

SGA derivation of matrix elements between spin-adapted perturbative wavefunctions

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Abstract

The Symmetric Group Approach (SGA) is used to derive formulas for the Hamiltonian matrix elements between perturbatively generated, highly contracted Configuration State Functions (CSF). The first order Møller–Plesset, Epstein–Nesbet and Krylov corrections are examples of such CSFs. They have been recently employed within the Superdirect Configuration Interaction (Sup-CI) method, which combines the efficiency and simplicity of the Many Body Perturbation Theory (MBPT) with the robustness of variational methods. The linear Sup-CI expansion in terms of such perturbative correction functions leads to a problem of efficient evaluation of matrix elements of the third power of the Hamiltonian in the usual CSFs. Using SGA and previously developed algebra of unitary group generators and circular operators one may express such matrix elements, similarly to MBPT, in terms of sums of products of two-electron integrals. Maple code enhancing greatly the algebraic manipulations has been developed and is available upon request. All the main steps in the derivation are discussed and the formulas are given in a compact form.

1 Introduction

The impressive development of the electronic structure methodology accompanied by the constant improvement of computer facilities has recently brought such achievements as the highly correlated *ab initio* study of the bacterial photosynthetic reaction center [1]. Reliable and simple enough approximations are required for routine treatment of systems of this size and complexity.

Efficient combinations of standard approaches, namely Configuration Interaction (CI), Perturbation Theory (PT) and Coupled Cluster (CC) method, proved to be especially useful when dealing with large systems. CAS-PT2 method [2] for instance starts from CI in a Complete Active Space space and then adds multireference perturbative corrections, whereas the Symmetry Adapted Cluster CI (SAC-CI) [3] is essentially CC approach formulated in the configurational space, allowing for the perturbative selection of configurations.

A new efficient scheme combining CI and many-body perturbation theory have been proposed recently, under the name Superdirect Configuration Interaction (Sup-CI) method [4]. As it is well known, the CI wavefunction is expressed in the form of a linear combination of N-electron functions, so-called Configuration State Functions (CSFs) [5]. This conceptually simple method of describing the electron correlation in practice has very serious limitations, associated with the slow convergence and thus the length of the CI expansion. Sup-CI method, following various forms of contracted CI [6], employs another possibility: projection into relatively small number of N-particle functions constructed as linear combination of CSFs, such as perturbatively generated Krylov or Nesbet correction vectors used in diagonalization methods [7].

Since the Hamilton operator contains one and two-body interactions only it should be possible to reduce the N-particle problem to the 2-particle equations. The *direct* CI method proposed by Roos [8] was the first step in this direction, getting rid of the N-particle matrix elements but leaving the coefficients of the N-particle CSFs. In the

Sup-CI approach one avoids construction of both the Hamiltonian matrix and the eigenvector, obtaining the energies and other properties from equations formulated directly at the 2-particle level.

Computing Hamiltonian matrix elements in highly contracted CSFs, arising as a result of acting with the Hamiltonian operator on some zeroth order approximation $|1\rangle = \hat{H}|0\rangle$, is not a trivial task however. Matrix elements of the third power of the Hamiltonian $\langle 0|\hat{H}^3|0\rangle$ have to be considered and reduced to the 2-particle level. The reference functions $|0\rangle$ are assumed to be of an arbitrary open shell type. In a similar effort Bendazzoli *et. al.* [9] developed the Fast CI method, which is a predecessor of the Sup-CI, for a limited case of several singlet open shell functions and they had to consider as many as 63 MBPT diagrams. For an arbitrary reference functions the problem is certainly more complex.

The Symmetric Group Approach (SGA) was previously used to derive formulas for the Hamiltonian matrix elements in the classical and direct CI [10]. It was later generalized [11] to provide matrix elements for the second power of the Hamiltonian, corresponding to the second order perturbation theory. Similar technique is employed now for the third power.

The spin and orbital subspaces or equivalently the spin and orbital parts of CSFs are treated separately in SGA. The non-relativistic Hamiltonians are spin free and they are also invariant with respect to the permutations of electron coordinates. Thus, the spin CSFs may be classified according to irreducible representations of the symmetric group and efficient group theory techniques may be used to compute the spin integrals taking the form of symmetric group representation matrices in expressions for the Hamiltonian matrix elements.

Products of unitary group generators [10], so-called replacement operators \hat{E}_{ij} occur in turn in the orbital integrals, due to a second quantization form of the Hamiltonian expressed in terms of two-electron integrals and \hat{E}_{ij} . They effectively define the the corresponding spin integrals to be calculated. In case of usual CI matrix elements

it is enough to consider only products of two replacement operators. Chains of up to six unitary group generators have to be considered, however, in case of $\langle 0|\hat{H}^3|0\rangle$.

The tedious algebraic manipulations and many terms that arise would be very difficult to handle. Therefore automatization of algebraic operations is mandatory. MapleV package for symbolic algebra is employed to derive the formulas presented here. Some of our Maple functions e.g. those dealing with the algebra of unitary group generators are of general use and are available upon request.

The paper is organized as follows. In the next section the SGA approach and Sup-CI method are briefly revisited. Then the derivation of the most complex matrix elements is discussed, with all the main logical steps highlighted. Due to the large number of terms it is impossible to present the final formulas in the explicit form. The readers are referred to the original work, which is available through Internet [12]. In the last section some conclusions and remarks on future development are included.

2 Theory

Sup-CI ansatz

In the externally contracted CI method [6] all CSFs sharing the same internal orbitals are contracted, using perturbation theory, into one contracted CSF (CCSF) in order to reduce the number of variational parameters. In Sup-CI [4] contractions are formed in a similar way, but disregarding internal-external division of orbitals:

$$\begin{aligned} |\Psi_{\text{SupCI}}\rangle &= \sum_{I,k} C_{I,k} |\text{CCSF}_{I,k}\rangle \\ |\text{CCSF}_{I,k}\rangle &= \hat{R}_k |\Phi_I\rangle = \sum_{ijab} C_{ij;k}^{ab} |\Phi_{I,ij}^{ab}\rangle \end{aligned} \quad (1)$$

The index k numbers different types of resolvent operators \hat{R}_k used to generate different trial functions. Since most chemical processes require multireference treatment the superdirect CI approach within a multireference scheme is used and $|\Phi_I\rangle$ denote reference functions. The Schrödinger equation $\mathbf{H}|\Psi\rangle = E\mathbf{S}|\Psi\rangle$ is projected into the

space of $|\text{CCSF}_{I,k}\rangle$ and coefficients $C_{I,k}$ are Sup-CI variational parameters, whereas $C_{ij;k}^{ab} = \langle \Phi_{I,ij}^{ab} | \hat{R}_k | \Phi_I \rangle$ are fixed using perturbation arguments. However, contrary to externally contracted CI, the contraction coefficients are not evaluated explicitly. They are instead implicitly taken into account while reducing the expressions for matrix elements to one-particle level. This is where both the difficulty and the key to efficiency lay [13].

