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Matrix elements of spin-adapted reduced Hamiltonians

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General formulas for matrix elements of the pth-order spin-adapted reduced Hamiltonian (p-SRH) are derived based on the theory of generalized reduced density operators. The method is illustrated by a diagrammatic technique developed in detail for $p=4$. The p-SRH is a matrix representing a p-particle operator in a finite-dimensional p-particle Hilbert space. It is related to the N-particle ($N \geq p$) Hamiltonian defined in an N-particle spin-adapted, finite-dimensional Hilbert space. The p-SRH's, apart from their importance in theory of atomic and molecular structure, may find applications in statistical theories of spectra and in nuclear shell theory.

I. INTRODUCTION

A reduction of the N-electron problem to a p-electron ($p \leq N$) one attracted much attention many years ago. The pioneering works by Löwdin,[1] Coleman,[2] Kummer,[3] McWeeny,[4] and others concentrated on studying properties of the reduced density matrices (or the reduced density operators). Efforts aimed at formulating an N-electron theory based on the reduced density matrix formalism and on the variational principle[1,2] have been frustrated by mathematical difficulties associated with the well-known N-representability problem. The present status of the theory is reported in the proceedings of a recent symposium.[5]

An approach to the reduction problem, in a sense complementary to the previous one, originates from the Bopp idea of the reduced Hamiltonian.[6] It is assumed that the electrons forming the N-electron system may be effectively described by a reduced Hamiltonian which acts in a p-particle (in practical terms in a two-particle) space. The reduced Hamiltonian is assumed to be independent of the finite-dimensional Hilbert space in which the N-electron problem is defined. This nonvariational approach has been applied in several contributions[7–9] however, it did not fulfill the high expectations which were originally associated with it.

Another method of dealing with the reduction problem has been formulated by Valdemoro.[10–13] In this approach the N-electron Hamiltonian $\hat{H}$ is determined in an antisymmetric and spin-adapted Hilbert space defined as a proper subspace of the N-fold tensorial product of a one-electron space V_{2K}. The one-electron space is a product of the K-dimensional orbital space

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

spanned by a set of K orthonormal orbitals and the two-dimensional spin space. The finite-dimensional Hilbert space is also referred to as the *full configuration-interaction* (full CI) space. Then, the N-electron Hamiltonian is here represented as a matrix, known as the full CI matrix.[1] Taking trace of a product of the full CI matrix and the pth order ($p \leq N$) reduced density-transition matrix we obtain a contraction of the Hamiltonian matrix from the N-particle spin-adapted space to a p-particle one. The resulting matrix is referred to as the p-particle (pth order) spin-adapted reduced Hamiltonian (p-SRH).[10–13] The p-SRH's possess many interesting mathematical properties. For $p=N$ their spectra are identical to the spectra of the corresponding full CI matrices. The eigenvalues of the p-SRH are only statistically related with the full CI spectrum since a given eigenvalue ${}^{p}\omega_I$ can exactly be expressed as

$${}^{p}\omega_I = \sum_{\mathcal{L}} \mathcal{E}_{\mathcal{L}}^{p} D_{II}^{\mathcal{L}} , \tag{2}$$

where $D_{II}^{\mathcal{L}}$ is the diagonal element of the pth-order reduced density matrix (p-RDM) corresponding to the N-electron full CI eigenstate of energy $\mathcal{E}_{\mathcal{L}}$. Although the p-RDM's cannot be derived in closed form from the p-SRH matrices, we have proposed a plausible model which permits the direct approximation of the p-RDM corresponding to a given eigenstate $|\mathcal{L}\rangle$. In this model the eigenvectors of the p-SRH matrix are assumed to describe sets of p electrons which on average can be considered to be independent. This approach has been successfully applied in the study of a series of atoms and ions[14,15] as well as to the study of the potential curves of the BeH and H_3 molecules.[16] These calculations were performed for $p=2$ and in the case of the beryllium isoelectronic series also $p=3$ was considered.[15] Another area of application of the p-SRH's is the statistical theory of spectra. It appears that the SRH's are most useful in deriving expressions for moments of the spectral density distributions of the original N-electron Hamiltonian.[17,18] Also some links between the SRH theory and the spectral distribution method of nuclear physics have been exposed.[19,20]

Recently general expressions for elements of 2-SRH (Ref. 21) and 3-SRH (Ref. 22) have been derived. The formalism used is based on the symmetric group approach (SGA) to the theory of many-electron systems.[23,24] In this formalism the N-electron Hilbert space is constructed as a direct product of two N-particle spaces: the spin space and the orbital space. The spin and the orbital spaces are then handeled separately.[18,23] The basic quantities of the theory, i.e., the Hamiltonian operator and the density operators, are expressed in terms of the replacement operators also referred to as the shift operators or the unitary group generators.[23-28] The replacement operators act in the orbital space only. Most of the theoretical considerations were concerned with the first-order replacement operators (Refs. 19, 20, and 24–26 and references therein). Properties of the higher-order replacement operators were studied rather scarcely.[25-28]

Since p-SRH is obtained through a linear transformation of the full CI matrix, its matrix elements are combinations of one- and two-electron integrals calculated in the orbital basis $\{\Phi_k\}_{k=1}^{K}$. The coefficients in these combinations may be expressed as traces of products of the pth and the second-order density operators.[22,28] A recently reported method of calculating these traces[28] allows us to derive a simple and efficient algorithm for evaluation of the p-SRH matrix elements for an arbitrary p. The main advantage of the new approach is a substantial simplification of the formulation resulting from using the generalized (pth order) replacement operators rather than the familiar first-order ones. In effect the pth-order reduced density operators (p-RDO) (and their traces) may be expressed in a compact way and using some rather simple algebra.[28]

The aim of this paper is to present a general method for evaluating p-SRH matrix elements. Though each single p-SRH matrix element may be, in principle, obtained using results of Ref. 28, relations between different elements and a general structure of the matrix were unknown. Exploring these relations and, in consequence, presenting a general and efficient algorithm for building up the p-SRH matrices is the aim of this paper. It is rather surprising that the number of different coefficients in a p-SRH matrix is very small. For $p=2,3,4$ there are, respectively, only 10,18,34 different coefficients. The present report terminates a series of papers concerned with the evaluation of p-SRH matrix elements.[20-22,28] The formalism developed in this paper contains our previous results for $p=2,3$ as special cases. It should be mentioned that the cases of $p\leq 4$ are of some special practical importance—the Schrödinger equation contracted to the two-electron space may be expressed in terms of the pth order density matrices with $2\leq p\leq 4$.[12,29,30] Therefore, the case of $p=4$ is discussed here in more detail.

