Transformations in the Theory of Complex Spectra

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Four transformations are considered in detail: that from the zero-order nlm_lm_s scheme to the *LS*-coupling scheme, that from the zero-order $nljm_j$ scheme to the *jj*-coupling scheme, that connecting these two zero-order schemes, and that connecting the *LS*- and the *jj*-coupling schemes. A correlation between the states of the configuration with ϵ electrons in shell S plus η other electrons and those of the configuration with ϵ electrons missing from shell S plus the same η other electrons is found such that all of these transformations are the same for the two configurations. The transformation between zero-order states in two different schemes is considered in general and a general expression (3.10) is found giving this transformation for an almost closed shell in terms of the transformation for the corresponding simple configuration. Finally, a direct method is found for obtaining the transformation from *LS*-coupling to *jj*-coupling for any two-electron configuration, and this transformation is given explicitly for all such configurations up to *dd*. This then furnishes the *LS-jj*-coupling transformation also for p^4, p^5s, p^5p, p^5d, d^8, d^9s, d^9p, and d^9d, the configurations for which the *jj*-coupling scheme is most useful.

IN the course of the calculations on the spectra of configurations containing almost-closed shells which the writer is making, it became desirable to use the *jj*-coupling scheme for certain configurations, such as p^5p and p^5d of the rare gases. The problem of transforming the electrostatic energy matrix to this scheme led to the following considerations of the transformations involved in the theory of complex spectra.

There are four representations which are of importance in the theory, the two zero-order schemes which we shall designate as the m_lm_s scheme and the jm_j scheme, and the two schemes characterized by quantized resultant J and M_J, which we shall call the *LS*-coupling scheme and the *jj*-coupling scheme. The four most interesting transformations between these schemes may be represented diagrammatically as follows:

$$\begin{array}{ccc} nljm_j & \rightleftharpoons & nlm_lm_s \\ \updownarrow & & \updownarrow \\ jjJM_J & \rightleftharpoons & LSJM_J. \end{array}$$

Our principal objective will be the determination of the relation between the *LS*- to *jj*-coupling transformation for a simple configuration and for the corresponding configuration involving an almost closed shell. To this end, we shall first consider this relation for each of the other transformations. We shall then obtain explicitly the *LS-jj* transformation by a direct method for all two-electron configurations up to *dd* (and hence for their almost-closed shell correspondents).

§1. The transformation $nlm_lm_s \rightleftharpoons LSJM_J$

In the m_lm_s scheme one specifies a set nlm_lm_s of quantum numbers for each electron in the configuration. In forming an antisymmetric zero-order wave function (cf. 3.2) these sets are arranged in a specified order. We shall take as standard an order in which sets of a given n and l, i.e., sets belonging to the same shell, are arranged in order of decreasing m_l, with $m_s=+\frac{1}{2}$ before $m_s=-\frac{1}{2}$ in case both occur for a given m_l. The transformation from this scheme to a scheme in which $\mathbf{L}^2$, $\mathbf{S}^2$ and $\mathbf{J}^2$ are diagonal may be obtained by several methods.[1] The relation between this transformation for a configuration ($\boldsymbol{L}$) containing ϵ electrons in shell S plus η electrons in other shells to that for the configuration ($\boldsymbol{R}$) having ϵ electrons missing from shell S plus the same η other electrons has been determined by the writer.[2] To a given zero-order state of $\boldsymbol{L}$ we correlate that state of $\boldsymbol{R}$ whose ϵ missing electrons have the negatives of the m_l and m_s values of the ϵ electrons of $\boldsymbol{L}$ and whose η additional electrons have the same quantum numbers as those of $\boldsymbol{L}$,

[1] See Ufford and Shortley, Phys. Rev. **42**, 167 (1932), §2.

[2] Shortley, Phys. Rev. **40**, 185 (1932). The letters $\boldsymbol{L}$ and $\boldsymbol{R}$ refer to left and right in the periodic table.

taken when in standard order with a phase (-1) to the sum of the m_l values of the electrons in shell S. With this correlation it was shown that the matrices of $\mathbf{L}^2$, $\mathbf{S}^2$ and $\mathbf{L}\cdot\mathbf{S}$ are the same in the two cases and hence that the transformation to LS-coupling is the same.

§2. The transformation $nljm_j \rightleftharpoons jjJM_j$

In the jm_j scheme a set $nljm_j$ of quantum numbers is specified for each electron in the configuration. Within a given shell we shall take for the standard order of arrangement of these sets, first those with $j=l+\frac{1}{2}$ in descending order of m_j, then those with $j=l-\frac{1}{2}$ in descending order of m_j. In the jj-coupling scheme, $\mathbf{J}^2$ has been diagonalized so that one obtains states characterized by a set of j values for the electrons and resultant J and M_J. The transformation between these two schemes may be obtained by methods analogous to those of reference 1.

