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Notes on the Stark Effect

E. U. Condon, *Princeton University*

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The theory of the Stark effect in atomic spectra is discussed in general terms and it is shown that large effects arise when two terms which are related to each other in such a way as to satisfy the optical combining rules come close together in the spectrum. Fairly good values of the Stark displacements in complicated atoms may be obtained simply by using the hydrogenic values of the matrix components involved in the theoretical formulas. The ideas are illustrated by discussion of the existing data on the spectra of nickel, lithium, carbon spark, and argon.

THERE exists in the literature of spectroscopy a large amount of experimental data referring to the Stark effect in atomic spectra which has not been hitherto brought into any kind of relation to the modern theory of atomic structure. Of course the effect, and its theoretical interpretation, for atomic hydrogen is very well known and has played an important rôle in development of the theory. Likewise the work of Foster[1] and of Dewey[2] on the effect in helium has brought the theory into satisfactory relation with experiment there. Some work has also been done on the small quadratic effect on the resonance lines of sodium and potassium, but in addition to these contributions a glance for example at the Stark effect chapter in the *Handbuch der Experimental Physik* (Volume 21) will show a considerable amount of uncorrelated experimental data. In this paper the aim is to show how the theory may be used to throw light on some of this material and to point the way for further work in this field.

§1. Theory of the Stark Effect

If H_0 is the Hamiltonian of the unperturbed atom and if $\mathbf{P}$ is the electric moment of the atom and $\mathbf{E}$ the applied electric field, then the Hamiltonian for the atom in the field is

$$H = H_0 - \mathbf{E}\cdot\mathbf{P}. \qquad (1)$$

The alteration of energy levels and proper states is therefore governed, in accordance with usual theory, by the matrix components of $\mathbf{P}$. Moreover the only component of $\mathbf{P}$ that is effective is that along $\mathbf{E}$ so we may choose axes so this is the z-component. Now P_z is the same quantity which governs that part of the dipole radiation of atoms which is polarized with its electric vector parallel to the z-axis. Therefore the selection rules and other calculations of its matrix components which have been made for the theory of line intensities are applicable here. Writing $(A|P|B)$ for the matrix component of P_z which connects two unperturbed energy states A and B we know that $(A|P|B)$ vanishes unless:

(a) A and B are of opposite parity (Laporte rule), (b) $J_B = J_A$ or $J_A \pm 1$ where J_B and J_A are the resultant angular momentum quantum numbers of B and A respectively,

(c) $M_{JA} = M_{JB}$ where M_{JA} and M_{JB} are the z-components of resultant angular momentum of the atom in the two states measured with $h/2\pi$ as unit.

These three properties are rigorous. In addition, insofar as it is accurate to assign electronic configuration labels to the terms we may say:

(d) Configuration A may differ from configuration B at most in regard to one electronic n, l value.

Likewise in case of Russell-Saunders coupling in which resultant spin angular momentum S and resultant orbital angular momentum L are quite accurately diagonal when H_0 is diagonal we may say that $(A|P|B)$ vanishes unless

(e) $S_A = S_B$.

(f) $L_B = L_A$, $L_A \pm 1$.

In addition for Russell-Saunders coupling the actual dependence on L, S, J and M_J is the same

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[1] Foster, Proc. Roy. Soc. **A114**, 47 (1927) and **A117**, 137 (1927).

[2] Dewey, Phys. Rev. **28**, 1108 (1926) and **30**, 770 (1927).

as that which in the intensity theory leads to the well-known Kronig-Russell-Hönl formulas.

So far as orders of magnitudes are concerned we may expect that the nonvanishing components will be of the same order as if calculated with hydrogen-like eigenfunctions for the individual electrons of the atom. For this reason we note that Schrödinger's calculations for hydrogen give

$$(n, l-1, m|EP|n, l, m) = \frac{3}{2} eEna_0 \left[\frac{(n^2-l^2)(l^2-m^2)}{4l^2-1}\right]^{\frac{1}{2}} \qquad (2)$$

for the matrix component connecting two states of equal n value and of l value differing by unity. Here a_0 is the first Bohr radius. Expressing energy in cm^{-1} and taking 100 kv/cm as the unit of E the coefficient of the irrational expression in (2) becomes

$$6.43n \quad \text{cm}^{-1} \text{ per } 100 \text{ kv/cm}.$$

The maximum value assumed by the radical for fixed n and varying l and m is about $n/3^{\frac{1}{2}}$ so far n not greater than 10 the matrix component is under 200 cm^{-1} in value in all cases for fields up to 100 kv/cm. This field is about the largest which has been used in ordinary Stark effect investigations.

