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THE THEORY OF COMPLEX SPECTRA

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Abstract

Extending the paper of Slater (Phys. Rev. **34**, 1293, 1929) on complex spectra, it is pointed out that assignment of definite electron configurations to spectral terms is an approximate procedure and only has meaning when the multiplet systems of the several configurations are widely separated. The effect of including spin terms is sketched. Non-diagonal matrix elements for the N-electron problem are reduced to corresponding elements for the 2-electron problem, as Slater did for the diagonal elements. Two-electron jumps occur because of the fact that spectral terms may not be precisely labelled by means of electron configurations.

IN A paper of this same name, Slater[1] has given a direct treatment of the application of the first order perturbation theory to the central field approximation to the atom model. He neglects spin forces in the Hamiltonian and so his results correspond to pure Russell-Saunders coupling of the angular momentum vectors, all intervals inside of the multiplets being zero. The electrostatic interaction gives the classification into multiplet levels and the calculations provide definite predictions concerning the intervals between the several multiplets which belong to the same electron configuration.

These intervals are found to be expressible in terms of certain double integrals over the radial factors of the eigen-functions of an electron moving in the central field which is made the starting-point of the perturbation calculation. For a configuration which gives n multiplets, there are thus $(n-1)$ intervals. Slater's first-order calculation expresses these $(n-1)$ intervals in terms of a fewer number (say, m) of integrals, usually, so even if one regards all of the integrals as independently adjustable, the theory predicts certain relations between the intervals. One may choose values for the m integrals as if they were independent so as to get the best fit possible in order to obtain a kind of test of Slater's results. Such a test of the results can be made comparatively simply without going into the more difficult question of determination of the best central field and the radial eigen-functions associated with it. If a good representation of the data is obtained on treating the m integrals as independent, the question still remains whether the m values assigned are compatible with the central field eigen-functions in view of the fact that they are not really independent. However, if a good representation cannot be obtained even by treating the integrals as independent, it certainly will not be improved when allowance is made for the fact that they are not independent

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[1] Slater, Phys. Rev. **34**, 1293 (1929).

With such considerations in mind an attempt was made to apply Slater's results to a larger number of cases than he has treated in the examples at the end of his paper. It quickly became apparent that the intervals between the multiplets usually disagree badly with the first-order calculations. It is therefore necessary for an adequate theory of complex spectra to extend the calculations to a higher degree of approximation. Some results in that direction are the subject of this paper.

1. **Definitions and Notation.** The starting point, as with Slater, is a model of the atom in which N electrons each move, without influencing each other, in the same central field which has the potential energy, $-U(r)$. Only eigen-functions that are anti-symmetric in all pairs of electrons are used and so an eigen-function is specified by giving a *complete set* of $4N$ quantum numbers. A complete set consists of N *individual sets* which are called (n, l, m, k) these being the (n, l, m_l, m_s) of Slater. Each electron has four coordinates (x, y, z, s). The first three give its position and the fourth the z-component of spin angular momentum. For short the Greek letters, $\alpha, \beta, \gamma, \delta \cdots$ are written for separate individual sets. Also the capitals $A, B, C, D \cdots$ are written as abbreviations for different complete sets.

By Pauli's exclusion principle all individual sets in a complete set must be different, and two complete sets are not considered as different if they differ merely in regard to the order of listing of the same N individual sets. Nevertheless for definiteness a definite order of writing the individual sets in a complete set is adopted and adhered to during the calculations.

Since anti-symmetric eigen-functions are used there is no one-to-one correspondence between individual electrons and individual sets of quantum numbers. This means that an expression commonly used in spectroscopy such as "the excited electron is in a $4f$ state" refers to the presence of a $4f$ individual set in the complete set of quantum numbers. The electron configuration of a given complete set means the list of n, l values of the individual sets. Thus there are generally a number of different complete sets belonging to each configuration. Since the energy of a particle in a central field depends only on n and l, all of the complete sets belonging to a certain configuration have the same energy in the zero$^{\text{th}}$ approximation from which the start is made.

