

the value for the water absorption. According to a formula developed by King,⁹ at the lowest frequency used, 84 percent of the sound energy is contained in a cone whose semi-vertical angle is 4 degrees and 20 minutes; at the highest frequency, 84 percent of the sound energy is contained in a cone whose semi-vertical angle is 1 degree and 40 minutes. This is an estimate which greatly exaggerates the spread, since most

⁹ L. V. King, *Can. J. Research* **11**, 135 (1934).

of the energy of the beam is contained within narrower limits than those here given. Nevertheless, the value of $\Delta(2\alpha)$ is independent of this slight spurious effect, since it represents the difference in absorption due to the addition of the suspension.

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The Computation of Quadrupole and Magnetic-Dipole Transition Probabilities

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The theory of quadrupole radiation is formulated in such a fashion as to make available all the methods of computation and sum rules which have been developed for electric-dipole radiation. Formulas for the strengths are given for the $SLM_S M_L$ scheme as well as the $SLJM$ scheme. The problem of the relative strengths of the multiplets in a transition array is treated, and formulae are given that explicitly solve this problem for all possible transitions between two-electron configurations. Values for $np\ n'p^4 \rightarrow np\ n''p$, $np\ n'p^4 \rightarrow np^2$, $np\ n'p \rightarrow np\ n'p$ and $np^2 \rightarrow np^2$ are tabulated. The spectroscopic stability method and the eigenfunction method of obtaining relative multiplet strengths are given a convenient formulation; and values are computed for $np^3 \rightarrow np^3$. A root $S^{\frac{1}{2}}$ of the line strength is defined in such a way that it transforms like a Hermitian matrix component. This enables convenient computation of line strengths in intermediate coupling. The J -file sum rule is shown to hold in intermediate coupling with the same degree of generality as for the electric-dipole case. Finally, closed formulas for the magnetic-dipole strengths in LS coupling are given and the method of transformation to intermediate coupling is indicated.

THE following considerations were developed in preparation for a complete tabulation of all quadrupole and magnetic-dipole strengths within the configurations p^2 , p^3 , and p^4 , for all possible cases of intermediate coupling, by a group at the Harvard College Observatory.¹

I. QUADRUPOLE RADIATION

For the case of quadrupole transitions, the *relative* strengths of the Zeeman components of a line and of the lines of a multiplet were first computed by Rubinowicz² and later, from group theory, by Brinkman.³ The J sum rule was shown to be obeyed within the multiplet. But nothing has been done, from a general point of view, in connection with the relative or absolute strengths of the multiplets in a transition array in LS coupling, and in connection with other coupling schemes of importance, such as intermediate coupling, the $SLM_S M_L$ scheme, and jj coupling. Condon⁴ has computed the absolute strengths of most of the lines of p^2 , p^3 , and p^4 , for LS coupling and small

¹ G. H. Shortley, L. H. Aller, J. G. Baker and D. H. Menzel, "Tabulation of Strengths of Forbidden Lines in p^2 , p^3 , p^4 as a Function of Coupling," to appear soon in the *Astrophysical Journal*.

² A. Rubinowicz, *Zeits. f. Physik* **61**, 338; **65**, 662 (1930).

³ H. C. Brinkman, *Zur Quantenmechanik der Multipolstrahlung*, Dissertation, Utrecht, 1932.

⁴ E. U. Condon, *Astrophys. J.* **79**, 217 (1934).

departures therefrom; but always by tediously writing explicitly one of the intermediate-coupling eigenfunctions in the $SLJM$ scheme for each separate level and computing from these the line strengths. It turns out, however, that all the simplifications which are used in the computation of ordinary dipole radiation⁵ are available also in the case of quadrupole radiation; similar methods of computation may be used and similar sum rules are obeyed. In this note we give a formulation of the theory which is very convenient in this connection, and outline, frequently by analogy with the dipole case, the necessary proofs.

Preliminaries

The strength $S_q(\alpha J, \alpha' J')$ of a quadrupole line, in terms of which the probability of spontaneous transition from the upper level αJ to the lower $\alpha' J'$ has the value

$$A_q(\alpha J, \alpha' J') = \frac{1}{2J+1} \frac{32\pi^6 \sigma^5}{5h} S_q(\alpha J, \alpha' J'),$$

is defined by
$$S_q(\alpha J, \alpha' J') = S_q(\alpha' J', \alpha J) = \sum_{M, M'} |(\alpha J M | \mathfrak{N}' | \alpha' J' M')|^2. \quad (1)^6$$

Here \mathfrak{N}' is the dyadic
$$\mathfrak{N}' = -e \sum_i (r_i r_i - \frac{1}{3} r_i^2 \mathfrak{S}), \quad (\mathfrak{S} = \mathbf{ii} + \mathbf{jj} + \mathbf{kk}) \quad (2)$$

the summation running over the electrons. In (1), the absolute square of a dyadic means the double-dot product of the dyadic and its complex conjugate, which is the sum of the absolute squares of the nine elements of the dyadic.

