MANY-ELECTRON SELECTION RULES

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ABSTRACT

Selection rules for many-electron transitions are derived by taking into account the first order perturbed eigenfunctions. The perturbations considered are the electrostatic interactions between the pairs of electrons, and the spin-orbit interaction of each electron. It was found that the possibly occurring terms in the first order eigenfunction were narrowly limited, and that this limitation provided the selection rules as follows: No more than three electrons can jump at a time. (a) when three electrons jump all change their n by an arbitrary amount, one changes its l by ± 1, the others by δ and ϵ, $\delta+\epsilon$ being even. (b) when two electrons jump both can change their n arbitrarily, one changes its l by $\delta \pm 1$, the other one by ϵ. Breaking off the series expansion for $1/r_{FG}$ in the electrostatic interaction after the second term gives for δ and ϵ only the values 0, ± 1. The Heisenberg two-electron selection rule is therefore to be considered as a special case of (b). The Laporte rule is verified making use only of the properties of spherical harmonics. Qualitative rules have been derived to tell when many-electron transitions may be expected to be strong. The first order terms also cause anomalies in the intensities of one-electron transitions.

I. INTRODUCTION

IN A recent paper* Condon considered the influence which neighboring electron configurations have upon each other when one treats the first order perturbation of the eigenfunctions. Condon also mentioned that the occurrence of two-electron transitions was closely connected with this mutual influence. In this paper we propose to study somewhat more in detail the possibilities for many-electron transitions by means of the method used by Condon. For our purpose it is necessary to investigate what type of terms occurs in the first order expansion of the eigenfunctions. The perturbations we shall consider are the electrostatic interaction between the different electrons, and the spin-orbit interaction for each electron.

2. ONE-ELECTRON TRANSITIONS IN THE MANY-ELECTRON PROBLEM

We shall first discuss the outline of the way in which our results were obtained, and at the end of the paper give the more detailed derivations and remarks.

Let

$$\psi^0(n_1l_1;\ n_2l_2;\ \cdots\ n_fl_f) \tag{2.1}$$

be a zeroth order eigenfunction for an f-electron problem, stabilized with respect to the electrostatic interaction between the different electrons, and for the spin-orbit interaction of each electron. For convenience we also assume

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* Condon, Phys. Rev. **36**, 1121 (1930).

that these functions are stabilized for the interaction with a homogeneous magnetic field. This symbol thus stands for a linear combination of eigenfunctions, each one being the product of single-electron eigenfunctions for all electrons. The single-electron eigenfunctions are the usual Schrödinger central field eigenfunctions with spin,

$$R_{nl}(r)P_l^{m_l}e^{im_l\phi}S(m_s/t).$$

The different terms of such a linear combination will all contain the same set of quantum numbers, n_i, l_i, but will differ in the permutations of the coordinates over these states. Moreover the same permutation will occur several times in the linear combination, each time with a different choice for the magnetic quantum numbers, m_l and m_s for each electron. This choice is restricted, however, by the fact that the total projection, M, given by,

$$M = \sum m_l + m_s$$

is the same for all terms of the linear combination and is a characteristic of the state under consideration. For our problem the magnetic quantum numbers are of no further interest. That is why we do not use them in the designation of the eigenfunctions.[1]

The intensity of a transition between two states, each one characterized by such a zeroth order eigenfunction, depends upon integrals of the form

$$\int \bar{\psi}^0(n_1'l_1';\ n_2'l_2';\ \cdots\ n_f'l_f')X\psi^0(n_1l_1;\ n_2l_2;\ \cdots\ n_fl_f)d\tau. \tag{2.2}$$

Primes are used for the quantum numbers of the final state. Here X stands for any one of the quantities

$$\begin{gathered}\sum_F r_F \sin\theta_F e^{i\phi_F}\\ \sum_F r_F \cos\theta_F\\ \sum_F r_F \sin\theta_F e^{-i\phi_F}.\end{gathered} \tag{2.3}$$

Considering the angles[2] θ_F one can derive first of all the well-known selection rule for M. For the first choice of X the integral (2.2) vanishes unless $M' = M+1$, for the second choice unless $M' = M$, and for the third choice unless $M' = M-1$. The middle choice gives a Zeeman component which is linearly polarized, parallel to the direction of the external field, the others give the circularly polarized components.

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[1] In the derivations at the end the magnetic quantum numbers will be included for the sake of clarity.

