Theory of Zeeman Effect in the Ground Multiplets of Rare-Earth Atoms*

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A number of corrections are made to the simple Landé formula for the g values of levels deriving from the ground term of configurations of the type $4f^n$. These include (a) the Schwinger correction, to give an accurate value of the gyromagnetic ratio for the electron spin; (b) a correction to allow for the deviations from perfect RS coupling; (c) a relativistic correction, which is directly related to the kinetic energy of the electrons; (d) a diamagnetic correction, depending on the electron density of the core. In order to calculate (b), the spin-orbit coupling constants and the Coulomb integrals F_k are estimated either from existing spectroscopic data or from a process of interpolation or extrapolation. An argument is presented for taking ratios of the integrals F_k corresponding to a hydrogenic eigenfunction. The various radial integrals required in the calculation of (c) and (d) are derived from a modified hydrogenic eigenfunction of the form $r^n e^{-ar}\cosh[\kappa(ar-n)]$. The parameter κ in this expression is estimated to be approximately 0.42 over the rare-earth series by comparison with available Hartree self-consistent field eigenfunctions. The second parameter a is chosen to give a fit with the spin-orbit coupling constants. The result of calculating (a), (b), (c), and (d) is to give atomic g values which agree remarkably well with the experimental data. This confirms that the ground configurations of PrI, NdI, PmI, SmI, EuI, DyI, HoI, ErI, and TmI are of the type $4f^n$, and that such a configuration is very low-lying in TbI. Tables of spin-orbit coupling constants and $\langle r^{-3}\rangle$ for both neutral and triply ionized rare earth atoms are given as well as of other radial integrals.

INTRODUCTION

IN the last few years a number of experiments have been set up to investigate the magnetic properties of beams of free rare-earth atoms.[1] Of the various nuclear and magnetic properties of the atoms obtained by these techniques, we shall direct our attention here to the interactions between the external field **H** and the electrons, and in particular to those contributions to the Hamiltonian which experimentally can be described by the effective Hamiltonian $g_J\mu_0\mathbf{H}\cdot\mathbf{J}$, where μ_0 is the Bohr magneton, **J** is the total angular momentum of the electron system, and g_J a suitably chosen constant referred to as the atomic g value. The elementary way of finding a theoretical value for g_J is to equate the eigenvalues of the operator $g_J\mathbf{J}$ to those of $\mathbf{L}+2\mathbf{S}$, where **L** and **S** are the total orbital and total spin angular momenta, respectively, of the electron system. When L and S are good quantum numbers, the value of g_J so obtained is the Landé g value.

This simple approach is complicated by a number of factors, which, although comparatively small, must be considered in any attempt to fit the accurate atomic beam data. These corrections to the elementary procedure have been described in detail by Abragam and Van Vleck, in their examination of the microwave spectrum of the oxygen atom,[2] and we shall simply enumerate them at this point.

To begin with, we must replace the factor 2 for the gyromagnetic ratio of the electron spin by

$$g_s=2(1+\alpha/2\pi+\cdots)=2.00232,$$

where α is the fine-structure constant. This will be called the Schwinger correction.

Next, it must be recognized that in order to find the eigenvalues of $\mathbf{L}+2\mathbf{S}$, we must have some knowledge of the eigenfunctions of the electron system. It has now become clear from the available experimental data that the lowest electronic configurations outside closed shells of the rare-earth atoms are nearly always of the type $4f^n$, and we shall confine our attention to these configurations. This allows us to extrapolate and interpolate the various radial integrals that occur in the calculations along the rare earth series. The lowest term in a configuration is given by Hund's rule, and is described by the two quantum numbers SL. When the spin-orbit interaction is included, however, these quantum numbers are separately not good quantum numbers, but only their resultant, J. For oxygen, it is a simple matter to allow for the departures from pure RS coupling, but for the rare-earth atoms, it is considerably more complex.

Also, for heavy atoms such as those considered here, the relativistic and diamagnetic effects become quite important. By the relativistic effect we mean here the correction, depending on the kinetic energy, which is a direct consequence of the Dirac equation for a single electron. The diamagnetic effect is caused by modifications in the interactions between the electrons due to the external field, and depends essentially on the electron density in the core. In contrast to oxygen, these effects for the rare-earth atoms usually predominate over the Schwinger correction.

The correction to the orbital gyromagnetic ratio caused by the motion of the nucleus, which was considered by Abragam and Van Vleck for oxygen,[2] is for the rare-earth atoms negligible compared with the experimental uncertainties.

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[1] A. Y. Cabezas, I. Lindgren and R. Marrus, preceding paper [Phys. Rev. **122**, 1796 (1961)]. In addition to the work on radioactive isotopes reported in that paper, we mention here the extensive experiments of Smith and Spalding on stable rare-earth isotopes at Cambridge; the examination of Sm by Sandars and Woodgate at Oxford; and the work on Tb by Penselin and Schlüpmann at Heidelberg. Some results for Eu have already been reported [P. G. H. Sandars and G. K. Woodgate, Proc. Roy. Soc. (London) **A257**, 269 (1960)].

[2] A. Abragam and J. H. Van Vleck, Phys. Rev. **92**, 1448 (1953).

STRUCTURE OF THE CONFIGURATION $4f^n$

Before we can begin an examination of the departures from *RS* coupling we must obtain the energy-level scheme in the *RS* limit; that is, in the limit where the Coulomb interaction between the $4f$ electrons,

$$\sum_{i>j} e^2/r_{ij}, \tag{1}$$

is very much greater than the spin-orbit interaction

$$\Lambda=\frac{1}{2m^2c^2}\sum_i\left(\frac{1}{r}\frac{dV}{dr}\right)_i \mathbf{s}_i\cdot\mathbf{l}_i. \tag{2}$$

The function V in (2) is the central field potential. We are obliged to perform this calculation because no experimental results are available on the positions of excited terms in the configurations $4f^n$ of neutral rare-earth atoms, and it is the admixtures of these excited terms in the ground term that produce the departures from *RS* coupling. To find the eigenvalues of (1), we write

$$\frac{1}{r_{ij}}=\sum_k \frac{r_<^k}{r_>^{k+1}}P_k(\cos\omega), \tag{3}$$

where $r_<$ and $r_>$ are the lesser and greater, respectively, of the two radii vectors r_i and r_j, and ω is the angle between them. This equation separates the radial and angular parts of the operator. The angular part can be treated exactly[3] and the energy of an *SL* term is expressed as a certain function of the radial integrals

$$F^k=e^2\int_0^\infty\int_0^\infty \frac{r_<^k}{r_>^{k+1}}[R(i)R(j)]^2 dr_i dr_j$$

for $k=2$, 4, and 6. The function $(1/r)R$ is the radial part of the $4f$ eigenfunction. In practice, it is more convenient to use the parameters F_k, where[4]

$$F_2=F^2/225, \quad F_4=F^4/1089, \quad F_6=F^6/7361.64.$$

It often turns out that the quantum numbers f^nSL are not sufficient to specify a term,[3] and the eigenfunctions are further classified according to their transformation properties under the groups G_2 and R_7. Irreducible representations of the first are specified by the two integers $(u_1u_2)=U$, where

$$u_1\geq u_2\geq 0,$$

and of the second by the three integers $(w_1w_2w_3)=W$, where

$$w_1\geq w_2\geq w_3\geq 0.$$

For terms of the highest and next-to-highest multiplicities of the configurations $4f^n$, the quantum numbers $f^nWUSLS_zL_z$ completely specify a state. Unlike S and L, the irreducible representations W and U are not good quantum numbers, so that in general a term is defined by a certain linear combination of pure $WUSL$ terms.

