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INTENSITY SUMMATION RULES AND PERTURBATION EFFECTS IN COMPLEX SPECTRA*

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ABSTRACT

After reviewing the present status of the problem of line intensities in complex spectra, and commenting on the relationship of the sum rule, the extended sum rule, and the general sum rule, a new J-group sum rule is derived. A J-group is defined as the totality of lines arising from transitions between all terms from one electron configuration having a given value J_1 of the inner quantum number and all terms from a second having a given value J_2; it maintains its identity for all couplings. It is proved that the total intensity of the lines in a J-group is independent of coupling, provided a third configuration does not produce terms which perturb those considered; where such perturbation occurs an extension of the new sum rule to an enlarged J-group is required. One can accordingly calculate the intensities of the individual lines for LS coupling, and the total intensities found for each J-group or enlarged J-group should apply to jj and all intermediate couplings. Verification of the rule is found in special cases which have been calculated theoretically, and, after ν^4 and excitation corrections have been applied, in Dorgelo's measurements in neon. Where only certain terms of a J-group perturb one another lines arising from the remaining terms need not be considered in taking the sums; experimental verification of this is given by measurements in the spectrum of Ti I. Bartlett's statement that the extensions of the sum rule must be modified when configurations containing equivalent electrons are involved is discussed, and a procedure for applying them and the J-group sum rule in such cases is suggested. Finally, intensity data for a number of cases in Ti I are given to illustrate the method used in assigning the causes of intensity anomalies in lines to their originating terms, and qualitative results on relationships between term separations and intensity perturbations are given.

§1. INTRODUCTION

WITHIN recent years a considerable amount of quantitative experimental data has been accumulated on line intensities in complex spectra,[1] much of which could not be given exact interpretation in terms of the available theoretical formulas, applying as they do only to certain simple types of electron configuration and vector coupling. In view of the complexity of the general problem, and the great need for theoretical guidance in determining which experimental data it is most important to obtain, we discuss in this paper several points which appear to be of value in attempting the

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* This paper was presented at the Washington Meeting of the American Physical Society, May 1, 1931.

[1] J. B. van Milaan, Zeits. f. Physik **34,** 921 (1925); **38,** 427 (1926); R. Frerichs, Ann. d. Physik **81,** 807 (1926); G. R. Harrison, J.O.S.A. **17,** 389 (1928); G. R. Harrison, and H. Engwicht, J.O.S.A. **18,** 287 (1929); C. E. Hesthal, thesis not yet published; R. S. Seward, Phys. Rev. **37,** 344 (1931).

piece-meal interpretation of intensity anomalies in spectra arising from electron configurations of any degree of complexity.

We summarize the intensity rules and formulas now available:

1. The original *sum rule* of Burger and Dorgelo,[2] which applies to intensities within a multiplet and which holds only for *LS* coupling.
2. The extension of this rule which was predicted by Kronig,[3] experimentally verified by Ornstein and Burger,[4] and theoretically established on the basis of the new quantum mechanics by Houston,[5] which we shall refer to as the *extended sum rule*, which applies to the aggregate of lines arising from transitions between two two-electron configurations of which one electron in each case is in an *s* state. This rule holds for all couplings, and the triplet, singlet, and intercombination lines in the array together form an *enlarged* (*erweiterte*) *multiplet* (sometimes called a generalized multiplet).
3. The multiplet intensity formulas derived from the vector model by Kronig,[3] by Sommerfeld and Hönl,[6] and by Russell,[7] for *LS* coupling, and by Bartlett[8] for *jj* coupling. These in general serve only to determine the relative intensities of lines in special cases.
4. Houston's derivation of the general intensity formulas for all lines arising from transitions between two two-electron configurations, one electron in each case being in an *s* state.
5. Bartlett's[9] derivation of the general intensity formulas for all lines arising from the transition $sp-p^2$.
6. The results of Fermi[10] showing the effects of perturbations arising between various configurations in one-electron systems.
7. The extension of the original sum rule which should apply to the general case of all couplings, suggested by Landé,[11] derived from the vector model by Kronig,[3] and experimentally confirmed in a special case in neon by Dorgelo[12] (but see §3 below). This we shall call the *general sum rule* in the discussion which follows. In the most general case it would state that the total intensity sum of all the lines in a spectrum from (or to) all levels having the same *á priori* probability $2J+1$ will be proportional to that probability times the number of levels involved. In cases where certain states are free from perturbation by other states these can be considered alone, and the general sum rule then reduces to a simple extension of the original sum rule.
8. The various formulas for intensities of lines in series, in hyperfine struc-

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[2] H. C. Burger and H. B. Dorgelo, Zeits. f. Physik **23**, 258 (1924).

[3] R. deL Kronig, Zeits. f. Physik **31**, 885 (1925); **33**, 261 (1925).

[4] L. S. Ornstein and H. C. Burger, Zeits. f. Physik **46**, 303 (1926).

[5] W. V. Houston, Phys. Rev. **33**, 297 (1929).

[6] A. Sommerfeld and H. Hönl, Sitz. Preuss. Akad. Wiss. **9**, 141 (1925).

[7] H. N. Russell, Proc. Nat. Acad. Sci. **11**, 314, 322 (1925).

[8] J. H. Barlett, Jr., Phys. Rev. **34**, 1247 (1929).

[9] J. H. Bartlett, Jr., Phys. Rev. **35**, 229 (1930).

[10] E. Fermi, Zeits. f. Physik **59**, 680 (1930).

[11] v. H. B. Dorgelo, Phys. Zeits. **26**, 787 (1925).

[12] H. B. Dorgelo, ibid.; also Physica **5**, 90 (1925).

ture, and in the Zeeman and Stark effects, in which we are not at the moment interested.

To these, all of which except the general sum rule have been quite commonly used by experimenters in interpreting their data, we add three, discussion of which form the basis of this paper:

1. A new *J-group sum rule* derived theoretically in §2, which states that the total intensity of all lines arising from transitions between all states $J=J_1$ of one configuration and all states $J=J_2$ of a second configuration is independent of coupling, provided that none of the states are perturbed by those of a third configuration. Where such perturbation exists the rule must be extended to include lines from the proper states in the perturbing configuration. The general sum rule follows from this rule, but does not lead to it. As will be seen from the discussion which follows, the array of lines which we have tentatively called a *J-group* is a more fundamental concept than the multiplet, since it keeps its identity through all degrees of coupling.

2. The observation by Bartlett[13] which is of great importance but which appears neither to have been discussed nor applied previously, that none of the extensions of the sum rule can be applied directly to line arrays arising from configurations containing equivalent electrons. We discuss in §4 the modifications in the rules which must be made when Pauli's exclusion principle has operated to eliminate certain terms from the array.

3. The general result of quantum mechanics that similar (odd or even) terms of the same J value perturb one another, by amounts which depend on the magnetic and electrostatic interactions, but which have not yet been calculated in detail for configurations containing more than two electrons. It appears desirable, therefore, to endeavor to establish empirical criteria from experimental data, which may enable one to predict roughly from the energy values of the terms and their quantum designations the intensity anomalies to be expected from the perturbations in any given case. We make a beginning at this in §5.

In addition to the terminology used above for the various sum rules, we list here the designations for certain groups of lines and terms which we have found convenient. We restrict the term *supermultiplet* to the meaning originally given it by Russell,[14] namely, the group of related multiplets of similar multiplicity arising from configurations possessing a common parent term. Two supermultiplets of high and low multiplicity, from a common parent term, together with all intercombinations arising between their terms, form by analogy an *enlarged supermultiplet.* The entire group of spectral terms arising from a given electron configuration will be termed a *configuration array*, and the totality of lines resulting from the transitions occurring between two configurations then forms a *transition array* (sometimes erroneously called a supermultiplet). Finally, since in the discussion which follows it frequently becomes desirable to isolate those lines which arise from transitions between all levels having a given value of J in one configuration and those

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[13] J. H. Bartlett, Jr., reference 9, p. 233.

