Clifford algebra and unitary group formulations of the many-electron problem[*]

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An essential role of Clifford algebras for quantum-chemical finite-dimensional orbital models of many-electron systems is pointed out. The relationship between Clifford algebra matric units, the generators of the unitary group approach (UGA) and the higher order replacement or excitation operators, as well as between their first and second quantized realizations, is elucidated. The usefulness of higher order replacement operators in the spin-adaptation of various many-body theories is briefly outlined and illustrated on the orthogonally spin-adapted coupled-pair approach. A natural connection with the Clifford algebra UGA is explored and new possibilities for its exploitation in large scale configuration interaction calculations are suggested.

Key words: Many-electron correlation problem — Spin-adaption — Unitary group approach — Coupled-pair approach — Configuration interaction

1. Introduction

On the occasion of his 65th anniversary, we dedicate this paper to Professor Jaroslav Koutecký, who, in addition to his numerous pioneering contributions

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to theoretical electrochemistry, surface science and the theory of the chemical bond, was one of the first quantum chemists to formulate a second-quantization-like formalism [1], specific for the particle-number conserving systems. Following Matsen [2], Koutecký and Laforgue [1] call the relevant operators – which can also be viewed as unitary group generators – the basic symmetry operators or BSOs, employ their first and second quantized forms and consider their extension to nonorthogonal bases. Later, a similar formalism was also exploited in a general study of alternant systems [3] and biradicaloids [4, 5].

The realization of the importance of unitary or general linear groups for particle-number conserving systems can be traced back to the pioneering days of quantum mechanics [6]. It was not, however, till the late sixties and early seventies that the unitary group was exploited in the shell model description of nuclei [7], atoms [8] and molecules [2, 9–12] as a dynamical group[1] [13, 14]. In such a role it enables an automatic spin-adaptation of the theory by exploiting the chain

$$U(2n) \supset U(n) \otimes U(2),$$

for systems with spin-independent Hamiltonian, given as a bilinear form in terms of $U(n)$ generators. The exploitation of this formalism became particularly widespread after the realization that a rather complex $U(n)$ representation theory [16] can be drastically simplified in the many-electron case [12, 17]. This formalism became known as the unitary group approach (UGA)[2] to the many-electron correlation problem [12, 17–19], and has primarily been exploited in large scale configuration interaction (CI) calculations [20]. The interested reader can consult numerous reviews [17, 21–24] or monographs [25–27] dealing with this topic.

Recently, UGA was further extended through an embedding of $U(n)$ in a much larger unitary group $U(2^n)$ [15, 28]. This approach has been named the Clifford algebra UGA (CAUGA) in view of the key role played by the related Clifford algebra spinorial basis, which enables the representation of relevant N-electron spin-adapted states as linear combinations of totally symmetric two-box Weyl tableaux of $U(2^n)$. Since the $U(n)$ generators may be simply related with those of $U(2^n)$ [29], the action of any particle-number conserving operator (which is expressible in terms of $U(n)$ generators) in this basis is trivially determined. CAUGA seems to be also easily amenable to many-electron system partitioning [28] (for UGA system partitioning see [30]).

In this paper we wish to show that the operators considered by Koutecký and Laforgue [1] appear naturally in UGA and CAUGA descriptions, and may also

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[1]   A unitary group is not a symmetry (invariance, degeneracy) group of a general many-fermion system but rather – loosely speaking – its dynamical or noninvariance group [13, 14]. The latter, or the related spectrum generating algebra, are required to contain all the bound states in a single irreducible representation (irrep). In this sense, it is rather the larger group $U(2^n)$ of the Clifford algebra unitary group approach (CAUGA) [15], which plays this role, since all the possible multiplets are then contained in a single irrep of this group

[2]   Or GUGA (graphical UGA), emphasizing the graphical representation of the electronic Gel'fand–Tsetlin basis, which was introduced by Shavitt [18]

be generalized to higher than one- and two-particle operators, if desired. In particular we wish

(i) to stress the basic importance of Clifford algebras for many-fermion systems,

(ii) to elucidate the relationship between the first and second quantized realizations of $U(n)$ and $U(2^n)$ generators,

(iii) to point out the usefulness of higher-order analogues of $U(n)$ generators for various many-body theories, in particular for their spin adaptation, which we will illustrate for the coupled-cluster theory and, finally,

(iv) to outline some new possibilities of CAUGA in large scale CI calculations.

