diffusion coefficient with magnetic field to that without magnetic field is given. This agrees, as it should, with our α. In the latter, on page 51, the ratio of drift parallel to the electric field with magnetic field to that without is given and also the ratio of transverse drift with magnetic field to parallel drift without. These should, but do not, agree with our α and β, respectively. In the absence of references it has not been possible to determine the source of the differences, but it probably lies either in the method used in averaging over the velocity distribution or in the assumptions, perhaps tacit, regarding that distribution.

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The Coupling of p Electron Configurations

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The structure and type of coupling of the observed p^2, p^3, and p^4 configurations is considered in detail in terms of the intermediate-coupling theory, in particular for the long isoelectronic sequences which have recently been analyzed. The theoretical values of the ratios of various intervals in these configurations are plotted as functions of the single parameter which specifies the type of coupling. The experimental values have been fitted to these curves and the parameters evaluated. The points fit the theoretical curves fairly well; and the departures of the experimental points of an isoelectronic sequence from these curves are sufficiently regular to enable accurate prediction of unknown levels. This method has yielded new classifications in K IV and Ca VII. For the configurations p^3 and p^3s, interval ratios are found which are predicted to be entirely independent of coupling. The parameters are plotted for the isoelectronic sequences of sp, p, p^2, p^3, p^4, p^5, and p^5s configurations. The electrostatic interaction parameter F_2 is found to be a linear function of Z to a good approximation; the spin-orbit parameter ζ_p is accurately proportional to $(Z-S)^4$ for all but the first few members of each sequence. The screening constants (S) for ζ_p are much smaller than the corresponding screening constants for F_2. A complete bibliography of data for those atoms with p electrons in the normal configuration is appended.

Introduction

Recent progress[1] in the analysis of isoelectronic spectra has now made possible a thorough comparison of the intermediate-coupling theories with experiment for those elements containing equivalent p electron groups. The manner in which the energy of the various levels is predicted to vary with the coupling is shown by Fig. 1. These diagrams, but with only a few data superposed, were given by Condon and Shortley.[2] The size of the parameter χ measures essentially the departure from Russell-Saunders coupling ($\chi=0$). For pure jj coupling $\chi=\infty$ ($1/\chi=0$). χ is defined as the ratio of the spin-orbit interaction integral ζ_p (C-S 4^54) to the electrostatic integral $5F_2$ (C-S page 177). Diagrams of this type are very compact and give a clear picture of the manner in which the relative values of the various energy intervals vary with the coupling. In actual practice, however, they are inconvenient to apply to experimental results because of the various scale factors involved and are inadequate for either extreme, $\chi \ll 1$ or $\chi \gg 1$, where certain of the intervals become very small compared to the rest. These difficulties are obviated in what follows by using ratios between directly observed energy intervals; these are calculated from theory and plotted directly against χ.

In the theory for the p^2, p^3, and p^4 configurations, the ratio of any two intervals (e.g. ${}^1S_0-{}^1D_2$ and ${}^3P_2-{}^3P_1$) is completely determined by χ alone. Thus in these configurations, if *any* three levels are known, χ may be predicted and the positions of the other levels as well. For example, a knowledge of the Landé ratio for a triplet term should predict absolutely the position of the two singlet terms arising from a p^2 or p^4

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[1] For a complete bibliography see the last section of this paper.

[2] Condon and Shortley, *Theory of Atomic Spectra* (Cambridge, 1935). For the general theory and notation used in this paper see chapters XI and XIII of this book. In what follows this reference will be denoted as C-S.

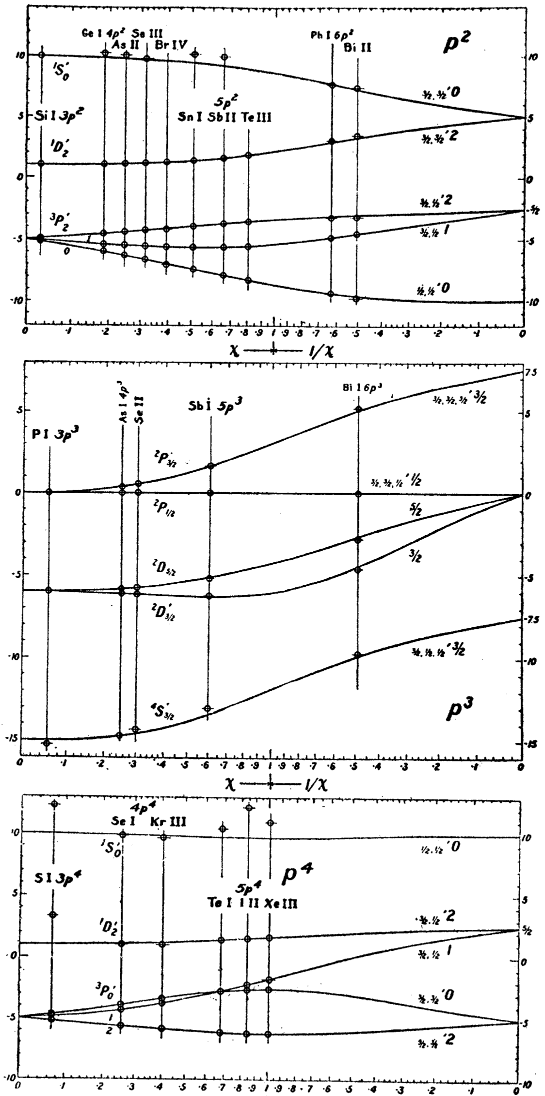

FIG. 1. *The configurations np^2, np^3, and np^4 in intermediate coupling.* Here are plotted quantities such as $({}^1D-F_0)/F_2(1+\chi^2)^{\frac{1}{2}}$ [cf. Eq. (1)], that is, the energy intervals here are measured in units $F_2(1+\chi^2)^{\frac{1}{2}}$. Superposed are all data for $n=4$, 5, 6, and the first member of each sequence for $n=3$. In the original figures of C-S, the χ value and scale to use for the p^2 and p^4 data was determined by making ${}^3P_1$, the mean of ${}^1S_0$ and ${}^3P_0$, and the mean of ${}^1D_2$ and ${}^3P_2$ fit exactly. Near LS coupling this method of choosing χ has little significance when the configurations are somewhat perturbed; e.g., it gives a *negative* value for χ for S I $3p^4$. Since $\chi=\zeta_p/5F_2$ and since the triplet splitting essentially measures ζ_p and the distance between terms is a measure of F_2, it seems most significant to choose χ by making a pair of intervals—one a term splitting, the other a distance between terms—fit precisely. The intervals chosen are: for p^2, ${}^3P_2-{}^3P_0$ and ${}^1D-{}^3P_c$; for p^3, ${}^2P_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}}$ and ${}^2P_c-{}^2D_c$; for $3p^4$ and $4p^4$, ${}^3P_1-{}^3P_2$ and ${}^1S-{}^1D$; for $5p^4$, ${}^3P_1-{}^3P_2$ and ${}^1D-{}^3P_c$. $6p^2$ and $6p^3$ are plotted as in C-S. This is the method used in obtaining the parameters of Tables VI, VII, and VIII.

configuration. It is our purpose to test these conclusions in detail.

