OCTOBER 1, 1933 PHYSICAL REVIEW VOLUME 44

Multiplet Separations and Perturbed Terms

N. G. Whitelaw, *University of Wisconsin*

(Received July 27, 1933)

It is well known that the multiplets in spectral series show an anomalous widening in regions where they are strongly perturbed by a vagrant term of large multiplet structure, which tends to impress its characteristics upon the series. Formulae are derived in this paper for the multiplet widths of perturbed terms, which enable one to calculate the separation of the multiplet levels providing the total shift of the "centers of gravity" of the multiplets from their unperturbed values is known. If a Ritz correction, $n^* = n - 0.03629 + 0.0399/n^2$, is assumed to give the positions of the terms exclusive of interaction with the perturbing $3p3d\,^3F$ term, one obtains excellent agreement between calculated and observed multiplet widths for the $3snf\,^3F$ series of Al II. Other examples treated are the ^2P series of Cu I and the $6snf\,^3F$ series of Ba I.

In investigating perturbed spectral series, one frequently finds that the multiplet separations behave anomalously in the region of the perturbing term. The $3smf\,^3F$ series of Al II shows a marked widening of the multiplets in the neighborhood of the intruding member, as can be seen in Fig. 1. This widening, of course, is due to the fact that because of the perturbation, the series members show some of the characteristics of the intruding term, which here has a wider multiplet structure than the members of the series proper. The importance of intruding members in spectral series is well known since the noteworthy paper of Shenstone and Russell.[1] Even before the day of quantum mechanics Schrödinger[2] noted that the anomalous behavior and positions of the multiplets of the ^3F series of Al II were to be attributed to some sort of a resonance phenomenon. The perturbation mechanism for this has been furnished by the new mechanics, as already noted by R. M. Langer.[3]

It is usually difficult to calculate by quadrature the off-diagonal matrix elements which embody the perturbing effect of an intruding term, since one rarely has accurate radial wave functions at his disposal for the states in question. We shall find, however, that knowledge of the wave functions is unnecessary for the calculation of the relative in distinction from absolute energies of the various members of the multiplet.

The secular determinant for the type of problem in which we are interested is of the form:

$$\begin{vmatrix} H(11)+\sigma_{11}{}^{(J)}-W^{(J)} & H(12) & H(13) & \cdots & H(1N) \\ H(12) & H(22)+\sigma_{22}{}^{(J)}-W^{(J)} & 0 & \cdots & 0 \\ H(13) & 0 & H(33)+\sigma_{33}{}^{(J)}-W^{(J)} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ H(1N) & 0 & 0 & \cdots & H(NN)+\sigma_{NN}{}^{(J)}-W^{(J)} \end{vmatrix} = 0. \tag{1}$$

Here, apart from the magnetic terms, $H(11)$ is the original position of the perturbing term, while $H(22), \cdots H(NN)$ have the same significance for the regular series members. The $H(1j)$ are the matrix elements of electrostatic energy, and the $\sigma_{ii}{}^{(J)}$ are those of the spin-orbit energy, given by

$$\sigma_{ii}{}^{(J)} = \tfrac{1}{2}A_i[J(J+1) - L(L+1) - S(S+1)]. \tag{2}$$

---

[1] Shenstone and Russell, Phys. Rev. **39**, 415 (1932).

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

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

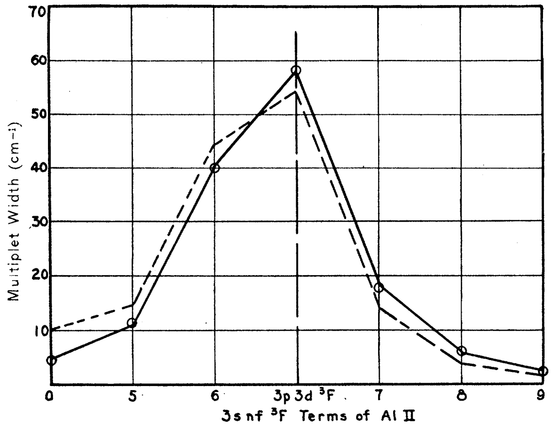

FIG. 1. The heavy line gives the calculated multiplet widths of the $3snf\,^3F$ series of Al II when the Ritz correction is used to find the unperturbed positions of the terms; the broken line gives the result obtained with no correction, and the circles are the observed widths. The vertical broken line (scale 0–150 instead of 0–70) is included to show that all the multiplet separation would belong to $3p3d\,^3F$ were there no perturbations.

