of this report, calculations of these wave functions using better approximations will be attempted when, shortly, a more powerful computer becomes available. In the case of ytterbium, at least, it will then be possible to determine with considerable accuracy the magnitudes of the relativistic and exchange effects. Further, it becomes possible to study in some detail certain fairly simple transformations which when applied to the corresponding hydrogen-like wave functions produce remarkably good approximations to the self-consistent field (SCF) functions.

The calculations reported on in this paper were carried out on a Burroughs 220 10K computer equipped with card input and output for data handling, and an IBM 407 for printed output. In addition, two magnetic tape units were required to accommodate the ALGOL compiler. Compile and running times for a typical iteration on 13 subshells total a little under three hours.

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# Hyperfine-Structure Measurements on Silver-105<sup>†</sup>

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The hyperfine-structure separation in the  ${}^{2}S_{1/2}$  electronic ground state of Ag<sup>105</sup> (40 day;  $I = \frac{1}{2}$ ) has been measured by atomic-beam methods. The result is  $\Delta \nu = 1529.057(20)$  Mc/sec, assuming either a positive or a negative nuclear moment. Combining this measurement with the known constants of Ag<sup>107</sup> gives a nuclear magnetic moment of magnitude  $|\mu_I|_{\text{uncorrected}} = 0.1009(10)$  nuclear magneton.

## I. INTRODUCTION

TOMIC-BEAM measurements on the "fieldindependent"  $\Delta F = 1$  hyperfine transition have given a new precision to the measured value of the hyperfine-structure (hfs) separation of 40-day Ag<sup>105</sup>. Preliminary work was done at several fields up to about 380 G, using the  $\Delta F = 0$  "standard transition." When the hfs separation was known well enough, a search for direct  $(\Delta F = 1)$  transitions was made successfully. Both  $\Delta F = 1$  lines were measured at low fields.

## II. THEORY OF THE EXPERIMENT

The theory of atomic-beam magnetic-resonance experiments has been developed in some detail since the method was introduced by Rabi.<sup>1</sup> Measurements of transition frequencies between pairs of hyperfine sublevels as split by a known magnetic field lead directly to a calculated value of the zero-field hfs separation. The hfs splitting, in turn, is a measure of the strength of the interaction between the electromagnetic moments of the nucleus and the electrons. If the electronic moments are known, the nuclear moments can be calculated. The results can then be compared with the predictions of various nuclear models.

For the alkali and alkali-like elements of Column I in the periodic table, the electronic ground state is  ${}^{2}S_{1/2}$ . The only electron-nuclear interaction is then the contact

interaction between the magnetic moments of the single-valence electron and the nucleus. The behavior of such a coupled spin system when a magnetic field is applied has been described by Breit and Rabi.<sup>2</sup> At low fields the two spins are tightly coupled and their resultants  $F = I \pm \frac{1}{2}$  behave like single dipoles, whose magnetic sublevels are split linearly by the field. At higher fields, the two spins are gradually decoupled until their magnetic splittings are virtually independent. The Breit-Rabi equation is an analytic description of this field behavior when  $J=\frac{1}{2}$ . If the nuclear moment  $\mu_I = g_I \mu_0 I$  and the electronic moment  $\mu_J = g_J \mu_0 J$  (where  $\mu_0$  is the magnitude of the Bohr magneton), then the energy of a magnetic sublevel is given by

$$\frac{W(H)}{h} = \frac{-\Delta\nu}{4(I+\frac{1}{2})} - g_I \frac{\mu_0}{h} Hm$$
  
with  $\pm \frac{1}{2} [(\Delta\nu)^2 + 2(\Delta\nu)\rho f + f^2]^{1/2},$  (1)

$$f = (-g_J + g_I)(\mu_0/h)H$$
 and  $\rho = m/F_{\text{max}} = \frac{m}{I + \frac{1}{2}}$ 

where  $h\Delta\nu = W_{I+1/2}(0) - W_{I-1/2}(0)$  is the zero-field hfs splitting between the two levels for  $F = I \pm \frac{1}{2}$  and f is a field parameter. The sign of the root is chosen positive or negative, respectively, depending on whether the level belongs to the group having larger or smaller F. Figure 1 illustrates this field dependence of the hyperfine sublevels for an isotope with  $I=\frac{1}{2}$  and a negative nuclear moment. (The assumption of a negative nuclear moment is proper for the stable silver isotopes Ag<sup>107</sup> and Ag<sup>109</sup>, and is probably correct for Ag<sup>105</sup> as well.)