[14] H. N. Russell and W. F. Meggers, Sci. Paper Bur. Stds. No. 558, and elsewhere.

having a given value of J in another configuration, we refer to this as a *J-group*. Where one or more configurations overlap we must consider also the *enlarged J-group*. By adding together those enlarged J-groups which belong in a given row or column of the usual type of intensity diagram, we form the array to which the general sum rule applies.

Where the word intensity is used, we refer always, of course, to the reduced intensity obtained after any necessary self-reversal, excitation, and ν^4 corrections have been applied.

§2. DERIVATION AND THEORETICAL DISCUSSION OF THE J-GROUP SUM RULE

Before discussing the intensities of lines in atomic spectra it is necessary to consider briefly the general problem of an isolated atomic system as it is treated in the quantum theory. For this purpose we suppose the Hamiltonian of the system to be

$$H = H_0 + H_1 + H_2 \tag{1}$$

where H_0 is the kinetic energy of the electrons moving around a fixed nucleus plus a spherically symmetric potential energy, determined by a modified Hartree method,[15] which is the same for each electron; H_1 is the energy of electrostatic repulsion between each pair of electrons minus the potential energy of H_0 arising from the repulsion between pairs of electrons; and H_2 is the magnetic energy arising from the interaction of the magnetic moment of each electron with the field in which it moves. The precise form of the Hamiltonian need not concern us here.

The first question that must be answered concerns the characteristic energy levels of this system. Slater[15] has shown how to find the characteristic values of H_0+H_1 by application of the first order perturbation theory. He starts from the well-known solutions for H_0 from which he constructs proper antisymmetric wave functions. Then treating H_1 as a perturbing potential he shows that the partial removal of the degeneracy in the unperturbed problem results in the classification of energy levels into multiplets. He is able to calculate the separation between the multiplets arising from a given electronic configuration in terms of certain radial integrals. Recently Condon[16] and Langer[17] have indicated how these results must be extended when two configurations lie so near one another that they must be considered together. It is expected that the inclusion of H_2 in the perturbation problem will further remove the degeneracy giving the separations within the multiplets.

Now the existence of certain integrals of the equations of motion greatly reduces the complexity of the problem. Thus when the magnetic interaction is omitted, the z components of the orbital and spin momenta, L_z and S_z, are such integrals. They therefore commute with H_0+H_1. Furthermore we find on computation that they are diagonal matrices in a representation with the above wave functions as a basis. It follows that the matrix of H_0+H_1 can only have components between states for which L_z and S_z are the same. Then

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[15] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[16] E. U. Condon, Phys. Rev. **36**, 1121 (1930).

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

the perturbation problem breaks up into a number of simpler problems, one for each value of L_z and S_z. If the magnetic interaction is included, L_z and S_z are not separately constants of motion, although the sum $J_z=L_z+S_z$ is. Then the perturbation problem reduces to separate problems for each value of J_z which are not quite as simple as before.

We ask ourselves if there are any other integrals which we may use to simplify further the problem. A well-known constant of motion which should be useful is J^2, the square of the total angular momentum. But on computation we find that it is not a diagonal matrix in the representation for which Slater's determinant wave-functions are used as a basis. However it has quite a simple form, all its components being pure numbers except for a common factor h^2. Moreover it has no components between states from different configurations. Furthermore we know that J_z commutes with J^2. It is then possible to find a transformation R to a new representation in which J^2 is a diagonal matrix,* the components of R being pure numbers. This transformation will leave J_z invariant. In our new representation with J^2 and J_z diagonal matrices, H_0+H_1 can only have components between states with the same value of J^2 and J_z. Consequently the perturbation problem reduces to separate problems for each value of J^2 and J_z. It is the possibility of the transformation R which enables us to say that only levels of the same J value perturb one another. It is essential for our later discussion to notice that this transformation is entirely independent of the electrostatic and the magnetic interaction.

We now turn to the question of intensities. We consider first transitions between the states of two configurations, A and B, which are sufficiently isolated so that a solution of the perturbation problem for each of these configurations taken by itself may be expected to yield a close approximation to an exact solution. To obtain the transition probabilities, neglecting quadrupole and other higher-pole radiation, we need the components of the electric moment matrix, P, between the states of A and B.** We find that in the initial representation these components are simple numerical terms except for a common radial factor which may be disregarded if we are only interested in relative intensities. We also find that in order to have some nonvanishing components A can differ from B in just one individual set of electron quantum numbers and that in this set l must change by ± 1. The first condition means that "two electron jumps" are not permitted. They can only occur when the configuration A (say) is strongly perturbed by another configuration which differs from B in only one set of individual electron quantum numbers. The second condition gives just the selection principle for the azimuthal quantum number.

Having obtained the matrix of the electric moment in the initial representation we must next pass to the representation in which J^2 is diagonal. Let

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* A detailed consideration of transformations that carry J^2 to a diagonal form will be presented in a later paper.

** It is only necessary to consider the z component of P because for an isolated atom there is no preferred direction in space.

R_A be the transformation that carries the portion of J^2 associated with the states of A, to a diagonal form and let R_B be the transformation that carries the part of J^2 associated with B, to a diagonal form. Then the components of P in which we are interested will be transformed to

$$P' = R_A P R_B^{-1}. \tag{2}$$

Inasmuch as the components of R are pure numbers, the relative magnitude of the transformed components of P will not involve the electrostatic or the magnetic interaction in any way. Now let S_A be the transformation that carries the energy matrix associated with the states of A to a diagonal form and let S_B perform a similar function for the part of the energy matrix associated with the states of B. As the energy matrix in the representation in which J^2 is diagonal only has components between states with the same J value, the same will also be true of the transformation S. The electric moment matrix now becomes

$$P'' = S_A P' S_B^{-1}. \tag{3}$$

The squares of the magnitudes of the components of P'' give directly the relative transition probabilities between the states of A and B for all electrostatic and magnetic interactions. Let us consider in detail the transition probability between a state n of A and a state m of B for some particular value of J_z. It is given by

$$\begin{aligned} \left| P''(nm) \right|^2 &= \left| \sum_{kl} S_A(nk) P'(kl) S_B^{-1}(lm) \right|^2 \\ &= \sum_{kk'll'} S_A(nk) S_A{}^*(nk') S_B{}^{-1}(lm) S_B{}^{*-1}(l'm) P'(kl) P'^*(k'l') \end{aligned} \tag{4}$$

where the summations k and k' are over all states of A with the same J value as n and the summations l and l' are over all states of B with the same J value as m. If we now sum over n and m, where n and m have the same range of values as k and l respectively, we obtain

$$\sum_{nm} \left| P''(nm) \right|^2 = \sum_{nmkk'll'} S_A(nk) S^*(nk') S_B{}^{-1}(lm) S_B{}^{*-1}(l'm) P'(kl) P^{*\prime}(k'l') \tag{5}$$

But from the general transformation theory we know that S is unitary so that

$$\begin{aligned} \sum_{n} S_A(nk) S_A{}^*(nk') &= \delta(kk') \\ \sum_{m} S_B{}^{-1}(lm) S_B{}^{*-1}(l'm) &= \delta(ll') \end{aligned} \tag{6}$$

Hence our sum reduces to*

$$\sum_{nm} \left| P''(nm) \right|^2 = \sum_{kl} \left| P'(kl) \right|^2 \tag{7}$$

We have already seen that the components of P' are independent of all interactions. This equation therefore means that the sum of the transition proba-

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* Van Vleck has given a proof of the invariance of an expression of the type $\sum_{kl} |P'(kl)|^2$ to a unitary transformation of both the initial and final states (Phys. Rev. **29,** 727 (1927)). We repeat the proof because of differences in notation.

bilities between states of A with J equal to J_1 and states of B with J equal to J_2 is independent of the electrostatic and the magnetic interaction for all values of J_1 and J_2. This we have shown to be true for a particular value of J_z. But the total transition probability is simply the sum of the transition probabilities over all values of J_z. Hence the above statement holds for the total transition probabilities.

