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Calculation of traces of Hamiltonian powers in finite-dimensional N-electron spin-adapted spaces: application to the determination of moments of spectral density distributions

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Abstract. Explicit formulae for the calculation of traces of N-order replacement operators in finite-dimensional, antisymmetric and spin-adapted N-electron Hilbert spaces are derived. These formulae are useful in the calculation of traces of Hamiltonian powers and provide an easier determination of moments of spectral density distributions according to the general procedure reported recently.

1. Introduction

Traces of products of pth-order replacement operators (p-RO) calculated in N-electron spin-adapted model spaces ($p \leqslant N$) are of importance in several areas of physics. These traces have been used in atomic spectroscopy to express moments of spectral density distributions which provide knowledge of the distribution function and consequently allow us to carry out simulations of spectra (Brody *et al* 1981, Bauche and Bauche-Arnoult 1990, Karwowski 1994). The propagation coefficients in the statistical theory of nuclear spectra are also calculated using similar types of traces (Brody *et al* 1981, Nomura 1988). Some computational approaches to many-electron theory (Diercksen *et al* 1990, Valdemoro *et al* 1992) have required an optimized evaluation of these expressions.

In a work by Torre *et al* (1993) the calculation of spin-adapted traces of p-ROs (that is the traces over the N-electron eigenfunctions of the $\hat{S}^2$ and $\hat{S}_z$ operators with determined quantum numbers S and S_z) has been carried out through a difference of S_z-adapted traces (that is the traces over the N-electron eigenfunctions of the $\hat{S}_z$ operator). This means that, in practice, the calculation of the spin-adapted traces is performed over Slater determinants. Using this procedure and expressing the N-electron Hamiltonian through the Nth-order spin-free replacement operators (N-ROs), general formulae have been found to evaluate the spin-adapted traces of any arbitrary power n of the Hamiltonian as a function of the S_z-adapted traces of the N-ROs (Torre and Lain 1995). In that reference, a technique to determine the S_z-adapted traces of the N-ROs has been described; this simplifies the calculation of the moments of the spectral density distributions of a set of Hamiltonian eigenvalues (Karwowski and Bancewicz 1987, Rajadell *et al* 1993).

This paper goes beyond showing the derivation of a general formula which calculates the S_z-adapted traces of any N-RO as a function of simple parameters which characterize the N-RO. Since these parameters can be determined systematically, our formulae provide

the means to construct a simple and general program for the calculation of the moments of spectral density distributions; only the standard integrals, the number of electrons N and the spin S are needed as data.

In section two we summarize the notation, main concepts and references. Section three describes the final formula for the calculation of S_z-adapted traces of N-ROs. Finally, the appendix shows some practical examples corresponding to the structure of the N-ROs.

2. The S_z-adapted traces of N-order replacement operators

Let us consider the N-electron Hamiltonian $\hat{H}$ which is represented in a finite-dimensional antisymmetric and spin-adapted Hilbert space. This model space is spanned by the N-electron antisymmetrized and spin-adapted products of orthonormal spin-orbitals and is known as the full configuration interaction (FCI) space. Choosing the origin of the energy scale so that $\bar{E} = 0$ (the first moment), the nth-order moment $M_n(\hat{H})$ of the Hamiltonian eigenvalue spectrum in that space is defined as

$$M_n(\hat{H}) = \frac{1}{D(N,S,K)} \operatorname{Tr}(\hat{H}^n) \tag{1}$$

where $D(N,S,K)$ is the Weyl–Paldus formula (Paldus 1974) defined as

$$D(N,S,K) = \frac{2S+1}{K+1} \begin{pmatrix} K+1 \\ \frac{1}{2}N - S \end{pmatrix} \begin{pmatrix} K+1 \\ \frac{1}{2}N + S + 1 \end{pmatrix} \tag{2}$$

that is, the dimension of the FCI space for N electrons, a spin S, any possible fixed value of the quantum number S_z and K one-electron orbital functions of an orthonormal basis set (Paldus 1976).