Elliott, Judd, and Runciman[5] have calculated the energies of all the terms of f^n possessing the highest and next-to-highest multiplicities on the assumption that the integrals F_6, F_4, and F_2 bear the same ratio to one another as they would if the radial eigenfunctions were hydrogenic, namely

$$F_4/F_2=0.138, \quad F_6/F_2=0.0151.$$

Although their work was directed at triply ionized rare-earth atoms, it seems unlikely that the ratios of these integrals would be appreciably different for the neutral atoms, particularly since the $4f$ electrons lie deep inside the atom and should be only slightly disturbed when outer electrons are removed. The use of hydrogenic ratios has met with considerable success,[6] a result which is rather surprising since it is quite clear that the actual radial eigenfunction has a much broader peak, and for this case the F_k ratios are significantly less than the hydrogenic ones. For example, Ridley,[7] in a recent Hartree self-consistent field (SCF) calculation for Pr^{3+}, gives

$$F_4/F_2=0.129, \quad F_6/F_2=0.0137.$$

Since we intend to use eigenfunctions of the broader kind in the determination of other radial integrals, we shall now give qualitative reasons for our present preference for F_k ratios based on a hydrogenic eigenfunction.

To begin with, we must recognize that electrons in closed shells can be polarized by electric fields and thereby produce screening effects. When a rare-earth ion is situated in a crystal, the electric field of the lattice is taken into account by including the expression

$$\sum_{i,k,q} A_k^q r_i^k Y_k^q(\theta_i,\phi_i) \tag{4}$$

in the Hamiltonian. It can be seen that the splittings in the J levels produced by the crystal field involve the products $A_k^q\langle r^k\rangle$, where $\langle r^k\rangle$ is the mean value of r^k for a $4f$ electron. Now A_k^q depends on the distance d from the nucleus of the rare-earth ion to neighboring lattice charges as the function d^{-k-1}; but in spite of the internal nature of the $4f$ electrons, which makes the theoretical values for $A_k^q\langle r^k\rangle$ decrease with k, it has been found experimentally[6,8] that in some cases these products actually increase. This result has been attributed to a screening effect by the closed shells of the rare earth ions, which increases in severity as k decreases.[9,10]

[3] G. Racah, Phys. Rev. **76**, 1352 (1949).
[4] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).
[5] R. J. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) **A240**, 509 (1957).
[6] B. R. Judd, Proc. Roy. Soc. (London) **A241**, 414 (1957).
[7] E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).
[8] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).
[9] R. A. Satten, J. Chem. Phys. **27**, 286 (1957).
[10] B. R. Judd, Proc. Roy. Soc. (London) **A251**, 134 (1959).

Returning to the problem of the integrals F_k, one sees that the electrostatic field of one $4f$ electron at another is likewise subject to these screening effects, though in a less striking manner, owing to the proximity of the electrons. In fact, we can write

$$\frac{r_<^k}{r_>^{k+1}}P_k(\cos\omega)=\frac{4\pi}{2k+1}\sum_m \frac{r_i^k}{r_j^{k+1}}Y_k^m(\theta_i,\phi_i)Y_k^m(\theta_j,\phi_j)^* +\frac{4\pi}{2k+1}\sum_m \frac{r_j^k}{r_i^{k+1}}Y_k^m(\theta_i,\phi_i)Y_k^m(\theta_j,\phi_j)^*,$$

where the first term applies to the region $r_i<r_j$, the second to $r_i>r_j$. If, in the first term, we regard electron i as moving in the potential produced by electron j, this expression takes the form of a term in the summation (4); hence we must include a reduction factor f_k in the calculation of the associated integral F_k. A similar argument applies to the second term. Moreover, that the screening increases as k decreases implies

$$f_6>f_4>f_2>0.$$

The effect of these factors is to increase the ratios F_4/F_2 and F_6/F_2 from the values given by Ridley for the Hartree SCF calculation, and also to bring her numerical value for F_2 nearer to experiment. We feel that the success of the hydrogenic ratios for the triply ionized rare-earth atoms makes them the most appropriate for our work.

The energies of the terms of the configurations $4f^n$ can now be expressed as multiples of F_2. As is seen in the next section, we are interested solely in those excited terms which differ at most by one unit in S and L from the ground term. As an example, we give the energies and eigenfunctions for relevant terms of Pr I $4f^3$, for which the ground term ^4I is the zero of the energy scale:

^2K $48.5F_2$ $|f^3(210)(21)^2K\rangle$,

^2I $77.5F_2$ $|f^3(210)(20)^2I\rangle$,

^2H $88.1F_2$ $0.3878|f^3(210)(21)^2H\rangle+0.9217|f^3(210)(11)^2H\rangle$,

^2H $32.9F_2$ $0.9217|f^3(210)(21)^2H\rangle-0.3878|f^3(210)(11)^2H\rangle$.

The eigenvalues of all the terms we shall need have been tabulated.[5]

DEPARTURES FROM RUSSELL-SAUNDERS COUPLING

The effect of the spin-orbit interaction is to split the terms up into levels, distinguished by the additional quantum number J. For a configuration of equivalent electrons, (2) can be written as

$$\Lambda=\zeta\sum \mathbf{s}\cdot\mathbf{l},$$

where

$$\zeta=\frac{1}{2m^2c^2}\int_0^\infty R^2\left(\frac{1}{r}\frac{dV}{dr}\right)dr. \quad (5)$$

In addition, Λ couples together states of the same J but different S and L, thus producing deviations from pure RS coupling. Elliott *et al.*[5] have given a general formula for the matrix elements

$$\langle 4f^nWUSLJ|\Lambda|4f^nW'U'S'L'J\rangle$$

in terms of a sum over the product of two 6-j symbols and the fractional parentage coefficients connecting the configurations f^n and f^{n-1}. The dependence on J is contained in a third 6-j symbol,

$$(-1)^J\begin{Bmatrix} J & L & S \\ 1 & S' & L' \end{Bmatrix}, \quad (6)$$

which may readily be evaluated from the formulas of Edmonds.[11] For our example, Pr I $4f^3$, we find

$$\langle f^3(111)(20)^4I_{9/2}|\Lambda|f^3(210)(21)^2H_{9/2}\rangle=(70/11)^{\frac{1}{2}},$$

and

$$\langle f^3(111)(20)^4I_{9/2}|\Lambda|f^3(210)(11)^2H_{9/2}\rangle=-(13/22)^{\frac{1}{2}}.$$

All but a few of the configurations $4f^n$ are extremely complex, and it would be a tedious process to diagonalize the combined Coulomb and spin-orbit interactions exactly. Fortunately ζ is sufficiently small to allow us to calculate the corrections to g_J by perturbation theory.