[2] One should not confuse the coordinates of the first, second . . . Fth electron, with the quantum numbers, e.g., n_1, n_2, n_3, $\cdots$ n_f. The number of quantum number sets f, of course equals the number of electrons F, but there is no connection between n_1, and r_I, n_2 and r_{II} etc. Because of the permutations n_1 is connected with all the r_I, r_{II}, $\cdots$ r_F. Similarly for n_2, n_3, $\cdots$ n_f. The difference is further brought out by using Roman numerals for subscripts of the coordinates and the capital letter for the running index.

After the M's for initial and final state have been fixed it is very essential for our purpose to remark that the integral (2.2) will vanish anyhow unless just one of the l_i' of the final state differs by $+1$ or -1 from one of the l_i of the initial state. All other l and n must be the same for both states, except that the n_i' with the same index as the differing l_i' may be different from n_i by an arbitrary amount. (See note A). If we denote the quantum numbers which differ by the index 1 we can write for the non-vanishing case

$$\int \bar{\psi}^0(n_1', l_1 \pm 1; n_2, l_2; \cdots n_f, l_f) X \psi^0(n_1, l_1; n_2, l_2; \cdots n_f, l_f). \qquad (2.4)$$

In the language of the atomic model this result would mean that only one electron could jump at a time, when we consider only zeroth order eigenfunctions, and that it's l changes by $+1$ or -1 and its n by an arbitrary amount.[3]

3. TERMS OCCURRING IN THE FIRST ORDER EIGENFUNCTIONS

3. In order to account for two-electron jumps we must now investigate what happens if we take the first order terms into account. For a qualitative discussion we need to consider such terms only in the initial or the final state; taking them for both states would not result in anything new. The first order eigenfunction will be of the form

$$\begin{aligned} \psi^1(n_1, l_1; \cdots n_f, l_f) = \psi^0(n_1, l_1; \cdots n_f, l_f) &+ \lambda \sum_a{}' c_a \psi^0(n_1^a, l_1^a; \cdots n_f^a, l_f^a) \\ &+ \mu \sum_b{}'' d_b \cdot \psi^0(n_1^b, l_1^b; \cdots n_f^b l_f^b) \end{aligned} \qquad (3.1)$$

The first sum with the coefficient λ we assume to arise from the spin-orbit interactions, the second sum with μ from the electrostatic interactions. *It is just these terms which cause the many electron transitions and therefore we are very much interested in finding out what terms may occur and what terms are excluded.* Though it does not help us in getting the many-electron transition selection rule, as a first limitation on the terms occurring in the two sums, we may cite the well-known matrix mechanics theorems that only such terms will occur that have the same total M, and J. Next, the primes at the summation signs mean that all eigenfunctions except the unperturbed one may occur in the sum. As we are dealing here with an originally degenerate system we must look at this fact more closely, since the prime excludes different eigenfunctions from the first than from the second sum. If we take for instance extreme Russell-Saunders coupling, the smaller spin-orbit interaction causes the splitting up of each multiplet (due to the Russell-Saunders coupling) into its levels. In the first sum are therefore excluded such eigenfunctions

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[3] It is perhaps not superfluous to note that this way of expressing our result may lead to the confusion mentioned in the footnote (2). One cannot say that one particular electron changes its quantum numbers, as all permutations of the electrons over the quantum numbers occur. If we consider the quantum state of the many-electron problem to be built up of a number of single electron states over which the electrons are distributed, one can say that in a transition only one electron *state* changes and the others remain unchanged.

of the different terms which belong to one and the same multiplet, but levels of other multiplets from the same configurations, that is, having the same[4] n's and l's may occur, as well as the eigenfunctions with different n's and l's.

The larger electrostatic interaction excludes from the sum all such eigenfunctions which belong to levels which fall together without this interaction. These are the multiplets with the same set of n's and l's. Thus the second sum will not contain eigenfunctions having this set of n's and l's. For extreme (jj) coupling on the other hand, the second sum may now contain terms having the same set of n's and l's as the unperturbed eigenfunction; the spin orbit sum (thus far) may or may not have the same set of l's, but must have at least one n different. These statements hold, of course, in extreme coupling only, in which case one can think of the perturbations as applied consecutively, the large one first and then the smaller.

For the spin-orbit interaction the perturbation is of the form,

$$\sum_F \frac{l_F \cdot s_F}{r_F{}^3} \cdot \qquad (3.2)$$

This requires that in the first sum only such terms remain that have all l's the same as the zeroth order eigenfunctions, and one of the n's but not more may different.[5] (See Note B.)

