SYMMETRIC GROUP APPROACH TO CONFIGURATION INTERACTION METHODS

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A self-contained review of the symmetric group approach to configuration interaction methods is given. Benefits resulting from an explicit separation of the N-particle configuration space to the orbital and the spin subspaces are discussed in detail. In particular, the internal structure of both the subspaces has been explored using their graphical representations. In effect an optimum configuration interaction algorithm has been formulated. Complete sets of formulae, necessary in both conventional and direct modes of implementation, are given in a compact, tabular form.

Preface

The paper presents a self-contained review of both conventional and direct configuration interaction methods within the symmetric group approach. Special attention has been paid to make the presentation complete. On the other hand, we avoided unnecessary formal considerations trying to make the approach easily accessible also to readers not willing to be involved in mathematical subtleties. A rather extensive list of references reflects a multiplicity of approaches to configuration interaction and related methods. It may be useful to a reader willing to find his own way of dealing with the problem. However, in order to understand and apply the formalism presented, no reference to other papers is necessary except for inessential details of some derivations.

The paper is divided into two parts. In the first part a general formulation of the theory is given. The second part contains explicit formulae and, where it is essential, information on the strategy of their implementation. The formulae are presented in a compact, tabular form, which makes their classification and computer representation particularly simple.

PART I. BASIC PRINCIPLES AND CONCEPTS

I.1. Introduction

The nonrelativistic one-particle model, culminating in the Hartree–Fock (HF) approximation, is certainly a basis for most of our intuitions, concepts and terminology in the field of quantum chemistry as well as of atomic and molecular physics. When the particles do not interact with each other, the model gives an exact solution of the Schrödiner equation. However, if we move closer towards the physical reality, the model becomes inadequate. First – if the particles interact by the Coulomb forces, the exact solution of the HF equations (where only an average interaction is taken into account) differs in an essential way from that of the corresponding Schrödinger equation. The energy difference, termed the *correlation energy* (E_{corr}) [1], is usually less than 1% of the total energy, but when the energy differences are concerned, the correlation energy constitutes often more than 100% of the difference (as e.g. in the case of atomic and molecular electron affinity values). Second – if the nonrelativistic approximation is not valid, the Schrödinger equation itself does not describe the system properly. The relativistic effects are small compared to the correlation ones only for the first row atoms and grow up very fast with the nuclear charge Z. Already for $Z = 14$ (silicon) the relativistic correction to the total energy (E_{rel}) exceeds the correlation energy and for $Z = 20$ (calcium) $E_{\mathrm{rel}} \approx 3E_{\mathrm{corr}}$. In consequence, beyond-Hartree–Fock methods of calculation are aimed at taking into account electron correlation and extending the basic formulation of the nonrelativistic theory. The first of these directions covers a vast majority of all the research works, including the present review. The second, though originated already in the thirties, received much interest only recently (for a review see ref. [2]) and culminated in excellent computer codes solving Dirac–Hartree–Fock equations for atoms [3]. Very little was done in studying correlation–relativistic cross effects, but it seems that also their role is far from being negligible [4].

The subject of the present study is the method of configuration interaction (CI) or, to be more precise, one out of many approaches to one out of many modes of its implementation. The method of configuration interaction is the most straightforward, the simplest and the most commonly used gateway beyond the one-particle model. It may also be very accurate – for small molecules it gave the most accurate results obtained so far [5] while for the medium size systems no real competition with CI exists. Various aspects of the CI method have been discussed in numerous papers, as e.g. excellent reviews by Shavitt [6] and by Roos [7], a monograph by Pauncz [8], proceedings of a workshop organized by Hinze [9], where further references may be found. The CI wavefunction becomes a formal solution of the nonrelativistic Schrödinger equation when the orbital basis set approaches completeness [10]. This property, combined with a rather slow convergence, stimulates a drive towards an extension of the length of the CI expansion. New concepts such as direct CI (DCI) method [11,12] and powerful graphical techniques based on group-theoretical properties of the CI wavefunction [13,14], allowed to overrun recently a limit of 10^6-term CI expansion [15].

The CI method originated from early papers of Hylleraas [16] and more extensive calculations of Boys [17], Parr et al. [18], Meckler [19] and others. Probably the first formally rigorous treatment of the method was given by Löwdin [10]. The conventional formulation of the method has been implemented in a number of laboratories. The most extensive and the best known CI procedures have been built into the systems MUNICH by Diercksen and Kraemer [20], ALCHEMY by Bagus et al. [21], POLYATOM by Neumann et al. [22], MOLECULE by Almlöf, Roos and Siegbahn [23,12].

The matrix element evaluation algorithms aimed at implementation in the conventional CI programs range from very simple rules of Reeves [24] extended by Sutcliffe [25] and by Cooper and McWeeny [26], valid for bonded functions only, to more sophisticated, based on group-theoretical techniques by Harris [27], Ruedenberg et al. [28,29], by one of us (JK) [30] and by many others. However, not the matrix element evaluation but rather storing CI matrices and searching for integrals appearing in a given matrix element, formed the real bottleneck of the conventional CI method.

A qualitative advance started with the idea of the direct CI formulated by Roos [11] a decade ago. In the conventional CI the Hamiltonian matrix elements are calculated explicitly to form the CI matrix. Next, a number of its eigenvalues and eigenvectors are obtained by a suitable iterative large-matrix procedure [31,32]. The core of such a procedure is always a multiplication of the matrix by a vector. The greatest advantage of the direct mode of calculation lies in constructing the product directly from a list of two-electron integrals, omitting the construction of the CI matrix itself. This kind of procedure reduces the storage requirements, but implies an increased mathematical complexity of the method. The formal problems connected with constructing general DCI algorithms have been solved by Paldus [13] and by Shavitt [14,33] using the unitary group approach (UGA) and by the present authors [34] within the symmetric group approach (SGA). Both the approaches allow to determine configuration pairs which may be coupled by a given two-electron integral and to evaluate the coupling constants.

The next milestone in development of the CI method was the concept of a global approach to the problem. Handling with entire spaces rather than with individual configurations was its essential novelty. The language of UGA introduced to CI methods by Paldus [13,74,75] and the direct mode of implementation, in a natural way suited to the global treatment of CI. Efficient implementations have been opened by Siegbahn's idea of dividing the orbital space into internal and external parts [35] and by the graphical representation of the CI basis by Shavitt [14,33]. In effect, graphical unitary group approach (GUGA) has been formulated outdating all previous achievements. The GUGA has been implemented in 3 different modes: integral driven [35], loop driven [38] and shape driven [15]. The maximum length of the CI expansion, used in a calculation, grows up very fast – from 6×10^4 in 1975 [39] to 10^6 in 1982 [15]. Of course, the increase is not only due to an improvement of the algorithms but also due to a development in the computer technology. The newest developments, aimed at vectorization of the global CI algorithms [53] seem to announce a new quantitative step forward.

Basic duality that exists between the symmetric and the unitary group causes that UGA and SGA are closely interrelated and that for each UGA result one can find its analog in SGA, and vice versa. Only recently, mainly due to work of Paldus and Wormer [85], these interrelations became clear. Though UGA is much younger than SGA [8], during the last decade the most important concepts have been developed within the UGA formalism [9]. Many of these concepts proved to be rather independent of the basic formulation of the theory. In particular, notions of the external and internal orbital spaces [35] or a graphical representation of the CI basis [14], originally introduced to UGA, are very general as far as their nature is concerned. Their transfer to SGA resulted in formulation of the symmetric group graphical approach (SGGA) [36,37]. In

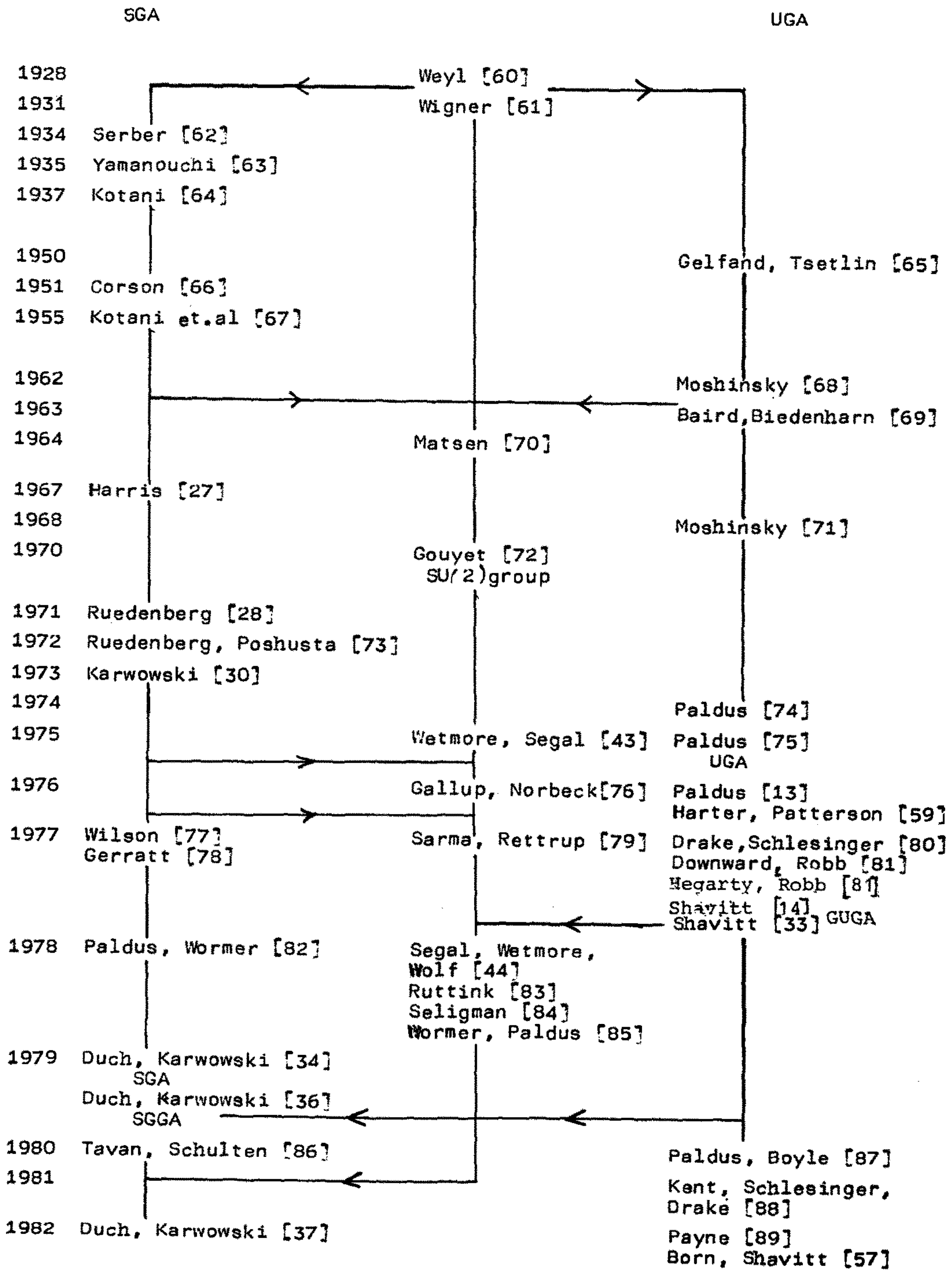

Fig. 1. Group theory based methods of matrix element evaluation.

fact, due to a separate treatment of the orbital and spin parts of the wavefunction, the global formulation of SGA proved to be even simpler than its UGA analogue. Nevertheless, to our knowledge, only one implementation of SGA has so far been done by Ruttink and Van Schaik [42].

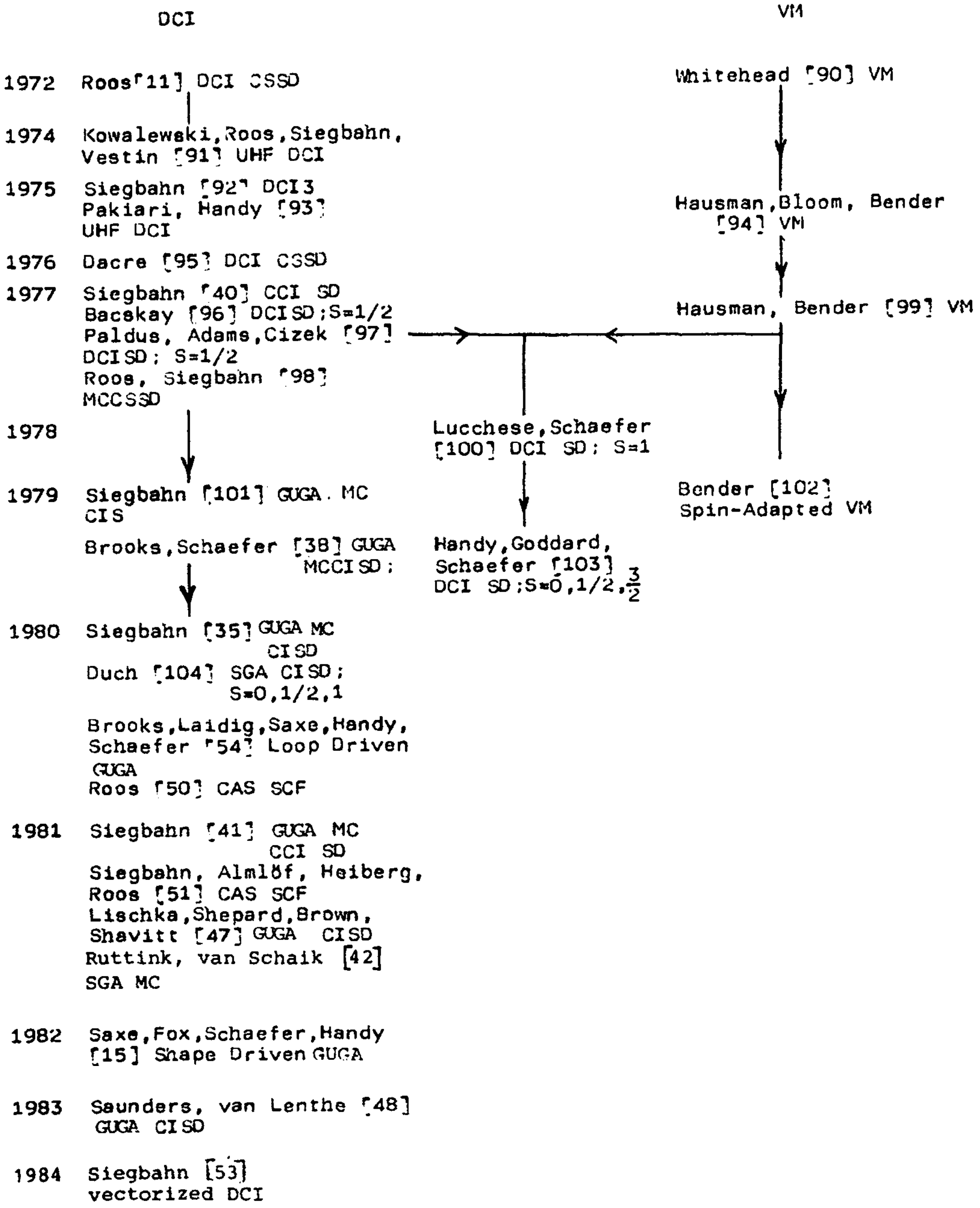

Fig. 2. Implementations of direct CI and vector methods. For explanation of the abbreviations used see list of abbreviations.

A number of simplifications of the general CI scheme has been proposed. In some methods a part of the variational parameters is kept fixed [40,41]. In others, a part of the Hamiltonian matrix is treated within a perturbational scheme [43,44]. To another class belong methods based on the electron-pair approximation [45,46]. We shall not discuss these approaches in any detail, though when a general CI algorithm is developed, it may be applied within any of the simplified theories.

The unitary group approach has been implemented not only in CI [15,35,47,48] but also in MCSCF [49], in complete active space SCF [50,51,52] and in CEPA [56] methods. Moreover, it was used in a formulation of an open-shell electron propagator theory [57], in the crystal field theory [58], in calculations of atomic properties [59], of one- and two-particle density matrices and of energy gradients [49,54]. We hope that SGA may constitute an useful alternative to UGA and that eventually, it will also be applied in equally many areas.

The present review is aimed at presentation of algorithms based on the symmetric group approach to DCI method. Similar aspects of UGA have recently been revived by Robb and Niazi [55]. A reader interested in conventional CI methods is referred to the already mentioned review by Shavitt [6]. Fig. 1 may serve as a guide to the sources and interrelations of the group-theory-based ideas useful in CI methods. A flow-chart of different DCI implementation is shown in fig. 2.

I.2. The method of configuration interaction – fundamentals

I.2.1. Preliminaries

The term *configuration interaction* method covers a class of approximate methods of solving an N-electron Hamiltonian eigenvalue problem

$$\hat{H}|\Phi\rangle = E|\Phi\rangle \tag{1}$$

based on the Ritz variational principle [105]. The problem is solvable if electron coordinates are the only variables in this equation. Therefore, if we are interested in solving the problem for a molecule, the nuclear positions are fixed to form a rigid frame. Since electrons are indistinguishable, the Hamiltonian is symmetric in electron coordinates. It is Hermitean, from the first principles of quantum mechanics. It contains only one- and two-electron terms, $\hat{h}_1(1)$ and $\hat{h}_2(1, 2)$, respectively. Hence,

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_1(i) + \sum_{i<j}^{N} \hat{h}_2(i, j), \tag{2}$$

where both $\hat{h}_1$ and $\hat{h}_2$ are Hermitean and $\hat{h}_2(i, j) = \hat{h}_2(j, i)$. The operator $\hat{h}_1$ includes operators describing interaction of an electron with an external field and the free-particle energy (kinetic energy in the nonrelativistic case) while $\hat{h}_2$ describes the electron–electron interaction. Though an exact Hamiltonian may consist of one- and two-electron terms only, in some approximate methods, as e.g. the ones based on cluster expansion techniques [46,106] or utilizing geminal-containing wavefunctions [107], many-electron terms appear in an effective Hamiltonian. We shall limit our discussion to the case of a Hamiltonian given by eq. (2) only, though in principle CI methods may be developed for a more general case.

CI method is distinguished by a special form of the trial function Ψ. Using the functional analysis language we may say that in an N-electron CI calculation we are looking for a solution of (1) in a subspace of a model space taken as the antisymmetric part of the N-fold tensorial product $H_N^{\mathrm{A}} = {}^{\mathrm{A}}(V_{2n}^{\mathrm{so}} \otimes^N)$ of the one-electron spaces $V_{2n}^{\mathrm{so}} = \{\chi_k\}_{k=1}^{2n}$ spanned by a set of $2n$ spin orbitals. The one-electron space itself is a product of the two-dimensional spin space $V_2^{\mathrm{s}} = \{\vartheta_i\}_{i=1,2}$ and the n-dimensional orbital space $V_n^{\mathrm{o}} = \{\varphi_k\}_{k=1}^{n}$ spanned by a set of n orbitals: $V_{2n}^{\mathrm{so}} = V_2^{\mathrm{s}} \otimes V_n^{\mathrm{o}}$. In practical terms it means that the trial function is taken in the form

$$\Psi(1, 2, \ldots, N) = \sum_L c_L \psi_L(1, 2, \ldots, N), \tag{3}$$

where $1, 2, \ldots, N$ stand for electron coordinates (including their spins), ψ_L are N-electron antisymmetrized products of spin orbitals (Slater determinants) and c_L are variational parameters. If the spin orbitals are chosen to be orthogonal, then the Slater determinants form an orthogonal system of the basis functions. Index L is an abbreviation for an ordered set of N indices of spin orbitals taken out of the set $\{\chi_k\}_{k=1}^{2n}$ i.e. $L = \{l_i\}_{i=1}^{N}$, $l_1 < l_2 < \ldots < l_N$, means that $\{\chi_{l_i}\}_{i=1}^{N}$ have been taken to construct ψ_L. The sets $L = \{l_i\}_{i=1}^{N}$ are often referred to as the *spin-orbital configurations*.

Depending on whether a spin orbital appears or not in a spin-orbital configuration we say that its occupation number in this configuration is, respectively, 1 or 0. Correspondingly we introduce also the orbital occupation numbers $n_i = 0, 1, 2$. If $n_i = 0$, the orbital φ_i does not appear, if $n_i = 1$ it appears once (associated with one of the two spin functions) and if $n_i = 2$ it appears twice (with both the spin functions) in the configuration. The singly occupied orbitals are referred to hereafter as *singles*, the doubly occupied as *doubles* and the empty ones as *virtuals*. The maximum number of spin-orbital configurations is equal to $\binom{2n}{N}$. If all of them are taken into account in the expansion (3), we call Ψ the *full CI* solution. This kind of calculation, for practical reasons, may be performed only if $2n - N$ is small enough. Usually *limited CI* calculations are performed with $K \ll \binom{2n}{N}$, where K is the number of terms included in expansion (3).

Application of the variational principle to (1) and (3) leads to a set of equations for c_L

$$\sum_L (H_{JL} - ES_{JL}) c_L = 0, \quad J = 1, 2, \ldots, K \tag{4}$$

being solvable under condition that

$$\det|H_{JL} - ES_{JL}| = 0, \tag{5}$$

where

$$H_{JL} = \langle \psi_J | \hat{H} | \psi_L \rangle, \tag{6}$$

$$S_{JL} = \langle \psi_J | \psi_L \rangle. \tag{7}$$

Eq. (4) may be rewritten in a matrix notation

$$\mathbf{H}c = E\mathbf{S}c, \tag{8}$$

where **H** and **S** are square matrices and c is a column vector. Eq. (8) is the matrix eigenvalue equation with an eigenvalue E and an eigenvector c. The K eigenvectors c_p (with components c_{Ip} and corresponding eigenvalues E_p) are subject to the condition

$$c_p^{\dagger}\mathbf{S}c_q = \delta_{pq} \tag{9}$$

and are numbered so that

$$E_1 \leqslant E_2 \leqslant \dots \leqslant E_K. \tag{10}$$

Each eigenvalue E_p of (8) is an upper bound to the corresponding eigenvalue of $\hat{H}$ [108]. As additional terms are added to the expansion (3), eigenvalues $E_p^{(K+1)}$ of the $(K+1)$-term expansion satisfy the inequalities

$$E_{p-1}^{(K)} \leqslant E_p^{(K+1)} \leqslant E_p^{(K)} \tag{11}$$

and as the orbital set $\{\varphi_k\}$ approaches completeness, the full CI solutions approach the exact solutions of eq. (1).

1.2.2. Configuration state functions

Methods based on eqs. (3)–(9) belong to the class of CI methods. In particular, one may formulate both relativistic and nonrelativistic CI methods though the former ones have never been implemented in large scale calculations. We consequently assume that the formulation is nonrelativistic, i.e. that the Hamiltonian does not depend upon spin variables. Then, all kinds of spin operators commute with $\hat{H}$. In other words, the total spin S and its projection M form, with energy E, a set of constants of motion. Hence, Ψ should be chosen as an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ operators. This requirement imposes upon the variational parameters in expansion (3) certain restrictions. The restrictions may be taken into account assuming that a number of Slater determinants corresponding to the same set of orbitals, but differing in their spin parts, are grouped together to form eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$. The spin adapted combination of the determinants is referred to as the *configuration state function* (CSF). The set of orbitals, common to all the Slater determinants forming a given CSF, is called the orbital configuration or simply *configuration*. Hence, a CSF $|\lambda;\, SM,\, l\rangle$, besides of being antisymmetric,

$$P\,|\lambda;\, SM,\, l\rangle = \epsilon(P)|\lambda;\, SM,\, l\rangle \tag{12}$$

fulfils the following eigenvalue equations

$$\hat{S}^2|\lambda;\, SM,\, l\rangle = S(S+1)|\lambda;\, SM,\, l\rangle, \tag{13}$$

$$\hat{S}_z|\lambda;\, SM,\, l\rangle = M|\lambda;\, SM,\, l\rangle, \tag{14}$$

where P is a permutation operator of electron coordinates, $\epsilon(P)$ is its parity ($\epsilon(P) = (-1)^m$, where m is the number of transpositions P is composed of), λ is an abbreviation for a set of the orbital indices used to construct a given CSF and index l has to distinguish independent eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ belonging to the same values of S and M. It may be shown (see e.g. ref. [8]) that $l = 1, 2, \ldots, f(S, s)$, where

$$f(S, s) = \frac{2S+1}{s+1}\binom{s \quad +1}{\frac{1}{2}s \quad -S} \tag{15}$$

and s is the number of singles in λ. Expansion (3) may then be replaced by a spin-adapted one

$$|\Psi; SM, k\rangle = \sum_{\lambda} \sum_{l=1}^{f(S,s)} C_{\lambda l}^{SMk} |\lambda; SM, l\rangle. \tag{16}$$

It means that instead of $^{\mathrm{A}}(V_{2n}^{\mathrm{so}} \otimes^{N})$ space, we take its subspace, $\Lambda(SM)$, spanned by all CSFs corresponding to a given pair of S, M quantum numbers. The dimension of $\Lambda(SM)$, i.e. the length of expansion (16) corresponding to full CI, is given by the Weyl–Paldus dimension formula [13,74]:

$$K(N, S, n) = \frac{2S+1}{n+1}\binom{n \quad +1}{\frac{1}{2}N \quad -S}\binom{n \quad +1}{\frac{1}{2}N \quad +S+1}. \tag{17}$$

Using the spin-adapted wavefunctions results in a very substantial reduction of the length of CI expansion. For example, in the case of a full CI calculation for $N = n = 6$, one can construct $\binom{12}{6} = 924$ Slater determinants, but only 175 singlet ($S = M = 0$) and 189 triplet ($S = M = 1$) CSFs.

Hamiltonian (2), apart from the invariance with respect to permutation and spin operators, is invariant with respect to all symmetry transformations of the external potential field. In the case of a molecule the group of invariance G, i.e. the symmetry group of the Hamiltonian, is determined by the space distribution of the nuclei. In the case of an atom, G is the orthogonal group $O(3)$. This kind of symmetry – the space symmetry – is more specific than those already discussed. In general, let $\hat{\Omega}_p \in G$, $p = 1, 2, \ldots, |G|$, be a set of symmetry operators such that

$$\left[\hat{H}, \hat{\Omega}_p\right] = 0. \tag{18}$$

Then, a symmetry adapted CSF (SACSF) $|\lambda, \Gamma, i; SM, l\rangle$ has to transform according to an irreducible representation Γ of the group G [109]. It means that

$$\hat{\Omega}_p|\lambda, \Gamma, i; SM, l\rangle = \sum_{j=1}^{d} \Gamma_{ji}(\Omega_p)|\lambda, \Gamma, j; SM, l\rangle, \quad i = 1, 2, \ldots, d, \tag{19}$$

where $\Gamma_{ji}(\Omega_p)$ is an element of the irreducible representation matrix of dimension d. Each $\Lambda(SM)$ space is reduced to a set of independent $\Lambda_\Gamma(SM)$ subspaces

$$\Lambda(SM) = \bigoplus_{\Gamma} \Lambda_\Gamma(SM). \tag{20}$$

In consequence, we have a separate CI expansion in each of the subspaces, i.e. for each of the irreducible representations Γ, and effectively the length of the expansion is further reduced.

SACSFs are, in general, linear combinations of CSFs. For each type of the point group different methods of constructing SACSFs have been developed. It is convenient to distinguish four different cases [6]. In order of increasing complexity they are: (I) Abelian groups, (II) non-Abelian axial groups, (III) cubic and icosahedral groups, (IV) the orthogonal group $O(3)$. Since we are concerned with a general formulation of the CI method rather than with specific features resulting from symmetry considerations, we shall disregard in the following the space symmetry restrictions, i.e. eqs. (19), except for the case of the Abelian groups. Moreover, the cases of non-Abelian groups (II)–(IV) have not been worked out in all details within the formalism we are concerned with, and their discussion here would be premature. An important progress in adaptation of UGA to non-Abelian symmetry groups has recently been achieved by Rettrup et al. [110] and by Chen and Chen [111]. An extensive list of references concerning applications of the point groups in CI is given in the review paper by Shavitt [6].

In the case of an Abelian group

$$[\hat{\Omega}_p, \hat{\Omega}_{p'}] = 0 \tag{21}$$

and $d = 1$. Eqs. (19) are then reduced to

$$\hat{\Omega}_p|\lambda^\Gamma; SM, k\rangle = \Gamma(\Omega_p)|\lambda^\Gamma; SM, k\rangle. \tag{22}$$

We have introduced here a single index λ^Γ since each orbital configuration λ corresponds to a single representation Γ of an Abelian group. In each $\Lambda_\Gamma(SM)$ space we have a separate CI expansion

$$|\Psi; \Gamma, SM, k\rangle = \sum_{\lambda^\Gamma} \sum_{l=1}^{f(S,s)} C_{\lambda^\Gamma l}^{SMk} |\lambda^\Gamma; SM, l\rangle, \tag{23}$$

where, for a given Γ, the set of SACSFs $|\lambda^\Gamma; SM, l\rangle$ is simply a subset of CSFs $|\lambda; SM, l\rangle$.

