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adapted spaces

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Abstract. This paper reports a calculation of moments of spectral density distributions which are used in statistical theory of spectra of many-electron systems. The procedure lead to formulae which are fit for computer evaluations. The method is based on the determination of spin-adapted traces of powers of the Hamiltonian operator, represented in a finite-dimensional antisymmetric and spin-adapted Hilbert space. A whole study of the traces which appear in this problem is described.

1. Introduction

In dealing with the study of discrete spectra of N-particle systems, the statistical method has proved to be a powerful tool. The determination of individual energy values is difficult in many experimental studies or it requires great effort in precise quantum mechanical calculations. Alternatively, general characteristics of the discrete spectra can be derived in the treatment which is known as statistical spectroscopy (Brody *et al* 1981, French and Kota 1982). The statistical techniques were first used in the analysis of nuclear spectra (Porter 1965, Nomura 1972, Nomura 1974). However they have been also applied to the description of spectra of N-electron systems, being particularly useful in situations where the number of levels is very large (Cowan 1981). Classical examples of application of the statistical approach are the studies of the emission spectra of highly ionized atoms, which appear in plasmas and astrophysics, where usually the lines corresponding to the transitions between the levels of two configurations are not well resolved (Bauche-Arnoult *et al* 1984, Bancewiz and Karwowski 1991, Bauche and Bauche-Arnoult 1990).

The statistical study of spectra is based on the treatment of the set of the eigenvalues of the Hamiltonian as a statistical ensemble. Hence, all the properties of the system can be derived from an appropriate knowledge of the distribution function. Two strategies may be applied to approximate the distribution function. Either its shape is assumed to depend on several parameters, which necessitates checking that asumption or, alternatively, the distribution function is expressed through a Gram–Charlier expansion (Bauche and Bauche-Arnoult 1990). In the latter case, calculation of the moments of the spectral density distribution to a determined order n is needed.

In the description of N-electron systems, the Hamiltonian is usually represented in a finite-dimensional, antisymmetric and spin-adapted Hilbert space which is also known as full configuration interaction (FCI) space (Paldus 1976). Hence, in statistical treatments of the N-electron systems, the calculation of the moments of spectral density distributions (basic tools in that approach) requires the evaluation of traces of powers of the N-electron

Hamiltonian (Cowan 1981, Bauche and Bauche-Arnoult 1990, Karwowski and Bancewicz 1987). This calculation of moments is useful not only to describe spectra. As they are invariants of unitary transformations of the basis in the model space, they characterize the space rather than a determined representation. This property has been applied to the location of errors in Hamiltonian matrices in CI programs (Diercksen *et al* 1990).

This paper approaches the problem of the determination of moments of spectral density distributions, in the FCI space, providing a simple procedure for the calculation of spin-adapted traces of powers of the Hamiltonian operator. An explicit formula for the moment of any order n of a spectral density distribution is obtained, which is worthwhile from a mathematical point of view as well as for computational purposes. The evaluation of that formula is based on the method described recently (Torre *et al* 1993) for calculating spin-adapted traces of spin-free p-order replacement operators (p-RO) ($p \leqslant N$) (Kutzelnigg 1985, Paldus and Jeziorski 1988).

The paper has been organized as follows. Section 2 describes the basic concepts which relate the nth order moment of a spectral density distribution to the spin-adapted traces of products of n 2-ROs. Section 3 reports one alternative approach. It shows that only spin-adapted traces of N-ROs are really needed for the calculation of traces of any power of an N-electron Hamiltonian. The explicit formulae for the $\hat{H}^2$ case are given in this section which is enlarged in the appendix with the formulae for the $\hat{H}^3$, $\hat{H}^4$ and $\hat{H}^n$ operators. Finally, section 4 presents a study of the spin-adapted traces of N-ROs which appear in this problem. Some examples to explain the calculation of this type of traces are included in this section.

