THE EFFECT OF CONFIGURATION INTERACTION

ON INTENSITY ANOMALIES

Thesis by

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ABSTRACT

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The problem of theoretical analysis of complex spectra is outlined with attention to various methods available for the computation of the Russell-Saunders wave functions, which form a basis for most other computations. In order to investigate intensity anomalies due to interconfiguration perturbations in two electron spectra, the non-diagonal matrix elements of the electrostatic interaction, between states describable by L-S wave functions, are computed by the symbolic "spinor" formulation of Weyl's group theory as developed by Kramers and Brinkman. A closed expression is obtained which embodies the results of what would be in the Schrodinger method a sum of integrals over angular wave functions; the radial integrals are still to be evaluated. A neat graphical method for computing the radial integrals, providing Slater's approximation to the Hartree wave functions can be used, is worked out.

Transition intensities are computed using this configuration interaction, and the effect of introducing as well that of the spin-orbit term is investigated. Formulae are derived which show that the first-order term in absolute intensity anomalies is due to the interconfiguration electrostatic term alone, which however leaves relative intensities within a given multiplet transition unaffected. The first-order correction term in the latter (second-order term for absolute intensities) depends upon a product of factors depending on the electrostatic and spin-orbit interactions respectively.

I. INTRODUCTION AND GENERAL OUTLINE OF THE PROBLEM.

The problem of analysis of the spectra emitted by
various atoms, and the corresponding one of accounting theoret-
ically for the particular spectrum observed was first attack-
ed with any degree of success by Niels Bohr in 1913. His
analyses, based mainly on classical dynamics, brought out the
conception of the atom as a minute solar system with the elect-
rons revolving about the nucleous in orbits whose energies were
predetermined and had certain discrete and fixed values. Later
modifications of Bohr's theory, together with the introduction
of the wave mechanics of Schrodinger, and the work of Sommer-
feld, made necessary the abandonment of the idea of discrete
particles revolving about the nucleous, but left intact the con-
ception of the existence within the atom of a set of discrete
energy levels characteristic of that particular atom. Furthur,
each of these energy levels was associated with a particular
state, of the electrons within the atom, which could be describ-
ed approximately in terms of a specific configuration of the
electrons, having definite values of their angular momentum, their
spins, and their modes of coupling with the nucleous and with
each other, but having no definite values assigned to the elect-
ron positions. That is to say, the electrons total energy was
perfectly described, and the component parts of that energy
were approximately so, although its position was not.

Each of these configuration states is describable,
according to the customary theory of wave mechanics, by means
of a wave- or eigen-function of the spatial coordinates alone,

which satisfies the Schrodinger wave equation

$$\nabla^2 \psi + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0$$

and through it is mathematically connected with a given total
energy level, or eigenvalue of the equation. According to
the usual theory this eigenfunction of the spatial coordinates
alone, describes the complete state of the system, including
all observable physical quantities, such as momentum, average
position in space, etc; all these quantities may readily be ob-
tained from the eigenfunction by means of simple quadratures.
This follows from the conception of the eigenfunction as the
amplitude function of a standing wave, which symbolically has
the same total energy (the connection between matter and wave
is contained in the Einstein equation for the energy associat-
ed with a wave, E=hν) as the particle whose state it describes,
and the square of whose amplitude (hence the square of the
eigenfunction) represents the probability of finding the part-
icle at the given point for which the amplitude is computed.

The basic units from which are built all atomic wave
functions for the various complicated cases are the simple
spherically symmetric wave functions (hydrogenic wave functions)

$$\psi = \text{Norm. factor} \cdot e^{im\varphi} \sin^{|m|}\vartheta \, P_\ell^{|m|}(\cos\vartheta)\, \rho^\ell e^{-\frac{\rho}{2}} L_{n+\ell}^{2\ell+1}(\rho)\, \sigma_{m_s}(\tfrac{1}{2})$$
$$= \psi(n_i/i) \qquad \rho = 2r/na \tag{2}$$

which are the solutions of the Schrodinger wave equation for
the Hydrogen atom (put $V = -e^2/r$ in 1).

In order to obtain wave functions for the various
states when we are dealing with atoms having more than one elec-
tron it is necessary to obtain first an approximate function
which describes the state assuming that no interactions exist

between the various electrons, and then, proceeding by one of
a number of methods, to obtain a more exact function which
takes account of the interactions. To get the approximate func-
tion we write the wave equation, omitting the interaction terms
in the potential energy,

$$\left(\sum_i \nabla_i^2\right)\Psi + \frac{8\pi^2\mu}{h^2}\left(E + \sum_i \frac{ze^2}{h_i}\right)\Psi = 0 \qquad \Psi = \psi(1)\,\psi(2)\cdots\psi(N)$$
$$i = 1, 2, \cdots N \qquad\qquad (3)$$

and since the electrons are then independent, we can separate
the equation into a series of equations, each of them functions
of the coordinates of a separate electron, and obtain the sol-
ution as a product of hydrogenic wave functions, each of the
coordinates (including spin) of a different electron.

$$\Psi = \psi(n_1|1)\,\psi(n_2|2)\cdot\cdot\cdot\cdot\cdot\psi(n_N|N) \qquad (4)$$

At this point it is necessary to introduce the Pauli
exclusion principle - which in one form says that only those
states are permissable in the atom, whose wave functions are
antisymmetric with respect to the exchange of any two electrons.
In order to satisfy this it is noted that since the electrons
are so far independent the coordinates of any two may be permut-
ed in (4) and the result is still a solution of (3); furthur
any sum of such permutations is a solution. Finally, Slater
has shown[*] that the particular sum of such permutations which is
completely antisymmetric in all electrons, and hence is the only
permissable solution, may be represented in the form of a det-
erminant.

$$\Psi^0(n_1, n_2 \cdots n_N | 1, 2, \cdots N) = \begin{vmatrix} \psi(n_1|1) & \psi(n_1|2) \cdots & \psi(n_1|N) \\ \psi(n_2|1) & & \\ \vdots & & \vdots \\ \psi(n_N|1) & \cdots & \psi(n_N|N) \end{vmatrix} \qquad (5)$$

[*] Dirac has shown that Slater has only made use of this theorem.

This, then, which we shall call the Slater wave function is our first, approximate, or zero-order wave function for an atom containing several electrons.

Now it can readily be shown that these zero-order wave functions form a complete and orthogonal set of solutions of the homogeneous wave equation (3) and hence that any solution of the inhomogeneous equation

$$\left(\sum_i \nabla_i^2\right)\Psi + \frac{8\pi^2\mu}{h^2}\left[E + \sum_i \frac{Ze^2}{h_i} + \sum_{i \neq j} \frac{1}{2}\frac{e^2}{h_{ij}} + \sum_i k_1 \frac{(\bar{\rho}_i \cdot \bar{s}_i)}{h_i^3} + \sum_{i \neq j} k_2 \frac{(\bar{s}_i \cdot \bar{s}_j)}{h_{ij}^3} + \cdots\right]\Psi = 0 \tag{6}$$

(which is the exact equation for the multiple electron case, and hence whose solution is the exact solution we wish) may be expressed as a linear sum of these zero-order functions with the proper coefficients[1]. Hence the problem devolves into one of finding the proper coefficients in the linear expansion which give the particular solution desired.

In order to find these proper coefficients we may proceed in one of a number of ways - one of which is the direct method of the Schrodinger perturbation theory. In this we consider the inhomogeneous term of (6) as a small perturbing potential consisting as it does of a series of small potentials each arising from a possible interaction between certain of the several electrons present. Hence as we make use of each small interaction potential as a perturbation, we build up as it were, a wave function which takes account of each interaction, step by step, and thus is at each step a closer approximation to the true function which takes into account all interactions which may be present in the atomic system. The formal procedure at each step is simple enough: we assume a linear combination of zero-order functions (solutions of the homogeneous equation),

substitute it into the inhomogeneous equation, and solve for
the coefficients by quadratures, obtaining for them certain
complex integrals involving the perturbing potential which the
wave function is to take into account.

Naturally since the total number of possible inter-
actions of different types among a group of several electrons
is manifold - furthur all interactions are not of the same or-
der of magnitude - we do not try to take them all into account,
but simply calculate wave functions which describe the more
important and spectroscopically distinctive interactions. This
means that, at best, we have only approximate wave functions,
and furthur, even these approximate wave functions are sometimes
extremely difficult to calculate by this direct process since
the expressions for the coefficients involve integrals which are
complicated and often impossible to evaluate.

In almost all spectroscopic problems the first and
most important interaction which is taken into account is the
electrostatic interaction of the separate electrons, which serves
to remove part of the degeneracy present and allows the system
to be expressed in terms of the total angular orbital momentum
L which may be thought of as a specific vector combination of
the individual angular momenta, l_i , of the separate electrons.
The next interaction to be considered is that of the separate
spin momenta, s_i , to form a total spin momentum S; and finally
the interaction of these total momenta L and S to form a total
angular momentum J for the entire system. It would be theoret-
ically possible to build up the wave functions which took into
account these particular interactions (these are known as the

Russell-Saunders wave functions or the functions for L-S coupling) by the above method, by introducing the various potential energy terms $\sum_{ij} \frac{1}{2} e^2/r_{ij}$, $\sum_{ij} k_1(r_{ij})(\bar{s}_i \cdot \bar{s}_j)$, $\sum_{i} k_2(r_i)(\bar{l}_i \cdot \bar{s}_i)$ into the wave equation, but the practical difficulties and computations as mentioned above are almost insurmountable. For this reason then, and since these Russell-Saunders wave functions approach very nearly to an accurate description of the states in most of the simple atoms, and hence form a starting point for the calculations to take into account various anomalies, it is necessary to turn to another method of computing the wave functions; that is, the proper coefficients in the linear expansions in terms of the Slater determinant functions.

It is perhaps advisable at this point to outline the procedure to be followed after these Russell-Saunders functions are obtained. It is desired to investigate the anomalies in intensities which are produced in the spectra of two-electron atoms by the fact that the energy levels are not accurately described by these L-S functions configuration by configuration, but rather that each configuration is somewhat distorted by the presence of the others. The important perturbing term in this case (this has been the consensus of opinion, its veracity will be examined later) is that of the electrostatic interaction, the non-diagonal elements of whose matrix are neglected in computing the energy levels of the various configurations when they are considered separately and describable by the L-S wave functions. Hence it is necessary to compute the interconfiguration electrostatic interaction, which is

$$H_{12} = \int \Psi^{o*}_{J_1,L_1,S_1} \frac{e^2}{r_{12}} \Psi^{\bullet}_{J_2,L_2,S_2} \tag{7}$$

where the ψ^os are the Russell-Saunders functions, already computed, which describe the levels in any one configuration considered separately. Knowing this interaction H_{12} it is possible to build up wave functions which take into account this interconfiguration perturbation to any desired degree of approximation by taking additional terms in the series

$$\psi_i' = \psi_i^o + \sum_{j \neq i} \frac{H_{ij}}{E_i^o - E_j^o} \psi_j^o + \cdots \qquad ; \; E_i^o = E_i - H_{ii} \qquad (8)$$

With these accurate wave functions it is simple to compute the theoretical intensities of the spectral lines, which can then be compared with those which would be observed if strict L-S coupling were present, i.e. if no interconfiguration interaction existed. These intensities, or transition probabilities, are proportional to the square of the amplitude of the electric moment between the two states involved.

$$I \propto [A_{ij}]^2 = [e \int \psi_i'^* \, \tau_{ij} \, \psi_j' \, d\tau]^2 \qquad (9)$$

The essential problem, then, is the computation of the interconfiguration interaction, and its precursor, the computation of the L-S wave functions. It will be seen later how both these steps may be accomplished in one process.

The Matrix Method.

A somewhat more elegant method than that of Schrodinger for computing these required functions is that followed by M. S. Johnson[a] which takes as its basis a combination of the matrix theory of Heizenberg and the operator calculus methods of Jordan. It is hardly necessary or possible here to go into all the intricacies of these theories; suffice it to say that the operators which are used to represent physical quantities

are symbolic in nature and are used as such purely as a mathematical device which serves to simplify the equations and achieve the same results as the fundamental Schrodinger theory. These operators which symbolize physical quantities are absolute in nature (as compared with the representation by means of a matrix), and as such are not physically observable. Physical quantities are also represented by matrices, but in this case we are dealing with a relative aspect of the physical quantity which is physically observable. The matrix elements, which may be written

$$a = \|a_{ij}\| \qquad a_{ij} = \int \psi_i^* \, a(\tau) \, \psi_j \, d\tau$$

, are considered the only part of the quantity "a" which can ever be observed in a physical sense; they are the different aspects of the quantity which can be observed when the system is in the state ψ_i, or undergoes a transition from the state ψ_i to the state ψ_j, and hence may be thought of as playing a role similar to that played by the separate Fourier components in ordinary analysis. It is obvious that they are relative since their form depends upon the particular set of wave functions which is used to describe the system, and hence upon the point of view. Since various sets of wave functions can be used to describe the same system (all that is required is a complete orthogonal set), and all must lead to the same absolute results as far as the constants of the system are concerned, the so-called transformation theory, which consists simply in establishing connections between the different points of view, was built up.

Johnson's method is a sort of composite based upon all of the above. In order to compute the wave functions for L-S coupling, it is noted that according to the definition of this

coupling scheme, heretofore given, L^2, S^2, either $L \cdot S$ or J^2, and J_z must be constants of the motion, and this in the matrix calculus means that the matrices which represent these quantities must be diagonal, after all degeneracies have been accounted for, when referred to L-S wave functions. It is only necessary then to compute the matrices of these quantities in terms of the zero-order, or Slater wave functions, and find the transformation matrix which carries them to diagonal form when applied in the usual manner. The elements in this transformation matrix then represent the coefficients in the linear expansion of the L-S wave functions in terms of the Slater functions. For example if R is a hermitian matrix which transforms the matrix A^o into a diagonal form

$$(R^{-1} A^o R)_{\rho\sigma} = A_{\rho\sigma} = A_{\rho\rho}\, \delta_{\rho\sigma} \qquad\qquad (a)$$

and the matrix A^o is computed from the wave functions ψ^o

$$A^o = \| A^o_{rs} \| = \| \int \psi_r^{o*} \mathcal{A} \, \psi_s^o \, d\tau \| \qquad\qquad (b)$$

then it is easily shown that the wave functions which make A a diagonal matrix are given by $\psi = R\psi^o$. For,

$$A_{\rho\sigma} = \int \psi_\rho^* \mathcal{A} \, \psi_\sigma \, d\tau = \int \sum_\mu \psi_\mu^{o*} R_{\rho\mu}^{-1} \mathcal{A} \sum_\lambda R_{\lambda\sigma} \psi_\lambda^o \, d\tau$$

$$= \sum_{\mu,\lambda} R_{\rho\mu}^{-1} R_{\lambda\sigma} \int \psi_\mu^{o*} \mathcal{A} \psi_\lambda^o \, d\tau = \sum_{\mu,\lambda} R_{\rho\mu}^{-1} A_{\mu\lambda}^o R_{\lambda\sigma} = A_{\rho\rho} \delta_{\rho\sigma} \qquad \text{by (a).}$$

The computation of the matrices for L^2, S^2, and $L \cdot S$ in the zero-order scheme is accomplished with the aid of the formulas developed by Condon[3], and the transformation matrix is determined in the manner in which any principle axis transformation is found. The procedure is relatively straightforward and is subject only to the drawback that is not general and the functions for each configuration must be computed individually from the beginning.

The Vector Addition Model.

A more general method, known as the "vector addition model", which allows us to carry out the process of finding the wave functions in terms of arbitrary l's, s's, and L, S, J and only substitute specific values for these variables in the final expression, is derived from the processes of group theory[4,5]. In this connection, it has been shown[6,7] that the problems involved in wave mechanics are analogous to those of linear orthogonal transformations in a vector space of n-dimensions (Hilbert Space), *n may be infinite* with the modification that in the wave-mechanical analogue the coordinates of a point are considered as complex, so that the distance between points becomes the sum of squares of moduli, rather than of coordinates themselves, and hence orthogonal transformations become unitary transformations. In particular, Weyl[8], in his analysis of group theory, studies the transformation properties of the solutions of the wave equation when the ordinary three dimensional coordinate system is subjected to a rotation, and uses them to derive many of the properties of the atom.

The wave functions which are correlated with a given vector l and a projection m_l are represented by a variable which behaves like this vector l when subjected to a space rotation, (i.e. to a unitary transformation in two dimensions). This means that when we have two variables ψ_{l_1} and ψ_{l_2}, i.e. two electrons, combined to form a new variable $\bar{L} = \bar{l}_1 + \bar{l}_2$, we must seek linear combinations of the products of the two original variables $\psi_{l_1}\psi_{l_2}$ which behave like the vector L when both l_1 and l_2 are subjected to the same rotation (the quantity L is to be

invariant to a rotation). (In all this work we are dealing with the angular parts of the wave function only; the group theory provides a representation of certain of the combination and transformation properties of spherical harmonics.) The process is somewhat as follows. First we seek the proper variable to represent $\psi_\ell^{m_\ell}$. The simple unitary transformation in two dimensions which corresponds to a space rotation is

$$\begin{cases} \xi' = \alpha\xi + \beta\eta \\ \eta' = -\beta^*\xi + \alpha^*\eta \end{cases}$$

$$\alpha\alpha^* + \beta\beta^* = 1$$

where ξ', η', ξ, η are complex variables in the *unitary* space and α, β are complex constants.
* denotes the complex conjugate.