For the one-electron eigen-function having the individual set α, written as a function of the first electron's coordinates, the notation $u_\alpha(1)$ is used, replacing Slater's $u(n_1/x_1)$. ψ is defined as

$$\psi = u_\alpha(1) \cdot u_\beta(2) \cdot u_\gamma(3) \cdots u_\xi(N)$$

so that the normalized eigen-function for the complete set A is

$$\Psi_A = (N!)^{-1/2} \sum_P (-1)^p P\psi$$

in which P stands for a permutation of the indices $1, 2, 3 \cdots N$ in ψ relative to the $\alpha, \beta, \gamma \cdots \xi$. The summation extends over all $N!$ such permutations and p has the parity of P.

For the matrix component of any quantity as H which connects the states having the complete sets A and B, the Dirac notation $(A\,|H|\,B)$ is used, so that

$$(A \mid H \mid B) = \int \bar{\Psi}_A H \Psi_B$$

where $\int$ means integration over the $3N$ position coordinates and summation over the N spin coordinates.

2. **Formulation of the energy level problem.** The starting point is an exact solution of the quantum mechanical problem for a fictitious atom whose Hamiltonian is E where

$$E = \sum_1 \left[\frac{1}{2\mu}(p_{x1}^2 + p_{y1}^2 + p_{z1}^2) - U(r_1) \right] \tag{2.1}$$

where Σ_1 means that the same functional form is to be written down successively as depending on the coordinates of all N electrons and the results added together.

A form of the Hamiltonian for real atoms that is much nearer to the truth is

$$H = \sum_1 \left[\frac{1}{2\mu}(p_{x1}^2 + p_{y1}^2 + p_{z1}^2) - \frac{ze^2}{r_1} + V(r_1) M_1 \cdot s_1 \right] + \frac{e^2}{2} \sum_{1,2} \frac{1}{r_{12}} \tag{2.2}$$

In this the terms $V(r_1)M_1 \cdot s_1$ represent the energy of interaction of each electron's spin with its own orbital angular momentum. $V(r_1)$ is to be chosen in some way along lines of the semi-empirical discussions of the "screening for the spin doublets" of other workers. The question will not be discussed further in this paper. $M \cdot s$ is the scalar product of orbital and spin angular momentum for an electron. $\Sigma_{1,2}$ means a summation over all pairs of electrons, the two indices varying independently so that each pair is counted twice. Since the operators for E and H do not commute with each other, the matrix for H will not be diagonal in terms of the representation that is based on the eigen-functions of E. The problem of finding the energy levels for H is that of finding a transformation to the diagonal form for the matrix for H.

How the function $U(r)$ is to be chosen will not be discussed here. An approximate theoretical treatment, such as that of Thomas and Fermi, or a semi-empirical method of the sort studied especially by Hartree may be used. Slater studied the Hamiltonian (2.2) with omission of the spin term. Houston,[2] Bartlett,[3] and Gaunt,[4] have considered special cases of (2.1) counting the spin term and Goudsmit[5] has recently extended their results by a clever device.

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[2] Houston, Phys. Rev. **33**, 297 (1929).

[3] Bartlett, Phys. Rev. **35**, 229 (1930).

[4] Gaunt, Proc. Roy. Soc. **A122**, 513 (1929).

[5] Goudsmit, Phys. Rev. **35**, 1325 (1930).

When the spin term is omitted the Hamiltonian H commutes with both the sum of the z-components of orbital angular momentum, and the sum of the z-components of spin angular momentum. Therefore H has no matrix components connecting states of E for which either of these sums is different. In terms of the quantum numbers introduced in §1 the quantities are Σm and Σk, the sums being over all the individual sets belonging to a complete set. Slater makes very good use of these results to calculate the energies of all the multiplets arising from a configuration (except for those configurations in which more than one multiplet of the same kind appears) without having to calculate any non-diagonal matrix components.