The only other configurations for which all interval ratios are a function of but one parameter are those of the type ls and $l^{m-1}s$ (ps, p^5s, ds, d^9s, etc.). These are considered in C-S, pp. 272, 304. In certain of these cases the theory has proved of considerable use in locating the singlet by means of the observed Landé ratio of the triplet.[3]

We shall consider only the "Russell-Saunders half" of the diagrams ($\chi=0$ to $\chi=1$) as most of the experimental values lie in this range. We shall for convenience use the LS term designation throughout. In general other types of ratios than those which we consider would be of interest in the "jj half" ($\chi=1$ to $\chi=\infty$).

The p^2 configuration

The secular equations for this configuration are given in C-S, page 274. If we write the equation for ${}^1D$ in the form

$$\begin{aligned}({}^1D-F_0)/F_2&=-2+\tfrac{1}{4}\zeta_p/F_2\\&\quad+[9-\tfrac{3}{2}\zeta_p/F_2+\tfrac{9}{16}(\zeta_p/F_2)^2]^{\frac{1}{2}}\\&=-2+\tfrac{5}{4}\chi+[9-\tfrac{15}{2}\chi+\tfrac{225}{16}\chi^2]^{\frac{1}{2}},\qquad(1)\end{aligned}$$

with similar equations for the remaining four terms, expressions for such ratios as $({}^3P_2-{}^3P_0)/$

TABLE I. *Configuration p^2: Theoretical interval ratios as a function of χ.*

χ	$\dfrac{{}^3P_2-{}^3P_0}{{}^1S-{}^1D}$	$\dfrac{{}^3P_2-{}^3P_0}{{}^1S-{}^3P_c}$	$\dfrac{{}^3P_2-{}^3P_0}{{}^1D-{}^3P_c}$	$\dfrac{{}^1S-{}^1D}{{}^1D-{}^3P_c}$	$\dfrac{{}^3P_2-{}^3P_1}{{}^3P_1-{}^3P_0}$
0	0	0	0	1.5	2
0.02	0.0168	0.0101	0.0252	1.4999	1.932
.04	.0335	.0201	.0503	1.4989	1.867
.08	.0674	.0404	.1009	1.4952	1.751
.12	.1015	.0607	.1510	1.4880	1.643
.16	.1357	.0810	.2010	1.4801	1.546
.20	.1700	.1012	.2495	1.4683	1.460
.24	.2040	.1210	.2970	1.4538	1.378
.28	.2380	.1402	.3415	1.4365	1.307
.32	.2720	.1598	.3860	1.4168	1.238
.36	.3060	.1782	.4270	1.3946	1.175
.40	.3400	.1962	.4655	1.3704	1.117
.48	.4065	.2307	.535	1.3168	1.012
.56	.473	.2640	.596	1.2584	0.926
.64	.539	.2940	.645	1.1975	0.844
.72	.605	.3215	.687	1.1361	0.774
.80	.670	.3470	.720	1.0760	0.713
.88	.736	.3713	.749	1.0180	0.659
1.00	.835	.403	.782	0.9367	0.592

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[3] E.g., H. A. Robinson, Phys. Rev. **49**, 301 (1935), Table V.

$({}^1S-{}^1D)$ in terms of χ follow immediately. The ratios whose numerical values are listed in Table I and plotted in Fig. 2 are of three types. The first type consists of ratios between the triplet splitting and the distances between terms; in what follows they will be called *coupling ratios* inasmuch as they are all zero for pure LS coupling and start increasing linearly with χ. If ${}^3P_c$ denotes the centroid of the triplet term (the mean of the levels weighted according to $2J+1$), these ratios are given by $({}^3P_2-{}^3P_0)/({}^1D-{}^3P_c)$; $({}^3P_2-{}^3P_0)/({}^1S-{}^1D)$; and $({}^3P_2-{}^3P_0)/({}^1S-{}^3P_c)$.

The second type is the familiar *Landé ratio* $({}^3P_2-{}^3P_1)/({}^3P_1-{}^3P_0)$. In the LS limit this ratio is 2 but it departs rapidly from this value, decreasing linearly with χ. When the triplet has as yet only 0.085 of the total configuration spread ($\chi=0.18$), it has already fallen to 1.5. It begins to decrease according to the relation

$$({}^3P_2-{}^3P_1)/({}^3P_1-{}^3P_0)=2-\tfrac{7}{2}\chi+\tfrac{125}{24}\chi^2+\cdots.$$

This relation may be obtained either from the energy formulas or from third-order perturbation theory.

The third type of ratio $({}^1S-{}^1D)/({}^1D-{}^3P_c)$ we shall call the *Slater ratio* inasmuch as Slater first showed that in pure LS coupling its value should be $\tfrac{3}{2}$. It decreases quadratically from this value according to the relation

$$({}^1S-{}^1D)/({}^1D-{}^3P_c)=\tfrac{3}{2}-\tfrac{25}{36}\chi^2+\cdots.$$

Of these five ratios only three are independent—the Landé ratio and any two of the other four ratios. If these three fit the observed data then the other two must also.

TABLE II. *Configuration p^4: Theoretical interval ratios as a function of χ.*

χ	$\dfrac{{}^3P_1-{}^3P_2}{{}^1D-{}^3P_c}$	$\dfrac{{}^3P_1-{}^3P_2}{{}^1S-{}^1D}$	$\dfrac{{}^3P_1-{}^3P_2}{{}^1S-{}^3P_c}$	$\dfrac{{}^1S-{}^1D}{{}^1D-{}^3P_c}$	$\dfrac{{}^3P_0-{}^3P_1}{{}^3P_1-{}^3P_2}$
0	0	0	0	1.5	0.5
0.04	0.0339	0.0226	0.01354	1.4989	.4653
.08	.0686	.0458	.02747	1.4959	.4313
.12	.1038	.0696	.04167	1.4914	.3984
.16	.1396	.0940	.0562	1.4870	.3653
.20	.1754	.1187	.0708	1.4778	.3333
.24	.2112	.1437	.0855	1.470	.3017
.28	.2467	.1688	.1002	1.461	.2706
.32	.2819	.1941	.1149	1.452	.2401
.36	.3164	.2192	.1295	1.4434	.2102
.40	.3503	.2443	.1439	1.4344	.1808
.48	.4157	.2934	.1720	1.4173	.1237
.56	.4775	.3407	.1988	1.4018	.0690
.64	.5354	.3857	.2242	1.388	.0168
.72	.5893	.4277	.2479	1.3777	−.0327
.80	.6392	.4670	.2698	1.3688	−.0797
.88	.6853	.5031	.2901	1.3622	−.1237
1.00	.7478	.5516	.3174	1.3558	−.1848

