

On the Inversion of Doublets in Alkali-Like Spectra

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(Received June 29, 1933)

Many of the doublets in the spectra of alkalis and alkali-like ions are inverted or anomalously narrow. This "tendency to inversion" may be explained by the polarizability of the core, which may be formulated as the repulsion by the excited core configuration states of the levels of the optical doublet. A study is made of the energies and wave functions of these states for the spectra Na I to S VI, on two coupling schemes which allow approximate computations to be made. On the assumption of *LS* coupling the separations of the excited core doublets turn out to be of the order of magnitude of the *2p* x-ray doublet; half the excited core doublets are inverted and half of them normal. The two sets of doublets repel the levels of the optical doublet unequally, and, in the series of spectra considered, the differential repulsion is of the right sign to give an inverting tendency of the same order, though somewhat less,

than the observed inversion. The same problem is then treated by another approximation, by assuming the *2p* x-ray doublet energy large compared to the electrostatic interaction energy of the *3p* and *3d* electrons. The results with both models are proportional to the spin orbit interaction energy of the "hole" in the *2p* shell. The condition that the effects studied should tend to invert and not to broaden the optical doublets, and the further conditions that they should produce an actual inversion are considered. In most cases these questions may be answered from a consideration of the quantum numbers associated with the states capable of perturbing the doublet, and the ratio of optical and x-ray doublet separations. In this way we can understand the observed incidence, both of the tendency toward inversion and of the inversion itself.

THE ordinary spin doublet formula may be derived from a consideration of the interaction of the magnetic moment of the electron and the magnetic field, $\mathbf{H} = 1/c[\mathbf{E} \times \mathbf{v}]$, produced by its velocity relative to the nucleus. For a Coulomb field the energy of this interaction is given by

$$W_s^l = \frac{Rhca^2 Z^4}{n^3 l(l + \frac{1}{2})(l + 1)} \frac{j(j+1) - l(l+1) - s(s+1)}{2}$$

The doublet separation in wave numbers is

$$\Delta\nu = R\alpha^2 Z^4 / n^3 l(l+1)$$

with the level of greater *j* value lying higher. This formula is applied to the spectra of alkalis and alkali-like ions, with an effective nuclear charge substituted for *Z* to take account of the screening by the core electrons. The formula often fails, however, and the occurrence of inverted or anomalously narrow doublets is frequent in alkali spectra.¹ Thus the *5f* doublet of Cs I is inverted, with $\Delta\nu = -0.16$; the *4f* doublet has not been resolved. The *d* and *f* doublets of Rb I are believed to be inverted.² We quote in Table

I the *3d* separations in frequency numbers for stripped atoms from magnesium through sulphur, as observed by Bowen and Millikan.³ The theoretical separations are calculated of the assumption of perfect screening, with

$$Z_{\text{eff}} = (Z - 10).$$

TABLE I. *3d* and *4d* separations. The observed values are from Bowen and Millikan.

	<i>3d</i>		<i>4d</i>	
	observed	from theory	observed	from theory
Mg II	-0.91	0.576		0.243
Al III	-1.70	2.92	-1.28	1.23
Si IV	1.57	9.2	0.08	3.9
P V	6.32	22.5	4.41	9.5
S VI	37.75	46.6		19.7

For an electron moving in a central static field the doublet separation is

$$W = (h/4\pi mc)^2 e \overline{E_r}/r$$

where E_r is the radial component of the electric intensity, and the bar denotes an average over the stationary state of the electron. Now for a neutral atom, and for all *r*, E_r is positive; this follows from Gauss' theorem, since the charge

¹ Bacher and Goudsmit, *Atomic Energy States*, 1932.

² Ramb, *Ann. d. Physik* 10, 311 (1931).

³ Bowen and Millikan, *Phys. Rev.* 25, 301 (1925).

within any spherical surface is necessarily positive. Thus the model of an electron moving in any central static field necessarily gives a normal doublet, with the level of greater j lying higher.

