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The Direct Configuration Interaction Method for General Multireference Expansions: Symmetric Group Approach

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A computer implementation of the direct configuration interaction method formulated within the symmetric group approach is discussed. The formulation allows for an open-shell as well as for a multiconfigurational reference state. The number of all necessary formulas, derived by a computer for each integral type rather than for the individual integrals, is lower than in the currently existing techniques, including the unitary group approach. The logical structure of a general program for singly and doubly excited configurations is outlined. The efficiency of the symmetric group approach is demonstrated on a recently developed program, restricted to one reference state only.

Key words: CI direct method – Multiconfigurational open-shell states – Symmetric group.

1. Introduction

The configuration interaction (CI) method used for calculations of the many-electron correlated wave functions, unlike many other methods can, in principle, yield exact results [1]. The CI space is taken as the antisymmetric part of the N-fold tensorial product $V_n \otimes^N$ of the one-electron space V_n, spanned by the set of orbitals $\{\varphi_k, k = 1, 2, \ldots, n\}$. The solution of the Schrödinger equation, restricted to that space V, may be represented as a linear combination of N-electron basis functions (configuration functions, CF):

$$\Psi = \sum_{\alpha} C_\alpha \phi_\alpha = \sum_{K=1}^{M} \left\{ C_{K,0}\phi_{K,0} + \sum_{\mu} C_{K,\mu}\phi_{K,\mu} \right\}. \tag{1}$$

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A few important functions $\phi_{K,0}$ (termed the reference or root CFs), usually obtained from MC-SCF calculations, give the dominant part of the correlation energy by taking care of all the degeneracy and near-degeneracy effects. The second part of the expansion takes into account the dynamical correlation of the motion of the electrons. The length of the CI expansion may be reduced by restricting the CI space to configurations with proper spin and space symmetry properties [2]. The concept of the first order interacting space [3–8] enables further reduction to the expansion in all single and double replacements from the reference configurations. As was demonstrated [9–14] this kind of model multi-reference expansion (MC-CI expansion) gives very accurate results. However, it becomes quickly very long, causing in the conventional CI approach, when the Hamiltonian matrix is constructed and processed, severe problems with computer storage and timings.

A straightforward way out of this problem is offered by the direct CI method [15, 16], developed extensively in many variants in recent years [17–31]. Despite of the great effort put into generalizations of this method only very recently it has been formulated in a form computationally well fitted for open shell MC-CI expansions. The generalization was made possible by turning into account the fact [32] that the CI space $V_n \otimes^N$ is the carrier space for representations of the permutation group S_N (permutations of the electrons) on the one hand and of the unitary group $U(n)$ (unitary transformations among the orbitals) on the other. Although the rapid development of the theory [33–40] and applications [20, 21, 31, 41] of the unitary group approach (UGA) overshadowed the development of the theory [42–53] and applications [54–56] of the symmetric group approach (SGA) one may argue that the SGA offers several advantages over UGA: the theory is simpler, one does not have to deal with spin couplings explicitly, the basis of the spin functions is very flexible, efficient treatment of spin-dependent operators is possible [48], the formalism may be used in conventional as well as in the direct CI approach [56].

Here we present an application of the SGA to the direct CI method. The approach suggested here has advantages of both the loop-driven implementation of UGA, by Brooks and Schaefer [31], and the integral-driven implementation by Siegbahn [20, 21] – the loops rather than individual integrals are processed and the formula tape is very short. The structure of the internal space (of orbitals occupied in at least one of the reference configurations) may be exploited fully during calculation of pertinent formulas and coupling coefficients. In SGA the number of coefficients which should be calculated is in many cases much lower than in the other approaches. This is a rather unimportant advantage[1] since in most practical cases the time used for their calculation by UGA programs is already quite short [21, 31].

[1] Consider, however, the case of full CI calculations for 4 valence electrons. The number of representation matrices is $4! = 24$ and their maximal dimension is 3 (for triplets), so the number of coefficients cannot exceed $24 \cdot 3 \cdot 3 = 216$ elements (in fact the relationships among the matrices allow us to reduce that number to 15). The number of coupling coefficients which should be calculated in the UGA depends on the size of the orbital basis and can reach several millions [20].