We have determined the χ values at which to plot the empirical ratios by making the observed value of $({}^3P_2-{}^3P_0)/({}^1D-{}^3P_c)$ fit the theoretical curve exactly. A coupling ratio was chosen inasmuch as near LS coupling it is related to ζ_p/F_2 more directly than the other types; the triplet splitting essentially measures ζ_p and the term separations F_2. We chose this particular coupling ratio because the ${}^1D$ is observed further along the sequence than is the ${}^1S$. With this choice of χ the other ratios are seen to fit rather poorly for $2p^2$, very well for $3p^2$ and $4p^2$, somewhat less well for $5p^2$. For $3p^2$ the discrepancy in the Landé ratio is of the order of the experimental uncertainty. There is a curious drop in the $4p^2$ Landé ratio at Br IV.

The p^4 configuration

The secular equations for the p^4 configuration are immediately obtained from those for p^2 by reversing the sign of ζ_p. The ratios of Table II and Fig. 3 are similar to those considered for p^2. The principal difference occurs in the Landé ratio which here *increases* rapidly according to the equation

$$\text{Landé ratio}=2+\tfrac{7}{2}\chi+\tfrac{125}{24}\chi^2+\cdots,$$

and becomes infinite at $\chi=\tfrac{2}{3}$ (cf. Fig. 1). For this reason we have plotted the reciprocal of the usual Landé ratio. This is positive for $\chi<\tfrac{2}{3}$, negative for $\chi>\tfrac{2}{3}$.

TABLE III. *The invariant ratio $({}^2P_{\frac12}-C_{1\frac12})/({}^2P_{\frac12}-{}^2D_{2\frac12})$ for p^3. (Theoretical value = 1.167.)*

$2p^3$ NORMAL		$3p^3$ NORMAL		$4p^3$ NORMAL	
N I	1.333	P I	1.182	As I	1.161
O II	1.320	S II	1.181	Se II	1.155
F III	1.316	Cl III	1.182		
Ne IV	—	A IV	1.181	$5p^3$ normal	
Na V	1.295*	K V	1.186*	Sb I	1.132
Mg VI	1.325*	Ca VI	1.20*		
Al VII	1.295*	Sc VII	1.195*	$6p^3$ normal	
Si VIII	1.301*			Bi I	1.093
$2p^3$ DISPLACED†		$3p^3$ DISPLACED			
C II	0.82	P III	0.872		
N III	0.87				
O IV	0.90*				
F V	0.93*				
Na VII	0.95*				

* No intercombinations; doublet-quartet intervals may be in error.

† Several such displaced configurations are known for p^2 and p^4, but have not been plotted. The displaced p^4 seem to show approximately the same χ values as the normal p^2 in the same ion.

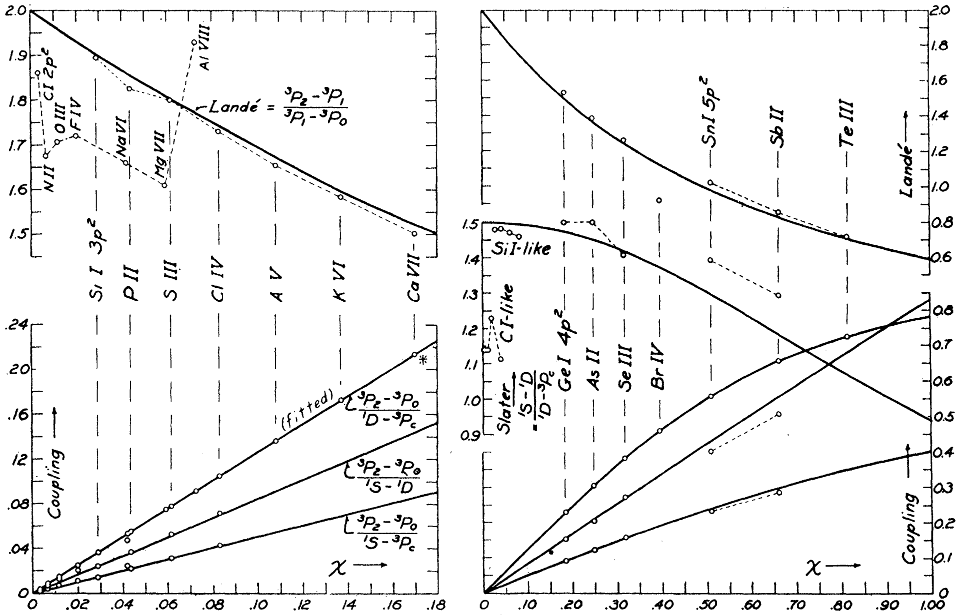

FIG. 2. Interval ratios for p^2 for $\chi=\zeta_p/5F_2\leq 1$. The plot on the left is an enlargement of part of that on the right. The curve coordinates are given in Table I.

In this case we have determined χ for $2p^4$, $3p^4$, and $4p^4$ from the coupling ratio[4] $(^3P_1-{}^3P_2)/(^1S-{}^1D)$ since many of the intercombinations are missing. For $2p^4$ the agreement with theory for the Slater ratio is poor but the Landé ratio agreement is much better than in $2p^2$; $3p^4$ is not so good as $3p^2$—it is poor at both ends of the sequence but good in the middle, although the Landé ratio is predicted remarkably well along the whole sequence; $4p^4$ is good. For $5p^4$ the Slater ratios have unreasonably large values.

