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On the Evaluation of CI Matrix Elements for a Canonically Ordered Basis

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Using the unitary group approach it is shown that the amount of storage needed for the construction of symbolic CI matrix element lists for N-electron basis functions with large numbers of open shells and arbitrary multiplicities may substantially be reduced compared to methods currently available in the literature.

Key words: CI matrix elements, construction of $\sim$ – Symbolic matrix elements

1. Introduction

The efficient generation of formulas for the calculation of CI matrix elements for functions with an arbitrary number of open shells has received much attention over a number of years [1, 2]. For calculations with singlet configurations with a small number of open shells (e.g. a closed-shell Hartree–Fock configuration with all single and double excitations) this presents little difficulty, since only a small number of different formulas is needed. However, even if an orthogonal basis is used, this number increases rapidly for larger numbers of open shells and for higher multiplicities and the direct implementation of this method soon becomes unwieldy [3]. We will assume a spin-independent Hamiltonian and real functions throughout this paper. A useful approach then consists of expressing the weights of the one- and two-electron integrals in the general expression for a CI matrix element

$$\langle \Psi_a | H | \Psi_b \rangle = \sum_{ij} C_{ij}^{ab} h_{ij} + \sum_{ijkl} C_{ijkl}^{ab} \langle ik \,|\, jl \rangle \tag{1}$$

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in terms of a number of standard coefficients. This list of standard coefficients should satisfy the following conditions:

1. the size of the list permits its storage in central memory;
2. information may be retrieved from it efficiently;
3. the relations between the weight factors in Eq. (1) and the elements of the standard list are relatively simple.

This standard list may then be calculated once and for all for use in any CI calculation, where the only restriction is that the number of open shells in the configuration set should be compatible with the standard list. In order to satisfy the above-mentioned conditions, various methods have been proposed, of which the so-called unitary group approach [4–7] seems to be promising but still not fully exploited. In this approach the properties of the unitary group U_n (n is the dimension of the spatial orbital basis) are used to obtain an orthogonal N-electron basis for the CI calculation at hand by constructing the relevant Gelfand–Tsetlin tableaux or by some other equivalent device (e.g. Wigner tableaux or Paldus graphs [4–5]). The second quantization representation of the Hamiltonian [5–7]

$$H = \sum_{ij} h_{ij} C_{i\to j} + \tfrac{1}{2} \sum_{ijkl} \langle ik|jl\rangle \, (C_{i\to j} C_{k\to l} - \delta_{il} \, C_{k\to j}) \tag{2}$$

is used, where the $C_{i\to j}$ operators are the group generators of U_n. Consequently the contributions of the one- and two-electron integrals to matrix elements such as given by Eq. (1) may be evaluated via a calculation of all possible matrix elements of the group generators and of the products of two group generators. However, since this method is only efficient for complete CI calculations [5], we will follow a slightly different method, suggested by Wetmore and Segal [7]. In their approach all possible matrix elements of the group generators are calculated by applying $C_{i\to j}$ to the complete set of canonical basis function $|w, \omega\rangle$, where w is the occupation vector and ω is a spin function label. The vector w has elements $w_i = 0$, 1 or 2 and ω defines a specific spin coupling scheme for the open shell orbitals. It will be assumed throughout that these orbitals are ordered in the same way for all basis functions. Following Wetmore and Segal we then have (Eq. (10) of [7]):

$$C_{i\to j}|w, \omega\rangle = \sum_{\omega'} \eta(w', \omega', w, \omega)|w', \omega'\rangle \quad (i \neq j) \tag{3}$$

where the summation may include all possible spin functions allowed for the occupation vector w' with elements

$$w_i' = w_i - 1, \qquad w_j' = w_j + 1, \qquad w_k' = w_k (k \neq i, j)$$

Because of the orthonormality of the basis the weight factors of the one-electron integrals in Eq. (1) are identical to the η-coefficients and the weight factors for the two-electron integrals are evaluated by using (Eq. (11) of [7]):

$$\langle w'', \omega''|C_{i\to j} C_{k\to l}|w, \omega\rangle = \sum_{\omega'} \eta(w'', \omega'', w', \omega')\eta(w', \omega', w, \omega) \tag{4}$$

In the method of Wetmore and Segal all possible η-coefficients are evaluated and stored once and for all for use in arbitrary CI calculations. However, the total

number of η-coefficients to be stored increases rapidly with the number of open shells [7].

In the following we will describe an algorithm for the evaluation of the η-coefficients, which uses a much smaller amount of storage while being comparable in speed. Special attention will be paid to the possibility of storing non-zero elements only, which leads to a substantial reduction of the number of coefficients actually needed. This will be done by expressing the η-coefficients in terms of the representation matrix elements for certain permutations of the spatial orbitals in the ordered basis $|w, \omega\rangle$, viz. those permutations which contain only one cycle with length greater than one. In our method the features of two existing methods for the calculation of CI matrix elements are used, viz. the method of Wetmore and Segal, i.e. calculation of the 4-index quantity C^{ab}_{ijkl} as a scalar product of the 2-index vectors η^a_{ij} and the approach of Ruedenberg *et al.* [2], i.e. calculations of C^{ab}_{ijkl} via the representation matrices of arbitrary permutations of the spatial orbitals.

2. Basic Formulas

2.1. Definitions

In the following the spin functions are assumed to be constructed according to the branching diagram method [8–11]. If a fixed ordering of the open shell orbitals is assumed, the N-electron functions thus obtained are (up to a phase factor) identical to the functions corresponding to Gelfand–Tsetlin tableaux [12]. The spin function label ω may be used to designate the branching diagram path or Yamanouchi symbol, corresponding to a particular spin function.

