

Relative Multiplet Transition Probabilities from Spectroscopic Stability

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A method analogous to the diagonal sum rule for term values is given for calculating the relative transition probabilities of the different multiplets in Russell-Saunders coupling. The method is based on the principle of spectro-

scopic stability. The relative multiplet transition probabilities are given for the transitions p^2d-p^3 , d^2p-d^3 , p^3d-p^4 and p^4d-p^5 .

THIS paper will give a method, based on the principle of spectroscopic stability, of calculating the relative transition probabilities of different multiplets in Russell-Saunders coupling. This principle allows one to use a method of finding the transition probabilities in Russell-Saunders coupling in terms of the transition probabilities between the zero order states analogous to the diagonal sum rule used by Slater¹ for the energy values. This method gives the same results as that used by Ufford² but avoids using the eigenfunctions in Russell-Saunders coupling.

We have the theorem³ analogous to the principle of spectroscopic stability, which states that the sum of the squares of the matrix elements connecting a set of states is invariant when these states are subjected to a unitary transformation. Since the transformation from zero order states to Russell-Saunders coupling states is unitary, this theorem will give us equations from which the matrix elements of the electric moment may be found in Russell-Saunders coupling. In cases where more than one term of a kind occurs in a configuration, this method will give only the sums of the squares of the matrix elements and not the elements themselves. The transition probabilities are proportional to the squares of these matrix elements of the electric moment. The transition probability for the entire multiplet may be determined from the transition prob-

ability for a transition between a single initial and final state by using the summation rules.

1. CALCULATION OF THE MATRIX ELEMENTS OF THE ELECTRIC MOMENT IN RUSSELL-SAUNDERS COUPLING

We are to calculate the matrix elements of the electric moment between a set of states belonging to a first electron configuration and a set belonging to a second electron configuration differing from the first in regard to just one nl value with a change in l equal to unity. Call the first configuration anl and the second $an'l'$. First, one draws up the zero-order scheme for each configuration, classified by M_L and M_S values; and the LSM_LM_S scheme for each configuration also classified by M_L and M_S values. As in the case of energies, only positive values of M_L and M_S need be considered.

The matrix components of $e\mathbf{r}$ will vanish between states of different M_S , so one may take each value of M_S separately, starting with the largest, and draw up the matrix for the different M_L values in each scheme. The matrix components of $e\mathbf{r}$ in the zero-order scheme may be obtained from the formulas given by Condon.⁴ The only nonvanishing matrix components are those in which but one individual set of quantum numbers changes, so that this must be the individual set referring to $(nl) - (n'l')$, where $l' = l \pm 1$.

¹ J. C. Slater, *Phys. Rev.* **34**, 1293 (1929).

² C. W. Ufford, *Phys. Rev.* **40**, 974 (1932).

³ M. Born, W. Heisenberg and P. Jordan, *Zeits. f. Physik* **35**, 557 (1926); J. H. Van Vleck, *Phys. Rev.* **29**, 740 (1927).

⁴ E. U. Condon, *Phys. Rev.* **36**, 1121 (1930). For the matrix elements between single electron states see for example, E. U. Condon and P. M. Morse, *Quantum Mechanics*, p. 100, McGraw-Hill (1929).

We want

$$|(nlm_i|er|n'l'm_i')|^2 = |(nl|er|n'l')(lm_i|r|l'm_i')|^2, \tag{1}$$

where $(lm_i|r|l'm_i')$ is the numerator of the factor given by Condon and Morse⁴ in Eqs. (35) which contains the dependence of $(nlm_i|er|n'l'm_i')$ on m_i and m_i' . Therefore $(nl|er|n'l')$ must be defined to include the denominator of the factor given by Condon and Morse, thus

$$(nl|er|n'l') = [(2l+1)(2l'+1)]^{-\frac{1}{2}} \int_0^\infty erR(nl)R(n'l')dr. \tag{2}$$

$$|(nl|er|n'l')|^2 \sum_{\substack{\text{zero order} \\ \text{states}}} |(lm_i|r|l'm_i')|^2 = \sum_{L \cdot S \text{ states}} |(LSM_L M_S|er|L'SM_L' M_S)|^2 = \sum_{L \cdot S \text{ states}} |(^{2S+1}L|er|^{2S+1}L')|^2 |(LM_L|r|LM_L')|^2. \tag{3}$$