Suppose now we put such a perturbing term into the Hamiltonian of an atom and consider what may be said in general about the result. The perturbed states will become linear combinations of such of the unperturbed states as are joined by nonvanishing matrix components of the perturbation. Therefore quantities which were quantum numbers in the unperturbed problem lose their significance after the perturbation. Thus it is no longer possible to speak of a state as being definitely odd or even, also the J value loses its precision, but M_J retains its status as an accurate quantum number.

The extent to which this tendency is realized the perturbation theory shows to be related to the nearness of the unperturbed terms. If W_A and W_B are the unperturbed energies of states A and B and $(A|EP|B)$ is the perturbation component connecting them then the perturbed states will be appreciable linear combinations of A and B if $(A|EP|B)$ is comparable with or large compared to (W_A-W_B). If $(A|EP|B) \ll (W_A-W_B)$ then the alteration in the perturbed states is relatively small as is also the change in energy. In this case so far as the change in energy is concerned due simply to the matrix component connecting A and B it is such as to displace the upper state upward and the lower state downward each by the same amount, namely.

$$|(A|EP|B)|^2/|W_A-W_B|. \qquad (3)$$

The states A and B thus seem to "repel" each other.

As to the amount of this "repulsion" of two terms it is generally rather small. For weaker fields a common value of $(A|EP|B)$ would be 15 cm^{-1} whereas the terms (A and B) may be separated by 1000 cm^{-1} so the perturbation of each would amount to 0.22 cm^{-1}. The small quadratic Stark effect of any state A is the sum of the actions of this type of all other states B of the atom which have matrix components connecting it with A. Most of the theoretical work on the Stark effect of alkalis, like that of Unsöld[3] and of Kirkwood,[4] is concerned with attempts to sum up, for particular states A, like the normal state, or the first resonance state, the whole effect of all other states which perturb it.

But such effects are never comparable with the relatively large effect in atomic hydrogen. Nevertheless such large Stark effects are observed in other atomic spectra. Large Stark shifts may occur in other atoms if two terms connected by a matrix component $(A|EP|B)$ are closer together in the unperturbed energy scheme than the energy value $(A|EP|B)$. In particular if A and B have zero interval in the unperturbed scheme then they will give rise to two levels in the perturbed scheme, one of which is moved up by $(A|EP|B)$ and the other down by the same amount. This makes it clear why large Stark effect displacements are relatively rare in spectra other than hydrogen. The matrix components $(A|EP|B)$ are rather severely restricted by the selection rules. Even when nonvanishing they are quite small so that it is something of an exceptional case when two states A and B which are connected by the perturbation matrix are close

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[3] Unsöld, Ann. d. Physik **82**, 355 (1927).

[4] Kirkwood, Phys. Zeits. **33**, 521 (1932).

together relative to the magnitude of $(A|EP|B)$.

The condition for large Stark effect just set out is more general than the one given by Bohr[5] before the new quantum mechanics which is usually used by experimental workers in qualitative discussions of their data. Bohr pointed out that we may expect large effects for a spectral term that is nearly hydrogen-like, i.e., one which if equated to Rh/n^{*2} leads to a nearly integral value of n^*. This was regarded as indicating that the electronic orbit was effectively in a Coulomb field and hence the hydrogen-like behavior was to be expected. But it did not give a means of estimating the magnitude of the effect. The account of the theory we have given shows clearly the justification of Bohr's rule. If a particular term is almost hydrogen-like then we may be fairly sure that terms arising from an electron configuration in which one of the electronic l values is increased by unity will also be hydrogen-like. If both are nearly hydrogen-like terms they will be near each other and so produce a large effect. The essential thing is nearness of W_A and W_B for nonvanishing $(A|EP|B)$ and Bohr's rule gives us a convenient way of noticing what is in point of fact a large class of the cases in which large Stark effects are observed. The rule is sufficient though not necessary so we may expect to find cases in which the effect is large even though the perturbed states are not hydrogen-like in their energy values.

