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Some results for symmetric-group-adapted reduced density operators

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Summary. Reduced density operators of the p-th order adapted to irreducible representations of the permutation group are expressed in terms of spin-adapted p-electron creation and annihilation operators. Simple rules for expressing products of two density operators as linear combinations of the symmetry-adapted density operators and formulas for calculating matrix elements of these operators are derived. The results may be useful in many-body perturbation theory, in coupled cluster methods, in theory of spin-adapted reduced Hamiltonians, and in statistical theories of spectra.

Key words: Reduced density operators – Spin-adaptation – Creation and annihilation operators

1 Introduction

Spin-free p-order reduced density operators (p-RDOs) [1] also referred to as excitation operators [2], replacement operators [3–5] and, in the first-order case, the unitary group generators [6], proved to be most useful in designing algorithms for evaluation of matrix elements in many areas of the N-electron system theory. Until recently, the properties of p-RDOs with $p > 2$ were investigated rather scarcely [1]. However, growing interest in extending the many-body perturbation theory and the coupled cluster expansions up to higher orders [2, 5, 7], developments in the theory of spin-adapted reduced Hamiltonians [8–11], and in the statistical theories of spectra [12] stimulated more research work on properties of the high-order p-RDOs [2, 5, 10, 11, 13].

In a recent work by Kutzelnigg [2], the importance of the permutation symmetry adaptation has been emphasized and methods for obtaining the symmetry-adapted operators have been developed. In the same paper a generalization of the Wick theorem allowing one to express products of p-RDOs as sums of single p-RDOs was given. A graphical representation of the Wick theorem allowing for an easy evaluation of products of the primitive (non-adapted) p-RDOs was presented in our recent paper [13]. The p-RDOs there are represented by means of p-electron creation and annihilation operators allowing for simple evaluation of their traces in finite-dimensional, spin-adapted, and antisymmetric Hilbert spaces.

In the present note we give a general procedure for constructing symmetry-adapted p-RDOs from spin-adapted p-particle creation and annihilation operators. The procedure is an alternative to the one given by Kutzelnigg [2]. Moreover, a simple scheme which allows one to express products of RDOs as linear combinations of the symmetry-adapted RDOs is outlined. Finally, formulas for calculating matrix elements of these operators are derived.

2 Spin-adapted second quantization operators

A primitive p-electron creation operator is defined as:

$$\bar{B}^{+}_{(i_1 i_2 \ldots i_p)\sigma_1\sigma_2\ldots\sigma_p} \equiv b^{+}_{i_1\sigma_1} b^{+}_{i_2\sigma_2} \ldots b^{+}_{i_p\sigma_p}, \tag{1}$$

where $(i_1 i_2 \ldots i_p)$ stands for orbitals, $\sigma_1\sigma_2\ldots\sigma_p$ for the one-electron spin functions and $b^{+}_{i\sigma}$ are the familiar one-electron creation operators. The notation is further generalized to describe p-particle states with a specific spin-coupling scheme. Thus, $B^{+}_{(i_1 i_2 \ldots i_p)SM\lambda}$ denotes a spin-adapted creation operator of a p-particle state. The spin-coupling scheme is labelled by λ and S, M denote the quantum numbers corresponding to the p-particle spin operators $\boldsymbol{S}^2$ and $\boldsymbol{S}_Z$, respectively. The spin-adapted creation operators may be expressed in terms of the primitive ones using the Clebsh–Gordan expansion [13, 14].

$$\{B^{+}_{(i_1 i_2 \ldots i_p)SM\lambda}\} = \{C^{\sigma_1\sigma_2\ldots\sigma_p}_{SM\lambda}\}\{\bar{B}^{+}_{(i_1 i_2 \ldots i_p)\sigma_1\sigma_2\ldots\sigma_p}\}, \tag{2}$$

where $\{C^{\sigma_1\sigma_2\ldots\sigma_p}_{SM\lambda}\}$ is the unitary matrix of the Clebsh–Gordan coefficients.