The formulas of Rubinowicz for the elements of the Hermitian matrix occurring in (1), but in a notation patterned after that used by TAS for the dipole components, and which will prove extremely convenient, are

$$\begin{aligned} (\alpha J M | \mathfrak{N}' | \alpha' J M \pm 2) &= (\alpha J; N; \alpha' J) \frac{1}{2} [(J \mp M)(J \mp M - 1)(J \pm M + 1)(J \pm M + 2)]^{\frac{1}{2}} \mathfrak{R}(\pm 2), \\ (\alpha J M | \mathfrak{N}' | \alpha' J M \pm 1) &= (\alpha J; N; \alpha' J) \frac{1}{2} (2M \pm 1) [(J \mp M)(J \pm M + 1)]^{\frac{1}{2}} \mathfrak{R}(\pm 1), \\ (\alpha J M | \mathfrak{N}' | \alpha' J M) &= (\alpha J; N; \alpha' J) 6^{-\frac{1}{2}} [3M^2 - J(J+1)] \mathfrak{R}(0), \\ (\alpha J M | \mathfrak{N}' | \alpha' J - 1 M \pm 2) &= (\alpha J; N; \alpha' J - 1) \\ &\quad (\pm \frac{1}{2}) [(J \mp M)(J \mp M - 1)(J \mp M - 2)(J \pm M + 1)]^{\frac{1}{2}} \mathfrak{R}(\pm 2), \\ (\alpha J M | \mathfrak{N}' | \alpha' J - 1 M \pm 1) &= (\alpha J; N; \alpha' J - 1) \frac{1}{2} (J \pm 2M + 1) [(J \mp M)(J \mp M - 1)]^{\frac{1}{2}} \mathfrak{R}(\pm 1), \\ (\alpha J M | \mathfrak{N}' | \alpha' J - 1 M) &= (\alpha J; N; \alpha' J - 1) M [\frac{3}{2}(J - M)(J + M)]^{\frac{1}{2}} \mathfrak{R}(0), \\ (\alpha J M | \mathfrak{N}' | \alpha' J - 2 M \pm 2) &= (\alpha J; N; \alpha' J - 2) \frac{1}{2} [(J \mp M)(J \mp M - 1)(J \mp M - 2)(J \mp M - 3)]^{\frac{1}{2}} \mathfrak{R}(\pm 2), \\ (\alpha J M | \mathfrak{N}' | \alpha' J - 2 M \pm 1) &= (\alpha J; N; \alpha' J - 2) (\pm) [(J - M)(J + M)(J \mp M - 1)(J \mp M - 2)]^{\frac{1}{2}} \mathfrak{R}(\pm 1), \\ (\alpha J M | \mathfrak{N}' | \alpha' J - 2 M) &= (\alpha J; N; \alpha' J - 2) [\frac{3}{2}(J - M)(J + M)(J - 1 - M)(J - 1 + M)]^{\frac{1}{2}} \mathfrak{R}(0). \end{aligned} \quad (3)$$

Here the $\mathfrak{R}(\Delta M)$ represent the dyadics

$$\mathfrak{R}(\pm 2) = \frac{1}{2} [\mathbf{ii} - \mathbf{jj} \pm i(\mathbf{ij} + \mathbf{ji})], \quad \mathfrak{R}(\pm 1) = \frac{1}{2} [\mathbf{ki} + \mathbf{ik} \pm i(\mathbf{kj} + \mathbf{jk})], \quad \mathfrak{R}(0) = \sqrt{\frac{2}{3}} [\mathbf{kk} - \frac{1}{2} \mathbf{ii} - \frac{1}{2} \mathbf{jj}]. \quad (4)$$

The factors $(\alpha J; N; \alpha' J')$ are expressible in terms of the factors $(\alpha J; r_i; \alpha' J')$ employed in the dipole discussion (TAS, pp. 63, 95) as linear combinations of quantities of the type

$$\sum_i \sum_{\alpha''} (\alpha J; r_i; \alpha'' J'') (\alpha'' J''; r_i; \alpha' J') = D(J, J'', J'), \quad (5)$$

namely
$$(\alpha J; N; \alpha' J) = D(J, J, J) - D(J, J - 1, J) - D(J, J + 1, J);$$

$$(\alpha J; N; \alpha' J - 1) = D(J, J, J - 1) + D(J, J - 1, J - 1); \quad (6)$$

$$(\alpha J; N; \alpha' J - 2) = D(J, J - 1, J - 2).$$

⁵ See E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Camb. Univ. Press, 1935), to which we shall refer by the letters TAS.