The Møller-Plesset resolvent \hat{R}_M leads for instance to the following first order correction vector with respect to some zeroth-order solution $|0\rangle$

$$|\text{CCSF}_{0,M}\rangle = \hat{R}_M|0\rangle = (\hat{H}_0 - E_0)^{-1} \hat{Q}_0 \hat{H}|0\rangle \quad (2)$$

Other correction vectors, like Krylov or Nesbet, are different only in the denominators and imply the same structure of the matrix elements formulae. Therefore, we shall call “diagonal” even those matrix elements that have been generated by different resolvent operators but with respect to a common reference e.g. $\langle \text{CCSF}_{0,M} | \hat{H} | \text{CCSF}_{0,K} \rangle$.

Symmetric group approach to CI methods

Formal developments due to Duch and Karwowski within SGA [10], used previously for efficient implementations of direct CI algorithms, may also provide a tool for deriving the MBPT-like formulas for the matrix elements between contracted functions, appearing in the superdirect CI approach [11]. We shall briefly recall the basic principles of the SGA – the readers are referred to original works [10] for details.

The non-relativistic spin-free electronic Hamiltonian may be represented in the finite Hilbert space \mathcal{H}^N in the following form [10]

$$\hat{H} = \sum_{ij}^k (i|j) \hat{E}_{ij} + \frac{1}{2} \sum_{ijkl}^k (ij|kl) (\hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il}) \quad (3)$$

with summation indices i, j referring to orthonormal orbitals $\{|\phi_i\rangle\}_{i=1}^k$. The one- and two-electron integrals are defined as follows

$$(i|j) = \langle \phi_i(1) | \hat{h}_1(1) | \phi_j(1) \rangle; \quad (ij|kl) = \langle \phi_i(1) \langle \phi_k(2) | \hat{h}_2(1, 2) | \phi_l(2) \rangle | \phi_j(1) \rangle \quad (4)$$

The operators $\hat{E}_{kl} = \sum_i^N |\phi_k(i)\rangle\langle\phi_l(i)|$ are known to be generators of the unitary group $U(k)$ and are also called the replacement operators since they replace $|\phi_l\rangle$ by $|\phi_k\rangle$ when acting on a product of orbitals. In terms of the usual annihilation and creation operators they are defined as $\hat{E}_{ij} = \sum_\sigma a_{i\sigma}^\dagger a_{j\sigma}$ and satisfy the following commutation rule

$$[\hat{E}_{ij}, \hat{E}_{kl}] = \delta_{kj} \hat{E}_{il} - \delta_{il} \hat{E}_{kj} \quad (5)$$

Since all kinds of spin operators commute with spin free \hat{H} the configuration state functions are chosen to be spin adapted linear combinations of a number of Slater determinants [5]. The CSFs will be denoted as $|\lambda; SM, l\rangle$ with λ standing for an orbital configuration. The index $l = 1, \dots, f(S, s_\lambda)$, depending on the number of singly occupied orbitals s_λ in λ , distinguishes independent eigenfunctions of \hat{S}^2 and \hat{S}_z belonging to the same values of S and M , respectively [10].

The SGA specific step consists in construction of separate N -particle orbital and spin spaces before the antisymmetrization is performed [10]. It results in N -electron CSFs of the form

$$|\lambda; SM, l\rangle = \xi_\lambda \hat{\mathcal{A}} [|\lambda\rangle |SM, l\rangle] \quad (6)$$

where $|SM, l\rangle \in \mathcal{H}_s^N$ is the pure spin function being an eigenfunction of \hat{S}^2 and \hat{S}_z and $|\lambda\rangle$ is a spin independent orbital function corresponding to the configuration λ . $\hat{\mathcal{A}}$ stands for antisymmetrizer operator and ξ_λ is the normalization constant. With each orbital configuration λ there is a vector of associated spin functions $|\mathbf{SM}\rangle_\lambda$ with the components $|SM, l\rangle$, $l = 1, \dots, f(S, s_\lambda)$.

Since the \hat{S}^2 and \hat{S}_z operators are symmetric in the coordinates of the electrons they commute with an arbitrary permutation i.e. for each $P \in S_N$ the new function $P|SM, l\rangle$ is an eigenfunction of \hat{S}^2 and \hat{S}_z with unchanged eigenvalues $S(S+1)$ and M . More precisely, the spin functions belonging to a pair of S, M ($S \geq |M|$) quantum numbers form a basis for an irreducible representation of the symmetric group S_N with the associated (M independent) matrix representation i.e. the set of matrices

$\{\mathbf{U}_S^N(P); P \in S_N\}$ where

$$U_S^N(P)_{kl} = \sigma(P)\langle SM, k|P|SM, l\rangle \quad k, l = 1, \dots, f(S, N) \quad (7)$$

Due to the separation of the spin and orbital parts in the CSFs one may perform separate integration over spin and orbital variables in the resulting Hamiltonian matrix elements. As a straightforward generalization of the previous result [10] one gets the following expression for the matrix elements of the Hamiltonian powers in the matrix block notation for $k = 1, \dots, f = f(S, s_\lambda)$ spin components of λ and $l = 1, \dots, g = f(S, s_\mu)$ components of μ

$$\mathbf{H}_{(\lambda)(\mu)}^p = 2^{-(d_\lambda+d_\mu)/2} \sum_q D_{\lambda\mu}^q [\mathbf{U}_S^N(P_q)]^{fg} \langle P_q \lambda | \hat{H}^p | \mu \rangle \quad (8)$$

where the summation runs over distinct double cosets $\Pi_\lambda P_q \Pi_\mu$ (Π_λ means a group generated by transpositions within d_λ doubly occupied orbitals of λ) of the dimensions $D_{\lambda\mu}^q$, generated by P_q . The permutations acting on the electron coordinates in the orbital integrals are replaced by their hermitian conjugate i.e. the same permutations but acting on the orbital indices. The full representation matrices are replaced by the small rectangular blocks $[\mathbf{U}_S^N(P_q)]^{fg}$ defined by the sets of singly occupied orbitals in $|\lambda\rangle$ and $|\mu\rangle$, respectively. As have been proved by Kotani *et. al.* [14] further (and essential) simplification is possible since all $[\mathbf{U}_S^N(P_q)]^{fg}$ blocks may be reduced to \mathbf{U}_S^s matrices, corresponding to appropriate permutations of singles only.

