In Fig. 3 are shown the L_{β_1} and $L_{\alpha_{1,2}}$ components. The upper curve shows the relative intensities observed in the spectrometer. The lower curve shows the attenuated spectrum when a 0.915-mg/cm^2 copper absorber is placed between the source and crystal. The L_{β_1} component in the attenuated beam represents less than 1% of the total.

It must be accepted that certain reservations must exist in applying the above conclusions to a series of experiments employing the more deeply penetrating protons. At the present time, however, there are no data available regarding relative intensity of lines, etc., originating from proton ionization. Therefore, the electron data must be used as a qualitative reference.

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Theory of Spin-Orbit Coupling in Atoms. III

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Spin-orbit coupling constants have been calculated for a number of $4d$ and $4f$ shell ions, as well as for some excited states of Li and Cu. The calculations are based on a theory in which the contribution of two-body spin-orbit interactions to the coupling constant is taken into account and exchange effects are included. Fair agreement with experiment is obtained, and several possible reasons for the discrepancies which do occur are discussed. The relation of spin-orbit coupling to hyperfine structure is also considered.

I. INTRODUCTION

IN two previous papers,[1] a theory of the spin-orbit coupling constant for many-electron atoms was developed and applied in calculations for a number of the lighter atoms and ions. In the present work, we wish to extend the previous calculations to atoms with unfilled $4d$ or $4f$ shells, to consider a number of special cases such as inversion of the Cu$(3d)^{10}4f$ doublet and the fine structure of the $(1s)^2 2p$, $(1s)^2 3p$, and $(1s)^2 3d$ states of Li, and to relate these observations to the problem of the calculation of hyperfine structures.

The experimental data available for $4d$ and $4f$ shell ions are less accurate and less extensive than was the case for the lighter ions which were considered in II. This makes the task of detailed comparison of our theoretical results with experiment more difficult, but, on the other hand, the importance of theoretical calculation is thereby enhanced, since it will provide added information for use in other work where spin-orbit coupling arises. Using the available experimental data, we find quite good agreement for the theoretical $4d$ shell results, while the theoretical coupling constants for the rare-earth ions lie somewhat higher than their experimental counterparts. We will compare the rare-earth calculations with those of Ridley,[2] where a use of Hartree functions and the familair $\langle (1/r)(\partial V/\partial r)\rangle$ expression for the coupling constant gave good agreement with experiment. The present method starts with a Hartree-Fock (H-F) wave function and properly evaluates the coupling constant for such a function. Since the radial integrals required for the calculation of the coupling constant resemble those used in the calculation of hyperfine interactions (a fact frequently exploited in the past[3–5]), we will estimate from the calculated coupling constants the usefulness of the H-F wave functions for the calculation of hyperfine structure. We shall see that the nonrelativistic $4d$ and $4f$ orbitals employed here are more appropriate for the discussion of hyperfine effects than one might have anticipated at first.

We also consider fine-structure doublets because of the historical role they have played in the understanding of spin-orbit coupling. The inadequacy of the standard

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[1] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A270**, 127 (1962), referred to as Paper I; **A271**, 565 (1963), referred to as Paper II.

[2] E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).

[3] B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961).

[4] I. Lindgren, Nucl. Phys. **32**, 151 (1962).

[5] See, e.g., R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953); **A219**, 387 (1953); and B. Bleaney, Proc. Phys. Soc. (London) **A68**, 937 (1955).

$\langle(1/r)(\partial V/\partial r)\rangle$ theory became apparent in the 1930's when it was observed that there existed doublets which were anomalously narrow or inverted and which could not be explained by such a theory. These occurred for single valence electrons outside of closed-shell cores such as for the $1s^22p$ state of Li and the $3d^{10}4f$ state of Cu. Controversy arose as to whether this was due to exchange effects[6,7] or to configuration interaction (i.e., correlation).[8] The calculations for Cu by Araki[6] and for Li by David,[7] among others, suggested that exchange was the dominant effect. We have reinspected these cases (and the $1s^23p$ and $1s^23d$ excited states of Li as well) making use of the better wave functions which are at our disposal. We shall see that the dominance of exchange is by no means as clear as it was once thought to be. These matters and the implications of correlation on spin-orbit coupling in general will be discussed.

In order to define the quantities under consideration, we summarize here some of the relevant results and definitions of Papers I and II. The spin-orbit coupling constant for a many-electron atom has, in the past, been defined by generalizing the constant for a one-electron atom. In the latter case, reduction of the Dirac equation to nonrelativistic form gives[9]

$$V_{\text{so}}=\frac{\alpha^2}{2}\left\langle\frac{1}{r}\frac{\partial V}{\partial r}\right\rangle\mathbf{l}\cdot\mathbf{s}=\frac{\alpha^2}{2}Z\left\langle\frac{1}{r^3}\right\rangle\mathbf{l}\cdot\mathbf{s}=\zeta\mathbf{l}\cdot\mathbf{s}\,, \tag{1}$$

where α is the fine structure constant and V is the Coulomb field of the nucleus of charge Z. This is generalized to a many-electron atom by summing over outer electrons and interpreting $V(r)$ to be the (assumed) spherical potential due to the nucleus and to all other electrons in the atom as seen by one of the outer electrons:

$$V_{\text{so}}=\frac{\alpha^2}{2}\left\langle\frac{1}{r}\frac{\partial V}{\partial r}\right\rangle\sum_i\mathbf{l}_i\cdot\mathbf{s}_i\,. \tag{2}$$

