PERTURBED SERIES IN LINE SPECTRA

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Abstract

There occur many line series in atomic spectra which do not even approximately fit a Ritz formula. They display either a sudden rise in the value of n^*-n towards high term values or a gradual fall of almost a unit. The latter type contains an extra term due to some other structure and becomes similar to the first type after the removal of that term. It is shown that all such series obey approximately a series formula of type $\nu_n = R/n^{*2}$, $n^* = \mu + \alpha\nu_n + (\beta/\nu_n - \nu_0)$ in which ν_0 is the wave number of some level of the same type from a different electron structure. The series in the spectra Ca I, Ba I, Hg I, Cu I, Al II are discussed in detail. The rules governing the occurrence of a perturbation are more restricted than the simple ones that can be deduced from the results in other perturbation problems. The constant β is always negative and the trems therefore appear to repel each other. The Ba I levels $5d6p\ ^{3\&1}P^0D^0F^0$ and the series $6snf\,^1F^0$ are given for the first time.

IN A letter to the Editor of the Physical Review[1] R.M. Langer has described a generalized form of the Rydberg-Ritz series formula, deduced from the perturbation theory of the wave mechanics. In the case of atoms containing more than one optical electron, the series formula is given by

$$\nu_n = \frac{R}{\left\{n + \sum \frac{p_{in}}{\nu_n - \nu_1}\right\}^2}$$

in which ν is the term value expressed in wave numbers. Normally this form reduces to a Ritz formula

$$\nu_n = \frac{R}{(n + \mu + \alpha\nu_n)^2}.$$

Cases arise, however, where the atom has states of nearly equivalent energies arising from different electron configurations, and the mutual perturbations must then be considered. Langer does not state the conditions necessary for the perturbations to occur, but one can deduce them with some degree of certainty from the results of similar calculations, for predissociation, auto-ionization, and band spectrum perturbations.

Perturbations will occur, in general, between terms having the same J-value and parity. In the special case of Russell-Saunders coupling, one must also add that they must have the same L and S values. Actually, this more restricted case is the one most frequently met with.

The object of this paper is to show how Langer's formula explains the

[1] R. M. Langer, Phys. Rev. **35**, 649 (1930).

anomalies which exist in a great many well-known series. It is found that the formula is inadequate to cover all the details, but its success is much beyond the expectations for a first approximation formula.

The type of perturbation most frequently met with occurs when a single term from some more complicated structure falls among the terms of a simple series. In that case, there is superimposed on the ordinary Ritz form, a quantity such as one meets in the formulae of anomalous dispersion, and we have

$$\nu_n = \frac{R}{n^{*2}} = \frac{R}{\{n + \mu + \alpha\nu_n + (\beta/\nu_n - \nu_0)\}^2}$$

in which ν_0 is the value of the foreign level.

The exhibition of term sequences is best accomplished by plotting $n^* - n$ against ν_n. The Rydberg formula is then represented by a straight line parallel to the ν axis, and the Ritz formula by a straight line of slope α and intercept μ. In fact, the best way to find the correct limit of an unperturbed series is to find the condition under which the plot is, as nearly as possible, a straight line.

The sensitivity of this method is very great if the lines involving the high series members are accurately measured. It should be remembered that the values of a set of terms are fixed by the lines, except for an additive constant. If we differentiate n^* with respect to ν_n, we obtain $dn^*/d\nu_n = -\frac{1}{2}(R)^{1/2}/\nu_n^{3/2}$, so that a constant change in the values of all the terms effects the n^*'s of the high terms very much more than those of the low terms. For instance, a change of 1 unit in the values of the terms changes n^* by 0.005 for a term at 1000 and by only 0.000005 for a term at 100,000. Practically, that means that, if a wrong limit is assumed, the end of the plot of $n^* - n$ against ν_n will show a deviation from a straight line of increasing amount as we proceed to smaller term values. If the series is strictly Ritzian, it is possible to make that last portion perfectly straight. In practice, one finds always that the high series members are known with insufficient accuracy, and the best one can do is to use the highest members which are based on accurate measurements. A case in point is the long ^3S series of Hg I in which no manipulation of the limit can even approximately straighten out the series tail. A series of three terms can, of course, always be fitted to a Ritz formula. In this case also the easiest method is trial and error to make the following relation true,

$$\frac{\nu_1 - \nu_2}{\nu_2 - \nu_3} = \frac{(n_1^* - n_1) - (n_2^* - n_2)}{(n_2^* - n_2) - (n_3^* - n_3)}.$$

This follows directly from the formula

$$n^* = n + \mu + \alpha\nu_n.$$

If the method of plotting which has been described is used for a series which obeys strictly Langer's formula, the curve obtained is a hyperbola having asymptotes $\nu = \nu_0$ and $n^* - n = \mu + \alpha\nu_n$. Such a curve is readily recognizable, and is very commonly found. The constants of the formula may be found very easily by the following method.

We first plot $(n^*-n)\ (\nu_n-\nu_0)=\beta+\mu'(\nu_n-\nu_0)+\alpha'(\nu_n-\nu_0)^2$. β is then found from the point where the parabola crosses the line $\nu=\nu_0$. Finally, we plot for each term the quantity $(n^*-n)-\beta/\nu_n-\nu_0=\mu+\alpha\nu_n$ and the remaining constants, μ and α are the intercept and slope of the straight line which represents the plotted points most nearly. In most cases the series fit into such a formula with reasonable accuracy; the greatest deviations being usually near the perturbation and in the first term of the series. The latter lack of agreement is quite usual in unperturbed series also.

In the quantum mechanics the existence of a perturbation implies at least a partial mutual sharing of identities by the terms involved. Such sharing may even become so great that it is impossible to tell which is the perturbing term. The perturbing term may show very nearly the same combining qualities as the series term, and be absorbed into the series as an extra member.

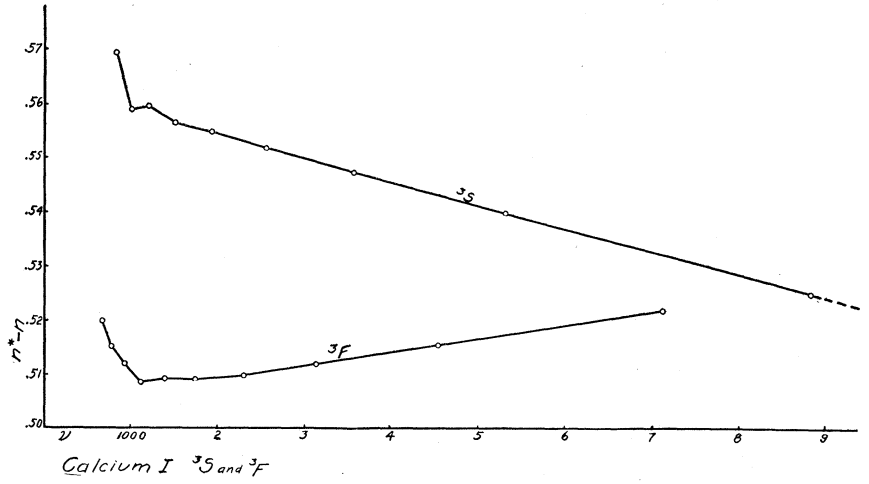

Fig. 1. Plot of ^3S and $^3F^0$ series of Ca I.