2. The first and second quantization formalisms

We shall consider an N-electron, n-level model system described by a spin-independent, particle-number conserving Hamiltonian H. In the usual wavefunction description, sometimes referred to as the first-quantization formalism, the appropriate space in which H acts is given by the antisymmetrized Nth tensor power of a one-electron space V_{2n} spanned by $2n$ orthonormal spinorbitals $|I\rangle$, $I = 1, \ldots, 2n$.

In the second quantized description one associates with each spinorbital $|I\rangle$ an annihilation operator X_I as well as a corresponding creation operator $X_I^\dagger$, given by the Hermitean conjugate of X_I, as the notation implies. These operators act in the appropriate Fock space $\mathscr{F}$ and satisfy the anticommutation relations

$$\{X_I, X_J\} = \{X_I^\dagger, X_J^\dagger\} = 0, \{X_I, X_J^\dagger\} = \delta_{IJ}, \tag{1}$$

where the anticommutator $\{A, B\}$ is defined as

$$\{A, B\} = AB + BA, \tag{2}$$

as well as the so called vacuum property

$$X_I|0\rangle = 0, \qquad\qquad (\forall I) \quad (3)$$

where $|0\rangle$ represents the physical (true) vacuum. We also define the corresponding number operators N_I in the usual way,

$$N_I = X_I^\dagger X_I, \tag{4}$$

as well as their complements $\bar{N}_I$,

$$\bar{N}_I = 1 - N_I = X_I X_I^\dagger. \tag{5}$$

We note that these operators form a system of mutually commuting Hermitean idempotents (projectors), namely

$$N_I^2 = N_I, \ \bar{N}_I^2 = \bar{N}_I, \ N_I^\dagger = N_I, \ \bar{N}_I^\dagger = \bar{N}_I, \tag{6}$$

$$[N_I, N_J] = [\bar{N}_I, \bar{N}_J] = [N_I, \bar{N}_J] = 0, \tag{7}$$

where

$$[A, B] = AB - BA.$$

Moreover,

$$N_I \bar{N}_I = 0, \qquad\qquad\qquad\qquad (\forall I). \quad (8)$$

The number operators (4) and (5) can be used in turn to define the following compound projectors

$$e_{\{I\}} \equiv e_{I_1 I_2 \cdots I_r} := N_{I_1} N_{I_2} \cdots N_{I_r} \bar{N}_{I_{r+1}} \cdots \bar{N}_{I_{2n}}, \qquad (9)$$

where $(I_1 I_2 \cdots I_{2n})$ is a permutation of $(12 \cdots (2n))$. We use curly braces for the set $\{I\}$ to emphasize the symmetric nature of the product involved, Eq. (9). If the set $\{I\}$ is empty, we have

$$e_{\{0\}} \equiv e_0 = \bar{N}_1 \cdots \bar{N}_{2n}. \qquad\qquad\qquad (10)$$

We easily find that

$$e_{\{I\}}^2 = e_{\{I\}}, e_{\{I\}}^\dagger = e_{\{I\}} \qquad\qquad\qquad (11)$$

and

$$e_{\{I\}} e_{\{J\}} = \delta_{\{I\},\{J\}} e_{\{I\}}. \qquad\qquad\qquad (12)$$

These orthognal projectors provide the resolution of identity, since

$$\sum_I e_{\{I\}} = \prod_{J=1}^{2n} (N_J + \bar{N}_J) = e. \qquad\qquad (13)$$

3. Clifford algebras

We recall that a Clifford algebra C_m is an *associative* algebra generated by the Clifford numbers α_i satisfying the anticommutation relations

$$\{\alpha_i, \alpha_j\} = 2\delta_{ij}, \qquad (i, j = 1, \ldots, m). \qquad (14)$$

A general monomial in C_m is a product of Clifford numbers $\alpha_1^{\nu_1} \alpha_2^{\nu_2} \cdots \alpha_m^{\nu_m}$ with $\nu_i = 0$ or 1 since, in view of Eq. (14), $\alpha_i^2 = 1$. We can thus establish a one-to-one correspondence between these monomials and binary strings $\{\nu_1 \nu_2 \cdots \nu_m\}$, so that $\dim C_m = 2^m$.

