In the case of sodium, Kapitza has not obtained sufficient data for determining the constant B, since the change in resistance for the lower fields was too small to measure. However, he does give $\Delta \rho / \rho$ for 300,000 gauss. Now B for sodium will be smaller than for lithium, and if we assume B=2.0, we obtain R=0.0042, while the observed value is 0.0021. In fact, if we study the effect of varying B, we find that for B=2.5, R=0.0049; while for B=1, R=0.0018. It is evident, then, that for lithium and sodium, the value of the Hall constant predicted by the theory of Sommerfeld and Frank is certainly of the correct order of magnitude and that there is a possibility of close agreement when complete data are obtained. In the case of potassium and caesium, since no values are available for the change of conductivity in a magnetic field, the results of the above theory cannot be found.

In conclusion it is a pleasure to acknowledge our indebtedness to Professor P. I. Wold for many valuable suggestions, and for the facilities put at our disposal.

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Line Strengths in Intermediate Coupling

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The sum rules applicable to intermediate coupling are discussed in §1; in §2 proofs are given for two which are essentially new: the J-file sum rule which states that for any coupling, in a transition array in which the jumping electron is not equivalent to any electron in the ion in either the initial or final configuration, the sum of the strengths of the lines originating in (or terminating on) a common level of quantum number J is proportional to 2J+1; and the J-group-file sum rule which says that for any transition array of this type in which the valence electron jumps from s to p or p to s, the individual J-groups may be split up

§1. SUM RULES IN INTERMEDIATE COUPLING

THE sum rules which are applicable to a transition array in intermediate coupling will be made most clear if we prove them first for a particular array such as $p^2s - p^2p$ (shown in Table I in LS coupling), and extend the proofs to more general arrays later.

All the sum rules apply to quantities of the type $S(\alpha J, \alpha' J')$, which we call the strength of the line from the level αJ to the level $\alpha' J'$, and which is defined as the sum $\Sigma_{M, M'} |(\alpha JM | \mathbf{P} | \alpha' J'M')|^2$ of the absolute squares of the components of electric moment. Under conditions of natural excitation the intensity of radiation of this line is

in one direction into invariant files. The dispersion measurements of Ladenburg and Levy on the neon transition array $2p^53p \rightarrow 2p^53s$ furnish in §3 an interesting experimental verification of these rules. The predictions of the usual first-order quantum-mechanical theory regarding the line strengths in this neon array are investigated in §4. It is concluded that this approximation does not enable the eigenfunctions to be determined with sufficient accuracy from the observed energy levels for quantitative intensity predictions.

given by

$$I(\alpha J \rightarrow \alpha' J')$$

$$= N(\alpha J) \cdot 64\pi^4 \nu^4 \mathbb{S}(\alpha J, \alpha' J')/3c^3(2J+1),$$

where $N(\alpha J)$ is the number of atoms in the level αJ . The line strengths are usually expressed in the form¹

$$S(\alpha J, \alpha' J') = (2J+1) | (\alpha J P \alpha' J') |^{2} \Xi(J, J'), (1)$$

where

$$\begin{split} \Xi(J, J+1) &= (J+1)(2J+3); \quad \Xi(J, J) = J(J+1); \\ \Xi(J, J-1) &= J(2J-1). \end{split}$$

The quantities $(\alpha J \stackrel{!}{!} P \stackrel{!}{!} \alpha' J')$ transform like the elements of the matrix of an observable in going

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¹See Born and Jordan, *Elementare Quantemmechanik*, p. 159, Eq. (10), or Güttinger and Pauli, Zeits. f. Physik 67, 754 (1931), Eq. (23).