Two distinct quantum mechanical aspects of the core are neglected in the one electron model. The first of these arises from the circumstance that the interaction of the valence electron and the electrons of the core is not completely represented by the field of the mean charge distribution of the core electrons; the application of the exclusion principle to the formulations of these interactions introduces, as is well known,⁴ terms which correspond to the interchange of core and valence electrons. These terms give contributions to the energy of the two states of the optical doublet which are in general unequal. Their effect has recently been investigated by Johnson and Breit,⁵ but is apparently too small to account for the observed inversions.

The second, which seems to us to give greater promise of an explanation, involves a consideration of the excited states of the core. This aspect may be stated in various ways: as a polarization of the core, expressed by transitions of the inner electrons to excited states; as an admixture of wave functions for the excited states in that for the true stationary state described approximately by the definite configuration of closed shells and the quantum numbers of the valence electron; or as a repulsion of the levels of the ordinary optical spectrum by those of the excited core configurations. These are three statements of the same effect, but one quite different from that mentioned in the preceding paragraph.

Strictly a level is said to be "perturbed" by another of the same parity (oddness or evenness of $\Sigma|l|$) and the same angular momentum, which lies close to it so that the nondiagonal element of the energy referring to the two states, in general small, is no longer negligible compared with the unperturbed energy difference. An example of a perturbation of this sort which anomalously inverts the doublets of certain terms is known in the spectrum of copper, in the configuration $(3d)^{10}(np)$. Shenstone and Russell⁶ have shown

that the perturbing levels in this case are the inverted doublets of $(3d)^9(4s)(np)$, and have given on this basis a complete explanation of the inversions observed. A similar explanation has been suggested at various times for the inverted doublets of alkalis.⁷ This case cannot really be an example of spectroscopic perturbation: the excited core states lie far from the optical ones, and the interaction energy is at best only a small fraction of this energy difference. The separations of states of the excited core configurations, however, are relatively enormous, arising partly from a deep lying unpaired spin, and in some of the states the j values will be inverted, analogous to those of x-ray doublets. It might be expected, then, that the existence of these higher states can totally alter the doublets of the optical terms, and that their arrangement may be such as to give a net inverting effect.

The atomic wave function for a true stationary state of an atom may be built up as a sum of wave functions for the approximately stationary states of definite configuration, and equal parity and angular momentum. In general nearly the whole of the true wave function is given by the term arising from one specific configuration, and this configuration is used (in addition to the quantum numbers $m_l m_s$) to index the state; the coefficients in the sum of wave functions referring to other configurations are small unless the conditions for a genuine perturbation are fulfilled. Thus we may write

$$\psi_i = \psi_{i_0} + \sum_j [V_{ij}/(E_i - E_j)] \psi_{j_0},$$

where ψ_{i_0} is the approximate function for a state of definite configuration i and V_{ij} is the matrix element of the electrostatic interaction energy corresponding to a transition between the configurations i and j . The two terms i and j repel each other by an amount

$$\Delta E = |V_{ij}|^2 / |E_i - E_j|.$$

Suppose that ψ_{i_0} represents a doublet of the same orbital angular momentum L as the optical doublet, and neglect the normal doublet splitting in comparison with that of the excited one, ϵ .

⁴ Fock, Zeits. f. Physik **81**, 195 (1933).

⁵ Johnson and Breit, Phys. Rev. **44**, 77 (1933).

⁶ Shenstone and Russell, Phys. Rev. **39**, 415 (1932).

⁷ H. E. White, Phys. Rev. **40**, 316 (1932); R. F. Bacher, Phys. Rev. **43**, 269 (1933).

$$(E_i - E_j)_{L+\frac{1}{2}} = E_0, \quad (E_i - E_j)_{L-\frac{1}{2}} = E_0 + \epsilon,$$

$$|V_{ij}|_{L-\frac{1}{2}} = |V_{ij}|_{L-\frac{3}{2}} - v.$$

The shift in doublet separation is given, to first order in ϵ and v , by

$$\delta E = \Delta E_{L+1/2} - \Delta E_{L-1/2} = |V_{ij}|^2 \epsilon / E_0^2 + 2V_{ij}v / E_0.$$