A more consistent procedure was followed in I, where it was shown that Eq. (2) is only approximate, and that "exchange" type terms must be included in the definition of the coupling constant. Beginning with the one- and two-body magnetic spin-orbit interactions[10]

$$V_m'=\frac{\alpha^2}{2}Z\sum_i\frac{1}{r_i^3}\mathbf{l}_i\cdot\mathbf{s}_i-\frac{\alpha^2}{2}\sum_{i\neq j}\left(\frac{\mathbf{r}_{ij}}{r_{ij}^3}\times\mathbf{p}_i\right)\cdot(\mathbf{s}_i+2\mathbf{s}_j)\,, \tag{3}$$

use was made of a relation due to Elliott,[11] which states that within the conventional Hartree-Fock description of the atom the two-body outer-electron-core interactions in Eq. (3) have matrix elements, which, within a given atomic configuration, are proportional to those of the operator $\sum_i\mathbf{l}_i\cdot\mathbf{s}_i$. This enabled Eq. (3) to be written as

$$V_m'=\zeta_c\sum_i{}'\,\mathbf{l}_i\cdot\mathbf{s}_i-\frac{\alpha^2}{2}\sum_{i\neq j}{}'\left(\frac{\mathbf{r}_{ij}}{r_{ij}^3}\times\mathbf{p}_i\right)\cdot(\mathbf{s}_i+2\mathbf{s}_j)\,. \tag{4}$$

The primes on the summations indicate that only those electrons in unfilled shells are to be included, and it is understood that the equality holds only for matrix elements within a given configuration. Equation (4) provides a definition of ζ_c, which was expressed in I in terms of radial integrals. These integrals were calculated for a number of ions using Hartree-Fock wave functions, and a comparison of these results with experiment was given in II. In order to derive the expressions for ζ_c, a single matrix element of Eq. (4) is calculated and equated to the same matrix element of Eq. (3). In doing this it was assumed that the atomic wave functions were written in determinantal form, so that exchange type terms entered into the matrix elements of the two-body operations in Eq. (4) as well as ζ_c. A further rearrangement of Eq. (4) was carried out by Horie[12] who showed that part of the two-body outer-electron interaction could also be represented as a one-body spin-orbit term so that

$$V_m'=\zeta'\sum{}'\,\mathbf{l}_i\cdot\mathbf{s}_i-\left\{\frac{\alpha^2}{\infty}\sum_{i\neq j}{}'\left(\frac{\mathbf{r}_{ij}}{r_{ij}^3}\times\mathbf{p}_i\right)\cdot(\mathbf{s}_i+2\mathbf{s}_j)\right.$$
$$\left.+(\zeta'-\zeta_c)\sum_i\mathbf{l}_i\cdot\mathbf{s}_i\right\}\,. \tag{5}$$

The constant ζ' is chosen so that the expression in brackets has no additive terms whose matrix elements are proportional, throughout a given configuration, to $\sum_i\mathbf{l}_i\cdot\mathbf{s}_i$; we refer to I for tables of this quantity. Ignoring the two-electron term of Eq. (5), the many-electron constant appropriate to $\lambda\mathbf{L}\cdot\mathbf{S}$ for the ionic ground state is given by

$$\lambda=\pm\zeta'/2S\,, \tag{6}$$

where plus and minus signs hold for ions with less-than- and more-than-half-filled shells, respectively. The two-electron terms of Eq. (5) cause deviations from this relation. These deviations were seen to be appreciable for $3d$ ions in II and we will briefly consider their role for $4d$ and $4f$ ions here. The two-electron effects involve radial integrals of the form

$$M_k(aa)\equiv\frac{a^2}{4}\int_0^\infty r^2dr\int_0^r r_1^2dr_1R_a^2(r)R_a^2(r_1)\frac{r_1^k}{r^{k+3}}\,, \tag{7}$$

where $R_a(r)$ is the valence shell radial orbital. This integral also appears in valence shell spin-spin and orbit-orbit interactions.[13]

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[6] G. Araki, Proc. Phys. Math. Soc. Japan **21**, 592 (1939).

[7] E. David, Z. Physik **91**, 289 (1934).

[8] M. Phillips, Phys. Rev. 44, 644 (1933).

[9] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955).

[10] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).

[11] J. P. Elliott, Proc. Roy. Soc. (London) **A218**, 345 (1953).

[12] H. Horie, Progr. Theoret. Phys. (Kyoto) **10**, 296 (1953).

[13] See, e.g., D. F. Johnston, in Proceedings of the International Conference on Paramagnetic Resonance, Israel, 1962 (unpublished).

TABLE I. Results for $4d$ shell ions.