The electrostatic perturbation is of the form

$$\sum_{FG} \frac{e^2}{r_{FG}} \cdot \qquad (3.3)$$

This necessitates that only such terms occur in the second sum for which two and no more than two of the l's may be different from two of the l's of the zeroth order eigenfunction. (See Note C_1.)

If we denote these changes by ∂ and ϵ their sum must be even. (see Note C_2.)

If we restrict ourselves to the first term of the expansion of the electrostatic perturbation in spherical harmonics, we find that none of the l's may change, and that one of the n's may be different.[6] (See Note C_3.)

The next term in the expansion for $1/r_{FG}$ gives two l's different, each by $+1$ or by -1, and the n's connected with them maybe different by an arbitrary amount.[7] (See Note C_4.)

The results of this section may then be summed up as follows: If we take

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[4] In the case that *all* the n's and l's are the same, the eigenfunction in the sum must be a different linear combination than the unperturbed one, namely, a combination belonging to another multiplet of the same configuration.

[5] As mentioned just before with reference to Note B, for extreme (jj) coupling one of the n's *must* be different.

[6] This is the same result that we got from the spin-orbit interaction.

[7] In general, if we consider the kth term of the expansion, taking the two differing l's as the first two, and calling them l_{1b}, l_{2b}, we find that in order that the integral does not vanish, l_1, l_{1b}, k, must be the side of a triangle of even perimeter; Similarly for l_2, l_{2b}, k. Thus, for example, $l_1 - l_{1b}$, may have the values, k, $k-2$, $k-4 \cdots$. The n's again are arbitrary. See Gaunt, Camb. Phil. Trans. 1929.

as an example those terms out of the sums for which the first quantum numbers are different, we may write them[8]

$$\begin{array}{ll} \lambda c\psi^0(n_1'', l_1; \cdots n_f, l_f) & \text{first order spin orbit terms} \\ \left.\begin{array}{l} \mu d_0\psi^0(n_1''', l_1; \cdots n_f, l_f) \\ \mu d_1\psi^0(n_1^{\mathrm{IV}}, l_1 \pm 1; n_2^{\mathrm{IV}} l_2 \pm 1; \cdots n_f l_f) \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ \mu d_k\psi^0(n_1^{\mathrm{V}}, l_1 + \partial_k; n_2^{\mathrm{V}} l_2 + \partial_k; \cdots n_f, l_f) \end{array}\right\} & \begin{array}{l} \text{first order} \\ \text{electrostatic} \\ \text{terms} \\ (\partial + \epsilon = \text{even}). \end{array} \end{array} \tag{3.4}$$

At this point we need say nothing more about the terms occurring in the spin-orbit sum (we again refer the reader to note B). But about the terms of the second sum we can say something further not only about what terms are excluded, but with what relative strength the allowed terms may occur. This is due to the fact that the coefficients of the terms of the second sum involve a product of two integrals, each of which contains a product of three spherical harmonics, the harmonic on which we sum occurring in the same way in both integrals (see notes C_1 and C_2). This latter property is the important one in excluding certain states from the sum and assigning the relative strength with which others occur. As mentioned in note C_2, the integral of a product of three spherical harmonics vanishes unless the absolute value of any two of the l's is equal to or less than the third l. This fact lends itself nicely to a chessboard diagram. We give the results which can easily be verified by examining the integrals for a few cases.

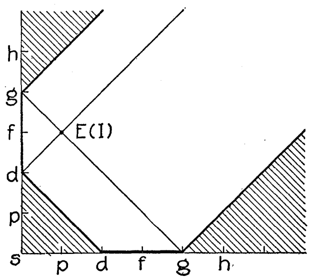

Fig. 1.

In Fig. 1 the abscissas and ordinates stand for the two l's (of the terms of the electrostatic interaction sum) which are allowed to be different from two of the unperturbed eigenfunction. Pick out any initial point or state, $E(I)$. Draw the two forty-five degree lines through it and complete the figure as shown by the heavy lines. Then

(a) the states which can occur in the sum, with respect to the chosen initial state, lie within the region bounded by the heavy line. Those, in the shaded region, are excluded by reason of the vanishing of the integrals.

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[8] It can be understood from what follows that the terms for which all quantum numbers are the same as those of the unperturbed state, do not contribute to two-electron jumps, but are important in accounting for anomalies in one-electron intensities.

(b) states lying within the region bounded by the heavy lines, but which have $\partial + \epsilon \neq$ even, are also excluded. This gives the Laporte rule when one considers the transitions. One can easily show that the Laporte rule holds for higher perturbations as well, since for these perturbations the same type of integrals is involved.