This J-group sum rule can be tested in a number of cases where the intensities have been worked out theoretically for both LS and jj coupling. As an example we consider the transition $dp \rightarrow ds$ for which the intensities in jj coupling have been given by Bartlett[19] and in LS coupling can be obtained from Kronig's formulas.[20] Tables I*a* and I*b* give the intensities in the two limiting types of coupling. Comparison of the two tables shows the sums of the lines in any given rectangle to be the same in each. This, in essence, is the J-group sum rule, except that in addition it predicts that the same will be true for all intermediate types of coupling.

TABLE Ia. *Line intensities for the transition $dp-ds$ in LS coupling, as calculated from Kronig's formulas.*

dp

	J	0	1			2				3			4
	1	36	0	27	81	0	1.8	27	151	x			x
ds	2	x	108	0	0	180	0	0	0	252	0	0	x
			0	81	27	0	27	125.1	27.9	0	27.9	224.1	
	3	x	x			0	151.2	27.9	0.9	0	224.1	27.9	324

TABLE Ib. *Line intensities for the transition $dp-ds$ in jj coupling, as calculated by Bartlett.**

dp

	J	0	1			2				3			4
	1	36	18	90	0	90	90	0	0	x			x
ds	2	x	90	18	0	90	90	0	0	252	0	0	x
			0	0	108	0	0	40	140	0	140	112	
	3	x	x			0	0	140	40	0	112	140	324

* We do not attempt to correlate the levels in *jj* coupling with those in *LS* coupling, as this correlation will depend on circumstances and we are only interested in the invariant intensity sums.

A simple special case of this rule is worth noting. Suppose there are two levels in the configuration A which are the only ones having their particular J values, and suppose there is one level in B which is the only one with its particular J value. Then the J-group sum rule levels tells us that the intensities of the two lines arising from these levels are independent of the magnetic interaction. Thus their intensity ratio should be normal no matter how

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[19] J. H. Bartlett, Jr., reference 8.

[20] R. deL. Kronig, Zeits. f. Physik **33**, 261 (1925).

anomalous the rest of the lines may be. In the example given in Tables I*a*–I*b* two such levels occur in *dp* for J equal to 0 and 4. In *ds* the levels for J equal to 1 and 3 are also isolated. Of the four possible lines,* two are forbidden by the selection rules for J and hence will always be of zero intensity (represented in the tables by x). The remaining two lines will have a constant ratio of 9 to 1 for all possible coupling schemes.**

Now we consider the relation of the J-group sum rule to other sum rules that have been proposed. It is evident that the original sum rule cannot be expected to hold in intermediate coupling because of the perturbations between terms from different multiplets. We might expect, however, that a rule similar to the extended sum rule will hold in the general case for intermediate coupling. If we sum over m in the expression which we have given for the transition probability in Eq. (4), and use (6) we find that

$$\sum_{m} |P''(nm)|^2 = \sum_{kk'l} S_A(nk)S_A{}^*(nk')P'(kl)P^{*\prime}(k'l). \tag{8}$$

Now to have such a rule hold, the components of the matrix S_A which involve the magnetic interaction must disappear from the sum. Of course we have only summed over a row of one J-group but it is certain that when we extend the sum over different J-groups to obtain the sum over a row of a transition array, the components of S_A will not in general disappear from the result. The special cases in which they do can only be determined by a more detailed consideration of the components of S_A and P'. We may mention one case in which the above sum is independent of the magnetic interaction. If we set

$$P'(kl)P^{*\prime}(k'l) = |P'(kl)|^2\delta(kk') \tag{9}$$

and if $\sum_l |P'(kl)|^2$ is independent of k, then it immediately follows from the unitary character of S_A that

$$\sum_{m} |P''(nm)|^2 = \sum_{l} |P'(kl)|^2. \tag{10}$$

Hence if in each column of a J-group there is only one nonvanishing transition probability in LS coupling, and if the sum of the transition probabilities in LS coupling over each row of the J-group has the same value for every row, then this sum over each row is independent of the magnetic interaction.† It is easily verified from Kronig's formulas that these conditions are satisfied if A is a two-electron configuration which contains one s electron and B is any other configuration.†† From these sums it follows therefore that a rule

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* In so far as dipole radiation is concerned the selection rule for J is rigorous for an isolated atomic system. This follows immediately from the facts that it holds in LS coupling and that only levels of the same J value can perturb one another.

** This conclusion must be modified if either *dp* or *ds* is perturbed by a third configuration in a manner which will be obvious after the discussion on page 765.

† It is assumed the transformation R is appropriate for LS coupling. This may be accomplished by making the transformation R such that it carried L^2, S^2 and $L\cdot S$ to a diagonal form simultaneously, a process made possible by the fact that these matrices all commute with one another.

†† An exception to this is the transition array $p^2 \to sp$. The second condition above is not satisfied due to the exclusion of some of the terms from $p\cdot p$.

similar to the extended sum rule holds in the general case of two electron systems in the direction of the sums for lines to or from a level in the configuration containing an s electron. We note that the sums over a row of a J-group give us considerably more detailed information than does this modification of the extended sum rule. In Tables Ia–Ib we see that for the J-group with $J=1$ for the levels of ds, the sums over each row of any of these J-groups has the same value in LS and jj coupling.

The J-group sum rule enables us to prove immediately the general sum rule. We observe that the sum contemplated in the general sum rule has the proper value in LS coupling. Since this sum is made up of a number of J-group sums it follows that the general sum rule holds in intermediate coupling. We note that it can never tell us more than the J-group sum rule, and in general the relations among the J-group sums which are given by this rule are insufficient to determine them completely.

It is interesting to note that the proof of the J-group sum rule does not depend on any specific characteristics of the components of P'. It is therefore valid when multipole radiation of all kinds is taken into account as well as dipole radiation.

We next inquire what modification must be introduced if the two configurations A and B are not sufficiently isolated, so that a solution of the perturbation problem for these two configurations taken by themselves cannot be expected to yield accurate results.* Let us suppose the levels of A are perturbed by the levels of a third configuration C. If A and C were well separated we could solve the problem for each configuration separately thus obtaining two transformations S_A and S_C which would carry the energy for the states of A and C respectively to a diagonal form. The transformations would not have any rows or columns in common. But now if A and C perturb one another, there will be matrix components between states of A and C so that the transformation S_{AC} that carries the energy to a diagonal form will involve states of A and C mixed together. It will only factor into the product S_AS_C in the limit when A and C are far apart and the intercombination matrix components are small. Now if we examine the proof of our sum rule, we see that Eq. (7) will still be true if we extend the summations n and k over all levels of A and C with the same J value, i.e. an enlarged J-group. But now the result is not independent of the electrostatic interaction for we remember that the components of P' associated with the states of A are multiplied by one radial integral whereas those associated with the states of C will be multiplied by a different radial integral. The sum will, however, be independent of the magnetic interaction. If we knew the radial part of the wave functions involved, we could calculate the ratio of these integrals which enters in the relative values of the sums we are trying to obtain. In general a great deal of labor is involved in finding these functions so that it is much easier to follow the less satisfactory method of introducing a parameter for this ratio which is adjusted to fit the experimental data.