If the spin term is not omitted one still has the result that H commutes with the total sum of the z-components of both orbital and spin angular momentum although it no longer commutes with each sum separately. Therefore, even with spin counted there will be no matrix components of H connecting states for which the values of $\Sigma(m+k)$ differ.

There is another important property of the Hamiltonian which arises from its isotropy with regard to different orientations of the coordinate axes. The isotropy means that there is still a degeneracy, that of space quantization, associated with the Hamiltonian, so that the degeneracy of E is not completely removed by the inclusion of the spin and electrostatic repulsion terms which are the essence of the transformation from E a diagonal matrix to H a diagonal matrix. With each eigen-value of H can be associated a maximum value of $\Sigma(m+k)$ which is represented among the eigen-functions belonging to that eigen-value. This number is the quantum number J of that energy level. The isotropy then brings with it the result that there are other eigen-functions for which $\Sigma(m+k)$ has the values $J-1$, $J-2 \cdots$, $-J$ all of which have the same eigen-value. The proof of this is best obtained by appeal to group theory.

If one uses the perturbation theory to find approximately the transformation from E diagonal to H diagonal, by treating $(H-E)$ as a perturbation, the success of the calculation in the first-order requires that the eigen-values of H which "grow out of" a particular eigen-value of E remain close together compared with the distance of the particular eigen-values of E from its nearest neighbor in the spectrum of E. This is a well known property of the perturbation theory and shows itself in many particular instances. Perhaps the Paschen-Back effect in the anomalous Zeeman effect is the best known of these. In it the effect of a uniform magnetic field on an atomic energy level is required. The first-order calculation is correct only if the spread of the energy levels growing out of the unperturbed level is small compared to the distance from the unperturbed level to its nearest neighbor in the unperturbed scheme. If this condition is not fulfilled then the second order perturbation becomes important. An important second-order correction implies that an important alteration of the eigen-function has taken place so that, when it is expanded in terms of the eigen-functions of E, it begins to have an important component of the eigen-function of the neighboring level of E in addition to the eigen-function of the level from which it grew.

Therefore as the second-order correction becomes more important the quantum numbers which were appropriate to labelling the different eigenvalues of E become less and less appropriate for the labelling of the eigenvalues of H. They cease to be "good quantum numbers" to use a curiously apt expression introduced by Mulliken[6] in a discussion of the correlation of atomic energy levels with those of diatomic molecules.

3. Validity of configuration assignments. All discussions of complex spectra have hitherto been based on the idea that an electron configuration could be assigned uniquely to each energy level. That this procedure is only of approximate validity is seen at once from the foregoing discussion. The criterion can be so formulated: *The assignment of a definite electron configuration to a group of multiplets is only exact insofar as the spread of the levels belonging to one configuration is small compared to the distance (on the energy level diagram) of the spread of levels belonging to the neighboring configurations.*

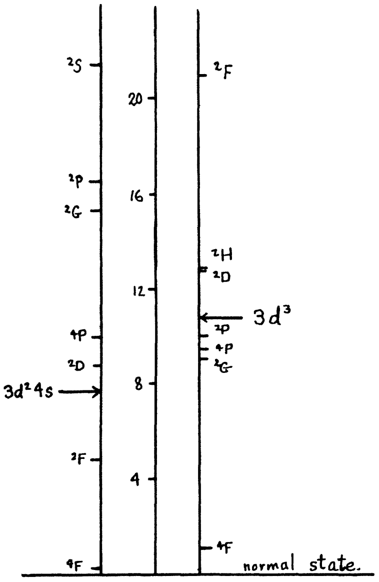

Fig. 1. *The two lowest configurations in Ti II.* Theory predicts another ^2D for $(3d)^3$ which has not been found; the arrow shows the center of gravity of the known terms, which is therefore not the exact center of gravity of the whole configuration. The center scale is in thousands of cm^{-1}.

It is evident that this criterion for the case of the electron configuration quantum numbers is of the same form as the well known criterion for deciding between "weak" and "strong" magnetic fields in the Paschen-Back effect.