I.2.3. Hamiltonian in the orbital space

A specific choice of the set $\{\varphi_i\}_{i=1}^n$ of orbitals is one of the most important steps in a CI calculation. Usually, the orbitals are taken to be orthonormal, but methods based on nonorthogonal orbitals have also been formulated [112]. The only assumption we shall make about the orbitals is that they form an orthonormal set. One may show [113] that in the nonrelativistic case, i.e. when $\hat{h}_1$ and $\hat{h}_2$ do not contain spin variables, Hamiltonian (2) in the model space H_N^A, as defined in section I.2.1, may be represented in an equivalent form

$$\hat{H} = \sum_{kl}^{n} (k|l) E_{kl} + \tfrac{1}{2} \sum_{ijkl}^{n} (ij|kl)(E_{ij}E_{kl} - \delta_{jk} E_{il}), \tag{24}$$

where

$$(i|j) = \langle \varphi_i | \hat{h}_1 | \varphi_j \rangle, \tag{25}$$

$$(ij|kl) = \langle \varphi_i(1) | \langle \varphi_k(2) | \hat{h}_2(1, 2) | \varphi_l(2) \rangle | \varphi_j(1) \rangle \tag{26}$$

are the one- and two-electron integrals, we shall refer to as the *molecular integrals* (though the orbitals may describe atoms, crystals, etc. as well). The operators E_{kl} are defined as [115]

$$E_{kl} = \sum_{i=1}^{N} |\varphi_k(i)\rangle\langle\varphi_l(i)| . \tag{27}$$

When they act on a product of orbitals they replace φ_l by φ_k. Therefore we can call them *replacement operators* *. They also may be expressed in terms of the fermion creation and annihilation operators [13,71]. Besides one may show that they are generators of the unitary group $U(n)$ [71] which is an invariance group of V_n^0. The last property is a basis for developing the unitary group approach in CI methods [13,55,114]. From (27) immediately results an important commutation rule

$$\left[E_{ij}, E_{kl}\right] = \delta_{kj} E_{il} - \delta_{il} E_{kj}. \tag{28}$$

The main advantage of representing the Hamiltonian in the form (24) as far as applications in CI methods are concerned, is that a CI matrix element (6) between SACSFs may now immediately be expressed in terms of one- and two-electron integrals:

$$H^{\Gamma}_{pq} = \sum_{kl}^{n} A^{kl}_{pq}(\Gamma)(k|l) + \tfrac{1}{2} \sum_{ijkl}^{n} B^{ijkl}_{pq}(\Gamma)(ij|kl), \tag{29}$$

where

$$A^{kl}_{pq}(\Gamma) = \langle \lambda^{\Gamma}; SM, m | E_{kl} | \mu^{\Gamma}; SM, m' \rangle \tag{30}$$

and

$$B^{ijkl}_{pq}(\Gamma) = \langle \lambda^{\Gamma}; SM, m | E_{ij} E_{kl} - \delta_{jk} E_{il} | \mu^{\Gamma}; SM, m' \rangle \tag{31}$$

are known as the *coupling constants* [12,34]. The indices p and q stand here as abbreviations for (λ^{Γ}, m) and (μ^{Γ}, m') respectively. Henceforth, the point-group symmetry label, Γ, is omitted. As it is seen from (27), a matrix element of E_{kl} between products of orbitals is equal to a combination of products of the overlap integrals

$$\langle \varphi_k | \varphi_l \rangle = \delta_{kl} \tag{32}$$

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* Let us note that the replacement operators are non-Hermitean ($E^{\dagger}_{kl} = E_{lk} \neq E_{kl}$). The Hamiltonian expansion is Hermitean because, due to Hermicity of $\hat{h}_1$ and $\hat{h}_2$, the conjugate operators appear there with equal weights.

and, in consequence, an evaluation of the constants A and B may be reduced to simple algebraic manipulations, see e.g. refs. [37,79,85]. In particular the values of A and B are independent of the nature of the orbitals.

I.2.4. Molecular integrals

The set of molecular orbitals $\{\varphi_k\}_{k=1}^{n}$ is usually constructued as a linear transformation of basis set orbitals $\{\o_p\}_{p=1}^{n'}$, $n \leqslant n'$

$$|\varphi_k\rangle = \sum_{p=1}^{n'} |\o_p\rangle b_{pk}, \quad k = 1, 2, \dots, n, \tag{33}$$

transforming according to an irreducible representation Γ of the pertinent molecular symmetry group

$$\hat{\Omega}_p \, |\varphi^{\Gamma}_{mi}\rangle = \sum_{j=1}^{d} \Gamma_{ji}(\Omega_p) \, |\varphi^{\Gamma}_{mj}\rangle, \quad i = 1, 2, \dots, d. \tag{34}$$

In order to simplify the notation, we use a single orbital index (k in eq. (33)) rather than the set of three indices ((Γ, m, i) in eq. (34)). Symbol Γ^k is used henceforth to denote the symmetry of $|\varphi_k\rangle$.

Most commonly the basis set consists of atom centered basis functions, the coefficients b_{pk} being determined in a Roothaan–Hartree–Fock SCF procedure [116], though any other reasonable set of orbitals may be used instead. The molecular integrals can be obtained from analogous basis-set integrals by means of the transformation (33)

$$(i|j) = \sum_{pq}^{n'} b^*_{pi} b_{qj} \langle \o_p | \hat{h}_1 | \o_q \rangle, \tag{35}$$

$$(ij|kl) = \sum_{pqrs}^{n'} b^*_{pi} b_{qj} b^*_{rk} b_{sl} \langle \o_p | \langle \o_r | \hat{h}_2 | \o_s \rangle | \o_q \rangle. \tag{36}$$

The integral transformation, though formally very simple, in the case of large basis sets requires extensive computational resources. In fact, it is also one of the most time-consuming steps in a CI calculation. The number of terms in the two-electron transformation formula (eq. (36)), is proportional to n'^4; the number of molecular integrals is proportional to n^4. Hence, the total number of terms to be computed, when eq. (36) is applied in a straightforward way, is $(nn')^4 \approx n^8$. A number of methods aimed at an efficient performing of the transformation has been developed [48,117–119]. Roughly speaking, they are based on breaking up the four-fold sum in eq. (36) into a sequence of four partial summations. In effect the transformation becomes n^5 rather than n^8 process. Since the integral transformation problem is common to all kinds of CI calculations it will not be discussed here. It has been treated extensively in the papers by Shavitt [6] and by Saunders and Van Lenthe [48] (see also proceedings of the NRCC workshop [119]).

A further reduction of the amount of computations necessary to perform the integral transformation procedure may be reached by an explicit use of symmetry. One may distinguish two kinds of the integral symmetry: the index permutation symmetry and the point-group symmetry.

1. Index permutation symmetry. Since $\hat{h}_2$ is Hermitean and symmetric in electron coordinates, the following relations hold:

$$(i|j) = (j|i) \tag{37}$$

and

$$(ij|kl) = (kl|ij) = (ji|lk) = (lk|ji). \tag{38}$$

Hence, out of 4! = 24 two-electron integrals corresponding to four different orbitals, only 6 are different:

$$J_1 = (ij|kl), \quad J_2 = (il|jk), \quad J_3 = (ik|jl), \tag{39}$$

$$J_1' = (ij|lk), \quad J_2' = (il|kj), \quad J_3' = (ik|lj). \tag{40}$$

In the most common case the orbitals are real. Then

$$J_p = J_p', \quad p = 1, 2, 3 \tag{41}$$

and the number of different integrals is reduced to 3. In the following we shall assume the orbitals to be real. In general, as a consequence of the index permutation symmetry, the number of different one-electron integrals is

$$n_{\mathrm{I}} = n(n+1)/2 \approx n^2/2 \tag{42}$$

and similarly of the two-electron ones is

$$n_{\mathrm{II}} = n_{\mathrm{I}}(n_{\mathrm{I}}+1)/2 \approx n^4/8. \tag{43}$$

2. Point-group symmetry. The point-group symmetry of integrals results from the symmetry of molecular orbitals. Its practical importance results from a theorem stating that integrals $(i|j)$ (and $(ij|kl)$) vanish, unless in the products of representations $\Gamma^i \otimes \Gamma^j$ (and $\Gamma^k \otimes \Gamma^l$) appears the identity representation [109]. In the case of an Abelian group it means that $\Gamma^i = \Gamma^j$ (and $\Gamma^k = \Gamma^l$). Hence, the nonzero integrals may be collected into blocks labeled by the symmetry group representation indices. The number of one-electron integrals in each of the blocks is equal to

$$n_{\mathrm{I}}(\Gamma) = n(\Gamma)(n(\Gamma)+1)/2, \tag{44}$$

where $n(\Gamma)$ is the number of MOs belonging to the representation Γ. Similarly, in the case of two-electron integrals

$$n_{\mathrm{II}}(\Gamma_1, \Gamma_2) = \begin{cases} n_{\mathrm{I}}(\Gamma)(n_{\mathrm{I}}(\Gamma)+1)/2, & \text{if } \Gamma_1 = \Gamma_2 = \Gamma, \\ n_{\mathrm{I}}(\Gamma_1) n_{\mathrm{I}}(\Gamma_2), & \text{if } \Gamma_1 \neq \Gamma_2. \end{cases} \tag{45}$$

Since usually $n_{\mathrm{I}} \gg \Sigma_p n_{\mathrm{I}}(\Gamma_p)$ and $n_{\mathrm{II}} \gg \Sigma_{p<q} n_{\mathrm{II}}(\Gamma_p, \Gamma_q)$, taking into account the point-group symmetry, results in an essential reduction of the necessary computations and of the storage requirements.

Efficient procedures for determining the smallest set of the symmetry-distinct integrals have been developed by Davidson [120] and implemented in his algorithm for the integral transformation. An extensive review of this subject has been given by Shavitt [6].

I.2.5. The matrix eigenvalue problem

The CI energy and the corresponding wavefunction are obtained by solving the eigenvalue equation (8). In a general case, when the CSFs are nonorthogonal eq. (8) defines a generalized eigenvalue problem. Though efficient methods which can treat also the nonorthogonal problems have been developed [121], it seems to be preferable either to transform first the **H** matrix to a basis of orthonormal CSFs or to start with orthonormal CSFs. Therefore we shall consider only an orthonormal eigenvalue equation

$$\mathbf{H}c = Ec. \tag{46}$$

In the case of a small-size CI calculations (matrices of order up to about 300), any standard method for finding the eigenvalues is appropriate (as e.g. Householders' tridiagonalization method [123] with a subsequent use of the QR algorithm [124]). An extensive discussion of the algebraic eigenvalue problem has been given by Wilkinson [125].

In the case of large matrices, more suitable are iterative methods as e.g. the Davidson's modification [32] of the Lanczos method [126] or a version of the optimum relaxation method [31,127]. It seems to be commonly accepted that the Davidson's algorithm is the most convenient because of its fast convergence and numerical stability even in case of nearly degenerate roots.

The most time-consuming part of all the iterative methods consists of a multiplication of the Hamiltonian matrix by its approximate eigenvector

$$b^{(k+1)} = \mathbf{H}c^{(k)}, \tag{47}$$

where the superscripts refer to the iteration number. At this step two alternative strategies have been proposed. In the first one, known as the *conventional CI* [6], the Hamiltonian matrix elements are computed in a systematic sequence and stored. Then the eigenvalue equation is solved iteratively. The main disadvantages encountered in this mode of operation are: the need of a random access to the molecular integral file during H_{ij} evaluation, an extensive storage required to accommodate the **H** matrix and, as a consequence, a very high proportion of the computation time expanded in locating and accessing data and in general organizational tasks. In the second strategy, known as the *direct CI* (DCI) method [12], first formulated by Roos [11], the product vector $b^{(k+1)}$ is constructed directly from the list of molecular integrals, without the construction of the **H** matrix. This avoids the auxiliary storage problems and dramatically reduces the data transferring tasks. Moreover, it is possible to optimize the DCI procedures in a way not accessible to the conventional ones [48]. In consequence, a comparison of the direct and the conventional modes of calculation shows that the former one, if properly implemented, is more economic (except for very limited CI expansions) [48].

In the next parts of this paper we shall give a detailed presentation of an approach to DCI method employing the permutational symmetry of the wavefunction.

I.3. Symmetric group approach

I.3.1. Configuration state functions

A spin-adapted and antisymmetric (i.e. fulfilling eqs. (12)–(14)) CSF may be expressed in the form [28–30,66,67]

$$|\lambda;\, SM,\, l\rangle = \xi_\lambda \hat{A}\big[|\lambda\rangle|SM,\, l\rangle\big], \tag{48}$$

where

$$\hat{A} = \frac{1}{N!}\sum_P \epsilon(P)P \tag{49}$$

is the antisymmetrization operator,

$$\xi_\lambda = (N!/2^d)^{1/2} \tag{50}$$

is the normalization constant, $|SM,\, l\rangle$ is a pure spin function being an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ and $|\lambda\rangle$ is a spin-independent orbital function. The orbital function is chosen to be a product of N orthonormal orbitals defining configuration λ, s_λ of them being singly- and d_λ doubly-occupied:

$$\langle \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N|\lambda\rangle = \prod_{i=1}^{s} \lambda_i(i) \prod_{j=1}^{d} \lambda_{s+2j-1}(s+2j-1)\lambda_{s+2j}(s+2j), \tag{51}$$

where $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$ stand for the coordinates of electrons and, for simplicity, we write $\lambda_i(j)$ rather than $\varphi_{\lambda_i}(\boldsymbol{r}_j)$ and s/d rather than s_λ/d_λ. The numbers of singles and doubles in λ are connected by the obvious relation

$$s_\lambda + 2d_\lambda = N. \tag{52}$$

We adopt hereafter a convention that in all products of orbitals the position index of an orbital in the product is equal to the designation index of the electron described by this orbital, i.e. if

$\varphi_{\lambda_i}(\boldsymbol{r}_j)$ is contained in a product, then $i=j$ (unless otherwise stated). As a consequence of this convention we usually omit the electron designation indices in products of orbitals.

We need two kinds of identification of an orbital: the first is the orbital index (λ_i in the case of φ_{λ_i}), the second is the position index of the orbital in a configuration (i in the case of φ_{λ_i}). In what follows, unless otherwise stated, we employ small latin letters to represent the orbital indices. The position index of an orbital is indicated by adding a bar to its orbital index, i.e. if $\varphi_{\lambda_i}=\varphi_k$, then $i=\bar{k}$. In a process of matrix element evaluation two configurations are involved. If the position index refers to the ket configuration, then it will be supplied with a prime. We assume that in the orbital parts (51) of CSFs the position indices of singles are always less than those of doubles. Moreover, both the singles and doubles stand in (51) in an ascending order of their orbital indices, i.e.

$$\lambda_1<\lambda_2<\ldots<\lambda_s, \quad \lambda_{s+1}=\lambda_{s+2}<\lambda_{s+3}=\lambda_{s+4}<\ldots<\lambda_{N-1}=\lambda_N. \tag{53}$$

Since $|\lambda\rangle$, as described by eq. (51), is symmetric with respect to transpositions within doubles, the corresponding spin function must be antisymmetric. Therefore the spins of those electron pairs which correspond to doubles must be coupled in $|SM,\, l\rangle$ to two-electron singlets, i.e.

$$\langle\sigma_1,\sigma_2,\ldots,\sigma_N|SM,\, l\rangle=\langle\sigma_1,\sigma_2,\ldots,\sigma_s|SM,\, l\rangle\prod_{j=1}^{d}\langle\sigma_{s+2j-1},\sigma_{s+2j}|00,\, 1\rangle, \tag{54}$$

where $\sigma_1,\sigma_2,\ldots,\sigma_N$ stand for spin coordinates of electrons and $\langle\sigma_{s+2j-1},\sigma_{s+2j}|00,\, 1\rangle$ is a singlet-coupled pair (SCP) spin function. The spin functions having property (54) are called geminally antisymmetric spin functions [29,85] (they change their sign upon a transposition of electrons forming a double). Their properties were discussed in detail by Paldus and Wormer [85]. Examples of spin functions which can be defined to fulfil condition (54) are Yamanouchi–Kotani [63,64,67], Serber [62] and spin-bonded [24,25] functions. Condition (54) implies that with each orbital configuration there is associated a vector $|\boldsymbol{SM}\rangle$ with the components $|SM,\, l\rangle$, $l=1,2,\ldots,f(S,s)$. Consequently, we define a configuration state vector (CSV) $|\lambda;\,\boldsymbol{SM}\rangle$, whose components are given by eq. (48) with $l=1,2,\ldots,f(S,s)$.

Spin functions belonging to a pair of S, M ($S\geqslant|M|$) quantum numbers form a basis for an irreducible representation of S_N [67]. In other words, the set of matrices $\{\mathbf{U}_S^N(P);\ P\in S_N\}$, where

$$U_S^N(P)_{kl}=\epsilon(P)\langle SM,\, k|P|SM,\, l\rangle, \quad k,\, l=1,2,\ldots,f(S,N), \tag{55}$$

is an irreducible representation of S_N [66,67] *. One may easily prove that the matrices are M-independent [67]. Property (55) is valid for all kinds of linearly independent spin functions, including the nonorthogonal ones (as e.g. bonded functions). We assume that the spin functions are orthonormal. Then the representation matrices are unitary, i.e.

$$\mathbf{U}_S^N(P^{-1})=\mathbf{U}_S^N(P)^{\dagger}. \tag{56}$$

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* Two sets of matrices, $\mathbf{U}_S^N(P)$ and $\epsilon(P)\mathbf{U}_S^N(P)$, $P\in S_N$, form two, mutually dual representations of S_N. Definition (55) allows us to absorb the parity factor $\epsilon(P)$ into the representation matrix, so that it does not appear explicitly in Hamiltonian matrix element formulae.

Orthogonality of the spin functions implies that also CSFs are orthogonal. We designate $[\mathbf{U}_S^N]^{fg}$ an $f\times g$ block of $\mathbf{U}_S^N$ and assume the block to consist of the first f rows and g columns of $\mathbf{U}_S^N$, unless stated otherwise.

The same CSF may be expressed in many forms, being equivalent from the formal point of view. However chosing one of these forms determines the way of the further proceeding, aimed at the coupling constant (or matrix element) evaluation. If CSF is represented by eq. (48), the spin eigenfunction is constructed *before* the antisymmetrization is performed. In consequence we have an explicit separation of the orbital part of the CSF from its spin part. As we shall see, in this approach the coupling constants (eqs. (30) and (31)) are expressed in terms of the representation matrices of S_N. Therefore it is named *symmetric group approach* (SGA). Let us note, that if we start with the Slater determinants and construct spin eigenfunctions as their linear combinations, then the spin eigenfunctions are constructed *after* the antisymmetrization and a separation of the spin and orbital parts is more complicated. Also in UGA the separation, though may be performed [89], is not so simple and direct as in SGA.

I.3.2. Hamiltonian matrix elements: general considerations

A choice of an algorithm for Hamiltonian matrix element evaluation plays a central role in each CI scheme. The entire computational strategy depends upon the way the coupling constants are determined. A currency of the bonded functions, despite of the inconvenience resulting from their nonorthogonality, was mainly caused by a simplicity of the Boys–Reeves matrix element evaluation method [24–26]. In SGA the splitting of the spin and orbital parts in CSFs makes a separate integration over spin and orbital variables particularly easy. In consequence also the SGA matrix element evaluation algorithm proves to be exceptionally simple [28–30].

Let $H_{kl}^{(\lambda\mu)} = \langle\lambda;\ SM,\ k|\hat{H}|\mu;\ SM,\ l\rangle$. Then, using eq. (48), after some algebra, we get [30]

$$H_{kl}^{(\lambda\mu)} = 2^{-(d_\lambda+d_\mu)/2} \sum_{P\in S_N} \epsilon(P)\langle SM,\ k|P|SM,\ l\rangle\langle\lambda|\hat{H}P|\mu\rangle,$$

$$k = 1, 2, \dots, f(S,\ s_\lambda);\ l = 1, 2, \dots, f(S,\ s_\mu). \tag{57}$$

Let $\{\Pi_\lambda\}$ be a subgroup of S_n consisting of all products of transpositions within doubles in $|\lambda\rangle$. Let a similar subgroup, $\{\Pi_\mu\}$, be connected with $|\mu\rangle$. A set $\{\Pi_\lambda P_q \Pi_\mu\}$ is called the double coset generated by P_q. Since all permutations belonging to the same double coset give the same contribution to the sum in eq. (57), it may be replaced by [30]

$$\mathbf{H}^{(\lambda\mu)} = 2^{-(d_\lambda+d_\mu)/2}\sum_q D_{\lambda\mu}^q\left[\mathbf{U}_S^N(P_q)\right]^{fg}\langle P_q\lambda|\hat{H}|\mu\rangle, \tag{58}$$

where $\langle P_q\lambda|$ means that P_q acts on the orbital indices in the product (51) rather than on electron coordinates and $D_{\lambda\mu}^q$ is the dimension of $\{\Pi_\lambda P_q \Pi_\mu\}$. In eq. (58) we have applied the matrix notation, defined in the preceding section, with $f = f(S,\ s_\lambda)$ and $g = f(S,\ s_\mu)$.

One may show [30,37], that if $|\mu\rangle$ is the configuration with more doubles than $|\lambda\rangle$, then

$$D_{\lambda\mu}^q = 2^{d_\mu + t_q}, \tag{59}$$

where t_q is equal to the number of these transpositions within doubles in $|\lambda\rangle$ which do not commute with P_q. In other words, t_q is equal to the number of doubles which in $\langle P_q\lambda|$ do not occupy any of the positions occupied by a double in $\langle\lambda|$, i.e. any of $s_\lambda + 2j - 1$, $s_\lambda + 2j$, $j = 1, 2, \ldots, d_\lambda$, positions. In brief we say, that it is the number of doubles being "broken" by P_q.

Eq. (58) is valid for an arbitrary set of CSFs (including the case of nonorthogonal orbitals and/or nonorthogonal spin functions) if the Hamiltonian is Hermitean and symmetric in electron coordinates. In our case further simplifications can be done [30,37].

I.3.3. Integrals over orbital variables

If the Hamiltonian is expressed according to eq. (24), the integration over orbital variables in eq. (58) is reduced to an evaluation of two kinds of matrix elements: $\langle P_q\lambda|E_{kl}|\mu\rangle$ and $\langle P_q\lambda|E_{ij}E_{kl}|\mu\rangle$. Let n_k^λ and n_k^μ be the occupation numbers of φ_k in $|\lambda\rangle$ and in $|\mu\rangle$, respectively. According to (27) E_{kl}, when acting on $|\mu\rangle$, changes the occupation number n_k^μ to $n_k^\mu + 1$ and n_l^μ to $n_l^\mu - 1$. Effectively it is equivalent to transforming $|\mu\rangle$ into a linear combination of n_l^μ orbital products in which one of the orbitals φ_l is replaced by φ_k. Using eq. (27) we have for example

$$E_{kl}|\varphi_k\varphi_l\rangle = \sum_i |\varphi_k(i)\rangle\langle\varphi_l(i)|\varphi_k(1)\rangle\ |\varphi_l(2)\rangle = |\varphi_k\varphi_k\rangle. \tag{60}$$

And similarly

$$E_{kl}\ |\varphi_k\varphi_l\varphi_l\rangle = |\varphi_k\varphi_k\varphi_l\rangle + |\varphi_k\varphi_l\varphi_k\rangle,$$

$$E_{kl}\ |\varphi_k\varphi_k\varphi_l\varphi_l\rangle = |\varphi_k\varphi_k\varphi_k\varphi_l\rangle + |\varphi_k\varphi_k\varphi_l\varphi_k\rangle, \tag{61}$$

$$E_{kl}\ |\mu\rangle = 0, \quad \text{if } n_l^\mu = 0. \tag{62}$$

Eq. (61) may seem to violate the Pauli principle. However, one should remember that eqs. (60)–(62) represent intermediate results in matrix element evaluation procedure and have no physical meaning.

Let $\hat{\Omega}$ stand for either E_{kl} or $E_{ij}E_{kl} - \delta_{jk}E_{il}$ and let n_p^Ω be the "occupation number" of φ_p in $\hat{\Omega}|\mu\rangle$. Then $n_p^\Omega = n_p^\mu + \Delta_p$, where $\Delta_p = 0$, ± 1, ± 2 depending on the relation between p and the orbital indices involved in $\hat{\Omega}$. An integral $\langle P_q\lambda|\hat{\Omega}|\mu\rangle$ is equal to 0, unless $n_p^\lambda = n_p^\Omega$, $p = 1, 2, \ldots, n$, and P_q brings orbitals of λ into a complete coincidence with those in one of the products composing $\hat{\Omega}|\mu\rangle$. This specific permutation is called the *line-up permutation*, and denoted P_0.

Since, in general, $\hat{\Omega}|\mu\rangle$ is a linear combination of several orbital products, there are several line-up permutations. However, all of them belong to the double coset $\{\Pi_\lambda P_0 \Pi_\mu\}$. Hence, for given λ, μ and $\hat{\Omega}$, at most one of the permutations P_q in eq. (58) is the line-up permutation, and

$$\langle P_q\lambda|\hat{\Omega}|\mu\rangle = \begin{cases} m, & \text{if } P_q \in \{\Pi_\lambda P_0 \Pi_\mu\} \text{ and } n_p^\lambda = n_p^\mu + \Delta_p,\ p = 1, 2, \ldots, n, \\ 0, & \text{otherwise,} \end{cases} \tag{63}$$

where, depending upon the case, $m = 0, 1, 2, 4$ [37].

Table 1
Nonzero $\langle P_q\lambda|\hat{\Omega}|\mu\rangle$ matrix elements: $\Delta_p = n_p^\lambda - n_p^\mu$

$\hat{\Omega}$	P_0	m
1. $\lambda = \mu$:		
E_{ll}	I	n_l
$E_{jj}E_{ll} - \delta_{jl}E_{jl}$	I	$n_l(n_j - \delta_{jl})$
$E_{lj}E_{jl} - E_{ll}$	$(\bar{j}, \bar{l})$, if $n_j n_l \neq 0$	1
2. λ and μ differ by 1 orbital: $\Delta_k = 1$, $\Delta_l = -1$		
E_{kl}	$P_{[\bar{k}\bar{l}]}$	1
$E_{il}E_{ki} = E_{ki}E_{il} - E_{kl}$, $i \neq k, l$	$(\bar{i}, \bar{k})P_{[\bar{k}\bar{l}]}$, if $n_i^\mu \neq 0$	1
$E_{kl}(E_{ii} - \delta_{il}) = (E_{ii} - \delta_{ik})E_{kl}$	$P_{[\bar{k}\bar{l}]}$	$n_i^\mu - \delta_{il} = n_i^\lambda - \delta_{ik}$
3. λ and μ differ by 2 orbitals: $\Delta_k = \Delta_i = 1 + \delta_{ik}$, $\Delta_l = \Delta_j = -1 - \delta_{jl}$		
$E_{ij}E_{kl}$	$P_{[\bar{i}\bar{j},\bar{k}\bar{l}]}$	$1 + \delta_{ik}\delta_{jl}$
$E_{kj}E_{il}$	$P_{[\bar{k}\bar{j},\bar{i}\bar{l}]}$	

We denote by I the identity operator, by $(\bar{k}, \bar{l})$ a transposition of φ_k and φ_l, by $P_{[\bar{k}\bar{l}]}$ – a line-up permutation which puts φ_k at the position $\bar{l}$ and shifts the orbitals located in the orbital product between $\bar{k}$ and $\bar{l}$, and by $P_{[\bar{i}\bar{j},\bar{k}\bar{l}]}$ – a line-up permutation which puts φ_i at the position $\bar{j}$ and φ_k at the position $\bar{l}$ and shifts the orbitals located in between. Each line-up permutation may be assigned to one of the above mentioned kinds of permutations. Explicit expressions for the line-up permutations are given later in this work (table 9). All types of line-up permutations and the values of $\langle P_q\lambda|\hat{\Omega}|\mu\rangle$ matrix elements, classified according to λ, μ and $\hat{\Omega}$ are listed in table 1. Only nonzero Δ_p values are specified in the table.

