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Traces of powers of the Hamiltonian operator in finite-dimensional antisymmetric model spaces

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Abstract. A general method of evaluation of traces of arbitrary powers of Hermitian operators containing one- and two-body interactions and defined in a finite-dimensional model space is presented. The model space is taken as the antisymmetric and spin-adapted part of an N -fold Cartesian product of a one-electron space. The method is based on the symmetric group approach to the theory of many-electron systems.

1. Introduction

Information on the discrete spectra of the Hamiltonian operators describing systems of N identical fermions have mainly been derived from studies of projections of these operators onto some model spaces, usually finite-dimensional antisymmetric Hilbert spaces. In the case of many-electron systems, the most commonly used model space is that spanned by the N -electron antisymmetrized and spin-adapted products of orthonormal spinorbitals (Ruedenberg 1971), known also as the full configuration interaction (FCI) space (Paldus 1976, Duch and Karwowski 1985, Duch 1986). From a formal point of view, the spin-adapted spaces corresponding to a specific configuration of an atom within the electron-shell model theory belong to the same class. The model space of the nuclear-shell theory has a very similar structure.

Two different strategies may be applied to study the eigenvalue spectrum of a Hamiltonian in a FCI space. In the first one the individual eigenvalues are evaluated by diagonalizing the Hamiltonian matrix. This approach is most useful when one is interested in a few, well characterized energy levels, as for example in the case of studies of electronic molecular states. However, it becomes prohibitively inefficient when the number of levels is very large, as, for example, in complex atomic or nuclear configurations. In the second strategy, global characteristics of the spectra are derived, usually from a knowledge of the appropriate distribution moments (Brody *et al* 1981). The set of eigenvalues is here treated as a statistical ensemble. Then, the larger is the ensemble, the more precise is the treatment. The resulting approach is often referred to as *statistical spectroscopy* (French 1974, French and Kota 1982). Usually in statistical spectroscopy we formulate different questions from those in the conventional one. The statistical approach is the best suited to describe the whole spectrum while the conventional one is best to determine properties

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of individual eigenvalues. Nevertheless, situations do arise when the statistical approach yields results normally associated with the conventional one. For example, the spectral distribution function has successfully been applied to predict locations of individual energy levels in both nuclear (Ratcliff 1971) and atomic (Bancewicz and Karwowski 1987, 1991) spectra.

The statistical spectroscopy originates from works of Bethe (1936), and of van Lier and Uhlenbeck (1937). Early results in this field have been collected by Porter (1965). Applications to nuclear physics have been reviewed by Brody *et al* (1981). More recent contributions by Nomura (1985, 1986) should also be mentioned. Reviews of statistical studies of atomic spectra have been recently published by Bauche *et al* (1988), Bauche and Bauche-Arnoult (1990) and by Karazija (1991). Some applications of the energy level density distribution moments in the crystal field theory have been presented by Yeung and Newman (1985, 1986).

Among the basic quantities of the statistical spectroscopy, of particular importance are the moments of the spectral density distribution, being closely related to traces of powers of the Hamiltonian matrix (Chang *et al* 1971, Nomura 1972, Cowan 1981, Bauche and Bauche-Arnoult 1990, Karazija 1991). Traces of powers of the Hamiltonian matrices were studied by many authors. The earliest works, by Ginocchio (1973) and by Mon and French (1975), were concerned with operators represented in nuclear shell model Hilbert spaces. More recent contributions by Nomura (1974, 1985, 1986) also address mainly problems in nuclear physics. In the atomic structure theory important contributions are due to Bauche-Arnoult *et al* (1979, 1982, 1985), Karazija (1989), and Rudzikaite and Karazija (1989). In the case of N electrons coupled to a given value of the total spin, general formulae for the first two moments of the spectral density distribution were derived Karwowski and Bancewicz (1987) using the formalism of spin-adapted reduced Hamiltonians (Karwowski *et al* 1986).

One can mention three different areas of physics in which the moments are useful: atomic and nuclear spectroscopy, the reduction problem, and studies on structure and properties of the model spaces.

(i) In spectroscopy most interesting applications are connected with the generation of detailed spectra from the moments (Ratcliff 1971, Brody *et al* 1981, Bancewicz and Karwowski 1987, 1991) and with deriving envelopes of spectra in transition arrays from the knowledge of moments (Bauche *et al* 1988, Bauche-Arnoult and Bauche 1992).

(ii) Reduction of the N -electron problem to an effective two-electron problem is one of the most tantalizing tasks in the theory of atoms and molecules (cf Erdahl and Smith 1987). The spectral distribution moments of a many-electron system may be expressed as linear combinations of products of two-electron integrals determined by a two-electron reduced Hamiltonian. In this expression, the information about specific properties of the interactions is contained in the integrals, while the dependence upon the number of electrons and their total spin is described by the expansion coefficients known as the *propagation coefficients*. The propagation coefficients may be derived analytically as rational functions of N and of the quantum numbers (Brody *et al* 1981, Karazija 1991). In this way the specific information about the system, contained in the reduced Hamiltonian, is reshaped, depending on the number of electrons and the total spin, by the propagation coefficients which are independent of the interaction.

(iii) The moments are invariants of the transformations of the basis in the model space. Therefore they characterize the space and may be used to study its general properties. A rather trivial though important application of this invariance was used by Dierksen *et al* (1987, 1990) to locate errors in numerically constructed Hamiltonian matrices. Among

trivial applications one can mention searching for hidden constants of motion (Rosenzweig and Porter 1960, Porter 1965) or determining conditions under which the spectra exhibit certain properties, as, for example, the particle-hole symmetry (Karwowski and Bancewicz 1987).

In the present paper a general algorithm for the evaluation of traces of arbitrary powers of the N -electron Hamiltonian matrix in a spin-adapted space is derived. The derivation is based on the symmetric group approach, in particular on results of recent works by Planelles *et al* (1990, 1991). The paper is organized as follows. In the next section some general concepts and notations are introduced. In section 3, being the central part of this paper, traces of products of the second-order reduced density operators are analysed and a theorem about the repeated indices is presented. A general expression for the traces of H^n and its applications to evaluating of moments of the spectral density distributions are discussed in the next two sections. In the last two sections simplifications of the general expression for the trace of H^n resulting from the symmetry properties of the sums of products of the two-electron integrals are analysed. As an example of application of the formalism, general expressions for traces of H^2 and H^3 are derived.

2. Definitions and basic properties

We are concerned with the N -electron Hamiltonian determined in the FCI space $\mathcal{H}^A(N, K, S, M)$. The FCI space is defined as the antisymmetric and spin-adapted part of the N -fold tensorial product of a $2K$ -dimensional one-electron space V_{2K} :

$$\mathcal{H}^A(N, K, S, M) = [V_{2K}^{\otimes N}]_{SM}^A \quad (1)$$

where A stands for antisymmetry and S, M refer to the total spin operators (S^2 and S_z respectively). The one-electron space is spanned by a set of $2K$ orthonormal spinorbitals. Each spinorbital is a product of a spin function σ_i , $i = 1, 2$ and an orbital ϕ_k , $k = 1, 2, \dots, K$. The dimension of \mathcal{H}^A is given by the Weyl-Paldus formula (Paldus 1976):

$$D(S, N, K) = \frac{2S+1}{K+1} \binom{K+1}{N/2-S} \binom{K+1}{N/2+S+1} \quad (2)$$

The Hamiltonian may be expressed in \mathcal{H}^A as (Planelles *et al* 1990):

$$H = \frac{1}{2} \sum_{ijkl} \{ij|kl\} {}^2E_{ji}^{ik} \quad (3)$$

where

$$\{ij|kl\} = \langle \Phi_i(1)\Phi_k(2) | h(1, 2) | \Phi_l(2)\Phi_j(1) \rangle \quad (4)$$

are generalized two-electron integrals and

$${}^2E_{ji}^{ik} = \sum_{\sigma_1\sigma_2} b_{i\sigma_1}^+ b_{k\sigma_2}^+ b_{l\sigma_2} b_{j\sigma_1} \quad (5)$$

are the second-order reduced density operators (2-RDOs), with b^+ / b^- being the usual fermion creation/annihilation operators. The operator $h(1, 2)$ is defined as

$$h(1, 2) = \frac{1}{N - 1} [h_1(1) + h_1(2)] + h_2(1, 2) \tag{6}$$

where h_1 and h_2 describe, respectively, the one- and two-body interactions. We assume that $h(1, 2) = h(2, 1)$ and that $h(1, 2)$ is Hermitian. Alternatively, Hamiltonian (3) may be expressed in terms of the quantities adapted to the permutation group S_2 of two particles:

$$H = \frac{1}{2} \sum_{ijkl}^K ({}^{[+] } R_{jl}^{ik} {}^{[+] } E_{ji}^{ik} + {}^{[-] } R_{jl}^{ik} {}^{[-] } E_{ji}^{ik}) \tag{7}$$

where

$${}^{[\pm] } R_{jl}^{ik} = \frac{1}{2} (\{ij|kl\} \pm \{il|kj\}) \tag{8}$$

and

$${}^{[\pm] } E_{jl}^{ik} = \frac{1}{2} ({}^2 E_{jl}^{ik} \pm {}^2 E_{ji}^{ki}). \tag{9}$$

This formulation may seem more complex than its equivalent given by (3). Nevertheless it has some significant advantages when analysing the structure of the final formulae. Developing the formalism within this framework goes beyond our present purpose. It will be discussed in a separate paper.

