Magnetic moments of atomic nitrogen in the ^4S and ^2D levels of its ground-state configuration

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(Received 31 August 1988)

The magnetic moments of atomic nitrogen in the ^4S and ^2D levels of its ground-state configuration are measured by microwave Zeeman absorption spectroscopy and compared to previous experimental and theoretical values. The values obtained for the corresponding g_J factors are $g_J(^4S_{3/2})=2.002\,136\,7(22)$, $g_J(^2D_{5/2})=1.200\,318\,(5)$, and $g_J(^2D_{3/2})=0.799\,483\,(15)$. The $g_J(^4S_{3/2})$ value disagrees with the early experimental value obtained with the same technique but agrees with the more precise ones obtained by other techniques. The $g_J(^2D_J)$ values disagree significantly with the early experimental values previously known. The three g_J values are found to be in agreement, to within a few ppm, with theoretical values obtained from detailed calculations within the Hartree-Fock self-consistent-field approximation.

INTRODUCTION

The magnetic moments of light atoms have been measured and calculated with precision of a few ppm over the last three decades with the general purpose of testing the theory of atomic magnetism [Refs. 1–18 (experimental); Refs. 19–30 (theoretical)]. The point of contact between theory and experiment is the value of the atomic g_J factor. This departs from the rational Landé value by the contributions of order α and higher which result from the spin-factor anomaly, by the contributions of order α^2 arising from relativistic and diamagnetic effects, and by the contribution due to the effect of the nuclear motion, which is linear in the ratio of the electronic and the nuclear masses.[19–23] A further deviation from the rational Landé value is also present if pure LS coupling is broken down by the admixture of states with different L,S values via the spin-orbit interaction.[21] Since the electron spin-factor anomaly is known to a precision of about 0.009 ppm,[31] the problem of calculating an atomic g_J factor to within a few ppm can then be considered either as a problem in atomic structure if the theory of the relativistic and diamagnetic corrections is regarded as reliably known, or vice versa. The agreement to 1 ppm between theory and experiment for g_J (He; $^3S_1$) (Refs. 19 and 20) indicates that the problem for heavier atoms lies on the knowledge of their structure.

The $2p$-row atoms are the natural candidates for further testing of the theory of atomic magnetism, insofar as atomic structure is concerned. The g_J factors of B, C, N, O, and F have been measured with precision of a few ppm, or better, in their ground-state levels (Refs. 14; 10; 1, 12, 13, 15; 3; 5, 8, respectively) and to about 10 ppm in two metastable-state levels in N.[7] These g factors have been calculated with different atomic structure theories, Hartree Fock (HF),[24–27] spin-extended HF,[29] and many body,[30] and with varying degrees of success. The HF calculations are of particular interest because they provide a definite theoretical reference value, with respect to which the effect of correlation in the g_J factor can be assessed, and also because some of the HF calculations, $g_J(\mathrm{F};^2P_{3/2})$ and g_J (O; $^3P_{1,2}$), show a remarkably good agreement with experiment[24,25] while others, $g_J(F;^2P_{1/2})$ and $g_J(N;^4S_{3/2})$ show, then, a remarkably poor one.[8,26]

The magnetic moments in the ground-state levels of atomic nitrogen are particularly interesting for several reasons. The theoretical g_J factor in the $^4S_{3/2}$ level is quite simple to calculate on account of the vanishing of the nuclear, the diamagnetic, and the "relativistic proper" corrections for this level in a central-field scheme.[21,26,29,30] Its HF value should then agree very well with experiment if correlation effects are negligible in N, or point to them if they are present. On the other hand, the g_J factor for the metastable $^2D_{5/2}$ level is free from the correction due to breakdown of LS coupling and consequently from the influence of the imperfectly known ζ_{2p} spin-orbit parameter. Precise measurements and good theoretical values for the g_J factors of these levels should then greatly help us to understand the effect of structure in atomic magnetism.

We have remeasured the values of the g_J factors in ^4S and ^2D ground-state atomic nitrogen and reviewed their calculated values in a central field HF basis. These results provide better experimental and theoretical values and a more clear view of the effect of atomic structure in these factors.

EXPERIMENTAL

Measurements were made with a Varian E-9 electron paramagnetic resonance (EPR) spectrometer adapted for precision measurements in a flowing gas.