Many such cases can be found in the literature of spectra. The resulting plot of n^*-n shows at some point in the series a rather rapid fall of almost a unit. The perturbing term must lie somewhere in the middle of the drop, and its removal displaces vertically upwards the whole curve below its position by a unit, producing the usual hyperbola. This phenomenon occurs in the ^3F series of A1 II, which Schroedinger[2] endeavoured to explain by assigning two terms to the same total quantum number.

There is a surprising number of well-known spectra which contain perturbed series, and some spectra in which almost every series is more or less influenced by a foreign term. The following spectra will be considered in some detail; Ca I, Ba I, Hg I, Al II, Cu I.

Ca I

Before dealing with the perturbed series it is necessary to find as accurate as possible a limit for the whole term system. This must be obtained in Ca I

[2] Schroedinger, Ann. d. Physik **77**, 43 (1925).

from the ^3S and $^3F^0$ series. The ends of both series deviate considerably from a straight line, but the chief portions are certainly most consistent if we retain the limit used by Fowler.[3] The plot of these two series is shown in Fig. 1.

The ^3D sequence is the familiar series in which the intervals at first decrease, then increase to a maximum, and finally fall off to unobservable quantities. The plot of n^*-n shows the characteristic rapid fall of almost a unit, with the term of maximum interval in the middle of the fall. The removal of

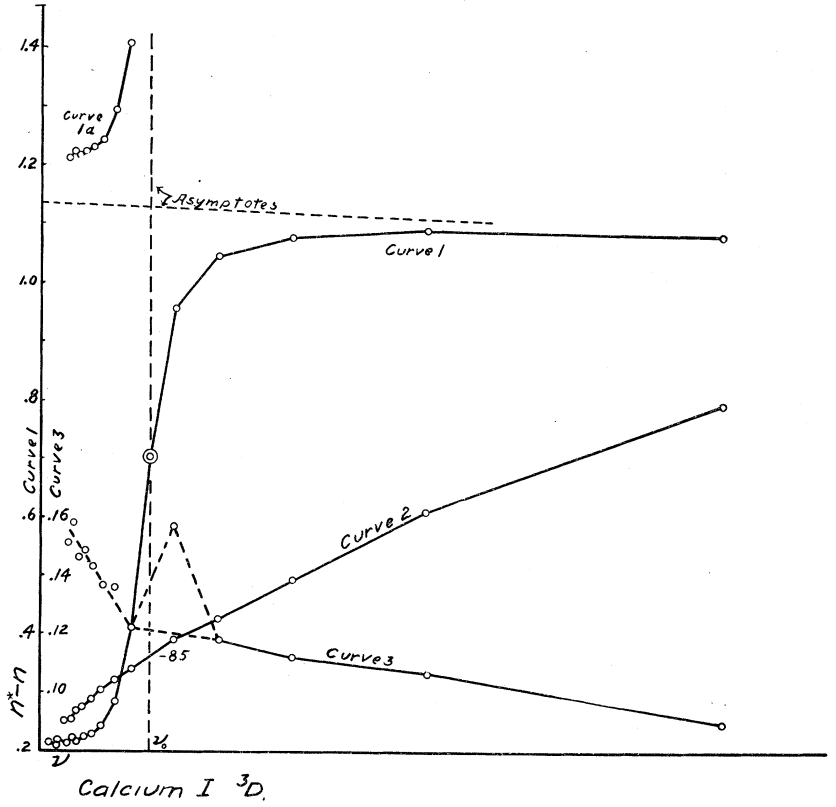

Fig. 2. $^3D_1$ of Ca I. Abscissae $=\nu_n$. Ordinates: Curve 1 n^*-n as the series is usually given. Curve 1(a) n^*-n after removal of perturbing level. Curve 2 (n^*-n) $(\nu_n-\nu_0)$ (No scale shown). Curve 3 $(n^*-n)-(\beta/\nu_n-\nu_0)$. (Scale 5 times scale for curve 1.)

that term from the series leaves the typical hyperbolic curve. It remains to identify the origin of the surplus term and to calculate the series formula. The identity is not difficult to discover, since the term must be of even ^3D nature. It is in the correct position for a structure of very probable occurrence, $3d5s\,^3D$. The assumption of such an origin makes the energy differences $3d5s-3d4d$ and $4s5s-4s4d$ almost exactly equal, as they should be. Additional evidence is given by the following consideration. The two terms $3d4s\,^3D$ and $3d5s\,^3D$ can be considered as successive terms of a series whose limit is $3d\,^2D$ of

[3] Fowler, Report on Series in Line Spectra (1922).

Ca II. On that basis, the two terms have Rydberg denominators of 1.604 and 2.640, which are very reasonable values. The third term of the series should be at about -5500, but should not be found because of the effect of auto-ionization.[4]

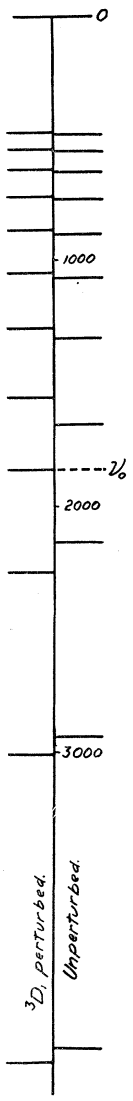

Fig. 3. Energy levels of $^3D_1$ Ca I, as usually given and after removal of the perturbation.

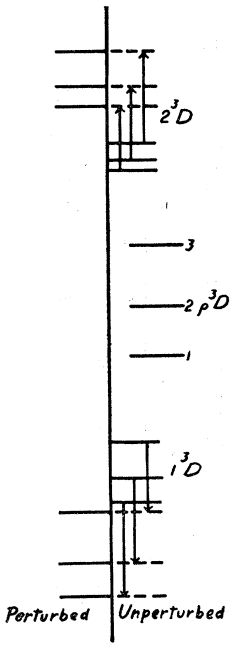

Fig. 4. To show change in term intervals in a perturbed series.

The complete calculations and curves for the $^3D_1$ series are given below. For the remaining series there are given only the series formula, the origin of

[4] A. G. Shenstone, Phys. Rev. **38**, 873 (1931).

TABLE I. *Calculations for series formula to represent the $4snd^3D_1$ series of Ca I.*

1	2	3	4	5	6	7	8	9	10	11	12
28969.1	27120.2	1.9463	−0.0537	−1456.4	−0.0031	−0.0506	−0.0982	0.0476	∽2.0258	∽26465	∽+2504
11556.4	9707.5	3.0815	+0.0815	+791.2	−0.0088	+0.0903	−0.0392	0.1295	3.0815	11556	0
6561.4	4712.5	4.0896	+0.0896	422.2	−0.0180	0.1076	−0.0222	0.1298	4.0893	6562	−1
4255.5	2406.6	5.0780	+0.0780	187.7	−0.0353	0.1133	−0.0144	0.1277	5.0798	4252	+3
3002.4	1153.5	6.0456	+0.0456	+52.6	−0.0737	0.1193	−0.0102	0.1295	6.0456	3002	0
2268.3	419.4	6.9552	−0.0448	−18.8	−0.2026	0.1578	−0.0077	0.1655	6.9260	2287	−19
(1848.9)	0										
1551.3	−297.6	8.4105	+0.4105	−122.2	+0.2856	0.1249	−0.0053	0.1302	8.4105	1551	0
1273.1	−575.8	9.2840	+0.2840	−163.5	+0.1476	0.1364	−0.0043	0.1407	9.2728	1276	−3
1045.6	−803.3	10.2445	+0.2445	−196.4	+0.1058	0.1387	−0.0035	0.1422	10.2318	1048	−2
869.8	−979.1	11.2323	+0.2323	−227.4	+0.0868	0.1455	−0.0029	0.1484	11.2134	873	−3
734.0	−1114.9	12.2273	+0.2273	−253.4	+0.0762	0.1510	−0.0025	0.1535	12.2033	737	−3
628.0	−1220.9	13.2190	+0.2190	−267.3	+0.0696	0.1494	−0.0021	0.1515	13.1970	630	−2
542.2	−1306.7	14.2265	+0.2265	−296.0	+0.0650	0.1615	−0.0018	0.1633	14.1927	545	−3
473.9	−1375.0	15.2172	+0.2172	−298.6	+0.0618	0.1554	−0.0016	0.1570	15.1897	476	−2