The p-SRH's, apart from the already-mentioned applications in theory of atomic and molecular structure, may be used in deriving expressions for higher moments of the spectral density distribution.[18] Their usefulness in developing new approximate methods in many-particle theories and, in particular, in nuclear shell theory[19,20] still has to be explored. Finally, using N-SRH instead of the corresponding CI matrix may lead to interesting computational approaches.

The paper is organized as follows. In Sec. II we give the basic formalism of the p-SRH and several theorems concerning relations between the coefficients met in the matrix element expressions. Some properties of the traces of the p-RDO's are discussed in Sec. III. In Sec. IV the general structure of the p-SRH matrix elements is explored in detail. Finally, in Sec. V a graphical representation of the formalism is given and applied to the case of $p=4$.

II. DEFINITIONS AND BASIC FORMULAS

The pth-order reduced transition matrix is defined as

$$^{p}D^{\Lambda\Omega}_{i_1 i_2\cdots i_p;j_p\cdots j_2 j_1}=\frac{1}{p!}\langle\Lambda|^{p}E^{i_1 i_2\cdots i_p}_{j_1 j_2\cdots j_p}|\Omega\rangle\ , \tag{3}$$

where $|\Lambda\rangle$ and $|\Omega\rangle$ are N-electron eigenfunctions of the total spin operators $\hat{S}^2$ and $\hat{S}_z$, $p\leq N$, and

$$^{p}E^{i_1 i_2\cdots i_p}_{j_1 j_2\cdots j_p}=\sum_{\sigma_1\sigma_2,\ldots,\sigma_p} b^{\dagger}_{i_1\sigma_1}b^{\dagger}_{i_2\sigma_2}\cdots b^{\dagger}_{i_p\sigma_p}\times b_{j_p\sigma_p}\cdots b_{j_2\sigma_2}b_{j_1\sigma_1} \tag{4}$$

is the p-RDO with $b^{\dagger}_{i\sigma}$ ($b_{i\sigma}$) being the creation (annihilation) fermion operator associated with the orbital Φ_i and spin σ. In the case of $\Lambda=\Omega$ the quantity defined in Eq. (3) is referred to as the pth-order reduced density matrix corresponding to state Λ in the orbital representation. Equation (3) implies that

$$\operatorname{tr}{}^{p}\underline{D}=\begin{bmatrix}N\\p\end{bmatrix}\ . \tag{5}$$

Please note that different normalizations are used by different authors and in different papers.[1,2,4,21,22]

In the following, in order to simplify the notation, we shall write $^{p}D_{qrs\cdots;\cdots cba}$ and $^{p}E^{qrs\cdots}_{abc\cdots}$ avoiding the multiple indices and assuming that the superscript p determines the number of indices in each case.

The N-electron Hamiltonian may be expressed in terms of the second-order density operators and the generalized two-electron integrals $\{ij|kl\}$ as[21,28]

$$\hat{H}=\tfrac{1}{2}\sum_{i,j,k,l}{}^{2}E^{ik}_{jl}\{ij|kl\}\ . \tag{6}$$

Its matrix representation in our Hilbert space is

$$H_{\Lambda\Omega}=\sum_{i,j,k,l}{}^{2}D^{\Lambda\Omega}_{ik;lj}\{ij|kl\}\ . \tag{7}$$

The contraction procedure[11,12] applied to $H_{\Lambda\Omega}$ leads to the following expression for the p-SRH:

$$^{p}H^{qrs\cdots}_{abc\cdots}=\sum_{i,j,k,l}\{ij|kl\}\sum_{\Lambda,\Omega}{}^{2}D^{\Lambda\Omega}_{ik,lj}\ {}^{p}D^{\Omega\Lambda}_{qrs\cdots;\cdots cba}\ . \tag{8}$$

Using the resolution of identity in the spin-adapted Hilbert space we may express Eq. (8) in an equivalent form

$$ {}^{p}H^{qrs\cdots}_{abc\cdots} = \frac{1}{2!p\,!} \sum_{i,j,k,l} \{ij|kl\} \langle {}^{2}E^{ik}_{jl}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle \ , \tag{9} $$

where $\langle \hat{O} \rangle$ stands for $\sum_{\Lambda} \langle \Lambda | \hat{O} | \Lambda \rangle$.

Equation (9) may be further simplified if we note that the coefficients of the generalized two-electron integrals (i.e., the traces of products of the RDO's) fulfill several simple and general relations. Some of them have already been used in different context by other authors.[25–28] Let us first consider the relations which are straightforward consequences of Eq. (4).

(1) If $\hat{P}$ and $\hat{Q}$ are arbitrary permutations of the indices, then

$$ \langle {}^{2}E^{\hat{Q}[ik]}_{\hat{Q}[jl]}\ {}^{p}E^{\hat{P}[qrs\cdots]}_{\hat{P}[abc\cdots]} \rangle = \langle {}^{2}E^{ik}_{jl}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle \ . \tag{10} $$

(2) Since a trace is invariant with respect to a Hermitian conjugation of the operator, we have

$$ \langle {}^{2}E^{ik}_{jl}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle = \langle {}^{2}E^{jl}_{ik}\ {}^{p}E^{abc\cdots}_{qrs\cdots} \rangle \ . \tag{11} $$

(3) The trace

$$ \langle {}^{2}E^{ik}_{jl}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle = 0 $$

unless the sets of numbers $\{i,k,q,r,s,\ldots\}$ and $\{j,l,a,b,c,\ldots\}$ are the same.

(4) A trace is invariant with respect to the numbering of the orbitals. Therefore, coefficients of the integrals in Eq. (9) depend on mutual relations between the indices involved rather than on their specific values. Moreover it holds that

$$ \langle {}^{2}E^{ik}_{jl}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle = \langle {}^{p}E^{qrs\cdots}_{abc\cdots}\ {}^{2}E^{ik}_{jl} \rangle \ . $$

(5) Since more than two creation or annihilation operators acting on the same orbital must produce zero,

$$ {}^{p}H^{qrs\cdots}_{abc\cdots} = 0 $$

if in either $\{q,r,s,\ldots\}$ or in $\{a,b,c,\ldots\}$ there are more than two identical values. We distinguish indices that appear once in a sequence and those that appear twice.

Let us denote by ρ the number of indices by which the sets $\{q,r,s,\ldots\}$ and $\{a,b,c,\ldots\}$ differ. Relations (3)–(9) imply that

$$ \text{if } \rho > 2, \quad \text{then } {}^{p}H^{qrs\cdots}_{abc\cdots} = 0 \ . \tag{12} $$

If $\rho \le 2$ we may distinguish three cases.