2. Moments of spectral density distributions

The spin-free non-relativistic N-electron Hamiltonian, in second quantization, is written as

$$\hat{H} = \frac{1}{2} \sum_{i,j,k,l} {}^2H_{jl}^{ik} \, {}^2E_{jl}^{ik} \tag{1}$$

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

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

$(ij|kl)$ are the standard two-electron integrals following the Mulliken convention and ϵ_{ij} are the one-electron integrals. ${}^2E_{jl}^{ik}$ are the second-order, spin-free replacement operators (2-RO) whose p-order version is (Kutzelnigg 1985, Paldus and Jeziorski 1988)

$$ {}^pE_{j_1\cdots j_p}^{i_1\cdots i_p} = \sum_{\sigma_1} \cdots \sum_{\sigma_p} b_{i_1\sigma_1}^+ \cdots b_{i_p\sigma_p}^+ b_{j_p\sigma_p} \cdots b_{j_1\sigma_1} \tag{3}$$

and where $b_{i_k\sigma_k}^+/b_{j_k\sigma_k}$ are the usual creation/annihilation fermion operators; $\sigma_1, \ldots, \sigma_p$ are the spin coordinates and $i_1, \ldots, i_p, j_1, \ldots, j_p \ldots$ are the K orbital functions of an orthonormal basis set.

Usually the Hamiltonian $\hat{H}$ is projected onto a model space which is an antisymmetric and spin-adapted subspace $H^A(N, K, S, S_z)$ of a finite-dimensional Hilbert space. The subspace $H^A(N, K, S, S_z)$ is defined as the antisymmetric and spin-adapted part of the N-fold tensorial product of a one-electron space

$$ H^A(N, K, S, S_z) = (V_{2K}^{\otimes N})_{S,S_z}^A \tag{4}$$

where A stands for antisymmetric and S and S_z refer to the standard spin quantum numbers. The one-electron space V_{2K} is spanned by a set of $2K$ spin-orbitals and is a product of the K-dimensional orbital space

$$V_K = \{\Phi_k\}_{k=1}^K \tag{5}$$

spanned by a set of K orthonormal orbitals and the two-dimensional spin space. The $H^A(N, K, S, S_z)$ subspace is also known as the full configuration interaction (FCI) space (Paldus 1976).

The dimension of the $H^A(N, K, S, S_z)$ subspace, $D(N, S, K)$, is given by the well known Weyl–Paldus formula (Paldus 1974)

$$D(N, S, K) = \frac{2S+1}{K+1} \left(\begin{array}{c} K+1 \\ \frac{N}{2} - S \end{array} \right) \left(\begin{array}{c} K+1 \\ \frac{N}{2} + S + 1 \end{array} \right) \tag{6}$$

where, obviously, the H^A subspace refers to a fixed value of the S_z quantum number, although its dimension is identical for all the S_z values corresponding to a determined S.

An analysis of equation (6) shows a very fast growth of the dimension of the FCI space with N. Since *ab initio* calculations need to use $K > 2N$ one-electron funtions in order to get an appropriate accuracy, the diagonalization of the FCI matrix becomes intractable except for systems with very few electrons. Hence, the altenative procedure to describe the FCI spectrum is the statistical treatment, which requires the calculation of moments of the spectral density distribution. Fortunately, in most situations only the lowest-order moments are needed (Bauche and Bauche-Arnoult 1990).

Choosing the origin of the energy scale so that $\bar{E} = 0$ (the first moment), the nth order moment of the spectral density distribution, $M_n(\hat{H})$, is defined as

$$M_n(\hat{H}) = \frac{1}{D} \operatorname{Tr}(\hat{H}^n) \tag{7}$$

where

$$\operatorname{Tr}(\hat{H}^n) = \sum_\Lambda \langle \Lambda | \hat{H}^n | \Lambda \rangle \tag{8}$$

and $\Lambda, \ldots$ are the basis functions of the FCI space, that is, the N-electron functions, eigenfunctions of the $(\hat{S}^2, \hat{S}_z)$ operators, corresponding to the spin quantum numbers S and S_z, which can be constructed with the K orbital functions of the basis set employed.