Now a tensor of order v which is built up out of these quantities ξ, η , has v+1 components of the form $\xi^{v-i}\eta^i$, which transform as follows under the above transformation.

$$\xi'^{v-i}\eta'^i = (\alpha\xi + \beta\eta)^{v-i}(-\beta^*\xi + \alpha^*\eta)^i = \sum_{\kappa=0}^{v} S_{i\kappa}^{(v)}\xi^{v-\kappa}\eta^\kappa$$

where $S_{i\kappa}^{(v)}$ is the tensor of the transformation and involves α, β , α^*, β^*. In order to make this transformation unitary, it is necessary to introduce a constant factor, and choose as the variable

$$q_\kappa^v = \frac{\xi^{v-\kappa}\eta^\kappa}{\sqrt{(v-\kappa)!\,\kappa!}}$$

To correlate this with the wave-mechanical problem put v=21, and m_1= 1-k, whereupon the variable becomes

$$q_{m_\ell}^\ell = \frac{\xi^{\ell+m_\ell}\eta^{\ell-m_\ell}}{\sqrt{(\ell+m_\ell)!\,(\ell-m_\ell)!}} \qquad m_\ell = \ell,\ \ell-1,\ \cdots -\ell+1,\ -\ell$$

It is easily seen that this variable is associated with the quantity ℓ and has $2\ell+1$ components, and thus may be used to represent $\psi_\ell^{m_\ell}$ in the space spanned by the one electron. The monomials $\xi^{\ell+m_\ell}\eta^{\ell-m_\ell}$, where ξ and η undergo a unitary trans-

or conversely, contragrediently with a form of the type

$$X_{M_L}^L = \frac{\alpha^{L+M_L} \beta^{L-M_L}}{\sqrt{(L+M_L)!\,(L-M_L)!}}$$

In order to obtain this linear combination it is convenient to form the invariant expression

$$A = (\xi_1 \eta_2 - \eta_1 \xi_2)^\lambda (\alpha \xi_1 + \beta \eta_1)^{2L-\lambda}(\alpha \xi_2 + \beta \eta_2)^{2L-\lambda}$$
$$= \sum_{M_L} W_{M_L}^L X_{M_L}^L \qquad \text{where} \quad L = \ell_1 + \ell_2 - \lambda$$

Hence since A is an invariant $W_{M_L}^L$ must transform contragrediently to $X_{M_L}^L$ and it is easily seen that the coefficients of $X_{M_L}^L$ in A, that is

$$W_{M_L}^L = \sum_{m_{\ell_1}, m_{\ell_2}} \rho_L \, C_{m_{\ell_1}, m_{\ell_2}}^L \, Q_{m_1, m_2}^{\ell_1, \ell_2} \qquad \begin{array}{l} M_L = m_{\ell_1} + m_{\ell_2} \\ \rho_L = \text{normalizing factor} \end{array}$$

are the proper linear combinations which give the linear expansion of $\psi_{M_L}^L$ in terms of $\psi_{m_{\ell_1}}^{\ell_1}, \psi_{m_{\ell_2}}^{\ell_2}$ in the form

$$\psi_{M_L}^L = \sum_{m_{\ell_1}, m_{\ell_2}} \rho_L \, C_{m_{\ell_1}, m_{\ell_2}}^{\ell_1, \ell_2; L} \, \psi_{m_{\ell_1}}^{\ell_1} \psi_{m_{\ell_2}}^{\ell_2}$$

$$C_{m_{\ell_1}, m_{\ell_2}}^{\ell_1 \ell_2; L} = \sum_\nu (-1)^\mu \frac{\sqrt{(\ell_1+m_1)!\,(\ell_1-m_1)!\,(\ell_2+m_2)!\,(\ell_2-m_2)!\,(L+M_L)!\,(L-M_L)!}}{(\ell_1-m_1-\mu)!\,(\ell_1+m_1-\lambda+\nu)!\,(\ell_2+m_2-\mu)!\,(\ell_2-m_2-\lambda+\nu)!\,\nu!\,(\lambda-\nu)!} \quad (10)$$

$$M_L = m_1 + m_2 \qquad \lambda = \ell_1 + \ell_2 - L$$

and this is valid for l_1, l_2, L either integral or half-integral.

The above expression gives, then, the proper coefficients to provide for the coupling of l_1 and l_2 to obtain L. It however is perfectly general and is equally applicable to the coefficients which are required when any two integral or half-integral vectors are coupled to give a third such vector. Thus, it is only necessary to apply the same formula in order to couple s_1 and s_2 to obtain S. The two functions which are then obtained may be regarded as simple functions and L and S coupled to obtain J, by a repetition of the same process. The resultant function $\psi_{M_J}^J$ is thus expressed as a linear combination of the original one-electron functions.

$$\psi_{M_J}^{J} = \rho_{JLS} \sum_{M_S} C_{M_J; M_L, M_S}^{J; L, S} \sum_{M_{\ell_1}} C_{M_L; m_{\ell_1}m_{\ell_2}}^{L; \ell_1, \ell_2} \sum_{m_{S_1}} C_{M_S; m_{S_1}m_{S_2}}^{S; S_1, S_2} \left(\psi_{m_{\ell_1}}^{\ell_1} \psi_{m_{\ell_2}}^{\ell_2} \sigma_{m_{S_1}}^{S_1} \sigma_{m_{S_2}}^{S_2} \right)$$

$$M_J = M_L + M_S \quad ; \quad M_L = m_{\ell_1} + m_{\ell_2} \quad ; \quad M_S = m_{S_1} + m_{S_2}$$

where the C's are determined as above and ρ_{LSJ} is a normalization factor for the linear sum (the one electron functions are assumed as already normalized). This process may seem somewhat complex, but specific cases may be written quickly from this formula directly, without having to go through the entire computation from the beginning for each configuration as is necessary when using the Johnson method.

Although the vector addition model, as has been seen, provides a quick and direct means of writing down the linear combinations of the unperturbed functions which provide a description of L-S coupling, this is only half the problem. The matrix elements which measure the interconfiguration interaction remain to be computed. It was thought possible to proceed as follows: Simply write down the ordinary expression for the matix element between two such ψ_J's as have been computed above.

$$H_{12} = \int \psi_{M_{J_1}; L_1 S_1}^{J_1 *} e^2/_{R_{12}} \psi_{M_{J_2}; L_2 S_2}^{J_2} d\tau$$

$$= \rho_{J_1 L_1 S_1} \rho_{J_2 L_2 S_2} \sum \cdots \sum c^{J_1 *} \cdots c^{S_2} \int \psi^{\ell_1 *} \cdots \frac{e^2}{R_{12}} \cdots \sigma^{S_2} d\tau$$

The integral breaks up into a series of normalization and orthogonality integrals, which simplify the expression somewhat, and finally, after a few integrals involving three spherical harmonics of the type considered by Gaunt[9] have been evaluated, reduces to a series of finite summations involving the numerical coefficients, and a single finite summation, having only a few terms, taken over the radial integrals of simple one-electron wave functions (this latter sum is independent of the first group). If the first summations, involving the coefficients,

could be carried out in general, a concise formula for the matrix of electrostatic interaction between L-S wave states would be the result. Unfortunately this is impossible, since no matter what method of attack is used, eventually there appears for summation an expression of the type

$$\sum_{\nu} \frac{(-1)^{\nu}}{\nu!} g_{\pi}(\ell_1 \ell_2 L M_L \nu) = \sum_{\nu} \frac{(-1)^{\nu} A! (B+A)! C! (D+A)! E!}{(A-\nu)!(B+\nu)!(C-\nu)!(D+\nu)!(E-\nu)! \nu!}$$

$$A = \ell_1 - \mu \ ; \ B = L - \ell_2 + \mu \ ; \ C = \ell_2 + M_L - \mu \ ; \ D = L - \ell_1 - M_L - \mu \ ; \ E = \ell_1 + \ell_2 - L$$

$$|\mu| \le \ell_1$$

This function seems to be allied closely with some of the generalized hypergeometric functions considered by Dixon and Whipple[10], but the peculiar relations which exist between A, B, C, D, and E do not fit into any of the situations there considered which permit summation. Furthur, due to various singularities which this function possesses it seems impossible to relate it in any usuable fashion to a summable function by the process of analytic continuation. This of course means that in order to evaluate the desired matrix elements, it is necessary to substitute into the general formula specific values of the quantum numbers from the beginning, and write out the sums term by term. This we could have done using the Johnson evaluation of the L-S wave functions. It then appears that the introduction of the symbolic methods of group theory have gained us nothing when they are only used to determine the wave functions, and we rely upon straightforward integration between two of the predetermined wave functions to obtain the matrix element.

The Spinor Method of Kramers.

These difficulties are surmounted by the very elegant and general formulation of Weyl's group theory methods which

has been developed by Kramers[11] through the use of symbolic

representations of not only wave functions but also of opera-

tors with properties which are well known from the theory of

invariants. It will be remembered that, in evaluating the L-S

wave functions by the group theory method above, certain invar-

iant expressions (see page 13) were written down which contain-

ed the desired functions in the form of coefficients of certain

variables. These coefficients were picked out and set down as

the proper L-S functions with which to proceed in the evalua-

tion of the matrix elements by ordinary integration. The ess-

ence of Kramer s method is to leave the entire expression as a

symbolic representation of the whole group of wave functions,

and to introduce this into the integral for the matrix element,

after replacing the perturbing operator e^2/r_{12} by its corres-

ponding symbolic expression derived from its behavior under a

space rotation. It is then possible to work out the entire int-

egral (except for the radial part) in general, without substi-

tuting any specific values until the work is completed. Thus

the two essential steps in our problem (before transition proba-

bilities can be computed) are combined into one process. In

carrying out Kramers procedure, which is also known as the "Spin-

or Method" since the wave functions and operators are represent-

ed in terms of the behavior of spinors (a two-dimensional com-

lex vector with components ξ , η ,[12]), it is convenient to eval-

uate the function and matrix elements between states defined on-

ly for orbital momentum L at first and later to introduce the

spin and spin-orbit coupling factors. The method of evaluation

follows. Brinkman[13] has carried out some similar calculations

along the same lines, but he dealt with a simpler problem which involved only one configuration.

II. COMPUTATION OF THE MATRIX ELEMENTS (ANGULAR PART).

We now proceed to the computation, by the direct 'spinor' method, of the interconfiguration interactions which we require in order to compute the transition probabilities for the two electron atom in intermediate coupling. This spinor method, as we have seen above, precludes the necessity of formally computing the Russell-Saunders, or L-S , wave functions for the unperturbed states, since the proper coefficients which are required are already contained in the linear transformations which we use in group theory to represent wave functions. Furthur, we may first compute the interaction between states which are described by only the angular momentum of their electrons, and later modify this according to their spins and spin-orbit coupling (J).

Hence we now concern ourselves with the non-diagonal matrix elements of the electrostatic interaction (e^2/r_{12}) between states in different configurations, neglecting the spin of both electrons. The angular momentum of the electrons in configuration I will be denoted by l_1, l_2 and in configuration II by λ_1, λ_2 . For our unperturbed wave functions we shall take those linear combinations of $\psi_{l_1 l_2}$, and of $\psi_{\lambda_1 \lambda_2}$, for which L^2 is a diagonal matrix, and denote them by $\Psi_{l_1 l_2 L}$ or $\Psi_{\lambda_1 \lambda_2 \Lambda}$, according to the configuration to which they refer.

The symbolical representation methods of group theory as developed by Kramers[11], and Brinkman[12,13] enable us to represent directly, as space rotations, the transformation properties of $\psi_{l_1 l_2}$, $\Psi_{l_1 l_2 L}$ and their analogues for the λ elec-

trons. If we represent

the $2l_1 + 1$ wave functions for l_1 by the monomes $\xi_1^{l_1+m_1} \eta_1^{l_1-m_1}$

the $2l_2 + 1$ wave functions for l_2 by the monomes $\bar{\xi}_2^{l_2+m_2} \bar{\eta}_2^{l_2-m_2}$

the $2\lambda_1 + 1$ wave functions for λ_1 by the monomes $\bar{\bar{\xi}}_1^{\lambda_1+\mu_1} \bar{\bar{\eta}}_1^{\lambda_1-\mu_1}$

the $2\lambda_2 + 1$ wave functions for λ_2 by the monomes $\bar{\bar{\xi}}_2^{\lambda_2+\mu_2} \bar{\bar{\eta}}_2^{\lambda_2-\mu_2}$

then the functions $\psi_{l_1 l_2}$ transform like the $(2l_1+1)(2l_2+1)$

expressions
$$\phi_{l_1 l_2}^{m_1 m_2} = \xi_1^{l_1+m_1} \eta_1^{l_1-m_1} \bar{\xi}_2^{l_2+m_2} \bar{\eta}_2^{l_2-m_2}$$

and a similar expression may be written for $\psi_{\lambda_1 \lambda_2}$.

In these expressions (ξ_1, η_1), $(\bar{\xi}_2, \bar{\eta}_2)$, $(\bar{\bar{\xi}}_1, \bar{\bar{\eta}}_1)$, $(\bar{\bar{\xi}}_2, \bar{\bar{\eta}}_2)$ are variable spinors. The subscript 1 refers to a function of the first electron, 2 to a function of the second electron, while the bars are introduced to denote that the radial part of the wave function may differ in each case. The angular parts are all the same intrinsically - the differences being taken care of by the powers to which the various spinor components occur.

The transformation properties of the 2L+1 functions $\Psi_{l_1 l_2 L}$, and the $2\Lambda+1$ functions $\Psi_{\lambda_1 \lambda_2 \Lambda}$ may be described by those of the expressions

$$\phi_{l_1 l_2 L} = P_1^{\alpha_1} Q_1^{\beta_1} \bar{R}_1^{\gamma_1}$$
$$\phi_{\lambda_1 \lambda_2 \Lambda} = P_2^{\alpha_2} Q_2^{\beta_2} \bar{R}_2^{\gamma_2}$$

where

$$P_1 = -\bar{\eta}_2 \xi_1 + \eta_1 \bar{\xi}_2 \qquad\qquad P_2 = -\bar{\bar{\eta}}_2 \bar{\bar{\xi}}_1 + \bar{\bar{\eta}}_1 \bar{\bar{\xi}}_2 \qquad (11)$$

$$Q_1 = -b\xi_1 + a\eta_1 \qquad\qquad Q_2 = -b\bar{\bar{\xi}}_1 + a\bar{\bar{\eta}}_1$$

$$\bar{R}_1 = -b\bar{\xi}_2 + a\bar{\eta}_2 \qquad\qquad R_2 = -b\bar{\bar{\xi}}_2 + a\bar{\bar{\eta}}_2$$

$$\alpha_1 = l_1 + l_2 - L \qquad\qquad \alpha_2 = \lambda_1 + \lambda_2 - \Lambda$$

$$\beta_1 = L + l_1 - l_2 \qquad\qquad \beta_2 = \Lambda + \lambda_1 - \lambda_2$$

$$\gamma_1 = L + l_2 - l_1 \qquad\qquad \gamma_2 = \Lambda + \lambda_2 - \lambda_1$$

and (a,b) is an arbitrary constant spinor (does not transform).

Thus $\Phi_{\ell_1\ell_2 L}$ is a homogeneous invariant of degree 2L in the components of the constant spinor (a,b), and the coefficients of the 2L+1 monomes $a^{L+M_L} b^{L-M_L}$ are linear combinations of the functions $\phi_{\ell_1\ell_2}^{m_1 m_2}$, which, because of the invariance of Φ, transform like the 2L+1 wave functions diagonal in L^2. These then are our unperturbed wave functions mentioned above. The same may be said of $\Phi_{\lambda_1\lambda_2\Lambda}$.