(i) If $\rho = 2$ and, say, $\{q,r\} \neq \{a,b\}$ then the only nonzero terms in Eq. (9) are the ones for which $\{i,k\} = \{a,b\}$ and $\{j,l\} = \{q,r\}$. Thus,

$$ {}^{p}H^{qrst\cdots}_{abcd\cdots} = {}^{p}H^{qrst\cdots}_{ab\hat{P}[st\cdots]} = A\{aq|br\} + A'\{ar|bq\} \ , \tag{13} $$

where

$$ A = \frac{1}{p\,!} \langle {}^{2}E^{ab}_{qr}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle \ , \tag{14} $$

$$ A' = \frac{1}{p\,!} \langle {}^{2}E^{ab}_{rq}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle \ , \tag{15} $$

and $ab\hat{P}[st\ldots]$ mean that the first and second subscripts are, respectively, a and b while the remaining ones are a permutation of $s,t,\ldots$.

(ii) If $\rho = 1$ and say $q \neq a$, then

$$ {}^{p}H^{qrs\cdots}_{abc\cdots} = {}^{p}H^{qrs\cdots}_{aP[rs\cdots]} = \sum_{k} (\beta_k\{kk|qa\} + \gamma_k\{ka|qk\}) \ , \tag{16} $$

$$ \beta_k = \frac{1}{p\,!} \langle {}^{2}E^{ka}_{kq}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle \ , \tag{17} $$

$$ \gamma_k = \frac{1}{p\,!} \langle {}^{2}E^{ka}_{qk}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle \ . \tag{18} $$

(iii) If $\rho = 0$, i.e., $\{q,r,s,\ldots\} = \{a,b,c\ldots\}$, then

$$ {}^{p}H^{qrs\cdots}_{abc\cdots} = {}^{p}H^{qrs\cdots}_{\hat{P}[qrs\cdots]} = \sum_{k,l} (\mu_{kl}\{kk|ll\} + \nu_{kl}\{kl|lk\}) \ , \tag{19} $$

$$ \mu_{kl} = \frac{1}{p\,!} \langle {}^{2}E^{kl}_{kl}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle \ , \tag{20} $$

$$ \nu_{kl} = \frac{1}{p\,!} \langle {}^{2}E^{kl}_{lk}\ {}^{p}E^{qrs\cdots}_{abc\cdots} \rangle \ , \tag{21} $$

As one can see, the general structure of a p-SRH is very similar to that of a CI matrix.[23] Another important conclusion from Eqs. (12)–(21) is that p-SRH is a matrix representation of an operator containing at most two-body interactions. The explicit form of this operator has recently been derived for $p=2$ (Ref. 31).

Applying relations (3)–(7) to Eqs. (12)–(21) allows us to reduce the number of different coefficients A, β, γ, μ, and ν in a very substantial way. For example, if $p=2$ then there are only two different coefficients of each kind,[21] if $p=3$ then there are four different coefficients A, β, and γ and three different coefficients μ and ν.[22] Then, 2-SRH is defined by 10 different coefficients and 3-SRH by 18. As we show later in this paper, in the case of $p=4$ the number of different coefficients is 34. Determining the number of different coefficients for an arbitrary p is certainly an interesting exercise on group theory, however, we do not discuss it in detail in this paper.

III. RELATIONS BETWEEN TRACES OF DENSITY OPERATORS

The traces of products of the RDO's, which appear in the expressions for p-SRH matrix elements [Eqs. (13), (16), and (19)] may, in principle, be calculated using a recently formulated method.[28] However, in order to reveal some links between different coefficients and to reduce the number of cases to be considered we present here several relations between the traces of density operators. Proofs of these relations are based on rather involved algebra and, in some cases, are far from being trivial. They extensively exploit the general formalism described in our previous paper.[28] In the following relations the indices 1,2,3,4,. . . refer to *different* orbitals, and symbols X, Y, W, and Z represent sequences of indices which are different from those explicitly specified. The sequences X, Y, W, and Z do not have to be necessarily different and may have common elements.

The relations may be divided into two groups.

(1) Relations that replace a doubly occurring index by two singly occurring indices in traces of RDO's:

$$\langle {}^pE^{11X}_{\hat{P}[11Y]}\rangle = \langle {}^pE^{12X}_{\hat{P}[12Y]}\rangle + \langle {}^pE^{12X}_{\hat{P}[21Y]}\rangle\ , \tag{22}$$

where $\hat{P}$ is an arbitrary permutation of the indices. In order to prove this identity, we first demonstrate by adding the two terms in the right-hand side of the equations that the orbitals 1 and 2 form a singlet-coupled pair. Then using the "freezing theorem"[28] we obtain an obvious identity in the space of $N-2$ electrons and $K-1$ orbitals.

(2) Relations concerning products of RDO's.

(a) The orbitals involved in the p-RDO are singly occurring ones

$$\langle {}^pE^{X1}_{\hat{P}[Y1]}\,{}^2E^{W1}_{\hat{Q}[Z1]}\rangle = \langle {}^pE^{X1}_{\hat{P}[Y1]}\,{}^2E^{W2}_{\hat{Q}[Z2]}\rangle + \langle {}^pE^{X1}_{\hat{P}[Y2]}\,{}^2E^{W2}_{\hat{Q}[Z1]}\rangle\ , \tag{23}$$

$$\langle {}^pE^{X1}_{\hat{P}[Y1]}\,{}^2E^{11}_{11}\rangle = \langle {}^pE^{X1}_{\hat{P}[Y1]}({}^2E^{32}_{32}+{}^2E^{32}_{23})\rangle + 2\langle {}^pE^{X1}_{\hat{P}[Y2]}({}^2E^{32}_{31}+{}^2E^{32}_{13})\rangle\ . \tag{24}$$

(b) The orbital involved in the p-RDO is the doubly occurring one

$$\langle {}^pE^{X11}_{\hat{P}[Y11]}\,{}^2E^{W1}_{\hat{Q}[Z1]}\rangle = \langle ({}^pE^{X12}_{\hat{P}[Y12]}+{}^pE^{X12}_{\hat{P}[Y21]})\,{}^2E^{W3}_{\hat{Q}[Z3]}\rangle + 2\langle ({}^pE^{X12}_{\hat{P}[Y32]}+{}^pE^{X12}_{\hat{P}[Y23]})\,{}^2E^{W3}_{\hat{Q}[Z1]}\rangle\ , \tag{25}$$

$$\begin{aligned}\langle {}^pE^{X11}_{\hat{P}[Y11]}\,{}^2E^{11}_{11}\rangle = {}& \langle ({}^pE^{X12}_{\hat{P}[Y12]}+{}^pE^{X12}_{\hat{P}[Y21]})({}^2E^{34}_{34}+{}^2E^{34}_{43})\rangle + 4\langle ({}^pE^{X12}_{\hat{P}[Y13]}+{}^pE^{X12}_{\hat{P}[Y31]})({}^2E^{34}_{24}+{}^2E^{34}_{42})\rangle \\ & + \langle ({}^pE^{X12}_{\hat{P}[Y34]}+{}^pE^{X12}_{\hat{P}[Y43]})({}^2E^{34}_{12}+{}^2E^{34}_{21})\rangle\ .\end{aligned} \tag{26}$$

In the proof, the traces of products of RDO's are first transformed into traces of single RDO's.[28] Then, relations (22) as well as the general properties of the traces [as Eqs. (10) and (11)] are applied to demonstrate the validity of the identities (23)–(26).