The line-up permutations may be expressed as products of at most 4 cycles [37,79]. A cycle $(p..q)$ is defined as follows:

$$(p..q) = (p, p \pm 1, p \pm 2, \ldots, q) = (p, p \pm 1)(p \pm 1, p \pm 2)\ldots(q \mp 1, q), \tag{64}$$

where the upper sign corresponds to $p < q$ and the lower one to $p > q$. As an example let us consider the case of $n_k^\lambda = n_i^\lambda = n_l^\mu = n_j^\mu = 1$, $k < i$, $l < j$. The two sets of singly occupied orbitals are represented as a *configuration pair diagram* [30] in fig. 3. In the diagram, the orbitals forming λ and μ are represented by asterisks being set in two rows in the order of their position indices in the orbital product (51). The lower row stands for λ, the upper one for μ. The identical orbitals are linked together. Then the line-up permutation may be defined as the one which rearranges the asterisks in λ so that all the links are represented by the vertical arcs, while the orbitals which appear in λ only, are lined in a way determined by the operator $\hat{\Omega}$ *. In the case displayed in fig.

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* A reader familiar with UGA may notice that an analog of the configuration pair diagram would have to contain also the empty orbitals. As a consequence the configuration pair diagram is then trivial since the orbitals are always lined up. However, the noncoincidences of the orbitals in matrix elements are then due to $\hat{\Omega}$ operators and the final result is exactly the same.

3 the line-up permutations consist of two cycles:

$$P_{[\bar i\bar j,\bar k\bar l]} = (\bar k..\bar l')(\bar i..\bar j'), \quad P_{[\bar k\bar j,\bar i\bar l]} = (\bar i..\bar l')(\bar k + 1..\bar j').$$

Using the formulae displayed in table 1, one may extract from the Hamiltonian (24) these parts which give nonzero contributions to matrix elements between two given configurations. We define an index

$$r_{\lambda\mu} = \tfrac{1}{2} \sum_{i=1}^{n} \left| n_i^\lambda - n_i^\mu \right| \tag{65}$$

equal to the number of orbitals configurations λ and μ differ by. Matrix elements (63) vanish unless $r_{\lambda\mu} = 0, 1, 2$. Hence, three cases may be distinguished:

1. Diagonal part ($r_{\lambda\mu} = 0$):

$$\hat H_0 = \sum_k \left[n_k (k|k) + \tfrac{1}{2} n_k (n_k - 1)(kk|kk) \right] + \tfrac{1}{2} \sum_{k \neq l} \left[n_k n_l (kk|ll) + (E_{lk} E_{kl} - n_l)(lk|kl) \right]. \tag{66}$$

2. λ and μ differ by one orbital ($r_{\lambda\mu} = 1$):

$$n_k^\lambda - n_k^\mu = 1, \quad n_l^\lambda - n_l^\mu = -1,$$

$$\hat H_1 = \left[(k|l) + \sum_i (n_i^\mu - \delta_{il})(ii|kl) \right] E_{kl} + \sum_{\substack{i \\ (i \neq k,l)}} (il|ki) E_{il} E_{ki}. \tag{67}$$

3. λ and μ differ by two orbitals ($r_{\lambda\mu} = 2$):

$$n_k^\lambda - n_k^\mu = n_i^\lambda - n_i^\mu = 1 + \delta_{ik}, \quad n_l^\lambda - n_l^\mu = n_j^\lambda - n_j^\mu = -1 - \delta_{jl},$$

$$\hat H_2 = 2^{-\delta_{ik}\delta_{jl}} (ij|kl) E_{ij} E_{kl} + (1 - \delta_{ik})(1 - \delta_{jl})(kj|il) E_{kj} E_{il}, \tag{68}$$

where $i \neq j$, l and $k \neq j$, l.

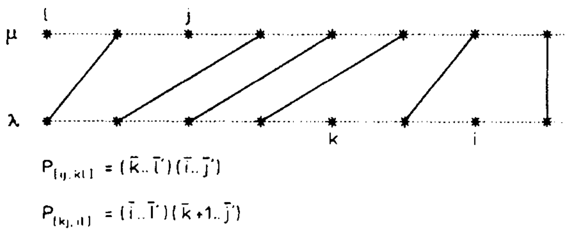


Fig. 3. Example of configuration-pair diagram and line-up permutations for the case of $\Delta_k = \Delta_i = 1$, $\Delta_l = \Delta_j = -1$, $n_k^\lambda = n_i^\lambda = n_l^\mu = n_j^\mu = 1$.

Eqs. (66)–(68) do not depend upon the form of the wavefunction and therefore are common for both SGA and UGA (see e.g. table II in the review paper by Paldus [13]).

I.3.4. Integrals over spin variables

In order to evaluate $\langle SM, k|P|SM, l\rangle$ integrals, we may exploit general properties of $\mathbf{U}_S^N$ matrices [67]. One easily notice that each permutation may be expressed as

$$P = P^{sd} P^s P^d, \tag{69}$$

where $P^s \in S_s$ acts on the singles only, P^d permutes doubles (singlet-coupled electron pairs) and P^{sd} consists of transpositions breaking doubles. For the Yamanouchi–Kotani (YK) spin functions [67]

$$\left[\mathbf{U}_S^N(P^{sd}P^sP^d)\right]^{fg} = \left[\mathbf{U}_S^N(P^{sd}P^s)\right]^{fg}, \tag{70}$$

where $f = f(S, s_\lambda)$ and $g = f(S, s_\mu)$. It can be shown [30] that if $P = P_0$ than $P^{sd} = P_0^{sd}$ breaks at most two doubles, i.e. only 5 types of P_0^{sd} permutations may appear: (d_a, d_b), (u, d), $(u_a, d)(u_b, d')$, $(d_a, d_b)(u, d'_a)$ and $(d'_a, d'_b)(u_a, d_a)(u_b, d_b)$, where u stands for a single, d, d' for two members of the same double and subscripts a, b are used to distinguish different singles and/or doubles. As has been proved by Kotani et al. [67], all $[\mathbf{U}_S^N]^{ff}$ blocks of the representation matrices may be reduced to $\mathbf{U}_S^s$ matrices corresponding to appropriate permutations of singles only. A complete set of the reduction formulae is given in table 2. For convenience the numerical factor resulting from eqs. (58) and (59) has also been there included.

The theorem of Kotani et al. is of a fundamental importance as far as implementations are concerned, since usually most of orbitals in CSFs are doubly occupied. In many methods its advantage has not been taken into account (as e.g. in refs. [28,29,85]. The resulting algorithms have to contain then a substantial redundancy. An elimination of doubles has been performed in the methods by Gallup and Norbeck [76] (note, that some cases are missing in their formulae), by Sarma and Rettrup [79] and by one of us [30]. There are many methods of constructing $\mathbf{U}_S^s$ matrices [8,62,63,67,77,82,86,128–132] and a general computer program has recently been made commonly available [132]. The algorithm we consider to be the most appropriate for large scale calculations [129] will be discussed in the next section. It is derived directly from the Yamanouchi–Kotani method [67]. Here we outline the fundamentals of the YK method and of

Table 2
Formulae for reduction of $[\mathbf{U}_S^N(P_0)]^{ff}$ blocks to $\mathbf{U}_S^s(P_0^s)$ matrices

No.	P_0^{sd}	$2^{t_q}[\mathbf{U}_S^N(P_0)]^{ff}$
1	(d_a, d_b)	$-2\mathbf{U}_S^s(P_0^s)$
2	(u, d)	$-\mathbf{U}_S^s(P_0^s)$
3	$(u_a, d)(u_b, d')$	$\mathbf{U}_S^s(P_0^s)+\mathbf{U}_S^s((u_a, u_b)P_0^s)$
4	$(d_a, d_b)(u, d'_a)$	$\mathbf{U}_S^s(P_0^s)$
5	$(d'_a, d'_b)(u_a, d_a)(u_b, d_b)$	$\mathbf{U}_S^s((u_a, u_b)P_0^s)$

its implementation by Rettrup [128], to a degree necessary in small-size CI calculations, when all information necessary to construct the CI matrix may be kept in the core memory of a computer.

Let $|SM, k\rangle$, $k = 1, 2, \ldots, f(S, s)$ be the YK functions. Then, by their proper ordering, we may assure that the matrices $\mathbf{U}_S^s(P^{s-1})$ for $P^{s-1} \in S_{s-1}$ have a reduced (block-diagonal) form [67]

$$\mathbf{U}_S^s(P^{s-1}) = \begin{bmatrix} \mathbf{U}_{S+1/2}^{s-1}(P^{s-1}) & \mathbf{0} \\ \mathbf{0} & \mathbf{U}_{S-1/2}^{s-1}(P^{s-1}) \end{bmatrix}. \tag{71}$$

If we take a sequence $P^{s-2} \in S_{s-2}$, $P^{s-3} \in S_{s-3}, \ldots$, then each of the matrices $\mathbf{U}_S^{s-1}$ may be further recursively reduced, according to eq. (71). On the other hand, a straightforward calculation shows that $\mathbf{U}_S^{s'}((s'-1, s'))$ has the following block structure [67]

$$\mathbf{U}_S^{s'}((s'-1, s')) = \begin{bmatrix} -\mathbf{I} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & a_S\mathbf{I} & b_S\mathbf{I} & \mathbf{0} \\ \mathbf{0} & b_S\mathbf{I} & -a_S\mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & -\mathbf{I} \end{bmatrix}, \tag{72}$$

where dimensions of the consecutive blocks (going from the top along the diagonal) are $f(S+1, s'-2)$, $f(S, s'-2)$, $f(S, s'-2)$, $f(S-1, s'-2)$ and $a_S = 1/(2S+1)$, $b_S = -\sqrt{1-a_S^2}$. Now, the matrices for $(s-1, s)$, $(s-2, s-1), \ldots, (1, 2)$ transpositions may be obtained combining eqs. (71) and (72).

We should note that the spin functions for which relations (71) and (72) hold, do not satisfy condition (54), since the electron pairs $(2j-1, 2j)$ rather than $(s+2j-1, s+2j)$, $j = 1, 2, \ldots, d$, are here coupled to two-electron singlets. Also the ordering of the spin functions which implies the block-diagonal form (71) and (72) of the representation matrices is different from the one resulting from eq. (54). Therefore, before further proceeding, one has to renumber the electrons and reorder the spin functions. In section I.4.1 of this paper we present an algorithm being free of this drawback.

After the appropriate reordering of the rows and columns in $\mathbf{U}_S^s((i-1, i))$ matrices and renumbering the electrons (i.e. replacing i by $N+1-i$), all the remaining $\mathbf{U}_S^s$ matrices can easily be constructued through matrix multiplication. For example, the relation

$$(i, j+1) = (j, j+1)(i, j)(j, j+1), \quad j \neq i \tag{73}$$

yields

$$\mathbf{U}((i, j+1)) = \mathbf{U}((j, j+1))\mathbf{U}((i, j))\mathbf{U}((j, j+1)). \tag{74}$$

According to eqs. (71) and (72) in each row/column of $\mathbf{U}((j, j+1))$ there are at most 2 nonzero elements. Hence, each element of $\mathbf{U}((i, j+1))$ may be expressed as a linear combination of at most 4 elements of $\mathbf{U}((i, j))$ [128].

The symmetric-group-based formalism of Kotani et al. [67], outlined in this section, may also be interpreted in terms of UGA. In fact, many of the Kotani et al. formulae have been independently rederived and generalized within the unitary group formalism. In particular, eq.

(72) corresponds to the matrix representation of the unitary group elementary generator in a basis of special Gelfand states [13].

I.3.5. Hamiltonian matrix element formulae

Collecting eqs. (29)–(31) and (66)–(68) together with those displayed in tables 1 and 2, we can express the general matrix element formulae as a set of directly programmable equations [37,79]. According to (24), (58) and (59), coupling constants (30) and (31) may be written as

$$\mathbf{A}^{kl}_{\lambda\mu} = 2^{(d_\mu - d_\lambda)/2} \sum_q 2^{t_q} \left[\mathbf{U}^N_S(P_q)\right]^{fg} \langle P_q\lambda | E_{kl} | \mu \rangle \tag{75}$$

and

$$\mathbf{B}^{ijkl}_{\lambda\mu} = 2^{(d_\mu - d_\lambda)/2} \sum_q 2^{t_q} \left[\mathbf{U}^N_S(P_q)\right]^{fg} \langle P_q\lambda | E_{ij}E_{kl} - \delta_{jk}E_{il} | \mu \rangle, \tag{76}$$

where $\mathbf{A}_{\lambda\mu}$ and $\mathbf{B}_{\lambda\mu}$ stand for $f \times g$ blocks ($f = f(S, s_\lambda)$, $g = f(S, s_\mu)$) corresponding to the pair of configurations λ, μ and $f \geqslant g$, i.e. λ is the configuration with at least as many singles as μ. Now, as it results from section I.3.3 and from table 1, for a given coupling constant, at most one permutation P_q gives a nonzero contribution to eqs. (75) and (76). Hence, the $\langle P_q\lambda | \hat{\Omega} | \mu \rangle$ matrix element is a permutation selector, reducing sums over all double cosets to single terms. According to eqs. (66)–(68) 3 cases should be distinguished:

1. $r_{\lambda\mu} = 0$

$$\begin{aligned}\mathbf{H}^{(\lambda\lambda)}_0 = {} & \sum_{k=1}^{n} \left\{ n_k(k|k) + \tfrac{1}{2}n_k(n_k - 1)(kk|kk) \right\} \mathbf{I} \\ & + \sum_{k<l} n_k n_l \left\{ (kk|ll)\mathbf{I} + (-2)^{(1-m)} \mathbf{U}^s_S\left((\bar{k}, \bar{l})^m\right)(kl|lk) \right\},\end{aligned} \tag{77}$$

where $\mathbf{I}$ stands for an $f \times f$ unit matrix, $m = \max(n_k, n_l)$ and $(\bar{k}, \bar{l})^2 = 1$, $(\bar{k}, \bar{l})^1 = (\bar{k}, \bar{l})$.

2. $r_{\lambda\mu} = 1$ ($\Delta_k = 1$, $\Delta_l = -1$)

$$\begin{aligned}\mathbf{H}^{(\lambda\mu)}_1 = {} & 2^t \left[\mathbf{U}^N_S(P_{[\bar{k}\bar{l}]})\right]^{fg} \left\{ (k|l) + \sum_i (n^\mu_i - \delta_{il})(ii|kl) \right\} \\ & + \sum_{\substack{i \\ (i \neq k,l)}} 2^t\left(1 - \delta_{n_i 0}\right)\left[\mathbf{U}^N_S\left((\bar{i}, \bar{k})P_{[\bar{k}\bar{l}]}\right)\right]^{fg}(il|ki).\end{aligned} \tag{78}$$

3. $r_{\lambda\mu} = 2$ ($\Delta_k = \Delta_i = 1 + \delta_{ik}$, $\Delta_l = \Delta_j = -1 - \delta_{lj}$)

$$\mathbf{H}^{(\lambda\mu)}_2 = \left\{ 2^t \left[\mathbf{U}^N_S(P_{[\bar{i}\bar{j},\bar{k}\bar{l}]})\right]^{fg}(ij|kl) + 2^t(1 - \delta_{ik})(1 - \delta_{jl})\left[\mathbf{U}^N_S(P_{[\bar{k}\bar{j},\bar{i}\bar{l}]})\right]^{fg}(kj|il) \right\}, \tag{79}$$

where $t = (d_\mu - d_\lambda)/2 + t_0$ and t_0 equals to the number of doubles in λ broken by P_0 (cf. eq. (59)).

The coupling constant blocks (75) and (76) have been expressed in eqs. (77)–(79) in terms of the representation matrices of S_N. A simple algorithm of constructing the representation matrices has been given in section I.3.4. Another one is discussed in detail in section I.4.3. For the reduction formulae from S_N to S_s see table 2. More explicit expressions for the Hamiltonian matrix elements are collected in tables 7 and 9. Details of derivations of the equations may be found in refs. [30,34].

Eqs. (77)–(79) (or rather their explicit counterparts in table 7) contain a complete information necessary for evaluation of an $f(S, s_\lambda) \times f(S, s_\mu)$ block of a CI matrix between two spin-adapted and antisymmetric CSVs corresponding to an arbitrary pair of configurations λ and μ constructed as products of orthonormal orbitals. The formulae are well suited to a conventional CI method. They may be applied according to the following scheme: take two configurations differing by at most 2 orbitals, select case, give designations λ, μ, i, j, k, l so that conditions of table 7 are valid, use the formulas to construct $\mathbf{H}$. The representation matrices may either be precalculated and kept in a tabular form or computed whenever they are needed. A reasonable compromise may be to precalculate and keep the representation matrices corresponding to single cycles and to transpositions while the remaining ones may be obtained through the matrix multiplication.

Due to their simplicity, the formulae may be used not only as a base for all kinds of computer programs, but also to derivations of specific formulae and desk calculations when only several matrix elements are needed. If the CI basis is small enough and we do not have to care about data manipulation problems, the formulae may be considered as the final result of the symmetric group approach. Most interesting physical and chemical problems lead to rather lengthy CI expansions and complicated data manipulation. For this kind of task the formulae derived here are inadequate – a global description of the entire CI problem is then necessary. This problem is discussed in the next section.

I.4. Global description of a CI problem

In this section we shall explore the structure of $A(SM)$ space. As has been explained, in SGA the $A(SM)$ space is separated into the spin and the orbital spaces and correspondingly, the matrix element evaluation procedure is separated into two parts. It is convenient to describe the structure of these two spaces using graphical methods. In the case of the spin space the graph, known as the branching diagram, was introduced at an early stage of development of the quantum theory by Van Vleck and Sherman [133]. Its analog for the orbital space was recently described by us [36,37]. The very idea of using this kind of graphical representations of A in CI methods is due to Shavitt [14,33] and most of the terminology has been adopted from him. Though both spin and orbital diagrams may be used for many purposes (e.g. to visualize the recursive building up procedure and the degeneracy of the spin states [8]), for us most important is that they give global descriptions of the entire spaces. As a consequence the diagrammatic methods facilitate a construction of efficient CI algorithms exploiting the global structure of $A(SM)$ space and avoiding repetitions and redundancy [9,14,33,37].

For the reader's convenience we tried to follow as closely as possible the way the graphical representation of the CI basis has been introduced to UGA [14,33]. In particular, the arrays $\mathbf{T}^S$ (eq. (80)) and $\mathbf{T}$ (eq. (93)) are analogues of the Paldus arrays of UGA. The way, the lexical path indices are defined and calculated corresponds to that of UGA, etc. In section I.4.1 the familiar spin branching diagram will be described in terms of the quantities specific for graphical representations of CI bases, so that it may also be considered as an educative example showing the way one constructs and uses graphs both in SGGA and in GUGA.

I.4.1. Spin functions: branching diagram

A YK spin function, corresponding to the total spin S, of an N-electron system may be represented by an array

$$\mathbf{T}^S(l) = [S_0, S_1, \ldots, S_N], \quad l = 1, 2, \ldots, f(S, N), \tag{80}$$

where S_k is the resultant spin obtained by coupling spins of the first k electrons. Then, $S_0 = 0$, $S_1 = \frac{1}{2}$, $S_2 = 0, 1, \ldots, S_N = S$. The array may be represented graphically on a grid in which the vertical position equals S_k and the horizontal one k. The graphical representation of $\mathbf{T}^S(l)$ is a directed path consisting of segments (*arcs*) joining consecutively nodes $\{k, S_k\}_{k=0}^{N}$ of the grid (*vertices*). To an arc contained between $k-1$ and k we assign the number k. Its slope represents the way spin of the kth electron is coupled to S_{k-1} to form S_k. Since there are at most two ways of the coupling [67,8],

$$1. \quad S_k = S_{k-1} - 1/2, \quad \text{if } S_{k-1} > 0 \text{ and } S_{k-1} > S - (N-k)/2, \tag{81}$$

$$2. \quad S_k = S_{k-1} + 1/2, \quad \text{if } S_{k-1} < S + (N-k)/2,$$

$$k = 1, 2, \ldots, N, \tag{82}$$

there are at most two arcs off a vertex. The first constraint for the coupling ($S_{k-1} > 0$) is obvious, the two others ($S - (N-k)/2 < S_{k-1} < S + (N-k)/2$) are to secure that $S_N = S$.

Each path starts at (0, 0) vertex (*head*) and ends at (N, S) vertex (*tail*). A set of the paths forms a graph. A graph containing all paths which may be constructed for given N and S forms a *complete branching diagram*. Usually, we need only a properly selected subspace of the entire space of $\{|S, M, l\rangle\}_{l=1}^{f(S,N)}$ spin functions. Such a subspace is described by a *restricted branching diagram*. An example of a complete branching diagram for $S = 1$, $N = 6$, and its extension to $N = 8$, is shown in fig. 4.

We can establish a lexical ordering between different spin functions, i.e. between different $\mathbf{T}^S(l)$ arrays. We say that $\mathbf{T}^S(l)$ precedes $\mathbf{T}^S(l')$ if in the sequence of differences $\{T^S(l)_k - T^S(l')_k\}_{k=N}^{1}$ the first nonzero entry is positive. The consecutive paths (spin functions) are numbered, in lexical order, by a lexical index l_x. In order to facilitate a simple evaluation of l_x for an arbitrary path we assign to a vertex (k, S_k) a number $d_x(k, S_k)$ (*lexical weight of the vertex*) and to an arc contained between $k-1$ and k a *lexical arc index* $y_x^{\pm}(k, S_k)$, where y^+ means that $S_{k-1} < S_k$ while y^- means the opposite. The weight of a vertex is equal to the number of paths beginning at the head and passing through the vertex. It results from the mode of the construction, that

$$d_{\mathrm{x}}(k,\, S_k) = d_{\mathrm{x}}(k-1,\, S_k - 1/2) + d_{\mathrm{x}}(k-1,\, S_k + 1/2). \tag{83}$$

Moreover, by definition,

$$d_{\mathrm{x}}(k,\, S_k) = f(S_k,\, k). \tag{84}$$

The lexical arc indices are defined as

$$y_{\mathrm{x}}^{+}(k,\, S_k) = \begin{cases} d_{\mathrm{x}}(k-1,\, S_k + 1/2), & \text{if vertex } (k-1,\, S_k + 1/2) \text{ belongs to the graph} \\ 0, & \text{otherwise,} \end{cases} \tag{85}$$

$$y_{\mathrm{x}}^{-}(k,\, s_k) = 0. \tag{86}$$

It can easily be verified (for a detailed discussion see refs. [14,33]) that the lexical index l_{x} of the path passing through an ordered set of vertices $\{k,\, S_k\}_{k=0}^{N}$ is given by

$$l_{\mathrm{x}} = 1 + \sum_{k=1}^{N} y_{\mathrm{x}}(k,\, S_k), \tag{87}$$

where y_{x} stands for either y_{x}^{+} or y_{x}^{-}. The lexical vertex weights and the lexical arc indices are both shown in the diagram in fig. 4.

As already explained in section I.3.4, the spin functions coupled according to the branching diagram scheme do not satisfy condition (54). In consequence they cannot be coupled with the orbital products (51) to form the CSFs (48). This may be easily seen from fig. 5a, where the set of lexically ordered paths corresponding to the diagram from fig. 4 is presented. To remove this

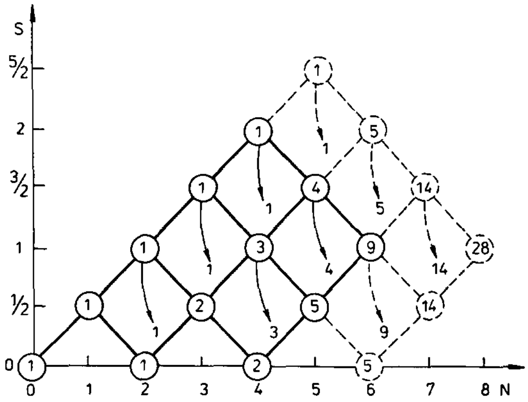


Fig. 4. Branching diagram for $S=1$, $N=6$ (full lines). The broken lines show an extension to the case of $S=1$, $N=8$. At arcs and vertices their weights (if different from 0) are shown. The origin of the arc weights is indicated by arrows.

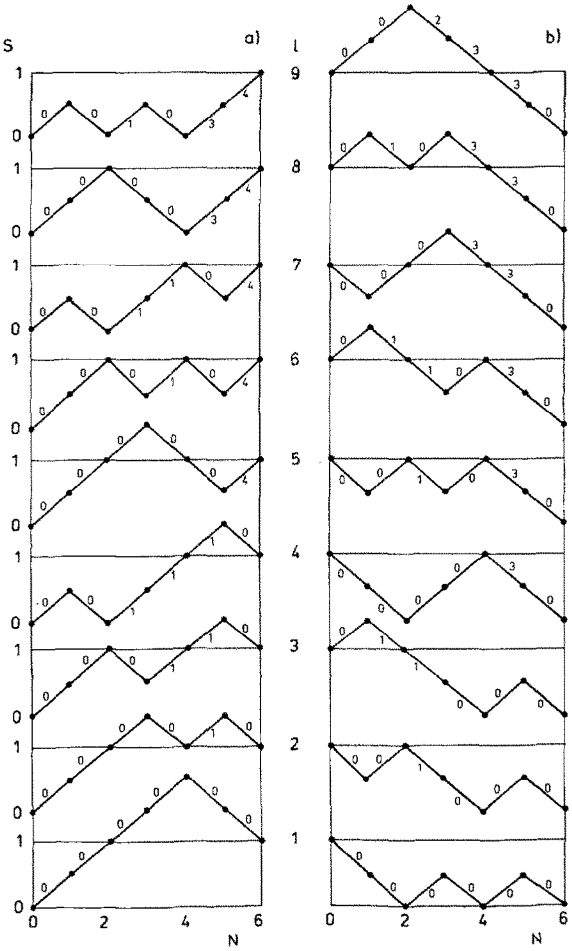


Fig. 5. The paths corresponding to 9 eigenfunctions of $\hat{S}^2$ for $S=1$, $N=6$ in the lexical order (a) and in the reversed lexical order (b). Each arc is supplied with its weight.

drawback, two operations should be performed: the reverse numbering of electrons and the reverse lexical ordering of the spin functions.

A branching diagram corresponding to the reverse electron numbering (reversed branching diagram) has a rather different interpretation than the ordinary one. In the reversed diagram vertex $(0, S)$ ((N, S) in the ordinary one) is its head and vertex $(N, 0)$ ($(0, 0)$ in the ordinary one) is its tail. In general, there is no relation between the weights $d_r(k, S_k)$ of the reversed diagram vertices and $f(S_k, k)$ numbers, except that $d_r(k, 0) = f(S, k)$. The weights of the vertices corresponding to $S \neq 0$ may be considered as counting indices only. The reversed lexical index l_r is given by

$$l_r = 1 + \sum_{k=1}^{N} y_r(k, S_k), \tag{88}$$

where y is either

$$y_{\mathrm{r}}^{-}(k,\, S_k) = \begin{cases} d_{\mathrm{r}}(k-1,\, S_k-1/2), & \text{if vertex } (k-1,\, S_k-1/2) \text{ belongs to the graph,} \\ 0, & \text{otherwise,} \end{cases} \tag{89}$$

or

$$y_{\mathrm{r}}^{+}(k,\, S_k) = 0. \tag{90}$$

Eqs. (88) and (89) are analogues of eqs. (87) and (85), respectively. There is, however, an important difference between eqs. (88) and (87). In the case of a reversed diagram the arc indices of SCPs are always 0. Therefore they do not contribute to l_{r} and in eq. (88) it is sufficient to extend the sum over singles rather than over all electrons. An example of a reversed branching diagram is shown in fig. 6. The corresponding paths (in reversed lexical order) are displayed in fig. 5b.

Since a contribution to l_{r} from a SCP is always 0, adding to the reversed diagram an arbitrary tail consisting of SCPs does not change neither the indexing of the remaining part of the diagram nor the numbering of the spin functions. A more general case is shown in fig. 7. Here we have two subsystems of electrons. The first one, consisting of s_1 electrons, is coupled to spin S ($S=1$ in fig. 7), the second one (s_2-electron) to a singlet. Then, the N-electron diagram is composed of two: s_1- and s_2-electron diagrams. There exists a simple relation between reversed lexical indices of N-, s_2- and s_1-electron cases:

$$l_{\mathrm{r}}(N) = (l_{\mathrm{r}}(s_2) - 1) f(S,\, s_1) + l_{\mathrm{r}}(s_1). \tag{91}$$

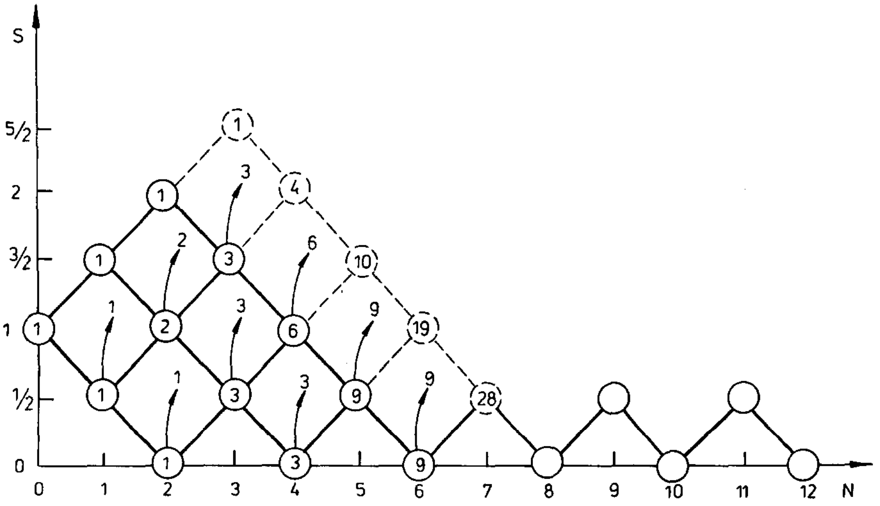


Fig. 6. Reversed branching diagram for $S=1$, $N=12$. Either 6 (full lines) or 8 (broken lines) electrons may be coupled in all the ways resulting from the YK scheme. The remaining electrons form SCPs. Designations as in fig. 4.