Thus we may write symbolically in one term the marix elements of e^2/r_{12} between the functions $\Psi_{\ell_1\ell_2 L}$ and $\Psi_{\lambda_1\lambda_2\Lambda}$ for all values of M_L and M_Λ .

$$\Omega_{\ell_1\ell_2 L}^{\lambda_1\lambda_2\Lambda} = \int \Phi_{\ell_1\ell_2 L}^* \frac{e^2}{r_{12}} \Phi_{\lambda_1\lambda_2\Lambda} \, d\tau \tag{12}$$

This expression must obviously be an invariant in a, a^*, b, b^*, or else zero. Now the only invariant built up of these quantities which exists everywhere in the space is of the form $C(aa^* + bb^*)^{P_{12}}$, so that in (12), a and a^*, as well as b and b^* must occur to the same degree. The condition for this is simply that $\beta_1 + \gamma_1 = \beta_2 + \gamma_2$

or $2L = 2\Lambda$ Therefor $\Lambda = L = L$

$$\therefore \quad \Omega_{\ell_1\ell_2 L}^{\lambda_1\lambda_2\Lambda} = C_{\ell_1\ell_2 L}^{\lambda_1\lambda_2} \delta_{L\Lambda} (aa^* + bb^*)^{2L}$$

In order to adapt our functions to the operator e^2/r_{12} which is a symmetric operator we must intruduce symmetry considerations into them. We put

$$\Phi_{\ell_1\ell_2 L}^S = \bar{P}_1^\alpha Q_1^{\beta_1} \bar{R}_1^{\gamma_1} \pm \bar{P}_1^{\alpha_1} \bar{Q}_1^{\gamma_1} R_1^{\beta_1}$$

where

$$\bar{P}_1 = -\bar{\eta}_1 \xi_2 + \eta_2 \bar{\xi}_1$$

$$\bar{Q}_1 = -b\bar{\xi}_1 + a\bar{\eta}_1 \tag{13}$$

$$R_1 = -b\xi_2 + a\eta_2$$

and

$$\Phi_{\lambda_1\lambda_2 L}^S = P_2^{\alpha_2} Q_2^{\beta_2} \bar{R}_2^{\delta_2} \pm \bar{P}_2^{\alpha} \bar{Q}_2^{\kappa} R_2^{\beta_2}$$

where

$$\overline{P_2} = -\overline{\overline{\eta}}_1\,\overline{\zeta}_2 + \overline{\overline{\eta}}_2\,\overline{\zeta}_1$$

$$\overline{Q_2} = -6\,\overline{\overline{\zeta}}_1 + a\,\overline{\overline{\eta}}_1 \qquad\qquad (13\text{con})$$

$$R_2 = -6\,\overline{\zeta}_2 + a\,\overline{\eta}_2$$

and P_1, Q_1, $\overline{R}_1$, P_2, Q_2, $\overline{R}_2$, are as before, so that these functions are then symmetric in the two electrons with the + sign and antisymmetric with the − sign. The index S has been added since the choice which is made later between the + and − signs will depend upon S, the spin.

Thus far we have not spoken of normalization factors -- however it is necessary to introduce them at this point in order to avoid ambiguity later on since what we wish eventually is a matrix element between wave functions which are normalized as far as angular momentum is concerned (i.e. $\ell_1 \ell_2 , \lambda_1 \lambda_2$,L ; the part for spin, etc., will be introduced later). First it will be assumed that the radial part of the function is normalized, and that for the angular normalization factor the following notation is to be used:

$$N_L^{M_L}(\ell_1 \ell_2) = N_\ell = N(\ell_1\ell_2;\ell_1\ell_2) = \int \Phi_{\ell_1\ell_2 L}^{*}\,\Phi_{\ell_1\ell_2 L}\,d\tau$$

$$N_L^{M_L}(\lambda_1 \lambda_2) = N_\lambda = N(\lambda_1\lambda_2;\lambda_1\lambda_2) = \int \Phi_{\lambda_1\lambda_2 L}^{*}\,\Phi_{\lambda_1\lambda_2 L}\,d\tau$$

$$N(12;12) = \int \Phi_{1,2,L}^{*}\,\Phi_{1,2,L}\,d\tau = N(12) \qquad (14)$$

$$N(12;21) = \int \Phi_{1,2,L}^{*}\,\Phi_{2,1,L}\,d\tau$$

and both the latter may refer to either the ℓ or λ electrons. In order to introduce these properly we note that in arriving at the expression flor the matrix element with the symmetry functions (13) we write,

$$\frac{e^2}{r_{12}}\,\frac{\Phi_{\lambda_1\lambda_2 L}^{S}}{\sqrt{N_\lambda}} = \sum_{j=\ell_2}^{\ell_1}\,Q_{\lambda_1\lambda_2 L}^{ij}\,\frac{\Phi_{ij,L}^{S}}{\sqrt{N(ij)}}$$

so that after multiplying through by $\Phi^{s*}_{\ell_1\ell_2 L}/\sqrt{N_\ell}$ and integrating

we have

$$\int \frac{\Phi^{s*}_{\ell_1\ell_2 L}}{\sqrt{N_\ell}} \frac{e^2}{r_{12}} \Phi^s_{\lambda_1\lambda_2 L}\,d\tau = \Omega^{\ell_1\ell_2}_{\lambda_1\lambda_2 L} \int \frac{\Phi^{s*}_{\ell_1\ell_2 L}}{\sqrt{N_\ell}} \frac{\Phi^s_{\ell_1\ell_2 L}}{\sqrt{N_\ell}}\,d\tau$$

*See below.

The right hand side becomes

$$\Omega^{\ell_1\ell_2}_{\lambda_1\lambda_2 L} \int \frac{(P_1^{*\alpha_1} Q_1^{*\beta_1} \bar{R}_1^{*\delta_1} \pm \bar{P}_1^{*\alpha_1} \bar{Q}_1^{*\delta_1} R_1^{*\beta_1})(P_1^{\alpha_1} Q_1^{\beta_1} \bar{R}_1^{\delta_1} \pm \bar{P}_1^{\alpha_1} \bar{Q}_1^{\delta_1} R_1^{\beta_1})}{\sqrt{N_\ell}}\,d\tau$$

$$= \Omega^{\ell_1\ell_2}_{\lambda_1\lambda_2 L} \left\{ \frac{N(12;12) + N(21;21) \pm N(12;21) \pm N(21;12)}{N_\ell} \right\}$$

$$= 2\,\Omega^{\ell_1\ell_2}_{\lambda_1\lambda_2 L} \left\{ \frac{N(12;12) \pm N(21;12)}{N_2} \right\}$$

$$= 2\,\Omega^{\ell_1\ell_2}_{\lambda_1\lambda_2 L} \cdot 1 \qquad \text{since } N(12;12)=N(21;21)$$
$$N(12;21)=N(21;12)$$

since if electrons ℓ_1 and ℓ_2 are not equivalent $N(21;12)=0$,
and if they are equivalent we have only one initial wave func-
tion as the one with the − sign is zero and has no meaning.

Thus,

$$\Omega^{\ell_1\ell_2}_{\lambda_1\lambda_2 L} = \tfrac{1}{2} \int \frac{\Phi^{s*}_{\ell_1\ell_2 L}}{\sqrt{N_\ell}} \frac{e^2}{r_{12}} \frac{\Phi^s_{\lambda_1\lambda_2 L}}{\sqrt{N_\lambda}}\,d\tau$$

is the element between completely normalized wave functions,
and can be expressed in terms of the symmetry functions (13) as

$$\Omega^{\ell_1\ell_2}_{\lambda_1\lambda_2 L} = 1/2\sqrt{N_\ell N_\lambda}\,(J_1 + J_2 \pm (J_3 + J_4))$$

where

$$J_1 = \int P_1^{*\alpha_1} Q_1^{*\beta_1} \bar{R}_1^{*\delta_1}\; e^2/r_{12}\; P_2^{\alpha_2} Q_2^{\beta_2} \bar{R}_2^{\delta_2}$$

$$J_2 = \int \bar{P}_1^{*\alpha_1} \bar{Q}_1^{*\delta_1} R_1^{*\beta_1}\; e^2/r_{12}\; \bar{P}_2^{\alpha_2} \bar{Q}_2^{\delta_2} R_2^{\beta_2} \qquad (15)$$

$$J_3 = \int \bar{P}_1^{*\alpha_1} \bar{Q}_1^{*\delta_1} R_1^{*\beta_1}\; e^2/r_{12}\; P_2^{\alpha_2} Q_2^{\beta_2} \bar{R}_2^{\delta_2}$$

$$J_4 = \int P_1^{*\alpha_1} Q_1^{*\beta_1} \bar{R}_1^{*\delta_1}\; e^2/r_{12}\; \bar{P}_2^{\alpha_2} \bar{Q}_2^{\delta_2} R_2^{\beta_2}$$

We must now compute these separate integrals.

In the usual manner we expand e^2/r_{12} into a sum
of Legendre polynomials,

$$e^2/r_{12} = \sum_\tau \Omega_\tau = \sum_\tau \frac{e^2 r_<^\tau}{r_>^{\tau+1}} P_\tau(\cos\alpha_{12})$$

Kramers[11] has shown that Ω_τ transforms like $c_\tau(-x_1y_2 + x_2y_1)^{2\tau}$,
where (x_1y_1) and (x_2y_2) are spinors depending on the compon-

* After replacing e^2/r_{12} by the operators Ω_τ, which do nothing to affect the value of M_L,
we get normalization integrals on the left side which insure that Ω^s_λ is _diagonal_ in M_L as
well as in L.

ents of either the first or second electron, and hence trans-
forming like these components. c_τ is a constant equal to
$\frac{e^2 h_\le^\tau}{h_> \tau+1}$. This symbolical expression is now substituted into
(15) and a new notation for the wave function is introduced.

$$J_1 = \sum_\tau J_1^\tau = \sum_\tau \int P_1^{*\alpha_1} Q_1^{*\beta_1} \overline{R}_1^{*\gamma_1} \Omega_\tau P_2^{\alpha_2} Q_2^{\beta_2} \overline{R}_2^{\gamma_2}$$

$$= \sum_\tau \int [\alpha_1 \beta_1 \gamma_1] \Omega_\tau [\alpha_2 \beta_2 \gamma_2] \qquad (16)$$

$$= \sum_\tau \int (\alpha_1 \beta_1 \gamma_1)(-x_1 y_2 + x_2 y_1)^{2\tau} (\alpha_2 \beta_2 \gamma_2) R^\tau (\alpha_1 \beta_1 \gamma_1 ; \alpha_2 \beta_2 \gamma_2)$$

So that $[\alpha_1 \beta \gamma] \equiv$ entire wave function with the electrons in
the first order - definition of symbols (11).

$[\alpha \gamma \beta] \equiv$ entire wave function with electrons in re-
versed order - definition of symbols (13).

$(\alpha \beta \gamma) \equiv$ angular part of wave function - first order.

$(\alpha \gamma \beta) \equiv$ angular part of wave function - second order.

$R^\tau(abc ; def) =$ integral over c_τ of the radial parts
of the wave functions.

It is now convenient to replace the operator[11,12]
for Ω_τ by a homogeneous one of degree 4τ in the variables
$\xi_\kappa, \eta_\kappa, \xi_\kappa^*, \eta_\kappa^*$ by means of the substitution

$$\begin{cases} x_\kappa = \xi_\kappa - \eta_\kappa^* \\ y_\kappa = \eta_\kappa + \xi_\kappa^* \end{cases} \qquad (17)$$

so that we then have all parts of the integral in terms of
the same variables. Furthur we can now drop all the bars
which were used over the spinor variables in the wave func-
tions to denote differences in the radial parts since we have
separated the angular and radial parts of the integral, and
the differences in behavior of the angular parts are complete-
ly determined by the coefficients $\alpha_1, \beta_1, \gamma_1, \alpha_2, \beta_2, \gamma_2$.

After introducing the substitution (17) it is possible to subdivide Ω_τ in terms of certain invariants which can be built up out of the ξ, η spinor components.

$$\Omega_\tau = c_\tau \left[\{3\} + \{4\} - \{5\} + \{6\} \right]^{2\tau}$$

where
$$\{1\} = \xi_1 \xi_1^{*} + \eta_1 \eta_1^{*} \qquad \{4\} = -\eta_2^{*}\xi_1^{*} + \eta_1^{*}\xi_2^{*}$$
$$\{2\} = \xi_2 \xi_2^{*} + \eta_2 \eta_2^{*} \qquad \{5\} = \xi_1 \xi_2^{*} + \eta_1 \eta_2^{*} \qquad (18)$$
$$\{3\} = -\eta_2 \xi_1 + \eta_1 \xi_2 \qquad \{6\} = \xi_2 \xi_1^{*} + \eta_2 \eta_1^{*}$$

The integral (16) is simplified somewhat when we introduce the operator (18) since many of the terms which result after multiplying out the integrand turn out to be zero. This is readily seen from an examination of the typical term from which is built up the integral. The term is of the type

$$\int \xi^{*\, l'+m'} \eta^{*\, l'-m'} \xi^{l+m} \eta^{l-m}$$

which is equal to zero unless $l' = l$ and $m' = m$ (it is equivalent to the orthogonality conditions on the spherical harmonics). Hence in each non-zero term ξ_k^{*} and η_k^{*} must occur to the same power as ξ_k and η_k. This gives us certain conditions between the relative powers of $\{3\}$, $\{4\}$, $\{5\}$, $\{6\}$, and the coefficients α, β, γ occurring in the integral which must be satisfied in order to obtain a non-zero result. For example, in the case of J_1^τ, one obtains from (15),(13), and (11) that outside of the term Ω_τ,

ξ_1^{*}, η_1^{*} occur to the power $2 l_1$

ξ_2^{*}, η_2^{*} occur to the power $2 l_2$

ξ_1, η_1 occur to the power $2 \lambda_1$

ξ_2, η_2 occur to the power $2 \lambda_2$

But in the term Ω_τ powers of,

$\zeta_1{}^+$ and $\eta_1{}^+$ are obtained from $\{4\}$ and $\{6\}$

$\zeta_2{}^+$ and $\eta_2{}^*$ are obtained from $\{4\}$ and $\{5\}$

ζ_1 and η_1 are obtained from $\{3\}$ and $\{5\}$

ζ_2 and η_2 are obtained from $\{3\}$ and $\{6\}$,

and hence if P_i denotes the power to which $\{i\}$ occurs in the integral, the condition that the powers of $\zeta_1{}^+$, $\eta_1{}^+$ be equal to those of ζ_1, η_1 gives

$$\begin{cases} 2\,\ell_1 + P_4 + P_6 = 2\,\lambda_1 + P_3 + P_5 \\ 2\,\ell_2 + P_4 + P_5 = 2\,\lambda_2 + P_3 + P_6 \end{cases}$$

and thus

$$\begin{aligned} P_4 - P_3 &= (\lambda_1 + \lambda_2) - (\ell_1 + \ell_2) = \alpha_2 - \alpha_1 = r \\ P_6 - P_5 &= (\lambda_1 - \lambda_2) - (\ell_1 - \ell_2) = \beta_2 - \beta_1 = \gamma_1 - \gamma_2 = s \end{aligned} \tag{19}$$

These equations will serve to define the quantities r and s, and we may furthur add a definition of a similar quantity q

$$(\lambda_1 - \lambda_2) + (\ell_1 - \ell_2) = \beta_2 - \gamma_1 = \beta_1 - \gamma_2 = q \tag{19}$$

Before substituting these conditions into the expansion of (18) we shall examine certain other conditions which serve to furthur limit the number of terms which actually contribute to $\Omega_{\lambda,L}^{\ell}$. Since each of the J^{τ} integrals (16) represents an integral over the entire range of variables for each electron, the integral will be zero if the integrand is an odd function in terms of the coordinates of any one electron, i.e., if it changes sign with the substitution

$$x'_k = -x_k \qquad y'_k = -y_k \qquad z'_k = -z_k \tag{20}$$

where k refers to the coordinates of the k'th electron. Now if this substitution is introduced into the symbolical integrals J^{τ} , the corresponding substitution in terms of the spinor components is $\zeta'_k = i\zeta_k$, $\eta'_k = i\eta_k$, since a

rotation of the axes through an angle π (to which 2θ corresponds) is equivalent to multiplying the spinor components by $e^{\frac{i\pi}{2}} = i$. If this is done we obtain for the product of the wave functions –

in J_1^τ ---- $F(\varsigma_1', \eta_1') = (-1)^{\frac{\alpha_1}{2} + \frac{\beta_1}{2} + \frac{\alpha_2}{2} + \frac{\beta_2}{2}} \, F(\varsigma_1, \eta_1) = (-1)^{\ell_1 + \lambda_1} \, F(\varsigma_1, \eta_1)$

$\qquad F(\varsigma_2', \eta_2') = (-1)^{\frac{\alpha_1}{2} + \frac{\gamma_1}{2} + \frac{\alpha_2}{2} + \frac{\gamma_2}{2}} \, F(\varsigma_2, \eta_2) = (-1)^{\ell_2 + \lambda_2} \, F(\varsigma_2, \eta_2)$

in J_2^τ ---- $F(\varsigma_1', \eta_1') = (-1)^{\frac{\alpha_1}{2} + \frac{\gamma_1}{2} + \frac{\alpha_2}{2} + \frac{\gamma_2}{2}} \, F(\varsigma_1, \eta_1) = (-1)^{\ell_2 + \lambda_2} F(\varsigma_1, \eta_1)$

$\qquad F(\varsigma_2', \eta_2') = (-1)^{\ell_1 + \lambda_1} \, F(\varsigma_2, \eta_2)$

in J_3^τ -----$F(\varsigma_1', \eta_1') = (-1)^{\ell_2 + \lambda_1} \, F(\varsigma_1, \eta_1)$

$\qquad F(\varsigma_2', \eta_2') = (-1)^{\ell_1 + \lambda_2} \, F(\varsigma_2, \eta_2)$

in J_4^τ -----$F(\varsigma_1', \eta_1') = (-1)^{\ell_1 + \lambda_2} \, F(\varsigma_1, \eta_1)$

$\qquad F(\varsigma_2', \eta_2') = (-1)^{\ell_2 + \lambda_1} \, F(\varsigma_2, \eta_2)$

Furthur the operator becomes,

$$\Omega_\tau(\varsigma_1', \eta_1') = (-1)^\tau \Omega_\tau(\varsigma_1, \eta_1)$$
$$\Omega_\tau(\varsigma_2', \eta_2') = (-1)^\tau \Omega_\tau(\varsigma_2, \eta_2)$$

since $P_\tau(\pi - \theta) = (-1)^\tau P_\tau(\theta)$ and the $r_<$ and $r_>$ functions are simply absolute lengths and do not change sign.