The roots $W^{(J)}$ of (1) are, of course, the actual term values. The spin-orbit interaction does not yield off-diagonal elements in (1) since it is diagonal in the individual azimuthal quantum numbers, whereas the perturbing term 1 will in general have different values of one or more l_i from the perturbed terms 2, 3, 4, $\cdots N$. All the terms in (1) have the same L, S and J. Each value of J in the sequence $|L-S|\cdots|L+S|$ gives rise to a different secular determinant, and a correspondingly different set of roots $W^{(J)}$. Under our hypotheses the various determinants have the same $H(1n)$ and differ solely in the $\sigma^{(J)}$. The superscript (J) has been affixed to all quantities which have a dependence on J.

The solution of a border determinant[4] such as (1) is given by:

$$H(11)+\sigma_{11}^{(J)}-W_n^{(J)} = \sum_{j=2}^{N} \frac{|H(1j)|^2}{H(jj)+\sigma_{jj}^{(J)}-W_n^{(J)}}. \quad (3)$$

It is apparent that if one possesses a set of unperturbed values $H(ii)+\sigma_{ii}^{(J)}$, $(i=1,\cdots N)$, for the spectral terms together with the corresponding set of actual levels $W_n^{(J)}$, then the off-diagonal electrostatic matrix elements may be computed.

The general procedure will then be: (a) given the $H(ii)+\sigma_{ii}^{(J)}$, $(i=1,\cdots N)$, and $W_n^{(J)}$ for one value of J, solve the linear Eqs. (3) for the $H(1j)$'s, (b) by means of this set of $H(1j)$'s, together with the $\sigma_{ii}^{(J)}$ furnished by (2) for the new values of J, calculate the actual values $W_n^{(J)}$ for the remaining components. The differences between the roots for the various determinants then furnish us with the multiplet widths. Step (a), unlike step (b), involves just the reverse of the usual perturbation calculation since in (a) we regard the matrix elements rather than the energy levels unknown.

The above assumption that the $H(1j)$'s are independent of J requires some comment. If the unperturbed system of representation is strictly Russell-Saunders in character, the assumption is, of course, entirely valid. However, if there is an appreciable tendency towards j-j coupling, there may be other important perturbations besides that due to state 1, namely, the perturbation due to spin-orbit interaction with states of similar l_i but different L, S, which are not represented in (1). Of course, one can imagine these interactions already allowed for in forming the unperturbed system, but then with given l_i, L, S the electrostatic part of the energy will no longer be independent of J, and the $H(1j)$ will not be independent of J. Thus our calculations are confined to configurations which are dominantly Russell-Saunders in character, and we must not be surprised to find that they do not work as well in Cu and Ba as in Al II.

Under certain conditions one can simplify the above procedure somewhat. If the multiplet separations before and after perturbation are small compared to the shift in energy of the terms caused by the perturbation, one may expand the Eqs. (3) in terms of the $\sigma_{ii}^{(J)}$ and $(W_n^{(J)}-W_n)$, retaining only first powers of the $\sigma_{ii}^{(J)}$ and $(W_n^{(J)}-W_n)$. The W_n denote the actual positions of the terms exclusive of magnetic energy. One finds by this method:

$$W_n^{(J)}-W_n = K^2\left[\sigma_{11}^{(J)}-\sum_{j=2}^{N}\frac{|H(1j)|^2}{[H(jj)-W_n]^2}\,\sigma_{jj}^{(J)}\right] \quad (4)$$

with

$$\frac{1}{K^2}=1+\sum_{j=2}^{N}\frac{|H(1j)|^2}{[H(jj)-W_n]^2}. \quad (5)$$

---

[4] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 220.