The importance of raising this point lies in the fact that complex spectra have already been analyzed in which the criterion for definite assignments

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[6] Mulliken, Reviews of Mod. Phys. **2**, 60 (1930).

of electron configurations is not fulfilled. A noteworthy instance[7] is that of Ti II as analyzed by Russell.[8]

In Fig. 1 are plotted the levels corresponding to the two lowest configurations in Ti II as assigned by Russell. The arrows in each column give the centers of gravity of all the terms in the column, weights being assigned according to their values of $(2J+1)$.

It is evident that here, if anywhere, one may expect an appreciable effect of what may be suitably called interaction of neighboring electron configurations. Except for the overlapping of $d^3\ {}^2H$ and ${}^2D$ and of $d^3\ {}^2P$ and ${}^4P$ the distance between multiplets is large compared to intervals inside the multiplets, so that the criterion for Russell-Saunders coupling is fulfilled. The ${}^2H$ and ${}^2D$ can show no interaction, though, since they have no common value of J, whereas it is expected that the nearness of ${}^2P$ to ${}^4P$ will disturb the intervals. This is in fact the case, the ratio of the observed intervals being 3.82 against a theoretical (Landé) value of 1.67.

Perhaps the best way to present the situation is by reference to Slater's diagrams (loc. cit. p. 1301) of the energy matrix. Referring to his Fig. 2, one may suppose that the upper double-shaded square is the matrix for the different complete sets belonging to $(3d)^2 4s$ and the next double-shaded square is the similar matrix for complete sets belonging to $(3d)^3$. Slater says that the terms in the singly-shaded rectangles (these are the matrix components connecting the complete sets in $(3d)^2 4s$ with those in $(3d)^3$) are negligible. This is often the case but the point that is made here is that they are not negligible in a case where the distance between the centers of gravity of the terms coming from the same configuration is small or comparable with the spread of the multiplets arising from the two configurations separately. In case the configurations overlap, as they do in the special instance of Ti II one needs to consider the larger square which includes the two doubly-shaded squares and the two singly-shaded rectangles that border them.

If one next makes use of the exact theorem that there are no matrix components connecting complete sets for which $\Sigma(m+k)$ differs the large square is considerably simplified. It can be rearranged so that complete sets belonging to either configuration but having the same $\Sigma(m+k)$ are in adjacent rows and columns and then the large square corresponding to the two configurations taken together will break up into a series of smaller squares. If one wishes further to neglect the spin terms, as Slater does, then these smaller squares may be broken up into still smaller ones since then both Σm and Σk separately have to be equal in the quantum numbers labelling rows and columns.

The actual procedure in applying the diagonal sum method will be illustrated in terms of d^2s and d^3 although the numerical application of the formulas to $(3d)^2 4s$ and $(3d)^3$ in Ti II will be reserved to a later paper. One has first to set up the scheme of complete sets of quantum numbers for each config-

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[7] I am indebted to my friend, Prof. J. E. Mack, for directing my attention to this case

[8] Russell, Astrophys. J. **66,** 283 (1927).

uration, just as Slater does. For example, Table I gives the quantum numbers for the (*dds*) configuration.

TABLE I. *Sets of quantum numbers for (dds) configuration.*

$\Sigma k=$	3/2 (+++)	1/2 (+−+)	(++−)
$\Sigma m=4$		(220)	
3	(210)	(210) (120)	(210)
2	(200)	(200) (020) (110)	(200)
1	(2–10) (100)	(2–10) (–120) (010) (100)	(2–10) (100)
0	(2–20) (1–10)	(2–20) (–220) (1–10) (–110) (000)	(2–20) (1–10)

In this table are listed the *m* values that may be associated with the sets of spin (*k*) values that head the columns. The corresponding table for d^3 is Table II.

