

 Open access • Journal Article • DOI:10.1063/1.1678616

Transformation properties of antisymmetric spin eigenfunctions under linear mixing of the orbitals — [Source link](#)

Paul E. S. Wormer, Ad van der Avoird

Published on: 15 Sep 1972 - Journal of Chemical Physics (American Institute of Physics)

Topics: Pauli exclusion principle, Spin quantum number, Spin (physics), Wave function and Permutation group

Related papers:

- [Group theoretical approach to the configuration interaction and perturbation theory calculations for atomic and molecular systems](#)
- [Group theory and second quantization for nonorthogonal orbitals](#)
- [Alternative Basis for the Theory of Complex Spectra](#)
- [Methods of molecular quantum mechanics](#)
- [Group Theory and the Many Body Problem](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/transformation-properties-of-antisymmetric-spin-24eryywo8k>

PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/16349>

Please be advised that this information was generated on 2022-05-30 and may be subject to change.

Transformation Properties of Antisymmetric Spin Eigenfunctions under Linear Mixing of the Orbitals

PAUL E. S. WORMER AND AD VAN DER AVOIRD

Institute of Theoretical Chemistry, University of Nijmegen, The Netherlands

(Received 8 May 1972)

After recalling the duality between the general linear group $GL(m)$, represented by its N -fold inner product, and the permutation group S_N , we have given a survey of its quantum chemical consequences. It causes the one-to-one correspondence between the total spin quantum number and the permutation symmetry of N -electron spin functions, and, via the Pauli principle which imposes permutation symmetry on the spatial part also, it leads to specific properties of antisymmetric spin eigenfunctions under orbital transformations. Such functions can be classified according to the irreducible representations of $GL(m)$. For special orbital transformations, often occurring in quantum chemistry, which mix only orbitals in different subsets among each other, we have derived how the transformation of the N -electron wavefunctions simplifies, by a reduction of the representations of $GL(m)$. The theory is illustrated by an example and some applications are discussed.

I. INTRODUCTION

The last years have shown among theoretical chemists a renewed interest in the applications of the permutation group to many-body problems. Kotani *et al.*¹ and Johnston² revived the early work of Hund, London, Heitler, Wigner, and, especially, Weyl.³ The theory was worked out further by Matsen and co-workers⁴ in a series on "spin-free quantum chemistry". It was applied to variational calculations by Goddard,⁵ Harris,⁶ and Morrison and Gallup,⁷ whereas van der Avoird,⁸ Amos and Musher⁹ and Klein¹⁰ continued the work of Eisen-schitz and London¹¹ on permutation symmetry adapted perturbation theory.

One aspect of the theory is missing in this recent work: The duality between the representations of the permutation group S_N on the one hand and the general linear group in m dimensions $GL(m)$ on the other. These groups are related via their representations carried by N th rank tensor space. Still, this relationship is of paramount importance. In the first place it forms the basis of the connection between the spin quantum number and permutation symmetry: N -electron eigenfunctions of S^2 , which carry irreducible representations of $GL(2)$ and its subgroup $SU(2)$, must span certain irreducible representations of the permutation group S_N . Secondly, the Pauli principle, requiring the anti-symmetry of the total many-electron wavefunction, imposes the permutation symmetry on the spatial part as well. Using the duality between S_N and $GL(m)$ again, it follows that the spatial function must have specific behavior under orbital transformations, which can be studied by considering the group $GL(m)$.

The global representation theory of $GL(m)$ on which this paper is based, originates from Schur and has been outlined in great detail by Weyl,³ who was the first to recognize its quantum mechanical importance. The

books by Boerner¹² and Murnaghan¹³ give a good survey of the mathematical background.

In many practical cases one is not interested in general orbital transformations, but, given a partitioning of the orbitals in different subsets, in those transformations which mix only orbitals belonging to the same subset. Examples are given by:

the hybridization of orbitals on the separate atoms in a molecular Valence Bond calculation,

orthogonalization of orbitals in different sets by intraset transformations (According to the pairing theorem such transformations can orthogonalize an orbital in a definite set to all orbitals except one in another set.),

mixing schemes in pair-correlated DODS methods, such as AMO¹⁴ or extended VB,¹⁵

Roothaan's procedure¹⁶ of simplifying the open-shell Hartree-Fock problem by transformation of the closed and open shell orbitals separately.

In this paper we have derived which antisymmetrized eigenfunctions of S^2 are mixed under such "partitioned" orbital transformations and indicated a way to calculate the mixing coefficients. The theory is outlined for a system consisting of two parts, but, by induction, is easily extensible to many subsystems. It could be considered as a supplement to Matsen and Klein's "aggregate theory,"⁴ regarding the transformation properties of aggregate states. Before we proceed to our results we shall give a brief survey of the general formalism which is extensively, but rather untrans- parently, described by Weyl.³

II. REVIEW OF THE DUALITY BETWEEN S_N AND $GL(m)$

For the construction of the wavefunction, let us begin with an m -dimensional orbital set spanning a linear

space V_m^r ,

$$V_m^r: \{\phi_i(r) | i=1, \dots, m\}. \quad (1)$$

The general linear group $GL(m)$ consists of all non-singular linear mappings (orbital transformations) γ ,

$$\gamma: V_m^r \rightarrow V_m^r. \quad (2)$$

Formation of all N -electron product functions amounts to constructing a tensorial product space spanned by N th rank (purely contravariant) tensors,

$$V_m^r \otimes^N: \{\Phi_{i_1, i_2, \dots, i_N} | i_1, i_2, \dots, i_N = 1, \dots, m\}, \quad (3)$$

where

$$\Phi_{i_1, i_2, \dots, i_N} = \phi_{i_1}(r_1) \otimes \phi_{i_2}(r_2) \otimes \dots \otimes \phi_{i_N}(r_N).$$

Similarly, the N -electron spin space $V_2^s \otimes^N$ is an N -fold tensorial product of 2-dimensional one-electron spin spaces V_2^s .

