THE
PHYSICAL REVIEW

THE THEORY OF COMPLEX SPECTRA II*

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(Received March 20, 1931)

ABSTRACT

Formulas for the relations between the energies of multiplets arising from the same electron configuration for all two-electron configurations up to ff and several cases of three-electron configurations are worked out following Slater's method; Slater's table of a's and b's being extended to cover f electrons. A systematic comparison of the known data with this first order perturbation theory shows poor agreement in many cases and good agreement in many. The theory predicts the observed alternation in the relative positions of singlet and triplet through S, P, D, F, etc. in the pp, pd, and pf triads, and the dd and df pentads. In general the p electron configurations fit very poorly; a uniform trend with atomic number is observed for p^3 and good fits are obtained for $4p3d$ in Ti III, V IV, and Cr V. For d electrons the theory fits very well in the first long period of the periodic table, and fairly well in the second. The ^1S of d^2 and the ^2D of d^2s are predicted much higher than the levels assigned to those multiplets when such an assignment is made. d^3 fits well except for ^2P. An energy level table of La II is given as recently analysed by Meggers and Russell. Here we have complete $5d4f$ and $4f^2$ configurations which fit the theory very well, these calculations having assisted in the assignment of some of the singlets and resulted in a rearrangement of singlet lines.

§1. INTRODUCTION

THIS paper is a sequel to one[1] published last fall in which the first steps were taken toward working out the second approximation for atomic spectra with Russell-Saunders coupling. Before going on with that work it was thought desirable to make a careful study of the application of the first approximation formulas, given by Slater's method,[2] to all of the known data. That is the subject of this paper.

It will be recalled that the first-order calculation gives formulas for the energy of each of the multiplets arising from a given electron configuration in terms of certain integrals taken over the radial factor of the wave function for an electron in the central force field that lies at the basis of the calculations. These integrals represent the perturbation energy due to the electro-

* This paper was presented at the New York Meeting of the American Physical Society, February 27, 1931.

[1] Condon, Phys. Rev. **36**, 1121 (1930).

[2] Slater, Phys. Rev. **34**, 1293 (1929).

static repulsion of the electrons. It is inconvenient to work out these integrals for they involve the unknown wave functions of the screened average force field in which the electrons move. Instead these integrals are treated as adjustable (except for restrictions such as that certain of them are essentially positive, etc.) in order to see how well the data can be represented. If a good fit is obtained that is, therefore, only a partial confirmation of the theory, for the question still remains open whether the relative magnitudes assumed for the several integrals are really compatible with their definition as integrals.

Since Meggers and Russell[3] have recently obtained for the first time, in La II, complete sets of multiplets involving the two-electron configurations pf, df, f^2 we have thought it worthwhile to extend Slater's tables of a's and b's to provide the necessary coefficients for applying the method to configurations involving f electrons. These results are presented in §2. In §3 and §4 the explicit formulas are given for the first-order energies in a number of important configurations and in §5, §6, and §7 comparison of the formulas with the data is made.

§2. Slater's Coefficients for f Electron Configurations

In Slater's paper[2] there are a few details connected with normalization that need to be straightened out. Slater, in his manuscript, had normalized his wave functions in an unusual way: namely, so that the normalizing integral over the spherical harmonic factor was set equal to 4π instead of 1. This requires the normalizing integral over the radial coordinate to be set equal to $1/4\pi$. When his paper went through the Physical Review office one of us (E.U.C.) thought that a mistake had been made in the normalizing factor and inserted a $(2\pi)^{-\frac{1}{2}}$ to normalize the $\Phi(m_l/\phi)$ on page 1308 in the usual way. As Slater was in Europe at the time he did not have an opportunity to set the matter straight again. Therefore this factor should be removed from the $\Phi(m_l/\phi)$ on page 1308 and then it should be borne in mind, what Slater does not mention, that the radial wave-function is to be normalized to $1/4\pi$ instead of 1. The usual normalization of each factor to 1, is the one we prefer. To have this one needs to leave the Φ factor as printed on page 1308, to insert $2^{-\frac{1}{2}}$ on the right side of the equation defining $\Theta(lm_l/\theta)$ on that page, to remove the factor 4π in the equation for $I(nl)$ on page 1310 and the factor $(4\pi)^2$ in the equations for F^k $(nl; n'l')$ and $G^k(nl; n'l')$ on page 1311.

We have also found it convenient to treat the a's and b's of page 1311 as integers by associating the denominator of the a's and b's as they occur in the tables of page 1312 with the corresponding F. Therefore we write

$$F_k(nl;\ n'l') = \frac{1}{D_k} F^k(nl;\ n'l')$$

where F^k is Slater's F and D_k is the denominator of the fractional value for $a^k(l,\ m_l;\ l'm_l')$ as given on page 1312. The corresponding definition of G_k is also made.

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[3] See §7 of this paper.

Having detected an error in Slater's table of b's by reaching an inconsistency in deriving the energy levels for the pd configuration it was thought worthwhile to check these tables by a complete recalculation using Gaunt's formulas[4] for the integrals. These formulas were also used to extend the tables to the pairs, sf, pf, df, ff. This straightforward but laborious computation makes us now feel confident that there are no errors in Slater's table of page 1312 except the one originally detected. The value

$$b^3(1, \pm 1; 2, \mp 2) = 45/245$$

is correct, instead of 9/245 as printed.

The extension to f electron values is covered in Tables I and II.

TABLE I. *Extension of table of* $a^k(lm_l; l'm_l')$

Electrons	l	m_l	l'	m_l'	$k = 0$	2	4	6
sf	0	0	0	± 3	1			
				± 2	1			
				± 1	1			
				0	1			
pf	1	± 1	3	± 3	1	5/75		
	1	± 1	3	± 2	1	0		
	1	± 1	3	± 1	1	-3		
	1	± 1	3	0	1	-4		
	1	0	3	± 3	1	-10		
	1	0	3	± 2	1	0		
	1	0	3	± 1	1	6		
	1	0	3	0	1	8		
df	2	± 2	3	± 3	1	10/105	3/693	
	2	± 2	3	± 2	1	0	-7	
	2	± 2	3	± 1	1	-6	1	
	2	± 2	3	0	1	-8	6	
	2	± 1	3	± 3	1	-5	-12	
	2	± 1	3	± 2	1	0	28	
	2	± 1	3	± 1	1	3	-4	
	2	± 1	3	0	1	4	-24	
	2	0	3	± 3	1	-10	18	
	2	0	3	± 2	1	0	-42	
	2	0	3	± 1	1	6	6	
	2	0	3	0	1	8	36	
ff	3	± 3	3	± 3	1	25/225	9/1089	1/7361.64
	3	± 3	3	± 2	1	0	-21	-6
	3	± 3	3	± 1	1	-15	3	15
	3	± 3	3	0	1	-20	18	-20
	3	± 2	3	± 2	1	0	49	36
	3	± 2	3	± 1	1	0	-7	-90
	3	± 2	3	0	1	0	-42	120
	3	± 1	3	± 1	1	9	1	225
	3	± 1	3	0	1	12	6	-300
	3	0	3	0	1	16	36	400

Note: In cases with two $\pm$ signs, the two can be combined in any of the four possible ways.