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* We assume that the transformation R which carries J^2 to a diagonal form has already been made.

As an example of the way in which the J-group sum rule can be applied, let us study the configuration transition $A \rightarrow B$ throughout an isoelectronic sequence. If no other configuration overlaps either A or B throughout the sequence, we should expect the J-group sums to have the same relative values for each member of the sequence. If however, another configuration overlaps A and B for some members of the sequence, we have to consider the enlarged J-groups. A parameter would have to be introduced to take care of the ratio of the radial integrals which would have different values for different members of the sequence. The way in which this parameter changes as we pass along the sequence could be approximately predicted by a study of the radial part of the wave functions involved for different members of the sequence.

To test this rule experimentally probably the best procedure is to calculate the intensities for LS coupling with Kronig's formulae. Then the sums can easily be calculated and may be compared with the experimental values. It should only be necessary to include in the sum, levels of the same J value which lie fairly close together as the usual perturbation theory expansions show. Unfortunately the theory gives no real criterion of just how neighborly levels must be before they begin to exert an appreciable influence on one another.

Finally we discuss the departures from normal intensities when the magnetic interaction is small. For this purpose we suppose that the transformation R is such that the diagonal terms of the transformed energy matrix give the energy levels in LS coupling.* Then for each value of J^2 and J_z the energy level problem is completely nondegenerate. We write

$$H_A = H_A{}^0 + \lambda H_A{}'$$

where $H_A{}^0$ is a diagonal matrix whose terms $E^0_{An}\delta(nm)$ give the LS coupling energies for the states of the configuration A and $\lambda H_A{}'$ is a matrix whose diagonal elements are all zero and whose non-diagonal elements depend only on the magnetic interaction. Now if the magnetic interaction is really small, we expect that a first order calculation will yield good results. From well-known formulae for the energy and the corresponding transformation[18] we have in the first order

$$E^0_{An} = E_{An}$$

$$S_A(nm) = \delta(nm) + \frac{\lambda H_A{}'(nm)}{E^0_{An} - E^0_{Am}}[1 - \delta(nm)]$$

Under this transformation the components of the electric moment matrix become

$$P'(nm) = P^0(nm) + \sum_k{}' \frac{\lambda H_A{}'(nk)}{E^0_{An} - E^0_{Ak}} P^0(km)$$

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* See footnote †† p. 764.

[18] J. H. Van Vleck Phys. Rev. **29**, 727 (1927).

where $|P^0(mn)|^2$ is the normal intensity in LS coupling. The summation k extends over all states of A with the same J values as n. Carrying out a precisely similar calculation for the states of B and keeping only terms of the first order, we find

$$\begin{aligned} P''(nm) &= P'(nm) + \sum_l \frac{\lambda H_B'(ml)}{E^0_{Bm} - E^0_{Bl}} P'(nl) \\ &= P^0(nm) + \sum_k{}' \frac{\lambda H_A'(nk)}{E^0_{An} - E^0_{Ak}} P^0(km) + \sum_l{}' \frac{\lambda H_B'(ml)}{E^0_{Bm} - E^0_{Bl}} P^0(nl) \end{aligned}$$

where the summation l is over all states of B with the same J value as m. Hence we obtain for the required intensities in the first order

$$\begin{aligned} |P''(nm)|^2 = P^0(nm) \Bigg[P^0(nm) &+ 2\sum_k{}' \frac{\lambda H_A'(nk)}{E^0_{An} - E^0_{Ak}} P^0(km) \\ &+ 2\sum_l{}' \frac{\lambda H_B'(ml)}{E^0_{Bm} - E^0_{Bl}} P^0(nl) \Bigg]. \end{aligned}$$

We see that there is a departure from normal intensity which is linear in the magnetic interaction. There is no such departure for the energy levels, for the normal energy level is defined so as to take account of the linear terms in the magnetic interaction. For energies the departures from normal energy begin with terms quadratic in the magnetic interaction. It therefore follows that for a weak magnetic interaction, intensities will be more sensitive to anomalies than energies. We note from our formula that in general we may expect the percentage departure to be greater for the weaker lines.

§3. Experimental Tests of the Sum Rules

As the original sum rule was discovered experimentally and has been amply confirmed by later measurements on many multiplets, departures from it are considered to be due to departures from LS coupling. The extended sum rule has better theoretical than experimental confirmation, since the only measurements which have been used to test it are those of Ornstein and Burger[21] in a very small number of cases. The general sum rule would of course be extremely difficult to test except in very simple transition arrays. The measurements of Dorgelo[22] on the intensities of the neon lines arising from the transition $2p^53s-2p^53p$ form the only case that we have been able to find in which its use has been invoked. This intensity array is shown in Table IIa, the tabular entries having been taken from Pauling and Goudsmit[23] and checked with Dorgelo's original paper.[24]

Inspection of Table IIa reveals that whereas the horizontal sums for $J=2$ and $J=0$ are proportional to $2J+1$, as is to be expected since these states

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[21] L. S. Ornstein and H. C. Burger, Zeits. f. Physik **46**, 303 (1926).

[22] H. B. Dorgelo, Phys. Zeits. **26**, 787 (1925).

[23] L. Pauling and S. Goudsmit, Structure of Line Spectra p. 142.

[24] H. B. Dorgelo, Physica **5**, 90 (1925).

are alone and hence unperturbed, the two horizontal sums for $J=1$ must be taken together, their *average* value being proportional to $2J+1$. The vertical sums for $J=2$ and $J=0$ can similarly be taken independently; although two of the latter are present they perturb each other but little. But the vertical sums for $J=2$ and $J=1$ must be averaged together due to the mutual perturbations of these states.

TABLE IIa. *Test of general sum rule by use of Dorgelo's original measurements on neon I.*

$p^5 \cdot p$

		8_0	10_0	1_1	4_1	6_1	9_1	3_2	5_2	7_2	2_3	Sum	Quotient
$p^5 \cdot s$	$^3P_2$	x	x	20	10	3	9	34	34	17.5	100	227.5	45.5
	$^3P_1$	15	1	20	32.5	0.1	4	39.5	10	20.5	x	142.6	2×43.3
	$^1P_1$	0.1	14	2	2	19.5	17	5	26	31.5	x	117.1	
	$^3P_0$	x	x	1	15	16	10.5	x	x	x	x	42.5	42.5
	Sum	15.1	15.0	43.0	59.5	38.6	40.5	78.5	70.0	69.5	100		
	Quotient	15.1	15.0	14.3	19.8	12.9	13.5	15.7	14.0	13.9		14.3	
		2×15.0		4×15.1				3×14.5				1×14.3	

TABLE IIb. *Test of J-group sum rule with same values as given in Table Ia. Upper values, J-group sums as calculated from Table Ia. Lower values, J-group sums calculated for LS coupling from Kronig's formulas.*

$p^5 \cdot p$

	8_0 10_0	1_1 4_1 6_1 9_1	3_2 5_2 7_2	2_3
$^3P_2$		42.0 42.8	85.5 71.4	100 100
$^3P_1$ $^1P_1$	30.1 28.6	97.1 85.6	132.5 142.8	x
$^3P_0$	x	42.5 42.8	x	x

In Table IIb we use the same data to test the J-group sum rule, the agreement being satisfactory, (ave. dev. 5 percent) but not so good as for the general sum rule, (ave. dev. 2.5 percent). We have some cause to be suspicious of the data, however, since from our discussion of this point in §2, one expects all the horizontal sums to split up no matter what the coupling, due to the fact that the horizontal configuration is equivalent to sp. We note that Dorgelo makes no mention of having applied a ν^4 correction to his results, and the fact that he used his data directly to calculate the luminous efficiency of his neon lamp source substantiates our belief that this correction was omitted, especially since the necessity for always introducing it was by no means so widely admitted in 1925 as it is at present. That no excitation correction was applied is certain since Dorgelo mentions that with slightly different conditions of excitation the relative intensities of many of the neon lines are greatly altered, and specifies that the general sum rule holds only for the conditions used. That such a correction is needed appears at once when we apply the ν^4 correction to Dorgelo's data, which has been done in Table IIIa.

