THE RELATIVE INTENSITIES OF SUPER-MULTIPLET LINES

By James H. Bartlett, Jr.

Institut f. Theoretische Physik, Leipzig

Abstract

A simple method is described by which one may construct wave functions for the case of (jj) coupling. The wave functions for $(2p)^2$, so determined, agree with those given in a previous paper, when one sets the electrostatic interaction equal to zero. It is shown how the ordinary multiplet intensity formulae may be modified to give the relative intensities in a super-multiplet for (jj) coupling. The modified formulae, applied to the transition $(2p)^2 \rightarrow 2p3s$, give relative intensities in agreement with those found in the above paper, for this limiting case. The sum-rules hold quite generally for non-equivalent electrons, and it is shown to what degree they hold for a transition such as $(2p)^2 \rightarrow 2p3s$.

ON THE basis of the Darwin-Pauli theory of the spinning electron it has been found possible[1,2] to calculate the relative intensities of super-multiplet lines for certain transitions, such as $(ds \rightarrow fs)$ and $(2p\ 2p \rightarrow 2p\ 3s)$. The intensities so found are dependent upon the strength of the electrostatic interaction between the electrons, as compared with that of the magnetic interactions between spin and orbital angular momenta. In the limiting case of strong electrostatic interaction, or $(1s)$ coupling, these intensities agree with those calculated from the formulae for relative intensities within an ordinary multiplet. In the other limiting case, that of (jj) coupling, where the spin-orbit interaction is predominant, analogous formulae can be set up and the intensities so obtained would agree with those found from more general formulae when the electrostatic interaction is set equal to zero. The difficulties involved in obtaining these general formulae for any degree of coupling have already been mentioned in a previous paper.[2] Accordingly, it seems expedient to calculate the theoretical intensities for the two limiting cases and to use some suitable method of interpolation when comparing with experiment.

1. The Wave Functions and Energy Value for (jj) Coupling

For simplicity, we shall at first deal with only two electrons. For (jj) coupling, we are to consider as a perturbation the magnetic interaction between each electron and its own orbit. Each electron can be considered

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

[2] J. H. Bartlett Jr., Phys. Rev. **34**, 1247 (1929). A sign error in the matrix components of the intercombination lines should be corrected. Both c_1 and c_5 should have the opposite sign. None of the conclusions of the paper are invalidated, to our degree of approximation. Furthermore, in the roots ϵ_3 and ϵ_4, one should substitute $+8$ for -8.

separately during this perturbation calculation and then the product functions, or a linear combination thereof, will represent the total system. As usual, we group those functions together which have a common $m = \sum m_l + m_s$, where m_l and m_s refer to the projections of l and s, the azimuthal and spin quantum numbers, on a preferred axis. For an externally undisturbed system, terms with different m's cannot combine, since m represents a constant of the motion. The wave functions are written

$$\psi_\alpha{}^m = R_{ln}(r) P_l{}^{m-1/2} S_\alpha \; ; \quad \psi_\beta{}^m = R_{ln}(r) P_l{}^{m+1/2} S_\beta.$$

The two possible values of the spin variable are S_α and S_β respectively, and

$$P_l{}^{m_l} = (l - m_l)! \sin{}^{m_l}\theta \left(\frac{d}{d \cos \theta} \right)^{l+m_l} \frac{(-\sin^2\theta)^l}{2^2 l!} e^{i m_l \phi}.$$

Let

$$\gamma_{ln} = \frac{h^2}{16\pi^2} \frac{Ze^2}{m_0{}^2 c^2} \int R_{ln}{}^2 \frac{1}{r^3} d\tau \quad \text{and} \quad \epsilon = \frac{\Delta E}{\gamma_{ln}} \cdot$$

For the perturbation arising from the interaction between spin and orbit, the secular equation is:

$$\begin{vmatrix} m - \tfrac{1}{2} - \epsilon & (l - m + \tfrac{1}{2})^{1/2}(l + m + \tfrac{1}{2})^{1/2} \\ (l - m + \tfrac{1}{2})^{1/2}(l + m + \tfrac{1}{2})^{1/2} & -m - \tfrac{1}{2} - \epsilon \end{vmatrix} = 0.$$

