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Transformation Properties of Many-Electron Wave Functions with Special Attention to the Relation Between Pair-Correlated DODS and Configuration Interaction

P. E. S. Wormer and A. Van Der Avoird
Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

Abstracts

A method is presented that leads to a simple derivation of the explicit relation between pair-correlated DODS schemes (e.g., the alternant molecular orbital method and the extended valence bond method) and configuration interaction.

This result is based on a reduction formula for the representations of the general linear group, \( GL(m) \), carried by the \( N \)-electron function space. Generally, this paper deals with the effect of “partitioned” orbital transformations on states with “local” permutation symmetry.

On présente une méthode qui fournit une dérivation simple de la relation explicite entre les procédés de type DODS-paires corrélées (par ex. la méthode des orbitales moléculaires alternantes et la méthode de la mésomerie généralisée) et l'interaction des configurations.

Ce résultat est basé sur une formule de réduction pour les représentations du groupe linéaire général, \( GL(m) \), portées par l'espace des fonctions de \( N \) électrons. En général l'article traite l'effet des transformations d'orbitales “partitionnées” sur les états avec une symétrie de permutation “locale”.

Eine Methode wird vorgelegt, die zu einer einfachen Herleitung der expliziten Beziehung zwischen paar-korrelierten DODS-Verfahren (z.B. der Methode mit alternierenden Molekül-orbitalen und der verallgemeinerten Valenzbindungsmethode) und Konfigurationswechselwirkung führt.

Das Ergebnis gründet sich auf eine Reduktionsformel für die Darstellungen der allgemeinen linearen Gruppe, \( GL(m) \), die von dem Raum der \( N \)-Elektronenfunktionen getragen werden. Im allgemeinen behandelt der Artikel die Wirkung von “partitionierten” Orbitaltransformationen auf Zustände mit “lokaler” Permutationssymmetrie.

1. Introduction

Starting from a molecular calculation by the Hartree–Fock self-consistent field procedure, various methods exist for the computation of the remaining correlation energy. One of the traditional methods is the configuration interaction technique, which permits the Hartree–Fock single configuration wave
function (which is an antisymmetrized \(N\)-electron eigenfunction of the total spin operator \(S^2\) in restricted Hartree–Fock) to be mixed with excited configuration wave functions (of the same spin multiplicity). Excited configurations are constructed from the original configuration by promoting electrons from occupied to virtual Hartree–Fock orbitals. By Hartree–Fock orbitals we do not necessarily understand the canonical Hartree–Fock orbitals; they may localized, for instance, and are even not required to be orthogonal.

Other methods for calculating correlation energy follow the different orbitals for different spins (\(\text{dods}\)) scheme described by Löwdin [1]. \(N\) different orbitals are obtained, for instance, by linear mixing between occupied and virtual Hartree–Fock orbitals. The correct \(N\)-electron wave function is formed from a product of such orbitals and a spin function product by antisymmetrization and spin projection. The mixing coefficients of the orbitals are considered as variation parameters which must be energy-optimized. Special forms of this \(\text{dods}\) method mix each occupied Hartree–Fock orbital with just one virtual orbital, which should already account for a substantial part of the pair-correlation energy between the electrons in the doubly occupied Hartree–Fock orbital. Examples of such methods, which we shall call pair-correlated \(\text{dods}\), are given by the alternant molecular orbital method [2] and by the extended valence bond method [3, 4].

Although it can be readily recognized that the mixing between virtual and occupied orbitals introduces excited configurations into the Hartree–Fock wave function, so that \(\text{dods}\) methods are in principle equivalent to configuration interaction with somewhat restricted interaction coefficients, it is not so easy to derive these coefficients explicitly. In a recent paper [5] we have reviewed the group-theoretical treatment of general orbital transformations as given by Weyl [6], and we have presented a new result which permits us to simplify the relation with \(\text{ci}\) considerably for pair-correlated \(\text{dods}\)-methods. This is worked out in the present paper.

Our result is not restricted to the special orbital transformations occurring in pair-correlated \(\text{dods}\), and we have also indicated the specific transformation properties of some currently used \(N\)-electron wave functions.

2. Transformation Properties of \(N\)-Electron Wave Functions

We discuss \(N\)-electron wave functions that are composed of spatial orbitals and spin functions. They are considered to satisfy the Pauli principle, and to be eigenfunctions of the total spin operator \(S^2\) with multiplicity \(2S + 1\). Given a certain basis set of \(m\) orbitals we can construct \(n_{(S)}\) linearly independent \(N\)-electron wave functions for a given \(S\) and \(S_z\) where \(n_{(S)}\) is determined by \(m\), \(N\) and \(S\) as described in ref. [5]. A linear transformation of the orbitals (e.g., a \(\text{dods}\) mixing) will mix these \(N\)-electron wave functions among each other.

The formal theory for general orbital transformations was treated by Weyl [6] using the duality between the group \(GL(m)\) of all linear (nonsingular) orbital
transformations and the permutation group $S_N$. This duality rests on the commutability of simultaneous orbital transformations for all $N$-electrons and the electron permutations. It implies that $N$-electron basis functions for a certain irreducible representation $[\lambda]$ of $S_N$ are also basis functions for an irreducible representation of $GL(m)$, denoted by $\langle \lambda \rangle$. Now, we know that spatial wave functions which span a certain irreducible representation $[\lambda]$ of $S_N$, must combine with spin functions spanning the associate representation $[\lambda']$ (because of the antisymmetry of the total wave function) and, moreover, that this is uniquely connected to the spin functions being eigenfunctions of $S^z$ with definite $S$.

Combining these results, we find that the antisymmetric eigenfunctions of $S^z$ with fixed $S$ form a basis for an irreducible representation $\langle \lambda \rangle$ of $GL(m)$. The irreducibility of $\langle \lambda \rangle$ implies that a general orbital transformation $D(y)$ (a non-singular $m \times m$ matrix) will mix all $n\langle \lambda \rangle$ $N$-electron antisymmetric wave functions belonging to the same $S$ (and $S_z$). The mixing coefficients are the matrix elements of $D(y)^{\langle \lambda \rangle}$, the irreducible matrix representation $\langle \lambda \rangle$ of $GL(m)$ (dimension $n\langle \lambda \rangle$). They are $N$th order homogeneous polynomials in the matrix elements of $D(y)$, which can be derived after the actual construction of the $N$-electron basis functions of $\langle \lambda \rangle$.