When these results are combined the result is obtained that the entire integrand of the various J^τ's will be odd, and hence the corresponding integral will vanish, unless the following conditions are satisfied.

For J_1^τ and J_2^τ $\qquad \left.\begin{array}{l} \ell_1 + \lambda_1 + \tau \\ \ell_2 + \lambda_2 + \tau \end{array}\right\}$ = even integer.

For J_3^τ and J_4^τ $\qquad \left.\begin{array}{l} \ell_2 + \lambda_1 + \tau \\ \ell_1 + \lambda_2 + \tau \end{array}\right\}$ = even integer.

These conditions are simply the mathematical statement of the condition that the interaction is restricted to between configurations of the same parity. If this is applied to (19)

it is quickly evident that s, q, and r must always be <u>even</u>

integers. Further, $\tau - \frac{q}{2} \pm \frac{|s|}{2}$ is always even.

We now proceed to the expansion of (18) in the usual manner by means of the binomial theorem. When account is taken of condition (19), the only non-zero terms are those included in the expression

$$\Omega_\tau = c_\tau \sum_{\mu = \Lambda/2}^{\tau - \frac{|s|}{2}} K_\mu \{3\}^{\mu - \frac{\Lambda}{2}} \{4\}^{\mu + \frac{\Lambda}{2}} \{5\}^{\tau - \frac{s}{2} - \mu} \{6\}^{\tau + \frac{s}{2} - \mu}$$

where $K_\mu = \begin{pmatrix} 2\tau \\ \tau - \frac{q}{2} - \frac{s}{2} \end{pmatrix} \begin{pmatrix} \tau - \frac{q}{2} - \frac{s}{2} \\ \mu - \Lambda/2 \end{pmatrix} \begin{pmatrix} \tau + \frac{s}{2} + \frac{\Lambda}{2} \\ \mu + \Lambda/2 \end{pmatrix} (-1)^{\tau - \frac{s}{2} - \mu}$

At this point it is necessary to distinguish between two cases, s positive and negative respectively, since either $\{5\}$ or $\{6\}$, which ever exists to the lower power, is to be eliminated by means of the relation

$$\{1\}\{2\} - \{3\}\{4\} = \{5\}\{6\}$$

For the case -- <u>s positive</u> we eliminate $\{5\}$ and obtain,

$$\Omega_\tau = c_\tau \sum_{\mu = \frac{\Lambda}{2}}^{\tau - \frac{|s|}{2}} K_\mu \{3\}^{\mu - \frac{\Lambda}{2}} \{4\}^{\mu + \frac{\Lambda}{2}} \{6\}^s \sum_{\lambda \geq \mu}^{\tau - \frac{|s|}{2}} (\{3\}\{4\})^{\lambda - \mu} (\{1\}\{2\})^{\tau - \frac{|s|}{2} - \lambda} \begin{pmatrix} \tau - \frac{|s|}{2} - \mu \\ \lambda - \mu \end{pmatrix} (-1)^{\lambda - \mu}$$

Now put $\mu = \sigma + \frac{\Lambda}{2}$ and collect terms,

$$\Omega_\tau = c_\tau \sum_{\sigma = 0}^{\tau - \frac{\Lambda}{2} - \frac{|s|}{2}} K_{\sigma + \frac{\Lambda}{2}} \{3\}^\sigma \{4\}^{\sigma + \Lambda} \{6\}^s \sum_{\lambda = \sigma}^{\tau - \frac{\Lambda}{2} - \frac{|s|}{2}} (\{3\}\{4\})^{\lambda - \sigma} (\{1\}\{2\})^{\tau - \frac{\Lambda}{2} - \frac{|s|}{2} - \lambda} \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} - \sigma \\ \lambda - \sigma \end{pmatrix} (-1)^{\lambda - \sigma}$$

$$= c_\tau \sum_{\lambda = 0}^{\tau - \frac{\Lambda}{2} - \frac{|s|}{2}} \{3\}^\lambda \{4\}^{\lambda + r} \{6\}^{|s|} (\{1\}\{2\})^{\tau - \frac{\Lambda}{2} - \frac{|s|}{2} - \lambda} \begin{pmatrix} 2\tau \\ \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \end{pmatrix} (-1)^{\tau - \frac{\Lambda}{2} + \lambda} \sum_{\sigma = 0}^{\lambda} \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} - \sigma \\ \lambda - \sigma \end{pmatrix} \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \\ \sigma \end{pmatrix} \begin{pmatrix} \tau + \frac{\Lambda}{2} + \frac{|s|}{2} \\ \sigma + \Lambda \end{pmatrix}$$

after the order of summation is interchanged. But

$$\sum_{\sigma = 0}^{\lambda} \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} - \sigma \\ \lambda - \sigma \end{pmatrix} \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \\ \sigma \end{pmatrix} \begin{pmatrix} \tau + \frac{\Lambda}{2} + \frac{|s|}{2} \\ \sigma + \Lambda \end{pmatrix} = \sum_{\sigma = 0}^{\lambda} \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \\ \lambda \end{pmatrix} \begin{pmatrix} \lambda \\ \Lambda - \sigma \end{pmatrix} \begin{pmatrix} \tau + \frac{\Lambda}{2} + \frac{|s|}{2} \\ \sigma + \Lambda \end{pmatrix}$$

$$= \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \\ \lambda \end{pmatrix} \sum_{\sigma = 0}^{\lambda} \begin{pmatrix} \lambda \\ \lambda - \sigma \end{pmatrix} \begin{pmatrix} \tau + \frac{\Lambda}{2} + \frac{|s|}{2} \\ \sigma + \Lambda \end{pmatrix} = \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \\ \lambda \end{pmatrix} \begin{pmatrix} \tau + \frac{\Lambda}{2} + \frac{|s|}{2} + \lambda \\ \lambda + \Lambda \end{pmatrix}$$

So finally,

$$\Omega_\tau^s(+) = c_\tau \sum_{\lambda = 0}^{\tau - \frac{\Lambda}{2} - \frac{|s|}{2}} K_\lambda \{3\}^\lambda \{4\}^{\lambda + r} \{6\}^{|s|} (\{1\}\{2\})^{\tau - \frac{\Lambda}{2} - \frac{|s|}{2} - \lambda}$$

(22)

where $K_\lambda = (-1)^{\tau + \lambda - \frac{\Lambda}{2} - \frac{|s|}{2}} \begin{pmatrix} 2\tau \\ \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \end{pmatrix} \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \\ \lambda \end{pmatrix} \begin{pmatrix} \tau + \frac{\Lambda}{2} + \frac{|s|}{2} + \lambda \\ \lambda + \Lambda \end{pmatrix}$

$$= (-1)^\lambda \begin{pmatrix} 2\tau \\ \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \end{pmatrix} \begin{pmatrix} \tau - \frac{\Lambda}{2} - \frac{|s|}{2} \\ \lambda \end{pmatrix} \begin{pmatrix} \tau + \frac{\Lambda}{2} + \frac{|s|}{2} + \lambda \\ \lambda + \Lambda \end{pmatrix}$$

For the case -- <u>s negative</u> we eliminate $\{6\}$ and get, in a

similar manner,

$$\Omega_{\tau}^{s}(\cdot)= c_{\tau} \sum_{\lambda=0}^{\tau-\frac{\Delta}{2}+\frac{|s|}{2}} \{3\}^{\lambda} \{4\}^{\lambda+\imath} \{5\}^{|s|} \left(\{1\}\{2\}\right)^{\tau-\frac{\Delta}{2}-\frac{|s|}{2}-\lambda} (-1)^{\tau-\frac{\Delta}{2}+\frac{|s|}{2}+\lambda} \binom{2\tau}{\tau-\frac{\Delta}{2}-\frac{|s|}{2}} \sum_{\sigma=0}^{\lambda} \binom{\tau-\frac{\Delta}{2}-\frac{|s|}{2}-\sigma}{\lambda-\sigma}\binom{\tau-\frac{\tau}{2}-\frac{|s|}{2}}{\sigma}\binom{\tau+\frac{\Delta}{2}+\frac{|s|}{2}}{\sigma+\imath}$$

$$= c_{\tau} \sum_{\lambda=0}^{\tau-\frac{\Delta}{2}-\frac{|s|}{2}} K_{\lambda} \{3\}^{\lambda} \{4\}^{\lambda+\imath} \{5\}^{|s|} \left(\{1\}\{2\}\right)^{\tau-\frac{\Delta}{2}-\frac{|s|}{2}-\lambda} \tag{23}$$

since s is always an even integer.

It is necessary to make one more change in the op-
erators (22) and (23) before introducing them into the inte-
gral. Since the meaning of the spinor components ξ^{*} and η^{*} ,
when used to operate on a wave function is rather ambiguous,
we replace them by the operators $\partial/\partial\xi$ and $\partial/\partial\eta$ which transform
in the same manner, --- and then write each of the operators
so that ξ occurs before $\partial/\partial\xi$, etc. (this is done to preserve the
relation that ξ^{*} commutes with ξ and should not operate upon
it). This substitution does not impair in any way the gen-
erality of the operators. Furthur it is necessary to arrange
the order of the separate terms so that they do not operate
upon each other but only consecutively upon the wave function,
(this would not have been possible if either $\{5\}$ or $\{6\}$ had
not been eliminated). It will also be noticed/that the indi-
vidual operators $\{i\}$ do not operate upon themselves except
in the case of $\{1\}$ and $\{2\}$. To eliminate the spurious terms
of degree less than 4τ (the entire operator must be homogen-
eous of degree 4τ) which occur because of the self-operating
character of $\{1\}$ and $\{2\}$, it is necessary to make the foll-
owing replacements,

$$\{1\}^{p} \longrightarrow ([1]-p+1)([1]-p) \cdots ([1]-1)([1]) = [1]'^{p}$$

$$\{2\}^{q} \longrightarrow ([2]-q+1)([2]-q) \cdots ([2]-1)([2]) = [2]'^{q}$$

$$\{3\}^{p} \to [3]^{p} \qquad\qquad \{5\}^{p} \to [5]^{p}$$

$$\{4\}^{p} \to [4]^{p} \qquad\qquad \{6\}^{p} \to [6]^{p}$$

where $[\cdot]$ denotes the operator after ζ^* has been replaced by $\partial/\partial\xi$, and η^* by $\partial/\partial\eta$.

After the above change has been made the operators (22) and (23) become,

$$\Omega_\tau^s(+) = c_\tau \sum_{\lambda=0}^{\tau-\frac{s}{2}-|\frac{s}{2}|} K_\lambda \ [3]^\lambda \ [1]'^{\tau-\frac{s}{2}-\frac{|s|}{2}-\lambda} \ [6]^{|s|} \ [2]'^{\tau-\frac{s}{2}-\frac{|s|}{2}-\lambda} \ [4]^{\lambda+\kappa}$$

$$\Omega_\tau^s(-) = c_\tau \sum_{\lambda=0}^{\tau-\frac{s}{2}-|\frac{s}{2}|} K_\lambda \ [3]^\lambda \ [2]'^{\tau-\frac{s}{2}-\frac{|s|}{2}-\lambda} \ [5]^{|s|} \ [1]'^{\tau-\frac{s}{2}-\frac{|s|}{2}-\lambda} \ [4]^{\lambda+\kappa}$$

(24)

These operators containing s apply to J_1^τ and J_2^τ, similar operators can be worked out where q replaces s to apply to J_3^τ and J_4^τ.

The next step is to apply these operators to the various wave functions. First of all, the result of applying the separate $[\iota]$ operators to the functions (notation defined in (16)) will be computed. A summary of the results follow.

$$[1] = \zeta_1 \frac{\partial}{\partial\zeta_1} + \eta_1 \frac{\partial}{\partial\eta_1} \qquad\qquad [4] = -\frac{\partial^2}{\partial\eta_2\partial\xi_1} + \frac{\partial^2}{\partial\zeta_2\partial\eta_1}$$

$$[2] = \zeta_2 \frac{\partial}{\partial\zeta_2} + \eta_2 \frac{\partial}{\partial\eta_2} \qquad\qquad [5] = \zeta_1 \frac{\partial}{\partial\zeta_2} + \eta_1 \frac{\partial}{\partial\eta_2}$$

$$[3] = -\eta_2\zeta_1 + \zeta_2\eta_1 \qquad\qquad [6] = \zeta_2 \frac{\partial}{\partial\zeta_1} + \eta_2 \frac{\partial}{\partial\eta_1}$$

$$(\alpha\beta\gamma) = (-\eta_2\zeta_1 + \zeta_2\eta_1)^\alpha \ (-b\zeta_1 + a\eta_1)^\beta \ (-b\zeta_2 + a\eta_2)^\gamma$$

$$(\alpha\gamma\beta) = (-\eta_1\zeta_2 + \eta_2\zeta_1)^\alpha \ (-b\zeta_1 + a\eta_1)^\gamma \ (-b\zeta_2 + a\eta_2)^\beta$$

The operations on $(\alpha\beta\gamma)$:

$$[1]\ (\alpha,\beta,\gamma) = (\alpha+\beta)\ (\alpha,\beta,\gamma)$$

(25)

$$[2]\ (\alpha,\beta,\gamma) = (\alpha+\gamma)\ (\alpha,\beta,\gamma)$$

$$[3]\ (\alpha,\beta,\gamma) = (\alpha+1,\ \beta,\ \gamma)$$

$$[4]\ (\alpha,\beta,\gamma) = \alpha\ (\delta+1)\ (\alpha-1,\ \beta,\ \gamma) \qquad\qquad \delta = \alpha+\beta+\gamma$$

$$[5]\ (\alpha,\beta,\gamma) = \gamma\ (\alpha,\ \beta+1,\ \gamma-1)$$

$$[6]\ (\alpha,\beta,\gamma) = \beta\ (\alpha,\ \beta-1,\ \gamma+1)$$

The operations on (α, δ, β):

$$[1] \; (\alpha, \delta, \beta) = (\alpha + \delta)(\alpha, \delta, \beta)$$
$$[2] \; (\alpha, \delta, \beta) = (\alpha + \beta)(\alpha, \delta, \beta)$$
$$[3] \; (\alpha, \delta, \beta) = -(\alpha + 1, \delta, \beta)$$
$$[4] \; (\alpha, \delta, \beta) = -\alpha \delta (\alpha - 1, \delta, \beta)$$
$$[5] \; (\alpha, \delta, \beta) = \beta (\alpha, \delta + 1, \beta - 1)$$
$$[6] \; (\alpha \delta, \beta) = \delta (\alpha, \delta - 1, \beta + 1)$$

$$(25)$$

These results are now combined into the $\Omega(\pm)$ operators, and we compute the result of operating with them upon the two wave functions $[\alpha_1, \beta_1, \delta_1]$ and $[\alpha_2, \delta_2, \beta_2]$.

$$\Omega_\tau^s(+)[\alpha_2, \beta_2, \delta_2] = c_\tau \, Q_\tau^s(\beta_2, \delta_2)\,[\alpha_2 - \pi, \, \beta_2 - |s|, \, \delta_2 + |s|]$$
$$\Omega_\tau^s(-)[\alpha_2, \beta_2, \delta_2] = c_\tau \, Q_\tau^s(\delta_2, \beta_2)\,[\alpha_2 - \pi, \, \beta_2 + |s|, \, \delta_2 - |s|]$$
$$\Omega_\tau^s(+)[\alpha_2, \delta_2, \beta_2] = c_\tau \, Q_\tau^s(\delta_2, \beta_2)\,[\alpha_2 - \pi, \, \delta_2 - |s|, \, \beta_2 + |s|]$$
$$\Omega_\tau^s(-)[\alpha_2, \delta_2, \beta_2] = c_\tau \, Q_\tau^s(\beta_2, \delta_2)\,[\alpha_2 - \pi, \, \delta_2 + |s|, \, \beta_2 - |s|]$$

$$(26)$$

where

$$Q_\tau^s(\beta_2, \delta_2) = \sum_{\lambda=0}^{\tau - \frac{s}{2} - \frac{|s|}{2}} K_\lambda \, \alpha_2^{(\lambda + \pi)} (\delta + 1)^{(\lambda + \pi)} (\alpha_2 + \delta_2 - \lambda - \pi)^{(\tau - \frac{s}{2} - \frac{|s|}{2} - \lambda)} \beta_2^{(|s|)} (\alpha_2 + \beta_2 - \lambda - \frac{|s|}{2})^{(\tau - \frac{s}{2} - \frac{|s|}{2} - \lambda)}$$

$$Q_\tau^s(\delta_2, \beta_2) = \sum_{\lambda=0}^{\tau - \frac{s}{2} - \frac{|s|}{2}} K_\lambda \, \alpha_2^{(\lambda + \pi)} (\delta + 1)^{(\lambda + \pi)} (\alpha_2 + \beta_2 - \lambda - \pi)^{(\tau - \frac{s}{2} - \frac{|s|}{2} - \lambda)} \delta_2^{(|s|)} (\alpha_2 + \delta_2 - \lambda - \frac{|s|}{2})^{(\tau - \frac{s}{2} - \frac{|s|}{2} - \lambda)}$$

and the notation $\varepsilon^{(\nu)} = \varepsilon(\varepsilon - 1) \cdots (\varepsilon - \nu + 1)$