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FIG. 1. Breit-Rabi diagram for Ag105, assuming a negative nuclear moment.

Three transitions between pairs of levels may be observed in the present atomic-beam apparatus. These are designated  $\nu_s$ ,  $\nu_1$ , and  $\nu_0$  in Fig. 1. Neglecting the  $g_I$  terms, the "standard transition" frequency  $\nu_s$  is given at low fields by

$$\nu_{s} = \frac{1}{2} (\rho_{1} - \rho_{2}) f [1 + \frac{1}{2} (\rho_{1} + \rho_{2}) (f / |\Delta \nu|) + \cdots ]. \quad (2)$$

The first term reduces to  $f/\lceil 2(I+\frac{1}{2}) \rceil$  for the  $\Delta m=1$ transition, so that at low fields the resonance frequency depends on nuclear and electron spin but not on  $\Delta \nu$ . After the spin has been determined, the resonance is observed at successively higher magnetic fields, where higher order terms in the expansion of Eq. (2) become important. These terms involve the hfs splitting  $\Delta \nu$  in a simple way. The hfs  $\Delta v$  may be calculated from the observed frequency of the standard transition at a known magnetic field by the equation

$$\Delta \nu = \left(\nu_s + g_I \frac{\mu_0}{h} H\right) \left[ \left(\nu_s + g_I \frac{\mu_0}{h} H\right) - f \right] / \left[ \frac{1}{2} (\rho_1 - \rho_2) f - \left(\nu_s + g_I \frac{\mu_0}{h} H\right) \right]. \quad (3)$$

The value of  $g_I$  is not known *a priori*, but may be estimated from the Fermi-Segrè formula.<sup>3</sup>

$$\left|\frac{g_I}{g_{I'}}\right| = \left|\frac{\Delta\nu}{\Delta\nu'}\right| \left(\frac{2I'+1}{2I+1}\right),\tag{4}$$

where the primed and unprimed quantities refer to different isotopes of the same element. Since the terms in  $g_I$  are small, Eq. (3) lends itself well to iterative

calculations using successively calculated values of  $g_I$ from Eq. (4) until consistent results are obtained for the two equations. However, the sign of  $g_I$  is not determined by Eq. (4). Thus, two calculations for  $\Delta \nu$  corresponding to the assumption of a positive or negative nuclear moment-must normally be made.

After  $\Delta v$  is known with sufficient accuracy, a search can be made for the  $\Delta F = 1$  direct transitions  $\nu_0$  and  $\nu_1$ in Fig. 1. These two frequencies are given for low fields  $\mathbf{b}\mathbf{v}$ 

$$\nu_{0} = |\Delta\nu| + \frac{1}{2}f^{2}/|\Delta\nu| + \cdots,$$
  

$$\nu_{1} = |\Delta\nu| + \frac{1}{2}f + \frac{1}{4}f^{2}/|\Delta\nu| + \cdots,$$
(5)

where the proper values of  $\rho_1$  and  $\rho_2$  for Ag<sup>105</sup> have been used. For low fields, the transition  $\nu_0$  has only a secondorder field dependence. Measurements of  $\nu_0$  near zero field can be expected to give the most precise value of  $\Delta \nu$ . Furthermore, since the linewidth in the present apparatus is caused primarily by inhomogeneities in the C field, the transition  $\nu_0$  will give a narrower line than  $\nu_1$ . Thus an initial search can best be made for the resonance  $\nu_1$ , while final results will be most precise for the resonance  $\nu_0$ .

## III. ISOTOPE PREPARATION

The Ag<sup>105</sup> used in this work was produced in the Crocker 60-in. cyclotron on the Berkeley campus. This cyclotron provided 12-MeV protons or 24-MeV deuterons in a beam of about 10<sup>15</sup> particles per second. The target was of natural palladium metal of sufficient thickness to stop the cyclotron beam. For proton irradiation this was 0.012 in., while for deuterons a thickness approximately twice as great was required.