Because orbital transformations do not affect the spin part of the wave functions, the theory is most easily formulated in a spinfree manner. The irreducible representations $[\lambda]$ of $S_N$, and also $\langle \lambda \rangle$ of $GL(m)$, are denoted by partitions of $N$ or Young diagrams. The two-valuedness of the electron spin permits only two-row diagrams $[\frac{1}{2}N + S, \frac{1}{2}N - S]$ for the electron spin functions, so that the spatial wave functions must be basis elements of a two-column representation $[\lambda] = [2^{1/2N-S}, 1^{2S}]$ of $S_N$ [7]. Such wave functions can be constructed by acting with the Wigner operators:

$$W^{[\lambda]}_{jk} = \frac{f^{[\lambda]}_j}{N!} \sum_{P \in S_N} D(P^{-1})_{kj} P$$

on an $N$-fold orbital product which corresponds to the desired electron-configuration ($f^{[\lambda]}_j$ is the dimension of the irreducible representation $[\lambda]$ of $S_N$). By the theory of ref. [5] it is easily proved that the $N$-electron eigenfunctions of $S^z$ with given $S$, taken as a basis for the irreducible representations $\langle \lambda \rangle = \langle 2^{1/2N-S}, 1^{2S} \rangle$ of $GL(m)$, generate a matrix representation $D(y)^{\langle \lambda \rangle}$ that is exactly identical to the one which is generated by the spinfree basis projected by $W^{[\lambda]}_{jk}$ for arbitrary, but fixed $j$. We denote the latter basis for the representation $\langle \lambda \rangle$ of $GL(m)$ by:

$$\Psi_i^{\langle \lambda \rangle}(1, \cdots, N) = W^{[\lambda]}_{jk} \Phi_{I}(1, \cdots, N); \quad i = 1, \cdots, n_{\langle \lambda \rangle}$$

with

$$\Phi_{I}(1, \cdots, N) = \varphi_{i_1}(1) \varphi_{i_2}(2) \cdots \varphi_{i_N}(N)$$

The index $I$ in principle runs over all orbital occupations ($i_1 = 1, \cdots, m; i_2 = 1, \cdots, m; \cdots; i_N = 1, \cdots, m$). Different choices of index $k$ with fixed $I$ project wave
functions which are either linearly independent or identical (except for a scalar factor which might be zero). The number of linearly independent wave functions that can be projected equals \( n_{(\lambda)} \).

Once we have constructed the spinfree basis functions of \( \langle \lambda \rangle \) we can proceed with the explicit derivation of the elements of the matrix \( D(\gamma)^{(\lambda)} \) by inspecting the result of an arbitrary orbital transformation \( D(\gamma) \) on these basis functions. If we realize that each orbital product in principle transforms into \( m^N \) products we can understand that this derivation is certainly not trivial. The complexity of the problem rapidly increases with \( N \) and \( m \). For instance, a transformation of four orbitals in a four electron system mixes twenty singlet configurations with coefficients that are fourth order polynomials; for the singlet states of eight electrons in eight orbitals we need already a 1764 dimensional transformation matrix of eighth order polynomials. If we wish to find the explicit relation between a dods treatment and a \( \alpha \) approach the expressions for the elements of these transformation matrices must be derived. Therefore it is very useful that we can simplify the transformation properties considerably if we restrict ourselves, for instance, to pair-correlated dods.

### 3. Partitioned Orbital Transformations

The orbital transformations occurring in pair-correlated dods are given by a direct sum of 2 x 2 matrices which mix every occupied Hartree–Fock orbital with one virtual orbital. They form a special case of “partitioned” orbital transformations, for which we have derived a simplified transformation formula for the \( N \)-electron wave functions. Partitioned orbital transformations are defined as follows:

\[
D(\gamma) = D(\gamma_1) \oplus D(\gamma_2)
\]

where \( D(\gamma_1) \) mixes only \( m_1 \) orbitals and \( D(\gamma_2) \) mixes only \( m_2 \) orbitals among each other \( (m_1 + m_2 = m) \).

Transformations of this type form a group \( GL(m_1 + m_2) \) which is a subgroup of \( GL(m) \). We derived in ref. [5] that the restriction to this subgroup reduces the irreducible representation \( \langle \lambda \rangle \) of \( GL(m) \) in the following way:

\[
D(\gamma)^{(\lambda)} \downarrow GL(m_1 + m_2) = \sum_{n=0}^{N} \sum_{(\mu)} \sum_{(\nu)} \oplus m_{\mu\nu} D(\gamma_1)^{(\mu)} \otimes D(\gamma_2)^{(\nu)}
\]

where \( \langle \mu \rangle \) are those irreducible representations of \( GL(m_1) \), the group of transformations \( D(\gamma_1) \), labelled by partitions of \( n \) and \( \langle \nu \rangle \) those irreducible representations of \( GL(m_2) \) labelled by partitions of \( (N - n) \). The outer direct products \( \langle \mu \rangle \otimes \langle \nu \rangle \) are irreducible representations of the outer product group \( GL(m_1) \otimes GL(m_2) \), which is isomorphic to \( GL(m_1 + m_2) \). The multiplicity coefficients
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\[ m_{\mu\nu\lambda} \] are obtained from an induction problem in the permutation group, namely the induction of the representations of the product group \( S_n \otimes S_{N-n} \) to the full permutation group \( S_N \):

\[ [\mu] \otimes [\lambda] \downarrow S_N = \sum_{\text{partitions} \lambda} \oplus m_{\mu\nu\lambda}[\lambda] \]

This reduction of the irreducible representations \( \langle \lambda \rangle \) of \( GL(m) \) for partitioned orbital transformations implies that no longer all \( n_{(\lambda)} \) basis functions of \( D(\gamma)^{([\lambda])} \) are mixed among each other, but only the \( n_{(\mu)} \times n_{(\nu)} \) basis functions of the product representations \( D(\gamma_1)^{([\mu])} \otimes D(\gamma_2)^{([\nu])} \). The last number usually is considerably smaller and, moreover, the form of the mixing coefficients for \( N \)-electron wave functions will be much simpler.

In order to obtain these mixing coefficients explicitly we have to construct the \( N \)-electron basis functions of \( D(\gamma_1)^{([\mu])} \otimes D(\gamma_2)^{([\nu])} \). These functions must simultaneously be basis elements of a two-column representation \( [\lambda] \) of \( S_N \). Wave functions which satisfy the latter condition (which is the spinfree equivalent of the total wave function satisfying the Pauli principle and being an eigenfunction of \( S^2 \)), we shall call Pauli kets. The duality between \( GL(m) \) and \( S_N \) implies that Pauli kets must also be basis elements of a two-column representation \( D(\gamma)^{([\lambda])} \) of \( GL(m) \) (see ref. [5]). Our special Pauli kets must therefore simultaneously be basis elements for \( \langle \lambda \rangle \) of \( GL(m) \) and for \( \langle \mu \rangle \otimes \langle \nu \rangle \) of \( GL(m_1 + m_2) \). We say that they are "sequence-adapted" to the two-membered sequence \( GL(m) \Rightarrow GL(m_1 + m_2) \).