Near the RS limit, S, L, and J are good quantum numbers. Within a manifold of states of constant J we can replace $\mathbf{L}+g_s\mathbf{S}$ by $g\mathbf{J}$, where g is the Landé factor, given by

$$g=\langle SLJ|g|SLJ\rangle=1+(g_s-1)\times\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}.$$

This is the zeroth-order contribution to g_J. There is no first-order contribution, since $\mathbf{L}+g_s\mathbf{S}$ cannot couple to any excited level. The second-order contribution is

$$\sum_m\langle 0|\Lambda|m\rangle\langle m|g|m\rangle\langle m|\Lambda|0\rangle/E_m^2 -\langle 0|g|0\rangle\sum_m\langle 0|\Lambda|m\rangle\langle m|\Lambda|0\rangle/E_m^2, \quad (7)$$

where $|0\rangle$ denotes the ground level and $|m\rangle$ an excited level at an energy E_m above it. Since these energies are calculated as multiples of F_2, and the matrix elements of Λ depend linearly on ζ, (7) can be expressed in terms of $(\zeta/F_2)^2$.

To estimate these parameters we make use of the corresponding values for the triply ionized atoms, which

[11] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

TABLE I. Spin-orbit coupling constants and Coulomb integrals (in cm^{-1}).

		Triply ionized atoms					Neutral atoms		
Nuclear charge	Ion	ζ' from expt.	Ref. No.	ζ' from Eq. (10)	F_2'	Atom	ζ from expt.	ζ from Eq. (11)	F_2
57						La		350	273
58	Ce^{3+}	640	a	619	298	Ce		482	285
59	Pr^{3+}	711	b	754	310	Pr		619	298
		737	c						
		781	c						
60	Nd^{3+}	860	d	895	322	Nd	770[g]	761	310
		906	e						
61	Pm^{3+}			1043	335	Pm		909	322
62	Sm^{3+}	1180	d	1196	347	Sm	1061[g]	1065	335
63	Eu^{3+}	1360	d	1361	360	Eu		1228	347
64	Gd^{3+}			1534	372	Gd		1402	360
65	Tb^{3+}	1720	d	1720	384	Tb		1587	372
66	Dy^{3+}	1920	d	1921	397	Dy		1787	384
67	Ho^{3+}	2080	d	2139	409	Ho		2004	397
68	Er^{3+}	2471	e	2380	422	Er		2242	409
69	Tm^{3+}	2575	c	2648	434	Tm	2506[h]	2507	422
		2709	c						
70	Yb^{3+}	2940	f	2951	446				

[a] R. J. Lang, Can. J. Research **14**, 127 (1936).
[b] See reference 6.
[c] W. A. Runciman and B. G. Wybourne, J. Chem. Phys. **30**, 1154 (1959).
[d] See reference 12.
[e] B. G. Wybourne, J. Chem. Phys. **32**, 639 (1960).
[f] H. Gobrecht, Ann. Physik **31**, 300 (1938).
[g] These values are taken from Table II of this paper.
[h] From reference 13.

we shall distinguish here by primes. Judd[12] has given the empirical formula

$$F_2'=12.4(Z-34), \tag{8}$$

and the various experimental values of ζ' are set out in the third column of Table I. Values are not tabulated if they have been unquestionably superseded by later work. In the case of the neutral atoms, suitable data for calculating ζ are available for NdI, SmI, and TmI only. The electronic configuration of TmI consists of a single hole in a full $4f$ shell, and only two levels, ${}^2F_{5/2}$ and ${}^2F_{7/2}$, occur. Their separation of 8771.25 cm^{-1} quoted by Meggers[13] yields at once $\zeta=2506$ for this atom. The experimental data for the other two atoms are set out in Table II. It can be seen from this table that appreciable departures from the Landé interval rule occur, and these must be ascribed almost entirely to second-order effects of the type

$$\sum_m \langle 0|\Lambda|m\rangle\langle m|\Lambda|0\rangle/E_m.$$

When one knows the matrix elements of Λ, which are needed in the calculation of the corrections to g_J, it is a simple matter to write down the second-order displacements of the levels as functions of ζ alone. The integral F_2, which is required in calculating the energies E_m, can be taken initially from (8), and preliminary values of ζ obtained for NdI and SmI. The first is found to be quite similar to the experimental value of ζ' for PrIV, and the second to the interpolated value for PmIV. This correspondence between ζ and ζ' suggests we take

$$F_2=12.4(Z-35), \tag{9}$$

as a better approximation for F_2. We can now fit the experimental positions of the levels quite closely with

TABLE II. Energy levels of the lowest multiplets of NdI and SmI in cm^{-1}.

	NdI; $\zeta=770$ cm^{-1}				SmI; $\zeta=1061$ cm^{-1}		
Level	Pure *RS* coupling	Corrected positions	Experiment[a]	Level	Pure *RS* coupling	Corrected positions	Experiment[b]
${}^5I_8$	5005	5051	5049	${}^7F_6$	3714	4017	4021
${}^5I_7$	3465	3676	3682	${}^7F_5$	2652	3146	3125
${}^5I_6$	2117	2343	2367	${}^7F_4$	1768	2288	2273
${}^5I_5$	962	1102	1128	${}^7F_3$	1061	1489	1490
${}^5I_4$	0	0	0	${}^7F_2$	530	798	812
				${}^7F_1$	177	280	293
				${}^7F_0$	0	0	0

[a] Ph. Schuurmans, Physica **11**, 419 (1946).
[b] W. Albertson, Phys. Rev. **52**, 644 (1937).

[12] B. R. Judd, Proc. Phys. Soc. (London) **A69**, 157 (1956).
[13] W. F. Meggers, Revs. Modern Phys. **14**, 96 (1942).

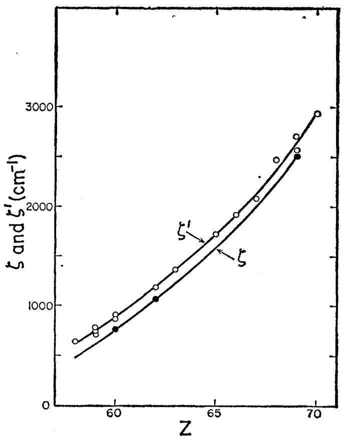

FIG. 1. Spin-orbit coupling constants. The full lines represent values taken from Eqs. (10) and (11) for the triply ionized and neutral atoms, respectively. The points are the experimental values given in Table I.

the values 770 and 1061 cm^{-1} for ζ (see Table II); indeed, the remaining discrepancies are only slightly larger than spin-spin effects, which also produce deviations from the Landé interval rule.[12] These results support the assumption of hydrogenic F_k ratios and also Eq. (9). The lowest ^5D term in SmI $4f^6$ possesses an exceptionally extended multiplet structure, and allowance was made for this by including diagonal spin-orbit matrix elements in estimates of the energies E_m. Strictly speaking, this accounts for some, but by no means all, of the third-order effects; but since the agreement between experiment and theory is improved by including it, it was felt better to do so, particularly since our present aim is to obtain the best value for ζ. Fortunately, $\langle {}^5D_J|g|{}^5D_J\rangle$ is identical to $\langle {}^7F_J|g|{}^7F_J\rangle$, so that the spread of ^5D has no effect on the calculations of g_J based on Eq. (7).