For definiteness we shall use this theory in an attempt to explain the data given in Table I, and in particular the inversion of the $3d$ doublet ($j=3/2, 5/2$) of Mg II, observed to have a separation of -0.9ν instead of 0.56ν as predicted by the spin theory. The normal Mg II atom consists of a single valence electron outside a completed $2p$ shell, so that a full description of the $3d$ configuration is $(1s)^2 (2s)^2 (2p)^6 (3d)$. We shall consider only transitions of the p electrons, and need not include $(1s)^2 (2s)^2$ in designating the configurations. The lowest even levels with $j=3/2, 5/2$ arising from core excitation are in $(2p)^5 (3s) (3p)$, but this involves a double jump from $(2p)^6 (3d)$, so that a much more considerable contribution may be expected from $(2p)^5 (3p) (3d)$. Higher terms, with transitions of one of the $2p$ electrons to $4p, 5p$, etc., will have similar but smaller effects. Unfortunately these states cannot be observed experimentally; the energy required to excite a core electron is much greater than the ionization potential of the valence electron, so that auto-ionization occurs.

The number of possible combinations of the individual l and s vectors of an almost closed shell is equal to that for the missing electrons. Thus in the elements of Table I the number of levels arising from $(2p)^5 (3p) (3d)$ is the same as that which would arise from $(2p) (3p) (3d)$, and we are justified, insofar as multiplicities are concerned, in treating the atom as a three electron atom, $2p$ representing a "hole" in the $2p$ shell. Two different coupling schemes for the excited core will be considered as limiting cases, although, since the electrostatic interactions and the $2p$ spin orbit interactions are of the same order of magnitude, the actual atom will be of some intermediate type. Calculations will be made first on the assumption of LS coupling, then according to a scheme in which the valence and excited electrons are coupled LS and then to the quantized j of the $2p$ hole. In the latter

case the levels fall into two groups, corresponding to the two members of the inverted x-ray doublet. It will be seen that the repulsion of both components of the optical doublet is the same if only the direct integrals of V_{ij} are considered, i.e., those which would appear even if the wave functions were not antisymmetrized. If exchange terms are included, however, there is a net effect, proportional on both models to the spin orbit interaction energy of the $2p$ hole.

EFFECT OF LS COUPLED EXCITED CORE STATES

Since the electrostatic energy commutes with L and S it has no matrix elements connected with transitions in which L and S change. Thus the whole effect of the excited core states, if LS coupled, comes from the 2D 's of the excited configuration. An enumeration of these relevant states may be made from the vector model. First couple the $3p, 3d$ electrons to form singlet and triplet P, D and F terms. One 2D ($L=2$) arises from each singlet and triplet of the two electron configuration, making six in all. There are no equivalent electrons and all states are allowed.

TABLE II. Diagonal elements of $\xi_1(l_1 \cdot s_1) + \xi_2(l_2 \cdot s_2)$.

Parent term	$\xi_1(l_1 \cdot s_1) + \xi_2(l_2 \cdot s_2)$		Separation
	$J=5/2$	$J=3/2$	
1P	$\frac{1}{2}\xi_1$	$-\frac{3}{4}\xi_1$	$\frac{5}{4}\xi_1$
1D	$\frac{1}{6}\xi_1$	$-\frac{1}{4}\xi_1$	$\frac{5}{12}\xi_1$
1F	$-\frac{1}{3}\xi_1$	$\frac{1}{2}\xi_1$	$-\frac{5}{6}\xi_1$
3P	$-\frac{1}{2}\xi_1 + \xi_P$	$\frac{3}{4}\xi_1 - \frac{3}{2}\xi_P$	$-\frac{5}{4}\xi_1 + \frac{5}{2}\xi_P$
3D	$-\frac{1}{6}\xi_1 + \frac{2}{3}\xi_D$	$\frac{1}{4}\xi_1 - \frac{5}{2}\xi_D$	$-\frac{5}{12}\xi_1 + \frac{5}{6}\xi_D$
3F	$\frac{1}{3}\xi_1 + \frac{2}{3}\xi_F$	$-\frac{1}{2}\xi_1 - 4\xi_F$	$\frac{5}{6}\xi_1 + 2\frac{2}{3}\xi_F$