TABLE I. The transition array $p^2p - p^2s$ in LS coupling as an illustration of the sum rules. The individual columns and rows of this array are each J files; the fourth column (containing the entries 32, 16, 80, 16, 144) is the J file referring to the level $p^2 ({}^3P) s {}^2P_{3/2}$; the third row (containing the entries 32, 16) is the J file referring to $p^2 ({}^3P) p {}^2P_{1/2}$. The rectangles set off by solid lines, of which there are eight in which transitions are allowed by the selection rules, are each J groups. The rectangle at the top center of the array (containing the entries 32, 16, 40, 8, 48) is the J group labeled by $J = \frac{1}{2}$ for p^2p and $J = \frac{3}{2}$ for p^2s . The broken lines break each J group up into two or three J-group files; the first file of the J group just mentioned contains the entries 32, 16; the second, 40, 8; the third the single entry 48.



from one coupling to another for a free atom. Hence the matrix of the quantities $S^{\frac{1}{2}}(\alpha J, \alpha' J')$, defined as the square roots of the strengths Staken + or - according to the sign of $(\alpha J \stackrel{!}{!} P \stackrel{!}{!} \alpha' J')$, transforms like the matrix of an observable since states of different J values do not become mixed up. These quantities $S^{\frac{1}{2}}(\alpha J, \alpha' J')$ are the most convenient to transform to intermediate coupling.

Table I gives, for *LS* coupling, the values of the line strengths S, and as superscripts the signs of $S^{\frac{1}{2}}$, for the transition array $p^2s \Rightarrow p^2p$ (the line strengths are symmetric in the initial and final states).²

In a transition array, the set of all lines originating in levels of one given J value and terminating on levels of a second given J value was called by Harrison and Johnson³ a J-group. In Table I all boxes set off by solid lines are J-groups. The J-group sum rule which they proved states that the strengths of the J-groups⁴ are independent of coupling. This follows immediately from the principle of spectroscopic stability for any transition array whatsoever.

In a transition array, the set of lines connecting a single given level of one configuration with all levels of the other configuration we shall call the J-file referring to that level. The different rows of Table I are J-files referring to the levels of p^2p , and the columns are J-files referring to the levels of p^2s . Now in LS coupling for a transition array in which the jumping electron is not equivalent to any in either ion, it follows from the known formulas for the relative strengths of the lines that the strengths of the different *J*-files referring to the levels of the same configuration are proportional to the values of 2J+1 for those levels. Thus the strengths of the rows and columns, shown at the right and bottom of Table I, are separately proportional to 2J+1. The same sum rule is known to hold for this same class of transition arrays in jj coupling. Hence it was immediately obvious from spectroscopic stability that the sum of the strengths of all the J-files of the array which refer to a given J value and a given configuration should be invariant and hence proportional to (2J+1)times the number of such files, in any coupling.5 These sums are shown in square brackets in Table I.

However Kronig,⁶ in considering on the basis of the old quantum theory the old vector model in which configuration assignments were only made for the valence electron, states that the "intensities" of the *separate J*-files should be invariant. This statement seems not to have been repeated elsewhere nor to have been investigated quantum mechanically. Now if we examine the

² Calculated by the method given in Johnson, Proc. Nat. Acad. Sci. **19**, 916 (1933) and Shortley, Proc. Nat.

Acad. Sci. 20, 591 (1934), for a particular choice of phases of the eigenstates.

³ Harrison and Johnson, Phys. Rev. 38, 757 (1931).

⁴ By the strength of a set of lines we mean the sum of the strengths of the lines in the set.

⁵ See, e.g., Pauling and Goudsmit, *Line Spectra*, p. 141. ⁶ Kronig, Zeits. f. Physik **33**, 268 (1925).

matrix of $S^{\frac{1}{2}}$ for $p^2p - p^2s$ (whose elements are the square roots of the strengths of Table I taken with the indicated signs) we note that any two rows or any two columns of $S^{\frac{1}{2}}$ headed by the same J value are orthogonal. This is sufficient to establish the invariance of the strengths of the separate files in this case, for if in any matrix the sum of the squares of the elements is the same for each row (or column) and the rows (columns) are orthogonal, these properties are independent⁷ of unitary transformations of the states labeling the rows and of the states labeling the columns.