	$Y^+(4d)^2$	$Y^{2+}(4d)^1$	$Zr^{2+}(4d^2)$	$Zr^{3+}(4d)^1$	$Nb^{2+}(4d)^3$	$Nd^{3+}(4d)^2$	$Mo^{2+}(4d)^4$	$Mo^{3+}(4d)^3$	$Ru^{2+}(4d)^6$
ζ_{nuc}	362	463	632	739	818	938	1025	1155	1506
ζ_{cd}	260	334	462	542	605	696	765	866	1147
ζ_c	242	311	432	506	567	652	719	813	1082
ζ_d'	259	334	462	542	598	688	763	864	1142
ζ'	242	312	432	507	560	644	717	812	1077
$2S\lambda$	241		430		556	642	710	806	1087
ζ_{exp}	210	300	425	500	555	670	695	800	1000
M^0	0.120	0.166	0.229	0.279	0.297	0.355	0.373	0.437	0.543
M^2	0.066	0.092	0.127	0.156	0.165	0.198	0.206	0.243	0.300

	$Ru^{3+}(4d)^5$	$Rh^{2+}(4d)^7$	$Rh^{3+}(4d)^6$	$Pd^{2+}(4d)^8$	$Pd^{3+}(4d)^7$	$Ag^{2+}(4d)^9$	$Ag^{3+}(4d)^8$	$Cd^{3+}(4d)^9$
ζ_{nuc}	1670	1789	1958	2101	2281	2446	2640	3037
ζ_{cd}	1274	1374	1506	1625	1768	1906	2060	2385
ζ_c	1202	1298	1423	1538	1673	1807	1952	2264
ζ_d'	1269	1366	1499	1615	1758	1892	2046	2368
ζ'	1197	1291	1416	1529	1664	1794	1940	2249
$2S\lambda$		1299	1430	1533	1676		1946	
ζ_{exp}	(1180)	1220	1400	1600	1640	1840	1930	2325
M^0	0.626	0.640	0.726	0.746	0.837	0.862	0.959	1.093
M^2	0.347	0.353	0.402	0.411	0.463	0.475	0.530	0.603

In the following sections we present calculated $4d$ and $4f$ ion values of ζ_c, ζ', M^k, ζ_{cd}, ζ_d', ζ_{nuc} and $2S\lambda$. The latter terms are defined by

$$\zeta_{cd}\equiv\tfrac{1}{2}\alpha^2\left\langle\frac{1}{r}\frac{\partial V_{\mathrm{core}}}{\partial r}\right\rangle, \tag{8}$$

i.e., just the conventional expression evaluated for a potential (V_{core}) due only to closed-shell electrons and

$$\zeta_d'\equiv\tfrac{1}{2}\alpha^2\left\langle\frac{1}{r}\frac{\partial V}{\partial r}\right\rangle, \tag{9}$$

or just the one-electron parameter appropriate to Eq. (2). The ζ_{nuc} is defined for a potential due only to the nucleus [i.e., for Eq. (1)] and is included to indicate the relative role of direct and exchange shielding. Values of $2S\lambda$, where λ is defined for the ground multiplet state of the ion, will be listed so as to indicate the importance of the two-electron-like effects [see Eqs. (5) and (6) and related discussion].

II. SPIN-ORBIT COUPLING FOR $4d$ IONS

Results for the $4d$ ions are listed in Table I. The calculations utilized recently obtained analytic nonrelativistic H-F functions.[14] The experimental ζ values come from the compilations of Griffith,[15] McClure[16] and Dunn.[17] These were not obtained with refined fitting procedures such as Horie's[12] (e.g., two-electron effects were not accounted for) and they are not necessarily accurate to the number of digits we quote. Comparing either ζ' or $2S\lambda$ values with experiment, the agreement between theory and experiment is seen to be good, i.e., generally to 5% or better. The traditional $\langle(1/r)(\partial V/\partial r)\rangle$ expression, indicated by the ζ_d' values, is less satisfactory. There is no clear trend in the differences which do occur between theory and experiment, largely, we believe, because of the uncertainties in the experimental values.

Comparison of ζ_{nuc} and ζ_{cd} values shows that the ion cores provide a direct shielding which reduces the coupling constant due to the field of the nucleus alone by 20 to 30%. The core exchange contributes an additional shielding which is 20%/(as compared with 25%/for the $3d$ ions[1]) of the direct effect. Neither the one-electron contributions to ζ' nor the two-electron effects (compare ζ' and $2S\lambda$) of the open valence shell are important. The two-electron-like terms make 1% contributions to the ground state spin-orbit coupling, contributions which are almost an order of magnitude less important than those seen (e.g., Table 6 of II) for the iron series ions. This decrease is due to an increase in the one-electron-like spin-orbit coupling, ζ', on the one hand, and to the more diffuse nature of $4d$ orbitals, which decreases spin-orbit, spin-spin, and orbit-orbit interactions within the $4d$ shell, on the other. These facts make it practicable to utilize the commonly made, and actually incorrect, assumption that spin-orbit coupling is a one-electron interaction (with a constant ζ within a configuration) when dealing with $4d$ ions.

