JULY 1, 1929 PHYSICAL REVIEW VOLUME 34

THE VECTOR COUPLING IN THE NICKEL-, PALLADIUM-, AND PLATINUM-LIKE SPECTRA

By J. E. Mack[1]
Palmer Physical Laboratory, Princeton University

(Received April 8, 1929)

Abstract

Spectroscopic data.—The $5d^96s$ and $5d^96p$ configurations are identified among the known levels of Pt I, and partly identified in Tl IV and Pb V. The lines observed in the condensed spark discharge of thallium λ868 to λ1070 and lead λ477 to λ1280 are listed.

Vector coupling.—The relative energies, line intensities, and g-values of the levels of the d^9s and d^9p configurations of the sequences Ni I-Ge V, Pd I-Sn V, and Pt I-Pb V show a gradual transition from LS or Russell-Saunders coupling to jj coupling with increasing atomic number and increasing net charge. In the "pure" jj coupling the levels are arranged in groups (two in d^9s and four in d^9p). The positions of the d^9p groups observed for Hg III, Tl IV, and Pb V agree well quantitatively with the positions independently calculated for jj coupling with the aid of the Sommerfeld regular doublet law. In the d^9p configuration of Tl IV and Pb V, only levels built upon $d^9\ ^2D_{5/2}$ are observed in spite of the fact that the $d^9{}_{3/2}+p_{1/2}$ levels are more stable than the $d^9{}_{5/2}+p_{3/2}$ levels.

Correlation of levels, with varying principal quantum number and varying nuclear charge.—In several cases among the spectra under consideration, levels of the same J-value cross when relative energy in a configuration is plotted against nuclear charge in an isoelectronic sequence. These levels, except in one case, happened to be recognizable on both sides of the "crossings" on account of their approximately normal intensities. But in general, correlation of levels and crossing or non-crossing in spectral series or isoelectronic sequences appears to be without meaning, for it necessitates considering quantum numbers or nuclear charges as continuous variables.

I. Introduction

Most of the progress made thus far in the classification of complicated atomic spectra, has been made among spectra of the "normal" or Russell-Saunders type.[2] Roughly speaking, the normal type is characteristic of all atoms except those "near the right-hand edge" or "near the bottom" of the periodic table—that is, of all atoms except those with nearly enough equivalent outer electrons to form a complete Pauli shell, or with high atomic number.

Platinum is the extreme case "in the lower right-hand corner" of the periodic table. The platinum-like spectra[3] are by no means completely known; but sufficient progress has been made in their classification to lend

---

[1] National Research Fellow.

[2] That is, spectra which satisfy approximately Landé's interval formula and g formula (A. Landé, Zeits. f. Physik **15**, 189 (1923)) and Russell's intensity formula (H. N. Russell, Nat. Acad. Sci. Proc. **11**, 314 (1925)).

[3] That is, the spectra of the isoelectronic sequence Pt I, $Z=78$; Au II, $Z=79$; etc.

interest to a study of them from the viewpoint of the vector model and a comparison with the analogous nickel-like and palladium-like spectra. Such a study is the main object of this paper; but certain new spectroscopic data pertinent to the study will be presented first.

II. DATA*

This paper will be confined largely to a consideration of the structure of atomic states wherein the outer electrons occur in configurations of nine *d* electrons and one *s* or *p* electron. The $3d^94s$, $3d^94p$ and $4d^95s$, $4d^95p$ configurations are already known for five spectra in each sequence.[4] The relative values of the levels arising from the $5d^96s$ and $5d^96p$ configurations are

---

* The work of numerial calculation for this paper has been materially lightened by the use of a calculating machine secured by this laboratory through the generosity of the Carnegie Corporation.

[4] Spectroscopic data from the following sources were used in the preparation of this paper (*l* means list of lines; *c*, list of levels; *i*, interpreted list of levels; *z*, Zeeman effect data):

Cr V *i*: R. C. Gibbs and H. E. White, Phys. Rev. **33**, 538 (1929).

Co I *i*: M. A. Catalán, Zeits. f. Physik **47**, 89 (1927); H. N. Russell, unpublished data.

Ni I *i*: K. Bechert and L. A. Sommer, Ann. d. Physik **77**, 351 (1925); *z*, O. Luttig (Peterko's data) Ann. d. Physik **38**, 43 (1912); *intensities*, quantitative measurements, F. Bouma, diss. Utrecht, and material about to be published in Dutch, obtained through the courtesy of Professor Ornstein.

Ni II *i*: A. G. Shenstone, Phys. Rev. **30**, 255 (1927); R. J. Lang, Phys. Rev. **31**, 773 (1928).

Cu I *i*: A. G. Shenstone, Phys. Rev. **28**, 449 (1926).

[a]Cu II *i z*: A. G. Shenstone, Phys. Rev. **29**, 380 (1927).

Cu III *i*: R. C. Gibbs and Alice M. Vieweg, Phys. Rev. **33**, 1092 (1929).

Zn II, Cd II *i*: G. v. Salis, Ann. d. Physik **76**, 145 (1925).

Zn III *i*: O. Laporte and R. J. Lang, Phys. Rev. **30**, 378 (1927).

[b]Zn III, Ga IV, Ge V *i*: J. E. Mack, O. Laporte, and R. J. Lang, Phys. Rev. **31**, 748 (1928).

[c]Cu-, Hg-, Au-like sequences *i*; Ga, Ge, Cd, In, Hg, Tl, Pb *l*: J. A. Carroll, Roy. Soc. Trans. **A225**, 357 (1925).

As VI (The paper of P. Pattabhiramiah and A. S. Rao, Zeits. f. Physik **53**, 587 (1929), has been consulted but its results have not been incorporated in this paper. A criticism is expected to appear shortly).

Pd I *c*: J. C. McLennan and H. G. Smith, Roy. Soc. Proc. **A112**, 110 (1926); *i*: Privately communicated by A. G. Shenstone; *z*: C. S. Beals, Roy. Soc. Proc. **A109**, 369 (1925) (*g*-values calculated by A. G. Shenstone).

Ag II *i z*: A. G. Shenstone, Phys. Rev. **31**, 317 (1928); and private communication.

[d]Cd III, In IV *i*: R. C. Gibbs and H. E. White, Phys. Rev. **31**, 773 (1928).

In III, Sn IV, Sb V *i*: R. J. Lang, Nat. Acad. Sci. Proc. **13**, 341 (1927).

Sn V *i*: R. C. Gibbs and H. E. White, Nat. Acad. Sci. Proc. **14**, 143 (1928).

[e]Pt, Au *l*: F. Exner and E. Haschek (Kayser's "Handbuch der Spektroscopie," vol. 6).

Pt *l*: W. F. Meggers, U. S. Bur. Stds. Sci. Papers **20**, 19 (1925).

Pt I *c*: J. C. McLennan and A. B. McLay, Roy. Soc. Canada Trans. **20**, 1 (1926); *i*: W. F. Meggers and O. Laporte (including Snyder's data), Phys. Rev. **28**, 642 (1926); *cz*: A. C. Haussmann, Astrophys. J. **66**, 333 (1927);

[f]*lz*: A. G. Shenstone and J. J. Livingood, unpublished data.

Au I *i*: J. C. McLennan and A. B. McLay, Roy. Soc. Proc. **112**, 95 (1926).

Au II *i*: J. C. McLennan and A. B. McLay, Roy. Soc. Canada Trans. **22**, 103 (1928).

Hg II *i*: F. Paschen, Preus. Akad. Sitzungsber. p. 536 (1928).

Hg III *i*: J. C. McLennan, A. B. McLay, and M. F. Crawford, Roy. Soc. Canada Trans. **22**, 247 (1928);

[g]*i*: R. J. Lang and J. E. Mack, unpublished data.

Hg *l*: T. Lyman, Astrophys. J. **38**, 282 (1913); G. Déjardin. Ann. de Physique **8**, 424 (1927).

collected in Table I. The conventional notation[5] has a significance somewhat more limited here than in cases of normal coupling; the discussion at the end of this paper should be consulted for its exact meaning.