(c) To find the relative strength with which the allowed states occur in the sum we proceed by the following rule: Go by the shortest number of unit "bishop's moves" from the initial state $E(I)$ to any allowed state in the sum. The number of unit moves which it takes to get there gives the lowest term in the expansion with which this state occurs (it may occur also in the higher terms). The states which are only one unit bishop move away occur with the largest coefficients, and are those which enter to give the Heisenberg selection rule.

4. TWO-ELECTRON AND THREE-ELECTRON TRANSITIONS

We now consider a final state of which we take only a zeroth order eigenfunctions. We chose it such that that there would be no transitions, if we had taken also only the zeroth order eigenfunction of the initial state; thus we take more than just one l and n different for the two states. We now investigate under what conditions the above given first order terms will cause the following integral, which governs the intensities, not to vanish

$$\int \bar{\psi}^0(u_1', l_1'; \cdots u_f', l_f') X \psi^1(n_1, l_1; \cdots n_f l_f) d\tau. \tag{4.1}$$

Substituting for ψ^1 leads to integrals of the following type

$$\lambda c \int \bar{\psi}^0(n_1', l_1'; \cdots n_f', l_f') X \psi^0(n_1'', l_1''; \cdots n_f l_f) d\tau \tag{4.2}$$

$$\mu d \int \bar{\psi}^0(n_1', l_1'; \cdots n_f', l_f') X \psi^0(n_1''', l_1 + \partial; n_2''', l_2 + \epsilon; n_3, l_3; \cdots n_f l_f) d\tau \tag{4.3}$$

and another integral like (4-2) due to the first term of $1/r_{FG}$. Of such integrals we know already that they will vanish, unless we have chosen the quantum numbers of the final state just right. Just one of the l's of the final state must differ by $+1$ or -1 from one of the l's of the other eigenfunction under the integral, the n's associated with these two l's may differ by an arbitrary amount, but all other l's and n's must be the same.

One will only get transitions with first order eigenfunctions when the quantum numbers of the final state are in a certain relation to the quantum numbers of the series expansion of the initial state.[9] Now we have seen that the quantum numbers in these series were related to the quantum numbers in the zeroth order eigenfunction, the quantum numbers by which we usually denote the state under consideration. It follows that one will only find transitions when the quantum numbers of the final state are related in a

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[9] A similar statement will be true if we interchange initial and final state.

certain way to those of the initial as required by the condition that at least one of the integrals (4.2), (4.3), does not vanish. This can be provided for in number of different ways and one can without much difficulty verify the following results, from which we omit the cases which give rise to an ordinary one-electron transition.

Combining statements just preceding references to notes A, B, and C_1, one finds that due to the first order terms of both the spin-orbit interaction and the first term of the electrostatic interaction, transitions may occur between two states:

(a) when there is a change in *two* electron states, one changing only its n, the other changing its l by $+1$ or -1, and its n by an arbitrary amount, thus:

$$\psi^1(n_1, l_1; \cdots n_f, l_f) \to \psi^0(n_1', l_1; n_2', l_2 \pm 1; \cdots n_f, l_f).$$

Combining statements just preceding references to notes A, C_2, C_3, C_4, one finds that due to the first order terms in the electrostatic interaction a transition may occur between two states,

(b) when there is a change in three electron states, all changing their n's by arbitrary amounts, two of them changing their l's by ∂ and ϵ ($\partial + \epsilon =$ even), the third one changing its l by $+1$ or -1. The values of $+1$ and -1 for ∂ and ϵ will be more probable. Thus,

$$\psi^1(n_1, l_1; \cdots n_f, l_f) \to \psi^0(n_1', l_1 + \partial; n_2', l_2 + \epsilon; n_3', l_3 \pm 1; \cdots u_f, l_f).$$

(c) when there is a change in two electron states, both changing their n's by arbitrary amounts, the one changing its l by ∂, the other changing its l by $\epsilon \pm 1$ ($\partial + \epsilon =$ even). Again the values $+1$, -1 for ∂ and ϵ will be more probable. Thus,

$$\psi^1(n_1, l_1; \cdots u_f, l_f) \to \psi^0(n_1', l_1 + \partial; n_2', l_2 + \epsilon \pm 1; n_3, l_3; \cdots n_f, l_f)$$

Case a (together with case c) if we choose ∂ and ϵ equal to ± 1 gives the well-known Heisenberg selection rule[10] for a two electron jump. All cases verify the Laporte rule.