Gas system

Nitrogen gas, pure or diluted in helium, was made to flow through a 0.9-m length of quartz tube by either one of three independent pump systems: a fast flow system, based on a Microvac-Stokes 66-L/s pump, capable of pumping up to 6-s L min of helium at average speeds and pressures of about 400 m/s and 0.1 kPa; a slow flow system, based on a bank of three 7-L/s Edwards mechanical pumps connected in parallel, capable of pumping up to about 2 s L min of helium at average speeds and pressures of about 60 m/s and 1 kPa; and a low-pressure system, based on an Edwards EO4 oil diffusion pump and backing mechanical pump, capable of pumping about 80 s cc min of nitrogen at pressures of 5 to 10 Pa. The gas mixture is regulated by three independent Teledyne-Hastings gas flow meters and controllers connected to the arms of a manifold. Pressure measurements are made by two Baratron manometers located near the ends of the flow line.

The quartz tube threads a discharge cavity, where the gas is excited, and the spectrometer X-band cavity. A small side tube attached to the flow tube near the X-band cavity can be used to add SF_6 to the flowing products of the excited gas when needed for reduction of electron noise.[32,33] The SF_6 flow, about 45 s cc min, is regulated by a Teledyne flow controller as well.

Discharge

Atoms were produced upstream from the X-band cavity by a 2450-MHz microwave discharge. The microwave power, from a voltage-regulated Raytheon MX-1 generator, is coupled to the streaming gas by means of a water cooled, resonating cavity of the Evenson type.[34] Power levels above 10 W were sufficient to produce ground-state atomic nitrogen, but about 50 and 80 W were found necessary for producing observable amounts of the metastable species. The discharge cavity can be moved along the discharge tube, by means of a vertical screw, in order to find the best operating regions, but most of the data were taken with the discharge cavity somewhere between 16.5 and 18 cm upstream from the X-band cavity.

The discharge tube is mounted in quick-connect fittings, so that it can be withdrawn from the X-band cavity in a short time (<1 min) when needed for making magnetic field measurements inside the X-band cavity after EPR runs.

Magnetic field

The magnetic field is provided by the 9-in pole face diameter electromagnet of the Varian E-9 EPR spectrometer and is held stable by its temperature-controlled Hall probe. Field measurements were made by a locally built nuclear magnetic resonance (NMR) magnetometer consisting of a tank circuit detector, a cascode radio frequency amplifier, a demodulator, and an audio frequency amplifier. A signal of the appropriate frequency, from a Hewlett-Packard 8640A generator, is fed to the tank circuit through a very small capacitance, and the demodulated output from the audio amplifier is connected to the phase detector in the EPR console. The NMR line can then be traced out by the same field sweep, and on the same graph used for recording the EPR lines, thus eliminating possible off-set errors resulting from separate recorders. Once warmed up, this system was capable of retracing and reproducing NMR lines with better than 1-ppm accuracy over time spans much longer than that elapsed between successive EPR and NMR runs.

The proton probe is a long cylindrical sample which fits accurately into the center of the X-band cavity, with the rf coil occupying exactly the effective EPR sample volume. The proton sample itself is a 0.1-molar aqueous solution of nickel sulfate. For this, a value of

$$-g_p = 0.003\,041\,987\,0(15), \ldots \quad (1)$$

is deduced from our sample molarity and the g_p value of water in a spherical sample at 25 °C, $-g_p = 0.003\,041\,986\,258\,(30)$,[31] which is realized with 0.5-ppm accuracy in a 0.2-molar nickel sulfate aqueous solution.[14]

Frequency measurements

Radio and microwave frequencies for, respectively, NMR and EPR transitions were measured with a crystal-controlled Hewlett-Packard 5340A frequency counter with high-stability time base, which is accurate to better than 0.1 ppm. Its overall performance was checked periodically by measuring the g_J/g_p ratios in $^3P_{1,2}$ atomic oxygen which, as is known, can be determined by frequency measurements only.[3]

