Precision measurement of $g_I(^{87}Rb^+)/g_J(^{87}Rb)$†

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A charge-exchange optical-pumping experiment has been performed to measure the ratio $g_I(^{87}Rb^+)/g_J(^{87}Rb)$. The NMR frequency of free $^{87}Rb^+$ ions polarized by charge-exchange collisions with optically pumped ^{87}Rb atoms was measured along with the $(F=2, M=-2 \longleftrightarrow F=2, M=-1)$ Zeeman transition frequency of ^{87}Rb in a magnetic field of ~55 G. The magnetic field was produced in a shielded solenoid. The 30-cm^3 cylindrical optical-pumping cells were filled with a Ne buffer gas, and the ions were produced in a weak continuous electrodeless rf discharge which was run in a sidearm attached to the cells. The NMR frequency was ~76 kHz and the charge-exchange and rf-broadened NMR linewidth was 60 Hz. The Zeeman frequency was ~39 MHz and the Zeeman linewidth was 80 Hz due to the inhomogeneity of the magnetic field. Our result is $g_I(^{87}Rb^+)/g_J(^{87}Rb) = -4.969\,934(12)\times10^{-4}$, which can be compared with a previously measured value of $g_I(^{87}Rb)/g_J(^{87}Rb) = -4.969\,914\,7(44)\times10^{-4}$ to obtain the difference in the shielding constants of the atom and ion, $\sigma(^{87}Rb) - \sigma(^{87}Rb^+) = (3.8\pm2.6)\times10^{-6}$.

I. INTRODUCTION

The diamagnetic shielding of the nuclear moment of an atom or ion in an external magnetic field by the atomic electrons is a subject of longstanding theoretical interest. The shielding was first calculated by Lamb[1] in 1941 for a spherically symmetric charge distribution. He showed that the induced shielding field depends directly on the electrostatic potential produced at the nucleus by the electrons. Using the Thomas-Fermi model of the atom, he derived for the ratio of the induced field $H'(0)$ at the nucleus to the external field H the expression

$$H'(0)/H = -3.19Z^{4/3}\times10^{-5}\ , \tag{1}$$

where Z is the nuclear charge.

This implies that the nuclear g factor g_I observed in rf spectroscopic experiments is less than the g factor $\bar{g}_I$ of the bare nucleus, and that

$$g_I = (1-\sigma)\bar{g}_I\ , \tag{2}$$

where the diamagnetic shielding constant σ is given by

$$\sigma = -H'(0)/H\ . \tag{3}$$

The calculation of σ for an atom or ion in an S state is in principle straightforward if the electronic wave function is known. As Hylleraas and Skavlem[2] and Dickinson[3] have shown,

$$\sigma = \tfrac{1}{3}\alpha^2\langle\psi|\sum_{i=1}^{N}\frac{1}{r_i}|\psi\rangle\ , \tag{4}$$

where α is the fine-structure constant, $|\psi\rangle$ is the N-electron wave function, and r_i is the distance from the ith electron to the nucleus in atomic units. The expression for σ in Eq. (4) can be evaluated with the aid of Hartree-Fock wave functions, and this has been done for the neutral and singly ionized alkali atoms by Malli and Fraga.[4]

Because the diamagnetic shielding constant is a property of the atom which depends in a simple way upon the electronic wave function, an experimental comparison of the shielding in a neutral alkali atom with the shielding in the singly ionized atom provides an interesting test of theoretical wave functions for the atom and ion. Recently, Mitchell and Fortson[5,6] introduced a charge-exchange optical-pumping technique which makes this kind of experiment possible. We have used their method to measure the ratio $g_I(^{87}Rb^+)/g_J(^{87}Rb)$. By combining the result of our experiment with a previously measured value[7] of $g_I(^{87}Rb)/g_J(^{87}Rb)$ we obtain the difference between the shielding constants in the Rb atom and the Rb positive ion.