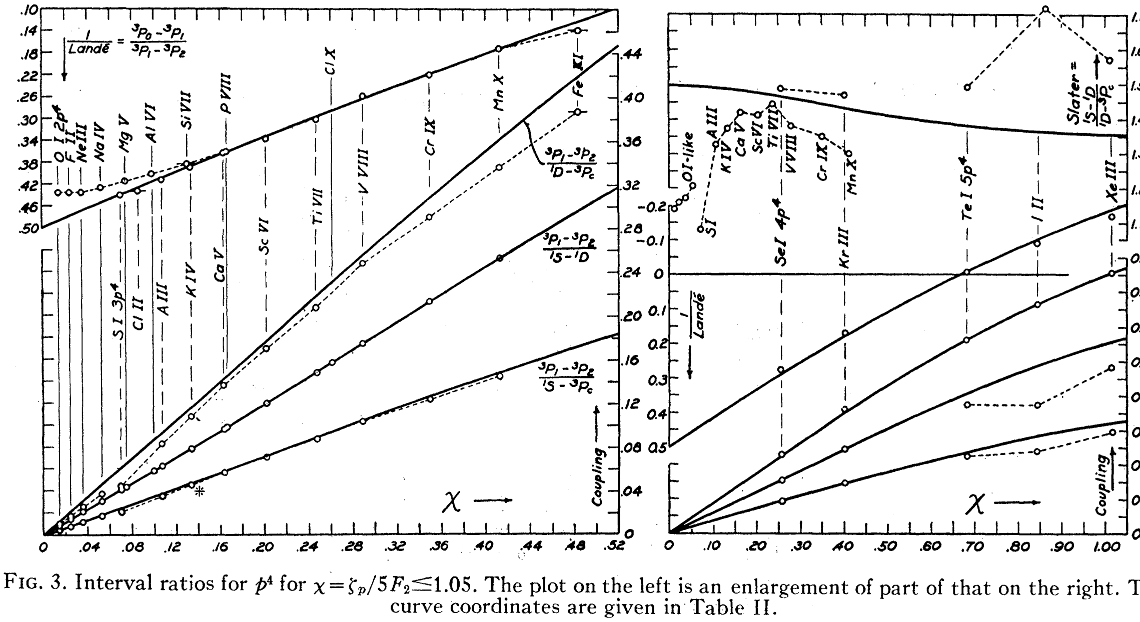

FIG. 3. Interval ratios for p^4 for $\chi=\zeta_p/5F_2\leq 1.05$. The plot on the left is an enlargement of part of that on the right. The curve coordinates are given in Table II.

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[4] For Cl II, Si VII and Fe XI this ratio is not observed; the χ values are interpolated or extrapolated values.

Reasonable χ values in this latter case can only be obtained from the coupling ratio $({}^3P_2-{}^3P_1)/({}^1D-{}^3P_c)$; this is seen in Fig. 3 to predict the Landé ratios very well. One would infer that it is only the ${}^1S$ which is badly perturbed but this is not sensible since any perturbations push the ${}^1S$ *down*, and it is *high* relative to the balance of the configuration.

The p^3 configuration

This configuration occupies an exceptional position because the diagonal elements of its spin-orbit interaction matrix are all zero in LS coupling. As a result, the term splitting near LS coupling is very small, a quadratic function of χ rather than the usual linear one. Because of the vanishing of the diagonal elements, the traces of the energy matrices are functions of F_2 alone, and we can find a ratio which is completely *independent of coupling.* Such an invariant ratio exists only for the configurations p^3 and p^3s. If we denote by $C_{1\frac{1}{2}}$ the centroid of the levels for which $J=\frac{3}{2}$ $[C_{1\frac{1}{2}}=\frac{1}{3}({}^2P_{1\frac{1}{2}}+{}^4S_{1\frac{1}{2}}+{}^2D_{1\frac{1}{2}})]$, then ${}^2P_{\frac{1}{2}}-C_{1\frac{1}{2}}=7F_2$; ${}^2P_{\frac{1}{2}}-{}^2D_{2\frac{1}{2}}=6F_2$; and in any coupling the ratio of these intervals is predicted to have the value $\frac{7}{6}$. The empirical values found for this ratio are listed in Table III. It will be noticed that even where they do not agree with the theoretical value, the ratios are approximately constant along an isoelectronic sequence.

TABLE IV. *Configuration p^3: Theoretical interval ratios as a function of χ.*

χ	$\frac{{}^2P_c-{}^2D_c}{{}^2D_c-{}^4S}$	$\frac{{}^2P_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}}}{{}^2P_c-{}^2D_c}$	$\frac{{}^2P_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}}}{{}^2D_{2\frac{1}{2}}-{}^2D_{1\frac{1}{2}}}$
0	0.667	0	1.32
0.06	.669	0.00392	1.32
.09	.674	.00911	1.32
.12	.678	.01603	1.32
.145	.683	.0230	1.32
.185	.693	.0367	1.34
.20	.697	.0424	1.34
.248	.718	.0627	1.347
.30	.730	.087	1.357
.35	.749	.113	1.37
.40	.770	.139	1.40
.45	.792	.167	1.41
.50	.815	.194	1.423
.55	.838	.222	1.450
.60	.862	.249	1.473
.65	.884	.275	1.495
.70	.905	.300	1.522
.75	.928	.325	1.545
.80	.947	.350	1.581
.85	.965	.372	1.613
.90	.983	.395	1.641
.95	.998	.416	1.672
1.00	1.010	.437	1.713

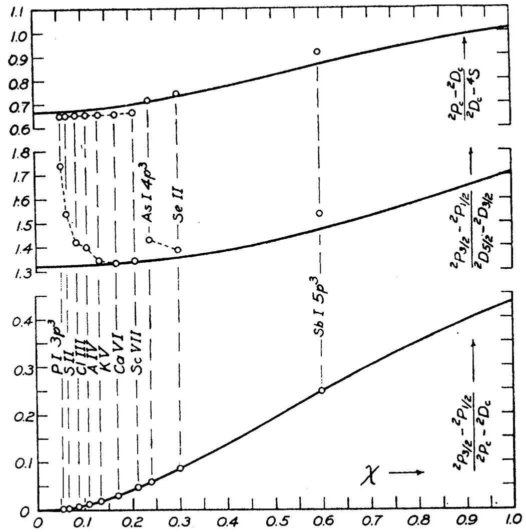

FIG. 4. Interval ratios for p^3 for $\chi=\zeta_p/5F_2\leq 1$. The curve coordinates are given in Table IV.