MEASUREMENTS

Ground-state $^4S_{3/2}$ atomic nitrogen

The magnetic substates of this level have been measured by microwave absorption,[1] atomic-beam,[12] optical-pumping,[13] and maser[15] techniques. The result from the first one, $g_J(N)/g_p$, combined with a similar measurement in atomic hydrogen[35] and the theoretical value for $g_J(\mathrm{H};\ ^2S_{1/2}) = g_s[1-(\alpha^2/3)]$ yields the value $g_J(\mathrm{N};\ ^4S_{3/2}) = 2.002\,117(3)$. The other three measurements, of 2.5-, 0.2-, and 0.03-ppm accuracies, respectively, are consistent with the best value $g_J(\mathrm{N};\ ^4S_{3/2}) = 2.002\,134\,652\,(64)$. We have remeasured this g_J factor mainly in order to check our g_p value of Eq. (1) and the overall performance of our apparatus, but also in order to check for possible unknown sources of errors in the microwave-absorption technique which might explain the large deviation of the early measurement made with this technique from the more modern ones, in case the same value was obtained.

A typical $\mathrm{N}(^4S_{3/2})M_J = \frac{1}{2} \leftrightarrow -\frac{1}{2}$, $M_I = 0$ EPR line is shown in Fig. 1 together with two NMR lines for interpolating the proton frequency f at the center of the nitrogen line. Center proton frequencies were determined for 10 runs like this, with 0.7-ppm accuracy. Substituting the values found for f and the corresponding microwave frequencies ν into the equation $-g_J(N)/g_p = (\nu/f)[1-(\Delta\nu/f)^2]$, with $\Delta\nu(\nu/f) = 10.45$ MHz,[1] the value

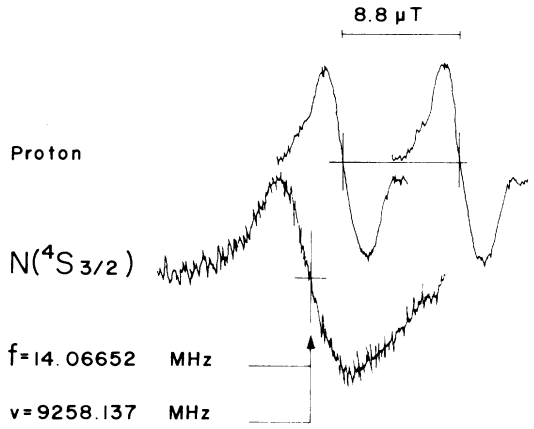

FIG. 1. Typical absorption $M_I=0$, $M_J=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ line of $N(^4S_{3/2})$ and field-calibrating NMR lines.

$$-g_J(\mathrm{N};^4S_{3/2})/g_p=658.167\,4(4),\ldots \quad (2)$$

is obtained. The histogram of the data is shown in Fig. 2.

Equations (1) and (2) now yield

$$g_J(\mathrm{N};^4S_{3/2})=2.002\,136\,7(22),\ldots . \quad (3)$$

This result brings, then, the measurement by the microwave-absorption technique into agreement with those made by other techniques.

Inversely, by using the best experimental value for the $g_J(N)$ factor, $g_J(\mathrm{N};^4S_{3/2})=2.002\,134\,652\,(64)$,[15] we find

$$-g_p=0.003\,041\,984\,(2),\ldots , \quad (4)$$

which agrees to within 1.0 ppm with the independently determined value of Eq. (1). We take this as the g_p value of our NMR probe.

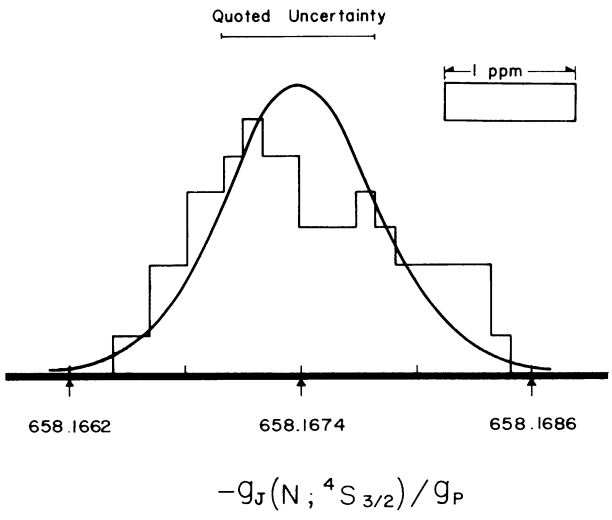

FIG. 2. Histogram of ten determinations of $-g_J(\mathrm{N};^4S_{3/2})/g_p$ from measurements of the $M_I=0, M_J=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ line.