The integrals in S_2 -adapted basis and the density operators are either symmetric or antisymmetric in the indices of the same level, i.e.

$$\begin{aligned} {}^{[\pm] } R_{jl}^{ik} &= \pm {}^{[\pm] } R_{ji}^{ki} = \pm {}^{[\pm] } R_{ij}^{ik} = {}^{[\pm] } R_{ij}^{ki} \\ {}^{[\pm] } E_{jl}^{ik} &= \pm {}^{[\pm] } E_{ji}^{ki} = \pm {}^{[\pm] } E_{ij}^{ik} = {}^{[\pm] } E_{ij}^{ki}. \end{aligned} \tag{10}$$

Besides, since $h(1, 2)$ is Hermitian

$${}^{[\pm] } R_{jl}^{ik} = {}^{[\pm] } R_{ik}^{jl} \tag{11}$$

however, E_{jl}^{ik} are, in general, non-Hermitian and

$${}^{[\pm] } E_{jl}^{ik} = ({}^{[\pm] } E_{ik}^{jl})^+. \tag{12}$$

Similarly, due to the Hermiticity of $h(1, 2)$

$$\{ij|kl\} = \{ji|lk\} \tag{13}$$

however

$${}^2 E_{jl}^{ik} = ({}^2 E_{ik}^{jl})^+ \neq {}^2 E_{ik}^{jl}. \tag{14}$$

The power of the Hamiltonian reads

$$H^n = \frac{1}{2^n} \sum_{(i)}^K \sum_{(j)}^K \sum_{(k)}^K \sum_{(l)}^K \left\{ \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ j_1 l_1, j_2 l_2, \dots, j_n l_n \end{matrix} \right\} \left\{ \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ j_1 l_1, j_2 l_2, \dots, j_n l_n \end{matrix} \right\} \tag{15}$$

where

$$\sum_{(i)} \text{ stands for } \sum_{i_1 i_2 \dots i_n}$$

and

$$\left\{ \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ j_1 l_1, j_2 l_2, \dots, j_n l_n \end{matrix} \right\} = \prod_{q=1}^n \{i_q j_q | k_q l_q\} \tag{16}$$

$$\left\langle \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ j_1 l_1, j_2 l_2, \dots, j_n l_n \end{matrix} \right\rangle = \prod_{q=1}^n 2 E_{j_q l_q}^{i_q k_q} \tag{17}$$

If the Hamiltonian is expressed in terms of S_2 -adapted quantities (equation (7)), then

$$H^n = \frac{1}{2^n} \sum_{(i)}^K \sum_{(j)}^K \sum_{(k)}^K \sum_{(l)}^K \sum_s^{2^n} [s] R_{j_1 l_1, j_2 l_2, \dots, j_n l_n}^{i_1 k_1, i_2 k_2, \dots, i_n k_n} [s] \mathcal{E}_{j_1 l_1, j_2 l_2, \dots, j_n l_n}^{i_1 k_1, i_2 k_2, \dots, i_n k_n} \tag{18}$$

Here $[s]$ is a sequence composed of n symbols $+$ or $-$ and the sum runs over all 2^n such sequences (for example, $[s] = ++, +-, -+, --$ in the case of $n = 2$),

$$[s] R_{j_1 l_1, j_2 l_2, \dots, j_n l_n}^{i_1 k_1, i_2 k_2, \dots, i_n k_n} = [s_1] R_{j_1 l_1}^{i_1 k_1} [s_2] R_{j_2 l_2}^{i_2 k_2} \dots [s_n] R_{j_n l_n}^{i_n k_n}$$

and

$$[s] \mathcal{E}_{j_1 l_1, j_2 l_2, \dots, j_n l_n}^{i_1 k_1, i_2 k_2, \dots, i_n k_n}$$

is defined in an analogous way.

The basis in \mathcal{H}^A is formed by a set of spin-adapted and antisymmetric products of the orbitals. Then, a basis vector may be expressed as (Ruedenberg 1971, Karwowski 1973, Duch and Karwowski 1985)

$$|SMl; \lambda\rangle = \hat{A}[|SMl\rangle|\lambda\rangle] \tag{19}$$

where \hat{A} is the antisymmetrizer, $|SMl\rangle$ is an eigenvector of the total spin (S^2 and S_z) operators, l numbers different spin coupling schemes and $|\lambda\rangle$ corresponds to a product of orbitals. The product λ is referred to as the *orbital configuration*. An orbital configuration is characterized by the corresponding *occupation numbers* $n_i^\lambda = 0, 1, 2, (i = 1, 2, \dots, k)$, of the orbitals. If an orbital does not appear in the product, then it is referred to as an *empty* or a *virtual orbital* and the corresponding occupation number is zero. If $n_i^\lambda = 1$ (singly occupied orbitals or *singles*), then the orbital Φ_i appears once in the product. If $n_i^\lambda = 2$ (doubly occupied orbitals or *doubles*), then Φ_i appears twice in the product. Due to the Pauli principle (antisymmetrization), configurations with $n_i^\lambda > 2$ are not allowed.

With this choice of the basis, a diagonal matrix element of any product of the 2-RDOS vanishes unless the sets of all upper and lower indices in the 2-RDOS are the same. Therefore the expectation value of H^n may be written as,

$$\langle H^n \rangle_{Av} = \frac{1}{2^n} \sum_{(i)}^K \sum_{(k)}^K \sum_{\mathcal{P} \in S_{2n}} \left\{ \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ \mathcal{P}[i_1 k_1, i_2 k_2, \dots, i_n k_n] \end{matrix} \right\} \left\langle \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ \mathcal{P}[i_1 k_1, i_2 k_2, \dots, i_n k_n] \end{matrix} \right\rangle_{Av} \tag{20}$$

where the last sum is extended over all $(2n)!$ permutations of the lower indices. Equation (20) is rather complicated and, in a general case, not easy to handle. In particular, the number of different types of the expectation values of the products of 2-RDOS is quite large.

3. Traces of products of 2-RDOS

The problem of calculating traces of H^n over $\mathcal{H}^A(N, K, S, M)$ appears to be simpler than that of calculating matrix elements. First, the trace of a product is invariant with respect to any cyclic permutation of the operators forming the product. Second, the trace is invariant with respect to a unitary transformation of the orbitals. In particular, it does not depend upon their numbering (Karwowski *et al* 1986). Since the numbering of the orbitals is irrelevant, we assume that the indices in the upper row of the product of 2-RDOS are always in ascending order. Then the traces of the 2-RDO products depend only on relations between the indices but not on their specific values. There are two different kinds of relations between the indices. The first one is concerned with equalities between the indices located in different rows, the second one with equalities between the indices located in the same row.