In Fig. 4 we have plotted three interval ratios as functions of χ. The lowest curve is the ratio of the ${}^2P$ splitting to the distance between the center of gravity of the ${}^2P$ and ${}^2D$ terms. This is analogous to a coupling ratio but starts quadratically in χ according to[5]

$$({}^2P_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}})/({}^2P_c-{}^2D_c)=\tfrac{55}{48}\chi^2-\tfrac{16555}{6912}\chi^4+\cdots.$$

The middle curve gives the ratio of the ${}^2P$ splitting to the ${}^2D$ splitting. This is therefore a Landé type ratio. It has the value $\frac{33}{25}=1.32$ for $\chi=0$ and departs from this slowly according to the relation

$$({}^2P_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}})/({}^2D_{2\frac{1}{2}}-{}^2D_{1\frac{1}{2}})=\tfrac{33}{25}+\tfrac{209}{450}\chi^2+\cdots.$$

The top curve gives the Slater ratio between the ${}^2P_c-{}^2D_c$ separation and the ${}^2D_c-{}^4S$ separation. This is $\frac{2}{3}$ in LS coupling and departs from this value slowly according to the relation

$$({}^2P_c-{}^2D_c)/({}^2D_c-{}^4S)=\tfrac{2}{3}+\tfrac{125}{162}\chi^2-\tfrac{23125}{23328}\chi^4+\cdots.$$

---

[5] Because of the occurrence of a cubic equation, the asymptotic forms for the p^3 levels are troublesome to compute. We give here explicitly the series for the energies (apart from the additive constant $3F_0$), as functions of $\chi=\zeta_p/5F_2$, measured in terms of F_2:

$$\begin{aligned}
{}^2D_{2\frac{1}{2}}/F_2&=-6,\\
{}^2D_{1\frac{1}{2}}/F_2&=-6-\tfrac{125}{24}\chi^2+\tfrac{71875}{10368}\chi^4+\cdots,\\
{}^2P_{1\frac{1}{2}}/F_2&=\tfrac{55}{8}\chi^2-\tfrac{2585}{384}\chi^4+\cdots,\\
{}^2P_{\frac{1}{2}}/F_2&=0,\\
{}^4S_{1\frac{1}{2}}/F_2&=-15-\tfrac{5}{3}\chi^2-\tfrac{65}{324}\chi^4+\cdots.
\end{aligned}$$

TABLE V. *Parameter values for normal p^2 configurations.*

$2p^2$	χ	F_2(cm^{-1})	ζ_p(cm^{-1})
C I	0.0032	1694	27.1
N II	.0067	2537	85.0
O III	.0120	3354	201
F IV	.0204	3970	405
Na VI	.0422	5826	1230
Mg VII	.0593	6554	1940
Al VIII	.0728	7282	2650
$3p^2$			
Si I	0.029	1020	148
P II	.044	1430	314
S III	.062	1790	555
Cl IV	.083	2130	885
A V	.108	2470	1330
K VI	.137	2800	1920
Ca VII	.170	3120	2650
$4p^2$			
Ge I	0.184	1000	924
As II	.248	1340	1660
Se III	.318	1600	2550
Br IV	.395	2050	4050
$5p^2$			
Sn I	0.510	875	2230
Sb II	.661	1120	3700
Te III	.815	1320	5370
$6p^2$			
Pb I	1.583	921	7290
Bi II	1.975	1168	11540

It is difficult to obtain accurate χ values for this configuration near *LS* coupling since all of these curves are very slowly varying in this region, and there are certainly perturbations on the levels which will have a large effect on the ratios involving the very narrow doublet splittings. The doublets are predicted to be *normal* at all values of χ, but in the $2p^3$ sequence, the perturbations are larger than the very small expected separations so that one or both doublets are narrow but *inverted* for the first six members of the sequence. Only for Al VII, Si VIII, and P IX are they both normal but the Landé ^2P-^2D splitting ratios are 4.63, 1.08, and 0.53, respectively, in place of the predicted 1.32. The Slater ratios, predicted to be 0.667, are: N I, 0.500; O II, 0.509; F III, 0.512; Ne IV, —; Na V, 0.527;[6] Mg VI, 0.528;[6] Al VII, 0.528;[6] Si VIII, 0.530.[6] It was not possible to obtain χ or ζ_p values for this sequence;[7] the F_2 values of Fig. 6 are calculated from the $^2P_c-{}^2D_c$ interval.

For the $3p^3$ sequence the χ values were determined from the coupling-ratio curve (drawn to a much larger scale than Fig. 4). The Slater ratio is very good; the Landé ratio improves along the sequence. For the known members of $4p^3$ and $5p^3$ the agreement is fair.

Parameter values

The parameters ζ_p, F_2 (and χ) are given in the theory in the form of integrals over the wave functions which in most cases have not been evaluated. As a result their values have only been obtained empirically by some method of fitting observed experimental results to theoretical curves. Where the theory is not exactly obeyed, the values obtained depend somewhat on the method of fitting, but even approximate values and their general trends when considered as a function of atomic number should be of considerable interest. Our values for these parameters, which appear in Tables V, VI, VII, have been obtained on the assumption that the two intervals (numerator and denominator) of the ratio which we used to obtain the χ values

TABLE VI. *Parameter values for normal p^3 configurations.*

$2p^3$	χ	F_2(cm^{-1})	ζ_p(cm^{-1})
N I		1600*	†
O II		2280*	
F III		2910*	
Ne IV		3520*	
Na V		4140*	
Mg VI		4740*	
Al VII		5360*	
Si VIII		6020*	
P IX		6690*	
$3p^3$			
P I	0.056	1220	343
S II	.067	1610	538
Cl III	.085	1940	825
A IV	.108	2270	1230
K V	.136	2580	1760
Ca VI	.169	2890	2440
Sc VII	.210	3190	3340
$4p^3$			
As I	0.240	1210	1450
Se II	.300	1540	2310
$5p^3$			
Sb I	0.598	1080	3230
$6p^3$			
Bi I	2.05	990	10,100

* For $2p^3$ the F_2 values were obtained from the observed value of $^2P_c-{}^2D_c$. The coefficients of F_2 for this separation were obtained from estimated χ values. These coefficients range from 6.00 for N I to 6.16 for P IX and are so insensitive to changes in χ that no significant error can thus have been introduced.

† Good estimates of these ζ_p values should be obtainable by interpolation between p^2 and p^4 in Fig. 5.

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[6] No intercombinations; doublet-quartet intervals may be in error.

[7] But see note to Table VI.