Using the notation of [11] in a slightly modified form the state functions $|w, \omega\rangle$ may be defined by

$$|w, \omega\rangle = \prod_{k \in \delta} D_k \prod_{k \in \sigma} C_k^{\pm} |0\rangle \tag{5}$$

where σ and δ are the sets of singly ($w_k = 1$) and doubly ($w_k = 2$) occupied orbitals respectively and $|0\rangle$ is the vacuum state, i.e. the state for which $w_k = 0\,(1 \leqslant k \leqslant n)$. $C_k^+ = C_k(1)$ and $C_k^- = C_k(-1, S)$ cf. Eqs. (1) of [11], i.e. C_k^+ and C_k^- correspond to a step up or down in ω respectively.

The dimension of the set σ, i.e. the number of open shells, will be denoted by m. Any function of the form (5) is normalized. In Eq. (5) the $C_k^{\pm}$ operators are ordered according to the fixed ordering condition. For simplicity we will assume that this condition is chosen such that the $C_k^{\pm}$ operators are applied in ascending order of k.

The explicit forms of the operators $C_k^{\pm}$, D_k and $C_{i \to j}$ in terms of the basic fermion operators $c_k^{\dagger}$, c_k, $\bar{c}_k^{\dagger}$ and $\bar{c}_k$ (the creation and annihilation operators for spatial orbital k with α and β spin respectively) are (Eqs. (1) and (5) of [11]).

$$\begin{aligned} C_k^+ &= c_k^{\dagger} \\ C_k^- &= [2S(2S+1)]^{-1/2}(-c_k^{\dagger} S_- + 2S\bar{c}_k^{\dagger}) \end{aligned} \tag{6}$$

where S_- is the step-down operator with respect to S_z.

$$D_k = \bar{c}_k^\dagger c_k^\dagger \tag{7}$$

$$C_{i\to j} = c_j^\dagger c_i + \bar{c}_j^\dagger \bar{c}_i \tag{8}$$

Using Eqs. (6–8) the following commutators, which will be needed in the following, are easily derived

$$[C_k^\pm, D_1] = 0 \tag{9}$$

$$[C_{i\to j}, D_k] = \delta_{ik}(\bar{c}_i^\dagger c_j^\dagger + \bar{c}_j^\dagger c_i^\dagger) \tag{10}$$

$$[C_{i\to j}, C_k^\pm] = \delta_{ik} C_j^\pm \tag{11}$$

$$[C_{i\to j}, C_{k\to l}] = \delta_{il} C_{k\to j} - \delta_{kj} C_{i\to l} \tag{12}$$

The branching diagram operators $C_k^\pm$ and the double occupation operators D_k act on the space and spin coordinates simultaneously. Since the $C_{i\to j}$ commute with all spin operators [7], one might suppose that these operators act on the space coordinates only. However, because of the anti-commutation properties of the fermion operators in Eq. (8), $C_{i\to j}$ also projects to the antisymmetrized N-electron space. Therefore the spin part of the function $|w, \omega\rangle$ on which $C_{i\to j}$ acts may also be affected if $C_{i\to j}$ changes the number of open shells (e.g. $w_i = w_j = 1$).

Further we introduce the permutations P which permute the indices of the singly occupied spatial orbitals in $|w, \omega\rangle$. Defining P_t and P_{spin} as the permutations of the fermion operators and the one-electron spin functions (α and β) respectively, the antisymmetrization yields

$$P_t|w, \omega\rangle = (-1)^{P_t}|w, \omega\rangle = P_{\text{spin}} P|w, \omega\rangle$$

Therefore

$$|w, \omega, P\rangle \equiv P|w, \omega\rangle = (-1)^{P_t} P_{\text{spin}}^{-1}|w, \omega\rangle \tag{13}$$

for a function where the spatial orbital indices of the $C_k^\pm$ operators are permuted with respect to the fixed ordering in $|w, \omega\rangle$. From Eq. (13) it follows that the (w, S) subspace spanned by all functions $|w, \omega\rangle$ with fixed w and S and all ω compatible with the chosen values of m and S is closed under these permutations. Therefore these functions form a basis for a representation of P.

The calculation of the η-vectors of Eq. (3) may be carried out in two steps. First we consider the effect of a generator $C_{i\to j}$ on a basis function $|w, \omega\rangle$ without taking account of the fixed ordering condition. In this step w and ω may both be affected. The other step consists of reordering the open shells. Since w is fixed in this step, this is a transformation within the (w, S) subspace of the antisymmetrized N-electron space.

2.2. *Application of a Generator $C_{i\to j}$ to a Function $|w, \omega\rangle$*

We start by observing that the generator $C_{i\to j}$ commutes with all operators with indices $k \neq i, j$ and that all operators D_l commute with all branching diagram

operators $C_k^{\pm}$. In order to describe the effect of $C_{i\to j}$ on $|w, \omega\rangle$ we define the intermediate function

$$|w_s, S_s\rangle = \prod_{k\in\sigma}^{k_s} C_k^{\pm}|0\rangle \tag{14}$$

where σ is the set of singly occupied orbitals in Eq. (5) and k_s is defined as follows (ignoring the cases $w_i = 0$ and $w_j = 2$, since in these cases $|w, \omega\rangle$ is annihilated by $C_{i\to j}$). If $w_i = 1$ or $w_j = 1$ in the function of Eq. (5), k_s is the index of the orbital preceding i or j respectively in the fixed ordering sequence. If $w_i = w_j = 1$, k_s precedes the lowest of i and j. In the only remaining case, i.e. $w_i = 2$, $w_j = 0$, k_s is chosen as the index of the orbital preceding i. From these definitions it follows that the orbitals i and j are empty in the intermediate function, implying

$$C_{i\to j}|w_s, S_s\rangle = 0 \tag{14a}$$

The function $|w_s, S_s\rangle$ is an eigenfunction of S^2 with spin quantum number S_s determined by the form of the branching diagram path corresponding to Eq. (14). In order to obtain explicit results, four cases, depending on the occupations of orbitals i and j in $|w, \omega\rangle$, have to be treated separately.