3.1. The case when all indices are different

Let us assume that the indices are all different. Then there are $(2n)!$ different traces of the products of p -RDOS, each of them labelled by a permutation $\mathcal{P} \in S_{2n}$:

$$\langle\langle \mathcal{P} \rangle\rangle \equiv \text{Tr} \left(\left\langle \begin{array}{c} 1 \ 2, \ 3 \ 4, \ \dots, \ 2n-1 \ 2n \\ \mathcal{P}[1 \ 2, \ 3 \ 4, \ \dots, \ 2n-1 \ 2n] \end{array} \right\rangle \right). \quad (21)$$

In order to divide the $(2n)!$ products into classes of equivalence, each of them containing products having the same trace, let us recall the definition of the p th-order density operator (Planelles *et al* 1990):

$${}^p E_{acd\dots}^{ijk\dots} = \sum_{\sigma_1 \dots \sigma_p} b_{i\sigma_1}^+ b_{j\sigma_2}^+ b_{k\sigma_3}^+ \dots b_{d\sigma_p} b_{c\sigma_2} b_{a\sigma_1}. \quad (22)$$

As has been proved by Planelles *et al* (1990), two density operators

$${}^p E_{\mathcal{P}(acd\dots)}^{ijk\dots} \quad \text{and} \quad {}^p E_{\mathcal{Q}(acd\dots)}^{ijk\dots} \quad (\mathcal{P}, \mathcal{Q} \in S_p)$$

have the same trace if \mathcal{P} and \mathcal{Q} belong to the same class of S_p i.e. if they have the same cycle structure. Product (17) of the primitive 2-RDOS, using the generalized Wick theorem (Kutzelnigg 1985, Planelles *et al* 1990), may be expressed in terms of sums of RDOS of orders $2n, 2n-1, \dots$. Hence, two traces $\langle\langle \mathcal{P} \rangle\rangle$ and $\langle\langle \mathcal{Q} \rangle\rangle$ defined by equation (21) are the same if the Wick expansions of

$$\left\langle \begin{array}{c} 1 \ 2, \ 3 \ 4, \ \dots, \ 2n-1 \ 2n \\ \mathcal{P}[1 \ 2, \ 3 \ 4, \ \dots, \ 2n-1 \ 2n] \end{array} \right\rangle \quad \text{and} \quad \left\langle \begin{array}{c} 1 \ 2, \ 3 \ 4, \ \dots, \ 2n-1 \ 2n \\ \mathcal{Q}[1 \ 2, \ 3 \ 4, \ \dots, \ 2n-1 \ 2n] \end{array} \right\rangle$$

are of the same form, i.e. they consist of the same number of p -RDOS possessing the same cycle structure.

To facilitate an easy classification of the Wick expansions let us introduce the concept of *upper links* between the indices involved in a cycle. Let us consider as an example $\text{Tr} [{}^2 E_{35}^{12} {}^2 E_{26}^{34} {}^2 E_{14}^{56}]$. The corresponding permutation is $(1325)(46)^\dagger$. We denote

$$\text{Tr} [{}^2 E_{35}^{12} {}^2 E_{26}^{34} {}^2 E_{14}^{56}] \equiv \langle\langle {}^2 E_{35}^{12} {}^2 E_{26}^{34} {}^2 E_{14}^{56} \rangle\rangle \equiv \langle\langle (1 \ 3 \ 2 \ 5)(4 \ 6) \rangle\rangle \quad (23)$$

† When expressing a permutation as a product of cycles we adopt a convention that in each cycle the lowest index stands at the first position and that the cycles in the product are written in a descending order of their lengths.

where m means that the 2-RDO in which m is a subscript stands to the left of a 2-RDO in which m is a superscript. An arc drawn between the lower and the upper index marked by a dot links two different 2-RDOs and ascends from the bottom row to the top row. Then, the dots indicate those creation operators (the top row indices) which in

$$\left\langle \begin{array}{c} 1 \dot{2}, 3 \dot{4}, \dots, 2n - 1 \dot{2n} \\ \mathcal{P}[1 \dot{2}, 3 \dot{4}, \dots, 2n - 1 \dot{2n}] \end{array} \right\rangle$$

stand to the right of the corresponding annihilators (the bottom row indices).

A very simple rule allows marking of the upper links in a permutation: if in a cycle two adjacent indices are associated with two different 2-RDOs and if the first index is smaller than the second, then the second index should be supplied with a dot.

Consulting the algorithm for the generalized Wick theorem (Kutzelnigg 1985, Planelles *et al* 1990) one can see that the following theorem concerning traces of products of 2-RDOs is fulfilled.

Theorem 1. If two permutations \mathcal{P} and \mathcal{Q} belong to the same class of the pertinent permutation group and if in $\langle\langle \mathcal{P} \rangle\rangle$ and in $\langle\langle \mathcal{Q} \rangle\rangle$ the number of the upper links in the corresponding cycles is the same, then $\langle\langle \mathcal{P} \rangle\rangle = \langle\langle \mathcal{Q} \rangle\rangle$.

As a consequence of this theorem it is convenient to denote a trace of a product of 2-RDOs by indicating only the cyclic structure of the permutation and the number of the upper links in each cycle. Then, the trace from equation (23) is denoted as

$$\langle\langle (1 \dot{3} 2 \dot{5})(4 \dot{6}) \rangle\rangle = \langle\langle 4_2 2_1 \rangle\rangle \tag{24}$$

where 4 and 2 refer to the lengths of the corresponding cycles (class [42] of S_6) and the subscripts correspond to the numbers of the upper links. In our example

$$\begin{aligned} \langle\langle 4_2 2_1 \rangle\rangle &= \langle\langle (1 \dot{3} 2 \dot{5})(4 \dot{6}) \rangle\rangle = \langle\langle (1 \dot{5} 2 \dot{3})(4 \dot{6}) \rangle\rangle \\ &= \langle\langle (1 \dot{4} 2 \dot{5})(3 \dot{6}) \rangle\rangle = \langle\langle (1 \dot{5} 2 \dot{4})(3 \dot{6}) \rangle\rangle \\ &= \langle\langle (1 \dot{4} 3 \dot{5})(2 \dot{6}) \rangle\rangle = \langle\langle (1 \dot{3} 4 \dot{5})(2 \dot{6}) \rangle\rangle \\ &= \langle\langle (1 \dot{6} 3 \dot{5})(2 \dot{4}) \rangle\rangle = \langle\langle (1 \dot{6} 2 \dot{5})(3 \dot{4}) \rangle\rangle \\ &= \langle\langle (1 \dot{3} 2 \dot{6})(4 \dot{5}) \rangle\rangle = \langle\langle (1 \dot{6} 2 \dot{3})(4 \dot{5}) \rangle\rangle \\ &= \langle\langle (1 \dot{4} 2 \dot{6})(3 \dot{5}) \rangle\rangle = \langle\langle (1 \dot{6} 2 \dot{4})(3 \dot{5}) \rangle\rangle \\ &= \langle\langle (1 \dot{4} 3 \dot{6})(2 \dot{5}) \rangle\rangle = \langle\langle (1 \dot{3} 4 \dot{6})(2 \dot{5}) \rangle\rangle \\ &= \langle\langle (1 \dot{5} 3 \dot{6})(2 \dot{4}) \rangle\rangle = \langle\langle (1 \dot{5} 2 \dot{6})(3 \dot{4}) \rangle\rangle. \end{aligned}$$

A simple formulation of the generalized Wick theorem for traces of products of the 2-RDOs, based on the notion of the upper links is given in appendix 1.

3.2. The case of repeated indices

Let us consider the case when at least one of the indices in the product of 2-RDOs (equation (17)) appears more than once. We shall prove that the trace of such a product may be expressed as a sum of traces of products of 2-RDOs in which all indices are different. To this aim we formulate two lemmas concerning RDOs of an arbitrary order.

Lemma 1. If $S_r \subset S_p$, $\mathcal{R} \in S_r$, $\mathcal{P} \in S_p$ and $r > 2$, then

$$\sum_{\mathcal{R} \in S_r} \langle\langle {}^p E_{\mathcal{R}\mathcal{P}}^Z(Z) \rangle\rangle = 0 \tag{25}$$

where Z denotes an arbitrary string of p indices.

Proof of this lemma is given in appendix 2.

Lemma 2. If X is a string of $(p - q)$ arbitrary indices and Y is a string of q identical indices, then

$$\langle\langle {}^p E_{\mathcal{P}(YX)}^{YX} \rangle\rangle = 0 \tag{26}$$

for an arbitrary $\mathcal{P} \in S_p$ and $q > 2$.

The proof is a direct consequence of the Pauli principle: if $q > 2$, then

$${}^p E_{\mathcal{P}(YX)}^{YX} |SMI; \lambda\rangle = 0.$$

Combining equations (25) and (26) we obtain a theorem concerning repeated indices in traces of the p th order RDOS:

Theorem 2. Let X be a string of $(p - q)$ arbitrary indices, Y a string of q identical indices and Z a string of p indices in which the last $p - q$ positions are the same as in X , while the first q positions are occupied by indices which are all different and which are different from any of the indices of X . Let $\mathcal{P} \in S_p$ and $\mathcal{R} \in G_q$, where G_q is a permutation group isomorphic to S_q but containing operators which act on the first q indices of Z only. Then,

$$\langle\langle {}^p E_{\mathcal{P}(YX)}^{YX} \rangle\rangle = \sum_{\mathcal{R} \in G_q} \langle\langle {}^p E_{\mathcal{R}\mathcal{P}}^Z(Z) \rangle\rangle. \tag{27}$$

This is obvious for $q > 2$, from the above lemmas (both sides of the equation are zero). The equality is also true for the case $q = 2$ (cf equation (22) in Planelles et al 1991), although in this case it is different from zero. Thus, (27) is valid for any q .