The next step is to introduce these results into the integrals for J^τ (16). We obtain,

$$J_1^\tau = \int [\alpha_1, \beta_1, \delta_1] \, \Omega_\tau^s(\pm)[\alpha_2, \beta_2, \delta_2]$$

$$= Q_\tau^s \left\{ \begin{matrix} (\beta_2, \delta_2) \\ (\delta_2, \beta_2) \end{matrix} \right\} R^\tau (\alpha_1 \beta_1 \delta_1 ; \alpha_2 \beta_2 \delta_2) \left\{ \begin{matrix} \int (\alpha, \beta, \delta)(\alpha_2 - \pi, \beta_2 - |s|, \delta_2 + |s|) \\ \int (\alpha, \beta, \delta)(\alpha_2 - \pi, \beta_2 + |s|, \delta_2 - |s|) \end{matrix} \right\}$$

where the upper expression in the bracket applies when $s = +$, and the lower when $s = -$. Condition (19) gives for this integral,

$$r = (\lambda_1 + \lambda_2) - (\ell_1 + \ell_2) = \alpha_2 - \alpha_1$$
$$s = (\lambda_1 - \lambda_2) - (\ell_1 - \ell_2) = \beta_2 - \beta_1 = \delta_1 - \delta_2$$

so that the integral becomes

$$J_1^\tau = Q_\tau^s \left\{ \begin{matrix} (\beta_2 \delta_2) \\ (\delta_2 \beta_2) \end{matrix} \right\} R^\tau(\alpha_1\beta_1\delta_1 ; \alpha_2\beta_2\delta_2) \left\{ \begin{matrix} \int(\alpha_1\beta_1\delta_1)(\alpha_1\beta_1\delta_1) \\ \int(\alpha_1\beta_1\delta_1)(\alpha_1\beta_1\delta_1) \end{matrix} \right\}$$

$$= N_L^{M_L}(\ell_1\ell_2) \; Q_\tau^s \left\{ \begin{matrix} (\beta_2\delta_2) \\ (\delta_2\beta_2) \end{matrix} \right\} R^\tau(\ell_1\ell_2 ; \lambda_1\lambda_2)$$

and it will be noted that a slightly different notation for the radial integral is introduced; the meaning is obvious.

Similar results are obtained for the other J^τ's.

$$J_2^\tau = \int [\alpha_1 \delta_1 \beta_1] \; \Omega_\tau^{s'}(\pm) [\alpha_2 \delta_2 \beta_2]$$

$$= Q_\tau^{s'} \left\{ \begin{matrix} (\delta_2\beta_2) \\ (\beta_2\delta_2) \end{matrix} \right\} R^\tau(\alpha_1\delta_1\beta_1 ; \alpha_2\delta_2\beta_2) \left\{ \begin{matrix} \int(\alpha_1\delta_1\beta_1)(\alpha_2-\alpha, \delta_2-|s|, \beta_2+|s|) \\ \int(\alpha_1\delta_1\beta_1)(\alpha_2-\alpha, \delta_2+|s|, \beta_2-|s|) \end{matrix} \right\}$$

$$= Q_\tau^{s'} \left\{ \begin{matrix} (\delta_2\beta_2) \\ (\beta_2\delta_2) \end{matrix} \right\} R^\tau(\ell_2\ell_1 ; \lambda_2\lambda_1) \left\{ \begin{matrix} \int(\delta_1\delta_1\beta_1)(\alpha_1\delta_1\beta_1) \\ \int(\alpha_1\delta_1\beta_1)(\alpha_1\delta_1\beta_1) \end{matrix} \right\}$$

$$= N_L^{M_L}(\ell_2\ell_1) \; Q_\tau^{s'} \left\{ \begin{matrix} (\delta_2\beta_2) \\ (\beta_2\delta_2) \end{matrix} \right\} R^\tau(\ell_2\ell_1 ; \lambda_2\lambda_1)$$

since (19) gives $s' = (\lambda_2-\lambda_1) - (\ell_2-\ell_1) = \beta_1-\beta_2 = \delta_2-\delta_1 = -s$

$$J_3^\tau = \int [\alpha_1 \delta_1 \beta_1] \; \Omega_\tau^{g}(\pm) [\alpha_2 \beta_2 \delta_2]$$

$$= Q_\tau^{g} \left\{ \begin{matrix} (\beta_2\delta_2) \\ (\delta_2\beta_2) \end{matrix} \right\} R^\tau(\alpha_1\delta_1\beta_1 ; \alpha_2\beta_2\delta_2) \left\{ \begin{matrix} \int(\alpha_1\delta_1\beta_1)(\alpha_2-\alpha, \beta_2-|g|, \delta_2+|g|) \\ \int(\alpha_1\delta_1\beta_1)(\alpha_2-\alpha, \beta_2+|g|, \delta_2-|g|) \end{matrix} \right\}$$

$$= Q_\tau^{g} \left\{ \begin{matrix} (\beta_2\delta_2) \\ (\delta_2\beta_2) \end{matrix} \right\} R^\tau(\ell_2\ell_1 ; \lambda_1\lambda_2) \left\{ \begin{matrix} \int(\alpha_1\delta_1\beta_1)(\alpha_1\delta_1\beta_1) \\ \int(\alpha_1\delta_1\beta_1)(\alpha_1\delta_1\beta_1) \end{matrix} \right\}$$

$$= N_L^{M}(\ell_2\ell_1) \; Q_\tau^{g} \left\{ \begin{matrix} (\beta_2\delta_2) \\ (\delta_2\beta_2) \end{matrix} \right\} R^\tau(\ell_2\ell_1 ; \lambda_1\lambda_2)$$

since (19) gives $q = (\lambda_1-\lambda_2) + (\ell_1-\ell_2) = \beta_2-\delta_1 = \beta_1-\delta_2$, and the upper expression prevails for $q = +$, the lower for $q = -$.

$$J_4^\tau = \int [\alpha_1 \beta_1 \delta_1] \; \Omega_\tau^{g'}(\pm) [\alpha_2 \delta_2 \beta_2]$$

$$= Q_\tau^{g'} \left\{ \begin{matrix} (\delta_2\beta_2) \\ (\beta_2\delta_2) \end{matrix} \right\} R^\tau(\alpha_1\beta_1\delta_1 ; \alpha_2\delta_2\beta_2) \left\{ \begin{matrix} \int(\alpha_1\beta_1\delta_1)(\alpha_2-\alpha, \delta_2-|g|', \beta_2+|g|') \\ \int(\alpha_1\beta_1\delta_1)(\alpha_2-\alpha, \delta_2+(g|'), \beta_2-|g|') \end{matrix} \right\}$$

$$= N_L^{M_L}(\ell_1\ell_2) \; Q_\tau^{g'} \left\{ \begin{matrix} (\delta_2\beta_1) \\ (\beta_2\delta_2) \end{matrix} \right\} R^\tau(\ell_1\ell_2 ; \lambda_2\lambda_1)$$

since (19) gives $q' = (\lambda_2-\lambda_1) + (\ell_2-\ell_1) = \delta_1-\beta_2 = \delta_2-\beta_1 = -q.$

If we now note that since it makes no difference how we label the electrons,

$$N_L^{M_L}(\ell_1\ell_2) = N_L^{M_L}(\ell_2\ell_1) \qquad R^\tau(\ell_2\ell_1;\lambda_1\lambda_2) = R^\tau(\ell_1\ell_2;\lambda_2\lambda_1)$$

$$R^\tau(\ell_2\ell_1;\lambda_1\lambda_2) = R^\tau(\ell_1\ell_2;\lambda_2\lambda_1)$$

and furthur that we may eliminate the use of s' and q' if we remember that the signs contained in the Ω_τ^s's and Ω_τ^g's must always be opposite as between J_1^τ and J_2^τ , and opposite as between J_3^τ and J_4^τ , and furthur that τ has the same range of summation in J_1^τ and J_2^τ , and the same range in J_3^τ and J_4^τ , we may combine the integrals as follows.

$$J_1^\tau + J_2^\tau = 2N_L^{M_L}(\ell_1\ell_2) \left\{ \begin{matrix} Q_\tau^s(\beta_2\delta_2) \\ Q_\tau^s(\delta_2\beta_2) \end{matrix} \right\} R^\tau(\ell_1\ell_2;\lambda_1\lambda_2)$$

$$J_3^\tau + J_4^\tau = 2N_L^{M_L}(\ell_1\ell_2) \left\{ \begin{matrix} Q_\tau^g(\beta_2\delta_2) \\ Q_\tau^g(\delta_2\beta_2) \end{matrix} \right\} R^\tau(\ell_1\ell_2;\lambda_2\lambda_1)$$

where the upper expression is used when s or q is positive and the lower if they are negative.

Furthur combining and we have,

$$J_1^\tau + J_2^\tau \pm (J_3^\tau + J_4^\tau) = 2N_L^{M_L}(\ell_1\ell_2) \left[\begin{matrix} Q_\tau^s(\beta_2\delta_2) \\ Q_\tau^s(\delta_2\beta_2) \end{matrix} R^\tau(\ell_1\ell_2;\lambda_1\lambda_2) \pm \begin{matrix} Q_\tau^g(\beta_2\delta_2) \\ Q_\tau^g(\delta_2\beta_2) \end{matrix} R^\tau(\ell_1\ell_2;\lambda_2\lambda_1) \right]$$

Finally we carry out the summation on τ (noting however that the range on τ in J_1^τ and J_2^τ is not necessarily the same as in J_3^τ and J_4^τ , so that we use another summation variable σ to avoid ambiguity) and introduce the expression into (15).

$$\Omega_{\lambda_1\lambda_2;LM_L}^{\ell_1\ell_2} = \sqrt{\frac{N_L^{M_L}(\ell_1\ell_2)}{N_L^{M_L}(\lambda_1\lambda_2)}} \left\{ \sum_\tau \begin{matrix} Q_\tau^s(\beta_2\delta_2) \\ Q_\tau^s(\delta_2\beta_2) \end{matrix} R^\tau(\ell_1\ell_2;\lambda_1\lambda_2) \pm \sum_\sigma \begin{matrix} Q_\sigma^g(\beta_2\delta_2) \\ Q_\sigma^g(\delta_2\beta_2) \end{matrix} R^\sigma(\ell_1\ell_2;\lambda_2\lambda_1) \right\}$$

(27)

These summations on τ and σ are restricted to a few values of τ and σ due to the fact that there are only certain values of these variables for which Q_τ and Q_σ are not zero.

These conditions are,

For $Q_r^s(\beta_2 \gamma_2)$ and $Q_r^s(\gamma_2 \beta_2)$

$$r/2 + s/2 \leq \tau \leq \alpha_2 + \beta_2 - r/2 - |s|/2$$

$$\tau \leq \alpha_2 + \gamma_2 - r/2 + |s|/2$$

$$\therefore \quad |\lambda_1 - \ell_1| \leq \tau \leq \lambda_1 + \ell_1$$
$$|\lambda_2 - \ell_2| \leq \tau \leq \lambda_2 + \ell_2$$

For $Q_\sigma^q(\beta_2 \gamma_2)$ and $Q_\sigma^q(\gamma_2 \beta_2)$ $\hspace{3cm}$ (28)

$$r/2 + q/2 \leq \sigma \leq \alpha_2 + \beta_2 - r/2 - |q|/2$$

$$\sigma \leq \alpha_2 + \gamma_2 - r/2 + |q|/2$$

$$\therefore \quad |\lambda_1 - \ell_2| \leq \sigma \leq \lambda_1 + \ell_2$$
$$|\lambda_2 - \ell_1| \leq \sigma \leq \lambda_2 + \ell_1$$

These conditions then, together with (21) must be satisfied if $\Omega_{\lambda_1 \lambda_1; LM_L}^{\ell_1 \ell_2}$ is not to vanish. It is to be noted that in the second part of (21) τ is to be replaced by σ .

$\hspace{2em}$ It is seen then that the matrix element, which is diagonal in both L and M_L, is only dependent on M_L through the normalization factors. From Brinkman[12] (page 55) it is obtained that $N_L^{M_L}(\ell_1 \ell_2)$ is the coefficient of $(aa^*)^{L+M_L} (bb^*)^{L+M_L}$ in the expression

$$\left(\begin{smallmatrix} 2L \\ L+M_L \end{smallmatrix} \right)^{-2} \int (P_1 P_1^*)^{\alpha_1} (Q_1 Q_1^*)^{\beta_1} (\bar{R}_1 \bar{R}_1^*)^{\gamma_1}$$

This is simply the normalization integral which corresponds to the process that has been used to evaluate the matrix element. The result is,

$$N_L^{M_L}(\ell_1 \ell_2) = \frac{(L+M_L)!(L-M_L)!}{(2L)!} \frac{(\delta_1+1)! \, \alpha_1! \, \beta_1! \, \gamma_1!}{(\beta_1+\delta_1+1)!(\alpha_1+\beta_1)!(\alpha_1+\delta_1)!} C_{2\ell_1} C_{2\ell_2}$$

where $C_{2\ell_i}$ is a constant which depends upon ℓ_i alone and its form is determined by the form of the initial wave function (for ordinary hydrogenic angular wave functions it is $(2\ell_i)!$).

The part depending on M_L is seen to be independent of l_1 and l_2 and entirely separate from the rest. Hence when we form the expression $N_L^{M_L}(l_1 l_2)/N_L^{M_L}(\lambda_1 \lambda_2)$ which occurs in the matrix element the part depending on M_L cancels out and leaves the matrix element entirely independent of M_L.

$$\Omega_{\lambda_1 \lambda_2}^{l_1 l_2} = \Omega_{\lambda, L}^{\ell} = \sqrt{\frac{(\delta_1 + 1)!\ \alpha_1!\ \beta_1!\ \delta_1!}{(\delta_2 + 1)!\ \alpha_2!\ \beta_2!\ \delta_2!}} \times$$

$$\left\{ \sum_{\tau}' \begin{array}{c} Q_\tau^s(\beta_2 \delta_2) \\ Q_\tau^s(\delta_2 \beta_2) \end{array} R^\tau(l_1 l_2; \lambda_1 \lambda_2) \pm \sum_\sigma' \begin{array}{c} Q_\sigma^g(\beta_2 \delta_2) \\ Q_\sigma^g(\delta_2 \beta_2) \end{array} R^\sigma(l_1 l_2; \lambda_2 \lambda_1) \right\} \quad (29)$$

It may be readily shown, by writing out the coefficients of the R's, that $\Omega_{\lambda, L}^\ell \equiv \Omega_{\ell, L}^\lambda$. This serves as a check.

In this expression the Q's, the numerical coefficients of the radial integrals, are defined by (26), and in order for a non-vanishing matrix element to exist τ and σ must be restricted by both conditions (21) and (28).

The Introduction of the Spin.

We have obtained a result for the matrix element of electrostatic interaction between two states, which were specified in terms of wave functions diagonal in L, from different configurations $(l_1 l_2)$ and $(\lambda_1 \lambda_2)$, which depends upon the values of $l_1, l_2, \lambda_1, \lambda_2$, and L. If we take into account the electron spin we can build up wave functions diagonal in S which are formed of linear combinations of individual electron spin functions. These will be denoted by $\psi_S^{M_S}$ and they will be, for the case of two electrons, symmetric if S=1, and antisymmetric if S=0.