Let us consider the matrix of $\mathbf{J}^2$ in the jm_j scheme. Its elements may be written down in exact analogy to those of $\mathbf{L}^2$ in the m_lm_s scheme.[3] It has nondiagonal elements only between states which differ in regard to two individual sets of quantum numbers; say that state A contains sets a and b where A' contains a' and b'. This element has the value

$$(A\,|\,\mathbf{J}^2\,|\,A')=\pm 4\{(a\,|\,J_x\,|\,a')(b\,|\,J_x\,|\,b')-(a\,|\,J_x\,|\,b')(b\,|\,J_x\,|\,a')\},$$

where

$$(a\,|\,J_x\,|\,b)=(n^al^aj^am_j^a\,|\,J_x\,|\,n^bl^bj^bm_j^b)=\delta(n^al^aj^a;\,n^bl^bj^b)\,\delta(m_j^a\pm 1,\,m_j^b)\tfrac{1}{2}\bar{h}[(j^b\pm m_j^b)(j^b\mp m_j^b+1)]^{\frac{1}{2}}.$$

The diagonal element of $\mathbf{J}^2$ is

$$(A\,|\,\mathbf{J}^2\,|\,A)=\bar{h}^2M_J{}^2+\bar{h}\sum_a\{j^a(j^a+1)-(m_j^a)^2\}-4\sum_{a<b}(a\,|\,J_x\,|\,b)^2.$$

Now to a given state of $\boldsymbol{L}$ (in the jm_j scheme) let us correlate that state of $\boldsymbol{R}$ whose ϵ missing electrons have the same j values but the negatives of the m_j values of the ϵ electrons of $\boldsymbol{L}$, and whose η additional electrons have the same quantum numbers. With this correlation it is easily seen, by an argument which is the direct analogue of that previously given for $\mathbf{L}^2$ in the m_lm_s scheme,[3] that the matrix of $\mathbf{J}^2$ is the same for the two configurations and hence that the same matrix will transform them to jj-coupling. Since the matrix of $\mathbf{J}^2$ is diagonal with respect to the number of electrons in shell S with $j=l-\frac{1}{2}$, this result still holds if our correlation involves a phase which depends in an arbitrary way on this number; this property will be of use later. In jj-coupling, to a given state of $\boldsymbol{L}$ is correlated that state of $\boldsymbol{R}$ of the same JM_J whose ϵ missing j values are those present in shell S of $\boldsymbol{L}$, and whose η additional j values are the same as those of $\boldsymbol{L}$.

§3. The transformation $nlm_lm_s \rightleftharpoons nljm_j$

Let us consider a k-electron configuration for which there are n possible sets of one-electron quantum numbers.[4] In the m_lm_s scheme let us denote these sets, in standard order, by the numbers $1, 2, \cdots n$, and the corresponding states by $\psi(1), \psi(2), \cdots \psi(n)$. In the jm_j scheme let us use the notation $1', 2', \cdots n'$ for the quantum numbers, and $\phi(1'), \phi(2'), \cdots \phi(n')$ for the states.[4] The transformation between these two one-electron systems[5] is given by

$$\psi(\alpha)=\sum_{\beta=1}^{n}\phi(\beta')(\beta'\,|\,\alpha). \tag{3.1}$$

The zero-order antisymmetric function belonging to the complete set $\alpha_1, \alpha_2, \cdots \alpha_k$ of quantum numbers is defined by

[3] Cf. §5 of reference 2 for details and notation.

[4] For example, for the configuration $2s3p^2$, $k=3$ and $n=8$, the possible sets of quantum numbers being given, for the m_lm_s scheme by $1=2s\,0^+$, $2=2s\,0^-$, $3=3p\,1^+$, $4=3p\,1^-$, $5=3p\,0^+$, $6=3p\,0^-$, $7=3p\,-1^+$, $8=3p\,-1^-$; and for the jm_j scheme by $1'=2s\,\frac{1}{2}\,\frac{1}{2}$, $2'=2s\,\frac{1}{2}\,-\frac{1}{2}$, $3'=3p\,\frac{3}{2}\,\frac{3}{2}$, $4'=3p\,\frac{3}{2}\,\frac{1}{2}$, $5'=3p\,\frac{3}{2}\,-\frac{1}{2}$, $6'=3p\,\frac{3}{2}\,-\frac{3}{2}$, $7'=3p\,\frac{1}{2}\,\frac{1}{2}$, $8'=3p\,\frac{1}{2}\,-\frac{1}{2}$.

[5] Most of the considerations of this section will be more general than is implied by the jm_j and m_lm_s designations; we shall prefer for a while the designations primed and unprimed schemes.

$$\Psi(\alpha_1, \alpha_2, \cdots \alpha_k) = \frac{1}{(k!)^{\frac{1}{2}}} \sum_P (-1)^p P \psi_1(\alpha_1)\psi_2(\alpha_2)\cdots\psi_k(\alpha_k), \tag{3.2}$$

where P is a permutation of the electron indices 1, 2, $\cdots$ k which are written as subscripts to the ψ's. α_1, α_2, $\cdots$ α_k are k numbers of the set 1, 2, $\cdots$ n, arranged in the order $\alpha_1 < \alpha_2 < \cdots < \alpha_k$.

