PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOL. 4, NO. 2 AUGUST 1971

Relativistic Effects in the Hyperfine Structure of $Sn^{117,119}$ †

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(Received 17 February 1971)

The atomic-beam magnetic-resonance technique has been used to measure the magnetic-dipole hyperfine-interaction constants A for the 8613-cm^{-1} $^1D_2$ metastable atomic state of $Sn^{117,119}$. The results are $A(Sn^{117}, {}^1D_2) = -1269.650(3)$ MHz and $A(Sn^{119}, {}^1D_2) = -1328.745(4)$ MHz. These results, together with the previous measurements of A for the $^3P_1$ and $^3P_2$ states, are considered (a) nonrelativistically, (b) relativistically, with Casimir correction factors, and (c) with relativistic Hartree-Fock radial wave functions. Procedure (c) is shown to be relatively successful in accounting for the hfs observations, and leads to a predicted mixing coefficient for the states $^3P_2$ and $^1D_2$ which is within 13% of the mutually consistent values found (i) by consideration of the $^3P_2 - {}^1D_2$ energy separation and (ii) from the precisely measured g_J values for the $^3P_2$ and $^1D_2$ states.

I. INTRODUCTION

The ground configuration ns^2np^2 of the group-IV elements is the simplest nontrivial two-electron configuration and has consequently been studied in detail by many authors[1] over the years. In addition to its simplicity, it is relatively well isolated from other even-parity configurations. In the atoms C, Si, and Ge, for which $n=2$, 3, and 4, LS coupling is a good approximation, while for Pb ($n=6$), jj coupling is a better approximation and relativistic effects become very important. The Sn atom is transitional between these extremes, both with regard to coupling and to the importance of relativistic effects. The present experiment completes the measurement of the hyperfine structure (hfs) of the odd-A stable Sn isotopes, and considers the excitation energies, g factors, and magnetic-dipole hfs constants A together for all $J \neq 0$ states of the configuration. A recent paper by Lurio and Landman[2] dealt with the corresponding situation in Pb^{207}

High-precision measurements of the g_J values of the three $J \neq 0$ $5s^25p^2$ states of Sn I ($^3P_1$, $^3P_2$, and $^1D_2$) have shown[3] that $^3P_1$ is an almost completely pure state, and that the $^3P_2$ and $^1D_2$ states are strongly intermixed. The perturbations of the g values of these two states were shown to be equal and opposite to within 0.2%. Subsequent experiments[4] were performed to measure the hfs of the $^3P_{1,2}$ states of the odd-A isotopes $Sn^{115,117,119}$, but at that time the sensitivity of the detector was inadequate to permit measurement of the hfs of the third $J \neq 0$ state, $^1D_2$. Improvement in sensitivity has now led to measurement of the hfs of the $^1D_2$ state in $Sn^{117,119}$, and improved values were obtained for the g values of the three $J \neq 0$ states as well.

With knowledge of the three A values, it is now possible to determine three parameters; those chosen are in effect $(\mu_I/I)\langle r^{-3}\rangle_{5p}$, the degree of core polarization, and the degree of mixing between the $J=2$ states. The deduction of parameter values from the hfs observation is done (a) nonrelativistically, (b) relativistically by means of the "Casimir correction factors," and (c) with relativistic Hartree-Fock radial wave functions. The results of the three treatments are somewhat different, since the way in which relativistic effects are treated is important (the $^3P_1$ state, for example, should have no hfs at all nonrelativistically and in the absence of configuration interaction). The value obtained for the mixing coefficient from study of the hfs is also compared with the values obtained from observation of the $J=2$ energy splitting and from the measured g_J values.

II. EXPERIMENTAL DETAILS

The atomic-beam magnetic-resonance technique has been described[5] too many times to need further discussion here. The apparatus used for the present experiment has also been previously described[6];

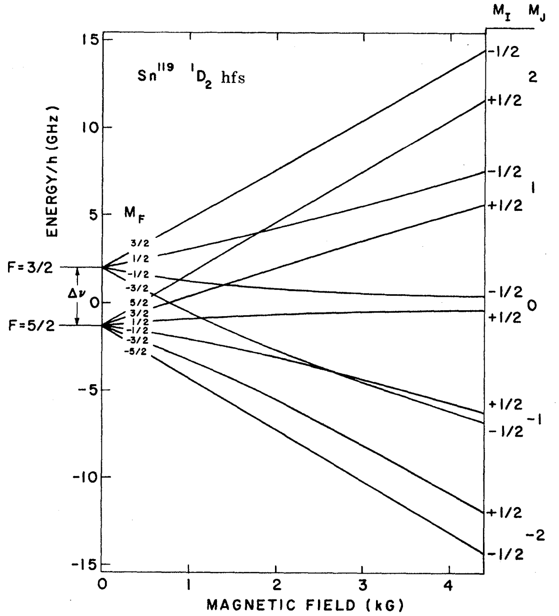

FIG. 1. Zeeman effect in the hyperfine structure of the 8613-cm^{-1} $^1D_2$ metastable atomic state of Sn^{119}. The corresponding figure for Sn^{117} differs only in scale. The relevant quantum numbers are indicated.

it is basically the same one used for earlier atomic-beam magnetic-resonance investigations of stable Sn isotopes. Two modifications of the data-handling techniques are responsible for the required improvement in sensitivity: the use of a swept rf signal in conjunction with a multichannel analyzer,[7] and a digital noise filter[8] for eliminating nonrandom bursts of counts arising from instabilities in the apparatus. Both modifications have been described. The improvement in sensitivity they made possible was only just adequate for the experiment on the metastable $^1D_2$ state at 8613 cm^{-1} in Sn^{117,119}.

The Hamiltonian used to describe the magnetic field dependence of the magnetic-dipole hfs of an isolated atomic state is

$$\mathcal{H} = hA\vec{I}\cdot\vec{J} + g_J\mu_B HJ_z + g_I\mu_N HI_z ,$$

in which A is the magnetic-dipole hyperfine-interaction constant, $\vec{I}$ and $\vec{J}$ are the nuclear-spin and electronic-angular-momentum operators, respectively, I_z and J_z are their z projections, g_J and g_I are the electron and nuclear g factors, μ_B and μ_N are the Bohr and nuclear magnetons, and H is the external magnetic field. Only the magnetic-dipole term of the hfs is included because $I = \frac{1}{2}$ for the stable odd-A Sn isotopes considered. The eigenvalues of this Hamiltonian have been given[4] analytically but are normally calculated digitally by computer. Figure 1 is a plot of the eigenvalues for the $^1D_2$ state of Sn^{119} on which most of the present experiment was performed.

The excitation energies[9] for the $5s^25p^2$ states of Sn I are given in Table I, along with the Boltzmann factors for the approximate oven temperature of 1412 °C. Since the relative intensities observed for hfs transitions in the odd-A isotopes are proportional to these factors, observation of such transitions in the $^1D_2$ state was expected to be very difficult.

With data-collection times on the order of 45 min, reproducible resonance curves could be obtained for the $F, M = \frac{5}{2}, \frac{3}{2} \longleftrightarrow F', M' = \frac{5}{2}, -\frac{1}{2}$ double-quantum transition in Sn^{119} at $H = 200$ G, although the signal-to-noise ratio was typically only about 4. At 400 G, the double-quantum transitions could not be seen, and efforts were therefore made to measure the $\Delta M_F = \pm 1$ intervals. The normal procedure for integral-J atoms such as Sn is to remove the central obstacle and to search for single-quantum flopout transitions. This procedure is difficult because of the large background of undeflected $M_J = 0$ atoms. Eventually these transitions were observed, but the high background kept the signal-to-noise ratios below 1.3–2.0.

The two-frequency technique of Prior, Dymanus, Shugart, and Vanden Bout[10] was then tried in an effort to get better-looking resonances. Since this technique was designed to induce two single-quantum transitions (of different frequency) successively, the flop occurs between states which have opposite values of M_J at high field and consequently a central obstacle can be used to reduce the beam background. In addition, because the transitions sought are single quantum, modest rf power may be used to reduce the likelihood of "frequency pulling." Since all of the relevant single-quantum intervals were previously measured to within less than a linewidth (though with considerable scatter of data points), there was no danger of misinterpreting a two-quantum ($\nu_\alpha + \nu_\beta = \Delta E/h$, $\nu_\alpha \neq \nu_\beta$) transition as arising from two successive single-quantum transitions.[11] Figure 2 shows the appearance of such a two-frequency observation in Sn^{119}, namely, the $\frac{5}{2}, \frac{3}{2} \longleftrightarrow \frac{5}{2}, \frac{1}{2}$ transition of $^1D_2$ at $H = 400$ G.

TABLE I. Excitation energies and Boltzmann factors (calculated for the oven temperature of 1412 °C) for the $5s^2 5p^2$ atomic levels of Sn I. For a given isotope, the relative intensities expected for hfs transitions are approximately proportional to the Boltzmann factors.

Atomic state	Excitation energy (cm^{-1})	Boltzmann factor ($T = 1412$ °C)
$^3P_0$	0.0	1.00
$^3P_1$	1691.8	0.24
$^3P_2$	3427.7	0.054
$^1D_2$	8613.0	0.0006
$^1S_0$	17162.6	very small

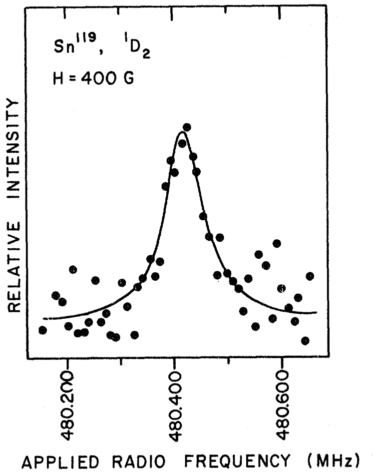

FIG. 2. The $\frac{5}{2}$, $\frac{3}{2} \longleftrightarrow \frac{5}{2}$, $\frac{1}{2}$ transition in the $^1D_2$ state of Sn^{119} as observed at $H = 400$ G. The two-frequency technique of Prior, Dymanus, Shugart, and Vanden Bout was used to enhance the signal-to-noise ratio. About 2 h data collection were required to obtain the spectrum shown.