Since there are six stable isotopes of palladium, a bombardment was expected to produce many different silver isotopes. However, the half-lives are sufficiently different that there is little possibility for confusion in isotope identification. Targets were normally allowed to decay for several days or weeks before an experiment was performed. Most short-lived components were thus eliminated from the sample. In making the spin assignment,<sup>4,5</sup> several checks of the decay curve were made, and these connected the  $I=\frac{1}{2}$  resonances with a 40-day activity that has long been established as Ag<sup>105</sup>.<sup>6,7</sup>

Chemical separation of silver from the palladium target is straightforward, involving no more than the dissolving of the target in aqua regia. The palladium goes into solution very easily, while the silver is precipitated as AgCl. Addition of a measured amount of silver carrier (as AgNO<sub>3</sub>) serves to bring down almost all the silver.

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Calibration							
Resonance number	Transition	Isotope	Frequency (Mc/sec)	Magnetic field (G)	Ag <sup>105</sup> frequency (Mc/sec)	${{ m Ag^{105}}\over{ m (Mc/sec)}}$	
**************************************			(a) $\Delta F = 0$ tran	sition: $\nu_s = (1,1) \leftrightarrow (1,0)$	)		
2161	νs	Rb <sup>87</sup>	9.85(2)	14.01(2)	19.90(10)	1500(1000)	
2431	$\nu_s$	Rb <sup>8</sup>	20.84(1)	29.52(1)	42.57(10)	1410(130)	
2432	V <sub>s</sub>	RD <sup>8</sup> '	94.05(2)	129.94(3) 120.07(2)	203.51(10) 203.61(10)	1520(8)	
2433	$\nu_s$	KD <sup>81</sup> DL87	94.07(2) 04.60(1)	129.97(3)	203.01(10) 202.48(10)	1522(8)	
2434	V <sub>s</sub>	KD <sup>87</sup> D 1.87	302.46(5)	129.00(1) 383 30(6)	203.48(10)	1519(7)	
2433	V <sub>8</sub>	(D h 85	27.96(3)	385.59(0)	101.82(20)	1521(5)	
4981	νs	) R h87	40 76(5)	57.26(6)	84.65(10)	1450(50)	
6991	ν <sub>s</sub>	Rb <sup>85</sup> Rb <sup>87</sup>	341.14(5) 395 47(5)	485.34(5)	938.80(20)	1529(2)	
		(10)		(0.0) (1.0)			
(b) $\Delta F = 1$ transitions: $\nu_0 = (0,0) \leftrightarrow (1,0)$ $\nu_1 = (0,0) \leftrightarrow (1,-1)$							
2436	νo	Rb <sup>87</sup>	2.45(2)	3.50(3)	1529.10(5)	1529.07(5)	
2437	$\nu_0$	$\mathbf{Rb^{87}}$	4.10(2)	5.85(3)	1529.13(2)	1529.04(2)	
2438	$\nu_0$	Rb <sup>87</sup>	3.98(2)	5.68(3)	1529.13(2)	1529.05(2)	
6031	$\nu_1$	${ m Rb^{85} \atop  m Rb^{87}}$	2.210(10) 3.290(15)	4.707(21)	1535.70(10)	1529.00(10)	
6032	$\boldsymbol{\nu}_0$	$\left\{ \begin{matrix} \mathrm{Rb^{85}} \\ \mathrm{Rb^{87}} \end{matrix}  ight.$	2.197(10) 3.267(10)	4.676(18)	1529.11(2)	1529.056(14)	
6033	$\nu_0$	{Rb <sup>85</sup> (Rb <sup>87</sup>	2.190(10) 3.270(10)	4.671(18)	1529.12(1)	1529.066(12)	
C	)ver-all least-sq	uares averag	e: $\Delta \nu_{\pm} = 1529.057(8)$	8) Mc/sec; $\chi^2$ of the fit:	15.7 with 13 degrees of	freedom.	
	(c) Constants used in calculation					References	
$\mu_0/h = 1.399677 \text{ Mc}/\text{sec-gauss}$					13		
$M_{p}/m_{e} = 1836.12^{a}$					13		
$g_J(Rb) = -2.002409$					14		
$g_J(Ag) = -2.002333$					15, 16		
$Rb^{s_0}: I = 5/2$					17		
$\Delta \nu = 3035./324$ MC/sec					18		
$\mu_{I} = \pm 1.34021$ IIII D187. $I = \frac{3}{2}$					10 17		
$KU^{-1}$ , $I = 3/2$ $\Lambda_{W} = 6834.6826 \text{ M}_{C}/\text{sec}$					17		
$\mu_{T} = +2.7414 \text{ nm}$					10 20		
$A_{\sigma^{105}} \cdot I = 1/2$					4.5		
	-	$ g_{\rm I}  = \left  \frac{\Delta \nu}{\Delta \nu} \right $	$\frac{(\mathrm{Ag^{105}})}{(\mathrm{Ag^{107}})}g_{\mathrm{I}}(\mathrm{Ag^{107}})$		,,,,		
$Ag^{107}$ : $I = 1/2$					21		
$\Delta \nu = -1712.56 \text{ Mc/sec}$					16		
$\mu_{\rm I}$ (uncorrected) = $-0.1130$ nm					22. 23		