§3. THE ENERGY LEVELS IN TWO-ELECTRON CONFIGURATIONS

Slater has treated in detail the method whereby the energy levels of the several multiplets are to be found in terms of the F and G perturbation integrals and has given some examples. He has shown that the electrons in

[4] Gaunt, Phil. Trans. Roy. Soc. **A228**, 151 (1929).

closed shells are without direct effect on the perturbation theory, although of course, they have the indirect effect of determining the nature of the best

TABLE II. *Extension of table of* $b^k(lm\ ;\ l'm_l')$

Electrons	l	m_l	l'	m_l'	$k=0$	1	2	3	4	5	6
sf	0	0	3	±3				1/7			
	0	0	3	±2				1			
	0	0	3	±1				1			
	0	0	3	0				1			
pf	1	±1	3	±3			45/175		1/189		
	1	±1	3	±2			30		3		
	1	±1	3	±1			18		6		
	1	±1	3	0			9		10		
	1	0	3	±3			0		7		
	1	0·	3	±2			15		12		
	1	0	3	±1			24		15		
	1	0	3	0			27		16		
	1	±1	3	∓3			0		28		
	1	±1	3	∓2			0		21		
	1	±1	3	∓1			3		15		
df	2	±2	3	±3		15/35		10/315		1/1524.6	
	2	±2	3	±2		5		20		5	
	2	±2	3	±1		1		24		15	
	2	±2	3	0		0		20		35	
	2	±1	3	±3		0		25		7	
	2	±1	3	±2		10		15		24	
	2	±1	3	±1		8		2		50	
	2	±1	3	0		3		2		80	
	2	0	3	±3		0		25		28	
	2	0	3	±2		0		0		63	
	2	0	3	±1		6		9		90	
	2	0	3	0		9		16		100	
	2	±2	3	∓3		0		0		210	
	2	±2	3	∓2		0		0		126	
	2	±2	3	∓1		0		10		70	
	2	±1	3	∓3		0		0		84	
	2	±1	3	∓2		0		25		112	
	2	±1	3	∓1		0		15		105	
ff	3	±3	3	±3	1		25/225		9/1089		1/7361.64
	3	±3	3	±2	0		25		30		7
	3	±3	3	±1	0		10		54		28
	3	±3	3	0	0		0		63		84
	3	±2	3	±2	1		0		49		36
	3	±2	3	±1	0		15		32		105
	3	±2	3	0	0		20		3		224
	3	±1	3	±1	1		9		1		225
	3	±1	3	0	0		2		15		350
	3	0	3	0	1		16		36		400
	3	±3	3	∓3	0		0		0		924
	3	±3	3	∓2	0		0		0		462
	3	±3	3	∓1	0		0		42		210
	3	±2	3	∓2	0		0		70		504
	3	±2	3	∓1	0		0		14		378
	3	±1	3	∓1	0		24		40		420

Note: In cases where there are two ± signs, the two upper or the two lower signs must be taken together.

central field on which to base the approximation. Therefore, we do not need to give the details of the calculations but merely summarize the results.

Slater's F^k integrals are necessarily positive and decreasing with increas-

ing k, from their definition. Therefore, since the denominator D in the definition of our F_k increases rapidly, F_k necessarily decreases very rapidly with increasing k. Since the G's are not essentially positive by definition, no definite statement can be made concerning their relative magnitudes; however, in every instance we have found, the G_k's have been positive and rapidly decreasing with k. Although not consistent with its definition as an integral, it is convenient to measure F_0, which occurs in the formula for each multiplet, from an arbitrary low level of the spectrum. (Slater's theory provides an integral I, dependent only on the configuration, to locate the height of the whole multiplet.)

If one electron is in an s state the result is simply a singlet and triplet whose L is the l of the other electron outside closed shells, as Slater shows on page 1315, duplicating by this method a result of Heisenberg.

For pp, non-equivalent p electrons, Slater gives the triplet intervals. The complete formulas are, if ^3P is written for "relative energy of the center of gravity of the ^3P terms,"

$$
\begin{aligned}
^1S &= F_0 + 10F_2 + G_0 + 10G_2 \\
^3S &= F_0 + 10F_2 - G_0 - 10G_2 \\
^1P &= F_0 - 5F_2 - G_0 + 5G_2 \\
^3P &= F_0 - 5F_2 + G_0 - 5G_2 \\
^1D &= F_0 + F_2 + G_0 + G_2 \\
^3D &= F_0 + F_2 - G_0 - G_2
\end{aligned}
\qquad (pp)
$$

We note that the arithmetic mean of the corresponding singlet and triplet energies is independent of the G's while corresponding singlet-triplet intervals are independent of F's. Also since $G_2 \ll G_0$ usually we have $^1S > {}^3S$ and $^1P < {}^3P$ and $^1D > {}^3D$; an alternation which is quite a general prediction of the theory.

For p^2, equivalent p electrons, the ^3S, ^1P and ^3D are ruled out by the exclusion principle and the formulas for what is left are the same as those for the arithmetic means of singlet and triplet in pp, namely

$$
\begin{aligned}
^1S &= F_0 + 10F_2 \\
^3P &= F_0 - 5F_2 \\
^1D &= F_0 + F_2.
\end{aligned}
\qquad (p^2)
$$

The formulas for dd and d^2, also ff and f^2, show similar relationships. For dd we have

$$
\begin{aligned}
^1S, {}^3S &= F_0 + 14F_2 + 126F_4 \pm (G_0 + 14G_2 + 126G_4) \\
^1P, {}^3P &= F_0 + 7F_2 - 84F_4 \mp (G_0 + 7G_2 - 84G_4) \\
^1D, {}^3D &= F_0 - 3F_2 + 36F_4 \pm (G_0 - 3G_2 + 36G_4) \\
^1F, {}^3F &= F_0 - 8F_2 - 9F_4 \mp (G_0 - 8G_2 - 9G_4) \\
^1G, {}^3G &= F_0 + 4F_2 + F_4 \pm (G_0 + 4G_2 + G_4)
\end{aligned}
\qquad (dd)
$$

where the upper sign is for the singlet and the lower for the triplet. For d^2 the multiplets are ^1S, ^3P, ^1D, ^3F, ^1G and their energies are given by the same formulas upon omitting the terms involving G integrals.