Since ${}^p E_{\mathcal{P}\mathcal{Q}A}^{\mathcal{Q}A} = {}^p E_{\mathcal{P}'A}^A$, where $\mathcal{P}, \mathcal{Q} \in S_p$, $\mathcal{P}' = \mathcal{Q}^{-1}\mathcal{P}\mathcal{Q}$ and A is an arbitrary string of p indices, theorem 2 may be formulated in a more general way. For an arbitrary $\mathcal{P} \in S_p$, $\mathcal{Q} \in S_p$ and $\mathcal{P}' = \mathcal{Q}^{-1}\mathcal{P}\mathcal{Q}$ we may rewrite (27) as

$$\langle\langle {}^p E_{\mathcal{P}\mathcal{Q}(YX)}^{\mathcal{Q}(YX)} \rangle\rangle = \sum_{\mathcal{R} \in G_q} \langle\langle {}^p E_{\mathcal{R}\mathcal{P}'}^Z(Z) \rangle\rangle. \tag{28}$$

Then, in (28) string $\mathcal{Q}(YX)$ contains repeated indices distributed in an arbitrary way (defined by the permutation \mathcal{Q}).

A similar relation is valid for arbitrary products of p -RDOS, in particular for products of 2-RDOS. Using the same symbols as in (28) we have

$$\langle\langle \begin{matrix} \mathcal{Q}(YX) \\ \mathcal{P}\mathcal{Q}(YX) \end{matrix} \rangle\rangle = \sum_{\mathcal{R} \in G_q} \langle\langle \begin{matrix} Z \\ \mathcal{R}\mathcal{P}'(Z) \end{matrix} \rangle\rangle. \tag{29}$$

It is worthwhile to note that the present results generalize the ones expressed by Planelles *et al* (1991) in equations (22)–(26).

The last equation may be proved by applying to both its sides the generalized Wick theorem (see appendix 1). Let us note, that if

$$\left\langle\left\langle \begin{matrix} 1 & 2 & 3 & 4 & \dots & 2n-1 & 2n \\ p & q & r & s & \dots & u & v \end{matrix} \right\rangle\right\rangle$$

is a product of n 2-RDOS, then the application of the Wick theorem will produce a combination of ${}^{2n}E, {}^{2n-1}E, {}^{2n-2}E, \dots$, with the corresponding strings of indices containing, respectively, all the indices of (YX) and (Z) , one index less, two indices less, ... Then, the RHS of (29) is a combination of expressions

$$W_{st} = \sum_{\mathcal{R} \in \mathcal{G}_s} \left\langle\left\langle {}^t E_{\mathcal{R}P''(Z_{st})}^{Z_{st}} \right\rangle\right\rangle$$

with $t = 2n, 2n - 1, 2n - 2, \dots, s = q, q - 1, \dots$ and P'' being modified accordingly. The string of indices Z_{st} contains t indices out of which $t-s$ belong to X .

According to lemma 1, $W_{st} = 0$ if $s > 2$. Similarly, the LHS of (29) is a combination of expressions

$$U_{st} = \left\langle\left\langle {}^t E_{\mathcal{P}''Q''(Y_s X_{t-s})}^{Q''(Y_s X_{t-s})} \right\rangle\right\rangle$$

where Y_s and X_{t-s} are strings containing, respectively, s and $t-s$ indices, and Q'' being modified accordingly. In this case, due to lemma 2, $U_{st} = 0$ if $s > 2$.

As one can check, the terms which remain in both sides of (29) correspond to each other in the sense of (28) and appear with the same coefficients. Instead of a general demonstration of this fact (which is rather tedious), we shall illustrate the procedure using an example. According to (29)

$$\left\langle\left\langle E_{11}^{11} E_{54}^{1\bar{4}} E_{11}^{\bar{5}1} \right\rangle\right\rangle = \sum_{\mathcal{R} \in \mathcal{G}_4} \left\langle\left\langle \begin{matrix} 1 & 2 & 3 & \bar{4} & \bar{5} & 6 \\ \mathcal{R}[1 & 2 & \bar{5} & \bar{4} & 3 & 6] \end{matrix} \right\rangle\right\rangle \tag{30}$$

where, for clarity, the indices corresponding to string X are marked by a tilde. The permutations \mathcal{R} act only on the indices which are not marked. Applying to the RHS of (30) the procedure described we get

$$\text{RHS} = 2 \sum_{\mathcal{R} \in \mathcal{G}_2} \left(\left\langle\left\langle {}^4 E_{\mathcal{R}[1\bar{5}42]}^{12\bar{4}\bar{5}} \right\rangle\right\rangle + \left\langle\left\langle {}^3 E_{\mathcal{R}[12\bar{4}]}^{12\bar{4}} \right\rangle\right\rangle \right). \tag{31}$$

In the calculation some identities like, for example

$$\sum_{\mathcal{R} \in \mathcal{S}_2} \left\langle\left\langle {}^4 E_{\mathcal{R}[5142]}^{1245} \right\rangle\right\rangle = \sum_{\mathcal{R} \in \mathcal{S}_2} \left\langle\left\langle {}^4 E_{5142}^{\mathcal{R}[1245]} \right\rangle\right\rangle = \sum_{\mathcal{R} \in \mathcal{S}_2} \left\langle\left\langle {}^4 E_{\mathcal{R}[1542]}^{1245} \right\rangle\right\rangle$$

are useful. Developing the LHS, we get two non-vanishing terms

$$\text{LHS} = 2 \left(\left\langle\left\langle {}^4 E_{1541}^{1145} \right\rangle\right\rangle + \left\langle\left\langle {}^3 E_{114}^{114} \right\rangle\right\rangle \right). \tag{32}$$

Applying (29) we have

$$\begin{aligned} \left\langle\left\langle {}^4 E_{1541}^{1145} \right\rangle\right\rangle &= \left\langle\left\langle {}^4 E_{1542}^{1245} \right\rangle\right\rangle + \left\langle\left\langle {}^4 E_{2541}^{1245} \right\rangle\right\rangle \\ \left\langle\left\langle {}^3 E_{114}^{114} \right\rangle\right\rangle &= \left\langle\left\langle {}^3 E_{124}^{124} \right\rangle\right\rangle + \left\langle\left\langle {}^3 E_{214}^{124} \right\rangle\right\rangle \end{aligned}$$

i.e. same as in (31).

3.3. Summary

Due to equation (29) only traces of products of 2-RDOs with all indices different are needed. In the case of all indices different, theorem 1 allows us to reduce the number of different traces very substantially. A list of all different traces of products of 2-RDOs which may appear when calculating traces of H , H^2 and H^3 are given in table 1. As we see, in these cases there are, respectively, 2, 8, and 30 different traces.

Table 1. List of all different traces of products of the second order density operators appearing in expressions for $\text{Tr}(H^n)$, $n < 4$. Each trace is identified by the class of S_{2n} with appropriately distributed upper links. If there are no upper links in a cycle, the corresponding index is omitted.