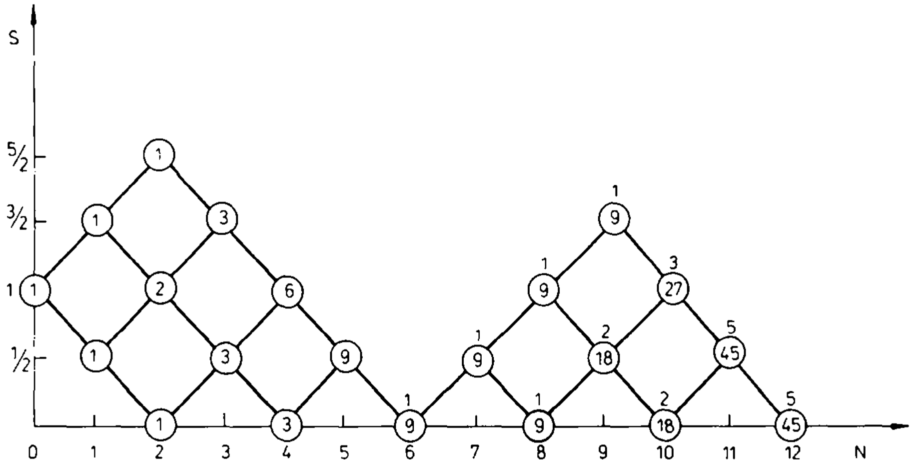


Fig. 7. Reversed branching diagram for a twelve-electron ($S=1$) system divided into two subsystems: the first 6 electrons are coupled to a triplet, the second 6 to a singlet. Only vertex weights are inscribed into the diagram. An independent indexing of the singlet part is inserted above the vertices.

Most important, the structure of the S-coupled (s_1-electron) part of the diagram does not depend upon a specific form of the singlet-coupled (s_2-electron) part. The total number of N-electron spin functions is then

$$f(0, s_1; S, s_2) = f(0, s_2) \times f(S, s_1). \tag{92}$$

Particularly useful kinds of the singlet-coupled parts correspond to $s_2 = 2$ (SCP, already discussed) and to $s_2 = 4$. The case of a singlet-coupled quadruplet (SCQ) appears to be of a fundamental importance when a general first-order-interaction space [134] is constructed. This subject will be discussed in more detail later in this work.

1.4.2. Orbital functions: configuration graph

A diagram representing a configuration set may be constructed in a complete analogy to the spin branching diagram. Similarly as in the spin case (eq. (80)), a configuration λ may be represented by an array

$$\mathbf{T}^{\lambda}(l) = [N_0, N_1, \dots, N_n], \quad l = 1, 2, \dots, K_c, \tag{93}$$

where K_c is the number of configurations, N_k is the number of electrons occupying the first k orbitals, i.e. $N_0 = 0$, $N_n = N$ and

$$n_k = N_k - N_{k-1} \tag{94}$$

is the occupation number of φ_k in λ. The array may be represented graphically on a grid in which the horizontal position equals N_k and the vertical one k. The graphical representation of

$\mathbf{T}^{(\lambda)}$ is a directed path consisting of arcs joining consecutively vertices $\{k, N_k\}_{k=0}^{n}$. To an arc contained between $k-1$ and k we assign the number k. The slope of the arc represents the occupation number n_k. Since $n_k = 0, 1, 2$, there are at most 3 arcs off a vertex. Each path starts at the head of the graph ((0, 0) vertex) and ends at its tail ((n, N) vertex). Similarly as in the case of the branching diagram we define a complete graph (describing a full CI basis) and a restricted one. Examples are shown in figs. 8 and 9.

To (k, N_k) vertex we assign the lexical weight of the vertex

$$D(k, N_k) = D(k-1, N_k) + D(k-1, N_k - 1) + D(k-1, N_k - 2) \tag{95}$$

equal to the number of paths beginning at the head and passing through the vertex. To the arc

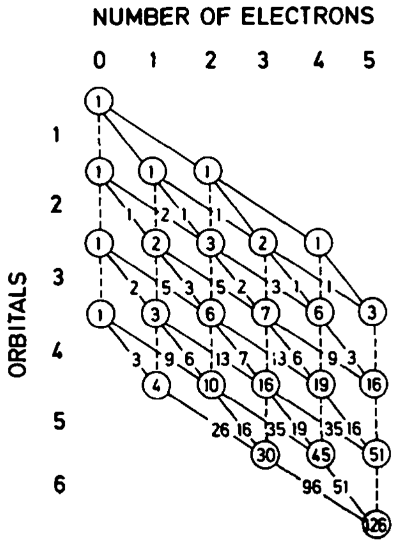


Fig. 8. Orbital graph describing full CI basis for the case of 5 electrons and 6 orbitals. The set of 126 configurations corresponds to 210 doublet, 84 quartet and 6 sextet CSFs. At the arcs and vertices their weights (if different from 0) are shown.

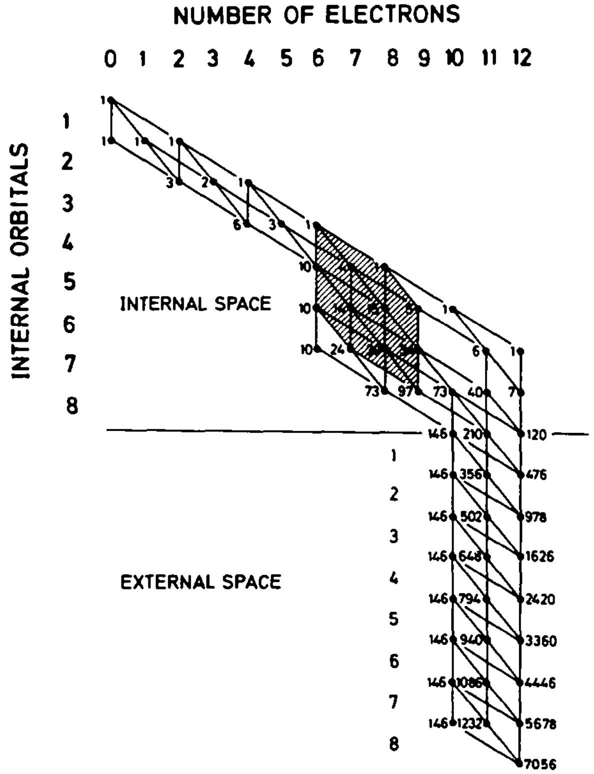


Fig. 9. Orbital graph for 12 electrons, 8 internal and 8 external orbitals. At least 6 electrons occupy the first 4 internal orbitals. The external space may be occupied by, at most, 2 electrons. Vertex (7, 10) and the arc contained between vertices (8, 9) and (9, 10) have been removed from the graph and, in consequence, the number of paths has been reduced from 11703 to 7056 (cf. ref. [37]). The shadow area indicates the part of the graph discussed in section II.1.2.

contained between $(k-1, N_k-n_k)$ and (k, N_k) vertices we assign the lexical arc index

$$Y(k, N_k)=\sum_{i=0}^{n_k-1} D(k-1, N_k-i). \tag{96}$$

If eq. (95) or (96) refers to a vertex that does not belong to the graph, then the corresponding contribution is 0, $D(0, 0)=1$, and $Y(k, N_k)=0$ if $n_k=0$. The lexical index m_λ of the path λ passing through the ordered set of vertices $\{k, N_k\}_{k=0}^{n}$ is given by [14,33]

$$m_\lambda=1+\sum_{k=1}^{n} Y(k, N_k). \tag{97}$$

Both lexical weights and lexical arc indices are shown in the graph in fig. 8.

As in the case of branching diagrams, the reversed lexical ordering may also be established in the case of configuration graphs. However, in this case it is not so important as in the spin case, though it may be sometimes helpful in forming loops over selected sets of configurations. The idea of the reversed lexical ordering is here similar to that in the spin case and therefore will not be discussed in more detail (in practice one may obtain the reversed lexical ordering by turning the graph upside down before assigning to it the indices).

Every path in the graph represents an orbital configuration $|\lambda\rangle$ and every configuration $|\lambda\rangle$ is associated with an $f(S, s)$ component configuration state vector $|\lambda; \boldsymbol{SM}\rangle$. A mapping of the lexical indices of the paths to the elements of the variational vector $\boldsymbol{C}$ of the CI method (eq. (16)) is facilitated by introducing the index vector $I(m_\lambda)$. The component C_I of the vector $\boldsymbol{C}$ corresponding to $|\lambda; SM, k\rangle$, $k=1$, has the address

$$I(m_\lambda)=1+\sum_{m=1}^{m_\lambda-1} f(S, s_m), \tag{98}$$

where s_m is the number of singles in the path with the lexical index m. The components of the index vector may be calculated recursively:

$$I(m+1)=I(m)+f(S, s_m). \tag{99}$$

The lexical indices of the paths may be mapped to the components of $\boldsymbol{C}$ in any other unique way. As a practical alternative of the lexical ordering it may be convenient to divide configurations into groups according to the number of singles, i.e. according to the number of components of the corresponding $|\lambda; \boldsymbol{SM}\rangle$ vectors. Then the elements of the index vector may be ordered with respect to two indices: the number of singles s and, for each s, the lexical index m_λ^s.

For practical purposes, some of the configurations – usually the ones giving the most important contributions to the CI expansion (eq. (16)) – are distinguished as the *reference configurations*. In discussing the strategy we assume that the only configurations to be included in the CI calculations are the ones which differ by at most two orbitals from at least one reference configuration. We say that only singly and doubly excited configurations are taken into account. A selection of the reference configurations may be based either upon physical intuitions or upon results of some preliminary calculations, but there exists no formal limitation as far as their number or structure is concerned. The assumptions on a division of configurations into two sets are aimed at a minimization of the length of the CI expansion and, though they lead to a complication of the formal structure of the algorithm, are necessary if we intend to have an efficient CI program. We should note that these assumptions offer some additional options and do not limit generality of the method. In particular, an expansion described by an arbitrary graph, with no path removed (also the full CI expansion), may be obtained as a special case of the one described here, if all configurations are handled as the reference configurations.

In connection with selecting the set of the reference configurations we divide the orbital space V_n^{o} into 3 major subspaces – the doubly occupied space $\mathscr{D}(n_{\mathrm{D}})$, the active space $\mathscr{A}(n_{\mathrm{A}})$ and the external space $\mathscr{E}(n_{\mathrm{E}})$, i.e.

$$V_n^{\mathrm{o}} = \mathscr{D}(n_{\mathrm{D}}) \oplus \mathscr{A}(n_{\mathrm{A}}) \oplus \mathscr{E}(n_{\mathrm{E}}),$$

where n_{D}, n_{A} and n_{E} are dimensions of the corresponding subspaces. The doubly occupied space consist of the orbitals $\{d_k\}_{k=1}^{n_{\mathrm{D}}}$, being doubly occupied in all the reference configurations. The external space consists of the orbitals being empty in all the reference configurations. All the other orbitals, $\{a_k\}_{k=1}^{n_{\mathrm{A}}}$, belong to the active space. The orbitals belonging to either $\mathscr{D}(n_{\mathrm{D}})$ or to $\mathscr{A}(n_{\mathrm{A}})$ are said to form the internal space $\mathscr{I}(n_{\mathrm{I}})$

$$\mathscr{I}(n_{\mathrm{I}}) = \mathscr{D}(n_{\mathrm{D}}) \oplus \mathscr{A}(n_{\mathrm{A}}).$$

Then

$$V_n^{\mathrm{o}} = \mathscr{I}(n_{\mathrm{I}}) \oplus \mathscr{E}(n_{\mathrm{E}}).$$

The last kind of division is most important as far as applications are concerned. The orbitals forming the internal space (internal orbitals) are designated i_k, $k = 1, 2, \ldots, n_{\mathrm{I}}$, or φ_i, φ_j, φ_k, φ_l. The external orbitals are designated e_k, $k = 1, 2, \ldots, n_{\mathrm{E}}$, or φ_a, φ_b, φ_c, φ_d.

Since in general the external space is on one hand rather large and on the other has a relatively simple structure, it is useful to consider the contributions from the internal and external spaces separately, as it was done by Siegbahn in the UGA context [35,101]. In fig. 10 several examples of external spaces of 6 orbitals are shown. The case presented in fig. 10a is particularly important. Therefore we shall discuss it in more detail. The external and internal spaces are joined together in 3 vertices labeled V, S, D. The paths, corresponding to configurations consisting of the internal orbitals only, pass through the vertex V. The paths which correspond to single and double excitations from the internal space pass through the vertices S and D, respectively. It is convenient to split vertex D into two subvertices D1 and D2 corresponding, respectively, to configurations with one external double and with two external singles. The numbers K_{V}, K_{S}, K_{D1} and K_{D2} of paths passing through the vertices indicated as the subscripts are:

$$\begin{aligned} K_{\mathrm{V}} &= D(n_{\mathrm{I}}, N), & K_{\mathrm{S}} &= n_{\mathrm{E}} D(n_{\mathrm{I}}, N-1), \\ K_{\mathrm{D1}} &= n_{\mathrm{E}} D(n_{\mathrm{I}}, N-2), & K_{\mathrm{D2}} &= \tbinom{n_{\mathrm{E}}}{2} D(n_{\mathrm{I}}, N-2), \end{aligned} \tag{100}$$

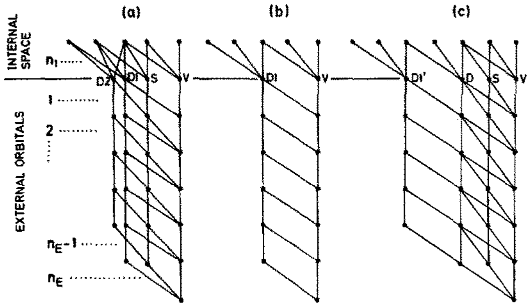


Fig. 10. External space. (a) The case discussed in detail in this paper. In configurations corresponding to the paths passing through vertices V, S, D, respectively, 0, 1, 2 electrons occupy the external space. Vertex D has been splited into subvertices D1 (1 external double) and D2 (2 external singles). (b) A simplified version of (a) with vertices D2 and S being removed. Only doubles are allowed in the external space. In this case separation of the external space is trivial (cf. sections I.5.2 and II.2.3). (c) An example of the case of 4 electrons, but at most 2 singles, in the external space. The algorithms discussed in sections I.5.2 and II.2.3 may be generalized in a rather straightforward way to cover also more general cases of 2 singles in the external space.

Now we adopt the following numbering of the paths. Let the paths in the internal space be numbered lexically and let the numbering of the paths passing through V, S, D vertices be independent The lexical indices of the internal paths connected with each of these vertices are

$$m_V = 1, 2, \ldots, D(n_I, N), \quad m_S = 1, 2, \ldots, D(n_I, N-1), \quad m_D = 1, 2, \ldots, D(n_I, N-2). \tag{101}$$

Then the consecutive numbers of the complete paths (including both internal and external space contributions) are

$$\begin{aligned} &M_V = m_V, \quad M_S = K_V + n_E(m_S - 1) + a, \\ &M_{D1} = K_V + K_S + n_E(m_D - 1) + a, \\ &M_{D2} = K_V + K_S + K_{D1} + \binom{n_E}{2}(m_D - 1) + \binom{\max(a, b) - 1}{2} + \min(a, b), \quad a, b = 1, 2, \ldots, n_E, \end{aligned} \tag{102}$$

where V, S, D1, D2 refer to the vertices the paths pass through, and a, b are the orbital indices of the occupied external space orbitals. As seen, the contributions from the external space to the lexical indices of the paths have a very simple form. Therefore it is sufficient to form the index vector for the internal space only. The external space contributions may easily be calculated using eqs. (102).

If the orbitals are symmetry-adapted then, in the case of the Abelian groups, the direct product of the orbital representations gives the representation of the wavefunction. The problem is essentially the same as in the GUGA. In the simplest method, proposed by Siegbahn [35,101], one removes the configurations with wrong symmetry by means of the index vector. One may also impose the symmetry restrictions upon the graph using separate labeling for different representations as proposed by Shavitt [135] or expanding the graph as it was done by Brooks and Schaefer [38]. A useful compromise is to introduce the symmetry vertices in the external space only, so that instead of S or D vertices we shall get a number of S and D vertices, one for each representation. In the internal part of the graph we have to use the index vector in which the additional information about the symmetry of the external part may be placed.

Finally, a few words should be added about a computer representation of the graph. The information required is: for every orbital φ_k a list of all possible values of N_k. For every (k, N_k) pair only 2 numbers are needed – the values of $Y(k, N_k)$ for $n_k = 1, 2$ (eq. (96)). A practical computer representation of the graph is given in part II of this paper.

The graphical ideas presented here are closely related to the Shavitt's graphical representation [14,33] of the Gelfand–Zetlin basis adapted to the molecular quantum mechanics by Paldus [13]. In particular, the spin branching diagram and the configuration graph, as described in this chapter, may be considered as subgraphs of the UGA graph. By removing from the UGA graph the vertices describing spin couplings, we obtain the orbital graph; if we draw the UGA graph for a single orbital configuration, we obtain the spin branching diagram (see also refs. [87]). In fact, the separate treatment of both the subgraphs (the branching diagram being completely independent of the CI basis actually used) is one of the most important advantages of SGGA. Due to removing the spin coupling information from the orbital graph, the number of paths is reduced and the index vector is much shorter than the vector C. For example, the length of the index vector (i.e. the weight of the tail) in the case presented in fig. 8 is 126 while the length of the vector C (i.e. the dimension of the CI basis) is, in the case of doublets, 210.

I.4.3. Representation matrices

A permutation P, acting on a spin eigenstate $|SM, i\rangle$, transforms it into a linear combination of several other states $|SM, j\rangle$, the coefficients of this combination being equal to $\epsilon(P)U_S^N(P)_{ji}$ (cf. eq. (55)). The state (path) $|SM, i\rangle$ is referred to as the *parent state* (*parent path*) and the set of the states $|SM, j\rangle$, $j \neq i$, for which $U_S^N(P)_{ji} \neq 0$ as the *daughter states* (*daughter paths*). The set of the daughter paths together with the parent one, is represented by the *P-generated graph*, being a part of the reversed branching diagram.

The parent and the daughter paths form loops in the P-generated graph. The concept of a loop is very useful in formulating matrix element evaluation procedures. In UGA a loop in the UGA graph is associated with segment values which depend upon its location in the graph [33,137]. The value of a coupling constant is expressed as a product of the segment values. A similar concept is applicable also in SGA, though in a simplified form. For example, in the case of the $\mathbf{U}_S^N$ matrix elements corresponding to single cycles (in UGA it corresponds to matrix elements of single unitary group generators), only two loops have to be considered [129].

a) Elementary transpositions

A transposition $(k, k-1)$ which interchanges two adjacent elements is called an elementary transposition. When acting on spin functions represented by a reversed branching diagram, it affects only arcs $k-1$ and k, i.e. the path segments contained between nodes with abscissae

$k-2$ and k (segments no. k). There are four kinds of the segments: two upright ones

$A^k_{-1} =$  , $A^k_1 =$  (103a)

and two bend ones

$B^k_{-1} =$  , $B^k_1 =$  , (103b)

where the graphical symbols visualise the appropriate fragments of the path. All paths in a branching diagram may be divided into four groups, according to the kind of segment formed by the arcs $k-1$ and k. To each of these groups a set of the reversed lexical indices of the corresponding paths is assigned. The sets of the indices are designated $\{A^k_{-1}\}$, $\{A^k_1\}$, $\{B^k_{-1}\}$ and $\{B^k_1\}$, according to the notation introduced by eqs. (103). If we wish to refer to a certain segment type (either to an upright or to a bend one), designations A^k and B^k will be used.

We denote $s(k-1, k)_i$ the kth segment of $|SM, i\rangle$. An individual spin function may then be denoted $|SM, i\rangle = |L_i, s(k-1, k)_i, R_i\rangle$ where L_i (R_i) are the parts of the path standing to the left (right) of the segment no. k. More explicitly, $|SM, i\rangle$ may be represented in one of the following ways: $|L_i A^k_{-1} R_i\rangle$, $|L_i A^k_1 R_i\rangle$, $|L_i B^k_{-1} R_i\rangle$, $|L_i B^k_1 R_i\rangle$. As results from eqs. (72) and (71)

$$(k, k-1)\ |L_i A^k R_i\rangle = |L_i A^k R_i\rangle, \tag{104}$$

$$(k, k-1)\ |L_i B^k_{-1} R_i\rangle = -a_k\ |L_i B^k_{-1} R_i\rangle + b_k\ |L_i B^k_1 R_i\rangle, \tag{105}$$

$$(k, k-1)\ |L_i B^k_1 R_i\rangle = a_k\ |L_i B^k_1 R_i\rangle + b_k\ |L_i B^k_{-1} R_i\rangle, \tag{106}$$

where

$$a_k = 1/(2S_k+1), \quad b_k = \sqrt{1-a_k^2}\,. \tag{107}$$

Then, according to eq. (55),

$$U^N_S((k, k-1))_{ii} = \begin{cases} -1, & \text{if } i \in \{A^k\}, \\ -m a_k, & \text{if } i \in \{B^k_m\}. \end{cases} \tag{108}$$

Similarly for the off-diagonal elements ($j > i$)

$$U^N_S((k, k-1))_{ji} = \begin{cases} -b_k, & \text{if } L_j = L_i,\ R_j = R_i,\ s(k-1, k)_j = B^k_{-1},\ s(k-1, k)_i = B^k_1, \\ 0, & \text{otherwise} \end{cases} \tag{109}$$

and $U_S^N((k, k-1))_{ij} = U_S^N((k, k-1))_{ji}$. Hence, a nonzero off-diagonal matrix element corresponds to the paths $|SM, j\rangle$ and $|SM, i\rangle$ forming a loop consisting of two bend segments.

It is convenient to distinguish two different types of the loops, depending on whether the parent path contributes B_{-1}^k or B_1^k segment to the loop. Having in mind a generalization for the single cycle matrix element case (cf. the next section) we define, within each of the two types, two forms of loops depending on which arc (rather than which segment) belongs to the parent path: form R if it is either the upper-right or the lower-right arc, and form L if it is either the upper-left or the lower-left arc. All these loops are shown in fig. 11. No other loops may appear if we limit our considerations to a single cycle. The arcs forming a loop are assigned with the arc values $\pm a_k$ and b_k, as shown in fig. 11. Though matrix elements of $\mathbf{U}_S^N((k, k-1))$ are determined by these values, their direct evaluation from eqs. (108), (109) is so simple that any reference to the corresponding loops is perhaps superfluous. As we shall see later, this is not the case if the permutation is more complicated.

Since the contribution of B_{-1}^k to the lexical index is equal to $d_r(k-1, S_k - 1/2)$ and that of B_1^k is $d_r(k-2, S_k - 1)$ (see eq. (89), the indices of nonzero off-diagonal matrix element (109) fulfil the relation

$$j - i = d_r(k-1, S_k - 1/2) - d_r(k-2, S_k - 1). \tag{110}$$

When combined with eq. (109) it gives the explicit structure of the representation matrix

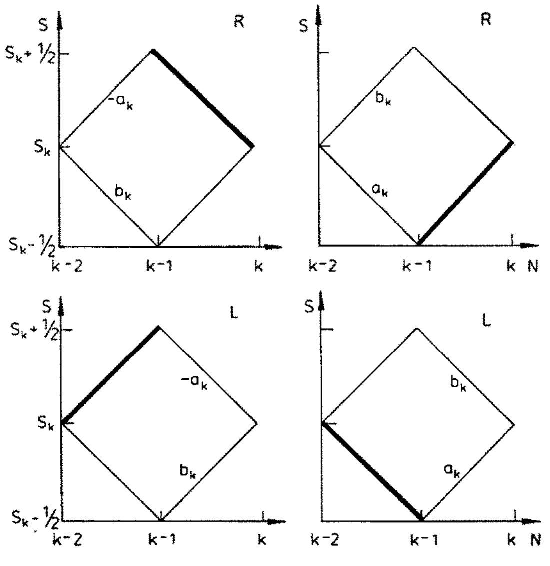
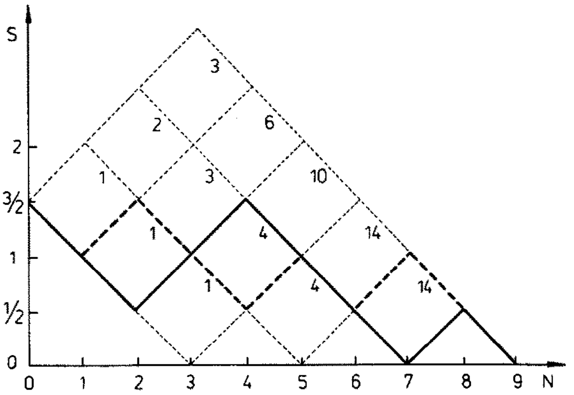


Fig. 11. Loops in a reversed branching diagram formed by two bend segments. Arcs of the parent paths used to determine the loop forms (either R or L) are indicated by heavy lines. In each case the arc values different from 1 are shown.



P	(12)	(23)	(34)	(45)	(56)	(67)	(78)	(89)
$U(P)_{99}$	-1	$-1/3$	-1	$1/3$	-1	-1	$-1/2$	1

$U(23)_{9,10} = U(45)_{6,9} = -\sqrt{8/3}$; $U(78)_{9,23} = -\sqrt{3/2}$

Fig. 12. Parent path (full line) and all the daughter paths (broken lines) generated from it by elementary transpositions in a reversed branching diagram (dotted lines). The arcs are provided with their nonzero weights. Nonzero matrix elements in which the parent path (no. 9) is involved are also given.

corresponding to an elementary transposition. An example of a parent path and of daughter paths generated by all elementary transpositions is shown in fig. 12. Nonzero matrix elements in which the parent path is involved, calculated directly from the graph according to eqs. (108), (109) and (110) are also displayed in the figure.

b) A single cycle

Let us consider a cycle $(k..l)=(k,\ k-1)(k-1,\ k-2)\ldots(l+1,\ l),\ k>l$. The sequence of the elementary transpositions transforms consecutive segments of the paths according to eqs. (104)–(106), and the cycle transforms the path representing $|SM,\ i\rangle$ into the cycle-generated graph. We may formulate the following rule for constructing the cycle-generated graph: take a path $|SM,\ i\rangle$ and move along it from the segment no. $l+1$ to the segment no. k; whenever a bent segment $B_m^j(j=l+1,\ l+2,\ldots,\ k;\ m=-1,\ 1)$ is met complete it to the loop corresponding to $(j,\ j-1)$ transposition; assign to the arcs no. $j-1$ of the loop the arc values $D(j-1)_i$ equal to $\pm a_j$ or b_j, as it is shown in fig. 11, loops R; if an edge of the newly formed loop makes together with an arc of the parent loop a bend segment, proceed in the same way. To the arcs of the cycle-generated graph to which no arc value has been assigned in the build-up procedure, assign value 1. Then,

$$D(j-1)_i=\begin{cases}\pm a_j, & \text{if in the } R \text{ loop arc no. } j-1 \text{ is perpendicular to arc no. } j \text{ of the parent path,}\\ b_j, & \text{if in the } R \text{ loop arc no. } j-1 \text{ is parallel to arc no. } j \text{ of the parent path,}\\ 1, & \text{otherwise.}\end{cases} \tag{111}$$

For the cycle $(l..k)=(k..l)^{-1}$ the procedure is the same, except that we start from the segment no. $k-1$ and that the loops L rather than R have to be used. Examples of the cycle-generated graphs are shown in fig. 13.