For pd the formulas are

$$^1P, \, ^3P \, = F_0 + 7F_2 \pm (\, G_1 + 63G_3)$$

$$^1D, \, ^3D = F_0 - 7F_2 \mp (3G_1 - 21G_3) \qquad (pd)$$

$$^1F, \, ^3F = F_0 + 2F_2 \pm (6G_1 + 3 \, G_3).$$

This shows the same alternation in sign of the leading G integral but differs from the preceding ones in that the F and G parts are not similar.

The formulas for pf are

$$^1D, \, ^3D = F_0 + 12F_2 \pm (\, 3G_2 + 36G_4)$$

$$^1F, \, ^3F = F_0 - 15F_2 \mp (15G_2 - 9G_4) \qquad (pf)$$

$$^1G, \, ^3G = F_0 + 5F_2 \pm (45G_2 + G_4).$$

The formulas for df are

$$^1P, \, ^3P \, = F_0 + 24F_2 + 66F_4 \pm (\, G_1 + 24G_3 + 330G_5)$$

$$^1D, \, ^3D = F_0 + 6F_2 - 99F_4 \mp (\, 3G_1 + 42G_3 - 165G_5)$$

$$^1F, \, ^3F = F_0 - 11F_2 + 66F_4 \pm (\, 6G_1 + 19G_3 + 55G_5) \qquad (df)$$

$$^1G, \, ^3G = F_0 - 15F_2 - 22F_4 \mp (10G_1 - 35G_3 - 11G_5)$$

$$^1H, \, ^3H = F_0 + 10F_2 + 3F_4 \pm (15G_1 + 10G_3 + G_5).$$

Finally the formulas for two non-equivalent f electrons are

$$^1S, \, ^3S \, = F_0 + 60F_2 + 198F_4 + 1716F_6 \pm (G_0 + 60G_2 + 198G_4 + 1716G_6)$$

$$^1P, \, ^3P \, = F_0 + 45F_2 + 33F_4 - 1287F_6 \mp (G_0 + 45G_2 + 33G_4 - 1287G_6)$$

$$^1D, \, ^3D = F_0 + 19F_2 - 99F_4 + 715F_6 \pm (G_0 + 19G_2 - 99G_4 + 715G_6)$$

$$^1F, \, ^3F = F_0 - 10F_2 - 33F_4 - 286F_6 \mp (G_0 - 10G_2 - 33G_4 - 286G_6) \qquad (ff)$$

$$^1G, \, ^3G = F_0 - 30F_2 + 97F_4 + 78F_6 \pm (G_0 - 30G_2 + 97G_4 + 78G_6)$$

$$^1H, \, ^3H = F_0 - 25F_2 - 51F_4 - 13F_6 \mp (G_0 - 25G_2 - 51G_4 - 13G_6)$$

$$^1I, \, ^3I = F_0 + 25F_2 + 9F_4 + F_6 \pm (G_0 + 25G_2 + 9G_4 + G_6),$$

from which the values for f^2 can be obtained by ignoring the part involving G integrals and remembering that the allowed terms are ^1S, ^3P, ^1D, ^3F, ^1G, ^3H and ^1I.

The most striking thing about these results perhaps is the uniform way in which an alternation of the relative height of singlet and triplet is predicted, since in most cases the G of lowest index will be enough larger than the others to dominate the whole expression in the G's. Russell and Meggers[5] called attention to this alternation in 1927 and "commended it to the attention of theoretical investigators." Its explanation by the quantum mechanics must be counted as an important success for the theory.

[5] Russell and Meggers, Sci. Papers Bur. Stand. **22**, 364 (1927).

§4. Three-Electron Configurations

It would be a waste of time to work out all possible three-electron configurations at present, therefore we confine ourselves to cases for which we have been able to find experimental data with which to check the results. The addition of an s electron to p^2, d^2 or pd gives three important cases.

According to the vector coupling viewpoint the addition of an s electron to p^2 gives the results $^1S \rightarrow {}^2S$, $^3P \rightarrow {}^2P$ and ^4P, and $^1D \rightarrow {}^2D$. In the formulas for p^2s the F integrals are of the type $F(np^2)$ while there now appears a G integral to represent the action of the s electron, which is $G_1(np, n's)$:

$$
\begin{aligned}
^2S &= F_0 + 10F_2 - G_1 \\
^2P &= F_0 - 5F_2 + G_1 \\
^4P &= F_0 - 5F_2 - 2G_1 \\
^2D &= F_0 + F_2 - G_1
\end{aligned}
\qquad (p^2s)
$$

where $F_0 = 2F_0(np, n's) + F_0(np^2)$. Thus $3G_1$ is the $^2P - {}^4P$ interval and the quantities ^2S, $(^2P + 2{}^4P)/3$ (which is the center of gravity of this combination), and ^2D have the same intervals as ^1S, ^3P and ^1D in p^2.

Similar results hold for d^2s. Here too the singlets of d^2 become doublets and the triplets split into doublets and quartets:

$$
\begin{aligned}
^2S &= F_0 + 14F_2 + 126F_4 - G_2 \\
^2P &= F_0 + 7F_2 - 84F_4 + G_2 \\
^4P &= F_0 + 7F_2 - 84F_4 - 2G_2 \\
^2D &= F_0 - 3F_2 + 36F_4 - G_2 \\
^2F &= F_0 - 8F_2 - 9F_4 + G_2 \\
^4F &= F_0 - 8F_2 - 9F_4 - 2G_2 \\
^2G &= F_0 + 4F_2 + F_4 - G_2
\end{aligned}
\qquad (d^2s)
$$

in which

$$
\begin{aligned}
F_0 &= F_0(nd^2) + 2F_0(nd, n's) \\
G_2 &= G_2(nd, n's).
\end{aligned}
$$

The relation to d^2 is evident on comparison. Further we see that the doublet-quartet interval is the same for the P and the F multiplets, being equal to $3G_2$.

In the case of pds we encounter the first instance in which it is impossible to get complete formulas by Slater's diagonal sum method since this configuration gives two different ^2P, ^2D and ^2F. This comes about because pd gives $^{1,3}P,D,F$ and the added s electron makes the singlets into $^2P,D,F$, and splits each triplet into $^{2,4}P,D,F$. In such a case the method gives simply the arithmetic mean of the two doublets of similar L value:

$$
\begin{aligned}
(^2P) &= F_0 + 7F_2 \\
^4P &= F_0 + 7F_2 - (\ G_1{}^{pd} + 63G_3{}^{pd}) - G_1{}^{sp} - G_2{}^{sd}
\end{aligned}
$$

$$(^2D) = F_0 - 7F_2$$

$$^4D = F_0 - 7F_2 + (3G_1{}^{pd} - 21G_3{}^{pd}) - G_1{}^{sp} - G_2{}^{sd}$$

$$(^2F) = F_0 + 2F_2$$

$$^4F = F_0 + 2F_2 - (6G_1{}^{pd} + 3\ G_3{}^{pd}) - G_1{}^{sp} - G_2{}^{sd}$$

$$(spd)$$

in which (^2P) indicates the mean of the two ^2P's and

$$F_0 = F_0(ns,\ n'p) + F_0(ns,\ n''d) + F_0(n'p,\ n''d)$$

$$F_2 = F_2(n'p,\ n''d)$$

$$G_1{}^{sp} = G_1(ns,\ n'p) \qquad G_2{}^{sd} = G_2(ns,\ n''d)$$

$$G_1{}^{pd} = G_1(n'p,\ n''d) \qquad G_3{}^{pd} = G_3(n'p,\ n''d).$$

Slater has worked out p^3, the result being that the energies increase in the order ^4S, ^2D, ^2P and the interval $(^2P-^2D)$ is to $(^2D-^4S)$ as $2:3$.