TABLE I. *The* $5d^96s$ *and* $5d^96p$ *energy levels of the platinum-like spectra. The* $5d^96s$ *levels are listed according to energy values; the* $5d^96p$ *levels, according to J-values. The numbers after the values of the Pt I levels, are the arbitrary symbols assigned to these levels by Haussmann.*

		Pt I		Au II	Hg III	Tl IV	Pb V
$5d^96s$	$^3D_3$	0		0	0	0	0
	$^3D_2$	775.9		2601.5	3179	3588	3944
	$^3D_1$	10132.0		12726.7	15556	18865	
	$^1D_2$	13496.3		14582.0	18235	21681	25234
$5d^96p$	$^3F_4$	37590.7	7	57455.7	75143	92617	110296
	$^3F_3$	34122.1	3	49964.2	62777	74783	86370
	$^3D_3$	40970.1	15	59752.1	78750	97217	115744
	$^1F_3$	49286.1	33	70660.8	(89637)		
	$^3P_2$	32620.0	1	48014.0	60699	72582	84043
	$^3D_2$	38815.9	10	58138.8	75698		
	$^3F_2$	44444.4	21	61620.5	78077	95285	113130
	$^1D_2$	51286.9	37	71526.0	91736		
	$^3P_1$	41802.7	16	58364.5	(75756)		
	$^1P_1$	49544.5	34	66620.2	83704	100233	?117075
	$^3D_1$	50055.3	36	70668.0	(93626)		
	$^3P_0$	46433.9	26	67574.5			

Several investigators have recently extended the wave-number system of Pt I, which was developed about thirty years ago by Snyder. Meggers and Laporte assigned the lowest levels to the configuration $5d^96s$, and the subsequent Zeeman effect work of Haussmann has confirmed their assignment. Mr. J. J. Livingood and Professor Shenstone have kindly put their unpublished data on the Zeeman effect in the platinum arc spectrum, at my disposal; this aid, and the wealth of material now available for comparison with other spectra, have made it possible to identify the $5d^96s$ and $5d^96p$ levels of Pt I.

In the palladium atom, the levels of the configuration d^9p are a good deal more stable than any other "odd" levels of the spectrum. In platinum, as in nickel, the levels of this configuration are sprinkled among those of the rich configuration d^8sp, which completely overlap it; but, as we shall see below, in platinum the usual criteria for sorting levels have almost completely broken down. Fortunately, three guides—first, the expectation of a fair degree of smoothness in the relative behavior of the energy levels in the isoelectronic sequence; second, the g-sum rule for the behavior of the levels in a weak magnetic field; the third, the relative intensities of the transitions $5d^86s^2 \leftarrow 5d^86s6p$, $5d^96s \leftarrow 5d^86s6p$, $5d^96s \leftarrow 5d^96p$ (one electron jump) and

---

[5] The orbital, spin, and total angular momenta of an atomic system as a whole are designated by capital letters L, S, J in accordance with a recommendation of the committee on spectroscopic notation, Phys. Rev. **33**, 900 (1929).

$5d^86s^2 \leftarrow 5d^96p$ (two electron jump)—were sufficient to allow the $5d^96p$ levels to be sorted from the others, with quite a high degree of certainty. The numbers after the values of the Pt I levels in Table I are the arbitrary numerical symbols used by Haussmann.

The levels of Au II were discovered and classified by McLennan and McLay. This classification was especially useful in the study of the d^9p levels, which again in Au II are considerably more stable than any other "odd" levels.

Table II. *Energy levels and lines of triply ionized thallium, Tl IV.*

			$(5d^9_{5/2}6s)_3$ or $5d^96s\,^3D_3$ 0	$(5d^9_{5/2}6s)_2$ or $5d^96s\,^3D_2$ 3588	$(5d^9_{3/2}6s)_1$ or $5d^96s\,^3D_1$ 18865	$(5d^9_{3/2}6s)_2$ or $5d^96s\,^1D_2$ 21681
$(5d^9_{5/2}6p_{1/2})_2$ or $5d^96p\,^3P_2$		72582	72582(7) 0	68995(5)+1	53717(3) 0	50901(3) 0
$(5d^9_{5/2}6p_{1/2})_3$	$^3F_3$	74783	74784(4)+1	71195(8) 0		53101(5)−1
$(5d^9_{5/2}6p_{3/2})_4$	$^3F_4$	92617	92617(6) 0			
$(5d^9_{5/2}6p_{3/2})_2$	$^3F_2$	95285	95285(2) 0	91684(4)−13	76423(2)+3	73606(5)+2
$(5d^9_{5/2}6p_{3/2})_3$	$^3D_3$	97217	97224(4)+7	93623(4)−6		75542(1C?)+6
$(5d^9_{5/2}6p_{3/2})_1$	$^1P_1$	100233		96643(3)−2	—	78553(3)+1

McLennan, McLay, and Crawford have recently published a classification of Hg III. Most of their levels are confirmed by an independent investigation by Lang and Mack; but three (shown in parentheses in Table I) were derived from lines which are classified elsewhere or show such great wave-length discrepancies that they can not be treated with the same certainty as the others. An attempt to find $d^9p\ ^3P_1$, $^3P_0$, $^1F_3$, $^3D_1$ and higher levels in Hg III has been, thus far, unsuccessful.

Table III. *Classified lines of triply ionized thallium, Tl IV.*

	Carroll		This investigation		
λ	ν	Int.	ν	Int.	Designation
1028.55	97224	4	97219	6	$d^9s\,^3D_3 - d^9p\,^3D_3$
1034.74	96643	3	96655	4	$^3D_2 -\ ^1P_1$
1049.48	95285	2	95277	5	$^3D_3 -\ ^3F_2$
1068.11	93623	4	93624	5	$^3D_2 -\ ^3D_3$
1079.71	92617	6	92622	6	$^3D_3 -\ ^3F_4$
1090.70	91684	4	91689	5	$^3D_2 -\ ^3F_2$
1273.03	78553	3	78557	6	$^1D_2 -\ ^1P_1$
1308.50	76423	2	76426	4	$^3D_1 -\ ^3F_2$
1323.76	75542	1 C?	75542	6	$^1D_2 -\ ^3D_3$
1337.19	74784	4	74781	7	$^3D_3 -\ ^3F_3$
1358.58	73606	5	73603	7	$^1D_2 -\ ^3F_2$
1377.75	72582	7	72579	7	$^3D_3 -\ ^3P_2$
1404.60	71195	8	71191	7	$^3D_2 -\ ^3F_3$
1449.37	68995	5			$^3D_2 -\ ^3P_2$
1861.6	53717	3			$^3D_1 -\ ^3P_2$
1883.2	53101	5			$^1D_2 -\ ^3F_3$
1964.6	50901	3			$^1D_2 -\ ^3P_2$

C? Possibly due to carbon.

The condensed spark spectra of thallium and lead were photographed on the University of Michigan's one meter, 15,000 lines/inch grating spectrograph; the generous cooperation of Professor Sawyer made this part of the investigation possible. For thallium, the data are in good agreement with Carroll's in the region of overlapping; since Carroll measured his lines in several orders, his values are used. For lead, the new values are preferred in the region of overlapping.