The transformation of this state to the primed scheme is given by the following calculation. From (3.2) and (3.1)

$$\Psi(\alpha_1, \alpha_2, \cdots \alpha_k) = \frac{1}{(k!)^{\frac{1}{2}}} \sum_P (-1)^p P \sum_{\beta_1=1}^{n} \phi_1(\beta_1')(\beta_1'|\alpha_1)\cdots \sum_{\beta_k=1}^{n} \phi_k(\beta_k')(\beta_k'|\alpha_k)$$

$$= \sum_{\beta_1, \cdots \beta_k} (\beta_1'|\alpha_1)\cdots(\beta_k'|\alpha_k) \frac{1}{(k!)^{\frac{1}{2}}} \sum_P (-1)^p P \phi_1(\beta_1')\cdots\phi_k(\beta_k').$$

If two of the β's are equal the antisymmetric factor $\sum_P \cdots$ vanishes, while for a given set of β's this term is the same, irrespective of the order of the β's, to within a sign which is just correct to give us a determinant of the transformation coefficients; i.e.,

$$\Psi(\alpha_1, \alpha_2, \cdots \alpha_k) = \sum_{\beta_1<\beta_2<\cdots<\beta_k} \boldsymbol{D}\begin{pmatrix}\beta_1'\cdots\beta_k'\\ \alpha_1\cdots\alpha_k\end{pmatrix} \Phi(\beta_1', \beta_2', \cdots \beta_k'), \tag{3.3}$$

where we use the notation

$$\boldsymbol{D}\begin{pmatrix}\beta_1'\cdots\beta_k'\\ \alpha_1\cdots\alpha_k\end{pmatrix} = \begin{vmatrix} (\beta_1'|\alpha_1) & \cdots & (\beta_1'|\alpha_k) \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ (\beta_k'|\alpha_1) & \cdots & (\beta_k'|\alpha_k) \end{vmatrix}. \tag{3.4}$$

The transformation coefficient connecting the state β_1', β_2', $\cdots$ β_k' with the state α_1, α_2, $\cdots$ α_k (quantum numbers in standard order) is given, then, by just this determinant:

$$(\beta_1', \beta_2', \cdots \beta_k'|\alpha_1, \alpha_2, \cdots \alpha_k) = \int \bar{\Phi}(\beta_1', \beta_2', \cdots \beta_k')\Psi(\alpha_1, \alpha_2, \cdots \alpha_k) = \boldsymbol{D}\begin{pmatrix}\beta_1'\cdots\beta_k'\\ \alpha_1\cdots\alpha_k\end{pmatrix}. \tag{3.5}$$

Suppose now that the configuration consists of g electrons in shell $\boldsymbol{S}$ and $k-g$ in other shells. Since the transformation (3.1) has no components connecting sets belonging to different shells, the coefficient (3.5) becomes just the product of two determinants:

$$(\beta_1', \cdots \beta_g', \beta_{g+1}', \cdots \beta_k'|\alpha_1, \cdots \alpha_g, \alpha_{g+1}, \cdots \alpha_k) = \boldsymbol{D}\begin{pmatrix}\beta_1'\cdots\beta_g'\\ \alpha_1\cdots\alpha_g\end{pmatrix} \boldsymbol{D}\begin{pmatrix}\beta_{g+1}'\cdots\beta_k'\\ \alpha_{g+1}\cdots\alpha_k\end{pmatrix}. \tag{3.6}$$

Because of this property, in considering the relation between these coefficients for $\boldsymbol{L}$ and $\boldsymbol{R}$ we may restrict ourselves purely to the shell $\boldsymbol{S}$ so long as the other quantum numbers are the same for the correlated states of $\boldsymbol{L}$ and $\boldsymbol{R}$. We shall suppose that there are altogether m states in the shell $\boldsymbol{S}$, and consider the relation of these components for the configuration consisting of ϵ electrons to that consisting of $m-\epsilon$ electrons in this shell.

Let us seek an invariant correlation between an ϵ-electron state and the $(m-\epsilon)$-electron state whose ϵ missing electrons have the same quantum numbers. This correlation is to be independent

of the system of zero-order states used in the description. We shall denote a given ϵ-electron state by $\Psi(\alpha_1, \alpha_2, \cdots \alpha_\epsilon)$ and the corresponding $(m-\epsilon)$-electron state by $\Psi(a_1, a_2, \cdots a_{m-\epsilon})$, where the α's and a's together make up the set 1, 2, $\cdots m$.