III. SPIN-ORBIT COUPLING FOR RARE-EARTH IONS

Results for the rare-earth ions are listed in Table II. These were evaluated with analytic nonrelativistic H-F functions[18] which are of inferior accuracy to those utilized in the preceding section. A more accurate nonrelativistic Ce^{3+} function, which has been obtained more

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[14] R. E. Watson and A. J. Freeman (to be published).

[15] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, England, 1961).

[16] D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 399.

[17] T. M. Dunn, Trans. Faraday Soc. **17**, 1441 (1961).

[18] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2059 (1962).

TABLE II. Results for rare-earth ions.

	$Ce^{3+}(4f)^1$	$Pr^{3+}(4f)^2$	$Nd^{3+}(4f)^3$	$Sm^{3+}(4f)^5$	$Eu^{2+}(4f)^7$	$Gd^{3+}(4f)^7$	$Tb^{3+}(4f)^8$
ζ_{nuc}	1600	1852	2114	2668	2773	3307	3638
ζ_{cd}	831	985	1149	1506	1585	1929	2153
ζ_c	737	879	1030	1361	1436	1755	1965
ζ_d'	831	981	1138	1432	1548	1884	2097
ζ'	740	878	1024	1342	1404	1717	1915
ζ_{exp}	640	750	900	1180			1620
ζ_d'	(Hartree functions)[a]	785					
M^0	1.95	2.24	2.52	3.08	3.06	3.70	3.99
M^2	1.10	1.26	1.42	1.73	1.71	2.08	2.24
M^4	0.74	0.85	0.96	1.18	1.16	1.41	1.52
	$Dy^{3+}(4f)^9$	$Ho^{3+}(4f)^{10}$	$Er^{3+}(4f)^{11}$	$Tm^{2+}(4f)^{13}$	$Tm^{3+}(4f)^{12}$	$Yb^{3+}(4f)^{13}$	
ζ_{nuc}	3987	4368	4773	4927	5184	5659	
ζ_{cd}	2392	2655	2936	3057	3225	3559	
ζ_c	2189	2436	2700	2817	2973	3288	
ζ_d'	2323	2572	2837	2940	3109	3423	
ζ'	2182	2360	2610	2708	2866	3161	
ζ_{exp}	1820	2080	2470	2500	2750	2950	
					2740		
M^0	4.29	4.62	4.96	4.89	5.28	5.69	
M^2	2.41	2.59	2.78	2.73	2.96	3.19	
M^4	1.64	1.76	1.89	1.85	2.01	2.17	

[a] See Ref. 3.

recently by Bagus,[19] yields a ζ' value equal to 743 cm^{-1}, in good agreement with the value reported in Table II, and suggests that wave function deficiencies have not seriously affected the values listed there. The experimental ζ values are compromises between those tabulated by Jørgensen,[20] Runciman,[21] Wybourne[22] and McClure.[16] These values are subject to the same uncertainties as their $4d$ counterparts and, with the exception of Ce^{3+}, were obtained for the ions in salts rather than in their free state. Environmental effects on a rare-earth ζ are expected to be small (perhaps causing up to a 1% lowering of its value), smaller, in fact, than other uncertainties in the quoted values.

Comparing ζ' values with experiment, we see that they are consistently high, ranging from 17% for Ce^{3+} to 7% for Yb^{3+}. The traditional $\langle(1/r)(\partial V/\partial r)\rangle$ values (i.e., ζ_d') lie even higher with roughly twice the discrepancy with experiment seen for ζ'. This is the first time that ζ' values have run higher than experiment. The $3p$ and $4p$ ions are the only other cases where significant disagreement has occurred between theory and experiment (see II). There the calculated ζ' values were generally smaller than the experimental values, a difference ascribed to relativistic effects. We believe relativistic effects to be the largest single source of the $4f$ ζ' deviations as well. The various possible sources of such deviations will be discussed later.

Inspection of ζ_{nuc} and ζ_{cd} values in Tables I and II shows the direct shielding is relatively more important for the rare earths, where it causes 40 to 45% shielding. Exchange effects, however, are relatively less important, contributing a shielding which is 15% of the direct terms.

Two-electron effects have not been included in Table II. Although small, they are more important than is the case for the $4d$ series. Contributions of as much as 2 or 3% to individual spin-orbit matrix elements are to be expected. These tend to reduce the disagreement with experiment for the under-half-filled shell ions while enhancing the disagreement for the others and causes the deviations to settle closer to 10 or 12% for all but Ce^{3+} and Yb^{3+}. Since these ions have, respectively, $4f$ and $4f^{13}$ configurations, they have no two-electron terms. While small, the two-electron effects in $4d$ and rare-earth ions cannot be ignored in any experimental fit involving more than a single multiplet state where 1% accuracy or better is desired.