This is the same as the formula:

$$W_n^{(J)} - W_n = \sum_{i=1}^{N} S(ki)\sigma_{ii}^{(J)} S^{-1}(ik), \qquad (6)$$

if the transformation matrix S is determined by solving the primary electrostatic problem. Eqs. (4) and (6) are identical inasmuch as the elements $S(ik)$ of the transformation matrix for a border determinant such as (1) with $\sigma_{ii}^{(J)}=0$ $(i=1, \cdots N)$ have the form:

$$S(ik) = K\frac{H(1j)}{H(jj)-W_k}, \quad (i \neq k); \quad S(ii) = K, \qquad (7)$$

where K is a normalization factor defined as in (5). The accurate transformation matrix is determined from a secular determinant in which the magnetic terms are included, but the modification in S resulting from these terms is unimportant if the σ's are small.

If the approximation (4) is allowable, the multiplets will still obey the interval rule (2), but the proportionality constants will no longer have the unperturbed values A_i.

APPLICATION TO THE ^3F SERIES OF AL II

The multiplet separations of the $3smf\ ^3F$ series of Al II are very irregular because of perturbation by a ^3F term identified by Shenstone and Russell,[1] and Van Vleck[4] as arising from the configuration $3p3d$. This term was so intimately absorbed into the regular $3smf\ ^3F$ series that it was classified as an ordinary member by Sawyer and Paschen.[5]

The conditions demanded by Eq. (4) were satisfied in this case so the determination of the multiplet widths was made by that method. The unperturbed multiplet separations of the $3smf\ ^3F$ series were taken to be zero, permitting us to set $\sigma_{ii}^{(J)}=0$, $(i=2, \cdots N)$. The multiplet separation of the unperturbed $3p3d\ ^3F$ term was assumed to be the sum of the observed multiplet separations of the $3smf\ ^3F$ series plus that of $3p3d\ ^3F$ (Fig. 1). This assumption is valid since the spur of the matrix of the σ's $(i=1, \cdots N)$, must be the same before and after perturbation. The multiplet width of a $3p3d\ ^3F$ term may also be calculated by Goudsmit's formula[6] with the screening constants obtained from the $3s3p\ ^3P$ and $3p^2\ ^3P$ terms. The values found for the unperturbed overall width of $3p3d\ ^3F$ were: (a) from the sum of the observed ^3F widths, 142 cm^{-1}, (b) from $3s3p\ ^3P$, 146 cm^{-1}, and (c) from $3p^2\ ^3P$ 144 cm^{-1}. This agreement is much better than one can normally expect.

If one includes all discrete and continuous levels belonging to the $3smf\ ^3F$ series, the secular determinant to be solved is infinite. However, nearly all the multiplet separation is absorbed by the first six members of the series showing that they are the most strongly perturbed. An approximate solution W_n^0 was obtained first by considering these six levels plus the intruder.

Effect of terms beyond $3s9f\ ^3F$ on the solution of (3). In order to take into account the effect of the remaining levels $3smf\ ^3F$, $(m=10, \cdots \infty)$, on the solution of the linear Eq. (3), the following procedure was adopted: The infinite secular problem was reduced to a finite one by assuming that W_n may be replaced by W_n^0 in terms representing the influence of levels beyond $3s9f\ ^3F$. The only effect then of the outer levels $n>7$ was the contribution of an additive term B to the right side of Eqs. (3) restricted to $n \overline{<} 7$, namely,

$$B = \sum_{j=8}^{\infty} \frac{|H(1j)|^2}{H(jj)-W_n^0}. \qquad (8)$$

The values of (8) were estimated by assuming that for the levels beyond $3s9f\ ^3F$:

$$H(1j) = C1/r^2(3d; mf). \qquad (9)$$

The basis of this assumption will be discussed in a paper immediately following this one; the point is not that (9) is strictly true but that it is a sufficient approximation for $H(1j)$, $(j>7)$, since $H(18) \cdots H(1N)$ need not be known as accurately as $H(12) \cdots H(17)$. The factor of proportionality, C, was determined so as to make the $H(1j)$, $(j<8)$, obtained by (9) agree as well as possible with the correct values found from (3). The matrix elements of $1/r^2(3d; mf)$ for discrete-discrete transitions were calculated by means of the well-known Laguerre functions. In the discrete-continuous case, one finds by a method

---

[5] R. A. Sawyer and F. Paschen, Ann. d. Physik **84**, 1 (1927).