The program, developed along the lines presented in that paper, has a very similar structure to the original direct CI program of Roos [15] and to the recent program of Siegbahn [21]. Although at the present stage it is not so general as UGA programs – covers the cases of single and double replacements from one reference configuration with no more than two open shells – further generalization for complete first-order active space is straightforward. The graphical form of SGA [53] presents a more efficient alternative than the present approach if configurations with more than two replacements should be included.

2. Symmetric Group Approach to the Direct Configuration Interaction Method

Only a brief summary is given here; for full presentation of the theory the reader is refered elsewhere [16, 43, 47, 53, 56].

Since at most two-particle interactions appear in the Hamiltonian H, it may be represented in the CI space in the following way [33]:

$$H = \sum_{i,j} (ij) E_{ij} + \tfrac{1}{2} \sum_{i,j,k,l} (ij|kl)(E_{ij}E_{kl} - \delta_{jk}E_{il}) \tag{2}$$

where (ij) and $(ij|kl)$ are one and two-electron integrals and E_{ij} are the generators of the unitary group $U(n)$.

The iterative methods, used for partial diagonalization of very large matrices [1, 17, 19, 57] make use of the Hamiltonian matrix H to find in each iteration the product vector:

$$\sigma_\mu = \sum_\nu H_{\mu\nu} C_\nu^{(n)}, \qquad H_{\mu\nu} = \langle \phi_\mu | H | \phi_\nu \rangle \tag{3}$$

where $\boldsymbol{C}^{(n)}$ is the approximate eigenvector in the n-th iteration. This can be written as:

$$\sigma_\mu = \sum_{i,j} (ij) \Big(\sum_\nu a_{ij}^{\mu\nu} C_\nu^{(n)} \Big) + \sum_{i,j,k,l} (ij|kl) \Big(\sum_\nu b_{ijkl}^{\mu\nu} C_\nu^{(n)} \Big) \tag{4}$$

where

$$a_{ij}^{\mu\nu} = \langle \phi_\mu | E_{ij} | \phi_\nu \rangle; \qquad b_{ijkl}^{\mu\nu} = \tfrac{1}{2} \langle \phi_\mu | E_{ij}E_{kl} - \delta_{jk}E_{il} | \phi_\nu \rangle \tag{5}$$

are the coupling constants.

To calculate the σ vector directly from the list of integrals – this is the main idea of the direct CI method – one should be able to identify, for a given integral, all pairs of configurations μ, ν, and calculate appropriate coupling constants (5). To that purpose let's define spin-adapted configuration:

$$\phi_{\lambda,S,M;k}(r, \sigma) = D \sum_P \varepsilon(P) P(\Theta_{S,M;k}(\sigma) \psi_\lambda(r)), \qquad k = 1, \ldots, f_\lambda \tag{6}$$

where P is a permutation operator acting on spatial and spin coordinates r, σ of electrons, $\varepsilon(P)$ is its parity, D is normalization constant, S and M refer to the eigenvalues of S^2 and S_z operators of the total spin, and f_λ is the number of

independent spin functions $\Theta_{S,M;k}$. The orbital part $\psi_\lambda(r)$ has the form:

$$\begin{aligned} &\psi_\lambda(r) = \prod_{i=1}^{N} \varphi_{\lambda i}(r_i), \qquad \varphi_{\lambda i} \in V_N, \\ &\lambda_1 < \lambda_2 < \cdots < \lambda_s: \qquad \lambda_{s+1} = \lambda_{s+2} < \cdots < \lambda_{N-1} = \lambda_N \end{aligned} \tag{7}$$

where λ is abbreviation for the set $\{\lambda_i, i = 1, \ldots, N\}$ and s denotes the number of singly occupied orbitals in λ. When evaluating a matrix element between two configurations, the integration over spin and orbital variables is performed separately and in the case of spin-free operators (spin-dependent case is described in [48]) the integrals over spin variables give:

$$\langle \Theta_{S,M;k} | P | \Theta_{S,M;l} \rangle = \varepsilon(P) \underline{U}^N_S(P)_{kl} \tag{8}$$

where $\underline{U}^N_S(P)$ is an irreducible representation matrix of the symmetric group S_N. This is one of the principal features responsible for high efficiency of SGA: all the spin coupling properties are hidden in the representation matrices and we have a freedom of choice of the representation. In fact we can treat all f_λ functions (6) as one function. Moreover, we can very easily keep strictly to the first order interacting space [29–31] deleting all rows and columns of $\underline{U}^s_S(P)$ matrices corresponding to spin functions which give zero matrix elements with the reference state.

