direction of polarization of the incident beam, and a polaroid disk was used to analyze the scattered beam. In addition, a polarization "scrambler" was positioned at the monochromator entrance slit to eliminate anomalous intensity effects arising from dependence of instrument sensitivity on the polarization of light reaching the gratings. Solution spectra were obtained from saturated solutions of trimethylplatinum hydroxide and iodide in carbon tetrachloride and trimethylplatinum chloride in chloroform. Part of the Raman spectrum of the hydroxide was also investigated in benzene solution. Solutions were contained in a small multipass cell.

Relative intensities were obtained by measuring the areas of Raman lines and correcting the results for instrument sensitivity. For trimethylplatinum chloride, a Du Pont Model 310 curve resolver was used to analyze the complex 200–300-cm^{-1} region.

Infrared spectra of the hydroxide and chloride were recorded on a Beckman IR-12 over the region 200–4000 cm^{-1}. Samples were examined as both KBr pellets and Nujol mulls held between polyethylene windows. For the iodide, the infrared spectrum of a Nujol mull was recorded on a Beckman IR-11 between 60 and 300 cm^{-1}.

Acknowledgments.—We wish to thank Miss B. Prescott of Bell Telephone Laboratories, Murray Hill, N. J., for recording the far-infrared spectrum of trimethylplatinum iodide and Mr. Aris Terzis for assistance in the mounting and orientation of single crystals.

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Atomic and Molecular Spin–Orbit Coupling Constants for 3d Transition Metal Ions[1]

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Linear equations have been obtained relating the interelectronic repulsion parameters F_2 and B and the spin–orbit coupling constant. The equations are obtained empirically from a least-squares fit of free-ion spectral data. Since reduction of the interelectronic repulsion parameters and the spin–orbit coupling constant for complexes relative to free-ion values may be treated as due to expansion of 3d radial wave functions, the equations may also be used to estimate effective spin–orbit coupling constants for complexes. Effective coupling constants, which compare favorably with those obtained from analyses of absorption spectra, are calculated for complexes of several metal ions.

Introduction

The spin–orbit (SO) interaction in transition metal complexes makes important contributions to the splittings and intensities of electronic spectra,[2] zero-field splitting,[3] g factors,[4] and line shapes[5] of electron resonance spectra and is related to the chemical shifts[6] and quadrupole splittings[7] observed in nuclear resonances for these systems. Unfortunately, the spin–orbit coupling constant is only rarely available as an experimental observable in a molecular environment. It is well known, however, that this constant is reduced from the free-ion value in complexes[4c] in similar fashion to the reduction of interelectron repulsion parameters (IRP).[8] These reductions may be explained by assuming that they result from radial expansion of the metal 3d atomic orbitals. Essentially the same results obtain by assuming that the charge on the metal in a complex is reduced relative to the free ion. Radial expansion of the metal ion 3d atomic orbitals thus provides an appropriate basis for correlation between the *effective* SO coupling constant and the interelectron repulsion parameters in both free atoms and complexes. This treatment should not be interpreted as a theoretical model. Rather it is an empiricism in which free-ion data for IRP's and SO coupling constants have been used with radial expectation values from self-consistent field wave functions to establish linear correlations for isoelectronic sequences and sequences of ions of a given nucleus. The empiricism is shown to be of predictive value for free ions and yields quite reasonable values for molecular SO coupling constants. We also note an interesting correlation between $\langle r^{-1}\rangle$ and the effective charge of the central metal ion in complexes which may be of value for comparison with the results of molecular orbital calculations.

Procedure

Assuming a spherical Coulomb potential the spin–orbit interaction may be written[9,10]

$$V_{\mathrm{SO}} = {}^1/_2\alpha^2 Z \sum_{i=1} \zeta_i(nl)\mathbf{l}_i \cdot \mathbf{s}_i \qquad (1)$$

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[1] Presented in part at the 1968 Fall meeting of the American Physical Society, Miami Beach, Fla., Nov 25, 1968; G. M. Cole, Jr., and B. B. Garrett, *Bull. Amer. Phys. Soc.*, **13**, 1396 (1968).

[2] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, Chapter 6.

