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Calculation of permutation matrices using graphical methods of spin algebras: Explicit expressions for the Serber-coupling case

J. Paldus* and P. E. S. Wormer†

Quantum Theory Group, Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

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We present a general method, based on the diagrammatic techniques of spin algebras, for the calculation of permutation matrices of two-rowed (two-columned) irreducible representations of the symmetric group $\mathcal{S}_N$ relative to a basis (or bases) adapted to the subgroup(s) $\mathcal{S}_{N_A} \otimes \mathcal{S}_{N_B} \subset \mathcal{S}_N$ or to (a) subgroup chain(s) which may be generated by a recursive application of the above-given chain. These matrix elements are needed in spin-adapted configuration interaction calculations. This general technique is applied to the Serber coupling scheme, and general and explicit closed formulas are obtained for the matrix elements of an arbitrary transposition. An extension of this formalism to cases with an arbitrarily large frozen core is also outlined using the same technique. A computer program based on these derivations was written and its effectiveness compared with that of other approaches is discussed. An extension of these applications to more complex permutations than transpositions, as well as to other coupling schemes, is also briefly discussed.

I. INTRODUCTION

The basic problem in the majority of atomic and molecular electronic structure calculations is the determination of eigenvalues and eigenstates of N-electron *spin-independent* Hamiltonians. The neglect of the explicit spin dependence endows a Hamiltonian with a rather high symmetry: in addition to being invariant under the *inner* direct product group $\mathcal{S}_N^{(r)} \boxtimes \mathcal{S}_N^{(s)}$ of the symmetric groups permuting the spatial ($\mathcal{S}_N^{(r)}$) and spin ($\mathcal{S}_N^{(s)}$) coordinates, which is a consequence of the fact that electrons are indistinguishable, the spin-independent Hamiltonian also commutes with the *outer* direct product group $\mathcal{S}_N^{(r)} \otimes \mathcal{S}_N^{(s)}$, and with the special unitary group SU(2).[1,2] Of course, the irreducible representations of SU(2) and $\mathcal{S}_N^{(s)}$ (henceforth designated simply as $\mathcal{S}_N$) are closely related[1,3,4]: $\mathcal{S}_N$-adapted spin states automatically span irreducible representations of SU(2). Conversely, adaptation to SU(2) symmetry imposes $\mathcal{S}_N$ symmetry on the spin functions (assuming that the spin states are connected via ladder operators[4]).

Thus, in order to utilize the symmetry of the spin-free Hamiltonian, we can either use the SU(2) calculus, developed originally by Wigner and Racah, or the $\mathcal{S}_N$ calculus pioneered by Young. Moreover, it may often be even more advantageous to exploit the pertinent dynamical group[2] $U(m)$, as indicated by a large number of recently published papers.[4-7] In fact, as will be seen later, it may be sometimes very convenient to combine several of these approaches.[6,7]

In many physical and chemical applications one not only wishes the spin states to be adapted to $\mathcal{S}_N$ [and SU(2)], but also to some subgroups $\mathcal{S}_{N_1} \times \mathcal{S}_{N_2} \times \cdots \times \mathcal{S}_{N_k}$ of $\mathcal{S}_N$ ($\sum_i N_i = N$). Reasons for this may be that the electrons form an "aggregate"[8] of weakly interacting subsystems of $N_1, N_2, \ldots, N_k$ electrons, or that the orbital states are required to span irreducible representations of certain subgroups of GL(m).[9] In order to project out states that have this latter property one needs irreducible representations of $\mathcal{S}_N$ simultaneously adapted to $\mathcal{S}_{N_1} \otimes \mathcal{S}_{N_2} \otimes \cdots \otimes \mathcal{S}_{N_k}$.

To our knowledge, no general prescription for the computation of such irreducible representations exists. In this paper, we present a prescription for irreducible representations of $\mathcal{S}_N$ having at most two rows (or columns) in their Young diagram. Our approach relies on the Wigner-Racah SU(2) calculus, and in particular on its graphical version pioneered by Jucys and co-workers.[10]

The diagrammatic techniques of spin algebras have great advantages arising from their universality and transparency in handling various coupling schemes. Although, in this paper, we apply them to the spin functions only, we must stress their suitability in conjunction with the graphical techniques based on the second quantization formalism and Wick's theorem, whenever the spin and/or angular momentum adapted theory is required. Let us at least mention their previous use in spin (and/or angular momentum) adaptation of perturbation theory and Green's-function approaches,[11] limited configuration-interaction (CI) matrix element evaluation[12,13] and generation of compact direct CI[14] expressions[12] or in the spin adapted coupled-cluster-theory derivation.[15] They were also successfully employed to calculate efficiently the matrix elements of the unitary group generators[6,7] or of their products.[7] Very recently,[16] they were also used to establish a transformation between dif-

ferent coupling schemes,[17] in particular between Serber-like and Young-Yamanouchi bases, which led to a new derivation of the Young-Yamanouchi formulas for elementary transpositions in the two-rowed irreducible representations.[16]

The objective of this paper is to present a rather general outline of the possible applications of the graphical methods of spin algebras to the calculation of matrix elements of spin-independent operators over "aggregate states",[8] using an approach via the symmetric and the SU(2) groups. As a specific application of this general technique we work out in detail the case in which the aggregate consists solely of electron pairs ($N_1 = N_2 = \cdots = N_k = 2$); we refer to this as the Serber case.

The Serber case has attracted much attention recently, and different ways of constructing Serber states[18] have been proposed.[19-24] However, in this connection, one must realize that the requirement that eigenstates of $\hat{S}^2$ transform according to irreducible representations of $\mathfrak{S}_2 \otimes \mathfrak{S}_2 \otimes \cdots \otimes \mathfrak{S}_2$ is not sufficient to specify states uniquely (up to phase); indeed, one commonly employs a canonical chain of subgroups of $\mathfrak{S}_N$ to achieve a unique state labeling. The chain originally used by Serber[25,26] is[18]

$$\mathfrak{S}_2 \subset \mathfrak{S}_4 \subset \mathfrak{S}_6 \subset \cdots \subset \mathfrak{S}_{N-2} \subset \mathfrak{S}_N \tag{1}$$

and, accordingly, we calculate representation matrices adapted to this chain. The same chain has been recently used by Carrington and Doggett,[22] who suggested a simple method for Serber-state construction, using formulas from an earlier work by Kotani *et al.*[27] A similar procedure has also been very recently proposed by Pauncz.[23] A completely different line of approach has been followed earlier by Ruedenberg and collaborators,[19-21] who diagonalize the $\hat{S}^2$ operator over all spin states of fixed magnetic quantum number and belonging to a certain irreducible representation of $\mathfrak{S}_2 \otimes \mathfrak{S}_2 \otimes \cdots \otimes \mathfrak{S}_2$. The resulting eigenvectors do not correspond to a definite coupling scheme, and hence are strictly speaking not Serber states. Very recently Vojtík and Fišer[24] showed that the Ruedenberg-Salmon scheme can be improved upon by including time reversal.

In all the work mentioned above the Serber states are constructed explicitly. However, as has been shown by Ruedenberg,[28] all one needs in the calculation of Hamiltonian matrix elements is the matrix of certain permutations (so-called line-up permutations) relative to the basis of eigenstates of $\hat{S}^2$. Thus, there is no need to calculate Serber states explicitly if one can derive formulas for the matrices of arbitrary transpositions relative to the Serber basis. Any permutation matrix can then be obtained from the latter ones by matrix multiplication. As will be discussed in this paper, our formulas for the matrix elements of arbitrary transpositions relative to the Serber basis have enabled us to write a very fast computer program requiring little main storage.

II. GENERAL OUTLINE OF THE METHOD

In this section, we briefly describe a general technique for obtaining the matrices of arbitrary permutations $\hat{P} \in \mathfrak{S}_N$ relative to eigenstates of $\hat{S}^2$, which may result from any coupling of the electron spins. Consequently the method, as we present it, is restricted to two-rowed and two-columned irreducible representations of $\mathfrak{S}_N$ which, however, are precisely the irreducible representations needed in a spin-free treatment of spin-$\frac{1}{2}$ fermions. With the aid of a generalization of the graphical techniques used in this paper to SU(m) (Ref. 29) one may be able to apply similar techniques in obtaining other irreducible representations of $\mathfrak{S}_N$.