The roots are $\epsilon_1 = l$ and $\epsilon_2 = -l - 1$, and the corresponding wave functions are:

$$\psi_1{}^m = (1/2l+1)^{1/2}[(l+m+\tfrac{1}{2})^{1/2}\psi_\alpha{}^m + (l-m+\tfrac{1}{2})^{1/2}\psi_\beta{}^m]$$

$$\psi_2{}^m = (1/2l+1)^{1/2}[-(l-m+\tfrac{1}{2})^{1/2}\psi_\alpha{}^m + (l+m+\tfrac{1}{2})^{1/2}\psi_\beta{}^m].$$

One sees that, for the state 1, $j = m_{\max} = l + \tfrac{1}{2}$ and for the state 2, $j = m_{\max} = l - \tfrac{1}{2}$.

The calculation thus far deals with coupling of the type $(s_1 l_1) = j_1$. In order to treat coupling of the type $(j_1 j_2) = j$ one must construct antisymmetric wave functions from products of functions such as $\psi_1{}^m$ and $\psi_2{}^m$. For instance, set[3]

$$\psi_{j_1 j_2}{}^m = (\tfrac{1}{2})^{1/2} \begin{vmatrix} \psi_{j_1}{}^{m_1}(1) \; ; \; \psi_{j_1}{}^{m_1}(2) \\ \psi_{j_2}{}^{m_2}(1) \; ; \; \psi_{j_2}{}^{m_2}(2) \end{vmatrix}.$$

If now, for a given m, the vectors j_1 and j_2 combine to give only one j, then the state is not degenerate for (jj) coupling and will be represented, except perhaps for a sign factor, by a function of the above type. Just as frequently, however, one finds a degeneracy and the correct wave functions for a given value of j are found by taking linear combinations, the coefficients being

[3] In the more general case of more than two electrons, the antisymmetric functions will have the determinant form. See J. C. Slater, Phys. Rev. (being published). The notation used above is similar to that of the paper to which reference is here made.

determined from a perturbation calculation, the electrostatic interaction between the electrons being the perturbation. This degeneracy is for a given set $(j_1 j_2)$ combining to give different j's. If one should take the wave functions for the same j, as determined by this process, but for different sets $(j_1 j_2)$, and repeated the process, this would give the correct wave functions for (ls) coupling. This is to be expected, since it should make no difference in which order the various perturbations are applied. In the previous paper,[2] the reverse order was employed, and the results agree, both for energy values and for wave functions.

The total energy of the two-electron system for (jj) coupling is given by

$$E = E(n_1 l_1) + \gamma_{l_1 n_1} \epsilon(j_1) + E(n_2 l_2) + \gamma_{l_2 n_2} \epsilon(j_2).$$

This agrees with the work of Goudsmit[4] if we make $\gamma = a/2$.

2. SELECTION RULES

Let us denote the set of quantum numbers $(nljm)$ by p. Then the matrix element for a transition involving two electrons will be a linear combination, in the zeroth approximation, of matrix elements of the type

$$z(p_1 p_2 ; p_3 p_4) \sim \delta(p_2 p_4) z(p_1 p_3) + \delta(p_1 p_3) z(p_2 p_4) - \delta(p_2 p_3) z(p_1 p_4) - \delta(p_1 p_4) z(p_2 p_3). \quad (1)$$

Thus, whether the coupling be of the (ls) (jj) type, as long as the wave functions are formed by the linear combinations of functions of the unperturbed system, then two-electron jumps are not permitted. This is true for any number of electrons, but only as a first approximation. According to Pauli's exclusion principle, no two electrons can have the same p and so, for any transition, we have only one term on the right-hand side of equation (1). Let this term be the first, i.e. $p_2 = p_4$. That is, for one of the two electrons, all four quantum numbers remain the same, and for the other, the ordinary selection rules hold. In the (jj) coupling case, therefore, j_1 can change by $0, \pm 1$ and j_2 does not change. If $p_1 = p_3$ instead, then $\Delta j_1 = 0$ and $\Delta j_2 = 0, \pm 1$.