[3] A. Abragram and H. M. L. Pryce, *Proc. Roy. Soc., Ser. A*, **205**, 135 (1951); **206**, 164 (1951).

[4] (a) A. A. Misetich and R. E. Watson, *Phys. Rev.*, **143**, 335 (1966); (b) B. B. Garrett, K. DeArmond, and H. S. Gutowsky, *J. Chem. Phys.*, **44**, 3393 (1966); (c) R. Lacroix and G. Emch, *Helv. Phys. Acta*, **35**, 592 (1962).

[5] N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961).

[6] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

[7] W. S. Childs and L. S. Goodman, *Phys. Rev.*, **170**, 50 (1968).

[8] C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

[9] M. Blume and R. E. Watson, *Proc. Phys. Soc., London, Sect. A*, **270**, 127 (1963).

[10] E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," 2nd ed, Cambridge University Press, Cambridge, England, 1963.

where

$$\zeta(nl) = \int_0^\infty \frac{|R(nl)|^2}{r^3}\,\mathrm{d}r \tag{2}$$

is the one-electron spin-orbit coupling constant. In the Russell-Saunders coupling scheme an average many-electron SO coupling constant may be defined as

$$V_{\mathrm{SO}} = \lambda \mathbf{L}\cdot\mathbf{S} \tag{3}$$

Within the ground state of a configuration[9]

$$\lambda = \frac{\pm\zeta}{2S} \tag{4}$$

where the plus sign is used for less than half-filled shells, and the negative sign, for more than half-filled shells; S is the total spin; α is the fine structure constant; $\mathbf{l}_i$ and $\mathbf{s}_i$ are the orbital and spin angular momenta of electron i. The interelectronic repulsion parameters F_k are defined[11] for equivalent electrons as

$$F_k = D\int_0^\infty |R(n_\mathrm{a}l_\mathrm{a})|^2 \frac{r_<^{\,k}}{r_>^{\,k+1}} |R(n_\mathrm{b}l_\mathrm{b})|^2 r_1^2\mathrm{d}r_1 r_2^2\mathrm{d}r_2 \tag{5}$$

D is a constant, and $R(nl)$ is a suitable radial function. An alternative notation[11] is

$$B = F_2 - 5F_4 \tag{6}$$

Thus one expects the approximate proportionalities: $F_2 \propto \langle r^{-1}\rangle$, $B \propto \langle r^{-1}\rangle$, and $\zeta \propto \langle r^{-3}\rangle$.

Calculated values of both $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ for 3d metal ions are given in Table I. We have chosen to use the "double ζ" functions of Richardson, *et al.*[12] These give results similar to those of the Watson[13] radial functions for $\langle r^{-1}\rangle$[14] and F_2.[15] There are a variety of other functions in current use, especially those of Clementi.[16] However, Watson's[13] functions seem to give better results for several observables, including interelectron repulsion parameters[13,17] and spin-orbit coupling constants.[18,19]

TABLE I

CALCULATED VALUES OF $\langle r^{-1}\rangle$ AND $\langle r^{-3}\rangle$ (IN PARENTHESES) FOR THE IONS M^{n+}, IN ATOMIC UNITS (1 AU = 0.529×10^{-8} CM)

	n					
	0	1	2	3	4	5
Ti	0.762	0.851	0.937	1.026	...	...
	(1.589)	(1.864)	(2.187)	(2.584)	...	...
V	0.849	0.939	1.020	1.099	1.174	...
	(2.076)	(2.402)	(2.754)	(3.141)	(3.550)	...
Cr	0.935	1.021	1.099	1.173	1.240	1.297
	(2.633)	(2.988)	(3.358)	(3.757)	(4.164)	(4.541)
Mn	1.018	1.104	1.174	1.243	1.307	1.367
	(3.248)	(3.644)	(4.014)	(4.421)	(4.845)	(5.266)
Fe	1.098	1.175	1.251	1.314	1.374	1.432
	(3.924)	(4.312)	(4.734)	(5.158)	(5.596)	(6.066)
Co	1.175	1.250	1.317	1.383	1.440	1.502
	(4.647)	(5.063)	(5.492)	(5.954)	(6.406)	(6.942)
Ni	1.246	1.320	1.388	1.450	1.506	1.564
	(5.395)	(5.852)	(6.325)	(6.801)	(7.278)	(7.842)
Cu	...	1.388	1.454	1.517	1.574	1.624
	...	(6.699)	(7.190)	(7.735)	(8.261)	(8.771)