It is well-known that an N-electron irreducible representation of SU(2), characterized by the total spin quantum number S, is related to an irreducible representation $[\lambda]$ of $\mathfrak{S}_N$, where the Young tableau $[\lambda]$ is given by

$$[\lambda] = [\tfrac{1}{2}N + S, \tfrac{1}{2}N - S]. \tag{2}$$

We consider irreducible representations of $\mathfrak{S}_N$ adapted to the chain $\mathfrak{S}_{N_A} \otimes \mathfrak{S}_{N_B} \subset \mathfrak{S}_N$, where $N = N_A + N_B$, and no other restriction is made on the particle numbers N_A and N_B. This chain clearly entails an arbitrary chain of subgroups, because we can repeatedly substitute the chain, with varying N_A and N_B, into the permutation subgroups which occur, i.e., $\mathfrak{S}_{N_A}$ and $\mathfrak{S}_{N_B}$. Most of the spin-functions used in the literature can be characterized by such a chain. We obtain, for instance, Young-Yamanouchi functions (cf., for example, Ref. 4) by taking $N_B = 1$ throughout the chain, while the Serber case arises when $N_B = 2$.

We write the N-electron spin functions as $|SM\gamma\rangle$, where S and M are defined by (using atomic units)

$$\begin{aligned} \hat{S}^2|SM\gamma\rangle &= S(S+1)|SM\gamma\rangle , \\ \hat{S}_z|SM\gamma\rangle &= M|SM\gamma\rangle . \end{aligned} \tag{3}$$

The third argument γ stands for a set of Young diagrams labeling irreducible representations of the subgroups of $\mathfrak{S}_N$ that occur in the chain under consideration. Because only two-rowed (columned) representations are considered, all subductions arising are multiplicity free.

That is, the frequency factors $m_{\lambda\mu\nu}$, defined by

$$[\lambda] \downarrow \mathfrak{S}_{N_A} \otimes \mathfrak{S}_{N_B} = \sum_{\mu,\nu} m_{\lambda\mu\nu} [\mu] \otimes [\nu], \tag{4a}$$

are zero or one. This implies that the different sets γ provide a unique state labeling.

If, instead, we express γ as a set of intermediate spin quantum numbers (as we do in this paper; cf., for an example, Table II in Appendix B), we write (4a) as

$$\begin{aligned}[\tfrac{1}{2}N+S, \tfrac{1}{2}N-S] \downarrow \mathfrak{S}_{N_A} \otimes \mathfrak{S}_{N_B} \\ = \sum_{S_A, S_B} \{S, S_A, S_B\} [\tfrac{1}{2}N_A + S_A, \tfrac{1}{2}N_A - S_A] \\ \otimes [\tfrac{1}{2}N_B + S_B, \tfrac{1}{2}N_B - S_B]. \end{aligned} \tag{4b}$$

Here,

$$\{S, S_A, S_B\} = \begin{cases} 1 & \text{for } S = |S_A - S_B|, |S_A - S_B| + 1, \ldots, S_A + S_B, \\ 0 & \text{otherwise,} \end{cases} \tag{5}$$

is the usual triangular δ symbol. One obtains states adapted to $\mathfrak{S}_N \supset \mathfrak{S}_{N_A} \otimes \mathfrak{S}_{N_B}$ by forming the Clebsch-Gordan series corresponding to (4b)

$$|SM\gamma\rangle = \sum_{S_A, S_B} \langle S_A M_A \; S_B M_B | SM \rangle |S_A M_A \gamma_A\rangle |S_B M_B \gamma_B\rangle, \tag{6}$$

where $|S_A M_A \gamma_A\rangle$ and $|S_B M_B \gamma_B\rangle$ are the spin eigenfunctions associated with the subsystems containing N_A and N_B electrons, respectively, and where $\langle S_A M_A \; S_B M_B | SM\rangle$ is the usual Clebsch-Gordan (CG) coefficient. From (6) follows that

$$\gamma = \gamma_A \cup \gamma_B \cup \{S_A, S_B\}, \tag{7}$$

and so, using repeatedly Eq. (6) for the spin functions occurring on the right-hand side, we obtain γ as a set of intermediate spin quantum numbers.

After we have specified a state by a set of spin quantum numbers, its graphical representation is easily drawn.[10,12,30,31] A matrix element $\langle \tilde{S}\tilde{M}\tilde{\gamma}|\hat{P}|SM\gamma\rangle$ of an arbitrary permutation $\hat{P} \in \mathfrak{S}_N$ may then be calculated in the following way: We write down the graphs of $\langle \tilde{S}\tilde{M}\tilde{\gamma}|$ and $|SM\gamma\rangle$ (or, rather, the generalized CG coefficients defining these states), as shown schematically in Fig. 1. We let $\hat{P}$ act on the one-electron labels of the ket, and form the resulting diagram representing $\langle \tilde{S}\tilde{M}\tilde{\gamma}|\hat{P}|SM\gamma\rangle$ by interconnecting all the lines in the bra and the ket that label the same one-electron coordinate (i.e., we interconnect lines labeled $\tilde{i}$ and i, $i = 1, \ldots, N$, in Fig. 1). One can also connect the resulting total spin lines (labeled by $\tilde{S}, \tilde{M}$ and S, M) if one introduces the factor ϕ (Ref. 32) [cf., for example, rule (67) of Ref. 12].

$$\phi \equiv [S]^{-1} \delta(\tilde{M}, M) \delta(\tilde{S}, S). \tag{8}$$

The resulting diagram may then be simplified and evaluated using the standard rules of the graphical techniques of spin algebras[30,31] (for a brief list of the most useful rules see Appendix A of Ref. 12).

The diagram in Fig. 1 is completely general in the sense that the bra and ket may belong to different coupling schemes. We can even assume that $\tilde{N}_A \neq N_A$ as long as $\tilde{N}_A + \tilde{N}_B = N_A + N_B$. In such cases we compute a so-called "asymmetric" representation[33] of $\mathfrak{S}_N$. The calculation of recoupling coefficients is a special case of the method outlined here; it is simply a calculation of the identity permutation matrix in an asymmetric representation.

It is more common for the bra and ket to belong to the same coupling scheme. In that case one sees the subduction rule (4b) illustrated graphically. For, let $\hat{P} \equiv \hat{P}_A \otimes \hat{P}_B$ belong to $\mathfrak{S}_{N_A} \otimes \mathfrak{S}_{N_B}$: then no electrons are exchanged between the boxes A and B and the diagram can be broken over the lines $\tilde{S}_A, S_A$ and $\tilde{S}_B, S_B$ yielding three separate diagrams. One diagram represents the matrix element $\langle \tilde{S}_A \tilde{M}_A \tilde{\gamma}_A | \hat{P}_A | S_A M_A \gamma_A \rangle$, one represents $\langle \tilde{S}_B \tilde{M}_B \tilde{\gamma}_B | \hat{P}_B | S_B M_B \gamma_B \rangle$, and the third stands for $\{S, S_A, S_B\}$.

III. SERBER STATES

Consider, for the sake of simplicity, a system with an even number of electrons N,[34] $N = 2n$. In

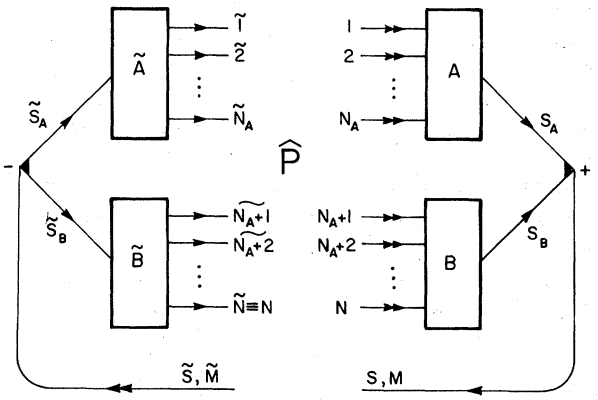

FIG. 1. A schematic representation of the formation of the resulting spin diagram used to evaluate the matrix elements of an arbitrary permutation $\hat{P} \in \mathfrak{S}_N$, relative to the bases adapted to subgroups $\mathfrak{S}_{\tilde{N}_A} \otimes \mathfrak{S}_{\tilde{N}_B}$ and $\mathfrak{S}_{N_A} \otimes \mathfrak{S}_{N_B}$, $N = \tilde{N}_A + \tilde{N}_B = N_A + N_B$. The triangular-shaped vertices are the Clebsch-Gordan vertices (cf. Ref. 12). See text for details.

order to define the N-electron Serber states, we first "precouple" the appropriate electron pairs as follows:

$$|S_i M_i\rangle = \sum_{m_{2i-1}} \sum_{m_{2i}} \langle \tfrac{1}{2} m_{2i-1} \ \tfrac{1}{2} m_{2i} | S_i M_i \rangle | \tfrac{1}{2} m_{2i-1} \rangle | \tfrac{1}{2} m_{2i} \rangle , \tag{9}$$

where $|\frac{1}{2}\ \frac{1}{2}\rangle$ and $|\frac{1}{2}\ -\ \frac{1}{2}\rangle$ designate the usual SU(2) spin-up and spin-down states. Clearly, only singlet ($S_i = 0$) or triplet ($S_i = 1$) pair states can be obtained, so that the *pair spin quantum numbers* S_i, $i = 1, \ldots, n$, can only equal zero or one, respectively.