TABLE IIIa. *Test of general sum rule with data of Table Ia, but with ν^4 correction applied.*
$p^5\cdot p$

		8_0	10_0	1_1	4_1	6_1	9_1	3_2	5_2	7_2	2_3	Sum	Quotient
$p^5\cdot s$	$^3P_2$	x	x	29.3	8.95	2.26	6.4	32.6	29	13	100	221.5	44.3
	$^3P_1$	12.2	0.51	33.0	32.2	0.08	3.24	42.3	9.5	16.8	x	149.8	49.8
	$^1P_1$	0.12	9.8	5.1	2.88	23.8	19.3	8.0	36.0	37.8	x	142.8	47.5
	$^3P_0$	x	x	1.84	16.3	14.8	9.02	x	x	x	x	42.0	42.0
	Sum	12.3	10.3	69.2	60.3	40.9	38.0	82.9	74.5	67.6	100		
	Quotient	12.3	10.3	23.0	20.1	13.6	12.7	16.6	14.9	13.5	14.3		

TABLE IIIb. *Test of J-group sum rule with data of Table IIa. Upper, measured; lower, calculated for LS case.*

J	0	1	2	3
2	x	46.9 42.8	74.6 71.4	100 100
1	22.6 28.6	119.6 85.6	150.4 142.8	x
0	x	42.0 42.8	x	x

Inspection of this table reveals that the horizontal sums have now split apart, as was expected, while the vertical sums have not. These, however, show a marked correlation in intensity with the energy values of the upper states, those lying highest in the atom being weakest (the main numbers in the term designations indicate their order in the energy level diagram, 10_0 lying highest and 1_1 lowest). It is apparent that the higher lying levels are not being filled properly, and an excitation correction must be applied. For completeness, however, we have given in Table IIIb the test of the J-group sum rule, with the data of Table IIIa; it now holds quite as well as the general sum rule, although the agreement of neither is so good as formerly.

The types of excitation involved in the production of light in the neon lamp are undoubtedly very complicated; we are justified, however, in seeing if the assumption of any equivalent temperature of excitation will improve the results. In Fig. 1 we plot the energy separations between the various upper terms and the upper term 2_3 against the common logarithm of the factor required to bring the intensity sum/$2J+1$ closest to a constant value, since we can reduce the Boltzmann excitation factor to the form $\Delta\sigma = 1.6T \log_{10} R$[25], where $\Delta\sigma$ is the term separation, T is the equivalent excitation tem-

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[25] G. R. Harrison and H. Engwicht, J.O.S.A. **18**, 287 (1929); G. R. Harrison, J.O.S.A. **19**, 109 (1929).

perature, and R is the reduction factor needed. The slope of the straight line which most closely fits all points will give us the best value to use for the equivalent excitation temperature, which in this case is 8000°K. Since perturbations are known to exist, however, we should draw our line only through those points which are least perturbed, namely 8_0, 10_0, and 2_3. The slope of this line as drawn gives the temperature 13,600°K, a value lying in the range of excitation temperatures found by this same method in titanium and other arcs,[26] and by the Langmuir probe method in numerous similar cases.[27] We

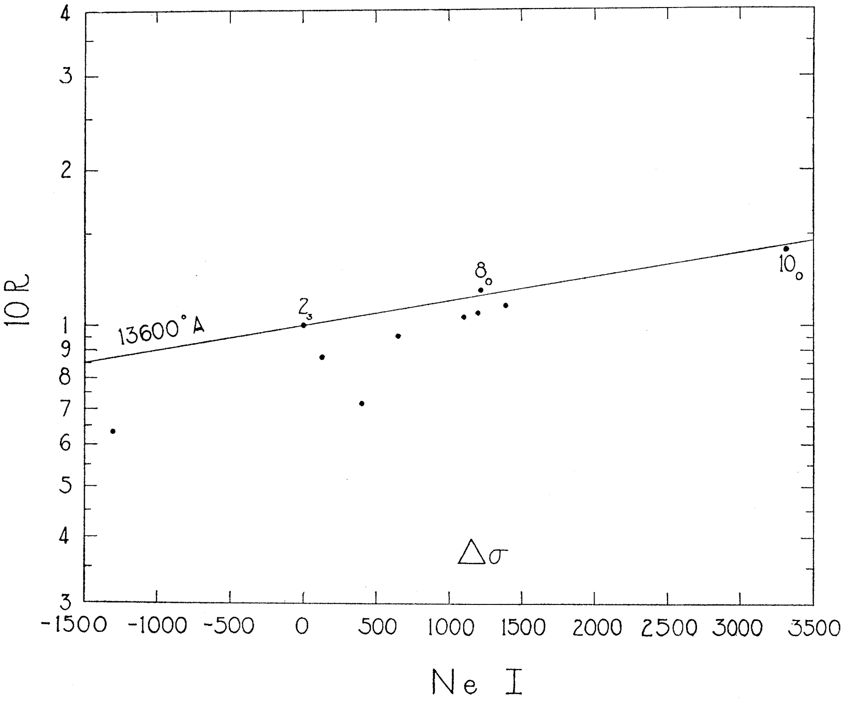

Fig. 1.

now apply an excitation correction to all the lines using this equivalent temperature, and obtain the results shown in Table IVa. The horizontal sums are still split apart, and it is seen that the special application of the extended sum rule given in §2 holds to within 6 percent. The individual vertical sums, on the other hand, vary on the average by over 13 percent from the mean, so that we must apply the general sum rule, taking the sums in groups, when we get agreement to within 7 percent. Again, we see from Table IVb that the J-group sum rule holds to within 7 percent also, which is doubtless within the experimental error, when we consider the broad spectral region covered and the complicated type of excitation involved, together with possible reversal effects. Two J-groups are responsible for almost all of the deviation from the

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[26] G. R. Harrison and H. Engwicht, reference 25.

[27] W. B. Nottingham, Jour. Frank. Inst. **206**, 43 (1928).