TABLE II

VALUES OF THE INTERELECTRON REPULSION PARAMETERS F_2, THE RACAH PARAMETER B (IN PARENTHESES), AND THE SPIN-ORBIT COUPLING CONSTANT ζ[15] [IN BRACKETS], FOR THE IONS M^{n+}, OF THE 3d TRANSITION SERIES IN KILOKAISERS

	n					
	0	1	2	3	4	5
Ti	0.552^a	0.860	1.110	...	...	...
	(0.334)^a	(0.575)	(0.700)	...	...	...
	[0.070]	[0.900]	[0.120]	[0.155]	...	...
V	0.735^a	0.902	1.171	1.407	...	...
	(0.482)^a	(0.521)	(0.756)	(0.862)	...	...
	[0.950]	[0.135]	[0.170]	[0.120]	[0.250]	...
Cr	0.664^a	1.048	1.202	1.443	1.673	...
	(0.513)^a	(0.647)	(0.691)	(0.918)	(1.013)	...
	[0.135]^c	[0.190]^c	[0.230]	[0.275]	[0.325]	[0.380]
Mn	0.687^a	1.013	1.331	1.467	1.687	1.919
	(0.296)^a	(0.513)	(0.790)	(0.839	(1.065)	(1.159)
	[0.190]	[0.255]	[0.300]^c	[0.355]	[0.415]	[0.475]
Fe	1.052^a	1.255	1.494	1.577	1.732	1.920
	(0.608)^a	(0.746)	(0.917)	(0.928)	(0.982)	(1.205)
	[0.255]	[0.345]	[0.400]	[0.461]^c	[0.515]	[0.555]
Co	...	1.424^a	1.572	1.796^b	1.808^a	1.976^a
	...	(0.843)	(0.971)	(1.100)^b	(1.047)^a	(1.114)^a
	...	...	[0.515]	[0.580]	[0.650]	[0.715]
Ni	...	...	1.774	1.894^b	...	2.034^a
	...	...	(1.056)	(1.115)^b	...	(1.165)^a
	...	[0.603]	[0.668)^d	[0.715]	[0.780]	[0.865]^c
Cu	...	...	...	1.893	1.904	...
	...	...	...	(1.216)	(1.238)	...
	...	...	...	[0.875]	[0.960]	[1.030]

[a] Values estimated by extrapolation of linear isoelectronic series data. [b] Values taken from J. Ferguson, H. J. Guggenheim, and D. L. Wood, *J. Chem. Phys.*, **40**, 822 (1964). [c] Estimated by extrapolation.[21] [d] J. Ferguson and H. J. Guggenheim, *J. Chem. Phys.*, **44**, 1095 (1966).

Values for F_2 (and B), which were determined from Moore's tables,[20] are given in Table II. The levels were selected such that they correspond to those observed in complexes, and are given in the Appendix. Most spin-orbit parameters were taken from the collection by Dunn[21] and are also listed in Table II. They are in agreement with values reported by other workers.[18,19] The correlation between F_2 and ζ is greatly simplified by the fact that $\langle r^{-1}\rangle^3$ and $\langle r^{-3}\rangle$ are linearly related as shown in Figure 1. For example, the relationship for vanadium is

$$\langle r^{-1}\rangle^3 = 0.6881\langle r^{-3}\rangle - 0.825 \tag{7}$$

Graphs of ζ *vs.* $\langle r^{-1}\rangle^3$ for the M^{n+} (n = 0-5) metal ion sequence (Figure 2) were linear, as were similar plots of F_2 and B *vs.* $\langle r^{-1}\rangle$ (Figure 3). A least-squares procedure was used to fit these plots to the equations

$$\zeta = s\langle r^{-1}\rangle^3 + t \tag{8}$$

$$F_2 = u\langle r^{-1}\rangle - v \tag{9}$$

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(11) Reference 2, Chapter 2.