[6] Pauling and Goudsmit, *The Structure of Line Spectra*, p. 99; W. Heisenberg, Zeits. f. Physik **32**, 841 (1925).

similar to that used by Sugiura[7] in his calculation of the number of dispersion electrons for discrete-continuous transitions in hydrogen that for the case $n_1=l_2=l_1+1$

$$\left[\frac{1}{r^2}(n_1l_1;\,El_2)\right]=\left[\left(\frac{2Z}{n_2a_0}\right)^3\frac{(n_1-l_1-1)\,!e^{2\pi x}(e^{2\pi x}-1)e^{-4x\ \arctan(n_1/x)}}{2n_1[(n_1+l_1)\,!]^3 8\pi^2Za_0(4E)^{l_2}(l_2\,!)^2\prod\limits_{\mu=1}^{l_2}(1+x^2/\mu^2)}\right]^{\frac{1}{2}}$$

$$\times\frac{(2Z/n_1)^{l_1}[(n_1+l_1)\,!]^2 2\pi i(n_1{}^2/E)^{l_2}(x^2+n_1{}^2)^{l_2}}{(e^{2\pi x}-1)(n_1/iE^{\frac{1}{2}})^{l_1+l_2}(-x+n_1)^{l_1+l_2}}K, \quad (10)$$

$$K=\sum_{p=0}^{l_1+l_2}\left\{\binom{l_2-ix}{p}\binom{l_2+ix}{l_1+l_2-p}\left(\frac{l_1-ix}{l_2+ix}\right)^p(-1)^p\right\}=\frac{(2l_2)^{2l_2}(ix+l_1-1)\cdots(ix-l_1+1)}{(2l_2-1)\,!(l_1+ix)^{l_1+l_2}}.$$

Here $x=Z/E^{\frac{1}{2}}$, and E denotes the energy measured in multiples of the Rydberg constant.[8] The variation of the square of the absolute value of (10) as a function of E may be seen in Fig. 2.[9]

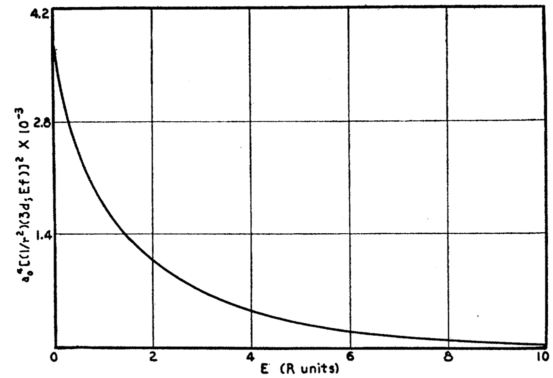

FIG. 2.

The inclusion of term B made a difference varying from six to one percent in the multiplet widths according as respectively the multiplet was far removed from or close to the intruder.

Positions of unperturbed levels. The unperturbed energy values of $3smf\ ^3F$, $(m=4, 5, \cdots 9)$, were obtained by applying an empirical Ritz correction:

$$n-n^*=0.03629-0.0399/n^2, \quad (11)$$

to a straight hydrogenic set of energy levels. A correction of this general nature was necessary since the unperturbed set should be unperturbed only in the sense that they have not felt the disturbing influence of $3p3d\ ^3F$. An attempt is made to justify the particular Ritz correction (11) in Section V of the following paper.[10] The calculated multiplet widths proved to be very sensitive to the Ritz correction assumed for the unperturbed positions. This was especially true for the multiplets of the first and last series members of the six treated, for which we do not obtain good agreement if much change is made in the constants of (11). For example if instead of (11) the Balmer formula, $n-n^*=0$, had been used, we would have obtained the dotted curve in Fig. 1. Since the quantum defect due to perturbation by $3p3d\ ^3F$ was very large for the middle members, they did not prove as sensitive as the outside

---

[7] Y. Sugiura, J. de Physique **8**, 113 (1927). Sci. Papers, Toyko Inst. Phys. and Chem. **11**, 1 (1929).