Let us define a linear operator Z by the relations

$$Z\Psi(\alpha_1, \alpha_2, \cdots \alpha_\epsilon) = (-1)^{\alpha_1+\alpha_2+\cdots+\alpha_\epsilon}\bar{\Psi}(a_1, a_2, \cdots a_{m-\epsilon}). \quad (3.7)$$

This operator is seen to be unitary, since the states on the right form a normalized orthogonal system. In the primed scheme we shall define a corresponding operator Z' by

$$Z'\Phi(\beta_1', \beta_2', \cdots \beta_\epsilon') = (-1)^{\beta_1+\beta_2+\cdots+\beta_\epsilon}\bar{\Phi}(b_1', b_2', \cdots b_{m-\epsilon}'). \quad (3.8)$$

The relation between Z' and Z is given by the following calculation.

$$\begin{aligned} Z'\Psi(\alpha_1, \alpha_2, \cdots \alpha_\epsilon) &= Z' \sum_{\beta_1<\cdots<\beta_\epsilon} D\begin{pmatrix}\beta_1' \cdots \beta_\epsilon' \\ \alpha_1 \cdots \alpha_\epsilon\end{pmatrix}\Phi(\beta_1', \beta_2', \cdots \beta_\epsilon') \\ &= \sum_{\beta_1<\cdots<\beta_\epsilon} D\begin{pmatrix}\beta_1' \cdots \beta_\epsilon' \\ \alpha_1 \cdots \alpha_\epsilon\end{pmatrix}(-1)^{\Sigma\beta_\nu}\bar{\Phi}(b_1', b_2', \cdots b_{m-\epsilon}') \\ &= \sum_{\beta_1<\cdots<\beta_\epsilon} (-1)^{\Sigma\beta_\nu} D\begin{pmatrix}\beta_1' \cdots \beta_\epsilon' \\ \alpha_1 \cdots \alpha_\epsilon\end{pmatrix} \sum_{c_1<\cdots<c_{m-\epsilon}} D\begin{pmatrix}b_1' \cdots b_{m-\epsilon}' \\ c_1 \cdots c_{m-\epsilon}\end{pmatrix}\bar{\Psi}(c_1, c_2, \cdots c_{m-\epsilon}) \\ &= (-1)^{\Sigma\alpha_\nu} D\begin{pmatrix}1' \cdots m' \\ 1 \cdots m\end{pmatrix}\bar{\Psi}(a_1, a_2, \cdots a_{m-\epsilon}), \end{aligned}$$

since the terms for $c_1 = a_1, \cdots c_{m-\epsilon} = a_{m-\epsilon}$ furnish just the Laplace expansion of $D\begin{pmatrix}1' \cdots m' \\ 1 \cdots m\end{pmatrix}$ while the other terms vanish. Since any state may be expressed in terms of the $\Psi(\alpha_1, \alpha_2, \cdots \alpha_\epsilon)$, we see by comparison with (3.7) that

$$Z' = D\begin{pmatrix}1' \cdots m' \\ 1 \cdots m\end{pmatrix} Z. \quad (3.9)$$

This shows the operator Z to be invariant to within a constant factor. If we apply this operator to an ϵ-electron state and then take the complex conjugate we obtain an invariantively correlated $(m-\epsilon)$-electron state.[6,7] We take the complex conjugate because by (3.7) Z acting on a state gives a state in the dual space, whereas we want a state in the same space.

We may now calculate the relation between the transformation coefficients:

$$\begin{aligned} (b_1', b_2', \cdots b_{m-\epsilon}' | a_1, a_2, \cdots a_{m-\epsilon}) &= \int \bar{\Phi}(b_1', b_2', \cdots b_{m-\epsilon}')\Psi(a_1, a_2, \cdots a_{m-\epsilon}) \\ &= (-1)^{\Sigma\alpha_\nu+\Sigma\beta_\nu}\int Z'\Phi(\beta_1', \beta_2', \cdots \beta_\epsilon')\overline{Z\Psi(\alpha_1, \alpha_2, \cdots \alpha_\epsilon)} \\ &= (-1)^{\Sigma\alpha_\nu+\Sigma\beta_\nu} D\begin{pmatrix}1' \cdots m' \\ 1 \cdots m\end{pmatrix}\int \overline{Z\Psi(\alpha_1, \alpha_2, \cdots \alpha_\epsilon)} Z\Phi(\beta_1', \beta_2', \cdots \beta_\epsilon') \\ &= (-1)^{\Sigma\alpha_\nu+\Sigma\beta_\nu} D\begin{pmatrix}1' \cdots m' \\ 1 \cdots m\end{pmatrix}(\alpha_1, \alpha_2, \cdots \alpha_\epsilon | \beta_1', \beta_2', \cdots \beta_\epsilon'), \end{aligned} \quad (3.10)$$

since a transformation coefficient is invariant under a unitary transformation.

[6] This correlation was suggested by Professor E. P. Wigner, whom I wish to thank for his kind assistance with this section.

[7] This correlation is not linear, since taking the complex conjugate is an invariant, but not linear, operation. A linear correlation such as is obtained directly by omitting the bar on the right side of (3.7) is invariant only under real orthogonal transformations of the zero-order states.