For the spectrum, two rf signals were applied to the same loop through a hybrid junction. One signal was held fixed at 473.174 MHz, the approximate frequency for the $\frac{5}{2}$, $\frac{1}{2} \longleftrightarrow \frac{5}{2}$, $-\frac{1}{2}$ interval, and the other was swept repeatedly through the interval shown on the abscissa. Two hours of data collection were required for the curve.

Similar measurements were made for all four observable $\Delta M_F = 1$ intervals in this way, and the results are summarized in Table II. On the basis of these observations, the zero-field $\Delta F = 1$ interval could be predicted with a small enough uncertainty to justify a search. Accordingly, the field was set to about 1 G, and the $\frac{3}{2}$, $\frac{1}{2} \longleftrightarrow \frac{5}{2}$, $-\frac{1}{2}$ direct transition was observed as expected. A phase-locked magnetron was used to induce the transition. It was then assumed that the ratio of the zero-field hyperfine interval for $^1D_2$ in Sn^{117} to the known interval for $^1D_2$ in Sn^{119} would be equal to the known[4] ratio $A(^3P_2, Sn^{117})/A(^3P_2, Sn^{119}) = 0.95552$. This proved to be true, and the $^1D_2$ $\Delta F = 1$ interval was observed in Sn^{117} at 1 G as shown in Table II. Because the interval happens to be almost identical to that[4] of the $^3P_2$ state in Sn^{119}, it was possible, by use of the predicted field dependences of the two transitions, to predict that at $H = 0.757$ G they should appear side by side. A run at this field, with the mass spectrometer of the detector set for $A = 117$, produced the spectrum shown in Fig. 3. Although (from Table I and the relative abundances of the isotopes) the peak at the left is expected to be about 100 times stronger than that on the right, they appear about equal in intensity because of the strong mass discrimination used. The results for the $^3P_2$ state of Sn^{119} are in agreement with the previously published results.[4]

Values of the magnetic-dipole hyperfine-interaction constant A deduced from the observed zero-field hyperfine intervals must be corrected for perturbations caused by other atomic states. The required corrections are discussed in Sec. III K; the corrected and uncorrected results are compiled in Table III. Corrected values are also given for the previously published,[4] but uncorrected, values of A for the $^3P_{1,2}$ states of $Sn^{115,117,119}$.

It should be mentioned that the algebraic sign of $A(^1D_2)$ was not determined for $Sn^{117,119}$ in the present experiment. The signs of $A(^3P_1)$ and $A(^3P_2)$ were measured,[4] however, for $Sn^{115,117,119}$ previously, and both nonrelativistic and relativistic theoretical predictions of $A(^1D_2)$ (based on these measured signs) are strongly negative for all three isotopes. That $A(^1D_2)$ is negative is assumed throughout in what follows.

Table IV presents various ratios between the corrected values of the hfs A constant of Table III.

TABLE II. Summary of observed transitions in the metastable $^1D_2$ atomic state of $Sn^{117,119}$. The magnetic field at which each observation was made was measured by observing resonances in an auxiliary atomic beam of K^{39}.

Isotope	Atomic state	Transition $(F, M \longleftrightarrow F', M')$	H (G)	Observed resonance frequency (MHz)	$\nu^{obs} - \nu^{calc}$ (kHz)
Sn^{119}	$^1D_2$	$(\frac{5}{2}, \frac{3}{2} \longleftrightarrow \frac{5}{2}, -\frac{1}{2})$	200	236.922(12)	0
		$(\frac{3}{2}, \frac{1}{2} \longleftrightarrow \frac{3}{2}, -\frac{3}{2})$	200	354.284(7)	−7
		$(\frac{5}{2}, \frac{3}{2} \longleftrightarrow \frac{5}{2}, \frac{1}{2})$	400	480.423(15)	−2
		$(\frac{5}{2}, \frac{1}{2} \longleftrightarrow \frac{5}{2}, -\frac{1}{2})$	400	473.182(15)	2
		$(\frac{3}{2}, -\frac{1}{2} \longleftrightarrow \frac{3}{2}, -\frac{3}{2})$	400	714.036(22)	7
		$(\frac{3}{2}, \frac{1}{2} \longleftrightarrow \frac{3}{2}, -\frac{1}{2})$	400	705.116(20)	8
		$(\frac{3}{2}, \frac{1}{2} \longleftrightarrow \frac{5}{2}, -\frac{1}{2})$	0.996	3323.340(10)	4
		$(\frac{3}{2}, \frac{1}{2} \longleftrightarrow \frac{5}{2}, -\frac{1}{2})$	0.987	3323.318(10)	−4
Sn^{117}	$^1D_2$	$(\frac{3}{2}, \frac{1}{2} \longleftrightarrow \frac{5}{2}, -\frac{1}{2})$	0.757	3175.233(10)	−11
		$(\frac{3}{2}, \frac{1}{2} \longleftrightarrow \frac{5}{2}, -\frac{1}{2})$	2.011	3177.100(7)	8

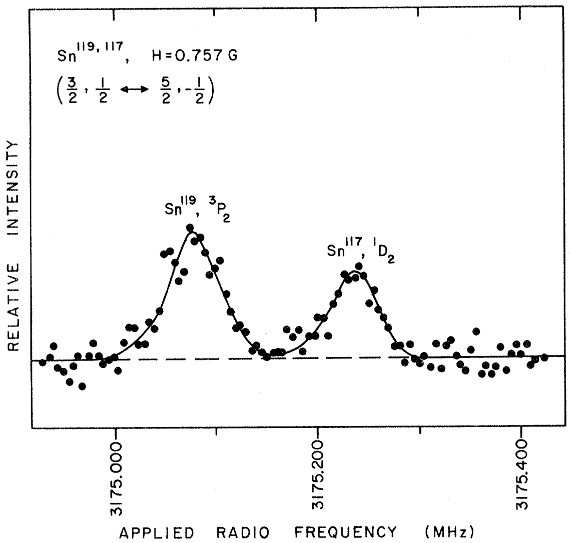

FIG. 3. Observation of the $\Delta F = 1$, $(\frac{3}{2}, \frac{1}{2} \leftrightarrow \frac{5}{2}, -\frac{1}{2})$ transition in the $^1D_2$ state of Sn^{117} and in the $^3P_2$ state of Sn^{119} at $H = 0.757$ G. Although the number of atoms undergoing the transition at the left is about 100 times greater than for that on the right, the peaks appear comparable because the mass spectrometer of the detector, set for $A = 117$, discriminated strongly against Sn^{119} atoms.

Although the general consistency is good, two points appear puzzling. First, although the differences in the ratio $A(^3P_2)/A(^3P_1)$ from isotope to isotope are within the quoted uncertainties, this consistency is deceptive. Most of the uncertainty in the ratio arises from the fact that different methods of calculating the correction to $A(^3P_1)$ (see Sec. III K) result in different values for the corrected A value. If the correction is made in the same way for each isotope, however, then the variation in the ratio $A(^3P_2)/A(^3P_1)$ from isotope to isotope is definitely larger than the experimental uncertainty. Second, both for $A(Sn^{117})/A(Sn^{115})$ and for $A(Sn^{119})/A(Sn^{117})$, the differences between the ratios for different states are also larger than the experimental uncertainty. These effects appear to be due partly to differences between the three nuclei and partly to the fact that the three atomic states $^3P_1$, $^3P_2$, and $^1D_2$ contain different amounts of the deeply probing $p_{1/2}$ electron, as viewed from the jj scheme. This may be seen from Eq. (5) of Sec. IIIA.

TABLE III. Summary of magnetic-dipole hyperfine-interaction constants A for the $^3P_{1,2}$ and $^1D_2$ states of $Sn^{115,117,119}$. The final values (on the right) have been corrected for hyperfine interactions with other atomic states; the quoted uncertainties include the uncertainty in the corrections applied. The uncorrected values for the $^3P_1$ and $^3P_2$ states were published previously.

Isotope	Atomic state	Uncorrected A (MHz)	Corrected A (MHz)
Sn^{115}	$^3P_1$	507.445(4)[a]	507.483(25)
	$^3P_2$	−1113.770(4)[a]	−1113.752(10)
	$^1D_2$		
Sn^{117}	$^3P_1$	552.608(4)[a]	552.653(25)
	$^3P_2$	−1212.956(3)[a]	−1212.935(10)
	$^1D_2$	−1269.652(3)	−1269.650(3)
Sn^{119}	$^3P_1$	578.296(4)[a]	578.345(25)
	$^3P_2$	−1269.419(3)[a]	−1269.396(10)
	$^1D_2$	−1328.747(4)	−1328.745(4)

[a] Reference 4.

TABLE IV. Ratios between various corrected values of the magnetic-dipole hyperfine-interaction constants A for the isotopes $Sn^{115,117,119}$

Ratio	Sn^{115}	Sn^{117}	Sn^{119}
$A(^3P_2)/A(^3P_1)$	−2.194 66(11)	−2.194 75(10)	−2.194 88(9)
$A(^1D_2)/A(^3P_2)$		1.046 76(1)	1.046 75(1)
Ratio	$^3P_1$	$^3P_2$	$^1D_2$
$A(Sn^{117})/A(Sn^{115})$	1.089 01(1)	1.089 05(1)	
$A(Sn^{119})/A(Sn^{117})$	1.046 49(1)	1.046 55(1)	1.046 54(1)

In addition to the g_J value obtained for the $^1D_2$ state through hfs studies of Sn^{119}, g_J was remeasured in all three states at fields to 1000 G with the even-even Sn isotopes for which there are no hfs complications. The results are presented in Table V, along with the LS-limit values and the differences. The results are discussed in Sec. III.

III. THEORY AND DISCUSSION

A. Description of $5s^2 5p^2$ $J \neq 0$ States

The lowest electron configuration in the neutral Sn atom is $5s^2 5p^2$, which comprises the five levels $^3P_{0,1,2}$, $^1D_2$, and $^1S_0$. Of the two levels with $J = 0$, $^3P_0$ lies lower and is the atomic ground state, and $^1S_0$ lies at 17 162 cm^{-1}. The three levels with nonzero angular momentum, $^3P_1$, $^3P_2$, and $^1D_2$, lie at 1691, 3427, and 8613 cm^{-1}, respectively. Since no other $J \neq 0$ even-parity levels lie within 35 000 cm^{-1} of them (the lowest even-parity configuration above $5s^2 5p^2$ is $5s^2 5p 6p$, which lies above 42 000 cm^{-1}), they may be expected to be rather free from configuration mixing. The excitation energies of the $5s^2 5p^2$ levels are given[9] in Table I.