A further calibration of our system is made by measuring g_J/g_p for ground-state $^3P_2$ atomic oxygen. The average of 20 runs over four transitions of its microwave Zeeman spectrum yields[3]

$$-g_J(\mathrm{O};^3P_2)/g_p=493.400\,95\,(50),\ldots . \quad (5)$$

This histogram of these data is shown in Fig. 3. Dividing Eq. (5) by Eq. (2) we find

$$g_J(\mathrm{O};^3P_2)/g_J(\mathrm{N};^4S_{3/2})=0.749\,658\,7(12),\ldots , \quad (6)$$

which is independent of the g_p value of the proton sample.

Multiplying now by the value of $g_J(\mathrm{N};^4S_{3/2})$ we obtain

$$g_J(\mathrm{O};^3P_2)=1.500\,917\,6(20),\ldots , \quad (7)$$

which is in agreement with the known value $g_J(\mathrm{O};^3P_2)=1.500\,921\,(2)$ for this g factor.[3]

Metastable ^2D_J atomic nitrogen

The magnetic parameters of this doublet were first measured by EPR in the rather weak lines that can be observed in a discharge in a hypersonic He-N_2 jet.[7] Much stronger lines can be observed in the products of a microwave discharge in a fast flowing He-N_2 gas stream.[32,33] This, and the poor agreement with theory of the known experimental g_J factors, stimulated this work.

The ^2D_J microwave Zeeman spectrum was observed in a fast flowing He-N_2 gas mixture with partial flows of 3 s L min of helium and 80 s cc min of nitrogen. About 45 s cc min of SF_6 were added, immediately before the mixture passed by the X-band cavity, in order to reduce the electron noise.[32] Total gas pressure at this point was about 0.1 kPa. Commercial high purity gases and long periods of clean-up pumping with the diffusion pump were found necessary to obtain good signals.

The EPR lines of the lowest, $J=\frac{5}{2}$, level of the D dou-

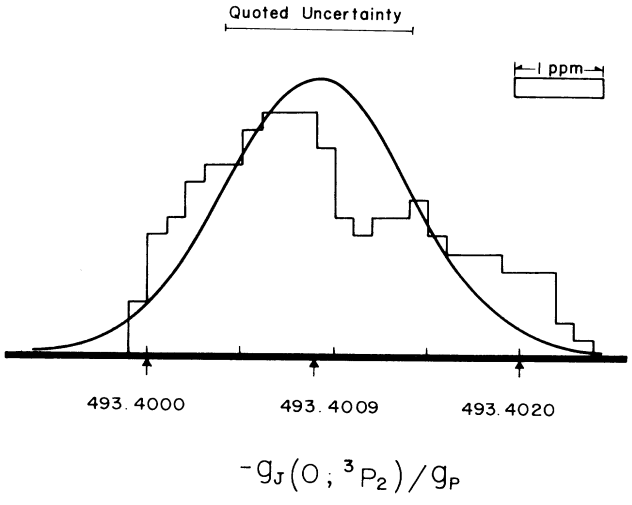

FIG. 3. Histogram of 20 determinations of $-g_J(\mathrm{O};^3P_2)/g_p$.

blet could be observed at a signal-to-noise ratio $S/N \simeq 30$ with a field modulation of 0.5 mT. At the 0.1 mT modulation used to prevent distorting the lines in actual measurements, S/N degraded to about 8. The linewidth under these conditions is about 200 ppm (Fig. 4). Line centers can then be determined with about 10-ppm accuracy, or slightly better with good statistics.

The $J=\frac{3}{2}$ lines were much weaker and had to be recorded at a field modulation of 0.2 mT in actual measurements (Fig. 5). This, of course, degraded the accuracy for center of line determinations by about a factor of 2 and also lowered considerably the number of useful observations.