1) $w_i = 1, \quad w_j = 0$
Eqs. (11) and (14) may be used to obtain

$$C_{i\to j}C_i^{\pm}|w_s, S_s\rangle = C_j^{\pm}|w_s, S_s\rangle \tag{15}$$

2) $w_i = 1, \quad w_j = 1$
We impose the condition that $C_i^{\pm}$ and $C_j^{\pm}$ are neighbours in the function on which $C_{i\to j}$ acts. This implies that the following relations can only be used *after* a permutation of the orbital indices in $|w, \omega\rangle$. Eqs. (11) and (14) lead to

$$C_{i\to j}C_i^{\pm}C_j^{\mp}|w_s, S_s\rangle = C_{i\to j}C_j^{\pm}C_i^{\mp}|w_s, S_s\rangle = C_j^{\pm}C_j^{\mp}|w_s, S_s\rangle \tag{16}$$

and Eqs. (6) and (7) may then be used to obtain

$$\begin{aligned} C_j^+C_j^-|w_s, S_s\rangle &= F_A(S_s)D_j|w_s, S_s\rangle \\ C_j^-C_j^+|w_s, S_s\rangle &= F_B(S_s)D_j|w_s, S_s\rangle \\ C_j^+C_j^+|w_s, S_s\rangle &= C_j^-C_j^-|w_s, S_s\rangle = 0 \end{aligned} \tag{17}$$

with

$$\begin{aligned} F_A(S_s) &= -[S/(S+\tfrac{1}{2})]^{1/2} \\ F_B(S_s) &= [(S+1)/(S+\tfrac{1}{2})]^{1/2} \end{aligned} \tag{18}$$

3) $w_i = 2, \quad w_j = 0$
By using Eqs. (10) and (6) we find

$$\begin{aligned} C_{i\to j}D_i|w_s, S_s\rangle &= [F_A(S_s)C_j^+C_i^- + F_B(S_s)C_j^-C_i^+]|w_s, S_s\rangle \\ &= [F_A(S_s)C_i^+C_j^- + F_B(S_s)C_i^-C_j^+]|w_s, S_s\rangle \end{aligned} \tag{19}$$

where $F_{A,B}(S_s)$ are given by Eqs. (18).

4) $w_i = 2, \quad w_j = 1$
This case differs only in sign from case 1):

$$C_{i\to j}D_iC_j^{\pm}|w_s, S_s\rangle = -D_jC_i^{\pm}|w_s, S_s\rangle \tag{20}$$

This relation may be obtained by using Eqs. (10), (11), (6) and (7).

2.3. The Transformation to a Basis with Fixed Spatial Orbital Ordering

The other part of the calculation, viz. adjusting the ordering of the spatial orbital indices, may be expressed by

$$|w, \omega, P\rangle = P|w, \omega\rangle = \sum_{\omega'} \pi_{m,S}(\omega', \omega \mid P)|w, \omega'\rangle \tag{21}$$

where P is a permutation of the spatial orbital indices and the summation is over all spin functions ω' compatible with m and S. $\pi_{m,S}(\omega', \omega \mid P)$ is the element with column index ω and row index ω' of the matrix $\pi_{m,S}(P)$ representing P in the basis $|w, \omega\rangle$ with fixed w and S. The labels m and S indicate that the representation depends on m and S. Since P only affects the *ordering* of the singly occupied orbitals in $|w, \omega\rangle$ the representation of P in this basis depends on w, but only through m (cf. Sect. 2.1). Therefore a set of dummy spatial orbitals, numbered from 1 to m may be used in this part of the calculation without loss of generality. Assuming m and S fixed, the basis for our representation of P may then be rendered in the form

$$|\omega\rangle = \prod_{k=1}^{m} C_k^{\pm}|0\rangle \tag{22}$$

For the derivation of an explicit form for $\pi_{m,S}(P)$ it is important to realize that the permutations needed in our method have a special structure due to the fact that only one orbital is out of place in $|w, \omega, P\rangle$, i.e. in the right hand side functions in Eqs. (15), (19) and (20) and the left hand side function in Eq. (16). Our problem thus reduces to moving one orbital index along the others until the desired ordering is obtained. The permutations needed therefore contain only one cycle with length greater than one.

This permutation, which moves orbital index k_1 to the position of orbital index k_2, may then be denoted by

$$P = (k_1 \ldots k_2) \quad (k_1 < k_2)$$

Because of the condition $k_1 < k_2$ we have restricted ourselves to permutations which correspond to moving an orbital index to the left in Eq. (22). Since P is unitary and the basis is orthogonal and real, the representation matrices will also be orthogonal. Consequently the representation matrix of a permutation corresponding to moving an orbital index to the right in Eq. (22), viz.

$$(k_2 \ldots k_1) = (k_1 \ldots k_2)^{-1} = P^{-1} \quad (k_1 < k_2)$$

is simply the transpose of the matrix for P. Therefore no information is lost by the restriction $k_1 < k_2$.

In order to arrive at an explicit expression for the matrix elements of P we use the decomposition in terms of the basic pair permutations $P_k = (k, k+1)$ as follows

$$P = (k_1 \ldots k_2) = P_{k_1} P_{k_1+1} \ldots P_{k_2-1} = \prod_{k=k_1}^{k_2-1} P_k \quad (k_1 < k_2) \tag{23}$$

where the last factor in the continued product is applied first to the function on which P acts.