Within the $5s^2 5p^2$ configuration, however, levels of the same J can mix. Thus, in the absence of configuration interaction, we may represent the $^3P_2$ and $^1D_2$ states of the atom as being linear combinations of the LS basis states of the same name. That is, we have

$$\begin{aligned} |^3P_2\rangle &= (1-\alpha^2)^{1/2} |^3P_2^{LS}\rangle + \alpha |^1D_2^{LS}\rangle , \\ |^1D_2\rangle &= -\alpha |^3P_2^{LS}\rangle + (1-\alpha^2)^{1/2} |^1D_2^{LS}\rangle , \end{aligned} \tag{1}$$

TABLE V. Values of g_J for the states ${}^3P_1$, ${}^3P_2$, and ${}^1D_2$ of Sn I. The observed values are weighted averages obtained from observations in both even-even and odd-A isotopes at a variety of values of the field H. The final column lists the departures of the observed g values from those calculated in the LS limit. The very small departure for the ${}^3P_1$ state and the (nearly) equal and opposite departures for the ${}^3P_2$ and ${}^1D_2$ states are discussed in the text.

Atomic state	Value of g_J Observed	 LS limit	$g_J^{\text{obs}} - g_J^{LS}$
${}^3P_1$	1.501 06(3)	1.501 16	− 0.000 10(3)
${}^3P_2$	1.448 70(5)	1.501 16	− 0.052 46(5)
${}^1D_2$	1.052 29(3)	1.000 00	+ 0.052 29(3)

where in this and following equations a superscript LS is used to distinguish the LS basis state from the actual state of the atom. There is a similar mixing of the ${}^1S_0^{LS}$ and ${}^3P_0^{LS}$ states, although the mixing coefficient is not the same as α. In the same approximation, the ${}^3P_1$ state of the atom is pure; i.e.,

$$|{}^3P_1\rangle = |{}^3P_1^{LS}\rangle \ . \tag{2}$$

The mixing is caused almost entirely by the spin-orbit interaction; i.e.,

$$\mathcal{H}_{\text{so}} = \zeta_{5p} \sum_{i=1}^{2} \vec{1}_i \cdot \vec{s}_i \ . \tag{3}$$

The remaining magnetic interactions (spin-spin, orbit-orbit, and spin-other-orbit) are very much smaller than the spin-orbit interaction, and Lurio and Landman[2] have recently shown that taking explicit account of them for the $6s^2 6p^2$ ground configuration of Pb I (for which the departure from the LS limit is still more severe then for Sn I) does not lead to improved understanding of the mixing. To the extent that all of the mixing arises from the spin-orbit interaction, the value of the mixing coefficient α may be estimated from perturbation theory to be

$$\alpha_{\text{pert}} = \frac{\langle {}^3P_2 M | \mathcal{H}_{\text{so}} | {}^1D_2 M\rangle}{E({}^3P_2) - E({}^1D_2)} = \frac{\zeta_{5p}/\sqrt{2}}{E({}^3P_2) - E({}^1D_2)}$$
$$\approx -0.30 \ , \tag{4}$$

in which the value[3] $\zeta_{5p} = 2171$ cm^{-1} is used.

The atomic states may alternatively be expressed in the jj scheme as

$$|{}^3P_2\rangle = \xi |p_{1/2}, p_{3/2}; 2\rangle + (1-\xi^2)^{1/2} |p_{3/2}, p_{3/2}, 2\rangle \ ,$$
$$|{}^1D_2\rangle = (1-\xi^2)^{1/2} |p_{1/2}, p_{3/2}; 2\rangle - \xi |p_{3/2}, p_{3/2}; 2\rangle \ , \tag{5}$$
$$|{}^3P_1\rangle = |p_{1/2}, p_{3/2}; 1\rangle \ ,$$

in which

$$\xi = (1/\sqrt{3})[\sqrt{2}\,\alpha - (1-\alpha^2)^{1/2}] \ ,$$
$$\alpha = (1/\sqrt{3})[\sqrt{2}\,\xi + (1-\xi^2)^{1/2}] \ . \tag{6}$$

From Eqs. (4) and (6), we expect $\xi \approx -0.80$.

B. Determination of α from Zeeman Effect of $J \neq 0$ Levels

One can predict the g_J values to be expected from the descriptions of the states given above. From Eqs. (1) and (2), we expect

$$g_J({}^3P_2) = (1-\alpha^2) g_J({}^3P_2^{LS}) + \alpha^2 g_J({}^1D_2^{LS})$$
$$= g_J({}^3P_2^{LS}) - \alpha^2 [g_J({}^3P_2^{LS}) - g_J({}^1D_2^{LS})] \ ,$$
$$g_J({}^1D_2) = \alpha^2 g_J({}^3P_2^{LS}) + (1-\alpha^2) g_J({}^1D_2^{LS}) \tag{7}$$
$$= g_J({}^1D_2^{LS}) + \alpha^2 [g_J({}^3P_2^{LS}) - g_J({}^1D_2^{LS})] \ ,$$
$$g_J({}^3P_1) = g_J({}^3P_1^{LS}) \ .$$

The electron g factors g_J have been measured for these states with high precision, and the results are presented in Table V. As can be seen from the last column of the table, the observed value of g_J for the ${}^3P_1$ state is almost exactly that of a ${}^3P_1$ LS basis state. In addition, the g_J values for the $J=2$ states depart from the LS-limit predictions by amounts that are almost exactly equal and opposite, as predicted by Eq. (7). The very small differences between these predictions of Eq. (7) and the numbers in the right-hand column of Table V probably arise mostly from failure to take into account the relativistic and diamagnetic corrections to the theoretical g values used for the basis states. The small differences could also be due in part to higher-order configuration-interaction effects.

Thus for the measured values of g_J for ${}^3P_2$ and ${}^1D_2$ one obtains from Eq. (7) the results $|\alpha({}^3P_2)| = 0.3235$ and $|\alpha({}^1D_2)| = 0.3230$, respectively. If one assigns the negative sign (the sign of α is shown to be negative from considerations of both spin-orbit mixing and hyperfine structure) and takes an average of these results, it is found that

$$\alpha_{g_J} = -0.323 \ . \tag{8}$$

It may be noted that small contributions from states of higher configurations may be mixed into $5s^2 5p^2$ ${}^3P_2$ and ${}^1D_2$ by the Coulomb interaction. Since this interaction is diagonal in S, L, and J, however, nearly all of the admixture will be characterized by the same value of g_J, and thus any shift in g_J will be very small—particularly since the closest even-parity states with $J=2$ lie 35 000 cm^{-1} away.[9] The effects of configuration interaction will be discussed in more detail in Sec. III J.

C. Determination of α from Energy Splitting of $J=2$ Levels

The simplest approach to understanding the energy spacings in the $5s^2 5p^2$ configuration is to ignore any possible configuration interaction, and to neglect the smaller magnetic interactions (which have been shown[2] to be very much smaller than the spin-orbit interaction). Condon and Shortley[1] give the results of such a treatment. Since there are four excitation energies to be fitted (${}^3P_1$, ${}^3P_2$, ${}^1D_2$, and ${}^1S_0$) and only two relevant adjustable parameters (F_2 and ζ_{5p}), it is clear that there are several possible ways of proceeding. The way adopted here is to fit the excitation energies of the two $J=2$ states exactly (i.e., to fit the energy splitting and the excitation energy of either state). From Condon and Shortley's expressions for the eigenvalues, we write

$$\begin{aligned} E({}^1D_2) - E({}^3P_2) &= 2F_2(9 - \tfrac{3}{2}x + \tfrac{9}{16}x^2)^{1/2} = 5185.3\ \mathrm{cm}^{-1}, \\ E({}^1D_2) - E({}^3P_0) &= F_2\left[-\tfrac{9}{2} + \tfrac{3}{4}x + (\tfrac{225}{4} + \tfrac{15}{2}x + \tfrac{9}{4}x^2)^{1/2} \right. \\ &\quad \left. + (9 - \tfrac{3}{2}x + \tfrac{9}{16}x^2)^{1/2}\right] = 8613.0\ \mathrm{cm}^{-1}, \end{aligned} \tag{9}$$

in which F_2 is the relevant Slater integral, $x = \zeta_{5p}/F_2$, and ζ_{5p} is the spin-orbit constant for the configuration. The solution is

$$\begin{aligned} \zeta_{5p} &= 2225\ \mathrm{cm}^{-1}, \\ F_2 &= 872.3\ \mathrm{cm}^{-1}, \\ x &= 2.551. \end{aligned} \tag{10}$$

For the value $x = 2.551$, consideration of the matrix given for the $J=2$ states by Condon and Shortley leads to the result

$$\alpha_{\mathrm{energy}} = -\frac{1}{\sqrt{2}}\left[1 + \frac{x-12}{[3(3x^2 - 8x + 48)]^{1/2}}\right]^{1/2} = -0.320. \tag{11}$$

This result is in remarkably close agreement with the value $\alpha_{g_J} = -0.323$ obtained from the observed values of g_J. Since the two determinations of α arise from different physical interactions, they are completely independent. The result of Eq. (11) is not independent of that of Eq. (4), however, since the latter deduces an approximate value of α from the same physical considerations (spin-orbit mixing) as did the more rigorous result of Eq. (11).

D. Nonrelativistic Treatment of Hyperfine Structure

The hyperfine structure of the ${}^3P_1$, ${}^3P_2$, and ${}^1D_2$ states has been measured[4] in Sn^{115}, Sn^{117}, and Sn^{119} (except for the ${}^1D_2$ state of Sn^{115}, for which the available intensity was inadequate). Since the nuclear spin I is $\frac{1}{2}$ for all three isotopes, only the magnetic-dipole interaction need be considered. The situation is virtually identical for the three isotopes except that the hyperfine energies are scaled by the ratio of the nuclear g factors,[12] μ_I/I. The description given will therefore be limited to the single isotope Sn^{119}.