Values of ζ for other rare-earth atoms must be obtained by interpolation. It is to be expected that the curve of ζ against Z will follow fairly closely the corresponding curve for the triply ionized atoms; for the latter we have used

$$\zeta'=77.4(Z-66.29)+28720(80.78-Z)^{-1}, \quad (10)$$

which fits the experimental data rather better than a curve of the type $A(Z-\sigma)^s$. Values of Eq. (10) are set out in Table I. It can be seen that ζ(NdI), ζ(SmI), and ζ(TmI) lie between the pairs ζ'(PrIV), ζ'(NdIV); ζ'(PmIV), ζ'(SmIV); and ζ'(ErIV), ζ'(TmIV), respectively, advancing slowly towards the second member of a pair as Z increases. We have assumed a linear shift with Z to obtain the formula

$$\zeta=81.2(Z-66.90)+27380(80.72-Z)^{-1}. \quad (11)$$

Values of Eq. (11) are given in Table I. The data on ζ and ζ' are illustrated in Fig. 1. The expression (7) has been calculated for all levels of the lowest multiplets of the configurations of the type $4f^n$ (irrespective of the fact that in some rare-earth atoms, e.g., LaI and GdI, they may not necessarily be the ground configuration) and entered in the column headed "spin-orbit correction" that will be found in Table III. This completes the calculation to second order of contributions to g_J produced by departures from pure RS coupling.

RELATIVISTIC AND DIAMAGNETIC CORRECTIONS

In the first-order theory the Hamiltonian for the interaction between the electrons and an external magnetic field is written

$$Z=\mu_0\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S}). \quad (12)$$

For a single electron the second-order correction to this operator can be obtained in a straightforward way from the Dirac equation by including terms of the order of v^2/c^2, where v is the velocity of the electron. This has been done by Breit[14] and Margenau,[15] and the result can be written as the following correction to the g value,

$$\delta g=-\alpha^2[(j+\tfrac{1}{2})^2/j(j+1)]\langle T\rangle, \quad (13)$$

which is usually called the Breit-Margenau correction. The kinetic energy T of the electron and all other quantities in this section are expressed in atomic units.

The many-electron problem has been treated by Perl[16] and Abragam and Van Vleck.[2] The part of the correction to the classical Zeeman operator (12) which corresponds to the Breit-Margenau correction becomes

$$\delta Z_1=-\alpha^2\mu_0\sum_i[\mathbf{H}\cdot(\mathbf{l}_i+2\mathbf{s}_i)T_i-\mathbf{s}_i\cdot(\nabla_iV_i\times\mathbf{A}_i)], \quad (14)$$

in a uniform magnetic field, where

$$V_i=-\frac{Z}{r_i}+\sum_{k\neq i}\frac{1}{r_{ik}},$$

and $\mathbf{A}_i$ is the magnetic vector potential for electron i. The first part of (14) can be regarded as a relativistic mass correction and the second part as a correction to the spin-orbit coupling. It is shown below that both these corrections depend essentially on the kinetic energy of the electron, and (14) is therefore referred to as the relativistic correction.

Like the spin-orbit coupling, the interactions between the electrons are modified in a magnetic field and therefore give rise to another correction to the classical Zeeman operator. This can be derived from Breit's equation for electron-electron interactions[17] and written[2,16]

$$\delta Z_2=\alpha^2\mu_0\sum_{i\neq k}\left[2\mathbf{s}_i\cdot\left(\nabla_k\frac{1}{r_{ik}}\times\mathbf{A}_k\right)-\frac{\mathbf{A}_k\cdot\mathbf{p}_i}{r_{ik}}-\frac{(\mathbf{r}_{ik}\cdot\mathbf{A}_k)(\mathbf{r}_{ik}\cdot\mathbf{p}_i)}{r_{ik}^3}\right]. \quad (15)$$

The first term in this expression is a correction to the

[14] G. Breit, Nature **122**, 649 (1928).
[15] H. Margenau, Phys. Rev. **57**, 383 (1940).
[16] W. Perl, Phys. Rev. **91**, 852 (1953).
[17] G. Breit, Phys. Rev. **34**, 553 (1929).

TABLE III. Atomic g values: theory and experiment.

