Nuclear Magnetic Moment of Pr¹⁴¹ from the Hyperfine Structure of Pr II

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From the hyperfine structure of Pr II lines measured by White the magnetic interaction constant a_{6e} = 0.416 ± 0.015 cm⁻¹ has been evaluated for the 6s electron in the configuration $4f^{3}(^{4}I)$ 6s. Application of the formula of Goudsmit and Fermi-Segrè yields the nuclear magnetic moment $\mu(Pr^{141}) = +3.9 \pm 0.3$ nuclear magnetons.

TO precise value, of the order of precision attainable in the method of nuclear induction, has yet been found for the nuclear magnetic moment μ of Pr¹⁴¹. A preliminary value $\mu = 3.8$ nuclear magnetons has been derived¹ from the magnetic hyperfine structure (hfs) interaction constant a_{6s} of the 6s electron in Pr II. Recently Lew² measured the hfs due to the $4f^3$ electrons in Pr I and, independently, obtained the same result for μ from a_{4f} . In view of the theoretical uncertainties involved in any calculation of nuclear moments from hfs data of complex spectra, the agreement is very remarkable. Praseodymium is the first element for which the hfs of electronic states as different as 6s and 4f can be thus compared. It, therefore, seems justifiable to give a brief report of the calculations for Pr II, especially since the knowledge of a_{4f} now makes possible a more complete presentation.

The hfs of 170 lines of Pr II were measured by White³ in 1929. Rosen, Harrison, and McNally⁴ later classified 100 of these lines as transitions between $4f^{3}(4I)6s \ a^{3,5}I^{\circ}$ and higher even levels which originate mainly from $4f^{3}(4I)6p$. They used the hfs data as a check on the analysis of the spectrum, and made a rough estimate of a_{fs} . Thus far, however, the large amount of information available from White's measurements had not been fully utilized.

The Pr II lines' show characteristic hfs "flag patterns" with six components (I=5/2). Since in the classified transitions the total quantum numbers F are high, only the strong components can be observed.⁵ For each line the separations of the components are simply given by the differences of the hfs intervals of the two levels involved. The hfs of the levels can, therefore, be deduced from White's data except for an additive constant which is the same for all levels. It is convenient to introduce a quantity Δ which is equal to the total hfs splitting of a level plus the separation between the hfs states with F=J+I-1 and F=J+I-2. The connection between Δ and the interval factor A is given by

$$\Delta = A(2IJ + 2I + J - 1)$$

This sum, Δ , can be shown to be nearly independent of nuclear quadrupole effects. One also has the advantage that the four best defined components out of each hfs pattern are used.

As an example, Table I shows the difference between the Δ values of $a^5I_6^{\circ}$ and $a^3I_6^{\circ}$ as obtained from combinations with various upper levels. The agreement is even better than that shown in Table I for most of the other levels belonging to the terms a^5I° and a^3I° . Up to ten independent determinations are available in some cases. The possibility of frequent cross checks indicates an accuracy of better than ± 0.05 cm⁻¹, corresponding to about ± 0.001 cm⁻¹ for the A values.

The g sums as observed in the study of the Zeeman effect⁴ show that $a^{3,5}I^{\circ}$ and $z^{3,5}H$, I, K originate from a 6s and 6p electron, respectively, coupled to $4f^3 4I^\circ$ and that good Russell Saunders coupling holds for the ${}^{4}I^{\circ}$. Under these assumptions the magnetic interaction constants of the 6s and 6p electrons can be evaluated in the usual way⁵ from the experimental data. Since relativity corrections are negligible for the 4f electrons, Goudsmit's⁶ formula for the hfs of a multiplet is applicable to the parent term $4f^{3} I^{\circ}$. The contributions of the $4f^3$ configuration to the hfs of the various levels considered turn out to be nearly the same in all cases (see Table II). Only the small variations in these contributions enter into the evaluation of a_{6s} and μ . The influence upon the final result is less than 2 percent, and can be taken into account using $a_{4f} = 0.02356$ cm⁻¹

TABLE I. Example of the evaluation of the hfs of Pr II levels from White's measurements: $\Delta(a^{5}I_{6}^{\circ}) - \Delta(a^{3}I_{6}^{\circ})$ as obtained from pairs of lines originating from various upper levels.

Upper level	$\frac{\Delta(^{5}I_{6})-\Delta(^{3}I_{6})}{\mathrm{cm}^{-1}}$		
	2.43 2.44 2.42 2.46 2.43 2.37 2.56		
201	Mean 2.44		

⁶ S. Goudsmit, Phys. Rev. 37, 663 (1931).

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P. Brix, unpublished calculations, quoted by A. Steudel, Z. Physik 132, 429 (1952).
² H. Lew, Phys. Rev. 89, 530 (1953).
³ H. E. White, Phys. Rev. 34, 1397 (1929).
⁴ Rosen, Harrison, and McNally, Phys. Rev. 60, 722 (1941).
⁵ See, e.g., H. Kopfermann, Kernmomente (Akademische Verlagsgesellschaft, Leipzig, 1940).</sup>

TABLE II. Calculated and observed values of $\Delta = (6J+4)A$ for the low odd levels of Pr II. The contributions due to the $4f^3$ elec-trons (according to Lew's value of a_{4f}) and to the 6s-electron (with $a_{6s}=0.416 \text{ cm}^{-1}$) have been listed separately. All values in cm⁻¹.