TABLE IVa. *Test of the general sum rule with the data of Table IIa, but with both* ν^4 *correction and excitation correction for 13,600° equivalent temperature applied.*

	8_0	10_0	1_1	4_1	6_1	9_1	3_2	5_2	7_2	2_3	Sum	Quotient
$^3P_2$	x	x	25.8	9.4	2.5	7.4	33.2	31	14.7	100	224	44.8
$^3P_1$	13.9	0.7	29	33.8	0.1	3.76	43.2	10.2	19	x	153.7	51.2
$^1P_1$	0.1	14.2	4.5	3.0	16.7	22.4	8.2	38.6	42.5	x	150.2	50.1
$^3P_0$	x	x	1.6	17.1	16.6	10.5	x	x	x	x	45.8	45.8
Sum	14.0	14.9	60.9	63.3	35.9	44.1	84.6	79.8	76.2	100		
Quotient	14.0	14.9	20.3	21.1	12.0	14.7	16.9	16.0	15.2	14.3		
	2×14.4		4×17.3				3×16.0			1×14.3		

TABLE IVb. *Test of the J-group sum rule with the data of Table IVa, the upper figures being the J-group sums as measured and corrected, and the lower figures being the sums calculated for LS coupling. The total intensity of the array has been made roughly the same for the two cases.*

J	0	1	2	3
2	x	41.0 42.8	71.6 71.4	90.7 100
1	26.3 28.6	103 85.6	147 142.8	x
0	x	41.6 42.8	x	x

J-group sum rule; one of these contains but a single strong line, and hence is subject to the greatest experimental error. The other anomalous group ($J=1$ to $J'=1$) contains the lines which are obviously most responsible for the deviations from the other sum rules, so that whatever may be the cause of the anomaly it affects new and old rules alike.

We have been able to find no other data which could be used for a general test of the new rules, since we are restricted to two-electron configurations where the intensities of all lines can be calculated for LS coupling by Kronig's formulas. On the theoretical side there would be much use for an extension of the correspondence principle formulas to the general case of multiplets not having a common parent term, while experimental data on line intensities in two-electron configuration transitions is badly needed.

§4. MODIFICATIONS IN USE OF THE GENERAL AND J-GROUP SUM RULES FOR CONFIGURATIONS CONTAINING EQUIVALENT ELECTRONS

It has been commonly assummed that all the intensity formulas and summation rules apply equally well to ordinary configuration arrays and to those in which Pauli's exclusion principle has operated to eliminate certain terms. Bartlett[28] has pointed out, however, that when one is dealing with the transition array from $sp-p^2$ the sums corresponding to the J's for sp cannot be

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[28] J. H. Bartlett, Jr., Phys. Rev. **35**, 229 (1930).

proportional to $2J+1$, even for LS coupling, since some of the terms are missing due to the equivalence of the two p electrons. Indeed it appears that this must be true for any transition array arising from configurations either or both of which contain two or more equivalent electrons. For since many of

TABLE VA. *Calculated intensities for LS coupling for the transition array* $pd-d\cdot d$ *and* $(pd-d^2)$.*

pd

	$^3F_4$	$^3F_3$	$^3D_3$	$^1F_3$	$^3F_2$	$^3D_2$	$^3P_2$	$^1D_2$	$^3D_1$	$^3P_1$	$^1P_1$	$^3P_0$	Sum $d\cdot d$, d^2	
$(^3G_5)$	(264)	x	x	x	x	x	x	x	x	x	x	x	264	0
$(^3G_4)$	(13)	(202)	(0)	(0)	x	x	x	x	x	x	x	x	216	0
$^3F_4$	67	4	144	0	x	x	x	x	x	x	x	x	216	216
$^1G_4$	0	0	0	216	x	x	x	x	x	x	x	x	216	216
$(^3G_3)$	(1)	(13)	(0)	(0)	(154)	0	0	0	x	x	x	x	168	0
$^3F_3$	4	46	13	0	4	100	0	0	x	x	x	x	168	168
$(^3D_3)$	(10)	(1)	(87)	(0)	(1)	(11)	(59)	0	x	x	x	x	168	0
$(^1F_3)$	0	0	(0)	(56)	(0)	(0)	(0)	(112)	x	x	x	x	168	0
$^3F_2$	x	4	1	0	35	13	0	0	67	0	0	x	120	120
$(^3D_2)$	x	(7)	(11)	(0)	(1)	(49)	(10)	(0)	(11)	(31)	0	x	120	0
$^3P_2$	x	0	25	0	0	5	67	0	1	23	0	x	120	120
$^1D_2$	x	0	0	8	0	0	0	70	0	0	42	x	120	120
$(^3D_1)$	x	x	x	x	(5)	(11)	(0)	(0)	(31)	(10)	(0)	(14)	72	0
$^3P_1$	x	x	x	x	0	13	23	0	5	13	0	18	72	72
$(^3S_1)$	x	x	x	x	(0)	(0)	(40)	(0)	(0)	(24)	(0)	(8)	72	0
$(^1P_1)$	x	x	x	x	(0)	(0)	(0)	(18)	(0)	(0)	(54)	(0)	72	0
$^3P_0$	x	x	x	x	x	x	x	x	6	18	0	x	24	24
$^1S_0$	x	x	x	x	x	x	x	x	0	0	24	x	24	24
Sum $d\cdot d$	360	280	280	280	200	200	200	200	120	120	120	40		
Sum d^2	72	54	181	224	39	127	90	70	79	54	66	18		

* The individual intensity values are not quite exact in many cases due to the adjustments required to keep small integral numbers.

TABLE VB. *J-group sums for* $pd-d\cdot d$ *and* $pd-d^2$.

pd

		$^3P_0$	$^1P_1$ $^3P_1$ $^3D_1$	$^1D_2$ $^3P_2$ $^3D_2$ $^3F_2$	$^1F_3$ $^3D_3$ $^3F_3$	$^3F_4$
	$^1S_0$ $^3P_0$	x	48 48	x	x	x
	$(^1P_1)$ $(^3S_1)$ $^3P_1$ $(^3D_1)$	40 18	138 18	109 36	x	x
$d\cdot d$ (d^2)	$^1D_2$ $^3P_2$ $(^3D_2)$ $^3F_2$	x	175 133	250 190	56 38	0 0
	$(^1F_3)$ $(^3D_3)$ $^3F_3$ $(^3G_3)$	x	x	438 111	218 60	16 5
	$^1G_4$ $^3F_4$ $(^3G_4)$	x	x	x	564 364	81 67
	$(^3G_5)$	x	x	x	x	264 0
	Sum $d\cdot d$ Sum d^2	40 18	360 199	800 327	840 462	360 72

the confirmatory measurements of the multiplet intensity formulas have been made on multiplets arising from systems containing equivalent electrons, we know that the internal multiplet intensities are the same, but certain multiplets are obviously completely omitted. We illustrate this in Table Va, where the intensities in LS coupling for the transition array arising from $pd-d\cdot d$ are given as computed from Kronig's formulas. We have placed in parenthesis those lines which fall out when the two d-electrons are equivalent, and the new sums arising when the transition is $pd-d^2$ are similarly marked. Apparently, then, when one is applying the general sum rule to lines arising from configurations containing any number of equivalent electrons, the correct procedure is to calculate the proper sums for the suitable nonequivalent case, and then subtract the theoretical values of the lines arising from terms which have been ruled out, these being obtainable in the general case by calculating them for LS coupling and applying the J-group sum rule. The configurations p^5, d^9, etc. should not require modification, since they have the same term content as p, d, etc.

The J-group sum rule will presumably still hold when equivalent electrons are present, but the sums used will be different, as seen in Table Vb, on account of the different term content of the J-groups.

It should be emphasized that while this suggested method of procedure appears perfectly straightforward and is given weight by the calculations of Bartlett, it lacks direct experimental testing and may lead to results which contradict our previous ideas of the role of the statistical weight in intensity determinations.

§5. Empirical Study of Perturbation Effects which Produce Intensity Anomalies in Complex Spectra

If we wish to cling to the useful fiction that each spectral term can be described by a single set of quantum numbers we must, as is well known, give up the ordinary selection principles which state that the azimuthal quantum number L can change only by ±1 or 0, and that combinations occur only between states of the same multiplicity. We also find it very convenient to retain the formal nomenclature of LS coupling in cases where the multiplet structures are not entirely broken down, and to explain the anomalies which arise as due to perturbation effects produced by near-lying terms. We turn now to a detailed examination of certain terms in a typical complex spectrum.