IV. *P*-SRH MATRIX ELEMENTS

As was mentioned before, the general properties of the traces of the RDO's discussed in Sec. II and in a recent paper,[28] as well as the relations between different kinds of products of these operators [Eqs. (22)–(26)], lead to some significant simplification of the p-SRH expressions [Eqs. (13), (16), and (19)]. It is convenient to consider first the case when only singly occurring indices appear in either $\{q,r,s,\ldots\}$ or $\{a,b,c\ldots\}$ sets and then to reduce the cases with occurrence of doubly occurring indices to the previously considered one.

A. Only singly occurring indices appear in the *p*-RDO

(i) $p=2$.

Let us note that, due to properties (1) [Eq. (10)] and (4) of Sec. II, as well as Eqs. (13)–(15), we have

$$A(Q) = \frac{1}{p!}\langle {}^pE^{123\ldots p-2,qr}_{\hat{Q}[123\ldots p-2,ab]}\,{}^2E^{ab}_{qr}\rangle\ , \tag{27}$$

$$A'(Q) = \frac{1}{p!}\langle {}^pE^{123\ldots p-2,qr}_{\hat{Q}[123\ldots p-2,ba]}\,{}^2E^{ab}_{qr}\rangle\ , \tag{28}$$

where $a,b,q,r > p-2$. Then,

$$A'(Q) = A(Q(p-1,p))\ , \tag{29}$$

where $(p-1,p)$ stands for the transposition.

As one can see, $A(Q)=A(Q')$ if $\hat{Q}$ and $\hat{Q}'$ have the same cyclic structure and if both permutations affect indices a and b in an equivalent way (i.e., if they appear in cycles of the same length in both cases). For example, in the case of $p=4$ we have only five different values of A and five different values of A':

$$\begin{aligned}&A(I)\ ,\\ &A((12))\ ,\\ &A((13))=A((23))=A((14))=A((24))\ ,\\ &A((13)(12))=A((23)(12))=A((14)(12))\\ &\qquad\qquad\qquad = A((24)(12))\ ,\\ &A((13)(24))=A((14)(23))\ .\end{aligned}$$

All distinct A and A' coefficients are collected in Table I.

(ii) $p=1$.

If $p=1$ [Eq. (16)], we have to distinguish three cases.

Case 1. $k\notin\{a,q,r,s\ldots\}$. In this case we have

$$B(Q)\equiv\beta_k = \frac{1}{p!}\langle {}^pE^{123\ldots p-1,q}_{\hat{Q}[123\ldots p-1,a]}\,{}^2E^{pa}_{pq}\rangle\ , \tag{30}$$

$$C(Q)\equiv\gamma_k = \frac{1}{p!}\langle {}^pE^{123\ldots p-1,q}_{\hat{Q}[123\ldots p-1,a]}\,{}^2E^{pa}_{qp}\rangle\ , \tag{31}$$

where $a,q>p$. Also here $B(Q)=B(Q')$ and $C(Q)=C(Q')$ if $\hat{Q}$ and $\hat{Q}'$ have the same cyclic structure and if both permutations affect index a in an equivalent way (i.e., if it appears in a cycle of the same length in both cases).

For example,

$$\begin{aligned}&B((12))=B((13))=\cdots=B((p-2,p-1))\ ,\\ &B((1p))=B((2p))=\cdots=B((p-1,p))\ ,\\ &B((12)(2p))=B((13)(3p))\\ &\qquad = \cdots = B((p-2,p-1)(p-1,p))\ ,\end{aligned}$$

etc. Let us note that B and C are k independent due to the invariance of a trace with respect to the numbering of orbitals. All distinct B and C coefficients for $p=4$ are collected in Table II.

TABLE I. Diagrams corresponding to 4-SRH matrix elements with all superscripts and all subscripts different in the case of $\rho=2$ and expressions for the corresponding A and A' coefficients. For simplicity the right-hand-side (rhs) expressions for all coefficients have been multipied by $p!=24$.

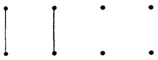
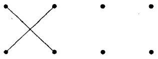
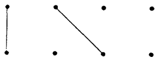
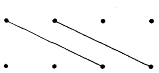
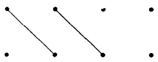
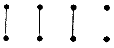
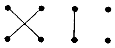
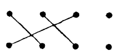
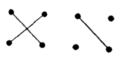
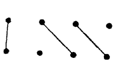
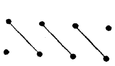
Graph	Coefficients
	$A_1=\langle E^{1234}_{1256}E^{56}_{34}\rangle$, $A'_1=\langle E^{1234}_{1256}E^{56}_{43}\rangle$
	$A_2=\langle E^{1234}_{2156}E^{56}_{34}\rangle$, $A'_2=\langle E^{1234}_{2156}E^{56}_{43}\rangle$
	$A_3=\langle E^{1234}_{1526}E^{56}_{34}\rangle$, $A'_3=\langle E^{1234}_{1526}E^{56}_{43}\rangle$
	$A_4=\langle E^{1234}_{5612}E^{56}_{34}\rangle$, $A'_4=\langle E^{1234}_{5612}E^{56}_{43}\rangle$
	$A_5=\langle E^{1234}_{5126}E^{56}_{34}\rangle$, $A'_5=\langle E^{1234}_{5126}E^{56}_{43}\rangle$

TABLE II. Diagrams corresponding to 4-SRH matrix elements with all superscripts and all subscripts different in the case of $\rho=1$ and expressions for the corresponding B and C coefficients. For simplicity the rhs expressions for all coefficients have been multiplied by $p!=24$.