Now the final atomic states are specified by values of J, L, S, M_J, where J is the result of the vector addition of L and S. We can build up the function for these final states

by taking linear combinations of products of wave functions of the form $\psi_L^{M_L}\psi_S^{M_S}$ where $\psi_L^{M_L}$ and $\psi_S^{M_S}$ are normalized wave functions for L and S, and $M_L + M_S = M_J$ (see page 13). We may suppose this to have been done so that there is obtained

$$\psi_{JLS}^{M_J} = \sum_{M_L} C_{JLS}^{M_J\,M_L}\, \psi_L^{M_L}\, \psi_S^{M_J-M_L}$$

The matrix element of e^2/r_{12} between two of these states will be

$$H_{J_2 M_{J_2} L_2 S_2}^{J_1 M_{J_1} L_1 S_1} = \frac{\int \psi_1^* \frac{e^2}{r_{12}} \psi_2}{\int \psi_1^* \psi_2} = \frac{\sum_{M_{L_1}}\sum_{M_{L_2}} C_{J_1 L_1 S_1}^{M_{J_1} M_{L_1}\,*}\, C_{J_2 L_2 S_2}^{M_{J_2} M_{L_2}} \int \psi_{L_1}^{M_{L_1}\,*} \psi_{S_1}^{M_{S_1}\,*} \frac{e^2}{r_{12}} \psi_{L_2}^{M_{L_2}} \psi_{S_2}^{M_{S_2}}}{\sum_{M_{L_1}}\sum_{M_{L_2}} C_{J_1 L_1 S_1}^{M_{J_1} M_{L_1}\,*}\, C_{J_2 L_2 S_2}^{M_{J_2} M_{L_2}} \int \psi_{L_1}^{M_{L_1}\,*} \psi_{S_1}^{M_{S_1}\,*} \psi_{L_2}^{M_{L_2}} \psi_{S_2}^{M_{S_2}}}$$

But e^2/r_{12} does not involve spins so the integral over the wave functions for spin becomes merely a normalization integral. Also $\int \psi_{L_1}^{M_{L_1}\,*} \frac{e^2}{r_{12}} \psi_{L_2}^{M_{L_2}}$ is just $\Omega_{\lambda,L}^{\ell}$ which has already been worked out, and is diagonal in both L and M_L.

$$\therefore\ H_{J_2 M_{J_2} L_2 S_2}^{J_1 M_{J_1} L_1 S_1} = \frac{\sum_{M_{L_1}} C_{J_1 L_1 S_1}^{M_{J_1} M_{L_1}\,*}\, C_{J_2 L_2 S_1}^{M_{J_2} M_{L_1}}\, \delta_{M_{L_1}, L_2}^{M_{L_1}, L_1}\, \delta_{M_{S_1}, S_2}^{M_{S_1}, S_1} \int \psi_{L_1}^{M_{L_1}\,*}(\ell, \ell_1) \frac{e^2}{r_{12}} \psi_{L_1}^{M_{L_1}}(\lambda, \lambda_1)}{\sum_{M_{L_1}} C_{J_1 L_1 S_1}^{M_{J_1} M_{L_1}\,*}\, C_{J_2 L_1 S_1}^{M_{J_1} M_{L_1}}}$$

But since J^2 is a constant of the motion when we use these wave functions, (it is invariant to a space rotation as is e^2/r_{12}) the operators J^2 and e^2/r_{12} commute and hence it can easily be shown that the matrix elements of e^2/r_{12} are diagonal in J.

$$H_{J M_J L S}^{J_1 M_{J_1} L_1 S_1} = \frac{\delta_{J_1 J}\, \delta_{M_{J_1} M_J}\, \delta_{L_1 L}\, \delta_{S S_1}\, \sum_{M_L} C_{JLS}^{M_J M_L\,*}\, C_{JLS}^{M_J M_L}\, \Omega_{\lambda, L, M_L}^{\ell}}{\sum_{M_L} C_{JLS}^{M_J M_L\,*}\, C_{JLS}^{M_J M_L}}$$

Now furthur we have shown that $\Omega_{\lambda, L, M_L}^{\ell}$ is independent of M_L so that we may take it outside of the summation, and the sum of constants cancel out, leaving,

$$H_{J M_J L S}^{J_1 M_{J_1} L_1 S_1}(\ell, \lambda) = H_{12} = \delta_{J_1 J}\, \delta_{M_{J_1} M_J}\, \delta_{L_1 L}\, \delta_{S S_1}\, \Omega_{\lambda, L}^{\ell} \qquad (30)$$

It is thus independent of J and M_J, but depends upon S through the choice of the ± signs in $\Omega_{\lambda, L}^{\ell}$.

III. COMPUTATION OF THE MATRIX ELEMENTS (RADIAL PART).

In attempting to evaluate the non-diagonal matrix elements of the electrostatic interaction the elements have thus far been reduced to a numerical factor times a radial integral. The typical radial integral, expressed in the previous section as $R^{\tau}(\ell_1 \ell_2; \lambda_1 \lambda_2)$, or

$$R^{\tau}(\ell \ell_2; \lambda_1 \lambda_2) = e^2 \iint_0^{\infty} \frac{r_<^\tau}{r_>^{\tau+1}} R(n_1 l_1/1) R(n_2 l_2/2) R(n_3 \lambda_1/1) R(n_4 \lambda_2/2) r_1^2 r_2^2 dr_1 dr_2$$

$$= R^{\tau}(n_1 l_1 n_2 l_2, n_3 \lambda_1 n_4 \lambda_2) \qquad \text{in the more famil-}$$

iar notation, where R(nl/i) is a normalized radial function of the i'th electron having quantum numbers n and l, must now be evaluated.

In order to obtain results which will not be limited to two electrons, we shall choose as our radial functions, Slater's approximation to the Hartree functions.

$$R(nl/i) = 1/N_{n\ell} \cdot r_i^{n^* - 1} \cdot e^{-\frac{z-s}{n^*} r_i}$$

(31)

where $N_{n\ell} = \left\{ \frac{(2n^* - 2)!}{\left[\frac{2(z-s)}{n^*} \right]^{2n^* - 1}} \right\}^{\frac{1}{2}}$ is the normalizing

factor, and n^* and s are parameters which are fixed when we are considering any given configuration in any given atom, and Z is the atomic number. The rules for finding n^* and s are as follows. If n = 1, 2, 3, 4, 5, 6

then n^* = 1, 2, 3, 3.7, 4.0, 4.2 .

s is obtained as a sum of terms contributed as follows -

a) Nothing from a shell outside the one considered.

b) 0.35 from each other electron in the group considered -
(except for the 1s group, where it is 0.30).

c) If the shell considered is an s or a p shell, an amount

0.85 from each electron with quantum number less by one, and an amount 1.00 from each electron still furthur in; for a _d_ or _f_ shell, an amount 1.00 from each electron inside it.

Using these radial functions we have,

$$R^{\tau}(n_1 l_1 n_2 l_2, n_3 \lambda_1 n_4 \lambda_2) = \frac{e^2}{N_{n_1 \ell_1} N_{n_2 \ell_2} N_{n_3 \lambda_1} N_{n_4 \lambda_2}} \int_0^{\infty}\int \frac{r_<^{\tau}}{r_>^{\tau}} r_1^{n_1^* + n_3^*} e^{-\left(\frac{z - s_1}{n_1^*} + \frac{z - s_2}{n_3^*}\right) r_1} \cdot$$

$$\cdot r_2^{n_2^* + n_4^*} e^{-\left(\frac{z - s_2}{n_2^*} + \frac{z - s_4}{n_4^*}\right) r_2} \, dr_1 dr_2$$

$$= \frac{e^2}{N_{n_1 \ell_1} N_{n_2 \ell_2} N_{n_3 \lambda_1} N_{n_4 \lambda_2}} \left\{ \int_0^{\infty}\int_{r_1 > r_2} r_2^{n_2^* + n_4^* + \tau} e^{-\eta_1 r_1} e^{-\eta_2 r_2} r_1^{n_1^* + n_3^* - \tau - 1} dr_1 dr_2 \right.$$

$$\left. + \int_0^{\infty}\int_{r_2 > r_1} r_1^{n_1^* + n_3^* + \tau} r_2^{n_2^* + n_4^* - \tau - 1} e^{-\eta_1 r_1} e^{-\eta_2 r_2} dr_1 dr_2 \right\}$$

$$= \frac{e^2}{N_{n_1 \ell_1} N_{n_2 \ell_2} N_{n_3 \lambda_1} N_{n_4 \lambda_2}} \left\{ \int_0^{\infty} r_1^{n_1^* + n_3^* - \tau - 1} e^{-\eta_1 r_1} dr_1 \int_0^{r_1} r_2^{n_2^* + n_4^* + \tau} e^{-\eta_2 r_2} dr_2 \right.$$

$$\left. + \int_0^{\infty} r_2^{n_2^* + n_4^* - \tau - 1} e^{-\eta_2 r_2} dr_2 \int_0^{r_2} r_1^{n_1^* + n_3^* + \tau} e^{-\eta_1 r_1} dr_1 \right\}$$

If we now place $\sigma_1 = n_1^* + n_3^*$, $\sigma_2 = n_2^* + n_4^*$

$$\eta_1 = \frac{z - s_1}{n_1^*} + \frac{z - s_3}{n_3^*} \quad , \quad \eta_2 = \frac{z - s_2}{n_2^*} + \frac{z - s_4}{n_4^*} \tag{32}$$

we can write - (after interchanging the name of the integration variables in the second term),

$$R^{\tau}(l_1 l_2; \lambda_1 \lambda_2) = \frac{e^2}{N_{n_1 \ell_1} N_{n_2 \ell_2} N_{n_3 \lambda_1} N_{n_4 \lambda_2}} \left\{ \int_0^{\infty} r_1^{\sigma_1 - \tau - 1} e^{-\eta_1 r_1} dr_1 \int_0^{r_1} r_2^{\sigma_2 + \tau} e^{-\eta_2 r_2} dr_2 \right.$$

$$\left. + \int_0^{\infty} r_1^{\sigma_2 - \tau - 1} e^{-\eta_2 r_1} dr_1 \int_0^{r_1} r_2^{\sigma_1 + \tau} e^{-\eta_1 r_2} dr_2 \right\}$$

$$\tag{33}$$

$$= \frac{e^2}{N_{n_1 \ell_1} N_{n_2 \ell_2} N_{n_3 \lambda_1} N_{n_4 \lambda_2}} \left\{ I(\sigma_1 \eta_1; \sigma_2 \eta_2) + I(\sigma_2 \eta_2; \sigma_1 \eta_1) \right\}$$

where $I(\sigma_i \eta_i; \sigma_j \eta_j) = \int_0^{\infty} y^{\sigma_i - \tau - 1} e^{-\eta_i y} dy \int_0^y x^{\sigma_j + \tau} e^{-\eta_j x} dx$

We now proceed to an evaluation of the "I" integral.

$$I(\sigma_1\eta_1;\sigma_2\eta_2) = \int_0^\infty y^{\sigma_1-\tau-1} e^{-\eta_1 y}\, dy \int_0^y x^{\sigma_2+\tau} e^{-\eta_2 x}\, dx = \int_0^\infty y^{\sigma_1-\tau-1} e^{-\eta_1 y}\mathcal{J}(\eta_2\sigma_2 y)\, dy$$

$$\mathcal{J}(\sigma_2\eta_2 y) = \int_0^y x^{\sigma_2+\tau} e^{-\eta_2 x}\, dx = \frac{(\sigma_2+\tau)!}{\eta_2^{\sigma_2+\tau+1}}\left[1 - e^{-\eta_2 y}\sum_{\alpha=0}^{\sigma_2+\tau}\frac{(\eta_2 y)^\alpha}{\alpha!}\right]$$

This result is of course the ordinary incomplete Gamma function integral, and holds as written only for values of α which are integral. We shall limit ourselves to this case for the moment. Now,

$$I(\sigma_1\eta_1;\sigma_2\eta_2) = \frac{(\sigma_2+\tau)!}{\eta_2^{\sigma_2+\tau+1}}\left\{\int_0^\infty y^{\sigma_1-\tau-1} e^{-\eta_1 y}\, dy - \int_0^\infty e^{-(\eta_1+\eta_2)y}\sum_0^{\sigma_2+\tau}\frac{\eta_2^\alpha\, y^{\sigma_1+\alpha-\tau-1}}{\alpha!}\, dy\right\}$$

$$= \frac{(\sigma_2+\tau)!}{\eta_2^{\sigma_2+\tau+1}}\left\{\frac{\Gamma(\sigma_1-\tau)}{\eta_1^{\sigma_1-\tau}} - \sum_{\alpha=0}^{\sigma_2+\tau}\frac{\eta_2^\alpha}{\alpha!}\int_0^\infty y^{\sigma_1+\alpha-\tau-1} e^{-(\eta_1+\eta_2)y}\, dy\right\}$$

> (the interchange of summation and integration being allowable by an application of Dini's theorem.)

$$= \frac{(\sigma_2+\tau)!}{\eta_2^{\sigma_2+\tau+1}}\left\{\frac{\Gamma(\sigma_1-\tau)}{\eta_1^{\sigma_1-\tau}} - \sum_{\alpha=0}^{\sigma_2+\tau}\frac{\eta_2^\alpha}{\alpha!}\frac{\Gamma(\sigma_1-\tau+\alpha)}{(\eta_1+\eta_2)^{\sigma_1-\tau+\alpha}}\right\}$$

We can write this in a slightly different form by taking out a term $\dfrac{\Gamma(\sigma_1-\tau)}{(\eta_1+\eta_2)^{\sigma_1-\tau}}$ and then have,

$$I(\sigma_1\eta_1;\sigma_2\eta_2) = \frac{(\sigma_2+\tau)!\,\Gamma(\sigma_1-\tau)}{\eta_2^{\sigma_2+\tau+1}(\eta_1+\eta_2)^{\sigma_1-\tau}}\left\{\left(\frac{\eta_1+\eta_2}{\eta_1}\right)^{\sigma_1-\tau} - \sum_{\alpha=0}^{\sigma_2+\tau}\frac{\Gamma(\sigma_1-\tau+\alpha)}{\Gamma(\sigma_1-\tau)}\frac{1}{\alpha!}\left(\frac{\eta_2}{\eta_1+\eta_2}\right)^\alpha\right\}$$

and furthur if we introduce the notation

$$w = \frac{n_2}{n_1+n_2} \qquad\qquad 1 - w = \frac{n_1}{n_1+n_2}$$

$$I(\sigma_1\eta_1;\sigma_2\eta_2) = \frac{(\sigma_2+\tau)!\,\Gamma(\sigma_1-\tau)}{\eta_2^{\sigma_2+\tau+1}(\eta_1+\eta_2)^{\sigma_1-\tau}}\left\{(1-w)^{\tau-\sigma_1} - \sum_{\alpha=0}^{\sigma_2+\tau}\frac{\Gamma(\sigma_1-\tau+\alpha)}{\Gamma(\sigma_1-\tau)}\frac{w^\alpha}{\alpha!}\right\} \tag{34}$$

This result, it will be remembered, was obtained under the condition that σ_2 be an integer. Since however $I(\sigma_1\eta_1;\sigma_2\eta_2)$ is quite obviously a continous function of σ_2, at least for small values, it is reasonable to generalize the expression for arbi-

trary values of σ_2 by writing

$$I(\sigma_1\eta_1;\sigma_2\eta_2) = \frac{\Gamma(\sigma_2+\tau+1)\,\Gamma(\sigma_1-\tau)}{(\eta_1+\eta_2)^{\sigma_1-\tau}\,\eta_2^{\sigma_2+\tau+1}}\left\{(1-w)^{\tau-\sigma_1}- \sum_{\alpha=0}^{\sigma_2+\tau} \frac{\Gamma(\sigma_1-\tau+\alpha)}{\Gamma(\sigma_1-\tau)} \frac{w^{\alpha}}{\alpha!}\right\} \tag{35}$$

where, by this sum terminating at a non-integral value of $\sigma_2+\tau$, we shall understand an interpolated value between values corresponding to the two integers nearest to $\sigma_2+\tau$.

Various other methods were experimented with in the attempt to evaluate $R^{\tau}(\ell.\ell_2;\lambda.\lambda)$, and it was found possible to express the radial integral as a remainder after a given number of terms in a Taylor series, or as a hypergeometric function of certain of the quantum numbers, both of course with appropriate coefficients depending on the quantum numbers, but neither seemed as readily adaptable to practical computation as the above.

In order to evaluate numerically the expression for I it is necessary to plot the function $\sum\limits_{\alpha=0}^{\sigma_2+\tau} \frac{\Gamma(\sigma_1-\tau+\alpha)}{\Gamma(\sigma_1-\tau)} \frac{w^{\alpha}}{\alpha!} = F_w^{\sigma_1-\tau}(\sigma_2+\tau)$ for different values of $\sigma_1-\tau$ and w as a function of $\sigma_2+\tau$, i.e. of the number of terms we take in the series. We will have then a family of curves, each of which has a fixed $\sigma_1-\tau$ and w, along which can be read off values corresponding to non-integral $\sigma_2+\tau$. For values of $\sigma_1-\tau$ and w for which curves are not drawn we may interpolate between various curves of the family.

A standard set of curves was computed for $F_w^{\sigma_1-\tau}(\sigma_2+\tau)$, using values of $\sigma_1-\tau$ from 2 to 5 and w = 0.4, 0.5, and 0.6, it being found that most practical cases had values of these variables lying between the above values. These curves are plotted as functions of $\sigma_2+\tau$ on the next page.