A similar expansion may be used to construct spin-adapted p-particle operators from products of the spin-adapted t- and u-particle operators, where $p = t + u$. For example, if $t = u = 2$, then:

$$B^{+}_{(abcd)SMs_1s_2} = \sum_{m_1=-s_1}^{s_1} \sum_{m_2=-s_2}^{s_2} \langle SMs_1s_2 \,|\, s_1m_1s_2m_2\rangle B^{+}_{(ab)s_1m_1} B^{+}_{(cd)s_2m_2}, \tag{3}$$

where s_1, $s_2 = 0, 1$ and $\langle SMs_1s_2 \,|\, s_1m_1s_2m_2\rangle$ are the Clebsh–Gordan coefficients for this specific coupling scheme. A generalization of Eq. (3) for arbitrary t and u is straightforward.

It is convenient to introduce a more compact notation for the spin-adapted creation and annihilation operators. We set:

$$B^{+}_{\alpha,SM\lambda} \equiv B^{+}_{(i_1 i_2 \ldots i_p)SM\lambda} \tag{4}$$

where α stands for the string of the orbital indices. The corresponding annihilator is $B_{\alpha,SM\lambda}$.

A spin-adapted creation operator, acting upon the vacuum state creates an antisymmetric, p-electron spin eigenfunction corresponding to a given orbital configuration, i.e.:

$$B^{+}_{\alpha,SM\lambda}|0\rangle = |\alpha, SM\lambda\rangle.$$

Hence, in the spin and in the orbital spaces the spin-adapted creation/annihilation operators corresponding to given α, S, M form bases for the pertinent irreducible representations of the symmetric group S_p of $p!$ elements[1].

[1] In order to simplify the discussion we assume, for the time being, that all indices in the α string are different. A generalization for the case of repeated indices follows the same line as in the theory of spin functions (see e.g. [16, 17])

In the coordinate representation $|\alpha, SM\lambda\rangle$ corresponds to a spin-adapted antisymmetrized product of orthonormal spin-orbitals [15]:

$$\Psi(\underline{r}, \underline{\sigma})^{\alpha}_{SM\lambda} = \langle \underline{r}, \underline{\sigma} \mid \alpha, SM\lambda \rangle. \tag{5}$$

If $\tilde{\mathscr{P}}_{\sigma}/\tilde{\mathscr{P}}_{r}$ denote a permutation $\mathscr{P}$ acting on the spin/orbital coordinates of electrons, then the Pauli principle gives:

$$\tilde{\mathscr{P}}_{r}\tilde{\mathscr{P}}_{\sigma}\Psi^{\alpha}_{SM\lambda} = \varepsilon(\mathscr{P})\Psi^{\alpha}_{SM\lambda} \tag{6}$$

where $\varepsilon(\mathscr{P})$ is the parity of $\mathscr{P}$. The transformation properties of the orbital and of the spin parts of $\Psi^{\alpha}_{SM\lambda}$ implies [16, 17] that:

$$\tilde{\mathscr{P}}_{\sigma}\Psi^{\alpha}_{SM\lambda} = \sum_{\mu=1}^{f(S,p)} V^{p}_{S}(\mathscr{P})_{\mu\lambda}\Psi^{\alpha}_{SM\mu} \tag{7a}$$

and

$$\tilde{\mathscr{P}}_{r}\Psi^{\alpha}_{SM\lambda} = \sum_{\mu=1}^{f(S,p)} U^{p}_{S}(\mathscr{P})^{+}_{\mu\lambda}\Psi^{\alpha}_{SM\mu} \tag{7b}$$

where V^{p}_{S} and U^{p}_{S} are matrices of mutually dual irreducible representations of S_p. Their dimension, $f(S, p)$, is given by the Heisenberg formula [17]:

$$f(S, p) = \frac{2S+1}{p+1}\binom{p+1}{p/2-S}. \tag{8}$$

The total spin quantum number designates the pertinent representation and V^{p}_{S}/U^{p}_{S} correspond to the Young diagrams containing at most two rows/columns. The representations V^{p}_{S} and U^{p}_{S} are related according to $U^{p}_{S}(\mathscr{P}) = \varepsilon(\mathscr{P})V^{p}_{S}(\mathscr{P}^{-1})^{+}$ [17]. We assume that $\Psi^{\alpha}_{SM\lambda}$ form an orthonormal set. Then the representation matrices are orthogonal, i.e.