The linear space $V_m^r \otimes^N$ is stable under both the permutation group S_N and the N -fold inner product group $[GL(m)]^N$. The latter consists of the tensor products of mappings $[\gamma]^N$,

$$[\gamma]^N: V_m^r \otimes^N \rightarrow V_m^r \otimes^N, \quad (4)$$

which are defined by

$$[\gamma]^N \Phi_{i_1, i_2, \dots, i_N} = \gamma \phi_{i_1}(r_1) \otimes \gamma \phi_{i_2}(r_2) \otimes \dots \otimes \gamma \phi_{i_N}(r_N), \quad (5)$$

that is, by a simultaneous transformation of all orbitals in $\Phi_{i_1, i_2, \dots, i_N}$ under γ . If $\mathbf{D}(\gamma)$ is the matrix of γ , then $[\mathbf{D}(\gamma)]^N$, the N th power Kronecker product of $\mathbf{D}(\gamma)$, is the matrix of $[\gamma]^N$. The group consisting of these Kronecker product matrices is a faithful representation of $GL(m)$ {and of the isomorphic group $[GL(m)]^N$ } carried by N th rank tensor space. This tensor space can be decomposed with respect to the permutation group S_N using the matrix element operators or Wigner operators (which generate minimal right-ideals of the group algebra of S_N ¹²):

$$W_{ij}^{[\lambda]} = (f_{[\lambda]}/N!) \sum_{P \in S_N} \mathbf{D}_{ji}^{[\lambda]}(P^{-1})P. \quad (6)$$

Here $\mathbf{D}_{ji}^{[\lambda]}$ is a matrix element of the $f_{[\lambda]}$ dimensional irreducible matrix representation $[\lambda]$ of S_N (which can be denoted by a partition of N). Because the elements of S_N commute with all the elements of the group $[GL(m)]^N$, it follows that a complete reduction of $V_m^r \otimes^N$ under S_N brings along the following complete reduction under $[GL(m)]^N$ and, consequently, under $GL(m)$ ¹⁷:

$$V_m^r \otimes^N = \sum_{(\lambda)} \oplus R^{(\lambda)} \quad (7)$$

partitions of N

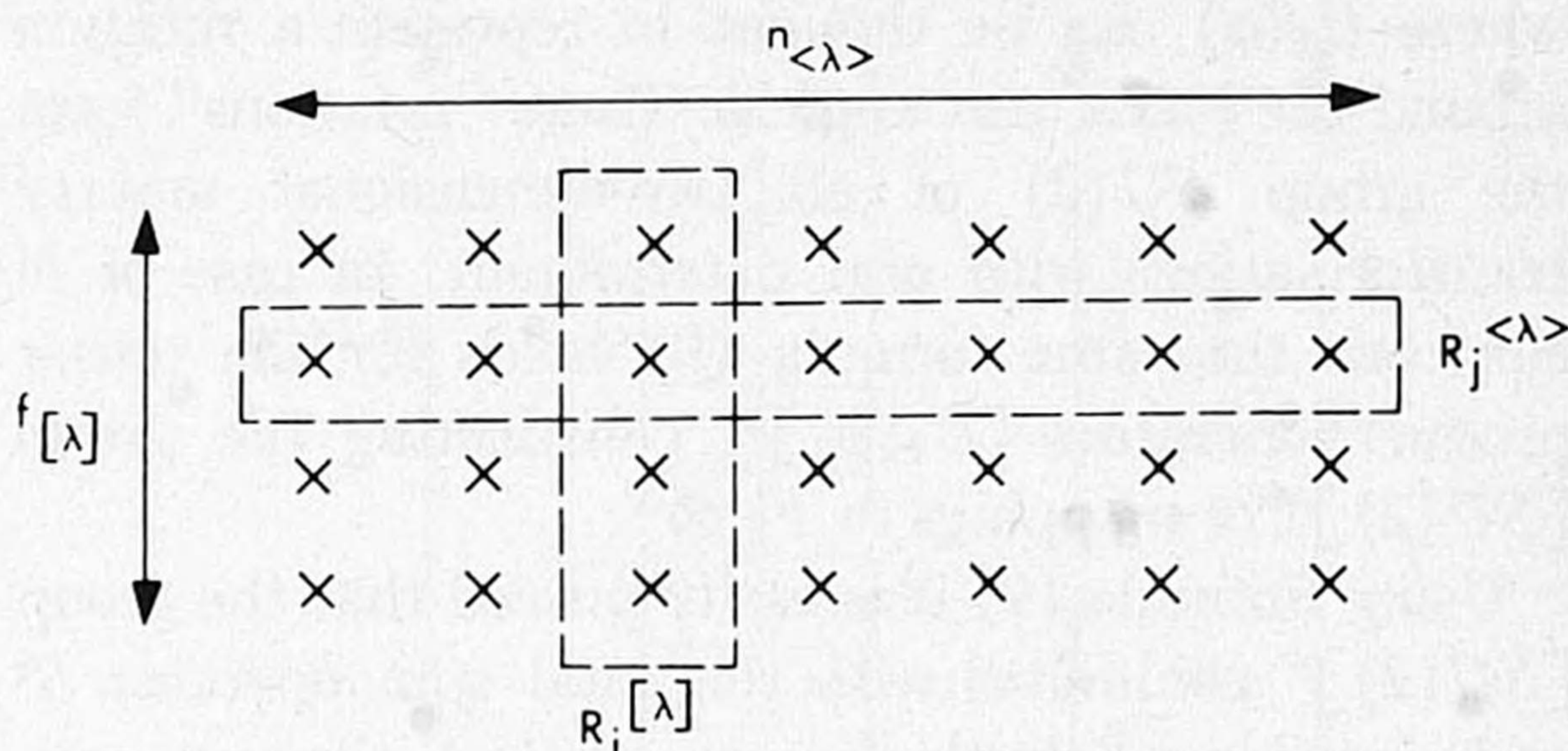


FIG. 1. Simultaneous decomposition of the space $R^{(\lambda)}$ in basis vectors of the irreducible representations $[\lambda]$ of S_N and $\langle \lambda \rangle$ of $GL(m)$. These basis vectors can be obtained by applying the Wigner operators $W_{jk}^{[\lambda]}$, $j=1, \dots, f_{[\lambda]}$, [Formula (6)] on different product configurations which can be constructed from the given orbital set.

with

$$R^{(\lambda)} = \sum_{i=1}^{n_{\langle \lambda \rangle}} \oplus R_i^{[\lambda]} = \sum_{j=1}^{f_{[\lambda]}} \oplus R_j^{\langle \lambda \rangle}.$$

$R_i^{[\lambda]}$ spans the $f_{[\lambda]}$ dimensional representation $[\lambda]$ of S_N which occurs $n_{\langle \lambda \rangle}$ times in $V_m^r \otimes^N$, whereas $R_j^{\langle \lambda \rangle}$ spans the $n_{\langle \lambda \rangle}$ dimensional representation $\langle \lambda \rangle$ of $GL(m)$ occurring $f_{[\lambda]}$ times. Here Robinson's¹⁸ notation is used. Both dimensions, $f_{[\lambda]}$ and $n_{\langle \lambda \rangle}$, are easily calculated by means of hook graphs and m graphs, respectively.^{18,19} Schematically this decomposition (7) is shown in Fig. 1.