The matrix elements for the basic pair permutations may be derived in various ways (see e.g. [9], where the results are given for the corresponding permutations in spin space, viz. P_{spin} in Eq. (13)). Using Eqs. (6) we find

$$P_k \begin{cases} C^-_{k+1} C^+_k = f_1(S_k) C^-_{k+1} C^+_k + f_2(S_k) C^+_{k+1} C^-_k \\ C^+_{k+1} C^-_k = f_2(S_k) C^-_{k+1} C^+_k - f_1(S_k) C^+_{k+1} C^-_k \\ C^+_{k+1} C^+_k = f_3 C^+_{k+1} C^+_k \\ C^-_{k+1} C^-_k = f_3 C^-_{k+1} C^-_k \end{cases} \tag{24a}$$

with

$$\begin{aligned} f_1(S_k) &= (2S_k + 1)^{-1} \\ f_2(S_k) &= -2[S_k(S_k+1)]^{1/2}(2S_k+1)^{-1} \\ f_3 &= -1 \end{aligned} \tag{24b}$$

and S_k is the spin quantum number of the (intermediate) function on which the operator $C^\pm_{k+1} C^\pm_k$ acts, i.e. the function with $k-1$ open shells and a branching diagram path identical to ω in the range $1 \leqslant k' < k$. The non-zero elements of the representation matrices of the basic pair permutations $\pi(\omega', \omega | P_k)$ are given by the coefficients $f_i(S_k)$ of the $C_{k+1} C_k$ operators in Eq. (24).

Using Eqs. (24) an explicit expression for the matrix elements of a general permutation as given by Eq. (23) may be derived. To this end we use a method analogous to the method used by Grein *et al.* [10] for the evaluation of branching diagram functions in terms of simple spin products. From Eq. (21) we have

$$\pi(\omega, \omega' \mid P) = \langle \omega \mid \omega \rangle \langle \omega | P | \omega' \rangle = \langle \omega | \Omega P | \omega' \rangle$$

where Ω is the projection operator [14] corresponding to $|\omega\rangle$.

Since, assuming a fixed ordering of the orbitals throughout, the function $|\omega\rangle$ is completely determined by the corresponding Yamanouchi symbol ω, we may decompose Ω as follows

$$\Omega = |\omega\rangle\langle\omega| = \prod_{k=1}^{m} \Omega_k \tag{25}$$

where Ω_k projects onto the components with the same sign in $C^\pm_k$ as in $|\omega\rangle$, Eq. (22). The basic pair permutations P_k commute with all projectors $\Omega_{k'}$, for which $k' \neq k$ and $k+1$, because these permutations do not affect the signs in the $C^\pm_{k'}$, operators.

Therefore, using Eqs. (23) and (25), the operator ΩP may be rewritten as follows

$$\Omega P = \prod_{k=1}^{k_1} \Omega_k \prod_{k=k_1}^{k_2-1} (\Omega_{k+1} P_k) \prod_{k=k_2+1}^{m} \Omega_k \tag{26}$$

Since Ω_k projects to one of the functions in the right hand side of Eq. (24) we have

$$\Omega_{k+1} P_k |\omega_k'\rangle = f_i(S_k) |\omega_{k+1}'\rangle \tag{27}$$

where $|\omega_k'\rangle$ is the (intermediate) function obtained by applying all preceding $\Omega_{k+1} P_k$ operators and $|\omega_{k+1}'\rangle$ is obtained from $|\omega_k'\rangle$ by applying Eq. (24) followed by a projection with Ω_{k+1}. Assuming that no projection with Ω_{k+1} annihilates the function on which it acts, successive applications of Eq. (27) yield

$$\Omega P |\omega'\rangle = \prod_{k=k_1}^{k_2-1} f_i(S_k) |\omega\rangle$$

i.e. any non-vanishing π-coefficient may be written in the form

$$\pi(\omega, \omega' \mid P) = \prod_{k=k_1}^{k_2-1} f_i(S_k) \tag{28}$$

In Eq. (28) it is implicitly assumed that the functions $|\omega_k'\rangle$ exist in each step. If any projection with $\Omega_k (k_1 \leqslant k \leqslant k_2)$ annihilates both functions generated by Eqs. (24) the π-coefficient vanishes. The same applies if any projection with $\Omega_k (1 \leqslant k < k_1$ or $k_2 < k \leqslant m)$ annihilates the function $|\omega'\rangle$, i.e. if the

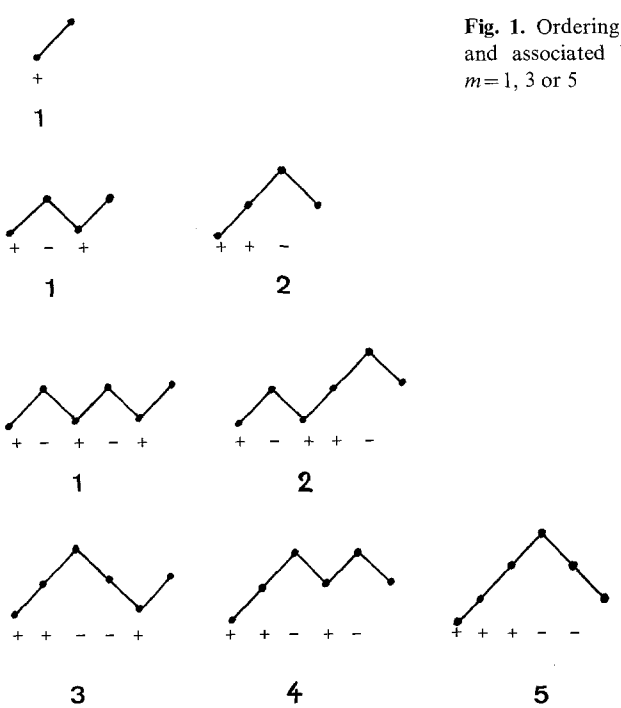

Fig. 1. Ordering of the branching diagram paths and associated Yamanouchi symbols for $S=\frac{1}{2}$, $m=1$, 3 or 5

Yamanouchi symbols ω and ω' are not identical in the ranges $1 \leqslant k < k_1$ and $k_2 < k \leqslant m$.