$$U^{p}_{S}(\mathscr{P}) = \varepsilon(\mathscr{P})V^{p}_{S}(\mathscr{P}). \tag{9}$$

Since using the occupation number rather than the coordinate representation appears to be more convenient, we introduce permutation operators $\mathscr{P}_{\sigma}/\mathscr{P}_{r}$ acting on the spin/orbital labels rather than on the corresponding electron coordinates. Taken into account that

$$\mathscr{P}_{r}\tilde{\mathscr{P}}_{r}\Psi^{\alpha}_{SM\lambda} = \mathscr{P}_{\sigma}\tilde{\mathscr{P}}_{\sigma}\Psi^{\alpha}_{SM\lambda} = \Psi^{\alpha}_{SM\lambda}, \tag{10}$$

the both kinds of the operators, when considered as elements of an abstract permutation group S_p, are related as

$$\mathscr{P}_{r} = \tilde{\mathscr{P}}^{-1}_{r}; \qquad \mathscr{P}_{\sigma} = \tilde{\mathscr{P}}^{-1}_{\sigma}. \tag{11}$$

The transformation properties of $\Psi^{\alpha}_{SM\lambda}$ expressed in Eq. (7) imply that

$$\mathscr{P}_{\sigma}B^{+}_{\alpha,SM\lambda} = \sum_{\mu=1}^{f(S,p)} V^{p}_{S}(\mathscr{P}^{-1})_{\mu\lambda}B^{+}_{\alpha,SM\mu}, \tag{12a}$$

$$\mathscr{P}_{r}B^{+}_{\alpha,SM\lambda} = \sum_{\mu=1}^{f(S,p)} U^{p}_{S}(\mathscr{P}^{-1})^{+}_{\mu\lambda}B^{+}_{\alpha,SM\mu}. \tag{12b}$$

Hereafter, wherever it does not lead to any confusion, we omit the subscripts r or σ in the symbols denoting permutation operators.

3 Symmetry-adapted p-RDOs

A primitive p-RDO is defined as [2, 13]:

$$ {}^{p}E^{i_1 i_2 \ldots i_p}_{a_1 a_2 \ldots a_p} = \sum_{\sigma_1 \sigma_2 \ldots \sigma_p} b^{+}_{i_1 \sigma_1} b^{+}_{i_2 \sigma_2} \ldots b^{+}_{i_p \sigma_p} b_{a_p \sigma_p} \ldots b_{a_2 \sigma_2} b_{a_1 \sigma_1}. \tag{13} $$

In particular, the 1-RDO:

$$ {}^{1}E^{i}_{a} = E_{ia} = \sum_{\sigma} b^{+}_{i\sigma} b_{a\sigma} \tag{14} $$

is the unitary group generator [6] also known as the replacement operator or the shift operator [3, 4]. If $i = a$ then E_{ii} is the orbital occupation number operator. Its eigenvalues $n_i = 0, 1, 2$ are the occupation number of the orbital i.

Then, according to [13]:

$$ {}^{p}E^{\alpha}_{\beta} = \sum_{\sigma_1 \sigma_2 \ldots \sigma_p} \bar{B}^{+}_{\alpha, \sigma_1 \sigma_2 \ldots \sigma_p} \bar{B}_{\beta, \sigma_1 \sigma_2 \ldots \sigma_p} \tag{15a} $$

$$ = \sum_{S = S_{\min}}^{p/2} \sum_{M = -S}^{S} \sum_{\lambda = 1}^{f(S,p)} B^{+}_{\alpha, SM\lambda} B_{\beta, SM\lambda} \tag{15b} $$

where $S_{\min} = 0$ if p is even and $S_{\min} = 1/2$ if p is odd. Equations (15) express the fact that for a given pair of the orbital index strings (α, β) the sets of all spin-adapted and of all non-adapted creation/annihilation operators span the same space.

