{10} + 2a_d^{10} - 3a^{01} - a^{12} \left[20 \left(\frac{30}{7} \right)^{1/2} \left(\frac{(2J+1)(J+1)(2J+3)}{(L+J+\frac{7}{2})(L+J-\frac{1}{2})(\frac{5}{2}+J-L)(\frac{3}{2}+L-J)} \right)^{1/2} \right. \\ \left. \cdot \begin{pmatrix} \frac{3}{2} & \frac{3}{2} & 1 \\ L & L & 2 \\ J & J+1 & 1 \end{pmatrix} \langle d^2 {}^3L \| V^{(12)} \| d^2 {}^3L \rangle \right], \quad (12)$$

where the fact that $I = \frac{7}{2}$ has been used for La¹³⁹. The last term of Eq. (12) is very small compared to the first three, and the dipole matrix element within either 4F or 4P terms is very nearly proportional to Θ' , where

$$\Theta' \equiv a_s^{10} + 2a_d^{10} - 3a^{01} \approx \Theta. \quad (13)$$

Shifts from the $\Delta F = 0$ transition frequencies predicted for 4F or 4P states from Eq. (1) are due mainly to other members of the same quartet and at fields up to about 1000 G are nearly proportional to both H and Θ' (i. e., they arise mostly from the hfs-Zeeman interference term). Thus, an increase in a_s^{10} will result in only a very small change in the calculated frequency shift if a_d^{10} is reduced so as to keep Θ' unchanged. (The change would be zero if the eigenvector contained no doublet component.)

Transition frequencies in quartet states may also be perturbed by doublet states by amounts that depend on the interaction ${}^4L \rightarrow {}^2L$, which is proportional not to Θ' but to Φ' , where

$$\Phi' = a_s^{10} - a_d^{10}. \quad (14)$$

Thus at low field for $\Delta F = \pm 1$ intervals in 4F or 4P states, the shifts due to quartet-quartet interactions are proportional to Θ'^2 and those due to quartet-doublet interactions are proportional to Φ'^2 . Although qualitative considerations of this type were extremely valuable in interpreting the data, they were not a part of the quantitative analysis. For the latter, the computer calculated the shifts directly from Eq. (10), using the proper form of the matrix elements.

F. Alternative Classification of Properties of States

The last column of Table III summarizes the corrected values of the hyperfine-interaction constants, g_J values, and χ^2 values achieved in the fit to the observed resonance frequencies. The uncertainties given for these corrected values are in some cases, particularly for the B values, much larger than the uncertainty derived from frequency measurements (which is given in the column of uncorrected values). The increased uncertainty reflects the uncertainties in the a 's and b 's used in calculating the frequency corrections of Eq. (10). While it is convenient (and conventional) to reduce

an ensemble of precisely measured resonance frequencies to a much smaller number of hfs constants and a g_J value in this way, it is disappointing to lose so much precision in the process.

It is possible to give an alternative reduction of the data which does not lead to such a loss of precision; one gives the zero-field hyperfine intervals and the g_J value instead of the hfs constants and the g_J value. Table V lists these results. For all but two of the intervals $\Delta\nu$ listed, the observation was made at $H \leq 4$ G and then corrected back to zero field for the table. This field correction is not subject to any of the off-diagonal corrections of Eq. (10), and can be done without loss of precision by the computer program. The results therefore do not depend on uncertainties in the values of A , B , C ; the a 's, b 's, or g_J ; nor on the size of χ^2 .

Two of the $\Delta F = \pm 1$ intervals listed were measured at strong field, but the interval can still be corrected to zero field with little loss of precision. The $F = 4 \rightarrow 5$ interval in $5d^2 6s {}^4F_{3/2}$ was observed with the $(4, 3 \rightarrow 5, 3)$ transition at 2873 G. If the corrections of Eq. (10) are applied to all the calculated frequencies of the state with each of several sets of values of the a 's and b 's, and a least-squares fit to the data is made for each set, different values of A , B , χ^2 (and g_J) are obtained for each set. If one uses these numbers, together

TABLE IV. Example of the calculated perturbation of a resonance frequency by hfs and Zeeman interactions with nearby levels. The case considered is the transition $(3, 1 \rightarrow 4, 2)$ in the $5d^2 6s {}^4F_{3/2}$ state. The calculation was carried out by computer in intermediate coupling (by use of the Wilson eigenvectors) and took account of all neighboring levels. Only those shown caused perturbations of 1 kHz or more. All calculated resonance frequencies were corrected for such shifts before the residuals listed in the last column of Table II were obtained by comparison with the observed frequencies.

Perturbing state ($5d^2 6s$)	Calculated frequency shift	
	At $H=0$ G (MHz)	At $H=1934$ G (MHz)
${}^4F_{5/2}$	+0.492	+1.128
${}^2F_{5/2}$	+0.071	+0.067
${}^2D_{5/2}$	+0.001	+0.001
${}^4P_{5/2}$	+0.003	+0.003
Total shift	+0.567	+1.199

TABLE V. List of zero-field hyperfine intervals $\Delta\nu$. Except for the two intervals denoted by asterisks, all the intervals shown were measured at $H \leq 4$ G and then corrected to zero field straightforwardly. Although the other two measurements were made at high field, the deduction of the quoted zero-field interval is thought to be free from error caused by perturbation by other states.