TABLE I. Resonances in Ag<sup>105</sup>.

<sup>a</sup> The ratio of proton to electron masses is used in the conversion between Bohr magnetons and nuclear magnetons.

For an atomic-beam experiment, the washed AgCl precipitate had to be reduced to metallic silver. This has been done in two ways. The first method involved solution of AgCl in dilute NH4OH from which the silver was recovered by electroplating. The second procedure was a precipitation of AgI in ammonia solution. This silver iodide precipitate was decomposed directly to silver metal and iodine gas by heating. In some cases this final decomposition was done in the atomic-beam apparatus. However, the silver iodide was quite bulky, so that more silver could be loaded into an atomic-beam oven if the precipitate had been heated strongly outside the apparatus.

### IV. EXPERIMENTAL PROCEDURE

The atomic-beam magnetic-resonance apparatus used for these measurements has been described elsewhere.<sup>8,9</sup> Calibration of the uniform transition field was made by using a beam of rubidium atoms that could be detected by a surface-ionization detector.<sup>10-12</sup> The calibration oven was mounted behind the one containing the radioactive silver. When a calibration was desired, the main oven was moved aside to allow the calibration beam to enter the magnet region of the apparatus.

The radioactive silver was contained in a tantalum oven that was heated by electron bombardment. The oven was aligned before each run with a small amount of an alkali compound that could be detected on the

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surface ionization detector. Radioactive detection was accomplished by collecting samples on sulfur-surfaced buttons, that were then counted in thin-crystal scintillation counters. The counters included a single-channel pulse-height analyzer so that only the palladium x rays from decaying silver atoms were accepted. A normalization procedure has been described previously9 in connection with work on gold and silver isotopes.

Transitions among the hyperfine sublevels were caused in the uniform C-field region of the apparatus by an oscillating magnetic field. This oscillating field was produced by passing an rf current through a simple "strap hairpin." Frequencies were measured with a Hewlett-Packard-524B frequency counter and associated plug-in units. For frequencies above 220 Mc/sec, the HP-540A transfer oscillator was also used. Periodically the internal 100-kc/sec standard of the frequency counter was compared with a 100-kc/sec signal from a National Company Atomichron. Errors in frequency measurement should not be a factor in setting the precision of these measurements.

Several different sources of rf power have been used, depending on the desired frequency range. A Tektronix-190 signal generator was used for frequencies less than 20 Mc/sec, while a HP-608A oscillator and two wideband amplifiers were used with higher frequencies to about 220 Mc/sec. First results with frequencies above 300 Mc/sec (including observations of the direct transition  $\nu_0$ ) were obtained by using an Airborne Instruments Power Oscillator, Model 124C. This oscillator is difficult to set accurately and is not sufficiently stable for precise measurements. Therefore, final results were obtained by using the Gertsch FM-4A signal generator with traveling-wave-tube amplifiers, as required. The FM-4A was locked to a harmonic of the Gertsch AM-1 for the most careful sweeps over the field-independent resonance. Under these last conditions, rf frequencies were held constant easily-within less than 1 kc/sec.



FIG. 2.  $\Delta F = 1$  transitions in Ag<sup>105</sup>.



FIG. 3. "Field-independent" line observed in Ag<sup>105</sup> at low field.