Eqs. (24) and (28) may be illustrated by some simple examples. For $m = 3$, $S = \frac{1}{2}$ we have, using Eqs. (24) (see Fig. 1).

$$\pi_{3,1/2}(1, 1 \mid (12)) = f_1(0) = 1$$

$$\pi_{3,1/2}(1, 2 \mid (12)) = \pi_{3,1/2}(2, 1 \mid (12)) = 0$$

$$\pi_{3,1/2}(2, 2 \mid (12)) = f_3 = -1$$

$$\pi_{3,1/2}(1, 1 \mid (23)) = -f_1(\tfrac{1}{2}) = -\tfrac{1}{2}$$

$$\pi_{3,1/2}(1, 2 \mid (23)) = \pi_{3,1/2}(2, 1 \mid (23)) = f_2(\tfrac{1}{2}) = -3^{1/2}/2$$

$$\pi_{3,1/2}(2, 2 \mid (23)) = f_1(\tfrac{1}{2}) = \tfrac{1}{2}$$

and from Eq. (28) we have

$$\pi_{3,1/2}(1, 2 \mid (123)) = f_2(\tfrac{1}{2}) f_1(0) = -3^{1/2}/2$$

$$\pi_{3,1/2}(2, 2 \mid (123)) = f_1(\tfrac{1}{2}) f_3 = -\tfrac{1}{2}$$

Finally we take $m = 5$, $S = \frac{1}{2}$ and we evaluate the matrix element

$$\pi_{5,1/2}(2, 1 \mid (12345)) = \langle 11111, 2 | (12345) | 11111, 1 \rangle$$

using the sequence of Fig. 2.

We start with the branching diagram path corresponding to $\omega' = 1$ (Fig. 1). The permutation is written as

$$P = (12345) = (12)(23)(34)(45)$$

and in each step we select that branching diagram path which resembles the final path $\omega = 2$ as closely as possible. The S_k values needed are the S-values for the intermediate functions as indicated by the open circles in Fig. 2. The corresponding $f_i(S_k)$ factors are

$$(45): f_2(\tfrac{1}{2}) = -3^{1/2}/2$$

$$(34): f_3 = -1$$

$$(23): -f_1(\tfrac{1}{2}) = -\tfrac{1}{2}$$

$$(12): f_1(0) = 1$$

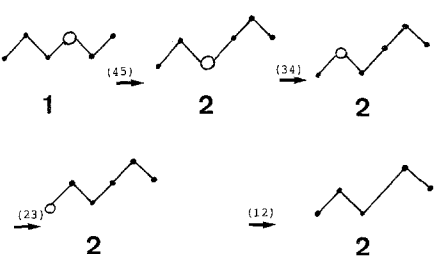

Fig. 2. Intermediate branching diagram paths needed for the calculation of the matrix element $\langle 11111, 2 | (12345) | 11111, 1 \rangle$ using $(12345) = (12)(23)(34)(45)$. The basic pair permutations $(k, k+1)$ used in each step are indicated between the paths and the S_k-values needed correspond to the positions indicated by open circles

and the result is thus

$$\pi_{5,1/2}(2, 1 \mid (12345)) = -3^{1/2}/4$$

3. Results

3.1. Formulas

The results of the preceding section may be combined as follows.

For case 1) ($w_i = 1$, $w_j = 0$) we have from Eqs. (15) and (21)

$$C_{i\to j}|w, \omega\rangle = |w', \omega, P\rangle = P|w', \omega\rangle = \sum_{\omega'} \pi_{m,S}(\omega', \omega \mid P)|w', \omega'\rangle \tag{29}$$

The function $|w', \omega, P\rangle$ generally does not satisfy the fixed ordering condition because $C_j^{\pm}$ occupies the position of $C_i^{\pm}$ in the original function. It follows that P is the permutation which moves orbital index j from its position in $|w', \omega\rangle$ (which satisfies the fixed ordering condition) to the position of orbital index i in the original function $|w, \omega\rangle$.

For case 2) ($w_i = w_j = 1$) the derivation is more complicated because Eq. (16) may only be used *after* a permutation has been applied, such that $C_i^{\pm}$ and $C_j^{\pm}$ are neighbours in $|w, \omega, P\rangle$, i.e. P is the permutation which moves the highest of i and j to the position next to the lowest of i and j. We then have

$$C_{i\to j}|w, \omega, P\rangle = F_{A,B}(S_s)|w', \omega'(\omega)\rangle \tag{30}$$

where the choice between F_A and F_B is determined by the sign in the branching diagram operator for the lowest of i and j.

Since $C_{i\to j}$ decreases the number of open shells by two, ω and ω' are different; ω' is obtained from ω by deleting the two steps corresponding to $C_i^{\pm}$ and $C_j^{\mp}$ in $|w, \omega, P\rangle$ from the corresponding branching diagram path. This involves one step up and one step down, since otherwise the contribution vanishes, cf. Eq. (17); if the signs in $C_i^{\pm}$ and $C_j^{\pm}$ are equal, the mapping ω' (ω) does not exist. Since the ordering of the other orbital indices $k \neq i, j$ is not affected by P, the functions $|w, \omega'\rangle$ automatically satisfy the fixed ordering condition. Using Eq. (21) we then have

$$C_{i\to j}|w, \omega, P\rangle = C_{i\to j} \sum_{\omega'''} \pi_{m,S}(\omega''', \omega \mid P)|w, \omega'''\rangle = F_{A,B}(S_s)|w', \omega'(\omega)\rangle$$

Multiplying both sides by $\pi_{m,S}(\omega'', \omega|P)$, summing over ω and using the orthogonality of the π-matrices then yields

$$C_{i\to j}|w, \omega''\rangle = F_{A,B}(S_s) \sum_{\omega} \pi_{m,S}(\omega'', \omega \mid P)|w', \omega'(\omega)\rangle \tag{31}$$

where it should be noted that only those terms contribute for which the mapping $\omega'(\omega)$ exists. S_s is the spin quantum number of the intermediate function $|w_s, S_s\rangle$ as defined by Eq. (14).