Graph	Coefficients
	$B_1=\langle E^{1234}_{1236}E^{56}_{54}\rangle$, $C_1=\langle E^{1234}_{1236}E^{56}_{45}\rangle$
	$B_2=\langle E^{1234}_{2136}E^{56}_{54}\rangle$, $C_2=\langle E^{1234}_{2136}E^{56}_{45}\rangle$
	$B_3=\langle E^{1234}_{3126}E^{56}_{54}\rangle$, $C_3=\langle E^{1234}_{3126}E^{56}_{45}\rangle$
	$B_4=\langle E^{1234}_{1263}E^{56}_{54}\rangle$, $C_4=\langle E^{1234}_{1263}E^{56}_{45}\rangle$
	$B_5=\langle E^{1234}_{2163}E^{56}_{54}\rangle$, $C_5=\langle E^{1234}_{2163}E^{56}_{45}\rangle$
	$B_6=\langle E^{1234}_{1623}E^{56}_{54}\rangle$, $C_6=\langle E^{1234}_{1623}E^{56}_{45}\rangle$
	$B_7=\langle E^{1234}_{6123}E^{56}_{54}\rangle$, $C_7=\langle E^{1234}_{6123}E^{56}_{45}\rangle$

Case. 2. $k\in\{r,s,\ldots\}$. In this case

$$\begin{aligned}\beta_k&=\frac{1}{p!}\langle {}^pE^{12\ldots k\ldots p-1,q}_{\hat{Q}[12\ldots k\ldots p-1,a]}\;{}^2E^{ka}_{kq}\rangle\;,\\ \gamma_k&=\frac{1}{p!}\langle {}^pE^{12\ldots k\ldots p-1,q}_{\hat{Q}[12\ldots k\ldots p-1,a]}\;{}^2E^{ka}_{qk}\rangle\;,\end{aligned}\tag{32}$$

Eqs. (32) may be rewritten in an equivalent form

$$\begin{aligned}\beta(Q_k)=\beta_k&=\frac{1}{p!}\langle {}^2E^{12\ldots p-1,q}_{\hat{Q}_k[12\ldots p-1,a]}\;{}^2E^{p-1,a}_{p-1,q}\rangle\;,\\ \gamma(Q_k)=\gamma_k&=\frac{1}{p!}\langle {}^pE^{12\ldots p-1,q}_{\hat{Q}_k[12\ldots p-1,a]}\;{}^2E^{p-1,a}_{q,p-1}\rangle\;,\end{aligned}\tag{33}$$

where $\hat{Q}_k=(k,p-1)\hat{Q}(k,p-1)$. Using Eq. (23) we get

$$\begin{aligned}\beta(Q_k)&=A(Q_k)+B(Q_k)\;,\\ \gamma(Q_k)&=A'(Q_k)+C(Q_k)\;,\end{aligned}\tag{34}$$

where $B(Q_k)=B(Q)$ and $C(Q_k)=C(Q)$ for all k, because $\hat{Q}$ and $\hat{Q}_k$ have the same cyclic structure and transposition $(k,p-1)$ does not change the position of a. Then, we finally have

$$\begin{aligned}\beta(Q_k)&=A(Q_k)+B(Q)\;,\\ \gamma(Q_k)&=A'(Q_k)+C(Q)\;.\end{aligned}\tag{35}$$

Case 3. $k=q$ or $k=a$ or $k=q=a$. In this case $\beta_k=\gamma_k$. Using the formulas for traces of products of the RDO's (Ref. 28) and applying Eqs. (23) and (24) we get

$$\beta_k=\gamma_k=B(Q)+C(Q)\;.\tag{36}$$

Hence, in the case of $\rho=1$ one matrix element is expressed in terms of two coefficients $B(Q)$ and $C(Q)$ specific for this case, and of several coefficients $A(Q_k)$ and $A'(Q_k)$, which appear also in the case of $\rho=2$ matrix elements. Combining together Eqs. (16)–(18) and (30)–(36) we get

$$\begin{aligned}{}^pH^{123\ldots p-1,r}_{Q[123\ldots p-1,q]}=&\sum_{k=1}^{p-1}[A(Q_k)\{rq|kk\}+A'(Q_k)\{rk|kq\}]\\ &+B(Q)\{rq|\alpha\alpha\}+C(Q)\{r\alpha|\alpha q\}\;,\end{aligned}\tag{37}$$

where

$$\begin{aligned}\{rq|\alpha\alpha\}&=\sum_{k=1}^{K}\{rq|kk\}\;,\\ \{r\alpha|\alpha q\}&=\sum_{k=1}^{K}\{rk|kq\}\;.\end{aligned}\tag{38}$$

A graphical rule which simplifies determination of these coefficients will be described in the next section.

(iii) $\rho=0$.

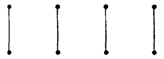
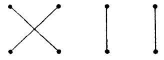
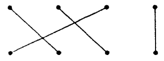
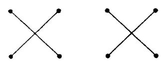
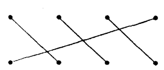
Also here three cases may be distinguished.

Case 1. $k,l\notin\{q,r,s,\ldots\}$. If $k\neq l$ then Eqs. (20) and (21) read

$$\begin{aligned}F(Q)=\mu_{kl}&=\frac{1}{p!}\langle {}^pE^{123\ldots p}_{\hat{Q}[123\ldots p]}\;{}^2E^{p+1,p+2}_{p+1,p+2}\rangle\;,\\ G(Q)=\nu_{kl}&=\frac{1}{p!}\langle {}^pE^{123\ldots p}_{\hat{Q}[123\ldots p]}\;{}^2E^{p+1,p+2}_{p+2,p+1}\rangle\;.\end{aligned}\tag{39}$$

From the invariance of traces with respect to the num-

TABLE III. Diagrams corresponding to 4-SRH matrix elements with all superscripts and all subscripts different in the case of $\rho=0$ and expressions for the corresponding F and G coefficients. For simplicity the rhs expressions for all coefficients have been multiplied by $p!=24$.