The nonrelativistic Hamiltonian for the magnetic-dipole hyperfine interaction of an atom with a single partially filled electron shell l^N is, in the absence of configuration interaction,

$$\mathcal{H}_{\mathrm{hfs}} = a_{nl} \sum_{i=1}^{N} [\vec{1}_i - (\sqrt{10})(\vec{s} \times \overleftrightarrow{C}^{(2)})_i^{(1)}] \cdot \vec{I} \tag{12}$$

for $l>0$, where $\overleftrightarrow{C}^{(2)}$ is a second-rank tensor operator proportional to a spherical harmonic of order 2. It is convenient to characterize the dipole hfs between any two LS basis states $\psi = |l^N \alpha SL\rangle$ and $\psi' = |l^N \alpha' S' L'\rangle$ of the same J by a generalized magnetic-dipole hyperfine-interaction constant $A(\psi, \psi')$ such that

$$\langle l^N \alpha SLJIFM | \mathcal{H}_{\mathrm{hfs}} | l^N \alpha' S' L' JIFM\rangle = \langle FM | \vec{I} \cdot \vec{J} | FM\rangle A(\psi, \psi'). \tag{13}$$

The form of $A(\psi, \psi')$ is completely specified by Eqs. (12) and (13), and the result is

$$\begin{aligned} A(\psi, \psi') &= A(\psi', \psi) \\ &= \left[(2 - g_J^*)\delta(\alpha SL, \alpha' S' L') \right. \\ &\quad + \left(\frac{30(2J+1)l(l+1)(2l+1)}{J(J+1)(2l-1)(2l+3)}\right)^{1/2} \\ &\quad \times \langle l^N \alpha SL \| V^{(12)} \| l^N \alpha' S' L'\rangle \\ &\quad \left. \times \begin{Bmatrix} S & S' & 1 \\ L & L' & 2 \\ J & J & 1 \end{Bmatrix}\right] a_{nl}, \end{aligned} \tag{14}$$

in which

$$g_J^* = 1 + [J(J+1) + S(S+1) - L(L+1)]/2J(J+1) \tag{15}$$

is the Landé value of the g factor, and we define

$$a_{nl} = 2\mu_B \mu_N (\mu_I/I)\langle r^{-3}\rangle_{nl}. \tag{16}$$

Because the dipole hyperfine interaction for a given nuclear dipole moment is basically a measure of the magnetic field at the nucleus, it is extremely sensitive to even a very slight admixture of states containing unpaired s electrons. This effect is known to be important in Sn I. It has been shown[13] that these effects, regardless of their origin, may be taken into account by adding to the Hamiltonian of Eq. (12) a contact term

$$C\vec{I}\cdot\vec{S}\ . \tag{17}$$

The result is that a corresponding term

$$C(g_J^*-1)\delta(\alpha SL,\alpha' S' L') \tag{18}$$

is added to Eq. (14). This contribution to the hfs of Sn may be viewed as arising from polarization of the inner electron orbits (core polarization). The quantity C may be regarded as a constant to be determined empirically.

From Eqs. (1) and (2), the A values expected for the states $^3P_1$, $^3P_2$, and $^1D_2$ may be written

$$\begin{aligned}
A(^3P_1) &= A(^3P_1^{LS},\ ^3P_1^{LS})\ ,\\
A(^3P_2) &= (1-\alpha^2)A(^3P_2^{LS},\ ^3P_2^{LS})+\alpha^2 A(^1D_2^{LS},\ ^1D_2^{LS})\\
&\quad +2\alpha(1-\alpha^2)^{1/2}A(^3P_2^{LS},\ ^1D_2^{LS})\ ,\\
A(^1D_2) &= \alpha^2 A(^3P_2^{LS},\ ^3P_2^{LS})+(1-\alpha^2)A(^1D_2^{LS},\ ^1D_2^{LS})\\
&\quad -2\alpha(1-\alpha^2)^{1/2}A(^3P_2^{LS},\ ^1D_2^{LS})\ ,
\end{aligned} \tag{19}$$

and the required expressions for $A(\psi,\psi')$ may be found from Eqs. (14) and (18) to be

$$\begin{aligned}
A(^3P_1^{LS},\ ^3P_1^{LS}) &= \tfrac{1}{2}C\ ,\\
A(^3P_2^{LS},\ ^3P_2^{LS}) &= \tfrac{1}{2}C+\tfrac{3}{5}a_{5p}\ ,\\
A(^1D_2^{LS},\ ^1D_2^{LS}) &= a_{5p}\ ,\\
A(^3P_2^{LS},\ ^1D_2^{LS}) &= -[3/10\sqrt{2}]a_{5p}\ .
\end{aligned} \tag{20}$$

We may collect these results by writing

$$A(^3P_1)=\tfrac{1}{2}C=+578.345(25)\text{ MHz}\ , \tag{21a}$$

$$\begin{aligned}
A(^3P_2) &= (1-\alpha^2)[\tfrac{3}{5}a_{5p}+\tfrac{1}{2}C]+\alpha^2 a_{5p}\\
&\quad +2\alpha(1-\alpha^2)^{1/2}[-3/10\sqrt{2}]a_{5p}\\
&= -1269.396(10)\text{ MHz}\ ,
\end{aligned} \tag{21b}$$

$$\begin{aligned}
A(^1D_2) &= \alpha^2[\tfrac{3}{5}a_{5p}+\tfrac{1}{2}C]+(1-\alpha^2)a_{5p}\\
&\quad -2\alpha(1-\alpha^2)^{1/2}[-3/10\sqrt{2}]a_{5p}\\
&= -1328.745(4)\text{ MHz}\ ,
\end{aligned} \tag{21c}$$

where the experimental results for Sn^{119} (from Table III) have been included on the right-hand side. Several features of Eqs. (21) should be noted. First, the hyperfine structure of the $^3P_1$ state should be precisely zero nonrelativistically and in the absence of core polarization ($C=0$), but is found experimentally to be large and positive. Second, the mixing coefficient α drops out if one forms the sum

$$\begin{aligned}
A(^3P_2)+A(^1D_2) &= A(^3P_2^{LS},\ ^3P_2^{LS})+A(^1D_2^{LS},\ ^1D_2^{LS})\\
&= \tfrac{8}{5}a_{5p}+\tfrac{1}{2}C=-2598.141(11)\text{ MHz}\ .
\end{aligned} \tag{22}$$

Hence a_{5p} and C can be evaluated independently of α from Eqs. (22) and (21a), with the result

$$a_{5p}=-1985\text{ MHz},\quad C=+1157\text{ MHz}\ . \tag{23}$$

Finally, the value of α may be found by combining the results of Eq. (23) with either Eq. (21b) or Eq. (21c), the result being

$$\alpha_{\text{hfs}}^{\text{nonrel}}=-0.472\ . \tag{24}$$

This value of α is seen to differ markedly from the value found from consideration of the fine-structure energies and from that found from the observed values of g_J. In addition, the value of a_{5p} is much larger than the value predicted by substituting the Hartree-Fock value[14] of $\langle r^{-3}\rangle_{5p}$ and the known value[12] $\mu_I(\text{Sn}^{119})=-1.046\mu_N$ into Eq. (16). The extremely large value found for C is also subject to question. It would appear that in permitting the three parameters a_{5p}, C, and α to vary freely to fit the observed values of $A(^3P_1)$, $A(^3P_2)$, and $A(^1D_2)$, the effects of relativity must be taken into account.

Before passing on to a discussion of the relativistic effects, it is of interest to ask what value would be predicted from the nonrelativistic theory for $A(^1D_2)$ from the previously known[4] values of $A(^3P_1)$ and $A(^3P_2)$. If the value $\alpha=-0.323$ obtained in Eq. (8) from the observed g_J values is used, one predicts $A(^1D_2)=-1859$ MHz, which is 40% larger than the experimental result -1329 MHz.

E. Relativistic Treatment of Hyperfine Structure

Breit and Wills[15] gave given the relativistic theory of the hyperfine structure of the p^2 configuration in terms of the natural jj-coupling scheme for the two electrons. More recently, Schwartz[16] has dealt in detail with relativistic effects in hyperfine structure. The theory has been summarized and applied to $\text{Pb}^{207}(6s^2 6p^2)$ by Lurio and Landman.[2]

It has been shown by Sandars and Beck[17] that hfs calculations can often be made more conveniently by using effective operators between nonrelativistic LS basis states, and this approach is used here. These authors have shown that all of the relativistic effects predicted by use of the classic jj-coupling scheme can be reproduced exactly if one uses the effective operator

$$\mathcal{H}_{\text{hfs}}=\sum_{i=1}^{N}[a^{01}\vec{l}_i-(\sqrt{10})a^{12}(\vec{s}\times\overleftrightarrow{C}^{(2)})_i^{(1)}+a^{10}\vec{s}_i]\cdot\vec{I}\ , \tag{25}$$

acting between the nonrelativistic LS basis states. This Hamiltonian replaces that of Eq. (12). In the absence of configuration interaction, the quantities

a^{01}, a^{12}, and a^{10} in this expression have the values

$$a^{01}=D(2l+1)^{-2}\left[2l(l+1)F_{++}+2l(l+1)F_{--}+F_{+-}\right]\,, \tag{26a}$$

$$a^{12}=\tfrac{1}{3}D(2l+1)^{-2}\left[-4l(l+1)(2l-1)F_{++}+4l(l+1)\times(2l+3)F_{--}-(2l+3)(2l-1)F_{+-}\right]\,, \tag{26b}$$

$$a^{10}=\tfrac{4}{3}Dl(l+1)(2l+1)^{-2}\left[(l+1)F_{++}-lF_{--}-F_{+-}\right]\,, \tag{26c}$$

in which $D=2\mu_B\mu_N\mu_I/I$, the signs + and − refer to the cases $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$, respectively, and the quantities

$$F_{jj'}=-2\left[\alpha a_0(K+K'+2)\right]^{-1}\int_0^\infty (PQ'+QP')r^{-2}\,dr \tag{27}$$

