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LOW-LYING ENERGY LEVELS OF LANTHANIDE ATOMS AND INTERMEDIATE COUPLING

Berkeley, California

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J. G. Conway and B. G. Wybourne

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ABSTRACT

A detailed examination of the effects of intermediate coupling on the properties of the low-lying levels of lanthanide atoms has been made. Particular attention has been given to the effects of a breakdown of Russell-Saunders coupling on the energies and magnetic properties of the levels of the ground multiplets. The energy levels were calculated by diagonalization of the combined electrostatic and spin-orbit matrices of the f^n configurations. It is found possible to fit the energy levels of the ground multiplets of NdI and SmI to within $2cm^{-1}$ of their observed energies using 4f-hydrogenic ratios for the Slater F_k integrals. The g values are found to agree within the experimental errors of the atomic beam measurements. An explanation for the apparent success of the 4f-hydrogenic eigenfunctions is offered and it is demonstrated that the success of these eigenfunctions does not imply that the actual eigenfunctions are hydrogen-like. Tables of the calculated energies and eigenvectors for low-lying levels are given together with the g values calculated in intermediate coupling. The effects of intermediate coupling on the relativistic and diamagnetic corrections to the g values are examined and shown to fall within the range of atomic beam measurements. The importance of intermediate coupling in the actinides is noted.

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INTRODUCTION

In recent years the application of the techniques of atomic beam resonances has led to very precise measurements of the g values associated with the levels of the ground multiplets of the atoms belonging to the first rare earth series, the lanthanides. Measurements of the hyperfine structure of the levels of these multiplets has permitted the evaluation of the nuclear magnetic and electric quadrupole moments of the atoms. Spectroscopic studies have succeeded in establishing all the energy levels of the ground multiplets of the NdI and SmI atoms. Except for CeI, GdI and TbI, the ground multiplets have been established as belonging to the $4f^n6s^2$ configurations.

In a recent paper Judd and Lindgren[1] have examined the Zeeman effect for the ground multiplets in considerable detail. They have made several corrections to the simple Lande' formula for the g values of the levels deriving from the ground terms of configurations of the type $4f^n$. Among these they attempted to (a) correct for deviations from perfect Russell-Saunders coupling, (b) correct for relativistic and diamagnetic effects. To calculate the spin-orbit corrections it was necessary to estimate the Slater integrals F_k and the spin-orbit coupling constants ζ_{4f}. The ratios of the integrals F_k were assumed to be those calculated for a 4f-hydrogenic

eigenfunction.

In the present paper it is shown that the energy levels of the ground multiplets of the lanthanide atoms are very sensitive to the magnitude of the spin-orbit coupling constants and relatively insensitive to the precise form of the Coulomb interaction. It is found that the remarkably close agreement between the calculated and experimental g values obtained by Judd and Lindgren[1] does not imply that the 4f-eigenfunctions for the lanthanides are necessarily even to a close approximation, hydrogen-like. Calculations of the spin-orbit corrections to the g values were made by diagonalizing the energy matrices of the appropriate $4f^n$ configurations. The eigenvectors obtained from these diagonalizations are tabulated and used to obtain accurate intermediate coupling corrections for the g values. An attempt has been made to obtain reliable estimates of the energies of the levels of the ground multiplets which in many cases still have to be established experimentally.

ENERGY LEVELS OF NdI AND SmI

Schuurmans[2] has established all the levels of the $4f^4(^5I)6s^2$ multiplet of NdI while Albertson[3] has established those of the $4f^6(^7F)6s^2$ multiplet of SmI. The complete energy matrices for the f^4 configuration have been calculated by Reilly[4], and Crozier and Runciman[5] while Ofelt[6] has calculated those of the three highest multiplicities of the f^6 configuration using the results of two earlier papers.[7,8] Following Judd and Lindgren it was assumed that the ratios of the Slater integrals F_4/F_2 and F_6/F_2 were those of a 4f-hydrogenic eigenfunction

i.e. $F_4/F_2 = 0.13805$ and $F_6/F_2 = 0.015108$

With this assumption it is then possible to express the elements of the energy matrices in terms of the two integrals F_2 and 4f. These two integrals

were then treated as freely variable parameters and the energy matrices of the f^4 and f^6 configurations diagonalized for several values of $X = \zeta_{4f}/F_2$.

It was found that for NdI the values

$$F_2 = 292.26\text{cm}^{-1} \quad \text{and} \quad \zeta_{4f} = 777.41\text{cm}^{-1}$$

produced a mean error between the calculated and experimental energy levels of $< 2\text{cm}^{-1}$ while for SmI it was found that the values

$$F_2 = 335.63\text{cm}^{-1} \quad \text{and} \quad \zeta_{4f} = 1062.27\text{cm}^{-1}$$

also produced a deviation of $< 2\text{cm}^{-1}$.

This agreement with experiment is better than might be expected when it is remembered that no attempt has been made to include the spin-spin, spin-other-orbit or configuration interactions which in general will be of larger magnitude than the mean deviations for these calculations. The calculation is even more impressive when it is realized that the eigenvectors obtained from the diagonalization of the energy matrices permit an almost exact treatment of the spin-orbit corrections to the g values to be made which results in the observed and calculated g values to agree almost within the experimental errors which for the most part occur in the fifth decimal place.