(12) J. W. Richardson, W. C. Nieuport, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(13) R. E. Watson, Technical Report No. 12, June 15, 1959, Solid-State and Molecular Theory Group, Massachustts Institute of Technology, Cambridge, Mass., unpublished; *Phys. Rev.*, **118**, 1036 (1960).

(14) Present work.

(15) E. Tondello, G. De Michelis, L. Oleari, and L. DiSipio, *Coord. Chem. Rev.*, **2**, 65 (1957).

(16) E. Clementi, "Tables of Atomic Functions," supplement to *IBM J. Res. Develop.*, **9**, 2 (1965).

(17) C. Fisk and S. Fraga, *Can. J. Phys.*, **46**, 1140 (1968).

(18) M. Blume and R. E. Watson, *Proc. Phys. Soc., London, Sect. A*, **271**, 565 (1963).

(19) J. Thorhallsson, C. Fisk, and S. Fraga, *J. Chem. Phys.*, **48**, 2925 (1968).

(20) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular No. 467, U. S. Government Printing Office, Washington, D. C., 1952.

(21) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

and

$$B = w\langle r^{-1}\rangle - x \qquad (10)$$

where $\langle r^{-1}\rangle$ is in atomic units and ζ, F_2, and B are in kilokaisers (kK). Values of s, t, u, v, w, and x are given in Table III.

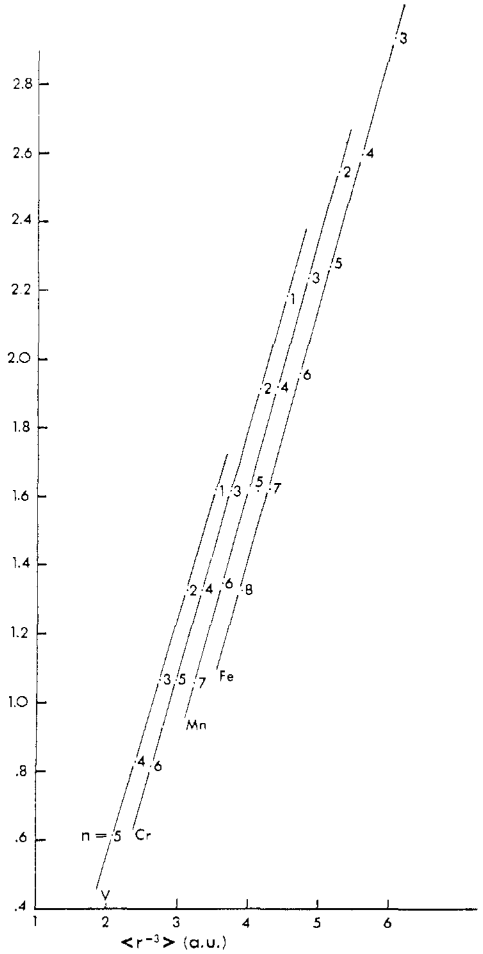

Figure 1.—Plots of $\langle r^{-1}\rangle^3$ *vs.* $\langle r^{-3}\rangle$ for V^{n+}, Cr^{n+}, Mn^{n+}, and Fe^{n+}.