The desired Serber states are then obtained by sequentially coupling the pair states (9). This introduces an additional $n-2$ *intermediate spin quantum numbers* $S_{(i)}$, $i = 2, \ldots, n-1$. It is convenient to make the definitions

$$S_{(1)} \equiv S_1, \quad M_{(1)} \equiv M_1 \tag{10a}$$

and

$$S_{(0)} = M_{(0)} \equiv 0 , \tag{10b}$$

and, similarly, for the resulting spin quantum numbers,

$$S \equiv S_{(n)} \quad \text{and} \quad M \equiv M_{(n)} . \tag{11}$$

The Serber states of multiplicity $(2S+1)$ are then defined as follows:

$$\begin{aligned} |\Gamma\rangle \equiv |SM\gamma\rangle \\ = \sum_{M_1, \ldots, M_n} \sum_{M_{(2)}, \ldots, M_{(n-1)}} |S_1 M_1\rangle \\ \times \prod_{i=2}^{n} \langle S_{(i-1)} M_{(i-1)} \ S_i M_i | S_{(i)} M_{(i)} \rangle \\ \times |S_i M_i\rangle , \end{aligned} \tag{12}$$

where

$$\gamma \equiv \{S_1, S_2, \ldots, S_n; S_{(2)}, \ldots, S_{(n-1)}\} \tag{13}$$

designates an index set containing both the pair and the intermediate spin quantum numbers S_i, $i = 1, \ldots, n$ and $S_{(i)}$, $i = 2, \ldots, n-1$, respectively (see, for an example, Table II of Appendix B). The summations extend over all possible values of the corresponding projections M_i, $|M_i| \leq S_i$ and $M_{(i)}$, $|M_{(i)}| \leq S_{(i)}$.

When the values of pair and intermediate spin quantum numbers contained in γ are not consistent with the triangular conditions implied by the pertinent CG coefficients in Eqs. (9) and (12), the Serber state (12) vanishes. Conversely, the set γ of pair and intermediate quantum numbers satisfying the triangular conditions provides a unique labeling scheme for Serber states of any desired multiplicity $(2S+1)$ that is consistent with the total electron number N.

The Serber states (12) may now be represented by the 3-*jm* graph[35] shown in Fig. 2, where the pertinent phase and normalization factor Φ, resulting from a transition from the CG representation to the 3-*jm* one, is

$$\Phi = (-1)^S [S_1, \ldots, S_n, S_{(2)}, \ldots, S_{(n)}]^{1/2} . \tag{14}$$

We use here the usual shorthand notation for the dimensions of the SU(2) irreducible representations, namely

$$[S] \equiv 2S+1 \tag{15}$$

and

$$[S_1, \ldots, S_i] \equiv \prod_{j=1}^{i} [S_j] . \tag{16}$$

The corresponding bra state is then represented by the diagram, which is obtained by (i) reflecting the diagram in the vertical plane, (ii) reversing the signs of all vertices, (iii) reversing the orientation of all lines, and (iv) reversing the variance of external lines (i.e., replacing the double arrows with single arrows and vice versa for the external lines). Further, the pair and intermediate spin quantum numbers, as well as the electronic coordinates of the bra state, or of its diagram, are designated by the corresponding

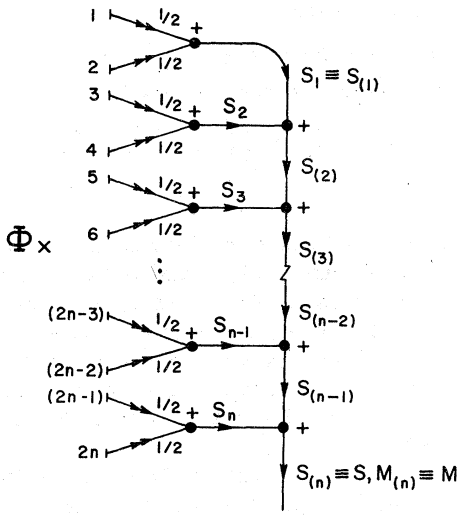

FIG. 2. 3-*jm* graph representing the Serber spin function $|SM\gamma>$, Eq. (12). The phase and normalization multiplicative factor Φ is given by Eq. (14). The orientation of internal lines can be dropped since the pair (S_k) and intermediate ($S_{(k)}$) spin quantum numbers, $k = 1, 2, \cdots, n$, can only take on integral values. The numbers on the left-hand side designate the appropriate electron coordinates.

symbols with tildes, i.e., $\tilde{S}_k, \tilde{S}_{(k)}, \tilde{S}, \tilde{M}, \tilde{\gamma}$, etc.

We also note that both pair and intermediate spin quantum numbers S_i and $S_{(i)}$, respectively, take on only integral values in the Serber case considered, so that we can ignore the orientation of all internal lines in the diagram in Fig. 2. This property is used to simplify the resulting diagrams.

IV. MATRIX ELEMENT EVALUATION

Following the general outline given in Sec. II, we form the resulting diagram by considering an arbitrary Serber bra $\langle \tilde{S}\tilde{M}\tilde{\gamma}|$ and ket $|SM\gamma\rangle$, and an arbitrary transposition $(i,j)\in \mathfrak{S}_N$. When we interconnect the resulting spin lines, this yields the factor ϕ, Eq. (8), and gives the resulting diagram shown schematically in Fig. 3, where the overall factor Ω multiplying this diagram is

$$\Omega \equiv \tilde{\Phi}\Phi\phi = (-1)^{S+\tilde{S}}[S]^{-1}\delta(\tilde{S},S)\delta(\tilde{M},M)[S_1,\ldots,S_n,S_{(2)},\ldots,S_{(n)},\tilde{S}_1,\ldots,\tilde{S}_n,\tilde{S}_{(2)},\ldots,\tilde{S}_{(n)}]^{1/2}$$
$$= \delta(\tilde{S},S)\delta(\tilde{M},M)[S_1,\ldots,S_n,S_{(2)},\ldots,S_{(n-1)},\tilde{S}_1,\ldots,\tilde{S}_n,\tilde{S}_{(2)},\ldots,\tilde{S}_{(n-1)}]^{1/2}. \tag{17}$$

Here we have used definition (11) and the notation (15), (16).

In view of the orbital pairings (9), we have to distinguish several cases of the transposition (i,j) depending on the evenness or the oddness of the indices involved. These four cases will only differ by an appropriate phase factor, and may be easily transformed one into the other, as can be seen from the diagram in Fig. 3(b). Thus, taking the transposition $(2i, 2j-1)$ as a standard one, we find that

$$\begin{aligned}
&\langle\tilde{\Gamma}|(2i-1,2j-1)|\Gamma\rangle = (-1)^{\tilde{S}_i+S_i}\langle\tilde{\Gamma}|(2i,2j-1)|\Gamma\rangle,\\
&\langle\tilde{\Gamma}|(2i,2j)|\Gamma\rangle = (-1)^{\tilde{S}_j+S_j}\langle\tilde{\Gamma}|(2i,2j-1)|\Gamma\rangle,\\
&\langle\tilde{\Gamma}|(2i-1,2j)|\Gamma\rangle = (-1)^{\tilde{S}_i+S_i+\tilde{S}_j+S_j}\langle\tilde{\Gamma}|(2i,2j-1)|\Gamma\rangle,
\end{aligned} \tag{18}$$

assuming that $i<j$.

For a transposition involving the same pair $(i=j)$ we have that

$$\langle\tilde{\Gamma}|(2i-1,2i)|\Gamma\rangle = (-1)^{1+S_i}\bar{\delta}(\emptyset,\emptyset), \tag{19}$$

where we have defined, generally,

$$\bar{\delta}(K,L) \equiv \delta(\tilde{M},M)\prod_{\substack{k=2\\ k\notin K}}^{n}\delta(\tilde{S}_{(k)},S_{(k)})\prod_{\substack{l=1\\ l\notin L}}^{n}\delta(\tilde{S}_l,S_l), \tag{20}$$

for arbitrary index sets K and L. In Eq. (19), both K and L are empty index sets $\emptyset$, so that $\bar{\delta}(\emptyset,\emptyset)$ vanishes unless $\tilde{\gamma}=\gamma$ (and, of course, $\tilde{S}=S, \tilde{M}=M$). Thus, the matrix $\langle\tilde{\Gamma}|(2i-1,2i)|\Gamma\rangle$ is a diagonal matrix with diagonal matrix elements equal to -1 and 1, depending on whether the ith pair in the state Γ is a singlet or a triplet, respectively.