In fact, as we shall show in §2, in any case in which the strengths of the files are known to be proportional to 2J+1 in LS coupling, they individually have the same values in all intermediate coupling. This theorem, which we shall call the *J*-file sum rule states that for any coupling, in a transition array in which the jumping electron is not equivalent to any electron in the ion in either the initial or final configuration, the strengths of the J-files referring to the levels of the initial (final) configuration are proportional to the values of 2J+1 for those levels. In addition, for the particular two-electron arrays $nlnl'' = nl^2$, the strengths of the *J*-files referring to nl^2 (but not those referring to nln'l') are proportional to 2J + 1.

In the particular cases of the arrays $\alpha s \Rightarrow \alpha p$, in which the valence electron jumps from s to por p to s and is not equivalent to any electron in the ion, we can further break the individual allowed J-groups up into invariant files referring to the levels of the configuration αs . These we shall call J-group files. In such a transition array in any coupling the strength of a J-group file anywhere in the array is equal to the strength of a J-file referring to the J-value of the configuration ap which labels the J-group. In Table I the J-group files are set off by broken and solid lines; their strengths (shown in parentheses) are equal to the strengths of the rows as given at the right of the table and are invariant since the different files in a J-group are obviously orthogonal. This J-group-file sum rule was recognized by Harrison and Johnson to hold in the particular

case of two-electron transitions ls = lp. We shall sketch a general proof in §2.

A further illustration of these three sum rules is furnished by the strengths in Table IIa, b of $p^5p \Rightarrow p^5s$ or $pp \Rightarrow ps$ in jj and LS coupling.

§2. Proof of the *J*-File and *J*-Group-File Sum Rules

In order to prove the invariance of the individual J-files it will be simplest to consider the scheme in which each electron is characterized by quantum numbers nlm_1m_s . Then if the valence electron is not equivalent to any in the ion in either the initial or final configuration, the matrix component of electric moment P vanishes unless all quantum numbers referring to the ion are the same in the initial and final states, in which case it equals the one-electron matrix component

$$(nlm_lm_s | \boldsymbol{P} | n'l'm_l'm_s')$$

if the valence electron initially has quantum numbers nlm_lm_s and finally quantum numbers $n'l'm_l'm_s'$.

Now from the dependence of this matrix component on m_l and m_l' as given by Born and Jordan¹ it follows that

$$\sum_{m_{l}'m_{s}'} (nlm_{l}m_{s} | \mathbf{P} | n'l'm_{l}'m_{s}') \cdot (n'l'm_{l}'m_{s}' | \mathbf{P} | nlm_{l}''m_{s}'') = \delta(m_{l}, m_{l}'') \delta(m_{s}, m_{s}'') | (nl! \mathbf{P} ! n'l') |^{2} \Xi(l, l').$$
(2)⁸

Hence in this scheme the sum of the absolute squares of the matrix elements of P having a common original state is independent of that state, and the files of matrix elements from two original states have vanishing scalar product. A simple extension of the proof cited in reference 7 shows these properties to be invariant under unitary transformations, so that in any scheme labeled by JM, the lines having the initial state αJM have the strength sum $|(nl : P : n'l')|^2 \Xi(l, l')$; hence the J-file referring to the initial level αJ has the strength

$$(2J+1) | (nl!P!n'l') | {}^{2}\Xi(l, l').$$
(3)

Symmetrically, the *J*-file referring to the final level $\beta J'$ has the strength

$$(2J'+1) | (n'l' P nl) |^{2} \Xi(l', l).$$
(4)

⁸ (n, l:P:n', l-1) =
$$-e(4l^2-1)^{-\frac{1}{2}}\int_0^{\infty} rR(n,l)R(n',l-1)dr.$$

 $^{^7\,\}rm{This}$ is proved in Eq. (9) of Harrison and Johnson (reference 3).

These equations show that rows and columns of a transition array labeled by the same J value have relative strengths $\Xi(l, l')/\Xi(l', l)$. This ratio $\Xi(p, s)/\Xi(s, p) = 1/3$ is seen to obtain in Tables I and II.