The factor $|(nl|er|n'l')|^2$ remains the same throughout the entire matrix so that, as we are interested only in relative values, it may be omitted. Also, the squares of the matrix elements contain the factor $\frac{1}{4}$ for the x and y components since $x = \frac{1}{2}(x+iy+x-iy)$ and the matrix element of either $x+iy$ or $x-iy$ is zero for a given transition. Since this factor, $\frac{1}{4}$, will occur in both the zero order and $LSM_L M_S$ schemes, on each side of Eq. (3), it also may be omitted. Then, beginning in the rectangle with the largest M_L , we solve the equation of each rectangle for the $|(^{2S+1}L|er|^{2S+1}L')|^2$'s using the values obtained from the rectangles of higher M_L . Thus we obtain an equation for each rectangle with only one unknown as long as only one multiplet of the same kind occurs in a configuration. An equation for the sum of the squares of the matrix components of the multiplets of the same kind is obtained. In some rectangles it often happens that all the elements are known, so that a check is obtained on the work up to this point.

The relative transition probability for the entire multiplet is then obtained from

$$|(^{2S+1}L|er|^{2S+1}L')|^2$$

by multiplying by the factors given by Güttinger and Pauli⁵ in Eq. (24) for the sum over the final

Again in the $LSM_L M_S$ scheme, we must separate from each matrix element $(LSM_L M_S|er|L'SM_L' M_S)$ the part, $(LM_L|r|L'M_L')$, depending on M_L , so that the remaining part $(^{2S+1}L|er|^{2S+1}L')$ will be independent of M_L , and hence the same in each rectangle characterized by a different value of M_L . It is the squares of these factors independent of M_L which we are then able to calculate by the invariance of the sum of their squares. The dependence of $(LSM_L M_S|er|L'SM_L' M_S)$ on M_L may be obtained from formulas given by Güttinger and Pauli.⁵

Now in each rectangle characterized by a given value of $M_S M_L$ and M_L' we write an equation.

states and by $(2S+1)(2L+1)$ for the sum over the initial states.

TABLE I. Calculation of the matrix elements of the electric moment in Russell-Saunders coupling for the quartets of d^2p-d^3 with $M_S=3/2$.

		d^3	
		M_L	
		3	
		Zero order states	$ 2^+1^+0^+ $
		$LSM_L M_S$ states	
		4F	
d^2p	4	$ 1_p^+2^+1^+ $	4G $2 = 56 (d^2p^4G er d^3^4F) ^2$ $ (d^2p^4G er d^3^4F) ^2 = \frac{1}{3^8}$
	3	$ 1_p^+2^+0^+ $ $ 0_p^+2^+1^+ $	4G $3+4 = 7 (d^2p^4G er d^3^4F) ^2$ $+9 (d^2p^4F er d^3^4F) ^2$ 4F $7 = \frac{7}{3^8} (d^2p^4F er d^3^4F) ^2$ $ (d^2p^4F er d^3^4F) ^2 = \frac{3}{4}$
	2	$ 1_p^+2^+-1^+ $ $ 1_p^+1^+0^+ $ $ 0_p^+2^+0^+ $ $ -1_p^+2^+1^+ $	4G $2+12+6 = 2 (d^2p^4G er d^3^4F) ^2$ $+6 (d^2p^4F er d^3^4F) ^2$ 4F $+30 (d^2p^2^4D er d^3^4F) ^2$ $20 = \frac{2}{3^8} + 6(\frac{3}{8})$ 4D $+30 (d^2p^2^4D er d^3^4F) ^2$ 4D $ (d^2p^2^4D er d^3^4F) ^2 = \frac{1}{3^8}$

⁵ P. Güttinger and W. Pauli, Zeits. f. Physik **67**, 743 (1931); p. 761, Eq. (25). The $a_{L'}$ of this equation is $(^{2S+1}L|r|^{2S+1}L')$.

2. DETAILED CALCULATION OF QUARTET TRANSITIONS IN d^2p-d^3

The method of calculating relative multiplet transition probabilities is shown in Table I. To obtain, for example, the equation in the rectangle labeled $d^2pM_L=3, d^3M_L=3$, one has for the zero order states:⁴

$$\begin{aligned} |(|2+0+1_p+||z||2+1+0+||)^2 &= |(1_p+|z|1+)|^2 = (1+1+1)(1-1+1) = 3, \\ |(|2+1+0_p+||z||2+1+0+||)^2 &= |(0_p+|z|0+)|^2 = (1+0+1)(1+0+1) = 4. \end{aligned} \quad (4)$$