Henceforth we assume that the different spaces $R_i^{[\lambda]}$, $i=1, \dots, n_{\langle \lambda \rangle}$, which span the irreducible representations $[\lambda]$ of S_N , carry identical matrix representations. Weyl's proof shows that, in this case, the spaces $R_j^{\langle \lambda \rangle}$, $j=1, \dots, f_{[\lambda]}$, carry identical matrix representations $\mathbf{D}^{(\lambda)}$ of $GL(m)$, so that we obtain the following decomposition of $[\mathbf{D}(\gamma)]^N$:

$$[\mathbf{D}(\gamma)]^N = \sum_{(\lambda)} \oplus f_{[\lambda]} \mathbf{D}^{(\lambda)}(\gamma). \quad (8)$$

partitions of N

Since the elements of $\mathbf{D}^{(\lambda)}(\gamma)$ are integral functions (N th order homogeneous polynomials) of the elements of $\mathbf{D}(\gamma)$, these irreducible representations of $GL(m)$ are called integral.^{12,13} The reason that this one-to-one correspondence between the irreducible representations of S_N and $GL(m)$ has important consequences in the quantum mechanics of N -electron systems is explained in the next two sections.

III. SPIN QUANTUM NUMBER AND PERMUTATION SYMMETRY

The ξ -component of the spin operator, S_ξ , for one electron is related to the unitary mappings in two-dimensional spin space V_2^s by

$$U_\xi(\phi) = \exp(i\phi S_\xi), \quad (9)$$

where $U_\xi(\phi)$ can be thought to represent a rotation around the ξ axis over angle ϕ . These "rotations" form the group $SU(2)$ of all two-dimensional unitary transformations with unit determinant. In case of N electrons the same formula (9) holds for the tensor product operators $[U_\xi(\phi)]^N$, constituting the group $[SU(2)]^N$ of mappings in $V_2^s \otimes^N$.

Using Formula (9) it is easily proved that the group $[SU(2)]^N$ commutes with the total spin operator S^2 and, invoking Schur's lemma, that N -electron spin functions which are basis vectors for the irreducible representations of $[SU(2)]^N$, and of $SU(2)$, are eigenfunctions of S^2 . The duality between the representations of $[U(2)]^N$ and S_N and the property that irreducible representations of $U(2)$ stay irreducible under the subduction $U(2) \downarrow SU(2)$, then leads to the one-to-one correspondence between the irreducible representations of S_N and the total spin quantum number. Eigenfunctions of S^2 are basis vectors for the irreducible representations of S_N , corresponding to partitions of N , graphically represented by Young diagrams. The dimensionality 2 of the spin space causes at most two-element partitions (two-row diagrams) to occur, so that one can write a basis element of $V_2^s \otimes^N$ as

$$|[N/2+S, N/2-S], M_s, j\rangle, \quad (10)$$

where S denotes the total spin quantum number, M_s the z component of the spin, and the index $j=1, \dots, f_{[N/2+S, N/2-S]}$.

IV. TRANSFORMATION PROPERTIES OF THE SPATIAL WAVEFUNCTIONS

If one neglects spin-dynamics, then S and M_s are good quantum numbers and the spin part of the N -electron wavefunction must be an eigenfunction of S^2 . In order to construct the spatial wavefunction one must first select an appropriate configuration $|\Phi_{I_N}\rangle$, where I_N corresponds to a set of specific orbital indices $I_N = \{i_1, i_2, \dots, i_N\}$. The total N -electron wavefunction, which must be antisymmetrized according to the Pauli principle, can then be written as³

$$|\psi_{I_N, k}^{S, M_s}\rangle = \sum_{j=1}^{f_{[N/2+S, N/2-S]}} |[N/2+S, N/2-S], M_s, j\rangle \otimes W_{jk}^{[2^{N/2-S}, 1^{2S}]} |\Phi_{I_N}\rangle. \quad (11)$$

In this expression $[2^{N/2-S}, 1^{2S}]$ is the associate (two-column) representation of $[N/2+S, N/2-S]$. The index k of the Wigner operator has to be chosen such that the resulting tensor is not equal to zero. In general, several choices of k , resulting in tensors with different parentage, are possible.

Summarizing, it follows that spin symmetry together with the Pauli principle imposes definite permutation symmetry on the spatial part of the wavefunction. The latter symmetry in turn, because of the duality between S_N and $GL(m)$, causes a reduction of $V_m^r \otimes^N$ under $GL(m)$.

When neglecting spin terms in the Hamiltonian, a general Hamilton matrix element takes the form

$$\langle \psi_{I_N', k'}^{S', M_s'} | H | \psi_{I_N, k}^{S, M_s} \rangle = \delta_{S'S} \delta_{M_s' M_s} f_{[\lambda]} \times \langle \Phi_{I_N'} | H | W_{k'k}^{[\lambda]} \Phi_{I_N} \rangle, \quad (12)$$

where $[\lambda]$ stands for $[2^{N/2-S}, 1^{2S}]$.

For arriving at this result we used the property that the Wigner operators commute with H and the relation

$$W_{j'k'}^{[\lambda] \dagger} W_{jk}^{[\lambda]} = \delta_{[j'] [j]} \delta_{[k'] [k]} W_{k'k}^{[\lambda]}. \quad (13)$$

Formulas (12) and (13) show in the first place that the carrier spaces $R_j^{[\lambda]}$, $j=1, \dots, f_{[\lambda]}$, of $GL(m)$ are non-interacting for different $[\lambda]$ and different j . Secondly, instead of writing the matrix elements over antisymmetric space-spin functions $|\psi\rangle$, one can also write matrix elements over the space functions $W_{jk}^{[\lambda]} |\Phi_{I_N}\rangle$ only. The reason is that the matrix elements over such space functions are independent of j , and identical (except for multiplication by a constant) to the matrix elements over the space-spin functions. Concluding, we can take just one of the carrier spaces $R_j^{[\lambda]}$ of $GL(m)$ in order to construct all matrix elements in the secular problem. Neglecting spin dynamics, we may replace the Pauli principle and the spin symmetry by the single postulate: A physically allowable N -electron spatial wavefunction must be expanded in partner basis elements of an integral representation of $GL(m)$, characterized by a Young diagram with an most two columns.

Although this postulate is equivalent to Matsen's,²⁰ which concerns the permutation group S_N , the formulation in terms of $GL(m)$ emphasizes directly the spatial transformation properties of the wavefunction. This postulate has one drawback: We change the degeneracy of the system from $2S+1$ to $f_{[2^{N/2-S}, 1^{2S}]}$, where the latter degeneracy cannot be resolved by any physical means whatever (Ref. 3, p. 321).