The action of a permutation operator $\mathscr{P}$ on ${}^{p}E^{\alpha}_{\beta}$ is defined as:

$$ \mathscr{P}\, {}^{p}E^{\alpha}_{\beta} = {}^{p}E^{\mathscr{P}\alpha}_{\beta}. \tag{16a} $$

The Hermitean-conjugate equation reads:

$$ {}^{p}E^{\beta}_{\alpha}\, \mathscr{P}^{+} = {}^{p}E^{\beta}_{\mathscr{P}\alpha}. \tag{16b} $$

The symmetry-adapted p-RDO, following Kutzelnigg [2], is defined as:

$$ {}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]} = \mathbb{P}^{S}_{\mu\nu}\, {}^{p}E^{\alpha}_{\beta} \tag{17} $$

where:

$$ \mathbb{P}^{S}_{\mu\nu} = \frac{f(S,p)}{p!} \sum_{p \in S_p} U^{p}_{S}(\mathscr{P})_{\mu\nu} \mathscr{P}. \tag{18} $$

The operator $\mathbb{P}^{S}_{\mu\nu}$ is, in fact, a shift rather than a projection operator. If we used a projection operator:

$$ \mathbb{P}^{S}_{\mu} = \frac{f(S,p)}{p!} \sum_{\mathscr{P} \in S_p} U^{p}_{S}(\mathscr{P})_{\mu\mu} \mathscr{P} $$

instead, then:

$$ \mathbb{P}^{S}_{\mu}\, {}^{p}E^{\alpha}_{\beta} (\mathbb{P}^{S}_{\nu})^{+} = \delta_{\mu\nu}\, {}^{[S]}E^{\alpha[\mu]}_{\beta[\mu]} $$

where $(\mathbb{P}^{S}_{\nu})^{+}$ acts on the lower (β) indices. The last equation is a straightforward consequence of Eqs. (16) and of:

$$ {}^{p}E^{\mathscr{P}\alpha}_{\beta} = {}^{p}E^{\alpha}_{\mathscr{P}^{-1}\beta}. \tag{19} $$

Hence, although shift operators are not projection operators in the strict sense, they are more useful than the standard projection operators because they can be

used to build irreducible basis vectors from arbitrary vectors [18, 19], while projection operators do not have this property.

Substituting the primitive p-RDO in Eq. (17) by Eq. (15b) we can obtain another representation of the symmetry-adapted p-RDO. Making use of the orthogonality relation:

$$\frac{f(S,p)}{p!}\sum_{\mathscr{P}} U^p_S(\mathscr{P})_{\mu\nu} U^p_{S'}(\mathscr{P})_{\chi\lambda} = \delta_{SS'}\delta_{\mu\chi}\delta_{\nu\lambda} \tag{20}$$

and of Eqs. (12) we get:

$${}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]} = \sum_{M=-S}^{S} B^{+}_{\alpha,SM\mu} B_{\beta,SM\nu}. \tag{21}$$

Equation (21) may also be used as a definition of the symmetry-adapted p-RDO. It has a very straightforward physical meaning, expecially when combined with Eq. (15b). However, one has to remember that the p-RDOs act in the orbital space only. In particular, Eq. (21) should be interpreted in the sense of the spin-free formulation – the spin labels reflect the symmetry properties of the orbital-dependent operator.

Combining Eqs. (12), (15), and (21) we get another set of useful relations. The first one allows one to express the primitive RDOs in terms of symmetry-adapted ones:

$${}^{p}E^{\mathscr{P}\alpha}_{\beta} = \sum_{S=S_{\min}}^{p/2} \sum_{\mu,\nu=1}^{f(S,p)} U^p_S(\mathscr{P})_{\mu\nu}\, {}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]}. \tag{22}$$