Judd and Lindgren, in their estimates[3,4] of rare-earth hyperfine fields, relied on the observation that ζ_d''s computed with nonrelativistic Hartree functions[2] for Pr^{3+} and Tm^{3+} yielded remarkable good agreement with experiment. These ζ_d' values are also listed in Table II. Since agreement of this sort is not typical for other ions for which the $\langle(1/r)(\partial V/\partial r)\rangle$ expression has been evaluated with Hartree functions, one may consider it to be due to a cancelation of errors. Note that if one inserted the Hartree orbitals into an antisymmetric function and evaluated ζ', agreement with experiment would be destroyed. As discussed later, agreement of ζ_d' with experiment does not imply that Hartree $\langle r^{-3}\rangle$ values, of interest for hyperfine effects, show similar agreement.

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[19] P. Bagus (unpublished).

[20] C. K. Jørgensen, J. Inorg. Nucl. Chem. **1**, 301 (1955); C. K. Jørgensen, Kgl. Danske Videnskab. Selskab, Mat. Fyz. Medd. **29**, No. 11 (1955).

[21] W. A. Runciman, *Reports on Progress in Physics* (The Physical Society, London, 1958), Vol. 21, p. 30.

[22] W. A. Runciman and B. G. Wybourne, J. Chem. Phys. **31**, 1149 (1959); B. G. Wybourne, *ibid.* **32**, 639 (1960).

IV. INDIVIDUAL SHELL CONTRIBUTIONS TO ζ_c

Direct and exchange contributions per electron per shell are listed in Table III for the various closed shells of two ions (Pd^{2+} and Yb^{3+}). Values of $\zeta_{\rm nuc}/Z$ are also included in order to provide a basis for comparison.

The behavior observed here is the same as that seen in II. Only those shells lying inside the innermost loops of the open valence shell contribute significantly to the direct shielding and, in turn, only the outermost of this set of shells contribute substantially to the exchange shielding.

The direct shielding is also readily understood, as was seen in II. The one-electron spin-orbit coupling is closely associated with the r^{-3} behavior of the valence shell. The innermost loop of such a shell's radial function is almost entirely responsible for its $\langle r^{-3}\rangle$ value. The $\langle(1/r)(\partial V/\partial r)\rangle$ shielding is due to closed-shell contributions to the potential V, and for these shells to contribute significantly to the shielding they must lie within the innermost loop of the valence shell radial function.

The behavior of the exchange term is slightly more complex as it is dependent on the overlap between the shells in question. the $1s$ shell of Pd^{2+} and the $1s$, $2s$ and $2p$ shells of Yb^{3+} are so concentrated in the interior of their respective ions that they overlap their valence shells very little, and, hence, they contribute comparatively little exchange shielding. On the other hand, shells which overlap the bulk of the valence shell tend to have small exchange terms because of the dominant exchange integrals

$$V^k(\text{Val, Closed})$$

$$\equiv \tfrac{1}{4}\alpha^2 \int_0^\infty \int_0^\infty r_1^2 \cdot r_2^2 \cdot dr_1 dr_2 f_{\rm Val}(r_1) f_{\rm Cl}(r_2) \times \frac{r_<^k}{r_>^{k+3}} \left(r_2 \frac{\partial}{\partial r_1} - r_1 \frac{\partial}{\partial r_2} \right) f_{\rm Cl}(r_1) f_{\rm Val}(r_2)$$

(introduced in I). Given a closed shell which greatly overlaps the valence shell, the V^k integrand then varies in sign from one region to another. The resulting cancellations cause the small magnitude and variation in sign seen for the exchange terms of the outer closed shells. The largest exchange effects occur when the negative outer slope of the closed shell overlaps the rising positively sloped, inner loop of the valence shell.

It should be noted that individual shell exchange terms are not, of necessity, shielding. Unlike electrostatic exchange effects which are always of one sign, the spin-orbit terms take either sign.[23] Inspection of Table III shows some of the less important outer shell terms to be antishielding. We expect that the total exchange effect, coming from all closed shells, will always be shielding.

TABLE III. Contributions of individual shells to the coupling constants.

		Direct	Exchange	Total
Pd^{2+}	$\zeta_{\rm nuc}/Z$			45.7
	$1s$	−44.5	−6.7	−51.3
	$2s$	−25.1	−24.5	−49.6
	$3s$	−7.3	+1.7	−5.6
	$4s$	−2.5	−1.8	−4.3
	$2p$	−29.4	−25.6	−55.0
	$3p$	−7.7	+2.4	−5.3
	$4p$	−2.3	−1.0	−3.3
	$3d$	−8.0	+3.3	−4.7
Yb^{3+}	$\zeta_{\rm nuc}/Z$			80.9
	$1s$	−80.9	−0.1	−81.0
	$2s$	−78.0	−11.2	−89.2
	$3s$	−51.8	−28.3	−80.1
	$4s$	−15.6	−0.6	−16.2
	$5s$	−2.0	+0.7	−1.3
	$2p$	−79.0	−7.7	−86.7
	$3p$	−53.8	−28.1	−81.9
	$4p$	−15.3	+0.0	−15.3
	$5p$	−1.7	+0.6	−1.1
	$3d$	−60.0	−26.7	−86.7
	$4d$	−14.6	+1.4	−13.2

Finally, we see that some closed shells have overshielded the nucleus, i.e., the direct plus exchange shielding due to a single closed-shell electron has exceeded the spin-orbit coupling ($\zeta_{\rm nuc}/Z$) associated with a nuclear charge of 1. This has happened for the $1s$, $2s$ and $2p$ shells of Pd^{2+} and for the $3p$ and $3d$ shells in Yb^{3+} as well.