TABLE IV. *Lines of the condensed spark discharge between thallium electrodes (supplimentary to Carroll's* $\lambda > 1000$*).*

Carroll	This investigation			
λ	λ	ν	Int.	
	68.99	115076	2	
	872.06	1146[illegible]1	0	
	874.87	114303	1	
	879.68	113678	0	
	903.77	110648	3	C
	904.13	110604	5	C
	908.31	110095	1	
	909.43	109959	4	
	910.35	109848	2	
	911.70	109685	2	
	912.74	109560	3	
	916.93	109060	4	
	917.31	109014	5	
	919.73	108728	2	
	921.6	10851	0	
	922.42	108410	1	
	924.40	108178	1	
	925.34	108068	1	
	926.29	107958	2	
	928.01	107757	3	
	929.80	107550	1	
	930.80	107435	5	
	931.15	107394	1	
	931.88	107310	1	
	932.32	107260	1	
	933.11	107168	4	
	933.69	107102	3	
	934.70	106986	4	
	935.61	106882	4	
	936.87	106738	5	
	937.62	106653	2	
	938.91	106506	1	
	940.17	106394	3	
	940.59	106316	2	
	941.54	106209	2	
	941.99	106158	1	
	944.17	105913	?0	
	944.45	105820	?0	
	945.81	105729	2	
	948.28	105454	?0	
	948.82	105394	?0	
	950.09	105253	4	
	951.50	105097	1	
	952.24	105016	1	
	953.57	104869	2	
	954.57	104759	6	
	955.88	104616	0	
	956.8	10452	0	
	958.36	104345	5	
	958.69	104309	5	
	959.73	104196	2	
	960.16	104149	3	
	960.85	104075	1	
	962.00	103950	4	
	962.87	103856	1	
	964.75	103654	2	
	965.45	103579	3	
	966.60	103455	2	
	966.85	103429	5	
	967.51	103358	1	
	968.55	103247	4	
	970.39	103051	3	
	974.69	102597	0	
	976.00	102459	2	
977.02	977.03	102351	8	C977.031
	979.38	102123	0	
	989.57	101054	2	
993.66	993.73	100631	5	
995.5	995.57	100445	2	
	1001.50	99850	0	
	1002.25	99776	0	
	1005.41	99462	0	
	1006.17	99387	0	
	1010.35	98976	2*d*	C
	1022.9	9776	0	
	1025.85	97480	1	
	1030.07	97081	0	
1031.7	1031.85	96913	2	
	1035.42	96579	0	
1036.60	1036.52	96477	4	C?
	1036.92	96439	3	C?
1053.5	1053.50	94922	2	
1054.80	1055.01	94786	0	
1058.2	1058.21	94499	1	
1059.9	1059.98	94341	0*d*	
	1066.69	93748	1	
	1069.93	93464	0	

?0 Existence of line uncertain.
C Carbon.
d Diffuse.

Tables II and V show the wave-number schemes for Tl IV and Pb V, respectively. The alternative notation for the levels is explained on page 33. For each line, two numbers are given: the intensity, in parentheses, and the difference $\nu_{\text{obs}}-\nu_{\text{calc}}$ between the observed frequency of the line and the frequency calculated from the values assigned to the levels. The frequencies of the four thallium lines $d^9s\,^3D_3$, $^3D_2-d^9p\,^3F_2$, $^3D_3$ derived from Carroll's measurements, show relatively high discrepancies; but a careful remeasurement of the intervals has verified this classification.

TABLE V. *Energy levels and lines of quadruply ionized lead, Pb V.*

			$(5d^9{}_{5/2}6s)_3$ or $5d^96s\,^3D_3$ 0	$(5d^9{}_{5/2}6s)_2$ or $5d^96s\,^3D_2$ 3944	$(5d^9{}_{3/2}6s)_2$ or $5d^96s\,^1D_2$ 25234
$(5d^9{}_{5/2}6p_{1/2})_2$ or $5d^96p\,^3P_2$		84043	84044(6)+1	80097(3)−2	58813(00 Carroll)+4
$(5d^9{}_{5/2}6p_{1/2})_3$	$^3F_3$	86370	86368(8)−2	82427(6)+1	61136(00 Carroll) 0
$(5d^9{}_{5/2}6p_{3/2})_4$	$^3F_4$	110296	110296(8) 0		
$(5d^9{}_{5/2}6p_{3/2})_2$	$^3F_2$	113130	113128(x)−2	109192(6)+6	87892(8)−4
$(5d^9{}_{5/2}6p_{3/2})_3$	$^3D_3$	115744	115748(7)+4	111796(6)−4	90510(1) 0
$(5d^9{}_{5/2}6p_{3/2})_1$	$^1P_1$	?117075		113128(5−x)−3	91843(4)+2

? Existence of level uncertain.

TABLE VI. *Classified lines of quadruply ionized lead, Pb V.*

Carroll		This investigation			
λ	Int.	λ	ν	Int.	Designation
864.0	5	863.95	115748	7	$d^9s\,^3D_3-d^9p\,^3D_3$
883.9	4	883.95	113128	5	$\{^3D_3-\ ^3F_2$ $^3D_2-\ ?^1P_1$
894.4	4	894.49	111796	6	$^3D_2-\ ^3D_3$
906.7	7	906.65	110296	8	$^3D_3-\ ^3F_4$
915.9	3	915.82	109192	6	$^3D_2-\ ^3F_2$
1088.9	2	1088.82	91843	4	$^1D_2-\ ?^1P_1$
1104.8	00	1104.85	90510	1	$^1D_2-\ ^3D_3$
1137.8	5*d*	1137.76	87892	8	$^1D_2-\ ^3F_2$
1158.0	8	1157.83	86368	8	$^3D_3-\ ^3F_3$
1190.1	7	1189.85	84044	6	$^3D_3-\ ^3P_2$
1213.4	5	1213.20	82427	6	$^3D_2-\ ^3F_3$
1248.6	2	1248.49	80097	3	$^3D_2-\ ^3P_2$
1635.7	00				$^1D_2-\ ^3F_3$
1700.3	00				$^1D_2-\ ^3P_2$

d Diffuse.

Tables III and VI are lists of the newly classified lines.

Table IV is a list of the lines observed in the condensed spark spectrum of thallium, in the region λ868 to λ1070, supplementary to Carroll's list. For the lines not listed, the present measurements are in agreement with Carroll's, with an average discrepancy of 0.04A. Table VII, for lead in the region $\lambda < 1280$ is similar except that here all the lines in the region are listed. Hydrogen λ1215.680 and Bowen and Ingram's lines[6] were used as standards. Since it was necessary to extrapolate from λ833, the shorter wave-lengths in the thallium list may be in error by as much as 0.3A in absolute value. The probable random error is about 0.05A.

---

[6] I. S. Bowen and S. B. Ingram, Phys. Rev. **28**, 444 (1926).