The ordering of the orbitals in Eq. (7) allows us to express all the matrix elements using permutations among singly occupied orbitals only [47]. The coupling constants may now be written in a general form:

$$a_{\mu\nu}[\underline{A}_{\mu\nu}\underline{U}^s_S(P_0)]^{f_\mu f_\nu} \tag{9}$$

where $[\underline{U}]^{f_\mu f_\nu}$ is the rectangular part of the matrix $\underline{U}$ consisting of its first f_μ rows and f_ν columns, P_0 is the permutation "chosen" by the generators in Eq. (5) (integral over space variables is different from zero only for one permutation P_0 acting on indices of singly occupied orbitals in (7)), $a_{\mu\nu}$ are simple constants ± 1, $\pm\sqrt{2}$ or 2 and $\underline{A}_{\mu\nu}$ is usually a unit matrix except for a few cases when it is a unit matrix plus a representation matrix for a single transposition. The value of $a_{\mu\nu}$ does not depend on the actual form of μ and ν but only on the occupation numbers of orbitals corresponding to the integral indices i, j, k, l in the both configurations. Only a few different sets of occupation numbers are allowed – one can find them using the method presented in [56] or considering all possible types of generators (5). All the sets of the occupation numbers except for the trivial case of diagonal terms, are listed in Table 1.

For each case a number of different distributions of the occupation numbers is possible [56]. In order to obtain all the nonequivalent distributions one should perform P_J permutations, given in the third column, on columns of both μ and ν occupation numbers. In the last column values of $a_{\mu\nu}$ are given. The P_0 permu-

Table 1. Values of $a_{\mu\nu}$ coefficients and $\underline{A}_{\mu\nu}$ matrices for allowed occupation numbers of the orbitals involved in the integral. To obtain all nonequivalent distributions of the occupation numbers P_J permutations should be performed on the columns of the orbital occupances in μ and ν configuration

No.	Occupational numbers n_i^μ	n_j^μ	n_k^μ	n_l^μ	n_i^ν	n_j^ν	n_k^ν	n_l^ν	P_J	$a_{\mu\nu}$
$(ij\|kl)$ integrals. Four orbitals different. $\underline{A}_{\mu\nu} = I$ except case No. 4, $P_J = (23), (132), (234), (1342)$ when $\underline{A}_{\mu\nu} = -(I + \underline{U}^s_S((I_iI_j)))$ where I_i is the position of φ_i in μ.										
1	1	0	1	0	0	1	0	1	I, (12), (23)	1
2	1	0	1	1	0	1	0	2	I, (12), (14), (23), (24), (34), (124), (142), (234), (243), (12)(34), (14)(23)	$\sqrt{2}$
3	1	1	1	1	0	2	0	2	I, (12), (34), (12)(34), (23), (14)	2
4	1	0	1	2	0	1	2	1	I, (12), (13), (23), (24), (123), (132), (134), (234), (13)(24), (1324), (1342)	-1
5	1	2	1	1	2	1	2	0	as in case No. 2	$-\sqrt{2}$
6	1	2	1	2	2	1	2	1	as in case No. 1	1
$(ik\|kj)$ integrals									Three orbitals different	
7	1	2	0		0	1	2		I, (12)	-1
8	1	1	0		0	0	2		I	$\sqrt{2}$
9	1	1	2		2	2	0		I	$-\sqrt{2}$
No. 10: $(ij\|ij)$ integrals, No. 11–13: (ij) integrals										
									Two orbitals different	
10	0	2			2	0			I	1
11	1	0			0	1			I	1
12	2	1			1	2			I	-1
13	1	1			0	2			I, (12)	$\sqrt{2}$

$(ij|jj)$ integrals: as in cases No. 12–13.
$(ij|kk)$ integrals: as in cases No. 11–13 except that $a_{\mu\nu}$ should be replaced by $n_k a_{\mu\nu}$.
$(ik|kj)$ integrals: as in cases No. 11–13 except that $a_{\mu\nu}$ should be replaced by $-a_{\mu\nu}$ if $n_k = 2$ and $\underline{A}_{\mu\nu} = -(I + \underline{U}^s_S((I_jI_k)))$ in the case No. 12, $n_k = 1$.

tation may be given in the explicit form as a product of cycles [51, 53, 56] or may be found by proper ordering of the orbital indices in μ.