For the configuration d^3 we find the energy levels to be,

$$^2P = 3F_0 - 6F_2 - 12F_4$$

$$^4P = 3F_0 \qquad - 147F_4$$

$$(^2D) = 3F_0 + 5F_2 + 3F_4$$

$$^2F = 3F_0 + 9F_2 - 87F_4$$

$$^4F = 3F_0 - 15F_2 - 72F_4$$

$$^2G = 3F_0 - 11F_2 + 13F_4$$

$$^2H = 3F_0 - 6F_2 - 12F_4$$

$$(d^3)$$

where (^2D) indicates the mean of the two ^2D's.

§5. COMPARISON WITH EXPERIMENTAL DATA, CONFIGURATIONS WITH p ELECTRONS

The simplest case for comparison with the data is p^2, where the theory predicts that the multiplets come in the order ^3P, ^1D, ^1S, as Slater noted. From

TABLE III. p^2 configurations

Element	Config.	$(^1S-^1D)/(^1D-^3P)$	Reference
Theory		1.500	
C I	$2p^2$	1.13	1
N II	"	5. (? on ^1S)	2
O III	"	1.14	2
Si I	$3p^2$	1.48	3
Ca I	$4p^2$	−0.01	4
Ge I	"	1.50	5
Sn I	$5p^2$	1.39	5
Pb I	$6p^2$	0.62	6
Bi II	"	0.51	7

[1] Paschen and Kruger, Ann. d. Physik **7**, 1 (1930).
[2] Fowler and Selwyn, Proc. Roy. Soc. **A118**, 42 (1928).
[3] Slater, Phys. Rev. **34**, 1317 (1929).
[4] Russell, Astrophys. J. **66**, 190 (1927).
[5] Rao, Proc. Roy. Soc. **A124**, 475 (1929).
[6] Gieseler and Grotrian, Zeits. f. Physik **39**, 377 (1926); Sur, Phil. Mag. **3**, 736 (1927).
[7] McLennan, McLay, and Crawford, Proc. Roy. Soc. **A129**, 584 (1930).

§3 we see that the ratio $(^1S-{}^1D)/(^1D-{}^3P) = 3/2$ according to theory. Slater gives the normal configuration of Si I as an example, and we find several more, as given in Table III.

From this it would appear that some influence depresses the ^1S in general, and that the doubtful ^1S given by Fowler and Selwyn for N II is probably wrong. Pb I and Bi II are so far from Russell-Saunders coupling that a good fit would hardly be expected.

The configurations p^3 and p^4 may be discussed here because they are similar to p^2. For p^3 the theory says that the ratio $(^2P-{}^2D)/(^2D-{}^4S)$ equals $2/3$. Table IV gives the known instances.

TABLE IV. p^3 configurations

Element	Config.	$(^2P-{}^2D)/(^2D-{}^4S)$	Reference
Theory		0.67	
N I	$2p^3$	0.50	1
O II	"	0.51	2
F III*	"	0.46	3
S II	$3p^3$	0.65	4
As I	$4p^3$	0.72	5
Sb I	$5p^3$	0.91	6
Bi I	$6p^3$	1.12	6

[1] Compton and Boyce, Phys. Rev. 33, 147 (1929); Ekefors, Zeits. f. Physik 63, 442 (1930).
[2] Russell, Phys. Rev. 31, 27 (1928).
[3] Dingle, Proc. Roy. Soc. A122, 144 (1929).
[4] Ingram, Phys. Rev. 32, 172 (1928); L. and E. Bloch, C. R. 188, 160 (1929).
[5] Rao, Proc. Roy. Soc. A125, 240 (1929).
[6] Charola, Phys. Zeits. 31, 458 (1930).
* No intercombinations are found between the quartet and doublet systems, and the relative term values are probably quite inaccurate.

The continued increase in this ratio as the total quantum number increases is to be noted particularly. The closeness of the ratio for N I and O II would indicate that the ratio for the unreliable F III should perhaps be closer to 0.51.

For p^4 the theory gives the same result as for p^2. Table V gives the examples.

TABLE V. p^4 configurations

Element	Config.	$(^1S-{}^1D)/(^1D-{}^3P)$	Reference
Theory		1.50	
O I	$2p^4$	1.14	1
Se I	$4p^4$	1.71	2
Te I	$5p^4$	1.71	2

[1] Frerichs, Phys. Rev. 36, 398 (1930); Hopfield, Phys. Rev. 37, 160 (1931).
[2] McLennan and Crawford, Nature 124, 874 (1929).

The new data of Frerichs show that O I is not in as good agreement with the theory as indicated in one of Slater's examples, his ratio being 1.55. Slater took his data from a remarkable energy-level diagram by McLennan, McLeod and Ruedy, Phil. Mag. 6, 565 (1928), in which the wave number difference for $^1S-{}^1D$ is given as 39,500, although the main point of the paper is the identification of this transition with the auroral green line!

We have found two complete p^2s configurations, which should be similar to p^2 as indicated in §4. The ratio $(^2S-^2D)/(^2D-P)$, where $P = (2^4P+^2P)/3$, which should be 1.50, is 0.58 in As I[6] and 3.58 in Sb III.[7]

pp, pd, and pf give similar triads, in which the means of singlet and triplet should lie in the corresponding orders: $P\ D\ S$, $D\ F\ P$, $F\ G\ D$, lowest energy first, with the ratios $(S-D)/(D-P) = 9/6$; $(P-F)/(F-D) = 5/9$; $(D-G)/(G-F) = 7/20$, respectively.

We have found the pp complete only for C I[8], N II[9], and O III[10], but since these all occur with the means in the wrong order we do not give the details.