The rule was enunciated before the development of Pauli's principle with its sound basis for getting true n values. In those days if n^* was nearly an integer it was thought that the nearest integer was the true value of n. Now we know that n^*-n may become as great as several units so that a term may be apparently hydrogen-like through having (n^*-n) be almost exactly equal to an integer instead of zero. This is in fact the case in silver, where there is a good-sized Stark effect that comes about from the nearness of the $6d\,^2D$ to the $4f\,^2F$, both being very close to the hydrogenic value for $n=4$.

In what follows attention will be paid to the application of the perturbation theory to the discussion of the existing data for the spectra of several elements. The general standpoint will be that the effect has to be calculated by finding the allowed values of $H_0-\mathbf{E}\cdot\mathbf{P}$ which can be done in view of the smallness of the matrix components of $\mathbf{E}\cdot\mathbf{P}$ by solving the finite secular equation which represents the interaction of just those interacting terms which are within a few hundred wave numbers of each other on the energy scale.

§2. NICKEL

To illustrate how the principles of the preceding section may be used to throw some light on the experimental data, even in a case that is too complicated for detailed discussion at present, let us consider the Stark effect in nickel. The only observations apparently are those of Takamine,[6] which were made a decade before the analysis of the spectrum by Russell.[7] Of the fifty lines for which Takamine records Stark displacements, twenty-nine may be found in Russell's list of classified lines. These are all transitions from levels of the high even configurations d^8s5s, d^94d, d^96s, d^95d and d^8s4d to the intermediate odd configurations d^94p and d^8s4p. The final states have term values between 25,000 and 33,000 cm^{-1} above the normal state. As there are no even configurations in this region we conclude that the Stark displacement of these terms is very small.

The initial states involved in the identified lines fall into two groups, one between 49,000 and 51,000 cm^{-1}, and the other between 54,000 and 57,000 cm^{-1}. Taking the ionization limit to be 61,579 cm^{-1} we find that the hydrogenic terms are 49,400 cm^{-1} for $n=3$ and 54,730 cm^{-1} for $n=4$. For the lower group the configurations are $(3d)^94d$ and $(3d)^44s5s$, so these are not $n=3$ states for valence electrons. But these lower even configurations occupy the same region in the energy diagram as does the odd d^95p which is known from Russell's analysis. So it is more in accord with our general principles to regard the Stark effect as an interaction of d^94d and d^8s5s with d^95p which is induced by the applied field and to regard the nearness to a hydrogenic value as accidental. Similarly the upper group of even terms is in the correct position to interact with d^96p but as this configuration has not been identi-

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[5] Bohr, Proc. Phys. Soc. London **35**, 275 (1923) and Ann. d. Physik **71**, 228 (1923).

[6] Takamine, Astrophys. J. **50**, 1 (1919).

[7] Russell, Phys. Rev. **34**, 821 (1929).

fied in the spectrum as yet we must confine our attention to the lower group of initial states.

This further restriction reduces the number of identified lines for which Takamine gives Stark displacements to twelve, listed in Table I. The first column gives Takamine's wave-length, the second that of the identified line in Russell's paper which I take to be the same line (there is a systematic difference of about 0.2A). The third column gives the identification in terms of Russell's multiplet analysis, the fourth and fifth are the shifts in wave numbers of the parallel and perpendicular polarized components as observed by Takamine for the values of the field strength given in the sixth column of the table. The line 5142.77 is given two alternative identifications by Russell both of which are listed in the table.

It will be noticed that e^3F_4 occurs as initial state for the first, second, fifth and eleventh lines in the table. The nearness of the equality of their Stark displacements, when these are reduced to the same field strength assuming a variation with E^2, is an indication of the accuracy to which the whole effect may be attributed to the upper state. In the twelve lines there are eight different initial states represented. All the terms show a displacement upward in energy except e^3P_1 and e^3F_2. According to the ideas of §1 we therefore expect that the nearest odd combining term to each of these terms will be below the perturbed term, except for these two for which the nearest combining term is above. This is in fact the case as Table II shows. In Table II are listed in the successive columns: the name of the term, its configuration, the name and configuration of the nearest term which could perturb it, and the interval between the perturbed term and this nearest term in cm^{-1} counted negative if the perturbing term is below the perturbed term and positive if it is above. Of course the designations perturbed term and perturbing term are simply relative to the particular lines under discussion; actually the perturbation is mutual and (if it existed) Stark effect data on lines involving the terms called "perturbing" here should show that they are perturbed by amounts equal and opposite to their perturbing action on the terms here called "perturbed."