Let us illustrate the quantum chemical application of this theory by an example. The O_2 molecule counts 10 atomic orbitals in the K and L shells that can be considered in a valence bond calculation, or the same number of molecular orbitals if we start with an MO treatment on that basis. Suppose we wish to construct an antisymmetric wavefunction for the triplet ground

state of O_2 containing 16 electrons. This triplet function must be a basis element of the representation $\langle 2^7, 1^2 \rangle$ of $GL(10)$. A simplification is obtained by noting that this representation has the same dimension as the representation $\langle 2^7, 1^2 \rangle$ of $SU(10)$, which is equivalent to the "hole" representation $\langle 2, 1^2 \rangle$ of $SU(10)$.²¹ This hole representation is defined such that its Young diagram added to the original diagram as in Fig. 2 yields the Young diagram for m doubly occupied orbitals.

The dimension $n_{\langle 2, 1^2 \rangle}$, which equals the number of triplet configurations that can be constructed from the given orbital basis, is easily calculated by Robinson's formula¹⁸

$$n_{\langle \lambda \rangle} = G_{\langle \lambda \rangle}(m) / H_{\langle \lambda \rangle}, \quad (14)$$

where $G_{\langle \lambda \rangle}(m)$ is the product of numbers in the m graph and $H_{\langle \lambda \rangle}$ is the product of hook lengths. The dimension is 990.



This means that an orbital transformation of the original 10 orbital basis set, for instance a Löwdin orthogonalization of the VB orbitals or a DODS mixing of the MO's, would mix 990 triplet states of O_2 . If the applied orbital transformation $\mathbf{D}(\gamma)$ is predetermined, as for the Löwdin orthogonalization, the weights of all mixed configurations are fixed: they are the matrix elements of $\mathbf{D}(\gamma)^{\langle 2^{N/2-S}, 1^{2S} \rangle}$. In the case of the DODS procedure, the matrix elements of $\mathbf{D}(\gamma)$ are used as variation parameters. The theory of this section then tells immediately that the DODS approach is equivalent to a full configuration interaction with somewhat restricted CI coefficients that are homogeneous polynomials of the DODS parameters.

V. PARTITIONED ORBITAL TRANSFORMATIONS

So far we have outlined the basic theory derived by Schur and Weyl. From this theory follows the manner in which an antisymmetric spin eigenfunction behaves under arbitrary orbital transformations. In many practical cases, however (examples are given in the introduction), one can divide the orbitals in different subsets and restrict the transformations between orbitals of the same subset. In these cases the matrix $\mathbf{D}(\gamma)$ has a blocked form. We have derived explicitly how the transformation of the many-electron wave-

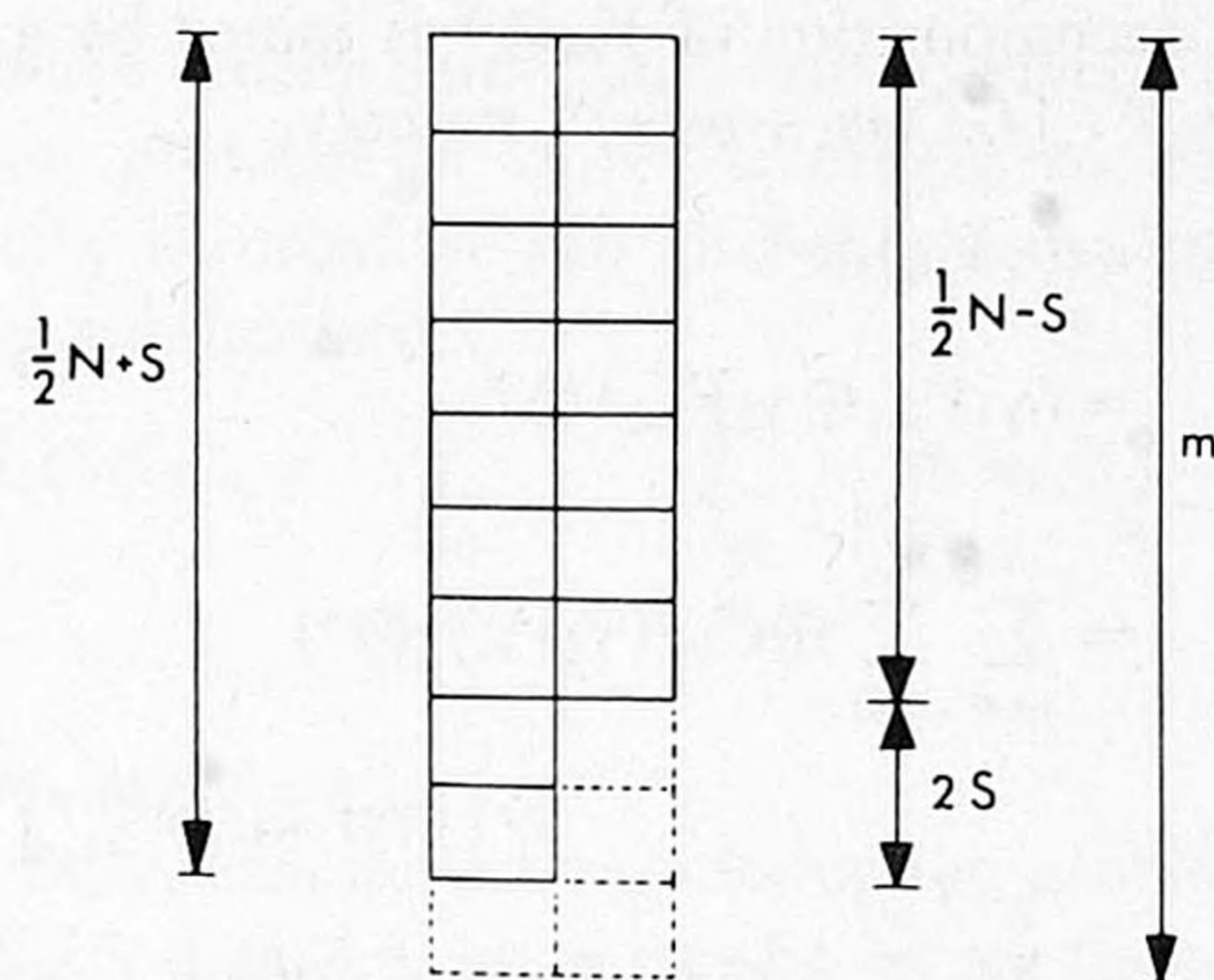


FIG. 2. Young diagram for the triplet ($S=1$) state of O_2 ; number of electrons $N=16$, number of orbitals $m=10$.

function simplifies under such orbital transformations. The result is described in this section for a two-subset partitioning of the orbital set, but, by induction, can be easily extended to the general case.