The procedure will then be to compute the term $(1-w)^{\tau-\sigma_1}$ and measure graphically the distance between the straight line
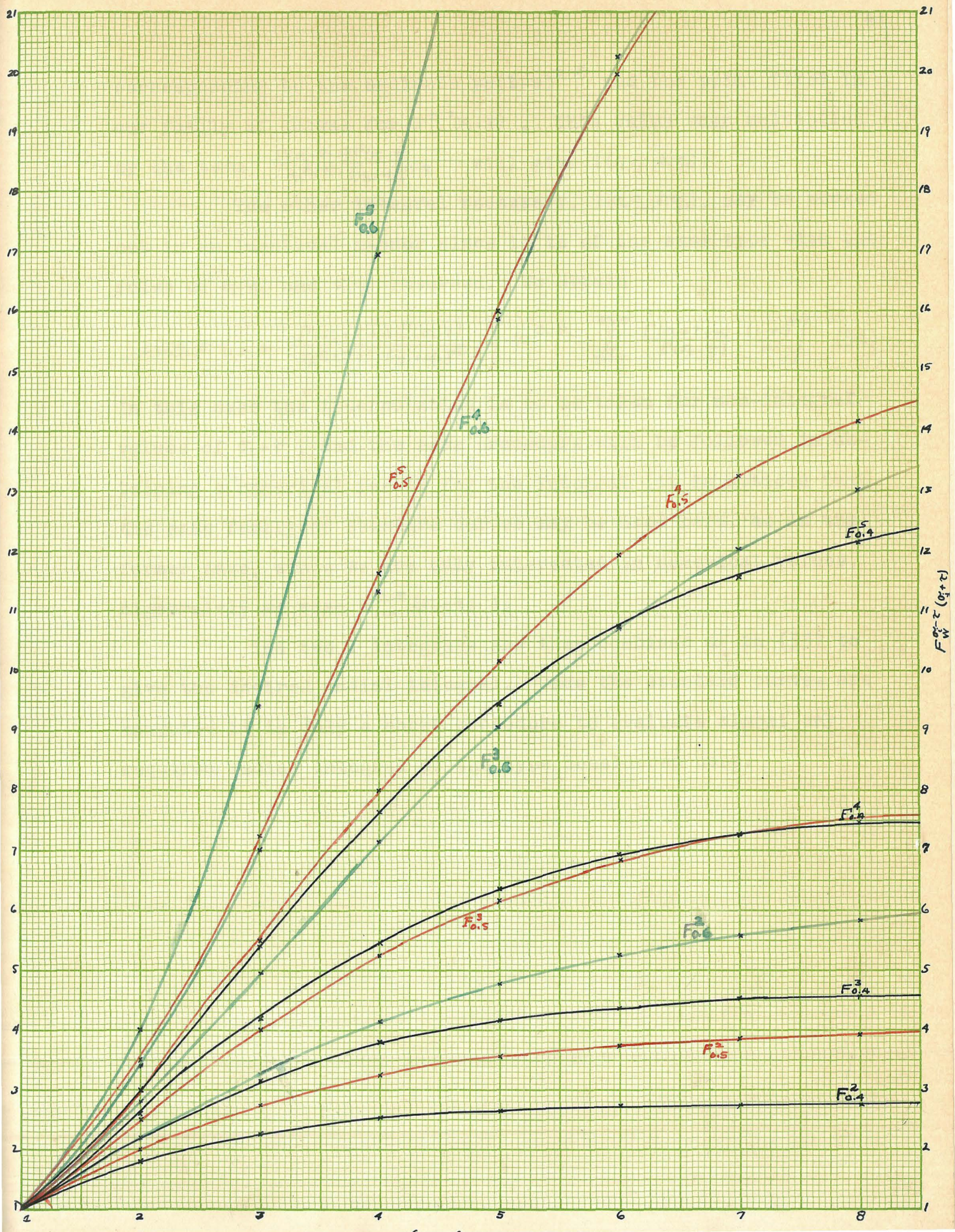
corresponding to the ordinate $y = (1-w)^{\tau - \sigma_1}$ and the point fixed in our family of curves for $F_w^{\sigma_1 - \tau}(\sigma_1 + \tau)$. This value when multiplied by the term $\dfrac{\Gamma(\sigma_2 + \tau + 1)\,\Gamma(\sigma_1 - \tau)}{\eta_2^{\sigma_1 + \tau + 1}\,(\eta_1 + \eta_2)^{\sigma_1 - \tau}}$ will give $I(\sigma_1 \eta_1; \sigma_2 \eta_2)$.

The other integral necessary, $I(\sigma_2 \eta_2; \sigma_1 \eta_1)$, may be worked out in an identical manner since it is of the same type with the roles of σ_2, η_2 and σ_1, η_1 reversed. We obtain

$$I(\sigma_2 \eta_2; \sigma_1 \eta_1) = \frac{\Gamma(\sigma_1 + \tau + 1)\,\Gamma(\sigma_2 - \tau)}{\eta_1^{\sigma_1 + \tau + 1}\,(\eta_1 + \eta_2)^{\sigma_2 - \tau}} \left\{ w^{\tau - \sigma_2} - \sum_{\alpha = 0}^{\sigma_1 + \tau} \frac{\Gamma(\sigma_2 + \tau + \alpha)}{\Gamma(\sigma_2 - \tau)} \frac{(1-w)^{\alpha}}{\alpha!} \right\} \quad (36)$$

In this case the interpolation is to be taken for non-integral values of $\sigma_1 + \tau$, and the same procedure will be followed in obtaining a numerical result for the integral (it is noticed that the same family of standard curves may be used here, as in the former case, since we are only interested in numerical values. Algebraicly we wish $F_{1-w}^{\sigma_2 - \tau}(\sigma_1 + \tau)$).

The two I integrals are then combined as in (33) to give the desired radial integral. Once the standard curves are computed it is only a short procedure to evaluate almost any required radial integral of the type considered here.

IV. TRANSITION INTENSITIES.

The matrix elements of the electrostatic interaction between configurations have been obtained in the form (30),

$$H^{J M_J \Lambda, S,}_{J M_J L S} (l_1 l_2, \lambda_1 \lambda_2) = H_{12} = \delta^{J, M_J, \Lambda, S,}_{J \ M_J L S} \ \Omega^{\ell, \ell_2}_{\lambda, \lambda_2; LS}$$

where $\Omega^{\ell, \ell_2}_{\lambda, \lambda_2; LS}$ is independent of J, M_J, and M_L.

To proceed with computations concerning the transition probabilities the proper wave functions for the system which includes the above interaction as a perturbation are built up, in the usual manner of the Schrodinger perturbation theory, out of linear combinations of the Ψ^o's (the Russell-Saunders wave functions describing the separate configurations) in which the H_{ij}'s enter as part of the coefficients.

$$\Psi_i = \Psi_i^o + \sum_{j \neq i}' \frac{H_{ij}}{E_i^o - E_j^o} \Psi_j^o + \sum_{j \neq i}' \left\{ \sum_{t \neq j} \frac{H_{it} H_{tj}}{(E_i^o - E_j^o)(E_t^o - E_j^o)} \right\} \Psi_j^o + \cdots$$

$$\Psi_K = \Psi_K^o + \sum_{\ell \neq k}' \frac{H_{K\ell}}{E_K^o - E_\ell^o} \Psi_\ell^o + \sum_{\ell \neq k}' \left\{ \sum_{s \neq \ell} \frac{H_{Ks} H_{s\ell}}{(E_K^o - E_\ell^o)(E_s^o - E_\ell^o)} \right\} \Psi_\ell^o + \cdots \quad (37)$$

It will be noted that the coefficients of the Ψ^o's are entirely independent of J; the H_{ij}'s have been found so in II, while the E^o's represent the energy levels before they are corrected with the diagonal elements of the perturbing matrix, i.e., the electrostatic energy which serves to split the configurations into multiplets, and hence are the centroid energies of the configurations which are obviously independent of J.

The transition intensity between two states is proportional to the square of the amplitude of the electric moment between the states, which in the quantum mechanical analogue of classical electromagnetic theory is expressed as $e \int \Psi_i^* r \ \Psi_K d\tau = \bar{A}$. We first compute the matrix elements of the components of this

quantity which will be associated with the various Zeeman components of a spectral line. The procedure for this is analogous to that used in evaluating the interaction matrix elements in the preceding section, in that symbolic spinor functions, transforming under a space rotation in a similar fashion, are substituted for the angular part of the factors ψ_i^*, ψ_k, and $\bar{r}$ occurring in the integral, and the integration worked out using the operational character of these functions. The method has been used by Brinkman[12] in evaluating the ordinary Russell-Saunders intensity relations. In writing out the expressions we shall use only the first order perturbation term in the proper wave functions, although it will be seen later that this is an unnecessary restriction and that the same type of a result is obtained no matter how many terms we take in the expression for ψ.

The components of $e\bar{r}$ which are desired for intensity relationships, $A_x + iA_y$, $-A_x + iA_y$, A_z, transform like the quantities X^2, Y^2, and $-XY$,[4] where X and Y are the components of a spin-vector, so that by introducing the operator $(-BX+AY)^2$, (A,B a constant spinor), for $e\bar{r}$, the requisite components are obtained. The same expressions are used for the wave functions as in section II, except that J,L,S replace the vectors L,l_1,l_2. The details of the procedure are much the same as before, in that differential operators are substituted for the X's and Y's and the indicated operations performed. The results for the case $J+1 \rightarrow J$ may be expressed as follows(the primes denote that the matrix elements have been computed between unnormalized wave functions).

$$(A'_x + iA'_y)_{J \; M}^{J+1 \; M+1}(ik) = \int \Psi_{i \; J+1}^{*\; M+1} (A_x + iA_y) \Psi_{K \; J}^{M} \, d\tau$$

$$= (A'_x + iA'_y)_{J \; M}^{J+1 \; M+1}(ik)^0 + \sum_j{}' R_{ij} (A'_x + iA'_y)_{J \; M}^{J+1 \; M+1}(jk)^0$$

$$+ \sum_\ell{}' R_{K\ell} (A'_x + iA'_y)_{J \; M}^{J+1 \; M+1}(i\ell)^0 + \sum_j{}' \sum_\ell{}' R_{ij} R_{K\ell} (A'_x + iA'_y)_{J \; M}^{J+1 \; M+1}(j\ell)^0$$

$$= \binom{2J+2}{J+M+2}^{-1} \left\{ C_J^{J+1}(ik)^0 + \sum_j{}' R_{ij} C_J^{J+1}(jk)^0 + \sum_\ell R_{K\ell} C_J^{J+1}(i\ell)^0 + \sum_j \sum_\ell R_{ij} R_{K\ell} C_J^{J+1}(j\ell)^0 \right\} \quad (38)$$

where $R_{ij} = H_{ij}/E_i^0 - E_j^0$

(ik) means that the function shown is taken between Ψ_i and Ψ_K

(ik)^0 " " " " " " " " " Ψ_i^0 and Ψ_K^0

$C_{J_z}^{J}(ij)^0$ = result of integrating the particular Ψ^0's shown

over the operator $(-BX+AY)$ [a] and does not depend upon M.

$$(-A'_x + iA'_y)_{J \; M}^{J+1 \; M-1}(ik) = \binom{2J+2}{J+M}^{-1} \left\{ \text{same expression as above} \right\}$$

$$(A'_z)_{J \; M}^{J+1 \; M}(ik) = \binom{2J+2}{J+M+1}^{-1} \left\{ \text{same expression as above} \right\}$$

In order to obtain the matrix elements between normalized wave functions it is noted that the normalization integral may be written

$$N_J^M = \int \Psi_J^{0 \; M *} \Psi_J^{0 \; M} d\tau = C_J \binom{2J}{J+M}^{-1} \quad (39)$$

where C_J is the part of this integral independent of M.
Hence if each Ψ^0 is divided by the proper $\sqrt{N_J^M}$ and the entire expression for the matrix element is divided by $\sqrt{N} = \sqrt{(1 + \sum_j R_{ij}^2)(1 + \sum_\ell R_{K\ell}^2)}$
(the normalization factors for the linear expansion), the matrix elements between normalized wave functions will be the result.

$$(A_x + iA_y)_{J \; M}^{J+1 \; M+1}(ik) = \sqrt{\frac{(J+M+2)(J+M+1)}{(2J+1)(2J+2) \, N}} \left\{ \frac{C_J^{J+1}(ik)^0}{\sqrt{C_{J+1}(i)^0 \, C_J(k)^0}} + \right.$$

$$\quad (40)$$

$$\left. \sum_j{}' \frac{R_{ij} C_J^{J+1}(jk)^0}{\sqrt{C_{J+1}(j)^0 C_J(k)^0}} + \sum_\ell{}' \frac{R_{K\ell} C_J^{J+1}(i\ell)^0}{\sqrt{C_{J+1}(i)^0 C_J(\ell)^0}} + \sum_j \sum_\ell \frac{R_{ij} R_{K\ell} C_J^{J+1}(j\ell)^0}{\sqrt{C_{J+1}(j)^0 C_J(\ell)^0}} \right\}$$

$$(-A_x + iA_y)^{J+1 \ M-1}_{J \ \ \ M}(i\kappa) = \sqrt{\frac{(J-M+2)(J-M+1)}{(2J+2)(2J+1)N}} \quad \Big\{ \quad \text{same as above} \Big\}$$

$$(A_z)^{J+1 \ M}_{J \ \ \ M}(i\kappa) = \sqrt{\frac{(J+M+1)(J-M+1)}{(2J+2)(2J+1)N}} \quad \Big\{ \quad \text{same as above} \Big\}$$

It will be noted that the expression in the bracket is entirely independent of M since both the $C^{J_i}_{J_2}$'s and the R_{ij}'s are independent of M; it will hereinafter be denoted by $\mathcal{A}^{J+1}_{J}(i\kappa)^\circ$.

To obtain the total intensity (total radiation in all directions) of a line $J+1 \rightarrow J$ which is not split into Zeeman components, the squares of the above matrix elements for the amplitudes of the components of the electric moment are integrated over all directions in space and the results summed (a factor $\frac{2}{3}\frac{(2\pi\nu)^4}{c^3}$, which comes from the fact that the true amplitude squared is a time average of the energy flow, must also be added). This gives the total intensity of a line $J+1 \rightarrow J$ which goes to the final state J,M. This result turns out to be independent of M, since this factor cancels out in the coefficients and $\mathcal{A}^{J+1}_{J}$ is already known to be independent. Hence the sum over all end states M, to give the total intensity of the transition $J+1$ to J, introduces simply a factor of $2J+1$. The resultant total intensity denoted by I^{J+1}_{J} is

$$I^{S' \ L' \ J+1}_{S \ L \ J} = \frac{2}{3}\frac{(2\pi\nu)^4}{c^3}\frac{(2J+3)}{N}\left[\mathcal{A}^{J+1}_{J}(i\kappa)^\circ\right]^2 \tag{41}$$

By a similar procedure the corresponding intensities for transitions $J \rightarrow J$ and $J-1 \rightarrow J$ are obtained.

$$I^{S' \ L' \ J}_{S \ L \ J} = \frac{2}{3}\frac{(2\pi\nu)^4}{c^3}\frac{(2J+1)(J+1)}{2JN}\left[\mathcal{A}^{J}_{J}(i\kappa)^\circ\right]^2$$

$$I^{S' \ L' \ J-1}_{S \ L \ J} = \frac{2}{3}\frac{(2\pi\nu)^4}{c^3}\frac{(2J+1)}{N}\left[\mathcal{A}^{J-1}_{J}(i\kappa)^\circ\right]^2$$

These intensities have been denoted as occurring for transitions

S', L', to S, L since the factors $\mathcal{A}_J^{J'}$ are still dependent, through

the expressions $C_J^{J'}$ and C_J, upon S and L as well as upon J. The

next step is to obtain this dependence, and separate the factors

depending on J.

The factors $C_J(i)^0$ resulting from the normalization

integral (39) may be separated into a product of two factors,

$C_J(i)^0 = f(J,L,S) C_L(i)^0$ where f is independent of the values l_1,

l_2, etc., out of which the state i is built, while $C_L(i)^0$ con-

tains this dependence but is independent of J.

The factors $C_J^{J'}(ij)^0$ are simply the results of integrat-

ing the Russell-Saunders wave functions $\psi_i^0(J'L'S')$ and $\psi_j^0(JLS)$ over

the operator $(-BX+AY)^2$ and have been evaluated partially by Brink-

man[12]. They may be written as a product of two factors

$$C_J^{J'}(ij)^0 = g(J,J',L,L',S,S') \; C_L^{L'}(ij)^0 \qquad (42)$$

where g is completely independent of the factors $l_1, l_2, \lambda_1, \lambda_2$, etc,

as well as the manner in which the states L, L', and S, S', are

built up out of them, while $C_L^{L'}(ij)^0$ contains this dependence but

is completely independent of J. Now the function $\mathcal{A}_J^{J'}(ik)^0$ into

which the values of $C_J^{J'}$ and C_J are to be substituted consists of

four terms, three of which involve sums over certain L-S wave

functions. However it will be remembered that the matrix element

R_{ij} (or H_{ij}) was found to be diagonal in J, L, and S, so that all

the L-S wave functions associated with the initial state $\psi_i^{J'L'S'}$

have the same values J', L', S', and all the L-S functions asso-

ciated with the final state ψ_k^{JLS} have the same values J, L, S.