These considerations have been rather more general than we need for the schemes $m_l m_s$ (unprimed) and jm_j (primed) in which we are particularly interested. In this case the transformation (3.1) is completely real, and its inverse is given by

$$\phi(nl, l\pm\tfrac{1}{2}, m_j) = \pm\left(\frac{l\pm m_j+\frac{1}{2}}{2l+1}\right)^{\frac{1}{2}}\psi(nl, m_j-\tfrac{1}{2}, \tfrac{1}{2}) + \left(\frac{l\mp m_j+\frac{1}{2}}{2l+1}\right)^{\frac{1}{2}}\psi(nl, m_j+\tfrac{1}{2}, -\tfrac{1}{2}), \qquad (3.11)$$

where the $\psi(nlm_l m_s)$ are chosen with such phase that the matrix of L_x is entirely positive (cf. reference 1). The determinant of this transformation for an l shell is easily shown to be $(-1)^l$. This value is to be inserted in (3.10). Moreover from the standard order of listing quantum numbers (§§1 and 2) it is seen that $(-1)^{\Sigma\alpha_\nu} = (-1)^{M_S+\epsilon/2}$, and $(-1)^{\Sigma\beta_\nu} = (-1)^{-M_J+q+\epsilon(l-\frac{1}{2})}$, where ϵ is the number of electrons in the configuration and q is the number in $\Phi(\beta_1', \beta_2', \cdots\beta_\epsilon')$ with $j=l-\frac{1}{2}$. Since $M_J = M_L + M_S$, (3.10) becomes

$$(b_1', b_2', \cdots b_{m-\epsilon}' | a_1, a_2, \cdots a_{m-\epsilon}) = (-1)^{-M_L+q+l(\epsilon+1)}(\beta_1', \beta_2', \cdots \beta_\epsilon' | \alpha_1, \alpha_2, \cdots \alpha_\epsilon). \qquad (3.12)$$

The states on the right side of this equation have just the quantum numbers which are missing on the left; we should prefer (because later we shall add η electrons in other shells and should then like to compare states of the same M_L, M_S, M_J) them to have the negatives of the m_l, m_s, and m_j values missing on the left. But this is easily accomplished. Let the coefficient on the right of (3.12) be

$$(l+\tfrac{1}{2} : m_j^1, m_j^2, \cdots m_j^p; l-\tfrac{1}{2} : m_j^1, m_j^2, \cdots m_j^q | m_l^1 m_s^1, m_l^2 m_s^2, \cdots m_l^\epsilon m_s^\epsilon), \qquad (3.13)$$

where $p+q=\epsilon$. The coefficient we would like to compare with this is

$$(l+\tfrac{1}{2} : -m_j^p, \cdots, -m_j^1; l-\tfrac{1}{2} : -m_j^q, \cdots, -m_j^1 | -m_l^\epsilon - m_s^\epsilon, \cdots, -m_l^1 - m_s^1). \qquad (3.14)$$

If (3.13) is in standard order, (3.14) is seen to be also. Now from a comparison of the two determinants of type (3.5) which give the values of these two coefficients, and by using the relations (cf. 3.11)

$$(l+\tfrac{1}{2}, m_j | m_l, m_s) = (l+\tfrac{1}{2}, -m_j | -m_l, -m_s),$$
$$(l-\tfrac{1}{2}, m_j | m_l, m_s) = -(l-\tfrac{1}{2}, -m_j | -m_l, -m_s),$$

it is seen that

$$(3.14) = (-1)^{\epsilon q}\cdot(3.13).$$

Hence, returning to (3.12), it is seen that the ratio of the transformation coefficient for the almost closed shell to that of the ϵ-electron configuration whose electrons have the negatives of the m_l, m_s, m_j values of those missing from the closed shell is

$$(-1)^{M_L+(\epsilon+1)(q+l)}. \qquad (3.15)$$

If we make the correlation of §1 which includes a phase factor $(-1)^{M_L}$ for the $m_l m_s$ scheme, and if in the jm_j correlation we insert a phase $(-1)^{(\epsilon+1)(q+l)}$—a function of the number of electrons with $j=l-\frac{1}{2}$ for which provision was made at the end of §2—we may say that the $m_l m_s$-jm_j transformation is the same for the two configurations.

These same results hold, as shown by (3.6), when we add η electrons in other shells with the same quantum numbers to both configurations.