[8] The second form of the expression for K is obtained from the first by expressing the sum as a coefficient in a multinomial expansion, after removal of a factor $1/(l_1+ix)^{l_1+l_2}$. This coefficient can be proved to be a polynomial in ix, and can be evaluated since its zeros can be obtained by inspection.

[9] As a check on the correctness of (10), we have verified that formula (17) of the following paper is satisfied, specialized to $s=-2$, $n=3$, $l=l'-1=2$. The right and left sides of (17) are then found to agree to within 5 percent, which is as good as can be expected since the integration over the continuum can only be performed graphically and high numerical precision was not attempted. In (17) the summation is, of course, to be understood to include this integration. The matrix elements (10) are so normalized that their contribution to (17) is obtained by squaring and integrating over E from 0 to ∞. As an additional check, it was verified that the discrete and continuous elements join together at $E=0$ in the fashion discussed in connection with reference 28 of the following paper (Phys. Rev. **44**, 551 (1933)). Only the discrete-continuous matrix elements are exhibited in Fig. 2. The discrete-discrete elements are found in our case to contribute only 13 percent of (17).

[10] Van Vleck and Whitelaw, Phys. Rev. **44**, 551 (1933).

ones to the unperturbed positions assumed. In the case of the outside members, the Ritz correction and the quantum defect due to perturbation by $3p3d\ {}^3F$ were of the same order of magnitude.

The unperturbed position of the intruding term $H(11)$ was located for the solution of the six levels alone plus the intruder by making use of the theorem[11] that for a unitary transformation the spur of the energy matrix is invariant. Given all the actual term values plus the unperturbed ones of the regular series members, one easily locates the intruder at 11,568 cm^{-1}.

Results. A table of the calculated *versus* the observed multiplet widths, and of the off-diagonal elements $H(1j)$ is given in Table I.

TABLE I.

Term	Calc. Sep.	Obs. Sep.	$H(1j)$
$3s4f\,{}^3F$	4.77 cm^{-1}	4.92 cm^{-1}	2948 cm^{-1}
$5f$	11.98	12.29	2056
$6f$	40.67	40.44	1502
$3p3d$	57.90	58.10	
$3s7f$	18.36	17.83	1176
$8f$	5.61	5.70	940
$9f$	2.46	2.42	778

Insensitivity of multiplets to distant perturbations. In a great many cases one finds multiplets which have been displaced as a whole, but the relative positions of the components remain unaltered. This is to be expected unless the perturbing member is nearby or unless either the perturbing term or the perturbed member has an extremely wide multiplet structure. If $H(ij)$ is the matrix element of perturbation between two remote terms, the energy shift of the perturbed term as a whole is approximately:

$$\Delta W = |H(ij)|^2/[H(ii)-H(jj)], \tag{12}$$

whereas the new multiplet separation absorbed from the perturbing term is:

$$\sigma_{jj}{}'^{(J)} = |H(ij)|^2\sigma_{ii}{}^{(J)}/|H(ii)-H(jj)|^2, \tag{13}$$

if $\sigma_{ii}{}^{(J)}$ is the unperturbed multiplet width of the intruder. One sees then that it may be possible to have large perturbing matrix elements and still have little effect on multiplet widths provided the perturbing term is sufficiently far removed, since (12) has the first power and (13) the second of $[H(ii)-H(jj)]$ in the denominator.