State of $5d^26s$	$F \rightarrow F'$	$\Delta\nu$ (MHz)
$^4F_{3/2}$	$5 \rightarrow 4^*$	2390.631(11)
$^4F_{3/2}$	$4 \rightarrow 3$	1925.510(11)
$^4F_{5/2}$	$6 \rightarrow 5$	1808.938(12)
$^4F_{5/2}$	$5 \rightarrow 4$	1503.210(18)
$^4F_{5/2}$	$4 \rightarrow 3$	1199.787(15)
$^4F_{7/2}$	$7 \rightarrow 6$	3247.744(6)
$^4F_{7/2}$	$6 \rightarrow 5$	2779.047(7)
$^4F_{7/2}$	$5 \rightarrow 4$	2312.531(20)
$^4F_{7/2}$	$4 \rightarrow 3$	1847.837(12)
$^4F_{9/2}$	$8 \rightarrow 7$	3928.536(27)
$^4F_{9/2}$	$7 \rightarrow 6$	3430.754(13)
$^4F_{9/2}$	$6 \rightarrow 5$	2935.669(10)
$^4F_{9/2}$	$5 \rightarrow 4$	2442.885(22)
$^4F_{9/2}$	$4 \rightarrow 3$	1952.018(20)
$^2F_{5/2}$	$6 \rightarrow 5$	1840.665(15)
$^2F_{5/2}$	$5 \rightarrow 4$	1522.871(15)
$^2F_{5/2}$	$4 \rightarrow 3$	1211.072(15)
$^2F_{7/2}$	$5 \rightarrow 4$	989.482(20)
$^2F_{7/2}$	$4 \rightarrow 3$	796.567(12)
$^4P_{1/2}$	$4 \rightarrow 3^*$	9840.632(15)
$^4P_{3/2}$	$4 \rightarrow 3$	3707.836(22)
$^4P_{5/2}$	$4 \rightarrow 3$	3216.524(20)

with the corresponding values of the a 's and b 's, to predict the zero-field interval in question, he finds that the corrected value predicted for the $F = 4 \rightarrow 5$ zero-field interval is the same to within 1 kHz regardless of the a 's and b 's used. The situation is similar for the $5d^26s$ $^4P_{1/2}$ state, for which the $F = 4 \rightarrow 3$ interval was measured at 1702 and 1987 G by using several different transitions. The predicted value of the zero-field $F = 4 \rightarrow 3$ interval again turns out to be nearly independent of the values of the a 's and b 's used.

Only hfs intervals actually measured can be given to high precision in this way. Prediction of others depends ultimately on the values of the a 's and b 's used in the prediction. Table V lists the zero-field intervals in the $5d^26s$ configuration for which accurate values can be given. The intervals measured in the $5d6s^2$ configuration are given by Ting.³

G. Signs of A Values

Before describing the fit of the theoretical expressions for the A or B values to the observed values, several comments concerning the signs of the measured quantities should be made. The Hamiltonian of Eq. (1) has the property that it is insensitive to the absolute sign of A except for data

taken at large enough H ($H \geq 1000$ G) that the term in $g_I \mu_B H$ becomes large compared with experimental uncertainty. Thus, with the exception of the $^4F_{3/2,5/2}$ and $^4P_{1/2}$ states for which very high-field observations were made, the data reported are not capable of determining the signs of the A values. [Even for these states, the calculated frequencies at large H depend – through the corrections of Eq. (10) – on the values of the a 's and b 's used. Thus, although it would appear that the sign of A was actually measured for each of these states, the possibility that a new set of a 's and b 's could be found which could account for the observed resonance frequencies for the other sign of A has not been systematically examined.] It is therefore not claimed that the signs of the A values have been measured. The sign of B/A was measured for each state, however, and the sign of B therefore follows from any assumed sign of A .

The procedure used to assign signs to the measured A values is as follows. For states of $5d^26s$, one takes the LS-limit expressions for the A values in terms of the three parameters $a^{01} = a^{12}$, a_d^{10} , and a_s^{10} , and selects "reasonable" values for these parameters. (Values for a^{01} and a_s^{10} may be deduced from the spin-orbit parameter ζ_{sd} , g_I , and certain term-value differences in $5d^2ns$.) If the A values are then calculated from these LS-limit expressions (using the parameter values from the upper right section of Table VII, for example), it is found that none of the predicted values lie near zero, and that the magnitudes are all within 130 MHz of the observed ones except for $^2D_{3/2}$. For this state, the magnitude of the large negative calculated value is even larger than that observed. Because of the close agreement between the magnitudes of the calculated and observed A values, the calculated algebraic signs are adopted for the $5d^26s$ states.

For the $5d6s^2$ $^2D_{3/2,5/2}$ states, the procedure just outlined fails because of the importance of s -electron admixture (in this case, there are contributions both from core polarization and from configuration interaction with $5d^26s$). It can be shown, however, that contributions of this sort are about equal and opposite for the two states, and that the sum of the two values of A should be very close to the LS-limit prediction based on the parameter values of Table VII again. On this basis, one can unambiguously assign positive signs to the A values of these two states.

H. Least-Squares Fits to Corrected Values of A and B

It has been shown (Sec. VD) how parametrized theoretical expressions are developed for the A and B values for each of the observed states, and (in Sec. VE) how the experimental A and B values

are corrected by Eq. (10) for hyperfine and Zeeman interactions with neighboring levels. The procedure followed is iterative and proceeds as follows. The observed A and B values are fitted with the expressions of the form of Eqs. (8) and (9), and rough values of the a 's and b 's are thereby obtained. These are then used in Eq. (10) to calculate the corrections to the calculated resonance frequencies, from which corrected values of A and B are determined. The latter are then refitted to obtain better values for the a 's and b 's, and so forth. The procedure is very tedious, so it is fortunate that two such iterations were sufficient.