Let us start the construction of these Pauli kets by taking the basis functions for the irreducible representations \( D(\gamma_1)^{([\mu])} \) and \( D(\gamma_2)^{([\nu])} \), which are also basis functions of the representations \( [\mu] \) of \( S_n \) and \( [\nu] \) of \( S_{N-n} \) respectively. (Again, because of the duality between the general linear group and the permutation group).

Such basis functions can be obtained by projection with the Wigner operators of \( S_n \) and \( S_{N-n} \) (compare formula (2)):

\[ \Psi_{p}(1, \cdots, n) = W_{qr}^{[\mu]} \Phi_{p}(1, \cdots, n); \quad p = 1, \cdots, n_{(\mu)} \]
\[ \Psi_{s}(n + 1, \cdots, N) = W_{tu}^{[\nu]} \Phi_{s}(n + 1, \cdots, N); \quad s = 1, \cdots, n_{(\nu)} \]

The (tensorial) products of these basis functions

\[ \{ \Psi_{p}^{([\mu])} \otimes \Psi_{s}^{([\nu])} ; \quad p = 1, \cdots, n_{(\mu)} ; \quad s = 1, \cdots, n_{(\nu)} \} \]

form a basis for the representations \( D(\gamma_1)^{([\mu])} \otimes D(\gamma_2)^{([\nu])} \) of \( GL(m_1 + m_2) \). They are not Pauli kets, however, although they are adapted to the permutation symmetry of the group \( S_n \otimes S_{N-n} \), because they do not span an irreducible representation of the full permutation group \( S_N \). Pauli kets can be generated by acting with the left coset generators \( \{ C_l ; \quad l = 1, \cdots, N \} \) of the subgroup \( S_n \otimes S_{N-n} \) in \( S_N \) on the product functions, which yields a basis for the induced representation.
and a subsequent basis transformation which corresponds to the reduction (5). This induction-reduction process with respect to $S_N$ does not influence the transformation properties of the wave functions, so that they still form a basis for $D(\gamma_1)^{(\mu)} \otimes D(\gamma_2)^{(\nu)}$. In fact, this construction forms an essential part of the derivation of formula (4), as described in ref. [5].

One way to obtain the proper Pauli kets is by direct action with the Wigner operators $W_{jk}^{[\lambda]}$ of the full permutation group $S_N$ on the product functions $\Psi_p^{(\mu)} \otimes \Psi_s^{(\nu)}$. Thus, we can be sure of the correct permutation symmetry. It is better, however, to take advantage of the permutation symmetry which is already present in the product functions by using the “reduced Wigner operators”:*  

\[ W_{jk}^{[\lambda]} = \frac{f_1^{[\lambda]}}{f_{[\mu]} f_{[\nu]}} \left( N \right)_0^{1} \sum_{l=1}^{N} D(C_l^{-1})_{K,l}C_l \]

with $J = (\mu', \nu', v, w)$ and $K = (\mu, \nu, q, t)$

In this formula $D^{[\lambda]}$ must be an irreducible matrix representation of $S_N$ which is “sequence adapted” to the subgroup $S_n \otimes S_{N-n}$. A method for deriving such representations is described by Matsen and Klein (ref. [8], Appendix 3). Acting with the reduced operators, which only contain the coset generators $C_l$ of $S_n \otimes S_{N-n}$ in $S_N$, on a function which is already symmetry adapted to $S_n \otimes S_{N-n}$ we can obtain the same result as by acting with the full Wigner operator. This is expressed by the following relation:

\[ W_{[\lambda]}^{[\mu, v', v, w]}(\mu, v, r, u) = \sum_{q=1}^{f_{[\mu]}} \sum_{l=1}^{f_{[\nu]}} W_{[\mu, v', v, w]}^{[\lambda]}(\mu, v, q, t) W_{[\lambda]}^{[\mu] W_{[\nu]}}^{[v]} \]

The form of a sequence-adapted representation, the derivation of expression (8) and the meaning of all indices is shown in the Appendix.

Using this property of the reduced Wigner operators, we can write the resulting Pauli kets as follows:

\[ \Psi_{p, s}^{(\mu) \otimes (\nu)}(1, \cdots, N) = \sum_{q=1}^{f_{[\mu]}} \sum_{l=1}^{f_{[\nu]}} W_{[\mu, v', v, w]}^{[\lambda]}(\mu, v, q, t) \Psi_p^{(\mu)}(1, \cdots, n) \otimes \Psi_s^{(\nu)}(n+1, \cdots, N) \]

where $p = 1, \cdots, n_{(\mu)}$, $s = 1, \cdots, n_{(\nu)}$ and the functions on the right-hand side are given by (6). The reduced Wigner operator being a linear combination of left coset generators, Equation (9) is the algebraic analogue of the induction-reduction process described before.

* This problem of obtaining the correct overall permutation symmetry for wave functions which are already permutation symmetry adapted to certain subsystems forms the basis of what is called by Matsen and Klein “the aggregate theory” [8, 9].
It is easily proved [5], by using the commutation of the matrices representing \( GL(m_1 + m_2) \) and the coset generators \( C_i \), that expression (9) indeed produces basis elements for the irreducible representation \( \langle \mu \rangle \otimes \langle \nu \rangle \) of \( GL(m_1 + m_2) \). Moreover, it produces proper Pauli kets with the representation \( [\lambda] \) of \( S_N \) and \( \langle \lambda \rangle \) of \( GL(m) \), so that we now have obtained basis vectors which are adapted to the sequence \( GL(m) \supset GL(m_1 + m_2) \). Equation (4) then shows the way to obtain a full basis of \( GL(m) \).

The irreducibility of the representations \( \langle \mu \rangle \otimes \langle \nu \rangle \) with respect to the group of partitioned orbital transformations \( GL(m_1 + m_2) \) implies that the basis functions which we have now constructed give maximum simplification of the transformation matrix for the \( N \)-electron wave functions. Moreover, their expression by means of the reduced Wigner operators appears to be particularly convenient for deriving the remaining matrix elements explicitly. This we will demonstrate by an example in the next section.