Elements of the first long period give rise to many multiplets which obey the ordinary (LS) multiplet intensity formulas almost exactly, and to others which are entirely anomalous, while in between lie multiplets containing various percentages of normal and anomalous lines. In particular titanium (Ti I and Ti II)[29] gives rise to many lines of both types, while vanadium,[30] chromium,[31] manganese,[32] iron,[33] cobalt,[34] and nickel[34] show increasing per-

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[29] G. R. Harrison, J.O.S.A. **17**, 389 (1928).

[30] G. R. Harrison, unpublished material.

[31] C. E. Hesthal, thesis not yet published.

[32] R. S. Seward, Phys. Rev. **37**, 344 (1931).

centages of anomalous lines. This is to be expected, since the internal multiplet separations become greater as one passes from left to right across the table, so that the tendency of multiplet levels to overlap with a resulting departure from *LS* coupling increases.

In Ti I we consider the triads d^3D', c^3F, c^3G; and c^5D', b^5F, b^5G', arising from the configuration $(3d)^3 4p$[35]. The relative positions of these terms in the energy level diagram are shown in Fig. 2. We note that b^5F is comparatively isolated, while in particular $c^3G_3{}'$ and $d^3D_3{}'$ practically coincide. In addition $c^5D'_{4321}$ lie very close to the $^3G'$ and $^3D'$ terms. To make the relationships more clear we plot the same energy levels, together with all others lying near them, in Fig. 3, where the terms have been arranged according to their *J* values,

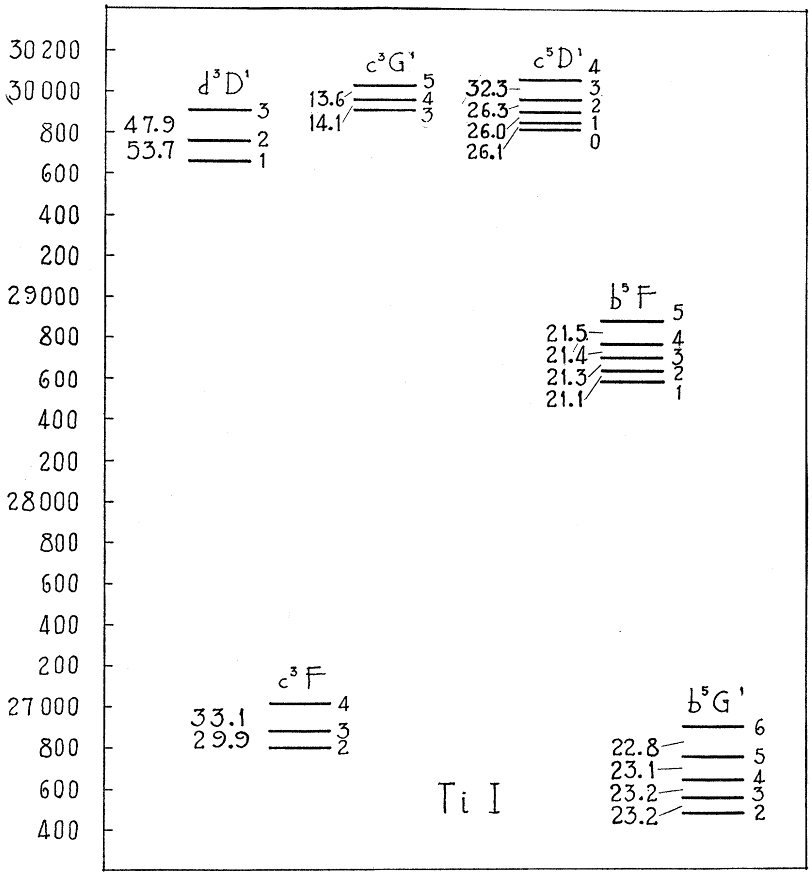

Fig. 2.

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[33] J. B. van Milaan, Zeits. f. Physik **34,** 921 (1925); **38,** 427 (1926); R. Frerichs, Ann. d. Physik **81,** 807 (1926).

[34] L. S. Ornstein and T. Bouma, Phys. Rev. **36,** 679 (1930).

[35] H. N. Russell, Astrophys. J. **66,** 335 (1927), but modified later, see J.O.S.A. **18,** 296 (1929).

which have been marked across the top of the diagram. We are led to expect from this figure that c^3G_5' and c^5D_0' will be unperturbed, as will b^5G_{56}' and all of the b^5F terms.

In Table VI are given the relative intensities of the lines in various sets of multiplets arising between c^3G', c^5D', and d^3D' and the terms marked in the left hand column. The values are relative only within a group pertaining to a given set of lower terms, and while quantitative measurements were made

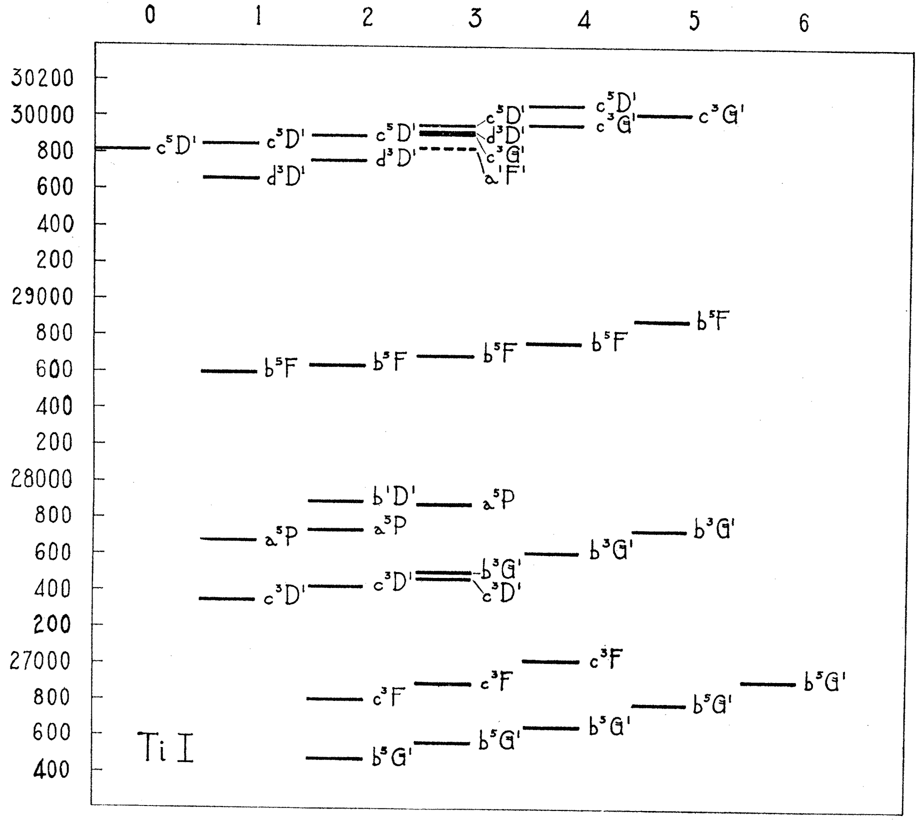

Fig. 3.