The applicability of the *J*-file sum rule to the files referring to nl^2 in the array $nl^2 = nln'l'$ arises from the fact that the strengths of the allowed lines in this array are just twice those of the corresponding lines of nln''l = nln'l',⁹ and that none of the lines in the nl^2 files are forbidden.

This completes the proof of the *J*-file sum rule.

The J-group-file sum rule states that for the transition array $\alpha s \Rightarrow \alpha p$ in any coupling characterized by J values, the sum of the strengths of all lines in the J-group $J \nleftrightarrow J'$ having a common level of the configuration αs equals (2J'+1) $|(p P s)|^2 \Xi(p, s)$. The quantum numbers which characterize the levels in *jj* coupling are a set I referring to the ion, nsj or n'pj' for the valence electron, and the resultant J value. In *jj* coupling two files in the same J-group are obviously orthogonal since they refer to different ionic quantum numbers I. The strength of a *J*-group file is $\Sigma_{j'} S(I, nsj, J; I, n'pj', J')$ where j=1/2 and j'=1/2, 3/2. This sum may without difficulty be evaluated directly from formulas given by Güttinger and Pauli¹ for the three special cases J' = J + 1, J, and J - 1, and shown to have the value stated in the theorem.

§3. Application to the Neon Red-Yellow Lines

The neon transition array $2p^{5}3p \rightarrow 2p^{5}3s$, which, with the old intensity measurements of Dorgelo, has been used to infer that the *J*-file sum rule should not hold in intermediate coupling, will, with the new dispersion measurements of Ladenburg and Levy,¹⁰ furnish us with instead a very interesting experimental verification.

The relative line strengths calculated from the Einstein A values of L. and L. by the relation $S(p, s) = 3hc^3(2J_p+1) A(p, s)/64\pi^4\nu^3$ are given in Table IIc.¹¹ The ratios of the sums which should be invariant to their values in IIa and IIb are shown in parentheses. To the first order of the perturbation theory, which is expected to be rather good in this particular case, these ratios should all be equal.

Now the relative strengths of lines having a given final level were obtained by L. and L. by measurements of anomalous dispersion to an accuracy of perhaps 10 percent, while the strengths in different rows of the diagram were only related by direct measurements of much less accuracy of relative intensity of lines having the same initial level. This suggests that we try relating the strengths in the different rows by requiring the *J*-file sum rule to hold exactly with respect to the rows; this amounts to discarding the direct intensity measurements and using only the dispersion measurements. Such a procedure seems further justified by the fact that the ratios for the three *J*-group files in each row are of approximately the same size but that these ratios differ much between rows; there is a real discrepancy in the first row for which we have no explanation. The test of this procedure will come from an examination of the sums of the columns in the modified array, for one would not in general expect an improvement in these sums upon multiplication of the rows by arbitrary factors.

Table IId shows the array modified so that the sums of the rows have exactly the theoretical relative values, and it is seen that there is a great improvement in the ratios of the sums of the columns to their theoretical values. In fact, this agreement becomes almost as good as one could expect from the accuracy of the data.

§4. DIRECT QUANTUM-MECHANICAL CALCULATIONS

While considering neon $2p^{5}3p \rightarrow 2p^{5}3s$, it seems of interest to see what the first-order perturbation theory has to say about the detailed linestrength pattern when we use only the ordinary electrostatic and spin-orbit interaction terms and evaluate the coupling constants (radial integrals) from the observed energy values. In order to do this, we first calculate the transformations from *LS* coupling to the actual coupling for $p^{5}s$ and $p^{5}p$, and then transform the matrix of $S^{\frac{1}{2}}$ from *LS* coupling to the actual coupling.

⁹ Shortley, Phys. Rev. 40, 185 (1932), §8.

¹⁰ Ladenburg and Levy, Zeits. f. Physik **88**, 461 (1934). ¹¹ The notation of Bacher and Goudsmit is used for the levels of $p^{b}p$. The three bracketed values in this table are very rough estimates, from the measurements of Dorgelo, of the strengths of lines which were not measured by L. and L. The designation v.s. means 'very small.'