Let us consider the fits of the expressions for the A and B values to the observed values. We assume that all corrections for the effects of Eq. (10) have been made and that the values of A and B being fitted are the corrected values. For the quadrupole interaction, accurate values have been determined not only for the two B 's of the $5d6s^2$ $^2D_{3/2, 5/2}$ states but also for the six B 's of the $^4F_{9/2, 7/2, 5/2, 3/2}$ and $^2F_{7/2, 5/2}$ states of $5d^26s$. Two types of fits are possible: One may let the parameters b^{02} , b^{13} , and b^{11} vary independently, or one may assume the interrelationships between them given by Eq. (7). Consider the first type of fit first. Since no B 's were measured in the $5d^3$ configuration, it was felt that all parameters relating to it must be held fixed. Because the amount of $5d^3$ present in the measured B 's is very small, the parameter values assumed for $5d^3$ are not critical. It was assumed for this purpose that $b^{02}(5d^3) = 100$ MHz (i. e., about the same as for $5d^26s$ and $5d6s^2$), and that $b^{11}(5d^3) = -4$ MHz and $b^{13}(5d^3) = 25$ MHz as predicted by Eq. (7). Since only two B 's were known for $5d6s^2$ (only the $^2D_{5/2, 3/2}$ states exist), only two free parameters could reasonably be retained for this configuration, and the smallest coefficient $b^{11}(5d6s^2)$ was held to be -4 MHz as for $5d^3$. Variation of the five remaining b 's (b^{02} , b^{11} , b^{13} for $5d^26s$ and b^{02} , b^{13} for $5d6s^2$) could not fit the eight accurately known B 's to better than 12% in the worst case. This failure will be discussed in Sec. V K.

However, variation of the five parameters to fit the six B 's of $5d^26s$ 4F and $5d6s^2$ 2D produced an excellent fit (to within 1.1%, which is about the uncertainty of the corrected B 's). It is interesting to note that for this fit the best-fit values found for the b 's of $5d^26s$ agree remarkably well with the ratios of Eq. (7), which were calculated from the relativistic theory¹⁶ and the Casimir factors. Thus it was found that

$$b^{02}(5d^26s) = 108 \text{ MHz}, \quad b^{13}(5d^26s) = 22 \text{ MHz},$$

$$b^{11}(5d^26s) = -3 \text{ MHz}$$

and that

$$b^{02}(5d6s^2) = 124 \text{ MHz}, \quad b^{13}(5d6s^2) = 40 \text{ MHz}. \quad (15)$$

The large size of $b^{13}(5d6s^2)$ is not considered meaningful since (i) the value used for $b^{11}(5d6s^2)$ may not be the best value and (ii) two states are not really enough for the determination. If the ratios of Eq. (7) are forced and if $b^{02}(5d^3)$ is held at 100 MHz, one may make a two-parameter relativistic fit (which takes account of all three types of tensor operators for each of the three configurations). The six B 's of $5d^26s$ 4F and $5d6s^2$ 2D may be fitted to 1.5% in this way. The values found for the parameters are $b^{02}(5d^26s) = 109$ MHz and $b^{02}(5d6s^2) = 126$ MHz. As before, it is not possible to fit the 4F and 2F B values together. Table VI gives the values calculated with these parameter values and compares them with experiment. It is seen that they are all within the experimental uncertainty except for the 2F states. Discussion of this discrepancy is deferred to Sec. V K.

For the magnetic-dipole hyperfine-interaction constants A , one may follow the same fitting procedure as for the quadrupole case. For the fit to the six A values of $5d6s^2$ 2D and $5d^26s$ 4F , the number of free parameters must again be limited. Since no A 's are to be fitted in $5d^3$ (none have been measured), we cannot allow the $5d^3$ parameters to vary. From the known values of $\zeta_{sd}(5d^3)$ and g_I , we hold

$$a^{01}(5d^3) = a^{12}(5d^3) = 140 \text{ MHz}.$$

The results are not sensitive to the core-polarization parameter $a^{10}(5d^3)$ and we set it equal to zero. Since only two states exist for $5d6s^2$, we can use only two free parameters for this configuration;

TABLE VI. Comparison of the observed B values (corrected for perturbations as discussed in the text) with the two-parameter relativistic theoretical expressions calculated from the Wilson eigenvectors. The parameters were adjusted to fit the B 's of the first six states, and the remainder then calculated from them. The values predicted for the $5d^26s$ $^2F_{7/2, 5/2}$ states are not consistent with the observed values. The problem is discussed in the text.

Electron configuration	State	Observed B (MHz)	Calculated B (MHz)	$B^{\text{obs}} - B^{\text{calc}}$ (%)
$5d6s^2$	$^2D_{5/2}$	54.2 (Ref. 3)	55.0	-1.5
$5d6s^2$	$^2D_{3/2}$	44.8 (Ref. 3)	44.1	1.5
$5d^26s$	$^4F_{9/2}$	31.9 ± 0.2	31.8	0.3
$5d^26s$	$^4F_{7/2}$	19.3 ± 0.2	19.4	-0.7
$5d^26s$	$^4F_{5/2}$	14.0 ± 0.3	13.8	1.3
$5d^26s$	$^4F_{3/2}$	14.2 ± 0.2	14.3	-0.9
$5d^26s$	$^2F_{7/2}$	41.4 ± 0.2	34.1	18
$5d^26s$	$^2F_{5/2}$	27.8 ± 0.1	22.6	19
$5d^26s$	$^4P_{1/2}$	-40 ± 8	-37	8 ± 20
$5d^26s$	$^4P_{3/2}$	37.2 ± 2.5	35	6 ± 7
$5d^26s$	$^4P_{1/2}$	0	0	0
$5d^26s$	$^2D_{1/2}$	22 ± 36	-16	
$5d^26s$	$^2D_{3/2}$	-13 ± 4	-19	

TABLE VII. Comparison of the observed A values (corrected for perturbations as discussed in the text) with the five-parameter theoretical expressions calculated from the Wilson eigenvectors. Two fits are given; only the first 6 states were considered in the first fit, while all 13 were included in the second. The largest discrepancy, that for ${}^2F_{7/2}$, is discussed in the text.