TABLE II. *Sets of quantum numbers for (ddd) configuration.*

$\Sigma k=$	3/2 (+++)	1/2 (++−)
$\Sigma m=6$		
5		(212)
4		(211) (202)
3	(210)	(210) (201) (2–12) (102)
2	(21–1)	(21–1) (200) (2–11) (2–22) (101) (1–12)
1	(21–2) (20–1)	(21–2) (20–1) (2–10) (2–21) (100) (1–11) (1–22) (0–12)
0	(20–2) (10–1)	(20–2) (2–1–1) (2–20) (10–1) (1–10) (1–21) (0–11) (0–22)

In these tables it is not necessary to list the quantum numbers for negative values of Σm and Σk as these do not give additional information.

The multiplet schemes corresponding to the two configurations are given superposed in the Table III, the first line in each cell being the contribution from d^2s and the second that from d^3.

TABLE III. *Multiplets for d^2s and d^3.*

$\Sigma k=$	3/2		1/2								
$\Sigma m=6$											
5			^2H								
4				^2G							
			^2H	^2G							
3	^4F			^2G	^2F					^4F	
	^4F		^2H	^5G	^2F					^4F	
2	^4F			^2G	^2F	^2D				^4F	
	^4F		^2H	^2G	^2F	^2D	^2D			^4F	
1	^4F	^4P		^2G	^2F	^2D		^2P		^4F	^4P
	^4F	^4P	^2H	^2G	^2F	^2D	^2D	^2P		^4F	^4P
0	^4F	^4P		^2G	^2F	^2D		^2P	^2S	^4F	^4P
	^4F	^4P	^2H	^2G	^2F	^2D	^2D	^2P		^4F	^4P

Now if the interaction between configurations can be neglected the diagonal sum method gives a value for the sum of the energies of all the multiplets lying on each line separately in each cell. But if the interaction is important then the diagonal sums must be taken simply cell by cell, this gives only half as many equations and so the power of the diagonal sum method is greatly diminished (just as it is greatly diminished when spin is not neglected). Neglecting the interaction the diagonal sum method in this case is capable of giving the energy of each multiplet except that it can only give the arithmetic mean of the two ${}^2D$'s which arise from d^3. Allowing for the interaction it gives much less: now the ${}^2H$ and the ${}^2S$ are the only ones given directly, also given are the arithmetic means of the two ${}^4P$'s the two ${}^4F$'s, the three ${}^2D$'s, the two ${}^2P$'s, the two ${}^2F$'s and the two ${}^2G$'s.

In order to get the actual separation of the terms of similar multiplet character whose sums only are given one needs to have the non-diagonal elements of the energy matrix.

With these at hand one can set up the secular determinants for each cell and get the roots of the secular equations. This looks formidable at first sight because the determinants are of the order equal to the number of multiplets in each cell. But the diagonal sum method can be used to depress the order of the secular equations so that one needs only to solve a quadratic where there are two multiplets of the same kind, a cubic if there are three, and so on.

Perhaps it is helpful here to point out how the diagonal sum method works when spin is not neglected. In that case one can not write an equation that the sum of the terms in each cell of the Σm, Σk diagram is equal to the sum of the corresponding diagonal elements of the energy matrix. Also one needs a complete table covering the negative values of Σk as well as the positive. For simplicity the argument will be presented in terms of the *sp* configuration, which has already been fully treated by Houston.[9] One has for $\Sigma m, \Sigma k$:

sp

$\Sigma k=$	$1\ (++)$	$0\ (+-)\ (-+)$	$-1\ (--)$
$\Sigma m=1$	(01)	(01) (01)	(01)
0	(00)	(00) (00)	(00)
-1	(0–1)	(0–1) (0–1)	(0–1)

Arranging by values of $\Sigma(m+k)$ one sees that the values of $\Sigma(m+k)$ and the number of complete sets by which each value is realized is

$\Sigma(m+k)$	Realizations	Terms represented			
2	1	${}^3P_2$			
1	3	${}^3P_2$	${}^3P_1$		${}^1P_1$
0	4	${}^3P_2$	${}^3P_1$	${}^3P_0$	${}^1P_1$
-1	3	${}^3P_2$	${}^3P_1$		${}^1P_1$
-2	1	${}^3P_2$			

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[9] Houston, Phys. Rev. **33**, 297 (1929).