This remarkable agreement might be thought to justify the simple expedient of taking the ratios of the Slater integrals as those of the 4f-hydrogenic eigenfunction. It might also be thought possible to make accurate predictions of the energies of the levels of the higher multiplets using these parameters. Such conclusions are erroneous. This may be readily seen by considering the calculation of the energies of the ground multiplets from the standpoint of perturbation theory. The splittings of the ground multiplet will be given to second order by

$$(0|\Lambda|0) - \frac{\sum_m (0|\Lambda|m)(m|\Lambda|0)}{E_m} \tag{1}$$

where $|0$ denotes the ground level and $|m)$ an upper level at an energy E_m above it while Λ is the spin-orbit interaction operator. The eigenfunctions for the perturbed levels of the ground multiplet will be given by

$$|0') = \left(1 - \left[\frac{\sum_m (0|\Lambda|m)}{E_m}\right]^2\right)|0) - \frac{\sum_m (0|\Lambda|m)|m}{E_m} \tag{2}$$

The energy denominators appearing in these equations will be equal to the difference in the Coulombic energy of the upper state $|m)$ and the lower state $|0)$. These energies have been tabulated by Elliott, Judd and Runciman.[9] An inspection of their tables shows that in almost every case the energy denominators appearing in these equations will be quite large. This gives the reason for the apparent success of the hydrogenic approximation for the ground multiplets of the lanthanides. Since the energy denominators are large slight changes in the energy denominators will not affect the levels of the ground multiplets to any appreciable extent. Departures of the ratios of the Slater integrals from those of the 4f-hydrogenic eigenfunction will result in changes in the energy denominators but their effect for the most part will not be felt by the low lying levels of the ground multiplets. We conclude that for the ground multiplets of the atoms of the lanthanides the splittings of the levels will not be a sensitive function of the choice of Slater integrals. To test this conclusion the energy matrices of the f^6 configuration were diagonalized taking the ratios of the Slater integrals to be those of the 5f-hydrogenic eigenfunction

$$F_4/F_2 = 0.14218 \qquad \text{and} \qquad F_6/F_2 = 0.016104$$

It was then found that the energy levels of the ^7F multiplet of SmI could be fitted to the observed energy levels with a mean error of $<2cm^{-1}$ using the parameters

$$F_2 = 316.68cm^{-1} \qquad \text{and} \qquad \zeta_{4f} = 1064.04cm^{-1}$$

The eigenvectors of the states of the ground multiplet were found to be the same as those for the earlier 4f-hydrogenic calculation to better than four significant figures. The g values again were found to be almost within the experimental error. It will be noted that F_2 differs considerably in the two calculations whereas ζ_{4f} differs by $<2cm^{-1}$. From these results we conclude that the ζ_{4f} values obtained from analyses of the structure of the ground multiplets of the lanthanides are insensitive to the choice of the Slater integrals. The values of ζ_{4f} obtained for NdI and SmI agree very closely with those of Judd and Lindgren and it appears unlikely that any substantial improvement can be made to their interpolated values. Since the values of ζ_{4f} deduced from the structure of the ground multiplets are insensitive to the choice of the Slater integrals and are unlikely to be affected appreciably by configuration interaction it would seem that these values should closely define the spin-orbit coupling constants for all the levels of the f^n configuration. It has been a tradition of theoretical spectroscopy to treat both the Slater integrals <u>and</u> the spin-orbit coupling constants as parameters to be freely varied. When these parameters are derived by a least-squares analysis of the energy levels of the f^n configuration it is usually found that the parameters so obtained lead to appreciable

deviations between the calculated and experimental energy levels of ground multiplets. The reason for these deviations would seem to be due to the tendency for the spin-orbit coupling constant to change from that deduced from considerations of the energy level structure of the ground multiplet alone so as to accomodate part of the changes in the energies of the upper terms produced by configuration interaction. The deviations due to configuration interaction are associated in the main part with the Coulomb interactions. It would appear to be more realistic in making energy level calculations to first derive accurate values of ζ_{4f} from the levels of the ground multiplet and then to treat the Slater integrals as free variables, keeping the spin-orbit coupling constant fixed. The remaining deviations should then give a truer indication of the extent of configuration interaction effects.

THE GROUND MULTIPLETS

The results obtained for NdI and SmI show that if 4f-hydrogenic ratios for the Slater radial integrals are used an excellent fit of both the energy levels and the g values of the levels of the ground multiplets can be made by treating F_2 and ζ_{4f} as parameters. The values of ζ_{4f} obtained are consistent with those of Judd and Lindgren.

Using the energy matrices for the three highest multiplicities of all the f^n configurations we have endeavoured to determine the values of $X = \zeta_{4f}/F_2$ that most closely reproduce the observed g values for the ground multiplets, including the relativistic and diamagnetic corrections given by Judd and Lindgren. The values of X obtained are given in Table I. Using the ζ_{4f} values given by Judd and Lindgren, except for NdI and SmI where slightly more accurate values were possible the energy levels were calculated

for the ground multiplets of all those lanthanides having the $4f^n$ configuration lowest. Experience with the levels of the ground multiplets of NdI and SmI would seem to indicate that the calculated energy levels are probably correct to within a few cm^{-1} apart from the possible exception of ErI where the intermediate coupling effects are considerable even for the ground multiplet. These calculated energy levels should be of assistance in establishing the energy levels by spectroscopic methods. All the energy levels of the f^n configurations were calculated and the levels below $\sim 12{,}000 cm^{-1}$ are tabulated in Table II. The higher energy levels cannot be expected to have anywhere near the preciseness of those of the ground multiplets since they will be extremely sensitive to the choice of Slater integrals. They are tabulated solely as a guide to spectroscopists engaged in determining the energy levels experimentally. The energy ordering of the levels of the same J quantum numbers is unlikely to change. The deviations between the energies of the observed and experimental levels will in some cases be as large or larger than $1500 cm^{-1}$ with a mean error of approximately $500 cm^{-1}$.