⁶ TAS, p. 93 *et seq.*; E. C. Kemble, *Quantum Mechanics* (McGraw-Hill, 1937), p. 469, p. 462 (footnote).

The factors $(\alpha J; N; \alpha' J')$ form a Hermitian matrix which transforms like the matrix of an observable:

$$(\beta J; N; \beta' J') = \sum_{\alpha, \alpha'} (\beta J | \alpha J) (\alpha J; N; \alpha' J') (\alpha' J' | \beta' J'). \quad (7)$$

This may be easily demonstrated from the known transformation properties (TAS 9³12, p. 64) of the separate factors of (5).

The $SLM_S M_L$ scheme

Computations in Russell-Saunders coupling are frequently simplified by using states characterized by the quantum numbers $M_S M_L$ in place of JM . For example, one can obtain the dependence of the matrix components of \mathfrak{N}' on $M_S M_L$ much more simply than on JM . They are diagonal in S and M_S , and by exactly the arguments used in the computation of (3), we see that the dependence on M_L is

$$(\gamma S L M_S M_L | \mathfrak{N}' | \gamma' S L' M_S M_L') = (\gamma S L; N; \gamma' S L') \times \text{factor given by (3) with } JM \text{ replaced by } LM_L. \quad (8)$$

The elements $(\gamma S L; N; \gamma' S L')$ are given by (5) and (6) with α and J replaced by γS and L (cf. 11³9, p. 70 TAS). From this Eq. (8) we see at once that the selection rules forbidding transitions $J=0 \rightarrow 0$, $\frac{1}{2} \rightarrow \frac{1}{2}$, $0 \rightleftharpoons 1$, which are embodied in (3), apply also to L ; *transitions* $L=0 \rightarrow 0$, $0 \rightleftharpoons 1$, *i.e.*, $S \rightarrow S$ and $S \rightleftharpoons P$ are forbidden.

The $SLJM$ scheme

The matrix components of \mathfrak{N}' in this scheme should be expressible in terms of the same elements as occur on the right of (8). This may be done by using 11³8, p. 69 TAS to express the factors (6) in terms of $(\gamma S L; N; \gamma' S L')$. This rather tedious calculation was carried out by Rubinowicz; we give a typical formula:

$$\begin{aligned} (\gamma S L J; N; \gamma' S L - 1 J + 1) &= -(\gamma S L; N; \gamma' S L - 1) \\ &\times \frac{[(S+L-J)(S+L-J-1)(J+S-L+1)(J+S-L+2)]^{\frac{1}{2}}}{2J(J+1)(J+2)[(2J+1)(2J+3)]^{\frac{1}{2}}} [J(J+1) - S(S+1) + (J+L)(L+1)]. \end{aligned} \quad (9)$$

Sum rules, line and multiple strengths

From (3) we easily evaluate the sums corresponding to 13³1, TAS, which we need for the line strength formulas and the proof of the J -file sum rule:

$$\sum_{M'} (\alpha J M | \mathfrak{N}' | \alpha' J' M') : (\alpha' J' M' | \mathfrak{N}' | \alpha'' J'' M'') = \delta_{J J''} \delta_{M M''} (\alpha J; N; \alpha' J') (\alpha' J'; N; \alpha'' J) H(J, J''), \quad (10)$$

where

$$\begin{aligned} H(J, J) &= \frac{1}{6} J(J+1)(2J-1)(2J+3), \\ H(J, J-1) &= \frac{1}{2} J(J+1)(J-1)(2J-1), & H(J, J+1) &= \frac{1}{2} J(J+1)(J+2)(2J+3), \\ H(J, J-2) &= J(J-1)(2J-1)(2J-3), & H(J, J+2) &= (J+1)(J+2)(2J+3)(2J+5). \end{aligned} \quad (11)$$

These are not symmetric in J and J' , but become so when multiplied by $2J+1$ to accomplish the summation over M . This gives the formula for the *line strength*:

$$S_q(\alpha J, \alpha' J') = \sum_{M, M'} |(\alpha J M | \mathfrak{N}' | \alpha' J' M')|^2 = (2J+1) H(J, J') |(\alpha J; N; \alpha' J')|^2. \quad (12)$$