3. A General Strategy

As it was pointed out by Siegbahn [21], it is not enough to calculate quickly all the coupling constants, but one should also store and retrieve them efficiently. We shall now present a general strategy of the symmetric group approach to the direct CI method in case of single and double replacements out of a general multireference state.

Two distinct steps may be distinguished: at first all necessary formulas and coupling constants are found and recorded on the external file, to be processed in the second part. In contrast to the "formula tape" technique [27–31] the formulas are derived not for each integral separately, but for a small number of the integral types, i.e. for all the integrals with the same occupances of the orbitals involved (compare [29, 30]).

We introduce the symbol ${}_{\alpha_1}\langle\mu\|\nu\rangle_{\alpha_2}$ for the matrix element $\langle\phi_\mu|H|\phi_\nu\rangle$ where configuration μ is defined by excitations from the reference configuration α_1 and ν from α_2. Two separate cases are possible: the root configurations α_1 and α_2 are the same, $\alpha_1=\alpha_2$, or they are different. In the first case for a given integral type we shall find all possible pairs of configurations μ, ν at most doubly excited relatively to α_1, such that ${}_{\alpha_1}\langle\mu\|\nu\rangle_{\alpha_2}$ contains integrals of this type. We shall use the method presented in [56] which may be summarized as follows: in the pair of interacting configurations the actual occupances of the orbitals involved in the integral may take only one of the values listed in Table 1. Comparing these allowed occupances with the occupation numbers of the orbitals in the reference configuration α_1 we can easily find what excitations should be performed to obtain the allowed occupances. By systematic inspection of the rows of Table 1, we shall find all possible types of configuration pairs, given in the form of excitations from/to orbitals involved in the integral and from/to some additional orbitals appearing in both configurations. For example, for the integral $(ab|ij)$, where φ_a, φ_b are virtual and φ_i, φ_j are doubly occupied in α_1 one of possible pairs of configurations is ${}_{\alpha_1}\langle\mu\|\nu\rangle_{\alpha_1}={}_{\alpha_1}\langle ki\to bc\|kj\to ac\rangle_{\alpha_1}$. The indices k and c do not appear in the integral and refer to doubly occupied and virtual orbitals respectively. The contributions to σ vector may be written in this case as:

$$\Delta\sigma_{(ki\to bc)_{\alpha_1}}=(ab|ij)b^{\mu\nu}_{abij}C^{(n)}_{(kj\to ac)_{\alpha_1}} \tag{10}$$

To find all the contributions from $(ab|ij)$ integral we should make a loop over k and c indices (referred to as the loop indices) and repeat the procedure for all other types of μ, ν pairs.

Now let us consider the contributions from the elements ${}_{\alpha_1}\langle\mu\|\nu\rangle_{\alpha_1}$ where α_i is a reference configuration different than α_i. These elements may be expressed as:

$${}_{\alpha_1}\langle\mu\|\nu\rangle_{\alpha_i}={}_{\alpha_i}\langle\mu\|\nu',\ \alpha_i\to\alpha_1\rangle_{\alpha_i}={}_{\alpha_1}\langle\mu\|\nu'\rangle_{\alpha_1} \tag{11}$$

where $(\alpha_i\to\alpha_1)$ denotes an $\bar{\alpha}_i$-fold excitation of α_i which has to be performed in order to obtain α_1. If $\bar{\nu}'\le 2$, $\bar{\mu}\le 2$, i.e. the level of excitation of μ and ν is not greater than 2 the element (11) was already taken into account when all excitations from α_1 were considered. Therefore it is enough to consider only the cases of $\bar{\nu}'>2$ and $\bar{\nu}\le 2$, $\bar{\mu}\le 2$. Using the same method as before we may find all the configuration pairs μ, ν' defined relatively to α_1, for which $\bar{\mu}\le 2$ and $2<\bar{\nu}'\le\bar{\alpha}_i+2$. Then, by inspection of the occupation numbers we check whether the resulting configuration ν is not more than doubly excited relatively to α_i – if it is not the pair μ, ν is accepted. We should also include the elements ${}_{\alpha_1}\langle\mu\|\nu'\rangle_{\alpha_1}={}_{\alpha_1}\langle\nu'\|\mu\rangle_{\alpha_1}$ for which $\bar{\mu}>2$, $\bar{\nu}'\le 2$; this is done by reversing the role of μ and ν' configurations (ν' is taken as μ and μ is taken as ν'). In consequence it may happen that the number of singly occupied orbitals in μ is lower than in ν (Table 1, cases No. 2, 3, 5, 8, 9, 13) – then the P_0 permutation should be transposed and act on ν.