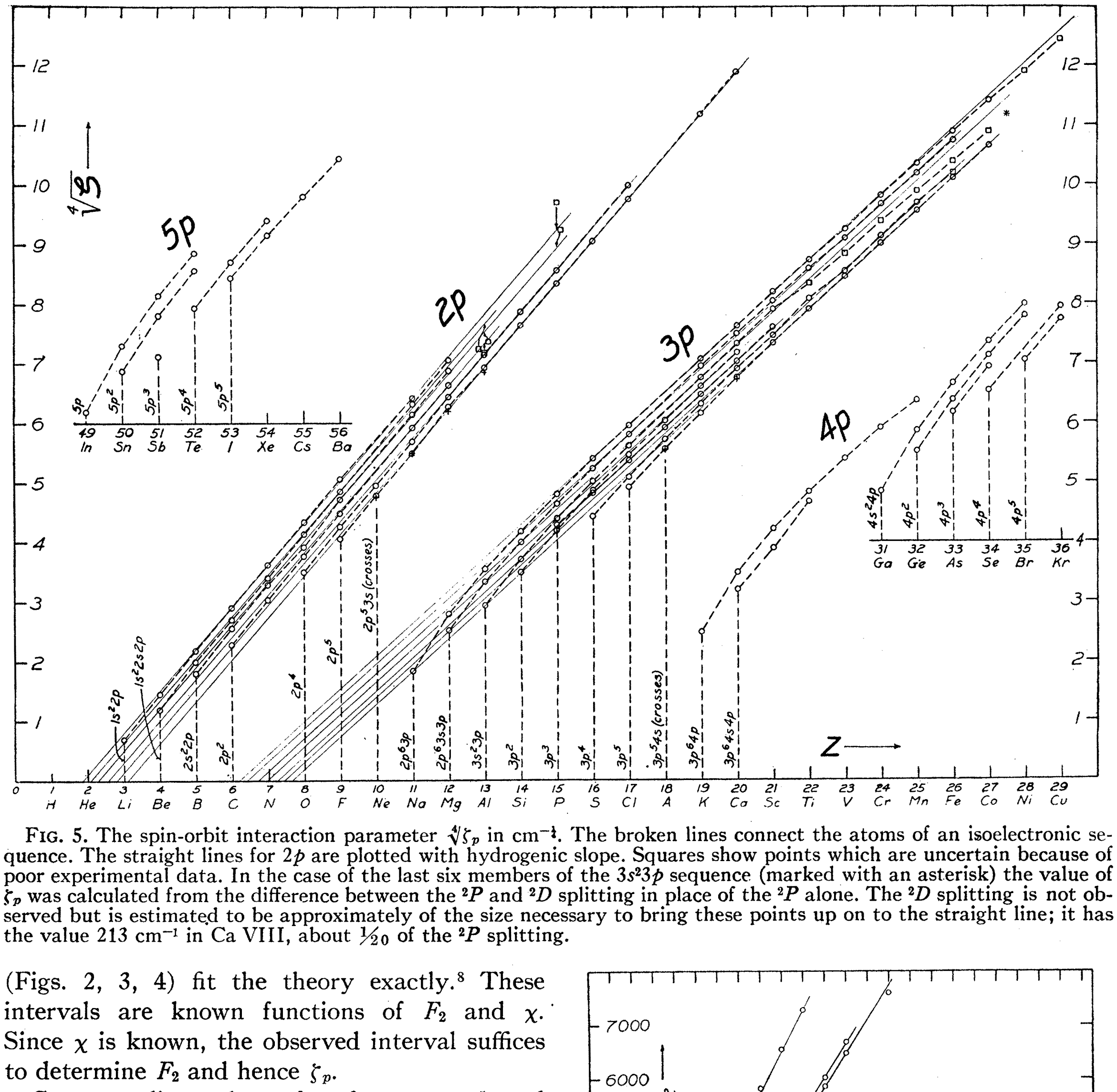

FIG. 5. The spin-orbit interaction parameter $\sqrt[4]{\zeta_p}$ in cm$^{-\frac{1}{4}}$. The broken lines connect the atoms of an isoelectronic sequence. The straight lines for $2p$ are plotted with hydrogenic slope. Squares show points which are uncertain because of poor experimental data. In the case of the last six members of the $3s^23p$ sequence (marked with an asterisk) the value of ζ_p was calculated from the difference between the ${}^2P$ and ${}^2D$ splitting in place of the ${}^2P$ alone. The ${}^2D$ splitting is not observed but is estimated to be approximately of the size necessary to bring these points up on to the straight line; it has the value 213 cm^{-1} in Ca VIII, about $\frac{1}{20}$ of the ${}^2P$ splitting.

(Figs. 2, 3, 4) fit the theory exactly.[8] These intervals are known functions of F_2 and χ. Since χ is known, the observed interval suffices to determine F_2 and hence ζ_p.

Corresponding values of ζ_p for p, sp, p^5, and sp^5 may also be found. In the p and p^5 configurations, $\zeta_p=\pm\frac{2}{3}$ the doublet splitting; in sp and sp^5, $\zeta_p=\pm\frac{2}{3}({}^3P_2-{}^3P_0)$ for any coupling. Values of $\sqrt[4]{\zeta_p}$ are plotted in Fig. 5 against Z. In the lower stages of ionization for the several sequences the curves bend down, but after this the relation $\zeta_p=K(Z-S)^4$ is remarkably well obeyed as is shown by the straight solid lines. Values of S may, of course, be found from the intercepts of the straight lines with the Z axis. The hydrogenic ζ are given by the

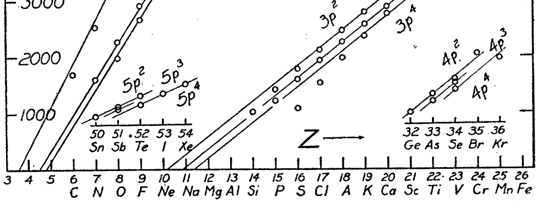

FIG. 6. The electrostatic interaction parameter F_2 in cm^{-1}. The straight lines for $2p^2$, $3p^2$, $3p^3$, $3p^4$ are drawn with hydrogenic slope.

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[8] Compare with the legend of Fig. 1.

well-known formula

$$\zeta_{nl}=\frac{5.822\,Z^4}{n^3l(l+\frac{1}{2})(l+1)}\ \text{cm}^{-1}.$$

Thus

$$\sqrt[4]{\zeta_{2p}}=0.702\,Z\ \text{cm}^{-\frac{1}{4}};\qquad \sqrt[4]{\zeta_{3p}}=0.518\,Z\ \text{cm}^{-\frac{1}{4}}.$$

The straight lines drawn through the $2p$ points have just the hydrogenic slope 0.702. The $3p$ points are not well represented by lines of slope 0.518. The slope chosen is 0.550. This corresponds to $n^*=2.86$ in place of $n=3$ in the hydrogenic formula. The data are as yet insufficient to decide whether the curves become linear at high ionization for $4p$ and $5p$.

The hydrogenic values of F_2, on the other hand, are linear in Z, so in Fig. 6 we plot F_2 directly against Z; the points lie fairly well on the indicated straight lines. It will be noticed that the screening constants corresponding to these lines are much larger than those found in Fig. 5. This may crudely be explained by the fact that ζ_p is essentially the average value of $1/r^3$ and so depends very strongly on the fields near the nucleus, where the screening is small. (Note that the ζ_p screening factors increase by only about $\frac{1}{5}$ for the addition of each $2s$ or $2p$ electron.) The contributions to F_2 are more uniformly distributed over the whole wave function. The hydrogenic values are $F_2(2p, 2p) = 770\,Z$ cm^{-1}; $F_2(3p, 3p) = 320\,Z$ cm^{-1}. The curves for $2p^2$, $3p^2$, $3p^3$, $3p^4$ are drawn with hydrogenic slopes!