The Schwinger g values were calculated in Russell-Saunders coupling and then transformed to intermediate coupling using the complete eigenvectors obtained from the diagonalization of the energy matrices. The relativistic and diamagnetic corrections of Judd and Lindgren[1] were then added to the intermediate coupling corrected g values to give the final calculated g values. The calculated g values are compared with the observed g values[10] for the ground multiplets in Table II.

The eigenvectors were calculated to seven significant figures and their accuracy verified in all cases to be better than six significant figures. Due to the bulk of the computer output it is not feasible to

tabulate all the components of the eigenvectors. In most practical applications it is unnecessary to use more than the components of the eigenvectors originating from the states of the two highest multiplicities to obtain by far the major part of the intermediate coupling corrections. In Table III the eigenvectors for the energy levels below 5000cm^{-1} of the ground multiplets are given to four significant figures ommiting components $<10^{-3}$ and components originating from states of the third highest multiplicity except for the special case of EuI $4f^7(^8S_{7/2})$.

An inspection of Table III allows several conclusions as to the importance of intermediate coupling in the lanthanides to be drawn. In many cases the levels of the ground multiplets are better than 95% pure Russell-Saunders states. This might be taken as indicating that <u>all</u> the levels of the configurations are fairly closely Russell-Saunders coupled states. Such is not however the case.

The ground multiplets of the $4f^n$ configurations tend to exhibit close Russell-Saunders coupling simply because the perturbing states are so far from the levels of the ground multiplet in comparison with the magnitudes of the perturbing interactions. The spin-orbit coupling constants are a steadily increasing function of atomic number with the result that the breakdown of Russell-Saunders coupling increases with increasing atomic number. Of considerably greater importance is the rapid increase in the density of the upper states that occurs as the half-filled shell of electrons or holes is approached. As the density of states increases the spacings between interacting states decreases with the result that for the upper states the effects of spin-orbit interaction becomes increasingly larger and hence the breakdown of Russell-Saunders coupling increases. These effects lead to a considerable breakdown of Russell-Saunders coupling in

f^n configurations where $10 \geq n \geq 4$, particularly for the upper states. In many cases the breakdown of Russell-Saunders coupling is so great that the usual LS labels of this coupling scheme lose all meaning.

Using the eigenvectors of Table III it is possible to examine the effects of intermediate coupling on several important quantum mechanical operators. Of considerable topical importance are the effects of intermediate coupling on the g values and on the calculation of nuclear moments from hyperfine strucure measurements.

In making the calculations of the g values for Table II it was assumed that the relativistic and diamagnetic corrections are those for the pure Russell-Saunders ground multiplets. This same assumption is also explicit in the work of Judd and Lindgren.[1] The relativistic and diamagnetic corrections are not however diagonal in the LSJ quantum numbers. It is of some interest to examine the effect of a breakdown of Russell-Saunders coupling on these corrections since they will be of particular importance when detailed studies of the second rare earth series, the actinides, are undertaken where the breakdown of Russell-Saunders coupling is considerable even for the ground multiplets.[11-13]

The levels of the ground multiplets are sufficiently separated from one another and the corrections are sufficiently small to allow us to neglect the coupling of levels of different J. Judd and Lindgren[1] have shown that for a system of n-equivalent electrons the relativistic and diamagnetic corrections may be represented by the matrix elements of the operator

$$H_{op} = -\alpha^2 \left[\sum_{i=1}^{n} (\underset{\sim}{\ell}_i + 2\underset{\sim}{s}_i)\langle T+Y\rangle - \sum_{i=1}^{n} \left(\underset{\sim}{s}_i - \frac{\underset{\sim}{r}_i(\underset{\sim}{r}_i \cdot \underset{\sim}{s}_i)}{\underset{\sim}{r}_i^2}\right)\langle T+U\rangle \right] \qquad (3)$$

where α is the fine structure constant and $\langle T+Y \rangle$ and $\langle T+U \rangle$ are the expectation values of the radial integrals defined in their paper. For the f^n configuration the matrix elements of H_{op} diagonal in J will be given by

$$(f^n \alpha SLJ | H_{op} | f^n \alpha' S' L' J') = - \alpha^2 \, [g \, \langle T+Y \rangle - h \, \langle T+U \rangle] \tag{4}$$

where g is the classical Lande' g values and h is the matrix element of the operator appearing in the second part of the r.h.s. of eqn (3).