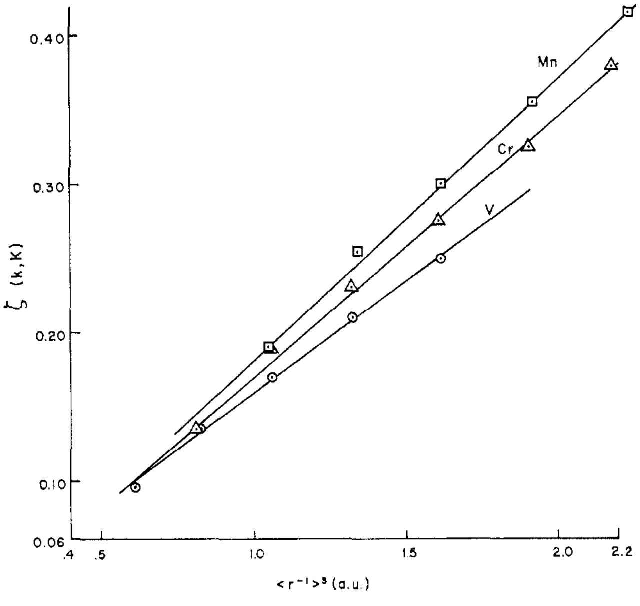

Figure 2.—Radial dependence of the spin–orbit coupling constant, ζ: Mn^{n+}, ⊡; Cr^{n+}, ⚠; V^{n+}, ⊙ (n = 0–5).

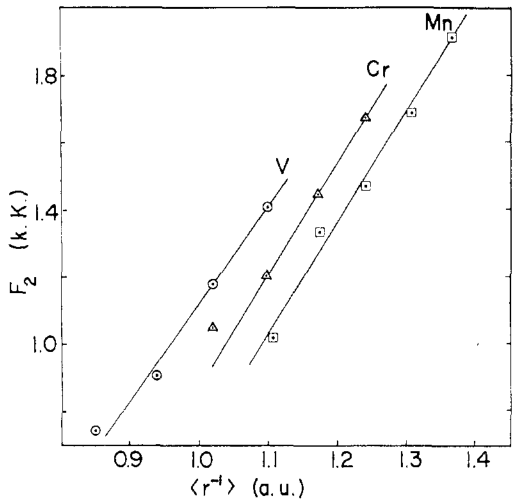

Figure 3.—Radial dependence of the interelectron repulsion parameter, F_2, for the free ions of vanadium (⊙), chromium (⚠), and manganese (⊡).

TABLE III

RADIAL DEPENDENCE OF THE SPIN–ORBIT AND INTERELECTRON REPULSION PARAMETERS FOR 3d TRANSITION METAL IONS: ζ, F_2, AND B IN kK; $\langle r^{-1}\rangle$ IN ATOMIC UNITS

	$\zeta = s\langle r^{-1}\rangle^3 + t$		$F_2 = u\langle r^{-1}\rangle - v$		$B = w\langle r^{-1}\rangle - x$	
	s	t	u	v	w	x
Ti	0.1347	0.0090	...	...	...	...
V	0.1459	0.0149	2.74	1.62	1.37	0.64
Cr	0.1599	0.0187	3.34	2.47	1.69	1.08
Mn	0.1884	−0.0048	3.31	2.61	2.55	2.31
Fe	0.1766	0.0573	2.48	1.65	1.77	1.33
Co	0.1850	0.0921	2.27	1.41	1.92	1.56
Ni	0.1684	0.2180	1.96	0.96	0.95	0.25
Cu	0.1695	0.2990	...	...	...	...
d^2	0.1913	−0.0374	1.89	0.66	1.08	0.32
d^3	0.2026	−0.0418	1.82	0.69	1.09	0.36
d^4	0.2070	−0.0334	1.90	0.89	1.06	0.47
d^5	0.2474	−0.0891	1.81	0.79	0.96	0.33

Some scatter was obtained in graphs of F_2 and B with F_2 displaying less scatter is every case. Where significant scatter occurred in the individual metal ion sequences, points representing the more important chemical oxidation numbers were given extra weight in the least-squares procedure.

We make the further assumption that eq 8–10 remain valid for metal ions in complexes. The justifications for this extension are discussed below. The important point is that if either F_2 or B for a complex is available, the fitting parameters of Table III may be used (eq 9 or 10) to obtain a corresponding value of $\langle r^{-1}\rangle$ which is then used to calculate an *effective* spin–orbit coupling constant *via* eq 8. We shall denote an effective coupling constant calculated in this manner as ζ^*.

The SO coupling constant obtained from splittings in atomic spectra[20] is the average many-electron parameter λ (eq 3). Throughout this work we have used the one-electron parameter ζ, since it is the relevant constant for our correlations. Many of the SO coupling constants cited for comparison in later sections were originally reported in terms of λ. Equation 4 was used to convert these to the corresponding one-electron values. (Note is made of these conversions.) Since eq 4 is not exact even for free ions,[22] some errors are introduced by its use; however, these errors do not significantly affect our results.