It is now easy to see that the fermionic algebra, defined by the second quantization creation and annihilation operators, Eqs. (1)–(3), is isomorphic with the Clifford algebra C_{4n}. Indeed, we find easily that the following linear combinations

$$\begin{aligned} \alpha_I &= X_I + X_I^\dagger, \qquad (I = 1, \ldots 2n) \\ \alpha_{I+2n} &= i(X_I - X_I^\dagger), \end{aligned} \qquad (15)$$

satisfy the relations (14) for Clifford numbers. Conversely, we have that

$$\begin{aligned} X_I &= \tfrac{1}{2}(\alpha_I - i\alpha_{I+2n}), \\ X_I^\dagger &= \tfrac{1}{2}(\alpha_I + i\alpha_{I+2n}). \end{aligned} \qquad (16)$$

We can also easily construct a matric basis for this algebra [31]. For this purpose we introduce the following notation for arbitrary products of the creation and corresponding annihilation operators,

$$X^\dagger_{[I]} = X^\dagger_{I_1} X^\dagger_{I_2} \cdots X^\dagger_{I_r},$$
$$X_{[I]} = X_{I_r} \cdots X_{I_2} X_{I_1},$$

(17)

where $[I]$ designates[3] the ordered set $\{I_1, I_2, \ldots, I_r\}$, $I_1 < I_2 < \cdots < I_r$. Note that $X^\dagger_{[I]}$ is again the Hermitean conjugate of $X_{[I]}$. It can be easily shown that

$$X_{[I]} e_0 = e_0 X^\dagger_{[I]} = 0,$$

(18)

which implies that

$$e_0 X_{[I]} X^\dagger_{[J]} e_0 = \delta_{[I],[J]} e_0.$$

(19)

We can thus define the matric units by

$$e_{[I][J]} = X^\dagger_{[I]} e_0 X_{[J]}.$$

(20)

Using Eq. (19) we see immediately that indeed

$$e_{[I][J]} e_{[K][L]} = \delta_{[J][K]} e_{[I][L]}.$$

(21)

We note also that

$$e_{\{I\}} = e_{[I][I]},$$

(22)

since

$$[\bar{N}_I, X_J] = \delta_{IJ} X_J,$$

(23)

so that

$$e = \sum_{[I]} e_{[I][I]}.$$

(24)

4. The relationship between the first and the second quantization formalisms

The projector $e_0 \equiv e_{\{0\}}$, Eq. (10), associated with the empty set $\{0\} \equiv \varnothing$, projects onto the true vacuum state $|0\rangle$, so that clearly

$$e_0 |0\rangle = |0\rangle \quad \text{and} \quad \langle 0| e_0 = \langle 0|,$$

(25)

while any other state containing at least a single particle, e.g. $|[\cdots I_k \cdots]\rangle$, where

$$|[I]\rangle \equiv |[I_1 I_2 \cdots I_r]\rangle = X^\dagger_{I_1} X^\dagger_{I_2} \cdots X^\dagger_{I_r} |0\rangle = X^\dagger_{[I]} |0\rangle$$

(26)

is annihilated, i.e.

$$e_0 |[\cdots I_k \cdots]\rangle = 0 = \langle [\cdots I_k \cdots]| e_0.$$

(27)

We can thus identify this operator with the ket–bra vacuum product,

$$e_0 = |0\rangle\langle 0|,$$

(28)

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[3]   We now enclose I in square brackets to emphasize the antisymmetric nature of these products

so that

$$e_{[I][J]} = X^{\dagger}_{[I]}|0\rangle\langle 0|X_{[J]} = |[I]\rangle\langle[J]|. \tag{29}$$