Consequently, according to equation (1) the expression for the nth order moment is

$$M_n(\hat{H}) = \frac{1}{D\, 2^n} \sum_{\{i\}} \sum_{\{j\}} \sum_{\{k\}} \sum_{\{l\}} {}^2H_{j_1l_1}^{i_1k_1} \ldots {}^2H_{j_nl_n}^{i_nk_n} \sum_\Lambda \langle \Lambda | {}^2E_{j_1l_1}^{i_1k_1} \ldots {}^2E_{j_nl_n}^{i_nk_n} | \Lambda \rangle \tag{9}$$

where we have adopted the shorthand notation $\sum_{\{i\}} \equiv \sum_{(i_1, \ldots, i_n)}$.

Equation (9) allows the calculation of the nth order moment, $M_n(\hat{H})$, through the generalized two-electron integrals and the spin-adapted trace of the product of n spin-free 2-ROs, $\sum_\Lambda \langle \Lambda | {}^2E_{j_1l_1}^{i_1k_1} \ldots {}^2E_{j_nl_n}^{i_nk_n} | \Lambda \rangle$, which is also referred in the literature as propagation coefficient (Brody *et al* 1981, Rajadell *et al* 1993)

3. The traces of the Hamiltonian powers

A direct evaluation of the spin-adapted trace of the product of n 2-ROs, in equation (9), is a cumbersome task. In fact, the first step in this calculation is to carry out the product of two 2-ROs (Planelles *et al* 1990, Valdemoro *et al* 1992). Then each term of this result must be multiplied by the third operator ${}^2E_{j_3l_3}^{i_3k_3}$, giving higher order ROs, etc., so that a lot of ROs

of different orders are obtained. Finally, the traces of all the resulting operators must be evaluated.

Some treatments of those products of n 2-RO, in the calculation of traces of powers of the Hamiltonian, has been reported (Rajadell *et al* 1993). However, a simpler and more systematic formulation of the problem can be got when the equation (1) is expressed in the N-electron space. The N-electron Hamiltonian operator can also be written as (Torre *et al* 1991)

$$\hat{H} = \frac{1}{N!} \sum_{(i_1\ldots i_N),(j_1\ldots j_N)} {}^N H^{i_1\ldots i_N}_{j_1\ldots j_N} \, {}^N E^{i_1\ldots i_N}_{j_1\ldots j_N} \tag{10}$$

where

$$ {}^N H^{i_1\ldots i_N}_{j_1\ldots j_N} = \sum_{k<l} {}^2 H^{i_k i_l}_{j_k j_l} \, \delta^{i_1\ldots i_{(k-1)}}_{j_1\ldots j_{(k-1)}} \, \delta^{i_{(k+1)}\ldots i_{(l-1)}}_{j_{(k+1)}\ldots j_{(l-1)}} \, \delta^{i_{(l+1)}\ldots i_N}_{j_{(l+1)}\ldots j_N} \tag{11}$$

and $\delta^{i_1\ldots i_p}_{j_1\ldots j_p}$ are the product of the Kronecker deltas

$$\delta^{i_1\ldots i_p}_{j_1\ldots j_p} = \delta_{i_1 j_1} \cdots \delta_{i_p j_p} \tag{12}$$

Hence, the elements of the N-electron Hamiltonian matrix ${}^N H^{i_1\ldots i_N}_{j_1\ldots j_N}$ are easily calculated through the sum of a few generalized two-electron integrals ${}^2 H^{i_k i_l}_{j_k j_l}$. It means, in computational terms, that the N-electron matrix does not need to be stored.