Matrix elements of the Hamiltonian powers (8) are in general sums of a number of terms $\Upsilon^{(\lambda)(\mu)} = \gamma(\Upsilon)[\mathbf{U}_S^N(P_q)]^{fg} \langle P_q \lambda | \Upsilon | \mu \rangle$, where $\gamma(\Upsilon)$ is an appropriate product of one- or two-electron integrals associated with a chain (product) of replacement operators Υ occurring in $\mathbf{H}_{(\lambda)(\mu)}^p$ e.g. $\Upsilon_{efgh\dots pq} = \hat{E}_{ef} \hat{E}_{gh} \dots \hat{E}_{pq}$. A given $\Upsilon^{(\lambda)(\mu)}$ is not equal to zero only if the occupation schemes (i.e. assignment of electrons to orbitals) of $|\lambda\rangle$ and $|\mu\rangle$ are the same. From the practical point of view it is crucial that only at most one of the permutations P_q , called line-up permutation, leads to complete coincidence between $|P_q \lambda\rangle$ and each non-vanishing chain $\Upsilon|\mu\rangle$ and,

subsequently, to an orbital integral $\langle P_q \lambda | \Upsilon | \mu \rangle = 1$ and the corresponding spin integral $[\mathbf{U}_S^N(P_q)]^{fg}$. Several very efficient and suitable procedures for evaluating the matrices of the symmetric group representations have been proposed [10].

Circular operators and spin integrals

We have to learn first how to generate the non-vanishing chains of replacement operators. The most difficult is diagonal case with $|\lambda\rangle = |\mu\rangle$. The non-diagonal matrix elements can be reduced to diagonal ones with smaller number of free indices [12]. Let $|0\rangle$ denote the total, orbital or spin N -electron function (or their set $|\mathbf{SM}\rangle_0$) depending on the context. Using such simplified notation one may write

$$\langle 0 | \hat{H}^p | 0 \rangle = \sum_{\Upsilon'} \gamma(\Upsilon) \langle 0 | P(\Upsilon) | 0 \rangle = \sum_{\Upsilon'} \gamma(\Upsilon) \sum_{\mathcal{E}(\Upsilon)} \langle 0 | P(\mathcal{E}(\Upsilon)) | 0 \rangle \quad (9)$$

where all the numerical factors are absorbed either in γ or in the spin integrals $\langle 0 | P(\Upsilon) | 0 \rangle$ which are square representation matrices $[\mathbf{U}_S^{s_0}(P)]^{ff}$ in this case. The chains leading to orbital integrals equal to zero are excluded from summation $\sum_{\Upsilon'}$ and those for non-vanishing integrals define a permutation $P(\Upsilon)$ such that $\langle P(\Upsilon) 0 | \Upsilon 0 \rangle = 1$. The second sum runs over a set of the so-called circular operators [11] arising from a given chain Υ and denoted as $\mathcal{E}(\Upsilon)$. Circular operators are chains of the form

$$\mathcal{E}_{efh\dots mne} = \Upsilon_{effh\dots mnne} = \hat{E}_{ef} \hat{E}_{fh} \dots \hat{E}_{mn} \hat{E}_{ne} \quad (10)$$

where the subsequent orbitals we excite from are the same as those we excite to in the nearest right hand side neighbor, regarding the first and the last index as neighbors.

The summation over distinct, non-vanishing chains in eq. (9) may be indeed expressed as a sum over circular operators only. If Υ is to give a non-zero contribution it cannot change the occupation of any orbital in $|0\rangle$ i.e. each index m must appear $2i$ times in Υ , i times as left index E_{mp} and i times as right one E_{qm} . Commuting the replacement operators one may end up with the circular chain and then subsequently permute to the circular form the additional terms that may appear by applying

the commutation rule (5). This will be our general strategy: to specify all non-vanishing chains of operators in the orbital integral and transform them to sums of circular chains, having the advantage of very simple structure of the corresponding permutation and spin integral.

From now on, we shall distinguish the occupation of orbitals by the respective Latin letters: arbitrary indices with occupations $n_x = 0, 1, 2$ will be denoted as e, f, g, h, m, n, p, q , unoccupied indices ($n_x = 0$) as a, b, c, d , singly occupied indices ($n_x = 1$) as s, t, u, w, y, z and doubly occupied ones ($n_x = 2$) as i, j, k, l . We shall further divide the set of arbitrarily occupied indices into two subsets: those we may excite from ($n_x = 2, 1$) e, f, m, n and those we may excite to ($n_x = 1, 0$) g, h, p, q . An unspecified index will be denoted by r and ρ will stand for a set of such indices.

One may demonstrate [11] that all the unoccupied indices may be eliminated from the diagonal matrix elements of the circular chains. Moreover, contributions of doubly occupied orbitals are very simple. As a result the only non-trivial spin integrals will appear when considering matrix elements of chains $\mathcal{E}_{st\dots s}$ involving singly occupied orbitals only, for which the related permutations are easy to find. Consider for example \mathcal{E}_{sts} acting on the orbital product $|\psi_s\rangle \cdots |\psi_t\rangle$. The result is equivalent to action of the $1 + (s, t)$ operator, where (s, t) denotes the transposition of s -th and t -th orbitals [11]. For longer chains we simply have $\mathcal{E}_{stus} = (1 + (s, t))(1 + (s, u))$ etc.

Thus, the spin integrals $\langle 0|P(\mathcal{E}_{st\dots s})|0\rangle$ may be, without any ambiguity, denoted as $\langle 0|\mathcal{E}_{st\dots s}|0\rangle$ with $|0\rangle$ standing for a set of spin functions. In general

$$\langle 0|\mathcal{E}_{stu\dots ws}|0\rangle = (1 + \langle s, t \rangle)(1 + \langle s, u \rangle) \cdots (1 + \langle s, w \rangle) \quad (11)$$

i.e. diagonal elements of the circular operators may be reduced to products of basic integrals $\langle s, t \rangle = \langle 0|(s, t)|0\rangle$, corresponding to the transpositions of spins with numbers s and t . They are equal to ± 1 in the determinantal basis. In case of spin adapted basis they are appropriate representation matrices of the transpositions (s, t) and are easily calculated from the branching diagram [10].