Column (1) Term value ν_n; (2) $\nu_n-\nu_0$; (3) n^*; (4) n^*-n; (5) $(n^*-n)(\nu_n-\nu_0)$; (6) $(-85/\nu_n-\nu_0)$; (7) $n^*-n-(-85/\nu_n-\nu_0)$; (8) $\alpha\nu_n$; (9) $n^*-n-(-85/\nu_n-\nu_0)-\alpha\nu_n$; (10) n^*(calc.); (11) ν_n(calc.); (12) ν_n(obs.) $-\nu_n$(calc.).

$4snd^3D_1$

$\nu_n=R/n^{*2}$

$n^*=n+\mu+\alpha\nu_n+(\beta/\nu_n-\nu_0)$

$\mu=-0.8705$

$\alpha=-3.39\times10^{-6}$

$\beta=-85$

$\nu_0=1849=3d5s^3D_1$

$n=3, 4, \cdots$

Residuals $=\backsim+2504, 0, -1, +3, 0, -19, (\nu_0), 0, -3, -2, -3, -3, -2, -3, -2$

$4snd^3D_2$

$\mu=-0.8678$

$\alpha=-3.571\times10^{-6}$

$\beta=-86$

$\nu_0=1839=3d5s^3D_2$

$n=3, 4, \cdots$

Residuals $=\backsim+2210, 0, +1, +3, 0, -20, (\nu_0), 0, -3, -2, -2, -2, -2, -2, -1.$

$4snd^3D_3$

$\mu=-0.8656$

$\alpha=-3.665\times10^{-6}$

$\beta=-90$

$\nu_0=1829=3d5s^3D_3$

$n=3, 4, \cdots$

Residuals $=\backsim+2172, 0, +1, +2, -3, -27, (\nu_0), -1, -1, -1, -1, -2, -1, -2, -1.$

the perturbing term, and the differences between observed and calculated term values.

Fig. 2, curve 1 shows the plot of n^*-n against ν_n, as the series is given in Fowler; and curve Ia after removal of the perturbing term and the consequent addition of a unit to the ordinates of the higher series members. Curve 2 exhibits the values of $(n^*-n)(\nu_n-\nu_0)$ plotted against ν_n, from which the value of β is found at approximately -85, where the curve crosses the abscissa ν_0. Curve 3 is the plot of the remainders on a 5 times greater scale after the subtraction of $\beta/\nu_n-\nu_0$ from n^*-n. This should be a straight line, but shows the same type of deviation in the higher terms as was evident in the supposedly unperturbed ^3S and ^3F series. In addition, one point next to the perturbation shows a rather large deviation. In Table I are shown the various steps in the calculation, and the differences between the observed and calculated terms.

Fig. 3 shows the effect of the perturbation. The energy levels as they are observed and approximately as they would be without the perturbation are shown beside each other to illustrate the magnitude of the effect.

It will be noticed that the constants of the perturbations in the three component series are of about the same magnitude, and that the perturbing term has wider intervals than would normally appear at that position in the series. These two facts explain the anomalous opening out of the intervals in the series terms near the perturbation. The reason for this can best be understood by considering an hypothetical much exaggerated case. (Fig. 4).

The perturbation has the effect of a repulsion proportional to the *nearness* of the perturbed and perturbing levels. The diagram makes it evident that the repulsive effect of the components of p^3D on 2^3D will be greatest for the level of $J=3$ and least for $J=1$. In other words the displacement of $J=3$ will be greater than the displacement of $J=2$ and $J=1$, with the result that 2^3D in its perturbed state will have larger intervals than normal. The same considerations applied to the interaction of p^3D and 1^3D show that 1^3D also will have its intervals increased. If p^3D were an inverted term, we would expect the intervals of 1^3D and 2^3D to be decreased or even inverted. The ^2P series of Cu I is of that type.

^1D series.

This series has apparently two perturbations. One is, undoubtedly, due to the level $4p^2\,{}^1D$ at 8585 and the other to a possible level at 1492 which may be either $3d^2\,{}^1D$ or $3d5s\,{}^1D$. The number of members available and the very irregular behaviour makes a calculation unwarranted.

$^3P^\circ$.

There are only three members known in the $^3P_1^\circ$ and $^3P_0^\circ$ series, and four in the $^3P_2^\circ$. The series are perturbed by the known $3d4p\,{}^3P^\circ$ term. The formula has been fitted to the first three members of the $^3P_2^\circ$ series and gives an error of eight units for the fourth member. The constants are as follows:

$$\mu = -1.9489$$
$$\alpha = -7.48 \times 10^{-6}$$

$$\beta = -62.9$$
$$\nu_0 = 9964 = 3d4p\,^3P_2{}^0$$
$$n = 4, 5 \text{ etc.}$$

$^1P^0$.

This series and the equivalent one in Sr I do not yield to the usual methods. There can be no doubt from the evidence of intensities and position that the level 12573 is foreign to the series and originates principally in the structure $3d4p$. The use of that level as ν_0 requires a value of $\beta = -4500$ and the terms deviate from the formula by very large amounts. If we judge entirely from the plot of $n^* - n$, the level at 5372 can be logically removed from the series. The constants of the series are then of reasonable magnitudes and the residuals are quite small. Another possibility is that the second member of the series is actually missing. The formula then requires very large values of α and β. The theoretical elucidation of this series would seem to be of considerable importance.

^1S.

This series is perturbed by $p^2\,{}^1S$ at 8614. The agreement is very poor near the perturbation. The constants are as follows.

$$\mu = -2.3495$$
$$\alpha = -1.066 \times 10^{-6}$$
$$\beta = -100$$
$$\nu_0 = 8614 = p^{21}S$$
$$\text{Res.} = \sim +6191, 0, (\nu_0), -245, +2, 0, -1, -1, -1, 0.$$
$$n = 4, 5 \text{ etc.}$$

$^1F^\circ$.