The separations ϵ of the individual doublets are given by the matrix of the spin orbit interaction energy. This matrix is not diagonal in the LS scheme but we may assume the diagonal elements large and calculate them for the 2D 's formed by the addition of $2p$ to ${}^1PDF, {}^3PDF$. A method for obtaining the spin orbit interactions in LS coupling directly from the matrix equations has been given by Johnson.⁸ Table II contains the diagonal elements of $\xi_1(l_1 \cdot s_1) + \xi_2(l_2 \cdot s_2)$, where

$$\xi_1 = R\alpha^2 Z_{\text{eff}}^4 / n^3 l(l+\frac{1}{2})(l+1)$$

⁸ M. H. Johnson, Phys. Rev. **38**, 1628 (1931).

for $2p$, and ξ_2 is the corresponding parameter associated with the ionic multiplet. It may be assumed that these parameters for the ionic multiplets are negligibly small compared with ξ_1 . As has been pointed out by Shortley⁹ the spin orbit parameter of a missing electron in an otherwise closed shell is negative. Those doublets arising from 1P , 1D , 3F are thus seen to be inverted, while the other three are normal. The orientation of the doublets with P and F parent terms could have been predicted from the vector model.

The linear combinations of determinantal eigenfunctions to represent the various D doublets were obtained by using angular momentum operators, a method given by Gray and Wills.¹⁰ The valence and excited electrons are first combined, then coupled with $2p$, so that correlations with the individual doublets shown by the vector model may be made. No constant factor arises in the V_{ij} because of the presence of six electrons in the p shell. Specifying the quantum numbers of $3p$ (of which there are six possibilities) in the excited core wave functions automatically selects terms in the antisymmetrized function for the ordinary 2D which combine. There are $3!$ nonvanishing terms for each pair of determinantal functions in the three electron case, and this factor is cancelled by the normalizing factor $1/(3!)^{\frac{1}{2}}$. If the problem is done explicitly in all seven electrons the $7!$ terms in V_{ij} are taken care of by the $1/(7!)^{\frac{1}{2}}$ of the antisymmetric permutations. The coefficients of the first direct and interchange radial integrals of V_{ij} , the matrix element of e^2/r_{12} , where 1 and 2 refer to $3d$ and the electron making the transition $2p \rightarrow np$, then, are found by multiplying the coefficients of determinantal functions which combine with the optical doublet by the proper angular integrals (tables of which may be constructed from Slater's b 's) and summing. This result is independent of the m of the $j=5/2$, of course, and is the same for both members of the doublet. Because of the antisymmetry in spin of the singlet the sign between the direct and exchange integrals is different according to whether the parent term of state j is a singlet

or a triplet. To this order, then:

$$V_{ij}(^1P) = \left(\frac{3}{10}\right)^{\frac{1}{2}} \left(F_0 + \frac{1}{15}G\right)$$

$$V_{ij}(^3P) = \frac{3}{10^{\frac{1}{2}}} \left(F_0 - \frac{1}{15}G\right)$$

$$V_{ij}(^1D) = \frac{1}{2^{\frac{1}{2}}} \left(F_0 - \frac{1}{5}G\right)$$

$$V_{ij}(^3D) = \left(\frac{3}{2}\right)^{\frac{1}{2}} \left(F_0 + \frac{1}{5}G\right)$$

$$V_{ij}(^1F) = \left(\frac{7}{10}\right)^{\frac{1}{2}} \left(F_0 + \frac{2}{5}G\right)$$

$$V_{ij}(^3F) = \left(\frac{21}{10}\right)^{\frac{1}{2}} \left(F_0 - \frac{2}{5}G\right).$$