A division of the orbital set into two subsets is equivalent to the following decomposition of the orbital space:

$$V_m = V_{m_1} \oplus V_{m_2}. \quad (15)$$

We consider orbital transformations of the form

$$\gamma = \gamma_1 \oplus \gamma_2, \quad (16)$$

where γ_1 is the restriction of γ to V_{m_1} and γ_2 to V_{m_2} . The mappings γ of this form constitute a group which we denote by $GL(m_1 + m_2)$. Since $m_1 + m_2 = m$, this group is clearly a subgroup of $GL(m)$. Thinking in terms of matrices instead of linear mappings, $GL(m_1 + m_2)$ can be defined as the group of matrices with the blocked structure

$$\mathbf{D}(\gamma) = \mathbf{D}(\gamma_1) \oplus \mathbf{D}(\gamma_2), \quad (17)$$

where $\mathbf{D}(\gamma_1)$ is a $m_1 \times m_1$ matrix and $\mathbf{D}(\gamma_2)$ a $m_2 \times m_2$ matrix.

The problem we have to solve is to find the behavior of the irreducible representations $\langle \lambda \rangle$ of $GL(m)$ under the subduction $GL(m) \downarrow GL(m_1 + m_2)$. First we decompose the N th rank tensor space $V_m \otimes^N$ by a generalization of Newton's binomial theorem for noncommuting factors:

$$\begin{aligned} V_m \otimes^N &= (V_{m_1} \oplus V_{m_2}) \otimes^N \\ &= \sum_{n=0}^N \sum_{k=1}^{\binom{N}{n}} \oplus C_k (V_{m_1} \otimes^n) \otimes (V_{m_2} \otimes^{N-n}). \end{aligned} \quad (18)$$

The elements $C_k \in S_N$ which take care of the proper ordering of the factors in the tensorial products are the coset generators of the subgroup $S_n \otimes S_{N-n}$ in S_N . Note

that this decomposition of $V_m \otimes^N$ is joined by a reduction of $[\gamma]^N \in [GL(m_1+m_2)]^N$, namely,

$$\begin{aligned}
 [\gamma]^N V_m \otimes^N &= (\gamma V_m) \otimes^N \\
 &= (\gamma_1 V_{m_1} \oplus \gamma_2 V_{m_2}) \otimes^N \\
 &= \sum_{n=0}^N \sum_{k=1}^{\binom{N}{n}} \oplus C_k \{ (\gamma_1 V_{m_1}) \otimes^n \} \\
 &\quad \otimes \{ (\gamma_2 V_{m_2}) \otimes^{N-n} \} \\
 &= \sum_{n=0}^N \sum_{k=1}^{\binom{N}{n}} \oplus C_k [\gamma_1]^n \otimes [\gamma_2]^{N-n} (V_{m_1} \otimes^n) \\
 &\quad \otimes (V_{m_2} \otimes^{N-n}) \\
 &= \sum_{n=0}^N \sum_{k=1}^{\binom{N}{n}} \oplus \{ C_k [\gamma_1]^n \otimes [\gamma_2]^{N-n} C_k^{-1} \} \\
 &\quad \times \{ C_k (V_{m_1} \otimes^n) \otimes (V_{m_2} \otimes^{N-n}) \}. \quad (19)
 \end{aligned}$$

Hence,

$$[\gamma_1 \oplus \gamma_2]^N = \sum_{n=0}^N \sum_{k=1}^{\binom{N}{n}} \oplus C_k [\gamma_1]^n \otimes [\gamma_2]^{N-n} C_k^{-1}, \quad (20)$$

where the summand is the restriction of $[\gamma_1 \oplus \gamma_2]^N$ to $C_k(V_{m_1} \otimes^n) \otimes (V_{m_2} \otimes^{N-n})$.

If we choose the basis elements in each of the spaces $C_k(V_{m_1} \otimes^n) \otimes (V_{m_2} \otimes^{N-n})$ such that they are obtained from an original basis in $(V_{m_1} \otimes^n) \otimes (V_{m_2} \otimes^{N-n})$ by the permutations C_k , it follows that all elements $C_k[\gamma_1]^n \otimes [\gamma_2]^{N-n} C_k^{-1}$ for

$$k = 1, \dots, \binom{N}{n}$$

have the same matrix,

$$[D(\gamma_1)]^n \otimes [D(\gamma_2)]^{N-n}. \quad (21)$$

This is easily proved since C_k is a linear operator which does not act on the transformation coefficients of $[D(\gamma_1)]^n \otimes [D(\gamma_2)]^{N-n}$. We thus arrive at a reduction of the matrix representation of $GL(m)$ carried by the complete tensor space $V_m \otimes^N$ under $GL(m_1+m_2)$.

We must now look for the reduction of the irreducible representations $\langle \lambda \rangle$ of $GL(m)$ under $GL(m_1+m_2)$. To this end we reduce the spaces $V_{m_1} \otimes^n$ and $V_{m_2} \otimes^{N-n}$ according to Formula (7):

$$\begin{aligned}
 V_{m_1} \otimes^n &= \sum_{(\mu)} \sum_{i=1}^{f_{[\mu]}} \oplus R_i^{\langle \mu \rangle}, \\
 &\quad \text{partitions of } n \\
 V_{m_2} \otimes^{N-n} &= \sum_{(\nu)} \sum_{j=1}^{f_{[\nu]}} \oplus R_j^{\langle \nu \rangle}, \quad (22) \\
 &\quad \text{partitions of } N-n
 \end{aligned}$$

where $R_i^{\langle \mu \rangle}$ is irreducible under $[GL(m_1)]^n$ and $R_j^{\langle \nu \rangle}$ is irreducible under $[GL(m_2)]^{N-n}$. Therefore the tensor product space $R_i^{\langle \mu \rangle} \otimes R_j^{\langle \nu \rangle}$ is irreducible under $[GL(m_1)]^n \otimes [GL(m_2)]^{N-n}$ and, consequently, under $GL(m_1+m_2)$.²² Since we just derived [see Expression (21)] that all spaces $C_k(V_{m_1} \otimes^n) \otimes (V_{m_2} \otimes^{N-n})$ span the same matrix representation of $GL(m_1+m_2)$, it follows that all spaces $C_k(R_i^{\langle \mu \rangle} \otimes R_j^{\langle \nu \rangle})$ for

$$k = 1, \dots, \binom{N}{n}, \quad i = 1, \dots, f_{[\mu]}, \quad j = 1, \dots, f_{[\nu]}$$

are irreducible under $GL(m_1+m_2)$ and span the same matrix representation $D^{\langle \mu \rangle} \otimes D^{\langle \nu \rangle}$.