Electron config- uration	State	Observed A (MHz)	$A^{\text{obs}} - A^{\text{calc}}$ (%)	
			-param- fit to first 6 states	5-param- eter fit to all 13 states
$5d6s^2$	${}^2D_{5/2}$	182(Ref. 3)	0	0
$5d6s^2$	${}^2D_{3/2}$	141(Ref. 3)	0	0
$5d^26s$	${}^4F_{9/2}$	490	0	-4
$5d^26s$	${}^4F_{7/2}$	463	-1	-3
$5d^26s$	${}^4F_{5/2}$	301	0	-1
$5d^26s$	${}^4F_{3/2}$	(-)480	0	-4
$5d^26s$	${}^2F_{7/2}$	(-)197	-16	-5
$5d^26s$	${}^2F_{5/2}$	304	-4	-2
$5d^26s$	${}^4P_{5/2}$	802	4	0
$5d^26s$	${}^4P_{3/2}$	930	4	1
$5d^26s$	${}^4P_{1/2}$	2460	5	2
$5d^26s$	${}^2D_{5/2}$	881	8	8
$5d^26s$	${}^2D_{3/2}$	(-)425	7	10

we choose $a^{01}(5d6s^2) = a^{12}(5d6s^2)$ and $a^{10}(5d6s^2)$. For $5d^26s$, we again require $a^{01}(5d^26s) = a^{12}(5d^26s)$. We are then left with five parameters ($a^{01} = a^{12}$ and a^{10} for $5d6s^2$; $a^{01} = a^{12}$, a_d^{10} , and a_s^{10} for $5d^26s$; and no free parameters for $5d^3$) to fit the six measured A 's of $5d6s^2{}^2D$ and $5d^26s{}^4F$. The six A 's are fitted to within 0.6% in the worst case; the results are shown in the next to the last column of Table VII. The parameter values obtained are given in the middle column at the top of Table VIII. These values were then used to predict the A values of the remaining states of interest in $5d^26s$, and the differences of these predictions from the experimental results are also given in percent in Table VII.

Unlike the quadrupole case, A values have been accurately measured for 13 states, and one may attempt to fit all of them by varying the five parameters. The results of this fit are given in the right-hand columns of Tables VII and VIII (upper half).

J. Determination of Parameter Values by High-Field Observations Within a Single State

The mechanics of making least-squares fits of the parametrized theoretical expressions for the hfs constants A and B to the measured values have been described in Sec. V H. The quality and interpretation of the fits and the parameter values obtained will be discussed in Secs. V K and V L, respectively. It is desirable, however, to consider first the extent to which the high-field observations of Table II can yield independent values

for some of the parameters discussed.

It is clear that the $g_I \mu_B H$ term of Eq. (1) becomes arbitrarily large as H increases, and the magnetic-dipole moment of the nucleus may be measured from this effect. If the value of g_I is unknown, it may in principle be deduced by careful comparison between high-field observations and the transition frequencies predicted by Eq. (1). It must be noted, however, that at large field the hyperfine and Zeeman interactions with other atomic states may shift the transition frequency by amounts comparable to $g_I \mu_B H$. In other words, the contribution of Eq. (10) to the transition frequency may be comparable in magnitude to the $g_I \mu_B H$ term of Eq. (1). Thus, if the dipole moment is to be measured by high-field observations, one must have either an isolated atomic state or a very good knowledge of the a 's and b 's of Eqs. (3)

TABLE VIII. Parameter values found from several fits of theoretical expressions to the data. Values in the top half of the table are for the Wilson eigenvectors; those in the bottom half result from similar fits in the LS limit. The first column of parameter values is for the case in which no terms of $5d^26s$ other than 4F are considered, and the last is for equal weighting of all states for which experimental uncertainty is not too large. The values are discussed in the text.

Eigenvectors used	Parameter	Parameter values (MHz)	
		Fit to $5d^26s{}^4F$ and $5d6s^2{}^2D$ only	Fit to all states
Wilson	$\left\{ \begin{array}{l} a^{01}(5d^26s) \\ a^{12}(5d^26s) \end{array} \right\}$	132	137 ± 30
	$a_d^{10}(5d^26s)$	-381	-297 ± 150
	$a_s^{10}(5d^26s)$	4378	4356 ± 200
	$b_{sd}(5d^26s)$	103	99 ± 11
	Θ'	3220	3351 ⁺ 150 -100
	Φ'	4759	4653 ± 300
	$\left\{ \begin{array}{l} a^{01}(5d6s^2) \\ a^{12}(5d6s^2) \end{array} \right\}$	128	128 ± 12
	$a^{10}(5d6s^2)$	-174	-170 ± 140
	$b_{sd}(5d6s^2)$	118	125 ± 8
	LS Limit	$\left\{ \begin{array}{l} a^{01}(5d^26s) \\ a^{12}(5d^26s) \end{array} \right\}$	130
$a_d^{10}(5d^26s)$			-181
$a_s^{10}(5d^26s)$			3883
$b_{sd}(5d^26s)$		105 ± 4	
Θ'		3111	3116
Φ'			4064
$\left\{ \begin{array}{l} a^{01}(5d6s^2) \\ a^{12}(5d6s^2) \end{array} \right\}$		141	141
$a^{10}(5d6s^2)$		426	426
$b_{sd}(5d6s^2)$		96 ± 4	96

and (4) and of the eigenvectors and relative excitation energies of the nearby states. The present case of La^{139} is of interest in this situation because the value of μ_I is precisely known from NMR studies and thus the procedures can be checked. Knowledge of μ_I makes it possible to reduce the uncertainties on the values of the a 's, particularly of the linear combination Θ' . If μ_I were not known, its value could be deduced from the present experiment, but uncertainties in the a 's and b 's would have to be represented in the uncertainty quoted for μ_I . Figure 5 shows the hyperfine diagram (to scale) for the $5d^26s\ ^4P_{1/2}$ state at 7231 cm^{-1} as a function of H . In the approximation that the state is completely isolated from neighbors [i. e., that corrections of the type treated by Eq. (10) vanish], it can be shown from Eq. (1) that

$$\nu_b - \nu_a = -2g_I \mu_B H \quad (16)$$

at all H . A convenient field for measuring $\nu_b - \nu_a$ is 1702 G, for which it can be shown that

$$\frac{\partial \nu_b}{\partial H} \approx \frac{\partial \nu_a}{\partial H} \approx 0.$$