Graph	Coefficients
	$F_1=\langle E^{1234}_{1234}E^{56}_{56}\rangle$, $G_1=\langle E^{1234}_{1234}E^{56}_{65}\rangle$
	$F_2=\langle E^{1234}_{2134}E^{56}_{56}\rangle$, $G_2=\langle E^{1234}_{2134}E^{56}_{65}\rangle$
	$F_3=\langle E^{1234}_{3124}E^{56}_{56}\rangle$, $G_3=\langle E^{1234}_{3124}E^{56}_{65}\rangle$
	$F_4=\langle E^{1234}_{2143}E^{56}_{56}\rangle$, $G_4=\langle E^{1234}_{2143}E^{56}_{65}\rangle$
	$F_5=\langle E^{1234}_{4123}E^{56}_{56}\rangle$, $G_5=\langle E^{1234}_{4123}E^{56}_{65}\rangle$

bering of orbitals it follows again that the values of $F(Q)$ and $G(Q)$ are k,l independent. Besides, if $\hat{Q}$ and $\hat{Q}\,'$ belong to the same class then $F(Q)=F(Q')$ and $G(Q)=G(Q')$. A list of all $F(Q)$ and $G(Q)$ coefficients for $p=4$ is given in Table III. If $k=l$ then one gets a rather trivial modification of Eq. (39). In this case

$$\mu_{kk}=\nu_{kk}=F(Q)+G(Q)\ .$$

Case 2. One of the indices k,l belongs to the set $\{q,r,s,\ldots\}$ and the other does not. Then

$$\begin{aligned}\mu(Q_k)=\mu_{kl}&=\frac{1}{p!}\langle {}^pE^{12\ldots k\ldots l\ldots p}_{\hat{Q}_k[12\ldots k\ldots l\ldots p]}\;{}^2E^{p,p+1}_{p,p+1}\rangle\ ,\\ \nu(Q_k)=\nu_{kl}&=\frac{1}{p!}\langle {}^pE^{12\ldots k\ldots l\ldots p}_{\hat{Q}_k[12\ldots k\ldots l\ldots p]}\;{}^2E^{p,p+1}_{p+1,p}\rangle\ .\end{aligned}\tag{40}$$

Similarly as in the previous case, Eq. (23) gives

$$\begin{aligned}\mu(Q_k)&=B(Q_k)+F(Q_k)\ ,\\ \nu(Q_k)&=C(Q_k)+G(Q_k)\ ,\end{aligned}\tag{41}$$

with $\hat{Q}_k=(kp)\hat{Q}(pk)$. Also now, $F(Q_k)$ and $G(Q_k)$ are k independent because in the corresponding expressions resulting from Eq. (23) $\hat{Q}_k$ does not affect the labels in p-RDO, which also appear in 2-RDO [similarly as in Eq. (39)] and because the traces are invariant with respect to the numbering of orbitals. Therefore, in Eq. (41) we can put $F(Q_k)=F(Q)$ and $G(Q_k)=G(Q)$. However $B(Q_k)$ and $C(Q_k)$ depend upon k since in the corresponding expressions transposition (pk) acts on a label which appears in both p-RDO and 2-RDO.

Case 3. Both k and l belong to $\{q,r,s,\ldots\}$. If $k\neq l$ then Eqs. (20) and (21) become

$$\begin{aligned}\mu(Q_{kl})=\mu_{kl}&=\frac{1}{p!}\langle {}^pE^{12\ldots k\ldots l\ldots p}_{\hat{Q}_{kl}[12\ldots k\ldots l\ldots p]}\;{}^2E^{p-1,p}_{p-1,p}\rangle\ ,\\ \nu(Q_{kl})=\nu_{kl}&=\frac{1}{p!}\langle {}^pE^{12\ldots k\ldots l\ldots p}_{\hat{Q}_{kl}[12\ldots k\ldots l\ldots p]}\;{}^2E^{p-1,p}_{p,p-1}\rangle\ .\end{aligned}\tag{42}$$

By using Eq. (23) twice we finally obtain

$$\begin{aligned}\mu(Q_{kl})&=A(Q_{kl})+B(Q_k)+B(Q_l)+F(Q)\ ,\\ \nu(Q_{kl})&=A'(Q_{kl})+C(Q_k)+C(Q_l)+G(Q)\ ,\end{aligned}\tag{43}$$

with

$$\begin{aligned}\hat{Q}_{kl}&=(k,p-1)(lp)\hat{Q}(lp)(k,p-1)\ ,\\ \hat{Q}_k&=(kp)\hat{Q}(kp)\ ,\\ \hat{Q}_l&=(lp)\hat{Q}(lp)\ .\end{aligned}$$

If $k=l$, Eq. (24) gives

$$\mu(Q_k)=\nu(Q_k)=2B(Q_k)+2C(Q_k)+F(Q)+G(Q)\ .\tag{44}$$

Combining Eqs. (39)–(44) we get the following expression for the p-SRH matrix element:

$$\begin{aligned}H^{123\ldots p}_{\hat{Q}[123\ldots p]}=&\sum_{\substack{k=1\\k<l}}^{p}[A(Q_{kl})\{kk|ll\}+A'(Q_{kl})\{kl|lk\}]\\ &+\sum_{k=1}^{p}[B(Q_k)\{kk|\alpha\alpha\}+C(Q_k)\{k\alpha|\alpha k\}]\\ &+F(Q)\{\alpha\alpha|\beta\beta\}+G(Q)\{\alpha\beta|\beta\alpha\}\ ,\end{aligned}\tag{45}$$

where

$$\begin{aligned}\{\alpha\alpha|\beta\beta\}&=\tfrac{1}{2}\sum_{k,l=1}^{K}\{kk|ll\}\ ,\\ \{\alpha\beta|\beta\alpha\}&=\tfrac{1}{2}\sum_{k,l=1}^{K}\{kl|lk\}\ .\end{aligned}\tag{46}$$

B. At least one doubly occurring index in p-RDO

As it may be seen from the formalism presented in Secs. II and III and, in particular, from Eqs. (22)–(26), the case of a doubly occurring index in the p-RDO may always be reduced to the cases in which this specific index has been replaced by several singly occurring indices. The cases of several doubly occurring indices may be treated applying the same procedure repeatedly to each of these indices. In the preceding section we considered all cases of traces of products of p-RDO's and 2-RDO's, in which the p-RDO's do not contain any doubly occurring indices. Therefore this procedure can generate only traces which were already considered. In consequence the coefficients of the integrals in the resulting p-SRH matrix elements are always expressible in terms of A, B, C, F, and G.

As an example let us consider the coefficient of the

$\{43|11\}$ integral in H^{2311}_{2411}. According to Eq. (25) we have

$$T\equiv\langle {}^4E^{2311}_{2411}\,{}^2E^{41}_{31}\rangle=2\langle({}^4E^{2315}_{2465}+{}^4E^{2315}_{2456})\,{}^2E^{46}_{31}\rangle+\langle({}^4E^{2315}_{2415}+{}^4E^{2315}_{2451})\,{}^2E^{46}_{36}\rangle\ .$$

Now, according to Eqs. (27)–(31),

$$T=2[A(I)+A'(I)]+B(I)+B((34))\ .$$

Using Tables I and II we get

$$T=2(A_1+A_1')+B_1+B_2\ .$$

Let us note, that the indices appearing in a p-RDO are the same as the indices in the corresponding p-SRH matrix element. Therefore we refer to the matrix elements in which some of upper and/or lower row indices repeat as matrix elements that contain doubly occurring indices.