TABLE I. *Stark effect in nickel I.*

(Takamine)	(Russell)	Identification	$\Delta\nu$ (cm^{-1})		Field (kv/cm)
			$\parallel$	$\perp$	
4410.66	4410.50	$z^5D_3^0-e^3F_4$	+6.1	+4.1	39
4937.45	4937.33	$z^5F_4^0-e^3F_4$	+5.0	+5.5	38.5
5018.48	5018.30	$z^3D_1^0-e^3F_2$	−2.8	0.0	38.5
5082.55	5082.38	$z^3P_1^0-e^3P_1$	−1.7	−0.97	38.5
5084.20	5084.07	$z^3D_3^0-e^3F_4$	+5.0	+5.4	38.5
5142.91	5142.77	$z^3D_2^0-f^3D_2$ $z^5F_3^0-f^3D_3$	+0.34	+0.26	21.8
5146.61	5146.48	$z^3D_2^0-e^5F_4$	+0.44	+0.26	21.8
5155.90	5155.76	$z^1D_2^0-e^1F_3$	+3.0	+3.0	21.8
5176.72	5176.56	$z^1D_2^0-f^1D_2$	+0.56	+0.34	21.8
5184.78	5184.59	$z^3D_2^0-e^3P_1$	−1.1	−1.1	21.8
5462.69	5462.48	$z^1F_3^0-e^3F_4$	+2.9	+1.9	21.8
5588.09	5587.85	$a^3P_2-y^3D_3^0$	+0.48	+0.35	21.8

TABLE II.

Perturbed term	Configuration	Nearest perturbing term	Interval (cm^{-1})
e^3F_4	d^94d	$3D_3^0d^95p$	−5.2
e^3F_2	d^94d	$3D_1^0d^95p$	+16.7
e^1F_3	d^94d	${}^3F_4^0d^85p$	−42.5
e^3P_1	d^94d	${}^3D_2^0d^95p$	+12.0
e^5F_4	d^8s5s	$6^0J=3$	−53.3
f^3D_2	d^94d	${}^3D_3^0d^95p$	−0.5
f^3D_3	d^94d	${}^3D_2^0d^95p$ ${}^3D_3^0d^95p$	−86.5 +56.1
f^1D_2	d^94d	${}^1D_2^0d^95p$	−65.0
$y^3D_3^0$	d^8s4p	${}^3D_3d^95s$	−15.11

The table shows that we should expect f^3D_2 to show a strong upward perturbation whereas f^3D_3 would probably show a very small perturbation since the nearest terms are relatively far from it and there are two, one above and one below of roughly the same distance whose effects tend to cancel. Since the Stark effect for 5142.77 is actually quite small this tells us unambiguously that this line is to be identified with the second of the two alternatives offered by Russell's analysis. It is believed that this is the first time that a doubtful point in an analysis of a complex spectrum has been settled by reference to the expected Stark effect of the lines.

In the absence of more complete experimental data it is not thought worthwhile to attempt more precise discussion of the relations involved in the theory. It is felt, however, that even these rough agreements suffice to show that the Takamine data are in accord with the general outlines of the theory of the Stark effect.

§3. LITHIUM

The experimental data for lithium are summarized in the *Handbuch der Experimental*

Physik (Volume 21) article by Stark, page 479. All of it refers to combinations in which $2s$ or $2p$ are the final states. Either of these should have extremely small effects owing to their great separation from the nearest terms of opposite parity. Therefore we expect the line shifts to be essentially those of the corresponding upper states. Evidence for this is found in comparing the recorded shifts of $2s$–$5p$ and $2p$–$5p$, assuming these to be quadratic effects. The former is -5.5 cm^{-1} at 0.26 unit (1 unit $=10^5$ volt/cm) while the latter is -45.5 cm^{-1} at 0.8 unit. Writing $\Delta\nu = kE^2$ corresponding values of k are 81. and 72. respectively.