It is known¹² that $\mu_I = +2.778(1)\ \mu_N$, $I = \frac{7}{2}$, and hence at 1702 G, the difference $\nu_b - \nu_a$ should be 2.058(1) MHz. The observed separation of the two frequencies is, from Table II, 2.702(20) MHz, about 31% more than the value calculated for an isolated $J = \frac{1}{2}$ state. The difference arises from perturbations of the type treated by Eq. (10). Calculations show that the perturbations produce a contribution

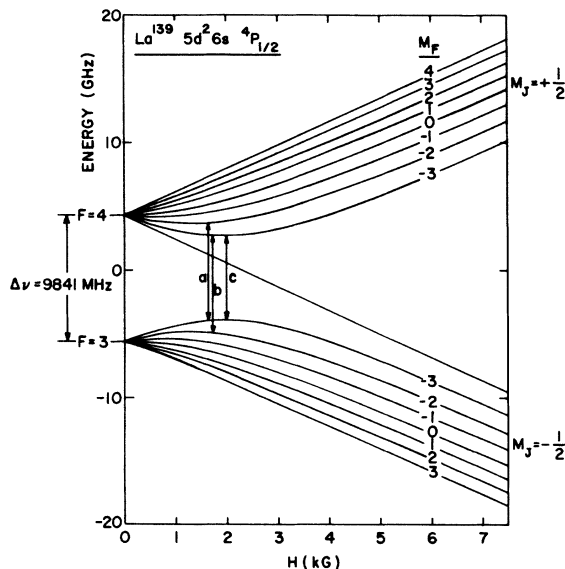


FIG. 5. Scale-drawing of the Zeeman effect of the hfs of the $5d^26s\ ^4P_{1/2}$ level of La^{139} at 7231 cm^{-1} . The transitions a , b , and c were observed at the field values indicated.

to $\nu_b - \nu_a$ which, since it is due primarily to the $^4P_{1/2} - ^4P_{3/2}$ interaction, depends on Θ' , and is nearly proportional to Θ' even at 1700 G. When detailed calculations of the shifts caused by all states of $5d^26s$ are applied to the frequencies calculated from Eq. (1), they lead to the residuals given in the last column of Table II, and to the values of A , g_J , and χ^2 given in the "corrected" column of Table III. The value determined for Θ' in this way is

$$\Theta'(^4P_{1/2}) = 3250 \pm 100\text{ MHz}, \quad (17)$$

which may be compared with the value 3351_{-100}^{+150} MHz given in Table VIII as determined from a fit to the A 's of all the states observed. The difference between these numbers is just on the edge of being significant as indicated by the quoted uncertainties. Another way of seeing this is to note that if the parameter values of Table VIII are used for the corrections and μ_I is treated as a free parameter, one finds that $\mu_I = 2.75 \pm 0.02\ \mu_N$, which is just on the edge of being consistent with the NMR result given above.

The situation is not so simple to analyze analytically for the $^4F_{3/2}$ state at 2668 cm^{-1} , but it presents no problem for the computer programs. If the parameter values of Table VIII are used for the corrections and if μ_I is again treated as a free parameter, it is found that $\mu_I = +2.69 \pm 0.02\ \mu_N$, a value not consistent with the NMR value. Conversely, if the NMR value is forced, it enables us to determine Θ' more accurately and one obtains

$$\Theta'(^4F_{3/2}) = 3130 \pm 175\text{ MHz}, \quad (18)$$

which is about 7% smaller than the "average" value given at the upper right in Table VIII. It is difficult to determine $a_s^{10}(5d^26s)$ and $a_d^{10}(5d^26s)$ separately (or, equivalently, to determine the values of both Θ' and Φ' in either the $^4P_{1/2}$ or $^4F_{3/2}$ states because the two parameters have different effects only to the extent that the states depart from the LS limit as discussed above). According to the Wilson eigenvectors, the $^4P_{1/2}$ state is 98.9% pure, and the $^4F_{3/2}$ state is 98.5% pure.

The only other state for which sufficient high-field data could be obtained was the $^4F_{5/2}$ state at 3010 cm^{-1} . When the parameter values of Table VIII were used to make the required frequency corrections, the result obtained was $\mu_I = +2.88 \pm 0.17\ \mu_N$. Since this is consistent with the NMR result, it is concluded that $\Theta(^4F_{5/2}) \approx 3350\text{ MHz}$. No attempt was made to assign an uncertainty.

K. Comparison of Observed and Calculated Values of hfs Constants A and B

The eigenvector of any atomic state should be consistent with all the observed properties of the state. The consistency of the Wilson⁴ eigenvectors

with the optically measured term energies and the present g_J values is generally good, and is discussed by Wilson.⁴

Our procedure for obtaining theoretical values of the hyperfine-interaction constants A and B for comparison with the observed values has been discussed in Sec. VD. Briefly, for each observed quantity (either A or B), the expectation value of the appropriate operator is calculated for the eigenvector of each state in terms of the relevant radial integrals. These radial quantities are then treated as adjustable parameters in making least-squares fits to the observed quantities. Tables VI and VII contain the results of such fits for the quadrupole and dipole hfs constants, respectively.