The $^1F^\circ$ series is peculiar in being perturbed by a term $3d4p\,^1F^\circ$ at 8767 which is lower than the first series member. The formula gives a very good agreement with all eight numbers.

$$\mu = -0.0955$$
$$\alpha = 2.90 \times 10^{-5}$$
$$\beta = -80$$
$$\nu_0 = 8767 = 3d4p\,^1F^0$$
$$\text{Res.} = -2, -1, +2, +2, +2, +1, +1, -1.$$
$$n = 4, 5 \text{ etc.}$$

Ba I

The series of Ba I are so irregular that it is impossible to calculate a limit with any certainty; but, from a survey of all the series, it is considered that an improvement can be made by increasing all of the term values given in

Fowler's tables by 3 units. The chief perturbed series is the $6snf\,^3F^\circ$ series (Fig. 5). The perturbation arises from a $^3F^\circ$ term, which is part of a triad $^{3\&1}P^\circ$, D°, F° recently discovered by one of us (H. N. R.) and probably arising

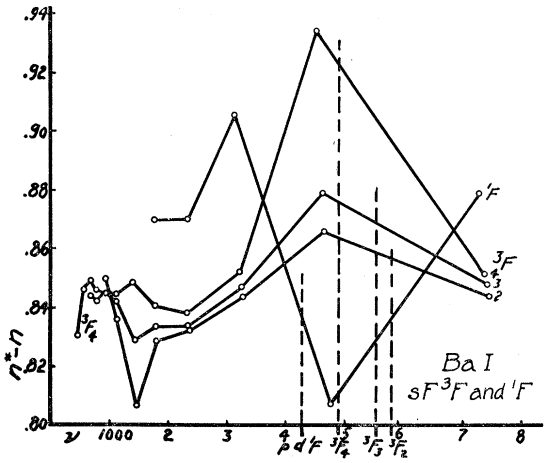

Fig. 5. Plot of ^3F and ^1F series of Ba I.

from $5d7p$. The multiplets are given below in Table II. It will be noticed that two levels, 5039.5 and 3529.9, were previously assigned to the $6snp\,^1P^\circ$ series, The $6snf\,^1F^\circ$ series has also been replaced (H. N. R.) by an entirely new set of terms, which are now found to show a perturbation exactly where expected.

TABLE II. *New multiplets in Ba I. The term values are all measured from* $s^2\,^1S_0$. To obtain value used in this paper, subtract from 42031.4.

	$6s^2\,^1S_0$ 0.00	$6s5d\,^3D_3$ 9596.39	$^3D_2$ 9215.33	$^3D_1$ 9033.87	$^1D_2$ 11395.36
		40 III			
$5d7p\,^3F_4^\circ$ 37131.91		27535.52			
			(4) 15 III		(2u)
$^3F_3^\circ$ 36511.22			27295.84		25115.90
			(2)	(1u) 2 III	
$^3F_2^\circ$ 36235.13			27019.81	27201.18	
		30 III	15 III		
$^3D_3^\circ$ 37540.02		27943.63	28324.72		
		2 III	3 III	10 III	
$^3D_2^\circ$ 37063.18		27466.88	27847.62	28029.46	
	(4) 3 IV		(1u) 3 III	(3) 10 III	(1) 2 III
$^3D_1^\circ$ 36495.65	36495.66		27280.38	27461.78	25100.20
		15 n III	10 III		(2u) 15 III
$^3P_2^\circ$ 37282.08		27685.62	28066.59		25886.64
	(6r) 8 IV		15 III	10 III	(2u) 2 III
$^3P_1^\circ$ 36989.86	36989.82		27774.54	27955.97	25594.55
				10 III	
$^3P_0^\circ$ 36908.21				27874.37	
		(1u)			(5u) 15 III
$^1F_3^\circ$ 37739.96		28142.77 ?			26344.60
			10 III		(2u) 20 III
$^1D_2^\circ$ 37077.44			27861.99		25682.17
	(6r) 8 n IV		3 n III		(3r) 20 NIII
$^1P_1^\circ$ 38499.32	38499.24		29284.20		27103.80

The details of the $^3F^\circ$ and $^1F^\circ$ series are given below. The $^1F^\circ$ series is given in full, since it has not previously been published.

TABLE III. *Constants for $^3F^\circ$ and $^1F^\circ$ series of Ba I.*

Ba

$6snf\,^3F_4$
$\mu = -0.1980$
$\alpha = 8.33 \times 10^{-6}$
$\beta = -33$
$n = 4, 5$
$\nu_0 = 4900.5 = 5d7p\,^3F_4$
Res. = 0, (ν_0), −13, −1, 0, −3, −3, −2, −1, −1, 0, 0, +1

$6snf\,^3F_3$
$\mu = -0.1956$
$\alpha = 8.016 \times 10^{-6}$
$\beta = -32.3$
$n = 4, 5$
$\nu_0 = 5521.2 = 5d7p\,^3F_3$
Res. = 0, (ν_0), 0, 0, +2, 0, +1, −2, −1, 0, 0

$6snf\,^3F_2$
$\mu = -0.1934$
$\alpha = 7.23 \times 10^{-6}$
$\beta = -28$
$n = 4, 5$
$\nu_0 = 5797.3 = 5d7p\,^3F_2$
Res. = 0, (ν_0), 0, 0, +3, +2, +9, 0, −2

$6snf\,^1F_3$
$\mu = -0.1497$
$\alpha = 5.25 \times 10^{-6}$
$\beta = -31.5$
$n = 4, 5$
$\nu_0 = 4292.4 = 5d7p\,^1F_3$
Res. = 0, 0, (ν_0), −9, +7, +5

TABLE IV. $5^1D - n^1F^\circ$ *series of Ba I.* $5^1D = 30637.1$.

λ	*I*	Auth.	ν	*n* ^1F
4283.11	40II	K	23340.9	(4) 7296.2
3861.905	8III	K	25886.6	(5) 4750.5
3636.832	40III	K	27488.7	(6) 3148.4
3531.345	40III	K	28309.8	(7) 2327.3
3463.741	40III	K	28862.3	(8) 1774.8
3921.476	30III	K	29217.8	(9) 1418.3

E & H = Exner and Haschek. K = King.

The F° series are all, undoubtedly, perturbed by the levels given above, but they also show a second possible small disturbance at about $\nu = 1000$. At that position there would be expected the terms arising from the structure $5d4f$.

$^1P^0$.

The $^1P^0$ series of Ba I is given quite incorrectly in Paschen-Götze and in Fowler. One of us (H. N. R.) has recently rearranged the terms of this spectrum and has fixed the following as the $^1P^0$ series.

$mp\,^1P^0 = 23972, 9485, 6140, 4257, 2724, 2047, 1609 \quad n = 6, 7$ etc.