This failure of C I, N II, and O III to agree with the theory appears also in the known pd configurations, the mean of the F's being low in every case.[8,9,10] Yt II,[11] La II,[12] and Ge I[13] $4p5d$, also have the pd means in the wrong order. The means of Ge I $4p4d$, and Zr III $5p4d$[14] come in the right order with the ratio $(P-F)/(F-D)$, which is theoretically 0.555, having the value 0.28 and 3.58, respectively. More interesting is the behavior of $4p3d$ in the isoelectronic sequence Ca I[15], Sc II[16], Ti III[17], V IV[18] and Cr V[18]. The first two come in the wrong order, giving $(P-F)/(F-D) = -0.15$ and -0.06, respectively, but the last three agree satisfactorily, the ratios being $+0.45$, 0.49, and 0.548. Since $P-F = 10F_2(4p3d)$ and $F-D = 18F_2(4p3d)$, we can get two values of F_2 for each of these last three ions. Taking the average of these two, we have $F_2(4p3d)$ for Ti III, 427; V IV, 569; Cr V, 707 cm^{-1}. These are perfectly linear, as shown by the plot in Fig. 2, together with corresponding F's for d^2. We have a further check on the three singlet-triplet separations in terms of the two parameters G_1 and G_3, which it is fruitless to apply to the cases in which the means fitted poorly, but interesting in the other three cases.

TABLE VI.   *3p 4d singlet -triplet separations*

	Ti III		V IV		Cr V	
	obs.	calc.	obs.	calc.	obs.	calc.
$^1P-^3P$	2810	2785	4761	4873	6894	7208
$^1D-^3D$	−2056	−1970	−1588	−1935	− 826	−1704
$^1F-^3F$	5270	5310	6784	6590	8161	7648
G_1	435		534		614	
G_3	15.2		30.2		47.4	
G^1	6520		8000		9200	
G^3	3720		7400		11600	

[6] Rao, Proc. Roy. Soc. **A125**, 240 (1929).

[7] Lang, Phys. Rev. **35**, 445 (1930).

[8] Paschen and Kruger, Ann. d. Physik **7**, 1 (1930).

[9] Ingram, Phys. Rev. **34**, 427 (1929).

[10] Fowler and Selwyn, Proc. Roy. Soc. **A118**, 42 (1928).

[11] Meggers and Russell, B. S. Jl. of Res. **2**, 733 (1929).

[12] Meggers and Russell, see §7.

[13] Rao, Proc. Roy. Soc. **A124**, 467 (1929).

[14] Kiess and Lang, B. S. Jl. of Res. **5**, 311 (1930).

[15] Russell, Astrophys. J. **66**, 190 (1927).

[16] Russell and Meggers, Sci. Papers Bur. Stand. **22**, 329 (1927).

[17] Russell and Lang, Astrophys. J. **66**, 19 (1927).

[18] White, Phys. Rev. **33**, 542 (1929).

Ti III, V IV and Cr V all alternate properly, as pointed out in §3. Table VI shows the results of fitting the data to the formulas for the separations by least squares.

It is seen that, in the opposite order from the means, Ti III fits best and V IV next. The G's are again approximately linear functions of the ionic charge. G^3 becomes greater than G^1, which is allowed.

For pf in La II[12] the ratio $(D-G)/(G-F)$ is 1.05 instead of the theoretical 0.35.

There is one more instance of a configuration with p electrons in which one gets a determined ratio, namely pds. In this case (see §4) nothing can be pre-
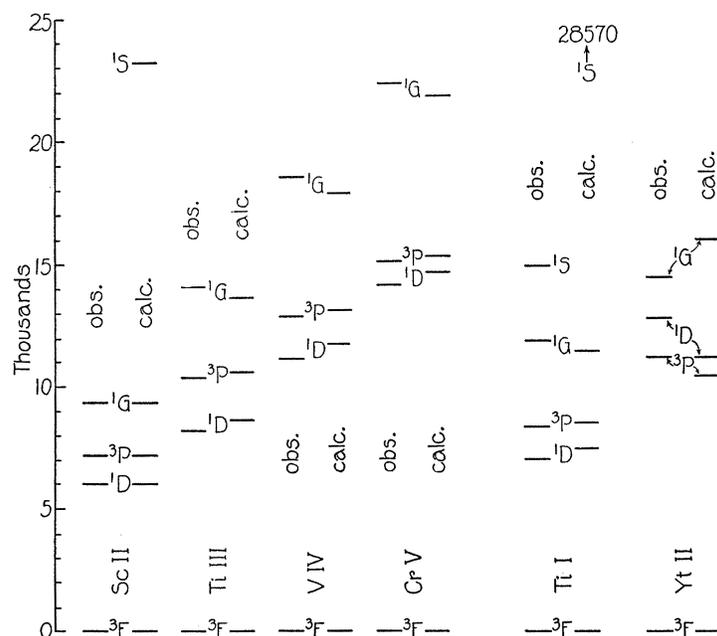
Fig. 1. The configuration d^2.

dicted concerning the quartets, ^4P, ^4D, ^4F; but the theory predicts a constant ratio between the means of the two ^2P's, the two ^2D's, and the two ^2F's which occur. If we designate these means by P D F, we have the order D F P as in pd, with the same ratio $(P-F)/(F-D) = 5/9$. In Sc I[16] these means have the wrong order, D P F; and in Yt I[11] and Zr II[19] the above ratio has the values 1.86 and 2.08, respectively, much too large.

In general the predictions of the theory have been seen to fit very poorly for configurations with p electrons, a uniform trend having been observed in p^3, and good fits having been obtained for pd in the higher members of the Ca I isoelectronic sequence.

[19] Kiess and Kiess, B. S. Jl. of Res. **5**, 1210 (1930).

§6. COMPARISON WITH EXPERIMENTAL DATA, d ELECTRONS

For d^2 the theory predicts (see §3) the energies of the five multiplets ^1S, ^3P, ^1D, ^3F, ^1G in terms of three integrals, the ^1S being predicted extremely high. In no instance, where a ^1S is reported, is it anywhere nearly high enough, and so we have investigated the other four levels, making a least-squares fit of the separations of ^3P, ^1D, ^1G from the low ^3F, which three separations the theory gives in terms of the two parameters F_2 and F_4.

In the isoelectronic sequence Sc II[16], Ti III[17], V IV[18], and Cr V[18], it was found possible to make the excellent fits plotted in Fig. 1 for $3d^2$. The predicted height of ^1S in Sc II is shown, the other ^1S's being correspondingly high. Russell and Meggers reported a ^1S between the ^1D and ^3P of Sc II, but later, in a note to their Yt paper[11] they ascribe this not to $3d^2$ but to $4s^2$. The $3d^2$ ^1S as predicted would be in the midst of the configuration $4p3d$ with which they get their strong combinations, and so difficult to find. In Ti III, Russell
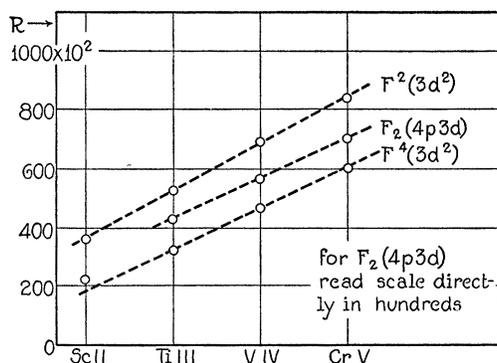
Fig. 2. Values of some integrals for the Ca I isoelectronic sequence.

and Lang report a ^1S just under the ^1G, but with a question mark. This undoubtedly does not belong to $3d^2$. In V IV and Cr V, White reports a ^1S just above the ^1G, but since these spectra were analyzed practically by extrapolation from Sc II and Ti III these levels also are probably not part of $3d^2$. The values of F^2 and F^4 as determined in this way show a striking linearity as plotted in Fig. 2. Slater's $F^2(3d^2)$ and $F^4(3d^2)$ are plotted in place of our F_2 and F_4 in order to show their relative magnitudes. Table VII gives these values $(D_2 = 49, D_4 = 441)$:

TABLE VII.