For the $5d6s^2^2D$ ground term only two parameters directly relating to $5d6s^2$ are allowed to vary to fit the two A values, and the good fit of Table VII is therefore expected. Because the large admixture of $5d^26s$ found in these states by Wilson was explicitly taken into account, the values found for the parameters should be physically meaningful. For the fit to the B values, a good fit is obtained even though only one parameter directly relating to $5d6s^2$ is allowed to vary.

For the 4F term of $5d^26s$, good fits to both the A and B values are obtained for all four states. The fourth column of Table VI lists the calculated B values for all 13 states, even though only the first six were used for the fit. The experimental uncertainties on the B 's for the 4P and 2D terms (of $5d^26s$) are too large to allow a meaningful comparison with the calculated values. For the 2F term, however, the calculated B values are about 20% smaller than the observed. Although some of the discrepancy might be due to error in the eigenvectors, the difference is the same for both states and, in addition, appears rather large to be due entirely to this cause. Wilson and Fred²³ have recently shown both empirically and by Hartree-Fock calculations that for some atoms, certain radial integrals (such as ζ_{nl} or $\langle r^{-3} \rangle_{nl}$) appear to vary with excitation energy. The measured B values of the 2F term might be understood if $\langle r^{-3} \rangle_{5d}$ were larger for 2F than for 4F .

The fourth column of Table VII gives the results of fitting the A values of the first six states and then calculating the remainder with the parameter values held fixed. The only state for which the calculated value differs markedly from the observed is $^2F_{7/2}$. The reason for the discrepancy is not clear. In contrast to the quadrupole case, any possible variation of $\langle r^{-3} \rangle_{5d}$ with excitation energy is of only minor importance in understanding the dipole effects because of the overriding importance of the contact hfs due to the $6s$ electron in $5d^26s$. The result that the difference $A^{\text{obs}} - A^{\text{calc}}$ is much smaller for $^2F_{5/2}$ than for $^2F_{7/2}$ may pos-

sibly be associated with the fact that while the contribution to A due to the $6s$ electron is 120% of the total for $^2F_{7/2}$, it is only 34% for $^2F_{5/2}$. The final column of Table VII gives the results of fitting the A values of all 13 states simultaneously, again with five parameters. The parameter values obtained in the two fits are slightly different, and are given in the upper section of Table VIII.

L. Discussion of the Parameter Values Found

Table VIII summarizes the values found for the different parameters from least-squares fits to the hyperfine observations. In the upper half of the table, the theoretical expressions which were fitted to the data were for the Wilson⁴ eigenvectors which span the three configurations $(5d + 6s)^3$ in intermediate coupling. Separate fits (both dipole and quadrupole) are given for (i) the six states $5d6s^2^2D$ and $5d^26s^4F$ and (ii) all states for which A and B values are known. The details of the fits have been given in Sec. VH. Comparison of the table with Eq. (18) shows that the value of Θ' found for the $^4F_{3/2}$ state alone is in better agreement with the Θ' found by fitting the A 's of the 4F states than with that found by fitting all the A 's. The amount of core polarization (most of a_d^{10} is probably due to polarization of the core by the $5d$ electrons) appears larger for 4F than for the average of all the states. Eight values of the difference $|A^{\text{obs}} - A^{\text{calc}}|$ are less than $\frac{1}{2}\%$, and are rounded off to 0% in Table VII. Perfect fits are unlikely since, in each case, the number of adjustable parameters is less than the number of A values being fitted.

It is interesting to compare the parameter values obtained from fitting procedures using the Wilson eigenvectors with those that are found if LS-limit eigenvectors are used instead for all states. The parameter values obtained by fitting LS-limit expressions to the data are summarized in the bottom section of the table. The single-configuration LS limit is an extremely poor representation of the states; for example, if b^{02} ($5d^26s$) is evaluated from LS-limit expressions for the B values, the predicted value of $B(^4P_{5/2})$ is large and positive, while the observed value is large and negative. Note that in the LS-limit fit to the A 's of $5d^26s^4F$, it is impossible to distinguish between the two contact terms characterized by a_s^{10} and a_d^{10} ; only the value of Θ' can be given. [This can be seen from Eq. (12) by noting that the coefficients of a_s^{10} and a_d^{10} are independent of J . This is no longer true if, as occurs in the real eigenvectors, doublet states are mixed in differently for different J 's.] Perhaps the most interesting difference between the top and bottom parts of Table VIII is the value found for a^{10} ($5d6s^2$); in the LS limit it is +426 MHz, while for Wilson's

eigenvectors it becomes -170 MHz. The change is due to his taking explicit account of the strong configuration interaction with $5d^26s$ and $5d^3$. The -170 MHz not due to configuration interaction with $(5d+6s)^3$ is probably due to core polarization.

A relativistic fit to the B factors of $5d6s^2$ in the LS limit predicts B 's which differ from experiment by more than 4% for both states; this figure is reduced to 1.5% by Wilson's eigenvectors. The one-parameter relativistic fit to the four B 's of $5d^26s^4F$ is improved even more (to within experimental error) in going from the LS limit to the Wilson eigenvectors.