Atom	Level	Landé value with Schwinger correction	h	Spin-orbit correction	Relativistic and diamagnetic corrections	Theoretical g_J	Experimental g_J (Ref. 1)
(LaI)	$^2F_{5/2}$	0.85681	$-6/35$	0	-0.00084	0.8560	
	$^2F_{7/2}$	1.14319	8/63	0	-0.00079	1.1424	
(CeI)	$^3H_4$	0.79954	$-348/2025$	0.00675	-0.00090	0.8054	
	$^3H_5$	1.03341	17/1350	0	-0.00092	1.0325	
	$^3H_6$	1.16705	7/54	-0.00021	-0.00092	1.1659	
PrI	$^4I_{9/2}$	0.72664	$-212/1089$	0.00500	-0.00095	0.7307	0.7311 ±0.0002
	$^4I_{11/2}$	0.96495	$-1258/42471$	0.00126	-0.00100	0.9652	
	$^4I_{13/2}$	1.10794	628/8775	-0.00045	-0.00103	1.1065	
	$^4I_{15/2}$	1.20046	94/675	-0.00098	-0.00104	1.1984	
NdI	$^5I_4$	0.59907	$-25/99$	0.00461	-0.00098	0.6027	0.6032 ±0.0001
	$^5I_5$	0.89977	$-23/396$	0.00178	-0.00106	0.9005	0.9002 ±0.0002
	$^5I_6$	1.07159	713/13860	-0.00020	-0.00112	1.0703	1.0715 ±0.0020
	$^5I_7$	1.17899	149/1260	-0.00182	-0.00115	1.1760	
	$^5I_8$	1.25058	29/180	-0.00320	-0.00117	1.2462	
PmI	$^6H_{5/2}$	0.28406	$-398/945$	0.00967	-0.00091	0.2928	
	$^6H_{7/2}$	0.82499	$-1156/14175$	0.00358	-0.00110	0.8275	0.831 ±0.005
	$^6H_{9/2}$	1.07087	1526/22275	0.00055	-0.00120	1.0702	1.068 ±0.004
	$^6H_{11/2}$	1.20327	13972/96525	-0.00136	-0.00125	1.2007	
	$^6H_{13/2}$	1.28271	326/1755	-0.00281	-0.00129	1.2786	
	$^6H_{15/2}$	1.33411	28/135	-0.00405	-0.00133	1.3287	
SmI	$^7F_1$	1.50116	7/18	-0.00203	-0.00138	1.4978	1.49838±0.00005
	$^7F_2$	1.50116	103/270	-0.00233	-0.00140	1.4974	1.49777±0.00003
	$^7F_3$	1.50116	10/27	-0.00279	-0.00141	1.4970	1.49705±0.00003
	$^7F_4$	1.50116	16/45	-0.00340	-0.00143	1.4963	1.49623±0.00004
	$^7F_5$	1.50116	91/270	-0.00416	-0.00146	1.4955	1.49531±0.00006
	$^7F_6$	1.50116	17/54	-0.00507	-0.00149	1.4946	1.49417±0.00010
EuI	$^8S_{7/2}$	2.00232	2/3	-0.00729	-0.00175	1.9933	1.99337±0.00007
(GdI)	$^7F_1$	1.50116	7/18	-0.00304	-0.00159	1.4965	
	$^7F_2$	1.50116	103/270	-0.00349	-0.00160	1.4961	
	$^7F_3$	1.50116	10/27	-0.00418	-0.00162	1.4954	
	$^7F_4$	1.50116	16/45	-0.00509	-0.00164	1.4944	
	$^7F_5$	1.50116	91/270	-0.00623	-0.00168	1.4932	
	$^7F_6$	1.50116	17/54	-0.00759	-0.00171	1.4919	
TbI	$^6H_{5/2}$	0.28406	$-398/945$	0.02214	-0.00119	0.3050	
	$^6H_{7/2}$	0.82499	$-1156/14175$	0.00821	-0.00145	0.8318	
	$^6H_{9/2}$	1.07087	1526/22275	0.00127	-0.00157	1.0706	
	$^6H_{11/2}$	1.20327	13972/96525	-0.00312	-0.00165	1.1985	
	$^6H_{13/2}$	1.28271	326/1755	-0.00643	-0.00171	1.2746	
	$^6H_{15/2}$	1.33411	28/135	-0.00928	-0.00175	1.3231	1.3225 ±0.003
DyI	$^5I_4$	0.59907	$-25/99$	0.01653	-0.00149	0.6141	
	$^5I_5$	0.89977	$-23/396$	0.00638	-0.00162	0.9045	
	$^5I_6$	1.07159	713/13860	-0.00072	-0.00168	1.0692	
	$^5I_7$	1.17899	149/1260	-0.00653	-0.00174	1.1707	
	$^5I_8$	1.25058	29/180	-0.01180	-0.00178	1.2370	1.24166±0.00007; 1.2414 ±0.0003
HoI	$^4I_{9/2}$	0.72664	$-212/1089$	0.02948	-0.00167	0.7544	
	$^4I_{11/2}$	0.96495	$-1258/42471$	0.00743	-0.00177	0.9706	
	$^4I_{13/2}$	1.10794	628/8775	-0.00265	-0.00182	1.1035	
	$^4I_{15/2}$	1.20046	94/675	-0.00578	-0.00205	1.1926	1.19516±0.00010
ErI	$^3H_4$	0.79954	$-348/2025$	0.0709	-0.00184	0.8048	
	$^3H_5$	1.03341	17/1350	0	-0.00190	1.0315	
	$^3H_6$	1.16705	7/54	-0.00219	-0.00192	1.1629	1.1638 ±0.0002
TmI	$^2F_{5/2}$	0.85681	$-6/35$	0	-0.00204	0.8548	
	$^2F_{7/2}$	1.14319	8/63	0	-0.00198	1.1412	1.14122±0.00015

spin-other-orbit coupling and the last two terms are corrections to the orbit-orbit coupling. These corrections depend essentially on the electron density in the core and we refer to (15) as the diamagnetic correction.

In order to calculate the matrix of (14) and (15) we shall, in principle, follow the approximate method which Abragam and Van Vleck used in their discussion of the Zeeman effect in atomic oxygen. We transform the two-electron operators appearing in these expressions into single-electron operators by integrating over one of the electrons. Of course, in doing this all exchange integrals are dropped as well as all elements between states that differ by two single-electron states. In this approximation it is also assumed that the charge density from all electrons is spherically symmetric. It turns out that these approximations have only a small effect on the final result. One may note here the close relationship with Hartree's SCF method.

Integration over electron k yields for V_i in (14)

$$V_i=-\frac{Z}{r_i}+\int\sum_{k\neq i}\psi_k^*(\mathbf{r}')\frac{1}{|\mathbf{r}_i-\mathbf{r}'|}\psi_k(\mathbf{r}')d\tau'$$

$$=-\frac{Z}{r_i}+\int\frac{\rho_i(\mathbf{r}')}{|\mathbf{r}_i-\mathbf{r}'|}d\tau',$$

where

$$\rho(r')=\sum_{k\neq i}\psi_k^*(\mathbf{r}')\psi_k(\mathbf{r}')$$

is the density of all electrons except i. If ρ_i is spherically symmetric, V_i becomes exactly the central potential used in the Hartree method.

We then have, dropping the subscript i,

$$\mathbf{s}\cdot(\nabla V\times\mathbf{A})=\frac{1}{2r}\frac{dV}{dr}\mathbf{s}\cdot[\mathbf{r}\times(\mathbf{H}\times\mathbf{r})]$$

$$=\frac{r}{2}\frac{dV}{dr}\mathbf{H}\cdot\left(\mathbf{s}-\frac{(\mathbf{s}\cdot\mathbf{r})}{r^2}\mathbf{r}\right),$$

and Eq. (14) becomes

$$\delta Z_1=-\alpha^2\mu_0\mathbf{H}\cdot\sum\left[(\mathbf{l}+2\mathbf{s})T-\frac{1}{2}\left(\mathbf{s}-\frac{(\mathbf{s}\cdot\mathbf{r})}{r^2}\mathbf{r}\right)r\frac{dV}{dr}\right]. \quad (16)$$

In the same way we get from (15)

$$\delta Z_2=\alpha^2\mu_0\sum\int\left[2\mathbf{s}\cdot\left(\nabla'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\times\mathbf{A}'\right)\right.$$

$$\left.-\left(\frac{\mathbf{A}'}{|\mathbf{r}-\mathbf{r}'|}+\frac{(\mathbf{r}-\mathbf{r}')\cdot\mathbf{A}'}{|\mathbf{r}-\mathbf{r}'|^3}(\mathbf{r}-\mathbf{r}')\right)\cdot\mathbf{p}\right]\rho(\mathbf{r}')d\tau'. \quad (17)$$

Abragam and Van Vleck have shown that if ρ is spherically symmetric the operator (17) is equivalent to

$$\delta Z_2=\alpha^2\mu_0\sum\{-2\mathbf{s}\cdot[\nabla\times\mathbf{A}Y(r)]-\mathbf{H}\cdot\mathbf{l}Y(r)\},$$

where

$$Y(r)=\frac{1}{3}\left[\frac{1}{r^3}\int_0^r r'^2\rho'(r')dr'+\int_r^\infty\frac{\rho'(r')}{r'}dr'\right].$$