they are in many cases not much better than estimates, due to overlapping lines, to the comparative weakness of certain lines, and to the presence of bands. The accuracy is sufficient, however, to indicate qualitatively the validity of the J-group sum rule as applied to partial J-groups, where only those lines are considered which arise from terms which mutually perturb one another. The measured intensities are written in two parts in the case of unforbidden lines; thus if a line is predicted to be of intensity 56 in LS coupling, and is found actually to be 48, it is written as 56–8. To test the sums it is then only necessary to add the three (or fewer) numbers in any row of any rectangle in Table VI; the excess or deficiency values of the allowed lines plus the intensities of the forbidden lines, marked (), should total zero. We note

TABLE VI. *Intensities in typical partial J-groups of Ti I with perturbing levels.*

Upper states												
c^3G'		5	4		3							
→c^5D'				4		3		2		1		0
d^3D'							3		2		1	
Lower states →	5	(–)	(–)	220	x	x	x					
	4	(–)*	(–)	30	(<2)	150– 30	(35– lap)	x	x			
a^5F'	3	x	(–)	∽2	(–)	42– 9	(<15)	96– 1	(<2)	x	x	
	2		x	x	(–)	lap	(<1)	40– 1	(<2)	56	(<1)	x
	1				x	x	x	4	(«1)	28	(<1)	28
	4	1230	63– ?	(<3)	1+ 54	(50 « 150)	700– 110	x	x			
a^3F'	3	x	940	(–)	63	(20)	lap	(50)	lap	x	x	
	2		x	x	720– ?	(2)	2+ 19	(2)	61	(15)	328	x
	4	5	—	(–)	—	(10)	41– 15?	x	x			
b^3F'	3	x	2	(–)	—	(<1)	4– 1	(<2)	28+ lap	x	x	
	2		x	x	<1	(–)	—	(–)	4	(–)	19+ lap	x
	2		x	x	(3)	(15)	84– 20	(–)	15	(–)	∽1	x
a^3P'	1				x	x	x	(∽2)	lap	(–)	15	(--)
	0							x	x	(–)	lap	x

* Although Russell lists a line with this designation, it is an exact lap with a strong line, and lies 7 wave-numbers from the proper position, so that its existence is very doubtful.

— indicates line too weak to observe.

(—) indicates line forbidden by L or R selection principles which is too weak to observe.

( ) enclose observed intensities of lines forbidden by L or R selection principles.

x indicates transition forbidden by J selection principle.

that where forbidden lines exist their intensities are taken from some allowed line which is made abnormally weak; that perturbations may produce increased as well as decreased intensities in allowed lines; that the perturbations are here greatest in the columns with $J=3$, and that all lines in the columns with $J=5$ or 0 appear normal.

We may evaluate somewhat more closely the amount of perturbation existing between two levels by observing the ratio of intensity of a forbidden line to that of the allowed line or lines from which its intensity has obviously been abstracted. This ratio multiplied by 100 we call P; while we do not expect P to be a constant for all of the lines arising from any two mutually perturbing upper states, it appears to remain fairly constant in order of magnitude. For example, between d^3D_3' and c^5D_3' we get the following values of P from Table VI: 19.3; 21.6; 8.0; 24; 25; 18. We use the average value 19.3

TABLE VII. *Measurements of perturbations between states from the data of Table VI.*

Perturbed states		Separation	P
$c^3G'_5$		—	0
$c^3G'_4$	$c^5D'_4$	89	<1
$c^3G'_3$	$c^5D'_3$	72	<1
$c^3G'_3$	$d^3D'_3$	2.4	5
$d^3D'_3$	$c^5D'_3$	74	19.3
$d^3D'_2$	$c^5D'_2$	139	2.5
$d^3D'_1$	$c^5D'_1$	194	<2
	$c^5D'_0$		0

as a rough intensity indication of the degree of perturbation between these two terms. In Table VII we give the values of P obtained for various mutually perturbing upper terms as computed from the date of Table VI.

We note in particular the much greater perturbations between the d^3D' and c^5D' terms than between either and c^3G'. If we are correct in assuming that all three come from the same configuration, the close coupling between the triplet and quintet D terms can probably be traced to the fact that they differ only in spin orientation.

We note also from Table VII that the mutual perturbations between two given sets of multiple terms increase rapidly as the energy differences between the perturbing states decrease, as is to be expected.

We may briefly summarize the available intensity measurements dealing with some of the other upper states shown in Figs. 2 and 3 as follows: b^5F, comparatively isolated, gives the practically normal multiplet (#172) $a^5F'-b^5F$. The only forbidden lines to which b^5F gives rise are extremely weak, with the exception of a few which can be traced to perturbations of the other states giving rise to them. c^3F, on the other hand, shows many intensity anomalies, which can be traced to perturbations with b^5G'.

A great deal of useful information can of course be obtained without quantitative intensity measurements by observing the estimated intensities of lines forbidden by the L and R selection principles. One first seeks to determine whether they arise from perturbations of the upper or lower states, or both. This is usually easiest to do in the case of lines forbidden by both selection principles; consider for example lines of the type $a^1D_2-{}^3G_3'$, of which there are several in Ti I. We observe that such a combination can only be produced by perturbation of the lower term by one of the type ${}^3F_2'$, or of the upper term by one of the type ${}^1F_3$. But the terms a^3F_2' and b^3F_2' are respectively 7250 and 4280 wave numbers from a^1D_2, and experience with other terms in Ti I indicates that ordinarily perturbations are not noticeable between terms more than 2000 wave numbers apart in this element. We may check this conclusion, however, by listing the estimated intensities of all lines of type $a^3F_2'-{}^3G'$ and $a^1D_2-{}^3G'$, as in Table VIII.

TABLE VIII.

$a^3F'_2-a^3G'_3$	30	$a^1D_2-a^3G'_3$	(−)
$-b$	100	b	(−)
$-c$	80	c	(−)
$-d$	100	d	(1)
$-e$	20	e	(10)
$-f^3G'_3$	10	$f^3G'_3$	(3)

From the absence of the first three forbidden lines in Table VIII, we see that the presence of the last three is probably due to perturbations of the upper states by ${}^1F_3$ terms. In Table IX we list the various ${}^3G'$ upper states of Table VIII, the nearest ${}^1F_3$ terms to them, when within 2000 wave-numbers, the wave-number separations between ${}^3G_3'$ and ${}^1F_3$, the estimated intensities of the forbidden $a^1D_2-{}^3G_3'$ lines, the estimated intensities of the corresponding $a^1D_2-{}^1F_3$ lines, and the approximate ratios of the two latter, obtained by squaring the estimated ratios.[36] We note that where perturbations exist they increase greatly as the term separation decreases.

TABLE IX.

$a^3G'_3$	a^1F_3	930	(–)	12	
b	–	–	(–)	–	
c	–	–	(–)	–	
d	b	1480	(1)	40	1/1600
e	c	68	(10)	20	1/4
f	e	415	(3)	40	1/170

The intensity anomalies produced by terms a given distance apart will of course depend on the magnetic separations within the multiplet terms, on the relationship of the perturbing terms, and on the quantum numbers involved. Detailed investigation of these factors is beyond the scope of the present paper; a large amount of interesting data of this type is being accumulated in the spectra of Ca, Ti, Zr, V, Cr, Mn and Ni, which will be published at a later date. Where the internal multiplet separations become relatively great, as in Zr I, while the general character of *LS* coupling is roughly preserved, we can obtain much information on perturbations not only from the intensity anomalies within multiplets and the presence of forbidden lines, but from the anomalous *g* values and departures from Landé's interval rule, as has been mentioned recently by Kiess and Kiess.[37] While there are a number of such departures in Ti I their specific causes are usually more difficult to determine than in Zr I.

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