We conclude this section by summarizing the above considerations in a corollary, while at the same time extending the theory to an arbitrary number of subsystems. Assume that the spatial wave function \( \Phi^{(1)}(1, \cdots, n_1) \) is an orbital product, or a linear combination of orbital products, constructed from the first \( m_1 \) orbitals of the \( m \)-dimensional orbital basis. (It forms an element of the \( n_1 \)-fold tensor product space \( V_{m_1} \otimes^{n_1} \)). Analogously, \( \Phi^{(2)}(n_1 + 1, \cdots, n_1 + n_2) \) is constructed from the second set of \( m_2 \) orbitals. We continue until \( \Phi^{(k)}(N - n_k + 1, \cdots, N) \), which is built from the last set of \( m_k \) orbitals.

\[
(m_1 + m_2 + \cdots + m_k = m; \ n_1 + n_2 + \cdots + n_k = N)
\]

Let the Wigner operator \( W^{[\lambda]}_{JK} \) be constructed on the basis of an irreducible representation \( [\lambda] \) of \( S_N \) that is sequence adapted to

\[
S_N \supset S_{n_1} \otimes S_{n_2} \otimes \cdots \otimes S_{n_k}
\]

The column index \( K \) of the Wigner operator corresponds with the irreducible representation \( [\mu_1] \otimes [\mu_2] \otimes \cdots \otimes [\mu_k] \) of the subgroup (see Appendix). By an easy generalization of the contents of this section one can show that the Pauli ket

\[
\Psi = W^{[\lambda]}_{JK} \Phi^{(1)}(1, \cdots, n_1) \otimes \Phi^{(2)}(n_1 + 1, \cdots, n_1 + n_2) \\
\otimes \cdots \otimes \Phi^{(k)}(N - n_k + 1, \cdots, N)
\]

is an element in the basis of the irreducible representation \( \langle \mu_1 \rangle \otimes \langle \mu_2 \rangle \otimes \cdots \otimes \langle \mu_k \rangle \) of the group \( GL(m_1 + m_2 + \cdots + m_k) \). If the functions \( \Phi^{(i)} \) are already symmetry adapted to the permutation group \( S_{n_i}(i = 1, \cdots, k) \), we can use the reduced Wigner operators in order to replace (10) by an expression which is the generalization of (9) to an arbitrary number of subsystems.
By constructing basis functions that are sequence adapted to the permutation group sequence $S_N \supset S_{n_1} \otimes \cdots \otimes S_{n_k}$—Matsen and Klein [8] call such functions “aggregate states”—we have obtained a basis that is also sequence adapted to the orbital transformation groups $GL(m) \supset GL(m_1 + m_2 + \cdots + m_k)$. In other words, by fixing the parentage of the Pauli kets with respect to the permutation groups $S_{n_1}, S_{n_2}, \cdots, S_{n_k}$, we have completely determined their transformation behaviour under partitioned orbital transformations belonging to the group $GL(m_1 + m_2 + \cdots + m_k)$.

4. Relation between Pair-Correlated DODS and CI

The matrix of a pair-correlated DODS transformation is a direct sum of $2 \times 2$ matrices (not necessarily orthogonal), which mix pairs of orbitals that for physical reasons are chosen to be coupled. Matrix elements are the mixing coefficients which serve, according to the DODS formalism on a finite basis, as variation parameters. Mathematically, this pair-correlated DODS matrix is an element of a matrix group isomorphic to $GL(2 + 2 + \cdots + 2)$. In order to project Pauli kets transforming to irreducible representations of this group, one needs, according to the above prescription, representations $[\lambda]$ of $S_N$ adapted to $S_2 \otimes S_2 \otimes \cdots \otimes S_2$. This type of representation is known as Serber representation [10]. The corollary of the previous section states that the DODS wave function projected by a Wigner operator on basis of a Serber representation transforms according to an irreducible representation of $GL(2 + 2 + \cdots + 2)$. Knowing this, we can readily derive the explicit expansion of the DODS wave function in terms of configurations, without necessity to write out the projection of any wave function involved in the expansion.

Let us illustrate the characteristic features of the theory by a rather simple example: the DODS treatment of a four electron system. Due to the simplifications which the theory permits for pair-correlated DODS, this treatment can easily be extended to larger systems.

We start with a basis set of four orbitals $\{ \varphi_1, \varphi_2, \varphi_3, \varphi_4 \}$, e.g., two occupied and two virtual molecular orbitals from a SCF–LCAO calculation. (In the AMO method these MO’s are the canonical ones, in extended valence bond they are localized). The DODS scheme allows these four orbitals to be mixed in order to form four different orbitals $\{ \psi_1, \psi_2, \psi_3, \psi_4 \}$, in each of which one electron is placed. This can be achieved by a $4 \times 4$ orbital transformation matrix $D(\gamma)$. The theory for general orbital transformations then tells us that we mix twenty singlet configurations: the SCF ground state with two doubly occupied MO’s: $\varphi_1^2 \varphi_2^2$ and all excited singlet configurations which can be constructed within the given basis. The mixing coefficients of the four-electron configurations, which form a $20 \times 20$ matrix, are fourth order homogeneous polynomials of the elements of $D(\gamma)$.

If we restrict ourselves to pair-correlated DODS the matrix $D(\gamma)$ has the following
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In this example the occupied orbitals \( \varphi_1 \) and \( \varphi_2 \) are mixed with the virtual orbitals \( \varphi_3 \) and \( \varphi_4 \), respectively. Partitioned orbital transformations of this type cause the following reduction of the twenty-dimensional singlet representation of \( GL(4) \) into outer direct products of representations of \( GL(2) \):

\[
\langle 2^2, 0^2 \rangle = \langle 2^2 \rangle \otimes \langle 0^2 \rangle \oplus \langle 2, 1 \rangle \otimes \langle 1, 0 \rangle \oplus \\
\langle 2, 0 \rangle \otimes \langle 2, 0 \rangle \oplus \langle 1^2 \rangle \otimes \langle 1^2 \rangle \oplus \\
\langle 1, 0 \rangle \otimes \langle 2, 1 \rangle \oplus \langle 0^2 \rangle \otimes \langle 2^2 \rangle
\]

with dimensionality \( 20 = 1 \times 1 + 2 \times 2 + 3 \times 3 + 1 \times 1 + 2 \times 2 + 1 \times 1 \).

In order to indicate clearly to which group the representations belong we have placed zeros for the nonoccurring rows in the Young diagrams. Note that the representation \( D(\gamma)^{(0^2)} \) is the identity representation of \( GL(2) \) and that the representation \( D(\gamma)^{(1,0)} \) is identical to \( D(\gamma) \) itself.