V. SPIN-ORBIT COUPLING IN EXCITED STATES OF ATOMIC Li AND Cu

The possibility that a closed shell's exchange spin-orbit contribution can lead to overshielding suggests that ions with a single valence electron external to closed shells (for which strong shielding is already available from the direct terms) might very well have anomalously narrow or inverted doublet levels. The observation of such cases supplied the first indication that the $\langle(1/r)(\partial V/\partial r)\rangle$ expression was inadequate. In this section we report on a repetition of the original calculations of David[7] for Li $1s^22p$ and of Araki[6] for Cu $3d^{10}4f$.

Results obtained with analytic H-F functions of Weiss[24] for the $1s^22p$, $1s^23p$ and $1s^23d$ states of Li are listed in Table IV. The present $1s^22p$ state results are in substantial agreement with those of David. (The other two states were not considered by him.) The $1s^22p$ and $1s^33p$ behavior is much the same: In both cases exchange is important, causing us to go from ζ_{cd}'s which are a factor of 2 too large to ζ_c's which are one-third smaller than experiment. Better, but by no means detailed, agreement with experiment is obtained with the more exact theory.

The situation is different from the $1s^23d$ state. Here,

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[23] The sign of the spin-orbit exchange term is associated with that of the V^k integral. The standard arguments which lead to a plus sign for electrostatic exchange integrals do not hold for this integral.

[24] A. Weiss (to be published).

the direct terms contribute to a complete shielding (equivalent to a nuclear charge of 2), making ζ_{cd} equal to one third of ζ_{nuc}, and the exchange term is almost zero, seen in the preceding section for the $1s$ shells of Pd^{2+} and Yb^{3+}. The $3d$ shell has almost no overlap with the $1s$ shell, causing a minimal exchange term and a complete direct shielding. Interestingly, there is better agreement with experiment for this case than was seen for the $1s^22p$ and $1s^23p$ states.

The $(3d)^{10}4f$ state of Cu is an inverted doublet. The $4f$ shell is sufficiently external to the ion so that the closed shells screen all but a nuclear charge of one, so that

$$\zeta_{cd}\sim(\alpha^2/2)\langle r^{-3}\rangle\approx 0.002\ \text{cm}^{-1}. \tag{11}$$

To obtain a negative coupling constant, it is necessary for the exchange terms to be larger than and of opposite sign to ζ_{cd}. Araki's calculation[6] showed such a sign reversal. The present results, relying on an analytic H-F function obtained by the authors, do not give such an effect (See Table V). The situation is similar to that discussed for the Li $1s^23d$ state, where the maximum attainable direct shielding has been achieved at the price of the exchange terms. The present calculation suggests that exchange plays but a minor role in spin-orbit coupling of states whose valence electron is truly outside the core.

It should be noted that cases such as those considered in this section make severe demands of numerical accuracy. Very strong differencing occurs which amplifiers any errors in the wave function. This problem was considered in more detail for the Li $1s^22p$ state, for which a number of approximate H-F functions are available. Values of ζ_c as small as 0.12 cm^{-1} were obtained with functions whose total (ion) energy was almost identical to that of the function used for the Table IV estimate. This result is illustrative of the numerical uncertainties which may be ecountered and which are particularly severe for ions with single valence electrons. We believe that the value of $\zeta_c(0.16\ \text{cm}^{-1})$ given in Table IV represents an accurate H-F estimate and that wave function accuracy has not affected the qualitative features of the Cu results shown in Table V.

TABLE IV. Results for some excited states of Li.

	Present calculations	David	Experiment
$1s^22p$			
ζ_{nuc}	1.01		
ζ_{cd}	0.48	0.57	
ζ_c	0.16	0.17	0.23
$1s^23p$			
ζ_{nuc}	0.309		
ζ_{cd}	0.149		
ζ_c	0.044		0.066
$1s^23d$			
ζ_{nuc}	0.0435		
ζ_{cd}	0.0146		
ζ_c	0.0144		0.01_6

TABLE V. $\text{Cu}(3d)^{10}4f$.

$\zeta_{\text{nuc}}=0.0632\ \text{cm}^{-1}$
$\zeta_{cd}\ =0.0021\ \text{cm}^{-1}$
$\zeta_c\ \ =0.0021\ \text{cm}^{-1}$

VI. RELATIVISTIC AND CORRELATION EFFECTS

The results of the preceding sections were obtained with conventional H-F functions which are neither relativistic nor, by definition, correlated. Let us consider how the inclusion of these effects might affect the computed coupling constants.