In the case of a pair of configurations defined relatively to an arbitrary pair of α_k, αl reference configurations the double-level indexing scheme [16, 19] may be applied to delete the redundant pairs. The position of a given doubly excited

configuration in the configuration list is calculated from the following formula:

$$\text{Address}\,(ij \to ab)_{\alpha_k} = N(N_1(N_2(i)+j)+N_3(a)+b+N_{\alpha_k}) \tag{12}$$

where N_1, N_2, N_3 are short auxiliary vectors and N_{α_k} is the starting position of the configuration α_k in the index vector N.

The index vector contains the address of the first entry for f_μ coefficients $C_\mu = C_{(ij\to ab)_{\alpha_k}}$. The address of a configuration which has to be deleted because of redundancy or because of symmetry restrictions is equal zero (compare [16]).

Now let us consider the dependence of the coupling constants $a_{ij}^{\mu\nu}$, $b_{ijkl}^{\mu\nu}$ on the i, j, k, l orbital indices and on μ, ν configurations. The values of $a_{\mu\nu}$ are uniquely determined by the set of the occupation numbers from which μ and ν were derived (a row in Table 1) while $\underline{A}_{\mu\nu}$ (if $\underline{A}_{\mu\nu} \neq I$) and P_0 depend only on the positions of these orbitals which are singly occupied in the configurations μ and ν. In the product (7) the orbitals are placed in order of their growing indices: for a general doubly excited configuration $\mu = (ij \to ab)$, $i \leq j$, $a \leq b$ the order of the singly occupied orbitals can be changed only if the inequalities between i, j and a, b indices change, or if the indices in the excitation correspond to singly occupied orbitals. Therefore the ranges of the indices for which the coupling constants have the same value may be found easily and the structure of the internal space may be fully exploited. Moreover, many P_0 permutations are the same for different ranges of the indices and for many pairs of configurations. The matrices corresponding to these permutations should be stored only once and used for many different types of matrix elements.

The contributions from the external space (the space of the orbitals absent in all the reference configurations) is particularly simple – because the indices of the external orbitals are the greatest these orbitals are always placed at the positions s and $s-1$ in the product (7) (for no more than doubly excited configurations). In consequence P_0 is factorized to a product $P_e P_i$, where P_e is I or $(s-1, s)$ transposition, depending on the order of external orbitals in the configuration pair and P_i is the ordering permutation for $P_e = I$. In standard representations the matrices corresponding to P_e permutation are diagonal with ± 1 elements [43, 58]. In particular it is easy to show that when all the integral indices correspond to orbitals from the external space P_i is always identity. The coupling constants are then ± 1 or $\sqrt{2}$ (compare [21]).

For every type of μ and ν configurations we must store the value of $a_{\mu\nu}$, the dimensions of the configurations (f_μ, f_ν in (9)), and information about the loop structure (i.e. what kind of the loop indices appear in the configuration) and the pointers to the array of $[\underline{U}_S^s(P_0)]^{f_\mu f_\nu}$ matrices for every region in which P_0 is fixed. Some additional symmetries of the integral indices may be used to minimize the number of formulas derived. For example integrals $(ij|kl)$, $(ik|jl)$, and $(il|jk)$ may be treated simultaneously.

To illustrate the method presented let us consider the integral $(nm|ij)$, where i, j are the indices of a closed-shell orbital and the two reference configurations α_1, α_2