This condition is quite generally found in the low lying multiplets of two electron spectra. The perturbing terms usually lie near or outside the series limit, and shift the terms downward as a whole without disturbing their multiplet structure to any extent. As noted by Shenstone and Russell, the lowest ${}^3P$ terms of Zn, Cd and Hg, all lie much deeper than a linear extrapolation of the quantum defect for higher lying terms would indicate. However, if one examines the multiplet separations in the above series, one finds them to be quite regular. In the case of Al II the positions of the $3smf\ {}^3F$ terms are influenced by $3pmg\ {}^3F$. The effect of this influence, by no means insignificant (cf. next paper), is incorporated in our "unperturbed" levels (11). Nevertheless due to the large energy separation, a negligible amount of the multiplet separation of $3p5g\ {}^3F$ is shared, although its multiplet width is of the same order of magnitude as that of $3p3d\ {}^3F$.

Hyperfine structure. The hfs of the F terms of Al II is mainly due to the $3s$ electron. Hence the perturbation by $3p3d$ diminishes the hfs of a term $3snf\ {}^3F$ by a fractional amount equal to the ratio of its multiplet separation, as given in the table, to the intruder's original separation 142 cm^{-1}. The perturbed $3p3d\ {}^3F$ state should have a hfs of $(142-58)/142=0.59$ times the width of that of an unperturbed $3snf\ {}^3F$ term.[12] The existing spectral measurements are not refined enough to test these predictions.

Si III. The $snmf\ {}^3F$ series of Si III shows a perturbation and anomalous multiplet width similar to that in Al II, but extensive calculations are not feasible since only the two lowest terms have been identified.

THE ${}^2P$ SERIES OF COPPER

The ${}^2P$ series of copper is perturbed[13] by two levels and consequently only a rough correlation

---

[11] There is no essential modification of the theorem necessary when the additional terms (8) are included in the secular problem, as all one needs to do is to regard the original levels in the secular problem of the six lowest states as inclusive of the displacement (8).

[12] This behavior is a rather extreme example of the modulation of hfs by electrostatic perturbations, an effect stressed recently by Fermi and Segre, Zeits. f. Physik **82**, 729 (1933).

[13] Shenstone, Phys. Rev. **34**, 1623 (1929). Also private communication in regard to perturbing terms in Cu.

can be made between the term displacements and the multiplet separations. The multiplet separations of these levels are not small compared to the displacements caused by the perturbation, and so Eq. (4) cannot be used. The perturbation matrix elements, if one assumes Russell and Saunders coupling will, however, still be independent of J. One may work out the perturbation matrix elements between the $^2P_{\frac{3}{2}}$ terms and the chief perturbing term, and use these perturbation elements to calculate the perturbed positions of the $^2P_{\frac{1}{2}}$ terms.

The selection of the unperturbed positions of the $^2P_{\frac{3}{2}}$ series is quite critical as there is only a narrow range for the quantum defect which will yield a sensible solution. The equation $n-n^*=2.08-1.66\times 10^{-6}\nu_n$ was found empirically to give the best agreement with experiment, and made the observed and unperturbed positions of the first series member agree.

The resulting term values are given in Table II.

TABLE II.

	$^2P_{\frac{1}{2}}$		$^2P_{\frac{3}{2}}$	
n	Observed	Calculated	Observed	Assumed
4	31,780.8 cm^{-1}	—	31,532.4 cm^{-1}	31,532.4 cm^{-1}
5	12,932.7	12,929	12,933.1	12,566
6	7,288.3	7,377	7,531.9	7,185
7	4,897.4	4,941	4,366.8	4,543
8	2,993.2	2,890	3,040.1	3,135

A better idea of the agreement is perhaps furnished by the graph of quantum defect against term value in Fig. 3. The perturbing multiplet $^2P_{\frac{1}{2},\frac{3}{2}}$ is located at 3952.3, 5972.7 cm^{-1}. From the constancy of the diagonal sum of the energy matrix, the corresponding unperturbed position is found to be 4498, 6426 cm^{-1}. There is also the other perturbing multiplet $P_{\frac{1}{2},\frac{3}{2}}$ at 16,495.2, 16,436.9 cm^{-1}, but we have neglected its disturbing influence, which is small except perhaps on $5p\,^2P$.