In the N-electron space, the spin-free N-electron Hamiltonian $\hat{H}$ can be expressed in the form (Torre *et al* 1991)

$$\hat{H} = \frac{1}{N!} \sum_{\substack{(i_1 \ldots i_N) \\ (j_1 \ldots j_N)}}^{N} H_{j_1 \ldots j_N}^{i_1 \ldots i_N N} E_{j_1 \ldots j_N}^{i_1 \ldots i_N} \tag{3}$$

where

$${}^N H_{j_1 \ldots j_N}^{i_1 \ldots i_N} = \sum_{k<l} {}^2H^{i_k i_l}{}_{j_k j_l} \delta_{j_1 \ldots j_{(k-1)}}^{i_1 \ldots i_{(k-1)}} \delta_{j_{(k+1)} \ldots j_{(l-1)}}^{i_{(k+1)} \ldots i_{(l-1)}} \delta_{j_{(l+1)} \ldots j_N}^{i_{(l+1)} \ldots i_N} \tag{4}$$

$\delta_{j_1 \ldots j_s}^{i_1 \ldots i_s}$ are the product of the Kronecker deltas

$$\delta_{j_1 \ldots j_s}^{i_1 \ldots i_s} = \delta_{i_1 j_1} \ldots \delta_{i_s j_s} \tag{5}$$

${}^2H_{jl}^{ik}$ are the generalized two-electron integrals (Valdemoro 1992)

$${}^2H_{jl}^{ik} = (ij|kl) + \frac{1}{N-1}(\delta_{kl}\epsilon_{ij} + \delta_{ij}\epsilon_{kl}) \tag{6}$$

and $(ij|kl)$ and ϵ_{ij} are the standard two-electron (in the Mulliken convention) and one-electron integrals respectively.

${}^N E_{j_1 \ldots j_N}^{i_1 \ldots i_N}$ are the Nth-order spin-free replacement operators (N-ROs) (Kutzelnigg 1985, Paldus and Jeziorski 1988)

$${}^N E_{j_1 \ldots j_N}^{i_1 \ldots i_N} = \sum_{\sigma_1} \cdots \sum_{\sigma_N} b_{i_1\sigma_1}^{+} \ldots b_{i_N\sigma_N}^{+} b_{j_N\sigma_N} \ldots b_{j_1\sigma_1} \tag{7}$$

where $b^{+}_{i_k\sigma_k}$ and $b_{j_k\sigma_k}$ are the usual creation and annihilation fermion operators respectively, $\sigma_1, \ldots, \sigma_N$ are the spin coordinates and $i_1, \ldots, i_N$, $j_1, \ldots, j_N$ ... are the K one-electron orbital functions of the orthonormal basis set.

If $\Lambda, \Omega, \ldots$ are the N-electron functions and eigenfunctions of the operators $\hat{S}^2$ and $\hat{S}_z$ corresponding to the spin quantum numbers S and S_z that can be constructed with K orbital functions, then the spin-adapted trace of the nth power of the Hamiltonian operator is given by (Torre and Lain 1995)

$$\begin{aligned}\mathrm{Tr}(\hat{H}^n) = \frac{1}{(N!)^n} \sum_{\{i^1\}} \sum_{\{j^1\}} \cdots \sum_{\{i^n\}} \sum_{\{j^n\}}^{N} H^{i_1^1 \ldots i_N^1}_{j_1^1 \ldots j_N^1} \cdots {}^{N}H^{i_1^n \ldots i_N^n}_{j_1^n \ldots j_N^n} \\ \times \sum_{P_1 \in S_N} \cdots \sum_{P_{(n-1)} \in S_N} \sum_{\Lambda} \langle \Lambda |^N E^{i_1^1 \ldots i_N^1}_{P_{(n-1)}(j_1^n \ldots j_N^n)} | \Lambda \rangle_{N,S,K} \delta^{j_1^1 \ldots j_N^1}_{P_1(i_1^2 \ldots i_N^2)} \delta^{P_1(j_1^2 \ldots j_N^2)}_{P_2(i_1^3 \ldots i_N^3)} \\ \ldots \delta^{P_{(n-2)}(j_1^{(n-1)} \ldots j_N^{(n-1)})}_{P_{(n-1)}(i_1^n \ldots i_N^n)}\end{aligned} \tag{8}$$

where the shorthand notation $\sum_{\{i^1\}} \equiv \sum_{(i_1^1, \ldots, i_N^1)}$ etc has been used. $P_1(i_1^2 \ldots i_N^2)$ is a permutation of the set $(i_1^2 \ldots i_N^2)$, belonging to the symmetric group S_N and $P_{n-1}(j_1^n \ldots j_N^n)$ is the same concept referred to the indices $(j_1^n \ldots j_N^n)$.