Because in the \( \text{dods} \) scheme we assign four different orbitals to the four electrons, thus placing two electrons in each orbital pair, the \( \text{dods} \) four-electron singlets can only span the representations \( \langle 2, 0 \rangle \otimes \langle 2, 0 \rangle \) or \( \langle 1^2 \rangle \otimes \langle 1^2 \rangle \). (The other representations occurring in (12) correspond physically with one or two orbitals being doubly occupied.) In fact, from the configuration \( \psi_1 \psi_3 \psi_2 \psi_4 \) we can construct two linearly independent singlet wave functions, one of which spans the representation \( \langle 1^2 \rangle \otimes \langle 1^2 \rangle \), whereas the other one is a basis element of \( \langle 2, 0 \rangle \otimes \langle 2, 0 \rangle \). In order to derive the explicit relation between the \( \text{dods} \) wave functions and a ci basis we construct these wave functions and show their transformation behaviour.

In the first step we use the Wigner operators of the group \( S_4 \):

\[
W^{[2,0]} \psi_1 \psi_3 = \frac{i}{2} (\psi_1 \psi_3 + \psi_3 \psi_1) = d_{11}d_{13}W^{[2,0]} \varphi_1 \varphi_1 + \\
+ d_{31}d_{33}W^{[2,0]} \varphi_3 \varphi_3 + (d_{11}d_{33} + d_{13}d_{31})W^{[2,0]} \varphi_1 \varphi_3
\]

\[
W^{[1^2]} \psi_1 \psi_3 = \frac{i}{2} (\psi_1 \psi_3 - \psi_3 \psi_1) = (d_{11}d_{33} - d_{13}d_{31})W^{[1^2]} \varphi_1 \varphi_3
\]

We note that for the triplet state several terms cancel. One proceeds analogously for the other electron pair.

The next step is to find an irreducible matrix representation \([2^2, 0^2]\) of \( S_4 \)
which is sequence adapted to $S_2 \otimes S_2$. Accidentally, in this case the Serber representation is identical with the Young–Yamanouchi representation [11, 12]. We do not need this Serber representation explicitly, we only need to know the parentage of its different columns. The operator $W_{11}^{[2^2,0^0]}$ has the parentage $[2,0] \otimes [2,0]$, whereas $W_{12}^{[2^2,0^0]}$ corresponds with $[1^2] \otimes [1^2]$. Therefore, we can write the DODS wave functions as follows:

\[
\Psi^{(2,0) \otimes (2,0)} = W_{11}^{[2^2,0^0]} \psi_1 \psi_3 \psi_2 \psi_4 \\
= \tilde{W}_{11}^{[2^2,0^0]}(W_{11}^{[2,0]} \psi_1 \psi_3) \otimes (W_{11}^{[2,0]} \psi_2 \psi_4)
\]

(14)

\[
\Psi^{(1^2) \otimes (1^2)} = W_{12}^{[2^2,0^0]} \psi_1 \psi_3 \psi_2 \psi_4 \\
= \tilde{W}_{12}^{[2^2,0^0]}(W_{12}^{[1^2]} \psi_1 \psi_3) \otimes (W_{12}^{[1^2]} \psi_2 \psi_4)
\]

Substituting the formula (13) and using relation (8) again, we can easily express the DODS wave functions in terms of the MO configurations that form the basis of a CI treatment (they should be Pauli kets also):

\[
\Psi^{(2,0) \otimes (2,0)} = d_{11}d_{13}d_{23}d_{24}W_{11}^{[2^2,0^0]} \psi_1 \psi_3 \psi_2 \psi_4 \\
+ d_{11}d_{13}d_{44}d_{44}W_{11}^{[2^2,0^0]} \psi_1 \psi_4 \psi_2 \psi_4 \\
+ d_{24d_{23}d_{23}d_{24}}W_{11}^{[2,0]} \psi_2 \psi_2 \psi_2 \psi_4 \\
+ d_{24d_{33}d_{44}d_{44}}W_{11}^{[2,0]} \psi_3 \psi_3 \psi_4 \psi_4 \\
+ d_{11d_{13}d_{22}d_{24}} + d_{24d_{42}}W_{11}^{[2^2,0^0]} \psi_1 \psi_1 \psi_2 \psi_4 \\
+ (d_{11d_{23}} + d_{13d_{3l}})d_{22d_{24}}W_{11}^{[2^2,0^0]} \psi_1 \psi_3 \psi_2 \psi_2 \\
+ d_{31d_{33}d_{23}d_{24}}W_{11}^{[2^2,0^0]} \psi_3 \psi_3 \psi_2 \psi_4 \\
+ (d_{11d_{23}} + d_{13d_{31}})d_{22d_{44}}W_{11}^{[2^2,0^0]} \psi_1 \psi_3 \psi_2 \psi_4 \\
+ (d_{11d_{23}} + d_{13d_{31}})d_{22d_{44}} + d_{24d_{42}}W_{11}^{[2^2,0^0]} \psi_1 \psi_3 \psi_2 \psi_4
\]

(15)

\[
\Psi^{(1^2) \otimes (1^2)} = (d_{11d_{33}} - d_{13d_{31}})(d_{22d_{24}} - d_{24d_{42}})W_{12}^{[2^2,0^0]} \psi_1 \psi_3 \psi_2 \psi_4
\]

This result tells us explicitly which configurations are mixed in a pair-correlated DODS wave function and how the mixing coefficients vary as a function of the orbital mixing coefficients.

In the special case of the AMO method, where the orbital transformation matrices have the form:

\[
D(\gamma_1) = \begin{pmatrix} \cos \theta_1 & \cos \theta_1 \\ \sin \theta_1 & -\sin \theta_1 \end{pmatrix}, \quad D(\gamma_2) = \begin{pmatrix} \cos \theta_2 & \cos \theta_2 \\ \sin \theta_2 & -\sin \theta_2 \end{pmatrix}
\]

(16)
various terms cancel and we find the following simple relation:

\[
\Psi^{(2,0)\otimes(2,0)} = \cos^2 \theta_1 \cos^2 \theta_2 W_{11}^{(2,0,0)} \varphi_1 \varphi_1 \varphi_2 \varphi_2 \\
- \cos^2 \theta_1 \sin^2 \theta_2 W_{11}^{(2,0,0)} \varphi_1 \varphi_4 \varphi_4 \\
- \sin^2 \theta_1 \cos^2 \theta_2 W_{11}^{(2,0,0)} \varphi_3 \varphi_3 \varphi_2 \varphi_2 \\
+ \sin^2 \theta_1 \sin^2 \theta_2 W_{11}^{(2,0,0)} \varphi_3 \varphi_3 \varphi_4 \varphi_4
\]

\[
\Psi^{(1)\otimes(1)} = 4 \cos \theta_1 \sin \theta_1 \cos \theta_2 \sin \theta_2 W_{12}^{(2,0,0)} \varphi_1 \varphi_3 \varphi_2 \varphi_4
\]

No singly or triply excited states occur in the singlet AMO wave functions.