§4. The transformation $jjJM_J \rightleftharpoons LSJM_J$

We have found a correlation between the zero-order states of $\boldsymbol{L}$ and $\boldsymbol{R}$ such that the transformations $jjJM_J \rightleftharpoons nljm_j$, $nljm_j \rightleftharpoons nlm_l m_s$, and $nlm_l m_s \rightleftharpoons LSJM_J$ are the same for the two configurations. This is seen to imply that the transformation $jjJM_J \rightleftharpoons LSJM_J$ is the same. More explicitly, the situation is as follows: A given state of the configuration $\boldsymbol{L}$ characterized by the quantum numbers $LSJM_J$ (this state is not uniquely determined for two reasons—first, there is an arbitrary phase; second, the set $LSJM_J$ of quantum numbers is not in general complete for more than two electrons so there may be two independent states characterized by the same $LSJM_J$) is a certain linear combination of the $m_l m_s$ states; the same linear combination of the correlated $m_l m_s$ states of $\boldsymbol{R}$ is a state of $\boldsymbol{R}$ characterized by this same $LSJM_J$. A similar

statement holds for a $jjJM_J$ state except that the *missing* j's of $\boldsymbol{R}$ are those of $\boldsymbol{L}$. The transformation between the LS- and jj-coupling states of $\boldsymbol{R}$ obtained in this way is the same as the corresponding transformation for $\boldsymbol{L}$.

Now to obtain this LS-jj transformation by the combination of the other three is in general a very tedious process involving the multiplication of three matrices of high order, for no two of the three transformations are diagonal in common with respect to more than M_J. On the other hand the resulting transformation is diagonal with respect to both J and M_J and splits in general into steps of a relatively low order. For example, no two-electron configuration or its equivalent can have more than four states of the same J and M_J, while pp or p^5p has altogether 10 states of $M_J=0$, dd or d^9d has 19.

It seems, then, to be desirable to find a direct method which will enable this transformation to be calculated with greater ease. The following accomplishes this result for two-electron configurations, this being in general the only case in which the quantum numbers $LSJM_J$ or $jjJM_J$ define a unique state (to within a phase).

The procedure we shall follow is that of calculating the matrices of $\mathbf{L}^2$ and $\mathbf{S}^2$ in the jj-coupling scheme and then diagonalizing them to obtain the transformation to LS coupling. Since these matrices will split into steps of at most fourth order, and since their eigenvalues are known, this diagonalization is a very simple procedure.

The matrices of $\mathbf{L}^2$ and $\mathbf{S}^2$ in a non-antisymmetric scheme in which the first electron has quantum numbers n_1, l_1, j_1, and the second electron has quantum numbers n_2, l_2, j_2, with resultant J, M_J, may be obtained by the method of Güttinger-Pauli and Johnson.[8] $\mathbf{L}^2=\mathbf{L}_1^2+\mathbf{L}_2^2+2\mathbf{L}_1\cdot\mathbf{L}_2$. The first two terms have known diagonal matrices. The matrix of the third term is diagonal with respect to n_1l_1, n_2l_2, JM_J. If we omit these quantum numbers, using simply the notation $(j_1, j_2|2\mathbf{L}_1\cdot\mathbf{L}_2|j_1', j_2')$, the elements of this matrix are given, with the abbreviation

$$w_i=l_i+\tfrac{1}{2},$$

by

[8] Güttinger and Pauli, Zeits. f Physik **67**, 743 (1931). The formulas given are exactly analogous to those obtained by M. H. Johnson, Phys. Rev. **38**, 1628 (1931) for the matrix of $\mathbf{L}_1\cdot\mathbf{S}_1$ in the LS-coupling scheme.

$$\left.\begin{aligned}
&(l_1\pm\tfrac{1}{2}, l_2\dot{\pm}\tfrac{1}{2}|2\mathbf{L}_1\cdot\mathbf{L}_2|l_1\pm\tfrac{1}{2}, l_2\dot{\pm}\tfrac{1}{2})\\
&\qquad=\frac{(2w_1\mp1)(2w_2\dot{\mp}1)}{4w_1w_2}\{J(J+1)-w_1(w_1\pm1)-w_2(w_2\dot{\pm}1)\}\\
&(l_1\pm\tfrac{1}{2}, l_2+\tfrac{1}{2}|2\mathbf{L}_1\cdot\mathbf{L}_2|l_1\pm\tfrac{1}{2}, l_2-\tfrac{1}{2})\\
&\qquad=\frac{2w_1\mp1}{4w_1w_2}\{(J\mp w_1+w_2)(J\pm w_1-w_2+1)(J\pm w_1+w_2+1)(w_2\pm w_1-J)\}^{\frac{1}{2}}\\
&(l_1+\tfrac{1}{2}, l_2\pm\tfrac{1}{2}|2\mathbf{L}_1\cdot\mathbf{L}_2|l_1-\tfrac{1}{2}, l_2\pm\tfrac{1}{2})\\
&\qquad=-\frac{2w_2\mp1}{4w_1w_2}\{(J+w_1\mp w_2)(J-w_1\pm w_2+1)(J+w_1\pm w_2+1)(w_1\pm w_2-J)\}^{\frac{1}{2}}\\
&(l_1+\tfrac{1}{2}, l_2+\tfrac{1}{2}|2\mathbf{L}_1\cdot\mathbf{L}_2|l_1-\tfrac{1}{2}, l_2-\tfrac{1}{2})\\
&\qquad=-\frac{1}{4w_1w_2}\{(J+w_1+w_2+1)(J+w_1+w_2)(w_1+w_2-J)(w_1+w_2-J-1)\}^{\frac{1}{2}}\\
&(l_1-\tfrac{1}{2}, l_2+\tfrac{1}{2}|2\mathbf{L}_1\cdot\mathbf{L}_2|l_1+\tfrac{1}{2}, l_2-\tfrac{1}{2})\\
&\qquad=\frac{1}{4w_1w_2}\{(J-w_1+w_2)(J-w_1+w_2+1)(J+w_1-w_2)(J+w_1-w_2+1)\}^{\frac{1}{2}}
\end{aligned}\right\}. \qquad (4.1)$$