The ^2D_J Zeeman spectrum has been analyzed by Radford and Evenson.[7] We have reviewed their analysis and agree with it except for minor details: a factor of $\frac{1}{4}$ multiplying a_J and a_{J-1} in the quadratic term of their Eq. (7), and a missing minus sign in the third one of their Eqs. (8). From this analysis it can be seen that the best lines for measuring g_J in either spectrum are the $M_I=0, M_J=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ central lines. Their field positions are given by

$$h\nu/\mu = g_J H \mp (12/125)(g_S - g_L)^3 (H/\delta)^2 H + a_J^2/(g_J H) ,$$

where $J=2\pm\frac{1}{2}$, $\delta=-18.615$ T is the fine-structure interval in magnetic field units, $a_{5/2}=8.1944$ mT and $a_{3/2}=4.67$ mT are the hfs constants,[7] and the other symbols have their usual meanings.

The histogram of 15 determinations of the $g_J(^2D_{5/2})$ factor is shown in Fig. 6, and that of five determinations of $g_J(^2D_{3/2})$ is shown in Fig. 7. The values obtained for these factors are

$$g_J(^2D_{5/2}) = 1.200\,318\,(5)$$

and

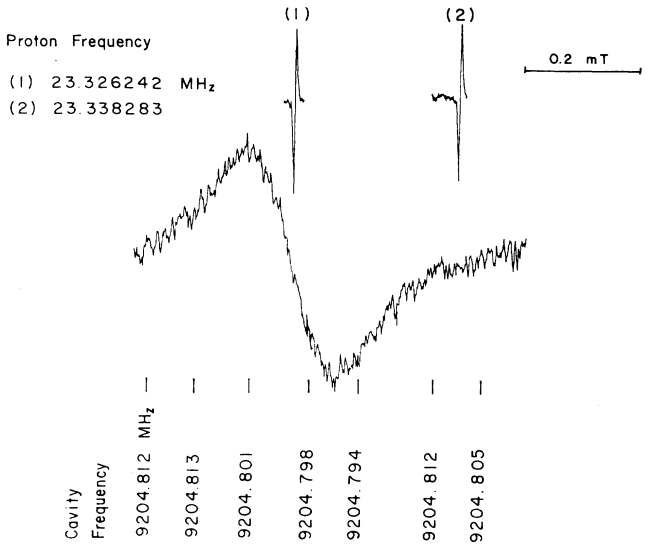

FIG. 4. Typical absorption $M_I=0, M_J=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ line of $N(^2D_{5/2})$ and field-calibrating proton NMR lines.

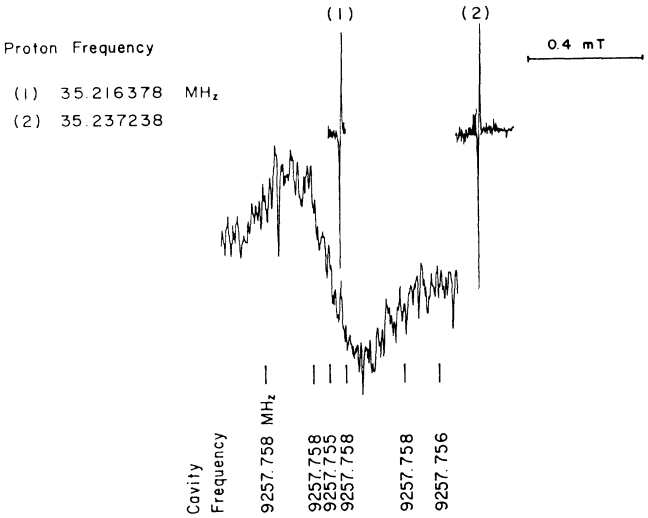

FIG. 5. Typical absorption $M_I=0, M_J=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ line of $N(^2D_{3/2})$ and field-calibrating proton NMR lines.

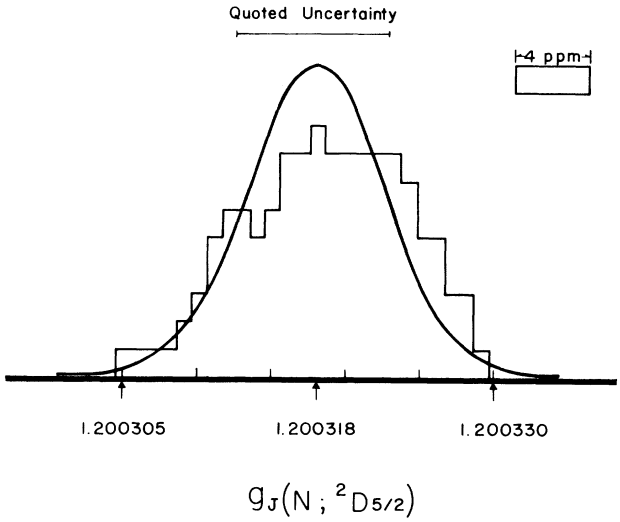

FIG. 6. Histrogram of 15 determinations of $g_J(N;^2D_{5/2})$.