In this spectrum the doublet separations are negligibly small. Also the excited states are fairly hydrogen-like. Let us first consider the effect of the field on the states with $n=4$. The unperturbed energy values relative to the $4d$ term are:

$4s$	-1611.7 cm^{-1}	$4d$	0.0
$4p$	-154.7	$4f$	$+7.4$

The matrix components of electric interaction we may expect to be close to the values given by (2) for hydrogen. In any case the relative magnitudes will be given quite accurately by (2) and this is all that matters for a description of the pattern. We may expect a fairly strong interaction between $4d$ and $4f$, a smaller effect on $4p$ and a quite small effect on $4s$. The secular equation for $m=3$ is linear and tells us that this substate of the $4f$ term is not affected by the field. Owing to the selection rule on m this does not show up in combinations with $2p$. For $m=2$ it is a quadratic equation connecting these substates of $4d$ and $4f$. Using the matrix components for (2) and the empirical $4d$–$4f$ separation we find the roots to be

$$\lambda = 3.7 \pm [3.7^2 + 25.8^2E^2]^{\frac{1}{2}}$$

when measured from the $4d$ level.

Likewise for $m=1$ the secular equation is a cubic connecting corresponding substates of the $4p$, $4d$ and $4f$ terms:

$$\begin{vmatrix} -154.7-\lambda & -39.8E & 0 \\ -\ 39.8E & -\lambda & -32.5E \\ 0 & -32.5E & 7.4-\lambda \end{vmatrix} = 0.$$

For $m=0$ the secular equation is a quartic but here the $4s$ term is so far away compared to the size of the perturbation that its effect may be neglected. The matrix component connecting $4s$ and $4p$ has the value 56.9 for unit field strength so the perturbation due to interaction of these terms is $(56.9)^2/1457.0 = 2.2$ cm^{-1} which is negligible compared to the main effect. Even the $4p$–$4d$ interaction is quite small so that all of the secular equations may with good accuracy be taken simply as quadratics connecting the $4d$ and $4f$ levels. If we do this we obtain as the levels

$$\lambda_2 = 3.7 \pm [(3.7)^2 + 25.8^2E^2]^{\frac{1}{2}}$$

$$\lambda_1 = 3.7 \pm [(3.7)^2 + 32.5^2E^2]^{\frac{1}{2}}$$

$$\lambda_0 = 3.7 \pm [(3.7)^2 + 34.5^2E^2]^{\frac{1}{2}}.$$

In Fig. 1 these levels are plotted against E. The experimental points are from the date of Snyder[8] on $\lambda 4602$ which is the combination with $2p$. The agreement is quite good. This calculation makes no reference to the doublet character of the spectrum and so is not in accord with Snyder's suggestion concerning the line's behavior.[9]

Similar remarks may be made concerning the group of levels for $n=5$. In combination with $2p$ only the substates with $m=0$, 1 and 2 are effec-

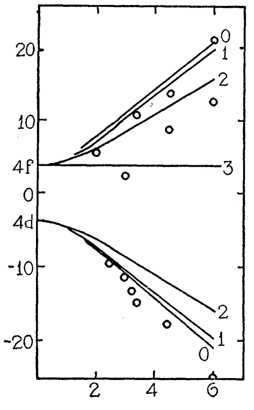

Fig. 1.

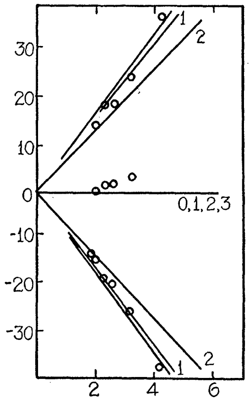

Fig. 2.

Fig. 1. Stark displacements due to interaction of $4d$ and $4f$ terms in lithium. Ordinates, displacement in cm^{-1}; abscissas, field strength in 10^4 volt/cm. The points are observed displacements of the lines $4d-2p$ and $4f-2p$.

Fig. 2. Stark displacements due to interaction of $5d$, $5f$ and $5g$ terms in lithium. Ordinates, displacement in cm^{-1}; abscissas, field strength in 10^4 volt/cm. The points are observed displacements of the combinations with the $2p$ term.

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[8] Snyder, Phys. Rev. **33**, 354 (1929).