Consider now the matrix elements of a standard transposition $(2i, 2j-1)$ appearing on the right-hand side of Eqs. (18). The pertinent resulting diagram shown in Fig. 3 may then be factored[36] by separating over each pair of lines labeled $\tilde{S}_{(k)}$ and $S_{(k)}$ for $k=1,2,\ldots,i-1,j,j+1,\ldots,n-1$, and each resulting component (except the first one) may be further factored by separation over the pair of lines labeled $\tilde{S}_k$ and S_k for $k=2,\ldots,i-1,j+1,\ldots,n$. Each separation introduces a factor $[S_{(k)}]^{-1}\delta(\tilde{S}_{(k)},S_{(k)})$ and $[S_k]^{-1}\delta(\tilde{S}_k,S_k)$, respectively, and the "oyster-type" graphs [cf. Eq. (74) of Ref. 12] representing the triangular δ functions $\{\frac{1}{2}\frac{1}{2}S_k\}$ and $\{S_kS_{(k-1)}S_{(k)}\}$, defined by Eqs. (5). All these symbols equal 1 when nonvanishing Serber states (12) are used.

In the remaining part of the diagram, involving the pairs of quantum numbers $\tilde{S}_i, S_i$ through $\tilde{S}_j, S_j$, we can further factor out the triangular δ graphs by separating over the pairs of lines labeled by $\tilde{S}_k$ and S_k with $k=i+1,i+2,\ldots,j-1$, to obtain finally the diagram shown in Fig. 4(a).[36] This diagram represents a $3nj$ symbol of the first kind, where $n=j-i+3$. Thus, already for the elementary transposition of the type considered $(j=i+1)$ this diagram represents a $12j$ symbol of the first kind.

Designating the diagram in Fig. 4(a) by $\mathfrak{D}$, we can write for the desired matrix element

$$\langle\tilde{\Gamma}|(2i,2j-1)|\Gamma\rangle = \bar{\delta}(K_{ij},L_{ij})[S_i,\tilde{S}_i,S_j,\tilde{S}_j]^{1/2}\left(\prod_{k=i}^{j-1}[\tilde{S}_{(k)},S_{(k)}]^{1/2}\right)\mathfrak{D}, \tag{21}$$

where K_{ij} and L_{ij} are the index sets

$$\begin{aligned}
K_{ij} &\equiv \{i,i+1,\ldots,j-1\},\\
L_{ij} &\equiv \{i,j\}
\end{aligned} \tag{22}$$

and $\bar{\delta}(K,L)$ is defined by Eq. (20). Bringing the $3nj$ symbol in Fig. 4(a) to a standard form we find that

$$\mathfrak{D} = (-1)^{1+\tilde{S}_{(i)}+S_{(i)}+\tilde{S}_{(j-1)}+S_{(j-1)}}\left\{\begin{array}{ccccccc|c}
\frac{1}{2} & S_i & S_{(i)} & S_{(i+1)} & \cdots & S_{(j-2)} & S_{(j-1)} & S_j \\
\frac{1}{2} & S_{(i-1)} & S_{i+1} & S_{i+2} & \cdots & S_{j-1} & S_{(j)} & \frac{1}{2} \\
\frac{1}{2} & \tilde{S}_i & \tilde{S}_{(i)} & \tilde{S}_{(i+1)} & \cdots & \tilde{S}_{(j-2)} & \tilde{S}_{(j-1)} & \tilde{S}_j
\end{array}\right\}. \tag{23}$$

It is well known[30,31] that the $3nj$ symbol $\mathfrak{D}$ can be reduced to the sum of products of $6j$ symbols. This is easily achieved in diagrammatic form by applying the rule shown in Fig. 5 to the pair of intersecting lines, labeled with angular momentum $\frac{1}{2}$ in Fig. 4(a). Clearly, the sum over the intermediate angular momentum line labeled X contains only two terms, namely $X=0$ and $X=1$. The diagrams corresponding to these two terms ($X=0$ and $X=1$) are shown in Figs. 4(b) and 4(c), respectively, where in the first diagram 4(b) we have already eliminated the zero angular momentum line [cf. rule (68) of Ref. 12] yielding a factor $\frac{1}{2}$. Thus, the first diagram [Fig. 4(b)] yields simply a contribution $\frac{1}{2}\delta(\emptyset,\emptyset)$, since the separation over each pair of lines labeled $\tilde{S}_{(k)},S_{(k)}$, $k=1,\ldots,j-1$ and $\tilde{S}_k,S_k$, $k=i$ and j, yields factors $[S_{(k)}]^{-1}\delta(\tilde{S}_{(k)},S_{(k)})$ and $[S_k]^{-1}\delta(\tilde{S}_k,S_k)$, respectively (in addition to the triangular δ factors which must equal 1 if proper Serber states are involved).

The second graph [Fig. 4(c)] may then be separated over the three lines for each triple of lines involving always the central line with angular momentum 1, and the appropriate pair of lines on the perimeter of the diagram in Fig. 4(c), labeled $\tilde{S}_{(k)},S_{(k)}$, $k=i,i+1,\ldots,j-1$ and $\tilde{S}_k,S_k$, $k=i$ and j, and in each case a $6j$ graph is obtained. Bringing these $6j$ graphs to one of the standard forms [cf. Eq. (75) of Ref. 12] and using explicit expressions for the $6j$ symbols involving $\frac{1}{2}$-angular momenta [$6j$ graphs separated on each end of the graph in Fig. 4(c)] we find, finally, an explicit expression for the desired matrix elements $\langle\tilde{\Gamma}|\,(2i,2j-1)\,|\Gamma\rangle$, $i<j$,

$$\langle\tilde{\Gamma}|\,(2i,2j-1)\,|\Gamma\rangle=\tfrac{1}{2}\bar{\delta}(\emptyset,\emptyset)+(-1)^{Q_{ij}}\Delta_{ij}\begin{Bmatrix} S_i & \tilde{S}_i & 1\\ \tilde{S}_{(i)} & S_{(i)} & S_{(i-1)}\end{Bmatrix}\begin{Bmatrix} S_j & \tilde{S}_j & 1\\ \tilde{S}_{(j-1)} & S_{(j-1)} & S_{(j)}\end{Bmatrix}\prod_{k=i}^{j-2}\begin{Bmatrix} S_{(k+1)} & \tilde{S}_{(k+1)} & 1\\ \tilde{S}_{(k)} & S_{(k)} & S_{k+1}\end{Bmatrix}, \tag{24}$$

where

$$Q_{ij}\equiv j-i+S_{(i-1)}+S_{(i)}+\tilde{S}_{(j-1)}+S_{(j)}+\sum_{k=i}^{j-2}(S_{k+1}+\tilde{S}_{(k+1)}+S_{(k)}), \tag{25}$$

$$\Delta_{ij}\equiv\bar{\delta}(K_{ij},L_{ij})\left[\left(\prod_{k\in K_{ij}}[\tilde{S}_{(k)},S_{(k)}]\right)\left(\prod_{l\in L_{ij}}[\tilde{S}_l,S_l][\tfrac{1}{2}(\tilde{S}_l+S_l)]^{-1}\right)\right]^{1/2}\prod_{l\in L_{ij}}\{S_l\tilde{S}_l 1\}, \tag{26}$$

with $\bar{\delta}(K,L)$ defined by Eq. (20) and the index sets K_{ij} and L_{ij} by Eqs. (22). As above, $\emptyset$ designates the empty set and $[S]\equiv 2S+1$ [cf. definitions (15) and (16)]. The $6j$ coefficients appearing in this expression may be easily evaluated and their explicit form is given in Appendix A.

V. PRESENCE OF A FROZEN CORE

In this section, we show how to apply the formula derived in the foregoing section in the case that an indefinitely large frozen core is present. By a frozen core we mean a set of n_c orbitals, which are doubly occupied in all the states under consideration.

It will be convenient to associate the first n_c pairs in our Serber state (12) with the frozen core orbitals. Clearly, then $S_k=S_{(k)}=0$ for $k=1,\ldots,n_c$. Considering, thus, as the A part in Fig. 1 the frozen-core part ($\tilde{N}_A=N_A=2n_c$), we can represent schematically our Serber state by the diagrams shown in Fig. 1, since the diagram may always be broken on a zero angular momentum line or, conversely, the disconnected parts may be connected via a zero angular momentum line.