This example can be easily extended to systems with more than four electrons by using the results of the previous section, formula (10) in particular. The complete pair-correlated AMO wave functions can be built up from the singlets and triplets of formula (13) by using the reduced Wigner operators based on the Serber representations of \( S_N \). If one wants to derive which configurations occur in a certain AMO wave function and to calculate the configuration interaction coefficients as functions of the orbital mixing coefficients, it is not necessary to construct these complete wave functions, however. Only knowing their parentage with respect to \( S_2 \otimes S_2 \otimes \cdots \otimes S_2 \), i.e., the singlet and triplet states from which they are built, is sufficient.

5. Transformation of Some Common Antisymmetric Spin Eigenfunctions

We have seen in the previous section that the transformation properties of antisymmetric spin eigenfunctions under pair-correlated AMO mixing become particularly simple if we project such wave functions by means of Wigner operators based on the Serber representations of \( S_N \). Although Serber functions have found recent interest in quantum chemistry [13], many other projectors have been used in the literature to construct antisymmetric eigenfunctions of \( S^2 \). We shall briefly discuss the transformation properties of some of these other Pauli kets also.

The general section about partitioned orbital transformations tells us that the transformation behaviour of Pauli kets can be largely simplified if one knows the permutational genealogy of their projectors.

Let us first look at some Wigner operators based on the orthogonal Young–Yamanouchi representations [12], called orthogonal units by Rutherford [11]. We shall label the basis functions for a given irreducible representation \([\lambda]\) = \([2^{1/2N–S}, 1^{2S}] \) of \( S_N \) according to decreasing Yamanouchi symbols, using Hamermesh's [14] definition of these symbols. It follows immediately from the construction rules for the Young–Yamanouchi representations (ref. [14], Section 7-7) and from the form of the first standard Young tableau that the Wigner operator \( W_{11}^{[\lambda]} \) is invariant under all transpositions \((12), (34) \cdots, (N – 2S – 1, N – 2S)\)
and spans an antisymmetric representation of all permutations among the last \( 2S \) electrons. Thus, the Wigner operator \( W^{[A]}_{11} \) generates spatial functions that carry the representation

\[
\frac{1}{2}N - S \text{ factors}
\]

of the group \( S_2 \otimes S_2 \otimes \cdots \otimes S_2 \otimes S_{2S} \). Such functions are also sequence adapted to

\[
GL(m) \supset GL(m_1 + m_2 + \cdots + m_{1/2N-S}) \quad \text{and transform according to the representation:}
\]

\[
\langle 2 \rangle \otimes \langle 2 \rangle \otimes \cdots \otimes \langle 2 \rangle \otimes \langle 1^2S \rangle \text{ of the latter group.}
\]

In order to get nontrivial results the partitioning of the orbital basis \( m = m_1 + m_2 + \cdots + m_{1/2N-S+1} \) must satisfy the relations

\[
m_1, m_2, \ldots, m_{1/2N-S} \geq 1; \quad m_{1/2N-S+1} \geq 2S
\]

This projector is used by Goddard in his \( GL \)-method \([15]\).

Basis functions projected by this operator transform identically to one of the Serber basis functions under \( GL(m_1 + m_2 + \cdots + m_{1/2N}) \), namely according to

\[
\langle 2 \rangle \otimes \cdots \otimes \langle 2 \rangle \otimes \langle 1^2 \rangle \otimes \cdots \otimes \langle 1^2 \rangle \\
\frac{1}{2}N - S \text{ factors} \quad S \text{ factors}
\]

Consequently, this projector connects pair-correlated \( \text{d} \)\( \text{d} \)s and \( \text{c} \) in the manner described in the previous section.

Another Wigner operator with a physically interesting parentage is \( W^{[A]}_{f[X], f[X]} \), where \( f[A] \) is the dimension of the irreducible representation \([\lambda] = [2^{1/2N-S}, 1^2S] \).

It is sequence-adapted to \( S_N \supset S_{1/2N+S} \otimes S_{1/2N-S} \) and corresponds to the representation \([1^{1/2N+S}] \otimes [1^{1/2N-S}] \). Pauli kets which are projected by this operator transform according to \( \langle 1^{1/2N+S} \rangle \otimes \langle 1^{1/2N-S} \rangle \) of \( GL(m_1 + m_2) \). The partitioning of the orbital basis must satisfy \( m_1 \geq \frac{1}{2}N + S, \quad m_2 \geq \frac{1}{2}N - S \). If the equal signs hold, the irreducible representation \( \langle 1^{1/2N+S} \rangle \otimes \langle 1^{1/2N-S} \rangle \) is one-dimensional, and the functions carrying \( \langle 1^{1/2N+S} \rangle \) and \( \langle 1^{1/2N-S} \rangle \) are simply Slater determinants composed of \( \frac{1}{2}N + S \) and \( \frac{1}{2}N - S \) spatial orbitals, respectively. In general, this projector corresponds to a physical system with antiferromagnetic coupling between two subsystems with \( \frac{1}{2}N + S \) and \( \frac{1}{2}N - S \) parallel spins. This projector is also of importance if one fills up degenerate \( \text{d} \)\( \text{d} \)s orbitals according to Hund’s rules \([16]\).
Also a common way of constructing antisymmetric eigenfunctions of $S^2$ is by acting with the Young operators $[17]$, $P_iN_i$ or $N_iP_i$, either on the spin part or on the spatial part of a wave function.