[9] Reference 8, bottom of page 359.

tive. The energies relative to $5d$ are:

$5s$	-798.2	$5f$	$+7.8$
$5p$	-84.0	$5g$	$7.8<?<10$
$5d$	0.0		

where probable limits for the unknown $5g$ are merely suggested. In the field the perturbed eigenstates become linear combinations of the almost coincident $5d$, $5f$, $5g$ terms. The $5p$ is not so far away but that its displacement is appreciable. With the second-order perturbation formula this term must be pushed up by $5s$ and down by $5d$ giving as its displacement in unit field -57 cm^{-1} which is in fair agreement with the values -81 and -72 obtained experimentally. The displacement of the line $2p$–$5s$ corresponds to a downward displacement in unit field of the $5s$ term of 28 cm^{-1}. The theoretical value is 12. cm^{-1}.

The group $2p-(5d+5f+5g)$ may be discussed easily by omitting the $5p$ interaction and neglecting the small and empirically uncertain intervals between these initial state terms. Doing this the energy levels are given by

$$\lambda_2=\pm 64.2E, \quad \lambda_1=\pm 77.5E, \quad \lambda_0=\pm 81.4E.$$

In Fig. 2 the data of Snyder are plotted together with the straight lines given by the theory.

Similarly the line $2p$–$6s$ shows a shift corresponding to a displacement of $6s$ of -32 cm^{-1} in unit field whereas the theoretical push from $6p$ is -45 cm^{-1}. The displacement of the $6p$ term in unit field as inferred from the $2p$–$6p$ line is -163 cm^{-1}. The theoretical value is the difference between the upward push from $6s$ and the downward push of $6d$ which comes out to be -200 cm^{-1}. Since the experimental data are rough and the theoretical values depend on the square of matrix components which are taken from hydrogen it is felt that the agreement here presented is good enough to indicate that the ideas of §1 are adequate for a discussion of the main effect.

§4. Carbon Spark

The data are some observations made by Ishida and Fukushima[10] and are believed to be the only data on a nonhydrogenic ion spectrum. The displacements, as is to be expected, correspond to smaller values of the matrix components than in arc spectra. The matrix components are in fact roughly half the hydrogenic values which is the factor of reduction to be expected for orbits in a Coulomb field with $Z=2$.

Their Fig. 2a gives the results of observation on λ2747.31 and λ2746.50 which is the transition, $s^23p^2P-s^24d^2D$, in CII. The shift is to longer wave-lengths and corresponds to $k=-0.004$ in the equation $\Delta\nu=kE^2$ where $\Delta\nu$ is in cm^{-1} and E is in 10^4 volt/cm. Likewise their Fig. 2b gives the data on λ4267.27 and λ4267.02 which is s^23d-s^24f. Here the k is about $+0.002$ in the same units. Attributing these shifts to the upper states we see that they are due to the interaction of the s^24d term and the s^24f term. The $4d$ term is 855 cm^{-1} below the $4f$ term and so the $4d$ term is pushed down in energy and the $4f$ term is pushed up, which is in accord with the facts.

An interesting feature of their Fig. 2b is the fact that there is an unshifted component in the $\perp$ polarization which is absent in the $\|$ polarization. This is due to the fact that the $m=3$ substates in ^2F are unperturbed since there is no $m=3$ substate in ^2D to perturb them. In combining with ^2D to form a radiative transition the $m=3$ substate of ^2F must jump into an $m=2$ substate of ^2D which accounts for the presence of the unshifted component in the $\perp$ but not in the $\|$ polarization.

The hydrogenic matrix component for $m=0$ connecting the $4d$ and $4f$ states for a field of 10^4 volt/cm is 3.44 cm^{-1} from Eq. (2). The value of the matrix component corresponding to empirical k of 0.002 and $\Delta\nu$ of 855 is 1.37 cm^{-1} or roughly half of the hydrogenic value. This is largely due to the fact that we are dealing with an ion rather than a neutral atom, also to the fact that the pictures are blends of components for $m=1$ and $m=2$ for which the matrix components are smaller.

Their data on λ2992.63 furnish an excellent example of the interaction of terms as sketched in §1. This is the transition s^23d-s^25f. The experimental value of k is -0.018. At first sight this appears to be an exception to our general rules as the field makes it go down in energy and yet the $5d$ term, below it, should push it up.

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[10] Ishida and Fukushima, Sci. Papers Inst. Phys. Chem. Research **14**, 123 (1930).