TABLE VII. *Lines of the condensed spark discharge between lead electrodes.*

Carroll		This investigation			
λ	Int.	λ	ν	Int.	Assignment
		474.81	210610	3	
		477.75	209314	2	
		495.92	201645	4	
		497.8	20090	?0	
		499.39	200244	4	
		514.49	194367	2	
		529.5	18886	1	
		541.11	184805	1	
		542.31	184396	3	
		569.77	175509	4	
		572.36	174715	3	
		648.22	154279	2*d*	
		652.56	153243	3*pd*	
		653.46	153032	?0	
		655.82	152439	3	
		689.8	14498	0	
		694.35	144020	1	
		703.63	142120	2	0? 703 blend
		706.06	141631	0	
		707.39	141365	1	
		708.97	141050	2	
		717.05	139460	1	
		718.07	139262	2	
		719.17	139049	1	
		721.46	138608	1	
		728.59	137251	4	
		739.49	135228	1	
		741.89	134791	4	
		749.09	133495	3*p*	
		752.6	13288	1*p*?	
		754.93	132463	4	
		755.73	132322	3	
		760.9	13142	0	
		762.85	131087	1	
		764.57	130792	2	
		765.74	130593	1	
767.5	0	767.38	130314	6	
		769.48	129958	4	
		771.28	129655	5	
		772.51	129448	2	
		775.58	128936	3	
		781.3	12798	2*p*	
		782.14	127854	4	
		783.40	127649	2	
786.48	1				
787.73	2	787.74	126945	4	0 787.716
790.21	3	790.21	126549	1	0 790.205
		795.35	125731	4	
796.58	0	796.8	12550	1*d*	0? 796.665
		798.79	125189	0*d*	
		799.76	125076	1*d*	
		800.37	124942	1*d*	
802.07	1	802.03	124684	5	
		802.96	124539	0	
804.8	00?	804.55	124293	1	
806.3	00?	806.09	124056	2	
		807.12	123897	0	
		808.40	123701	2	
		809.59	123519	3	
		811.8	12319	?1	
		812.58	123065	4	
		813.26	122962	2	
815.91	1	815.76	122585	3*v*	
		816.96	122405	3	
		818.15	122227	2	
819.5	0	819.25	122063	3	
		821.32	121728	0	
		822.86	121527	1	
		826.1	12105	?0	
826.9	0	826.72	120960	3	
827.8	0	827.63	120827	2	
		828.63	120681	3	
829.32	0	829.28	120587	2	
830.3	0	830.10	120467	6	
834 group		832.7	12009	1*d*	0 832 blend
834.5	3	834.46	119838	4	0 834.459
835.4	3	835.4	11970	1	0 835 blend
		836.03	119613	0	
		838.42	119272	1*d*	
		839.6	11911	?0*d*	
		840.99	118908	5	
		842.33	118718	2*d*	
		842.81	118651	1*d*	
		844.84	118366	4*v*	
		845.96	118209	4	
		847.8	11795	0	
849.6	00	849.57	117707	6	
852.1	00	851.98	117374	2	
		853.07	117224	2	
		854.46	117033	0	
854.9	00?	854.81	116985	?0	
857.8	0	857.63	116600	6	
		858.91	116427	1	
		860.6	11620	?0	
862.5	0	862.36	115961	5	
864.0	5	863.95	115748	7	Pb V
		865.4	11555	0	
		867.16	115319	0	
		867.94	115215	0	
870.5	3	870.44	114884	5	
		872.57	114604	2	
		879.9	11364	0*d*	
883.9	4	883.95	113128	5	Pb V
885.0	1	884.98	112997	6	
		887.3	11271	1	
888.5	3	888.41	112561	5	
890.8	4	890.78	112261	7	Pb IV?
894.4	4	894.49	111796	6	Pb V
		896.10	111595	5	
903.6	3	903.7	11065	?0	C
		904.17	110599	4	C
		904.74	110529	0	
906.7	7	906.65	110296	8	Pb V
908.5	0	908.54	110067	5	
		915.08	109280	0	
915.9	3	915.82	109192	6	Pb V
916.8	0				
918.1	1*d*	917.96	108937	6	
920.4	3	920.32	108658	5	
		920.95	108584	1	
922.5	4	922.48	108403	10	Pb IV?
923.4	1	923.52	108281	2	
924.5	0	924.59	108156	3	
		926.32	107954	4	
927.7	3	927.70	107794	6	
		930.50	107469	1	
932.3	3	932.23	107270	7	
933.7	0*d*	933.8	10708	?0	
937.2	2*d*	937.10	106712	5	
		940.74	106299	1	
944.6	00?				
946.4	00?				
		953.00	104932	4	
954.4	5	954.34	104784	6	
955.5	00?	955.33	104676	3	
		959.01	104274	2	
		960.93	104066	5	
		967.15	103396	4*d*	
970.3	0?	970.28	103063	1	
		974.27	102641	2*d*	
977.0	4	977.03	102351	8	C 977.031
		978.4	10221	0	
		979.47	102096	2	
981.2	0	981.07	101930	6	
		982.20	101812	1	
		989.15	101097	3	
		991.43	100864	2	
995.8	2	995.74	100428	8	
		997.0	10030	1	
		1002.9	9971	0	
1005.5	1	1005.56	99447	7	
		1007.7	9924	0	
		1009.5	9906	1	
		1011.05	98907	2*d*	
1012.5	00	1012.45	98770	3	
1021.4	00				
1022.2	00	1022.06	97842	0	
		1024.30	97628	2	

? (before intensity) Existence of line uncertain.
d Diffuse.
p Pair.
v Diffuse toward shorter wave-lengths.

TABLE VII. (continued)

Carroll		This investigation			
λ	Int.	λ	ν	Int.	Assignment
1028.7	10	1028.57	97222	8	Pb IV?
1030.5	3	1030.36	97054	6	
		1032.04	96896	2	
		1036.3	9650	0	
		1037.02	96430	2	
1041.3	3*d*	1041.10	96052	4*d*	
		1044.3	9576	2*d*	
1048.9	12	1048.84	95344	12	
1051.4	0				
1052.3	2	1052.21	95038	5	
		1053.8	9490	0	
		1056.43	94658	3	
		1059.3	9440	1	
1060.6	0	1060.63	94284	5	
1062.8	1*d*	1062.63	94106	0*d*	
1068.0	00				
1069.2	4	1069.07	93539	8	
		1070.83	93386	0	
1072.1	1	1072.05	93279	6	
1073.1	1	1073.1	9319	0	
1074.7	3	1074.63	93055	7	
1076.8	3	1076.72	92875	4	
		1079.81	92609	3	
1080.8	0	1080.85	92520	3	
		1082.51	92378	2	
		1084.12	92241	3	
1087.6	1	1087.34	91968	2	
1088.9	2	1088.82	91843	4	Pb V?
1090.1	0	1089.90	91752	1	
1094.3	00	1094.1	9140	1*d*	
1096.5	1*d*	1096.47	91202	2	
		1097.34	91129	0	
1098.4	0*d*	1098.37	91044	6	
		1098.7	9102	0	
1099.2	1*d*				
		1100.46	90871	2	
1103.6	0*d*	1103.7	9061	6*d*	
1104.8	00	1104.85	90510	1	
1105.6	00				
1108.7	1	1108.40	90220	5	
		1109.69	90115	3	
		1111.43	89974	1	
		1112.89	89856	0	
1115.0	2	1114.93	89692	7	
1116.2	4	1116.09	89598	7	
1117.4	0				
1118.9	00?	1118.60	89397	3	
1119.9	00	1119.56	89321	4	
		1121.19	89191	3	
1123.7	3	1123.45	89012	3	
1131.9	00				
1133.2	2	1133.09	88254	5	
1137.8	5*d*	1137.76	87892	8	Pb V
1142.9	1	1142.86	87500	6	
1145.0	3	1144.83	87349	6	
		1146.6	8722	0	
1148.3	0	1148.17	87095	4	
		1150.8	8690	0	
		1155.88	86514	2	
1158.0	8	1157.83	86368	8	Pb V
1165.1	4	1164.96	86840	8	
1167.0	4	1166.89	86698	8	
		1170.75	86415	1	
		1171.68	85347	2	
		1174.93	85111	2	C 1174.922
1176.0	00	1175.66	85059	4	C blend
		1176.32	85011	2	C 1176.359
		1178.47	84856	1	
1185.6	6	1185.37	84362	6	
1190.1	7	1189.85	84044	6	Pb V
1197.8	2	1197.68	83495	5	
1199.5	0				
1203.6	3	1203.4	8310	7	
1206.6	0	1206.61	82877	3	
1213.4	5	1213.20	82427	6	
		1214.21	82358	?1	
1215.8	2	1215	plate broken here		H 1215.680
1231.3	1	1231.15	81225	5*d*	
1233.6	3	1233.53	81068	5	
		1247.39	80167	0	C 1247.391
1248.6	2	1248.49	80097	3	Pb V
1250.6	4	1250.36	79977	6	
		1258.19	79479	?0	
		1260.94	79306	2	
		1264.52	79081	1*d*	
1266.9	1	1266.64	78949	7	
1274.6	0	1274.45	78465	5	
		1275.53	78399	2	
1279.5	3	1279.31	78167	6	

TABLE VIII. *Regular doublet screening numbers, $Z-Z_{eff}$, for shells lacking one d electron.*

Spectrum		I		II		III		IV		V	X-rays
$3d^9$	^2D 27 Co I, etc.	*1232.45a* 13.398	**−0.299**	*1507* 13.697	**0.182**	*2070* 13.515					
		−0.295		**0.181**		**0.145**					
$3d^94s$	^3D 28 Ni I, etc.	*1508.29* 13.693	**0.177**	*2069.7* 13.516	**0.146**	*2754* 13.370	**0.121**	*3575* 13.249	**0.088**	*4536* 13.161	
		0.127		**0.094**							
$3d^94s^2$	^2D 29 Cu I, etc.	*2042.9* 13.566	**0.144**	*2719.06* 13.422							
$3d^94s^24p^6$....											13.0
$4d^9$	^2D 45 Rh I, etc.	*2348.1* 25.171	**1.141**	*3539* 24.030							
		1.115		**0.457**							
$4d^95s$	^3D 46 Pd I, etc.	*3529.8* 24.056	**0.483**	*4574.8* 23.573	**0.395**	*5766.1* 23.178	**0.333**	*7108* 22.845	**0.293**	*8620* 22.552	
				0.252							
$4d^95s^2$	^2D 47 Ag I, etc.			*5634.8* 23.321							
$4d^95s^25p^6$....											24
$5d^9$	^2D 77 Ir I, etc.										
$5d^96s$	^3D 78 Pt I, etc.	*10132.0* 44.215	**0.982**	*12726.7* 43.233	**0.841**	*15556* 42.392	**0.857**	*18865* 41.535		*(22.6·10³)* (40.7)	
		0.660		**0.532**							
$5d^96s^2$	^2D 79 Au I, etc.	*12274* 43.555	**0.854**	*15038* 42.701							

a Possibly belongs to the configuration d^7s^2
( ) Extrapolated.