are the relativistic radial integrals required. Here a_0 is the Bohr radius; K and K' are associated with j and j' and are given by K, $K'=-(l+1)$ for j, $j'=l+\frac{1}{2}$ and by K, $K'=l$ for j, $j'=l-\frac{1}{2}$; and, in Eq. (27) only, α is the fine-structure constant instead of the mixing coefficient. In the integral, P is the large component of the relativistic radial wave function and Q the small component as discussed by Sandars and Beck.[17] It can be shown that in the nonrelativistic limit $F_{jj'}$ approaches $\langle r^{-3}\rangle_{nl}$ for all j, j' and consequently the quantity $DF_{jj'}=2\mu_B\mu_N(\mu_I/I)F_{jj'}$ approaches a_{nl} [defined in Eq. (16)] in the same limit. Examination of Eq. (26) shows that in the nonrelativistic limit,

$$a^{01}\to a_{nl}\,,\quad a^{12}\to a_{nl}\,,\quad a^{10}\to 0\,. \tag{28}$$

It is convenient to express the coefficients a^{01}, a^{12}, and a^{10} in terms of correction factors defined by

$$a^{01}=a_{nl}R^{01},\quad a^{12}=a_{nl}R^{12},\quad a^{10}=a_{nl}R^{10}, \tag{29}$$

in which a_{nl} retains its nonrelativistic definition, Eq. (16). Although the values required empirically for these parameters may, in principle, be distorted from the predictions of Eq. (26) by configuration interaction,[18] such effects are normally very small for a^{01} and a^{12}. As discussed in the nonrelativistic treatment in Sec. III D, however, any s admixture can lead to a substantial contribution to the hfs and must be explicitly taken into account by adding[13] the term $C\vec{I}\cdot\vec{S}$ [Eq. (17)] to the Hamiltonian of Eq. (25). Although this term has precisely the tensor character[7] of the final term of Eq. (25), it is nevertheless convenient to introduce it explicitly as in the nonrelativistic case, and to regard a^{10} as due solely to relativistic effects and as being given by Eq. (26c). With this interpretation, the extent of relativistic effects may be measured by noting the departure of R^{01}, R^{12}, and R^{10} from their nonrelativistic limits of 1, 1, and 0, respectively. Although C may be much larger than a^{10} and is independent of it, only the sum of the two can be determined experimentally; the relative size (and sign) of a^{10} and C must be obtained from theoretical considerations.

In calculating the hyperfine-structure constants A expected relativistically for the states ${}^3P_1$, ${}^3P_2$, and ${}^1D_2$, we use the eigenvector descriptions of Eqs. (1) and (2) and the definition of A implied by Eq. (13). We therefore retain Eqs. (19); but when we replace the nonrelativistic Hamiltonian of Eq. (12) by Eq. (25), we must modify Eq. (14) to contain a different a for each of the three terms. Thus we have

$$A(\psi,\psi')=A(\psi',\psi)=(2-g_J^*)\delta(\alpha SL,\alpha'S'L')a^{01}+\left[\frac{30(2J+1)l(l+1)(2l+1)}{J(J+1)(2l-1)(2l+3)}\right]^{1/2}\times\langle l^N\alpha SL\,\|V^{(12)}\|\,l^N\alpha'S'L'\rangle\times\begin{Bmatrix}S & S' & 1\\ L & L' & 2\\ J & J & 1\end{Bmatrix}a^{12}+(g_J^*-1)\delta(\alpha SL,\alpha'S'L')(a^{10}+C)\,, \tag{30}$$

where we have added the core-polarization term in C to take explicit account of possible s admixture, as in the nonrelativistic case.

The A factors for the required LS basis states may be evaluated from Eq. (30). The result is

$$\begin{aligned}
&A({}^3P_1^{LS},\,{}^3P_1^{LS})=\tfrac{1}{2}(R^{01}-R^{12}+R^{10})a_{5p}+\tfrac{1}{2}C\,,\\
&A({}^3P_2^{LS},\,{}^3P_2^{LS})=\tfrac{1}{2}(R^{01}+\tfrac{1}{5}R^{12}+R^{10})a_{5p}+\tfrac{1}{2}C\,,\\
&A({}^1D_2^{LS},\,{}^1D_2^{LS})=R^{01}a_{5p}\,,\\
&A({}^3P_2^{LS},\,{}^1D_2^{LS})=-\left[3/10\sqrt{2}\,\right]R^{12}a_{5p}\,.
\end{aligned} \tag{31}$$

These expressions, which reduce to those of Eq. (20) in the nonrelativistic limit, are given in terms of F_{++}, F_{--}, F_{+-}, and C in Eq. (50) in the Appendix. Finally, the relativistic equivalent of Eq. (21) for Sn^{119} may be written as

$$\begin{aligned}
A({}^3P_1)&=\tfrac{1}{2}(R^{01}-R^{12}+R^{10})a_{5p}+\tfrac{1}{2}C=+578.345(25)\ \text{MHz}\,,\\
A({}^3P_2)&=(1-\alpha^2)\left[\tfrac{1}{2}a_{5p}(R^{01}+\tfrac{1}{5}R^{12}+R^{10})+\tfrac{1}{2}C\right]+\alpha^2\left[R^{01}a_{5p}\right]+2\alpha(1-\alpha^2)^{1/2}\left[-(3/10\sqrt{2}\,)a_{5p}R^{12}\right]\\
&=-1269.396(10)\ \text{MHz}\,,
\end{aligned} \tag{32}$$

$$A(^1D_2)=\alpha^2\left[\tfrac{1}{2}a_{5p}(R^{01}+\tfrac{1}{5}R^{12}+R^{10})+\tfrac{1}{2}C\right]+(1-\alpha^2)[R^{01}a_{5p}]-2\alpha(1-\alpha^2)^{1/2}\left[-(3/10\sqrt{2})a_{5p}R^{12}\right]=-1328.745(4)\text{ MHz}\ .$$

Equation (32) could have been written in terms of F_{++}, F_{--}, and F_{+-} instead of R^{01}, R^{12}, and R^{10} by making use of Eqs. (26) and (29). Also $A(^3P_2)$ and $A(^1D_2)$ can be expressed in terms of ξ and the A values of the jj basis states of Eq. (5). Some of these expressions are given in the Appendix.

In comparing Eq. (32) with the nonrelativistic equivalent, Eq. (21), it is seen that instead of the three unknowns a_{5p}, C, and α of the nonrelativistic case, we now have five unknowns $R^{01}a_{5p}$, $R^{12}a_{5p}$, $R^{10}a_{5p}$, C, and α—but still only three equations. Two procedures are used to introduce additional constraints by approximating the relativistic integrals of Eq. (27): (a) the Casimir approximation and (b) the use of relativistic Hartree-Fock radial wave functions.

F. Casimir Approximation

For an atom with a known nuclear magnetic-dipole moment, theoretical prediction of the quantities a^{01}, a^{12}, and a^{10} is equivalent to evaluation of the integrals F_{++}, F_{--}, and F_{+-} as can be seen from Eq. (26). The Casimir approach[19] to evaluation of these integrals is to approximate the relativistic radial wave functions near the origin analytically with suitable Bessel functions, normalized to fit the observed fine-structure splitting, and then to carry out the integrals. The details have been summarized by several writers,[20] and it is sufficient here to give the pertinent results. The procedure usually followed is to express the integrals $DF_{jj'}$ in terms of the nonrelativistic limit a_{nl} by use of correction factors F_r and G_r (normally near unity). The expressions are

$$\begin{aligned}DF_{++}&=F_r(j=l+\tfrac{1}{2},\ Z_{\text{eff}})a_{nl}\ ,\\ DF_{--}&=F_r(j=l-\tfrac{1}{2},\ Z_{\text{eff}})a_{nl}\ ,\\ DF_{+-}&=G_r(l,\ Z_{\text{eff}})a_{nl}\ .\end{aligned}\qquad(33)$$

These "Casimir factors" have been tabulated by Kopfermann.[20] It has been found empirically that the best value to use for Z_{eff} is less than Z because of screening effects. The value used depends on l, and is commonly taken[21] to be $Z-4$ for p electrons. When this is done, the results are $F_r(p_{3/2},\ \text{Sn})=1.0458$, $F_r(p_{1/2},\ \text{Sn})=1.2493$, and $G_r(p,\ \text{Sn})=1.0511$. These can be used in Eqs. (26) and (29) to give $R^{01}=1.1368$, $R^{12}=1.3463$, and $R^{10}=-0.0619$ for the p electrons of Sn.

If these numerical values are put into Eq. (31), it is found that

$$A(^3P_1^{LS},\ ^3P_1^{LS})=-0.1357a_{5p}+\tfrac{1}{2}C\ ,\qquad(34\text{a})$$

$$A(^3P_2^{LS},\ ^3P_2^{LS})=+0.6721a_{5p}+\tfrac{1}{2}C\ ,\qquad(34\text{b})$$

$$A(^1D_2^{LS},\ ^1D_2^{LS})=+1.1368a_{5p}\ ,\qquad(34\text{c})$$

$$A(^3P_2^{LS},\ ^1D_2^{LS})=+1.3463\left[-3/10\sqrt{2}\right]a_{5p}\ .\qquad(34\text{d})$$

In comparing these results with the nonrelativistic equivalent [Eq. (20)], the most striking difference is the appearence of the new term $-0.1357a_{5p}$ in the hfs constant for the $^3P_1$ state. Thus, even in the absence of core polarization, relativity predicts hfs for the $^3P_1$ state, while the nonrelativistic theory predicts none at all. Perhaps the next most striking change produced by relativity is the 34% increase in the strength of the cross term given by Eq. (34d).

With these results, Eqs. (32) are reduced to three equations in three unknowns (a_{5p}, C, and α) as in the nonrelativistic treatment. The solution for a_{5p} and C is again independent of α, as was shown in the nonrelativistic treatment above. The results for Sn^{119} are

$$a_{5p}=-1634\text{ MHz}\ ,\quad C=+714\text{ MHz}\ ,\quad \alpha=-0.405\ .\qquad(35)$$

These results appear considerably more reasonable than do those of Eqs. (23) and (24), which were obtained nonrelativistically. The magnitude $|a_{5p}|=1634$ MHz, though still larger than the Hartree-Fock estimate,[14] is 18% smaller than that obtained nonrelativistically. The quantity C, which measures the amount of core polarization which must be invoked to account for the observed hfs, has dropped 38%. Most impressive, perhaps, is the fact that the value required for α has moved 45% of the way from the nonrelativistic value -0.472 toward the (presumably more physical) value -0.323 obtained from the Zeeman effect. There is still, however, considerable room for improvement. It is indeed disappointing to find that the value of α obtained from the hfs is still about 25% larger than the mutually consistent values found from the energy splitting and the Zeeman effect.