The other equations determine transformation properties of the symmetry-adapted p-RDOs. In particular:

$$\mathscr{P}\,{}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]} = {}^{[S]}E^{\mathscr{P}\alpha[\mu]}_{\beta[\nu]} \tag{23a}$$

$$= \sum_{\lambda=1}^{f(S,p)} U^p_S(\mathscr{P})_{\lambda\mu}\, {}^{[S]}E^{\alpha[\lambda]}_{\beta[\nu]} \tag{23b}$$

and

$${}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]}\mathscr{P}^{+} = {}^{[S]}E^{\alpha[\mu]}_{\mathscr{P}\beta[\nu]} \tag{23c}$$

$$= \sum_{\lambda=1}^{f(S,p)} U^p_S(\mathscr{P})^{+}_{\lambda\nu}\, {}^{[S]}E^{\alpha[\mu]}_{\beta[\lambda]}. \tag{23d}$$

Finally, Eq. (22) may be rewritten in a simple form as:

$${}^{p}E^{\mathscr{P}\alpha}_{\beta} = \sum_{S=S_{\min}}^{p/2} \sum_{\nu=1}^{f(S,p)} {}^{[S]}E^{\mathscr{P}\alpha[\nu]}_{\beta[\nu]}. \tag{24}$$

4 Products of p-RDOs

One of the most important tasks in the theory of p-RDOs is expressing their products in terms of single p-RDOs [2, 13]. In the case when a symmetry-adapted p-RDO is multiplied by a primitive 1-RDO, we first apply Eqs. (13), (14), and (17) in order to express E^i_a and ${}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]}$ in terms of the creation and annihilation operators. Then the standard commutation rules are applied.

Finally using the appropriate Clebsh–Gordan expansion (an analog of Eq. (3)), we obtain:

$$
\begin{aligned}
{}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]}E^{i}_{a} = \delta(i \in \beta)\{{}^{[S]}E^{\alpha[\mu]}_{\beta(a\to i)[\nu]} + {}^{[S]}E^{\alpha[\mu]}_{\beta(a\to i')[\nu]}\} \\
+ {}^{[S+1/2]}E^{\alpha i[\mu']}_{\beta a[\nu']} + {}^{[S-1/2]}E^{\alpha i[\mu'']}_{\beta a[\nu'']}
\end{aligned}
\tag{25}
$$

where

$$
\delta(i \in \beta) = \begin{cases} 1, & \text{if } i \text{ appears in } \beta \\ 0, & \text{otherwise} \end{cases}, \tag{26}
$$

$\beta(a \to i)$ means that index i has been replaced in β by a (the second term, with $\beta(a \to i')$ replacement, is present only if index i appears twice in β) and $\alpha i/\beta a$ mean that the strings α/β have been appended by i/a. Values of the counting indices μ', ν' (μ'', ν'') depend upon the adopted convention in defining basis for the pertinent irreducible representation. Let us note that the orbital indices in Eq. (25) appear in a specific order: in $[S \pm 1/2]$ operators the indices i and a are put at the end of α and β strings respectively and in $[S]$ operator index a replaces i in the β string. If another sequence of the indices is required, Eqs. (23) may be applied.

The second-order primitive RDOs are related to the first-order ones by a simple relation [1]:

$$
E^{ij}_{ab} = E^{i}_{a}E^{j}_{b} - \delta_{ja}E^{i}_{b}. \tag{27}
$$

Then, the corresponding formula for the appropriate products of the symmetry-adapted p-RDOs and the primitive 2-RDOs may be readily obtained by a twofold application of Eq. (25). The same holds, of course, for the higher-order primitive RDOs.

Equation (25) may be written in a more compact way as:

$$
{}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]}E^{i}_{a} = \delta(i \in \beta)\,{}^{[S]}E^{\alpha[\mu]}_{\beta\{a\to i\}[\nu]} + {}^{[S\otimes 1/2]}E^{\alpha i[\mu']}_{\beta a[\nu']}, \tag{28}
$$

where $\{a \to i\}$ means that terms corresponding to all possible replacements of i by a must be included (in this case the number of terms is equal to the occupation number of i in β; cf. Eq. (25)), and $[S \otimes 1/2]$ is a shorthand designation for the sum of $[S + 1/2]$ and $[S - 1/2]$ operators. Using this notation one can easily express products involving higher-order primitive p-RDOs. For $p = 2$ we have:

$$
\begin{aligned}
{}^{[S]}E^{\alpha[\mu]}_{\beta[\nu]}E^{ij}_{ab} = \delta(i \in \beta)\delta(j \in \beta)\,{}^{[S]}E^{\alpha[\mu]}_{\beta\{a\to i,\, b\to j\}[\nu]} \\
+ \delta(i \in \beta)\,{}^{[S\otimes 1/2]}E^{\alpha j[\mu']}_{\beta\{a\to i\}b[\nu']} + \delta(j \in \beta)\,{}^{[S\otimes 1/2]}E^{\alpha i[\mu'']}_{\beta\{b\to j\}a[\nu'']} \\
+ {}^{[S\otimes(1\oplus 0)]}E^{\alpha ij[\mu''']}_{\beta ab[\nu''']}
\end{aligned}
\tag{29}
$$

where obvious generalizations of the previously defined symbols have been used. It is worthwhile to stress some very close structural similarity of Eqs. (25), (28), and (29) to the generalized Wick theorem for the primitive p-RDOs [2, 13]. In fact, the building principle expressed by these equations may be considered as another version of the generalized Wick theorem.

5 Matrix elements of p-RDOs

Several efficient algorithms of evaluation matrix elements of non-adapted one- and two-body RDOs are available, within frameworks of both unitary group

[1, 6] and symmetric group [3, 20] approaches. A recently proposed method of constructing the symmetry adapted p-th order reduced density matrices [2] took an advantage of these algorithms. In essence, the method consists of the following steps:

(1) Expressing the symmetry adapted p-RDOs in terms of the primitive p-RDOs (using, e.g., Eq. (17)).

(2) Reducing the p-RDO matrix elements of p-RDOs in the 1-RDO and 2-RDO ones (using p-particle generalizations of Eq. (27)).

(3) Applying the standard algorithms to calculate the matrix elements of 1-RDOs and 2-RDOs.

In this section equations for direct evaluation of the p-RDO matrix elements are presented. Since the symmetry-adapted p-RDOs transform according to irreducible representations of S_p, we found the symmetric group approach to be most appropriate for deriving the formulas. The strings of N orbital labels in the standard order are denoted Λ, Γ, Ω. The same strings in non-standard orders are denoted $\Lambda', \Gamma', \Omega', \Lambda'', \Gamma'', \Omega''$, etc. In this section we allow some indices in the orbital label strings to appear twice. The repeated indices are referred to as *doubles* and their number in a given string is denoted d.

5.1 Primitive p-RDOs

Let E_i^j be a 1-RDO which does not affect the doubles in Γ and let us consider $i \neq j$. Then:

$$E_i^j|\Gamma; SM\gamma\rangle = \begin{cases} |\Lambda'; SM\gamma\rangle, & \text{if } i \in \Gamma \text{ and } n_j \neq 2 \\ 0, & \text{otherwise.} \end{cases} \tag{30}$$

If $\mathscr{P}$ is the permutation operator which acting on the orbital labels transform Λ' into Λ then, for $i \in \Gamma$ and $n_j \neq 2$, due to Eqs. (12):

$$E_i^j|\Gamma; SM\gamma\rangle = |\mathscr{P}^{-1}\Lambda; SM\gamma\rangle \tag{31}$$

$$= \sum_{\lambda}^{f(S,N)} U_S^N(\mathscr{P})_{\gamma\lambda}|\Lambda; SM\lambda\rangle. \tag{32}$$

Therefore:

$$\langle\Omega; SM\omega|E_i^j|\Gamma; SM\gamma\rangle = U_S^N(\mathscr{P})_{\gamma\omega}\delta_{\Lambda\Omega}\delta(i \in \Gamma). \tag{33}$$