#### V. RESULTS

The results of these measurements are given in Table I. The table is in three parts. Part (a) lists calibration and resonance data for the several observations of the standard  $\Delta F = 0$  transition ( $\nu_s$  in Fig. 1). Part (b) of the table lists similar information for observations of the direct  $\Delta F = \pm 1$  transitions ( $\nu_0$  and  $\nu_1$  in Fig. 1). Values of the various nuclear constants used to calculate the hfs  $\Delta \nu$  for Ag<sup>105</sup> from resonance data are summarized<sup>4,5,13-23</sup> in Part (c) of Table I, along with the calculated  $\Delta v$  for each resonance. The number in parentheses after each measured value or calculated result represents the uncertainty in the least significant digit, e.g., Resonance 2161, the observed frequency of the Rb<sup>87</sup> resonance is given as  $9.85 \pm 0.02$  Mc/sec.

Figure 2 compares the resonance frequencies and resonance heights of the two observable direct transitions. The advantages of measuring a field-independent line are clear, especially when the apparatus has a relatively low-quality C magnet. The difference in width between the two lines  $\nu_0$  and  $\nu_1$  in Fig. 2 corre-

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sponds to an average field inhomogeneity along the hairpin of approximately 3% at about 5 G.

The apparent split of the resonance  $\nu_1$  shown in Fig. 2 is not considered significant, since the low button was taken at a time of rapidly changing beam intensity. The normalization, therefore, may be questionable.

All calculations implied by Table I have been performed on digital computers, most recently the IBM 7090. Original results of the program<sup>24</sup> HYPER-FINE 3 have been verified by a second program, OMNI. The interpretation of results must be made in the usual least-squares sense of statistical reliability.

The uncertainty in the final value of hfs  $\Delta \nu$  is determined almost entirely by the measured width of the field-independent  $\Delta F=1$  direct transition. The full width at half-maximum of this line is about 90 kc/sec (Fig. 3). The peak can be located with an accuracy of about 20 kc/sec. The consistency of the resonance data, as demonstrated by the value of  $\chi^2$  (Table I), is sufficient to justify the usual  $\approx 30\%$  confidence level in the computer's choice of  $\sigma=8$  kc/sec. To allow for the possibility of systematic errors in the apparatus, as well as to compensate for the relatively poor shape of the resonance line in Fig. 3, we choose to give our result an uncertainty of 20 kc/sec, i.e.,

$$\Delta \nu(\mathrm{Ag^{105}}) = \pm 1529.057(20)$$
 Mc/sec.

Of course, the sign of the nuclear moment (and hence of the hfs  $\Delta \nu$ ) cannot be determined from these data.

The magnitude of the nuclear moment of Ag<sup>105</sup> can be estimated from the Fermi-Segrè relation (Eq. 4) by using previous determinations of hfs  $\Delta \nu$  and nuclear magnetic moment for any other isotope of silver. By use of the constants listed in Table I(c) for Ag<sup>107</sup>, the uncorrected nuclear magnetic dipole moment of Ag<sup>105</sup>

is calculated to be

 $\mu_I(Ag^{105}) = \pm 0.1009(10)$  nuclear magneton.

The uncertainty in the value of  $\mu_I$  is determined not by this measurement but by the uncertainty in the Fermi-Segrè relation itself. The hfs anomaly, a measure of the inaccuracy of the Fermi-Segrè formula, has been determined<sup>16,22,23</sup> to be 0.41% between Ag<sup>107</sup> and Ag<sup>109</sup>. A similar deviation may be expected between Ag<sup>105</sup> and Ag<sup>107</sup>. Therefore, an accuracy of less than  $\approx 1\%$  for the moment of Ag<sup>105</sup> is probably not realistic.

## VI. DISCUSSION

The magnitude of the nuclear moment of  $Ag^{105}$  is sufficiently small to confirm the previous assignment of the odd proton to a  $p_{1/2}$  shell-model level.<sup>25</sup> This agrees with previous results<sup>16,26,27</sup> for  $Ag^{107}$ ,  $Ag^{109}$ , and  $Ag^{11}$ . For the two stable isotopes the sign of the nuclear dipole moment has been measured to be negative. Although this experiment has been unable to make a direct determination of the sign, it is probable that a negative sign should be assigned also to  $Ag^{105}$  as has been assigned already to  $Ag^{111}$ .

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