In this way, the traces of the operator $\hat{H}^n$ are calculated using the expressions $\sum_{\Lambda} \langle \Lambda |^N E^{i_1 \ldots i_N}_{j_1 \ldots j_N} | \Lambda \rangle_{N,S,K}$, which are the spin-adapted traces of the N-ROs ${}^{N}E^{i_1 \ldots i_N}_{j_1 \ldots j_N}$. These traces vanish unless the sets $(i_1 \ldots i_N)$ and $(j_1 \ldots j_N)$ are composed by identical orbital functions and, for a given spin S, their numerical values are independent of the quantum number S_z (Lain *et al* 1988). An optimized calculation of $\sum_{\Lambda} \langle \Lambda |^N E^{i_1 \ldots i_N}_{j_1 \ldots j_N} | \Lambda \rangle_{N,S,K}$ is carried out using the formula (Torre *et al* 1993)

$$\begin{aligned}\sum_{\Lambda} \langle \Lambda |^N E^{i_1 \ldots i_N}_{j_1 \ldots j_N} | \Lambda \rangle_{N,S,K} = \sum_{\mathcal{SD}(S)} \langle \mathcal{SD}(S) |^N E^{i_1 \ldots i_N}_{j_1 \ldots j_N} | \mathcal{SD}(S) \rangle \\ - \sum_{\mathcal{SD}(S+1)} \langle \mathcal{SD}(S+1) |^N E^{i_1 \ldots i_N}_{j_1 \ldots j_N} | \mathcal{SD}(S+1) \rangle\end{aligned} \tag{9}$$

where $\mathcal{SD}(S)$ denotes the N-electron Slater determinants that can be constructed with a basis set of K orbital functions, having the biggest eigenvalue $S_z = S$ of the $\hat{S}_z$ operator for a determined spin quantum number S, that is, having $N_\alpha = \frac{1}{2}N + S$ α-electrons and $N_\beta = \frac{1}{2}N - S$ β-electrons. This means that the spin-adapted trace of the N-ROs can be evaluated through a difference of S_z-adapted traces of those operators.

According to the above equations, the use of N-ROs provides explicit and general formulae to evaluate the trace of any power of the Hamiltonian (equation (8)) and the nth-order moment of a Hamiltonian eigenvalue distribution (equation (1)) which is worthy of statistical studies. The N-electron matrix elements which are involved in equation (8) are calculated using a function corresponding to formula (4) so that only the two-electron matrix must be stored in computing programs. The calculation requires the determination of spin-adapted traces of N-ROs which is carried out in terms of the S_z-adapted ones (equation (9)). Although a technique to evaluate these traces has been described (Torre and Lain 1995), in the next section explicit formulae for the calculation of S_z-adapted traces of an N-RO for any value of the S_z quantum number are derived. These formulae provide a straightforward calculation of the traces of Hamiltonian powers and moments through algorithms which can easily be programmed.

3. The explicit calculation of S_z-adapted traces of N-ROs

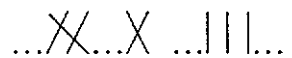
The aim of this section is the derivation of a mathematical formula which can be used in computer evaluations of S_z-adapted traces of N-ROs, that is, in the calculation of

$$\sum_{\mathcal{SD}(S)} \langle \mathcal{SD}(S)|^N E^{i_1 \dots i_N}_{j_1 \dots j_N} |\mathcal{SD}(S)\rangle \tag{10}$$

where it is assumed that the sets $(i_1 \dots i_N)$ and $(j_1 \dots j_N)$ are composed by identical orbitals (otherwise the value of the trace is zero).