The shift of optical doublet separation may be calculated from the formula $\delta E = |V_{ij}|^2 \epsilon / E_0^2$, substituting the values of the separations from Table II. The terms in F_0^2 cancel, but the further terms in V_{ij}^2 give a net result. Since the exchange integral G_1 is much smaller than the direct integral F_0 we shall here record only the first nonvanishing terms (Table III). Whether this

TABLE III.

$$\begin{aligned} \delta E(^1P) &= \frac{1}{2} F_0 (F_0 G / E_0^2) \xi_1, & \delta E(^3D) &= -\frac{1}{4} (F_0 G / E_0^2) \xi_1, \\ \delta E(^3P) &= \frac{3}{2} F_0 (F_0 G / E_0^2) \xi_1, & \delta E(^1F) &= -\frac{1}{5} (F_0 G / E_0^2) \xi_1, \\ \delta E(^1D) &= -\frac{1}{12} (F_0 G / E_0^2) \xi_1, & \delta E(^3F) &= -\frac{1}{5} (F_0 G / E_0^2) \xi_1, \\ & & \Sigma \delta E &= -2 (F_0 G / E_0^2) \xi_1. \end{aligned}$$

result means inversion depends on the relative sign of F_0 and G_1 , on their magnitudes, and the energy differences of the levels, but before making an application to an actual case we shall investigate the other coupling scheme outlined above.

EFFECT OF jJ COUPLED EXCITED CORE STATES

In this scheme the quantized j of $2p$ is coupled to the ionic multiplets of the outer two electron configuration. Since the total orbital angular momentum of the three electrons is no longer quantized there will be matrix elements V_{ij} between the optical 2D and all the $J=3/2, 5/2$ states of the excited core, of which there are altogether thirty-six. The appropriate angular

⁹ Shortley, Phys. Rev. **40**, 185 (1932)

¹⁰ Gray and Wills, Phys. Rev. **38**, 248 (1931).

momentum operators were used to obtain the three electron eigenfunctions. Products of coefficients of combining terms of the excited core and optical state wave functions were multiplied by the appropriate angular integrals and summed, for each of the relevant excited core levels. The contributions to the energy of the mutual repulsion are proportional to the squares of these sums. Since the levels from a single multiplet coupled to a particular j of $2p$ lie very close together, the inverting effect of such a set of levels is proportional to $\Sigma(|V_{ij}|^2_{5/2} - |V_{ij}|^2_{3/2})$. The results are given in terms of the first direct and interchange integrals.

$$j_{2p} = 3/2: \quad \Sigma(|V_{ij}|^2_{5/2} - |V_{ij}|^2_{3/2}) = -\frac{2}{3}F_0G_1,$$

$$j_{2p} = 1/2: \quad \Sigma(|V_{ij}|^2_{3/2} - |V_{ij}|^2_{5/2}) = \frac{2}{3}F_0G_1.$$

The coupling scheme here assumed implies that all states associated with a definite j of $2p$ are grouped together, and their spread of energies is neglected. The two sets of levels act in opposite ways on the optical doublet separation, but they are separated by ϵ , the width of the $2p$ x-ray doublet. The sum of their effects is

$$\Sigma\delta E = \frac{2}{3}F_0G_1(-1/E_0 + 1/(E_0 + \epsilon)),$$

since the $2p_{3/2}$ group lies nearer the optical doublet.

$$\Sigma\delta E = -\frac{2}{3}\epsilon(F_0G_1/E_0^2).$$

Now, since

$$\epsilon = \frac{1}{2}(2l+1)\xi_1 = (3/2)\xi_1,$$

$$\Sigma\delta E = -(F_0G_1/E_0^2)\xi_1.$$

The net effect in this case is due entirely to the difference in the sign between F_0 and G_1 for excited core levels with singlet and triplet parent terms, and is equal to that portion of the LS result which arises from the same cause. Because of the different enumeration and character of the states no extra contribution from the triplets occurs here. Owing to the quantization of the j of the $2p$ "hole" instead of the total orbital angular momentum the electrostatic interaction energy associated with the transition $2p \rightarrow np$ must be calculated separately for the $J=3/2, 5/2$ states arising from each component of a triplet, and the individual elements squared before summing. Thus the weighting of terms from

triplet parents, which appears in LS coupling, is lost, and the whole effect comes from the difference in symmetry between singlets and triplets.