The value 4356 ± 200 MHz found for $a_s^{10}(5d^26s)$ is in good agreement with the value 4544 MHz calculated²⁴ from the energies of the states $5d^2ns^4F_{3/2}$ for $n=6,7$. The values found for a^{01} may be compared with those calculated by the expression of Trees²⁵ from the values of ζ_{sd} found by Wilson.⁴ For the configurations $5d6s^2$ and $5d^26s$, one thus finds

$$a^{01}(5d6s^2) = 133 \text{ MHz} \quad \text{and} \quad a^{01}(5d^26s) = 115 \text{ MHz} .$$

The first value is in good agreement with Table VIII, while the second is 13% low. This difference might be caused by forcing a^{01} to be the same as a^{12} for $5d^26s$. The ratio $b_{sd}(5d6s^2)/b_{sd}(5d^26s)$ is expected to be 1.16 from the ratio of the ζ 's, and is in fact 1.15.

M. Electric-Quadrupole Moment of the La^{139} Nuclear Ground State

The value of the nonrelativistic parameter b_{nl} for any electron configuration is directly proportional to the electric-quadrupole moment Q of the nuclear ground state. The relationship is just

$$b_{nl} = e^2 Q' \langle r^{-3} \rangle_{nl} , \quad (19)$$

where Q' is the electric-quadrupole moment uncorrected for Sternheimer shielding.²⁶ It is proportional to Q . Two methods are commonly used for evaluating the quantity $\langle r^{-3} \rangle_{nl}$. The first method is to note that nonrelativistically at least, the dipole and quadrupole hyperfine interactions both involve $\langle r^{-3} \rangle_{nl}$, and thus one may use the dipole interaction, together with the NMR value for μ_I , to measure the value of $\langle r^{-3} \rangle_{nl}$ needed to obtain Q' . Thus,

$$a_{nl} = 2(\mu_I/I) \mu_B \mu_N \langle r^{-3} \rangle_{nl} . \quad (20)$$

In analogy to Eq. (7), it can be shown by the analysis of Sandars and Beck¹⁶ (with the use of the appropriate Casimir factors) that for the $5d$ electrons of La

$$a^{01} \approx 1.031 a_{sd} . \quad (21)$$

Thus, we have

$$Q' = \frac{2\mu_B \mu_N}{e^2} \frac{\mu_I}{I} \left(\frac{b_{sd}}{a_{sd}} \right) = +0.322 \left(\frac{b_{sd}}{a_{sd}} \right) b . \quad (22)$$

Before this expression is applied to the values of b_{sd} and a_{sd} listed in Table VIII, it would perhaps be wise to take note of its limitations and weaknesses. First of all, it assumes that the dipole and quadrupole hyperfine interactions have precisely the same radial dependence - i.e., both vary as r^{-3} . Although this is exactly true in the nonrelativistic limit, it is well known that the relativistic radial integrals for the two interactions in the $5d6s^2D$ states are not exactly the same. For the $5d^26s$ configuration, three different radial integrals are required to describe the quadrupole hfs interaction in the Sandars-Beck scheme, and Eq. (7) shows that one of the two introduced by relativity is 20% as large as the nonrelativistic one. Although attempts have been made to take account of these effects by using Casimir factors to estimate the relativistic integrals, such factors are known to be imprecise.

Another problem in deducing $\langle r^{-3} \rangle_{nl}$ from the magnetic-dipole hfs constant A is that all sources of the hfs contributing to A must be understood, and in particular, the contact part must be properly excluded. Consider the term $5d6s^2D$, for example. If all of the dipole hfs were due to the $5d$ electron, we should have, relativistically, $A(^2D_{3/2})/A(^2D_{5/2}) = 2.39$; the experimental value is 0.77. It has been assumed in the past that this discrepancy is all due to contact interaction of the $\vec{I} \cdot \vec{S}$ type (core polarization). This assumption leads of necessity to the use of two parameters (a_{sd} and one additional parameter for core polarization) to fit the two measured values of A . Although a perfect fit results, it does not follow that the value of a_{sd} (and hence $\langle r^{-3} \rangle_{sd}$) obtained is realistic. It has been pointed out in Sec. V L that Wilson's eigenvectors, which should be much more realistic, result in a value for the core-polarization constant which is not even of the same sign as the large value deduced without taking explicit account of configuration interaction within $(5d+6s)^3$. The use of Wilson's eigenvectors also result in a 9% decrease in the value found for $a^{01}(5d6s^2)$ and consequently of $\langle r^{-3} \rangle_{sd}$.

From this discussion it should be clear that attempts to evaluate $\langle r^{-3} \rangle_{sd}$ from the magnetic-dipole hyperfine interaction are subject to considerably more uncertainty than is at first apparent, and values of Q which depend on this process are therefore subject to this uncertainty. With the limitations of Eq. (21) in mind, however, let us apply it to the values of b_{sd} and a_{sd} of Table VIII. For the situation in which one fits the hfs constants of $5d^26s^4F$ and $5d6s^2D$ simultaneously with the Wilson eigenvectors, one obtains

$$\begin{aligned} Q'(5d^26s^4F) &= 0.26 \text{ b}, \\ Q'(5d6s^2D) &= 0.30 \text{ b}. \end{aligned} \quad (23)$$

If one uses the fit to all states instead, one obtains $Q'(5d^26s) = 0.23 \text{ b}$ and $Q'(5d6s^2D) = 0.31 \text{ b}$. Ting,³ working in the single-configuration LS limit but allowing for core polarization, obtains

$$Q'(5d6s^2D) = 0.230 \pm 0.010 \text{ b},$$

which is somewhat smaller than the value above. Less precise measurements of quadrupole hfs were made by Luhrs¹ and by Murakawa² by detailed analysis of the hfs of optical transitions.