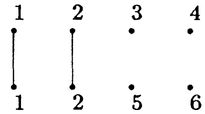
V. DIAGRAMMATIC RULES FOR CALCULATING THE p-SRH MATRIX ELEMENTS

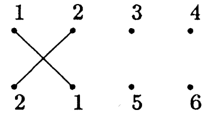
The equations derived in the preceding section may be represented in a graphical form. The graphical representation of the p-SRH matrix elements visualizes the rules for their construction and is particularly useful in decomposing these matrix elements that contain doubly occurring indices into the ones without such indices. For simplicity, we describe in this section the diagrammatic rules using an example of $p=4$. A generalization for the case of an arbitrary p is straightforward.

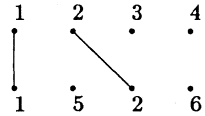
A. Only singly occurring indices appear in the p-RDO

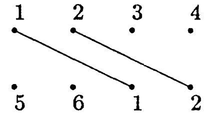
(i) $p=2$.

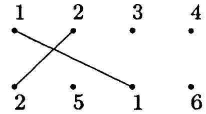
Let us consider a set of $4!=24$ matrix elements $H^{1234}_{\hat{P}[1256]}$. As it was discussed in Sec. IV, the matrix elements may be divided into five sets so that the elements in each set are the same. Here is a list of the representatives of each of the sets, of the corresponding diagrams, and of the formulas [explicit forms of Eqs. (13), (27), and (28)].

$H^{1234}_{1256}=$  $=A(I)\{35|46\}+A((34))\{36|45\}$

$H^{1234}_{2156}=$  $=A((12))\{35|46\}+A((12)(34))\{36|45\}$

$H^{1234}_{1526}=$  $=A((23))\{35|46\}+A((23)(34))\{36|45\}$ (47)

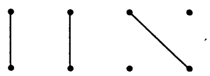
$H^{1234}_{5612}=$  $=A((13)(24))\{35|46\}+A((13)(24)(34))\{36|45\}$

$H^{1234}_{2516}=$  $=A((13)(12))\{35|46\}+A((13)(12)(34))\{36|45\}$.

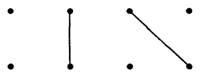
In the diagrams each of the superscripts (subscripts) is represented by a dot in the upper (lower) row of a two-row array. The same indices are linked by arcs. Let us note that the permutations which define the coefficients of the integrals are the ones which acting on the lower row indices put the linked dots into coincidence (after these permutations are executed, all arcs are vertical). The indices of the integrals are the ones which correspond to the unlinked dots.

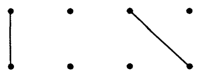
(ii) $p=1$.

There are seven sets of different matrix elements. They are all shown in Table II. From Eq. (37) we see that each matrix element consists, in this case, of two parts. The first part comprises sums $\{rq|\alpha\alpha\}$ and $\{r\alpha|\alpha q\}$ of integrals [Eqs. (38)] multiplied, respectively, by the coefficients B and C. The coefficients are specific for each class of the matrix elements. The second part of the formulas contains $\{rq|kk\}$ and $\{rk|kq\}$, $k\le p$, integrals multiplied, respectively, by coefficients A and A'. An inspection of Eqs. (32)–(37) leads us to a conclusion that the coefficients of the integrals are equal to the sums of the corresponding coefficients appearing in matrix elements represented by diagrams that contain one arc less than the diagrams representing the original matrix element. To be more specific, let us consider matrix element H^{1236}_{1243}. It is represented by a diagram

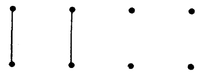


From Table II we see that it is associated with coefficients B_4 and C_4. Removing one arc from it we obtain three diagrams with $\rho=2$:





and



According to Table I the pairs of coefficients associated with these diagrams are, respectively, A_3, A'_3; A_3, A'_3, and A_1, A'_1. Then, the rule formulated above says that

$$\begin{aligned} H^{1236}_{1243} = {} & A_3\{46|11\}+A'_3\{41|16\} \\ & +A_3\{46|22\}+A'_3\{42|26\} \\ & +A_1\{43|36\}+A'_1\{46|33\} \\ & +B_4\{46|\alpha\alpha\}+C_4\{4\alpha|\alpha 6\} \ . \end{aligned} \tag{48}$$

This rule appears to be quite general and it is valid for all kinds of p-SRH matrix elements. In order to facilitate a simple use of this rule, in Table IV we give the "hierar-

TABLE IV. The hierarchy of diagrams corresponding to 4-SRH in the case of all superscripts and all subscripts different. Note that due to Eq. (10) more than one diagram corresponds to the same coefficient because some of the diagrams are equivalent.

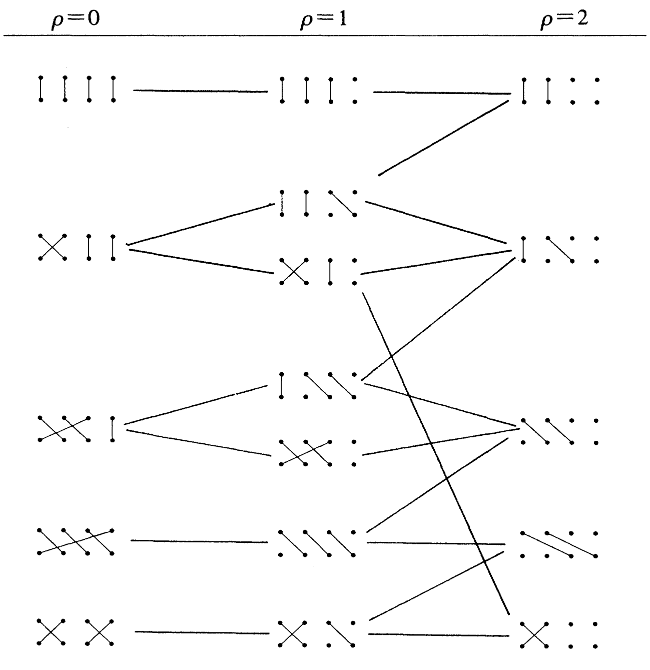


TABLE V. Decomposition of a matrix element in which all superscripts and all subscripts are different.