It has been shown by Ruedenberg[28] that all one needs for a calculation of Hamiltonian matrix elements on the basis of spin-adapted antisymmetrized functions are the matrices $\langle\tilde{S}\tilde{M}\tilde{\gamma}|\hat{L}|SM\gamma\rangle$ and $\langle\tilde{S}\tilde{M}\tilde{\gamma}|(k,l)\hat{L}|SM\gamma\rangle$, $k<l$. Here $\hat{L}$ is the permutation that lines up the orbitals in the ket so as to minimize the number of noncoincidences between bra and ket (a so-called line-up permutation); and (k,l) is an arbitrary transposition. Because the order of the orbitals in the core is fixed, $\hat{L}$ never permutes core electrons, or in other words $\hat{L}\in\mathfrak{S}_{N_B}$, $[\tilde{N}_B=N_B=2(n-n_c)]$. In contrast, the transposition (k,l) may act on any pair of electron coordinates, so that $(k,l)\in\mathfrak{S}_{2n}$.

Clearly, the matrix elements of $\hat{L}$ are given directly by Eq. (24), where $N=N_B=2(n-n_c)$, and are independent of any frozen core altogether.

On the other hand, the transposition $(k,l)\in\mathfrak{S}_{2n}$ may interchange the $\frac{1}{2}$-angular momentum lines between the frozen core and valence shell. However, since the frozen core may always be disconnected from the rest of the diagram by separation over the zero line(s) ($\tilde{S}_{(n_c)}=S_{(n_c)}=0$), the only link between the two parts of the diagram will be via the $\frac{1}{2}$-angular momentum lines. We can separate over these two lines [rule (70) of Ref. 12] yielding a factor $(\frac{1}{2})$ and two disconnected diagrams

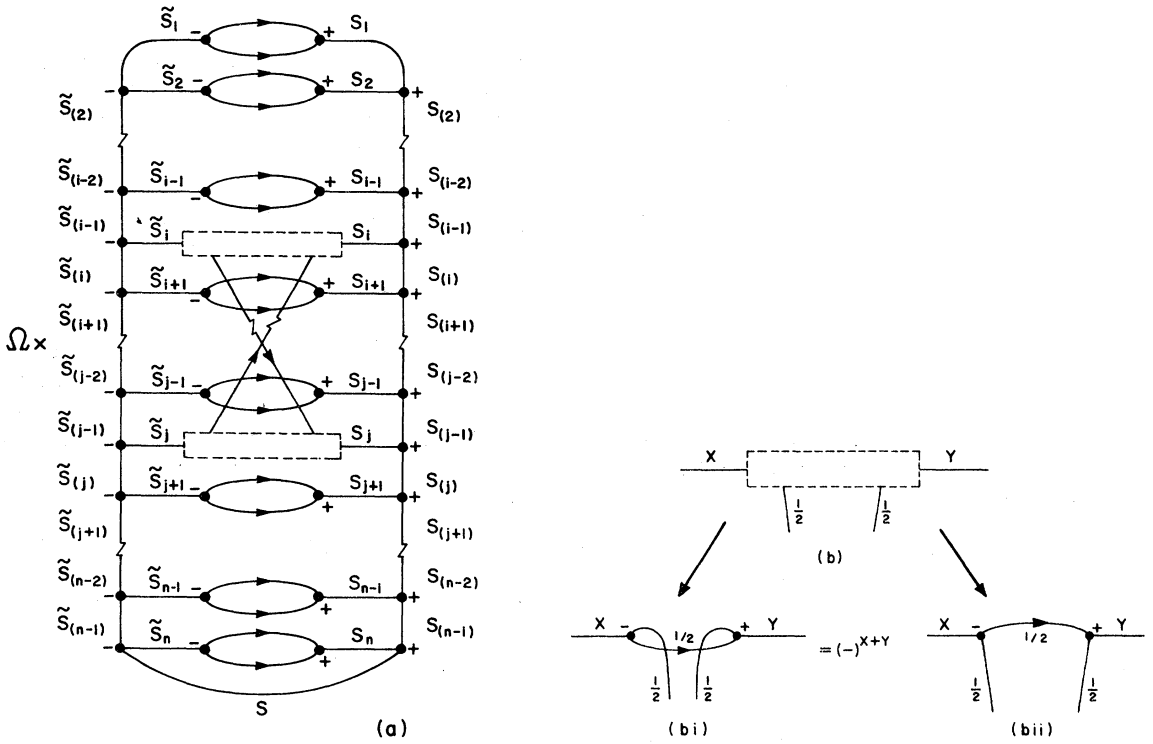

FIG. 3. A schematic representation (a) of the resulting spin diagram associated with the matrix elements appearing in relations (18). All oriented lines carry the angular momentum $\frac{1}{2}$. The phase and normalization multiplicative factor Ω is given by Eq. (17). The dashed rectangles (b) can be replaced by either one of the diagrams (bi) or (bii) as indicated. Making the replacements at $\tilde{S}_i$, S_i and $\tilde{S}_j$, S_j of the types (i), (i); (ii), (ii); (i), (ii) and (ii), (i) yields the spin diagrams for matrix elements of transpositions $(2i-1,\ 2j)$, $(2i,\ 2j-1)$, $(2i-1,\ 2j-1)$, and $(2i,\ 2j)$, respectively.

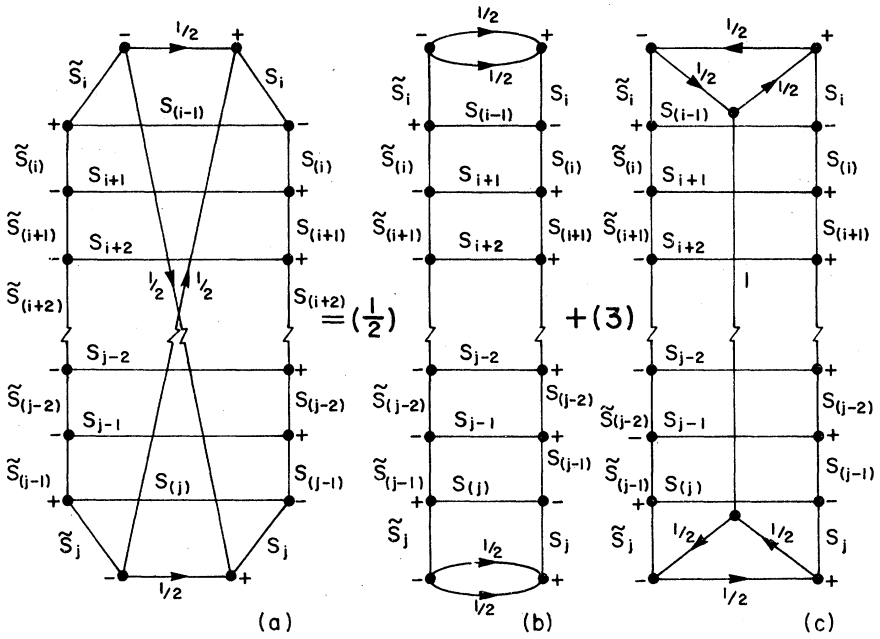

FIG. 4. (a) The spin diagram $\mathfrak{D}$, Eqs. (21) and (23), and its decomposition into the diagonal (b) and off-diagonal (c) parts using the summation rule shown in Fig. 5.

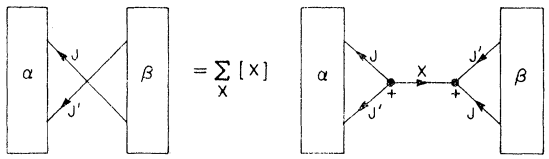

FIG. 5. Summation rule based on the orthonormality relation for $3jm$ symbols involving the summation over the two magnetic quantum numbers. The rectangles labeled α and β represent schematically an arbitrary angular momentum diagram. For greater convenience in applying this rule to the diagram $\mathfrak{D}$, Fig. 4(a), it is formulated for the case of crossing lines.

representing the normalization diagram for the frozen core and the diagram of $\hat{L}$ in the basis of the valence shell.

We can thus conclude that the matrix elements $\langle \tilde{S}\tilde{M}\tilde{\gamma}|(k,l)\hat{L}|SM\gamma\rangle$ are given by

$$\sum_{\gamma_B'} \langle S_B M_B \tilde{\gamma}_B|(k,l)|S_B M_B \gamma_B'\rangle \langle S_B M_B \gamma_B'|\hat{L}|S_B M_B \gamma_B\rangle , \tag{27}$$

if $k, l > 2n_c$, and by

$$\tfrac{1}{2}\langle S_B M_B \tilde{\gamma}_B|\hat{L}|S_B M_B \gamma_B\rangle , \tag{28}$$

if $k \leq 2n_c$ and $k \neq l-1$.