Using that formulation, the trace of the $\hat{H}^2$ operator, which is related to the variance, is

$$\text{Tr}(\hat{H}^2) = \frac{1}{(N!)^2} \sum_{\{i\}} \sum_{\{j\}} \sum_{\{k\}} \sum_{\{l\}} {}^N H^{i_1\ldots i_N}_{j_1\ldots j_N} \, {}^N H^{k_1\ldots k_N}_{l_1\ldots l_N} \sum_{\Lambda} \langle \Lambda | {}^N E^{i_1\ldots i_N}_{j_1\ldots j_N} \, {}^N E^{k_1\ldots k_N}_{l_1\ldots l_N} |\Lambda\rangle \tag{13}$$

where the evaluation of the trace $\sum_{\Lambda} \langle \Lambda | {}^N E^{i_1\ldots i_N}_{j_1\ldots j_N} \, {}^N E^{k_1\ldots k_N}_{l_1\ldots l_N} |\Lambda\rangle$ would require one to carry out the product of the operators ${}^N E^{i_1\ldots i_N}_{j_1\ldots j_N} \cdot {}^N E^{k_1\ldots k_N}_{l_1\ldots l_N}$, which produces a sum of a large number of ROs of orders between N and $2N$ (Valdemoro *et al* 1992).

However, those operators are applied to the N-electron functions $|\Lambda\rangle$. Consequently, the orders higher than N can be ignored and so only the N-RO must be taken into account. Straightforward application of the rules of the product of spin-free ROs (Valdemoro *et al* 1992) now leads to the trace

$$\sum_{\Lambda} \langle \Lambda | {}^N E^{i_1\ldots i_N}_{j_1\ldots j_N} \, {}^N E^{k_1\ldots k_N}_{l_1\ldots l_N} |\Lambda\rangle = \sum_{P \in S_N} \sum_{\Lambda} \langle \Lambda | {}^N E^{i_1\ldots i_N}_{P(l_1\ldots l_N)} |\Lambda\rangle \, \delta^{j_1\ldots j_N}_{P(k_1\ldots k_N)} \tag{14}$$

where $P(k_1\ldots k_N)$ means a permutation of the set $(k_1\ldots k_N)$, belonging to the symmetric group S_N and $P(l_1\ldots l_N)$ is the same permutation referred to the indices $\{l\}$.

Due to the Kronecker deltas, the sets $(j_1\ldots j_N)$ and $(k_1\ldots k_N)$ must be constituted by the same functions and so when the set $(j_1\ldots j_N)$ has no repetition of indices, the right hand side of the equation (14) is reduced to the unique term $\sum_{\Lambda} \langle \Lambda | {}^N E^{i_1\ldots i_N}_{l_a\ldots l_b} |\Lambda\rangle \, \delta^{j_1\ldots j_N}_{k_a\ldots k_b}$, where the indices a and b mean the position in the set $(k_1\ldots k_N)$ which fulfill $j_1 = k_a$ and $j_N = k_b$ and similarly for the intermediate cases $j_2\ldots j_{(N-1)}$.

Since the indices of the N-RO refer to fermion operators, each index in the set $(j_1\ldots j_N)$ or $(k_1\ldots k_N)$ can be repeated only once. Consequently, a repeated index produces two terms similar to that described above. In conclusion, the original $N!$ traces of N-ROs, included in equation (14), are reduced to a few terms (one term when there is no repetition of indices). Furthermore, the sets $(i_1\ldots i_N)$ and $(l_a\ldots l_b)$ must be constituted by the same functions, otherwise the trace is zero (Lain *et al* 1988).

According to those equations, the spin-adapted trace of the $\hat{H}^2$ operator can be expressed by

$$\text{Tr}(\hat{H}^2) = \frac{1}{(N!)^2} \sum_{\{i\}} \sum_{\{j\}} \sum_{\{k\}} \sum_{\{l\}} {}^N H^{i_1 \dots i_N}_{j_1 \dots j_N} {}^N H^{k_1 \dots k_N}_{l_1 \dots l_N} \sum_{P \in S_N} \sum_{\Lambda} \langle \Lambda |^N E^{i_1 \dots i_N}_{P(l_1 \dots l_N)} |\Lambda\rangle \, \delta^{j_1 \dots j_N}_{P(k_1 \dots k_N)}$$

(15)

where a large number of terms are zero due to the Kronecker deltas which appear in this equation explicitly and implicitly (see equation (11)). It provides an easy handling in a computational point of view.