5. Qualitative Remarks on Intensities of Many-Electron Transitions

5. Though it is difficult to give quantitive statements about the intensities of the two or more electron jumps, we can tell in which cases we can expect them to be strong. At the outset we can state that the three-electron transitions will be less probable, since an atom with three excited electrons is in a very high and improbable energy state, often corresponding to an energy higher than that of the ionized atom. The coefficients with which $E(I^a)$ occurs in the electrostatic expansion of $E(I)$ are given by,

$$\int \bar{\psi}^0(n_1^a, l_1^a; n_2^a, l_2^a; \cdots n_f^a, l_f^a) \frac{l^2}{r_{FG}} \psi^0(n_1, l_1; n_2, l_2; \cdots n_f l_f) d\tau$$

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[10] W. Heisenberg, Zeits. f. Physik. **32,** 841 (1925).

The superscript, a, is used to denote the quantum numbers of the a^{th} eigenfunction occurring in the first expansion.

One of the conditions that the coefficients be large is that the levels $E(I)$ and $E(I^a)$ lie near together. This is a necessary but not a sufficient condition. For even though two states may lie close together they will only disturb each other when the quantum numbers obey the demands of (a) and (b) of section 3. We may say that the coefficients will be larger or smaller according to (c) of section 3.

The results obtained in Section 4 can be given the following interpretation. In order that a many electron transition between a state $E(I)$ and a state $E(II)$ be possible, it is necessary that there exist a state $E(I^a)$ which occurs in the first order expansion of $E(I)$ and which has the property that there can be a one electron transition between $E(I^a)$ and $E(II)$. The larger the coefficient and the stronger the one electron transition is, the more probable it will be to actually observe the many electron transition.

6. NOTES

Note A.

The expression (2.2) written out completely is, if we take the first of (3:1) as an example,

$$\sum_{\substack{\alpha k \beta j \\ F}} \int d\tau \left[P_\alpha p_{\alpha k} \psi_1(m_1{}^k/x_{\mathrm{I}}) \cdots \psi_f(m_f{}^k/x_f)\right] r_F \sin\theta_F e^{i\phi_F}$$
$$\left[P_\beta q_{\beta j} \psi_{1'}(m_{1'}{}^j/x_{\mathrm{I}}) \cdots \psi_{f'}(m_{f'}{}^j/x_F)\right]$$

Here:

1. $m_1{}^k, \cdots, m_f{}^k$ are the m's occurring in the k^{th} combination giving $\Sigma m = M$

2. $m_{1'}{}^j, \cdots, m_{f'}{}^j$ are the m's occurring in the j^{th} combination giving $\Sigma m' = M'$. Primes denote quantum numbers of the final state.

3. The subscripts of the ψ's stand for the n, l of the eigenfunctions.

4. P_α stands for the α^{th} permutation (of the coordinates) of each combination of the initial state.

5. P_β stands for the β^{th} permutation (of the coordinates) of each combination of the final state.

6. It must be remembered that $m_1{}^k = m_{l_1}{}^k + m_{s_1}{}^k$;

7. $p_{\alpha k}$ and $q_{\beta j}$ are the coefficients of each product of ψ's in the linear combinations forming stabilized eigenfunction, ψ^0

Fix all the summation indices except j and let us look at the first term of the sum on F, namely, $r_I \sin\theta_I e^{i\phi_I}$. The integral vanishes unless $m_{s_1}{}^j = m_{s_1}{}^k$; $m_{l_1}{}^j + 1 = m_{l_1}{}^k$; $l_1' = l_1 \pm 1$; $\psi_{2'} = \psi_2$; $\cdots$, $\psi_{f'} = \psi_f$. With these fixed conditions all the other integrals of the sums over F and j vanish either because of the ϕ or the θ part of the eigenfunctions. It is obvious that instead of starting with $r_I \sin\theta_I e^{i\phi_I}$ we might have started with any $r_F \sin\theta_F{}^{i\phi_F}$ and the result would have been the same.

Similar reasoning will show that the integral is zero unless the permutation β is the same as α (for the sake of clearness the integral as written has been taken for the case $\alpha=\beta$). For each k one will have for each term the same conditions $l_1'=l_1\pm 1$; $\psi_{2'}=\psi_2$; $\cdots$, $\psi_{f'}=\psi_f$. Thus the 5-fold sum reduces to a 2-fold sum over the permutations α and the combinations k

$$\sum_{\alpha k} P_\alpha\, p_{\alpha k}\, q_{\alpha k} \int d\tau \bar{\psi}_{n_1 l_1}(m_1{}^k/x_\alpha) r_\alpha \sin\theta_\alpha e^{i\phi_\alpha} \psi_{n_1' l_1 \pm 1}(m_1{}^k - 1/x_\alpha).$$

The calculations show there is no restriction on $n_1'-n$. Similar computations show that the rule $l_i'=l_i\pm 1$ is the same for the cases (3:2) and (3:3).