The most obvious by-product of the inclusion of relativistic terms would be a contraction of the ionic charge density in the immediate vicinity of the nucleus. We believe this to be the primary source of the $3p$ and $4p$ ion ζ' discrepancies reported in II. The computed ζ' values were smaller than experiment, with the deviations more severe for the $4p$ case. The relativistic contraction would improve the agreement with experiment, with a larger shift for the $4p$ ions than for the $3p$ ions. An f or d shell electron does not, however, penetrate too close to the nucleus. Comparison of relativistic and nonrelativistic Hartree functions[25] suggests that while s and p shells undergo a contraction, d and f shells expand due to increased s and p shell shielding of the nuclear potential. These higher order expansions are, of course, far less severe than the s and p contractions. Estimates of this effect have yet to be made for the rare earths, but an expansion of this sort would reduce the ζ' discrepancies of Table III.

"Correlation" effects can be roughly divided into two sorts: First, there is the classical interelectronic correlation associated with the fact that H-F theory does not properly account for the presence of interelectronic (e^2/r_{12}) terms in the Hamiltonian. This type of correlation is associated with doubly substituted configurations in the configuration interaction scheme[26] and is generally thought to have little effect on the expectation value of a one-electron operator.[27] The effect on the expectation value of an operator of the form of Eq. (3) is not, however, obvious. The dominant two-electron spin-orbit terms are the valence electron closed-shell direct shielding and we do not expect these (and in turn ζ') to be seriously affected.

The second type of correlation is associated with the

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[25] D. F. Mayers, Proc. Roy. Soc. (London) **A241**, 93 (1957); R. G. Boyd, A. C. Larson, and J. T. Waber, Phys. Rev. **129**, 1629 (1963).

[26] See R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955); also Rev. Mod. Phys. **33**, 28 (1961) for a discussion of single and double substitution configuration interaction and the role H-F theory plays in this approach.

[27] For a recent investigation into the matter, see J. W. Cooper and J. B. Martin, Phys. Rev. **131**, 1183 (1963).

fact that we normally utilize H-F theory in a restricted form when dealing with open-shell systems. The restrictions lead (among other things) to a description in which closed shells have closed, inert ^1S character. Aspherical, nonsinglet open shells will, on the other hand, induce distortions within the closed (and valence) shells, distortions which should contribute to the spin-orbit coupling. Sternhimer[28] used perturbation techniques to investigate the effect of these distortions on hyperfine interactions and found them to be significant. One can alternatively approach the problem using singly substituted configuration interaction[26] or the unrestricted H-F method.[29] The perturabtion and H-F methods suffer symmetry difficulties[30] and cause a breakdown of Elliott's theorem as soon as closed shells are in any way distorted.

In addition to the question of relativistic and correlation corrections, there is, of course, the larger question of the definition of a proper relativistic many-electron theory and of whether an adequate approximation to it is being used. We do not believe it relevant to inquire into the implications of this question to the discrepancies at hand until the other matters of this section are better understood. Of these, we believe relativistic shifts to be most important for the $3p$, $4p$, and $4f$ ion deviation, though not for the Cu and Li results of the preceding section. Hopefully, considerably more will be known about relativistic effects in the not too distant future.

VII. SPIN-ORBIT COUPLING AND HYPERFINE INTERACTIONS

The orbital and spin dipolar magnetic and electric quadrupole hyperfine interactions of non-S-state ions are proportional to the valence shell $\langle r^{-3}\rangle$ integral within the RHF description. Since the nuclear spin-orbit term is also proportional to this (and the closed-shell direct shielding is approximately so), a close connection between the two types of interaction is suggested. This observation has led to some remarkably accurate[3,5] estimates of rare-earth hyperfine field behavior based on observed spin-orbit coupling constants.[30a] It also suggests that for a given wave function, it is possible to correlate to some extent its fine- and hyperfine-structure predictions. For example, it appears that the deviation between a predicted ζ' and experiment implies a similar deviation in hyperfine predictions.

With the above factors in mind, let us examine rare-earth $\langle r^{-3}\rangle$ hyperfine parameters. These are listed in Table VI and include Lindgren's Hartree predictions[14] and the restricted H-F values.[18] Estimates of experimental $\langle r^{-3}\rangle$'s present certain difficulties. There have been recent determinations of the nuclear magnetic moments of isotopes of Nd,[31] Er,[32] Yb,[33] Tm,[34] and Eu.[35] Experimental hyperfine data are also available for trivalent Nd^{3+}, Er^{3+}, and Yb^{3+}, and experimental $\langle r^{-3}\rangle$ parameters are thus available for these three ions. Unfortunately, lack of detailed knowledge of rare-earth wave function behavior renders the evaluation of the necessary spin and angular matrix elements, and in turn the $\langle r^{-3}\rangle$'s, uncertain (see, for example, Elliott and Stevens[5]). For experimental values we list those computed by Bleaney,[36] by the experimenters (when available) and by use of Lindgren's analysis. The resulting variation in $\langle r^{-3}\rangle$ values suggests a 5% uncertainty from this source. In addition, the ± 0.5 listed for Er^{3+} reflects the uncertainty which Doyle and Marrus attach to their experimental moment. Values quoted for ions other than Nd^{3+}, Er^{3+}, and Yb^{3+} are those interpolated by Bleaney.[36] The valence electron relativistic effects discussed in the preceding section would affect fine and hyperfine interactions in much the same way. Closed s- and p-shell contractions would not affect hyperfine interactions but could, however, lead to an increase in the spin-orbit shielding. Such effects would tend to reduce the deviations of Table III. Assuming the valence shell shifts to dominate, relativistic corrections would be similar, but not identical, for the two interactions.