The number of paths in a cycle-generated graph, $r(k-l)_i$, ranges from 1 – if all the segments of the cycle-affected part of $|SM,\ i\rangle$ are the upright ones – to $r(k-l)_{\max}$, where $r(1)_{\max}=2$, $r(2)_{\max}=3$ and $r(n+1)_{\max}=r(n)_{\max}+r(n-1)_{\max}$ – if $|SM,\ i\rangle$ consists of the bend segments only. The value of $r_{\max}$ is equal to the number of nonzero elements in one row (column) of the representation matrix. It is interesting to note, that $r_{\max}$ depends on the cycle length only and does not depend on the matrix size [129] *.

Matrix elements $U_S^N((k..l))_{ji}$, for a given i, may be obtained by a successive application of eqs. (104)–(106) to the elementary transpositions forming the cycle. The matrix element is equal to the product of contributions from consecutive segments forming the jth path, multiplied by $\epsilon((k..l))=(-1)^{k-l}$. However, the simplest way to evaluate all nonzero elements of the ith column of $\mathbf{U}_S^N((k..l))$ is to use the cycle-generated graph. As one can easily see

$$U_S^N((k..l))_{ji}=(-1)^{k-l}\prod_{n_j=l}^{k}D(n_j)_i, \tag{112}$$

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* The sequence $r(n)_{\max}$ is the Fibonacci sequence [136].

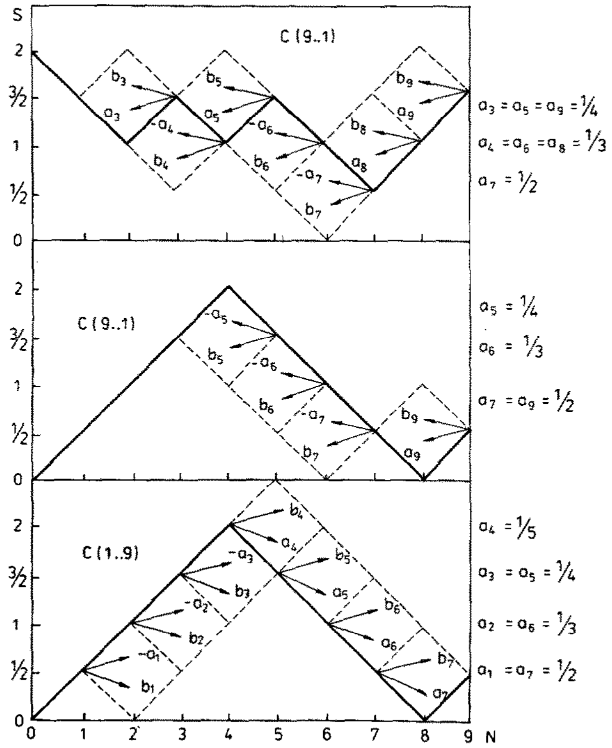

Fig. 13. Examples of cycle generated graphs. At each arc its arc value (if different from 1) is shown. The origin of the arc values is indicated by arrows.

where $D(n_j)_i$ are the arc values of the arcs forming the path which corresponds to $|SM, j\rangle$. Examples are shown in fig. 13.

When constructing $\mathbf{U}_S^N((k..l))$ one can evaluate all nonzero elements of the ith column simultaneously. All of the $r(k-l)_i$ products given by eq. (112) can be calculated in one loop. Since many fragments of the paths in a cycle-generated graph are the same, it allows us to avoid reiterated multiplications. A detailed discussion of the optimization of the algorithm based on eqs. (111) and (112) is given in ref. [129].

c) Shift of a singlet-coupled pair

Using relations (105) and (106) one may easily construct combinations of the YK spin functions which possess some required transformation properties. In particular, a combination

$$|L_i \circ\!\!-\!\!\circ R_i\rangle = \sqrt{\frac{1+a_k}{2}}\ |L_i B_{-1}^k R_i\rangle - \sqrt{\frac{1-a_k}{2}}\ |L_i B_1^k R_i\rangle \tag{113}$$

is antisymmetric with respect to $(k-1,\ k)$ transposition

$$(k-1,\ k)\ |L_i \circ\!\!-\!\!\circ R_i\rangle = -\ |L_i \circ\!\!-\!\!\circ R_i\rangle, \tag{114}$$

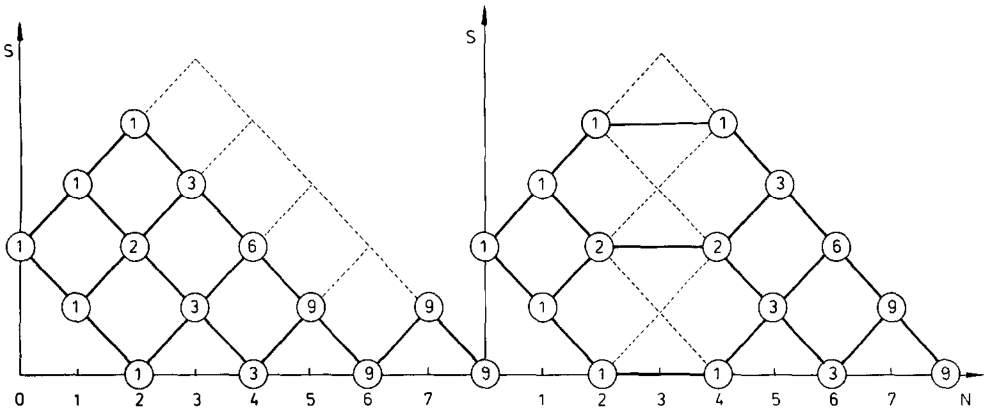

Fig. 14. Shift of a singlet-coupled pair from 7, 8 to 3, 4 position in $N=8$, $S=1$ reversed branching diagram.

i.e. represents spins $k-1$ and k being coupled to a singlet. Similarly, the combination orthogonal to (113)

$$|L_i \circ\!\!-\!\!\times\!\!-\!\!\circ\, R_i\rangle = \sqrt{\frac{1-a_k}{2}}\;\; |L_i B^k_{-1} R_i\rangle + \sqrt{\frac{1+a_k}{2}}\;\; |L_i B^k_1 R_i\rangle \tag{115}$$

is symmetric with respect to $(k-1,\ k)$, i.e. spins $k-1$ and k are here coupled to a triplet.

Let us assume that a SCP has to be shifted from the position $N-1$, N (in the reversed branching diagram) to the k, $k+1$ one. The corresponding transformation of the branching diagram is shown in fig. 14. Since a SCP shift does not change the coupling schemes, except for a renumbering of spins in the part of the diagram affected by the shift, we may write for a spin eigenfunction $|SM,\ i\rangle \equiv |L_i(1, 2, \ldots, k-1) R_i(k, \ldots, N-2) \circ\!\!-\!\!\circ\rangle$

$$\begin{aligned}(k..N)(k..N)\ & |L_i(1, \ldots, k-1) R_i(k, \ldots, N-2) \circ\!\!-\!\!\circ\rangle \\ =\ & |L_i(1, \ldots, k-1) \circ\!\!-\!\!\circ\, R_i(k+2, \ldots, N)\rangle,\end{aligned} \tag{116}$$

where L_i and R_i stand for the pertinent parts of the path. Then, due to eq. (113),

$$U^N_S((k..N)(k..N))_{ji} = \begin{cases} -m\sqrt{(1-ma_{k+1})/2}\,, & \text{if } \langle SM,\ j| \ = \langle L_i B^{k+1}_m R_i|\ , \\ 0, & \text{otherwise.}\end{cases} \tag{117}$$

Eq. (116) leads to another useful relation

$$(k..l)\ |\ldots R_i(k,\ k+1, \ldots, l-2) \circ\!\!-\!\!\circ\ \ldots\rangle = (l..k)\ |\ldots \circ\!\!-\!\!\circ\, R_i(k+2,\ k+3, \ldots, l) \ldots\rangle, \tag{118}$$

where only the parts of the paths affected by the cycles are written explicitly.

Let $y_r^-(p, S_p)_i$ and $y_r^-(p, S_p)_j$ be the reversed lexical arc indices (89) corresponding to the paths $|SM, i\rangle$ and $|SM, j\rangle$, respectively. The reversed lexical indices j and i of the paths giving nonzero matrix elements (117) are connected in a simple way

$$y_r^-(p, S_p)_i = \begin{cases} y_r^-(p, S_p)_j, & \text{if } p < k, \\ 0, & \text{if } p = k,\ k+1, \\ y_r^-(p-2, S_p)_j, & \text{if } p > k+1, \end{cases} \tag{119}$$

and the indices i and j are given by eq. (88). The matrix given by eqs. (117) and (119) is a rectangular one: since the spins $N-1$ and N in $|SM, i\rangle$ form a SCP, we have $i = 1, 2, \ldots, f(S, N-2)$, while $j = 1, 2, \ldots, f(S, N)$. The structure of this matrix is very simple – there is at most one nonzero element in a row and either one or two nonzero elements in a column.

The results may be generalized in a straightforward way for the case of a shift of two (or more) SCPs. Eq. (116), generalized for the case of two SCPs, says:

$$\begin{aligned} &(l..N-2)^2(k..N)^2\ |L_i(1, \ldots, k-1)R_{1i}(k, \ldots, l-3)R_{2i}(l-2, \ldots, N-4)\circ\!\!-\!\!\circ\ \circ\!\!-\!\!\circ\rangle \\ &\quad = |L_i(1, \ldots, k-1)\circ\!\!-\!\!\circ\, R_{1i}(k+2, \ldots, l-1)\circ\!\!-\!\!\circ\, R_{2i}(l+2, \ldots, N)\rangle \end{aligned} \tag{120}$$

and eq. (117)

$$\begin{aligned} &U_S^N\big((l..N-2)^2(k..N)^2\big)_{ji} \\ &\quad = \begin{cases} m_1 m_2\sqrt{(1-m_1 a_{k+1})(1-m_2 a_{l-1})}\,/2, & \text{if } \langle SM, j| = \langle L_i B_{m_1}^{k+1} R_{1i} B_{m_2}^{l+1} R_{2i}|\ , \\ 0, & \text{otherwise}, \end{cases} \\ &\quad j = 1, 2, \ldots, f(S, N), \quad i = 1, 2, \ldots, f(S, N-4), \end{aligned} \tag{121}$$

where at most 4 nonzero elements may appear in a column and at most 1 in a row, independently of the dimension of $\mathbf{U}_S^N$. Similarly as in the previous case, the relation between the reversed lexical indices of $|SM, i\rangle$ and $|SM, j\rangle$ may easily be expressed in terms of the pertinent reversed lexical arc indices.

d) Products of two cycles

As will be shown in the next section, eqs. (116) and (117) allows us to express all permutations met in the Hamiltonian matrix element formulae as products of at most two cycles and of a permutation shifting at most two SCPs

$$P_0 = (k..l)(i..j)P_S, \tag{122}$$

where P_S is the SCP shift operator. In particular,

$$(k, l) = (k..l + \epsilon_{kl})(l..k) = (l..k)(k - \epsilon_{kl}..l),$$

where $\epsilon_{kl} = \mathrm{sgn}(k - l)$. Therefore, the last algorithm we need to complete the considerations on the spin space properties, is the one to calculate the representation matrix elements of products of two cycles. Two cases should be considered: (i) nonoverlapping cycles, i.e. having at most one element in common, and (ii) overlapping cycles.

Matrix elements for nonoverlapping cycles may be calculated using exactly the same method as the one developed for a single cycle. The graph generated by a product of two nonoverlapping cycles has the same properties as the one generated by a single cycle. Matrix elements of the representation matrix are given by eq. (112), except that the range of the product is extended over the two cycles.

If the cycles do overlap, the overlapping part must be treated in a different way. Also in this case each $\mathbf{U}_S^N$ matrix element may be expressed as a product (or rather as a linear combination of two products) of appropriate segment values. However, on one hand, the algorithm is more complicated and, on the other, the overlapping parts of cycles are relatively rarely met. Therefore it seems to be more convenient to use the following very simple method based on the idea of multiplying properly chosen, sparse, single-cycle representation matrices [129]:

- Express the overlapping part P^{o} of a two-cycle product in terms of two- and three-element cycles

  $$P_0 = P^n P^{\mathrm{o}} P^{n'} = P^n P_q \dots P_2 P_1 P^{n'}, \tag{123}$$

  where P^n and $P^{n'}$ are the nonoverlapping parts of P_0 and $P_1, P_2, \dots, P_q$ are two- or three-element cycles. For example,

  $$\begin{aligned} P_0 &= (3..8)(4..12) = (3,\,4)(4..8)(4..8)(8..12) \\ &= (3,\,4)(6..4)(7..5)(8..6)(8..12) = P^n P_3 P_2 P_1 P^{n'}. \end{aligned}$$

- Construct the ith column of $\mathbf{U}_S^N(P^{n'})$ matrix corresponding to the nonoverlapping part of the cycle according to eq. (112). In the example $P^{n'} = (8..12)$.
- Calculate nonzero elements of the consecutive rows of $\mathbf{U}_S^N(P_1)$, according to eqs. (108), (109) or (112) and then the elements of the ith column of $\mathbf{U}_S^N(P_1 P^{n'})$. Since in a row of a two-element (three-element) cycle representation matrix three are at most $r(1)_{\max} = 2$ ($r(2)_{\max} = 3$) nonzero elements, an element of the new column is expressed as a linear combination of at most 2 (3) elements of the column already in the computer memory.
- Repeat the same procedure calculating recurrently $P_2(P_1 P^{n'})$, $P_3(P_2 P_1 P^{n'}), \dots$.

Calculating elements of a single column of $\mathbf{U}_S^N$ rather than of the whole matrix may be essential as a space-saving approach, when dimensions of $\mathbf{U}_S^N$ are very large. Since

$$\mathbf{U}_S^N(P^+) = \mathbf{U}_S^N(P)^{\mathrm{T}}, \tag{124}$$

where T means transposition, a row of $\mathbf{U}_S^N$ matrix rather than a column may be constructed using the same procedure. If the method is used within a DCI approach the column (row) of $\mathbf{U}_S^N(P_0)$, after being constructed, may be multiplied by the appropriate part of the CI vector.

1.4.4. An analysis of the configuration graph

In order to calculate a block $\mathbf{H}^{(\lambda\mu)}$ one has to check in how many orbitals configurations λ and μ differ by and, if the number is 1 or 2, find the line-up permutations. The comparison of all the configuration pairs appears to be one of the most time-consuming steps in a large-scale calculation. No such comparison is necessary in the DCI approach. However, the final expressions for the coupling constants depend upon the line-up permutations, many of them being either identical or related to each other. Therefore it is desirable to divide the configuration pairs into sets, gathering in one set all the pairs for which the line-up permutations are the same. The classification of the permutations and of the configuration pairs is facilitated by the configuration graph. A detailed discussion of the subject is given in our recent paper [37]. Here we shall give a brief review of the basic concepts and a summary of the results. One should note, however, that the final formulae presented here differ from those in ref. [37]; in the present paper, due to taking an advantage of the SCP-shift permutation, we have reduced the number of cycles in the line-up permutations to at most two.

a) A single path

A path in the configuration graph represents a symmetry adapted (for an Abelian symmetry group) orbital configuration λ^Γ. The index vector components (99) for the symmetry under consideration should be calculated during construction of the graph. The representation Γ to which configuration λ^Γ belongs is given by the direct product of the representations according to which the orbitals forming λ^Γ transform

$$\Gamma = \bigotimes_{i=1}^{N} \Gamma^{\lambda_i}. \tag{125}$$

Let $n_\lambda(\Gamma^k)$ be the number of orbitals in λ^Γ belonging to Γ^k. Since, for an Abelian group, the square of a representation gives always I (identity), the contribution to Γ from the orbitals belonging to Γ^k is either I (if $n_\lambda(\Gamma^k)$ is even) or Γ^k (if $n_\lambda(\Gamma^k)$ is odd). Then

$$\Gamma = I \,\tilde{\bigotimes_{k}}\, \Gamma^k, \tag{126}$$

where the tilde means that the product is extended only over these orbital symmetries for which the number of orbitals in λ^Γ is odd. In optimizing the molecular symmetry dependent procedures it is helpful if orbitals of the same symmetry are grouped together, within each subspace of the orbital space.

Each path in the configuration graph is associated with a diagonal block $\mathbf{H}_0^{(\lambda\lambda)}$ (eq. (77)). There are two kinds of coupling constants in $\mathbf{H}_0^{(\lambda\lambda)}$.

1) The coupling constants proportional to $[\mathbf{I}]^{\mathrm{ff}}$. They are associated with $(k|k)$, $(kk|ll)$ and, if $n_k n_l \neq 1$, with $(kl|lk)$ integrals and depend only upon the occupation numbers of the orbitals in the path. The whole contribution may be calculated as one number for each path.
2) The coupling constants associated with $(kl|lk)$ integrals, where $n_k n_l = 1$. Blocks of these coupling constants are given by appropriate $\mathbf{U}_S^s((\bar{k}, \bar{l}))$ matrices.

If a kind of tree-search algorithm [138] is used to run over the graph, then the computation of the diagonal block contributions may be organized in such a way that repetitive calculations of the same contributions to different diagonal blocks are avoided (see part II of this paper). Since a diagonal block consists of many terms (approximately $n(n+1)$), the optimum strategy is to precalculate and store all the blocks.

b) Loops in the graph

Two paths λ and μ in the graph coincide in some arcs and in some others run separately. The nonparallel arcs of the two paths form a *loop in the configuration graph*. The shape of the loop determines the type of the matrix element formula. It remains in a one-to-one correspondence with the sets of the occupation numbers and with the appropriate configuration pair diagrams. Therefore, as far as the evaluation of a single matrix element is concerned, all these structures may be utilized alternatively. However, since a loop is associated with the graph, i.e. with the whole CI basis, we may easily identify all configuration pairs being connected by the same kind of loop, i.e. giving the same type (or even the same value) of matrix elements.

Let us consider the case of configurations λ and μ differing by 1 orbital: $(n_k^\lambda - n_k^\mu) = -(n_l^\lambda - n_l^\mu) = \pm 1$. Assume that $l < k$ and $s_\lambda \geqslant s_\mu$. Moreover, if $s_\lambda = s_\mu$, then let $m_\lambda < m_\mu$ if $\min(n_l^\lambda, n_l^\mu) = 1$ and $m_\lambda > m_\mu$ if $\min(n_l^\lambda, n_l^\mu) = 0$ *. In consequence, four different sets of the occupation numbers are possible:

$$\begin{array}{c} n_l \\ n_k \end{array} \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}, \quad \begin{vmatrix} 2 & 1 \\ 1 & 2 \end{vmatrix}, \quad \begin{vmatrix} 1 & 2 \\ 1 & 0 \end{vmatrix}, \quad \begin{vmatrix} 1 & 0 \\ 1 & 2 \end{vmatrix}, \tag{127}$$

where the first column corresponds to λ and the second one to μ. The corresponding paths coincide between the head of the graph and level l, they branch into two parallel paths (diverge) at level l, join together (converge) at level k and coincide again between level k and the tail of the graph.

All loops and configuration pair diagrams, which correspond to configurations differing by one orbital, are shown in fig. 15. A row in the array of occupation numbers representing a loop is called an *orbital segment* or simply a *segment* (not to be confused with segments in the branching diagram). In particular, the arrays (127) represent two-segment loops. Each orbital segment may be interpreted as the ternary representation of a single integer in the decimal system, i.e. $|0\ 1| \leftrightarrow 1$, $|0\ 2| \leftrightarrow 2$, $|1\ 0| \leftrightarrow 3, \ldots, |2\ 1| \leftrightarrow 7$. A compact representation of a loop is then obtained by arranging consecutively the decimal representations of the segments in an one-row array. For example, the two-segment loops (127) in the compact notation are

$$\{1\ 3\}, \quad \{7\ 5\}, \quad \{5\ 3\}, \quad \{3\ 5\}. \tag{127a}$$

In the case of configurations differing by two orbitals, the loop may be composed of two, three or four segments. If in eq. (68) $i = k$ and $j = l$ (i.e. $n_k^\lambda = n_k^\mu + 2$, $n_l^\lambda = n_l^\mu - 2$) then we have a

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* These assumptions lead to a unique assignment of one of the configurations forming a loop as bra (i.e. λ) and the other one as ket (i.e. μ). Conditions determining the assignment have been chosen in a way which allows for a compact classification of the loops and, in consequence, of the line-up permutations.

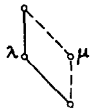
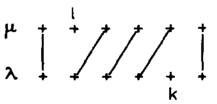
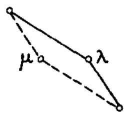
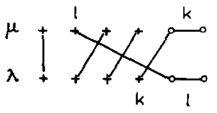
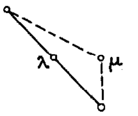
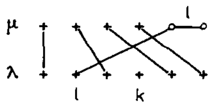
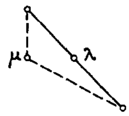
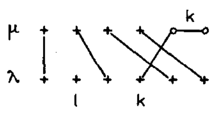
Case No	Occupation numbers	Loop	Configuration-pair diagram
1	$\begin{array}{c\|cc\|} & \lambda & \mu \\ l & 0 & 1 \\ k & 1 & 0 \end{array}$		
2	$\begin{array}{c\|cc\|} l & 2 & 1 \\ k & 1 & 2 \end{array}$		
3	$\begin{array}{c\|cc\|} l & 1 & 2 \\ k & 1 & 0 \end{array}$		
4	$\begin{array}{c\|cc\|} l & 1 & 0 \\ k & 1 & 2 \end{array}$		

Fig. 15. Loop shapes and configuration-pair diagrams corresponding to the pairs of configurations differing by one orbital, see also refs. [30,37].

two-segment loop. The loops consist of three segments if $i = k$ and $j \neq l$, or $i \neq k$ and $j = l$ and of four if all the indices are different. One can show [37] that if $r_{\lambda\mu} = 2$ then there exist 1 two-segment loop, 12 three-segment loops and 48 four-segment loops. The two-segment loop consists of two segments with no singles ($|0\ 2|$ and $|2\ 0|$), the three-segment one contains one segment with no singles. In each segment of a four-segment loop one single appears.

All loops in which the distribution of singles is the same form a *chain of loops*. The number of members in a chain is equal to the number of different distributions of doubles and virtuals satisfying the condition that the sum of the occupation numbers in both columns of the array is the same. The chains consisting of two-, three- and four-segment loops we designate (A), (B) and (C), respectively. Different chains within each of the groups will be distinguished by an index [(A1), (A2), ...]. Cases no. 1 and 2 of fig. 15 belong to one chain and cases no. 3 and 4 to another one. There are 3 chains of two-segment loops

$$(\mathrm{A1}): \begin{vmatrix} \times & 1 \\ 1 & \times \end{vmatrix}, \quad (\mathrm{A2}): \begin{vmatrix} 1 & \times \\ 1 & \times \end{vmatrix}, \quad (\mathrm{A3}): \begin{vmatrix} \times & \times \\ \times & \times \end{vmatrix}, \tag{128}$$

two chains of three-segment loops

$$(\mathrm{B1}): \begin{vmatrix} \times & 1 \\ 1 & \times \\ \times & \times \end{vmatrix}, \quad (\mathrm{B2}): \begin{vmatrix} 1 & \times \\ 1 & \times \\ \times & \times \end{vmatrix} \tag{129}$$

and eight chains of four-segment loops

$$\underset{(\mathrm{C1}),}{\begin{vmatrix} \times & 1 \\ \times & 1 \\ 1 & \times \\ 1 & \times \end{vmatrix}} \underset{(\mathrm{C2}),}{\begin{vmatrix} \times & 1 \\ 1 & \times \\ \times & 1 \\ 1 & \times \end{vmatrix}} \underset{(\mathrm{C3}),}{\begin{vmatrix} \times & 1 \\ 1 & \times \\ 1 & \times \\ \times & 1 \end{vmatrix}} \underset{(\mathrm{C4}),}{\begin{vmatrix} \times & 1 \\ 1 & \times \\ 1 & \times \\ 1 & \times \end{vmatrix}} \underset{(\mathrm{C5}),}{\begin{vmatrix} 1 & \times \\ \times & 1 \\ 1 & \times \\ 1 & \times \end{vmatrix}} \underset{(\mathrm{C6}),}{\begin{vmatrix} 1 & \times \\ 1 & \times \\ \times & 1 \\ 1 & \times \end{vmatrix}} \underset{(\mathrm{C7}),}{\begin{vmatrix} 1 & \times \\ 1 & \times \\ 1 & \times \\ \times & 1 \end{vmatrix}} \underset{(\mathrm{C8}),}{\begin{vmatrix} 1 & \times \\ 1 & \times \\ 1 & \times \\ 1 & \times \end{vmatrix}} \qquad (130)$$

where × means 0 or 2. Since $n^{\lambda} \neq n^{\mu}$ in each of the loop segments (otherwise the arcs of λ and μ are either parallel or overlap and do not belong to the loop), $|\times \ \times|$ means either $|0 \ 2|$ or $|2 \ 0|$. As one can check (for details see ref. [37]) the (A3) chain consists of only one loop, (A1), (A2), (B1) and (B2) of two and (C1)–(C8) of six loops. Besides, each of the chains (B1) and (B2) represents three different cases, since the $|\times \ \times|$ segment may be located at the top, in the middle and in the bottom (as it is in (129)) of a loop. However, the matrix element formulae appear to be independent of the location of the $|\times \ \times|$ segment.

As one can see in table 2, the form of the permutations determining the coupling constants depends only upon the distribution of singles in the pair of configurations. Therefore the concept of a chain of loops facilitates selection of configuration pairs for which the line-up permutations are the same. A complete set of formulae for all chains of loops is given in part II of this paper. Details of derivations are, in some cases, rather tedious and are omitted. In principle they are based on an explicit consideration of each case and on a reduction of the line-up permutations to the products of cycles and SCP-shifting permutations. As an illustration we outline the derivations for (A1), (A2) and (A3) chains.

Chains (A1) and (A2) correspond to the pairs of configurations differing by one orbital. Let us rewrite eq. (78) in the form

$$\mathbf{H}_1^{(\lambda\mu)} = \mathbf{A}_{\lambda\mu}(P_a)\left[(k|l) + \sum_i (n_i - \delta_{il})(ii|kl)\right] + \sum_i{}' \left(1 - \delta_{n,0}\right)\mathbf{A}_{\lambda\mu}(P_i)(il|ki), \qquad (131)$$

where prime means $i \neq k$, l and $\mathbf{A}_{\lambda\mu}(P)$ are $f \times g$ matrices. In the case of chain (A1) an inspection of fig. 15 and table 2 leads in a rather straightforward way to the following results:

$$(\mathrm{A1}): \begin{cases} \begin{array}{c|cc|} & \lambda & \mu \\ l & 0 & 1 \\ k & 1 & 0 \end{array} = \{1 \ 3\}, & \begin{array}{|cc|} \lambda & \mu \\ 2 & 1 \\ 1 & 2 \end{array} = \{7 \ 5\}, \\ P_a = [P_0], & [-P_0], \\ P_i = \left[-\delta_{n,2}P_0 + \delta_{n,1}P_1\right], & \left[P_0 + \delta_{n,1}P_1\right], \end{cases} \qquad (1.32)$$

where $P_0 = (\bar{k}..\bar{l}')$, $P_1 = (\bar{k}..\bar{i} + \epsilon_{ki})(\bar{i}..\bar{l}')$, $\epsilon_{ki} = \mathrm{sgn}(\bar{k} - \bar{i})$ and $P = [aP_0 + bP_1]$ means that

$$\mathbf{A}_{\lambda\mu}(P) = 2^{|d_\lambda - d_\mu|/2}\left(a\left[\mathbf{U}_S^s(P_0)\right]^{fg} + b\left[\mathbf{U}_S^s(P_1)\right]^{fg}\right). \qquad (133)$$

To obtain P_1 the rule

$$(i,\ k)(k..l) = (k..i + \epsilon_{ki})(i..l)$$

has been applied. It is worth-while to note that if $\bar{k} < \bar{i} \leqslant \bar{l}'$, then the cycles forming P_1 do not overlap.