3 Algorithm and formulae

We are ready now to reduce matrix elements, occurring in the multireference third order Sup-CI method, to sums of products of one- and two-electron integrals and proper spin coupling constants (spin integrals). We shall explicitly consider only the most complicated case, namely the diagonal elements of the type

$$\langle 0 | \hat{R}_1 \hat{H} \hat{R}_2 | 0 \rangle = \sum_{L \neq 0} \sum_{K \neq 0} d_1(L) d_2(K) \langle 0 | \hat{H} | L \rangle \langle L | \hat{H} | K \rangle \langle K | \hat{H} | 0 \rangle \quad (12)$$

where $|0\rangle$ is an arbitrary open shell function and \hat{R}_1, \hat{R}_2 are different operators generating perturbative corrections with the corresponding denominators d_1, d_2 . The CSFs L, K are at most doubly excited with respect to $|0\rangle$ and with respect to each other. Notice that Møller–Plesset corrections $\hat{R}_1, \hat{R}_2 = \hat{R}_M$ lead to the core of E_3 MBPT formula.

The most complicated term in expression (12) is associated with intermediate doubles $K, L \in D_0$; $K \in D_L$ (D_K stands for a set of all CSFs that are doubly excited with respect to K). It may be written as

$$S1 = \sum_{m \leq n} \sum_{p \leq q} \sum_{e \leq f} \sum_{g \leq h} d_1^{mnpq} d_2^{efgh} \langle 0 | \hat{B}_2^{mnpq} |_{mn}^{pq} \rangle \langle pq | \hat{B}_2^\rho |_{ef}^{gh} \rangle \langle gh | \hat{B}_2^{gh} |_{ef}^{ef} \rangle | 0 \rangle \quad (13)$$

where \hat{B}_2^{efgh} denotes the part of the Hamiltonian connecting states differing on two orbitals, e.g. reference function and double excitation with respect to it $\langle 0 | \hat{B}_2^{efgh} |_{ef}^{gh} \rangle$

$$\hat{B}_2^{efgh} = 2^{-\delta_{ef}\delta_{gh}} (eg|fh) \hat{E}_{eg} \hat{E}_{fh} + (1 - \delta_{ef})(1 - \delta_{gh})(eh|fg) \hat{E}_{eh} \hat{E}_{fg} \quad (14)$$

One may similarly extract from the definition of the Hamiltonian those terms which do not vanish between CSFs differing by only one orbital index \hat{B}_1^{eg} or having all orbital indices in common \hat{B}_0 [10].

Contractions

The computational complexity of the third order formulas scales as n^6 , where n is the size of basis set. It is clear that summation over doubles $|_{ef}^{gh}\rangle$ of eq. (13)

cannot be completely unrestricted, since they are also doubles with respect to the first intermediate double $L = |_{mn}^{pq}\rangle$. Only two of indices e, f, g, h may differ from the indices m, n, p, q . This gives six possible contractions of eight orbital indices, reducing the sums to 6-fold only and defining four non-specified indices ρ in (13). If for instance $e = m, f = n$ then $\rho \equiv p, q, g, h$. Exchanging summation indices such that the free ones are always denoted as e, g we may gather four contraction schemes together and using $\delta'_{mn} = 1 - \delta_{mn}$ we get

$$\begin{aligned}
S1 = & \sum_{m \leq n} \sum_{p \leq q} d_1^{mnpq} \langle 0 | \hat{B}_2^{mnpq} \{ \sum_{g \leq h} d_2^{mng h} \hat{B}_2^{pqgh} \hat{B}_2^{ghmn} + \\
& + \sum_{e \leq f} d_2^{efmn} \hat{B}_2^{efmn} \hat{B}_2^{pqef} + \sum_e \sum_g [d_2^{megp} \hat{B}_2^{eqng} \hat{B}_2^{pgme} + \delta'_{mn} d_2^{enpg} \hat{B}_2^{eqmg} \hat{B}_2^{pgen} + \\
& + \delta'_{pq} d_2^{megq} \hat{B}_2^{epng} \hat{B}_2^{gqme} + \delta'_{mn} \delta'_{pq} d_2^{engq} \hat{B}_2^{epmg} \hat{B}_2^{gqen}] \} | 0 \rangle \quad (15)
\end{aligned}$$

Notice that the intermediate states may be dropped in the above expression, since for example $\langle 0 | \hat{B}_2^{mnpq} \hat{B}_2^{eqng} |_{me}^{pg}\rangle = \langle 0 | \hat{B}_2^{mnpq} \hat{\mathbf{1}} \hat{B}_2^{eqng} |_{me}^{pg}\rangle = \langle 0 | \hat{B}_2^{mnpq} |_{mn}^{pq}\rangle \langle_{mn}^{pq} | \hat{B}_2^{eqng} |_{me}^{pg}\rangle$.

Constraints for the subsequent summations in the first and second sum of $S1$ are obvious: the second pair of orbitals is taken from an appropriate subset of orbitals with first pair excluded etc. Sum over $\sum_e \sum_g$ is associated with up to four different categories of right hand side intermediate configurations K and, except for common $e \neq g$, there are different constraints associated with each category. For instance $|_{me}^{pg}\rangle \in D_0 \cap D_L$ implies that $e \neq p, g \neq m$ and $e \neq n, g \neq q$, respectively. Thus, there are further contractions implicitly generated by each such term with e and/or g equal to some still not excluded indices of the first intermediate double.

It should be also kept in mind that by different contraction schemes we mean distinct categories of relative doubles $K \in D_L$ generating distinct summation patterns and chains of unitary group generators. If for instance $m = n$, then $|_{me}^{pg}\rangle$ and $|_{en}^{pg}\rangle$ of the third $S1$ summation become equivalent and only one summation $\sum_{e \neq m}$ with the chain $\hat{B}_2^{mmpq} \hat{B}_2^{eqmg} \hat{B}_2^{pgme}$ has to be considered (if $m \neq n$ two separate sums arise, namely $\sum_{e \neq n}$ and $\sum_{e \neq m}$ associated with $\hat{B}_2^{mmpq} \hat{B}_2^{eqng} \hat{B}_2^{pgme}$ and $\hat{B}_2^{mmpq} \hat{B}_2^{eqmg} \hat{B}_2^{pgen}$,

respectively). The same concerns terms with $p = q$ and this is why only some chains related to K survive in (15), depending on the structure of L .