The series has two perturbations by known terms, $5d6p\,^1P^0$ at 13478 and $5d7p\,^1P^0$ at 3532, but a formula containing two β's can be fitted to it with reasonable accuracy. The constants are as follows:

$$\mu = -3.9192$$
$$\alpha = 4.635 \times 10^{-6}$$
$$\beta_1 = -1179$$
$$\beta_2 = -110$$
$$\nu_{01} = 13478$$
$$\nu_{02} = 3532$$
$$n = 6, 7 \text{ etc.}$$
$$\text{Residuals} = -1380, (\nu_{01}), 0, 0, 0, (\nu_{02}), -6, -30, -5.$$

HG I

The mercury spectrum contains long series but none of them is capable of giving an accurate limit. The ^3S series is known to the sixteenth member,

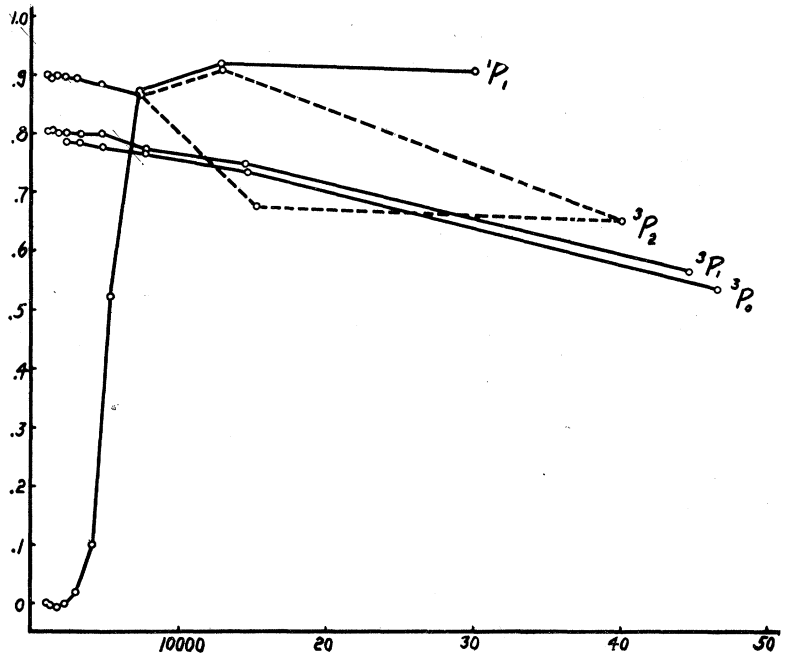

Fig. 6. $^3P^0$ and $^1P^0$ series of Hg I. The second member of $^3P_2{}^0$ may be chosen either way, as indicated in the plot.

but a plot of n^*-n shows a very rapid rise towards the end of the series. The same is true of ^3D. If we accept the usual limit and calculate a Ritz formula for ^3S the residuals are:—

0, 0, +0.5, 0, −0.5, −1.1, −1.7, −0.9, −1.9, −3.5, −3.4, −4.2, −4.3, −3.3.

If we change the limit by +1.5, the agreement is slightly better, except that now the first member is quite far from the calculated position. The residuals are:—

24, 0, 0.2, 0, 0, −0.2, −0.6, −0.4, −1.1, −2.2, −1.9, −2.8, −2.9, −1.7.

For the purpose of the following calculations of the perturbed series, the original limit has been retained, but errors of the magnitude of those above are to be expected. The details of the $^3P^\circ$ series have been taken from a recent paper by Paschen.[5]

The plots of the component $^{3\&1}P^\circ$ series (Fig. 6) indicate that the $^3P_0^\circ$ is unperturbed; that $^3P_1^\circ$ has a small perturbation between the third and fourth members; and that $^3P_2^\circ$ has a large perturbation near the beginning of the series. The origin of the disturbance of the $^3P_2^\circ$ series has been discussed elsewhere.[6] It is attributed to the presence of $5d^9 6s^2 6p\,^3P_2^\circ$, and it has been shown that either the old second member 12974, or the new level 15295, could be attributed to that structure, as far as energy is concerned. It is also true that either one may be taken as a series member and the other as the perturbing level. Both cases have been calculated and can be represented about equally well by a formula. The constant of the perturbation is rather large when the old second member is retained, and we are inclined to believe, therefore, that the other choice is the better. The formulae for both cases are given below. No attempt has been made to include the very low first member.

$\mathrm{HgI}\,^3P_2^0$ (a). $\nu_0 = 15295$

$\mu = -4.0993$

$\alpha = -1.152 \times 10^{-5}$

$\beta = -365$

$n = 6.7$ etc.

Res. $= 0, (\nu_0), 0, 0, 0, +4, +5, +6, +2.$

(b). $\nu_0 = 12974$

$\mu = -4.0842$

$\alpha = -1.129 \times 10^{-5}$

$\beta = -150$

Res. $= 0, 0, (\nu_0), 0, +2, +5, +6, +7, +4.$

In the paper referred to above, it was stated that a possible perturbing term for the series $^3P_1^\circ$ is 7273, calculated from two combinations. That level is, of course, of doubtful reality, but its use does give a very reasonable fit. We are inclined, now, to believe that the perturbation is actually caused by the same level which perturbs the $^1P_1^\circ$ series. Such an assignment is possible because of the fact that the coupling is very far from Russell-Saunders type in Hg I. The perturbation of the $^3P_1^\circ$ series is a very small one, as might be expected in such a case.

$\mathrm{HgI}\,^3P_1^0$ (a). $\nu_0 = 7273? = d^9 s^2 p\,^3P_1^0?$

$\mu = -4.1900$

[5] Paschen, Ann. d. Physik **6**, 47 (1930).

[6] Shenstone, Phys. Rev. **38**, 873 (1931).

$\alpha = -4.15 \times 10^{-6}$
$\beta = -3$
$n = 6, 7$ etc.
Res. $= +2, -1(\nu_0), -10, -1, +1, 0, 0, +1.$

(b) $\nu_0 = 5368 = d^9s^2p\,{}^1P_1{}^0$
$\mu = -4.1925$
$\alpha = -4.02 \times 10^{-6}$
$\beta = -6$
Res. $= -8, +8, (\nu_0), +2, -1, 0, 0, 0, 0.$

If we are correct in choosing the ${}^1P_1{}^\circ$ as the term perturbing the ${}^3P_1{}^\circ$ series, it must be assigned to the structure d^9s^2p. In that case, the corresponding ${}^3P_1{}^\circ$ must be considerably higher. This is the reverse of what would be expected from analogy with similar structures, e.g., d^9sp, d^9p. The ${}^1P_1{}^\circ$ series is interesting because its perturbation also explains the anomalous opening out of the isotope displacements observed by Schüler and Keyston.[7] The plot of n^*-n (Fig. 6) makes it evident that the term 5368 is the logical one to remove. The formula gives a very good agreement except for the low first member and the first one above the perturbation.

$\nu_0 = 5368$
$\mu = -4.0425$
$\alpha = -1.587 \times 10^{-6}$
$\beta = -145.5$
Res. $= \sim -141, 0, 0, (\nu_0), -33, -5, 0, +1, -1, -2.$

The observations of isotopic displacements indicate that they are greatest for terms arising from complicated structures. In Hg I, Schüler and Keyston observe an isotopic shift in the ${}^1S$ series, decreasing for higher members.

In the ${}^1P^\circ$ series they observe zero displacement for the lowest level, a large displacement for the level 5318 and a smaller one for 4217. Unfortunately their observations cannot include the second and third levels, 12886.2 and 7318. The second of these is given in the paper by Paschen quoted above. The level 5318 which shows the large displacement is the one now assigned to the complicated structure d^9s^2p. Its effect as a perturbing term must naturally be treated separately for each isotope, with the result that the series members will show isotopic displacements depending on their nearness to the perturbing term. The case is analogous to the opening out of the intervals in the ${}^3D$ series of Ca I. The presence of two 6s electrons seems to be requisite for a large isotopic displacement.

Al II

The spark spectrum of aluminium has been beautifully analysed by Sawyer and Paschen.[8] It is a two electron spectrum like calcium, and long series

[7] Schüler and Keyston, Zeits. f. Physik **72,** 423 (1931).
[8] Sawyer and Paschen, Ann. d. Physik **84,** 1 (1927).

of type $3snx$ have been recognised. In addition a number of terms have been found which originate in other structures. In particular, the $3p^2\ ^3P$ has been found and a $^3P^\circ$ combining with it. The latter term is incorrectly attributed to $3p3d$. Its position and intervals both indicate the origin $3p4s$.