By exact analogy with the simple transformation argument used to obtain the similar dipole sum on p. 72 TAS we may write the value of the sum over J' in the $SLJM$ scheme:

$$\begin{aligned} \sum_{J' M'} (\gamma S L J M | \mathfrak{N}' | \gamma' S L' J' M') : (\gamma' S L' J' M' | \mathfrak{N}' | \gamma'' S L'' J'' M'') \\ = \delta_{J J''} \delta_{M M''} \delta_{L L''} (\gamma S L; N; \gamma' S L') (\gamma' S L'; N; \gamma'' S L'') H(L, L''). \end{aligned} \quad (13)$$

Since the right member is independent of J and M , dropping the double primes and multiplying by $2J+1$ to accomplish the summation over M gives us the ordinary J sum rule which holds within a multiplet. If instead we multiply by $(2S+1)(2L+1)$ to sum over J and M , we get the total *multiplet strength*

$$S_q(\gamma SL, \gamma' SL') = \sum_{J, J'} S_q(\gamma SLJ, \gamma' SL'J') = (2S+1)(2L+1) H(L, L') |(\gamma SL; N; \gamma' SL')|^2. \quad (14)$$

The strengths of the individual lines of the multiplet are to be obtained by substituting in (12) the formulas of the type (9) to obtain, e.g.

$$\begin{aligned} & S_q(\gamma S L J, \gamma' S L - 1 J + 1) \\ &= (-)^2 \frac{(S+L-J)(S+L-J-1)(J+S-L+1)(J+S-L+2)[J(J+1)-S(S+1)+(J+L)(L+1)]^2}{8J(J+1)(J+2)} \\ & \qquad \qquad \qquad \times |(\gamma S L; N; \gamma' S L - 1)|^2, \quad (15a) \end{aligned}$$

or in general

$$S_q(\gamma SLJ, \gamma' SL'J') = (2J+1) H(J, J') |(\gamma SLJ; N; \gamma' SL'J')|^2 = f_q(SLJ, SL'J') |(\gamma SL; N; \gamma' SL')|^2. \quad (15b)$$

In this notation the value of $f_q(SLJ, SL'J')$ is $\frac{1}{16}$ the coefficient of G^2 , H^2 , or I^2 in the table of p. 253, TAS.⁷

Multiplet strengths in a transition array. Two different configurations. Coupled groups

We now turn to the question of the relative strengths of the different multiplets in a transition array in LS coupling. The transition array must either connect two different configurations, differing in regard to the nl value of one electron, or be entirely within the same configuration. For two different configurations all the arguments of §3⁹, p. 244 TAS may be repeated in the quadrupole case. If the configurations are expressible in the forms I+II and I+IV, respectively,⁸ we may reduce the strengths to those connecting II and IV. The parent term $\gamma^I S^I L^I$ cannot change. Only the part, \mathfrak{N}'^{II} , of \mathfrak{N}' which refers to the electrons jumping from II to IV enters the consideration. This part commutes with L^I and from the known properties of the dipole components we see that the factor⁹ $(\gamma^I S^I L^I, \gamma^{II} S^{II} L^{II}, SL; N^{II}; \gamma^I S^I L^I, \gamma^{IV} S^{IV} L^{IV}, SL')$ which enters (14) and (15) is independent of S and is the same function of $L^I L^{II} L$, $L^I L^{IV} L'$ as $(\gamma SLJ; N; \gamma' SL'J')$ is of $SLJ, SL'J'$, cf. (9). With this knowledge, a comparison of (14) with (15b) gives us the formula

$$\begin{aligned} & S_q(\gamma^I S^I L^I, \gamma^{II} S^{II} L^{II}, SL; \gamma^I S^I L^I, \gamma^{IV} S^{IV} L^{IV}, SL') \\ &= (2S+1) f_q(L^I L^{II} L, L^I L^{IV} L') |(\gamma^{II} S^{II} L^{II}; N^{II}; \gamma^{IV} S^{IV} L^{IV})|^2. \quad (16) \end{aligned}$$

That the last factor is independent of $\gamma^I S^I L^I$ is shown by the fact that the matrix components

$$(\gamma^I S^I L^I M_S^I M_L^I, \gamma^{II} S^{II} L^{II} M_S^{II} M_L^{II} | \mathfrak{N}' | \gamma^I S^I L^I M_S^I M_L^I, \gamma^{IV} S^{IV} L^{IV} M_S^{IV} M_L^{IV}),$$

which are given by formulas like (3) in terms of the same factors, are independent of $\gamma^I S^I L^I$ (see the discussion in §1⁸ TAS of vector coupling in antisymmetric states). If we sum (16) over all values of L and L' consistent with the given values of L^I , L^{II} , and L^{IV} , we obtain, in analogy with (14)

⁷ There is one error in this table, in the ninth row, for the entry given explicitly in (15a), the $-$ sign before $J(L+1)$ in the bracket should be changed to $+$.