The complete expression for $\langle 0|R_1HR_2|0\rangle$ with contributions of the intermediate singles and all the general contraction schemes is given in Table 1. According to our strategy, as specified by the equation (9), we shall now expand explicitly all the chains of operators to transform them to circular form.

Chains and spin integrals

As the first step all possible repetitions of indices or, in other words, all the implicitly included contraction schemes should be extracted. They occur due to summations over pairs (e.g. $\sum_{m \leq n}$), as we may promote two electrons from or to a given orbital, and due to the presence of singly occupied indices resulting in excitation from and to singly occupied orbitals. Next, one may apply commutation rule (5) to transform products of \hat{E}_{eh} into circular form.

As some of the partial summations may still extend over different sets of orbitals e.g. e being doubly or singly occupied, all the possible occupation schemes have to be explicitly distinguished. For each occupation pattern the unoccupied and effectively also doubly occupied indices are then removed and spin integrals corresponding to circular operators involving single indices only may be calculated. Unfortunately, it also means that the general summations, as those of $S1$, break into a number of partial summations that are associated with distinct occupation patterns.

For each summations over pairs of indices we get two sums with different chains of indices involving e.g. $m < n$ and $m = n$, respectively. Thus, the first $S1$ sum $\sum_{m \leq n} \sum_{p \leq q} \sum_{g \leq h}$ generates eight partial sums with the distinct chains of operators. In one extreme case $m = n$, $p = q$, $g = h$ and the associated integral $\langle 0|\hat{E}_{mp}\hat{E}_{mp}\hat{E}_{pg}\hat{E}_{pg}\hat{E}_{gm}\hat{E}_{gm}|0\rangle$ takes a simple numerical form, as it involves only doubly occupied $n_m = 2$ and unoccupied $n_p = n_g = 0$ indices and we may use $\mathcal{E}_{mpgm}|0\rangle = \mathcal{E}_{mm}|0\rangle = n_m$. In another extreme case, with all the indices of three

summation pairs different, we have as many as 27 possible occupation patterns because for each pair there are three possibilities:

$$m, n \rightarrow (2, 2); (2, 1); (1, 1); \quad p, q; g, h \rightarrow (1, 1); (1, 0); (0, 0) \quad (16)$$

where (2, 1) for instance means a pair with one doubly and one singly occupied index. The corresponding partial sums run over the respective subsets of all indices. The most complicated is the occupation pattern with all the indices singly occupied (1, 1)(1, 1)(1, 1) which is taken into account through the partial sum $\sum_{s<t} \sum_{u<w} \sum_{y<z}$ (for a fixed s, t the second sum runs over pairs $u < w$ with s, t excluded etc.) and leads to circular chains involving up to 7 indices (i.e. to products of up to 5 basic spin integrals $\langle s, t \rangle$) e.g. $\langle 0 | \hat{E}_{mq} \hat{E}_{np} \hat{E}_{pg} \hat{E}_{qh} \hat{E}_{gm} \hat{E}_{hn} | 0 \rangle$ leads to $\langle \mathcal{E}_{swztuys} - \mathcal{E}_{swzuyts} \rangle$. The total number of partial summations is equal to 64: 27 for all indices different (only these sums are 6-fold), 9 for each pair of equal indices and all the remaining being different e.g. $m = n, p < q, g < h$ ($3 \cdot 9 = 27$), 3 for each two pairs of equal indices ($3 \cdot 3 = 9$) and 1 term for all three pairs collapsing to a single index.

Similarly one gets 64 partial summations extracted from the second general contraction scheme in the expression (15), namely $\sum_{m \leq n} \sum_{p \leq q} \sum_{e \leq f}$. Some contractions lead however to equivalent sums and may be gathered together with appropriate chains of the first general contraction scheme. For instance, if all indices are singly occupied we again get sum $\sum_{s<t} \sum_{u<w} \sum_{y<z}$ associated with the intermediate doubles $L \equiv | \begin{smallmatrix} uw \\ st \end{smallmatrix} \rangle$, $K \equiv | \begin{smallmatrix} uw \\ yz \end{smallmatrix} \rangle$. Previously it was related to $L \equiv | \begin{smallmatrix} uw \\ st \end{smallmatrix} \rangle$, $K \equiv | \begin{smallmatrix} yz \\ st \end{smallmatrix} \rangle$ and to different chains of replacement operators. Therefore, including terms corresponding to previously occurring patterns in the first general sum of eq. (15), we actually obtain only 18 6-fold, 21 5-fold, 8 4-fold and one 3-fold sum i.e. 48 new sums.

The third contraction scheme $\sum_{m \leq n} \sum_{p \leq q} \sum_e \sum_g$ is more complicated, since indices e and g belong to two different sets: those we may excite from and those we may excite to, respectively. As we have seen, each of up to four chains entails slightly different summation imposing different restrictions on e and g indices. Taking prod-

uct of summation ranges due to these constraints i.e. assuming that $e \neq g$ and both e and g are not equal to any other summation index, we may exclude for a moment additional possible repetitions getting common sums for all the four chains. This leads again to 64 partial summations. When $m < n$, $p < q$ the 6-fold sums arise and the possible occupations schemes for e and g , namely $(2, 0)$; $(2, 1)$; $(1, 0)$; $(1, 1)$, together with those of m, n and p, q pairs, as defined in eq. (16), generate 36 partial summations. For $m = n$, $p < q$ and $m < n$, $p = q$ one gets 12 summations in each case and for $m = n$, $p = q$ there are 4 summations. All the occupation patterns except for $(2, 0)$ were included already previously, thus we actually have only 9 6-fold, 6 5-fold and 1 4-fold new partial summations. Since e and g belong to different categories of indices the summation pattern $(1, 1)$ is associated with a sum $\sum_y \sum_{z \neq y}$ and not $\sum_{y < z}$. Thus, adding such terms to previous partial summation of this type, we have to also perform summation $\sum_{y > z}$ over them. The so far obtained 192 different terms (with up to four chains of operators) may be rearranged to form 128 different partial sums, 54 among them being 6-fold, 54 5-fold, 18 4-fold and 2 3-fold.