	Sc II	Ti III	V IV	Cr V
$F^2(3d^2)$	36180	52840	69300	84330
$F^4(3d^2)$	22740	32520	47020	60880

These values are in good accord with Slater's rough estimate that F^4 is approximately half of F^2.

Russell[20] has completed the $3d^2$ also in Ti I, the levels being shown in Fig. 1, together with the theoretical levels with $F_2(3d^2) = 899.5$ and $F_4(3d^2) = 66.15$. This is again an excellent fit except for ^1S, as was pointed out by Slater. Meggers and Russell[11] have found all but the ^1S in the $4d^2$ of Yt II, but here, see Fig. 1, not a very good fit is obtained of the rest of the levels, although the perturbations are not great. This plot is made with $F_2(4d^2) = 625.2$ and $F_4(4d^2) = 55.1$.

In contrast to these reasonable fits we have the Zr III $4d^2$ of Kiess and Lang,[14] in which not only is the ^1S much too low, but the *two* intervals between *no three* of the other levels may be fitted with possible values of the *two* parameters F_2 and F_4; either it is necessary to assume that one of the integrals is
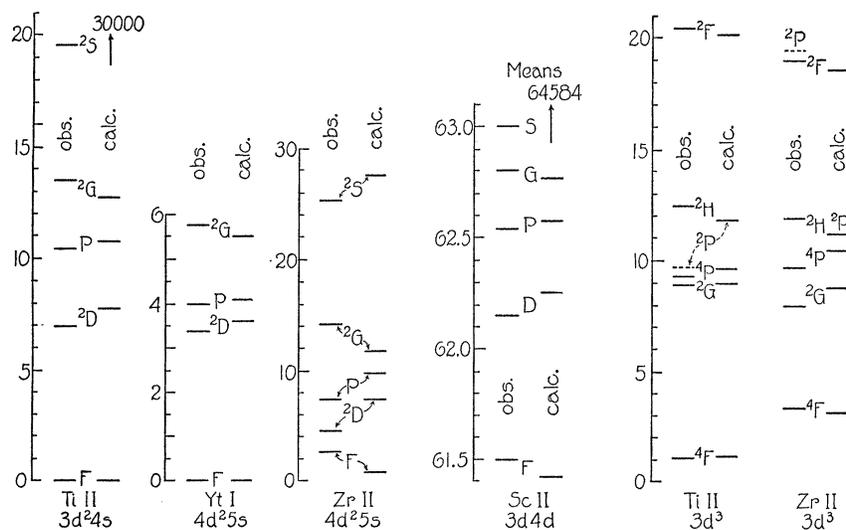
Fig. 3. The configurations d^2s, dd, and d^3. (Scale in thousands of wave numbers.)

negative or that F^4 is many times greater than F^2. In the $5d^2$ of La II (see §7 for energy levels) we have a somewhat different situation. No ^1S is reported, and of the four remaining levels there are three, and just three, which may be fitted with possible values of the parameters. These are ^3P, ^3F, ^1G with $F_2 = 495$ and $F_4 = 35.4$. (The two parameters fit the two intervals exactly, of course.) This leaves the ^1D almost 5000 cm^{-1} too high.

In d^2s we have exactly the same situation as in d^2 when we take the weighted means of ^2P and ^4P, and ^2F and ^4F, as analogous to ^3P and ^3F, respectively. Here again we can get good least squares fits of the F, ^2D, P, ^2G levels of $3d^24s$ of Ti II[21] and $4d^25s$ of Yt I[11]. These are plotted in Fig. 3. In Ti II a ^2S is observed at about the same relative position as the ^1S of Ti I, while calculated it should be much higher. Again in Yt I no ^2S is observed. The values of the parameters are, for Ti II, $F_2 = 1014.7$, $F_4 = 59.2$ and for Yt I, $F_2 = 433.6$, $F_4 = 32.1$. We have $F^2 = 1.91F^4$ and $1.51F^4$ respectively in these

[20] Russell, Astrophys. J. **66**, 347 (1927).
[21] Russell, Astrophys. J. **66**, 283 (1927).

two cases. In Zr II[19], $4d^25s$, we have the first instance in which a ^2S is found reasonably high. In this configuration, although we cannot get a very good fit, in contrast to the $4d^2$ of Zr III almost any three of the five levels will give reasonable values of the parameters, and we can get an approximate fit of all five by taking $F_2 = 905$, $F_4 = 55$ as indicated in Fig. 3 ($F_0 - G_2 = 8000$ cm^{-1} measured from Kiess and Kiess' low $^4F_{1\frac{1}{2}}$, see §3). The fit would not be much improved by omitting any one of the multiplets from consideration so here we have probably a generally large second order perturbation. We have a further check in this configuration on the doublet-quartet separations, which should be the same for P and F terms, being equal to $3G_2$. We have for Ti II, $^2P - {}^4P = 6620$, $^2F - {}^4F = 4558$; and for Yt I, $^2P - {}^4P = 3964$, $^2F - {}^4E = 4357$. These show reasonable agreements, but Zr II is badly off, for here we have $^2P - {}^4P = -1877$, and $^2F - {}^4F = +5404$.

The dd configuration gives us a pentad, $^{1,3}SPDFG$, with three F's to fit the means and three G's to fit the separations. The first and best instance of this configuration is the Sc II $3d4d$ of Russell and Meggers.[16] Here we can fit the $PDFG$ means as shown in Fig. 3 using $F_2(3d4d) = 107$, $F_4(3d4d) = 6$ ($F_0 = 62330$). The S mean is observed some 1600 cm^{-1} too low, which could be caused by the ^1S being about 3000 cm^{-1} too low. When we consider the separations (singlet — triplet) we find that we can obtain a fairly good fit of the P D F G separations, with the observed S separation much too small, as shown by Table VIII.