II. EXPERIMENT

A. Charge-exchange optical pumping

The charge-exchange optical-pumping technique used in this experiment is analogous to spin-exchange optical pumping.[8] Rb atoms were polarized in a magnetic field of ~55 G by optical pumping. The optical-pumping cells were 30-cm^3 Pyrex cylinders, and they were filled with a Ne buffer gas. Rb^+ ions were produced by a continuous weak electrodeless rf discharge which was run in a tubulation attached to the side of the cell. The Rb^+ ions diffused into the optical-pumping region and underwent charge-exchange collisions with the optically pumped neutral Rb atoms. The charge-exchange collisions transfered part of the polarization of the neutral atoms to the nuclei of the ions. Because the charge transfer is a resonant process, the charge-exchange cross section is large ($\sim 10^{-14}$ cm^2). Furthermore, the nuclear spins are not easily disoriented by collisions with the buffer gas because the ions are in a $^1S_0$ ground state. The charge-exchange collisions with the neutral Rb atoms are the principal relaxation mechanism for the nuclear spins. For these reasons a substantial nuclear polarization is built up. When an rf field was applied at the NMR frequency of the ions, the nuclear spins were depolarized, and the charge-exchange collisions partially depolarized the neutral Rb atoms. This resulted in a decrease in the intensity of the pumping light transmitted by the cell. The amplitude of the NMR signals which were obtained in this experiment was of the same order of magnitude as those obtained in conventional spin-exchange optical-pumping experiments.

The Zeeman transitions in the neutral Rb atoms were observed by directly depolarizing the atoms with an rf field applied at the Zeeman transition frequencies. By measuring the ion NMR frequency and the ($F=2$, $M=-2 \rightarrow F=2$, $M=-1$) Zeeman transition frequency, we obtained a value for $g_I(^{87}Rb^+)/g_J(^{87}Rb)$. Isotopically pure ^{87}Rb was used rather than natural Rb in order to increase the amplitude of the NMR signal. We chose ^{87}Rb rather than ^{85}Rb to take advantage of the larger nuclear moment.

B. Apparatus

A block diagram of the apparatus is shown in Fig. 1. The important feature of the apparatus is the solenoid-shield system which was used to produce a stable and homogeneous magnetic field. The solenoid had a 36-in. length and a 12-in. diameter and was surrounded by three concentric cylindrical Mollypermalloy shields. The solenoid was equipped with field correction coils to improve the axial homogeneity of the field. The solenoid was powered by a current regulated supply which had a short-term stability of 10^{-7}. The inhomogeneity of the field across the 30-cm^3 volume of the buffered cells produced a linewidth of 80 Hz for the ^{87}Rb Zeeman transition which ocurred at $\sim$39 MHz. The NMR transition occurred at a frequency of $\sim$76 kHz, and the magnetic field contribution to the NMR linewidth was only 0.15 Hz. The linewidth of the NMR transition was 60 Hz and was due to a combination of charge-exchange and rf power broadening.

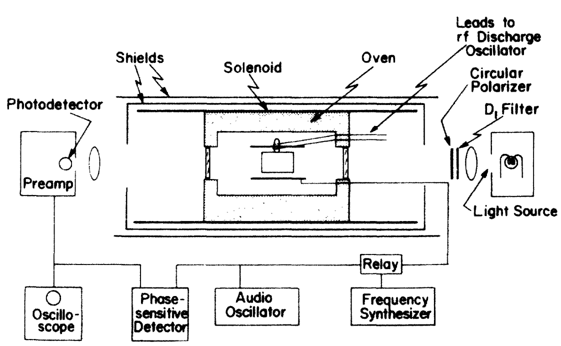

FIG. 1. Block diagram of the apparatus.

The rf for the NMR and Zeeman transitions was generated by a frequency synthesizer and fed into a Helmholtz pair surrounding the optical-pumping cell. The dimensions of the Helmholtz coils were made as large as possible ($\sim$20 cm in diameter) in order to minimize asymmetries in the Zeeman line shape due to a combination of the inhomogeneities in the rf and static fields.[7] It was necessary to amplify the output of the frequency synthesizer for the NMR transition because the nuclear magnetic moment is weak.