differ in one closed shell orbital: $(\alpha_1 \to \alpha_2) = (mm \to nn)$. The same example was considered also by Roos and Siegbahn [19]. The integral, relatively to α_1, is of 0, 2, 2, 2 type. The excitation $(\alpha_1 \to \alpha_2)$ is composed of two one-electron excitations, therefore $\bar{\mu} \leq 2$, $2 < \bar{\nu} \leq 4$. It is easy to notice that the condition $\bar{\mu} \leq 2$ may be fulfilled only in cases No. 3–6 of Table 1. In order to find the first type of interacting configurations discussed in [19] let us take the set of occupation numbers (1, 0, 1, 2), (0, 1, 2, 1) (case No. 4, $P_J = I$). Subtracting these occupation numbers from the occupation numbers in α_1 we get the differences 1, −2, −1, 0 and 0, −1, 0, −1. Hence $\bar{\mu} \geq 3$ and $\bar{\nu}' \geq 2$. Reversing the role of μ and ν' we obtain $\mu = (mj \to xy)_{\alpha_1}$, where x, y are the loop indices. To find ν we must add the excitation $(\alpha_2 \to \alpha_1) = (nn \to mm)$ to ν', i.e. substract 2 from the occupation number of φ_n and add 2 to the occupation number of φ_m. As the result, the differences are −1, 0, −1, 0. Therefore $\nu = (ni \to xy)$ and the configuration pair is ${}_{\alpha_1}\langle \mu \| \nu \rangle_{\alpha_2} = {}_{\alpha_1}\langle mj \to xy \| ni \to xy \rangle_{\alpha_2}$. In the same way the second type of interacting pairs discussed in [19] may be obtained – the pair ${}_{\alpha_1}\langle jx \to ny \| ix \to my \rangle_{\alpha_2}$, corresponding to the case No. 6, $P_J = (12)$ (also in this case the order of μ and ν should be reversed).

Now we shall derive the coupling constants for the case of two different conventions of the ordering of orbitals. Case A, used in [56], when the excitation from a pair of doubles to a pair of virtuals $(ij \to ab)$ leads to a, i, b, j order of the orbitals in the configuration (this case corresponds to *ph-ph* spin coupling scheme [24]) and case B, in agreement with (7) (this case corresponds to *pp-hh* spin coupling scheme [24]). If α_1, α_2 are closed shell configurations then using the standard Yamanouchi-Kotani representation matrices [43] we have:

$$ {}_{\alpha_1}\langle mj \to xy \| ni \to xy \rangle_{\alpha_2}; \qquad a_{\mu\nu} = -1; \qquad \underline{A}_{\mu\nu} = I \tag{13} $$

	Case A	Case B
$j < m, i < n$ or $j > m, i > n$	$\underline{U}_0^4(I) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$;	$\underline{U}_0^4(I) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$.
$j > m, i < n$ or $j < m, i > n$	$\underline{U}_0^4((24)) = \begin{pmatrix} -1/2 & \sqrt{3}/3 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$;	$\underline{U}_0^4((12)) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

In the case of open-shell reference configurations and x, y corresponding as before to the virtual orbitals the matrices $\underline{U}_S^{s+4}((hs+1, s+2))$, where s is the number of singles in α_1 and S is the desired value of spin, should be taken instead of $\underline{U}_0^4((12))$.

The representation matrix for a general permutation P_0 may be obtained as a product of matrices for transpositions. Although most of the permutations needed are single transpositions or unity, the computation time in this part of the program is spent mainly on the multiplications of the matrices.

The frozen-core orbitals may be easily taken into account by repartitioning the Hamiltonian by means of the Fock operator $F = \sum_i (J_i - 1/2K_i)n_i$, where J_i and K_i are Coulomb and exchange operators and n_i are the most common occupations in the reference states. In consequence the integrals comprising the frozen-core orbitals may be deleted from the list of integrals. The additional advantage of the repartitioning is a reduction of the number of formulas for $(ij|kk)$, $(ik|kj)$ integrals and a significant simplification of the diagonal matrix elements.

In the second part of the program the formulas and the coupling constants are retrieved and used for each type of integrals separately. To minimize the number of input/output operations the integrals should be presorted into blocks of a given type. Then for one iteration only one pass through the list of integrals and through the list of formulas and coupling constants is needed. Every loop over the orbital indices should be broken into regions of constant P_0 values and before looping over a given region the pair of integrals J_1, J_2 appearing in the same matrix element is combined in one entity $a_1 J_1 \underline{U}_1 + a_2 J_2 \underline{U}_2$ where a_1, a_2 are $a_{\mu\nu}$ coefficients and $\underline{U}_1$, $\underline{U}_2$ are the representation matrices.