⁸ For example, I+II might be $p^2 \cdot sd$, I+IV, $p^2 \cdot d^2$. The invariant part p^2 may be considered as the parent configuration to which the groups sd and d^2 are added. It is necessary that none of the electrons in either II or IV be equivalent to any in I.

⁹ The functional dependence follows clearly from the definition of this factor and the discussion of §11³, p. 67 TAS. The argument of TAS (top of p. 70, bottom of p. 237) for the independence of S is, however, not clear. That in this case any matrix component of \mathfrak{N}' in the $SLM_S M_L$ scheme, and hence (cf. 8) the factor in question, is independent of S may be shown at once by transformation to a scheme employing quantum numbers $S^I S^{II} M_S^I M_S^{II}$, where the components are known to be independent of M_S^I and M_S^{II} by a standard theorem (TAS 3⁸, p. 49).

and (15), for the total strength of all multiplets of spin S built on $S^I L^I$ by the addition of $S^{II} L^{II}$ and $S^{IV} L^{IV}$ the value

$$S_q(\gamma^I S^I L^I, \gamma^{II} S^{II} L^{II}, S; \gamma^I S^I L^I, \gamma^{IV} S^{IV} L^{IV}, S) = (2S+1)(2L^I+1)(2L^{II}+1) H(L^{II} L^{IV}) |(\gamma^{II} S^{II} L^{II}; N^{II}; \gamma^{IV} S^{IV} L^{IV})|^2. \quad (17)$$

But the last two factors here are those in terms of which the multiplet strengths in the transition $II \rightarrow IV$ are expressed by (14). Hence we may set (17)

$$= \frac{(2S+1)(2L^I+1)}{2S^{II}+1} S_q(\gamma^{II} S^{II} L^{II}, \gamma^{IV} S^{IV} L^{IV}). \quad (17')$$

This completes the reduction of the strengths to those of $II \rightarrow IV$. In particular it is interesting to note that in the case in which I involves only closed shells, so that $S^I = L^I = 0$, $S = S^{II}$, $L = L^{II}$, $L' = L^{IV}$, (17') reduces to an equation which says that the closed shells do not influence the strengths.

Addition of an electron to an ion

For the case in which the jumping electron is not equivalent to any in the ion in either the initial or the final configuration, the total strength of a supermultiplet is given by (17) and the strengths of the multiplets in a supermultiplet by (16). We let $\gamma^I S^I L^I$ represent the parent term of the ion, $\gamma^{II} L^{II} = nl$ and $\gamma^{IV} L^{IV} = n'l'$, the nl values of the jumping electron in the initial and final states ($nl \neq n'l'$), and $S^{II} = \frac{1}{2}$. The multiplet strength is

$$S_q(\gamma^I S^I L^I nl SL, \gamma^I S^I L^I n'l' SL') = (2S+1) f_q(L^{II} L, L^{IV} L') |nl; N; n'l'|^2. \quad (18)$$

The relative strengths of the multiplets in a supermultiplet are thus the same functions of $L^{II} L$, $L^{IV} L'$ as the relative strengths of the lines in a multiplet are of SLJ , $SL'J'$. To obtain absolute strengths we need to evaluate the last factor of (18), which is just the factor which arises in connection with intensities in one-electron spectra. This is easily done by expressing one of the 9 components of the dyadic $-err$ in terms of this factor by (8) and then expressing this component as an integral. In this way we find

$$\begin{aligned} (n l; N; n' l) &= \frac{2e}{(2l-1)(2l+3)} \int_0^\infty r^2 R(n l) R(n' l) dr = s_q(n l, n' l), \\ (n l; N; n' l-1) &= 0, \\ (n l; N; n' l-2) &= -\frac{e}{(2l-1)[(2l-3)(2l+1)]^{\frac{1}{2}}} \int_0^\infty r^2 R(n l) R(n' l-2) dr = s_q(n l, n' l-2). \end{aligned} \quad (19)$$

The short s_q -notation for these components is in practice convenient.

Two-electron configurations. Transitions involving an electron jump

If neither initial nor final configuration is composed of equivalent electrons, the multiplet strengths are given at once by (18). If the two electrons of *one* of the configurations are equivalent, Eq. 6⁸17, p. 232 TAS, shows that the strengths of the allowed multiplets have just *twice* the values given by (18). The numerical values for $np n' p' \leftarrow np n'' p$ and $np n' p' \leftarrow np^2$ are given in Table II.