Another method of assessing the validity of the relativistic treatment using the Casimir correction factors is to use the previously known[4] values of $A(^3P_1)$ and $A(^3P_2)$, together with the Zeeman result $\alpha=-0.323$, to predict the A value of the $^1D_2$ state. In this way, it is predicted that $A(^1D_2)=-1571$ MHz, while the value observed in the present experiment is -1329 MHz. Although the prediction is off by 18%, it is 46% closer to the observed value than was the nonrelativistic prediction given above.

G. Use of Relativistic Hartree-Fock Radial Wave Functions

With the advent of modern high-speed digital computers, it is no longer necessary to rely on analytic approximations to the relativistic radial wave functions. Mann[22] has recently calculated relativistic Hartree-Fock radial wave functions for the $5p$ electrons of Sn in each of the configurations $5p_{1/2}5p_{1/2}$, $5p_{1/2}5p_{3/2}$, and $5p_{3/2}5p_{3/2}$. It can be seen from Eq. (5) that only the last two sets are required for the states of interest. From these wave functions, the value of F_{++} was calculated for each of the configurations $5p_{1/2}5p_{3/2}$ and $5p_{3/2}5p_{3/2}$ and found to be the same to within about 0.5%. The $5p_{1/2}5p_{3/2}$ configuration was then used to obtain the values[22]

$$F_{++}=6.778a_0^{-3}\ ,\qquad F_{--}=9.117a_0^{-3}\ ,\qquad F_{+-}=7.408a_0^{-3}\ . \tag{36}$$

[If one uses Mann's[14] nonrelativistic Hartree-Fock result $\langle r^{-3}\rangle_{5p}=6.747a_0^{-3}$, it follows that the equivalents of the Casimir correction factors (which are just $F_{jj'}/\langle r^{-3}\rangle nl$) are $F_r(p_{3/2},\ \mathrm{Sn})=1.005$, $F_r(p_{1/2},\ \mathrm{Sn})=1.351$, and $G_r(p,\ \mathrm{Sn})=1.098$. These may be compared with the Casimir[20] values 1.0458, 1.2493, and 1.0511, respectively.]

When the results of Eqs. (36) and the known value[12] of the dipole moment of Sn^{119} are used in Eq. (26), the results are

$$a^{01}=-1574\ \mathrm{MHz}=a_{5p}R^{01}\ ,\qquad a^{12}=-2021\ \mathrm{MHz}=a_{5p}R^{12}\ ,\qquad a^{10}=+176\ \mathrm{MHz}=a_{5p}R^{10}\ . \tag{37}$$

If these three values are used in Eq. (32), it is seen that the two remaining unknowns (C and α) are overdetermined by the three measured A values. Indeed, no values of C and α can be found which allow Eq. (37) to satisfy Eq. (32). In view of this, it was decided to relax one constraint by allowing the *relative* sizes of a^{01}, a^{12}, and a^{10} to be given by the calculated integrals as in Eqs. (36) and (37), but to allow a single free scaling factor for all three a's.

Thus, from Eq. (37) we find

$$R^{12}=1.284R^{01},\quad R^{10}=-0.112R^{01}\ . \tag{38}$$

When these values are put into Eq. (32), we now have three equations in the three unknowns $R^{01}a_{5p}$, C, and α. The solution for the first two is again independent of α, and we obtain

$$a^{01}=R^{01}a_{5p}=-1795\ \mathrm{MHz}\ ,\qquad C=+447\ \mathrm{MHz}\ ,\quad \alpha=-0.366\ . \tag{39}$$

While the relativistic theory says nothing about a_{5p}, a nonrelativistic quantity, Mann's nonrelativistic Hartree-Fock result[14] $\langle r^{-3}\rangle_{5p}=6.747a_0^{-3}$ for Sn may be used in Eq. (37) to obtain

$$R^{01}=1.169\ ,\quad R^{12}=1.501\ ,\quad R^{10}=-0.130\ , \tag{40}$$

which may be compared with the corresponding numbers obtained with the Casimir procedure, namely, 1.1368, 1.3463, and −0.0619, respectively. On using the result $R^{01}=1.169$ we find that the value of a_{5p} required to fit the observed hfs is

$$a_{5p}=-1535\ \mathrm{MHz}\ . \tag{41}$$

It may be noted from Eqs. (29), (40), and (41) that the value required for the relativistic contact parameter a^{10} is +201 MHz. This is by no means negligible in comparison with the core-polarization parameter $C=+447$ MHz in Eq. (39).

The results just obtained for a_{5p}, C, and α are presented in Table VI, along with the corresponding values obtained both in the nonrelativistic limit and by the use of the Casimir factors. The column at the right, labeled "experimental," needs a word of explanation. The value given for α is that obtained from measurement of the g_J values (Zeeman effect), since this method of determining α appears to be the least susceptible to such distortions as configuration interaction. The value given in the table for $A(^1D_2)$ is indeed the experimental result, and the "experimental" value given for R^{12}/R^{01} will be discussed in Sec. III H.

It can be seen that the value obtained for α from the relativistic Hartree-Fock treatment is indeed considerably closer to the "experimental" value than is the value obtained with Casimir factors. It may also be noted that the amount of core polariza-

TABLE VI. Comparison of the results of treating the observed Sn^{119} hfs (a) nonrelativistically, (b) relativistically, with Casimir correction factors, and (c) with relativistic Hartree-Fock wave functions. Use of the relativistic Hartree-Fock wave functions leads to values of α (the $^3P_2$-$^1D_2$ mixing coefficient), $A(^1D_2)$, and a^{12}/a^{01} which are considerably closer to experiment than are those obtained either nonrelativistically or with the Casimir correction factors.

Quantity[a]	Nonrelativistic	Casimir approximation	Relativistic Hartree-Fock	"Experimental"
α	−0.472	−0.405	−0.366	−0.323
a_{5p} (MHz)	−1985	−1634	−1535	
C (MHz)	+1157	+714	+447	
$A(^1D_2)$ (MHz)	−1859	−1571	−1446	−1329
R^{12}/R^{01}	1	1.184	1.284	1.399

[a] The values of α, a_{5p}, and C are those that fit the measured values of A for all three states. The values of $A(^1D_2)$ are predictions based on fitting the A's and g_J's of the $^3P_1$ and $^3P_2$ states. The ratios R^{12}/R^{01} are predicted.

tion (measured by the value of C) required is much smaller than for the other treatments. The true value cannot be determined with assurance because it is indistinguishable experimentally from a^{10}. The value found for $R^{01}a_{5p}$, as given in Eqs. (39), is also smaller and is in fact only 14% larger than the Hartree-Fock value as given in Eqs. (37). Finally, if the value expected for $A(^1D_2)$ is predicted on the basis of the relativistic Hartree-Fock treatment, by making use of the previously measured[4] values of $A(^3P_1)$ and $A(^3P_2)$ and the Zeeman value $\alpha = -0.323$, one obtains $A(^1D_2) = -1446$ MHz. This is within 9% of the experimental result.

H. Value of R^{12}/R^{01}

The basic equations which describe the hfs constants of interest are Eqs. (32). If one requires that $\alpha = -0.323$ as required to fit the known $J = 2$ energy splitting and the observed g_J values, and if it is further noted that $R^{10}a_{5p} + C$ may be replaced by a single parameter, the three equations (32) involve only three unknowns, $a_{5p}R^{01}$, $a_{5p}R^{12}$, and $a_{5p}R^{10} + C$. The solution is

$$a^{01} = R^{01}a_{5p} = -1727 \text{ MHz} , \tag{42a}$$

$$a^{12} = R^{12}a_{5p} = -2416 \text{ MHz} , \tag{42b}$$

$$a^{10} + C = R^{10}a_{5p} + C = +468 \text{ MHz} . \tag{42c}$$

By dividing Eq. (42a) by (42b), we see that to fit the energy splitting, g_J values, and hfs simultaneously, we must have

$$R^{12}/R^{01} = 1.3986 . \tag{43}$$

This is called the "experimental" value of the ratio. The experimental value may be compared with the theoretical values: (a) the nonrelativistic value 1, (b) the Casimir value 1.184, and (c) the relativistic Hartree-Fock result 1.284. Again, the relativistic Hartree-Fock wave functions appear to give much more realistic results than does the use of the Casimir correction factors; both procedures are a great improvement over the nonrelativistic treatment—as expected.

J. Further Examination of Configuration-Interaction Effects

It was pointed out in Sec. III A that the importance of configuration interaction for the states of the $5s^25p^2$ configuration of Sn I should be very small because of the high degree of isolation of the levels Therefore, both in Eq. (1), which defines the mixing coefficient α, and in Eq. (2), it was explicitly assumed that the only impurities in the $5s^25p^2$ eigenvectors are due to other states of the same configuration. The comparison (Sec. III B) of the theoretical and experimental g_J values gives good support for this assumption. Excitation energies are considerably more sensitive to configuration interaction than are g values, however, and no values of the Slater integrals F_0 and F_2 and the spin-orbit constant ζ_{5p} for the $5s^25p^2$ configuration can be found[1,3] which will satisfy the precisely known energy separations to better than about 2% if configuration interaction is ignored; the experimental uncertainties are very much smaller.

It is known[18] that to first approximation the effects of configuration interaction on the hfs can be taken into account by treating the radial integrals as parameters, free to vary to permit a fit to the observed A values. While this procedure allows better fits to the experimental results, it may lead to distorted values for such quantities as a_{5p} and α. Thus, the difference between the value $\alpha = -0.366$ found from experiment by use of relativistic Hartree-Fock radial wave functions and the value $\alpha = -0.323$ found by consideration of the energy splitting and Zeeman effect might be due to distortions of configuration interaction.