APPLICATION OF THEORY TO MG II. EVALUATION OF INTEGRALS

F_0 and G_1 are the first two radial integrals of

$$V_{ij} = \int \int \psi_i(e^2/r_{12})\psi_j d\tau_1 d\tau_2,$$

when $1/r_{12}$ is expanded in spherical harmonics. In the evaluation of these integrals for a particular case, Mg II, hydrogen like one electron functions were used, with screening constants derived by interpolation from those given by Pauling and Sherman.¹¹ For the configuration whose energy lies closest to the optical state, $(2p)(3p)(3d)$, the values of Z_{eff} were 7 for $2p$, 3.7 for $3p$ and 2 for $3d$. The results were found to be surprisingly stable under a reasonable variation of screening constants.

$$F_0 = e^2 \int \int R_1(2p)R_1(3p)R_2^2(3d)(1/r_1)r_1^2r_2^2 dr_1 dr_2 \\ \simeq 1.73 \text{ volts}$$

where R is the radial factor of the one electron eigenfunction.

$$G_1 = e^2 \int \int R_1(3p)R_1(3d)R_2(2p)R_2(3d)(r_2/r_1^2) \\ \times r_1^2r_2^2 dr_1 dr_2 \simeq -0.43 \text{ volt electron.}$$

The radial wave function corresponding to spins parallel and antiparallel to the orbital angular momentum are not identical. This difference is appreciable only for the $2p$ electron, since only there are the energies for the two spin orientations considerably separated. Thus V_{ij} for levels associated with $2p_{3/2}$ and $2p_{1/2}$ are different. $|V_{ij}|_{3/2} - |V_{ij}|_{1/2} = v$ is small but since it is associated with only one set of the perturbing levels $V_{ij}v$ is weighted by a factor E_0/ϵ in comparison with $|V_{ij0}|^2$.

To ascertain a correction for this difference we may write

¹¹ Linus Pauling and J. Sherman, *Zeits. f. Krist.* **81** (1932).

$$F_0 \text{ }_{3/2} - F_0 \text{ }_{1/2} = f, \quad G_1 \text{ }_{3/2} - G_1 \text{ }_{1/2} = g,$$

$$f = e^2 \int_0^\infty \int_0^\infty R_2^2(3d)R_1(3p)\rho_1(2p)(1/r_1)r_1^2r_2^2dr_1dr_2,$$

where $\rho_1 = R_1(2p)_{3/2} - R_1(2p)_{1/2}$. The relativistic radial wave functions for a Coulomb field have been given as series in r by Darwin¹²:

$$R(2p)_{3/2} = re^{-cr} \left(1 - \frac{\alpha_1^2}{4} \ln 2cr + \frac{3}{8} \alpha_1^2 \right),$$

$$R(2p)_{1/2} = re^{-cr} \left\{ 1 - \frac{\alpha_1^2}{2} \ln 2cr - \frac{\alpha_1^2}{4} \left(-\frac{37}{8} \frac{cr}{2} + \frac{3}{4cr} \right) \right\},$$

where α_1 is the fine structure constant times the nuclear charge. $c = Z_{\text{eff}}/na$.

$$\rho = re^{-cr} \frac{\alpha_1^2}{4} \left(\ln 2cr - \frac{25}{8} + \frac{2(cr)^2 + 3}{4cr} \right).$$

To apply this to our problem we must determine what effective nuclear charge to use in evaluating α_1 . It is not possible to do this rigorously in any simple way; we have contented ourselves with elementary considerations which fix the possible limits of Z , and give us an estimate of the correction term. A mean for the parenthesis was estimated before integrating, and found to be approximately unity, so that the integral is merely $\alpha_1^2 F_0/4$. Since both $3d$ and $3p$ weight the difference $R(2p)_{3/2} - R(2p)_{1/2}$ far out from the nucleus the corresponding parenthesis in g is of the same sign, and is of the same order of magnitude. The overlapping coefficients are just as before, and the ratio of the correction to the effect previously considered is

$$\frac{F_0 g + G_1 f}{2 F_0 G_1} \frac{\alpha_1^2}{4} \frac{E_0}{\epsilon} \frac{\alpha_1^2}{4} \frac{E_0}{\epsilon}.$$