TABLE VIII. $ScII\ 3d\ 4d$ separations

	Obs.	Calc.
$^1S - {}^3S$	3872	6368
$^1P - {}^3P$	−4275	−4385
$^1D - {}^3D$	4384	4492
$^1F - {}^3F$	−3935	−3810
$^1G - {}^3G$	4864	4760

These are calculated using $G_0 = 2230$, $G_2 = 36.7$ and $G_4 = 3.5$, making $G^0(3d4d) = 2230$, $G^2(3d4d) = 1800$, $G^4(3d4d) = 1540$. (The G^0, unlike F^0, carries here its full meaning as an integral.) The S separation is about 2500 cm^{-1} too small, which would indicate a ^1S about that much too low. This is in good agreement with the predictions of the calculation of the means and indicates that this ^1S is perhaps incorrect, the correct one being some 2500–3000 cm^{-1} higher. An error in the assignment of a singlet term, especially a ^1S, is quite likely to occur, since the identification of such terms is very difficult. An interesting example of this sort will be discussed in §7.

The other instances of the dd configuration are not as good. Of the $4d5d$ of Yt II[11], no three of the means will fit with reasonable values of F_2 and F_4, the D and the S in particular being very low. Since the S separation was also large and negative where the theory, by comparison with the other separations, says it should be positive, Professor Russell assigned the 61367 ^1S to $4d5d$, discovering that the 59615 level he had assigned was not real; but this still is perhaps not the right level, since we have now a separation of only

$+167$ whereas the S separation should probably be a great deal larger. The other levels do not fit well enough to say anything definite. In the $4d5d$ of Zr III[14], Kiess and Lang do not find a ^1G, but of the means of the $S\ P\ D\ F$ singlets and triplets, no three will fit with positive values of F_2. Of the La II[12] $5d6d$ means the $P\ D\ F\ G$ will fit very well, with $F_2=115$, $F_4=4$ $(F_0=54430)$, with the S much too low, as in the case of Sc II, but this fit is not borne out by the separations, which are entirely skew, the P separation even being -2176 when it should probably be positive.

The other d configuration which we have found almost complete is d^3. Here we get ^2PFGH, ^4PF, and two ^2D's. Russell[21] in Ti II $3d^3$, has found all but one ^2D, and Kiess and Kiess have found all the multiplets of the $4d^3$ of Zr II.[19] The theory predicts, surprisingly, that ^2H and ^2P should have the same energy. Of these, in our two instances, the ^2H fits well, but the ^2P is considerably separated from it. Of the two ^2D's only the mean is given by the theory, but in Zr II this comes far from fitting well. However, in both cases we can fit the other five levels, ^2FGH and ^4PF surprisingly well with our three

TABLE IX. *La II*

6s²			^1D	40458	^1P	27424
			^3D	38835	^3P	23003
^1S	7473					
			^1F	37210	^1D	18895
6s6p			^3F	37034	^3D	22174
^1P	45692		^1G	39221	^1F	24523
^3P	32699		^3G	37479	^3F	18411
6s5d			**5d²**		^1G	16599
					^3G	21478
^1D	1394		^1S	—		
^3D	2760		^3P	5949	^1H	28525
			^1D	10095	^3H	18835
6s4f			^3F	1183		
			^1G	7473		
^1F	15773				**4f²**	
^3F	14888		**5d6d**			
					^1S	69505
6p²			^1S	54794	^3P	63960
			^3S	55230	^1D	59900
^1S	66592				^3F	57939
^3P	61779		^1P	56037	^1G	59528
^1D	62026		^3P	53861	^3H	56080
					^1I	62408
6p5d			^1D	55184[1]		
			^3D	53067		
^1P	30353					
^3P	28833		^1F	52138?		
			^3F	54819[1]		
^1D	24462					
^3D	27538		^1G	56036		
			^3G	53659		
^1F	32201					
^3F	27477		**5d4f**			
6p4f						

[1] The $^1D_2$ and $^3F_2$ of the $5d6d$ may possibly be interchanged. $(^3F_4=55321$, $^3F_3=54840$, $^3F_2=53885.)$

parameters, as indicated in Fig. 3. For Ti II we have $F_2(3d^2) = 845, F_4(3d^2) = 54$ $(3F_0 = 17750)$; corresponding to $F^2 = 1.74F^4$. The mean of the ^2D's is predicted at 22140, which would throw the ^2D not found at about 31000, very high indeed. For Zr II we have $F_2 = 683$, $F_4 = 36$ $(3F_0 = 16000)$; corresponding to $F^2 = 2.11F^4$. The mean of the ^2D's is predicted at 19523, observed at 14214 (multiplets at 13869 and 14559).

We have seen that the theory works much better for d electrons than for p. It has been good in every instance in the first long period of the periodic table, and better in the second than the third.

§7. La II and the f Electron Configurations

W. F. Meggers and H. N. Russell have recently completed the analysis of La II, obtaining the first complete pf, df and f^2 configurations. Through their kindness in allowing us to use these data we have been able to obtain two beautiful fits of the df and f^2 configurations, and to prove the actual service of this theory to spectroscopists by helping to straighten out the analysis at two or three points.

Since these data are unpublished as yet, Meggers and Russell have kindly allowed us to publish a preliminary energy table, the levels being measured up from the low $5d^2\,^3F_2$. We give only the centers of gravity of the multiplets in Table IX.

Of these the p^2, pd, pf, d^2, and dd have already been discussed, and were not found to agree particularly well with the theory. The new $5d4f$ and $4f^2$ remain to be considered, which will be done in some detail.
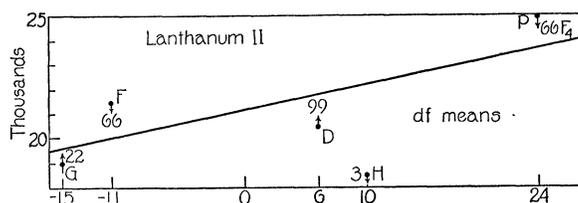
Fig. 4. Illustrating the method of locating poorly fitting multiplets and a method of estimating the values of the integrals.

As we received the data from Professor Russell, the $df\,^1H$ was placed at 18169, rather close to ^3H, instead of having the extremely great separation of about 10,000 units and being the highest level in the configuration. An attempt to fit the means by the method illustrated in Fig. 4 was made. This is incidentally the method used on many of the previous configurations. The formulas to which we are fitting these means are as follows:

$$
\begin{aligned}
& & & Calc. \\
P &= 25214 = F_0 + 24F_2 + 66F_4 & & 25216 \\
D &= 20534 = F_0 + 6F_2 - 99F_4 & & 20506 \\
F &= 21467 = F_0 - 11F_2 + 66F_4 & & 21191 \\
G &= 19038 = F_0 - 15F_2 - 22F_4 & & 19323 \\
H &= 18502 = F_0 + 10F_2 + 3F_4 & & 22598
\end{aligned}
$$

Since F_0 occurs uniformly, we plot in Fig. 4 the value of these means against the coefficients of F_2. Then the line determining F_2 must be so drawn that its separations from these points are as closely as possible proportional to the coefficients of F_4 and in the direction shown by the arrows. It is seen at once that we can thus fit G,F,D, and P quite well, but that H is far too low. From the slope of the line we get $F_2 = 115$, from the average separations $F_4 = 16$ (and from the height at zero abscissa, $F_0 = 21400$). From the level diagram in Fig. 5 we see that changing none of these values will tend to improve the general fit, so that these are approximately as good as can be found. A more exact determination of these values, such as a least squares fit, gives an accuracy which is meaningless. The calculated means are shown in the above table. From the calculated H mean it would seem that the ^1H should be about 8200 units higher.