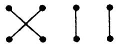
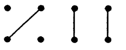
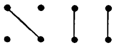
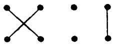
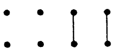
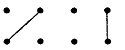
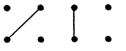
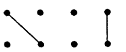
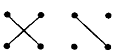
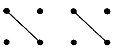
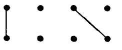
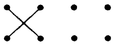
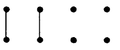
Matrix element	Contribution	Diagram
$H^{1234}_{2134}=$	$F_2\{\alpha\alpha|\beta\beta\}+G_2\{\alpha\beta|\beta\alpha\}$	
	$+B_4\{11|\alpha\alpha\}+C_4\{1\alpha|\alpha 1\}$	
	$+B_4\{22|\alpha\alpha\}+C_4\{2\alpha|\alpha 2\}$	
	$+B_2\{33|\alpha\alpha\}+C_2\{3\alpha|\alpha 3\}$	
	$+B_2\{44|\alpha\alpha\}+C_2\{4\alpha|\alpha 4\}$	
	$+A_1\{12|21\}+A'_1\{11|22\}$	
	$+A_3\{11|33\}+A'_3\{13|31\}$	
	$+A_3\{11|44\}+A'_3\{14|41\}$	
	$+A_3\{22|33\}+A'_3\{23|32\}$	
	$+A_3\{22|44\}+A'_3\{24|42\}$	
	$+A_2\{33|44\}+A'_2\{34|43\}$	

TABLE VI. Decomposition of a matrix element with one pair of identical superscripts and one pair of identical subscripts.

Matrix element	Contribution	Diagram
$H^{1134}_{1153}=$	$B_5\{45|\alpha\alpha\}+C_5\{4\alpha|\alpha 5\}$	
	$B_4\{45|\alpha\alpha\}+C_4\{4\alpha|\alpha 5\}$	
	$A_3\{11|45\}+A'_3\{15|41\}$	
	$A_4\{11|45\}+A'_4\{15|41\}$	
	$A_4\{11|45\}+A'_4\{15|41\}$	
	$A_3\{11|45\}+A'_3\{15|41\}$	
	$A_2\{35|43\}+A'_2\{33|45\}$	
	$A_1\{35|43\}+A'_1\{33|45\}$	

chy of the diagrams" showing the way they decompose.

(iii) $p=0$.

Since the permutation group S_4 contain five classes, there are five different values of F and G coefficients and there are five different diagrams. They are listed in Table III. In Table V the decomposition of a matrix element is presented. The same rule as the one leading to Eq. (48) applies, except that here this is a three-step procedure: from the original diagram we get F and G coefficients; from the ones obtained by removing one arc—B and C; finally, from the ones which result from removing two arcs—A.

B. At least one doubly occurring index in the p-RDO

The same rule of hierarchical decomposition applies to the case when one or several doubly occurring indices appear in the p-RDO, i.e., when in the matrix element we have at least one pair of the same superscripts and/or subscripts. Rather than giving a description of the specific variation of the general decomposition rule, we refer the reader to Table VI where an illustrative example is given.

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[1] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).
[2] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1965).
[3] H. Kummer, J. Math. Phys. **8**, 2063 (1967).
[4] R. McWeeny, Rev. Mod. Phys. **32**, 355 (1970).
[5] *Density Matrices and Density Functionals, Proceedings of the A. J. Coleman Symposium, Kingston, Ontario, 1985,* edited by R. Erdahl and V. Smith (Reidel, Dordrecht, 1987).
[6] F. Bopp, Z. Phys. **156**, 348 (1959).
[7] T. B. Grimley and F. D. Peat, Proc. Phys. Soc. **86**, 249 (1965).
[8] C. F. Bender, E. R. Davidson, and F. D. Peat, Phys. Rev. **174**, 75 (1968).
[9] A. J. Coleman and I. Absar, Int. J. Quantum Chem. **15**, 1279 (1980), and references therein.
[10] C. Valdemoro, An. R. Soc. Esp. Fis. **79**, 106 (1983).
[11] C. Valdemoro, Phys. Rev. A **31**, 2114 (1985).
[12] C. Valdemoro, in Ref. 5, p. 275.
[13] C. Valdemoro, in *Neuvas Tendecias en Química Teórica,* edited by S. Fraga (Consejo Superior de Investigaciones Científicas, Madrid, 1987), p. 95.
[14] C. Valdemoro, Phys. Rev. A **31**, 2123 (1985); L. Lain, C. Valdemoro, A. Torre, and M. Reguero, *ibid.* **35**, 3132 (1987); C. Valdemoro, L. Lain, F. Beitia, A. Ortiz de Zárate, and F. Castaño, *ibid.* **33**, 1525 (1986).
[15] L. Lain, A. Torre, and C. Valdemoro, Phys. Rev. A **37**, 2868 (1988).
[16] C. Valdemoro and M. Reguero, in *Quantum Chemistry—Basic Aspects, Actual Trends,* edited by R. Carbó (Elsevier, Amsterdam, 1989), p. 251; C. Valdemoro and L. Rodriguez-Monje (unpublished).
[17] J. Karwowski and M. Bancewicz, J. Phys. A **20**, 6309 (1987).
[18] J. Karwowski, in *Quantum Chemistry—Basic Aspects, Actual Trends,*. edited by R. Carbó (Elsevier, Amsterdam, 1989), p. 213.
[19] M. Nomura, Phys. Rev. A **37**, 2709 (1988).
[20] J. Karwowski and C. Valdemoro, Phys. Rev. A **37**, 2712 (1988).
[21] J. Karwowski, W. Duch, and C. Valdemoro, Phys. Rev. A **33**, 2254 (1986).
[22] L. Lain, A. Torre, J. Karwowski, and C. Valdemoro, Phys. Rev. A **38**, 2721 (1988).
[23] W. Duch and J. Karwowski, Comput. Phys. Rep. **2**, 95 (1985), and references therein.
[24] W. Duch, *GRMS or Graphical Representation of Model Spaces,* Vol. 42 of *Lecture Notes in Chemistry* (Springer, Berlin, 1986), and references therein.
[25] W. Kutzelnigg, J. Chem. Phys. **82**, 4166 (1985).
[26] J. Paldus and B. Jeziorski, Theoret. Chim. Acta (Berlin) **73**, 81 (1988).
[27] J. Hinze and J. T. Broad, in *The Unitary Group for the Evaluation of Electronic Energy Matrix Elements,* Vol. 22 of *Lecture Notes in Chemistry,* edited by J. Hinze (Springer, Berlin, 1981), p. 332.
[28] J. Planelles, C. Valdemoro, and J. Karwowski, Phys. Rev. A **41**, 2391 (1990).
[29] H. Nakatsuji, Phys. Rev. A **14**, 41 (1976).
[30] L. Cohen, C. Frishberg, Phys. Rev. A **13**, 927 (1976).
[31] J. Karwowski, C. Valdemoro, and L. Lain, Phys. Rev. A **39**, 4967 (1989).