For the LSM_LM_S states:⁵

$$\begin{aligned} |(d^2p4, 3/2, 3, 3/2|ez|d^33, 3/2, 3, 3/2)|^2 &= (4^2-3^2)|(d^2p^4G|er|d^3^4F)|^2 = 7|(d^2p^4G|er|d^3^4F)|^2, \\ |(d^2p3, 3/2, 3, 3/2|ez|d^33, 3/2, 3, 3/2)|^2 &= 3^2|(d^2p^4F|er|d^3^4F)|^2 = 9|(d^2p^4F|er|d^3^4F)|^2. \end{aligned} \quad (5)$$

Equating the sum of the elements of Eq. (4) to the sum of the elements of Eq. (5) gives the required equation. The value of $|(d^2p^4G|er|d^3^4F)|^2$ from the previous rectangle $d^2pM_L=4, d^3M_L=3$ is then substituted in this equation and the equation solved for $|(d^2p^4F|er|d^3^4F)|^2$. Now the relative multiplet transition probabilities are obtained from these elements by multiplying by the factors to sum over the initial and final states. Thus⁵

$$\begin{aligned} (d^2p^4G, d^3^4F) &= 1/28(4 \cdot 9)(4 \cdot 7) = 36, \\ (d^2p^4F, d^3^4F) &= 3/4(4 \cdot 7)(3 \cdot 4) = 252, \\ (d^2p2^2D, d^3^4F) &= 18/35(4 \cdot 5)(3 \cdot 7) = 216. \end{aligned} \quad (6)$$

(d^2p2^2D, d^3^4F) is the sum of the relative transition probabilities of the two $^4D-^4F$ multiplets.

3. RELATIVE MULTIPLY TRANSITION PROBABILITIES

The relative multiplet transition probabilities are shown in the tables as follows: p^2d-p^3 in Table II, d^2p-d^3 in Table III, p^3d-p^4 in Table IV, and p^4d-p^5 in Table V.

It must be remembered that a transition such as $d^2p3^2D-d^32^2D$ in Table III represents the sum of the relative transition probabilities of six $d^2p^2D-d^32^2D$ multiplets. As before,² the inter-system transitions forbidden by the selection rule for the spin quantum number, $\Delta S=0$, are marked

TABLE II. Relative multiplet transition probabilities in Russell-Saunders coupling for the transitions p^2d-p^3 .

		p^3		
		4S	2D	2P
p^2d	4F	y	x	x, y
	4D	y	x	x
	4P	24	x	x
	2G	x, y	y	y
	2^2F	x, y	42	y
	3^2D	x, y	15	25
	2^2P	x	3	9
	2S	x	y	2

TABLE III. Relative multiplet transition probabilities in Russell-Saunders coupling for the transitions d^2p-d^3 .

		d^3						
		4F	4P	2H	2G	2F	2^2D	2P
d^2p	4G	180	y	x	x	x	x, y	x, y
	4F	1260	y	x, y	x	x	x	x, y
	2^4D	1080	520	x, y	x, y	x	x	x
	4P	y	240	x, y	x, y	x, y	x	x
	4S	y	320	x, y	x, y	x, y	x, y	x
	2^2H	x, y	x, y	396	44	y	y	y
	2^2G	x	x, y	1584	576	180	y	y
	3^2F	x	x, y	y	1000	420	470	y
	3^2D	x	x	y	y	660	625	215
	3^2P	x, y	x	y	y	y	705	255
	2S	x, y	x	y	y	y	y	70

TABLE IV. *Relative multiplet transition probabilities in Russell-Saunders coupling for the transitions $p^3d - p^4$.*

		p^4		
		3P	1D	1S
p^3d	5D	x	x	x, y
	3G	y	x, y	x, y
	2^3F	y	x	x, y
	3^3D	120	x	x, y
	2^3P	45	x	x
	3S	15	x, y	x
	1G	x, y	y	y
	2^1F	x, y	63	y
	2^1D	x	30	y
	2^1P	x	7	20
1S	x	y	0	

TABLE V. *Relative multiplet transition probabilities in Russell-Saunders coupling for the transitions $p^4d - p^5$.*

		p^4d							
		4F	4D	4P	2G	2^2F	3^2D	2^2P	2S
p^5	2P	x, y	x	x	y	y	19	9	2

x ; and those forbidden by the selection rule for the total orbital angular momentum, $\Delta L = 0, \pm 1$, are marked y . Thus the method of spectroscopic stability is seen to aid effectively in the theoretical calculation of relative multiplet transition probabilities in Russell-Saunders coupling.