3. INTENSITIES

Consider the transition $(n_1' l_1' j_1' m_1' ; n_2 l_2 j_2 m_2) \rightarrow (n_1'' l_1'' j_1'' m_1'' ; n_2 l_2 j_2 m_2)$. The z-matrix will be a linear combination of a number of "unperturbed" z-matrices, which have the form $\int [R_{l_2 n_2}(2)]^2 r_2{}^2 dr_2 \int R_{l_1' n_1'}(1) R_{l_1'' n_1''}(1) r_1{}^2 dr_1 \int P_{l_1'}{}^*(1) z_1 P_{l_1''}(1) d\omega_1$ corresponding to the term $z(p_1 p_3)$ in Eq. (1). Thus, the radial integration gives a common factor and, since this is the only way in which the principal quantum numbers can enter, they have no influence on the relative intensities in a super-multiplet. It makes, therefore, no difference in the relative intensities as to whether the electrons are or are not equivalent. The equivalence is manifested, however, in the disappearance of certain states with the result that certain intensity sums are not proportional to statistical weights of the corresponding states.

[4] S. Goudsmit, Phys. Rev. **31**, 946 (1928).

For (jj) coupling, j_2 plays the same role as s, and j_1 the same role as l, respectively, in (ls) coupling. We can introduce a notation analogous to the Russell-Saunders notation, namely, $^r(j_1)_j$, where $r=2j_2+1$. The j_1 labels the valence electron, and r is the multiplicity. Even when the two electrons are equivalent, there is no ambiguity as to which is the valence electron, unless $j_1=j_2$. In this case one must double the intensity as calculated from the formulae to be given, to allow for the two possibilities.

The ordinary multiplet formulae can now be rewritten in terms of j_1 and j_2 instead of l and s. In the ordinary multiplet theory the statistical weight of an $^r(l)$ state is $r(ll+1)$, e.g. a ^3D state has a degeneracy of fifteen. For (jj) coupling, the statistical weight of an $^r(j_1)$ state is $r(2j_1+1)$, except for equivalent electrons with $j_1=j_2$, where it becomes $2rj_1$. The degeneracy of a ps $^4(1/2)$ state is eight, that for a $(2p)^2$ $^4(3/2)$ state is twelve, and that for a $(2p)^2$ $^4(1/2)$ the same as for $(2p)^2$ $^2(3/2)$, namely eight.

The formulae in terms of j_1 and j_2 follow:

$$\Delta_{j_1}=\pm 1 \qquad J_{-1}=G_j A^{j,j_1}_{j-1,j_1-1}=\frac{c}{4jj_1}P(j,j_1)P(j-1,j_1)$$

$$J_0=G_j A^{j,j_1}_{j,j_1-1}=\frac{c}{4jj_1}\frac{2j+1}{j+1}P(jj_1)Q(jj_1)$$

$$J_{+1}=G_{j-1}A^{j-1,j_1}_{j,j_1-1}=\frac{c}{4jj_1}Q(jj_1)Q(j-1,j_1)$$

$$\Delta j_1=0 \qquad J_0=G_j A^{j,j_1}_{j,j_1}=\frac{c}{4jj_1}\frac{2j+1}{j+1}\frac{2j_1+1}{j_1+1}R^2(j)$$

$$J\pm 1=G_j A^{j,j_1}_{j-1,j_1}=G_{j-1}A^{j-1,j_1}_{j,j_1}=\frac{c}{4jj_1}\frac{2j_1+1}{j_1+1}P(j,j_1)Q(j-1,j_1)$$

where

$$P(j)=(j+j_1)(j+j_1+1)-j_2(j_2+1)$$
$$-Q(j)=(j-j_1)(j-j_1+1)-j_2(j_2+1)$$
$$R(j)=j(j+1)+j_1(j_1+1)-j_2(j_2+1).$$

The A's are the squares of matrix elements. For any super-multiplet, or group of lines belonging to a transition such as $sp{\rightarrow}pp$, the value of C is the same for all lines. The sum of intensities form any state with equivalent electrons over all the states (with non-equivalent electrons) to which transitions can be made is, for a given super-multiplet, proportional to the statistical weight of the initial state. If these sums be taken horizontally, then in general the vertical sums will not be proportional to the corresponding statistical weights due to the exclusion of certain states which would be possible if the electrons were not equivalent.