Level	el Δ_{calc} for (Jj) coupling			$\Delta_{\mathbf{o}\mathbf{b}\mathbf{s}}$	Obs-calc
	from f ³	from 6s	total		
⁵ <i>I</i> ₄ °	+0.951	-1.165	-0.21	-0.21	0
⁵ <i>I</i> ⁵ ³ <i>I</i> ⁵	$^{+0.945}_{+0.915}$	$+1.414 \\ -1.179$	$^{+2.36}_{-0.26}$	$^{+2.20}_{-0.02}$	-0.16 + 0.24
${}^{5}I_{6}^{\circ}_{3}I_{6}^{\circ}$	$^{+0.910}_{+0.902}$	$+1.387 \\ -1.189$	$^{+2.30}_{-0.29}$	$^{+2.21}_{-0.23}$	-0.09 + 0.06
⁵ I7° ³ I7°	$^{+0.899}_{+0.901}$	+1.367 -1.196	$^{+2.27}_{-0.30}$	$^{+2.21}_{-0.27}$	-0.06 + 0.03
⁵ <i>I</i> ₈ °	+0.898	+1.352	+2.25	+2.25	0

as measured by Lew² for Pr I $4f^{3}6s^{2}$. No appreciable effect should arise from the slightly different screening of the 4f electrons in Pr I and Pr II. Assuming a ratio⁵ $a_{6p_{\frac{1}{2}}}/a_{6p_{\frac{3}{2}}}=6.66$, the following interaction constants have been obtained:

$a_{6s} = 0.416 \pm 0.015 \text{ cm}^{-1}$ $a_{6p_3} \approx 0.010 \text{ cm}^{-1}$.

For the odd levels the agreement between observed and calculated hfs is shown in Table II. The calculated Δ values are for (Jj) coupling with ${}^{5}I_{4}{}^{\circ}$ and ${}^{5}I_{8}{}^{\circ}$ independent of coupling. For Δ_{obs} the additive constant has been chosen to give agreement for ${}^{5}I_{4}^{\circ}$. As was already known from the atomic g values,⁴ Table II shows that a slight deviation from (J_i) coupling exists for the pairs of levels with equal J. For each of these pairs the differences o-c have the signs expected from a mutual perturbation, and the sum rule holds within the accuracy of the experimental data.

For an evaluation of the nuclear magnetic moment from a_{6s} the quantity $Z_a^2(dn_a/dn)/n_a^3$ is needed. Although neither n_a nor dn_a/dn are directly known from the spectrum of Pr II, the quantity as a whole can be fairly accurately derived^{7,8} from the position of the center of gravity of the $4f^{3}(4I)6p$ configuration with respect to the center of gravity of $4f^{3}(4I)6s$. From the value 23 600 cm⁻¹ so obtained,⁹ Fig. 7 of reference 8 gives

$$Z_a^2(dn_a/dn)/n_a^3 = 0.37_8$$
, for $4f^3(4I)6s$

This fits in well with the trend indicated by the directly known values for Ba II $4f^{0}6s$ (0.346) and Eu II $4f^{7}6s$ (0.406). The error for Pr II is not expected to exceed 5 percent.

The formula of Goudsmit and Fermi-Segrè,

finally yields

 $a_s = 0.008486 [Z_a^2 (dn_a/dn)/n_a^3]$

 $\mu(Pr^{141}) = +3.9 \pm 0.3$ nuclear magnetons.

 $\times \kappa(\mu/I)Z(1-\delta)(1-\epsilon)$ cm⁻¹,

The Rosenthal-Breit correction $\delta = 0.05$ has been taken from calculations of Crawford and Schawlow;¹⁰ the Bohr-Weisskopf correction ϵ can be neglected; and the relativity correction is $\kappa = 1.472$.

Lew,² using hydrogen like wave functions for the 4f electrons, obtained $\mu = +3.8 \pm \sim 10$ percent from the magnetic interaction constant a_{4f} . A comparison of the two results seems to indicate that the various formulas used are more reliable than could have been expected from the theoretical uncertainties involved. This is rather important with respect to the isotope shift constants of some rare earth elements (e.g., $cerium^7$) which also rely upon the validity, in complex spectra, of the Goudsmit-Fermi-Segrè formula and the determination of $Z_a^2(dn_a/dn)/n_a^3$ mentioned above.

I am very grateful to Dr. Lew for making available to me the results of his measurements in advance of publication.

⁹ Only four even levels with low statistical weight are missing in the analysis of Rosen, Harrison, and McNally (reference 4). Their positions have been estimated. ¹⁰ M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310

(1949).

⁷ P. Brix and H. Frank, Z. Physik **127**, 289 (1950). ⁸ P. Brix, Z. Physik **132**, 579 (1952).