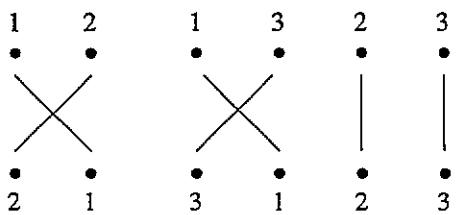
The Slater determinants $\mathcal{SD}(S)$ in the sum $\sum_{\mathcal{SD}(S)}$ are composed by $N_\alpha = \frac{1}{2}N + S$ α-spin orbitals and $N_\beta = \frac{1}{2}N - S$ β-spin orbitals. Hence, the problem we need to solve is the calculation of the number of terms derived from the expansion of the N-RO (given in equation (7)), which have the same spin-orbitals in the creation operators, the annihilation operators, and the Slater determinants of the sum $\sum_{\mathcal{SD}(S)}$. The number of these types of terms depends on the structure of the N-RO; each of the terms contribute to the trace (10) as $(-1)^\nu$, where ν is the number of transpositions required to pass from the ordered set $(i_1 \dots i_N)$ to the set $(j_1 \dots j_N)$.

According to equation (7), the indices occupying the same position in the creation and annihilation sets of the N-RO have the same spin-coordinate. Identical indices occupying the same position in the sets $\{i\}$ and $\{j\}$ will be called diagonal indices: they constitute the diagonal part of the N-RO. Similarly, in the N-RO it is possible to distinguish one or more blocks constituted by subsets of creation indices $(i_k \dots i_l)$ and annihilation indices $(j_k \dots j_l)$ containing identical orbitals (although in different positions) so that all the elements in a block must have, in the expansion of the N-RO, the same spin-coordinate (α or β). Blocks and diagonal indices allow us to represent the N-ROs through graphs of the type



where the lines join identical indices.

When there is no repetition of indices in the creation set (or in the annihilation set), the N-RO is represented by only one graph. The repetition of indices in the sets $\{i\}$ and $\{j\}$ produces different possibilities of how to divide the N-RO into blocks of indices with the same spin. Each of these possibilities corresponds to some terms of the N-RO expansion and will be represented by a graph. Since the indices of the N-RO refer to fermion operators, each index in the creation (or annihilation) set can be repeated only once. Consequently, an N-RO with q non-diagonal repeated indices will have 2^q different graphs due to there being 2^q ways to relate q pairs of creation indices to q pairs of annihilation indices. However, the graphs with repeated indices in the same block must be ignored because of the Pauli principle. In the same sense, it is possible to have graphs with repetition of indices between different blocks, between a block and the diagonal indices and between diagonal indices themselves, but repeated indices cannot belong to the same block. In order to clarify these aspects we will consider, as an example, the 6-RO ${}^6E^{121323}_{213123}$, where $1, 2, 3 \dots$ indicate different orbital functions. This RO has the graphs



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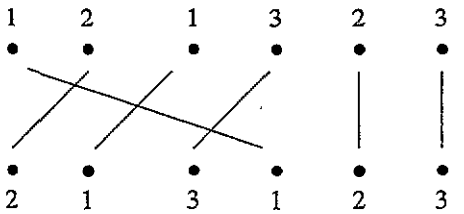

where, obviously, the last one must be neglected due to it having two identical indices in the same block.

Referring to a determined graph in what follows, the blocks, the diagonal indices and the relationships among them will be characterized by several parameters which we will define as follows:

b_i, the number of creation (or annihilation) indices in the block i;

r_{id}, the number of common indices between the block i and the diagonal part of the N-RO;

r_d, the number of repeated indices in the diagonal part of the N-RO;

$x_i = 1$, when the spin-coordinate of the block i is β;

$x_i = 0$, when the spin-coordinate of the block i is α;

$c_j^i = 1$, for the blocks i and j when $i \cap j \neq \emptyset$ and $c_j^i = 0$ otherwise;

m, the number of blocks in the graph;

ν, the number of transpositions required to pass from the ordered set $(i_1 \ldots i_N)$ to the set $(j_1 \ldots j_N)$.