VI. DISCUSSION

The technique employed to derive formula (24) can also be applied to general coupling schemes

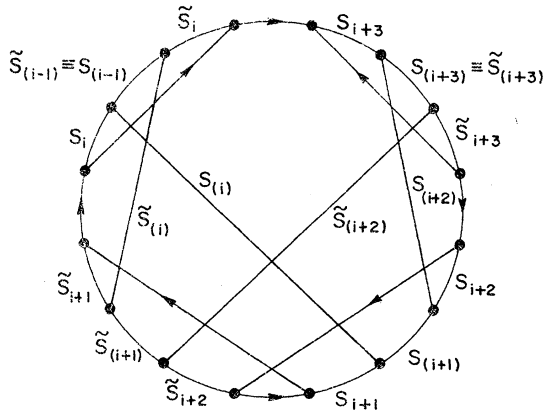

FIG. 6. $24j$ symbol appearing in the evaluation of matrix elements of cyclic permutations involving four pairs in a bra or a ket Serber state. All oriented lines carry the angular momentum $\frac{1}{2}$.

TABLE I. IBM 360/75 CPU times required for the calculation of the matrix of a transposition τ according to formula (24). The dimension of the matrix is given by the dimension $f_{[\lambda]}$ of the pertinent irreducible representations $[\lambda]$ of S_N.

N	S	$f_{[\frac{1}{2}N+S,\frac{1}{2}N-S]}$	τ	time (sec)
8	0	14	(6,8)	0.07
8	0	14	(1,8)	0.08
14	0	429	(12,14)	0.60
14	0	429	(1,14)	6.16
14	1	1001	(12,14)	2.43
14	1	1001	(1,14)	30.41

and arbitrary permutations. However, it is not always possible to break up a diagram in a general manner for an arbitrary number of electrons in order to obtain a relatively simple and closed formula.

For instance, we could try to generalize expression (24) to cyclic permutations of arbitrary length, which would be very useful in view of their relationship to the unitary group generators. However, one can easily convince oneself that the graph, representing the cyclic permutations $(2i-p, 2i-p+1, \ldots, 2(i+k)-q)$, where $p,q=0$ or 1, (i.e., cyclic permutations involving $(k+1)$ pairs in the Serber state) is a $6(k+1)j$ symbol of a more complicated nature than those of the first or second kind.

Indeed, in the case of a cyclic permutation involving three pairs we get an $18j$ symbol of the type $\{321\}$ (K diagrams, p. 213–214 of Ref. 30). This diagram can be expressed as a sum of products of one $6j$, one $9j$, and one $12j$ symbol of the first kind. Thus, expressing the $18j$ symbol in terms of $6j$ symbols, a triple summation will be involved.

Similarly, in the case of a cycle involving four pairs we get the $24j$ symbol shown in Fig. 6. It should be mentioned that there exist already 576 kinds of $24j$ symbols.[30]

Clearly, a general formula for a cyclic permutation involving an arbitrary number of Serber-coupled electrons would be cumbersome, if at all possible. A diagrammatic line of approach would probably be hardly more advantageous than the generation of permutation matrices by taking products of the representatives of transpositions.

On the other hand, even in such complicated cases, the graphical method can be useful as a qualitative tool providing an insight into the actual complexity of the problem. If one does not have to worry about the phase factors and multiplicative

TABLE II. Spin quantum numbers specifying the Serber eight-electron triplet states, cf. Eq. (13).

State	Pair quantum Nos.				Intermediate quantum Nos.		State	Pair quantum Nos.				Intermediate quantum Nos.	
No.	S_1	S_2	S_3	S_4	$S_{(2)}$	$S_{(3)}$	No.	S_1	S_2	S_3	S_4	$S_{(2)}$	$S_{(3)}$
1	1	1	1	1	2	1	15	1	1	1	0	2	1
2	1	1	1	1	1	1	16	1	1	1	0	1	1
3	1	0	1	1	1	1	17	1	0	1	0	1	1
4	0	1	1	1	1	1	18	0	1	1	0	1	1
5	1	1	1	1	0	1	19	1	1	1	0	0	1
6	0	0	1	1	0	1	20	0	0	1	0	0	1
7	1	1	0	1	1	1	21	1	1	0	0	1	1
8	1	0	0	1	1	1	22	1	0	0	0	1	1
9	0	1	0	1	1	1	23	0	1	0	0	1	1
10	1	1	1	1	1	0	24	1	1	1	1	1	2
11	1	0	1	1	1	0	25	1	0	1	1	1	2
12	0	1	1	1	1	0	26	0	1	1	1	1	2
13	1	1	0	1	0	0	27	1	1	0	1	2	2
14	0	0	0	1	0	0	28	1	1	1	1	2	2

constants, it usually does not take more than a few minutes to draw the pertinent diagram(s) and to determine which $3nj$ symbols will occur. In this manner one can explore the general appearance of the resulting formulas and find out immediately how many summations are involved and which $3nj$ symbols have to be evaluated in the final expressions. If these expressions seem tractable one can go back and take proper care of phases and constants.

The question may arise whether it is possible to generalize the method exploited in this paper to irreducible representations of $\mathcal{S}_N$ with m rows (or columns), where $m>2$. One must realize that such irreducible representations are in that case to be obtained from the irreducible representations of SU(m). Although graphical techniques for the SU(m) calculus have been discussed,[29] they are not so easy to apply, mainly because the special unitary group is not multiplicity free for $m>2$.

In order to test the feasibility of expression (24) for computer applications, we have programmed it using the values of the $6j$ symbols given in Appendix A. The resulting program is open ended in the sense that the only limitations on the spin and the number of electrons are core size and the CPU time. Some typical CPU times are given in Table I. In the largest case considered ($S=1$, 14 electrons, irreducible-representation dimension $f_{[8,6]}=1001$) the program required 82 kbytes of main storage.

In this connection it is perhaps instructive to examine the amount of computation required in the method of Salmon *et al.*,[19] taking as an example the 14-electron singlet case. In this case, Salmon *et al.* have to diagonalize a 393×393 matrix in order to obtain the 36 singlets characterized by all seven pair quantum numbers being one. Further, they have to diagonalize a 141×141 matrix, a 51×51 matrix, a 19×19 matrix, a 7×7 matrix, and a 3×3 matrix in

TABLE III. Symbols used in the tabulation of the representation matrices.

Symbol	·	a	b	c	d	e	f	g
Number	0	$\frac{1}{4}$	$\frac{1}{6}\sqrt{3}$	$\frac{1}{12}\sqrt{15}$	$\frac{1}{4}\sqrt{2}$	$\frac{1}{6}\sqrt{6}$	$\frac{1}{4}\sqrt{3}$	$\frac{1}{12}\sqrt{30}$
Symbol	h	j	k	m	n	p	q	1
Number	$\frac{1}{2}$	$\frac{1}{3}\sqrt{3}$	$\frac{1}{4}\sqrt{6}$	$\frac{1}{6}\sqrt{15}$	$\frac{1}{2}\sqrt{2}$	$\frac{3}{4}$	$\frac{1}{2}\sqrt{3}$	1

TABLE IV. The matrix $D^{[4,2]}(3,5)$.

	1	2	3	4	5	6	7	8	9
1	$-a$								
2	c	a							
3	$-g$	$-d$	h						
4	·	·	·	·					
5	·	j	e	·	h				
6	·	·	·	$-n$	·	h			
7	g	d	h	·	$-e$	·	h		
8	$-m$	h	·	·	$-b$	·	·	h	
9	·	·	·	n	·	h	·	·	h

order to obtain the states with, respectively, 6, 5, 4, 3, and 2 pair quantum numbers equal to one. Inclusion of time reversal roughly halves the dimension of the matrices involved.[24]

In a second stage Salmon *et al.*[19] operate with the required permutation on the ket and compute the matrix element. In this manner they avoid having to multiply large (but sparse) matrices, as has to be done in our method.

An example of eight-electron triplet matrices, complementing the results given by Serber[26] for the eight-electron singlet case, is given in Appendix B.

We remark that the number of electrons involved in our method, as well as in the method of Salmon *et al.*[19], is in fact the number of electrons in the valence shell, as pointed out above (cf. Sec. V). Thus, the 14-electron case corresponds to the inclusion of seven-fold excited spin-adapted states in a CI calculation of a closed-shell system. Hence, in practical applications we can usually restrict ourselves to eight or ten electrons in the valence shell.

To conclude, we want to remark that Serber spin functions are not as easy to handle as Yamanouchi-Kotani functions or spin-bonded functions, at least not by the technique presented in this paper. One can derive closed formulas for the matrix elements of more complicated permutations than transpositions relative to the basis consisting of either of these two kinds of functions. The formulas for cyclic permutations in the Yamanouchi-Kotani basis are equivalent to the expressions given by Drake and Schlesinger,[7] or earlier by Gouyet *et al.*,[6] for the matrix elements of the generators of the unitary group in a Gelfand basis. These expressions give the matrix elements of an arbitrary generator as a single product of $6j$ coefficients. In case of elementary transpositions one obtains the results for the elementary generators of U(m) derived earlier[5(d)] in a different manner (using the unitary group formalism[37]). Very recently, Shavitt[38] extended this approach to the matrix elements of nonelementary generators, expressing them as a single product of simple factors, while staying completely within the unitary group formalism.