This is due to the presence of a $5g$ term. This term is not known experimentally but we will not be far wrong if we place it at the exact hydrogenic value for $n=5$. The $5f$ term is 144 cm^{-1} lower than this and the $5d$ is 462 cm^{-1} lower than $5f$. Assuming hydrogen-like matrix components (divided by 2 because we have an ion) and these empirical term separations we calculate for k the value

$$k=-(2.43)^2/144+(3.45)^2/462=-0.015.$$

Here the first term is the downward push due to $5g$ and the second the upward push due to $5d$; the final value is in good agreement with the experimental, -0.018.

These are all the data on this spectrum which are available. Theory agrees with experiment as accurately as could be expected and, in particular, explains the difference in the behavior of the $4f$ and $5f$ terms.

§5. ARGON

The effect in argon has been investigated recently by Ryde.[11] He measured the displacements of a large number of lines and has given in his Table VII the displacement of the energy levels produced by a field of 100 kv/cm. The configuration $p^5 5d$ is given with some completeness and his Fig. 3 shows how the displacement of a term is greater the smaller its difference from the hydrogenic value for $n=5$. In argon the states may be separated into two sets, one built on the state $p^5\,{}^2P_{\frac{3}{2}}$ of the ion, the other on $p^5\,{}^2P_{\frac{1}{2}}$ of the ion. Combinations between the two sets are weak.

Looking at the data from the viewpoint of this paper, we see that the $p^5 5d({}^2P_{\frac{3}{2}})$ terms are perturbed downward because of a repulsion from the $p^5 5f({}^2P_{\frac{3}{2}})$ terms which lie in a close group at just the hydrogenic value reckoned down from ${}^2P_{\frac{3}{2}}$ of A II. Hence distance from hydrogenic value is here synonymous with distance from nearest perturbing term. At present we do not have very good knowledge of the coupling relations in argon so it is hard to give a detailed discussion of the interaction of the $5d$ with the $5f$ terms. Neglecting the separation between the $5f$ terms, the perturbation of any particular $5d$ term due to the $5f$ terms is

$$\Delta\nu=\sum_{\beta}\frac{|(5d_\alpha|E\cdot P|5f_\beta)|^2}{(W_{5d^\alpha}-W_{5f^\beta})},$$

where the sum extends over all the $5f$ terms in the group. If the numerator is about the same for all the d terms the $\Delta\nu$ values should lie on a hyperbola whose axis is the location of the $5f$ group, i.e., about 4400 cm^{-1}. Using the hydrogenic value with $m=0$ of the $5d$–$5f$ interaction from Eq. (2) for the numerator we have 5770. In Fig. 3 is plotted the curve $(5770)/(W_{5d}-W_{5f})$ together with points showing Ryde's experimental values for the corresponding term displacements in a field of 100 kv/cm. It is seen that the observed values agree with this curve in order of magnitude but drop to zero more rapidly than does the hyperbola representing interaction with $5f$. This might be due to a variation of the numerator with the $5d$, but another cause which is certainly acting is the upward push on the $5d$ terms from the $6p$ group which is not so very far below the $5d$ terms.

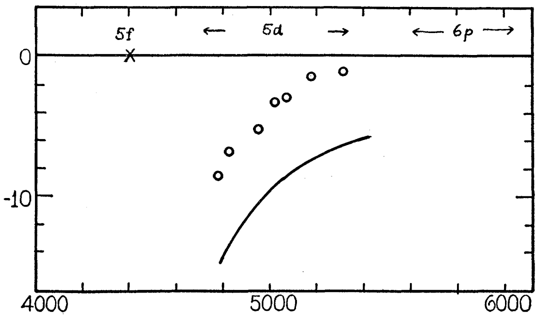

FIG. 3. Stark displacements of the several $p^5 5d({}^2P_{3/2})$ terms in argon, showing relation of the displacement to nearness to the perturbing $p^5 5f$ and $p^5 6p$ groups of terms. Ordinates, displacement in energy in field of 10^5 volt/cm; abscissas, term values of the terms in cm^{-1}. The hyperbola is drawn, using hydrogenic values of the matrix component connecting $5d$ and $5f$.

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[11] Ryde, Zeits. f. Physik **77**, 516 (1932).