We can distinguish the particle-number conserving operators $e_{[J][K]}$, when both sets $[J]$ and $[K]$ have the same cardinality, from the particle-number non-conserving ones, which transform between the subspaces with different particle numbers. Further, the set of particle-number conserving operators can be divided into $(2n+1)$ subsets according to different cardinalities of $[I]$ and $[J]$ in (29). We see immediately from the product property, Eq. (21), that any such subset is closed under multiplication and, hence, forms a subalgebra of C_{4n}. In particular, when the cardinality is one, so that we can make an identification $[I] = I$ and $[J] = J$, we obtain the set of operators

$$e_{IJ} = |I\rangle\langle J|, \tag{30}$$

which multiply in exactly the same way as the usual matric units, i.e.

$$e_{IJ}e_{KL} = \delta_{JK}e_{IL}. \tag{31}$$

It is well known that any associative algebra can be turned into a Lie algebra by defining the Lie product as a commutator. In the present case this gives

$$[e_{[I][J]}, e_{[K][L]}] = \delta_{[J][K]}e_{[I][L]} - \delta_{[L][I]}e_{[K][J]}, \tag{32}$$

which is isomorphic with the Lie algebra of $U(2^{2n})$ or, in the orbital case (see below), $U(2^n)$, i.e. the group exploited by CAUGA. Clearly, Lie-algebraizing the one-particle subalgebra spanned by the operators (30), we get the Lie algebra of $U(2n)$, which is exploited in UGA.

In the second quantization formulation we realize normally the $U(2n)$ generators by

$$e^I_J = X^{\dagger}_I X_J. \tag{33}$$

From now on we shall also consider the corresponding orbital generators given as partial traces of the generators (33). Writing the spinorbitals $|I\rangle$ as products of orbital and spin kets, $|I\rangle = |i\rangle|\mu\rangle$, we thus define

$$E^i_j = \sum_{\mu} e^{i\mu}_{j\mu} = X^{\dagger}_{i\alpha}X_{j\alpha} + X^{\dagger}_{i\beta}X_{j\beta}, \qquad (i, j = 1, \ldots, n). \tag{34}$$

These operators can be regarded as unitary group generators since they satisfy the commutation relations

$$[e^I_J, e^K_L] = \delta^K_J e^I_L - \delta^I_L e^K_J, \tag{35}$$

and similarly for the orbital group generators E^i_j. However, they no longer form an associative algebra, since

$$e^I_J e^K_L = e^{IK}_{JL} + \delta^K_J e^I_L, \tag{36}$$

where

$$e^{IK}_{JL} = X^{\dagger}_I X^{\dagger}_K X_L X_J \tag{37}$$

cannot be represented as a linear combination of e_J^I operators. The relationship (36) must be compared with the corresponding one given by Eq. (31). Clearly, both operator sets span isomorphic Lie algebras of $U(2n)$ but only the latter one also forms a corresponding associative algebra.

It should be pointed out, however, that for many applications the operators e_{IJ} [or, generally, the matric units of Eq. (20)] are not very convenient because of their high particle rank. By the particle rank of a particle-number conserving operator we understand, as usually, the number of creation-annihilation pairs that enter its second-quantized representation. Using Eqs. (10) and (20) we can easily verify that e_{IJ} is a $(2n-1)$-particle operator when $I \neq J$ and a $(2n)$-particle operator when $I = J$, while the particle rank of $e_{IK,JL}$ is $(2n-2)$, $(2n-1)$ or $2n$, depending on how many of the indices I, K, J, L are different. On the other hand, e_J^I or e_{JL}^{IK} are one- and two-particle operators, respectively. Being of such a low particle rank, these operators have proved to be particularly useful in various many-body theories, most notably in the coupled-cluster theory [32]. In fact, it is the possibility to generate higher rank operators as products of lower rank operators, as is exemplified in Eq. (36), that underlies one of the most powerful tools of the many-body theory: the exponential cluster ansatz [32–34].