(In the first formula either the upper or lower undotted sign is to be taken with either the upper or lower dotted sign.) The elements of the matrix of $2\mathbf{S}_1\cdot\mathbf{S}_2$ are exactly the same except that in the first two expressions the factor $(2w_1\mp1)$ is to be replaced by ∓1, in the first and third expressions the factor $(2w_2\mp1)$ is to be replaced by ∓1.

In terms of these non-antisymmetric matrix components, the components between antisymmetric states may be obtained by considerations such as previously used by the writer.[9] Let $\alpha=nl$, $\beta=n'l'$ and let all differences in quantum numbers be indicated by primes, subscripts merely denoting the electrons. Then unless $\alpha=\beta$ and $j=j'$, the antisymmetric

$$\Psi(\alpha j\beta j' JM_J)=2^{-\frac{1}{2}}[\Psi(\alpha_1 j_1\beta_2 j_2' JM_J) -\psi(\alpha_2 j_2\beta_1 j_1' JM_J)]. \quad (4.2)$$

Now if v is a symmetric observable diagonal with respect to n_1l_1 and n_2l_2 it is easily seen that for *non-equivalent electrons*

$$(\alpha j\beta j'|v|\alpha j''\beta j''') =(\alpha_1 j_1\beta_2 j_2'|v|\alpha_1 j_1''\beta_2 j_2'''), \quad \alpha\neq\beta \quad (4.3)$$

where we have for brevity omitted J and M_J throughout.

Consideration of the matrix element

$$(\alpha j\alpha j' JM_J|v|\alpha j''\alpha j''' JM_J)=(jj'|v|j''j''')$$

for *equivalent electrons* must be divided into three cases. First, if $j\neq j'$, $j''\neq j'''$, (4.2) applies to both states, and

$$(jj'|v|j''j''')=\tfrac{1}{2}[(j_1j_2'|v|j_1''j_2''')+(j_2j_1'|v|j_2''j_1''')-(j_1j_2'|v|j_2''j_1''')-(j_2j_1'|v|j_1''j_2''')]$$
$$=(j_1j_2'|v|j_1''j_2''')-(j_1j_2'|v|j_2''j_1''').$$

Now the order of the quantum numbers here is significant, and the second term must be evaluated by the relation

$$\psi(j_2''j_1''' JM_J)=(-1)^{j''+j'''-J}\psi(j_1'''j_2'' JM_J) \quad (4.4)$$

which has been given by Wigner,[10] with whose scheme of vector addition (4.1) are consistent. This gives us

$$(jj'|v|j''j''')=(j_1j_2'|v|j_1''j_2''')-(-1)^{j''+j'''-J}(j_1j_2'|v|j_1'''j_2''). \quad j\neq j',\ j''\neq j''' \quad (4.5a)$$

Second, if $j\neq j'$, $j''=j'''$, from (4.4) we see that $\psi(j_1''j_2'')$ is already either antisymmetric or symmetric, corresponding to allowed and excluded states.[11] For an allowed state we have

$$(jj'|v|j''j'')=2^{-\frac{1}{2}}[(j_1j_2'|v|j_1''j_2'')-(j_2j_1'|v|j_1''j_2'')]=2^{-\frac{1}{2}}[(j_1j_2'|v|j_1''j_2'')+(j_2j_1'|v|j_2''j_1'')]$$

or

$$(jj'|v|j''j'')=2^{\frac{1}{2}}(j_1j_2'|v|j_1''j_2''). \quad j\neq j' \quad (4.5b)$$

Third, if $j=j'$, $j''=j'''$, and both states are allowed, we have simply

$$(jj|v|j''j'')=(j_1j_2|v|j_1''j_2''). \quad (4.5c)$$

These formulas, then, enable us to calculate the matrices of $\mathbf{L}^2$ and $\mathbf{S}^2$ for antisymmetric states in jj-coupling using the non-antisymmetric values (4.1). These have been obtained and diagonalized for all two-electron configurations up to dd. The results are presented in the accompanying set of transformation matrices (see Fig. 1). On the left of the matrices are given the two j values of the state in jj-coupling, the J value being shown at the top in the Russell-Saunders notation. The transformations are independent of M_J. These matrices also give the transformations for the configurations p^4, p^5s, p^5p, p^5d, d^8, d^9s, d^9p, and d^9d, if the given j values are taken as the missing j values of the almost closed shells. It should be noted that while the phases in LS coupling are chosen here in no special way, the phases in jj coupling are those given by using Wigner's formula[10] for the vector addition of j_1 and j_2' (Wigner's l and $\bar{l}$) in the first term on the right of (4.2).