For case 3) ($w_i = 2$, $w_j = 0$) the result follows from Eqs. (19) and (21)

$$C_{i\to j}|w, \omega\rangle = \sum_{K=A,B} F_K(S_s)|w', \omega''_K(\omega), P\rangle$$
$$= \sum_{K=A,B} F_K(S_s) \sum_{\omega'_K} \pi_{m+2,S}(\omega'_K, \omega''_K(\omega) \mid P)|w', \omega'_K\rangle \quad (32)$$

where the first summation includes the two terms in the right hand side of Eq. (19). Since the signs in the $C_i^{\pm}$ operators in $|w', \omega'_A\rangle$ and $|w', \omega'_B\rangle$ are different, cf. Eq. (19), all branching diagram paths for $K = A$ are different from all branching diagram paths for $K = B$, i.e. the sets $\{\omega'_A\}$ and $\{\omega'_B\}$ are disjoint. Therefore the two summations in Eq. (32) ($K = A$ and $K = B$) may be treated separately.

$C_{i\to j}$ increases the number of open shells by two. Therefore ω'' is obtained from ω by inserting two steps (one step up and one step down or vice versa) in the position corresponding to orbital index i in the fixed ordering sequence. Therefore this index satisfies the fixed ordering condition in $|w', \omega''_K, P\rangle$ in Eq. (32). Since $C_i^{\pm}$ and $C_j^{\pm}$ are neighbours in this function, orbital index j generally does not satisfy this condition. It follows that P is the permutation which moves orbital index j from its position in the fixed ordering sequence to a position next to orbital index i. Finally, S_s is the spin quantum number corresponding to the intermediate function $|w_s, S_s\rangle$, which in this case contains all branching diagram operators $C_k^{\pm}$ contained in $|w, \omega\rangle$ with $k < i$.

For case 4) ($w_i = 2$, $w_j = 1$) the result is obtained analogous to case 1). Using Eqs. (20) and (21) we have

$$C_{i\to j}|w, \omega\rangle = -|w', \omega, P\rangle = -\sum_{\omega'} \pi_{m,S}(\omega', \omega \mid P)|w', \omega'\rangle \quad (33)$$

In $|w', \omega, P\rangle$ orbital index i is singly occupied. This orbital generally does not satisfy the fixed ordering condition, because it occupies the position of orbital index j in $|w, \omega\rangle$. It follows that P is the permutation which moves orbital index i to the position of orbital index j in the fixed ordering sequence for $|w, \omega\rangle$.

3.2. Some Examples

3.2.1. Case 1)

We take $m = 3$, $S = \frac{1}{2}$, $w = (01112)$, $\omega = 2$ (i.e. the Yamanouchi symbol is $++-$, see Fig. 1) $i = 4$ and $j = 1$. We then have

$$C_{4\to 1}|01112,2\rangle = C_{4\to 1} D_5 C_4^- C_3^+ C_2^+ |0\rangle$$

Eq. (15) yields

$$C_{4\to 1}|01112,2\rangle = D_5 C_1^- C_3^+ C_2^+ |0\rangle = (123) D_5 C_3^- C_2^+ C_1^+ |0\rangle = (123)|11102,2\rangle$$

where (123) is the permutation moving orbital index 1 to the position of orbital index 4 in the original function. Eq. (21) then yields

$$C_{4\to 1}|01112, 2\rangle = \sum_{\omega'=1}^{2} \pi_{3,1/2}(\omega', 2 \mid (123))|11102, \omega'\rangle$$

with $m=3$, $S=\frac{1}{2}$, $\omega=2$ and $\omega'=1, 2$. Using the results of the preceding section we finally obtain

$$C_{4\to 1}|01112, 2\rangle = -(3^{1/2}/2)|11102, 1\rangle - \tfrac{1}{2}|11102, 2\rangle$$

3.2.2. Case 2)

We take $m=3$, $S=\frac{1}{2}$, $w=(11120)$, $\omega=2$, $i=1$ and $j=3$, i.e.

$$|w, \omega\rangle = D_4 C_3^- C_2^+ C_1^+ |0\rangle.$$

In this case the orbital indices 2 and 3 have to be interchanged in order to put $C_3^{\pm}$ next to $C_1^{\pm}$, i.e. $P=(23)$. Further we have to take F_B because in $|w, \omega\rangle$ the branching diagram operator for orbital 1 corresponds to a step up in ω. The intermediate function $|w_s, S_s\rangle$ is identical to the vacuum state, i.e. $S_s=0$. Eqs. (31) thus yields

$$C_{1\to 3}|11120, 2\rangle = F_B(0) \sum_{\omega} \pi_{3,1/2}(2, \omega \mid (23))|01220, \omega'(\omega)\rangle$$

where ω' is obtained from ω by deleting the first two steps from the branching diagram paths $\omega=1, 2$. From Fig. 1 it is clear that in our case the mapping $\omega'(\omega)$ only exists for $\omega=1$ and that $\omega'(1)=1$. Therefore we find

$$C_{1\to 3}|11120, 2\rangle = F_B(0)\pi_{3,1/2}(2, 1 \mid (23))|01220, 1\rangle$$

and using Eq. (18) and the results of the preceding section we find

$$C_{1\to 3}|11120, 2\rangle = -(6^{1/2}/2)|01220, 1\rangle$$

3.2.3 Case 3)

We take $m=1$, $S=\frac{1}{2}$, $w=(01220)$, $\omega=1$, $i=3$ and $j=1$, i.e.