The procedure can easily be generalized to the calculation of traces of higher powers of the Hamiltonian. In the appendix we report the general case $\hat{H}^n$ as well as the cases $\hat{H}^3$ and $\hat{H}^4$, due to their importance in Statistics (skewness and kurtosis coefficient). In all cases, the determination of spin-adapted traces of N-ROs is needed. This determination is carried out in section 4.

4. The calculation of traces of N-RO

A whole study of spin-adapted traces of p-ROs over finite N-electron spaces has been reported by Torre *et al* (1993) for the general case $p \leqslant N$. However, the particular case $p = N$ allows a more direct treatment which is useful for the calculation of traces of the Hamiltonian powers.

Our method for the calculation of spin-adapted traces $\sum_{\Lambda} \langle \Lambda |^p E^{i_1 \dots i_p}_{j_1 \dots j_p} |\Lambda\rangle_{N,K,S}$ is based on the procedure (Torre *et al* 1993)

$$\sum_{\Lambda} \langle \Lambda |^p E^{i_1 \dots i_p}_{j_1 \dots j_p} |\Lambda\rangle_{N,K,S}$$

$$= \sum_{S(M)} \langle S(M) |^p E^{i_1 \dots i_p}_{j_1 \dots j_p} |S(M)\rangle - \sum_{S(M+1)} \langle S(M+1) |^p E^{i_1 \dots i_p}_{j_1 \dots j_p} |S(M+1)\rangle \qquad (16)$$

where $S(M)$ denotes the N-electron Slater determinants that can be constructed with a basis set of K orbital functions, having the largest eigenvalue, $S_z = M$, of the $\hat{S}_z$ operator for a determined spin quantum number S, that is, having $(N_\alpha = \frac{N}{2} + S)$ α-electrons and $(N_\beta = \frac{N}{2} - S)$ β-electrons. The subscripts N, K and S have been added in order to point out clearly the parameters which are used in the calculation of the trace. Equation (16) implies that the calculation of the spin-adapted trace of a p-RO can be carried out through a difference of traces taken over the Slater determinants corresponding to the eigenvalues M and $M + 1$.

Our treatment for the calculation of traces of $^p E^{i_1 \dots i_p}_{j_1 \dots j_p}$ operators, in the general case $p \leqslant N$, requires, at first, to classify the creation/annihilation sets $(i_1 \dots i_p)$ and $(j_1 \dots j_p)$, according to they have or do not have repetition of indices and according to the p-RO is diagonal, $(i_1 = j_1 \dots i_p = j_p)$, or off diagonal. In a second step, a progresive reduction of the p-RO to lower orders is carried out so that final formulae which are simple relationships between binomial coefficients are obtained (Torre *et al* 1993). In the particular case $p = N$, it is possible to carry out a direct calculation of those traces, avoiding both steps.

As has been mentioned above, the sets $(i_1 \dots i_N)$ and $(j_1 \dots j_N)$, in the N-RO, must be composed by identical orbital functions (otherwise the trace of the $^N E^{i_1 \dots i_N}_{j_1 \dots j_N}$ operator would be zero). Let us now consider that a given Slater determinant $|S(M)\rangle$ is constituted by a block of N_α α-spin orbitals and another one of N_β β-spin orbitals. Consequently, the calculation of the spin-adapted trace of a N-RO, through equation (16), requires to select

from the annihilation set $(j_1 \ldots j_N)$, that is, from the sum $\sum_{\sigma_1} \cdots \sum_{\sigma_N} b_{j_N \sigma_N} \cdots b_{j_1 \sigma_1}$, the terms containing the α- and β-spin functions which are coincident with the spin-orbitals which compose any of the Slater determinants of the sum $\sum_{S(M)}$. The same argument *must be applied simultaneously to the creation set* $(i_1 \ldots i_N)$. Hence, the application to a particular Slater determinant of the fermion operators derived from the sets $(i_1 \ldots i_N)$ and $(j_1 \ldots j_N)$ leads to zero unless each of these sets can be divided into two blocks of N_α and N_β spin functions, respectively, so that the α-blocks are composed by identical functions and similarly for the β-blocks.