The value of Q' may also be obtained from other determinations of $\langle r^{-3} \rangle_{5d}$ such as, for example, extraction from the measured value of the spin-orbit parameter ζ_{5d} or from Hartree-Fock calculations. If one uses Tree's expression²⁵ relating ζ_{5d} to $\langle r^{-3} \rangle_{5d}$, one obtains from Wilson's values of ζ_{5d} the result

$$\langle r^{-3}/a_0^{-3} \rangle_{5d} = 1.80 \text{ a.u.}$$

for $5d6s^2$ and 1.56 a.u. for $5d^26s$. For the fit to the B values of $5d6s^2D$ and $5d^26s^4F$, these numbers both lead to the same result, namely,

$$\begin{aligned} Q'(5d^26s^4F) &= 0.28 \text{ b}, \\ Q'(5d6s^2D) &= 0.28 \text{ b} \end{aligned} \quad (24)$$

for the Wilson eigenvectors. This result is midway between those obtained in Eq. (23), where $\langle r^{-3} \rangle_{5d}$ is obtained from the dipole hfs interaction. The applicability of this procedure for evaluating $\langle r^{-3} \rangle_{5d}$ depends on the degree to which the wave function is hydrogenic, but it is, at least, an independent method.

On the basis of these two experimental methods of estimating $\langle r^{-3} \rangle_{5d}$ then, one obtains for Q' the result

$$Q'(\text{La}^{139}) = 0.28 \pm 0.03 \text{ b}. \quad (25)$$

This result may be compared with the values deduced from theoretical calculations of $\langle r^{-3} \rangle_{5d}$. Recent Hartree-Fock calculations give $\langle r^{-3}/a_0^{-3} \rangle_{5d} = 2.32 \text{ a.u.}$ ²⁷ for $5d6s^2D$, and 1.94 a.u. ⁴ for $5d^26s^4F$; and from these one obtains

$$Q'(\text{La}^{139}) = 0.21 \text{ b}, \quad (26)$$

which is about 25% smaller than the estimates (25) in which $\langle r^{-3} \rangle_{5d}$ was estimated from the magnetic-dipole hfs and from the spin-orbit constant ζ_{5d} .

The sources of error in the "experimental" value of $\langle r^{-3} \rangle_{5d}$ used in (25) have been discussed; uncertainties in the Hartree-Fock results and thus in Eq. (26) may be comparable. Although the source of the difference is not really understood, Hartree-Fock estimates of $\langle r^{-3} \rangle_{n\ell}$ are usually somewhat larger than estimates based on parameter fitting of energy levels.

Sternheimer²⁶ has recently shown that the radial shielding correction is opposite to and larger than the previously calculated angular correction. The best value²⁸ is $R = -0.3$, so that the (antishielding) correction factor is $1/(1-R) = 0.769$, i. e.,

$$Q = 0.769Q'. \quad (27)$$

From Eq. (25), then, we have

$$Q(\text{La}^{139}) = 0.22 \pm 0.03 \text{ b}. \quad (28)$$

This result is in good agreement with Ref. 2.

Ting has shown that for La^{139} , which lacks one proton of having a complete $5g_{7/2}$ shell, the assumption that $\langle r_n^2 \rangle$ is half-way between that for a surface charge and a uniform charge distribution leads to the prediction $Q = 0.27 \text{ b}$. This is in reasonable agreement with the experimental result.

VI. CONCLUSIONS

The excitation energies, electron g factors, and particularly the hyperfine-interaction constants A and B of the atomic levels below 9000 cm^{-1} in La^{139} have been considered together and compared with predictions of a set of eigenvectors which spans the three principal competing configurations. As might be expected, it is not yet possible to fit all observables to within experimental error, but the self-consistency found is encouraging. The effective-operator interpretation of the hyperfine-interaction effects leads to evaluation of a number of characteristic parameters, and an improved value for the electric-quadrupole moment Q of the La^{139} nuclear ground state is found.

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LS-Term Dependence of Hyperfine-Interaction Parameters in d^2s Configurations*

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Hartree-Fock calculations have been made for the configurations $3d^24s$ of Sc I and $5d^26s$, $5d6s^2$, and $5d^3$ of La I. Attention is drawn to the variation of atomic quantities which influence hyperfine structures owing to the LS-term dependence of the radial wave functions. Theoretical calculations of the level structure of $(5d+6s)^3$ of La I are also presented.

I. INTRODUCTION

The traditional Hamiltonian for the magnetic-dipole hyperfine interaction in a configuration of the type $l^N s$ is of the form¹

$$H_{\text{dip}} = \left[a_I \sum_{i=1}^N (l_i - \sqrt{10} (sC^{(2)})_i^{(1)}) + a_s s \right] I,$$

where

$$a_I = 2\mu_B \mu_N \mu_I \langle r^{-3} \rangle_I / I$$

and

$$a_s = 16\pi \mu_B \mu_N \mu_I |\psi(0)|^2 / 3I,$$

μ_B is the Bohr magneton, μ_N the nuclear magneton, and μ_I the nuclear magnetic-dipole moment in nuclear magnetons.

Matrix elements of this Hamiltonian are usually expressed in terms of products of reduced matrix elements and certain angular coefficients. The reduced matrix elements depend on the radial parts of

the wave function and are often treated as adjustable parameters to be determined by fitting experimental hyperfine structure (hfs) data to the theoretical expressions. It is to be noted that a_I and a_s here are usually supposed constants for all the states of a given electron configuration.² This implies that the multiplet structure be ignored completely insofar as the radial functions are considered as being defined in terms of the occupation numbers of the various orbitals together with a single energy criterion.

Contributions to the hfs from the nuclear electric-quadrupole interaction serve to complicate further the interpretation of hfs splittings. Parametric treatments of this follow lines similar to those used for magnetic-dipole interaction in the use of a single parameter $b_i = e^2 Q \langle r^{-3} \rangle_i$ in the traditional approach. Again, it is to be noted that b_i is usually supposed a constant for all states of a given electron configuration.²

In recent years a variation of this approach has been used with some success in attempts to accom-