$$|w, \omega\rangle = |01220, 1\rangle = D_4 D_3 C_2^+ |0\rangle$$

Eq. (19) then yields functions where the orbital indices 1 and 2 are interchanged with respect to the fixed ordering sequence, i.e. $P=(12)$. The intermediate function is $|w_s, S_s\rangle = C_2^+|0\rangle$, i.e. $S_s=\frac{1}{2}$. ω_A'' and ω_B'' are obtained from ω by adding two steps in the positions 2 and 3, i.e. $\omega_A''=(+-+)$ and $\omega_B''=(++-)$. Eq. (32) thus yields

$$\begin{aligned} C_{3\to 1}|01220, 1\rangle = {} & F_A(\tfrac{1}{2}) \sum_{\omega_A'} \pi_{3,1/2}(\omega_A', 1 \mid (12))|11120, \omega_A'\rangle \\ & + F_B(\tfrac{1}{2}) \sum_{\omega_B'} \pi_{3,1/2}(\omega_B', 2 \mid (12))|11120, \omega_B'\rangle \end{aligned}$$

and using Eq. (18) and the results of the preceding section we obtain

$$C_{3\to 1}|01220, 1\rangle = -(2^{-1/2})|11120, 1\rangle - (6^{1/2}/2)|11120, 2\rangle$$

3.2.4. Case 4)

We take $m=3$, $S=\frac{1}{2}$, $w=(21110)$, $\omega=2$, $i=1$ and $j=4$, i.e.

$$|w, \omega\rangle = |21110, 2\rangle = D_1 C_4^- C_3^+ C_2^+ |0\rangle$$

Eq. (20) yields a function in which orbital index 1 occupies position 3 instead of position 1. Therefore we have to take $P=(123)$. Eq. (33) thus yields

$$C_{1\to 4}|21110, 2\rangle = -\sum_{\omega'} \pi_{3,1/2}(\omega', 2 \mid (123))|11120, \omega'\rangle$$

and using the results of the preceding section we find

$$C_{1\to 4}|21110, 2\rangle = -(3^{1/2}/2)|11120, 1\rangle - \tfrac{1}{2}|11120, 2\rangle$$

4. The List of Standard Coefficients

By comparing Eq. (3) with Eqs. (29), (31), (32) and (33) it is seen that the list of η-coefficients is equivalent to a list of all possible products of F- and π-coefficients. Therefore we may expect that the standard list of F- and π-coefficients will be considerably shorter than the list of η-coefficients. The calculation of the scalar product of two η-vectors in Eq. (4) corresponds to taking scalar products of two π-vectors, i.e. columns or rows of the relevant $\pi_{m,S}(P)$-matrices, and multiplying the results by the products of the relevant $F(S_s)$ factors. Therefore the algorithm for the construction of symbolic matrix element lists which uses this factorization is only slightly more time-consuming.

Regarding the first part of our calculation we note that the number of different $F(S_s)$ factors needed for a CI calculation with chosen maximal values of m and S is very small. This number follows directly from the form of the highest weight branching diagram path in the canonically ordered basis, i.e. the function

$$|\omega\rangle = \prod_{k=k_m+1}^{m} C_k^- \prod_{k=1}^{k_m} C_k^+ |0\rangle$$

with $k_m = m/2 + S$.

For the number of different $F(S_s)$ factors (which is twice the number of different intermediate S_s-values which may be encountered) we thus have

$$n(F(S_s)) = 2k_m = m + 2S$$

Therefore the storage of the F-factors does not lead to any problem at all. The π-coefficients are more difficult to handle than the F-factors, but the generation of all π-coefficients needed for fixed values of m and S is straightforward.

Moreover, the matrices turn out to be sparse, so that the numbers of non-zero elements are relatively small. Since the π-matrices are orthogonal, only the matrices for $P=(k_1 \ldots k_2)$ with $k_1 < k_2$ need to be stored. However, since only the non-zero elements are included in the list, the rows and columns have to be stored separately.

The length of the list of standard coefficients is determined by the maximal value of m for the configuration set used in the CI calculation at hand, i.e. for a CI calculation with up to m open shells only the π-matrices for m open shells are needed. This is not obvious because the π-matrices for $m+2$ open shells may be needed if Eq. (32) is used indiscriminately for the evaluation of Eq. (4). In this case the matrix element of Eq. (4) may either be reduced to a simpler form or it may be evaluated via an intermediate function $|w', \omega'\rangle$ containing $m-2$ open shells. In the first case we have e.g. (cf. Eqs. (1) and (2))

$$C^{ab}_{1212} = \tfrac{1}{2}\langle 02111, \omega''|C^2_{1\to 2}|20111, \omega\rangle$$

By using Eq. (8) and the anticommutation relations for the basic fermion operators we find

$$C^2_{1\to 2} = c_2^\dagger \bar{c}_2^\dagger \bar{c}_1 c_1$$

leading to

$$C^{ab}_{1212} = \langle 02111, \omega'' \mid 02111, \omega\rangle = \delta_{\omega''\omega}$$

Another example is

$$C^{ab}_{3112} = \langle 21011, \omega''|C_{3\to 1}C_{1\to 2}|20111, \omega\rangle$$

By using the commutator of Eq. (12) we now find

$$C^{ab}_{3112} = -\langle 21011, \omega''|C_{3\to 2}|20111, \omega\rangle = -\delta_{\omega''\omega}$$

These examples show how the use of the intermediate function $C_{1\to 2}|20111, \omega\rangle = |11111, \omega'\rangle$ with $m+2=5$ open shells may be avoided by evaluating C^{ab}_{ijkl} directly.