H	H^2	H^3
$\langle\langle 1 \rangle\rangle$	$\langle\langle 1 \rangle\rangle$	$\langle\langle 1 \rangle\rangle$
$\langle\langle 2 \rangle\rangle$	$\langle\langle 2 \rangle\rangle \langle\langle 2_1 \rangle\rangle$	$\langle\langle 2 \rangle\rangle \langle\langle 2_1 \rangle\rangle$
	$\langle\langle 3_1 \rangle\rangle$	$\langle\langle 3_1 \rangle\rangle \langle\langle 3_2 \rangle\rangle$
	$\langle\langle 4_1 \rangle\rangle \langle\langle 4_2 \rangle\rangle$	$\langle\langle 4_1 \rangle\rangle \langle\langle 4_2 \rangle\rangle$
	$\langle\langle 2^2 \rangle\rangle \langle\langle 2_2^2 \rangle\rangle$	$\langle\langle 2^2 \rangle\rangle \langle\langle 2_1^2 \rangle\rangle \langle\langle 2_2^2 \rangle\rangle$
		$\langle\langle 5_1 \rangle\rangle \langle\langle 5_2 \rangle\rangle \langle\langle 5_3 \rangle\rangle$
		$\langle\langle 3_1 2 \rangle\rangle \langle\langle 3_1 2_1 \rangle\rangle \langle\langle 3_2 2_1 \rangle\rangle$
		$\langle\langle 6_1 \rangle\rangle \langle\langle 6_2 \rangle\rangle \langle\langle 6_3 \rangle\rangle \langle\langle 6_4 \rangle\rangle$
		$\langle\langle 2^3 \rangle\rangle \langle\langle 2_1^3 \rangle\rangle \langle\langle 2_2^3 \rangle\rangle$
		$\langle\langle 4_1 2 \rangle\rangle \langle\langle 4_2 2 \rangle\rangle \langle\langle 4_1 2_1 \rangle\rangle \langle\langle 4_2 2_1 \rangle\rangle$
		$\langle\langle 3_1 3_1 \rangle\rangle \langle\langle 3_1 3_2 \rangle\rangle \langle\langle 3_2 3_2 \rangle\rangle$

4. General expression for traces of H^n

The traces of H^n , according to equation (20), may be expressed as

$$\text{Tr}(H^n) = \frac{1}{2^n} \sum_{\mathcal{P} \in S_{2n}} \left\langle\left\langle \begin{matrix} 1 & 2 & 3 & 4 & \dots & 2n-1 & 2n \\ \mathcal{P}[1 & 2 & 3 & 4 & \dots & 2n-1 & 2n] \end{matrix} \right\rangle\right\rangle \sum_{\substack{(i) \\ \text{all indices different}}}^K \sum_{(k)}^K \left\{ \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ \mathcal{P}[i_1 k_1, i_2 k_2, \dots, i_n k_n] \end{matrix} \right\} + [\text{terms with repeated indices}]. \tag{33}$$

The terms appearing in (33), depending upon the number of repeated indices, may be labelled by partitions of $2n$. For example, partition $[1^{2n}]$ corresponds to the term with all indices different (written explicitly in (33)), partition $[2 \ 1^{2n-2}]$ corresponds to the case of two repeated indices, $[2^2 \ 1^{2n-4}]$ to two (different) pairs of repeated indices, $[4 \ 1^{2n-4}]$ to four repeated indices, and $[2n]$ to the case when all indices are the same.

The number of different terms associated with each partition is equal to the number of compositions associated with this partition. Thus, it is equal to $\binom{2n}{k} (2n-k)!$ for $[k \ 1^{2n-k}]$, $\binom{2n}{k} \binom{2n-k}{l} (2n-l-k)!$ for $[kl \ 1^{2n-k-l}]$, and so on. The permutations \mathcal{P} , in the cases of repeated indices, run over appropriate subgroups of S_{2n} (the identical indices are not permuted between themselves). On the other hand, due to (29), each term with an index repeated q times contributes to $q!$ terms, each of them associated with a trace of a product of n 2-RDOs without repeated indices. The global effect results in a compression of (33) into a compact form:

$$\text{Tr}(H^n) = \frac{1}{2^n} \sum_{\mathcal{P} \in S_{2n}} \left\langle\left\langle \begin{matrix} 1 & 2 & 3 & 4 & \dots & 2n-1 & 2n \\ \mathcal{P}[1 & 2 & 3 & 4 & \dots & 2n-1 & 2n] \end{matrix} \right\rangle\right\rangle \sum_{(i)}^K \sum_{(k)}^K \left\{ \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ \mathcal{P}[i_1 k_1, i_2 k_2, \dots, i_n k_n] \end{matrix} \right\} \tag{34}$$

where all indices are included in the sums over $\{i\}$ and $\{k\}$. Equation (34) is the most compact and the most general expression for the trace of a power of an operator.

The sums of integrals appearing in (34) are, for a given \mathcal{P} , invariant with respect to unitary transformations of the orbital basis. Therefore, similarly to the case of the traces of the products of 2-RDOs, they depend upon relative arrangement of the indices (i.e. on the permutation \mathcal{P}) only. We denote

$$\langle\langle \mathcal{P} \rangle\rangle = \left\langle \left\langle \begin{matrix} 1 & 2, & 3 & 4, & \dots, & 2n-1 & 2n \\ \mathcal{P}[1 & 2, & 3 & 4, & \dots, & 2n-1 & 2n] \end{matrix} \right\rangle \right\rangle = \frac{1}{2^n} \sum_{(i)}^K \sum_{(k)}^K \left\{ \begin{matrix} i_1 k_1, i_2 k_2, \dots, i_n k_n \\ \mathcal{P}[i_1 k_1, i_2 k_2, \dots, i_n k_n] \end{matrix} \right\}. \quad (35)$$

In consequence, equation (34) may be rewritten in more condensed form as

$$\text{Tr}(H^n) = \sum_{\mathcal{P} \in S_{2n}} \langle\langle \mathcal{P} \rangle\rangle \langle\langle \mathcal{P} \rangle\rangle. \quad (36)$$

Equation (36) separates the effects which depend upon the specific form of the interactions in the system and on the properties of the one-electron (orbital) space from the ones which depend upon the number of electrons and the total spin \dagger .

The coefficients $\langle\langle \mathcal{P} \rangle\rangle$ describe the way in which one- and two-body effects contained in $\langle\langle \mathcal{P} \rangle\rangle$, which we refer to as the *interaction factors*, influence the system when the number of particles or their resultant spin changes. They are referred to as the *propagation coefficients* and have been subject of extensive studies in several contexts (cf Mon and French 1975, Brody *et al* 1981, Nomura 1972, 1974, 1985, 1986).

5. Basic properties of the interaction terms and the Hamiltonian moments

In the case of $n = 1$, equation (36) contains just two terms:

$$\text{Tr}(H) = \langle\langle (1) \rangle\rangle \left\langle \left\langle \begin{matrix} 1 & 2 \\ 1 & 2 \end{matrix} \right\rangle \right\rangle + \langle\langle (1 \ 2) \rangle\rangle \left\langle \left\langle \begin{matrix} 1 & 2 \\ 2 & 1 \end{matrix} \right\rangle \right\rangle. \quad (37)$$

The corresponding interaction factors

$$\left\langle \left\langle \begin{matrix} 1 & 2 \\ 1 & 2 \end{matrix} \right\rangle \right\rangle \quad \text{and} \quad \left\langle \left\langle \begin{matrix} 1 & 2 \\ 2 & 1 \end{matrix} \right\rangle \right\rangle$$

are referred to as the Coulomb and the exchange contributions, respectively (Karwowski and Bancewicz 1987) and are expressed as

$$\text{Tr}(\mathcal{J}) = \left\langle \left\langle \begin{matrix} 1 & 2 \\ 1 & 2 \end{matrix} \right\rangle \right\rangle = \frac{1}{2} \sum_{pk}^K \{pp|kk\} \quad (38)$$

$$\text{Tr}(\mathcal{K}) = \left\langle \left\langle \begin{matrix} 1 & 2 \\ 2 & 1 \end{matrix} \right\rangle \right\rangle = \frac{1}{2} \sum_{pk}^K \{pk|kp\}. \quad (39)$$

\dagger In fact, the interaction and the orbital-space-dependent part $\langle\langle \mathcal{P} \rangle\rangle$ depends, in a rather trivial way, upon the number of electrons through equation (6). This dependence can easily be eliminated by explicitly separating the generalized two-electron integrals into one- and two-electron ones. This step would, however, introduce unnecessary complications to the equations and we shall not do it at this stage.

Equations (38) and (39) are interpreted as traces of the Coulomb (\mathcal{J}_{pq}) and exchange (\mathcal{K}_{pq}) matrices defined over the entire one-electron space:

$$\mathcal{J}_{pq} = \sum_{k=1}^K \{pq|kk\} \quad (40)$$

and

$$\mathcal{K}_{pq} = \sum_{k=1}^K \{pk|kq\}. \quad (41)$$

In the majority of applications we are interested in moments of the spectral density distributions rather than in the traces. The first moment is, in our case, the average energy

$$\bar{H} = \frac{\text{Tr}(H)}{D(S, N, K)}. \quad (42)$$

The n th moment of the spectral density distribution is defined as

$$M_n = \frac{1}{D} \text{Tr}((H - \bar{H})^n). \quad (43)$$

If the interaction factors have correct asymptotic behaviour then the moments (contrary to the traces) converge to finite limits if $K \rightarrow \infty$.