As examples of applications of the formulae we give below the results (1) for a case with two non-equivalent electrons, and (2) for two equivalent electrons.

TABLE I. *Relative intensities in the super-multiplet dp→ds, for (jj) coupling.*

ds- \ dp	j	4(½)		4(3/2)				6(½)		6(3/2)				Sums	
		2	1	3	2	1	0	3	2	4	3	2	1		
4(½)	2	5	5	14	5	1	0	0	0	0	0	0	0	30	
4(½)	1	5	1	0	5	5	2	0	0	0	0	0	0	18	48
6(½)	2	0	0	0	0	0	0	$7^7/_9$	$2^2/_9$	0	$6^2/_9$	$7^7/_9$	6	30	
6(½)	3	0	0	0	0	0	0	$6^2/_9$	$7^7/_9$	18	$7^7/_9$	$2^2/_9$	0	42	72
Sums		10	6	14	10	6	2	14	10	18	14	10	6		
		16		32				24		48					
		48						72							

TABLE II. *Relative intensities in the super-multiplet $(2p)^2$→$2p3s$ for (jj) coupling.*

(2p)² \ 2p3s	j	4(½)		2(½)		Sums		
		1	2	1	0			
4(3/2)	0	2·2= 4	0	0	0	4	24	
4(3/2)	2	2·5=10	2·5=10	0	0	20		40
(4(½)	2	5	5	0	0	10	16	
(4(½)	1	1	5	0	0	6		
(2(3/2)	2	0	0	10	0	10	16	
(2(3/2)	1	0	0	2	4	6		20
2(½)	0	0	0	2·2=4	0	4	4	
Sums		20	20	16	4			
		40		20				

It is seen that the total intensity in a given system is proportional to the multiplicity of that system. For non-equivalent electrons both horizontal and vertical sums are proportional to the corresponding statistical weights, e.g. $^4(1/2){:}^4(3/2){:}^6(1/2){:}^6(3/2)=8{:}16{:}12{:}24$. For the equivalent electrons, the sums from the $(2p)^2$ states are likewise proportional to the statistical weights, e.g. $^4(3/2){:}^4(1/2){:}^2(3/2){:}^2(1/2)=12{:}8{:}8{:}2$.

However, this is not so for the sums from the $2p3s$ states, but would be true if the two p electrons were not equivalent. It should be noted that the $^4(1/2)$ and $^2(3/2)$ states of the $(2p)^2$ configuration have the same energy, but differ in the value of j which the valence electron has. (In the one case, $j_1=1/2$, $j_2=3/2$ and in the other case $j_1=3/2$, $j_2=1/2$ where j_1 denotes the

valence electron).   The intensities given above for the transition $(2p)^2\rightarrow$ $2p3s$ agree with those found from the general formulae of the previous paper,[2] when one sets the electrostatic interaction equal to zero.

As to the comparison with experiment, the observed intensities vary greatly from observer to observer, perhaps due to the excitation conditions. Furthermore, in some cases the identification of terms is in question. However, the intensities given by Mack[5] for the super-multiplet $d^9p\rightarrow d^9s$ in Ge V and SnV are not in any marked disagreement with what one should expect from Table I. Where (jj) coupling is not realized, it may sometimes be possible to interpolate between this case and that of (ls) coupling. This question, as well as the allied ones of term-crossing and co-ordination to series limits, is beyond the scope of the present paper, but in all probability can be treated by obtaining the general formulae for a few simple cases and by then applying the method of induction.   The calculations involved are not impossibly complicated for two electrons.

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[5] J. E. Mack, Phys. Rev. **34,** 17 (1929).