The expressions for spin-bonded functions are, of course, identical to those derived earlier by Reeves,[39] Cooper and McWeeny,[40] Sutcliffe[41] and others (for an excellent review, see Ref. 42). We intend to elaborate on these final remarks in a future paper.

ACKNOWLEDGMENTS

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TABLE V. The matrix $D^{[3,3]}(3,5)$.

	1	2	3	4	5
1					
2	$-n$	h			
3	·		$-h$		
4	n	h	·	h	
5			$-q$		h

TABLE VI. The matrix $D^{[5,1]}(3,5)$.

	1	2	3	4	5
1	p				
2	d	h			
3	·	·	1		
4	$-d$	h	·	h	
5	f	$-k$	·	k	a

TABLE VII. The matrix $D^{[5,3]}(5,7)$.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	p													
2	·	a												
3	·	·	a											
4	·	·	·	a										
5	·	·	·	·	·									
6	·	·	·	·	·	·								
7	·	$-d$	·	·	·	·	h							
8	·	·	$-d$	·	·	·	·	h						
9	·	·	·	$-d$	·	·	·	·	h					
10	·	j	·	·	·	·	e	·	·	h				
11	·	·	j	·	·	·	·	e	·	·	h			
12	·	·	·	j	·	·	·	·	e	·	·	h		
13	·	·	·	·	$-n$	·	·	·	·	·	·	·	h	
14	·	·	·	·	·	$-n$	·	·	·	·	·	·	·	h
15	$-d$	·	·	·	·	·	·	·	·	·	·	·	·	·
16	·	d	·	·	·	·	h	·	·	$-e$	·	·	·	·
17	·	·	d	·	·	·	·	h	·	·	$-e$	·	·	·
18	·	·	·	d	·	·	·	·	h	·	·	$-e$	·	·
19	·	·	·	·	n	·	·	·	·	·	·	·	h	·
20	·	·	·	·	·	n	·	·	·	·	·	·	·	h
21	·	h	·	·	·	·	·	·	·	$-b$	·	·	·	·
22	·	·	h	·	·	·	·	·	·	·	$-b$	·	·	·
23	·	·	·	h	·	·	·	·	·	·	·	$-b$	·	·
24	·	c	·	·	·	·	$-g$	·	·	·	·	·	·	·
25	·	·	c	·	·	·	·	$-g$	·	·	·	·	·	·
26	·	·	·	c	·	·	·	·	$-g$	·	·	·	·	·
27	d	·	·	·	·	·	·	·	·	·	·	·	·	·
28	f	·	·	·	·	·	·	·	·	·	·	·	·	·

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
15	h													
16	·	h												
17	·	·	h											
18	·	·	·	h										
19	·	·	·	·	h									
20	·	·	·	·	·	h								
21	·	·	·	·	·	·	h							
22	·	·	·	·	·	·	·	h						
23	·	·	·	·	·	·	·	·	h					
24	·	g	·	·	·	·	$-m$	·	·	$-a$				
25	·	·	g	·	·	·	·	$-m$	·	·	$-a$			
26	·	·	·	g	·	·	·	·	$-m$	·	·	$-a$		
27	h	·	·	·	·	·	·	·	·	·	·	·	h	
28	k	·	·	·	·	·	·	·	·	·	·	·	$-k$	a

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APPENDIX A: EXPLICIT EXPRESSIONS FOR THE REQUIRED 6j SYMBOLS

In this Appendix we present the explicit expressions for the 6j coefficients needed in the evalua-

tion of the matrix elements (24). These 6j coefficients are basically of three types, since the pair quantum numbers S_k ($k=1,\ldots,n$) can only equal zero or one. Thus, either at least one spin angular momentum vanishes [case (a)] or the 6j's are of the type [cases (b) and (c), respectively]

$$\begin{Bmatrix} 1 & 1 & 1 \\ S & S' & S'' \end{Bmatrix} \text{ and } \begin{Bmatrix} S & S' & 1 \\ S'' & S''' & 1 \end{Bmatrix}, \tag{A1}$$

where S, S', S'', S''' are nonvanishing integers.

Case (a). In the first case, the following well-known simple formula applies

$$\begin{Bmatrix} I & J & 1 \\ I' & J' & 0 \end{Bmatrix} = (-1)^{1+I+J}\{IJ1\}\delta_{II'}\delta_{JI'}[I,J]^{-1/2}, \tag{A2}$$

where we have used definitions (5), (15), and (16). In cases (b) and (c) the pertinent nonvanishing types are easily worked out and simple explicit expressions for them are derived, namely, case (b),

$$\begin{Bmatrix} 1 & 1 & 1 \\ I & I & I \end{Bmatrix} = (6I[\tfrac{1}{2}I, I])^{-1/2}, \tag{A3}$$

$$\begin{Bmatrix} 1 & 1 & 1 \\ I & I & I-1 \end{Bmatrix} = -\{(I+1)/6I[I]\}^{1/2}, \tag{A4}$$

$$\begin{Bmatrix} 1 & 1 & 1 \\ I & I & I+1 \end{Bmatrix} = (I/6[\tfrac{1}{2}I, I])^{1/2}, \tag{A5}$$

case (c),

$$\begin{Bmatrix} I & I+1 & 1 \\ I & I-1 & 1 \end{Bmatrix} = [I]^{-1}, \tag{A6}$$

$$\begin{Bmatrix} I & I-1 & 1 \\ I & I-1 & 1 \end{Bmatrix} = (I[I-1, I])^{-1}, \tag{A7}$$

$$\begin{Bmatrix} I & I & 1 \\ I & I-1 & 1 \end{Bmatrix} = -(I[I])^{-1}, \tag{A8}$$

$$\begin{Bmatrix} I & I & 1 \\ I & I+1 & 1 \end{Bmatrix} = [\tfrac{1}{2}I, I]^{-1}, \tag{A9}$$

$$\begin{Bmatrix} I & I & 1 \\ I & I & 1 \end{Bmatrix} = [I]^{-1}\{1-(I[\tfrac{1}{2}I])^{-1}\}, \tag{A10}$$

$$\begin{Bmatrix} I & I & 1 \\ I-1 & I-1 & 1 \end{Bmatrix} = -(I)^{-1}\left(\frac{I^2-1}{[I-1, I]}\right)^{1/2}, \tag{A11}$$

using again definitions (15) and (16). All the remaining 6j symbols needed in expression (24) for the desired matrix elements are related to those given above by 6j symmetry relations.

APPENDIX B: SERBER MATRICES FOR THE EIGHT-ELECTRON TRIPLET CASE

In this Appendix we list the matrices that are sufficient to generate the eight-electron triplet representation characterized by the Young diagram [5, 3]. All nontrivial elementary transpositions not given below follow by Eqs. (18) from the matrices in this Appendix. Only the lower triangles of the matrices are listed, as the matrices are symmetric. The Serber states, given in Table II, are ordered in such a way that maximal blocking is obtained in going through the chain $S_8 \supset S_6 \supset S_4 \supset S_2$. Within the blocks the ordering of Serber[26] is followed wherever possible. Since Serber gives matrices in the associated representation $\widetilde{[4,4]} \equiv [2^4]$, one can obtain from his tables also the subgroup representations [2, 2], [3, 1], [4, 2], and [3, 3]; these are identical with the ones given below.

Thus, we get

$$\begin{aligned} D^{[5,3]}(1,3) = \{&D^{[4]} \oplus D^{[3,1]} \oplus D^{[2,2]} \oplus D^{[3,1]} \\ &\oplus D^{[3,1]} \oplus D^{[2,2]} \oplus D^{[4]} \oplus D^{[3,1]} \\ &\oplus D^{[2,2]} \oplus D^{[3,1]} \oplus D^{[3,1]} \oplus D^{[4]} \\ &\oplus D^{[4]}\}(1,3), \end{aligned}$$

where

$$D^{[4]}(1,3) = (1),$$

$$D^{[3,1]}(1,3) = \begin{pmatrix} \cdot & & \\ n & h & \\ -n & h & h \end{pmatrix},$$

$$D^{[2,2]}(1,3) = \begin{pmatrix} -h & \\ -q & h \end{pmatrix},$$

(see Table III for the code used in these matrices), and

$$\begin{aligned} D^{[5,3]}(3,5) = \{&D^{[4,2]} \oplus D^{[3,3]} \oplus D^{[4,2]} \\ &\oplus D^{[5,1]}\}(3,5). \end{aligned}$$

See Tables IV, V, and VI for $D^{[4,2]}$, $D^{[3,3]}$ and $D^{[5,1]}$, respectively. The matrix $D^{[5,3]}(5,7)$ does not block, see Table VII.