Note B.

The perturbed part of the eigenfunction due to the spin-orbit interaction will now be written more fully,

$$\lambda \sum_a{}' c_a \psi^0(n_1{}^a, l_1{}^a; \cdots n_f{}^a, l_f{}^a)$$

$$\equiv \lambda \sum_a{}' c_a \left(\sum_{\beta t} q_{\beta t} \psi_{1a}(m_{1a}{}^t/x_{\mathrm{I}}) \cdots \psi_{fa}(m_{fa}{}^t/x_F) \right).$$

If one carries out the spin-orbit perturbation the coefficients of the λ part of the eigenfunction are given by,

$$c_a = \sum_{\substack{\alpha\beta k t\\ F}}{}' P_\alpha P_\beta p_{\alpha k} q_{\beta t} \frac{\displaystyle\int d\tau \left[\psi_{1a}(m_{1a}{}^t/x_{\mathrm{I}}) \cdots \psi_{fa}(m_{fa}{}^t/x_p)\right] \frac{l_F \cdot s_F}{r_F{}^3} \left[\psi_1(m_1{}^k/x_{\mathrm{I}}) \cdots \psi_f(m_F{}^k/x_F)\right]}{E_a - E}$$

Here

1. c_a stands for the coefficient occurring with the a^{th} set of n's and l's in the first order expansion. The bracket under the integral to the right of $l_F \cdot s_F/r_F{}^3$ is the given unperturbed eigenfunction, and hence does not need a running subscript with it's ψ's.

2. $m_{1a}{}^t, \cdots, m_{fa}{}^t$ are the m's occurring in the t^{th} combination of this product (state), giving a definite $\Sigma m_a = M_a$

3. P_β stands for the β^{th} permutation over the coordinates of this combination.

4. $m_1{}^k, \cdots, m_f{}^k$ are the m's occurring in the k^{th} combination of the unperturbed state giving a definite $\Sigma m = M$

5. P_α stands for the α^{th} permutation over the coordinates of this combination.

6. As given the states are for the $\alpha=1$ and $\beta=1$ permutations.

Let us fix our attention on $l_I \cdot s_I/r_I{}^3$. This operator does not work on $\psi_2, \cdots, \psi_f$. Thus the integral vanishes unless $\psi_{2a}=\psi_2, \cdots, \psi_{fa}=\psi_f$. We are left with the one-electron integrals

$$\sum_{\alpha} P_{\alpha} p_{\alpha k} q_{\alpha t} \frac{\int d\tau \bar{\psi}_{1a}(m_{1a}{}^{t}/x_{\alpha}) \dfrac{l_{\alpha} \cdot s_{\alpha}}{r_{\alpha}{}^{3}} \psi_{1}(m_{1}{}^{k}/x_{\alpha})}{E_{a} - E}$$

which are easily shown to vanish unless $m_{1a}{}^{t} = m_{1}{}^{k}$, $l_{1a} = l_{1}$. (In passing it might be mentioned that this demonstrates the fact that the Σm occurring in the perturbed terms, as well as in the unperturbed terms, must be the same.) One gets the same conditions starting with any other $l_{F} \cdot S_{F}/r_{F}{}^{3}$. n_{1a} may or may not be different from n_{1}. Let $n_{1a} = n_{1}$. With this condition and the fixed conditions $l_{1a} = l_{1}$; $\psi_{2a} = \psi_{2}$; $\cdots$, $\psi_{fa} = \psi_{f}$, the integrations over the other $l_{F} \cdot S_{F}/r_{F}{}^{3}$ will *not* vanish. This is the case mentioned in footnote 4. Although in this paper we are not interested in this case, for it provides only for one-electron jumps, it indicated at least the cause for the anomalies in the intensities of one-electron transitions; this is so because we see here that the coefficient of this first order term will be large, for in general the energy separations between multiplets of the same configuration (the case we have here) will be smaller than the energy separations between multiplets of different configurations.

It also must be mentioned that this case can occur only for extreme Russell-Saunders coupling. For extreme (*jj*) coupling, for example neon, one of the *n*'s must be different.

With $n_{1a} \neq n_{1}$ and the other fixed conditions the integrations over the other $l_{F} \cdot s_{F}/r_{F}{}^{3}$ vanish. Thus, the conditions for the non-vanishing of the coefficients are the same as in the case $n_{1a} = n_{1}$, but this time the coefficients will be much smaller.