The NMR and Zeeman signals were obtained by chopping the applied rf at a rate of 10 Hz so that at resonance the pumping-light intensity transmitted by the cell was amplitude modulated at this rate. The signal was detected by a photocell, amplified, and displayed on an oscilloscope and phase-sensitive detector.

The transition frequencies were measured with a digital frequency counter calibrated with the transmission from WWVB. The frequency of the NMR transition was counted for 10 sec with an accuracy of ± 0.1 Hz. The Zeeman transition frequency was counted for 1 sec with an accuracy of ± 1.0 Hz.

C. Measurements

Each measurement of $g_I(^{87}Rb^+)/g_J(^{87}Rb)$ was based upon two determinations of the NMR frequency sandwiched between two determinations of the Zeeman frequency to compensate for field drift. Each determination of the NMR frequency consisted of an average of two half-power point measurements. Less care was taken with the Zeeman transition and each determination of the Zeeman frequency was simply the average of two measurements of the frequency of the Zeeman signal peak. Measurements were made with alternately left- and right-circular polarization of the pumping light.

The results of our six final runs consisting of

TABLE I. Summary of the results from the final runs in this experiment.

Buffer gas pressure (Torr)	No. of measurements	$g_I(^{87}\text{Rb}^+)/g_J(^{87}\text{Rb})$	Std. dev.
190	20	$-4.969\,946\times 10^{-4}$	53×10^{-10}
190	15	$-4.969\,944\times 10^{-4}$	44×10^{-10}
190	21	$-4.969\,934\times 10^{-4}$	26×10^{-10}
190	27	$-4.969\,922\times 10^{-4}$	33×10^{-10}
190	19	$-4.969\,933\times 10^{-4}$	42×10^{-10}
60	24	$-4.969\,932\times 10^{-4}$	28×10^{-10}

approximately 20 g-factor ratio measurements each are shown in Table I. The principal limitation of the precision of the measurements was the width of the NMR resonance, and the variation in the results from run to run appeared to be statistical. This is in sharp contrast to the nonstatistical variations from run to run which are common in optical-pumping experiments with buffered cells and which are due to asymmetries in the magnetic-field-broadened line shapes. These asymmetries result from the combination of rf and static magnetic field inhomogeneities.[7] This was not a significant source of error in this experiment because of the small contribution of the field inhomogeneity to the NMR linewidth. The precision with which the NMR frequency could be determined was not sufficient to reveal the effects of the asymmetries introduced by the magnetic field. A histogram of the measurements from all six runs is shown in Fig. 2.

Light-intensity shifts[7] of the ^{87}Rb Zeeman transitions were too small to be a source of error in this experiment. Within the precision of the present experiment, no shifts of the NMR frequency were observed due to the polarization of the pumping light, the strength of the rf field, or the density of Rb atoms in the cell. The measurements of the NMR frequency were made with rf field

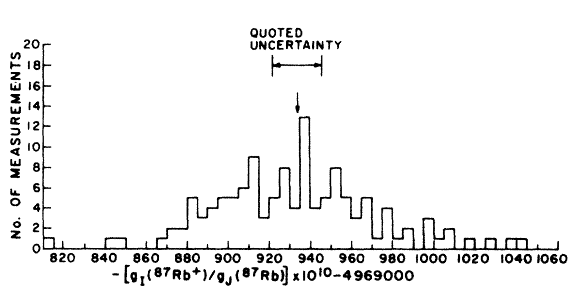

FIG. 2. Histogram of the measurements from all six runs.

strengths of the order of 15 mG. The rf field strength was measured by observing the "wiggle" frequency[9] of the ^{87}Rb magnetic moment. In searching for rf-field-strength shifts and Rb density shifts, the rf field was increased by a factor of 3 and the Rb density by a factor of 2.