For (A2) – cases no. 3 and 4 in fig. 15 – permutation $(\bar{k}..s)(\bar{l}..s)$, where $s = s_\lambda$, brings orbitals of λ into the maximum coincidence with those of μ locating φ_k and φ_l at the positions $s-1$ and s, respectively. However, due to identity

$$(k..s)(l..s) = (l..k)(k-1..s)^2 = (k..l)(l..s)^2 \tag{134}$$

we may express the coupling constants using several equivalent expressions, as

$$\mathbf{U}\big((\bar{k}..s)(\bar{l}..s)\big) = \mathbf{U}\big((\bar{l}..\bar{k})(\bar{k}-1..s)^2\big) = \mathbf{U}\big((\bar{k}..\bar{l})(\bar{l}..s)^2\big). \tag{135}$$

The first of the representation matrices corresponds to a product of two overlapping cycles while the other two to a product of a single cycle by an SCP-shifting permutation. One can give a simple interpretation of this result. As it is seen from eq. (58), the $\mathbf{U}(P)$ matrix stands with the $\langle P\lambda|H|\mu\rangle$ integral over the orbital variables. However if $P = P_x P_y$, then

$$\langle P\lambda|\hat{H}|\mu\rangle = \langle\lambda|P\hat{H}|\mu\rangle = \langle P_x\lambda|\hat{H}|P_y^+\mu\rangle. \tag{136}$$

If $P_x = (\bar{l}..\bar{k})$ then $P_y^+ = (s..\bar{k}-1)^2$, i.e. P_y^+ moves a double in μ from $s-1$, s to $\bar{k}-1$, $\bar{k}$. It is clear from fig. 15 that after such a shift is performed, a single cycle $(\bar{l}..\bar{k})$ acting on λ, lines-up the orbitals in both configurations.

A representation matrix of a permutation shifting a SCP has a particularly simple structure. As one can easily deduce from eqs. (117), (119) and (112) matrix elements of $\mathbf{U}((\bar{k}..\bar{l})(\bar{l}..s)^2)$ are equal to the elements of $\mathbf{U}((\bar{k}..\bar{l}))$ multiplied by a numberical factor determined in eq. (117). Moreover, the result does not depend on whether the SCP was initially located at any of $(s+1,\ s+2)$, $(s+2,\ s+3), \ldots, (N-1,\ N)$ positions. Therefore it is convenient to introduce the notation

$$P|_{\bar{l}} \equiv P(\bar{l}..s)^2, \quad \mathbf{U}(P)|_{\bar{l}} \equiv \mathbf{U}\big(P(\bar{l}..s)^2\big). \tag{137}$$

The complete set of formulae for (A2) may then be written in the following compact way

$$\text{(A2)}: \begin{cases} \begin{array}{c|cc|} & \lambda & \mu \\ l & 1 & 2 \\ k & 1 & 0 \end{array} \equiv \{5\ \ 3\}, & \begin{array}{|cc|} \lambda & \mu \\ 1 & 0 \\ 1 & 2 \end{array} \equiv \{3\ \ 5\}, \\ P_a = [P_0], & [P_0], \\ P_i = \left[-\delta_{n_i 2} P_0 + \delta_{n_i 1} P_1\right], & \left[-\delta_{n_i 2} P_0 + \delta_{n_i 1} P_2\right], \end{cases} \tag{138}$$

where $P_0=(\bar l..\bar k)|_{\bar k-1}=(\bar k..\bar l)|_{\bar l}$, $P_1=(\bar k..\bar l+\epsilon_{kl})(\bar i..\bar l)|_{\bar l}$, $P_2=(\bar l..\bar i+\epsilon_{li})(\bar i..\bar k)|_{\bar k-1}$.

The last two-segment chain (A3) describes a pair of configurations differing by two orbitals and consists of one loop only. It corresponds to the case of $i=k$ and $j=l$ in eq. (79), i.e.

$$\mathbf{H}_2^{(\lambda\mu)}=\mathbf{A}_{\lambda\mu}(P_a)(kl\,|\,kl) \tag{139}$$

and

$$(\text{A3}):\ \begin{array}{c|cc|}
 & \lambda & \mu \\
l & 0 & 2 \\
k & 2 & 0
\end{array}\equiv\{2\ 6\},\quad P_a=[I]. \tag{140}$$

The formulae for all the chains of loops met in CI calculations are collected in part II of this paper. In the case of (C) loops

$$\mathbf{H}_2^{(\lambda\mu)}=\mathbf{A}_{\lambda\mu}(P_a)J_a+\mathbf{A}_{\lambda\mu}(P_b)J_b \tag{141}$$

(for (B) loops $\mathbf{H}_2^{(\lambda\mu)}=\mathbf{A}_{\lambda\mu}(P_a)J_a$), where J_a, J_b are defined in eqs. (39)–(41). In each of the chains the assignment of J_1, J_2 and J_3 to J_a and J_b in eq. (141) is different. Two simple rules are useful in classifying and programming the formulae [37]:

1) If in a loop all virtuals and doubles are replaced by each other, then the assignment does not change.
2) Let us take two chains with the same number of singles in each of the configurations, say (C1) and (C2). Then (C2) may be obtained from (C1) by a transposition of the second and the third row: (C2) → (23)(C1), i.e. the permutations P_a and P_b for the loops of (C1) transform into the corresponding permutations for (C2) under the transposition of the pertinent indices. If, simultaneously, in (C1) J_1 is replaced by J_3 and J_3 by J_1, then also the assignment of the two electron integrals is the same as in (C2).

Let us define an operator $J\begin{pmatrix}\alpha\beta\nu\\ pqr\end{pmatrix}$ which, acting on a chain of loops, replaces J_α by J_p, J_β by J_q and J_ν by J_r. Then we may write

$$(\text{C2})=(23)J\begin{pmatrix}123\\321\end{pmatrix}(\text{C1}) \tag{142}$$

and similarly

$$(\text{C3})=(234)J\begin{pmatrix}123\\231\end{pmatrix}(\text{C1}),\quad (\text{C5})=(12)J\begin{pmatrix}123\\132\end{pmatrix}(\text{C4}),$$
$$(\text{C6})=(123)J\begin{pmatrix}123\\312\end{pmatrix}(\text{C4}),\quad (\text{C7})=(1234)J\begin{pmatrix}123\\213\end{pmatrix}(\text{C4}). \tag{143}$$

From the second rule results, that only 3 independent chains ((C1), (C4) and (C8)) are needed to describe the four-segment loops. Note, that in (C1)–(C3) $s_\lambda = s_\mu$, in (C4)–(C7) $s_\lambda = s_\mu + 2$ and in (C8) $s_\lambda = s_\mu + 4$.

I.5. Strategy of DCI calculations

The general strategy of SGA CI calculations may follow the same lines as the one developed within the framework of UGA. Some ideas of GUGA implementations may also be translated in a simplified form to the language of SGGA. Differences result mainly from the simplicity of the SGA graph and from the presence of $[\mathbf{U}_S^s(P)]^{fg}$ matrices in the expressions determining $\mathbf{H}^{(\lambda\mu)}$.

The most complete account on the strategy problem in CI has been given by Saunders and Van Lenthe [48] but it was also discussed in various aspects by other authors [35,38,53,137]. The strategy problem itself is a very extensive one and we shall limit its general discussion to several remarks which are necessary to understand the more detailed analysis of the algorithm, as given in part II of this paper. Since the DCI approach proved to be superior to the conventional one, except for rather small-size calculations [48], we shall consider only the case of DCI calculations.

I.5.1. Integrals

An analysis of the problem in terms of the graph shape, symmetry, the number of internal and external orbitals must be performed at first. To facilitate an easy access to the integrals, the integral file should be resorted. Since some combinations of the integrals appear in all $\mathbf{H}_0^{(\lambda\lambda)}$ or $\mathbf{H}_1^{(\lambda\mu)}$ elements, they should be precalculated, preferably during the resorting. The combinations are usually referred to as the Fock matrix elements

$$(i|F|j) = (i|j) + \sum_{\substack{k\\(k\neq i,\, j)}} \eta_k\left[(ij|kk) - \tfrac{1}{2}(ik|jk)\right] \tag{144}$$

and the reference energy

$$E_0 = \tfrac{1}{2}\sum_i \eta_i\left[(i|i) + (\eta_i - 1)(ii|ii) + (i|F|i)\right], \tag{145}$$

where η_i are fixed, but arbitrary, occupation numbers.

The integrals should be divided into five classes:

$$\begin{array}{lll}
\text{(i)} & (i|F|i),\ (ii|jj), & i \geqslant j,\\
\text{(ii)} & (ij|ij), & i > j,\\
\text{(iii)} & (i|F|j),\ (ij|jj),\ (ii|ij), & i > j,\\
\text{(iv)} & (ij|kk),\ (ik|jk), & i > j,\\
\text{(v)} & (ij|kl),\ (il|jk),\ (ik|jl), & i > j > k > l.
\end{array} \tag{146}$$

Integrals (i) and (ii) appear in the diagonal blocks. The diagonal blocks, or at lest the "scalar" (proportional to $[\mathrm{I}]^{ff}$) contributions comprising class (i) of the integrals, should be precalculated and stored. Therefore there is no need for storing the first class integrals. Integrals (ii) enter, besides the diagonal blocks, matrix elements corresponding to (A3) loops. Chains of loops (A1) and (A2) comprise classes (iii) and (iv) of the integrals. The three-segment chains are connected with class (iv) and the four-segment ones with class (v) of the integrals.

Within classes (ii)–(v), the molecular integrals are divided into subclasses I0, I1, I2, I3, I4, depending on the number of the internal orbitals in an integral, where Ik contains integrals with k internal orbitals. The integrals in each of the subclasses are grouped in blocks. All integrals containing the same set of internal orbitals are collected in the same block. All integrals (at most 3) which depend upon the same set of indices are processed and stored together so that only one packed integer may be used for their identification. Within each of the blocks the integrals are ordered according to the indices of the external orbitals, so that they may be processed as elements of an array. The following relation between the orbital indices is assumed

I0:

$$(e_4e_3|e_2e_1):\ e_4 \geqslant e_3,\ e_2 \geqslant e_1,\ e_4 \geqslant e_2 \text{ and, if } e_4 = e_2, \text{ then } e_3 \geqslant e_1. \tag{147}$$

For the remaining subclasses of integrals relations (147) and $i_k < e_l$ (for all k, l), imply that

I1:

$$(e_3e_2|e_1i_1):\ e_3 \geqslant e_2,$$

I2:

$$(e_2e_1|i_2i_1):\ e_2 \geqslant e_1,\ i_2 \geqslant i_1,$$

$$(e_2i_2|e_1i_1):\ e_2 \geqslant e_1, \text{ and, if } e_2 = e_1, \text{ then } i_2 \geqslant i_1, \tag{148}$$

I3:

$$(e_1i_3|i_2i_1):\ i_2 \geqslant i_1,$$

I4:

$$(i_4i_3|i_2i_1):\ i_4 \geqslant i_3,\ i_2 \geqslant i_1,\ i_4 \geqslant i_2, \text{ and, if } i_4 = i_2, \text{ then } i_3 \geqslant i_1.$$

I.5.2. Separation of the external space

Since only double excitations from the reference configurations are allowed, there are at most 2 electrons in $\mathscr{E}(n_{\mathrm{E}})$ and at least $2(n_{\mathrm{D}}-1)$ in $\mathscr{D}(n_{\mathrm{D}})$. The group of configurations with 2 electrons in the external space is designated D_{ba}, $a \neq b$ (φ_a and φ_b are singly occupied) or D_{aa} (φ_a is doubly occupied). Configurations with one electron in the external space are designated S_a (φ_a is singly occupied), and configurations with all electrons in the internal space, V (compare fig. 10). The same symbols are used to designate individual members of each of these groups of configurations.

As resulting from, eq. (108), in the reversed lexical ordering of the spin functions

$$\mathbf{U}_S^s((s-1,\ s))_{ji} = \begin{cases} \delta_{ji}, & \text{if } j \leqslant f_2, \\ -\delta_{ji}, & \text{if } j > f_2, \end{cases} \tag{149}$$

where $s = s_\lambda$, $f_2 = f(S,\ s) - f(S,\ s-2)$. We assume that the external orbitals, if singly occupied, are located at the last positions (i.e. s and $s-1$) in the orbital product (51). In consequence the external space contributions to the coupling constants may be calculated independently of the internal ones [37]. This property of the external space, noticed in UGA by Siegbahn [35], is of fundamental importance in formulating a strategy of DCI calculations. In particular, it allows for including all the external space contributions in form of a DO-loop over the external orbitals. The complete set of formulae allowing for a separation of the external space is given in part II of this paper. Here we give only an example and some general remarks.

The coupling constants associated with I0 integrals correspond to the paths λ and μ which coincide in the internal part of the graph. Hence, the coupling constants are determined by the external part exclusively. The line-up permutation must be either I or $(s-1,\ s)$. As one can easily check (see also ref. [37]), I0 integrals (147) with a set of all indices different couple 3 pairs of configurations $\mathrm{D}_{e_3e_4}$, $\mathrm{D}_{e_1e_2}$; $\mathrm{D}_{e_1e_3}$, $\mathrm{D}_{e_2e_4}$ and $\mathrm{D}_{e_1e_4}$, $\mathrm{D}_{e_2e_3}$. The Hamiltonian matrix elements are expressed in terms of the unit matrix $\mathbf{I}$ and the diagonal matrix $\mathbf{U}_S^s$ (eq. (149))

$$\langle \mathrm{D}_{e_3e_4} | H | \mathrm{D}_{e_1e_2} \rangle = \mathbf{I}(e_4e_2|e_3e_1) + \mathbf{U}_S^s((s-1,\ s))(e_4e_1|e_3e_2). \tag{150}$$

The formulae for the two remaining configuration pairs are obtained by changing the orbital indices. If $e_3 = e_4$ or $e_1 = e_2$ then

$$\langle \mathrm{D}_{e_3e_4} | H | \mathrm{D}_{e_1e_2} \rangle = \sqrt{2}\,\mathbf{I}(e_4e_2|e_3e_1). \tag{151}$$

Then, in the case of I0 integrals the coupling constants are either ± 1 or $\sqrt{2}$. Let us note, that the same integral and the same coupling constant correspond to *all* internal paths passing through the vertex D (see fig. 10). Similarly, $(e_2|F|e_1)$, $e_2 \geqslant e_1$, couples a set of pairs S_{e_1}, S_{e_2} and n_E sets of pairs $\mathrm{D}_{e_1e_k}$, $\mathrm{D}_{e_2e_k}$, where $k = 1, 2, \ldots, n_\mathrm{E}$. Also in this case the coupling constants are either ± 1 or $\sqrt{2}$ [37].

In the case of I1 integrals only D_{ab}, S_c or S_a, V pairs may be coupled. The integrals of (iv) and (v) classes (eq. (146)) may couple D_{ab}, S_c pairs only. The class (iii) may couple both D_{ab}, S_c and S_a, V pairs. The coupling constants are factorized to the external space contribution being ± 1 or $\sqrt{2}$ and to the internal one which is expressed in terms of a representation matrix of a single cycle.

The cases of I2 and I3 are more complicated, therefore the internal parts of the coupling constant formulae are represented as chains of loops. In the case of I2 there are two kinds of internal loops: closed loops, if both paths enter the external space at the same vertex (either S or D) and open loops, if the paths enter the external space in two different vertices (V and D). In the case of I3 only open loops are possible (the paths pass either through V and S or through S and D). Finally, in the case of I4 both paths overlap in the external space. A discussion of this case follows exactly the one in section I.4.4 of this paper.

Let us divide λ and μ into their internal (λ_{I}, μ_{I}) and external (λ_{E}, μ_{E}) parts, i.e. let $\langle\lambda| = \langle\lambda_{\mathrm{I}}\lambda_{\mathrm{E}}|$, $|\mu\rangle = |\mu_{\mathrm{I}}, \mu_{\mathrm{E}}\rangle$. In a similar way we distinguish in the corresponding loops their internal and external segments. Since in a configuration at most 2 electrons may be located in the external space, at most 4 external orbitals may be occupied when a configuration pair is considered. This case corresponds to $\lambda_{\mathrm{E}} = \mathrm{D}_{ba}$, $\mu_{\mathrm{E}} = \mathrm{D}_{dc}$. The occupation numbers of the external orbitals are then $n_a^\lambda = n_b^\lambda = n_c^\mu = n_d^\mu = 1$, $n_a^\mu = n_b^\mu = n_c^\lambda = n_d^\lambda = 0$. Therefore the 4-segment external loops may contain only $|10|$ and $|01|$ segments and only 3 different loops({1133}, {1313}, {1331}), being the first members of (C1), (C2) and (C3) chains may be formed. The other 3 loops, being their Hermitean conjugate, do not have to be considered

Table 3
Classification of the external parts of configuration pairs and the optimum strategy of DCI calculation

No.	λ_{E}	μ_{E}	External segments	$r_{\lambda\mu}^{\mathrm{E}}$	Subclasses of two-electron integrals coupling λ and μ		Optimum strategy [a]
					$r_{\lambda\mu} = 1$	$r_{\lambda\mu} = 2$	
	Closed loops						
1	V	V	{0}	0	I4	I4	PMED
2	S_a	S_a	{4}	0	I4, I2	I4	PMED
3	D_{aa}	D_{aa}	{8}	0	I4, I2	I4	PMED
4	D_{ba}	D_{ba}	{44}	0	I4, I2	I4	PMED
5	S_a	S_b	{13}	1	I2	I2	EID [1], ISD [2,3]
6	D_{bb}	D_{ba}	{71}	1	I2, I0	I2	EID
	D_{ba}	D_{bb}	{53}				ISD
7	D_{ca}	D_{cb}	{413}	1	I2, I0	I2	EID [1], ISD [2,3]
8	D_{aa}	D_{bb}	{26}	2		I0	PMED
9	D_{aa}	D_{cb}	{116}	2		I0	PMED
	D_{cb}	D_{aa}	{332}				
10	D_{ba}	D_{dc}	{1133}	2		I0	PMED
	Open loops						
11	V	S_a	{1}	1	I3	I3	EID
	S_a	V	{3}				ISD
12	S_a	D_{aa}	{5}	1	I3, I1	I3	PMED
	D_{aa}	S_a	{7}				
13	S_b	D_{ba}	{41}	1	I3, I1	I3	EID
	D_{ba}	S_b	{43}				ISD
14	V	D_{aa}	{2}	2		I2	EID
	D_{aa}	V	{6}				ISD
15	V	D_{ba}	{11}	2		I2	EID
	D_{ba}	V	{33}				ISD
16	S_b	D_{aa}	{32}	2		I1	EID
	D_{aa}	S_b	{16}				ISD
17	D_{ba}	S_c	{133}	2		I1	EID [1], ISD [2]
	S_c	D_{ba}	{311}				EID [2], ISD [3]

[a] Both $s_\lambda \geqslant s_\mu$ and $s_\lambda < s_\mu$ are allowed: [1] $s_\lambda > s_\mu$, [2] $s_\lambda = s_\mu$, [3] $s_\lambda < s_\mu$.

explicitly because there are no internal loops in this case (four-segment external loops are complete).

Three-segment external loops are not complete in this sense. Therefore, both the ones corresponding to $\lambda_E = D_{ba}$, $\mu_E = S_c$ ({133}, {313}, {331}), and their Hermitean-conjugate counterparts corresponding to $\lambda_E = S_c$, $\mu_E = D_{ba}$ ({311}, {131}, {113}) must be considered separately.

To give a complete description of the external parts of configuration pairs we extend the notation of section I.4.4. We introduce symbol {0} to designate the case of an empty external space and we write explicitly in the loop symbols all the external segments, including those with the same occupation numbers in λ and in μ, as for example {134} for the case of D_{ba}, D_{ca} pair.

The external parts of configuration pairs are displayed in table 3. The sequence $a > b > c > d$ is assumed for the external orbital indices. Each of the loops specified in the table corresponds to one specific assignment of the segments to the external orbitals, i.e. to one specific sequence of the segments. For example, {413} (entry no. 7) means that $\{4\} = |1\ 1|$ corresponds to φ_c, $\{1\} = |0\ 1|$ to φ_b and $\{3\} = |1\ 0|$ to φ_a. However, the information shown in the table, i.e. the number of external orbitals λ and μ differ by ($r^E_{\lambda\mu}$), the subclasses of two-electron integrals which may couple a given type of configuration pairs, and the optimum strategy of a DCI calculation (cf. the next section), does not depend upon the assignment of the segments to the orbitals. Then, each entry in the table, in fact, represents a set of the external loops corresponding to all nonequivalent assignments of the external segments to the external orbitals. Coming back to our example of the entry no. 7, we see that it stands for 6 different λ_E, μ_E pairs: {413}, {431}, {143}, {134}, {341}, {314} (all 3! ways the segments may be assigned to φ_a, φ_b and φ_c). If both pairs of the mutually Hermitean conjugate external configuration pairs have to be considered explicitly they are set in table 3 under the same number.

I.5.3. First-order-interaction space

In formulating criteria for an optimum choice of the CI expansion, the concept of the first-order-interaction space (FOIS) is particularly important [134]. FOIS is spanned by the set of excited CSFs which give nonzero matrix elements with the reference CSFs. In this section we describe a method of construction FOIS in SGA.

The set $\{\mu\}_R$ of all the *reference configurations* spans the reference configuration space. Let $\lambda \notin \{\mu\}_R$. A block $\mathbf{H}^{(\lambda\mu)}$ is nonzero if λ is either singly or doubly excited relatively to μ. Hence, FOIS contains only singly and doubly excited configurations. Simple selection of these configurations is facilitated by a proper choice of the external space (see fig. 10).

Each of the reference configurations contains not less than n_D doubles and not more than $s = N - 2n_D$ singles. Then, the spin functions associated with the reference configurations contain at least n_D SCPs, located as in eq. (54). These functions span the $f(S, s)$ dimensional *reference spin space*. An example of the reference spin space for a 12-electron triplet ($s = 6$, $n_D = 3$) is shown in fig. 6. A double excitation can, in general, break two SCPs and increase the dimension of the spin space up to $f(S, s+4)$. This increase may be very substantial – e.g., if $S = 1$, $s = 6$, then $f(S, s) = 9$ but $f(S, s+4) = 90$. However, as we shall see, only $2f(S, s)$ spin functions out of $f(S, s+4)$ belong to the FOIS.

Let λ-FOIS be the subspace of FOIS corresponding to a doubly excited configuration λ. It is spanned by the spin functions which for at least one $\mu \in \{\mu\}_R$ give a nonzero contribution to

$\mathbf{H}^{(\lambda\mu)}$. In other words, λ-FOIS is spanned by the spin functions giving nonzero contributions to $P_a|SM, i\rangle$ or to $P_b|SM, i\rangle$ where P_a and P_b are the permutations appearing in eqs. (139) and (141) while $|SM, i\rangle$, $i = 1, 2, \dots, f(S, s)$ are the reference spin functions. Then, the reversed branching diagram describing λ-FOIS may be generated by P_a and P_b from the diagram describing the reference spin space. It is clear that both dimension and structure of λ-FOIS depend upon the specific form of P_a and P_b. The least dimensions and the simplest structures are obtained if the orbitals are in $a_k < d_l < e_m$ order, where $1 \leqslant k \leqslant n_{\mathrm{A}}$, $1 \leqslant l \leqslant n_{\mathrm{D}}$, $1 \leqslant m \leqslant n_{\mathrm{E}}$. Therefore we assume that in an orbital graph the doubly occupied orbitals are always located between the active ones and the external ones.

If s' is the maximum number of singles in λ, then 3 cases should be examined:

1. $s' \leqslant s$. The spin functions belonging to λ-FOIS are contained in the reference spin space.
2. $s' = s + 2$. There are 4 double excitation types corresponding to this case:

   $d_l d_l \to e_l e_2$, $d_l d_2 \to e_l e_l$, $d_l d_2 \to a_l e_l$ and $d_l a_l \to e_l e_2$.

   For the first two types $P_a = I$ and P_b is zero. In consequence the dimension of λ-FOIS remains equal to $f(S, s)$. For the last two excitation types, $P_a = (s + 2..\bar{a}_1)$, $P_b = (s + 1..\bar{a}_1)$. This part of the graph generated by P_a and P_b which is not contained in the reference spin space is shown in fig. 16a. As seen the dimension of λ-FOIS for $d_1 d_2 \to a_1 e_1$ and $d_1 a_1 \to e_1 e_2$ is $2f(S, s)$.
3. $s' = s + 4$. The only excitation corresponding to this case is $d_1 d_2 \to e_1 e_2$. The line-up permutations are $\hat{I}$ and $(s + 2, s + 3)$. The graph generated by $(s + 2, s + 3)$ is shown in fig. 16b. Also here the dimension of λ-FOIS is $2f(S, s)$.

The arc values of the parts of λ-FOIS graphs which do not belong to the reference spin graph are shown in fig. 16. They are independent of the structure of the reference spin space. Also the reversed lexical indices of the λ-FOIS spin functions may easily be expressed in terms of the reversed lexical indices of the reference spin space functions (compare eq. (91)).

I.5.4. The optimum strategy

In order to illustrate the strategy optimization problem in DCI methods let us consider the contribution from $(e_2 i_2|e_1 i_1)$ type of integral in the case of the open loops formed by the D_{ab}, V

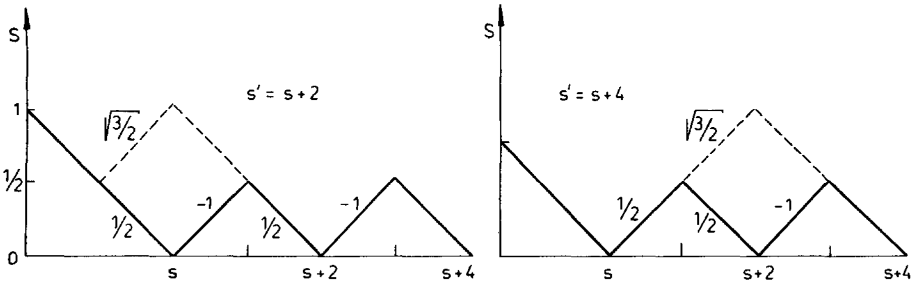


Fig. 16. The first-order-interaction spin space for the cases of $s' = s + 2$ and $s' = s + 4$. Only the spin functions represented by the broken lines interact with the reference onces (represented by the full lines) due to the line-up permutations.

pairs of configurations. Eq. (47) may be rewritten in the form

$$\begin{bmatrix} \boldsymbol{b}^{\mathrm{V}} \\ \boldsymbol{b}^{\mathrm{D}_2} \end{bmatrix} = \begin{bmatrix} \mathbf{H}^{\mathrm{VV}} & \mathbf{H}^{\mathrm{VD}_2} \\ \mathbf{H}^{\mathrm{D}_2\mathrm{V}} & \mathbf{H}^{\mathrm{D}_2\mathrm{D}_2} \end{bmatrix} \begin{bmatrix} \boldsymbol{c}^{\mathrm{V}} \\ \boldsymbol{c}^{\mathrm{D}_2} \end{bmatrix}, \tag{152}$$

where the superscripts stand for the vertices the paths corresponding to the respective configurations pass by. For simplicity, only the parts of the Hamiltonian matrix and of $\boldsymbol{b}$ and $\boldsymbol{c}$ vectors relevant to our example are shown in eq. (152). As one can see from fig. 10 and from eq. (100) there are $D(n_{\mathrm{I}}, N)$ configurations V and $N_p D(n_{\mathrm{I}}, N-2)$ configurations D_{ab}, where $N_p = \binom{n_{\mathrm{E}}}{2}$ is the number of different orbital pairs in the external space. Let us pick up, in the internal space, one path passing through vertex V and another one passing through D_2 and let the occupation numbers of only 2 internal orbitals be different from each other in both the paths, e.g. $n_i^{\mathrm{D}_2} = n_j^{\mathrm{D}_2} = 0$, $n_i^{\mathrm{V}} = n_j^{\mathrm{V}} = 1$. We shall calculate the contributions to the vector $\boldsymbol{b}$ from all the external space continuations of the paths and find the optimum strategy for this calculation.

From eq. (152) we have

$$\boldsymbol{b}^{\mathrm{V}} = \boldsymbol{b}^{\mathrm{V}}(\mathrm{V}) + \boldsymbol{b}^{\mathrm{V}}(\mathrm{D}_2), \tag{153}$$

$$\boldsymbol{b}^{\mathrm{D}_2} = \boldsymbol{b}^{\mathrm{D}_2}(\mathrm{V}) + \boldsymbol{b}^{\mathrm{D}_2}(\mathrm{D}_2), \tag{154}$$

where $\boldsymbol{b}^{\mathrm{V}}(\mathrm{D}_2) = \mathbf{H}^{\mathrm{VD}_2}\boldsymbol{c}^{\mathrm{D}_2}$ and similarly for the remaining symbols. The integrals considered by us appear in $\boldsymbol{b}^{\mathrm{D}_2}(\mathrm{V})$ and $\boldsymbol{b}^{\mathrm{V}}(\mathrm{D}_2)$ only:

$$\mathbf{Z}^{\mathrm{D}_2}(\mathrm{V})_{ab} = \left[(aj|bi)\mathbf{U}(P_0^s) + (ai|bj)\mathbf{U}(P_1^s)\right]\mathbf{C}_{ij}^{\mathrm{V}}, \tag{155}$$

$$\mathbf{Z}^{\mathrm{V}}(\mathrm{D}_2)_{ij} = \sum_{a<b} \left[(aj|bi)\mathbf{U}(P_0^s)^{\dagger} + (ai|bj)\mathbf{U}(P_1^s)^{\dagger}\right]\mathbf{C}_{ab}^{\mathrm{D}_2}, \tag{156}$$

where $\mathbf{Z}$ and $\mathbf{C}$ are appropriate $f = f(S, s)$ dimensional parts of $\boldsymbol{b}$ and $\boldsymbol{c}$ vectors. The subscripts *ab* and *ij* refer, respectively, to the external and internal parts of the paths. To evaluate the contributions to the vector $\boldsymbol{b}$ (eqs. (155) and (156)), three different strategies may be applied [48]. Each of the these strategies consists of two steps. In the following we write the formulae for each step, in the order of their execution in a computer.