Table VIII is an extension of a table started by Laporte[7] when he applied the regular doublet law of x-ray spectroscopy (below, Eq. (3)) to d^9 doublets in the optical region. The doublet or triplet separation, and the screening number, are given for every spectrum with a configuration d^9, d^9s, or d^9s^2. The corresponding x-ray $M_{32}M_{33}$ and $N_{32}N_{33}$ screening numbers are included. The regularity of the separations is now recognized as a special case of Goudsmit's Γ sum rule.[8] Separations are given in italic, screening numbers in ordinary light face, and screening number differences in bold face type.

The slight increase in screening which occurs with the addition of an s electron (except in the case of Ni II, where the decrease is about as large as the probable error) becomes increasingly important with increasing atomic number. The addition of a second outer s electron to form a stable shell, has naturally more effect on the screening than the addition of the first. This property has often been observed in connection with the first order screening, that is with absolute term values; here we see it influencing the separations.

The downward slope of the screening number in an isoelectronic sequence also, becomes considerably greater as we go down in the periodic table; this fact, combined with the great magnitude of the separations themselves, made the predictions in the platinum-like sequence crude compared with those for the lighter atoms.

TABLE IX. *Mean distances (centroid distances) between configurations:* d^9s-d^9p *and* $d^{10}s-d^{10}p$.

Spectrum	I		II		III		IV		V
$3d^94s-3d^94p$ Ni I, etc.	28740		46705		63247		79459		95550
		17965	**1423**	*16542*	**330**	*16212*	**121**	*16091*	
$3d^{10}4s-3d^{10}4p$ Cu I, etc.	30700		49063		66313		83169		99875
		18363	**1113**	*17250*	**394**	*16856*	**150**	*16706*	
$4d^95s-4d^95p$ Pd I, etc.	28913		43879		57677		71067		84305
		14966	**1168**	*13798*	**408**	*13390*	**152**	*13238*	
$4d^{10}5s-4d^{10}5p$ Ag I, etc.	30165		45790		60080		73894		87557
		15625	**1335**	*14290*	**476**	*13814*	**151**	*13663*	
$5d^96s-5d^96p$ Pt I, etc.	36836		54308		(70600)		(86600)		(102500)
		17472		*(16300)*		*(16000)*		*(15900)*	
$5d^{10}6s-5d^{10}6p$ Au I, etc.	39902		57571		74032		90190		
		17669	**1208**	*16461*	**303**	*16158*			

( ) Extrapolated.

Table IX shows the progress of the "irregular doublet" separation $s-p$ for atomic systems built upon the ion configurations d^9 and d.^{10} The centroid (with each level assigned the weight $2j+1$) is taken as the best representative energy value for the configuration. The regularity of the other sequences indicates that the extrapolated values for Hg III, Tl IV, and Pb V are probably correct within about 200 units. First differences are in italic, and second differences in bold face type.

The spectra of the systems built upon the ion d^9 are very much like those built upon d^{10}, so far as the mean differences $s-p$ are concerned. The distance is about the same for Ni I as for Pd I; but its slope with increasing

---

[7] O. Laporte, Phys. Rev. **29**, 650 (1927).

[8] S. Goudsmit, Phys. Rev. **31**, 946 (1928).

nuclear charge is much greater in the first sequence than in the second. For Pt I the distance is more than one-fourth greater than for Ni I and Pd I, and the initial slope is almost as great in the third sequence as in the first; so the separation in Pb V is about ten percent greater than in Ge V and twenty percent greater than in Sn V.

III. THE VECTOR COUPLING

The absolute energy of an atom with a given net nuclear charge and a given electronic configuration may be determined approximately by certain well-known laws which apply quite independently of whether the spectrum is of the normal type.[4b] The special interest attached to the spectra we are considering lies in the relative behavior of the levels within each configuration. Naturally our study is based on the fundamental work of Goudsmit[9] and Uhlenbeck,[10] who pointed out the significance of the departures from the normal type, from the viewpoint of the vector model, using the $2p^53s$ and $2p^53p$ configurations of neon as an example. The configurations d^9s and d^9p are in fact close analogues of the famous example. The nickel-like spectra $3d^94s$, $3d^94p$ have already been treated in detail, under Professor Laporte's direction.[4b] We can now study the relative trends in fifteen spectra, in three closely analogous sequences.

First, however, let us glance at two theoretical "pure" coupling schemes.[10] In the normal, Russell-Saunders, or LS coupling scheme

$$(l_1l_2)(s_1s_2)=(LS)=J \qquad (1)$$

the atom is characterized by a constant or "quantized" resultant orbital angular momentum L and a constant angular momentum of electronic spin S. The subscripts 1 and 2 refer to the ion and the added electron, respectively. In the jj coupling scheme

$$(l_1s_1)(l_2s_2)=(j_1j_2)=J \qquad (2)$$

the ion (that is, the whole system except the most loosely bound electron) is characterized by a total angular momentum j_1; and the electron by a total angular momentum j_2.

There are three criteria for the empirical study of the vector coupling in a complex spectrum: (a) relative energy values, (b) behavior in a magnetic field, and (c) line intensities. The spectra in our sequences will be compared among themselves and with these "pure" cases, with respect to these properties.

(*a*) *Relative energy values*. Figures 1, 2, and 3 show the relative positions of the levels in each configuration. Unit distance for each spectrum is taken to be the total separation of the $d^9s\ ^3D$ (Table VIII). The zero of the figure, for each configuration, is arbitrarily chosen at the centroid.

The LS equation (1) yields, of course, normal triplets and singlets. The separations within a triplet are proportional to the higher j-values (Landé's

---

[9] S. Goudsmit, Zeits. f. Physik **32,** 794 (1925).

[10] S. Goudsmit and G. E. Uhlenbeck, Zeits. f. Physik **35,** 618 (1926).

[11] S. Goudsmit and C. J. Humphreys, Phys. Rev. **31,** 960 (1928).

rule[2]); the relative separations of the several d^9p triplets might be determined, with the use of one more empirical constant (Goudsmit's rule[11]). But the theory can not yet tell us the distance between multiplets; it can only say, that the distances between certain of them are large compared with the unit chosen in the figures. Due to this incompleteness of the theory it would be impossible to show the LS case in the figures.

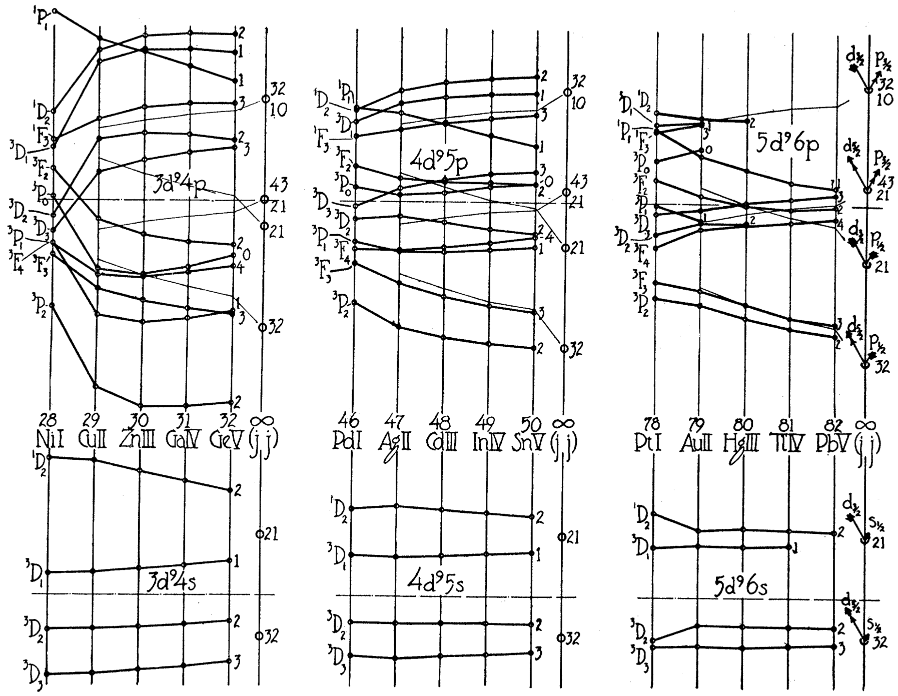

Fig. 1. Fig. 2. Fig. 3.