Let us imagine that we place the $n_{\langle \mu \rangle} \times n_{\langle \nu \rangle}$ basis vectors of $R_i^{\langle \mu \rangle} \otimes R_j^{\langle \nu \rangle}$ in rows. Taking these rows for $i = 1, \dots, f_{[\mu]}, j = 1, \dots, f_{[\nu]}$, we obtain a scheme comparable to Fig. 1. We construct identical schemes for the spaces $C_k(R_i^{\langle \mu \rangle} \otimes R_j^{\langle \nu \rangle})$ and place these directly under the first scheme, getting

$$\binom{N}{n}$$

blocks with each $f_{[\mu]} \times f_{[\nu]}$ rows. As shown above, each row carries the same irreducible matrix representation $D^{\langle \mu \rangle} \otimes D^{\langle \nu \rangle}$ of $GL(m_1+m_2)$. Using Weyl's result [Eq. (7)] again, we find that each column in the first block spans the irreducible representation $[\mu] \otimes [\nu]$ of $S_n \otimes S_{N-n}$. The columns of the next blocks are generated from the first block by the coset generators C_k of $S_n \otimes S_{N-n}$ in S_N . We can prove that a full column spans the induced representation of S_N denoted by $[\mu] \otimes [\nu] \uparrow S_N$. Every one of the $n_{\langle \mu \rangle} \times n_{\langle \nu \rangle}$ different columns spans an identical induced representation, thus assuring that all these induced representations can be reduced by the same basis transformation. But, if we perform the same basis transformation on all columns, we do not disturb the matrix representation of $GL(m_1+m_2)$ afforded by the rows.

Let the reduction of every column be written as follows:

$$[\mu] \otimes [\nu] \uparrow S_N = \sum_{(\lambda)} m_{\mu\nu\lambda} [\lambda], \quad (23)$$

partitions of N

and let us perform on the columns the basis transformation corresponding to this reduction. In our scheme we then have blocks in which the columns span the irreducible representations $[\lambda]$ of S_N , the same block appearing $m_{\mu\nu\lambda}$ times. The rows still span the representation $D^{\langle \mu \rangle} \otimes D^{\langle \nu \rangle}$ of $GL(m_1+m_2)$. This result is

expressed mathematically as

$$\sum_{k=1}^{(N)} \sum_{i=1}^{f[\mu]} \sum_{j=1}^{f[\nu]} \oplus C_k(R_i^{(\mu)} \otimes R_j^{(\nu)}) = \sum_{(\lambda)} \oplus m_{\mu\nu\lambda} \sum_{\tau=1}^{f[\lambda]} R_\tau^{(\mu) \otimes (\nu)}. \quad (24)$$

partitions of N

Note that the space $R_\tau^{(\mu) \otimes (\nu)}$ cannot be written as a tensor product, although it spans the representation $D^{(\mu)} \otimes D^{(\nu)}$.

We now consider the complete reduction of the full space $V_m \otimes^N$ under $GL(m_1+m_2)$:

$$V_m \otimes^N = \sum_{n=0}^N \sum_{k=1}^{(N)} \oplus C_k(V_{m_1} \otimes^n) \otimes (V_{m_2} \otimes^{N-n}) = \sum_{n=0}^N \sum_{k=1}^{(N)} \sum_{(\mu)} \sum_{(\nu)} \sum_{i=1}^{f[\mu]} \sum_{j=1}^{f[\nu]} \oplus C_k R_i^{(\mu)} \otimes R_j^{(\nu)}. \quad (25)$$

part. of n part. of $N-n$

Substituting Formula (24) yields

$$V_m \otimes^N = \sum_{n=0}^N \sum_{(\mu)} \sum_{(\nu)} \sum_{(\lambda)} m_{\mu\nu\lambda} \times \sum_{\tau=1}^{f[\lambda]} \oplus R_\tau^{(\mu) \otimes (\nu)}. \quad (26)$$

part. of n part. of $N-n$ part. of N

Comparing this to the original reduction of $V_m \otimes^N$ under $GL(m)$,

$$V_m \otimes^N = \sum_{(\lambda)} \sum_{\tau=1}^{f[\lambda]} \oplus R_\tau^{(\lambda)}, \quad (27)$$

part. of N

we find

$$R_\tau^{(\lambda)} = \sum_{n=0}^N \sum_{(\mu)} \sum_{(\nu)} \oplus m_{\mu\nu\lambda} R_\tau^{(\mu) \otimes (\nu)}. \quad (28)$$

part. of n part. of $N-n$

This reduction is accompanied by a decomposition of the matrix representation:

$$D^{(\lambda)}(\gamma_1 \oplus \gamma_2) = \sum_{n=0}^N \sum_{(\mu)} \sum_{(\nu)} \oplus m_{\mu\nu\lambda} D^{(\mu)}(\gamma_1) \otimes D^{(\nu)}(\gamma_2). \quad (29)$$

part. of n part. of $N-n$

With this result we have fulfilled our aim: the decomposition of the irreducible representations $\langle \lambda \rangle$ of $GL(m)$ with respect to $GL(m_1+m_2)$. They are expressed in tensor products of irreducible representations $\langle \mu \rangle$ and $\langle \nu \rangle$ of $GL(m_1)$ and $GL(m_2)$, respectively, with

multiplicity coefficients that are derived from an induction problem in S_N .²³ According to Frobenius' reciprocity theorem we can also obtain the coefficients from the subduction

$$[\lambda] \downarrow S_n \otimes S_{N-n} = \sum_{(\mu)} \sum_{(\nu)} \oplus m_{\lambda\mu\nu} [\mu] \otimes [\nu], \quad (30)$$

part. of n part. of $N-n$

where $m_{\mu\nu\lambda} = m_{\lambda\mu\nu}$.

Generally, this induction/subduction problem is not multiplicity free, i.e., $m_{\mu\nu\lambda}$ can be larger than 1. If we restrict the problem to many-electron systems, however, only representations are allowed with Young diagrams of two columns at most, and $m_{\mu\nu\lambda}$ can just become 0 or 1. A constructive method of calculating these multiplicity factors has been given by Littlewood²⁴ and by Robinson.¹⁸ Extensive tables can be found in Appendix B of Ref. 25.