The change in the optical 2D splitting predicted by the theory depends on the data assumed and on the coupling. $\epsilon = 2219\nu$, the separation of 2P in Mg IV. The energy difference between the excited core and optical states is that of the transition $2p \rightarrow 3p$, approximately $480,000\nu$ or 60 volts, from the spectrum of Mg III. The

effective charge which enters the ν correction through must lie between 7 and 11, and about 9 seems a reasonable choice for it. This leads to $1/3$ as the value of the ratio above. On LS coupling the shift in the $3d$ doublet separation is

$$\delta E = (4/3)\epsilon(F_0 G_1/E_0^2)(1 + \frac{1}{3}) \approx 0.9\nu,$$

sufficient to invert the levels, although not to the extent of the 1.5ν discrepancy indicated by observation. The jJ result is half this, and the actual Mg II atom must lie somewhere between. Further contributions toward inversion may be expected from transitions of a core electron to other p orbits. The direct integrals for transitions to $4p$ and $5p$ were calculated, and found to be 0.9 and 0.56 volt electrons, respectively. The corresponding exchange integrals are small, so that the computations cannot be rigorous. If they diminish in the same ratio as the F_0 's the combined inverting tendency of these configurations is about 0.4 times that of the first excited core level. We shall see, moreover, that all the inverting effects would be somewhat larger if more accurate radial wave functions were used. We are thus led to believe that the observed inversion of the $3d$ doublet may be wholly accounted for by the effect treated in this paper.

CONCLUSIONS

The effect of excited core states on the optical doublet separation is toward inversion if F_0 and G_1 are of opposite sign. A general argument for the signs of these radial integrals can be made for the elements of Table I. For the nearest perturbing state, $(2p)^5(3p)(3d)$, F_0 and G_1 are opposite in sign. Only one wave function, that of $3p$, has a node. In the direct integral the function is weighted by $2p$, which has its maximum far in; for the exchange integral the important region is that of greater r , because of the overlapping with $3d$. The node will always fall between these two weighted regions. While the largest contribution may be expected from this configuration similar effects arise from transitions to other p levels, the magnitude of whose cumulative shifting tendency it is difficult to estimate. More nodes occur in the np wave functions, ($n > 3$), but the principal contribution to G_1 will come between the first two nodes, and that to

¹² C. G. Darwin, Proc. Roy. Soc. A118, 673 (1928).

F_0 before the first one, so that the difference in sign persists. In a non-Coulomb central field, such as Hartree's, all the nodes are farther in than those of hydrogen-like functions, making $|-G_1|$ greater. It seems not likely that the accompanying diminution in F_0 would entirely compensate this increase, so that the numerical answer should be larger than that calculated for the $2p \rightarrow 3p$ transition in Mg II.

For actual inversion there must be, in addition to the tendency toward inversion due to different signs of F_0 and G_1 , an enormously larger spin orbit interaction energy for the x-ray levels than for the optical ones. This condition is satisfied for the first few elements of Table I.

In the inversion of $4d$ the argument is analogous. The overlapping for $np \cdot 4d$ is in general

farther out and opposite in sign to that of $2p \cdot np$, but the shift, even where the condition on the separation ratio is satisfied, should be less than that for $3d$. This is in accord with the observations in Al III. The $5f$ term of Cs I is analogous to the $4d$ of Al III.

Thus it appears that both the tendency toward inversion and the inversion itself can be roughly predicted from a consideration of the quantum numbers associated with the states capable of perturbing the doublet, and the ratio of the optical and x-ray doublet separations.

The writer is deeply indebted to Professor J. R. Oppenheimer, with whom this investigation was carried out, and to the Physics Department of the University of California for a Whiting Fellowship during the past year.