Inasmuch as χ is proportional to the ratio ζ_p/F_2 one would expect χ to vary as $(Z-S)^3$. This it does to a very good approximation. Because of the difference between the screening constant for ζ_p and the screening constant for F_2 there is some tendency for the curves of $\sqrt[3]{\chi}$ *vs.* Z to bend upward at low stages of ionization. Such an argument will perhaps account for the anomalous behavior of the ratio $\frac{3}{4}\zeta_p/G_1(s, p)$ in the sequence Ne I, Na II, Mg III ($2p3s$) and A I, K II, Ca III ($3p4s$) as shown in C-S, page 304. The ratio appears first to decrease and then to increase. The K II value shows also the effects of a perturbation from the configuration $3p3d$ with which it is completely mixed up.

TABLE VII. *Parameter values for normal p^4 configurations.*

$2p^4$	χ	F_2(cm^{-1})	ζ_p(cm^{-1})
O I	0.015	1990	150
F II	.025	2670	330
Ne III	.036	3320	600
Na IV	.053	3960	1050
Mg V	.075	4590	1720
Al VI	.100	5230	2620
Si VII	.129*	5870*	3840*
P VIII	.166	6480	5370
Cl X	.262	7600	9950
$3p^4$			
S I	0.071	1090	386
Cl II	.087*	1540*	670*
A III	.108	1980	1070
K IV	.134	2370	1590
Ca V	.164	2770	2270
Sc VI	.202	3070	3100
Ti VII	.247	3370	4160
V VIII	.290	3670	5320
Cr IX	.350	3980	6950
Mn X	.413	4240	8760
Fe XI	.484*	4510*	10,910*
$4p^4$			
Se I	0.258	1410	1821
Kr III	.402	1980	3980
$5p^4$			
Te I	0.682	1160	3970
I II	.844	1360	5760
Xe III	1.014	1530	7780

* From interpolated or extrapolated χ values.

Prediction of unknown levels

Figures 2, 3, and 4 show that the deviations of the experimental ratios from the theoretical curves are sufficiently regular that unknown interval ratios may be predicted by interpolation or extrapolation on the curves through the empirical points. Furthermore, the approximate linear variation of $\sqrt[3]{\chi}$, $\sqrt[4]{\zeta_p}$, and F_2 with Z may be used to predict unknown parameter values, where needed.

At the time that Fig. 3 was drawn the low states of Sc VI were unknown, but have since been published. As a typical example of the accuracy to be expected in interpolation, the following calculation was made (without recourse to the data) for this ion. The $\sqrt[3]{\chi}$ *vs.* Z was first plotted for the $3p^4$ sequence. The curve was smooth and gave the result $\chi=(0.588)^3 =0.203$. The following ratios were read immediately from the dashed curves of Fig. 3:

$$({}^3P_1-{}^3P_2)/({}^1S_0-{}^3P_c)=0.071,$$
$$({}^3P_1-{}^3P_2)/({}^1S_0-{}^1D_2)=0.121,$$
$$({}^3P_1-{}^3P_2)/({}^1D_2-{}^3P_c)=0.170,$$
$$({}^3P_0-{}^3P_1)/({}^3P_1-{}^3P_2)=0.330.$$

Now near LS coupling any Landé interval such as ${}^3P_1-{}^3P_2$ will vary approximately as $(Z-S)^4$ along an isoelectronic sequence. We may therefore interpolate, numerically or graphically, in the table of $({}^3P_1-{}^3P_2)^{\frac{1}{4}}$ to find for Sc VI, ${}^3P_1-{}^3P_2=(7.607)^4=3350$. Knowing this one value the other intervals follow at once. The results are listed in Table VIII. It will be noticed that the accuracy obtainable is about that which one would obtain by using the irregular-doublet law. In cases where predictions by means of the latter are precarious (as for example in interpolation between the first and third members of the sequence), the method here outlined may well give valuable information about the trend of the first difference.

Two other predictions made in this manner have allowed plausible classifications of hitherto unknown levels. These predictions are marked by means of an asterisk in Figs. 2 and 3. In these cases χ was known from the other levels. In the case of K IV $3p^4$ the ${}^1S$ was unknown. From Fig. 3 the ratio $({}^3P_1-{}^3P_2)/({}^1S-{}^3P_c)$ was predicted to be 0.0450. This predicts the unknown term at 37,160 cm^{-1}; two combinations have been found which locate the term at 37,778 cm^{-1}. In the case of Ca VII both the ${}^1S$ and ${}^1D$ were unknown. The ${}^1D$ was predicted at 21,910 cm^{-1} and found at 21,872 cm^{-1}. Lines giving the ${}^1S$ term could not be identified. The newly classified lines are listed in the following paper in this issue of the *Physical Review.*

Remarks on other configurations

The sp^3 configuration.—As mentioned previously, there exists for this configuration a ratio which is independent of the coupling. If 2_c denotes the centroid of the levels of $J=2$ $[2_c=\frac{1}{4}({}^1D_2+{}^3D_2+{}^3P_2+{}^5S_2)]$ and 1_c denotes the centroid of the levels of $J=1$ $[1_c=\frac{1}{4}({}^1D_1+{}^3P_1+{}^1P_1+{}^3S_1)]$, the ratio

$$\frac{16({}^3P_0)+4(1_c)-20(2_c)}{{}^3P_0-{}^3D_3}=19.$$

That this relation holds fairly well may be seen from Table IX. Other relations may be expected to hold near LS coupling, e.g.

$${}^1P-{}^3P_c={}^1D-{}^3D_c=\tfrac{1}{2}({}^3S-{}^5S).\quad \text{(C-S page 199.)}^{9}$$

TABLE VIII. *Observed and estimated intervals for Sc VI 3p⁴.*

INTERVAL	ESTIMATED (this method)	OBSERVED	ESTIMATED (irregular-doublet law)
${}^3P_1-{}^3P_2$	3350 cm^{-1}	3350 cm^{-1}	
${}^3P_1-{}^3P_0$	1110	1126	
${}^1D-{}^3P_2$	21,300	21,397	21,330 cm^{-1}
${}^1S-{}^3P_2$	48,800	49,238	49,180
${}^1S_0-{}^1D_2$	27,700	27,841	27,870

TABLE IX. *The invariant ratio $[16({}^3P_0)+4(1_c)-20(2_c)]/({}^3P_0-{}^3D_3)$ for sp^3. (Theoretical value = 19.)*

ELEMENT	CONFIGURATION	RATIO
N II	$2s2p^3$	18.21
O II	—	17.94
F IV	—	17.88
Na VI	—	18.32*
Mg VII	—	18.50*
Al VIII	—	18.56*
O I	$2p^33s$	21.35†
F II	—	20.27
P II	$3s3p^3$	19.4*
S I	$3p^34s$	19.20
Se I	$4p^35s$	19.09
Kr III	—	16.95†
Xe III	$5p^36s$	17.55†

* In these cases certain intercombinations are not accurately known.
† Partial overlapping with the p^3d configuration.