Here $\rho'(r')=4\pi r'^2\rho(\mathbf{r}')$ is the radial electron density. Now

$$\nabla\times[\mathbf{A}Y(r)]=\mathbf{H}Y(r)-\tfrac{1}{2}(\mathbf{r}\times(\mathbf{H}\times\mathbf{r})/r^2)U(r),$$

where

$$U(r)=\frac{1}{r^3}\int_0^r r'^2\rho'(r')dr',$$

and (12) becomes

$$\delta Z_2=-\alpha^2\mu_0\mathbf{H}\cdot\sum\left[(\mathbf{l}+2\mathbf{s})Y-\left(\mathbf{s}-\frac{(\mathbf{s}\cdot\mathbf{r})\mathbf{r}}{r^2}\right)U\right]. \quad (18)$$

Except for the radial parts this is identical to the relativistic correction operator (16), and therefore the total correction can be written

$$\delta Z=\delta Z_1+\delta Z_2=-\alpha^2\mu_0\mathbf{H}\cdot\sum\left[(\mathbf{l}+2\mathbf{s})(T+Y)\right.$$

$$\left.-\left(\mathbf{s}-\frac{(\mathbf{s}\cdot\mathbf{r})\mathbf{r}}{r^2}\right)(T+U)\right]. \quad (19)$$

We have here replaced $\frac{1}{2}r(dV/dr)$ by T, which, from the virial theorem, is correct as long as we stay within a given configuration. Obviously, only electrons outside closed shells contribute in this summation.

In a state defined by only one determinantal product of single-electron states the expectation value of (19) becomes

$$\langle\delta Z\rangle=-\alpha^2\mu_0H\sum[(m_l+2m_s)\langle T+Y\rangle$$

$$-m_s\langle\sin^2\theta\rangle\langle T+U\rangle]. \quad (20)$$

θ is here the angle between $\mathbf{r}$ and the magnetic field and hence we have

$$\langle\sin^2\theta\rangle=2[l(l+1)-1+m_l^2]/(2l-1)(2l+3).$$

The off-diagonal elements of (19) between two single-electron states are

$$\langle nlm_sm_l|\delta Z|nl\ m_s\pm1\ m_l\mp1\rangle$$

$$=\alpha^2\mu_0H\frac{1}{2}\int_0^\pi\theta(lm_l)\theta(lm_l\mp1)\sin^2\theta\cos\theta d\theta\langle T+U\rangle$$

$$=\alpha^2\mu_0H[(2m_l\mp1)/2(2l-1)(2l+3)]$$

$$\times[l(l+1)-m_l(m_l\mp1)]^{\frac{1}{2}}\langle T+U\rangle, \quad (21)$$

with the notations of Condon and Shortley. The integral has been evaluated by means of Gaunt's formula.[18]

If all electrons outside closed shells are equivalent,

[18] J. A. Gaunt, Phil. Trans. Roy. Soc. A228, 151 (1929).

the total correction to the g value obtained from (19) is of the form

$$\delta g=-\alpha^2[g\langle T+Y\rangle-h\langle T+U\rangle], \tag{22}$$

where g is the classical g value and h is another factor, depending only on the angular part of the eigenfunction. It turns out that the first term in (22) usually predominates, which means that an estimate of the correction is obtained directly from this expression if the radial integrals $\langle T\rangle$ and $\langle Y\rangle$ are known, without the usually lengthy calculation of h.

The operator (19) is very similar to the magnetic hyperfine-structure operator and can therefore be conveniently treated by tensor operators.[11] In the case of equivalent electrons and a Hund's-rule ground state, the factor h in Eq. (22) is given by

$$h=-\frac{2(2l-2n+1)}{3n(2L-1)(2l-1)(2l+3)}\left[\frac{L(L+1)[J(J+1)-L(L+1)+S(S+1)]}{2J(J+1)}\right.$$
$$\left.-\frac{3}{4}\frac{[J(J+1)-L(L+1)-S(S+1)][J(J+1)+L(L+1)-S(S+1)]}{J(J+1)}\right]+\frac{1}{3}\frac{J(J+1)-L(L+1)+S(S+1)}{J(J+1)}. \tag{23}$$

Here n is the number of electrons or holes in the unfilled shell, whichever is the smaller. This expression is very similar to the corresponding formula for the magnetic hfs,[19] the reason being that both operators involve the tensor $(\mathbf{s}\mathbf{C}^{(2)})^{(1)}$, with the notations of Edmonds.[11] For $J=L+S$, Eq. (23) simplifies to

$$h=n[12l(l+1)-3n(2l+1)+2n^2-5]/6J(2l-1)(2l+3).$$

Relevant values of h for the rare-earth atoms are given in Table III.

EVALUATION OF THE RADIAL INTEGRALS

The evaluation of the various radial integrals appearing in the relativistic and diamagnetic corrections discussed above requires some approximate radial eigenfunction for the $4f$ electrons. No SCF calculations are available for any rare-earth atom, but a good estimate of the shape of the eigenfunction can be made from calculations in the triply ionized atoms of Pr and Tm[7] and in heavier atoms like W and Hg.[20] For interpolation and extrapolation from the existing SCF eigenfunctions it is very convenient to have an analytic approximation of these functions. A simple form, which has been used by Cabezas and Lindgren[21] in the examination of the Zeeman effect in thulium, is

$$R(r)=Nr^ne^{-ar}\cosh[\kappa(ar-n)], \tag{24}$$

which is a modification of the hydrogenic eigenfunction for $n=l+1$. The extra factor has the effect of broadening out the eigenfunction without shifting the position of its maximum. With suitable values of the parameters, good agreement is obtained between Eq. (24) and the corresponding SCF functions.[16]

As mentioned above, the shape of the $4f$ eigenfunction is expected to differ only slightly between the neutral and triply ionized atoms; and for the same reason we expect a similar result between neighboring atoms in the series. By comparing eigenfunctions of the type (24) with available SCF functions in this region, we have obtained the κ values given in Table IV. These values have been determined so that the values of $\langle r^{-1}\rangle$, $\langle r^{-2}\rangle$, and $\langle r^{-3}\rangle$ become approximately the same for the two functions. Exact formulas for these integrals with the eigenfunction (24) are given in reference 21. Of course, one can fit only two of these integrals exactly with a two-parameter eigenfunction, but the difference in κ value for different pairs is very small, which indicates that the approximation is satisfactory. We have chosen these negative powers of r to determine κ, since all the radial functions that we want to average are decreasing with r.

It is seen from Table IV that κ is a very slowly varying function of Z, but, as one would expect, decreases with increasing atomic number. This reflects the fact that the functions become more hydrogen-like deeper inside the core. Quite accurate values of κ can therefore be obtained by interpolation from this table.

Although the other parameter of the wave function (24), a, could also be easily obtained by interpolation, we prefer to determine it from the experimental spin-orbit coupling constant. This probably gives more reliable eigenfunctions than if they were entirely based on SCF functions. For the calculation of the spin-orbit coupling [Eq. (5)] one also needs an estimation of the central potential V. The Thomas-Fermi potential is quite accurate for heavy atoms such as those considered here, but can probably be further improved by writing[4] $V(r)=Zv(r/b)$, where $b=0.88534Z^{-\frac{1}{3}}$ and the function v is determined so that V agrees with a suitable SCF

TABLE IV. Values of κ from Hartree functions.