For demonstrating the application of our result (29) we again turn to the example of the O_2 molecule. Suppose that we first wish to separate the core orbitals and then to perform an orbital transformation (e.g., hybridization or orthogonalization) which mixes only the valence orbitals of each atom among each other. For the separation of the two core orbitals we consider the reduction of the triplet representation $\langle 2^7, 1^2 \rangle$ of $GL(10)$ under $GL(2+8)$:

$$\begin{aligned} \langle 2^7, 1^2 \rangle &= \langle 1 \rangle \otimes \langle 2^7, 1 \rangle \\ \text{triplet } O_2 & \quad \text{doublet core} \quad \text{doublet valence} \\ (16 \text{ electrons}) & \quad (1 \text{ el.}) \quad (15 \text{ el.}) \\ \text{dimension } 990 &= 2 \times 8 \\ &\oplus \langle 2 \rangle \otimes \langle 2^6, 1^2 \rangle \oplus \langle 1^2 \rangle \otimes \langle 2^7 \rangle \\ &\quad \text{singlet c.} \quad \text{triplet v.} \quad \text{triplet c.} \quad \text{singlet v.} \\ &\quad (2) \quad (14) \quad (2) \quad (14) \\ &+ 3 \times 28 + 1 \times 36 \\ &\oplus \langle 1^2 \rangle \otimes \langle 2^6, 1^2 \rangle \oplus \langle 2, 1 \rangle \otimes \langle 2^6, 1 \rangle \\ &\quad \text{triplet c.} \quad \text{triplet v.} \quad \text{doublet c.} \quad \text{doublet v.} \\ &\quad (2) \quad (14) \quad (3) \quad (13) \\ &+ 1 \times 28 + 2 \times 168 \\ &\oplus \langle 2, 1 \rangle \otimes \langle 2^5, 1^3 \rangle \oplus \langle 2^2 \rangle \otimes \langle 2^5, 1^2 \rangle \\ &\quad \text{doublet c.} \quad \text{quartet v.} \quad \text{singlet c.} \quad \text{triplet v.} \\ &\quad (3) \quad (13) \quad (4) \quad (12) \\ &+ 2 \times 56 + 1 \times 378 \end{aligned}$$

We are only interested in those states with 4 electrons in the core forming a singlet, so that we are left with 12

electrons in the 8 valence orbitals carrying the triplet representation $\langle 2^5, 1^2 \rangle$ of $GL(8)$. Formula (14) shows that we find 378 such states. The second step of our procedure amounts to the reduction of the latter representation under $GL(4+4)$, which reads (indicating the atoms by A and B):

$$\begin{aligned}
 \langle 2^5, 1^2 \rangle &= \langle 2, 1^2 \rangle \otimes \langle 2^4 \rangle \\
 \text{valence triplet} & \quad \text{triplet } A^{2+} \quad \text{singlet } B^{2-} \\
 (12 \text{ electrons}) & \quad (4 \text{ el.}) \quad (8 \text{ el.}) \\
 \text{dimension } 378 &= 15 \times 1 \\
 \\
 \oplus \langle 2, 1^3 \rangle \otimes \langle 2^3, 1 \rangle \oplus \langle 2^2, 1 \rangle \otimes \langle 2^3, 1 \rangle \\
 \text{quartet } A^+ & \quad \text{doublet } B^- \quad \text{doublet } A^+ \quad \text{doublet } B^- \\
 (5) & \quad (7) \quad (5) \quad (7) \\
 + 4 \times 4 & + 20 \times 4 \\
 \\
 \oplus \langle 2^3 \rangle \otimes \langle 2^2, 1^2 \rangle \oplus \langle 2^2, 1^2 \rangle \otimes \langle 2^2, 1^2 \rangle \\
 \text{singlet } A & \quad \text{triplet } B \quad \text{triplet } A \quad \text{triplet } B \\
 (6) & \quad (6) \quad (6) \quad (6) \\
 + 10 \times 6 & + 6 \times 6 \\
 \\
 \oplus \langle 2^2, 1^2 \rangle \otimes \langle 2^3 \rangle \oplus \langle 2^3, 1 \rangle \otimes \langle 2^2, 1 \rangle \\
 \text{triplet } A & \quad \text{singlet } B \quad \text{doublet } A^- \quad \text{doublet } B^+ \\
 (6) & \quad (6) \quad (7) \quad (5) \\
 + 6 \times 10 & + 4 \times 20 \\
 \\
 \oplus \langle 2^3, 1 \rangle \otimes \langle 2, 1^3 \rangle \oplus \langle 2^4 \rangle \otimes \langle 2, 1^2 \rangle \\
 \text{doublet } A^- & \quad \text{quartet } B^+ \quad \text{singlet } A^{2-} \quad \text{triplet } B^{2+} \\
 (7) & \quad (5) \quad (8) \quad (4) \\
 + 4 \times 4 & + 1 \times 15
 \end{aligned}$$

One could imagine that the secular problem including all configurations mixed by $GL(8)$ is too large. In this case, we can, for instance, consider only the triplet ground state which is formed by covalent interaction between the atomic ground state triplets. We then find 36 states which transform as

$$\begin{aligned}
 \langle 2^2 \rangle \otimes \langle 2^2, 1^2 \rangle \otimes \langle 2^2, 1^2 \rangle \\
 \text{core} \quad \text{atom A} \quad \text{atom B} \\
 \text{singlet} \quad \text{triplet} \quad \text{triplet} .
 \end{aligned}$$

It is important to note, as we remarked before, that the product notation for the representations does not imply that the wavefunctions are simple tensorial products; they should have the proper symmetry also with respect to permutations exchanging electrons between subsystems. Still, they are basis elements of tensorial product representations. We have developed a method²⁶

to construct such wavefunctions by means of reduced Wigner operators, which is closely related to the aggregate theory of Matsen and Klein.⁴

VI. DISCUSSION

Starting from Weyl's theory which describes the behavior of antisymmetric spin eigenfunctions under general orbital transformations, we have derived how this behavior simplifies for partitioned orbital mixings. This simplification can be considerable, as in the example of the preceding section, where a full valence bond calculation is restricted to include only covalent states. Both the general result and its specification for partitioned transformations have numerous applications in quantum mechanical methods applied to atoms and molecules.

An example for the use of the general result is given by a complete orthogonalization of a linearly independent basis set. This orthogonalization of the orbital set can significantly change the interaction energy between atoms or molecules calculated with a limited number of atomic or molecular orbital configurations. In practice, this effect was noticed by Magnasco and Musso²⁷ in their computation of the interaction between two H_2 molecules and by Vonsovsky and Karpenko²⁸ in discussing superexchange by Anderson's model. The results of both studies depend sensitively on whether the atomic orbitals are orthogonalized or not. Weyl's theory tells in this case which configurations should be included in order to obtain a result which is independent of orbital mixing and, in case one takes fewer configurations, which new ones are introduced and how the weights are changed by a given orbital transformation.