Summary

For transitions involving an electron jump, the jumping electron not equivalent to any in the ion (but see the previous paragraph), the computation of the line strengths in terms of s_q (19) involves successive application of the following three formulas, which are very convenient as soon as tables of $F_q(SLJ, SL'J')$ are available:

Line strength in terms of multiplet strength, from (14) and (15)

$$S_q(\gamma SLJ, \gamma' SL'J') = \frac{f_q(SLJ, SL'J')}{(2S+1)(2L+1)H(L, L')} S_q(\gamma SL, \gamma' SL') = F_q(SLJ, SL'J') S_q(\gamma SL, \gamma' SL'). \quad (20)$$

Multiplet strength in terms of supermultiplet strength, from (17) and (18)

$$\begin{aligned} S_q(\gamma^I S^I L^I nl SL, \gamma^I S^I L^I n'l' SL') &= \frac{f_q(L^I l, L^I l')}{(2L^I+1)(2l+1)H(l, l')} S_q(\gamma^I S^I L^I nl S, \gamma^I S^I L^I n'l' S) \\ &= F_q(L^I l, L^I l') S_q(\gamma^I S^I L^I nl S, \gamma^I S^I L^I n'l' S). \end{aligned} \quad (21)$$

Strength of supermultiplet, from (17)

$$S_q(\gamma^I S^I L^I nl S, \gamma^I S^I L^I n'l' S) = (2S+1)(2L^I+1)(2l+1)H(l, l') s_q^2(nl, n'l'). \quad (22)$$

Spectroscopic stability method. Any transition array

For any transition array we may obtain the relative strengths of the multiplets by a method, based on the principle of spectroscopic stability, similar to that sketched in §4⁹, p. 249 TAS. This method, while quick and convenient, has the disadvantage of giving only the amplitudes and not the phases in the matrix of \mathfrak{N}' . Hence it is of no value for departures from LS coupling. For this reason we do not give detailed formulas. Roughly, in this method, one first computes the absolute squares of all matrix components of \mathfrak{N}' in the $nl m_s m_l$ orbital scheme in terms of the s_q 's, making use of (8) for the one-electron components. Then the quantities $|(\gamma S L M_S M_L | \mathfrak{N}' | \gamma' S' L' M_S' M_L')|^2$ are expressed in terms of $|(\gamma SL; N; \gamma' S' L')|^2$ by (8). Applying the principle of spectroscopic stability to each $M_S M_L$ partition then gives equations to determine $|(\gamma SL; N; \gamma' S' L')|^2$, and hence from (14) the multiplet strengths, in terms of the s_q 's.

Eigenfunction method. Any transition array

This method is the only one available in cases not falling in the categories covered by the matrix methods when it is desired to relate the phases of the strengths (see definition later) to those of the eigenfunctions. It requires writing just one eigenfunction in the $SLM_S M_L$ scheme for each term of the initial and final configuration. From these eigenfunctions we may calculate one component of \mathfrak{N}' in the $SLM_S M_L$ scheme for each multiplet, employing the standard techniques for reducing the matrix components of an observable of this type to one-electron components and evaluating these from (8) in terms of s_q . This same matrix component is, on the other hand, *directly* expressible by (8) in terms of $(\gamma SL; N; \gamma' S' L')$. This enables us to obtain this last quantity in terms of the s_q 's with proper phase for the particular choice of eigenfunctions. The multiplet strengths and line strengths are then obtained from this by (14) and (20).

The methods of the previous two paragraphs are applicable in cases of transition between two terms of the same configuration as well as in cases in which an electron jumps. Before considering matrix methods available for such cases, it will be desirable to consider the transformation to intermediate coupling.

Intermediate coupling. Computation of line strengths

In any coupling, the strength of a line $\alpha J, \alpha' J'$ is given in terms of $(\alpha J; N; \alpha' J')$ by (12). The transformation properties of $(\alpha J; N; \alpha' J')$ are known from (7). If we introduce a quantity $S_q^{\frac{1}{2}}(\alpha J, \alpha' J')$ defined as the square root of the line strength taken with the sign of the matrix component $(\alpha J; N; \alpha' J')$, we obtain the transformation formula

$$S_q^{\frac{1}{2}}(\beta J, \beta' J') = \sum_{\alpha, \alpha'} (\beta J | \alpha J) S_q^{\frac{1}{2}}(\alpha J, \alpha' J') (\alpha' J' | \beta' J'). \quad (23)$$

This enables us, in particular, to obtain the line strengths in intermediate coupling in terms of those in LS coupling if the intermediate-coupling eigenfunctions are known in terms of the LS -coupling functions and the values of $S_q^{\frac{1}{2}}$ are known for the *same* Russell-Saunders functions *with the same phases*.