It might be mentioned incidentally that these transformations furnish a very simple means of

[9] See Part II of reference 2.

[10] Wigner, *Gruppentheorie*, p. 206.

[11] This gives us the general rule for the allowed states in jj-coupling for two equivalent electrons, *viz.*, all J values for $j\neq j'$, even J values for $j=j'$.

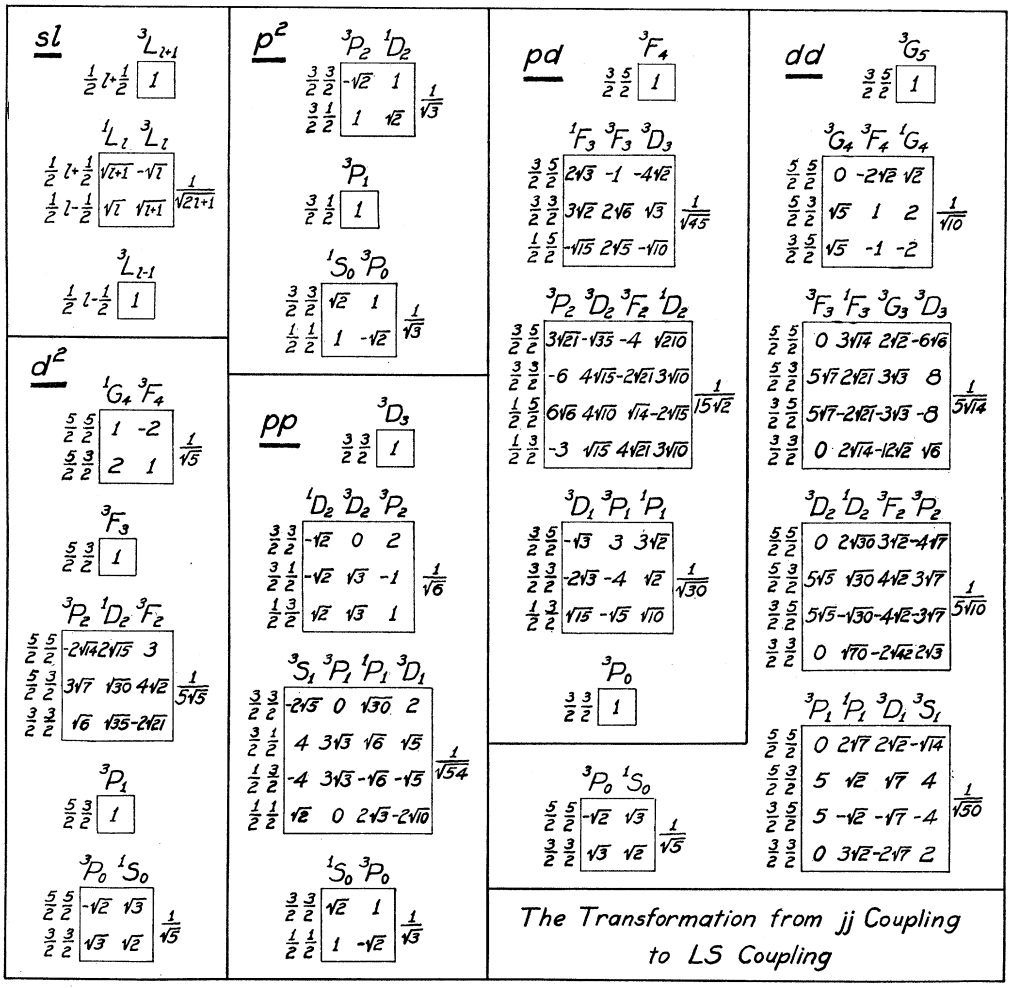

FIG. 1.

obtaining the matrix of spin-orbit interaction in LS-coupling, since this matrix has a simple diagonal form in jj-coupling. As a check of the transformations, this matrix has been obtained in this way and compared with that given by Johnson.[12] The transformation to jj coupling can alternatively be obtained by diagonalizing the matrix of spin-orbit interaction in LS coupling. This method applies not only to two-electron configurations but to any configuration in which the matrix of spin-orbit interaction is nondegenerate.

[12] Johnson, reference 8. We find no error in Johnson's matrices other than that pointed out by Inglis and Ginsburg, Phys. Rev. **43**, 194 (1933); that for pp the $^3P_0$-$^1S_0$ element should read a_1+a_2 in place of a_1-a_2.