An easier explanation of these arguments can be obtained when the operator ${}^N E^{i_1 \ldots i_N}_{j_1 \ldots j_N}$ is represented by the graph

where, according to equation (3), the functions occupying the same position have identical spin-coordinate. The vertical lines define two subsets, $(i_k \ldots i_l)$ and $(j_k \ldots j_l)$, constituted by identical orbital funtions, having all of them the same spin (α or β). Consequently, the subsets $(i_1 \ldots i_{k-1}, i_{l+1} \ldots i_N)$ and $(j_1 \ldots j_{k-1}, j_{l+1} \ldots j_N)$ must also have the same spin but it must be the opposite one (β or α) to that of the previous subsets.

The contribution of a particular choice of the subsets $(i_k \ldots i_l)$ and $(j_k \ldots j_l)$ to the sum $\sum_{S(M)} \langle S(M) |^N E^{i_1 \ldots i_N}_{j_1 \ldots j_N} | S(M) \rangle$ is $(-1)^{\nu_\alpha + \nu_\beta}$, where ν_α and ν_β are the number of transpositions required to pass from the ordered subset $(i_k \ldots i_l)$ to the $(j_k \ldots j_l)$ one and from $(i_1 \ldots i_{k-1}, i_{l+1} \ldots i_N)$ to $(j_1 \ldots j_{k-1}, j_{l+1} \ldots j_N)$, respectively. Obviously, the correct calculation of the trace of the ${}^N E^{i_1 \ldots i_N}_{j_1 \ldots j_N}$ operator requires that one take into account all the possibilities for constructing the subsets $(i_k \ldots i_l)$ and $(j_k \ldots j_l)$ derived from the sets $(i_1 \ldots i_N)$ and $(j_1 \ldots j_N)$.

In order to clarify these aspects, let us consider the simple numerical example $\sum_\Lambda \langle \Lambda |^6 E^{123456}_{214365} | \Lambda \rangle_{N=6, S=1}$. The graph of that 6-RO is

where the numbers $1, 2, 3 \ldots$ mean different orbital functions and the subscript K has been dropped due to the value of the trace of a N-RO is independent of that parameter.
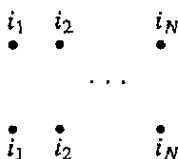
According to the values $S = 1$, $N = 6$, $N_\alpha = 4$ and $N_\beta = 2$, the Slater determinants which contribute with a non-zero value to the trace are determined by the graphs

The values of the $\nu_\alpha + \nu_\beta$ transpositions in each graph make $(-1)^{\nu_\alpha + \nu_\beta} = -1$ so that the sum $\sum_{S(M)} \langle S(M) |^6 E^{123456}_{214365} | S(M) \rangle_{N=6, S=1}$ is -3. As can easily be checked, the term

$\sum_{S(M+1)}\langle S(M+1)|^6 E_{214365}^{123456}|S(M+1)\rangle_{N=6,S=1}$ $(N_\alpha = 5, N_\beta = 1)$ is zero and, consequently, according to equation (16), the total trace $\sum_\Lambda \langle \Lambda|^6 E_{214365}^{123456}|\Lambda\rangle_{N=6,S=1}$ has the value -3.