As noted previously, even if $e = n$ the intermediate doubles $| \begin{smallmatrix} pq \\ mn \end{smallmatrix} \rangle$ and $| \begin{smallmatrix} qq \\ en \end{smallmatrix} \rangle \equiv | \begin{smallmatrix} qq \\ nn \end{smallmatrix} \rangle$ are doubly excited with respect to each other (implying in this case $n_n = 2$, $n \neq m$) and we have to consider terms with e and/or g equal to another index of the pair they belong in. There are 16 such terms and they are displayed as a second group of special $S1$ contractions in Table 2. Distinguishing explicitly all the possible occupation patterns one is lead to 93 different chains gathered within 24 5-fold and 12 4-fold partial summations with up to four chains associated with each of them. The chains corresponding to 12 5-fold and 8 4-fold summation patterns that already occurred may be rearranged, leaving only 16 new partial sums.

Other possible repetitions arise due to electrons promoted both from and to singly occupied orbitals. The intermediate doubles $| \begin{smallmatrix} pq \\ mn \end{smallmatrix} \rangle$ and $| \begin{smallmatrix} qq \\ en \end{smallmatrix} \rangle$ are doubly excited with respect to each other and $e \neq m, g \neq p$. Within a given configuration the indices we excite from must be different from those we excite to e.g. $g \neq e, q \neq n$. In the open

shell case, however, further repetitions are still possible, $e, p = s$ and/or $g, m = t$. For example $\begin{smallmatrix} sq \\ mn \end{smallmatrix}$ and $\begin{smallmatrix} qq \\ sn \end{smallmatrix}$ are still relative doubles. Using decoupled summation convention $\sum_{m \leq n} \sum_s \sum_{q \neq s} \sum_g$ (i.e. gathering the terms related to $\sum_{m \leq n} \sum_{p < s} \sum_g$ and $\sum_{m \leq n} \sum_{s < q} \sum_g$) we get 13 such terms - see the last group of special $S1$ contractions in Table 2. The possible occupation patterns lead to 72 different chains that may be gathered in 24 5-fold and 18 4-fold and 2 3-fold partial summations with up to two chains of operators. They are rather short as they involve at least one singly occupied index, but it may still be worth to collect together chains associated with 12 5-fold and 4 4-fold sums already considered.

The total number of terms arising from $S1$ is large. There are $272 = 192 + 80$ partial summations, each associated with up to four different replacement operator chains. As we have seen, they may be rearranged in $172 = 128 + 44$ distinct partial sums (54 among them being 6-fold) with a larger number of different chains. Notice that chains considered on this level become in fact sums of a number of circular chains (i.e. spin integrals), once we transform them to this form. Certainly, all the partial summations considered here run over subsets of all indices only and, moreover, they may be divided into groups with a particular structure (out of 16 possible) of the left intermediate double $\begin{smallmatrix} pq \\ mn \end{smallmatrix}$ in common. As can be seen from Table 1 the inclusion of singles does not bring many terms (there are few implicit contractions due to possible repetitions of indices) and they are certainly of a lower complexity.

In practice all the terms are generated by proper Maple functions that apply rules derived from the above analysis to deal with contractions and summation patterns. This is also the reason for very compact and computer oriented notation, employed in Tables 1 and 2. To obtain circular form of chains via commutations rules (5) other Maple functions dealing with the algebra of the unitary group generators are used. Substituting the definitions of all quantities involved, one gets an expression in terms of sums over orbital indices with some products of appropriate denominators, one- and two-electron integrals and representation matrices (spin integrals). More explicit

formulas for the diagonal matrix elements (12), are given in ref. [12].

4 Discussion

The separation of spin and orbital spaces in SGA is an important advantage, resulting in CSFs defined in terms of orbitals only and spin coupling constants depending on the relative structure of bra and ket functions. Simplicity of the underlying algebra, enabling the use of MapleV symbolic algebra package, is crucial while considering matrix elements of the third power of the Hamiltonian. In order to evaluate spin integrals it is necessary to distinguish possible occupation patterns for the summation indices, with different subsets of singly occupied ones. As the number of open shells is not restricted, there are many different cases that have to be explicitly considered. Certainly, one may significantly reduce complexity of the problem, limiting the number of open shells. Some constraints seem to be necessary while going to higher order Sup-CI method, with second order perturbative corrections.

Complex structure of some spin integrals is another problem related to the efficiency of matrix elements evaluation. As shown in the previous section, in case of all indices being singly occupied the spin integrals are products of up to 5 basic representation matrices $\langle s, t \rangle$, which could mean significant numerical burden. Fortunately, in practice the subset of singly occupied orbitals in a given reference function is rarely large enough to make the sum over three pairs of singly occupied indices long.

As shown in ref. [12] one may factorize long chains of replacement operators and the corresponding summations by means of various conveniently chosen intermediate states, such that products of shorter chains, corresponding to products of up to 3 basic integrals $\langle s, t \rangle$ may be considered. This step has not yet been implemented in our Maple code and the final formula presented in [12] is given on the level where both strategies can be applied: either simple deconvolution of all compressed expressions or factorization of some terms. The latter imposes additional logics on the structure

of the loops and whether it is more effective would depend on the actual architecture.

The derivation of non-diagonal elements, defined by $|0\rangle \neq |0'\rangle$, is also presented in ref. [12]. In the non-diagonal case the complexity of the evaluation of matrix elements is certainly lower and it depends on the relative structure of $|0\rangle$ and $|0'\rangle$. The formula for the diagonal matrix elements of the second order type i.e. $\langle 0|\hat{R}_1\hat{R}_2|0\rangle$ (equivalent to $H_{0R_1,0}$ and overlap S_{0R_1,R_20}) has been previously derived by Duch [11].

Concerning the efficiency of the algorithm proposed here it is worth stressing that, in contrast to MR-CISD methods, it is not an iterative method and there is no need to repeat the n^6 summation in each iteration. Secondly, although the general loop is broken into subsums over different subsets of indices (corresponding to a number of third order diagrams in MBPT language) it may then be again reorganized, so that the number of numerical operations is minimized. For instance, if we gather together all the terms with a given structure of a left intermediate double, the multiplications by two-electron integrals associated with it are not repeated. Furthermore, parallelization of the matrix elements evaluation is quite natural. Once the matrix elements are calculated solving small eigenvalue problem is trivial.