If E_i^j changes the number of doubles in Γ or if $i = j$, then the normalization factor in the resulting vector changes. For example, in the case of a two-electron singlet:

$$E_i^j B_{(ii)00}^+ = 2^{1/2} B_{(ij)00}^+$$

$$E_i^j B_{(ij)00}^+ = 2^{1/2} B_{(jj)00}^+$$

$$E_i^i B_{(ii)00}^+ = 2 B_{(ii)00}^+.$$

In a general case, whenever E_i^j either creates or destroys a double, a factor $2^{1/2}$ appears (the case of E_i^i may be interpreted as a destruction and a subsequent creation of the same double, leading to the factor $2^{1/2} \cdot 2^{1/2}$). Then, Eq. (33) in a general case of 1-RDOs reads:

$$\langle\Omega; SM\omega|E_i^j|\Gamma; SM\gamma\rangle = 2^{\Delta d/2} U_S^N(\mathscr{P})_{\gamma\omega}\delta_{\Lambda\Omega}\delta(i \in \Gamma) \tag{34}$$

where $\Delta d = 0, 1, 2$ says how many times a double has been either created or annihilated.

Let us generalize the above result to the case of a primitive p-RDO, $p \leqslant N$. Similar reasoning leads to the following equation:

$$ {}^{p}E^{\alpha}_{\beta}|\Gamma; SM\gamma\rangle = 2^{\Delta d/2}|\mathscr{P}^{-1}\Lambda; SM\gamma\rangle\delta(\beta \in \Gamma) \tag{35} $$

where Δd, Λ, and $\mathscr{P}$ are the appropriate generalizations of the quantities already defined. The right-hand side of Eq. (35) vanishes if any of the resulting occupation numbers in Λ violates the Pauli principle (is greater than 2). Hence, the corresponding matrix element may be written as:

$$ \langle\Omega; SM\omega|{}^{p}E^{\alpha}_{\beta}|\Gamma; SM\gamma\rangle = 2^{\Delta d/2}U^{N}_{S}(\mathscr{P})_{\gamma\omega}\delta_{\Lambda\Omega}\delta(\beta \in \Gamma). \tag{36} $$

5.2 Symmetry-adapted p-RDOs

In order to calculate matrix elements of the symmetry-adapted p-RDOs, let us start with the following lemma ([19], Chap. 7-7):

> If $\mathscr{R} \in S_p$, $p \leqslant N$, i.e., if $\mathscr{R}$ does not affect the last $(N-p)$ orbital labels in a string of N labels, then the matrices $U^{N}_{S}(\mathscr{R})$ are the direct sums of $U^{p}_{T}(\mathscr{R})$.

We can choose the representation so that $U^{N}_{S}(\mathscr{R})$ is in explicit reduced (block diagonal) form. Let $n(T, S)$ be the number of times $U^{p}_{T}(\mathscr{R})$ occurs in $U^{N}_{S}(\mathscr{R})$ and let $\{i_1, i_2, \ldots, i_n\}$ be the addresses of the $U^{p}_{T}(\mathscr{R})$ blocks in $U^{N}_{S}(\mathscr{R})$ so that:

$$ U^{N}_{S}(\mathscr{R})_{a+j,a+k} = U^{p}_{T}(\mathscr{R})_{j,k} \quad \text{if } a = i_1, i_2, \ldots, i_n \text{ and } j, k = 1, 2, \ldots, f(T, p). \tag{37} $$

Then, according to the orthogonality theorem:

$$ \frac{f(T,p)}{p!}\sum_{\mathscr{R}\in S_p} U^{p}_{T}(\mathscr{R})_{jk}U^{N}_{S}(\mathscr{R})_{lm} = \sum_{q=i_1}^{i_n}\delta_{j,l-q}\delta_{k,m-q}. \tag{38} $$

The vector ${}^{p}E^{\mathscr{R}\alpha}_{\beta}|\Gamma; SM\gamma\rangle = {}^{p}E^{\alpha}_{\mathscr{R}^{-1}\beta}|\Gamma; SM\gamma\rangle$ vanishes, unless Γ contains all the orbitals which appear in the β string. Let $\mathscr{Q}^{-1}$ be a permutation which reorders Γ in such a way that the first p labels of the resulting string Γ' coincide with β. The Pauli principle implies that:

$$ \mathscr{Q}^{-1}|\Gamma; SM\gamma\rangle = \varepsilon(\mathscr{Q})|\Gamma; SM\gamma\rangle = |\Gamma'; \mathscr{Q}^{-1}SM\gamma\rangle. \tag{39} $$