Results

Reliable experimental measurements of spin–orbit coupling constants for 3d transition metal complexes are quite difficult to obtain due to the existence of additional interactions of similar magnitude to the SO interaction. However, in recent years Ferguson and coworkers have analyzed spectra of various complexes of Co^{2+}, Cr^{3+}, Mn^{2+}, and Ni^{2+}.[23–26] The spectra were analyzed in terms of a four-parameter ligand field theory,[27] although details varied from one case to another. The four parameters are the crystal field splitting Dq, the SO coupling constant ζ, and two IRP's—either F_2 and F_4 or B and C. Since SO splittings are small (0.2–0.8 kK) compared to electronic transitions in 3d transition metal complexes, variations in ζ of up to 10% or so cause relatively minor energy shifts. Thus, even though a given set of parameters may give a good fit to a spectrum, the SO coupling constant will usually be accurate only to within about 10%. Thus, for example, the literature values for ζ cited in Table IV for Cr^{3+} and Co^{2+} were chosen somewhat arbitrarily due to a relatively small effect on the spacing of the energy levels. Nevertheless, as these numbers are among the best available, we compare them to our calculated values in Table IV.

TABLE IV
COMPARISON OF CALCULATED VALUES OF ζ^* WITH THOSE OBTAINED FROM ABSORPTION SPECTRA FOR COMPLEXES OF SEVERAL TRANSITION METAL IONS

Ion	Absorption spectra B, kK	Absorption spectra ζ, kK	Present work ζ^*, kK	Complex
Co^{2+} [a]	0.880	0.471	0.471	$KMgF_3Co^{2+}$
	0.780	0.420	0.426	$CoCl_2$
	0.760	0.420	0.418	$CoBr_2$
	0.760	0.420	0.418	$CoWO_4$
Cr^{3+} [b]	0.570	0.170	0.167	$Y_3Ga_5O_{12}$–Cr^{3+} [e]
	0.640	0.170	0.187	Al_2O_3–Cr^{3+} [f]
	0.740	0.170	0.218	CrF_3
	0.550	0.170	0.161	$CrCl_3$
	0.370	0.170	0.120	$CrBr_3$
Mn^{2+} [c]	0.700	0.300–0.400	0.304	$RbMnF_3$, $KMnF_3$
Ni^{2+} [d]	0.950	−0.610 to −0.640 [g]	−0.568	$KNiF_3$
	0.950	−0.620 [g]	−0.568	$KMgF_3$–Ni^{2+}
	0.990	−0.600 [g]	−0.604	$KZnF_3$–Ni^{2+}

[a] Reference 23. [b] Reference 24. [c] Reference 25. [d] Reference 26. [e] Yttrium gallium garnet. [f] Ruby. [g] Reference 28.

The Racah parameters B, in column 2 (which are known with considerably more accuracy than ζ), were used to obtain the ζ^* which appear in column 4. The first column gives the ion and the fifth lists the complexes (which are all nearly ocathedral). In each case there is good agreement between the predicted and "observed" coupling constants. The agreement is particularly satisfying considering the fact that the two sets of numbers represent essentially independent methods of determining coupling constants in complexes.

The most accurately known value in Table IV is the coupling constant for Ni^{2+}. In an octahedral environment the ^3F ground state is split into $^3A_{2g} + {}^3T_{2g} + {}^3T_{1g}$ with $^3A_{2g}$ lowest. The range[28] $\zeta = -0.610$ to -0.640 kK resulted from very good fits of both the $^3T_{2g}$ and $^3T_{1g}{}^a$ bands in the absorption spectra of $KNiF_3$.[26a] Misetich and Watson[4a] have made approximate calculations of the SO interaction in $KNiF_3$. They obtained[28] $\zeta(^3T_{2g}) = -0.642$ kK and $\zeta(^3A_{2g}) = -0.630$ kK. Assuming a single coupling constant appropriate to all $3d^8$ levels they estimated[28] $\zeta = -0.616$ to -0.636 kK (compared with the free-ion value of -0.668 kK). The fact that the calculated value of ζ^* is too low (by about 0.03–0.04 kK) is not surprising. It reflects the fact that our model tends to overemphasize somewhat the effect of changes in the outer part of the d orbitals.