The third column gives the energy levels whose sum is given by applying the diagonal sum method to all complete sets which have the same value of $\Sigma(m+k)$. Just as the diagonal sums, without spin, fails to give the separation between two multiplets of the same kind, so here with spin it fails to give the separation between two levels having the same J value. To get the separation one would need to solve a quadratic equation, which is what Houston did. And generally, the diagonal sums alone will give simply the arithmetic mean of all the terms in the configuration that have the same J value. To get them separately one has to use the non-diagonal elements and solve an algebraic equation whose degree is equal to the number of times the particular J value occurs. This statement is the starting point of Goudsmit's recent work on the transition from Russell-Saunders to *jj*-coupling.

Of course it is evident that if perturbations by an external magnetic field are included the method of diagonal sums gives the derivation of the g-sum rules that play such an important role in the theory of the anomalous Zeeman effect. But similarly if one wants to find the individual g's for n terms of the same J value then an algebraic equation of the n^{th} degree has to be solved, and this is true whether the n terms come from the same configuration or not.

4. Non-diagonal matrix elements. The diagonal sum method works only with the diagonal matrix elements of the energy and is quite powerful. It gives the energies of each multiplet belonging to a configuration if the interaction between configurations is neglected and if all multiplets are of a different kind. To go beyond this and find the separations between two multiplets of the same kind, or to allow for interaction of configurations and for other questions it is necessary to know the non-diagonal elements.

Two types of symmetrical function of the electron coordinates are of especial importance. One is of the form $F=\Sigma_1 f(1)$, that is, the sum of the same function of each one of the electron's coordinates occurring one at a time. The other is $G=\Sigma_{12}g(1,2)$, that is, the sum over all possible pairs of electrons, of a symmetrical function of the coordinates of both of them. Slater has carried out the calculation for the diagonal elements, the extension to the non-diagonal elements is very easy and almost exactly like Slater's work so only the results will be stated.

For a quantity of the type F, the matrix components, $(A\,|F|B)$, connecting states with the complete sets A and B are as follows:

(a) They vanish if B differs from A in regard to more than one individual set.

(b) If B differs from A solely in regard to one individual set then

$$(A\,|\,F\,|\,B) = \int_1 \bar{u}_\alpha(1)f(1)u_{\alpha'}(1)$$

where α and α' are the only individual sets of A and B respectively which are not equal.

(c) The diagonal element $(A\,|F|A)$ is worked out by Slater. Its value is

$$(A\,|\,F\,|\,A) = \sum_{\alpha}\int_{1} \bar{u}_{\alpha}(1)f(1)u_{\alpha}(1)$$

where the sum extends over all the individual sets in the complete set A.

An immediate corollary of the results (a) and (b) is that if $f(1)$ is a quantity which is a diagonal matrix in the one-electron problem, then F is a diagonal matrix in the N-electron problem. This is perhaps the simplest way of proving that the total z-component of spin and the total z-component of orbital angular momentum are diagonal matrices in the representation used for this approach to the theory of complex spectra.

Similarly the matrix components, $(A\,|G|B)$, for a quantity of the type G can be reduced as follows:

(d) They vanish if B differs from A in regard to more than two individual sets.

(e) If B differs from A only in that two of its individual sets which one may call α', β' differ from the individual sets of A, called α, β, then

$$\begin{aligned}(A\,|\,G\,|\,B) = \Big[2\int_{1,2} & \bar{u}_{\alpha}(1)\bar{u}_{\beta}(2)g(1,\,2)u_{\alpha'}(1)u_{\beta'}(2) \\ -2\int_{1,2} & \bar{u}_{\alpha}(1)\bar{u}_{\beta}(2)g(1,\,2)u_{\beta'}(1)u_{\alpha'}(2)\Big].\end{aligned}$$

(f) If B differs from A only in that its individual set, α', differs from the individual set, α, in A then

$$\begin{aligned}(A\,|\,G\,|\,B) = 2\sum_{\beta}\Big[\int_{1,2} & \bar{u}_{\alpha}(1)\bar{u}_{\beta}(2)g(1,\,2)u_{\alpha'}(1)u_{\beta}(2) \\ -\int_{1,2} & \bar{u}_{\alpha}(1)\bar{u}_{\beta}(2)g(1,\,2)u_{\beta}(1)u_{\alpha'}(2)\Big]\end{aligned}$$

where Σ_{β} means a summation in which β runs over the $N-1$ individual sets that are common to A and B.