The coding may be greatly simplified if the loops over the internal space orbitals are separated from the loops over the external space orbitals. The addresses of the internal part of the loop may then be calculated and stored during generation of the formulas, giving entries for the external loops. The structure of the loops used in actual processing of the integrals is then very simple. The formula tape generated in such a manner should be very compact as the internal space is usually rather small and the matrix of coupling coefficients may be used for a whole set of states in the internal space and in the external space. That approach is very similar to the integral-driven implementation of UGA made by Siegbahn [20, 21], but the structure of the internal space may be exploited in greater extent. Moreover, the matrix form of the coupling constants allows us to treat all the interactions between configurations with given orbital occupancy and all different spin-couplings simultaneously. As we shall see in the next section the efficiency of the program based on such approach grows with the growing dimensions of coupling constants matrices.

4. The Program

To test the efficiency of the method presented above a FORTRAN program was developed[2] for the special case of one reference configuration with no more than two open shells. This particularly simple case served mainly to gather experience for a more general program. It shows however general trends in the SGA approach and therefore it is reported here.

The program is composed of two separate parts. The first part generates the formulas for all the integral types in sequence of their appearance in the reordered

[2] All calculations were done on the ES-1032 computer (404 Kbytes of core memory available to the user, about 60 times slower than IBM 360/90) in the Computer Center of Nicholas Copernicus University.

integral list. For given value of spin and the number of open shells the formulas do not depend on the number of doubles and virtuals (if these numbers are greater than 3 – if not, some of the cases never appear and the corresponding formulas do not have to be generated). Therefore the set of the formulas is universal – once generated it may be used in many calculations.

The frozen-core orbitals are completely removed from our considerations. They are all included into the matrix elements of the Fock operator, calculated during the reordering of the list of integrals. Two-electron integrals depending on the same orbitals are treated simultaneously. In the integral list they are grouped together and only one packed-integer word is needed to identify them.

To illustrate the amount of storage needed for different cases, in Table 2 are given: the number of the integral types and of the formulas, the maximum lengths of the vectors where the formulas and the representation matrices are stored, needed in core for one integral type, and the total lengths of these vectors. In the last two columns the percentage of elements of the representation matrices which are equal to zero and the running times are given. As one can see even in the most complex case the generation of the formulas would take a fraction of a second on a fast computer. No care was taken to optimize this part of the program. In the Yamanouchi–Kotani representation, used in that calculations, only $\underline{U}^s_S((s, s-1))$ matrices are diagonal. Considerable savings could be made by changing to the Serber representation [43, 58], since the matrices for (12), (34) . . . transpositions are then diagonal. Taking it into account in matrix multiplications and in storage one should be able to reduce the total as well as the maximum number of the coupling constants several times. This should also reduce the large number of zero coupling constants. The simplest way to avoid such coupling constants is to store only non-zero elements of representation matrices. More specific choice of representation is also worth considering [60].

Due to the advantages of the matrix operations the running time grows much slower than the total number of calculated coupling constants. The dimensions of the representation matrices grow very fast with an increase of the number of the open shells. Therefore for a large number of the open shells both the storage

Table 2. Comparison of different sets of formulas for cases treated by the program. N_T – number of integral types, N_F – number of formulas, M_F and M_U are, respectively, the maximum length of arrays containing formulas and matrices for one integral type, L_F and L_U are the total length of these arrays. The percentage of zero elements of the representation matrices is given in the next column. Time t for generation of each case is given in CPU seconds on ES-1032 computer

No. of open shells	Spin	N_T	N_F	M_F	M_U	L_F	L_U	% of zeros	t
0	0	20	87	447	108	2478	384	12	4.0
1	$\frac{1}{2}$	37	273	685	637	7279	3339	34	10.0
2	0	47	502	801	639	14342	5303	24	21.4
2	1	47	429	766	1834	12952	13223	46	34.0

requirements and the running times will be much larger. This is inevitable in any approach unless we reduce the number of the spin functions keeping strictly to the first-order interacting space [3–8, 29–31]. For a large number of singles a direct determination of non-zero elements of the representation matrices [59–61], instead of matrix multiplications, should be the most efficient way of their generation. It is clear however that in any reasonable case of a large-scale calculations the generation of the formulas and of the coupling constants takes a negligible computer time compared to other steps.

In the second part of the program the Davidson's diagonalization procedure [57] is performed. The diagonal elements, needed in that procedure in explict form, are calculated in the conventional way. Three sets of formulas are used: for singly and doubly excited configurations interacting with the ground state only (in the first iteration), interacting with the ground state and singly excited states (in the next few iterations), and interacting with all configurations (in the last few iterations). Another choice of "important" formulas for a few first iterations is also possible. The total time needed for diagonalization is thus greatly reduced.