Atom or ion	Z	κ
Pr^{3+}	59	0.432
Tm^{3+}	69	0.418
W	74	0.382
Hg	80	0.343

[19] J. C. Hubbs, R. Marrus, W. A. Nierenberg, and J. L. Worcester, Phys. Rev. **109**, 390 (1958).
[20] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A149**, 210 (1935); M. F. Manning and J. Millman, Phys. Rev. **49**, 848 (1936).
[21] A. Y. Cabezas and I. P. K. Lindgren, Phys. Rev. **120**, 920 (1960).

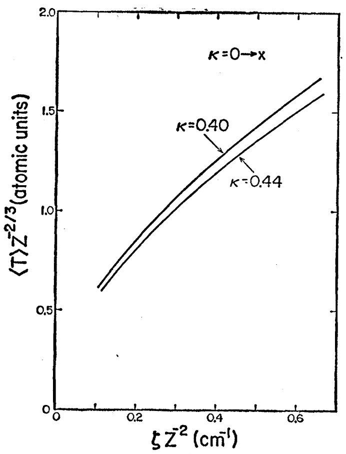

FIG. 2. Variation of the kinetic energy T with the spin-orbit coupling constant ζ.

potential. We have here used tungsten for this purpose, since this is the nearest atom for which SCF calculations have been made. The difference between this potential and the Thomas-Fermi potential is, however, quite small.[21]

We have determined the radial eigenfunctions of all the rare-earth atoms in this way, using the spin-orbit coupling constants given by Eq. (11). For convenience we have used the same value of κ throughout the whole series and have chosen $\kappa=0.42$ as a reasonable value in view of Table IV. The corresponding values of the integrals $\langle T\rangle$, $\langle U\rangle$, and $\langle Y\rangle$ are given in Table V. $\langle T\rangle$ is calculated from the formula given in reference 21, and $\langle U\rangle$ and $\langle Y\rangle$ have been integrated numerically with the electron density from the Thomas-Fermi model. The variation of these integrals with the spin-orbit coupling constant is shown in Figs. 2 and 3. The quantities involved are here divided by appropriate powers of Z, which makes the same diagram valid for all elements. The values are given for two different κ values, 0.40 and 0.44, which shows the dependence on the shape of the eigenfunctions. For comparison we have also marked a point for a hydrogenic eigenfunction. From these diagrams it is easy to estimate the corrections to the

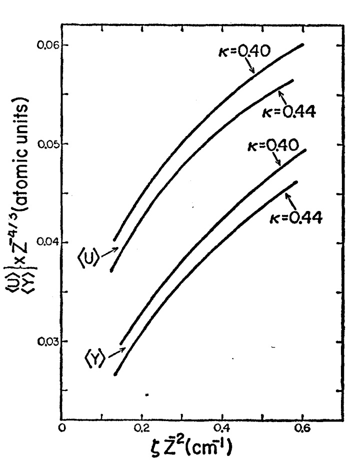

FIG. 3. Variation of the radial integrals U and Y with the spin-orbit coupling constant ζ.

integrals, corresponding to a small change in the spin-orbit coupling constant.

We are now ready to calculate the relativistic and diamagnetic corrections to the g values, and from Eqs. (22) and (23) and Table V we get the results shown in Table III for all levels of the ground terms.

Although they are not needed for the calculations here, the values of $\langle r^{-3}\rangle$ have also been determined with the same type of eigenfunction for the neutral as well as the triply ionized atoms, and are given in Table VI. The eigenfunctions have been chosen to reproduce the spin-orbit coupling constants given by (10) and (11), and the corresponding a values are included in the table. We have used $\kappa=0.42$ in all cases.

Figure 4 shows, for the neutral atoms, the variation of Z_i with the spin-orbit coupling constant for two values of κ, where Z_i is defined by

$$\left\langle \frac{1}{r}\frac{dV}{dr}\right\rangle = Z_i\left\langle\frac{1}{r^3}\right\rangle,$$

TABLE V. The radial integrals (in atomic units) for $\kappa=0.42$.

Atom	Z	$\langle T\rangle$	$\langle Y\rangle$	$\langle U\rangle$
La	57	9.2	5.8	8.3
Ce	58	10.5	6.4	9.0
Pr	59	11.8	7.0	9.7
Nd	60	13.1	7.6	10.4
Pm	61	14.4	8.2	11.1
Sm	62	15.6	8.8	11.7
Eu	63	16.8	9.4	12.4
Gd	64	17.9	10.0	13.0
Tb	65	19.1	10.6	13.6
Dy	66	20.3	11.1	14.2
Ho	67	21.5	11.7	14.8
Er	68	22.7	12.3	15.4
Tm	69	24.0	12.9	16.0

and some results with a Thomas-Fermi potential are also given for comparison. As one would expect, the values of $\langle r^{-3}\rangle$ determined in this way are quite insensitive to the shape of the eigenfunction, and it is also seen from the figure that the actual choice of potential is not critical either.

The values in Table VI differ considerably from those given by Bleaney,[22] which were calculated by use of hydrogenic eigenfunctions. We believe, however, that our values are much more accurate, since our assumptions about the spin-orbit coupling and the eigenfunctions have been very successful in our calculations.

DISCUSSION OF RESULTS

The experimental and theoretical values for g_J are compared in Table III. It can be seen that the agreement is extraordinarily good for the early members of the rare-earth series, but less so for the later members, particularly DyI. The large second-order contributions

[22] B. Bleaney, Proc. Phys. Soc. (London) A68, 937 (1955).

to g_J due to departures from pure *RS* coupling make it seem likely that higher-order effects are not negligible in these cases. This hypothesis is consistent with the good agreement which has been obtained for the early members of the series. In the case of HoI $4f^{11}$, for example, third-order effects are

$$(2004/619)^3(298/397)^3=14.5$$

times as large as for PrI $4f^3$, so that the discrepancy of 0.0023 for $g_{15/2}$ would be less than 0.0002 for the corresponding atomic g value in PrI. Fortunately, it is not difficult to include third-order effects for levels that satisfy $J=L+S$. This is because all possible linkages of

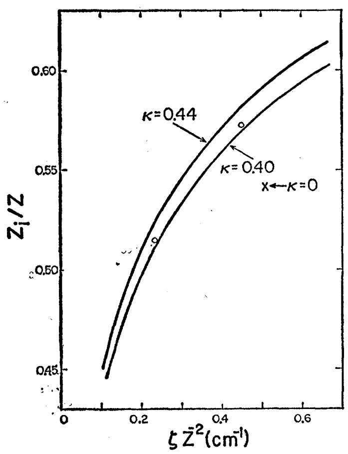

FIG. 4. Variation of Z_i with the spin-orbit coupling constant ζ. The open circles represent values obtained with a Thomas-Fermi potential.

the type

$$\langle 0|\Lambda|m\rangle\langle m|\Lambda|n\rangle\langle n|g|n\rangle\langle n|\Lambda|0\rangle,$$

which includes three spin-orbit matrix elements, involve very few states $|m\rangle$ and $|n\rangle$. To produce the proper value of J while at the same time having a nonzero matrix element with the ground level, the quantum numbers S and L of a state of this type must be respectively one unit less than and one unit greater than the corresponding quantum numbers of the ground state. The large value of L favors the occurrence of very few terms of the same kind (i.e., terms with the same S and L); for ErI and HoI there is only one, while for DyI there are but two, one of which possesses an exceptionally small matrix element of Λ connecting it to

TABLE VI. Values of a and $\langle r^{-3}\rangle$ for neutral and triply ionized atoms (in atomic units).