The lowest-order effects of configuration interaction on the $5s^25p^2$ eigenvectors of interest may be considered by letting

$$\begin{aligned}
|^3P_2\rangle &= (1 - \alpha_P^2 - \textstyle\sum_i \lambda_i^2)^{1/2} |5s^25p^2\ {}^3P_2^{LS}\rangle \\
&\quad + \alpha_P |5s^25p^2\ {}^1D_2^{LS}\rangle + \textstyle\sum_i \lambda_i |(\text{config})_i\ {}^3P_2^{LS}\rangle , \\
|^1D_2\rangle &= (1 - \alpha_D^2 - \textstyle\sum_i \mu_i^2)^{1/2} |5s^25p^2\ {}^1D_2^{LS}\rangle \\
&\quad - \alpha_D |5s^25p^2\ {}^3P_2^{LS}\rangle + \textstyle\sum_i \mu_i |(\text{config})_i\ {}^1D_2^{LS}\rangle , \qquad (44) \\
|^3P_1\rangle &= (1 - \textstyle\sum_i \lambda_i^2)^{1/2} |5s^25p^2\ {}^3P_1^{LS}\rangle \\
&\quad + \textstyle\sum_i \lambda_i |(\text{config})_i\ {}^3P_1^{LS}\rangle ,
\end{aligned}$$

in which cross-configuration mixing that is off-diagonal in L and S is ignored as likely to be much smaller than the diagonal mixing. The configuration-mixing coefficients λ_i and μ_i obtained from first-order perturbation theory are

$$\begin{aligned}
\lambda_i &= \frac{\langle 5s^25p^2\ {}^3P^{LS} \| H_{\text{NC}} \| (\text{config})_i\ {}^3P^{LS}\rangle}{E(5s^25p^2\ {}^3P_J) - E((\text{config})_i\ {}^3P_J)} , \\
\mu_i &= \frac{\langle 5s^25p^2\ {}^1D^{LS} \| H_{\text{NC}} \| (\text{config})_i\ {}^1D^{LS}\rangle}{E(5s^25p^2\ {}^1D_2) - E((\text{config})_i\ {}^1D_2)} ,
\end{aligned} \tag{45}$$

where H_{NC} is the noncentral part of the Coulomb interaction.

In Eq. (44), the sum over i omits the configuration $5s^25p^2$, which is considered explicitly. The values of $\sum_i \lambda_i^2$ and $\sum_i \mu_i^2$ are likely to be very small, probably not more than 1–2%, since (a) the excitation energies of the $5s^25p^2$ levels can be fitted to within about 2% without invoking configuration interaction at all, and (b) the value found for α from the $J=2$ energy splitting agrees to within 1% with that found from the g values.

From Eq. (44) and the measured g_J values, it follows that $\alpha_P=\alpha_D=-0.323$ as before. Thus, as mentioned above, configuration interaction does not affect the g_J values in lowest order.

In order to calculate the effects of configuration interaction on the energy separations or the hyperfine structure, it is necessary to consider each perturbing configuration individually. Morrison[23] has pointed out that the largest cross-configuration admixtures (except for core polarization, for which the effects on the hfs have already been considered) will very likely be from the $5p^4$ configuration because the principal quantum numbers are the same as for $5s^2 5p^2$ and consequently the radial integrals in λ and μ may be relatively large. The change in the $J=2$ energy splitting is given by

$$\delta E(^1D_2)-\delta E(^3P_2)$$
$$=\frac{|\langle 5s^2 5p^2\ {}^1D^{LS}\,\|\sum e^2/r_{ij}\,\|\,5p^4\ {}^1D^{LS}\rangle|^2}{E(5s^2 5p^2\ {}^1D_2)-E(5p^4\ {}^1D_2)}-\frac{|\langle 5s^2 5p^2\ {}^3P^{LS}\,\|\sum e^2/r_{ij}\,\|\,5p^4\ {}^3P^{LS}\rangle|^2}{E(5s^2 5p^2\ {}^3P_2)-E(5p^4\ {}^3P_2)}\ . \qquad (46)$$

Morrison[23] has shown that the matrix elements in Eq. (46) [and consequently those of Eq. (45) for the case in which the configuration labeled i is $5p^4$] have the same value. The energy denominators are on the order of 80 000 cm^{-1} and probably differ by a few thousand cm^{-1}, so that λ and μ for the admixture of $5p^4$ into $5s^2 5p^2$ are probably the same to within a few percent, and the change in the $J=2$ energy splitting is most likely much smaller. The actual shifts in excitation energy caused by configuration interaction probably arise from many configurations rather than from a few dominant ones.

In calculating the hfs A values expected for the eigenvectors of Eq. (44) for the case in which only the one perturbing configuration $i=5p^4$ is considered, we first note that the cross terms of the hfs operator between the two configurations vanish because the hfs Hamiltonian is a single-particle operator. The A values for the LS basis states of $5p^4$ differ from those of $5s^2 5p^2$ only by an over-all radial scaling factor. This may be seen by consideration of the angular parts of the three operators of the dipole Hamiltonian of Eq. (25) separately. The angular part of the $\vec{I}\cdot\vec{L}$ and $\vec{I}\cdot\vec{S}$ contributions to A (i.e., the first and third terms of the Hamiltonian) depend only on $2-g_J^*$ and g_J^*-1, respectively, and are therefore identical for p^2 and p^4. The corresponding contribution of the middle term to A is also unchanged since p^4 is conjugate to p^2 and

$$\langle p^2\alpha SL\,\|\,V^{(12)}\,\|\,p^2\alpha' S'L'\rangle$$
$$=+\langle p^4\alpha SL\,\|\,V^{(12)}\,\|\,p^4\alpha' S'L'\rangle\ .$$

With these considerations and the knowledge that $\lambda\approx\mu$, as shown by Morrison, it can be shown that as μ is allowed to increase from zero, the magnitude of α required to fit the observed A values departs still further from those found in Eqs. (24), (35), and (39) for $\mu=0$.

It would therefore appear that the difference between the value $\alpha=-0.366$ found by using the relativistic Hartree-Fock radial wave functions and the presumably more physical value $\alpha=-0.323$ found from the Zeeman effect does not arise primarily from interaction between the $5s^2 5p^2$ and $5p^4$ configurations. It may well be, however, that the cumulative effect of configuration interaction with many configurations is responsible for the difference.

K. Perturbation of g_J Values and hfs Constants by Other Atomic States

It is well known that each hyperfine level in one atomic state may be perturbed by hyperfine interactions with levels of the same F in other states. Since levels of different F are perturbed by different amounts, the observed size of the zero-field separations $\Delta\nu$, and consequently of the A values inferred from them, is affected by these second-order effects. Suitable corrections should be made before the measured A values are compared with theoretical predictions in which such effects are ignored.

The situation is further complicated when observations are made in nonzero magnetic field, since the Zeeman operator can produce similar perturbations which may be coherent with the hfs perturbations and therefore cannot be considered independently. For a magnetic substate $\mathfrak{F}$, M of the state Ψ, the energy shift due to perturbations caused by other atomic states Ψ' may be expressed[24] at arbitrary field H by the relation

$$\delta E(\Psi, I\mathfrak{F}M)\approx\sum_{\Psi'\neq\Psi}\sum_{F'}\frac{|\langle\Psi, I\mathfrak{F}M\,|\,\mathcal{H}\,|\,\Psi', IF'M\rangle|^2}{E(\Psi)-E(\Psi')}\ , \qquad (47)$$

in which the nuclear spin I is $\frac{1}{2}$ for Sn^{117,119}, and $\mathfrak{F}$, M represents the particular combination of zero-field basis states F, M for the real state at the field H. The Hamiltonian in Eq. (47) is

$$\mathcal{H}=\mathcal{H}_{\mathrm{hfs}}+\mathcal{H}_z\ , \qquad (48)$$

where $\mathcal{H}_{\mathrm{hfs}}$ is the hyperfine Hamiltonian defined in Eq. (25) and $\mathcal{H}_z$ is the electronic Zeeman operator

$$\mathcal{H}_z=\mu_B\vec{H}\cdot(\vec{L}+2\vec{S})\ . \qquad (49)$$

TABLE VII. Shifts in $\Delta\nu$ and A as a result of hfs interactions with other atomic states in Sn^{119}. They were calculated for three sets of parameter values: (a) the nonrelativistic set, (b) the relativistic set, with Casimir correction factors, and (c) the set obtained by using relativistic Hartree-Fock wave functions.

Calculation	Parameter values used	Calculated shift in $\Delta\nu$ (MHz)	Resulting shift in inferred A value (MHz)
Nonrelativistic	$\alpha = -0.472$	$-0.174(^3P_1)$	$+0.116(^3P_1)$
	$a_{5p} = -1985$ MHz	$+0.125(^3P_2)$	$+0.050(^3P_2)$
	$C = +1157$ MHz		
Casimir approximation	$\alpha = -0.405$	$-0.100(^3P_1)$	$+0.067(^3P_1)$
	$a_{5p} = -1634$ MHz	$+0.074(^3P_2)$	$+0.030(^3P_2)$
	$C = +714$ MHz	$+0.005(^1D_2)$	$+0.002(^1D_2)$
Relativistic Hartree-Fock	$\alpha = -0.366$	$-0.074(^3P_1)$	$+0.049(^3P_1)$
	$a_{5p} = -1535$ MHz	$+0.057(^3P_2)$	$+0.023(^3P_2)$
	$C = +447$ MHz	$+0.004(^1D_2)$	$+0.002(^1D_2)$

The energy shifts may be calculated even for states far removed from the LS limit by using the intermediate-coupling eigenvectors for Ψ and Ψ' explicitly in Eq. (47).