The application of this procedure is particularly simple when diagonal N-ROs are considered. In the case of a diagonal N-RO, such as $^N E_{i_1...i_N}^{i_1...i_N}$, the graph is

$$
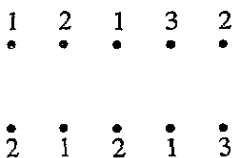\begin{array}{cccc}
i_1 & i_2 & & i_N \\
\bullet & \bullet & & \bullet \\
& & \cdots & \\
\bullet & \bullet & & \bullet \\
i_1 & i_2 & & i_N
\end{array}
$$

Consequently, the value of expression $\sum_{S(M)}\langle S(M)|^N E_{i_1...i_N}^{i_1...i_N}|S(M)\rangle$ is the number of possibilities for constructing the blocks of N_α and N_β functions, which is the same than the number of the N-electron Slater determinants, having N_α α-electrons and N_β β-electrons, that can be constructed with those N orbital functions that is, $\binom{N}{N_\alpha} = \binom{N}{N_\beta}$. In a similar way, the value of the expression $\sum_{S(M+1)}\langle S(M+1)|^N E_{i_1...i_N}^{i_1...i_N}|S(M+1)\rangle$ is $\binom{N}{N_\alpha+1} = \binom{N}{N_\beta-1}$.

Hence, a direct application of equation (16) to the case of diagonal N-ROs leads to

$$
\sum_\Lambda \langle \Lambda|^N E_{i_1...i_N}^{i_1...i_N}|\Lambda\rangle_{N,S} = \begin{pmatrix} N \\ \frac{N}{2}+S \end{pmatrix} - \begin{pmatrix} N \\ \frac{N}{2}+S+1 \end{pmatrix}
$$

$$
= \begin{pmatrix} N \\ \frac{N}{2}-S \end{pmatrix} - \begin{pmatrix} N \\ \frac{N}{2}-S-1 \end{pmatrix} \tag{17}
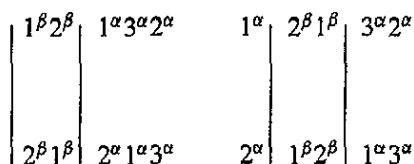$$

which is a simple and useful equation for the calculation of spin-adapted traces of diagonal N-ROs.

The general procedure can be also applied to the N-ROs which have repetition of indices in the sets $(i_1 \ldots i_N)$ and $(j_1 \ldots j_N)$ but in these situations the Pauli principle must be taken into account for constructing the blocks of N_α and N_β functions. According to that principle, a determined index can be only repeated twice and so those kind of indices must be separated in the α and β blocks; they cannot be repeated in the same block. Graphs having blocks (α or β) with repetition of indices must be neglected. An appropriate example to illustrate this case is $\sum_\Lambda \langle \Lambda|^5 E_{21213}^{12132}|\Lambda\rangle_{N=5,S=\frac{1}{2}}$. The graph of the 5-RO is

$$
\begin{array}{ccccc}
1 & 2 & 1 & 3 & 2 \\
\bullet & \bullet & \bullet & \bullet & \bullet \\
\\
\bullet & \bullet & \bullet & \bullet & \bullet \\
2 & 1 & 2 & 1 & 3
\end{array}
$$

and $N_\alpha = 3$ $N_\beta = 2$.

The Slater determinants which contribute to the trace value correspond to the graphs

$$
\begin{vmatrix} 1^\beta 2^\beta \\ \\ 2^\beta 1^\beta \end{vmatrix} \begin{matrix} 1^\alpha 3^\alpha 2^\alpha \\ \\ 2^\alpha 1^\alpha 3^\alpha \end{matrix} \quad \begin{vmatrix} 1^\alpha \\ \\ 2^\alpha \end{vmatrix} \begin{matrix} 2^\beta 1^\beta \\ \\ 1^\beta 2^\beta \end{matrix} \begin{matrix} 3^\alpha 2^\alpha \\ \\ 1^\alpha 3^\alpha \end{matrix}
$$

which lead to $\sum_\Lambda \langle \Lambda|^5 E_{21213}^{12132}|\Lambda\rangle_{N=5,S=\frac{1}{2}} = -2$

Note, finally, that the value of the traces of N-ROs is independent on the type and the number, K, of orbital functions of the employed basis set.