For the matrix computation summarized above, the phases of $S_q^{\frac{1}{2}}(\gamma SLJ, \gamma' SL'J')$ are given, in terms of the standard system of eigenfunction phases employed in TAS, by (20), (21), (22) if in taking the roots we use for the phases of $f_q^{\frac{1}{2}}$ or of $F_q^{\frac{1}{2}}$ those in the table of p. 253 of TAS. These phases are those in the column marked "Sign" multiplied by the sign of the quantity in the bracket which occurs squared in some of the elements.

Intermediate coupling. Sum rules

The J -group sum rule of course holds because of the principle of spectroscopic stability. This sum rule says that the sum of the strengths of the lines connecting all the levels of a given J in the initial configuration with all the levels of a given J' in the final configuration is independent of coupling. For the case in which the initial and final configuration are identical, it is clear that in those groups with $J=J'$ we must include the strengths of the "lines" connecting a level with itself and must double the strength of all other lines.

In case the initial and final configuration are different, the J -file sum rule obtains. A J file is the set of all lines connecting a single given level of one configuration with all levels of the other configuration. The sum rule states that *for any coupling, the strengths of the J files referring to the levels of the initial (final) configuration are proportional to $2J+1$ provided that the jumping electron is not equivalent to any other in the final (initial) configuration*. The proof parallels exactly that for the dipole case on pp. 279–281 of TAS since the sum relations (10) and (13) are similar to the corresponding dipole sums. In particular, if the nl electron which jumps is equivalent to $k-1$ other nl electrons in the configuration to which the J files refer, and jumps to an $n'l'$ orbit, the invariant strengths of the J files are

$$k(2J+1)H(l,l')s_q^2(nl, n'l'). \tag{24}$$

Matrix calculation for transitions between states of the same configuration (no-electron jumps)

For a configuration I+II consisting of inequivalent coupled groups, the strengths may be reduced to those within configuration I and II separately by methods similar to those used for the spin-orbit interaction in §1¹¹ p. 266 TAS. The procedure will be clear from the discussion of the important two-electron case, to which we proceed at once.

In the case of transition $nl n'l' \rightarrow nl n'l'$ the roots of the multiplet strengths are (cf. 14)

$$S_q^{\frac{1}{2}}(nl n'l' SL, nl n'l' SL') = [(2S+1)(2L+1)H(L,L')]^{\frac{1}{2}}(nl n'l' L; N; nl n'l' L'), \tag{25}$$

the last factor being independent of S because \mathfrak{N}' commutes with the spins of both electrons. The arguments of pp. 216, 232 TAS show that the last factor may be evaluated by ordinary vector-coupling methods, writing $N=N_1+N_2$, giving the first electron the quantum numbers nl , the second the quantum numbers $n'l'$, and ignoring considerations of antisymmetry. *This is true whether or not nl and $n'l'$ are equivalent*.

The part $(nl n'l' L; N_2; nl n'l' L')$ of this factor is the same function of WL, WL' as $(\gamma SLJ; N; \gamma' SL'J')$ is of $SLJ, SL'J'$. Hence its contribution to $S_q^{\frac{1}{2}}$ is, cf. (15b), $(2S+1)^{\frac{1}{2}} f_q^{\frac{1}{2}}(WL, WL') s_q(n'l', n'l')$. The factor $(nl n'l' L; N_1; nl n'l' L')$ is the same function of $l'l', l'l'$ as $(\gamma SLJ; N; \gamma' SL'J')$ is of $SLJ, SL'J'$, *except for phase*. The reversal of the rôles of the added vectors makes a phase change of $(-1)^{l+l'-L+l'+l'-L'} = (-1)^{L+L'}$ (cf. 14³⁷, p. 78 TAS). In this way we find for the total root multiplet strength

$$S_q^{\frac{1}{2}}(nl n'l' SL, nl n'l' SL') = (2S+1)^{\frac{1}{2}} [f_q^{\frac{1}{2}}(WL, WL') s_q(n'l', n'l') + (-1)^{L+L'} f_q^{\frac{1}{2}}(l'l', l'l') s_q(nl, nl)], \tag{26}$$

in terms of which the root line strength with the standard phase choice is given by (20).

In this case the J -file sum rule does not hold unless either $s_q(nl, nl)$ or $s_q(n'l', n'l')$ vanishes.