$$\text{Writing} \quad H'_{op} = \sum_{i=1}^{n} \frac{(\underset{\sim}{s}_i - \underset{\sim}{r}_i (\underset{\sim}{r}_i \cdot \underset{\sim}{s}_i))}{r_i^2}$$

$$= \frac{1}{3} \sum_{i=1}^{n} [2\underset{\sim}{s}_i + 10^{1/2} (\underset{\sim}{s}_i^{(1)} \times \underset{\sim}{C}^{(2)})_i^{(1)}] \tag{5}$$

we obtain

$$h = (f^n \alpha SLJ | H'_{op} | \alpha' S' L' J)$$

$$= \frac{2}{3} \left[(g-1) - \left(\frac{14(2J+1)}{J(J+1)} \right)^{1/2} \begin{Bmatrix} S & S' & 1 \\ L & L' & 2 \\ J & J & 1 \end{Bmatrix} (f^n \alpha SL | \, |V^{12}| \, | f^n \alpha' S' L') \right] \tag{6}$$

$$= \frac{2}{3} \left[(g-1) - \mathscr{S} \right] \tag{6'}$$

where $(f^n \alpha SL \| V^{12} \| f^n \alpha' S' L') = n[3(2S+1)(2S'+1)(2L+1)(2L'+1)/2]^{1/2}$

$$\times \sum_{\bar{\psi}} (\psi\} | \bar{\psi}) (\psi'\} | \bar{\psi}) \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \bar{S} \end{Bmatrix} \begin{Bmatrix} L & L' & 2 \\ 3 & 3 & \bar{L} \end{Bmatrix} (-L)^{\bar{L}+\bar{S}+L+S+1/2} \tag{7}$$

The calculation of the matrix elements of the double tensors V^{12} has been discussed elsewhere.[14,15]

Using eqns (4) to (7) the matrix elements of the relativistic and diamagnetic correction operator H_{op} may be evaluated in the αSLJ representation and then a transformation to intermediate coupling made using the eigenvectors of Table III. In general these calculations tend to be lengthy and tedious. The $4f^{12}$ configuration of ErI forms a simple system in which to examine the effect of a breakdown of Russell-Saunders coupling on the relativistic and diamagnetic corrections. For pure Russell-Saunders coupling the relativistic and diamagnetic correction for the $^3H_6$ ground state is given by

$$\delta g = -\alpha^2\left(\frac{7}{6}\langle T+Y\rangle - \frac{7}{54}\langle T+U\rangle\right) = -0.00198 \qquad (8)$$

Evaluating the matrix elements of H_{op} for the remaining interactions within the J=6 manifold of the f^{12} configuration one obtains $(^1I_6|H_{op}|^1I_6) = -\alpha^2\langle T+Y\rangle$ and $(^1I_6|H_{op}|^3H_6) = -\alpha^2 \frac{2^{1/2}}{54}\langle T+U\rangle$

Using the eigenvectors of Table III it is easily seen that the intermediate coupling relativistic and diamagnetic correction becomes

$$\delta g' = -\alpha^2\left[\frac{7}{6}(0.99885)\langle T+Y\rangle - \frac{7}{54}(0.95604)\langle T+U\rangle\right]$$

$$= -0.00199 \qquad (9)$$

Comparison of eqns (8) and (9) shows that the effect of intermediate coupling is to change the relativistic-diamagnetic correction from its

Russell-Saunders value by one unit in the fifth decimal place. This change while small is well within the experimental error of the atomic beam measurements for ErI ($^3H_6$).[15] The ground state of ErI departs only slightly from Russell-Saunders coupling and hence the small change is hardly surprising. The J = 4 levels of the $4f^{12}$ configuration of ErI depart markedly from Russell-Saunders coupling. The lowest J = 4 level which would be expected to be $^3H_4$ actually contains a predominating admixture of the $^3F_4$ state. The three J = 4 states afford us the opportunity of examining the effect of a large breakdown of Russell-Saunders coupling on the relativistic-diamagnetic corrections in a relatively simple system. The eigenvectors of the three levels in order of increasing energy are as follows:

$$|^3F_4) = 0.76559|^3F_4) + 0.56664|^1G_4) - 0.30460|^3H_4)$$

$$|^3H_4) = 0.76164|^3H_4 - 0.33776|^1G_4) + 0.55301|^3F_4)$$

$$|^1G_4) = 0.75156|^1G_4) + 0.57194|^3H_4) - 0.32870|^3F_4)$$

where we label the eigenvectors by their principal component. The results of the intermediate calculations are given in Table IV. The changes from the Russell-Saunders corrections are seen to be $\sim 5 \times 10^{-6}$ which is well within the experimental errors of the usual measurements. It will be noted that the values of h in intermediate coupling differs considerably from its value in Russell-Saunders coupling. However, the magnitude of h is usually considerably smaller than g with the result that the large change in h is not usually of major importance in the total relativistic-diamagnetic correction.

In many cases it is impractical to attempt a complete calculation

of the relativistic-diamagnetic correction and a method of making an approximate correction is desirable. We have found the formula

$$\delta g = -\frac{\alpha^2}{3}\left[g(3\langle T+Y\rangle - 2\langle T+U\rangle) + 2\langle T+U\rangle\right] \qquad (10)$$

where the g on the r.h.s. is the intermediate coupling corrected Lande g value will usually result in relativistic-diamagnetic corrections which differ from those calculated using the complete formula of eqn (4) only in the fifth decimal place. This simple formula should be of considerable assistance in understanding the Zeeman effect of levels of actinide atoms and ions without requiring extensive calculations.