Each Young operator corresponds with a standard Young tableau $(i = 1, \cdots, f_{[\lambda]})$; the operator $N_i$ is a product of antisymmetrizers over the electron indices occurring in the columns of tableau $i$, $P_i$ symmetrizes over indices occurring in rows. These Young operators, which project nonorthogonal bases, can be related to the spinfree Wigner operators. In case they project spin functions, the first step involves transferring the permutational symmetry from spin to spatial coordinates by using one of the relations:

\[
A(I \otimes P_iN_i^{[\lambda]}) = A(P_iN_i^{[\lambda]} \otimes I)
\]

\[
A(I \otimes N_iP_i^{[\lambda]}) = A(N_iP_i^{[\lambda]} \otimes I)
\]

where the first factor acts on the spatial coordinates and the second on the spin coordinates, $I$ is the identity operator and $A$ is the antisymmetrizer over spatial and spin coordinates. The representation $[\tilde{\lambda}]$ is associate to $[\lambda]$ and $i = f_{[\lambda]} + 1 - i$ counts according to increasing Yamanouchi symbols. These two relations are easily proved following the arguments of Heldmann $[18]$. Furthermore, one can show, using elements of Goddard’s proof $[19]$, that the following expansions must hold:

\[
N_iP_i^{[\lambda]} = \sum_{i=1}^{f_{[\lambda]}} c_iW_{i,1}^{[\lambda]}
\]

\[
P_{f_{[\lambda]}}N_i^{[\lambda]} = \sum_{i=1}^{f_{[\lambda]}} c_i'W_{i,f_{[\lambda]}}^{[\lambda]}
\]

Because the second index of the Wigner operators determines their permutational genealogy, and therewith the transformation properties of projected wave functions, and we have already discussed the Wigner operators $W_{11}^{[\lambda]}$ and $W_{f_{[\lambda]}1}^{[\lambda]}$, relations $(18)$ and $(19)$ are sufficient to uncover these properties for the given Young operators.

The projector $N_{f_{[\lambda]}}P_{f_{[\lambda]}}$ acting on a spin function $\alpha\beta\alpha\beta\cdots\alpha\beta\alpha\cdots\alpha$ generates the Boys-Reeves “spin-bonded” functions $[20]$. Using $(18)$ and $(19)$ we conclude that such functions transform according to $\langle 2 \rangle \otimes \langle 2 \rangle \otimes \cdots \otimes \langle 2 \rangle \otimes \langle 1^{2S} \rangle$ under $GL(m_1 + m_2 + \cdots + m_{1/2N-S} + m_{1/2N-S+1})$. The projector $P_iN_i^{[\lambda]}$ acting on:

\[
\left\{\begin{array}{c}
\alpha\alpha\cdots\alpha\beta\beta\cdots\beta \\
\frac{1}{2}N + S \\
\frac{1}{2}N - S
\end{array}\right\}
\]

yields the same result as the Löwdin operator $[21]$ acting on this function $[22]$. The Pauli kets corresponding to this choice transform as $\langle 1^{2N+S} \rangle \otimes \langle 1^{2N-S} \rangle$. 
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under $GL(m_1 + m_2)$. If we have just $N$ orbitals, these Pauli kets are invariant (except for a scalar factor) under mixing the spin-up and the spin-down orbitals among themselves. This result lies at the basis of the pairing theorem [23, 24].

6. Conclusion

In this paper we have treated the effect of orbital transformations on some commonly used many-electron wave functions, that are antisymmetric eigenfunctions of $S^2$. Especially, orbital mixings occurring in pair-correlated dods-schemes were considered in more detail, in order to find the explicit relation between such schemes and the configuration interaction method. Orbital transformations were regarded as elements of the general linear group, $GL(m)$, and their effects were studied group theoretically. Although some of the transformation properties that we have discussed in this paper have already been derived for special cases [2, 25], the group theoretical approach places these results in a general and more formal framework. It gives much deeper insight as it clearly shows the relation between the permutational characteristics of wave functions and their transformation behaviour. Moreover, by using a group-theoretical formula that we have derived for the subduction of the representations of $GL(m)$, we can very often simplify complicated transformation matrices to a large extent and, thus, save much labour.

Appendix

We have shown in this paper that the transformation properties of $N$-electron wave functions under partitioned orbital transformations can actually be simplified if we construct basis functions of the type (9) by means of the "reduced" Wigner operators which satisfy relation (8). We will now show the derivation of this relation (8) and explain the meaning of all occurring indices. (A similar result has been derived by Klein et al. [9], using the theory of semi-simple algebras, and by Jahn [26] and Gerrat [16], who both restrict their attention to one- and two-column representations only).

Start with an irreducible representation $[\lambda]$ of $S_N$ which is "sequence adapted" to the subgroup $S_n \otimes S_{N-n}$.

By definition such a representation $[\lambda]$ is completely decomposed if it is restricted to the subgroup $S_n \otimes S_{N-n}$. Therefore we can write for an arbitrary element $PQ$ of this subgroup ($P \in S_n$, $Q \in S_{N-n}$):

$$\mathbf{D}(PQ)[\lambda] = \sum_{(\mu)} \sum_{(\nu)} \oplus m_{\lambda \mu} \mathbf{D}(P)[\mu] \otimes \mathbf{D}(Q)[\nu]$$

(According to Frobenius' theorem the multiplicity coefficients in this subduction
Figure 1. Form of a representation \([\lambda]\) which is adapted to the sequence \(S_N \supset S_n \otimes S_{N-n}\).

The matrix \(D(PQ)^{[\lambda]}\) has a diagonal blocked form with the Kronecker products \(D(P)^{[\mu]} \otimes D(Q)^{[v]}\) occurring \(m_{\lambda \mu v}\) times on the diagonal (see Figure 1). If we want to write out relation (A1) in terms of matrix elements we necessarily have to introduce a large number of indices. The rows of the matrix \(D(PQ)^{[\lambda]}\) are numbered by:

- \(\mu\) (running over partitions of \(n\)),
- \(\nu\) (running over partitions of \(N - n\)),
- \(\alpha = 1, \cdots, m_{\lambda \mu v}\) (numbering multiple occurrences of \([\mu] \otimes [v]\)),
- \(r = 1, \cdots, f_{(\mu)}\) (running over the rows of \(D(P)^{[\mu]}\)),
- \(u = 1, \cdots, f_{(v)}\) (running over the rows of \(D(Q)^{[v]}\)).

All these indices can be collected in one index \(K\), numbering the rows of \(D(PQ)^{[\lambda]}\), such that there is a unique relation \(K = (\mu, \nu, \alpha, r, u)\). In the same manner we label the columns by \(L = (\mu', \nu', \alpha', q, t)\). Then, the following relation is obtained:

\[
D(PQ)^{[\lambda]}_{KL} = \delta_{\mu \mu'} \delta_{\nu \nu'} \delta_{\alpha \alpha'} D(P)^{[\mu]}_{rr} D(Q)^{[v]}_{ut}
\]

with \(K = (\mu, \nu, \alpha, r, u)\) and \(L = (\mu', \nu', \alpha', q, t)\).