Our special result for partitioned orbital transformations has been used in two different subjects so far:

(1) In connection with Roothaan's open-shell Hartree-Fock method¹⁶ we have proved, very compactly, that

an antisymmetric spin eigenfunction is invariant under mixing of the closed-shell orbitals,

an antisymmetric spin eigenfunction transforms under mixing of the open-shell orbitals as if the closed shells were not present.

Using the latter theorem one shows very easily that by mixing of the open shells also non-degenerate states (with the same spin multiplicity but different spatial symmetry) can be mixed.

(2) we have derived the explicit relation between a pair-correlated DODS method and the CI approach. Particularly, the effect that various matrix elements in the DODS secular equations do not depend on some mixing parameters could be explained.

These results will be elaborated in a forthcoming publication.²⁶

ACKNOWLEDGMENT

This research was supported by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) via the Netherlands Foundation for Chemical Research (S.O.N.).

¹ M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen, Tokyo, 1955).

² D. F. Johnston, Rept. Progr. Phys. **23**, 66 (1960).

³ H. Weyl, *The Theory of Groups and Quantum Mechanics* (Methuen, London, 1931).

⁴ F. A. Matsen and D. J. Klein, J. Phys. Chem. **75**, 1860 (1971) and references therein.

⁵ W. A. Goddard III, Phys. Rev. **157**, 81 (1967).

⁶ F. E. Harris, Advan. Quantum Chem. **3**, 61 (1967).

⁷ R. C. Morrison and G. A. Gallup, J. Chem. Phys. **50**, 1214 (1969).

⁸ A. van der Avoird, "Perturbation Theory for Intermolecular Forces," thesis, Eindhoven, 1968.

⁹ A. T. Amos and J. I. Musher, Chem. Phys. Letters **3**, 721 (1969).

¹⁰ D. J. Klein, Intern. J. Quantum Chem. **4S**, 271 (1971).

¹¹ R. Eisenschitz and F. London, Z. Physik **60**, 491 (1930).

¹² H. Boerner, *Darstellungen von Gruppen* (Springer, Berlin, 1967), 2nd ed.

¹³ F. D. Murnaghan, *The Theory of Group Representations* (Johns Hopkins U. P., Baltimore, 1938).

¹⁴ R. Pauncz, *Alternant Molecular Orbital Method* (Saunders, Philadelphia, 1967).

¹⁵ A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, Proc. Roy. Soc. (London) **A220**, 446 (1953).

¹⁶ C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

¹⁷ This is a group theoretical generalization of the theorem that two commuting operators have a set of common eigenfunctions. In his proof of this relation (7), Weyl used the property that the enveloping algebra of $[GL(m)]^N$ is the commuting algebra of the group algebra of S_N . Since the enveloping algebra of $[GL(m)]^N$ is also the enveloping algebra of $[U(m)]^N$, one finds that the (integral) representations $\langle \lambda \rangle$ of the general linear group $GL(m)$ stay irreducible under the restriction of $GL(m)$ to $U(m)$, the group of unitary transformations (see Refs. 12 and 13).

¹⁸ G. de B. Robinson, *Representation Theory of the Symmetric Group* (Edinburgh U. P., 1961).

¹⁹ A. J. Coleman, Advan. Quantum Chem. **4**, 83 (1968).

²⁰ F. A. Matsen, J. Am. Chem. Soc. **92**, 3525 (1970).

²¹ B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).

²² The first part of this assertion is a consequence of the theorem that the tensor products of the irreducible representations of two different groups form the irreducible representations of their outer product group. This theorem was proved by Weyl (Ref. 3, p. 164) for the compact group $U(m)$, but it is also valid for integral representations of $GL(m)$ which stay irreducible under $U(m)$ (see Ref. 17). The second statement holds because $[GL(m_1)]^n \otimes [GL(m_2)]^{N-n}$ is isomorphic to $GL(m_1) \otimes GL(m_2)$, which in its turn is isomorphic to $GL(m_1+m_2)$.

²³ This result is a generalization of Weyl's branching theorem (Ref. 3, p. 391).

²⁴ D. E. Littlewood, *The Theory of Group Characters* (Oxford U. P., New York, 1950), 2nd ed.

²⁵ B. G. Wybourne, *Symmetry Principles and Atomic Spectroscopy* (Wiley-Interscience, New York, 1970).

²⁶ P. E. S. Wormer and A. van der Avoird (unpublished).

²⁷ V. Magnasco and G. F. Musso, J. Chem. Phys. **48**, 2657 (1968).

²⁸ S. V. Vonsovsky and B. V. Karpenko, *Encyclopedia of Physics, Vol. 18/1 Magnetism*, edited by H. P. J. Wijn (Springer, Berlin, 1968), p. 265.

Quantum Lattice Dynamics of Molecular Solids. I. General Theory*

NATHAN JACOBI†

Department of Chemistry, University of Southern California, Los Angeles, California 90007

(Received 24 March 1972)

A quantum lattice dynamics formulation is presented for molecular solids, including translational and librational modes. The variational principle is used to construct ground and excited state wavefunctions obeying the translational symmetry of the crystal. For translational modes the formalism reduces to a form similar to previous quantum lattice dynamics treatments. The results for librational modes are new. General properties of the librational wavefunctions and matrix elements are derived for linear molecules interacting through arbitrary anisotropic pair potentials.

I. INTRODUCTION

In recent years quantum lattice dynamics treatments¹ have proven essential in the study of translational phonons of systems of light particles and/or weak binding energies. Most of the applications have been to solid helium and solid molecular hydrogen, systems characterized by large amplitude vibrations and appreciable zero-point energies.

Molecular solids possess, in addition, rotational degrees of freedom, giving rise to librational phonons. There is a clear distinction between solid hydrogen, where the rotational spacing is much larger than the

librational excitation energy, and the other molecular solids, where the opposite holds. This distinction² is the reason that only solid hydrogen was treated quantum mechanically, and as J is a good quantum number, free rotor wavefunctions of definite J were used as a basis set.

However, some other molecular solids have low barriers to rotation and have, as a result, large root-mean-square librational displacements from the equilibrium orientations. For example, the angular displacement in solid α -nitrogen is about 20° ,³ while in adamantane the librational amplitude is estimated to reach 30° .⁴ This leads to the conclusion that "fresh thinking is called