(g) The diagonal element $(A\,|G|A)$ is given by Slater. It is

$$\begin{aligned}(A\,|\,G\,|\,A) = \sum_{\alpha,\beta}\Big[\int_{1,2} & \bar{u}_{\alpha}(1)\bar{u}_{\beta}(2)g(1,\,2)u_{\alpha}(1)u_{\beta}(2) \\ -\int_{1,2} & \bar{u}_{\alpha}(1)\bar{u}_{\beta}(2)g(1,\,2)u_{\beta}(1)u_{\alpha}(2)\Big]\end{aligned}$$

the summation running over all pairs of individual sets.

These results show further simplifications for quantities that are independent of spin. For $u_{\alpha}(1)$ one has

$$u_{\alpha}\,(1) = v_{\alpha}\,(1)\,\delta\,(s_1,\,k_{\alpha})$$

where $v_{\alpha}(1)$ is a function of the position coordinates only. In the preceding formulas $\int_1$ means integration over the position coordinates and summation over the spin coordinate. If $f(1)$ or $g(1,2)$ do not depend on spin the summation over s can be carried out at once. The results are:

$$\text{(b)}\quad (A\,|\,F\,|\,B) = \delta(k_\alpha, k_{\alpha'}) \int_1 \bar{v}_\alpha(1) f(1) v_{\alpha'}(1)$$

$$\text{(c)}\quad (A\,|\,F\,|\,A) = \sum_\alpha \int_1 \bar{v}_\alpha(1) f(1) v_\alpha(1)$$

$$\text{(e)}\quad (A\,|\,G\,|\,B) = 2\Big[\delta(k_\alpha, k_{\alpha'})\delta(k_\beta, k_{\beta'}) \int_{1,2} \bar{v}_\alpha(1)\bar{v}_\beta(2) g(1,2) v_{\alpha'}(1) v_{\beta'}(2) - \delta(k_\alpha, k_{\beta'})\delta(k_\beta, k_{\alpha'}) \int_{1,2} \bar{v}_\alpha(1)\bar{v}_\beta(2) g(1,2) v_{\beta'}(1) v_{\alpha'}(2)\Big]$$

$$\text{(f)}\quad (A\,|\,G\,|\,B) = 2\delta(k_\alpha, k_{\alpha'}) \sum_\beta \Big[\int_{1,2} \bar{v}_\alpha(1)\bar{v}_\beta(2) g(1,2) v_{\alpha'}(1) v_\beta(2) - \int_{1,2} \bar{v}_\alpha(1)\bar{v}_\beta(2) g(1,2) v_\beta(1) v_{\alpha'}(2)\Big].$$

$$\text{(g)}\quad (A\,|\,G\,|\,A) = \sum_{\alpha,\beta} \Big[\int_{1,2} \bar{v}_\alpha(1)\bar{v}_\beta(2) g(1,2) v_\alpha(1) v_\beta(2) - \delta(k_\alpha, k_\beta) \int_{1,2} \bar{v}_\alpha(1)\bar{v}_\beta(2) g(1,2) v_\beta(1) v_\alpha(2)\Big].$$

A consequence of the limitation (d) is that there is no first-order inteaction between two neighboring configurations that differ in regard to more than two electrons. This result is hardly likely to be of much importance for two configurations that differ in regard to as many as three electrons will, in general, lie in widely separated parts of the energy level diagram so the interaction would be negligible anyway.