The terms in the expansion of the N-RO that contain the same spin-orbitals as the Slater determinants of the sum $\sum_{\mathcal{SD}(S)}$ will be obtained by appropriate assignations of α- and β-spin to the different blocks and diagonal indices of each graph. The number of indices which have no restriction on their distribution in the α or β part of the terms of the N-RO expansion is

$$N - \sum_i (b_i + r_{id}) - 2r_d \tag{11}$$

and the number of indices that have a determined spin (α or β) assigned is

$$\sum_i [x_i b_i + (1 - x_i) r_{id}] - r_d \tag{12}$$

where the factors x_i and $(1 - x_i)$ exclude the contribution when a block and a diagonal index which also appear in that block have the same spin-coordinate.

Consequently, the number of places in the β part of the terms of the N-RO expansion to be occupied by the indices given by expression (11) is

$$\tfrac{1}{2}N - S - \sum_i [x_i b_i + (1 - x_i) r_{id}] - r_d. \tag{13}$$

A similar expression can be obtained for the α part: $\frac{1}{2}N + S - \sum_i [x_i b_i + (1 - x_i) r_{id}] - r_d$. Hence, the number of possibilities for distributing the indices expressed by formula (11) over the available places (expression (13)), without violating the Pauli principle, is described by the binomial coefficient

$$\begin{pmatrix} N - \sum_i (b_i + r_{id}) - 2r_d \\ \frac{1}{2}N - S - \sum_i [x_i b_i + (1 - x_i) r_{id}] - r_d \end{pmatrix}. \tag{14}$$

The sum for all the possible values of the parameters x_i calculates the contribution of a graph to the value of the trace given by formula (10), that is

$$(-1)^{\nu}2^{r_d}\sum_{x_1}\cdots\sum_{x_m}\prod_{i<j}(1-\delta_{x_j}^{x_i}c_j^i)\begin{pmatrix} N-\sum_i(b_i+r_{id})-2r_d \\ \frac{1}{2}N-S-\sum_i[x_ib_i+(1-x_i)r_{id}]-r_d \end{pmatrix} \tag{15}$$

where the factors $\prod_{i<j}(1-\delta_{x_j}^{x_i}c_j^i)$ have been included to avoid binomial coefficients containing blocks with common indices and the same spin. The factor 2^{r_d} arises from the two possible spin-coordinates (α or β) which can be assigned to the r_d repeated indices in the diagonal part.

In conclusion, the possible graphs for an N-RO and their corresponding parameters $b_i, c_j^i, r_{id}, r_d, \nu, m$ can be easily calculated using a simple computer program. The use of formulae (15) and (9) leads to a straightforward evaluation of the spin-adapted traces of the N-RO which depend on the number of electrons N, the spin S and the structure of the operator. These tools provide a suitable calculation of traces of Hamiltonian powers and moments of spectral density distributions which can be carried out by a computer program that only needs the parameters N, S and the integrals corresponding to the K orbital functions of the basis set.

Some examples of the calculation of S_z-adapted traces of N-ROs corresponding to their structure are given in the appendix.

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Appendix. Examples

(i) Let us consider as a first example the calculation of S_z-adapted traces of the operator ${}^8E^{12231434}_{21324134}$. This operator has $q = 2$ non-diagonal repeated indices, so that it has $2^2 = 4$ graphs which can be described as

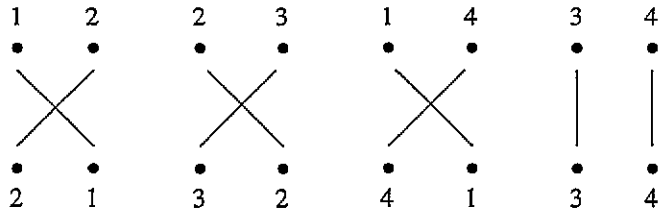
(a) block 1 $i_1 = j_2 = 1i_2 = j_1 = 2$; block 2 $i_3 = j_4 = 2i_4 = j_3 = 3$; block 3 $i_5 = j_6 = 1i_6 = j_5 = 4$; diagonal indices $i_7 = j_7 = 3$ and $i_8 = j_8 = 4$.