The eigenvectors of Table III may also be used in calculating nuclear magnetic and electric quadrupole moments from hyperfine measurements with correction for intermediate coupling effects. The method of making these corrections has been outlined in an earlier paper.[16] These corrections result in changes of the calculated nuclear moments for lanthanide atoms of 2-4%

CONCLUSIONS

It has been shown that quite different sets of Slater radial integrals may be chosen to reproduce the observed energy levels and g values for either the NdI or SmI ground multiplet with remarkable accuracy. This result emphasizes the great need for caution in trying to deduce the properties of the higher energy levels from a study of the ground multiplets alone. Clearly the hydrogenic approximation is a very crude guess of the ratios of the Slater radial integrals and is of little physical significance. It is unfortunate that a better choice of the Slater radial

integrals does not seem possible at the present time. Attempts to calculate the radial integrals from Hartree-Fock wave functions have not led to integrals that will reproduce the observed energy levels or g values with any appreciable accuracy.[17] The alternative approach is to deduce the magnitudes of the integrals from the experimental data as has been the tradition of theoretical spectroscopy.[18] However, if the integrals are to be deduced from experimental data with any reliability considerable extensions will have to be made to the existing data. In particular it is urgently necessary to establish the higher energy levels of the f^n configurations. Until this is done there is little hope of progress in determining the integrals empirically. Data limited to the ground multiplets clearly will not suffice.

The inclusion of the higher spin-orbit interactions which were neglected by Judd and Lindgren[1] leads to a considerable improvement in the calculation of the properties of the ground multiplets of NdI and SmI. It will be difficult to make meaningful improvements to these calculations. Judd, Rajnak and Wybourne[19] have shown that the effects of configuration interaction in the f^n configurations are by no means negligible though their effects are unlikely to be significant as far as the levels of the ground multiplets are concerned. The levels of the ground multiplets are probably more seriously affected by the failure to include the effects of spin-spin and spin-other-orbit interactions. In NdI spin-spin effects produce relative shifts of the levels of the ground multiplet $\sim 5 cm^{-1}$ while contact spin-spin produces shifts of a similar order.[20] It will be noted that these shifts are larger than the discrepancies between the calculated and experimental energies given in this paper where these effects have been

neglected. From a general study of spin-spin and spin-other-orbit effects Horie[21] has concluded that these effects are probably quite small for the heavy elements. In any improved treatment it would be necessary to consider spin-spin, spin-other-orbit, and configuration interactions simultaneously as they almost certainly produce effects of approximately equal importance. A partial treatment of any one of these interactions alone would almost certainly give a meaningless result.

The actinides are likely to behave quite differently from the corresponding lanthanides. The extreme breakdown of Russell-Saunders coupling makes the interpretation of the energies and magnetic properties of the low-lying levels very difficult. The treatment of the relativistic and diamagnetic corrections for the g values of the ground states can not be made on the basis of Russell-Saunders coupling as has been done for the lanthanides. Equation (10) should however, make it possible to correct for the greater part of the effects of intermediate coupling however, as yet the appropriate radial integrals are unknown.

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Table I. Values of $X(\zeta/F_2)$ for the Lanthanide atoms.

ATOM	Pr	Nd	Pm	Sm	Eu	Tb	Dy	Ho	Er
X	2.45	2.7	3.17	3.165	3.49	4.0	4.2	4.5	5.3

Table II. Energy Levels and g values of the Low Lying Levels.

Atom	SLJ	E Experimental	E Calculated	g Intermediate	g Calculated	g Experimental
PrI	$^4I_{9/2}$		0	0.7319584	0.7310084	0.7311±0.0002
	$^4I_{11/2}$		1307.10	0.96618		
	$^4I_{13/2}$		2705.30	1.07889		
	$^4I_{15/2}$		4163.33	1.19882		
	$^4F_{3/2}$		8678.38	0.42473		
	$^2H_{9/2}$		9174.79	0.98193		
	$^4F_{5/2}$		9399.90	1.03178		
	$^4S_{3/2}$		9990.01	1.96248		
	$^4F_{7/2}$		10071.20	1.21173		
NdI	$^5I_4$	0	0	0.6039981	0.6030181	0.6032±0001
	$^5I_5$	1128.04	1126.81	0.9014648	0.9004048	0.9002±0002
	$^5I_6$	2366.58	2367.22	1.0709314	1.0698114	1.0715±0020
	$^5I_7$	3681.65	3684.01	1.17628		
	$^5I_8$	5048.54	5049.34	1.24596		

Table II. Energy Levels and g values of the Low Lying Levels. (Cont.)