The second case may be illustrated by

$$\langle 11021, \omega''|C_{3\to 4}C_{1\to 2}|20111, \omega\rangle = \langle 11021, \omega''|C_{1\to 2}C_{3\to 4}|20111, \omega\rangle$$

where we have used $[C_{3\to 4}, C_{1\to 2}]=0$. In the left hand side the intermediate function $C_{1\to 2}|20111, \omega\rangle = |11111, \omega'\rangle$ contains $m+2=5$ open shells, whereas in the right hand side the intermediate function $C_{3\to 4}|20111, \omega\rangle = |20021, \omega'\rangle$ contains $m-2=1$ open shell.

By considering the explicit expressions [15] for the H-matrix elements over configurations with 0, 1 or 2 orbital differences it may readily be shown that all difficult matrix elements may be handled in this way. Since the π-matrices for m open shells contain all information needed for the calculation of matrix elements over configurations with $m' < m$ open shells, we conclude that only the π-matrices for m open shells are needed in a CI calculation with a configuration set involving variable numbers of open shells, i.e. $0 \leqslant m' \leqslant m$.

We have used the method described in Sect. 2.3 to calculate the non-zero elements of the representation matrices $\pi_{m,S}(P)$ for various values of m and S. The numbers of coefficients needed are given in Table 1, with the corresponding numbers of η-coefficients given in parentheses for comparison. Clearly our method uses a much smaller amount of storage than the method which uses the η-coefficients

Table 1. Numbers of non-zero π-coefficients 'the numbers of η-coefficients are in parentheses)

	S			
m	$0, \frac{1}{2}$	$1, \frac{3}{2}$	$2, \frac{5}{2}$	$3, \frac{7}{2}$
2	1 (4)	1 (3)		
3	10 (31)	3 (6)		
4	20 (56)	34 (111)	6	
5	117 (506)	81 (286)	10	
6	185 (731)	381 (2217)	160	15
7	1008 (7464)	949 (6950)	281	21
8	1464 (9747)	3364 (37497)	2016	455
9	7928 (108012)	8852 (134822)	3847	694
10	11070 (133227)	27359 (596397)	20109	6790
11	60634	75642	41239	11290
12	82971	216173	181896	78352

directly. Moreover, storing only the non-zero elements has the advantage that only the non-zero contributions to the scalar product of Eq. (4) have to be calculated when using the standard list in the construction of a symbolic matrix element list.

A further analysis yields the numbers of unique (numerically different) π-coefficients, as given in Table 2. These numbers appear to be small even for large m. However, since the mapping from given values of ω, ω' and P to the index of the unique π-coefficient needed is generally rather complicated, additional information must be stored to use this list efficiently.

The following method may then be useful for large values of m. Since both columns and rows may be needed in an actual calculation, these are stored separately.

Table 2. Numbers of unique (numerically different) π-coefficients

	S			
m	$0, \frac{1}{2}$	$1, \frac{3}{2}$	$2, \frac{5}{2}$	$3, \frac{7}{2}$
2	1	1		
3	6	2		
4	6	18	2	
5	28	38	2	
6	28	82	66	2
7	98	222	98	2
8	98	300	460	142
9	312	862	806	184
10	312	988	1836	1414
11	996	2624	3836	2004
12	996	2802	5980	7056

Instead of the non-zero π-coefficients themselves references to the unique list are stored together with the indices of the relevant branching diagram paths ω. In this way a number of references may be stored together in one computer word. Since the numbers of non-zero elements per column or row depend on ω and P, we also need information as to the first word addresses of the various columns and rows of the π-matrices. The mappings $\omega'(\omega'')$ and $\omega''(\omega)$ needed for Eqs. (31) and (32) are stored separately. Finally all possible products $F(S_s)F(S_s')$ may be included in the standard list.

Using 60-bit computer words we have generated the lists of standard coefficients needed for CI calculations with some selected values of S and m (as mentioned above the list for m open shells may be used for CI calculations with any number of open shells $m' < m$ if S is fixed). In the construction of these lists much computer time may be saved by using integer arithmetic as much as possible. This may be done by observing that all π-coefficients are constructed by using a very small number of numerically different $f_i(S_k)$ factors, cf. Eqs. (18), (24b) and (28).

Therefore it is advantageous to characterize each π-coefficient by the $f_i(S_k)$ factors it contains. While constructing the standard list the evaluation of a π-coefficient as a real number is then only necessary if it is not already included in the list of numerically different coefficients. Using this method, about 10 min. CP time is needed for the construction of the standard list for $m=10$, $S=3$ (CD/CYBER 73). The lengths of the standard lists are given in Table 3.

Table 3. Lengths of standard lists for CI calculations with selected maximal values of m and fixed S (60-bit words are used)

	S		
m	$0, \frac{1}{2}$	$1, \frac{3}{2}$	$2, \frac{5}{2}$
6	216	413	288
7	832	941	424
8	1076	2731	2002
9	5493	8132	3607
10	7285	22358	17858

5. Conclusions

We have shown that our method leads to a substantial reduction in the size of the standard list of coefficients which may be used for the calculation of symbolic matrix element lists for use in CI calculations with large numbers of open shells. Since our method may be expected to be comparable in speed to the method of Wetmore and Segal, we conclude that our method will be useful for large-scale CI calculations. Further reductions in the length of the standard list are possible, e.g. by considering the simplifications caused by equivalently occupied orbitals (orbitals which are purely singlet or triplet coupled), but these will not be further commented upon because the savings in storage are relatively small, whereas the structure of the standard list is considerably more complicated. Our method is also useful for hand calculations, because the number of non-zero contributions to

the scalar product in Eq. (4) is usually small and because the π-coefficients may be expressed as a continued product of a small number of $f_i(S_k)$ factors.

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