*Also, Dept. of Chemistry, University of Waterloo and the Guelph-Waterloo Center of Graduate Work in Chemistry.

†On leave from the University of Nijmegen, The Netherlands.

[1]H. Weyl, *Gruppentheorie und Quantenmechanik*, 2nd ed (Hirzel, Leipzig, 1931), Chap. V, Sec. 12 [*The Theory of Groups and Quantum Mechanics* (Dover, New York, 1964)].

[2]It is worth mentioning that while $\mathcal{S}_N^{(r)} \otimes \mathcal{S}_N^{(s)}$ (and, of course, $\mathcal{S}_N^{(r)}$ and $\mathcal{S}_N^{(s)}$ separately) and SU(2) are symmetry (invariance) groups of the spin-independent Hamiltonian, its dynamical group is much larger [namely GL(m) or U(m)] and depends on the model space in which the Hamiltonian is defined. (By a dynamical group of a system we mean a Lie group with a sufficient number of generators to express the Hamiltonian of the system as a function of these generators).

[3](a) H. Weyl, *The Classical Groups*, 2nd ed. (Princeton U.P., Princeton, N. J., 1946); (b) H. Boerner, *Darstellungen von Gruppen*, 2nd ed. (Springer, Berlin, 1967) [*Representations of Groups* (North-Holland, Amsterdam, 1970)].

[4]P. E. S. Wormer, Ph.D. thesis (University of Nijmegen, The Netherlands, 1975) (unpublished).

[5](a) M. J. Downward and M. A. Robb, Theor. Chim. Acta 46, 129 (1977); (b) W. G. Harter, Phys. Rev. A 8, 2819 (1973); W. G. Harter and C. W. Patterson, *ibid.* 13, 1067 (1976); *A Unitary Calculus for Electronic Orbitals*, Lecture Notes in Physics No. 49 (Springer, New York, 1976); (c) F. A. Matsen, Int. J. Quantum Chem. Symp. 8, 379 (1974); 10, 525 (1976); (d) J. Paldus, J. Chem. Phys. 61, 5321 (1974), Int. J. Quantum Chem. Symp. 9, 165 (1975); in *Theoretical Chemistry Advances and Perspectives*, edited by D. Henderson and H. Eyring (Academic, New York, 1976), Vol. 2 p. 131; Phys. Rev. 14, 1620 (1976); in *Electrons in Finite and Infinite Structures*, edited by P. Phariseau and L. Scheire (Plenum, New York, 1977), p. 411; (e) I. Shavitt, Int. J. Quantum Chem. Symp. 11, 131 (1977); (f) P. E. S. Wormer and A. van der Avoird, J. Chem. Phys. 57, 2498 (1972).

[6]J. F. Gouyet, R. Schranner, and T. H. Seligman, J. Phys. A 8, 285 (1975).

[7]G. W. F. Drake and M. Schlesinger, Phys. Rev. A 15, 1990 (1977).

[8]F. A. Matsen and D. J. Klein, J. Phys. Chem. 75, 1860 (1971).

[9]P. E. S. Wormer and A. van der Avoird, Int. J. Quantum Chem. 8, 715 (1974).

[10]A. P. Jucys, I. B. Levinson, and V. V. Vanagas, *Mathematical Apparatus of the Theory of Angular Momentum* (Israel Program for Scientific Translations, Jerusalam, 1962, and Gordon and Breach, New York, 1964).

[11]V. V. Tolmachev, Adv. Chem. Phys. 14, 471 (1969).

[12]J. Paldus, B. G. Adams, and J. Čížek, Int. J. Quantum Chem. 11, 813 (1977).

[13](a) B. G. Adams, J. Paldus, and J. Čížek, Int. J. Quantum Chem. 11, 849 (1977); (b) B. G. Adams, M. Math. thesis (University of Waterloo, 1974) (unpublished).

[14]B. O. Roos and P. E. M. Siegbahn in *Electronic Structure: Ab Initio Methods*, Vol. III of *Modern Theoretical Chemistry* edited by H. F. Schaefer, III, (Plenum, New York, 1977).

[15]J. Paldus, J. Chem. Phys. 67, 303 (1977).

[16]S. Wilson, J. Chem. Phys. 67, 5088 (1977).

[17]For a similar application yielding a transformation between particle-particle and particle-hole coupled CI states, see Refs. 12 and 13.

[18]These are sometimes referred to as Jahn-Serber states. However, J. P. Elliott, J. Hope, and H. A. Jahn [Trans. R. Soc. (Lond.) A 246, 241 (1953)] exploit a different chain of groups, namely the chain $\mathcal{S}_N \supset \mathcal{S}_{N-2} \otimes \mathcal{S}_2 \supset \mathcal{S}_{N-3} \supset \mathcal{S}_{N-4} \supset \cdots \supset \mathcal{S}_1$, which they refer to as the $(N, N-1)$ diagonalized Young-Yamanouchi-Rutherford representation.

[19]W. I. Salmon, K. Ruedenberg and L. M. Cheung, J. Chem. Phys. 57, 2787 (1972).

[20]W. I. Salmon and K. Ruedenberg, J. Chem. Phys. 57, 2791 (1972).

[21]W. I. Salmon, Adv. Quantum Chem. 8, 37 (1974).

[22]P. J. Carrington and G. Doggett, Mol. Phys. 30, 49 (1975).

[23]R. Pauncz, Int. J. Quantum Chem. 12, 369 (1977).

[24]J. Vojtík and J. Fišer, Theor. Chim. Acta 45, 301 (1977).

[25]R. Serber, Phys. Rev. 45, 461 (1934).

[26]R. Serber, J. Chem. Phys. 2, 697 (1934).

[27](a) M. Kotani, K. Ohno and K. Kayama, in *Encyclopedia of Physics*, Vol. 37/2, edited by S. Flügge (Springer, Berlin, 1961). (b) M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Tables of Molecular Integrals*, 2nd ed. (Maruzen, Tokyo, 1963).

[28]K. Ruedenberg, Phys. Rev. Lett. 27, 1105 (1971); K. Ruedenberg and R. D. Poshusta, Adv. Quantum Chem. 6, 267 (1972).

[29]V. P. Karasev, in *Group-Theoretical Methods in Physics*, edited by D. V. Skobel'tsyn, translated by J. B. Barbour, Vol. 70 of *Proceedings of the P. N. Lebedev Physics Institute* (Consultants Bureau, New York, 1975).

[30]A. P. Jucys and A. A. Bandzaitis, *The Theory of Angular Momentum in Quantum Mechanics* (Institute of Physics and Mathematics of the Academy of Sciences of the Lithuanian Soviet Socialist Republic, Mintis, Vilnius, 1964) (in Russian).

[31]E. El Baz and B. Castel, *Graphical Methods of Spin Algebras* (Dekker, New York, 1972).

[32]In order to avoid multiple indices we define $\delta_{ij} \equiv \delta(i,j)$ wherever expedient.

[33]I. G. Kaplan, *Symmetry of Many-Electron Systems* (Academic, New York, 1975).

[34]Modifications pertaining to systems with an odd number of electrons may be easily obtained by replacing the last spin angular momentum numbers $\frac{1}{2}, m_{2n}$ by zero angular momentum numbers.

[35]The graphical techniques of spin algebras are based either on the CG coefficients or the corresponding 3-jm symbols. Since the former ones have rather cumbersome symmetry properties, we exploit here the diagrams based on 3-jm symbols. A transition from the CG graphs to the 3-jm graphs and vice versa is easily achieved using simple rules [cf., for example, Eqs. (64) of Ref. 12].

[36]In fact, in the case of the resulting diagram in Fig. 3, we can achieve the desired separation by repeatedly applying a simple rule based on the orthogonality rela-

tion for CG coefficients which involves a summation over the magnetic numbers of the subsystems (cf. Rules 2.3.1 and 2.6.1 of Ref. 31).

[37]Cf., for example, M. Moshinsky, *Group Theory and the Many-Body Problem* (Gordon and Breach, New York, 1968), J. D. Louck, Amer. J. Phys. 38, 3 (1970).

[38]I. Shavitt, Int. J. Quantum Chem. Symp. 12 (to be published).

[39]C. M. Reeves, Ph.D. thesis (University of Cambridge, 1957) (unpublished).

[40]I. L. Cooper and R. McWeeny, J. Chem. Phys. 45, 226 (1966).

[41]B. T. Sutcliffe, J. Chem. Phys. 45, 235 (1966).

[42]I. Shavitt, in *Electronic Structure: Ab Initio Methods*, Vol. III of *Modern Theoretical Chemistry*, edited by H. F. Schaefer, III (Plenum, New York, 1977).