Atom	SLJ	E Experimental	E Calculated	g Intermediate	g Calculated	g Experimental
PmI	$^6H_{5/2}$		0	0.2970411		
	$^6H_{7/2}$		816.12	0.8294469	0.8283461	0.82836±.0006[a]
	$^6H_{9/2}$		1768.62	1.0712606	1.0700600	1.068±004
	$^6H_{11/2}$		2815.51	1.20096		
	$^6H_{13/2}$		3924.44	1.27835		
	$^6F_{1/2}$		4915.31	-0.64916		
	$^6H_{15/2}$		5070.83	1.32688		
	$^6F_{3/2}$		5097.40	1.05718		
	$^6F_{5/2}$		5477.91	1.30334		
	$^6F_{7/2}$		6152.83	1.38925		
	$^6F_{9/2}$		7077.38	1.42937		
	$^6F_{11/2}$		8170.88	1.45068		
SmI	$^7F_0$	0	0	0/0	0/0	0/0
	$^7F_1$	292.58	291.39	1.499868	1.49849	1.49838±.00005
	$^7F_2$	811.92	812.13	1.499261	1.49786	1.49777±.00003
	$^7F_3$	1489.55	1490.28	1.498498	1.49707	1.49705±.00003
	$^7F_4$	2273.09	2274.81	1.497712	1.49628	1.49623±.00004
	$^7F_5$	3125.46	3126.72	1.496808	1.49535	1.49531±.00006
	$^7F_6$	4020.66	4020.67	1.495726	1.49424	1.49417±.00010

[a] B. Budick, Lawrence Radiation Laboratory Report UCRL-10245, 1962 (Unpublished).

Table II. Energy Levels and g values of the Low Lying Levels. (Cont.)

Atom	SLJ	E Experimental	E Calculated	g Intermediate	g Calculated	g Experimental
EuI	$^8S_{7/2}$		0	1.9951404	1.9933909	1.99337±.00007
Tb	$^6H_{15/2}$		0	1.3258045	1.3240545	1.3225±0.003
	$^6H_{13/2}$		2810.19	1.27766		
	$^6H_{11/2}$		4791.64	1.20332		
	$^6H_{9/2}$		6334.04	1.07365		
	$^6F_{11/2}$		7172.93	1.44654		
	$^6H_{7/2}$		7489.15	0.83339		
	$^6F_{9/2}$		8326.10	1.42119		
	$^6H_{5/2}$		8419.21	0.30365		
	$^6F_{7/2}$		9901.14	1.38564		
	$^6F_{5/2}$		11066.32	1.30735		
	$^6F_{3/2}$		11749.20	1.06866		
	$^6F_{1/2}$		12196.08	-0.61494		
DyI	$^5I_8$	0	0	1.2432171	1.2414371	1.24166±.00007
	$^5I_7$		4160.15	1.175089		
	$^5I_6$		7148.23	1.07260		
	$^5I_5$		9376.25	0.90874		
	$^5I_4$		11126.59	0.61622		

Table II. Energy Levels and g values of the Low Lying Levels. (Cont.)

Atom	SLJ	E Experimental	E Calculated	g Intermediate	g Calculated	g Experimental
HoI	$^4I_{15/2}$		0	1.1972224	1.1951724	1.19516±.00010
	$^4I_{13/2}$		5428.06	1.07845		
	$^4I_{11/2}$		8722.08	0.98101		
	$^4I_{9/2}$		10979.62	0.80095		
ErI	$^3H_6$		0	1.1657185	1.1637985	1.163801±.000001
	$^3F_4$		4962.72	1.12827		
	$^3H_5$		6972.45	1.03341		
	$^3H_4$		10762.25	0.96034		

Table III. Eigenvectors for levels below 5000cm^{-1}.

Atom	SLJ	Eigenvector
PrI	$^4I_{9/2}$	$0.9856\|^4I)+0.0564\|^2_3H_{11})-0.1579\|^2_3H_{21})-0.0158\|^2_3G_{20})+0.0140\|^2_3G_{21})$ $+0.0068\|^4G)+0.0027\|^4F)$
	$^4I_{11/2}$	$0.9950\|^4I)+0.0358\|^2_3H_{11})-0.0915\|^2_3H_{21})-0.0142\|^2I)+0.0064\|^4G)$
	$^4I_{13/2}$	$0.9938\|^4I)+0.0605\|^2K)-0.0214\|^2I)$
	$^4I_{15/2}$	$0.9939\|^4I)+0.1104\|^2K)-0.0078\|^2L)$
NdI	$^5I_4$	$0.9879\|^5I)-0.0081\|^3_4H_{11})+0.0777\|^3_4H_{21})-0.1138\|^3_4H_{30})+0.0678\|^3_2H_{11})$ $-0.0037\|^5G)+0.0028\|^3_4G_{20})+0.0120\|^3_4G_{21})-0.0074\|^3_4G_{30})+0.0012\|^5F)$ $+0.0016\|^3_4F_{30})$
	$^5I_5$	$0.9932\|^5I)-0.0194\|^3_4I_{20})+0.0175\|^3_4I_{30})-0.0039\|^3_4H_{11})+0.0583\|^3_4H_{21})$ $-0.0835\|^3_4H_{30})+0.0484\|^3_2H_{11})-0.0043\|^5G)+0.0015\|^3_4G_{20})+0.0086\|^3_4G_{21})$ $-0.0052\|^3_4G_{30})+0.0012\|^5F)$
	$^5I_6$	$0.9947\|^5I)-0.0287\|^3_4I_{20})+0.0248\|^3_4I_{30})-0.0323\|^3_4K_{21})+0.0607\|^3_4K_{30})$ $+0.0350\|^3_4H_{21})-0.0492\|^3_4H_{30})+0.0277\|^3_2H_{11})-0.0033\|^5G)$
	$^5I_7$	$0.9910\|^5I)-0.0317\|^3_4I_{20})+0.0257\|^3_4I_{30})-0.0585\|^3_4K_{21})+0.1125\|^3_4K_{30})$ $-0.0130\|^3_4L_{21})$
	$^5I_8$	$0.9818\|^5I)-0.0830\|^3_4K_{21})+0.1683\|^3_4K_{30})-0.0198\|^3_4L_{21})+0.0361\|^3_4M_{30})$

Table III. Eigenvectors for levels below 5000cm^{-1}. (Cont.)