In Fig. 7 are given the usual plots of all the series of Al II. By using a different scale for each series, the series have all been reduced to an arbitrary length of 100 to make their peculiarities more easily comparable. It is obvious that the ^3G series is accurately Ritzian, and that $^3S\,^1S\,^3D\,^1F^\circ$ and possibly $^3P^\circ$ are nearly so. The series $^3F^\circ\,^1D\,^1P^\circ$ are very far from being Ritzian, and all exhibit the rapid fall in n^*-n towards small term values, which is characteristic of perturbed series into which the perturbing term has been absorbed.

Let us consider the possible foreign terms. They are $3p4s\,^3P^\circ\,^1P^\circ$; $3p^2\ ^1S$, ^1D; $3p3d\,^3P^\circ$, $^3F^\circ$, $^1P^\circ$, $^1F^\circ$. Of these, the only one certainly known is $3P4s\,^3P^\circ$,

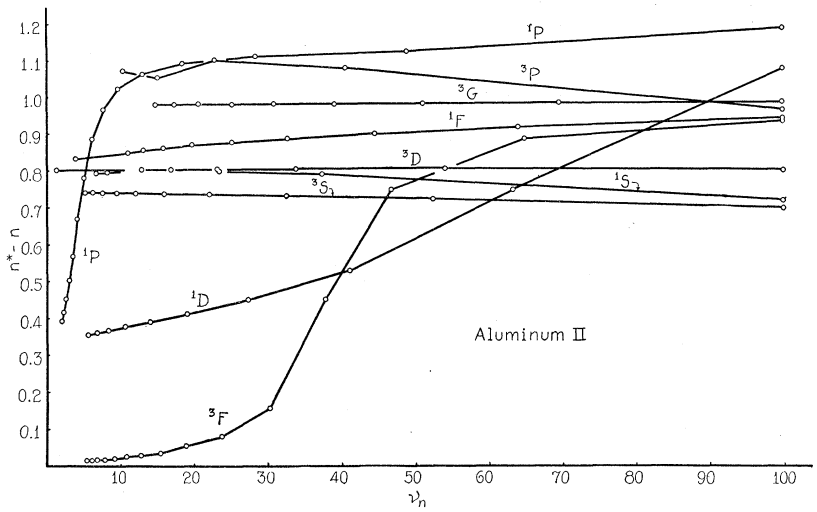

Fig. 7. Series of Al II. The horizontal scale is different for each series in order to reduce them to equal lengths for purposes of comparison. The ordinates of the ^1D series have been reduced by 0.5.

but the positions of the others can be reasonably estimated. From the known $p^2\ ^3P$, and by analogy with other spectra, we can place $s^2\ ^1D$ at about 50,000 to 56,000. The ^1D series contains terms at 66,381 and 41,773, one of which should be $p^2\ ^1D$. In this connection it should be remembered that the perturbing term is also itself displaced. For that reason we believe that the level 66381 is $p^2\ ^1D$, its position being so low because of the repulsion of all of the series terms. The displacement corresponds to a change of about 0.1 in the Rydberg denominator with respect to its own limit. The $p^2\ ^1S$ is either ineffective in producing a perturbation or it lies above the series limit.

The $^3P_2^\circ$ series is given as certain to the fifth member only, and is rather irregular even there. It is probably perturbed by the known $3p4s\,^3P_2^\circ$ at 5903 and also by $3d3p\,^3P^\circ$, the position of which will be discussed below. The $^1P^\circ$ has a disturbance between 5000 and 3000 and probably also above 2000. The

perturbations can be assigned to $3p4s\,^1P^\circ$ and $3d3p\,^1P^\circ$ both unidentified. The remaining irregular series is $^3F^\circ$. The perturbing term is almost certainly the one at 10700. Its separations are large and its position is correct for the term $3d3p^3F^\circ$. In that case $3d3p^3P^\circ$ should not be far away. At λ1910 in Sawyer and Paschen's list we find three lines with approximately the separations of $p^2\,^3P$. If we assume that they are the transition $p^2\,^3P - pd^3P^\circ$, and that the multiplet has the theoretical intensities, we obtain the approximate values

$$\begin{aligned} 3p3d^3P_2^0 \quad & 5262.8 \\ {}^3P_0^1 \quad & 5267.7 \\ {}^3P_0^0 \quad & 5266.8 \end{aligned}$$

The combination $4^3S - pd^3P^\circ$ would then fall about $\nu = 55326$ and there is an unidentified broad line at $\nu = 55328$. (λ1807.40). No other combinations are found, but we believe that the evidence is conclusive for the reality of that term. The $3snf\,^1F^\circ$ series shows a falling off of $n^* - n$ towards the end of the series which may indicate the presence of $3p3d\,^1F^\circ$ near the limit. As was remarked above, the $^1P^\circ$ series indicates a second perturbation above 2000 which is an indication that $3p3d\,^1P$ is also near the series limit. The remaining unidentified terms of this structure, $3p3d^3D^\circ$ and $^1D^\circ$, cannot perturb the ordinary D-series since the parities are opposite.

The calculations for the various perturbed series of Al II are as follows:

^1D Series

$$\begin{aligned} \nu_0 &= 66381 = p^2\,{}^1D? \\ \mu &= -0.3603 \\ \alpha &= 2.096 \times 10^{-6} \\ \beta &= -1300 \\ n &= 3, 4 \text{ etc.} \end{aligned}$$

$$\text{Residuals } \left(\frac{\nu_n}{4}\right)$$

$$(\nu_0),\ +55,\ 0,\ 0,\ -1,\ 0,\ 0,\ 0,\ 0,\ 0.$$

The only large deviation is at the usual point, i.e., in the term nearest to the perturbation.

$^1P_1^\circ$.

As was remarked above, this series is perturbed by $3p4s\,^1P^\circ$ and probably, above the known terms, by $3p3d\,^1P$. But the series has so completely absorbed the $3p4s\,^1P^\circ$ term that it is impossible, and indeed meaningless, to remove any one level from the series and assign it to that structure. The added complication of the probable higher unknown perturbing level makes a series calculation useless. As could be foreseen in such a case, no reasonable fit can be obtained, even though the assignment of any one of a number of terms as $3p4s\,^1P$ gives a curve resembling closely the usual hyperbola.

^3F.

In this series also, the perturbing term is rather intimately absorbed into the series, but it is possible to obtain a formula which gives a very reasonable agreement. The details are as follows. (Table V).