This means that when we put the above expressions for $C_J^{J'}$ and C_J

into $\mathcal{A}_J^{J'}$, the part $F(J,J',L,L',S,S') = \dfrac{g(J,J',L,L',S,S')}{\sqrt{f(J,L,S) \; f(J',L',S')}}$ is not only

independent of the inner summations but is also the same for each of the four terms. The result may be written,

$$\mathcal{A}_J^{J'}(i\kappa)^\circ = \mathcal{A}_J^{J'}\left[C_J^{J'}(i\kappa)\cdots\right] = F(JJ'LL'SS')\mathcal{A}_L^{L'}\left[C_L^{L'}(i\kappa)^\circ\cdots\right] = F(JJ'LL'SS')\mathcal{A}_L^{L'}(i\kappa)^\circ$$

If this form of $\mathcal{A}_J^{J'}$ is introduced into (41) and the particular values of $F(J,J',L,L',S,S')$ are written out (these coefficients have been evaluated numerous times[4,5,8,12]) for the only cases of L' and S' for which the intensity is not zero, we obtain for the transition probabilities,

$$
\left\{
\begin{aligned}
I_S^{S\ L+1\ J+1}_{\ \ L\ \ \ J} &= \frac{(2\pi\nu)^4}{3c^3}\ \frac{(\alpha+\beta+\gamma+3)(\alpha+\beta+\gamma+2)(\beta+2)(\beta+1)}{(J+1)(2L+2)(2L+1)N}\left[\mathcal{A}_L^{L+1}(i\kappa)^\circ\right]^2 \\
I_S^{S\ L+1\ J}_{\ \ L\ \ \ J} &= \frac{(2\pi\nu)^4}{3c^3}\ \frac{(2J+1)(\alpha+\beta+\gamma+2)(\alpha+1)(\beta+1)\gamma}{J(J+1)(2L+2)(2L+1)N}\left[\mathcal{A}_L^{L+1}(i\kappa)^\circ\right]^2 \quad (43)\\
I_S^{S\ L+1\ J-1}_{\ \ L\ \ \ J} &= \frac{(2\pi\nu)^4}{3c^3}\ \frac{(\alpha+2)(\alpha+1)\gamma(\gamma-1)}{J(2L+2)(2L+1)N}\left[\mathcal{A}_L^{L+1}(i\kappa)^\circ\right]^2
\end{aligned}
\right.
$$

$$
\left\{
\begin{aligned}
I_S^{S\ L\ J+1}_{\ \ L\ J} &= \frac{(2\pi\nu)^4}{3c^3}\ \frac{(\alpha+\beta+\gamma+2)\alpha(\beta+1)(\gamma+1)}{(J+1)(2L)^2 N}\left[\mathcal{A}_L^{L}(i\kappa)^\circ\right]^2 \\
I_S^{S\ L\ J}_{\ \ L\ J} &= \frac{(2\pi\nu)^4}{3c^3}\ \frac{(2J+1)(\beta^2+\beta\gamma+\alpha\beta-\alpha\gamma+2\beta)^2}{J(J+1)(2L)^2 N}\left[\mathcal{A}_L^{L}(i\kappa)^\circ\right]^2 \quad (44)\\
I_S^{S\ L\ J-1}_{\ \ L\ J} &= \frac{(2\pi\nu)^4}{3c^3}\ \frac{(\alpha+\beta+\gamma+1)(\alpha+1)\beta\gamma}{J(2L)^2 N}\left[\mathcal{A}_L^{L}(i\kappa)^\circ\right]^2
\end{aligned}
\right.
$$

where $\alpha = L+S-J$, $\beta = J+L-S$, $\gamma = J+S-L$

and the transition probabilities for $L-1 \to L$ can be obtained from (43) by interchanging initial and final states. The $\mathcal{A}_L^{L'}(i\kappa)^\circ$'s are entirely independent of J but depend upon L and S. They are of the form,

$$\mathcal{A}_L^{L'}(i\kappa)^\circ = \frac{C_L^{L'}(i\kappa)^\circ}{\sqrt{C_{L'}(i)^\circ C_L(\kappa)^\circ}} + \sum_j \frac{R_{ij}\ C_L^{L'}(j\kappa)^\circ}{\sqrt{C_{L'}(j)^\circ C_L(\kappa)^\circ}} + \sum_\ell \frac{R_{\kappa\ell}\ C_L^{L'}(i\ell)^\circ}{\sqrt{C_{L'}(i)^\circ C_L(\ell)^\circ}} +$$

$$\sum_j \sum_\ell \frac{R_{ij}\ R_{\kappa\ell}\ C_L^{L'}(j\ell)^\circ}{\sqrt{C_{L'}(j)^\circ C_L(\ell)^\circ}} + \cdots \quad (45)$$

Now it will be noted that in this entire process the first term which appears in the matrix elements (38)(40) and in the expressions for $\mathcal{A}_J^L$ and $\mathcal{A}_L^{L'}$ corresponds to the transition intensity which would be obtained had there been no interconfiguration perturbations. The various multiplicative factors which were obtained in (38), (40), (41), and (43), (44) and are dependent upon J, L, S, are independent of the fact that the extra terms arising from the perturbation are present in the matrix element of the electric moment. Thus, <u>the only difference between the above intensity expressions and those which would be obtained for the unperturbed case of strict L-S coupling is the presence of the extra normalizing factor N and the additional terms in $\mathcal{A}_L^{L'}$.</u>

It will be remembered that in carrying out the above calculation only the first order correction to the wave function was used. However the same sort of a result is obtained no matter how many terms we take in the expression (37) for the proper wave functions, since the coefficients are built up out of H_{ij}'s which are diagonal in J, L, and S and all the ψ^{o}'s in the expansion of any ψ_i have the same value of J, L, and S and hence give rise to identical factors as far as the dependence on these variables is concerned. <u>The only new thing which is introduced is the presence of additional terms in the expression for $\mathcal{A}_L^{L'}(iN)$.</u>

Since when we deal with the relative transition intensities within a given multiplet transition $L' \rightarrow L$, $S \rightarrow S$, the factors N and $\mathcal{A}_L^{L'}(iN)^{o}$ cancel out (they are independent of J), the result is obtained that <u>these relative intensities are unaffected by the interconfiguration perturbation of the electrostatic interaction, a result which is true no matter how accurate an approx-</u>

imation to the perturbed wave functions is used. (This, of course, is with the neglect, as far as the energies are concerned, of the spin-orbit term in the Hamiltonian.) However the absolute intensities, and the relative intermultiplet intensities, may be affected considerably, especially if two interacting configurations happen to lie close to one another and thus give rise to small values for some of the denominators occurring in the expressions for R_{ij}.

This rule is of course subject to the slight error due to the factor ν^4 which occurs in the expression for intensity. However this same factor affects in like order of magnitude the intensity relations in strict L-S coupling, and in general is quite negligible when relative intensities for a given multiplet transition are dealt with.

This result is dependent upon two factors -- first, the fact that the matrix element H_{ij} is independent of J, and second, the fact that the expressions which arise in the application of group theory to quantum mechanics involving two vector quantities and their sum (e.g. $\bar{J} = \bar{L} + \bar{S}$) may be written as a product of two terms one of which contains the entire dependence on the sum (J) and is entirely independent of the subconstituents of the other two (i.e. $l_i \ldots l_j$, $s_i \ldots \ldots s_j$).

V. SUMMARY AND DISCUSSION.

The result which has been obtained, namely, that the relative intensities of the lines within a given multiplet transition are independent of the interconfiguration perturbation of the electrostatic interaction, no matter how accurate an approximation is taken for the proper wave functions describing the perturbation, is consequent upon the following general process of building up the atomic system of energy levels. First of all the ordinary wave equation is solved in its elementary form which takes into account only the interaction of the individual electrons with the central field, and values are obtained for the so-called centroid energy levels of the different configurations. Next, the electrostatic interaction is introduced and the consideration of the diagonal elements of its matrix serves to split the configurations into multiplets which still possess the degeneracy that is to be later removed by the introduction of the spin-orbit interaction. The formal introduction of this interaction which splits the multiplets into J-energy levels is omitted for the time being, but the results of it are assumed in so far as we pick out of the various wave functions for the multiplets those particular ones associated with the J-levels, for purposes of computation of the non-diagonal matrix elements of the electrostatic interaction. When these non-diagonal elements between configurations are introduced, and the consequently modified wave functions used to compute transition intensities, the above theorem is obtained. The complete nuclear(central field), and electrostatic interactions have then been introduced into the energy levels, but not the spin-

orbit interaction.

If now the diagonal elements of the spin-orbit term in the Hamiltonian are taken into account the usual system of energy levels in terms of configurations, L's, S's, and J's, is obtained, except that furthur the energy perturbations due to interconfiguration interactions of the electrostatic term are already included. However, the relative intensity theorem above is still valid, since the E°'s appearing in the expressions from which it was derived are those present before the diagonal elements of whatever interconfiguration term we are considering have been taken into account, and the interconfiguration part of the spin-orbit term is as yet unintroduced. This requires some amplification --- since the strict division into definite configurations has already been scrambled by the interconfiguration terms of e^2/r_{12}, the complete diagonal elements of the spin-orbit term contain some of the interconfiguration part, but we may think of considering first only that part of the complete diagonal elements which is strictly diagonal in terms of the L-S wave functions, and then later the part which is "interconfiguration" in terms of these functions.

When the "interconfiguration" interaction caused by the non-diagonal matrix elements of the spin-orbit term in the Hamiltonian is taken into account, together with that "interconfiguration" part of the diagonal elements mentioned above, two new features are introduced. First, if it is assumed that these non-diagonal elements are negligible either in absolute magnitude or in comparison with similar terms of the electrostatic interaction, then the same form is obtained for the perturbed wave functions(37)

as before(since there are no new or additional H_{ij}'s), with the difference that now the E^o's which appear in the denominators of the R_{ij}'s are the energy levels before the diagonal elements of the spin-orbit term are introduced, but after the diagonal elements of the electrostatic term are taken into account. Hence, they are the centroid energy levels of the separate multiplets, and as such , are still independent of J; thus the theorem is still valid. Secondly, if these non-diagonal matrix elements are not neglected they will introduce certain additional terms in the expression for the perturbed wave functions(37). Since the matrix elements are diagonal in J but not in L and $S^{13,15}$, as were the corresponding elements of the electrostatic interaction, the additional terms which are introduced involve multiplets of different types than the original. This destroys the simple form of the intensity expressions and makes impossible the step in which a common factor depending on J, $F(J,J',L,L',S,S')$, was taken out of all the $C_J^{J'}$'s. Hence, the dependence on J does not cancel out when we compute relative intensities within a given multiplet transition, and these relative intensities are distorted from their normal values.

Before proceeding furthur in the effort to obtain an estimation of the magnitude of these anomalies, we must consider a few facts concerning the spin-orbit interaction between configurations. Shortley[15] has investigated some phases of this interaction and found that terms existed only between configurations which differ only in the $\underline{n}$ of one electron. Such configurations can be considered as two members of the same series, and in general lie far apart in the spectrum. Because of this, and the

fact that it is not true of the interconfiguration electrostatic interaction, we must come to the conclusion that as far as energy perturbations are concerned, the electrostatic interaction is alone of importance. In the case of intensity anomalies, however, it has been seen that the electrostatic term alone, even when the energies of the configurations involved overlap, can have no effect on certain of the relative intensities. It is only when the two interactions are combined that the anomalies may be accounted for.

The method of introducing the various interactions that has been outlined above served to make this clear. At the end it was apparent that only the introduction of the interconfiguration spin-orbit interaction yielded anomalies, and hence since it was the only term present it could not be neglected. Nevertheless, the above restriction on it, to between members of the same "configuration" series, makes all of its terms small. In order to avoid computing and introducing all these small terms (which serve to connect different types of multiplets, and thus destroy the simple separation into multiplet types which existed previously), it is desirable to examine an alternative order of introduction of the various interactions which makes possible a more practical computation of the intensity anomalies.

The alternative procedure is as follows. After the central field interaction with the electrons is taken into account, the diagonal and non-diagonal elements within a configuration of the spin-orbit term are introduced. Next the diagonal elements of the electrostatic interaction are taken into account, so that thus far each configuration is independent. Finally we compute the interconfiguration interaction caused by the perturbing terms

in the Hamiltonian (both e^2/r_{12} and spin-orbit). This will consist of two parts, one from e^2/r_{12} and one from the spin-orbit term; however the latter is small(see above) and can be neglected here in comparison to the electrostatic term. Hence we obtain for the entire interconfiguration interaction just those terms which have already been computed, which are diagonal in J, M_J, L, ans S, and hence connect only multiplets of identical type. However, in this case, the E°'s which appear in the denominators of the expansion coefficients, R_{ij}'s, are no longer independent of J, but are just the ordinary energy levels specified by J, L, and S. The intensity anomalies exist then because of the combination of both spin-orbit and electrostatic interaction. The $\mathcal{A}_L^{L''}$'s do not cancel out since they are not independent of J due to the presence of the spin-orbit term; but there would be no anomalous terms to be cancelled out were it not for the presence of non-zero interconfiguration elements of the electrostatic term.

The expressions which are obtained for the intensities are identical with (43) and (44) except that the R_{ij}'s which occur in the $\mathcal{A}_L^{L'} GK\rho$'s (45) must be written,

$$R_{ij} = \frac{H_{ij}}{E_i^\circ - E_j^\circ} \qquad \text{where } E_i^\circ = E_i + \Delta_i(J_i)$$

E_i = centroid energy of multiplet(independent of J)

$\Delta_i(J_i)$ = spin-orbit splitting factor $\qquad\qquad$ (46)

This may be written,

$$R_{ij} = \frac{H_{ij}}{E_i - E_j + \left[\Delta_i(J_i) - \Delta_j(J_j)\right]} = \frac{H_{ij}}{E_i - E_j} + \frac{H_{ij}\left[\Delta_i(J_i) - \Delta_j(J_j)\right]}{(E_i - E_j)^2}$$

since $\Delta_i - \Delta_j \ll E_i - E_j$ in general.

When this value of R_{ij} is substituted, $\mathcal{A}_L^{L'}$ may be conveniently separated into two parts, the first of which is the same as we had previously and the second of which is a second order term depending on J and containing factors which measure the spin-orbit interaction.

$$\mathcal{A}_L^{L'}{}_{(LK)^0} = \mathcal{A}_L^{L'}{}_I + \mathcal{A}_L^{L'}{}_{II}$$

When this is put into the expressions for intensity and squared, the square of $\mathcal{A}_{L\,II}^{L'}$ may be neglected and we obtain,

$$I_{SLJ}^{SL'J'} = \frac{(2\pi\nu)^4}{3c^3}\ \frac{K(J,J',L,L',S)}{N}\ \left[\mathcal{A}_{L\,I}^{L'}\right]^2\left(1+\frac{\mathcal{A}_{L\,II}^{L'}}{\mathcal{A}_{L\,I}^{L'}}\right) \tag{47}$$

where K is given in (43) and (44), and

$$\mathcal{A}_{L\,I}^{L'}{}_{(LK)^0} = \frac{C_L^{L'}{}_{(LK)^0}}{\sqrt{C_{L'}{}_{(L)^0}C_L{}_{(K)^0}}} + \sum_j{}' \frac{H_{ij}\,C_L^{L'}{}_{(jK)^0}}{(E_i-E_j)\sqrt{C_{L'}{}_{(j)^0}C_L{}_{(K)^0}}} + \sum_\ell{}' \frac{H_{K\ell}\,C_L^{L'}{}_{(L\ell)^0}}{(E_K-E_\ell)\sqrt{C_{L'}{}_{(L)^0}C_L{}_{(\ell)^0}}} +$$

$$\sum_j{}'\sum_\ell{}' \frac{H_{ij}\,H_{K\ell}\,C_L^{L'}{}_{(j\ell)^0}}{(E_i-E_j)(E_K-E_\ell)\sqrt{C_{L'}{}_{(j)^0}C_L{}_{(\ell)^0}}} + \ -\ -\ -\ -$$

$$\mathcal{A}_{L\,II}^{L'}{}_{(LK)^0} = \sum_j{}' \frac{H_{ij}\left[\Delta_i(J')-\Delta_j(J')\right]C_L^{L'}{}_{(jK)^0}}{(E_i-E_j)^2\sqrt{C_{L'}{}_{(j)^0}C_L{}_{(K)^0}}} + \sum_\ell{}' \frac{H_{K\ell}\left[\Delta_K(J')-\Delta_\ell(J')\right]C_L^{L'}{}_{(L\ell)^0}}{(E_K-E_\ell)^2\sqrt{C_{L'}{}_{(L)^0}C_L{}_{(\ell)^0}}} +$$

$$\sum_j{}'\sum_\ell{}' \frac{H_{ij}\,H_{K\ell}\left[\Delta_i(J')-\Delta_j(J')\right]\left[\Delta_K(J')-\Delta_\ell(J')\right]C_L^{L'}{}_{(j\ell)^0}}{(E_i-E_j)^2(E_K-E_\ell)^2\sqrt{C_{L'}{}_{(j)^0}C_L{}_{(\ell)^0}}} + \ -\ -\ -\ - \tag{48}$$

The first term in (47) then is entirely dependent on the electrostatic interaction and is the first-order term as far as anomalies in absolute intensities and in relative inter-multiplet intensities are concerned. It leaves relative intensities for a a given multiplet transition unchanged. The second term in (47) is the second-order term in absolute intensity anomalies and involves a product of factors depending on the electrostatic and spin-orbit interactions respectively; it is the first-order term as far as anomalies in relative intensities within a given multiplet transition are concerned.

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