

Π_a shows that for small K the calculated curve for $M=K$ will lie below the limiting case b' curve ($\alpha > 0$) and that the difference between the two will increase rapidly with K . The equation for δ_0 , which is the limiting case for a Π_a state with uncoupling, shows that for $\alpha > 3$ the calculated curve lies below the limiting curve but that the difference decreases rapidly with increasing K . For $M=K$ both limiting curves lie for all K above the curve for $M=0$. The calculated curves start out for small K below the first limiting curve and then approach the second limiting curve from below. For the $4d\pi\Pi_a$

state the extreme levels cross over at about $K=10$. For α slightly greater than 20, the extreme levels would cross over first for small K and a second time for very large K .

Curves of a similar nature could be drawn for the magnetic levels of the three states of a p -complex using Eq. (6). The Π state correlated to the δ_{-1} state would show a crossing over of the levels for suitable α and K in a manner very similar to that shown in the cases described above.

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On Perturbed Series, Especially in C III, B I and O IV

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Consideration of possible extra-configurational perturbations in atomic spectral series shows that often some series are preferable to others for the determination of series limits. In particular: In C III, several $2snd\ ^3D$ terms are recalculated, but Edlén's series limit value is verified in spite of perturbations; in B I, the term values are increased by 90 cm^{-1} or 0.011 volt, so that B I $2s^2 2p\ ^2P_{3/2}$ - B II $2s^2\ ^1S_0 = 66,930\text{ cm}^{-1} = 8.257$ volts; and in O IV, the old $5s\ ^2S_1$ term is replaced by a new one at $85,440\text{ cm}^{-1}$, $?4p\ ^2P$ and $?6f\ ^2F$ are repudiated, and $?7f\ ^2F$ and $?8f\ ^2F$ are verified.

ALTHOUGH the term values in most of the spectra of the lightest elements have recently been determined with a high degree of accuracy and completeness by Edlén,¹ there are a few instances in which series limits may be slightly altered and term assignments reconsidered after a study of the influence of extra-configurational perturbing terms.^{2, 3} The purpose of this note is to point out the general preferability of some series over others in the determination of series limits, and to make minor alterations in three of Edlén's spectra.

An irregular relationship between the term values and the corresponding quantum defects for a spectral series generally is an indication of the presence of a perturbing series, of which

usually only one or two terms appreciably affect the series in question. The extra-configurational series members have the same Laporte parity and (in the LS coupling case, which is all that need be considered in Edlén's spectra) the same multiplicity and L value as the series under consideration. Irregularity arises when the two series overlap or nearly overlap, in which case the members of the one series share their properties with neighboring members of the other with a consequent ambiguity as to configuration. Thus the members of a series may show an energy trend leading toward a false series limit, even though the term or terms mainly responsible for the complication may remain undiscovered. Although perturbing terms can be pointed out for almost all of Edlén's spectral series, we shall list here only those cases in which an analysis appears to lead to definite improvements in term values,

¹ B. Edlén, *Nova Acta Reg. Soc. Scient. Upsaliensis*, Ser. IV IX, No. 6 (1933).

² A. G. Shenstone and H. N. Russell, *Phys. Rev.* **39**, 415 (1932).

³ N. G. Whitelaw, *Phys. Rev.* **44**, 544 (1933).

C III: The $2snd\ ^3D$ series has been used to determine the series limit for C III. In the case of series members for $n \geq 7$, it seems impossible to assign J values and consequently the energies should be calculated with respect to the center of gravity of the $2s2p\ ^3P$ term. If this is done one obtains the following recalculated term values:

	ν	n^*
$2s7d\ ^3D$	20,575 cm^{-1}	6.9283
$8d$	15,722	7.9258
$9d$	12,412	8.9202

The resulting $n - n^*$ versus ν plot exhibits quite a curvature near $\nu = 0$ as is to be expected because of the presence of the $2p4p\ ^3D$ term near the series limit. The reason for the smallness of the shift of the $2s3d\ ^3D$ term due to perturbation by $2p3p\ ^3D$ is not apparent. In spite of the perturbations present, the 3D series is probably the most reliable from which to determine the series limit because of its length. The 1F and 3F series are very badly perturbed as is easily seen from the variation of the quantum defect with ν . Also the separation of the components of $2s4f\ ^3F$ would be nearly zero except that because of the perturbation, the term acquires part of the multiplet width of $2p3d\ ^3F$.

B I: The series limit of B I was determined by Selwyn.⁴ He fitted both the 2S and 2D series to a Ritz formula and took an average value for the series limit. However, upon examination of the series, one finds that a term, $2s2p^2\ ^2S$ lies near to the $5s\ ^2S$ series member and undoubtedly perturbs that term. The $2s2p^2\ ^2S$ term has not been found experimentally but by examining the $2s - 2p$ energy differences in members of the isoelectronic sequence, one can place it within the range 5000 to 9000 cm^{-1} , whereas $5s\ ^2S$ lies in the neighborhood of 6694 cm^{-1} . The $nd\ ^2D$ series

is perturbed by a $2s2p^2\ ^2D$ term which lies much deeper than any of the 2D regular series members and consequently the 2D series is not seriously perturbed. It seems more reasonable therefore to determine a series limit from the 2D series alone, and if this is done, we find a value about 90 cm^{-1} greater than the Selwyn value.

O IV: The series limit of O IV is quite accurately determined by the (experimentally) unperturbed 2D series. However, several other series are badly perturbed, and we think involve several wrong classifications. (a) The quantum defect of the $5s\ ^2S$ term as classified is impossible. The perturbing term, $2s2p3p\ ^2S$ lies below $4s\ ^2S$ and consequently should not affect $5s\ ^2S$ as much as $4s\ ^2S$. We have identified a line⁵ of intensity = 1, $\lambda = 185.544\text{\AA}$, $\nu = 538,956\ \text{cm}^{-1}$, attributed by Edlén to O IV on experimental grounds, which we think gives a more probable quantum defect for the $5s\ ^2S$ term. The new term value for $5s\ ^2S$ becomes 85,440 cm^{-1} . (b) Edlén questions his classification of $4p\ ^2P$ and one can reason that it must be wrong since the relative quantum defect for $3p\ ^2P$ and $4p\ ^2P$ is opposite to what it should be, because of the presence of the perturbing $2s2p3s\ ^2P$ term between them. (c) Edlén also questions his $nf\ ^2F$ terms for $n \geq 6$. The terms for $n = 7$ and $n = 8$ seem all right but $6f\ ^2F$ must be wrong. The nearest perturbing term, $2s2p4d\ ^2F$, lies just below $8f\ ^2F$, and $2s2p3d\ ^2F$ lies below $4f\ ^2F$ so the abnormal quantum defect of the present $6f\ ^2F$ term would seem to disqualify it.

It is easy to determine what series are likely to be free from disturbance by extra members in any particular case, although there seems to be no rule for them except to study the list of terms yielded by each configuration.

⁴ E. H. W. Selwyn, Proc. Phys. Soc. **41**, 392 (1929).

⁵ B. Edlén, Zeits. f. Physik **85**, 85 (1933).