Relative positions of the levels in each configuration.

In the jj case, Eq. (2), on the other hand, we have definite knowledge of the gross structure of each configuration, at the expense of exact knowledge of the fine structure. This definite knowledge of the gross structure is given by the Sommerfeld regular doublet law

$$\Delta\nu = \frac{\alpha^2 R Z_{\mathrm{eff}}{}^4}{n^3 l(l+1)} \cdot \qquad (3)$$

The d^9s configuration splits into two groups; the duplicity arises from the doublet nature of the ion d^9. The d^9p configuration splits into four groups, due to the doublet nature of both d^9 and p.[12]

We can easily determine the interval between the states arising in the case of jj coupling from the two values $j_1 = 5/2$ and $j_1 = 3/2$ of the ion d^9 or

---

[12] It was supposed in a previous paper (4b) that the separation due to the p electron would be negligible, in this asymptotic case. The authors of that paper are indebted to Professor Goudsmit for pointing out this error.

minus d doublet, provided j_2 be kept constant. This interval is the same for both configurations d^9s and d^9p (neglecting a slight difference in screening). It is simply the total separation of the d^9s ^3D (unity, in the figure); this is the special case of the Γ sum rule, mentioned in connection with Table VIII.

The calculation of the interval between $j_2=1/2$ and $j_2=3/2$ (with j_1 kept constant) for d^9p is a little more complicated. We shall consider two cases: large net charge, and small net charge. As the nuclear charge increases in a given sequence, the system approaches asymptotically a condition in which we may neglect the penetration of the p orbit and the difference between Z_{eff} for the p separation and Z_{eff} for the d separation. Then the ratio of the p separation to the minus d separation (cancelling the numerators on the right-hand side of Eq. (3)) is

$3^3\cdot 2\cdot 3/4^3\cdot 1\cdot 2=1.27$ for the nickel-like spectra,
$4^3\cdot 2\cdot 3/5^3\cdot 1\cdot 2=1.54$ for the palladium-like spectra, and
$5^3\cdot 2\cdot 3/6^3\cdot 1\cdot 2=1.74$ for the platinum-like spectra.

The relative positions of the several groups of levels for this case, are plotted in the figures, in the columns labeled "∞_{jj}".

Where the net charge for the outer part of the orbit under consideration is small compared with the Z_{eff} of Eq. (3), as it is for the p separations of all our spectra, we must use the modification of (3) introduced by Landé for penetrating orbits:

$$\Delta\nu=\frac{\alpha^2 R Z_{\text{inner}}{}^2\, Z_{\text{outer}}{}^2}{n_{\text{eff}}{}^3 l(l+1)}\,. \tag{4}$$

We can calculate the separation for the d^9p configurations of the spark spectra of our sequences, by comparison with the principal doublet $d^{10}p$ ^2P separation, for the copper-, silver-, and gold-like spectra of the same atoms. It is not even necessary to calculate any new screening numbers. The effect of the tenth d electron, on the inner effective charge Z_{inner} may be neglected; while the outer effective charge Z_{outer} is given by the roman numeral which designates the spectrum. The following table gives the (configuration centroid) values of n_{eff} for the added p electron, calculated from the first two members of the s series, uncorrected:

d^9p	Ni I 1.87	Cu II 2.13				
$d^{10}p$		Cu I 1.82	Zn II 2.11	Ga III 2.31	Ge IV 2.46	As V 2.58
	Pd I 1.83	Ag II 2.17				
		Ag I 1.83	Cd II 2.16	In III 2.41	Sn IV 2.58	Sb V 2.74
	Pt I 1.72	Au II 2.11				
		Au I 1.73	Hg II 2.10	Tl III (2.40)	Pb IV(2.60)	Bi V (2.77)

The numbers in parentheses are extrapolations. Whenever this approximate n_{eff} is known for a d^9p configuration, it is almost the same as for the corresponding $d^{10}p$ configuration with the same net charge. We may use this fact in extrapolating the values of n_{eff} for the d^9p configurations. The errors due to the crudity of this approximation will tend to cancel out in the ratio, which is all that is needed for our purposes. Let us consider an example. For Hg II $d^{10}p$ the p separation is 9123. For Hg III it will be, by Eq. (4),

$9123\cdot 3^2\cdot 2.10^3/2^2\cdot 2.40^3=15720$. The approximate positions of the four groups into which the d^9p configurations would fall for the jj coupling case, calculated in this way, are shown by the light lines in the figures, connected with their respective "∞_{jj}" groups. It will be noticed that these calculations are completely independent of the empirical d^9p separation data.

Among empirical data, the comparison of energy values is the most accurately measurable of the three criteria for the study of coupling; it is also generally the first to indicate a breaking away from normal coupling. The figures show hardly any indication of similarity to normal spectra, even for Ni I, the most nearly normal of all; but we shall see below, that the Zeeman effect and line intensity data clearly show the *LS* character of several of these spectra.

Many of the levels show certain trends with increasing nuclear charge in an isoelectronic sequence, and the same trends with constant net charge but "passing down the column" in the periodic table; that is, Figs. 2 and 3 act something like successive extrapolations to the right, of Fig. 1. This behavior is most easily apparent in the simpler configuration d^9s. A table started earlier[4b] can be extended now, showing numerically the progress of the distance $d^9s\ ^3D_2-{}^3D_3$ in the figures; the values are:

LS coupling:	0.600				
Ni I, Cu II, etc.:	0.448	0.444	0.428	0.407	0.384
Pd I, Ag II, etc.:	0.337	0.345	0.330	0.309	0.287
Pt I, Au II, etc.:	0.077	0.204	0.204	0.190	0.170
jj coupling:	0.000				

Though the trend is not monotonically downward the tendency is unmistakable.

There is an anomalous break in the $d^9s\ ^3D_2$, $^1D_2$ curves at Pt I. This is the only exception to a regularity that persists among all the other known triplet-singlet configurations (except where the triplet separation is quite small). But the present assignment of d^9s levels in Pt I can not be avoided without making the anomaly much worse.

The d^9p levels show a decided tendency among the more highly ionized members of the palladium-like sequence, to form four groups. The grouping there agrees with the calculated *jj* grouping except that the levels $J=4$ and $J=0$ are too low. Although the data for the platinum-like sequence unfortunately are incomplete, the indications are that the configuration has arrived at a state of more nearly pure *jj* coupling. Toward the right-hand side of Fig. 3 both of the well-developed groups $J=2$, 3 and $J=4$, 2, 3, 1, are relatively much more concentrated than in Fig. 2, and here the quantitative agreement of the energies with the values independently calculated for the *jj* coupling (light lines in the figures) is quite satisfactory.