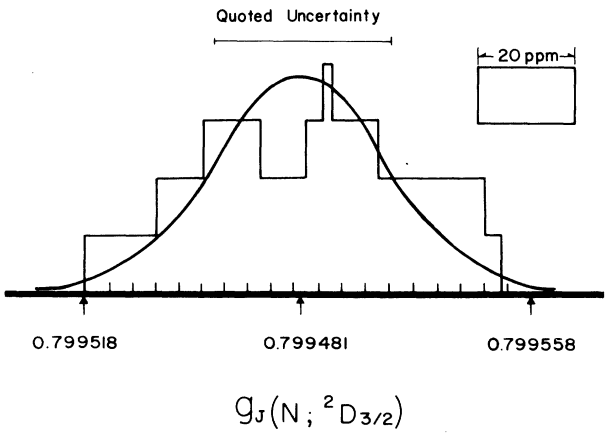

FIG. 7. Histogram of five determinations of $g_J(N;^2D_{3/2})$.

TABLE I. Experimental and calculated g_J factors of S and D levels in the ground-state configuration of atomic nitrogen. The value in square brackets denotes power of ten to which the value is raised.

Level	Landé g_J +SFA	δg_J(calc.)	δg_J(expt.)	calc.-expt. (ppm)
$^4S_{3/2}$	$2+\delta g_{\rm SFA}$	$-177.7[-6]$	$-184.6[-6]^a$	3.5
$^2D_{5/2}$	$(6+\delta g_{\rm SFA})/5$	$-140.8[-6]$	$-145.3(5)[-6]$	3.8(4)
$^2D_{3/2}$	$(4-\delta g_{\rm SFA})/5$	$-58.1[-6]$	$-55.1(15)[-6]$	$-3.8(18)$

$^a g_J(^4S_{3/2})$ is taken as exact for comparison with its calculated value since it is known to 0.03 ppm (Ref. 15).

$$g_J(^2D_{3/2}) = 0.799\,483\,(15)\ .$$

These are 35 and 10 ppm, respectively, below the previously known experimental values.[7]

DISCUSSION

The g_J factors of atomic nitrogen for all the levels of the ground-state configuration have been calculated to order α^2 with the theory of Abragam—Kambe–Van Vleck and with accurate Hartree-Fock wave functions.[26] The deviations of these calculated values from their respective Landé-plus-spin-factor-anomaly (SFA) values are shown in Table I together with their experimental counterparts as determined in this work. The experimental value of the $g_J(^4S_{3/2})$ factor is known to a much higher precision, 0.03 ppm, so it is taken as exact for purposes of comparison with the calculated value. The theoretical value, on the other hand, being free from the diamagnetic and the nuclear motion correction,[26] is quite simple and its calculation involved only one empirical parameter, the spin-orbit parameter ζ_{2p}, whose value is rather well established at about 70 $\rm cm^{-1}$ and has been shown to agree well with calculations made with Hartree-Fock wave functions.[36] The 3.5-ppm difference between the calculated and the experimental values in Table I can then be taken with fair degree of confidence as a measure of the effect of polarization on the $g_J(^4S_{3/2})$ factor. Polarization effects are, of course, also responsible for the nonzero value of the hfs constant in N $(^4S_{3/2})$ (Ref. 38) and for the differences between the observed ^2D and ^2P splittings and their calculated HF values.[34,36] Well-tailored superposition of configurations wave functions could probably bring all calculated values of the above parameters into agreement with experiment. Spin-extended HF calculations have already been shown to improve somewhat the $g_J(^4S_{3/2})$ value.[29]

The g_J $(^2D_{5/2})$ experimental and calculated values of Table I give additional support to the above conclusions. This factor is free from the effect of departures from LS coupling, i.e., it is not affected by the value of ζ_{2p}.[26] The correction to its Landé-plus spin-factor-anomaly value is calculated wholly from the HF wave functions and it is also seen to deviate from experiment by, at most, a few ppm.

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