To calculate contributions to vector (4) a block of the integrals (all of the same type) is read into the core. If the integrals in the block are of a different type than in the previous one the new formula vector and the new vector with representation matrices are read. Then the integral indices are unpacked and the information about the first formula is restored from the formula vector. The loop over the integrals of the block in core is started and for every integral the symbolic indices in the configuration pairs are replaced by the actual indices of that integral. For each type of the pair of configurations the subroutine which determines the loop structure (makes loops over the loop indices) is called. The loops over the internal and over the external orbitals were not separated in the present program, giving rise to rather lengthy code. The loops are divided into a few regions in which the coupling constants do not change. To avoid unnecessary repetitions pairs of two-electron integrals J_1, J_2 and coupling constants $a_1\underline{U}_1$, $a_2\underline{U}_2$ are combined in one matrix $a_1J_1\underline{U}_1 + a_2J_2\underline{U}$ before loops in each region are started. After using up all the formulas a new block of the integrals is read and the process repeated. The organization of the program minimizes the numbers of necessary multiplications and logical operations.

Test calculations on various systems (a few examples are given in Table 3) displayed the following features of the program:

The input/output efficiency is very high, rising with the length of the expansion from about 80% for medium scale closed-shell calculations to over 90% for open-shell large scale calculations. The percentage of the time used for multiplications, which must be performed independently of the logical structure of the algorithm used, changes similarly like the I/O efficiency (60%–85% for calculations without symmetry).

The time per one iteration is roughly proportional to the length of the expansion in power: 1.6 for closed-shell singlet, 1.35 for the doublet and open-shell singlet, 1.3 for the triplet case (least-squares fits to the calculations on the same system with

Table 3. Timings and loop statistics for the DCI program. % of multiplications is the percentage of the total CPU time used for actual multiplications in Eq. (4). % of unity is the percentage of loops corresponding to one pair of configurations only. Mean dimensions of the coupling constant matrices (9) are given in the last row. Time per iteration in minutes

Open shells, spin	0, 0		1, 1/2		2, 0		2, 1	
Doubles	4	8	4	6	4	4	4	4
Virtuals	34	16	20	12	10	17	8	14
Configuration functions	9453	8385	9645	7633	3246	8776	3331	9640
Configurations	6086	5024	3325	2521	1516	3686	1067	2642
Integrals	275652	45450	53300	18355	9452	38502	5670	22365
Time per iteration	38.3	20.7	20.8	12.9	5.5	22.0	4.0	20.4
% of multiplications	62	69	75	78	73	80	81	84
No. of loops	714251	242068	255192	132058	88041	305230	52586	183101
Elements per loop	10.5	20.2	35.9	48.0	19.9	26.6	45.7	65.8
% of unity	26	35	37	43	50	45	50	45
Mean dimension	1.5	1.7	2.8	3.2	2.5	2.6	3.9	4.1

different numbers of virtuals). The dependence on the number of integrals is almost linear. Calculation of diagonal matrix elements and the first iteration take no more than 5% of time needed for the last iteration, while the other iterations with reduced formulas take about 20% of that time. The timing and storage requirements for calculation of the size presented in Table 3 make them prohibitive using conventional CI programs on our computer. For the direct CI program they are of medium-size and quite easy to perform.

Most of the time during the iteration is spent on actual multiplications. The rest of the time (15–40%) is used mainly for evaluation of the addresses in the loops. Only a very small portion of the time goes for reading the formula vector. In the general case of an MC-CI expansion the formula vector may be very long, but the total number of individual terms in the loops is lower than in the case of one reference state with the same number of configurations (the H matrix is more dense for one reference configuration [19]). Therefore the high efficiency and weak dependence of the time on the length of expansion should remain.

To increase the efficiency even further another scheme of addressing could be used (see preceding part of this paper). One may propose a useful compromise between the formula tape approach and the direct CI method. All the loops which give only one contribution and the loops over singly occupied orbitals may be separated from the other loops, and a short formula tape may be formed for them directly from the list of integrals. For the remaining loops the number of elements per one loop, which is already quite high (Table 3), will be much greater, and the processing of the loops more efficient.

Obviously there is large number of other improvements which could be incorporated in future programs. It is clear that the use of the symmetric group allows for deep insight into the structure of Hamiltonian matrix and, thanks to that, for a very useful and general approach to the configuration interaction method.

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