(i) Partial matrix element driven (PMED) strategy

1. $$\mathbf{H}_{ab,ij} = (aj|bi)\mathbf{U}(P_0^s) + (ai|bj)\mathbf{U}(P_1^s) \quad \text{for all } a<b. \tag{157}$$

2. $$\mathbf{Z}^{\mathrm{D}_2}(\mathrm{V})_{ab} = \mathbf{H}_{ab,ij}\mathbf{C}_{ij}^{\mathrm{V}}, \tag{158}$$

$$\mathbf{Z}^{\mathrm{V}}(\mathrm{D}_2)_{ij} = \sum_{a<b} \mathbf{H}_{ab,ij}^{\dagger}\mathbf{C}_{ab}^{\mathrm{D}_2}. \tag{159}$$

(ii) Internal spin driven (ISD) strategy

$$1.\quad \boldsymbol{d}_m^{ij} = \mathbf{U}(P_m^s)\mathbf{C}_{ij}^{\mathrm{V}}, \quad m = 0, 1, \tag{160}$$

$$\boldsymbol{d}_m^{ab} = \mathbf{U}(P_m^s)^\dagger \mathbf{C}_{ab}^{\mathrm{D}_2}, \quad m = 0, 1, \text{ all } a < b. \tag{161}$$

$$2.\quad \mathbf{Z}^{\mathrm{D}_2}(\mathrm{V})_{ab} = (aj|bi)\boldsymbol{d}_0^{ij} + (ai|bj)\boldsymbol{d}_1^{ij}, \tag{162}$$

$$\mathbf{Z}^{\mathrm{V}}(\mathrm{D}_2)_{ij} = \sum_{a<b} \left[(aj|bi)\boldsymbol{d}_0^{ab} + (ai|bj)\boldsymbol{d}_1^{ab}\right]. \tag{163}$$

(iii) External integral driven (EID) strategy

$$1.\quad \mathbf{G}_0^{ab} = (aj|bi)\mathbf{C}_{ij}^{\mathrm{V}}, \quad \mathbf{G}_1^{ab} = (ai|bj)\mathbf{C}_{ij}^{\mathrm{V}}, \tag{164}$$

$$\mathbf{G}_0^{ij} = \sum_{a<b} (aj|bi)\mathbf{C}_{ab}^{\mathrm{D}_2}, \quad \mathbf{G}_1^{ij} = \sum_{a<b} (ai|bj)\mathbf{C}_{ab}^{\mathrm{D}_2}. \tag{165}$$

$$2.\quad \mathbf{Z}^{\mathrm{D}_2}(\mathrm{V})_{ab} = \mathbf{U}(P_0^s)\mathbf{G}_0^{ab} + \mathbf{U}(P_1^s)\mathbf{G}_1^{ab}, \tag{166}$$

$$\mathbf{Z}^{\mathrm{V}}(\mathrm{D}_2)_{ij} = \mathbf{U}(P_0^s)^\dagger\mathbf{G}_0^{ij} + \mathbf{U}(P_1^s)^\dagger\mathbf{G}_1^{ij}. \tag{167}$$

The number of multiplications necessary to perform in each of these strategies is shown in table 4. As can be seen from the table, when searching for the optimum strategy we should compare 3

Table 4
Comparison of different DCI strategies, as applied to evaluate the D_{ab}, V contribution. In each case the number of multiplications necessary to calculate the contribution from $(bi_2|ai_1)$ integrals to $\mathbf{Z}$ for all $a < b$ pairs and one i_2, i_1 pair is given. The optimum strategy is marked by an asterisk; $N_p = \binom{n_E}{2}$

Strategy	Step	Number of multiplications	
		$\mathbf{Z}^{\mathrm{D}_2}(\mathrm{V})_{ab}$	$\mathbf{Z}^{\mathrm{V}}(\mathrm{D}_2)$
PMED	1	$2f^2N_p$	
	2	f^2N_p	f^2N_p
	1+2	$4f^2N_p$	
ISD	1	$2f^2$	$2f^2N_p$
	2	$2fN_p$	$2fN_p$
	1+2	$*2f(f+N_p)$	$2f(f+1)N_p$
EID	1	$2fN_p$	$2fN_p$
	2	$2f^2N_p$	$2f^2$
	1+2	$2f(f+1)N_p$	$*2f(f+N_p)$

cases:

- PMED: $M_1 = 4f^2N_p$, (168)
- ISD for $b^{\mathrm{V}}(\mathrm{D}_2)$ and EID for $b^{\mathrm{D}_2}(\mathrm{V})$: $M_2 = 4f(f+1)N_p$, (169)
- EID for $b^{\mathrm{V}}(\mathrm{D}_2)$ and ISD for $b^{\mathrm{D}_2}(\mathrm{V})$: $M_3 = 4f(f+N_p)$, (170)

where M_1, M_2 and M_3 are the numbers of multiplications. Then,

$$M_2/M_1 = 1 + 1/f \tag{171}$$

and

$$M_3/M_1 = 1/N_p + 1/f. \tag{172}$$

Therefore always $M_2 > M_1$. Since N_p is usually rather big, we have

$$M_3 \approx M_1/f. \tag{173}$$

i.e., comparing to the PMED strategy, the number of multiplications is reduced as much as f times.

The only case when $M_3 > M_1$ is that of $f = 1$. However, then $M_3 - M_1 = 4$, i.e. the difference is negligibly small comparing to M_3.

It is clear from this example that no single optimum strategy exists and that the strategy optimization may result in an important increase of efficiency of the algorithm. Recommended strategies for different external parts of configuration pairs are given in table 3. Some cases with $r_{\lambda_\mu} = 1$ may be improved by using more specialized strategies but the gain seems to be small comparing to additional complications of the algorithm.

PART II. ALGORITHMS AND FORMULAE

Problems encountered in implementations of SGGA may be solved in a number of ways. Searching for particular solutions we tried to find the simplest and the most efficient ones. We do not expect them to be ultimate, but they certainly offer a reasonable reference for more specialized formulations.

This part of the paper consists of two sections. In the first one we consider a computer representation of the orbital graph and describe an algorithm for search the paths in the graph. The second contains tables with the matrix element formulae. The formulae are given in 3 different forms:

- General formulae for the conventional CI suitable for any matrix-element-based CI-type method (table 7).
- Coupling constant formulae, classified using the chain of loops concept (cf. section I.4.4) and

constructed to meet the conditions of a general direct CI method with no separation of the external space (table 8).

Coupling constant formulae with separated contributions from the external space (table 10) and optimum strategy for dealing with the external space (table 3).

II.1. The graph in a computer

II.1.1. Computer representation of the configuration graph

The representation of the configuration graph in a computer, chosen by us, takes an advantage of its specific, simple structure and is perhaps one of the most economic, as far as an occupation of the computer memory is concerned. Assuming that the external space contributions are separated from the internal ones (cf. section I.5.2), we need a representation of the internal part of the graph only. The vertices $v(k, N_k)$ are numbered consecutively from $v(0, 0) = 1$ to $v(n_\mathrm{I}, N) = L$. The counting number of an arbitrary vertex is given by equation

$$v(k, N_k) = B_1(k) + N_k, \tag{174}$$

where $B_1(k)$, $k = 1, 2, \ldots, n_\mathrm{I}$ is an auxiliary array. Another auxiliary array, $B_2(k)$, $k = 1, 2, \ldots, n_\mathrm{I}$, describes the left-hand border of the graph. Its kth element is equal to the minimum value of N_k

$$B_2(k) = N_k^{\min}. \tag{175}$$

Then, the counting number of the leftmost vertex corresponding to the orbital φ_k is equal to

$$v\left(k, N_k^{\min}\right) = B_1(k) + B_2(k). \tag{176}$$

If, as an example, we take the internal part of the graph from fig. 9, then $n_\mathrm{I} = 8$, $L = 33$ and $B_1 = [2, 3, 4, 5, 8, 13, 18, 21]$, $B_2 = [0, 2, 4, 6, 6, 6, 8, 10]$.

This graph is represented by a 3-row and L-column array. The first row, $y_0(v)$, contains the lexical weights of the vertices

$$y_0\left(v(k, N_k)\right) = \begin{cases} \pm D(k, N_k), \\ 0, \text{ if the vertex is removed from the graph,} \end{cases} \tag{177}$$

where $+D$ is taken if the arc $(k, N_k) - (k+1, N_k)$ belongs to the graph and $-D$ if it does not. In the two remaining rows $(y_i(v), i = 1, 2)$ the lexical arc indices corresponding to $(k, N_k) - (k + 1, N_k + \mathrm{i})$ arcs are collected. If an arc does not belong to the graph then we set $y_i = -1$. An example is shown in table 5.

II.1.2. Searching paths in the graph

Finding all paths which connect two given vertices constitutes the most important among the elementary problems met in any implementation of a graphical representation of the CI basis.

Table 5
An array representating the internal part of the orbital graph from fig. 9

v	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
k	0		1			2			3			4				5		
N_k	0	0	1	2	2	3	4	4	5	6	6	7	8	6	7	8	9	10
y_0	1	−1	−1	1	−3	−2	1	−6	−3	1	10	4	1	10	14	15	5	1
y_1	0	−1	1	0	−1	1	0	−1	1	0	4	1	0	14	15	5	1	0
y_2	0	2	1	0	3	1	0	4	1	0	5	1	0	29	20	6	1	0

continuation

19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
			6						7				8	
6	7	8	9	10	11	12	8	9	10	11	12	10	11	12
−10	−24	39	34	21	6	1	−73	−97	94	61	28	−264	−252	−183
−1	39	34	21	6	1	−1	−1	94	61	28	−1	−1	−1	−1
63	73	55	27	7	−1	−1	191	155	89	−1	−1	−1	−1	−1

Here we describe one of the most straightforward and efficient algorithms solving this problem. Let us assume that we have to find all paths joining two vertices $v_1 = v(a, N_a)$ and $v_2 = v(b, N_b)$, $a < b$. First we determine the two extreme paths joining the two vertices: the leftmost, passing through the vertices $v_l(k)$, and the rightmost, passing through the vertices $v_r(k)$, $k = a$, $a+1, \ldots, b$. The paths, we are interested in, pass only through the vertices $v(k, N_k)$ contained, for each k, between $v_l(k)$ and $v_r(k)$, i.e.

$$v_l(k) \leqslant v(k, N_k) \leqslant v_r(k). \tag{178}$$

The set of the lexical path indices is constructed recursively. Let $\{m_\lambda^k(v)\}$ be the set of the lexical index contributions from the arcs contained between the vertex v_1 and another vertex $v(k, N_k)$, conforming to condition (178). The number of elements in this set is equal to the number of paths connecting these two vertices. The elements of the sets $(m_\lambda^{k+1}\}$ and $\{m_\lambda^k\}$ are related in the following way *:

$$m_\lambda^{k+1}(v(k+1, N_k+i)) = \begin{cases} m_\lambda^k(v(k, N_k)), & \text{if } i = 0, \\ m_\lambda^k(v(k, N_k)) + y_i(v(k, N_k)), & \text{if } i = 1, 2. \end{cases} \tag{179}$$

The procedure starts with

$$m_\lambda^{a+1}(v(a+1, N_a+i)) = \begin{cases} 0, & \text{if } i = 0, \\ y_i(v(a, N_a)), & \text{if } i = 1, 2, \end{cases} \tag{180}$$

---

* For simplicity we designate elements of $\{m_\lambda^k(v)\}$ as $m_\lambda^k(v)$ and do not supply them with any counting index.

and terminates when the set m_λ^b is constructed. At each step of the procedure (179) at most 3 values of m_λ^{k+1} may be obtained from one value of m_λ^k (since $i = 0, 1, 2$). If $y_i(v(k, N_k)) < 0$ or condition (178) is not satisfied, the corresponding case has to be skipped.

As an example let us find all the paths joining vertices $v_1 = v(3, 6) = 10$ and $v_2 = v(7, 9) = 27$ in fig. 9. It is easy to see that

$$v_l[10, 11, 14, 20, 27], \quad v_r = [10, 13, 17, 22, 27].$$

From table 5 and eq. (180) we have

$v(4, 6+i)$:	11	12	13
$\{m_\lambda^4(v)\}$:	0	0	0

Now, applying procedure (179) we obtain

$v(5, N_k+i)$, $N_k = 6, 7, 8$:	14	15	16	17
$\{m_\lambda^5(v)\}$:	0	4, 0	5, 1, 0	1, 0

where the case of $v = (5, 10) = 18$ has been skipped since it violates condition (178). The next step gives

$v(6, N_k+i)$, $N_k = 6, 7, 8, 9$:	20	21	22
$\{m^6(v)\}$:	14, 4, 0	29, 19, 15, 5, 1, 0	24, 20, 10, 6, 5, 1, 0

Table 6
Representations and the multiplication table for D_{2h} symmetry group and its subgroups

Γ	D_{2h}	D_2	C_{2h}	C_{2v}	C_2	C_s	C_i	C_1
1	AG	A	AG	A1	A	A′	AG	A1
2	B1G	B1	BU	A2	B	A″	AU	
3	B2G	B2	BG	B1				
4	B3G	B3	AU	B2				
5	AU							
6	B1U							
7	B2U							
8	B3U							

Multiplication table

1	2	3	4	5	6	7	8
2	1	4	3	6	5	8	7
3	4	1	2	7	8	5	6
4	3	2	1	8	7	6	5
5	6	7	8	1	2	3	4
6	5	8	7	2	1	4	3
7	8	5	6	3	4	1	2
8	7	6	5	4	3	2	1

where the cases of $v(6,6)$, $v(6,10)$ and $v(6,11)$ have been skipped. The next step terminates the procedure

$$\begin{array}{l|l} v(7, N_k+i),\ N_k=7,8,9: & 27 \\ \{m^7(v)\}: & 87, 77, 73, 63, 53, 49, 39, 35, 34, 24, 20, 10, 6, 5, 1, 0 \end{array}$$

As can be seen the algorithm may easily be organzed in such a way that as result an ordered set of the lexical indices of the paths joining two vertices is obtained. To execute the algorithm, only one pass over the set of vertices satisfying condition (178) is necessary. A generalization of the algorithm so that also a symmetry index and the number of singles along each path may be calculated is straightforward. The multiplication table for the point-group D_{2h} and for all its subgroups, necessary in determining the path symmetries, is given in table 6. For remarks on taking into account the point-group symmetry see section I.4.4.

II.2. Formulae

II.2.1. Notation

The general formulae for CI matrix elements and for the coupling constants are given in the next sections. The information adequate for programming CI methods is summarized in tables 7 (conventional CI), 8 (DCI, no external space) and 10 (DCI, external space separated). Table 9, being a supplement to tables 7 and 8, contains explicit expressions for the line-up permutations. All the formulae are complete in the sense that they cover the most general cases and are brought to the final, directly programmable form. The notation and the conventions used have been explained in detail in part I of this paper. However, for convenience, the symbols used in the tables are collected again at the end of section II.2. Moreover, in order to make the presentation compact and the classification of the formulae transparent several new symbols have been introduced. Notation specific to each table is described separately.

All CI formulae refer to a configuration pair. Therefore it is convenient to divide all symbols into two classes: to the first one belong the symbols describing the configuration pair, to the second the ones of more general character. In the lists of symbols, where it is possible, a reference to the corresponding equation in part I is given.

II.2.2. Matrix elements and coupling constant formulae

General matrix element formulae (for conventional CI calculations) and the coupling constants (for DCI) are collected in tables 7 and 8. The formulae are valid for the most general CSFs compatible with eq. (48) in which the orbital and the spin parts are determined by eqs. (51) and (54), respectively. The orbitals, configurations λ and μ differ by, are denoted i, j (if $r_{\lambda\mu}=1$) and i, j, k, l (if $r_{\lambda\mu}=2$). The orbitals which have the same occupation numbers both in λ and in μ are denoted p, r (if $r_{\lambda\mu}=0$) and p (if $r_{\lambda\mu}=1$).

In determining the line-up permutations particularly important are the position indices of the orbitals which are singly occupied in one of the configurations only. The number of these orbitals

Table 7
Matrix element formulae. Explicit forms of P_1, P_2, P_3 are given in table 9

$$\mathbf{H}_0^{(\lambda\lambda)} = \mathbf{I}\sum_{p=1}^{n}\left[n_p(p|p) + \delta(n_p, 2)(pp|pp)\right] + \mathbf{I}\sum_{p<r}^{n} n_p n_r\left[(pp|rr) - \tfrac{1}{2}\left(1 - \delta(n_p n_r, 1)\right)(pr|pr)\right]$$

$$+ \sum_{p<r}^{n} \delta(n_p n_r, 1)\mathbf{U}_S^s((\bar{p}, \bar{r}))(pr|pr)$$

$$\mathbf{H}_1^{(\lambda\mu)} = \mathbf{A}_{\lambda\mu}(P_x)\left\{(i|j) + \delta(n_j, 2)(ij|jj) + \delta(n_i, 2)(ij|ii) + \sum_p{}' \left[n_p^\lambda(ij|pp) - \delta\left(n_p^\lambda, 2\right)(ip|jp)\right]\right\}$$

$$+ \sum_p{}' \delta\left(n_p^\lambda, 1\right)\mathbf{A}_{\lambda\mu}\left(P_y(\bar{p})\right)(ip|jp)$$

$$\mathbf{H}_2^{(\lambda\mu)} = J^x\mathbf{A}_{\lambda\mu}(P_x) + J^y\mathbf{A}_{\lambda\mu}(P_y); \quad J^1 = (ij|kl), \quad J^2 = (il|jk), \quad J^3 = (ik|jl)$$

$r_{\lambda\mu}$	Δd	ν_0^λ	ν_1^λ	ν_2^λ	Chain	P_x	P_y
1	0	1	1	0	(A1)	P_1	P_2
		0	1	1		$-P_1$	P_2'
	1	0	2	0	(A2)	P_1	$\delta(n_j^\mu, 0)P_2 + \delta(n_j^\mu, 2)P_2'$
2	0	1	0	1	(A3)	P_2	
	0	1	1	1	(B1)	P_2	
	1	0	2	1	(B2)	$-P_2$	
		1	2	0		P_2	
	0	0	2	2	(C1)–(C3)	P_3	P_2
		1	2	1		$\begin{cases} -P_3, & \text{if } n_i^\mu = n_k^\lambda \\ -P_2, & \text{otherwise} \end{cases}$	P_1
		2	2	0		P_3	P_2
	1	0	3	1	(C4)–(C7)	$\begin{cases} -P_1, & \text{if } n_k^\mu = 2 \\ -P_2, & \text{otherwise} \end{cases}$	$\begin{cases} P_3', & \text{if } n_j^\mu = 2 \\ P_2', & \text{otherwise} \end{cases}$
		1	3	0		$\begin{cases} P_2, & \text{if } n_k^\mu = 2 \\ P_1, & \text{otherwise} \end{cases}$	$\begin{cases} P_2, & \text{if } n_j^\mu = 2 \\ P_3, & \text{otherwise} \end{cases}$
	2	0	4	0	(C8)	$\begin{cases} P_3, & \text{if } n_i^\mu = n_j^\mu \\ P_1, & \text{otherwise} \end{cases}$	$\begin{cases} P_3, & \text{if } n_j^\mu = n_k^\mu \\ P_2, & \text{otherwise} \end{cases}$

in λ (μ) is denoted ν_1^λ (ν_1^μ) and $\nu_1 = \nu_1^\lambda + \nu_1^\mu$. It is easy to check that ν_1 is even and $\nu_1 \leqslant 2r_{\lambda\mu}$. Under assumption that $\nu_1^\lambda \geqslant \nu_1^\mu$, i.e. that $s \geqslant s'$, 6 different partitions of ν_1 into ν_1^λ and ν_1^μ are possible. Depending on the case, the following designation for the orbital indices are used.

$\nu_1^\lambda = 4$, $\nu_1^\mu = 0$ $\quad i > j > k > l$ are all singles in λ;

Table 8
DCI formulae. Explicit forms of P_1, P_2, P_3 are given in table 9

Designation of integrals:

$$J^1=\begin{cases}(ij|ii) & \text{in } \{75\} \text{ and } \{35\}\\ (ij|jj) & \text{in } \{75\} \text{ and } \{53\}\\ n_p^{\lambda}(ij|pp),\ (i|j) & \text{in (A1) and (A2)}\\ (ij|kl) & \text{in (C1)}-\text{(C8)}\end{cases}\qquad J^2=\begin{cases}(ij|ij) & \text{in (A3)}\\ (ip|jp) & \text{in (A1), (A2), (B1), (B2)}\\ (il|jk) & \text{in (C1)–(C8)}\end{cases}$$

$$J^3=\ (ik|jl)\quad \text{in (C1)–(C8)}$$

Assignment of coupling constants to the integrals:

$J^x\mathbf{A}_{\lambda\mu}(P_x)$, $J^y\mathbf{A}_{\lambda\mu}(P_y)$, $x, y = 1, 2, 3.$

Assignment of coupling constants to the loops:

2. Two- and three-segment loops

	(A1), $i>j$		(A2), $i>j$		(A3)	(B1), $i>j$		(B2), $i>j$	
	{13}	{75}	{35}	{53}	{26}	{156}	{732}	{332}	{556}
P_x	P_1	$-P_1$	P_1	P_1	P_2	$-P_2$	$-P_2$	P_2	$-P_2$
P_y	P_2	P_2'	P_2	P_2'					

2. Four-segment loops

Chain	Indices	J^1	J^2	J^3	Loops					
(C1)	$i>j>k>l$	J_1	J_2	J_3	{1133}	{7755}	{7153}	{1735}	{7135}	{1753}
(C2)	$i>k>j>l$	J_3	J_2	J_1	{1313}	{7575}	{7513}	{1375}	{7315}	{1573}
(C3)	$k>i>j>l$	J_2	J_3	J_1	{1331}	{7557}	{7531}	{1357}	{7351}	{1537}
	P_x				P_3		$-P_3$		$-P_2$	
	P_y				P_2		P_1		P_1	
(C4)	$i>j>k>l$	J_1	J_2	J_3	{1353}	{7535}	{1335}	{7553}	{1533}	{7355}
(C5)	$i>j>l>k$	J_1	J_3	J_2	{3153}	{5735}	{3135}	{5753}	{5133}	{3755}
(C6)	$i>l>j>k$	J_3	J_1	J_2	{3513}	{5375}	{3315}	{5573}	{5313}	{3575}
(C7)	$l>i>j>k$	J_2	J_1	J_3	{3531}	{5357}	{3351}	{5537}	{5331}	{3557]
	P_x				P_1	$-P_1$	P_1	$-P_1$	P_2	$-P_2$
	P_y				P_2	P_2'	P_3	P_3'	P_3	P_3'
(C8)	$i>j>k>l$	J_1	J_2	J_3	{3553}	{5335}	{3535}	{5353}	{3355}	{5533}
	P_x				P_1		P_1		P_3	
	P_y				P_3		P_2		P_2	

$\nu_1^\lambda = 3,\ \nu_1^\mu = 1$ $i > j > k$ are singles in λ, l is a single in μ;
$\nu_1^\lambda = 2,\ \nu_1^\mu = 2$ $i > j$ are singles in λ, $k > l$ are singles in μ;
$\nu_1^\lambda = 2,\ \nu_1^\mu = 0$ $i > j$ are singles in λ; moreover, if $r_{\lambda\mu} = 2$, then $k = l$ is a double either in λ or in μ;
$\nu_1^\lambda = 1,\ \nu_1^\mu = 1$ i is a single in λ, j is a single in μ; moreover, if $r_{\lambda\mu} = 2$, then $k = l$ is a double either in λ or in μ;
$\nu_1^\lambda = 0,\ \nu_1^\mu = 0$ $k = i$, $l = j$ are two (different) doubles: one in λ, another one in μ.

In the part of table 7 corresponding to $r_{\lambda\mu} = 2$, the assignment of permutations P_1, P_2, P_3 to P_x and P_y determines also the integral to appear in the matrix element formula; e.g., if $P_x = P_1$, $P_y = P_2'$, then $\mathbf{H}^{(\lambda\mu)} = J^1\mathbf{A}_{\lambda\mu}(P_1) + J^2\mathbf{A}_{\lambda\mu}(P_2')$. If P_y is not specified, then $\mathbf{H}^{(\lambda\mu)} = J^x\mathbf{A}_{\lambda\mu}(P_x)$.

In some cases it is convenient to define the Fock matrix $(i|F|j)$ (eq. (144)), the reference energy E_0 (eq. (145)) and a set of the reference occupation numbers η_i, $i = 1, 2, \ldots, n$ and express $\mathbf{H}_0^{(\lambda\mu)}$ and $\mathbf{H}_1^{(\lambda\mu)}$ in terms of these quantities. The corresponding formulas are:

$$\begin{aligned}\mathbf{H}_0^{(\lambda\mu)} = {} & \mathbf{I}E_0 + \mathbf{I}\sum_p \left[\left(\delta(n_p, 2) - \delta(\eta_p, 2)\right)(pp|pp) + (n_p - \eta_p)(p|F|p)\right] \\ & + \mathbf{I}\sum_{p<r} (n_p - \eta_p)(n_r - \eta_r)\left[(pp|rr) - \tfrac{1}{2}\left(1 - \delta(n_p n_r, 1)\right)(pr|pr)\right] \\ & + \sum_{p<r} \left[\mathbf{U}_S^s((\bar{p}, \bar{r})) + \tfrac{1}{2}\mathbf{I}(\eta_p + \eta_r - \eta_p\eta_r)\right]\delta(n_p n_r, 1)(pr|pr) \end{aligned} \tag{181}$$

and

$$\mathbf{H}_1^{(\lambda\mu)} = \mathbf{A}_{\lambda\mu}(P_x)(i|G|j) + {\sum_p}' \delta\left(n_p^\lambda, 1\right)\mathbf{A}_{\lambda\mu}(P_z(\bar{p}), (ip|jp), \tag{182}$$

where

$$\begin{aligned}(i|G|j) = {} & (i|F|j) + \delta(n_j, 2)(ij|jj) + \delta(n_i, 2)(ij|ii) \\ & + {\sum_p}' \left[\left(n_p^\lambda - \eta_p\right)(ij|pp) + \Delta\left(n_p^\lambda, \eta_p\right)(ip|jp)\right], \end{aligned} \tag{183}$$

$$\Delta\left(n_p^\lambda, \eta_p\right) = \tfrac{1}{2}\eta_p\left(1 - \delta\left(n_p^\lambda, 1\right)\right) - \delta\left(n_p^\lambda, 2\right), \tag{184}$$

$$P_z(\bar{p}) = P_y(\bar{p}) + \tfrac{1}{2}\eta_p P_x. \tag{185}$$

For explanation of the remaining symbols see section II.2.4.

Table 8 gives an assignment of the coupling constants to the integrals and to the configuration pairs (to the loops). This information is basic for all DCI algorithms. The table is, in principle, self-explanatory. The only comment regards a specific convention concerning the two-electron integrals. The integrals J_1, J_2, J_3 are stored in an integral list in the standard sequence defined by eq. (146). It implies that $J_1 = (ij|kl)$, $J_2 = (il|jk)$, $J_3 = (ik|jl)$ while $i > j > k > l$. Since the sequence of the orbital indices is not retained in neither table 7 nor 8 (it may be different in different chains of loops, cf. section I.4.4), the integrals appearing in the tables are designated J^1, J^2, J^3. Their assignment to J_1, J_2, J_3 depends upon the sequence of the orbital indices i, j, k, l and is shown explicitly in the table. Also all the chains of loops together with the corresponding sequences of the orbital indices, are specified there.

When the line-up permutations are known, the coupling constant values may be determined by eq. (133). A list of the permutations is given in table 9. As can be seen, for each case (i.e. for $r_{\lambda\mu}$, Δd, ν_1^λ set, i.e. for a chain of loops) we need at most 3 different permutations. A permutation in the table is expressed in 3 different forms: as a product of at most 4 cycles, as a product of a transposition and one (selected for each case) permutation, as a product of at most 2 cycles and a permutation shifting at most two SCPs. The first two forms are valid independently of the specific spin-coupling scheme, under condition that the spin function is compatible with eq. (54).