In this paper we have described Symmetric Group Approach based algorithm for evaluation of the third order type formulas for the Hamiltonian matrix elements in the basis of highly contracted, perturbatively generated CSFs. Such first order perturbative corrections have been employed within recently developed Superdirect Configuration Interaction method. The Sup-CI method may be viewed as the next logical step from classical CI through direct CI to complete reduction of equations to the single-particle level, leading to a non-iterative approximation to the MR-CISD without storage of very long eigenvectors.

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Appendix

Expressions in Tables 1 and 2 are automatically generated by means of the symbolic algebra program, written in the Maple language, and they employ a compact summation convention. According to this convention all sums are associated with the ordered orbital indices occurring as arguments of the denominators functions d_1^ρ , d_2^ρ generated by left and right intermediate configurations, respectively (ρ stands for two or four orbital indices for singly or doubly excited configurations, respectively). For example

$$d_1^{mp} d_2^{mp} \dots \longrightarrow \sum_m \sum_p d_1^{mp} d_2^{mp} \dots \quad (17)$$

$$d_1^{mp} d_2^{efph} \dots \longrightarrow \sum_m \sum_p \sum_{e \leq f} \sum_h d_1^{mp} d_2^{efph} \dots \quad (18)$$

$$d_1^{mnpq} d_2^{efpq} \dots \longrightarrow \sum_{m \leq n} \sum_{p \leq q} \sum_{e \leq f} d_1^{mnpq} d_2^{efpq} \dots \quad (19)$$

$$d_1^{mnpq} d_2^{engq} \dots \longrightarrow \sum_{m \leq n} \sum_{p \leq q} \sum_e \sum_g d_1^{mnpq} d_2^{engq} \dots \quad (20)$$

The general rule is clearly visible from the above examples. Constraints imposed on the subsequent summations (allowing or not some repetitions among the summation indices for instance) depend on the relative structure of the intermediate configurations that we sum over i.e. they are uniquely defined by the associated chains of \hat{B}_i^ρ operators (denoted as b_i^ρ) connecting configurations differing by two (b_2^ρ), one (b_1^ρ) or none (b_0^ρ) orbital indices.

As an example, the second term of the first row in Table 2 will be given in an explicit form (note that there are no implicit repetitions of indices on this level):

$$\begin{aligned} d_1^{mnpq} d_2^{mngg} &\equiv d_1^{mnpq} d_2^{mnaa} \equiv d_1^{mnpq} d_2^{mnaa} \langle b_2^{mnpq} b_2^{pqaa} b_2^{aamn} \rangle \equiv \\ d_1^{mnpq} d_2^{mnaa} (p_a | q_a) (a_m | a_n) &[(m_p | n_q) \langle 0 | \hat{E}_{mp} \hat{E}_{nq} \hat{E}_{pa} \hat{E}_{qa} \hat{E}_{am} \hat{E}_{an} | 0 \rangle + \\ &(m_q | n_p) \langle 0 | \hat{E}_{mq} \hat{E}_{np} \hat{E}_{pa} \hat{E}_{qa} \hat{E}_{am} \hat{E}_{an} | 0 \rangle] \equiv \end{aligned}$$

$$d_1^{mnpq}d_2^{mnaa}(pa|qa)(am|an) [(mp|nq)\langle\mathcal{E}_{mpm}\mathcal{E}_{nqn} + \mathcal{E}_{nqmpn} - \mathcal{E}_{nqpn}\rangle + \\ (mq|np)\langle\mathcal{E}_{mqm}\mathcal{E}_{npn} + \mathcal{E}_{mqnqm} - \mathcal{E}_{mqpm}\rangle] \quad (21)$$

Since there are two electrons promoted to orbital g in this contraction scheme, it may be replaced by a , denoting unoccupied orbital, and then it may be dropped in the resulting circular operators. The general summation related to denominators of eq. (21) i.e. $\sum_{m<n} \sum_{p<q} \sum_a$ has to be now partitioned into nine partial summations with different occupation schemes for indices m, n and p, q , in order to evaluate explicitly the spin integrals. Thus, $d_1^{mnpq}d_2^{mngg}$ represents a sum of nine terms. If $n_m = n_n = 2$ and $n_p = n_q = 0$, then according to rules described in Sec. 2 and in ref. [11] we get for example $\langle\mathcal{E}_{ici}\mathcal{E}_{jdj} + \mathcal{E}_{jdicj} - \mathcal{E}_{jdcj}\rangle = \langle\mathcal{E}_{ii}\mathcal{E}_{jj} - \mathcal{E}_{jj}\rangle = 2$ and the partial sum takes the following form:

$$\sum_{i<j} \sum_{c<d} \sum_a d_1^{ijcd}d_2^{ijaa}(ca|da)(ai|aj) 2 [(ic|jd) + (id|jc)]$$

If m and n are still doubly occupied, but p and q are singly occupied ($n_p = n_q = 1$), then $\langle\mathcal{E}_{isi}\mathcal{E}_{jtj} + \mathcal{E}_{jtisj} - \mathcal{E}_{jtsj}\rangle = \langle\mathcal{E}_{tst}\rangle$ and we get

$$\sum_{i<j} \sum_{s<t} \sum_a d_1^{ijst}d_2^{ijaa}(sa|ta)(ai|aj) \langle\mathcal{E}_{tst}\rangle [(is|jt) + (it|js)]$$

The integrals $\langle\mathcal{E}_{tst}\rangle$ are tabulated in ref. [11]. The most complicated partial sum arises when all m, n, p, q indices are singly occupied:

$$\sum_{u<w} \sum_{s<t} \sum_a d_1^{uwst}d_2^{uwaa}(sa|ta)(au|aw) [(us|wt)\langle\mathcal{E}_{usu}\mathcal{E}_{wtw} + \mathcal{E}_{wtusw} - \mathcal{E}_{wtsw}\rangle + \\ (ut|ws)\langle\mathcal{E}_{utu}\mathcal{E}_{wsw} + \mathcal{E}_{utwsu} - \mathcal{E}_{utsu}\rangle]$$

The above sum is already quite short, as it involves four different singly occupied (in the reference function) indices, and the long spin integrals \mathcal{E}_{wtusw} can be simply calculated on the fly, using eq. (11). The remaining six partial sums can be extracted in the similar way.