TABLE V. *Constants of $^3F^\circ$ series of Al II.*

Al II	
$^3F_4^\circ$	
	$\nu_0 = 10720 = 3d3p\,^3F_4^\circ$
	$\mu = -0.0579$
	$\alpha = +0.575 \times 10^{-6}$
	$\beta = -530$
	$\eta = 4, 5, 6$
	Res.$(\nu_n/4) = 0, +4, 0, (\nu_0), +20, +1, -1, +1, -3, 0, 0, +4, +2, +1, 0$
$^3F_3^\circ$	
	$\nu_0 = 10753$
	$\mu = -0.0636$
	$\alpha = 0.754 \times 10^{-6}$
	$\beta = -536$
	$\eta = 4, 5, 6$
	Res.$(\nu_n/4) = 0, 0, 0, (\nu_0), +21, +1, -1, -1, -2.$
$^3F_2^\circ$	
	$\nu_0 = 10778$
	$\mu = -0.0613$
	$\alpha = 0.701 \times 10^{-6}$
	$\beta = -550$
	$\eta = 4, 5, 6$
	Res.$(\nu_n/4) = 0, 0, 0, (\nu_0), +25, +4, 0, -1, 0.$

Cu I

The arc spectrum of copper contains probably the most distorted series known, the $np\,^2P^\circ$ series. The lowest member of that series produces the resonance lines in combination with $4s^2S$, and a single second member at 12933 with $J = 1\frac{1}{2}$ has also been recognised for a long time. The higher members of the series were only definitely settled when the spectrum had been so thoroughly analysed, that everything was accounted for except this series.[9] The evidence is now conclusive that the level at 12933 is, in reality, double and inverted, with a separation of about 0.4 wave numbers. The proof came from the accurate measurement of the $m^2D - 5^2P^\circ$ combination lines by Burns[10] and the observation that the Zeeman effect of λ2024 $1^2S - 5^2P^\circ$ is a Paschen-Back effect. The character of the higher members is fixed by Selwyn's[11] observation of the $1^2S - n^2P^\circ$ combinations in the Schumann region; and, in some cases, by Zeeman effects observed by one of us (A.G.S.) Fig. 8 is the plot of the $n^* - n$ against ν_n. The $J = 1\frac{1}{2}$ component is evidently strongly perturbed between the third and fourth members and the $J = \frac{1}{2}$ between the fourth and fifth. In just those positions 5973 and 3952 there are the two components of a wide $^2P^\circ$ arising from $3d^9 4s4p$. The higher series

[9] Shenstone, Phys. Rev. **34**, 1623 (1929).
[10] Burns, Allegheny Obs. Publications VIII 3.
[11] Selwyn, Proc. Phys. Soc. London **41**, 392 (1929).

members are not known with sufficient accuracy or in sufficient number to warrant an accurate calculation of Langer's formula, but a rough calculation gives an approximate fit with the constants for the two series about -100 and -200. There should be also a perturbation due to another $^2P^\circ$ from the same structure, but its effect is evidently much smaller. One would also expect a large perturbation in the $nf\,^2F^\circ$ series. There are only two members of that

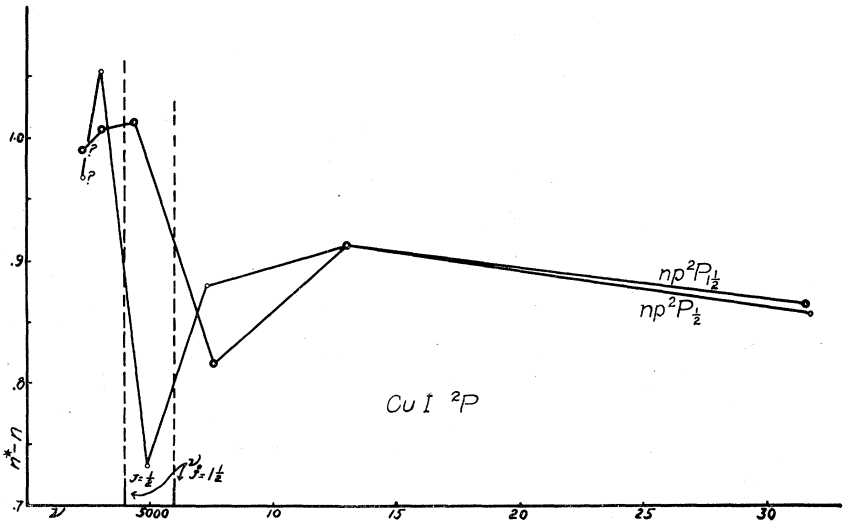

Fig. 8. $^2P^0$ series of Cu I.

series certainly known but they are just in the position to make the perturbation evident, if it existed. The lower of the two levels does show a small inversion but otherwise both members are practically Rydbergian. The exact reverse of this phenomenon is shown in the spectra Zn II and Cd II[12] which are equivalent in structure to Cu I. The $^2P^\circ$ series are quite regular, but the $^2F^\circ$ series exhibit perturbations. From the positions of the irregularities it can be predicted with reasonable certainty that there should be found the following terms in those two spectra.

Zn II

$3d^9 4s4p\ ^2F^0_{3\frac{1}{2}} \sim 13500$

$^2F^0_{2\frac{1}{2}} \sim 10500$

Cd II

$4d^9 5s5p\ ^2F^0_{3\frac{1}{2}} \sim 8500$

$^2F^0_{2\frac{1}{2}} \sim 3000$

There are without doubt many other known series where the methods used in this paper will reveal the presence of perturbations. For instance, the ^2D of Al I certainly contains an extra term whose origin can be safely ascribed to the structure $3s3p^2$. The Mg I ^1D series includes $p^2\ ^1D$ at 2631.6.[13]

[12] Takahashi, Ann. d. Physik **3**, 27 (1929).

[13] Sawyer, J.O.S.A. **13**, 431 (1926).

The Sr I $^1P^\circ$ series is exactly analogous to Ca I $^1P^\circ$. The second member, 11838.7, gives an anomalously weak line in combination with ^1S, but the curve for the series indicates that the level at 3474.7 is causing the perturbation. The ^1S of Sr I is perturbed by $p^2\,^1S$ at 8765.2. The ^3D of Sr I indicates the presence beyond the known terms of $4d6s^3D$, which can, from energy considerations, be placed in the neighborhood of 800.

While this paper was in preparation there appeared an analysis of the spectrum C III by Edlen.[14] The series contain several good examples of the type of disturbance described in this paper. It will be noticed that $2p3p^3S$ perturbs the ordinary ^3S series; $2p3p^3D$ perturbs the ^3D series and produces the very wide separations in the second member; $2p3d^3F^\circ$ perturbs the $^3F^\circ$ series. Other disturbances might be expected but are not found, e.g., the $^3P^\circ$ series by $2p3s^3P^\circ$.

It is probable that, in the spectra Ga II[15] and In II[16], which are similar to Al II, the $p^2\,^1D$ is the level assigned as the first member of the ordinary ^1D series.

The spectrum of lead[17] is interesting because the perturbations are between terms of similar electron structure. In it we have series of terms based on the $^2P_{\frac{1}{2}}$ limit perturbed by terms based on the $^2P_{1\frac{1}{2}}$ limit. Very few of the latter terms have been found and the presence of the perturbations may easily lead to new identifications. A similar type of perturbation is probably the cause of irregularities in Ne I, A I, etc.

In the following table (Table VI) there are collected the constants for all the series which have been considered in any detail. In comparing the values of the constants α and β, it should be noticed that in Al II, the values of α must be multiplied by 4 and β divided by 4 to make them comparable with arc spectrum values.

A review of the data of Table VI discloses the fact that the constant β is always negative. This is the same as saying that the foreign level attempts, by repulsion of neighboring terms, to make a place for itself in the series. The effect is strikingly shown in Fig. 3. In value, β ranges from -3 to -1200 but in most cases is in the range from -25 to -150 wave numbers.