TABLE II. Line strengths in the transition array $2p^53p-2p^53s$. In a and b, the sums in parentheses are predicted to be independent of coupling. The ratios of the actual sums in c and d to these predicted sums are shown in parentheses in c and d.



Neon $2p^53s$ fits Houston's formulas almost perfectly, giving for the eigenstates in the actual coupling

$$\psi({}^{1}P_{1}') = 0.964\psi({}^{1}P_{1}) + 0.266\psi({}^{3}P_{1})$$

$$\psi({}^{3}P_{1}') = 0.266\psi({}^{1}P_{1}) - 0.964\psi({}^{5}P_{1}).$$
 (5)

The agreement with the observed energy levels and Zeeman effect is so good that the error in these transformation coefficients is probably not more than 0.001.¹²

The situation with respect to $2p^{5}3p$ is unfortunately not so attractive. We use the electrostatic interactions in LS coupling as given in §4 of reference 9. The spin-orbit interaction is obtained from Johnson's¹³ matrix for pp by writing $-\zeta_{2p}$ for a_1 and ζ_{3p} for a_2 , where the ζ 's are the (essentially positive) integrals expressing the spin-orbit interaction of one electron in a central field. Inglis and Ginsburg found a fairly good agreement with the observed energy levels by use of the constants given under A in Table

TABLE III.

	Calc. A	Calc. B		Calc. A	Calc. B	
$F_0 \\ F_2 \\ 6G_0$	-339.1 157.7 4503	-334.9 166.6 4604.5	$\begin{array}{c} 12G_2\\ \varsigma_{3p}\\ \varsigma_{2p} \end{array}$	537 402.8 40.0	$482.8 \\ 385.6 \\ -8.4$	

¹³ Johnson, Phys. Rev. **38**, 1628 (1931). Note that a_1+a_2 should be written in place of a_1-a_2 in the matrix for J=0, as pointed out by Inglis and Ginsburg.

¹² This enables us to predict the relative intensity of the two resonance lines of neon as $({}^{1}P_{1}' \rightarrow {}^{1}S_{0})/({}^{8}P_{1}' \rightarrow {}^{1}S_{0}) = 13.2$ with an estimated error of about 0.1.

	Energy (cm ⁻¹)			g value		
	obs.	A	В	obs.	А	В
2 ₃ ³ D ₃	0.0	0.0	- 28.7	1.329	1.333	1.333
$3_2 {}^3D_2 \ 5_2 {}^1D_2 \ 8_2 {}^3P_2$	$167.2 \\ 658.8 \\ 1201.5$	$127.7 \\ 728.6 \\ 1171.2$	$149.2 \\ 667.8 \\ 1170.1$	1.137 1.229 1.301	$1.147 \\ 1.142 \\ 1.377$	1.146 1.106 1.415
$ \begin{array}{c} 1_1 {}^3S_1 \\ 4_1 {}^3D_1 \\ 7_1 {}^1P_1 \end{array} $	-1399.2 464.6 1115.1	-1271.4 378.2 1085.3	-1358.1 394.5 1144.1	1.984 .669 .999	1.994 .574 1.095	1.993 .561 1.105
$9_1 {}^{3}P_1$ $6_0 {}^{3}P_0$ $10_0 {}^{1}S_0$	1381.4 1260.4 3313.7	1369.7 1276.0 3298.3	1386.3 1325.0 3313.2	1.340	1.340	1,339

TABLE IV.

III.¹⁴ These constants lead to the energy levels and g values listed under A in Table IV. The matrix which expresses these levels in the *LS*coupling scheme is easily obtained; the Russell-Saunders level which occurs in largest proportion in each of these levels is listed in Table IV.¹⁵

The signs in the matrix of $S^{\frac{1}{2}}$ in Table IIb were obtained for states having the same phases as in the energy matrix we have used for p^5p and in (5). When we transform this matrix to the actual coupling of calculation A we obtain the line strengths of Table IIe, which show the general characteristics of the departures of the observed values from those in Russell-Saunders coupling, but disagree markedly in detail.