Equation (43) may be written alternatively as

$$M_n = \frac{1}{D} \text{Tr}(H^n) + \sum_{k=1}^n (-1)^k \binom{n}{k} \bar{H}^k \text{Tr}(H^{n-k}). \quad (44)$$

Hence, except for the terms appearing in M_n , $\text{Tr}(H^n)$ contains contributions from traces of H^k with $k = 0, 1, 2, \dots, n-1$. In order to simplify the algebra, it is convenient to redefine H by incorporating \bar{H} into it, i.e. by taking $\tilde{H} = H - \bar{H}$. Then

$$M_n = \frac{1}{D} \text{Tr}(\tilde{H}^n). \quad (45)$$

Formally this can be achieved by just setting $\bar{H} = 0$ or, equivalently,

$$\text{Tr}(\mathcal{J}) = \text{Tr}(\mathcal{K}) = 0. \quad (46)$$

The interaction factors containing $\text{Tr}(\mathcal{J})$ or $\text{Tr}(\mathcal{K})$ may be easily identified. If the elements of columns $2i-1, 2i$ ($i = 1, 2, \dots, n$) are not affected by the permutation \mathcal{P} , then these columns correspond to $\text{Tr}(\mathcal{J})$; if \mathcal{P} leaves the bottom row elements of these columns transposed, then these columns correspond to $\text{Tr}(\mathcal{K})$. For example

$$\left\{ \left\{ \begin{array}{cccccc} 1 & 2, & 3 & 4, & 5 & 6, & 7 & 8 \\ 5 & 6, & 3 & 4, & 1 & 2, & 7 & 8 \end{array} \right\} \right\} = \frac{1}{4} \text{Tr}(\mathcal{J})^2 \sum_{pqrs} \{pq|rs\} \{qp|sr\} \quad (47a)$$

$$\left\{ \left\{ \begin{array}{cccccc} 1 & 2, & 3 & 4, & 5 & 6, & 7 & 8 \\ 5 & 6, & 4 & 3, & 1 & 2, & 7 & 8 \end{array} \right\} \right\} = \frac{1}{4} \text{Tr}(\mathcal{J}) \text{Tr}(\mathcal{K}) \sum_{pqrs} \{pq|rs\} \{qp|sr\}. \quad (47b)$$

In general, if the permutation \mathcal{P} does not affect r integrals (r pairs of columns ($2i-1, 2i$)) and transposes indices in t integrals, then the corresponding interaction factor is proportional to $\text{Tr}(\mathcal{J})^r \text{Tr}(\mathcal{K})^t$.

6. Classification of the interaction terms

It is convenient to associate with each interaction factor an index $i = n - r - t$ which is equal to the number of the two-electron integrals being 'coupled' by the permutation \mathcal{P} . From our previous considerations (equations (44)–(46)) one concludes that only terms with $j = n$ are relevant for our discussion. However, for completeness, in some cases all terms are considered. Then, $\langle\langle \mathcal{P} \rangle\rangle_j$ denotes an interaction factor with j integrals coupled. If the index is omitted, it is assumed that $j = n$.

As we have demonstrated in section 3, the symmetry properties of the propagation coefficients allow us to divide all the coefficients onto *equivalence classes*, so that the coefficients belonging to each class are equal to each other. An equivalence class of the propagation coefficients may be labelled by two indices: one corresponding to the partition of $2n$ and the other one to the number of the upper links in each of the cycles defined by this partition.

Symmetry properties of the interaction factors are similar but not identical to those of the propagation coefficients. In particular no counterpart of the Wick theorem exist for the interaction factors. On the other hand, no symmetry element of the propagation coefficients exists which would correspond to the one resulting from equation (13) for the interaction factors. It appears that the index determining the number of integrals coupled by \mathcal{P} and the two indices identifying the equivalence classes of the propagation coefficients (the class of S_{2n} to which \mathcal{P} belongs and the number of upper links in each cycle) are not sufficient to identify the equivalence classes of the interaction factors. For example

$$\langle\langle {}^2E_{31}^{12} {}^2E_{56}^{34} {}^2E_{42}^{56} \rangle\rangle = \langle\langle {}^2E_{35}^{12} {}^2E_{26}^{34} {}^2E_{41}^{56} \rangle\rangle = \langle\langle 6_3 \rangle\rangle. \tag{48}$$

The corresponding interaction factors are

$$A \equiv \left\langle\left\langle \begin{array}{cccccc} 1 & 2, & 3 & 4, & 5 & 6 \\ 3 & 1, & 5 & 6, & 4 & 2 \end{array} \right\rangle\right\rangle = \frac{1}{4} \sum_{pqrst}^k \mathcal{K}_{pq} \{qr|ts\} \{rt|sp\} = \langle\langle (1 \overset{\cdot}{3} \overset{\cdot}{5} 4 \overset{\cdot}{6} 2) \rangle\rangle_3 \tag{49}$$

and

$$B \equiv \left\langle\left\langle \begin{array}{cccccc} 1 & 2, & 3 & 4, & 5 & 6 \\ 3 & 5, & 2 & 6, & 4 & 1 \end{array} \right\rangle\right\rangle = \frac{1}{8} \sum_{pqrst}^K \{uq|pr\} \{qp|ts\} \{rt|su\} = \langle\langle (1 \overset{\cdot}{3} 2 \overset{\cdot}{5} 4 \overset{\cdot}{6}) \rangle\rangle_3. \tag{50}$$

The number of integrals coupled by both permutations is 3, but evidently $A \neq B$.

A complete classification of the interaction factors requires an introduction of several labels which allow an identification of non-equivalent classes. As an example of such a label we introduce as a classification index the number of *lower links* in a cycle. We attach a lower link to an index s in a cycle if the index is associated with two different integrals and if in the bottom row of the symbol

$$\left\langle\left\langle \begin{array}{c} 1 \ 2, \ 3 \ 4, \ \dots, \ 2n - 1 \ 2n \\ \mathcal{P}[1 \ 2, \ 3 \ 4, \ \dots, \ 2n - 1 \ 2n] \end{array} \right\rangle\right\rangle$$

it stands at a position $q > s$. An index with a lower link is marked as $\overset{\cdot}$. An arc which connects the indices with lower links in the corresponding two-row symbols descends from the upper to the lower row. For example,

$$A = \left\langle\left\langle \begin{array}{cccccc} 1 & 2, & 3 & 4, & 5 & 6 \\ 3 & 1, & 5 & 6, & 4 & 2 \end{array} \right\rangle\right\rangle = \langle\langle (1 \overset{\cdot}{3} \overset{\cdot}{5} 4 \overset{\cdot}{6} 2) \rangle\rangle_3 \tag{51a}$$

$$B \equiv \left\langle\left\langle \begin{array}{cccccc} 1 & 2, & 3 & 4, & 5 & 6 \\ 3 & 5, & 2 & 6, & 4 & 1 \end{array} \right\rangle\right\rangle = \langle\langle (1 \overset{\cdot}{3} 2 \overset{\cdot}{5} 4 \overset{\cdot}{6}) \rangle\rangle_3 \tag{51b}$$

and we write

$$A = \{\{6_{3,2}\}\}_3 \quad B = \{\{6_{3,3}\}\}_3. \tag{52}$$

Note that a lower link is attached to an index if the preceding index in the same cycle is larger and belongs to another 2-RDO. When applying this rule one should remember that the last index of a cycle precedes the first one.

In general, if \mathcal{P} belongs to a class $C^{(i)} = [c^{(1)}c^{(2)} \dots c^{(t)}]$ of S_{2n} composed of t cycles, we denote

$$\langle\langle \mathcal{P}_{kl}^{(i)} \rangle\rangle_j \equiv \langle\langle C_{k_1 l_1}^{(1)} C_{k_2 l_2}^{(2)} \dots C_{k_t l_t}^{(t)} \rangle\rangle_j \tag{53}$$

where $c_{k_m l_m}^{(m)}$ means that there are k_m upper links and l_m lower links in the cycle $c^{(m)}$. The indices k, l stand, respectively, for the sets $\{k_m\}_{m=1}^t$ and $\{l_m\}_{m=1}^t$. The index i identifies the class of S_{2n} and j denotes the number of integrals coupled by the permutation.