The Mn^{2+} ion presents a more difficult problem. Ferguson's[25] analysis of the $^6A_{1g} \rightarrow {}^4T_{2g}$ transition in $RbMnF_3$ and $KMnF_3$ yields an SO coupling constant in the range 0.300–0.400 kK for the $^4T_{2g}$ state. This transition has also been observed by Mehra and Venkateswarlu.[29] They extracted a value of 0.320 kK for the coupling constant. The calculated value is $\zeta^* = 0.304$ kK. Although there is clearly no well-defined value for comparison, it appears to be quite reasonable.

As a final result we have included Figure 4 which is similar to the grids used by Tanabe and Sugano[30] and by Watson,[13] except that these authors used F_2 instead of $\langle r^{-1}\rangle$ as the ordinate. It is apparent that the variation of $\langle r^{-1}\rangle$ with charge is very nearly linear. This provides the interesting result that the effective charge on the central metal ion can be directly related to a readily available experimental observable, *viz.*, the IRP, F_2, or B.

Discussion

Application to Free Ions.—As mentioned in the Introduction, we are not proposing a theoretical model for SO coupling in complexes. While radial expansion probably should be included in a proper treatment of SO coupling, other factors are equally important. One of the benefits of an empirical correlation is that there is an implicit inclusion of other physical interactions. Our assertion is simply that radial expectation values are an appropriate basis for correlation between IRP's and SO coupling constants. A correlation of this

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(22) Reference 9, Section 1.2.

(23) J. Ferguson, D. L. Wood, and K. Knox, *J. Chem. Phys.*, **39**, 881 (1963).

(24) D. L. Wood, J. Ferguson, K. Knox, and J. F. Dillon, *ibid.*, **39**, 890 (1963).

(25) J. Ferguson, *Aust. J. Chem.*, **21**, 307 (1968).

(26) (a) J. Ferguson, H. J. Guggenheim, and D. L. Wood, *J. Chem. Phys.*, **40**, 822 (1964); (b) J. Ferguson and H. J. Guggenheim, *ibid.*, **44**, 1095 (1966).

(27) Reference 2, Chapters 4 and 5.

(28) Originally reported in terms of λ; converted to one-electron parameter, ζ, *via* eq 4. See Procedure.

(29) A. Mehra and P. Venkateswarlu, *Phys. Rev. Lett.*, **19**, 145 (1967).

(30) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jap.*, **9**, 735 (1964).

nature would be expected for equivalent electrons in a spherical, central-field potential. Within this context the validity of the procedure for free ions is obvious since it was derived from free-ion data. In Table V free-ion SO coupling constants for some highly charged ions are compared with the predictions of our empiricism. The excellent agreement demonstrates that it may successfully be used for ions other than those used to fit eq 8–10.

Table V

Spin-Orbit Coupling Constants (in kK) Calculated for M^{n+} ($n > 5$) Ions with $\langle r^{-1}\rangle^3$ (in au) Values Extrapolated from Figure 4

	n	$\langle r^{-1}\rangle^3$	ζ^*(calcd)	ζ(exptl)[a]
Mn	6	2.894	0.540	0.542
Fe	6	3.308	0.641	0.640
	7	3.652	0.701	0.750
Co	6	3.760	0.788	0.742
	7	4.096	0.850	. . .
Ni	6	4.212	0.927	0.859
	7	4.657	1.002	1.000

[a] Computed from ref 20.