This completes the reduction of the non-diagonal elements to integrations over the coordinates of only one or two electrons. If in particular $g(1,2)$ is of the form $1/r$ additional developments may be made in which $1/r_{12}$ is expanded in a series of spherical harmonics and so all the integrals can be expressed, as Slater does for the ones occurring in the diagonal elements, as a sum of certain integrals over the radial eigen-functions multiplied by coefficients that are certain integrals of spherical harmonics. The calculations involve some more general coefficients than Slater's a's and b's. Detailed developments of this part of the reduction will be reserved for a later paper.

5. Two-electron jumps. An immediate application of the results of the preceding section is to the question of "two-electron jumps." These are transitions between energy levels whose configurations differ in regard to two of the sets of nl values. Such transitions are usually weak compared to the more usual one-electron jumps. One may also have "zero-electron jumps," that is, transitions between terms arising from the same configuration. This is the usual way of stating the case, in which one speaks as though each term is uniquely associated with a single configuration of the central field approximation.

The interaction between a light wave whose vector potential is given by $A(x, y, z)$ and an atom consisting of N electrons is measured by a term in the Hamiltonian of the form

$$\sum_1 A(x_1, y_1, z_1) \cdot p_1$$

where p_1 is the momentum of the first electron. This form embraces quadrupole and all multipole radiations. The dipole radiation which is the first approximation is obtained by replacing $A(x, y, z)$ by its value at the center of the atom and writing

$$A(0, 0, 0) \cdot \sum_1 p_1$$

which is valid if the wave-length is great compared to the size of the atom so that A does not vary much over the size of the atom. Now even the exact interaction is of the form of the sum of the same operator function of the coordinates of each electron summed over each of the electrons. Therefore one sees that its matrix components connecting complete sets which differ in regard to more than one individual set vanish.

In other words, if assignment of electron configurations to energy levels were an exact procedure there would be no two-electron jumps. Thus the existence of two electron jumps is an indication of a break-down of exact configuration assignments.

This point is similar to the one that the existence of inter-system combinations, i.e. transitions between states of different multiplicities, is an indication of the break down of exact assignment of L and S values of the terms, i.e. break-down in the Russell-Saunders coupling scheme.

There is an interesting question of language involved here. If the expression "electron jump" is to be translated into quantum mechanics as meaning a change in an (nl) individual set in going from an initial state to a final state, then, strictly, only one-electron jumps occur. But the exact eigen-function of each energy level has in its make-up components belonging to several different configurations of the central field model, whereas it has been the custom to assign to the energy level one configuration which is presumed to be the one that has the largest component in the expansion of the exact eigen-function. One-electron jumps are the only ones really occurring but since the exact eigen-function has other configurations in it than the principal one from which it derives its configuration name, there will appear to be two-electron jumps when the transitions are described solely by reference to the single configuration name that is assigned to each level by the customary procedure. It is the same with inter-system combinations: the selection rule $\Delta S = 0$ is exact, but the actual energy levels have components in their eigen-functions corresponding to more than one value of S; then when one persists in labelling the terms simply with the value of S most strongly represented in the eigen-function he is confronted with apparent violations of this selection rule.

The break-down of exact configuration assignments also has important implications for the theory of relative intensity of spectral lines. Ornstein and Burger[10] have already shown that when inter-system combinations have appreciable intensity that they must be appropriately reckoned in the application of the intensity sum rules. This point is brought out clearly also in recent work by Harrison.[11] That is, the sum rules have to be applied to all the lines arising from transitions between all the terms of the initial and final configurations. Evidently all this has to be extended one step further for cases in which the interaction between two configurations is important. For simplicity suppose the initial state levels can be all given a fairly exact configuration assignment but that for the final state there are two configurations in interaction. Then the sum rules for intensities will have to be extended to summations over all lines terminating on any of the levels belonging to both of the interacting configurations. Detailed consideration of the intensity relations will be postponed to a later paper.

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[10] Ornstein and Burger, Zeits. f. Physik **40**, 403 (1926).

[11] Harrison, J. Opt. Soc. Amer. **19**, 109 (1929).