(b) block 1 $i_1 = j_6 = 1i_2 = j_1 = 2i_5 = j_2 = 1i_6 = j_5 = 4$; block 2 $i_3 = j_4 = 2i_4 = j_3 = 3$; diagonal indices $i_7 = j_7 = 3$ and $i_8 = j_8 = 4$.

(c) block 1 $i_1 = j_2 = 1i_2 = j_4 = 2i_3 = j_1 = 2i_4 = j_3 = 3$; block 2 $i_5 = j_6 = 1i_6 = j_5 = 4$; diagonal indices $i_7 = j_7 = 3$ and $i_8 = j_8 = 4$.

(d) block 1 $i_1 = j_6 = 1i_2 = j_4 = 2i_3 = j_1 = 2i_4 = j_3 = 3i_5 = j_2 = 1i_6 = j_5 = 4$; diagonal indices $i_7 = j_7 = 3$ and $i_8 = j_8 = 4$.

Starting with graph (a), that is



its corresponding parameters are $m = 3, b_1 = 2, b_2 = 2, b_3 = 2, c_2^1 = 1, c_3^1 = 1, c_3^2 = 0, r_{1d} = 0, r_{2d} = 1, r_{3d} = 1, r_d = 0, \nu = 3$. The application of formula (15) for the case of $S_z = 0$, that is, when $\frac{1}{2}N - S = 4$, leads to the value -2. The contributions of graphs (b), (c) and (d) are zero due to the fact that they all have repetition of indices in a block. Hence, for the operator ${}^8E^{12231434}_{21324134}$, the value of trace (10) for $S_z = 0$ is -2

(ii) As a second example we consider the operator ${}^5E^{12132}_{21213}$. *Again, the number of* non-diagonal repeated indices is two so that it has four graphs which are defined by

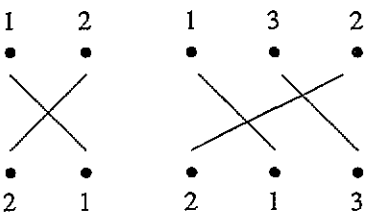
(a) block 1 $i_1 = j_2 = 1i_2 = j_1 = 2$; block 2 $i_3 = j_4 = 1i_4 = j_5 = 3i_5 = j_3 = 2$.

(b) block 1 $i_1 = j_2 = 1i_2 = j_3 = 2i_3 = j_4 = 1i_4 = j_5 = 3i_5 = j_1 = 2$.

(c) block 1 $i_1 = j_4 = 1i_2 = j_1 = 2i_3 = j_2 = 1i_4 = j_5 = 3i_5 = j_3 = 2$.

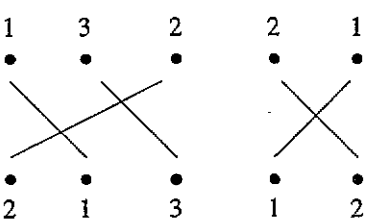
(d) block 1 $i_1 = j_4 = 1i_4 = j_5 = 3i_5 = j_1 = 2$; block 2 $i_2 = j_3 = 2i_3 = j_2 = 1$.

Since the graphs (b) and (c) have one block with repetition of indices, only the graphs (a) and (d) must be considered. Graph (a) is



and its parameters are $m = 2, b_1 = 2, b_2 = 3, c_2^1 = 1, r_{1d} = 0, r_{2d} = 0, r_d = 0, \nu = 3$, which for the case of $S_z = \frac{1}{2}$ (that is, $\frac{1}{2}N - S = 2$) give a value of -1 for formula (15).

Due to the fermion operator properties ${}^5E^{12132}_{21213} \equiv {}^5E^{13221}_{21312}$ so that graph (d) can be represented by



which has the same parameters and the same value from formula (15) as graph (a). Hence, for the operator ${}^5E^{12132}_{21213}$ the value of trace (10) for $S_z = \frac{1}{2}$ is -2.

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