As results from equation (13)

$$\left\langle\left\langle \begin{matrix} 1\ 2, & 3\ 4, & \dots, & 2n-1\ 2n \\ \mathcal{P}[1\ 2, & 3\ 4, & \dots, & 2n-1\ 2n] \end{matrix} \right\rangle\right\rangle = \left\langle\left\langle \begin{matrix} 1\ 2, & 3\ 4, & \dots, & 2n-1\ 2n \\ \mathcal{P}^{-1}[1\ 2, & 3\ 4, & \dots, & 2n-1\ 2n] \end{matrix} \right\rangle\right\rangle \tag{54}$$

i.e. the interactions are invariant with respect to transposition of the upper and the lower row in the corresponding symbol. For example

$$\left\langle\left\langle \begin{matrix} 1\ 2, & 3\ 4, & 5\ 6 \\ 3\ 1, & 5\ 6, & 2\ 4 \end{matrix} \right\rangle\right\rangle = \left\langle\left\langle \begin{matrix} 3\ 1, & 5\ 6, & 2\ 4 \\ 1\ 2, & 3\ 4, & 5\ 6 \end{matrix} \right\rangle\right\rangle = \left\langle\left\langle \begin{matrix} 1\ 2, & 3\ 4, & 5\ 6 \\ 2\ 5, & 1\ 6, & 3\ 4 \end{matrix} \right\rangle\right\rangle. \tag{55}$$

This operation transforms all the upper links into the lower ones and vice versa. Hence

$$\langle\langle \mathcal{P}_{kl}^{(i)} \rangle\rangle_j = \langle\langle \mathcal{P}_{lk}^{(i)} \rangle\rangle_j. \tag{56}$$

If the permutation \mathcal{P} consists of several cycles and different groups of cycles affect different groups of integrals, then the same symmetry applies to each of groups of cycles. For example

$$\begin{aligned} \text{Tr}(\mathcal{J}\mathcal{K}^2) \text{Tr}(\mathcal{J}^2\mathcal{K}) &= \langle\langle (1\ 2\ 6\ 4\ 3)(7\ 12\ 9\ 8) \rangle\rangle_6 \\ &= \langle\langle (1\ 2\ 6\ 4\ 3)(7\ 8\ 9\ 12) \rangle\rangle_6 \\ &= \langle\langle (1\ 3\ 4\ 6\ 2)(7\ 12\ 9\ 8) \rangle\rangle_6 \\ &= \langle\langle (1\ 3\ 4\ 6\ 2)(7\ 8\ 9\ 12) \rangle\rangle_6. \end{aligned} \tag{57}$$

The symmetry of the interaction factors resulting from equation (13) and described by equations (54)–(57) is referred to as the *reflection symmetry*. In general, this symmetry does not hold for the propagation coefficients (cf equation (14)). The propagation coefficients for a given cycle structure of \mathcal{P} depend only on the number of the upper links in each cycle. Therefore we can easily combine with each interaction term the corresponding propagation coefficients. For example, the contribution to $\text{Tr}(H^3)$ due to the interaction term A (equations (51) and (52)) is proportional to $\langle\langle \{6_{32}\}\rangle\rangle_3 (\langle\langle 6_3 \rangle\rangle + \langle\langle 6_2 \rangle\rangle)$ the one due to B is $\langle\langle \{6_3\ 3\}\rangle\rangle_3 \langle\langle 6_3 \rangle\rangle$. In the case of the contribution to $\text{Tr}(H^6)$ due to $\text{Tr}(\mathcal{J}\mathcal{K}^2) \text{Tr}(\mathcal{J}^2\mathcal{K})$ we have (equation (57)) $\langle\langle \{5_{12}4_{12}\}\rangle\rangle_6 (\langle\langle 5_{14} \rangle\rangle + \langle\langle 5_{14_2} \rangle\rangle + \langle\langle 5_{24_1} \rangle\rangle + \langle\langle 5_{24_2} \rangle\rangle)$. In general, a contribution to $\text{Tr}(H^n)$ due to terms associated with $\langle\langle \mathcal{P}_{kl}^{(i)} \rangle\rangle_j$ may be written as $\langle\langle \mathcal{P}_{kl}^{(i)} \rangle\rangle_j \langle\langle \bar{\mathcal{P}}_{kl}^{(i)} \rangle\rangle$, where $\langle\langle \bar{\mathcal{P}}_{kl}^{(i)} \rangle\rangle$ stands for an appropriate sum of the propagation coefficients. The bar means that only those cycles which affect different groups of integrals are considered when forming the sum.

7. The final formulae for traces of H^n

Equation (36) may be rewritten in the following form

$$\text{Tr}(H^n) = \sum_j^n \sum_i^l \sum_{kl}' n_{kl,j}^{(i)} \langle\langle \mathcal{P}_{kl}^{(i)} \rangle\rangle_j \langle\langle \bar{\mathcal{P}}_{kl}^{(i)} \rangle\rangle \tag{58}$$

where the prime means that sum extends only over those sets of the upper and lower links which give non-equivalent interaction terms. The integers $n_{kl,j}^{(i)}$ are equal to the number of elements in the corresponding classes of equivalence of the interaction factors. They are referred to as the *weights* of the corresponding permutations. They fulfil several useful relations, as

$$\sum_{ijkl} v_{kl,j}^{(i)} n_{kl,j}^{(i)} = (2n)! \tag{59}$$

$$\sum_{jkl} v_{kl,j}^{(i)} n_{kl,j}^{(i)} = g^{(i)} \tag{60}$$

where $v_{kl,j}^{(i)}$ is equal to the number of terms in the sum $\langle\langle \bar{\mathcal{P}}_{kl}^{(i)} \rangle\rangle$ and $g^{(i)}$ is the number of permutations in the class $C^{(i)}$ of S_{2n} .

The value of $n_{kl,j}^{(i)}$ may be obtained just by counting how many permutations belonging to a given class of S_{2n} and coupling j integrals have a given distribution of the upper and lower links. The following procedure may simplify the counting:

(1) Let us denote $t_m, m = 1, 2, \dots, n$, any of two indices $2m - 1, 2m$.

(2) Let us list all sets of permutations with given i, j, k , and l and with all possible distributions of the symbols t_m . If, for example, we are concerned with the permutation belonging to class [5] of S_6 , coupling three integrals, and having one upper and two lower links, then five types of the sets of these permutations are possible: $(t_1 t_1 t_3 t_2 t_2)$, $(t_1 t_1 t_3 t_2 t_1)$, $(t_1 t_3 t_2 t_2 t_1)$, $(t_1 t_3 t_3 t_2 t_1)$, $(t_1 t_3 t_3 t_2 t_2)$.

(3) The number of permutations in each of those sets (dimensions of the sets) may be obtained using several simple rules:

- put the cycles in the descending order of their length and, if they are of the same length, in the lexical order of the indices;
 - to the first cycle assign an index $(3 - M)2^{m-1}$ where m is the number of different t_m in cycle and M is the number of times t_1 it appears in the cycle (i.e. either $M = 1$ or $M = 2$);
 - to the consecutive cycles assign indices $(3 - M')2^{m'-1}$ where M' is the total number of times the first element of the current cycle has appeared in the current and in the preceding cycles and m' is the number of t_m which appear in the current cycle for the first time (they are not present in the preceding cycles);
 - if there are two cycles of identical type (as e.g. $(t_1 t_2 t_3)(t_1 t_2 t_3)$), then the second cycle index is $1/2$.
 - the number of permutations in each set is equal to the product of all the cycle indices.
- (4) The value of $n_{kl,j}^{(i)}$ is equal to the sum of the dimensions of all the sets.

As an example, general expressions for $\text{Tr}(H^2)$ and $\text{Tr}(H^3)$ are given here. In the case of H^2 ,

$$\begin{aligned} \text{Tr}(H^2) = & \langle\{1_{00}\}\rangle_1 \langle\{1_0}\rangle + 2 \langle\{2_{00}\}\rangle_1 \langle\{2_0}\rangle + \langle\{2_{00}2_{00}\}\rangle_1 \langle\{2_02_0}\rangle \\ & + 2 \langle\{4_{22}\}\rangle_2 \langle\{4_2}\rangle + 2 \langle\{2_{11}2_{11}\}\rangle_2 \langle\{2_12_1}\rangle + 4 \langle\{2_{11}\}\rangle_2 \langle\{2_1}\rangle \\ & + 8 \langle\{3_{11}\}\rangle_2 \langle\{3_1}\rangle + 4 \langle\{4_{11}\}\rangle_2 \langle\{4_1}\rangle. \end{aligned} \tag{61}$$

The contributions with $j = 1$ vanish when calculating $M_2(H)$. The remaining five terms correspond, respectively, to $\sum_{pqrs}\{pq|rs\}\{qr|sp\}$, $\sum_{pqrs}\{pq|rs\}\{qp|sr\}$, $\text{Tr}(\mathcal{J}^2)$, $\text{Tr}(\mathcal{JK})$ and $\text{Tr}(\mathcal{K}^2)$. This result may be compared with equations (47) and (49) of the work by Karwowski and Bancewicz (1987).