Note C₁.

The perturbed part of the eigenfunction due to the electrostatic interaction will now be written more fully

$$\mu \sum_{b}{}'' d_{b} \psi^{0}(n_{1}{}^{b}, l_{1j}{}^{b} \cdots n_{f}{}^{b}, l_{f}{}^{b})$$

$$\equiv \mu \sum_{b}{}'' d_{b} \Big(\sum_{\gamma r} P_{\gamma} u_{\gamma r} \psi_{1b}(m_{1b}{}^{r}/x_{\mathrm{I}}) \cdots \psi_{fb}(m_{fb}{}^{r}/x_{F}) \Big).$$

If one carries out the electrostatic perturbation the coefficients of the μ part of the eigenfunction are given by

$$d_{b} = \sum_{\substack{\alpha\gamma kr \\ FG}}{}'' P_{\alpha} P_{\beta} p_{\alpha k} u_{\gamma r} \frac{\int d\tau \overline{[\psi_{1a}(m_{1a}{}^{2}/x_{\mathrm{I}}) \cdots \psi_{fa}(m_{fa}{}^{r}/x_{F})]} \dfrac{e^{2}}{r_{FG}} [\psi_{1}(m_{1}{}^{k}/x_{\mathrm{I}}) \cdots \psi_{f}(m_{f}{}^{k}/x_{F})]}{E_{b} - E}.$$

The explanation of the symbols is the same as that given in note B.

Let us fix our attention on $e^{2}/r_{I\,II}$. With the given permutation the integral vanishes unless $\psi_{3b} = \psi_{3}$, $\cdots$, $\psi_{fb} = \psi_{f}$. With these fixed conditions the integrations over all the other e^2/r_{FG} give zero. Further one sees that the integral is zero unless $\alpha=\beta$. It is obvious that starting with any other e^2/r_{FG} we get the same results, namely, that only such coefficients occur for which two and no more than two of the n's and l's of the terms of the sum may be different from two of the n's and l's of the unperturbed eigenfunction. The summation reduces to

$$\sum_{\alpha kr} P_{\alpha} p_{\alpha k} u_{\alpha r} \frac{\displaystyle\int d\tau \psi_{1b}(m_{1a}{}^r/x_{\mathrm{I}})\psi_{2b}(m_{2a}{}^r/x_{\mathrm{II}}) \frac{e^2}{r_{\mathrm{I\,II}}} \psi_1(m_1{}^k/x_{\mathrm{I}})\psi_2(m_2{}^k/x_{\mathrm{II}})}{E_b - E}.$$

Note C$_2$.

Now puting in the value

$$\frac{1}{r_{\mathrm{I\,II}}} = \sum_{im} \frac{(i-|m|)!}{(i+|m|)!} \frac{r(I)^i}{r(II)^{i+1}} P_i{}^{|m|}(\cos\theta_{\mathrm{I}}) P_i{}^{|m|}(\cos\theta_{\mathrm{II}}) e^{im(\phi_{\mathrm{I}}-\phi_{\mathrm{II}})}$$

where $r(I)$, $r(II)$ are the radial distances of the two electrons, $(r(I)<r(II)\ )$, the non-radial part of the integral may be written, (dropping the denominator E_b-E)

$$\begin{aligned}\sum_{im}\ \sum_{\alpha kr} P_{\alpha} p_{\alpha k} u_{\alpha r} \int & [P_{l_{(1b)}}{}^{m_{l(1b)}{}^r}(\theta_{\mathrm{I}}) P_{l_{(1)}}{}^{m_{l(1)}{}^k}(\theta_{\mathrm{I}}) P_i{}^{|m|}(\theta_{\mathrm{I}})] \\ & [P_{l_{(2b)}}{}^{m_{l(2b)}{}^r}(\theta_{\mathrm{II}}) P_{l_{(2)}}{}^{m_{l(2)}{}^k}(\theta_{\mathrm{II}}) P_i{}^{|m|}(\theta_{\mathrm{II}})] d(\cos\theta_{\mathrm{I}}) d(\cos\theta_{\mathrm{II}}) \\ \times & \int [S(m_{s_{(1b)}}{}^r) S(m_{s_{(1)}}{}^k)][S(m_{s_{(2b)}}{}^r) S(m_{s_{(2)}}{}^k)] \\ \times & \int e^{-i(m_{l(1b)}{}^r - m_{l(1)}{}^k - |m|)\phi_{\mathrm{I}}} \cdot e^{-i(m_{l(2b)}{}^r - m_{l(2)}{}^k + m)\phi_{\mathrm{II}}} d\phi_{\mathrm{I}} d\phi_{\mathrm{II}}.\end{aligned}$$