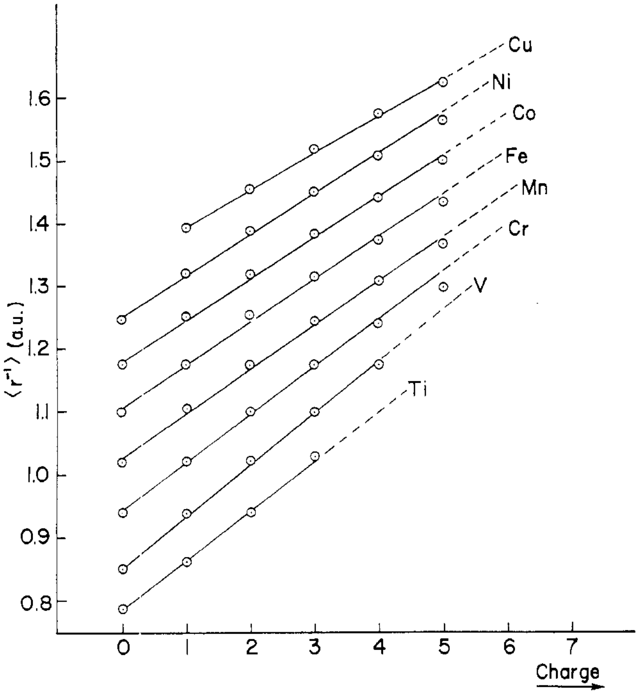

Figure 4.—Correlation between $\langle r^{-1}\rangle$ and charge for neutral atoms and the first four positive ions of the iron-series transition metals.

Application to Complexes.—Among the various assumptions involved in this work, the most crucial one is that eq 8–10, derived from free-ion data, are also valid for complexes. The justification for this is primarily based on the fact that a transition metal ion in a complex may be treated as an "almost free" ion with a reduced effective charge; *i.e.*, a radially expanded set of 3d orbitals (Figure 4). Accounting for all the effects of an ion's environment in terms of radial expansion would seem to neglect other physical interactions. However, as we have noted previously, many of these interactions are accounted for by the use of empirical IRP data. Since the final estimate for ζ^* is indirectly regulated by the initial value of the IRP, changes induced in outer regions of the 3d orbitals tend to be overemphasized. Thus, the procedure should lead to values of ζ^* which are slightly low.

Ideally, the best values for SO coupling constants in complexes would be those obtained from a well-developed theory. Although significant progress has been made in this direction,[4a] it is still in a formative state and involves considerable computational difficulties. The empirical procedure described in this work offers an internally consistent route to SO coupling constants for complexes which we feel are at least as reliable as those obtained by any other method.

Acknowledgments.—We wish to thank the Florida State University Computing Center for use of their facilities. We also acknowledge the assistance of Mr. Leonard Himes with some of the computations.

Appendix

The interelectron repulsion parameters F_2 and B were estimated from the atomic energy levels given by Moore.[20]

The IRP sets F_2 and F_4, or alternatively B and C, were fitted for each $3d^n$ sequence to the pair of low-lying transitions which gives the best agreement for the higher lying levels. The levels chosen for fitting correspond to the observable transitions for $3d^n$ complexes and are thus the appropriate choice for this analysis. The IRP fitting of the $3d^n$ sequences is described as follows. $3d^2$ (^3F, ^1D, ^3P, ^1G, ^1S): The levels ^3P and ^1G were fitted, and the ^1D level is predicted reasonably well by this choice. The ^1S level does not fit the theory very well when it is observed.[10] $3d^8$ (^3F, ^3P only observed): Data were available for Co^+ and Ni^{2+} and only B may be calculated. $3d^3$ (^4F, ^4P, ^2H, ^2G): The levels of ^4P and ^2G were fitted, and the ^2H level is predicted reasonably well. $3d^7$ (^4F, ^4P, ^2H, ^2G): Data were available for Fe^+ and Co^{2+} only. Fitting of the ^4P and ^2G levels predicts the ^2H level well. $3d^4$ (^5D, ^3H, ^3G, ^3D): For the sequence of ions V^+ to Co^{5+} a fitting to the ^3H and ^3G levels predicts the ^3D level quite well. $3d^6$: Data were available for Mn^+ and Fe^{2+} with fitting being similar to the $3d^4$ sequence. $3d^5$ (^6S, ^4G, ^4F, ^4D, ^4P): The levels ^4G and ^4D were used for fitting with the result that the ^4F prediction is good and the ^4P prediction is poor (see also ref 25). The IRP values obtained with these fittings are given in Table II along with several values which were estimated by extrapolation of the radial dependence curves for isoelectronic sequences.