		Atoms		Ions	
Element	Z	a ($\kappa=0.42$)	$\langle r^{-3}\rangle$	a ($\kappa=0.42$)	$\langle r^{-3}\rangle$
La	57	(4.95)	(2.34)	...	...
Ce	58	(5.37)	(3.00)	5.73	3.64
Pr	59	5.73	3.63	6.03	4.24
Nd	60	6.04	4.25	6.30	4.83
Pm	61	6.32	4.87	6.54	5.42
Sm	62	6.58	5.50	6.78	6.02
Eu	63	6.82	6.13	7.00	6.64
Gd	64	(7.05)	(6.78)	7.22	7.27
Tb	65	7.27	7.44	7.43	7.92
Dy	66	7.49	8.14	7.63	8.60
Ho	67	7.71	8.87	7.84	9.32
Er	68	7.93	9.66	8.05	10.10
Tm	69	8.16	10.51	8.27	10.95
Yb	70	...	...	8.50	11.89

the ground state. In these cases it is easier to set up the 2×2 secular determinants and solve them exactly than attempt to use higher-order perturbation theory. By the former course, a number of higher-order effects are taken into account, and the problem for ErI, for which $^3H_6$ and $^1I_6$ are the only levels in the configuration with $J=6$, is solved completely. For HoI and DyI there are other states with the same J value as the ground level, and the results are correct only to third order. The ground-level eigenfunctions are

$$0.9959|^3H_6\rangle+0.0917|^1I_6\rangle \text{ for ErI},$$

$$0.9860|^4I_{15/2}\rangle-0.1669|^2K_{15/2}\rangle \text{ for HoI},$$

$$0.9698|^5I_8\rangle-0.2438|^3K_8\rangle \text{ for DyI},$$

where

$$|^3K_8\rangle=0.4596|(211)(21)^3K_8\rangle-0.8882|(211)(30)^3K_8\rangle.$$

It is to be noted that the coefficients in these states depend on our choice of the integrals F_k and ζ. The final theoretical values for g_J, taking into account the Schwinger, relativistic, diamagnetic, and spin-orbit corrections (to third order), are set out in Table VII for these atoms.

The agreement between experiment and theory can be seen to be excellent. When these results are taken with others in Table III, there can be no doubt that the ground configurations of PrI, NdI, PmI, SmI, EuI, DyI,

TABLE VII. Atomic g values including third-order spin-orbit coupling effects.

					g_J	
Atom	Level	Landé value with Schwinger correction	Spin-orbit correction	Relativistic and diamagnetic corrections	Theoretical	Experimental
DyI	$^5I_8$	1.25058	−0.00743	−0.00178	1.2414	1.24166±0.00007 1.2414 ±0.0003
HoI	$^4I_{15/2}$	1.20046	−0.00371	−0.00205	1.1947	1.19516±0.00010
ErI	$^3H_6$	1.16705	−0.00140	−0.00192	1.1637	1.1638 ±0.0002

HoI, ErI, and TmI are of the type $4f^n$. Apart from LaI and GdI, which are known to have $4f^{n-1}5d$ as the ground configuration,[23] there remain CeI and TbI. The work of Smith and Spalding[1] on CeI and of Penselin and Schlüpmann[1] on TbI indicate that the simple configurations of the type $4f^n$ are not sufficient to account for the experimental results in these cases. For TbI, however, we can at least say that $4f^9$ is very low-lying.

The good agreement also gives us a great deal of confidence about the various radial integrals required in the calculations. The values of the spin-orbit coupling constants given by Eq. (11) should be accurate to at least 5% along the whole rare-earth series. The integrals F_2, which to some extent depend on the choice of the ratios F_4/F_2 and F_6/F_2, are probably given to within 10% by Eq. (9). The error in the relativistic and diamagnetic corrections should also be quite small, probably not exceeding 10%. This shows that the approximations made in the latter case are justified and also supports the type of eigenfunction used. It is easy to see, for instance, that if a hydrogenic eigenfunction is used instead of the modified type (24), the agreement would be poorer in almost all cases. As mentioned earlier, the shape of the eigenfunction has only a small effect on $\langle r^{-3}\rangle$, and we estimate that the errors in the tabulated values of these quantities are not greater than 5%.

In all the calculations it has been assumed that the electronic configuration is a pure $4f^n$ configuration. This is not so restrictive as it might appear at first sight. The Coulomb interaction is chiefly responsible for admixing other configurations, and it commutes with S, L, and J. The Landé formula, with the Schwinger correction, remains valid, and no corrections are necessary. The spin-orbit interaction can couple only to configurations of the type $4f^{n-1}5f$, $4f^{n-1}6f$, etc. These configurations are far removed from the ground configuration, and matrix elements of Λ between $4f$ and nf states are certainly small. The virtually perfect agreement that has been obtained for TmI,[21] where there are no corrections to g_J due to spin-orbit coupling effects within the ground configuration, supports the view that the effects of configuration interaction are negligible. It also indicates that the residual discrepancies between the theoretical and experimental g values of other rare-earth atoms are chiefly due to higher-order spin-orbit effects within the ground configurations, rather than to approximations made in estimating the relativistic and diamagnetic corrections. This conclusion is supported by the excellent agreement obtained for ErI, where the complete $J=6$ matrix is diagonalized.

It is interesting to note that when the Schwinger, relativistic, diamagnetic, and *second-order* spin-orbit corrections to the various g_J values of the levels of a given multiplet are made, the final calculated values satisfy an equation of the type

$$(J+1)g_J-(J-1)g_{J-1}=aJ^2+b, \qquad (25)$$

where a and b depend on the multiplet under examination and are independent of J. In deriving this equation, which is of a quite general validity, use was made of the detailed form of the 6-j symbol (6) and also the S, L, J dependence of h.

Finally, we should like to point out that some neglected corrections and errors in parameters such as ζ may produce effects which to some extent cancel, and therefore the remarkable agreement we have obtained between the experimental and theoretical g_J values may be partly accidental. However, since the results depend in so many ways on our various assumptions, and are so well checked by experiment, we feel that this could occur in only one or two instances, and our general conclusions concerning the accuracy of the spin-orbit coupling constants and other radial integrals should not be affected.

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