In order to see whether this disagreement is of the right order of magnitude to be accounted for by the fact that with our approximate formulas we could not fit the observed energy levels perfectly, we have in calculation B used a set of constants chosen so as to give approximately the best least-squares fit of the calculated to the observed energies.¹⁶ These constants give the energies listed in Table IV (B), which, while they fit better on the average, are not a great improvement over those of calculation A. The small shifts between A and B change the differences between energy levels of the same J value considerably, and this and the change in the constants change the eigenfunctions sufficiently to give the line strengths of Table IIf instead of IIe. The marked differences between these tables shows that we cannot expect, without further refinements in the theory, to get accurate quantitative intensity predictions in this case. The same observation with respect to g values has been made by Inglis and Ginsburg.

I wish here to express to Professors Harrison and Van Vleck and Dr. Kimball my appreciation for valuable discussions and suggestions concerning this work, and to thank Professor Ladenburg for calling my attention to his neon dispersion data before publication.

$$\partial \lambda_1 / \partial c_j = -\lambda_1^j / \prod_{i=2}^n (\lambda_1 - \lambda_i),$$

where λ_1 is any one of the roots.) From these we obtain $\partial \lambda_i / \partial F_j$. Now, knowing an approximate set $(F_1 \cdots F_6; \lambda_1' \cdots \lambda_1 o')$ of parameters and energy levels, we write $\lambda_i^{\circ} - \lambda_i' = \Sigma_j (\partial \lambda_i' / \partial F_j) \delta F_j$, where the λ_i° are the observed energies, and determine the six δF_j by a least-squares calculation to fit these equations as well as possible. Since the dependence of the roots on the parameters is only to a first approximation linear, this process may be repeated for greater accuracy. However in our case the dependence was sufficiently linear that there was no point in doing more than one calculation of this sort in getting from A to B.

¹⁴ Inglis and Ginsburg, Phys. Rev. **43**, 194 (1933). We find that the calculated energies given by Inglis and Ginsburg are not correct for the parameters they list. This statement is easily checked by an evaluation of the trace of say the J=2 matrix. The sum of the observed energies of the three levels of J=2 is 2027.5 cm⁻¹, the sum of their calculated energies 2058.5. Now the trace of the energy matrix is, in their notation, $\alpha + \gamma - \frac{3}{2}(a_1+a_2) = 2027.5$ —in agreement with the observed trace but not with their calculated trace as it should be. This discrepancy is entirely accounted for by an error of about 30 cm⁻¹ in their value 1201.5 for the level 8_2 . Similarly, we find their calculations for the levels of J=1 and 0 to be all in error by amounts ranging from 6 to 56 cm⁻¹. These discrepancies account for the difference between the energies and g values in Table IV (A) and those given by Inglis and Ginsburg.

in Table IV (A) and those given by Inglis and Ginsburg. ¹⁵ These proportions run from 60% for 7_1 (7_1 is 60% ¹⁹ P_1 , 29% ³ P_1 , 11% ³ D_1 , 0% ³ S_1 —in calculation B these proportions become 61%, 30%, 9% and 0%) to 100% for 2_3 ; on the average the levels contain 85% of the Russell-Saunders level indicated. In Tables IIc, d, e, f, these levels occupy the same columns as the corresponding Russell-Saunders levels in Table IIb.

¹⁶ This we may do in the following way. The energy levels $\lambda_1 \cdots \lambda_{10}$ are the roots of four polynomials whose coefficients $c_1 \cdots c_{10}$ are functions of six parameters $F_1 \cdots F_6$. We know $\partial c_k / \partial F_j$ and $\partial \lambda_i / \partial c_k$. (We have not succeeded in finding a reference to the formula for the rate of change of a root of a polynomial with respect to a coefficient, so we state the general formula here: If the *n*th degree equation $\lambda^n + \sum_{i=0}^{n-1} c_i \lambda^i = 0$ has roots $\lambda_1 \cdots \lambda_n$, then