The average of the results for $g_I(^{87}\text{Rb}^+)/g_J(^{87}\text{Rb})$ from each of the six runs is $-4.969\,935\times 10^{-4}$, and the value of $g_I(^{87}\text{Rb}^+)/g_J(^{87}\text{Rb})$ obtained by lumping the 126 measurements from all six runs together and averaging is $-4.969\,934(4)\times 10^{-4}$, where the error is the standard deviation divided by the square root of the number of measurements. We take as our final result

$$g_I(^{87}\text{Rb}^+)/g_J(^{87}\text{Rb}) = -4.969\,934(12)\times 10^{-4}\,,$$

where the quoted error includes our estimate of the upper limit of possible systematic errors due to rf power and Rb density-dependent frequency shifts.

In a Cs$^+$ charge-exchange optical-pumping experiment, Nienstadt *et al.*[10] observed a significant fractional frequency shift of the Cs$^+$ NMR frequency which was linear in the rf field strength, and which was attributed[11] to the charge-exchange process. Our upper limit for the magnitude of such a fractional shift at their reported rf field strength is a factor of 5 smaller than the fractional shift which they observed. We have been informed[12] that their reported shift was due to instrumental effects. In addition, they observed a small NMR signal when their source of ionization was turned off. Although our NMR signals were easily visible on an oscilloscope, we observed no ion signal when the rf discharge was turned off. Any such signal must have been more than a factor of 50 smaller than our discharge signal.

III. COMPARISON OF RESULTS WITH THEORY

In a spin-exchange optical-pumping experiment White *et al.*[7] found that

$$g_I(^{87}\text{Rb})/g_J(^{87}\text{Rb}) = -4.969\,914\,7(44)\times 10^{-4}\,.$$

Combining this number with our result gives

$$\sigma(^{87}\text{Rb}) - \sigma(^{87}\text{Rb}^+) = (3.8\pm 2.6)\times 10^{-6}$$

for the difference in the shielding constants for the Rb atom and ion.

The expression for σ in Eq. (1) derived by Lamb using the Thomas-Fermi model of the atom gives

$$[\sigma(^{87}\text{Rb}) - \sigma(^{87}\text{Rb}^+)]_L = 1.4\times 10^{-4}\,,$$

in clear disagreement with experiment.

Using Eq. (4), Malli and Fraga[4] calculated the difference in σ to be

$$[\sigma(^{87}\mathrm{Rb}) - \sigma(^{87}\mathrm{Rb}^+)]_{\mathrm{MF}} = -8.2\times 10^{-6}\ ,$$

which brings out the fact that the contribution of the valence electron to the shielding is expected to be small compared to the contribution of the core electrons. Our result is in qualitative agreement with this aspect of their calculation, although we find that the shielding is slightly larger in the atom than in the ions whereas they predicted that the reverse would be true.

IV. CONCLUSION

It is clear from this experiment that the contribution of the valence electron to the shielding of the Rb nucleus is small compared to the contribution of the core electrons as is expected on the basis of Hartree-Fock wave functions. We are in the process of modifying our apparatus to increase the magnetic field strength by a factor of 2. This should increase the precision of the measured value of $g_I(^{87}\mathrm{Rb}^+)/g_J(^{87}\mathrm{Rb})$ by the same factor by reducing the fractional linewidth of the NMR signal. We plan to extend our measurements to other alkali atoms and to continue to look for evidence of the type of rf-field-dependent frequency shift observed by Nienstadt *et al.*

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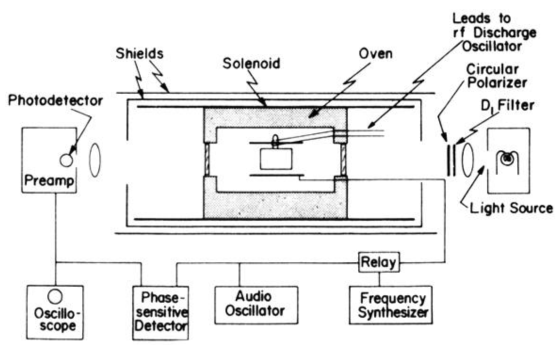

FIG. 1. Block diagram of the apparatus.