When we consider the separations we have the following formulas to determine the G's

$$\begin{array}{lllll} & & & & Calc. \\ ^1P - {}^3P = & -4421 = & -2(\ G_1 + 24G_3 + 330G_5) & & -4638 \\ ^1D - {}^3D = & 3279 = & 2(\ 3G_1 + 42G_3 - 165G_5) & & 3397 \\ ^1F - {}^3F = & -6112 = & -2(\ 6G_1 + 19G_3 + 55G_5) & & -5837 \\ ^1G - {}^3G = & 4879 = & 2(10G_1 - 35G_3 - 11G_5) & & 4987 \\ ^1H - {}^3H = & +666 = & -2(15G_1 + 10G_3 + G_5) & & -11330 \end{array}$$

It is inconvenient here to use such a method of fitting as described above, but such a diagram will readily show that the H separation relative to the others should be very large and negative. A least squares fit of the $P\ D\ F\ G$ separations gives $G_1 = 357.6$, $G_3 = 29.7$, $G_5 = 3.78$, and the calculated separations show in the table, a good fit. These values correspond to $G^1(5d4f) = 12,500$, $G^3 = 9350$, $G^5 = 5750$. This calculation shows that the ^1H should be about 12,000 units higher.

In the data as received from Professor Russell, the $4f^2\,{}^1I$ was placed at 52,052 instead of the value noted in the table, and two possibilities given for ^1S and ^1D, as noted below. The f^2 consists of seven levels to be fitted with four parameters as follows:

$$^1S = \left\{\begin{array}{c} 69505 \\ 66592 \end{array}\right\} = F_0 + 60F_2 + 198F_4 + 1716F_6$$

$$^3P = 63963 = F_0 + 45F_2 + 33F_4 - 1287F_6$$

$$^1D = \left\{\begin{array}{c} 59900 \\ 62026 \end{array}\right\} = F_0 + 19F_2 - 99F_4 + 715F_6$$

$$^3F = 57939 = F_0 - 10F_2 - 33F_4 - 286F_6$$

$$^1G = 59528 = F_0 - 30F_2 + 97F_4 + 78F_6$$

$$^3H = 56080 = F_0 - 25F_2 - 51F_4 - 13F_6$$

$$^1I = 52052 = F_0 + 25F_2 + 9F_4 + F_6.$$

Now from a diagram such as Fig. 4, it may be seen that F_6 will be extremely small, for a good fit of the high ^1S, the low ^1D, the ^3P, ^3F, ^1G, and ^3H may be obtained using just the parameters $F_2 = 94.0$, $F_4 = 22.1$. The ^1I is definitely observed 10000 units too low. The correct ^1S and ^1D are at once determined, since the other possibilities will not fit under any circumstances.

Thus we have seen that the theory predicted the ^1H of df and the ^1I of f^2 both about 10,000 units higher, and when this was called to the attention of Professor Russell, he discovered that he could make this shift by rearranging his lines as shown in Fig. 6. Upon doing this he immediately was able to check each of these levels by faint cross-combination lines, thus definitely proving
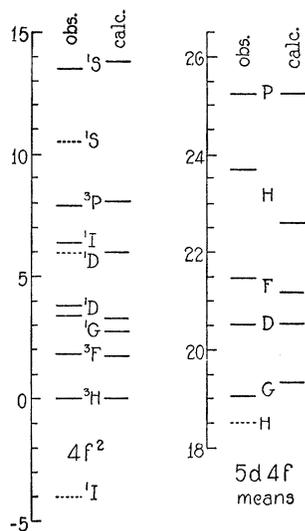
Fig. 5. The configurations df and f^2 of La II. (Scale in thousands of wave numbers.)
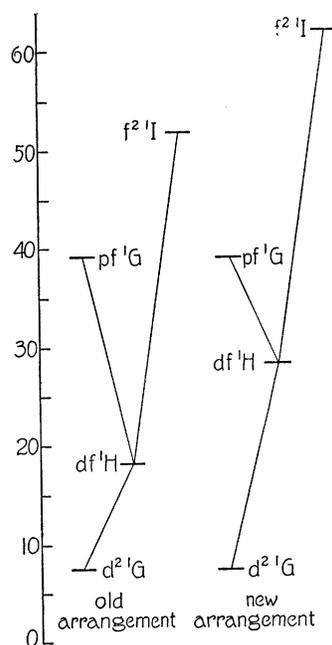
Fig. 6. Russell's rearrangement of the La II singlets according to the predictions of the theory. (Scale in thousands of wave numbers.)

the correctness of this arrangement. Both of these singlets were raised 10,356 units to the places shown in Table IX. In Fig. 5, the old levels are shown broken and the corrected levels by full lines. The df diagram is merely the old diagram determined from the means of P D F G, with the H mean put in its proper place. The $^1H - ^3H$ separation becomes now 9690 against the calculated 11330 from the other four separations. The ^1H was raised just about the average of the predictions from the means and from the separations. It is supposed that the $3d4d\,^1S$ of Sc II would behave in about this fashion. For the f^2 the ^1I is placed within 300 units of its prediction using the two coefficients above. Fig. 5, however, is a recalculation using least squares to fit the three

coefficients F_2, F_4, F_6 to the separations of all the levels from the low ^3H. This gives a surprisingly good fit of the 6 intervals in terms of the 3 integrals, with the value of $F^2 = 21,000$, $F^4 = 23,500$, $F^6 = 1930$. Unfortunately F^4 comes out a little larger than F^2 whereas it must be smaller.

Thus we have obtained quite pleasing results with these two f-electron instances, the theory having stood the test of prediction and been of actual service in the analysis of the spectrum, both in the assignment of ^1S and ^1D, f^2, the former of which Professor Russell says he had little possibility of assigning definitely, and in the rearrangement of the levels in both df and f^2.

Kiess and Lang[14] have completed the $4d4f$ configuration of Zr III except for the ^3H, but when the other four means are plotted as in Fig. 4, it is seen that no three of them will fit in any fashion. The P, D, and F separations alternate but the G does not.

In conclusion we may say that this first approximation seems to be most accurate for those configurations with lowest total quantum numbers in comparison with the angular momentum quantum numbers, the $3d$ and $4f$ in particular giving good results.