For H^3 we omit the terms coupling less than three integrals and, for simplicity, skip the subscript '3' in the interactions terms. Then

$$\begin{aligned} \text{Tr}(\bar{H}^3) = & 8\langle\langle 3_{12} \rangle\rangle \langle\langle \bar{3}_{12} \rangle\rangle + 24\langle\langle 4_{22} \rangle\rangle \langle\langle \bar{4}_2 \rangle\rangle + 24\langle\langle 4_{12} \rangle\rangle \langle\langle \bar{4}_{12} \rangle\rangle \\ & + 24\langle\langle 2_{11}^2 \rangle\rangle \langle\langle \bar{2}_1^2 \rangle\rangle + 24\langle\langle 5_{12} \rangle\rangle \langle\langle \bar{5}_{12} \rangle\rangle + 48\langle\langle 5_{22} \rangle\rangle \langle\langle \bar{5}_2 \rangle\rangle \\ & + 24\langle\langle 5_{32} \rangle\rangle \langle\langle \bar{5}_{32} \rangle\rangle + 48\langle\langle 3_{11} 2_{11} \rangle\rangle \langle\langle \bar{3}_1 2_1 \rangle\rangle \\ & + 24\langle\langle 3_{21} 2_{11} \rangle\rangle \langle\langle \bar{3}_{21} 2_{11} \rangle\rangle + 8\langle\langle 6_{12} \rangle\rangle \langle\langle \bar{6}_{12} \rangle\rangle \\ & + 24\langle\langle 6_{22} \rangle\rangle \langle\langle \bar{6}_2 \rangle\rangle + 24\langle\langle 6_{32} \rangle\rangle \langle\langle \bar{6}_{32} \rangle\rangle + 24\langle\langle 6_{33} \rangle\rangle \langle\langle \bar{6}_3 \rangle\rangle \\ & + 4\langle\langle 6_{42} \rangle\rangle \langle\langle \bar{6}_{42} \rangle\rangle + 8\langle\langle 2_{11}^3 \rangle\rangle \langle\langle \bar{2}_1^3 \rangle\rangle \\ & + 24\langle\langle 4_{21} 2_{11} \rangle\rangle \langle\langle \bar{4}_{21} 2_{11} \rangle\rangle + 24\langle\langle 4_{22} 2_{11} \rangle\rangle \langle\langle \bar{4}_2 2_1 \rangle\rangle \\ & + 24\langle\langle 3_{11}^2 \rangle\rangle \langle\langle \bar{3}_1^2 \rangle\rangle + 8\langle\langle 3_{12} 3_{21} \rangle\rangle \langle\langle \bar{3}_1 3_2 \rangle\rangle \\ & + 4\langle\langle 3_{21}^2 \rangle\rangle \langle\langle \bar{3}_{21}^2 \rangle\rangle. \end{aligned} \tag{62}$$

In this case all the sums of the propagation coefficients associated with a given interaction factor contain two terms, since

$$\langle\langle \bar{m}_{kl} \rangle\rangle = \langle\langle m_k \rangle\rangle + \langle\langle m_l \rangle\rangle \tag{63}$$

and

$$\langle\langle \bar{m}_{kl}^2 \rangle\rangle = \langle\langle m_k^2 \rangle\rangle + \langle\langle m_l^2 \rangle\rangle. \tag{64}$$

An explicit derivation of expressions for higher powers of H is rather straightforward. However, one should remember that the number of different terms in these expressions grows very fast with n . Therefore using symbolic program languages like MATHEMATICA, REDUCE or MAPLE is most appropriate in these cases.

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Appendix 1. Generalized Wick theorem for traces of products of 2-RDOs

A trace of a product of n second-order density operators containing m upper links may be expressed as a linear combination of traces of the density operators of orders $2n, 2n - 1, \dots, 2n - m$. The combination consists of traces of all density operators which may be obtained by formally removing indices with the upper links in all possible ways. for example

$$\begin{aligned} \langle\langle {}^2E_{35}^{12} {}^2E_{25}^{34} {}^2E_{14}^{56} \rangle\rangle &\equiv \langle\langle (1 \dot{3} 2 \dot{5}) (4 \dot{6}) \rangle\rangle && (65) \\ &= \langle\langle (1 3 2 5)(4 6) \rangle\rangle_{6E} && (0 \text{ indices removed}) \\ &+ \langle\langle (1 2 5)(4 6) \rangle\rangle_{5E} + \langle\langle (1 3 2)(4 6) \rangle\rangle_{5E} + \langle\langle (1 3 2 5) \rangle\rangle_{5E} && (1 \text{ index removed}) \\ &+ \langle\langle (1 2 5) \rangle\rangle_{4E} + \langle\langle (1 3 2) \rangle\rangle_{4E} + \langle\langle (1 2)(4 6) \rangle\rangle_{4E} && (2 \text{ indices removed}) \\ &+ \langle\langle (1 2) \rangle\rangle_{3E}. && (3 \text{ indices removed}) \end{aligned}$$

In this example $\langle\langle P \rangle\rangle_{qE}$ means the trace of the q th-order reduced density operator.

The theorem may be obtained in a rather straightforward way from the generalized Wick theorem for products of the density operators (Kutzelnigg 1985, Planelles *et al* 1990).

Appendix 2. Proof of lemma 1

Lemma 1 says that for an arbitrary string Z of p indices

$$\sum_{Q \in S_r, C S_p} \langle\langle {}^P E_{Q(PZ)}^Z \rangle\rangle = 0 \tag{66}$$

if $P \in S_p$ and $r > 2$. According to equation (32) of Planelles *et al* (1990)

$$\langle\langle {}^P E_{Q(PZ)}^Z \rangle\rangle = \epsilon(PQ) \sum_S \chi^{\Gamma(S)}(PQ) \left\langle\left\langle \sum_{|M| \leq S} B_{Z,SM}^+ B_{Z,SM} \right\rangle\right\rangle \tag{67}$$

where $P, Q \in S_p, B_{Z,SM}^+$ is a spin-adapted creation operator of a p -particle state (for details see Planelles *et al* 1990, Planelles and Karwowski 1992). In equation (67) $\Gamma(S)$ is an irreducible representation of S_p corresponding to the spin- S , i.e. to a Young diagram with at most two rows.

From equation (67) we have that

$$\sum_{Q \in S_r, C S_p} \langle\langle {}^P E_{Q(PZ)}^Z \rangle\rangle = \sum_S \left\langle\left\langle \sum_{|M| \leq S} B_{Z,SM}^+ B_{Z,SM} \right\rangle\right\rangle \sum_{Q \in S_r} \chi^{\tilde{\Gamma}(S)}(PQ) \tag{68}$$

where $\tilde{\Gamma}(S)$ is a representation conjugate to $\Gamma(S)$, i.e. it corresponds to a Young diagram with at most two columns. Let us choose the basis for the representation $\tilde{\Gamma}(S)$ in such a way that for $Q \in S_r$ the corresponding representation matrices are direct sums of matrices corresponding to $S_r \subset S_p$ (Hamermesh 1964),

$$D^{\tilde{\Gamma}}(Q) = \bigoplus_{\gamma} n_{\gamma} D^{\gamma}(Q) \tag{69}$$

where γ is an irreducible representation of S_r and $n_\gamma = 0, 1, 2, \dots$ says how many times γ appears in $\bar{\Gamma}$. The sum over \mathcal{Q} in (68) may be expressed as

$$\sum_{\mathcal{Q} \in \mathcal{S}_r} \chi^{\bar{\Gamma}}(\mathcal{P}\mathcal{Q}) = \sum_{kl} D_{kl}^{\bar{\Gamma}}(\mathcal{P}) \sum_{\gamma} n_{\gamma} \sum_{\mathcal{Q} \in \mathcal{S}_r} D_{kl}^{\gamma}(\mathcal{Q}). \quad (70)$$

According to the orthogonality theorem

$$\sum_{\mathcal{Q} \in \mathcal{S}_r} D_{kl}^{\gamma}(\mathcal{Q}) = 0$$

if γ is any but the totally symmetric representation of S_r , i.e. if $n_1 \neq 0$. However if $\bar{\Gamma}$ corresponds to a Young diagram with at least three rows and if $r > 2$ then, as results from the rules of decomposition of representations of the symmetric group, $n_1 = 0$. Therefore

$$\sum_{\mathcal{Q} \in \mathcal{S}_r} \chi^{\bar{\Gamma}}(\mathcal{P}\mathcal{Q}) = 0 \quad (71)$$

which proves the lemma.

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