One sees first that the integral is zero unless

$$m_{s_{(1b)}}{}^r = m_{s_{(1)}}{}^k; \qquad m_{s_{(2b)}}{}^r = m_{s_2}{}^k$$

$$m_{l_{(1b)}}{}^r - m_{l_{(\mathrm{I})}}{}^k = |m| = m_{l_{(2)}}{}^k - m_{l_{(2b)}}{}^r \quad \therefore \quad m_{l_{(1)}}{}^k + m_{l_{(2)}}{}^k = m_{l_{(1b)}}{}^r + m_{l_{(2b)}}{}^r$$

With the spin-orbit interaction we saw that only those terms might enter in the sum with $\Sigma m=$constant. Here the limitation is stricter, namely only those terms enter into the sum that have common Σm_l and Σm_s.

Now the important thing to notice is that the same $P_i{}^{|m|}$ comes in with both angles. Each of the product of the two integrals will vanish unless the sums of the three lower indices be an even number.[11] This fact in conjuction with the statement just preceding requires that if $\delta=|l_{1b}-l_1|$ and $\epsilon=|l_{2b}-l_2|$ that $\delta+\epsilon$ be even. This verifies the Laporte rule after one considers transitions.

Another important property of the integral of a product of three spherical harmonics, given by Gaunt, is that it vanishes unless the absolute value of the difference of any two of the subscripts is equal to or less than the third.

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[11] Gaunt, Cambridge Phil. Trans. 1929.

Note C_3.

For the first term of the expansion of $1/r_{I\,II}$, $i=0$, the non-radial part of the integral reduces to

$$\int [P_{l_{(1b)}}{}^{m}(\theta_{\mathrm{I}})P_{l_{(1)}}{}^{m}(\theta_{\mathrm{I}})][P_{l_{(2b)}}{}^{m}(\theta_{\mathrm{II}})P_{l_{(2)}}{}^{m}(\theta_{\mathrm{II}})]d(\cos\theta_{\mathrm{I}})d(\cos\theta_{\mathrm{II}}).$$

(We can now use the simple m, instead of $m_1{}^k$ etc., and leave off the summation sign since it does not affect the argument.)

This vanishes unless $l_{(b)}=l_{(1)}$; $l_{(2b)}=l_{(2)}$. The term $r(I)^i/r(II)^{i+1}$ reduces to $1/r(II)$. Thus in addition to the conditions for the l's and the initial conditions $\psi_{3b}=\psi_3; \cdots, \psi_{fb}=\psi_f$, in order that the radial part of the integral is not zero, one pair of n's must be equal. If both pair are equal we have the same situation mentioned in Note B, about one electron-jumps.

Note C_4.

The expansion of $1/r_{I\,II}$ decreases fairly rapidly because of the presence of the factor $(i-|m|)!/(i+|m|)!$. If we go to the second term of the expansion $i=1$, this approximation is sufficient to give the Heisenberg selection rule. The two possible integrals are

$$\int [P_{l_{(1b)}}{}^{m}(\theta_{\mathrm{I}})P_{l_{(1)}}{}^{m}(\theta_{\mathrm{I}})\cos\theta_{\mathrm{I}}][P_{l_{(2b)}}{}^{m}(\theta_{\mathrm{II}})P_{l_{(2)}}{}^{m}(\theta_{\mathrm{II}})\cos\theta_{\mathrm{II}}]d(\cos\theta_{\mathrm{I}})d(\cos\theta_{\mathrm{II}})$$

$$\int [P_{l_{(1b)}}{}^{m}(\theta_{\mathrm{I}})P_{l_{(1)}}{}^{m-1}(\theta_{\mathrm{I}})\sin\theta_{\mathrm{I}}][P_{l_{(2b)}}{}^{m}(\theta_{\mathrm{II}})P_{l_{(2)}}{}^{m-1}(\theta_{\mathrm{II}})\sin\theta_{\mathrm{II}}]d(\cos\theta_{\mathrm{I}})d(\cos\theta_{\mathrm{II}})$$

which do not vanish under the same conditions, namely, $l_{1(b)}=l_{(1)}\pm 1$, $l_{(2b)}=l_{(2)}\pm 1$. The n's are arbitrary in the radial part. As explained in the body of the paper this condition gives the Heisenberg rule, and in addition, the possibility of three and (up to this approximation) not more than three-electron transitions.