Transition arrays involving almost-closed shells. The array $np^4 \rightarrow np^4$

When we investigate the relation between transition arrays involving almost-closed shells and the corresponding simpler arrays, we find just as in the dipole case (p. 316 TAS) that if the transition is between two *different* configurations containing the *same* almost-closed shell the strengths are the same as for the simpler array in which the almost-closed shell is replaced by the missing electrons. But for quadrupole radiation we have another case to consider, the case of *no-electron jumps*. Here we find, by an examination of the corresponding matrix components in the m, m_1 -orbital scheme that *the strengths are the same for a pure almost-closed shell array (such as $p^4 \rightarrow p^4$) and for the complementary array (such as $p^2 \rightarrow p^2$).* The matrix components of \mathfrak{N}' and hence *the phases of $S_q^{\frac{3}{2}}$ are of opposite sign* in the two cases. Hence the strengths are not the same in an array such as $p^4 d \rightarrow p^4 d$ and in the corresponding array $p^2 d \rightarrow p^2 d$. Rather, the one set of strengths will be obtained from the other by reversing the sign of $s_q(p, p)$. This is analogous to the rule which holds for spin-orbit interaction.

***jj* coupling**

It is clear from the similarity of the above formulation to that for the dipole case that the methods used in the latter to obtain strengths in *jj* coupling (see TAS p. 264) are directly available here.

II. MAGNETIC-DIPOLE RADIATION

The strength $S_m(\alpha J, \alpha' J')$ of a magnetic-dipole line, in terms of which the probability of spontaneous transition from the upper level αJ to the lower level $\alpha' J'$ has the value

$$A_m(\alpha J, \alpha' J') = \frac{1}{2J+1} \frac{64\pi^4 \sigma^3}{3h} S_m(\alpha J, \alpha' J'), \quad (28)$$

is defined by

$$S_m(\alpha J, \alpha' J') = S_m(\alpha' J', \alpha J) = \sum_{M, M'} |(\alpha J M | \mathbf{M} | \alpha' J' M')|^2, \quad \text{where } \mathbf{M} = -\frac{e}{2\mu c} (\mathbf{L} + 2\mathbf{S}). \quad (29)$$

In LS coupling, magnetic-dipole transitions occur only between two levels of the same term. It does not seem to have been generally realized¹¹ that simple closed formulas can be obtained¹² for these strengths in *LS* coupling, and that these strengths can be used in transformations to intermediate coupling. By the same procedure as in the electric-dipole case (p. 99 TAS) we can write

$$S_m(\alpha J, \alpha' J') = (2J+1) \Xi(J, J') |(\alpha J; M; \alpha' J')|^2. \quad (30)$$

The last factor can be evaluated from 10³² pp. 64, 66 TAS to give

¹¹ For example, by Condon, reference 4.

¹² These formulas, at least for the nondiagonal elements, are given by Brinkman, reference 3. They are of considerable direct interest in connection with the excitation of the ground term in rarefied atmospheres. For example, Dunham, *Nature* **139**, 246 (1937), found four interstellar absorption lines from the lowest level ${}^4F_{3/2}$ of Ti II and none from the next level ${}^4F_{5/2}$ in spite of its low excitation potential of only 0.012 volt. The reason for the absence of absorption by ${}^4F_{5/2}$ is its short mean life for magnetic-dipole radiation of 7.6 hours, as determined from (28) and (31), whereas collisions occur much less frequently. This mean life was computed by Houston from Brinkman's formula and reported by Dunham, but with a numerical error of a factor of 10³, as Houston has kindly verified.

$$S_m(SL J, SL J+1) = [+]^2 \frac{(J-S+L+1)(J+S-L+1)(J+S+L+2)(S+L-J)}{4(J+1)} \left(-\frac{e\hbar}{2\mu c} \right)^2, \quad (31)$$

$$S_m(SL J, SL J) = [g(SLJ)]^2 J(J+1)(2J+1) \left(-\frac{e\hbar}{2\mu c} \right)^2,$$

where g is the Landé factor for the Zeeman effect. If we define $S_m^{\frac{1}{2}}(\alpha J, \alpha' J')$ as the root of S_m taken with the sign of $(\alpha J; M; \alpha' J')$ when measured in units $(-e\hbar/2\mu c)$, the transformation of coupling is effected exactly as in (23). In LS coupling, the sign of $S_m^{\frac{1}{2}}$ is the sign of the quantity in square brackets in (31), which is $+$ except in rare instances.

The magnetic-dipole strengths do not satisfy the ordinary J sum rule within a multiplet. Instead, one obtains the formula

$$\sum_{J'} S_m(SLJ, SLJ') = [2J(J+1) + 2S(S+1) - L(L+1)](2J+1). \quad (32)$$

In intermediate coupling, only the J -group sum rule is obeyed.

It is interesting to note that while one easily obtains the simple closed formulas (31) for the magnetic-dipole strengths in LS coupling, the strengths in jj coupling are relatively difficult to obtain; for many configurations the last factor of (30) cannot be evaluated by matrix methods and recourse must be had to the eigenfunctions or to transformation from LS coupling.