The theoretical problem presented by the failure of perturbations to occur is perhaps more important than the fact that many do occur. Some cases have been noted in the discussion of particular spectra but many more can certainly be found. The problem is being investigated in this laboratory from both the theoretical and the experimental sides.

It is evident from the data given that there are two places in a perturbed series which show poor agreement with the simple formula. The first disagreement is in the lowest term of the series. This is quite common in unperturbed series and will be discussed below. The second disagreement is in the terms next to the perturbing term. It might be assumed that this deviation could

[14] Edlen, Zeits. f. Physik **72**, 559 (1931).
[15] Sawyer and Lang, Phys. Rev. **34**, 712 (1929).
[16] Lang and Sawyer, Zeits. f. Physik **71**, 453 (1931).
[17] Giessler and Grotrian, Zeits. f. Physik **39**, 377 (1926).

TABLE VI. *Adopted series formula.* $n^*=n+\mu+\alpha\nu_n+(\beta/\nu_n-\nu_0)$. Constants for all the series which have been considered in detail. In the case of Al II, α should be multiplied by 4 and β divided by 4 to make them comparable with arc spectrum constants.

Spectrum	Series	μ	α	β	ν_0	(origin)	Remarks
Ca I	^1S	-2.3495	-1.066×10^{-6}	-100	8614	p^2	
	$^1P^\circ$ (a)	$\backsim-2.291$	$\backsim2.7\times10^{-5}$	$\backsim-4500$	12573	$3d4p$	Questionable
	(b)	-1.9753	1.42×10^{-7}	-526	5372	?	Questionable
	$^3P_2^\circ$	-1.9489	-7.48×10^{-6}	-62.9	9964	$3d4p$	
	^1D	$\backsim-0.8678$	$\backsim-4.4\times10^{-6}$	$\backsim-150$	8585	$4p^2$	Probably a second pert. at 1492 (d^2)?
	$^3D_3$	-0.8656	-3.665×10^{-6}	-90	1829	$3d5s$	
	$^3D_2$	-0.8678	-3.571×10^{-6}	-86	1839	$3d5s$	
	$^3D_1$	-0.8705	-3.39×10^{-6}	-85	1849	$3d5s$	
	$^1F^\circ$	-0.0955	2.90×10^{-5}	-80	8767	$3d4p$	
Ba I	$^3F_4^\circ$	-0.1980	8.33×10^{-6}	-33	4900.5	$5d7p$	
	$^3F_3^\circ$	-0.1956	8.016×10^{-6}	-32.3	5521.2	$5d7p$	
	$^3F_2^\circ$	-0.1934	7.23×10^{-6}	-28	5797.3	$5d7p$	
	$^1F_3^\circ$	-0.1497	5.25×10^{-6}	-31.5	4292.4	$5d7p$	
	$^1P^\circ$	-3.9192	4.635×10^{-6}	-1179	13478	$3d6p$	
				-150	3532	$3d7p$	Two perturbations
Hg I	$^3P_2^\circ$ (a)	-4.0993	-1.152×10^{-5}	-365	15295	$5d^96s^26p$	Reversal of roles of these two levels
	(b)	-4.0842	-1.129×10^{-5}	-150	12974	$5d^96s^26p$	
	$^3P_1^\circ$ (a)	-4.1900	-4.15×10^{-6}	-3	7273?	$5d^96s^26p^3P_1^\circ$	Questionable level
	(b)	-4.1925	-4.02×10^{-6}	-6	5368	$5d^96s^26p^1P_1^\circ$	$J-J$ coupling.
	$^1P^\circ$	-4.0425	-1.587×10^{-6}	-145.5	5368	$5d^96s^26p^1P_1^\circ$	
Al II	$^1P^\circ$	$\backsim-0.85$	$\backsim-0.3\times10^{-6}$	$\backsim-400$	3858?	$3p4s$	Very approximate
	^1D	-1.3603	2.096×10^{-6}	-1300	66381	$3p^2$	
	$^3F_4^\circ$	-0.0579	$+0.575\times10^{-6}$	-530	10720	$3p3d$	
	$^3F_3^\circ$	-0.0636	$+0.754\times10^{-6}$	-536	10753	$3p3d$	
	$^3F_2^\circ$	-0.0613	$+0.701\times10^{-6}$	-550	10778	$3p3d$	
Cu I	$^2P_{\frac{1}{2}}^\circ$	$\backsim-2.0572$	$\backsim-0.69\times10^{-6}$	$\backsim-196$	3952	$3d^94s4p$	Approximate only
	$^2P_{1\frac{1}{2}}^\circ$	$\backsim-2.0404$	$\backsim-2.56\times10^{-6}$	$\backsim-100$	5973	$3d^94s4p$	Approximate only

be removed by the consideration of an expression of type $\gamma/(\nu_n-\nu_0)^2$. Such can not be the case, however, because the deviation is never symmetrical and the large error frequently occurs for the term which is the further from the perturbation. The plot of the parabola $(n^*-n)\ (\nu_n-\nu_0)$ against ν_n, usually tells unambiguously which level it will be impossible to fit on the curve. In other words, it is not merely a question of fitting the formula to one or the other term by a change in the constants. It is really impossible to fit any formula of Langer's type without modification to give agreement at the points which, in the calculated series, show the large deviations.

As regards the large deviations from the Ritz formula shown by the first members of both regular and irregular series, it should be remarked that there is a very great distinction between one and two electron spectra. If one plots the curves for Na, K, Rb, Cs, ^2S, and $^2P^\circ$ series, the lack of linearity is very small indeed. The reverse is the case for the ^1S and $^3P^\circ$ series of Mg, Zn, Cd, Hg. The lowest terms are normally thousands of wave numbers below the position indicated by a linear extrapolation. The comparison is roughly as follows:

$^2P^0$ Na, K, Rb, Cs $= 0, 0 \sim 40 \sim 90$
^2S " " " " $= 0\ 0\ 0\ 0$
$^3P^0$ Mg Zn Cd Hg ~ 0 2300, 2200, 3500
^1S " " " " $\sim$ 6800, 9300, 8700, 9500.

The series of Ca, Sr. Ba are too perturbed to be of value in this comparison. It is also perhaps unfair to use the ^1S series at all, because the lowest member is due to a closed group s^2. The P series however show very clearly that the tendency of series is quite different in the one and two electron spectra.

Langer remarks that his result

$$n^* = n + \sum \frac{p_{in}}{\nu_n - \nu_i}$$

is obtained from a consideration of the perturbation theory for more than one electron. If we accept the experimental result from perturbed series that the p_{in} are always of such a sign as to cause repulsion, the lowest term of a series in a two-electron system experiences repulsions from all the higher members with no compensating repulsions from lower terms. One would then expect to find it moved toward lower term values, i.e., smaller values of n^*. This is in agreement with observation.

The numerical computations in this paper were greatly facilitated by a Rydberg term table calculated by Miss Janet MacInnes in this laboratory. The table contains the values of R_∞/n^{*2} for values of n^* from 1 to 11 in steps of 0.001. Fowler's table in steps of 0.01 and Paschen's table in steps of 0.05 are not sufficiently detailed to allow a linear interpolation. In one series, which was first calculated by using Fowler's table, errors of as much as 8 wave-numbers were detected when it was recalculated on the basis of the new table.

Miss MacInnes and Professors Condon and Turner have been very helpful in the preparation and criticism of this paper.