Then we have

$$ {}^{p}E^{\mathscr{R}\alpha}_{\beta}|\Gamma; SM\gamma\rangle = \varepsilon(\mathscr{Q}){}^{p}E^{\mathscr{R}\alpha}_{\beta}|\Gamma'; \mathscr{Q}^{-1}SM\gamma\rangle. \tag{40a} $$

The last equation can be rewritten as:

$$ = \varepsilon(\mathscr{Q}){}^{p}E^{\alpha}_{\beta}|\mathscr{R}\Gamma'; \mathscr{Q}^{-1}SM\gamma\rangle \tag{40b} $$

$$ = \sum_{\lambda,\omega}^{f(S,N)} U^{N}_{S}(\mathscr{R})_{\lambda\omega}U^{N}_{S}(\mathscr{Q})_{\omega\gamma}{}^{p}E^{\alpha}_{\beta}|\Gamma'; SM\lambda\rangle. \tag{41} $$

In Eqs. (40), (41) the permutation $\mathscr{Q} \in S_N$ while $\mathscr{R} \in S_p \subset S_N$. When acting on α, $\mathscr{R} \in S_p$ while acting on Γ', $\mathscr{R} \in S_N$. However, the operator $\mathscr{R}$ acts on the first p labels of Γ' only.

Multiplying the last equation by $(f(T,p)/p!)U^p_T(\mathscr{R})_{\mu\nu}$, summing over all $\mathscr{R} \in S_p$, and using Eqs. (38), (17) and (18), we get:

$$ {}^{[T]}E^{\alpha[\mu]}_{\beta[\nu]}|\Gamma; SM\gamma\rangle = \sum_{q=i_1}^{i_n} U^N_S(\mathscr{Q})_{\nu+q,\gamma}\, {}^pE^{\alpha}_{\beta}|\Gamma'; SM, \mu+q\rangle. \tag{42} $$

Finally, the matrix element of a symmetry-adapted p-RDO may be expressed in terms of the corresponding matrix elements of the primitive p-RDOs as:

$$ \langle \Omega; SM\omega|{}^{[T]}E^{\alpha[\mu]}_{\beta[\nu]}|\Gamma; SM\gamma\rangle = \sum_{q=i_1}^{i_n} U^N_S(\mathscr{Q})_{\nu+q,\gamma}\langle \Omega; SM\omega|{}^pE^{\alpha}_{\beta}|\Gamma'; SM, \mu+q\rangle. \tag{43} $$

By substitution of Eq. (36) for the primitive p-RDO matrix element, Eq. (43) obtains a more symmetric form:

$$ \langle \Omega; SM\omega|{}^{[T]}E^{\alpha[\mu]}_{\beta[\nu]}|\Gamma; SM\gamma\rangle $$

$$ = 2^{\Delta d/2}\delta(\alpha \in \Omega)\delta(\beta \in \Gamma)\delta(\Omega - \alpha, \Gamma - \beta) \sum_{q=i_1}^{i_n} U^N_S(\mathscr{P})^{+}_{\omega,\mu+q} U^N_S(\mathscr{Q})_{\nu+q,\gamma} \tag{44} $$

where $\Omega - \alpha/\Gamma - \beta$ stand for the orbital label strings obtained by removing α/β strings from Ω/Γ. The operator $\mathscr{P}$ has been defined in Eq. (35) by considering the effect of action of an RDO on a vector. Here the operators $\mathscr{P}$ and $\mathscr{Q}$ play analogous role with respect to Ω, α and Γ, β strings, respectively.

6 Concluding remarks

The matrix elements of p-RDOs are equal to the p-th-order density or transition matrix elements, i.e., to the coupling coefficients in general expressions for the matrices representing p-particle operators in N-fermion spin-adapted model spaces constructed from products of orthonormal orbitals. In these spaces most of methods of approximate solving the Schrödinger equation are defined. Therefore the results of this paper may be applied in many methods used in quantum chemistry. Also relations between different kinds of p-RDOs and between their different representations (cf. Eqs. (15), (17), (21), (22), (28), (29)) may be useful in both transforming specific equations met in the methods mentioned above and in designing new methods.

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