(*b*) *Behavior in a magnetic field.* Table X shows all the *g*-values available for our spectra, together with those calculated for the "pure" *LS* and *jj* cases:

$$g_{LS}=\frac{L}{J}g_L\cos(LJ)+\frac{S}{J}g_S\cos(SJ)=\frac{3J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

and

$$g_{jj}=\frac{j_1}{J}g_{j_1}\cos(j_1J)+\frac{j_2}{J}g_{j_2}\cos(j_2J)$$

$$=g_{j_1}\frac{J(J+1)+j_1(j_1+1)-j_2(j_2+1)}{2J(J+1)}+g_{j_2}\frac{J(J+1)+j_2(j_2+1)-j_1(j_1+1)}{2J(J+1)}.$$

TABLE X. *Zeeman effect data.*

Calculated *LS* coupling		Observed *g*-values					Calculated *jj* coupling		
structure	g_{LS}	Ni I	Cu II	Pd I	Ag II	Pt I	g_{jj}	J	structure
$d^9p\ {}^1F_3$	1.00		1.1	1.09	1.10	1.2	$1.07=\frac{16}{15}$	3	$-d_{3/2}+p_{3/2}$
${}^1D_2$	1.00		*n*	1.17	1.20	1.1	$1.07=\frac{16}{15}$	2	
${}^3D_1$	0.50		*n*	0.85	0.52	0.87	$1.07=\frac{16}{15}$	1	
${}^3P_0$	0/0						0/0	0	
${}^3F_4$	1.25		*n*	1.25	1.26	1.2	$1.25=\frac{5}{4}$	4	$-d_{5/2}+p_{3/2}$
${}^3D_3$	1.33		1.0	1.33	1.25	1.12	$1.24=\frac{223}{180}$	3	
${}^3F_2$	0.67		*n*	0.7	0.92	1.2	$1.21=\frac{109}{90}$	2	
${}^1P_1$	1.00	1.00	*n*	0.80	1.00	1.24	$1.10=\frac{11}{10}$	1	
${}^3D_2$	1.17		*n*	1.00	0.87	0.8	$0.77=\frac{23}{30}$	2	$-d_{3/2}+p_{1/2}$
${}^3P_1$	1.50		*n*	1.42	1.50	0.9	$0.83=\frac{5}{6}$	1	
${}^3F_3$	1.08		*n*	1.1	1.08	1.21	$1.11=\frac{10}{9}$	3	$-d_{5/2}+p_{1/2}$
${}^3P_2$	1.50		*n*	1.50	1.50	1.39	$1.29=\frac{58}{45}$	2	
$d^9s\ {}^1D_2$	1.00		*n*	1.00	1.03	1.17	$1.10=\frac{11}{10}$	2	$-d_{3/2}+s_{1/2}$
${}^3D_1$	0.50		*n*	0.50	0.50	0.50	$0.50=\frac{1}{2}$	1	
${}^3D_2$	1.17		*n*	1.15	1.13	1.01	$1.07=\frac{16}{15}$	2	$-d_{5/2}+s_{1/2}$
${}^3D_3$	1.33		*n*	1.33	1.33	1.3	$1.33=\frac{4}{3}$	3	

n Normal, within probable error of 0.1.

The empirical values were derived in a few cases from blends, by Russell and Shenstone's method;[13] but usually from resolved patterns. The largest probable errors (depending on blends) are about 0.1, but for most levels the probable errors are in the neighborhood of 0.03. In the interesting cases

TABLE XI. *Intensities.*

$3d4s$	$^3D_3$	$^3D_2$	$^3D_1$	$^1D_2$
	Cr V			
$3d4p\,^3F_4$	8			
$^3F_3$	0	7		—
$^3F_2$	—	0	6	—
$^3D_3$	7	1		—
$^3D_2$	3	5	1	—
$^3D_1$		2	4	—
$^3P_2$	7	5	—	—
$^3P_1$		5	3	—
$^3P_0$			3	
$^1F_3$	—	—		7
$^1D_2$	—	0	0	6
$^1P_1$		—	—	3

d^9s	$^3D_3$	$^3D_2$	$^3D_1$	$^1D_2$	$^3D_3$	$^3D_2$	D_1	$^1D_2$	$^3D_3$	$^3D_2$	D_1	$^1D_2$	$^3D_3$	$^3D_2$	$^3D_1$	$^1D_2$	$^3D_3$	$^3D_2$	$^3D_1$	$^1D_2$
	Ni I				Cu II				Zn III				Ga IV[4b]				Ge V[4c]			
$3d^94p\,^3F_4$	9.5				10				8				8				7			
$^3F_3$	6.6	8.6		7.8	4	10		6	4	5		4	5	8		2	5	5		0
$^3F_2$	0.9	5.2	9.1	2.7	3	4	8	0	4*c*	5	5	2	1	5	8	0	—	4	5	0
$^3D_3$	6.6	6.4		6.5	8	—		9	4	—		5	5	0		8	5	0		0
$^3D_2$	0.7	10.0	5.2	5.0	1	8	3	7	1	4	4*c*	4	0	5	3	6	—	6	3	5
$^3D_1$		0.1	8.8	0.2		2	7	4		3	3	4*c*		2	5	2		2	4	0
$^3P_2$	10.0	5.3	1.0	0.4	10	5	2	7	5	3	2	2	8	1	0	1	6	0	0	0
$^3P_1$		8.6	6.7	1.0		8	5	2		5	4	4		5	2	1		8*c*	1	4
$^3P_0$			7.0				5				4				3				5	
$^1F_3$	5.0	5.5		12.4	7	6		6	4	3		5	5	5		9*c*	6	5		5
$^1D_2$	0.3	1.3	0.2	9.3	2	2	5	5	3	4	4	4	1	3	4	5	2	3	4	8
$^1P_1$		4.0	1.7	10.6		1	1	5		2	3	5		0	2	6		—	1	4
	Pd I				Ag II				Cd III[4d]				In IV[4d]				Sn V			
$4d^95p\,^3F_4$	10				10				8				8				8			
$^3F_3$	5	10		2	7	9		8	6	8		4	3	5		1	3	6		2
$^3F_2$	—	0	5	2	—	5	7	8	1?	5	5	5	1	4	3	2	0	5	2	4
$^3D_3$	10	3		2	8	5		8	6	4		5	5	4		—	6	2?		2
$^3D_2$	1	5	2	2	1	8	8	1	1?	4	6	3	1	4	4	2	?	6	5	4
$^3D_1$		2	3	2		2	6	0		4	5	2		2	4	2		3	4	1
$^3P_2$	20	1	0	2	10	3	2	3	8	2	1?	2	6	?	—	3	8	?	—	1
$^3P_1$		10	1	1		8	6	6		6	3	3		4	1	1		5	2	3
$^3P_0$			3				7				4				4				4	
$^1F_3$	1	3		5	2	4		8	3	4		6	2	3		6	2	4		6
$^1D_2$	1	2	3	2	1	2	4	6	2	3	4	6	1	1	3	5	—	1	5	5
$^1P_1$		0	3	2		2	1	8		2	4	5		2	3	5		2	2	3
	Pt I[4e,f]				Au II				Hg III[4g]				Tl IV				Pb V			
$5d^96p\,^3F_4$	10				10				10				6				8			
$^3F_3$	7	10		—	8	9		6	8	8		3	4	8		5	8	6		0
$^3F_2$	0	1	3	2	1	2	7	6	9	6	8	7	2	4	2	5	5*c*	6		8
$^3D_3$	1	2*c*		3*c*	9	7		4	8	9		4	4	4		1*c*	7	6		1
$^3D_2$	—	3	3	1	4	9	7	1	5	8	6	6								
$^3D_1$		0	1	1		4	7	2												
$^3P_2$	17	3	1	1	10	7*c*	2	6	8	7	0	3	7	5	3	3	6	3		0
$^3P_1$		1	3	—		7	2	7												
$^3P_0$			1				6													
$^1F_3$	0	2		1	2	3		9												
$^1D_2$	0?	0	1	1	4	6	6	7	1	5	2	8								
$^1P_1$		—	0	1		6	3	8		6	5	6		3	—	3		?5*c*		?4

— Permitted line missing.
c Line also classified elsewhere.
? (before intensity) Existence of level uncertain.
? (elsewhere) Existence of line uncertain.

---

[13] A. G. Shenstone, article forthcoming in Phil. Mag.

of multiply ionized atoms the lines lie in the ultra-violet, generally beyond the reach of present day Zeeman-effect technique.

If only the g-values were considered, clearly the designations $^3D_2$ and $^1D_2$ of the d^9s configuration of Pt I would have to be interchanged. Similarly in the case of several of the d^9p levels the g's pass somewhat beyond the asymptotically expected values. Marked transient disturbances, too, occur in the intermediate coupling cases of Cu II $J=3$ and Pd I $J=1$. But for the rest, there appears to be a trend toward the g_{jj} values.