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Table 1: H^3 type diagonal matrix element: contractions

For the definition of notation see Appendix. Each term may represent a number of terms, corresponding to explicitly distinguished cases with all the indices being different and with some repetitions of indices e.g. due to promotion of two electrons from (to) the same orbital $m = n$ ($p = q$). The last three rows, referred to as $S1$ in eq. (15), correspond to intermediate doubles being also doubly excited with respect to each other and lead to 6-fold summations. In the explicit representation of all the $S1$ contractions (distinct summation patterns and chains of operators arising while distinguishing possible repetitions among indices) one gets except for the terms included here (with all the indices being different) the terms given in Table 2.

$$\begin{aligned}
\langle 0|R_1 H R_2|0\rangle := & d_1^{mp} d_2^{mp} \langle b_1^{mp} b_0^{mp} b_1^{pm} \rangle + \\
& d_1^{mp} [d_2^{ep} \langle b_1^{mp} b_1^{em} b_1^{pe} \rangle + d_2^{mg} \langle b_1^{mp} b_1^{pg} b_1^{gm} \rangle] + \\
& d_1^{mp} d_2^{mfph} \langle b_1^{mp} b_1^{fh} b_2^{phmf} \rangle + d_1^{mp} d_2^{eg} \langle b_1^{mp} b_2^{pemg} b_1^{ge} \rangle + \\
& d_1^{mp} [d_2^{efph} \langle b_1^{mp} b_2^{efmh} b_2^{phef} \rangle + d_2^{mfgh} \langle b_1^{mp} b_2^{pfg h} b_2^{ghmf} \rangle] + \\
& d_1^{mnpq} d_2^{mnpq} \langle b_2^{mnpq} b_0^{mnpq} b_2^{pqmn} \rangle + \\
& d_1^{mnpq} [d_2^{nq} \langle b_2^{mnpq} b_1^{pm} b_1^{qn} \rangle + d_2^{np} \langle b_2^{mnpq} b_1^{qm} b_1^{pn} \rangle \\
& + d_2^{mq} \langle b_2^{mnpq} b_1^{pn} b_1^{qm} \rangle + d_2^{mp} \langle b_2^{mnpq} b_1^{qn} b_1^{pm} \rangle] + \\
& d_1^{mnpq} [d_2^{enpq} \langle b_2^{mnpq} b_1^{em} b_2^{pqen} \rangle + d_2^{mepq} \langle b_2^{mnpq} b_1^{en} b_2^{pqme} \rangle \\
& + d_2^{mngq} \langle b_2^{mnpq} b_1^{pg} b_2^{gqmn} \rangle + d_2^{mnpq} \langle b_2^{mnpq} b_1^{qg} b_2^{pgmn} \rangle] + \\
& d_1^{mnpq} [d_2^{mg} \langle b_2^{mnpq} b_2^{pqng} b_1^{gm} \rangle + d_2^{ng} \langle b_2^{mnpq} b_2^{pqmg} b_1^{gn} \rangle \\
& + d_2^{ep} \langle b_2^{mnpq} b_2^{qemn} b_1^{pe} \rangle + d_2^{eq} \langle b_2^{mnpq} b_2^{pemn} b_1^{qe} \rangle] + \\
& d_1^{mnpq} [d_2^{efpq} \langle b_2^{mnpq} b_2^{efmn} b_2^{pqef} \rangle + d_2^{mng h} \langle b_2^{mnpq} b_2^{pqgh} b_2^{ghmn} \rangle \\
& + d_2^{engq} \langle b_2^{mnpq} b_2^{pemg} b_2^{gqen} \rangle + d_2^{enpq} \langle b_2^{mnpq} b_2^{qemg} b_2^{pgen} \rangle \\
& + d_2^{megq} \langle b_2^{mnpq} b_2^{peng} b_2^{gqme} \rangle + d_2^{mepq} \langle b_2^{mnpq} b_2^{qeng} b_2^{pgme} \rangle]
\end{aligned}$$

Table 2: Explicit expansion of $S1$ contractions

The most complicated part of $\langle 0|R_1HR_2|0\rangle$, referred to as $S1$ (see Section 3) expanded with respect to repetitions of indices. If all the indices are different one gets the last three rows of Table 1, without any further contractions implicitly included. The first four rows of the present Table correspond to repetitions in first two general summation schemes of $S1$, whereas the remaining two groups arise from the third sum $\sum_{m \leq n} \sum_{p \leq q} \sum_e \sum_g$. All the integrals are dropped for simplicity. Notice also that not all terms with the same structure of the left intermediate double $|_{mn}^{sq}\rangle$ are gathered together. For the definition of notation see Appendix.

$$\begin{aligned}
& d_1^{mnpq} [d_2^{eepq} + d_2^{mngg}] + \\
& d_1^{mmpq} [d_2^{efpq} + d_2^{eepq} + d_2^{mmgh} + d_2^{mmgg} + d_2^{emgq} + d_2^{empg}] + \\
& d_1^{mnpq} [d_2^{efpp} + d_2^{eepq} + d_2^{mngg} + d_2^{mngg} + d_2^{empg} + d_2^{enqp}] + \\
& d_1^{mmpq} [d_2^{efpp} + d_2^{eepq} + d_2^{mmgh} + d_2^{mmgg} + d_2^{emgp}] \\
+ \\
& d_1^{mnpq} [d_2^{mmgq} + d_2^{nngq} + d_2^{mmpg} + d_2^{nnpq}] + \\
& d_1^{mnpq} [d_2^{mepq} + d_2^{meqq} + d_2^{enpp} + d_2^{enqq}] + \\
& d_1^{mmpq} [d_2^{emgq} + d_2^{empp}] + d_1^{mnpq} [d_2^{mmgp} + d_2^{nngp}] + \\
& d_1^{mnpq} [d_2^{nnqq} + d_2^{nnpq} + d_2^{mmqq} + d_2^{mmpq}] \\
+ \\
& d_1^{mnpq} [d_2^{snpg} + d_2^{misp}] + d_1^{mmps} d_2^{smpp} + \\
& d_1^{mtpq} [d_2^{metq} + d_2^{mept}] + d_1^{mtpq} d_2^{metp} + \\
& d_1^{mtps} d_2^{mspt} + \\
& d_1^{mnsq} [d_2^{snqq} + d_2^{msqq}] + d_1^{mmsq} d_2^{smqq} + \\
& d_1^{mtpq} [d_2^{mmpt} + d_2^{mmtq}] + d_1^{mtpq} d_2^{mmpt}
\end{aligned}$$