Table 9
List of line-up permutations (supplement to tables 7 and 8)

$r_{\lambda\mu}$	Δd	Singles		Chain	Permutations
		in λ	in μ		
1	0	i	j	(A1)	$P_1=(\bar i..\bar j)$ $P_0=(\bar i,\bar p)P_1=(\bar i..\bar p+\epsilon_{ip})(\bar p..\bar j)$ $P_2=[\delta(n_p^\lambda,1)P_0-\delta(n_p^\lambda,2)P_1]$; $P_2'=[P_1+\delta(n_p^\lambda,1)P_0]$
1	1	$i>j$	–	(A2)	$P_1=(\bar i..s)(\bar j..s)=(\bar i..\bar j)\vert_{\bar j}$ $P_0=(\bar j,\bar p)P_1=(\bar j..\bar p+\epsilon_{jp})(\bar p..s)(\bar i-1..s)=(\bar j..\bar p+\epsilon_{jp})(\bar p..\bar i)\vert_{\bar i-1}$ $P_0'=(\bar i,\bar p)P_1=(\bar i..\bar p+\epsilon_{ip})(\bar p..s)(\bar j..s)=(\bar i..\bar p+\epsilon_{ip})(\bar p..\bar j)\vert_{\bar j}$ $P_2=[\delta(n_p^\lambda,1)P_0-\delta(n_p^\lambda,2)P_1]$: $P_2'=[\delta(n_p^\lambda,1)P_0'-\delta(n_p^\lambda,2)P_1]$
2	0	–	–	(A3)	$P_2=I$
2	0	i	j	(B1)	$P_2=(\bar i..\bar j)$
2	1	$i>j$	–	(B2)	$P_2=(\bar i..s)(\bar j..s)=(\bar i..\bar j)\vert_{\bar j}$
2	0	$i>j$	$k>l$	(C1)–(C3)	$\left.\begin{array}{l}P_2=(\bar i..\bar l)(\bar j+1..\bar k)\\ P_3=(\bar i,\bar j)P_2=(\bar j..\bar l)(\bar i..\bar k)\end{array}\right\}$ if $\bar l\leqslant\bar j$; $\left.\begin{array}{l}P_2=(\bar i..\bar l+1)(\bar j..\bar k)\\ P_3=(\bar i..\bar k)(\bar j..\bar l)\end{array}\right\}$ if $\bar l>\bar j$ $P_1=[P_2+P_3]$
2	1	$i>j>k$	l	(C4)–(C7) [a]	$P_1=(\bar i..s)(\bar j..s)(\bar k..\bar l)=(\bar i..\bar j)(\bar k..\bar l)\vert_{\bar j-\delta}$ $P_2=(\bar i,\bar k)P_1=(\bar k..s)(\bar j-1..s)(\bar i-2..\bar l)=(\bar j..\bar k)(\bar i..\bar l)\vert_{\bar k+\epsilon}$ $P_3=(\bar j,\bar k)P_1=(\bar i..s)(\bar k..s)(\bar j-1..\bar l)=(\bar i..\bar k)(\bar j+1..\bar l)\vert_{\bar k+\epsilon}$ $P_2'=[P_1+P_3]$; $P_3'=[P_1+P_2]$
2	2	$i>j>k>l$	–	(C8)	$P_1=(\bar i..s)(\bar j..s)(\bar k..s)(\bar l..s)=(\bar k..\bar l)(\bar i..\bar j)\vert_{\bar j,\bar l}$ $P_2=(\bar j,\bar l)P_1=(\bar i..s)(\bar j..s)(\bar k..s-1)(\bar l..s-2)=(\bar k..\bar j)(\bar i..\bar l)\vert_{\bar j,\bar l}$ $P_3=(\bar j,\bar k)P_1=(\bar i..s)(\bar j..s)(\bar k..s-1)(\bar l..s)=(\bar j..\bar l)(\bar i..\bar k)\vert_{\bar k,\bar l}$

[a] $\delta=\begin{cases}1, & \text{in (C6) and (C7)},\\ 0, & \text{otherwise},\end{cases}$ $\epsilon=\begin{cases}1, & \text{in (C4)},\\ 0, & \text{otherwise.}\end{cases}$

The last form is valid only under assumption of the YK spin coupling scheme.

In order to outline a DCI procedure based on Tables 8 and 9, let us consider the case of integrals with 4 different indices. Building up the DCI procedure comprises the following steps.

1. Make a DO-loop over integral indices.
2. Fix a set of 4 indices (4 levels in the orbital graph) and take the corresponding J_1, J_2, J_3 integrals.
3. Determine the numbers of singles which may appear between the levels and between the head of the graph and the uppermost level.
4. Make a DO-loop over all possible distributions of the singles.
5. Make a DO-loop over (C1)–(C8) chains.
6. Fix a chain, define J^1, J^2, J^3, determine P_1, P_2, P_3 (table 9), evaluate $\mathbf{A}(P_x)$, $x = 1, 2, 3$ (according to section I.4.3).
7. Form partial matrix elements $\mathbf{H}^{(\lambda\mu)} = J^x\mathbf{A}(P_x) + J^y\mathbf{A}(P_y)$ for all the loops of the chain, according to table 8.
8. Find all the paths, and in consequence the components of the index vector, compatible with the conditions determined so far (cf. section II.1.2).
9. Multiply $\mathbf{H}^{(\lambda\mu)}$ by the appropriate parts of the CI vector.

The analogous procedure in the case of separated external space contains additional DO-loops over the external orbitals and depends upon a specific strategy choice. This subject is discussed in the next section in more detail.

II.2.3. DCI formulae with the external space separated

Separation of the external space is aimed at the following algorithm: given an internal space contribution to a set of coupling constants, determine its external space complements and calculate the entire external space contribution to the CI vector within a simple-structured DO-loop. In this section there are collected coupling constant expressions in which the internal- and external-space counterparts are separated and the dependence on the external orbital indices is explicitly shown. We designate

$$\mathbf{H}_r^{(\lambda\mu)} = \mathbf{H}_r(\lambda_{\mathrm{E}}, \lambda_{\mathrm{I}}; \mu_{\mathrm{E}}, \mu_{\mathrm{I}}), \tag{186}$$

where $r = r_{\lambda\mu}$ and λ_{E}, $\mu_{\mathrm{E}} = \mathrm{V}, \mathrm{S}_a, \mathrm{D}_{aa}, \mathrm{D}_{ab}$. If $\lambda_{\mathrm{E}} = \mu_{\mathrm{E}}$ then the internal-space contribution is designated $\mathbf{H}_r(\lambda_{\mathrm{I}}^v, \mu_{\mathrm{I}}^v)$ where $v = \mathrm{V}, \mathrm{S}, \mathrm{D1}, \mathrm{D2}$ stand for the last vertex of the internal path. The expressions for $\mathbf{H}_r(\lambda_{\mathrm{I}}^v, \mu_{\mathrm{I}}^v)$ may be obtained from eqs. (181) and (182) of the preceding section by limiting the range of all the orbital indices to the internal space only. If $\lambda = \mu$ then we write $\mathbf{H}_r(\lambda_{\mathrm{I}}^v, \lambda_{\mathrm{I}}^v) = \mathbf{H}_r(\lambda_{\mathrm{I}}^v)$.

The coupling constant expressions are collected in table 10. The table is divided into two parts. In the first one, corresponding to $r_{\lambda\mu} = 0, 1$, explicit formulae for the coupling constants (and for the matrix elements as well) are given. In the second part, for $r_{\lambda\mu} = 2$, the line-up permutations and the coupling constants for I0, I1, I2 and I3 integrals are displayed. The case of I4 is omitted here since it is given in table 8.

Table 10
Separation of external space; no. refers to an entry in table 3

$r_{\lambda\mu}=0$; $a>b$;   eq. (181)

no.	λ_E	internal space	internal–external space cross terms	external space
1	V	$\mathbf{H}_0(\lambda_1^V)$		
2	S_a	$\mathbf{H}_0(\lambda_1^S)+$	$J_1^a+J_2^{a0}+J^a$	
3	D_{aa}	$\mathbf{H}_0(\lambda_1^D)+$	$2J_1^a+J^a$	
4	D_{ba}	$\mathbf{H}_0(\lambda_1^D)+$	$J_1^a+J_1^b+J_2^{a0}+J_2^{b1}+J^a+J^b+$	$\mathbf{I}(aa\|bb)+\mathbf{E}^s(ab\|ab)$

$$J^c=n_c(c|F|c)+(n_c-1)(cc|cc);\quad J_1^c=\sum_p(n_p-\eta_p)\left[(pp|cc)-\tfrac{1}{2}\left(1-\delta(n_pn_c,1)\right)(pc|pc)\right]$$

$$J_2^{c\nu}=\sum_p\delta(n_p,1)\left[\mathbf{U}_S^s((\bar{p},s-\nu))+\tfrac{1}{2}\eta_p\right](pc|pc);\quad c=a,b;\ \nu=0,1$$

$r_{\lambda\mu}=1$;   eqs. (182)–(185)

no.	λ_E	μ_E	internal space	internal–external space cross terms	external space
Loops formed by φ_i, φ_j orbitals, $a>b$					
1	V	V	$\mathbf{H}_1(\lambda_1^V,\mu_1^V)$		
2	S_a	S_a	$\mathbf{H}_1(\lambda_1^S,\mu_1^S)+$	$(aa\|ij)\mathbf{A}(P_x)+(ai\|aj)\mathbf{A}(P_y(s))$	
3	D_{aa}	D_{aa}	$\mathbf{H}_1(\lambda_1^D,\mu_1^D)+$	$[2(aa\|ij)-(ai\|aj)]\mathbf{A}(P_x)$	
4	D_{ba}	D_{ba}	$\mathbf{H}_1(\lambda_1^D,\mu_1^D)+$	$[(aa\|ij)+(bb\|ij)]\mathbf{A}(P_x)$ $+(ai\|aj)\mathbf{A}(P_y(s))+(bi\|bj)\mathbf{A}(P_y(s-1))$	
Loops formed by φ_i, φ_a orbitals: $a>b$					
11	V	S_a		$(a\|G\|i)\mathbf{A}(P_x)+\mathbf{K}^a$	
12	D_{aa}	S_a		$(a\|G\|i)\mathbf{A}(P_x)+\mathbf{K}^a+(ia\|aa)\mathbf{A}(P_x)$	
13	D_{ba}	S_b		$[(a\|G\|i)+(ai\|bb)]\mathbf{A}(P_x)+\mathbf{K}^a$ $+(ab\|ib)\mathbf{A}(P_y(s))$	
Loops formed by φ_a, φ_b orbitals; $a>b$ or $a<b$					
5	S_a	S_b		$(a\|G\|b)\mathbf{I}+\mathbf{K}^{ab}$	
6	D_{ba}	D_{bb}		$\sqrt{2}\,\boldsymbol{\delta}_{ab}^s[(a\|G\|b)+\mathbf{K}^{ab}]$	
7	D_{ca}	D_{cb}		$\boldsymbol{\delta}_{ca}^s[(a\|G\|b)+\mathbf{K}^{ab}]\boldsymbol{\delta}_{cb}^s+$	$\boldsymbol{\delta}_{ca}^s[(ab\|cc)+\mathbf{E}^s(ac\|bc)]\boldsymbol{\delta}_{cb}^s$

$$\mathbf{K}^a=\sum_{\substack{p=1\\(p\neq i)}}^{n_i}\delta\left(n_p^\lambda,1\right)\mathbf{A}(P_z(\bar{p}))(ap|ip);\ \mathbf{K}^{ab}=\sum_{p=1}^{n_i}\delta\left(n_p^\lambda,1\right)\mathbf{U}_S^s((\bar{p},s))(ap|bp).$$

$$\text{Sign matrix: }\boldsymbol{\delta}_{ab}^s=\begin{cases}\mathbf{E}^s & \text{if } a>b.\\ \mathbf{I} & \text{if } a\leqslant b.\end{cases}$$

$r_{\lambda\mu}=2$
(I) I0, I1, I2 (open loops): $a\geqslant b$, $i\geqslant j$

$$\mathbf{H}_2^{(\lambda\mu)}=\mathbf{J}\mathbf{A}_{\lambda\mu}(P);\ \mathbf{J}=\begin{cases}\mathbf{I}(aw_1|bw_2), & \text{if } a=b \text{ or } w_1=w_2\\ \mathbf{I}(aw_1|bw_2)+\mathbf{E}^s(aw_2|bw_1), & \text{otherwise}\end{cases}$$

case	no.	λ_E	μ_E	sequence of a, b, c, d	w_1	w_2	internal loops	P
I0	8, 9, 10	D_{ba}	D_{dc}	$c \geqslant d$	c	d	$\{0\}$	I
				$c < d$	d	c		
I1	16, 17	D_{ba}	S_c	$c \neq a, b$	c	i	$\{1\}$	$(s-1..\bar{i})$
							$\{5\}$	$(\bar{i}..s-1)$
I2 (open loops)	14, 15	D_{ba}	V		i	j	$\{11\}$	$(s-1..\bar{j})(s..\bar{i})$
							$\{55\}$	$(\bar{i}..s)(\bar{j}..s-2)$
							$\{15\}$	$(\bar{i}..s-1)(s-2..\bar{j})$
							$\{51\}$	$(\bar{j}..s-2)(s..\bar{i})$
					i	i	$\{2\}$	I

(II) I2 (closed loops): $i \geqslant j$

$$\mathbf{H}_2^{(\lambda\mu)} = J_x \mathbf{A}_{\lambda\mu}(P_x^e) + J_y \mathbf{A}_{\lambda\mu}(P_y^e); \quad J_1 = (e_1 e_2 | ij),\ J_2 = (e_1 j | e_2 i),\ J_3 = (e_1 i | e_2 j), \quad \begin{array}{l} e_1 = \max(a, b) \\ e_2 = \min(a, b) \end{array}$$

no.	λ_E	μ_E	sequence of a, b, c	P_x^e	P_y^e	internal loops	P_x	P_y	permutations
5	S_a	S_b		P_x	P_y	$\{13\}$	P_1	P_2	$P_1 = (\bar{i}..\bar{j})$
6, 7	D_{ca}	D_{cb}	$c < a, b$	P_x	P_y	$\{75\}$	$-P_1$	P_3	$P_2 = (\bar{i}..s-1)(s..\bar{j})$
									$P_3 = P_1 + P_2$
			$\left\{\begin{array}{l} a < c < b \\ b < c < a \end{array}\right.$	EP_x	$P_y E'$	$\{53\}$	P_1	P_2	$P_1 = (\bar{i}..s)(\bar{j}..s) = (\bar{i}..\bar{j})\|_j$
			$c \geqslant a, b$	P_x	$EP_y E'$	$\{35\}$	P_1	P_3	$P_2 = (\bar{i}..s-1)(\bar{j}..s)$
									$P_3 = (\bar{i}..s-1)(\bar{j}..s-2)$

1. $r_{\lambda\mu} = 0$ and $r_{\lambda\mu} = 1$

The external space and the cross-term internal–external space contributions presented in table 10 correspond to eqs. (181) and (182). We have assumed that $\eta_p = 0$ for $p = n_I + 1, \ldots, n$, since the simplest form of the external space contributions to $\mathbf{H}_1^{(\lambda\mu)}$ is then obtained. Usually, the optimum algorithms can be derived if we set $\eta_p = 2$ for $p = 1, 2, \ldots, n_I$. However, in special cases, other options may be more convenient. If $\eta_p = 0$ for $p = 1, 2, \ldots, n$, the formulae corresponding to the ones in tables 7 and 8 are obtained. For $r_{\lambda\mu} = 1$, permutation P_z is defined by eq. (185), while P_x and P_y are determined in tables 7 and 9 (chains (A1) and (A2)). In each case selection of the chain (either (A1) or (A2)) results from an analysis of the internal space contribution. For D_{ba}-type configurations relation $a > b$ is assumed, except for the case of $r_{\lambda\mu} = 1$, no. 5, 6, 7, where both $a > b$ and $a < b$ sequences are allowed.

2. $r_{\lambda\mu} = 2$

This part of table 10 is divided into two sections. In the first one (left-hand side) external space

(III) I3; conventions as in table 8

$\mathbf{H}_2^{(\lambda\mu)} = J_x \mathbf{A}_{\lambda\mu}(P_x^e) + J_y \mathbf{A}_{\lambda\mu}(P_y^e)$; $J_1 = (ai|jk)$, $J_2 = (ak|ij)$, $J_3 = (aj|ik)$

no.	λ_E	μ_E	sequence of a, b	P_x^e	P_y^e	assignment of permutations to internal loops				J^1	J^2	J^3	permutations
I1	V	S_a		P_x	P_y	(C1′):	{133}	{753}	{735}	J_1	J_2	J_3	$P_1 = (i..s)(j..\bar{k})$
I2,	D_{ba}	S_b	$a \geqslant b$	P_x	P_y	(C2′):	{313}	{573}	{375}	J_1	J_3	J_2	$P_3 = (j..s)(i-1..\bar{k})$
I3			$a < b$	$P_x E$	$P_y E$	(C3′):	{331}	{537}	{357}	J_3	J_1	J_2	$P_2 = P_1 + P_3$
						P_x:	P_1	$-P_1$	$-P_3$				
						P_y:	P_3	P_2	P_2				
						(C4′):	{533}	{353}	{335}	J_1	J_2	J_3	$P_1 = (i..s)(j..s)(\bar{k}..s)$
						P_x:	P_1	P_1	P_3				$= (i..s)(j..\bar{k})\|_{\bar{k}}$
						P_y:	P_3	P_2	P_2				$P_2 = (i..s)(j..s-1)(\bar{k}..s)$
													$= (j..s)(i-1..\bar{k})\|_{k}$
													$P_3 = (i..s)(j..s-1)(\bar{k}..s-2)$
													$= (\bar{k}..s)(i-1..j)\|_{j-1}$
						(B2′):	{65}			J_1	J_2	–	$P_2 = (i..s)$
						P_x:	$-P_2$						
I1	S_a	V		P_x	P_y	(C1″):	{755}	{135}	{153}				as for (C1′), (C2′), (C3′), except
I2,	S_b	D_{ba}	$a \geqslant b$	P_x	P_y	(C2″):	{575}	{315}	{513}				$P_2' = (i \ldots s-1)(j \ldots s-2)(s \ldots \bar{k})$
I3			$a < b$	EP_x	EP_y	(C3″):	{557}	{351}	{531}				$= (j \ldots i-1)(s \ldots \bar{k})\|_{i-\delta}$
						P_x:	$-P_1$	P_1	P_3				
						P_y:	P_3'	P_2'	P_2'				$P_3' = P_1 + P_2'$; $\delta = \begin{cases} 1, & \text{if } i < k \\ 0, & \text{otherwise} \end{cases}$
						(C4″):	{355}	{535}	{553}				as for (C4′)
						P_x:	P_1	P_1	P_3				
						P_y:	P_3	P_2	P_2				
						(B2″):	{23}						as for (B2′)
						P_x:	P_2						

Designations: $E = (s-1, s)$; $E' = (s'-1, s')$.

dependence of the coupling constants has been shown. In particular, their assignment to I0, I1, I2, I3 integrals and to the external configuration pairs λ_E and μ_E has been given. The second (right-hand side) section describes the internal space complements of λ_E and μ_E. Explicit expressions for the line-up permutations have been collected in the last column of the table.

Let us consider a pair of external paths, both of them passing through vertex D. This pair corresponds to a set of configurations, each of them containing two electrons in the external space. Let the λ, μ pair be a member of this set. The line-up permutations P depend only upon position indices of orbitals in λ and in μ. Then, P does not depend on whether the two electrons in the external space form two singles or one double. The representation matrices $\mathbf{U}_S^g(P)$, calculated for a given pair of the internal paths, under assumption that there are two external singles in λ and two in μ, may also be used if the electron pairs in $\mathscr{E}$ form one or two doubles. Taking into account this possibility results in a simplification of the algorithm since it significantly reduces the number of different cases to be considered. To this purpose we modify eq. (133) determining the coupling constants. Let $d_\lambda^\mathrm{E}(d_\mu^\mathrm{E})$ be the number of the external doubles and $s_\mathrm{m}(s'_\mathrm{m})$ the maximum number of singles in $\lambda(\mu)$. Then, the actual number of singles in the two configurations under consideration is

$$s_\lambda = s_\mathrm{m} - 2d_\lambda^\mathrm{E}, \quad s_\mu = s'_\mathrm{m} - 2d_\mu^\mathrm{E}. \tag{187}$$

Now eq. (133) may be written as

$$\mathbf{A}_{\lambda\mu}(P) = a_\mathrm{I} a_\mathrm{E} \left[\mathbf{U}_S^s(P)\right]^{fg}, \tag{188}$$

where $a_\mathrm{I} = 2^{\Delta s/4}$, $a_\mathrm{E} = 2^{\Delta d(\mathrm{E})/2}$, $\Delta s = |s_\mathrm{m} - s'_\mathrm{m}|$, $\Delta d(\mathrm{E}) = |d_\lambda^\mathrm{E} - d_\mu^\mathrm{E}|$, $f = f(S, s_\lambda)$, $g = g(S, s_\mu)$ and P has to be determined for $d_\lambda^\mathrm{E} = d_\mu^\mathrm{E} = 0$. All permutations in table 10 are determined under that assumption. The values of s_λ, s_μ and d^E used in eq. (188) are very easy to calculate when the loops are given. For example, if $\lambda_\mathrm{E} = \mathrm{D}_{ba}$, $\mu_\mathrm{E} = \mathrm{D}_{aa}$ are associated with the internal loop $\{53\}$, then $d_\lambda^\mathrm{E} = 0$, $d_\mu^\mathrm{E} = 1$, $s'_\mathrm{m} = s_\mathrm{m} - 2$ and $s_\lambda = s_\mathrm{m}$, $s_\mu = s_\mathrm{m} - 4$. The permutations, as displayed in table 10, have been determined for $\lambda_\mathrm{E} = \mathrm{D}_{ba}$, $\mu_\mathrm{E} = \mathrm{D}_{ca}$.

In the cases of I0, I1 and I2 (open loops) diagonal matrixes **J** (as defined in the table) should be processed rather than individual two-electron integrals. The chains of loops, as specified for I3, are subsets of the chains for the case of I4 (table 8). For example

$$\begin{array}{llllllll} (\mathrm{C1}): & \{1133\}, & \{1753\}, & \{1735\}, & & \{7755\}, & \{7135\}, & \{7153\}; \\ (\mathrm{C1}'): & \{133\}, & \{753\}, & \{735\}; & (\mathrm{C1}''): & \{755\}, & \{135\}, & \{153\}; \end{array}$$

i.e. (C1′) and (C1″) may be obtained by removing the first segment from appropriate members of (C1).

II.2.4. List of symbols and abbreviations

General symbols

N	no. of electrons,
n	no. of orbitals,
S	total spin quantum number,
$(i\|j)$	one-electron integral,
$(ij\|kl)$	two-electron integral,
η, $\eta_p = 0, 1, 2$	reference occupations numbers; eqs. (144), (145),
$\mathbf{H}^{(\lambda\mu)}$	$f \times g$ block of CI matrix; eq. (58),
P_x, P'_x	permutations,
$P_x(\bar{p})$	a permutation in which a dependence on an index $\bar{p}$ is explicitly indicated,
$\mathbf{U}_S^N(P_x)$	representation matrix of the N!-element permutation group; eq. (55),
$[\mathbf{U}_S^N(P_x)]^{fg}$	$f \times g$ block of $\mathbf{U}_S^N$ (the first g columns of $\mathbf{U}_S^s$),
$\mathbf{A}_{\lambda\mu}(P_x)$	$f \times g$ coupling constant matrix; eq. (133),

$(\bar{k}, \bar{l})$	transposition,
$(\bar{k}, \bar{l})^m =$	$\begin{cases} (k, l), & \text{if } m \text{ is odd}, \\ 1, & \text{if } m \text{ is even}, \end{cases}$
$\mathbf{E}^s = \mathbf{U}^s_S((s-1, s))$;	eq. (149),
$(\bar{k}..\bar{l})$	cycle; eq. (64),
$(\bar{k}..\bar{l})\|_j =$	$(\bar{k}..\bar{l})(\bar{j}..s'+2)^2$; eq. (137),
$(\bar{k}..\bar{l})\|_{ij} =$	$(\bar{k}..\bar{l})(\bar{i}..s'+2)^2(\bar{j}..s'+4)^2$,
(A1), (A2), (A3)	chains of two-segment loops; eq. (128),
(B1), (B2)	chains of three-segment loops; eq. (129),
(C1)–(C8)	chains of four-segment loops; eq. (130),
{13}, {75},	etc. two-segment loops; eq. (127a),
{156}, {1133},	etc. three- and four-segment loops,
V	configurations with no external orbitals,
S_a	configurations with one external orbital (φ_a) singly occupied,
D_{aa}	configurations with one external orbital (φ_a) doubly occupied,
D_{ba}	configurations with two external orbitals (φ_b and φ_a) doubly occupied,
$\mathscr{I}(n_\mathrm{I})$	internal space,
$\mathscr{E}(n_\mathrm{E})$	external space,
Ik, $k = 0, 1, 2, 3, 4$	a subclass of two electron integrals which depend upon indices of k internal orbitals; eqs. (147), (148),
e_k, $k = 1, 2, 3, 4$; $\varphi_a, \varphi_b, \varphi_c, \varphi_d (a, b, c, d = n_\mathrm{I} + 1, \ldots, n)$	external orbitals,
i_k, $k = 1, 2, 3, 4$; $\varphi_i, \varphi_j, \varphi_k, \varphi_l$ $(i, j, k, l = 1, \ldots, n_\mathrm{I})$	internal orbitals,
$\mathbf{I}$	$f \times f$ unit matrix,
$\delta_{ab} = \delta(a, b)$	Kronecker delta,
$\epsilon_{\mathrm{ik}} = \mathrm{sgn(i - k)}$.	

Configuration-pair symbols

λ, μ	configurations; eq. (51),
λ_E, μ_E	external parts of λ, μ,
λ_I, μ_I	internal parts of λ, μ,
$s = s_\lambda$, $s' = s_\mu$	no. of singles in λ, μ; $s \geqslant s'$, unless stated otherwise.
$d_\lambda (d_\mu)$	no. of doubles in λ (μ),
$\Delta d = d_\mu - d_\lambda = (s - s')/2$,	
d^E_λ (d^E_μ)	no. of external doubles in $\lambda(\mu)$,
$r = r_{\lambda\mu}$	the number of orbitals λ and μ differ by; eq. (65),
$f = f(S, s)$, $g = f(S, s')$	no. of independent spin functions associated with λ, μ; eq. (15),
$\nu^\lambda_p (\nu^\mu_p)$	no. of the orbitals whose occupations in λ and in μ are different and which are p-fold occupied in λ (μ),
i, j, k, l	indices of the orbitals λ and μ differ by,
$\bar{i}, \bar{j}, \bar{k}, \bar{l}$	position indices of $\varphi_i, \varphi_j, \varphi_k, \varphi_l$ in appropriate configuration,
p, r	indices of the orbitals whose occupations in λ and in μ are the same,
n^λ_k (n^μ_k)	occupation number of φ_k in λ (μ),
$n_k = \max(n^\lambda_k, n^\mu_k)$,	
$\sum_p{}' = \sum_{\substack{p \\ (p \neq i, j)}}$.	

Abbreviations

CAS	Complete Active Space (SCF),
CCI	Contracted CI,
CI	Configuration Interaction,
CS	Closed-Shell (reference state in CI),
CSF	Configuration State Function,
CSV	Configuration State Vector,
DCI	Direct CI,
DCI3	Direct CI for 3 electrons,
EID	External Index Driven (strategy),
FOIS	First-Order Interaction Space,
HF	Hartree–Fock,
ISD	Internal Spin Driven (strategy),
MC	Multi-Configuration (reference state in CI; SCF method),
MCCS	Multi-Configuration Closed-Shell (reference state in CI),
MO	Molecular Orbital,
PMED	Partial Matrix Element Driven (strategy),
S	Singly (excited configurations, e.g. CI S),
SACSF	Symmetry Adapted Configuration State Function,
SCF	Self-Consistent Field,
SCP	Singlet Coupled Pair,
SD	Singly and Doubly (excited configurations, e.g. CI SD),
SGA	Symmetric Group Approach,
SGGA	Symmetric Group Graphical (Global) Approach,
UGA	Unitary Group Approach,
GUGA	Graphical (Global) Unitary Group Approach,
UHF	Unrestricted Hartree–Fock,
VM	Vector Method,
YK	Yamanouchi–Kotani

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