(*c*) *Line intensities.* The evaluation of relative intensities is especially difficult for the heavy atoms, because of the large separations of related levels. For Pt I, for instance, the transition $d^9s \leftarrow d^9p$ extends from the green to the edge of the Schumann region; one "multiplet" $^3D-{}^3D$ covers the range from λ3485 to λ2028.

Table XI shows the relative intensities in our spectra, along with those for Cr V $3d4s-3d4p$, which is inserted as an example of a normal-type complex spectrum for a many times ionized atom. The intensities for some spectra have been multiplied by a factor so that the numbers for the several spectra are of the same order of magnitude.

Where the lists of several investigators are available for the lines of an element, even the best show wide disagreements in intensity, particularly in the Schumann region. For instance, the two available lists give the following intensities for the "multiplet diagonals" $^3D_3-{}^3F_4$, $^3D_2-{}^3F_3$, etc., of In IV:

Gibbs and White:	15, 10, 6; 10, 8, 7; 12, 7, 7
Carroll:	5, 6, 3; 5, –, 4; 2, 5, 3.

(The dash, –, indicates that the line $^3D_2$–$^3D_2$ is missing in Carroll's list, although it lies in the region reported by him.) It is impossible then in the present state of our knowledge of intensities, to distinguish between two influences: the crudity of the data, which has introduced spurious apparent changes; and actual changes in the character of the levels, which probably have influenced the relative intensities.

But at least we can say that in only three of our spectra, Ni I, Pd I, and Ag II, is the evidence of the intensities sufficient for the unambiguous assignment of complete names (including multiplicities and L-values) to the levels in these spectra. As examples of the ambiguities, the cases of $^3D_3$ and $^1F_3$ in the nickel-like spectra and $^3F_2$ and $^3D_2$ in the palladium-like spectra are instructive.

IV. DISCUSSION

Significance of the jj coupling. Three kinds of terms contributing toward the total energy, play important rôles in the relative separations of the levels of a configuration: first, the mutual spin interaction energy term[14]

---

[14] From the viewpoint of this vector model discussion it is immaterial whether the terms discussed are interaction terms in a strict sense, or not. Large (s_is_k) interaction, for instance, means here simply that levels whose vector pictures differ only in the resultant of s_i and s have greatly different energies.

whose importance in normal spectra is represented by the close coupling or association of the spins (s_is_k) in Eq. (1); second, the mutual orbital interaction (l_il_k), which shares the importance of (s_is_k) in Eq. (1); third, the orbit-spin interaction (l_is_i), which determines the multiplet separations or more generally the Goudsmit γ's.[8] This last term is small for normal coupling, but becomes predominant in the case of *jj* coupling, Eq. (2). (The small $(l_is_k)_{k\neq i}$ term may be neglected except for extremely light atoms.[15])

We were able to solve quantitatively for the asymptotic behavior of the separations in the *jj* case, because the predominant (l_is_i) contribution (the $\Delta\nu$ of Eq. (3)) is given by the solution of the one body problem. There is no such quantitatively useful theoretical expression yet for the (l_il_k) or (s_is_k) terms. It is an old empirical fact, that the (s_is_k) term (the "triplet-singlet distance") depends only slightly upon the atomic number, so that we were prepared to find the (s_is_k) interaction small compared with the fourth-power dependence of the (l_is_i) term for the more highly ionized members of an isoelectronic sequence, as well as for the heavier members of a column in the periodic table. The *jj*-like behavior of Tl IV and Pb V gives us the new empirical fact that here the (l_il_k) term also is small compared with the (l_is_i) term.

Non-occurrence of certain expected levels. Possibly the fact that only the levels built upon the lower level $d^9\ {}^2D_{5/2}$ have been found for the d^9p configuration of the spectra shown toward the right in Fig. 3, in spite of the stability of the missing $d^9\ {}^2D_{3/2}+p\ {}^2P_{1/2}$ levels, indicates a relatively high probability for levels built upon the more stable state of the ion. This is analogous to the occurrence of only the lower levels in the configuration $6p6d$ of Pb I; though the latter case is complicated by the relatively low ionizing potential of Pb I.

Naming the levels, and coordination of levels. The conventional notation, which has been used here, assigns an electronic configuration and quantum numbers J, L, and S to each level; that is, it is exactly suited to the description of normal spectra. We have seen that although the configuration and J-value are quite definite, for some of the levels in our spectra all the criteria for the assignment of L and S have broken down; there is no evidence that these symbols retain any meaning, in these cases. If we are to endow the symbols with a meaning, we must postulate that L and S would assume the assigned values, if the level were traced through a continuous change of coupling to the normal. In many of our cases it would be more natural to use a notation based on j_1 and j_2 (Table X, last two columns). Such a notation is used as an alternative, in Tables II and V.

The comparison of one spectrum with others in its column of the periodic table, and especially with others in its isoelectronic sequence, is a means frequently used in the naming of energy levels; it is only by this means that the levels newly named in this paper, could have been named according to the usual notation. The fact that levels of the same name are approaching

---

[15] W. Heisenberg, Zeits. f. Physik **39**, 499 (1926).

the same grouping in both Figs. 2 and 3 (for instance: ${}^3P_2$, ${}^3F_3 \sim d^9{}_{5/2}\, p_{1/2}$) is worth noting but probably not very important, as it might naturally have been expected from our extrapolative way of choosing the names.

The problem of naming levels is closely related to that of coordination. Hund[16] has recently advanced the conjecture that except where symmetry considerations demand it, levels do not cross each other. Figures 1 and 2 show three instances of levels with the same J, crossing: ${}^3D_2$ and ${}^3F_2$ near Ni I, and ${}^3D_1$ and ${}^1P_1$ near Zn III and again near Ag II.[17] But in order that the idea of "crossing" in general have meaning, it is necessary to identify a level at two points, between which it is "to cross" or "not to cross" another. We must treat the energy as a function of a continuous parameter. In questions of spectral series it is the dependence upon principal quantum number which is at issue; and in isoelectronic sequences, dependence upon electric charge. But the discreteness of quantum numbers lies at the very root of quantum mechanics; therefore it appears that coordination of levels to series limits, in general, is without physical meaning. Likewise there can be little serious doubt that the discreteness of electric charge is as deeply founded, although the present-day equations contain Ze as a continuous parameter. It is therefore doubtful whether the giving of "normal" names to levels has any meaning except in special cases.

Note added to proof, May, 1929. Professor Hund explains that the crossing of levels is never in disagreement with his conjecture, when supported by experimental evidence such as that of the intensities here; for, any such experimental evidence reveals a symmetry property of the system. The non-crossing conjecture may best be treated, then, simply as a convention for naming levels where experiment does not distinguish sharply in character between them.

Note added June 27, 1929. K. R. Rao, Phys. Soc. London Proc. *41*, 361 (1929) has classified Tl IV independently, using Carroll's data. Rao gives sixteen levels, of which six agree with six of the ten in this paper. Rao's $d^9s\,{}^3D_1 = 18614$ makes Table VIII look better ($s = 41.666$) than at present, but its existence depends largely upon that of the unverified levels above 100,000. Figure 3 of this paper decides in favor 92617 (Rao's alternative) for $d^9p\,{}^3F_4$.

---

[16] F. Hund, Zeits. f. Physik **52**, 601 (1928).

[17] Of course it would have been possible to connect the levels in the figures so that no two lines connecting levels with the same J, should cross. But these "crossing" levels, on the whole, retain nearly normal intensities, and the evidence of the intensities as well as the naturally expected curve smoothness, is in favor of crossing. (But for $d^9p\,{}^3D_1$, ${}^1P_1$ the nearly equal intensities in Zn III and nearly equal intensities and g-values in Pd I are interesting. The naming of Pd I d^9p ${}^3D_1$, ${}^1P_1$ is almost purely arbitrary.) On the other hand, Shenstone (4a, 13) has shown that if relative energy is plotted against total quantum number in any known d^9, s series, these criteria of intensities, g-values, and smoothness (in this case, fitting a Rydberg-Ritz formula) indicate non-crossing.