Although this factorization is only valid for the matrices \(D(PQ)^{[\lambda]}\) representing the subgroup \(S_n \otimes S_{N-n}\), we must realize that the sequence-adapted representation \(D(R)^{[\lambda]}\) is defined for all \(R \in S_N\). So, the labelling \(K = (\mu, \nu, \alpha, r, u), L = (\mu', \nu', \alpha', q, t)\) can be carried through for all \(R \in S_N\).
We now write a Wigner operator for the (sequence-adapted) representation $[\lambda]$ of $S_N$:

\[(A3) \quad W^{[\lambda]}_{JK} = \frac{f^{[\lambda]}_{J}}{N!} \sum_{R \in S_N} D(R^{-1})^{[\lambda]}_{KJR}\]

Every permutation $R \in S_N$ can be written as $R = C_l P Q$, where $P \in S_n$, $Q \in S_{N-n}$ and \{C\; ; \; l = 1, \cdots, (\frac{N}{n})\} are the (left) coset generators of $S_n \otimes S_{N-n}$ in $S_N$. Replacing the summation over all $R \in S_N$ by a threefold sum over $P \in S_n$, $Q \in S_{N-n}$ and $l = 1, \cdots, (\frac{N}{n})$ we obtain

\[(A4) \quad W^{[\lambda]}_{JK} = \frac{f^{[\lambda]}_{J}}{N!} \sum_{P \in S_n} \sum_{Q \in S_{N-n}} \sum_{l=1}^{(\frac{N}{n})} D(Q^{-1} P^{-1} C_l^{-1})^{[\lambda]}_{KJl} P Q\]

Substitution of expression (7) for the reduced Wigner operator yields

\[(A5) \quad W^{[\lambda]}_{JK} = \frac{f^{[\lambda]}_{J}}{n! (N-n)!} \sum_{L=1}^{\left(\frac{N}{n}\right)} \sum_{P \in S_n} \sum_{Q \in S_{N-n}} D(Q^{-1} P^{-1})^{[\lambda]}_{KLD} (C_l^{-1})_{LJl} P Q\]

Since the permutation $Q^{-1} P^{-1}$ is an element of the group $S_n \otimes S_{N-n}$ we can use the decomposition formula (A2):

\[(A6) \quad W^{[\lambda]}_{JK} = \frac{f^{[\lambda]}_{J}}{n! (N-n)!} \sum_{L=1}^{\left(\frac{N}{n}\right)} \sum_{P \in S_n} \sum_{Q \in S_{N-n}} \delta_{\mu \mu'} \delta_{\nu \nu'} \delta_{\alpha \alpha'} D(P^{-1})^{[\mu]}_{r} D(Q^{-1})^{[\nu]}_{u} P Q\]

Remember that $K = (\mu, \nu, \alpha, r, u)$ and $L = (\mu', \nu', \alpha', q, t)$. Because of the Kronecker delta's the summation over $L = (\mu', \nu', \alpha', q, t)$, which is in fact a fivefold summation, can be reduced to a twofold sum. Moreover, we can substitute formula (1) for the Wigner operators of $S_n$ and $S_{N-n}$ to obtain the final result:

\[(A7) \quad W^{[\lambda]}_{JK} = \sum_{q=1}^{\left(\frac{N}{n}\right)} \sum_{t=1}^{\left(\frac{N}{n}\right)} W^{[\lambda]}_{JL} W^{[\mu]}_{qt} W^{[\nu]}_{tu}\]

where $K = (\mu, \nu, \alpha, r, u)$, $L = (\mu, \nu, \alpha, q, t)$ and $J = 1, \cdots, f^{[\lambda]}$ is some arbitrary index, which could also be written as a contraction of the same type: $J = (\mu', \nu', \alpha', \nu, \omega)$. If we restrict ourselves to two-column representations of the permutation group, the induction-subduction problem (Equations (5) and (A1)) is multiplicity-free: $m_{\mu \nu}$ must be 0 or 1. In that case we can drop the indices $\alpha$ and $\alpha'$ to obtain Equation (8).
Formula (A7) can be easily generalized to an arbitrary number of subsystems. Suppose that we have $n_1$ electrons occupying the first $m_1$ orbitals, $n_2$ electrons in the second set of $m_2$ orbitals, etc., and $n_k$ electrons in the last $m_k$ orbitals, as in Equation (10). Irreducible representations of $S_{n_1}$, $S_{n_2}$, \ldots, $S_{n_k}$ are denoted by $[\mu_1]$, $[\mu_2]$, \ldots, $[\mu_k]$ and their rows and columns are numbered by $r_i = 1, \ldots, q_i$ and $q_i = 1, \ldots, f_{[\mu_i]}$, respectively, for $i = 1, \ldots, k$. The reduced Wigner operator $\tilde{W}^{[\lambda]}_{JK}$, which contains the left coset generators of the subgroup $S_{n_1} \otimes S_{n_2} \otimes \cdots \otimes S_{n_k}$ in $S_N$, is constructed on a representation $[\lambda]$ that is sequence-adapted to this subgroup. The rows and columns of $[\lambda]$ are numbered by $K = (\mu_1, \mu_2, \ldots, \mu_k, \alpha, r_1, r_2, \ldots, r_k)$ and $L = (\mu'_1, \mu'_2, \ldots, \mu'_k, \alpha', q_1, q_2, \ldots, q_k)$, respectively. The relation between a normal Wigner operator on the basis of this sequence-adapted representation $[\lambda]$ and the reduced Wigner operators becomes:

\begin{align*}
W^{[\lambda]}_{JK} = \sum_{q_1=1}^{\mu_1} \sum_{q_2=1}^{\mu_2} \cdots \sum_{q_k=1}^{\mu_k} \tilde{W}^{[\lambda]}_{JL} \tilde{W}_{q_1 r_1}^{[\mu_1]} \tilde{W}_{q_2 r_2}^{[\mu_2]} \cdots \tilde{W}_{q_k r_k}^{[\mu_k]},
\end{align*}

where $K = (\mu_1, \ldots, \mu_k, \alpha, r_1, \ldots, r_k)$, $L = (\mu'_1, \ldots, \mu'_k, \alpha', q_1, \ldots, q_k)$ and $J = (\mu'_1, \ldots, \mu'_k, \alpha', v_1, \ldots, v_k)$. This equation can be substituted into expression (10) in order to obtain a generalization of (9) for an arbitrary number of sub-systems.

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The referee has drawn our attention to a recent paper [27] which is concerned with the transformation properties of $N$-electron wave functions under general orbital transformations (with rectangular matrices). Moreover, he mentioned that the equivalence between Young operators ($PN$ or $NP$) and Löwdin projected determinants [19, 22] was also pointed out by Gallup [28].

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