Double substitution correlation effects would tend to be different for fine- and hyperfine-structure, since the former involve two-electron operators while the latter does not. In either case, they are probably small. Single substitition effects, on the other hand, need not be small. Sternhimer[28] investigated the effect of these on hyperfine interactions and his results suggest that these led to $\langle r^{-3}\rangle$ *parameters* which differ by as much as 30% from the $\langle r^{-3}\rangle$ *integral* values.[30] Less is known for the spin-orbit case but we expect shifts of significantly less than 10% to come from this source. An effect as large as 10%

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[28] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957).

[29] See, e.g., A. J. Freeman and R. E. Watson, in *Treatise on Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

[30] See also, R. Ingalls, Phys. Rev. **128**, 1155 (1962); A. J. Freeman and R. E. Watson, Phys. Rev. **131**, 2566 (1963).

[30a] *Note added in proof*. Judd [Proc. Phys. Soc. (London) **82**, 874 (1963)] in a paper published after this was submitted, has considered the effects of certain types of configuration interaction on spin-orbit coupling and orbital magnetic hyperfine structure for rare-earth ions. He uses a simplified one-electron form for the spin-orbit coupling operator and, on the assumption that the entire disagreement between theoretical and experimental spin-orbit coupling constants is due to configuration interaction, he derives numerical values for the screening of $\langle r^{-3}\rangle$ values to be used in orbital hyperfine calculations. The theoretical spin-orbit constants which he used did not include exchange effects, which halve the disagreement with experiment. Using these values and assuming Judd's analysis of the relation between spin-orbit and hyperfine constants, one concludes that the effect of configuration mixing is but a few percent of the theoretical values. Accordingly, further consideration must be given to the role of relativistic effects on the wave functions.

[31] D. Halford, Phys. Rev. **127**, 1940 (1962).

[32] W. M. Doyle and R. Marrus, Phys. Rev. **131**, 1586 (1963).

[33] A. C. Gossard, V. Jaccarino, and J. H. Wernick, Bull. Am. Phys. Soc. **7**, 482 (1962), and to be published.

[34] G. J. Ritter, Phys. Rev. **128**, 2238 (1962).

[35] P. G. H. Sandars and G. K. Woodgate, Proc. Roy. Soc. (London) **A257**, 269 (1960); F. M. Pichanick, P. G. H. Sandars, and G. K. Woodgate, *ibid.* **A257**, 277 (1960); and J. B. Baker and F. I. B. Williams, *ibid.* **A267**, 283 (1962).

[36] B. Bleaney (to be published).

TABLE VI. A comparison of $\langle r^{-3}\rangle 4f$ values for selected rare-earth ions (values quoted in atomic units).

	Pr^{3+}	Nd^{3+}	Sm^{3+}	Dy^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
H-F[a]	5.37	6.03	7.36	10.34	12.0	12.9	13.8
Lindgren[b]	4.26	4.86	6.07	8.74	10.3	11.2	12.2
Experiment	5.06[c]	5.64[d] 5.45[e] 5.53[f]	6.72[c]	9.20[c]	10.6[d] 10.5±0.5[f]	12.5±0.6[g] 11.7[c]	12.5[d] 12.9[h] 13.1[f]

[a] From Ref. 4.
[b] From Ref. 8.
[c] As interpolated by Bleaney (Ref. 36).
[d] As computed by Bleaney (Ref. 36).
[e] As computed by Halford (Ref. 31).
[f] As computed using Lindgren's analysis (see Ref. 4) and the observed moment.
[g] As measured by R. L. Cohen (to be published).
[h] As computed by A. C. Gossard, V. Jaccarino and J. H. Wernick (unpublished).

would be somewhat surprising in view of the agreement seen for the $4d$, and for that matter the $4f$, coupling constants. Again, we do not expect identical contributions to hyperfine and fine structure deviations from this source.

Lindgren's predictions[4] tend to be smaller than experiment, and do not reflect the exact agreement in spin-orbit coupling implicit in the Hartree parameterization which was used. As already noted, this is due to the accidental agreement between Hartree predictions and experiment for the rare-earth spin-orbit coupling. The RHF predictions, on the other hand, are approximately 10% too high. These deviations are very similar in behavior (in percentage and in sign) to those seen for the spin-orbit coupling in Table III. Experimental uncertainties make detailed comparisons impossible. The extent of the similarity is somewhat surprising in view of the discussion above and lends credence to the view that a wave function will product fine and hyperfine effects with similar accuracy.[37] As the deviations between theory and experiment become resolved, it will be of great interest to see if the same effect similarly improves both fine- and hyperfine-structure predictions.

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[37] In saying this we ignore any question of differing $\langle r^{-3}\rangle$ parameters for the different hyperfine interactions. See Refs. 16, 26, and 29. In such a case it would be most appropriate to use the orbital magnetic hyperfine $\langle r^{-3}\rangle$ parameter for comparisons.