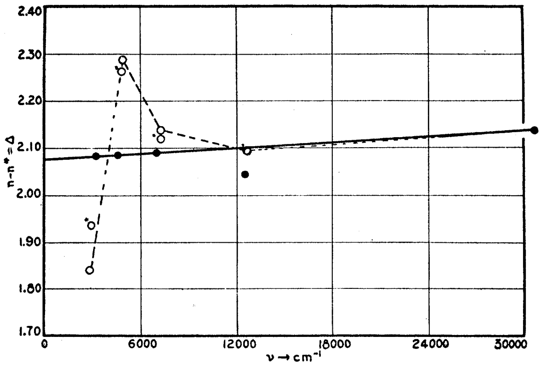

FIG. 3. The dots give the unperturbed defects assumed for the $^2P_{\frac{3}{2}}$ levels of Cu I. The circles give the calculated perturbed defects for the $^2P_{\frac{1}{2}}$ series. The asterisk indicates observed defects for the $^2P_{\frac{1}{2}}$ members.

THE ^3F SERIES OF BARIUM

As noted by Shenstone and Russell the $6snf\,^3F$ series is badly perturbed by a term arising from a $5d7p$ configuration. This perturbing term has such a wide multiplet structure that one must proceed as in the case of copper. A set of unperturbed energy values for the ^3F component was obtained by assuming the first and fourth members of the $6snf$ series to be undisturbed by the intruding $5d7p\,^3F$ term. A linear extrapolation of the quantum defect as a function of the term value then yielded unperturbed energy values for the second and third terms. Beyond the fourth term of the series a new perturbation enters which makes it impossible to treat the series further. The calculation of the $H(1j)$'s for the $^3F_2$ component was performed as in the case of copper, and the perturbed positions of the $^3F_3$ and $^3F_4$ components and $^1F_3$ computed. It was necessary, of course, to assume that the exchange portion of the $H(1j)$ vanished in this case in order to use the

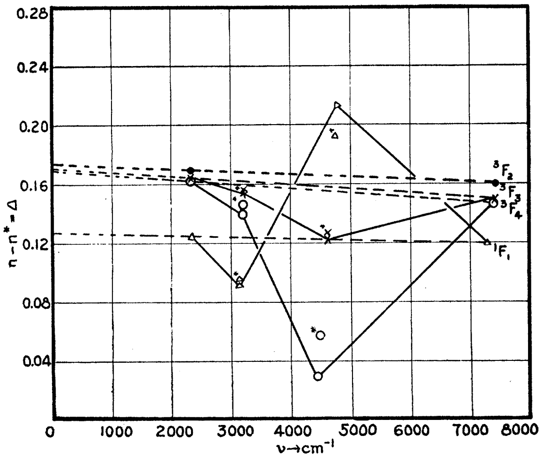

FIG. 4. The dotted lines give the unperturbed defects assumed for the indicated components of the $6snf\,^3F$ series and the ^1F series of Ba I. The heavy lines give the calculated perturbed defects, and the asterisk shows the observed defect.

$H(1j)$ calculated for the triplets for determining the perturbed positions of the singlets. Section VII of the following paper shows that this assumption is not an especially close approximation.

Table III gives the computed energy values. The corresponding quantum defects are illustrated in Fig. 4.

TABLE III.

	Calculated				Observed			
Term	$^3F_2$	$^3F_3$	$^3F_4$	$^1F_3$	$^3F_2$	$^3F_3$	$^3F_4$	$^1F_3$
4	—	—	—	—	7429.8	7415.8	7401.6	7296.2
5	—	4611	4445	4610	4637.6	4613.4	4508.3	4750.5
6	—	3210	3200	3180	3216.8	3213.3	3207.2	3148.4
7	—	—	—	—	2354.2	2351.7	2349.3	2327.3

The corresponding positions of the perturbing term are

$5d7p\ ^3F$	$^3F_2$	$^3F_3$	$^3F_4$	$^1F_3$
Observed	5796.3	5519.7	4899.5	4291.44
Unperturbed	5721.7	5429	4708	4400

In conclusion the writer wishes to thank Professor J. H. Van Vleck for suggesting the problem, and for helpful suggestions during the progress of the work. Also, the latter part of this paper as well as the following was partially supported (N. G. W.) by a grant from the Wisconsin Alumni Research Foundation.