Although the calculation of shifts according to Eq. (47) has been automated, there remains the problem of what numerical values to use for the parameters a^{01}, a^{12}, and C in the Hamiltonian, and for α in the eigenvector. It has been shown above that for Sn^{119}, the three observed A values (those for $^3P_2$, $^3P_1$, and $^1D_2$) may be fitted by a variety of choices of the parameter values. Because of this amibguity, the corrections to the $\Delta\nu$'s and A's were calculated separately for each of the sets of values of a_{5p}, C, and α, i.e., for (i) the nonrelativistic set given in Eqs. (23) and (24), (ii) the "Casimir" set given in Eq. (35), and (iii) the relativistic Hartree-Fock set given in Eqs. (39) and (41). The results are shown in Table VII. Although the values calculated from the relativistic Hartree-Fock set (at the bottom of the table) are probably the most realistic, the uncertainty assigned to each correction is chosen to be large enough to overlap that calculated with the Casimir set. The major source of uncertainty in the corrected values of $A(^3P_1)$ and $A(^3P_2)$ is the uncertainty in the correction. The corrections for the isotopes $\mathrm{Sn}^{115,117}$ are scaled from those for Sn^{119} in proportion to $(\mu_I/I)^2$. For the relativistic Hartree-Fock parameter set, Table VIII gives a breakdown of the contributions to $\Delta\nu(\mathrm{Sn}^{119})$ from the different states of the $5s^25p^2$ configuration. Contributions from higher states were ignored.

IV. COMPARISON OF RESULTS FOR Sn WITH THOSE FOR OTHER GROUP-IV NEUTRAL ATOMS

The lowest-lying configuration of the group-IV neutral atoms C, Si, Ge, Sn, and Pb is ns^2np^2, with $n = 2$, 3, 4, 5, and 6, respectively, and it is interesting to compare the present results for Sn with corresponding results for other atoms of the series. The value of α, as determined from the $J = 2$ energy splitting, is about -0.002 for C and -0.017 for Si, and the LS limit is clearly an extremely good approximation. The situation for Ge, Sn, and Pb is compared in Table IX. In Ge, as in Sn, the value of α deduced from the $J = 2$ splitting is in excellent agreement with that found from the g_J values.[3] The 4% difference in the corresponding values[25] for Pb probably reflects the increased importance of configuration mixing. Deduction of α for Pb^{207} from the hfs[2] must certainly be done relativistically, and a treatment using Casimir factors, though much better than the nonrelativistic treatment, still gives a result 46% larger than that found from the g_J values. No value has been obtained with relativistic Hartree-Fock wave functions, but it would presumably lie closer to that found from the g values.

V. CONCLUSIONS

It has been demonstrated that the $5s^25p^2$ configuration in Sn I appears to be well isolated to a high order. The excitation energies and g_J values may be accounted for to within about 2% without invoking configuration interaction. Although the coefficient that describes the mixing between the $^3P_2$ and $^1D_2$ states appears 46% too large when deter-

TABLE VIII. Breakdown of the calculated shifts of the $\Delta\nu$'s of Sn^{119} into contributions from each state of $5s^25p^2$ separately. The calculations were made with the relativistic Hartree-Fock parameter set ($\alpha = -0.366$, $a_{5p} = -1535$ MHz, and $C = +447$ MHz). As expected, the $^1D_2 \longleftrightarrow {}^3P_{1,2}$ interactions are much smaller than those for $^3P_J \longleftrightarrow {}^3P_{J'}$.

State in which $\Delta\nu$ is observed	Perturbing state	Perturbation of $\Delta\nu$ (MHz)	Total change in $\Delta\nu$ (MHz)
$^3P_1$	$^3P_0$	-0.014	
	$^3P_2$	-0.059	
	$^1D_2$	-0.001	
	$^1S_0$	0.000	-0.074
$^3P_2$	$^3P_0$	0.000	
	$^3P_1$	$+0.059$	
	$^1D_2$	-0.002	
	$^1S_0$	0.000	$+0.057$
$^1D_2$	$^3P_0$	0.000	
	$^3P_1$	$+0.001$	
	$^3P_2$	$+0.002$	
	$^1S_0$	0.000	$+0.004$

TABLE IX. Comparison of the value of the $^3P_2$-$^1D_2$ mixing coefficient α for the group-IV ns^2np^2 atoms C, Si, Ge, Sn, and Pb. Both C and Si are virtually nonrelativistic LS-limit atoms with $\alpha = -0.002$ and -0.017, respectively. For Pb^{207}, a jj atom, the hfs is highly relativistic, and the effects of configuration interaction are evident. Although the Sn atom falls between these extremes, relativistic effects are of great importance in understanding the hyperfine structure.

	Ge $4s^24p^2$	Sn $5s^25p^2$	Pb $6s^26p^2$
LS purity (%)	99	90	55
α_{energy}	-0.111	-0.320	-0.646
α_{g_J}	-0.114	-0.323	-0.672
α_{hfs}			
Nonrelativistic		-0.472	$+0.941$
Relativistic, with Casimir approx.		-0.405	-0.978
Relativistic Hartree-Fock		-0.366	

mined by a nonrelativistic treatment of the observed hyperfine structure, the difference drops to 13% when relativistic Hartree-Fock radial wave functions are used. It is not clear whether the remaining discrepancy is due to slight deficiencies in the relativistic wave functions or to the cumulative effect of configuration interaction with many configurations.

ACKNOWLEDGMENTS

The author would like to acknowledge many helpful discussions with L. S. Goodman, and to thank J. Morrison for establishing the equality of the matrix elements appearing in Eq. (46) and J. B. Mann for making available his unpublished relativistic Hartree-Fock wave functions. The use of these wave functions made possible a much more meaningful comparison of the experiment with the theory.

APPENDIX

Many of the hfs equations in the text could have been expressed in other forms because of (a) the equivalence of the LS and jj schemes for calculation and (b) the correspondence between (F_{++}, F_{--}, F_{+-}) and $(a^{01}/D, a^{12}/D, a^{10}/D)$ given in Eq. (26). Thus, Eqs. (31) giving the A values of the LS basis states could have been expressed as

$$A(^3P_1^{LS}, {}^3P_1^{LS}) = \tfrac{2}{3}D[F_{++} - F_{--}] + \tfrac{1}{2}C\,,$$

$$A(^3P_2^{LS}, {}^3P_2^{LS}) = \tfrac{1}{45}D[22F_{++} + 10F_{--} - 5F_{+-}] + \tfrac{1}{2}C\,,$$

$$A(^1D_2^{LS}, {}^1D_2^{LS}) = \tfrac{1}{9}D[4F_{++} + 4F_{--} + F_{+-}]\,, \tag{50}$$

$$A(^3P_2^{LS}, {}^1D_2^{LS}) = (\tfrac{1}{90}D/\sqrt{2})[8F_{++} - 40F_{--} + 5F_{+-}].$$

Thus Eq. (32), which give the A values as calculated in the LS scheme in terms of the correction factors R^{01}, R^{12}, and R^{10}, could have been written in terms of F_{++}, F_{--}, and F_{+-} if Eq. (50) had been used instead of Eq. (31).

The equations for the A values of the jj basis states are

$$\begin{aligned}
A(p_{1/2}p_{3/2}, 1; p_{1/2}p_{3/2}, 1) &= \tfrac{1}{2}(R^{01} - R^{12} + R^{10})a_{5p} + \tfrac{1}{2}C \\
&= \tfrac{2}{3}D(F_{++} - F_{--}) + \tfrac{1}{2}C\,, \\
A(p_{1/2}p_{3/2}, 2; p_{1/2}p_{3/2}, 2) &= \tfrac{1}{6}(5R^{01} + \tfrac{7}{5}R^{12} + R^{10})a_{5p} + \tfrac{1}{6}C \\
&= \tfrac{2}{15}D(3F_{++} + 5F_{--}) + \tfrac{1}{6}C\,, \\
A(p_{3/2}p_{3/2}, 2; p_{3/2}p_{3/2}, 2) &= \tfrac{2}{3}(R^{01} - \tfrac{1}{5}R^{12} + \tfrac{1}{2}R^{10})a_{5p} + \tfrac{1}{3}C \\
&= \tfrac{8}{15}DF_{++} + \tfrac{1}{3}C\,, \\
A(p_{1/2}p_{3/2}, 2; p_{3/2}p_{3/2}, 2) &= (\tfrac{1}{6}\sqrt{2})(R^{01} - \tfrac{1}{2}R^{12} - R^{10})a_{5p} - (\tfrac{1}{6}\sqrt{2})C \\
&= (\tfrac{1}{12}\sqrt{2})DF_{+-} - (\tfrac{1}{6}\sqrt{2})C\,.
\end{aligned} \tag{51}$$

The A values of the real states may be calculated in the jj scheme, and either set of radial integrals may be used. Thus by combining Eqs. (5), (13), and (51) we may write the equivalent of Eqs. (32) in the jj scheme as

$$\begin{aligned}
A(^3P_1) &= \tfrac{2}{3}D(F_{++} - F_{--}) + \tfrac{1}{2}C = +578.345(25)\ \text{MHz}, \\
A(^3P_2) &= \xi^2[(\tfrac{2}{15}D)(3F_{++} + 5F_{--}) + \tfrac{1}{6}C] + (1 - \xi^2)[\tfrac{8}{15}DF_{++} + \tfrac{1}{3}C] - 2\xi(1 - \xi^2)^{1/2}[(\tfrac{1}{12}\sqrt{2})DF_{+-} - (\tfrac{1}{6}\sqrt{2})C] \\
&= -1269.396(10)\ \text{MHz}\,, \\
A(^1D_2) &= (1 - \xi^2)[(\tfrac{2}{15}D)(3F_{++} + 5F_{--}) + \tfrac{1}{6}C] + \xi^2[\tfrac{8}{15}DF_{++} + \tfrac{1}{3}C] + 2\xi(1 - \xi^2)^{1/2}[(\tfrac{1}{12}\sqrt{2})DF_{+-} - (\tfrac{1}{6}\sqrt{2})C] \\
&= -1328.745(4)\ \text{MHz}\,.
\end{aligned} \tag{52}$$

These expressions contain five unknowns (DF_{++}, DF_{--}, DF_{+-}, C, and ξ) just as do Eqs. (32), and two additional constraints must be imposed as was done in Secs. III F and III G. If the ratios F_{--}/F_{++} and F_{+-}/F_{++} are assumed to be given correctly by Eqs. (36), for example, the values found for a^{01} and C are those of Eqs. (39), and in addition we find

$$\xi = -0.836 ,$$

from which, by Eqs. (6), we have $\alpha = -0.366$ as in Eqs. (39). Thus, the two calculational schemes, though entirely different, lead to identical results as expected.

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†Work performed under the auspices of the U. S. Atomic Energy Commission.

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