Atom	SLJ	Eigenvector
Pm I	$^6H_{5/2}$	$0.9781\|^6_5H_{11})+0.0019\|^4_5D_{20})-0.0024\|^4_5D_{21})+0.0017\|^4_3D_{20})+0.0120\|^6_5F_{10})$
		$-0.0175\|^4_5F_{21})-0.0079\|^4_5F_{30})+0.0075\|^4_3F_{10})+0.0345\|^4_5G_{20})$
		$+0.0321\|^4_5G_{21})-0.1546\|^4_5G_{30})-0.1257\|^4_3G_{20})$
	$^6H_{7/2}$	$0.9851\|^6_5H_{11})+0.0015\|^4_5D_{20})-0.0021\|^4_5D_{21})+0.0013\|^4_3D_{20})$
		$+0.0159\|^6_5F_{10})-0.0167\|^4_5F_{21})-0.0075\|^4_5F_{30})+0.0067\|^4_3F_{10})$
		$+0.0257\|^4_5G_{20})+0.0219\|^4_5G_{21})-0.1256\|^4_5G_{30})-0.1012\|^4_5G_{20})$
		$0.0217\|^4_5H_{11})+0.0319\|^4_5H_{30})$
	$^6H_{9/2}$	$0.9897\|^6_5H_{11})+0.0145\|^6_5F_{10})-0.0104\|^4_5F_{21})-0.0045\|^4_5F_{30})$
		$+0.0038\|^4_3F_{10})+0.0151\|^4_5G_{20})+0.0123\|^4_5G_{21})-0.0913\|^4_5G_{30})$
		$-0.0729\|^4_3G_{20})0.0333\|^4_5H_{11})+0.0015\|^4_5H_{21})+0.0475\|^4_5H_{30})$
		$+0.0449\|^4_5I_{30})+0.0234\|^4_3I_{20})$

Table III. Eigenvectors for levels below 5000cm^{-1}. (Cont.)

	$^6H_{11/2}$	$0.9903\|^6_5H_{11})+0.0093\|^6_5F_{10})+0.0055\|^4_5F_{10})+0.0049\|^4_5F_{21})$ $-0.0534\|^4_5F_{30})-0.0423\|^4_3F_{10})+0.0411\|^4_5H_{11})+0.0028\|^4_5H_{21})$ $+0.0566\|^4_5H_{30})+0.0866\|^4_5I_{30})+0.0441\|^4_3I_{20})-0.0086\|^4_5K_{21})$ $+0.0036\|^4_5K_{30})$
	$^6H_{13/2}$	$0.9860\|^6_5H_{11})+0.0403\|^4_5H_{11})+0.0044\|^4_5H_{21})0.0537\|^4_5H_{30})$ $+0.0053\|^4_5I_{20})+0.1350\|^4_5I_{30})+0.0661\|^4_5I_{20})+0.0165\|^4_5K_{21})$ $+0.0066\|^4_5K_{30})-0.0029\|^4_5L_{21})$
Pm	$^6F_{1/2}$	$0.9842\|^6_5F_{11})+0.1106\|^4_5D_{20})-0.1089\|^4_5D_{21})+0.0799\|^4_3D_{20})$ $+0.0042\|^4_5P_{30})-0.0042\|^4_5P_{11})$
Pm	$^6H_{15/2}$	$0.9769\|^6_5H_{11})+0.0161\|^4_5I_{20})+0.1903\|^4_5I_{30})+0.0882\|^4_3I_{20})$ $-0.0217\|^4_5K_{21})+0.0072\|^4_5K_{30})-0.0045\|^4_5L_{21})+0.0017\|^4_5M_{30})$

Table III. Eigenvectors for levels below 5000cm^{-1}. (Cont.)

SmI	$^7F_0$	$0.9712\|^7_6F_{10})+0.0022\|^5_6D_{20})+0.1580\|^5_6D_{21})-0.1733\|^5_4D_{20})$
	$^7F_1$	$0.9764\|^7_6F_{10})-0.0035\|^5_6P_{11})+0.0054\|^5_6D_{20})+0.1409\|^5_6D_{21})$
		$-0.1577\|^5_4D_{20})+0.0248\|^5_6F_{21})+0.0156\|^5_4F_{10})$
	$^7F_2$	$0.9833\|^7_6F_{10})-0.0040\|^5_6P_{11})+0.0102\|^5_6D_{20})+0.0111\|^5_6D_{21})$
		$-0.1307\|^5_4D_{20})+0.0445\|^5_6F_{21})+0.0273\|^5_4F_{10})-0.0047\|^5_6G_{20})$
		$-0.0136\|^5_6G_{21})+0.0148\|^5_4G_{20})$
	$^7F_3$	$0.9884\|^7_6F_{10})-0.0034\|^5_6P_{11})+0.0134\|^5_6D_{20})+0.0771\|^5_6D_{21})$
		$-0.0966\|^5_4D_{20})+0.0615\|^5_6F_{21})+0.0370\|^5_4F_{10})-0.0115\|^5_6G_{20})$
		$-0.0310\|^5_6G_{21})+0.0332\|^5_4G_{20})+0.0015\|^5_6H_{11})+0.0022\|^5_6H_{21})$
	$^7F_4$	$0.9905\|^7_6F_{10})+0.0119\|^5_6D_{20})+0.0417\|^5_6D_{21})-0.0575\|^5_4D_{20})$
		$+0.0723\|^5_5F_{21})+0.0419\|^5_4F_{10})-0.0222\|^5_6G_{21})-0.0535\|^5_6G_{20})$
		$+0.0568\|^5_4G_{20})+0.0036\|^5_6H_{11})+0.0051\|^5_6H_{21})$