TABLE X. *Intervals in sp^3 configurations.* (Theory predicts that these should be equal in LS coupling.)

	${}^1P-{}^3P_c$	${}^1D-{}^3D_c$	$\frac{1}{2}({}^3S-{}^5S)$
O I	2005	1526	1513
F II	−2324*	3189	3106
N II	57,547	51,943	54,231
O III	68,075	67,008	68,596
F IV	82,148	81,039	81,896
S I	1124	1407	1354
P II	26,011	12,462†	28,902

* Interaction between $sp^5\,{}^1P$ and $p^33s\,{}^1P$.
† The p^3 terms in P III are very irregular. There is also some interaction between sp^3 and s^2pd terms.

The empirical values are listed in Table X.

The pp configuration.—Early attempts to classify terms of this configuration in the first period led to erroneous term designations. As a result the relation[10] $R=(S_m-D_m)/(D_m-P_m)=3/2$ which was predicted for the LS coupling case was thought to be entirely disobeyed (C-S, page 200). Recent revisions of these spectra show that the terms really lie in the right order to make this ratio positive; for C I, $R=1.13$; N II, $R=1.135$; O III, $R=9.3$. In the second period

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[9] In this reference, the ${}^3S$, ${}^5S$ formula should read $+1$, $-3G_1$ in place of the coefficients given.

[10] The subscript $_m$ denotes the mean of the singlet and the centroid of the triplet; e.g. $D_m=\frac{1}{2}({}^1D+{}^3D_c)$.

Si I and P II give ratios which are negative because of the anomalous position of the ^1P term. In the third period the term order is correct: for As II, $R=1.20$. Ge I and Se III are not complete.

Sources of data

We present here a working bibliography which lists the sources of information on all ions having only s and p electrons in the normal configuration. In many cases the key paper only is given as usually previous data are therein listed. We have attempted to list also those papers which give supplementary data (usually by interpolation along an isoelectronic sequence) concerning a few terms in the spectra of other ions than those listed in the title. In several cases where more than one person has worked upon a single spectrum simultaneously we have only listed what appears to us on careful scrutiny to be the most reliable. Our choice has usually depended on further information which has appeared since the original publication and in no sense is to be construed as indicating that the efforts of a particular author are in general untrustworthy. In this list the roman numerals refer to the spectrum; the arabic to the reference.

This paper was completed while one of the writers (G. H. S.) was the guest of the physics department of Princeton University. He wishes to thank the members of this faculty for their generous hospitality.

Bibliography

He	I, 1, 18.
Li	I, 2; II, 1.
Be	I, 2, 3, 4; II, 2; III, 1; IV, 5.
B	I, II, III, 4; IV, 5.
C	I, 4; II, 4, 7; III, IV, 4; V. 1.
N	I, 2, 6; II, 4, 7, 15; III, IV, 4, 7; V, 4; VI, 1.
O	I, 2, 2a; II, III, IV, 4, 8; V, 4, 76; VI, 4; VII, 1.
F	I, 9, 10; II, III, 9, 11; IV, 11, 12; V, 11, 13; VI, 11, 14, 76; VII, 11, 14.
Ne	I, 2; II, III, IV, 16.
Na	I, 2; II–IX, 17.
Mg	I, 2, 3; II, 2; III–IX, 17.
Al	I, 2, 3, 18; II, 2, 3, 18; III, 2; IV–X, 17.
Si	I, 2, 19, 22; II, III, 2, 20; IV, 21; V–IX, 17.
P	I, 22; II, 22, 23; III, IV, V, 23; VI–XIII, 24.
S	I, 25, 26; II, 26, 27, 22; III, 2, 27, 28; IV, 2, 20; V, 20; VI, 2, 28; VIII, 28.
Cl	I, 2, 36; II, 2, 29; III, 30; IV, 30, 31; V, 30; VI, VII, 2; VIII, IX, 32.
A	I, 2; II, 33, 36; III, 33, 34; IV, 33; V, 33, 35.
K	I, 2, 10; II, 2; III, 2, 36, 41a; IV, 28, 37; V, 37; VI, 38, 28; VII, 38; VIII, 38, 39, 76; IX, 38, 40; X, 73; XI, 73, 76.
Ca	I, II, III, 2; IV, 2, 36, 41a; V, VI, 37; VII, 38, 28; VIII, 38; IX, 39, 76; X, 40; XI, 73; XII, 73, 76.
Sc	II, III, 2; IV–XI, 41, 41a, 41b, 41c; XII, 73.
Ti	IV, 2; V, 41b; VI, 36; VII, 42; X, XI, 39; XII, 40; XIII, 73.
V	V, 2; VII, 36; VIII, 42; XI, XII, 39; XIII, 40; XIV, 73.
Cr	VI, 2, 41d; VIII, 36; IX, 42; XII, XIII, 39; XIV, 40; XV, 73.
Mn	VII, 2, 41d; VIII, 41b; IX, 36; X, 42; XIII, XIV, 39; XV, 40.
Fe	VIII, 41d; IX, 41b; X, 36; XI, 42; XIV, XV, 39; XVI, 40.
Co	XI, 36; XV, XVI, 39; XVII, 40.
Ni	XVIII, 40.
Cu	XIX, 40.
Ga	I, 2.
Ge	I, 2, 43; II, 2.
As	I, 45, 75; II, 44, 75; III, 2, 46, 75; IV, 50.
Se	I, 47; II, 48; III, 49; IV, V, 50.
Br	I, 2; II, 62; IV, 51; V, 52.
Kr	I, 2; II–IV, 53, 54.
Rb	I, 2.
Sr	II, 2.
Y	III, 2.
Zr	IV, 2.
Cb	V, 55.
Mo	VI, 55.
In	I, 2.
Sn	I, II, 2.
Sb	I, 2; II, 56; III, 2, 57.
Te	I, 58; III, 59; IV, 60.
I	I, 61; II, 62; IV, 74.
Xe	I, 2; II, 63; III, 64.
Cs	I, 2; III, 65.
Ba	II, 2; IV, 65.
La	III, 2, 66.
Ce	IV, 66.
Tl	I, 2.
Pb	I, 2; II, 67.
Bi	I, 2; II, III, 68.
Ra	I, 69, 70; II, 71.
Th	IV, 72.

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