Acknowledgments

Appendix. Traces of the $\hat{H}^3$ and $\hat{H}^4$ operators: generalization

Explicit formulae for $\text{Tr}(\hat{H}^3)$, $\text{Tr}(\hat{H}^4)$ and $\text{Tr}(\hat{H}^n)$ are given in this appendix. They are a straightforward generalization of equation (15).

The trace of the $\hat{H}^3$ operator is

$$\text{Tr}(\hat{H}^3) = \frac{1}{(N!)^3} \sum_{\{i\}} \sum_{\{j\}} \sum_{\{k\}} \sum_{\{l\}} \sum_{\{p\}} \sum_{\{q\}} {}^N H^{i_1...i_N}_{j_1...j_N} \, {}^N H^{k_1...k_N}_{l_1...l_N} \, {}^N H^{p_1...p_N}_{q_1...q_N}$$

$$\times \sum_{P_1 \in S_N} \sum_{P_2 \in S_N} \sum_{\Lambda} \langle \Lambda |^N E^{i_1...i_N}_{P_2(q_1...q_N)} | \Lambda \rangle \, \delta^{j_1...j_N}_{P_1(k_1...k_N)} \, \delta^{P_1(l_1...l_N)}_{P_2(p_1...p_N)} \tag{A1}$$

with the condition that the set $P_2(q_1...q_N)$ must be a permutation of the ordered set $(i_1...i_N)$

The trace of the $\hat{H}^4$ operator is

$$\text{Tr}(\hat{H}^4) = \frac{1}{(N!)^4} \sum_{\{i\}} \sum_{\{j\}} \sum_{\{k\}} \sum_{\{l\}} \sum_{\{p\}} \sum_{\{q\}} \sum_{\{r\}} \sum_{\{s\}} {}^N H^{i_1...i_N}_{j_1...j_N} \, {}^N H^{k_1...k_N}_{l_1...l_N} \, {}^N H^{p_1...p_N}_{q_1...q_N} \, {}^N H^{r_1...r_N}_{s_1...s_N}$$

$$\times \sum_{P_1 \in S_N} \sum_{P_2 \in S_N} \sum_{P_3 \in S_N} \sum_{\Lambda} \langle \Lambda |^N E^{i_1...i_N}_{P_3(s_1...s_N)} | \Lambda \rangle \delta^{j_1...j_N}_{P_1(k_1...k_N)} \, \delta^{P_1(l_1...l_N)}_{P_2(p_1...p_N)} \delta^{P_2(q_1...q_N)}_{P_3(r_1...r_N)} \tag{A2}$$

again with the condition that $P_3(s_1...s_N)$ is a permutation of $(i_1...i_N)$.

The trace of any other power of the Hamiltonian can be obtained following this device without any difficulty:

$$\text{Tr}(\hat{H}^n) = \frac{1}{(N!)^n} \sum_{\{i^1\}} \sum_{\{j^1\}} \cdots \sum_{\{i^n\}} \sum_{\{j^n\}} {}^N H^{i^1_1...i^1_N}_{j^1_1...j^1_N} \cdots {}^N H^{i^n_1...i^n_N}_{j^n_1...j^n_N} \sum_{P_1 \in S_N}$$

$$\cdots \sum_{P_{(n-1)} \in S_N} \sum_{\Lambda} \langle \Lambda |^N E^{i^1_1...i^1_N}_{P_{(n-1)}(j^n_1...j^n_N)} | \Lambda \rangle \delta^{j^1_1...j^1_N}_{P_1(i^2_1...i^2_N)} \, \delta^{P_1(j^2_1...j^2_N)}_{P_2(i^3_1...i^3_N)} \cdots \delta^{P_{(n-2)}(j^{(n-1)}_1...j^{(n-1)}_N)}_{P_{(n-1)}(i^n_1...i^n_N)}$$

$$\tag{A3}$$

with $P_{(n-1)}(j^n_1...j^n_N) = (i^1_1...i^1_N)$

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