Table III. Eigenvectors for levels below 5000cm^{-1} (Cont.)

$^7F_5$	$0.9889\|^7_6F_{10})+0.0694\|^5_6F_{21})+0.0378\|^5_4F_{10})-0.0390\|^5_6G_{21})$
	$-0.0814\|^5_6G_{20})-0.0852\|^5_4G_{20})+0.0069\|^5_6H_{11})+0.0088\|^5_6H_{21})$
$^7F_6$	$0.9839\|^7_6F_{10})+0.0656\|^5_6G_{21})-0.1152\|^5_6G_{20})+0.1174\|^5_4G_{20})$
	$0.0091\|^5_6H_{11})+0.0102\|^5_6H_{21})-0.0013\|^5_6I_{20})$

Table III. Eigenvectors for levels below 5000cm^{-1}. (Cont.)

EuI	$^8S_{7/2}$	$0.9876\|^8_7S_{00})+0.1557\|^6_5P_{11})-0.0113\|^6_7D_{20})-0.0027\|^4_7D_{20})$
		$+0.0127\|^4_7D_{22}\|+0.0124\|^4_3D_{20})-0.0016\|^4_5F_{30})$
TbI	$^6H_{15/2}$	$0.9729\|^6_5H_{11})-0.0051\|^4_5I_{20})-0.0020\|^4_5I_{30})-0.032\|^4_5I_{20})$
		$-0.0221\|^4_5K_{21})+0.0089\|^4_5K_{30})+0.0044\|^4_5L_{21})+0.0012\|^4_5M_{30})$
	$^6H_{13/2}$	$0.9839\|^6_5H_{11})+0.0404\|^4_5H_{11})-0.0578\|^4_5H_{30})-0.0103\|^4_5I_{20})$
		$-0.1463\|^4_5I_{30})-0.0701\|^4_3I_{20})-0.0170\|^4_5K_{21})+0.0061\|^4_5K_{30})$
		$+0.0025\|^4_5L_{21})$
	$^6H_{11/2}$	$0.9747\|^6_5H_{11})+0.0859\|^6_5F_{10})-0.0220\|^4_5F_{10})-0.0401\|^4_5F_{21})$
		$+0.1069\|^4_5F_{30})+0.0917\|^4_3F_{10})-0.0550\|^4_5H_{11})-0.0760\|^4_5H_{30})$
		$-0.0126\|^4_5I_{20})-0.0945\|^4_5I_{30})-0.0420\|^4_3I_{20})-0.0090\|^4_5K_{21})$
		$-0.0025\|^4_5K_{30})$
DyI	$^5I_8$	$0.9710\|^5_4I_{20})+0.1089\|^3_4K_{21})-0.2086\|^3_4K_{30})-0.0276\|^3_4L_{21})$
		$-0.0051\|^3_4M_{30})$

	$^5I_7$	$0.9871\|{}^5_4I_{20})+0.0343\|{}^3_4I_{20})-0.0298\|{}^3_4I_{30})+0.0674\|{}^3_4K_{21})$
		$-0.1367\|{}^3_4K_{30})-0.0162\|{}^3_4L_{21})$
Ho I	$^4I_{15/2}$	$0.9879\|{}^4_3I_{20})-0.1545\|{}^2_3K_{21})-0.0140\|{}^2_3L_{21})$
Er I	$^3H_6$	$0.9960\|{}^3_2H_{11})+0.0893\|{}^1_2I_{20})$
	$^3F_4$	$0.7656\|{}^3_2F_{10})+0.5566\|{}^1_2G_{20})-0.3046\|{}^3_2H_{10})$

Table IV. Intermediate coupling and the relativistic-diamagnetic corrections for the J = 4 of ErI

SLJ	Russell-Saunders Coupling g	h	δg	Intermediate Coupling g	h	$\delta g'$
$^3F_4$)	$\frac{5}{4}$	$\frac{19}{108}$	-0.001973	$\frac{5}{4}$ (0.90215)	$\frac{19}{108}$(0.52764)	-0.001914
$^3H_4$)	$\frac{4}{5}$	$-\frac{348}{2025}$	-0.001840	$\frac{4}{5}$ (1.20053)	$-\frac{348}{2025}$(0.25132)	-0.001878
$^1G_4$)	1	0	-0.001864	1 (0.96158)	-0.053367	-0.001900

FOOTNOTES AND REFERENCES

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