To generalize definitions (33) and (37) to an arbitrary particle rank, we set

$$e_{[J]}^{[I]} = X_{[I]}^{\dagger} X_{[J]}, \tag{38}$$

which differs from Eq. (20) only in the absence of the vacuum projector between the strings of the creation and annihilation operators. The operators (38) will be referred to as the *spinorbital replacement operators*, since their action consists in replacing the spinorbitals from the set $[J]$ by the spinorbitals from the set $[I]$ in all the Fock space vectors on which $E_{[J]}^{[I]}$ acts. The operators $e_{[I][J]}$ performs essentially the same task, but only for one basis vector $|[J]\rangle$ from the Fock space, giving zero result when acting on all other basis vectors of the form (26).

Expanding Eq. (20) and solving recursively for $e_{[J]}^{[I]}$ (starting with $2n$-particle operators), we can easily verify that spinorbital replacement operators can be represented as follows

$$e_{[J]}^{[I]} = e_{[I][J]} + \sum_{I_1}{}' e_{[II_1][JI_1]} + \sum_{I_1 < I_2}{}' e_{[II_1I_2][JI_1I_2]} + \dots, \tag{39}$$

where the prime indicates that the summation extends over all spinorbitals not included in $[I]$ or $[J]$. All terms in Eq. (39) have the same sign, since the running indices I_1, I_2, $\dots$ are placed at the end of $[I]$ or $[J]$ indices, so that the combined indices $[II_1]$, $[JI_1]$, etc. are not properly ordered[4]. When the combined indices are brought to the natural order, each term in Eq. (39) must be multiplied by the sign of the permutation needed to perform the ordering.

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[4] Note that in Eq. (39) we do not require the sets $[II_1]$, $[II_1I_2]$, $\dots$, etc. to be ordered so that the generators $e_{[I\dots][J\dots]}$ are defined by generalizing Eqs. (29) and (26) to unordered spinorbital sets. Clearly, they will differ at most by a phase factor from the corresponding operators with ordered sets, Eq. (29)

Equation (39) and inverse equation expressing $e_{[I][J]}$ in terms of $e_{[J]}^{[I]}$ (i.e. Eq. (20)) show that the replacement operators constitute another basis of the Lie algebra of $U(2^{2n})$. Since the matrix transforming one of these basis sets into another is not unitary, the commutators of $e_{[J]}^{[I]}$ are not as simple as those of $e_{[I][J]}$, Eq. (32). In fact, only the set of one-particle operators e_J^I is closed under commutation. These operators form a basis for the Lie algebra of the $U(2n)$ group embedded into $U(2^{2n})$ via $SO(4n+1)$ [15]. Thus, Eq. (39) gives an important relationship between the $U(2n)$ and $U(2^{2n})$ generators, exploited in the development of CAUGA [15].

It is worthwhile to remark that the set of two-particle operators e_{JL}^{IK} is not closed under commutation (since the commutator of two two-particle operators is in general a three-particle operator). This unpleasant fact considerably complicates the many-body theory beyond the one-particle approximation.

There exists another relationship between the matric units $e_{[I][J]}$ and the replacement operators $e_{[J]}^{[I]}$, which is particularly important for the first-quantized applications [35]. Denoting by $A\!\upharpoonright\!\mathscr{F}_N$ the restriction of an arbitrary operator A to the N-electron layer of the Fock space $\mathscr{F}$ and assuming that the cardinality of $[I]$ and $[J]$ is k, we can write

$$e_{[J]}^{[I]}\!\upharpoonright\!\mathscr{F}_N = 0 \quad \text{for } N < k,$$

and

$$e_{[J]}^{[I]}\!\upharpoonright\!\mathscr{F}_N = \sum_{i_1 < \cdots < i_k}^{N} e_{[I][J]}(i_1 \cdots i_k) \quad \text{for } N \geq k, \tag{40}$$

where the operator $e_{[I][J]}(i_1 \cdots i_k)$, now acting only on the coordinates of electrons $i_1, \ldots, i_k$, can be represented as the integral operator with the kernel $\phi_{[I]}(i_1 \cdots i_k)\phi_{[J]}^*(i_1' \cdots i_k')$. The functions $\phi_{[I]}$ and $\phi_{[J]}$ are the first-quantized representatives (Slater determinants) of the state vectors $|[I]\rangle$ and $|[J]\rangle$ and i_k denotes here the set of spatial *and* spin coordinates of the electron i_k. In Eq. (40) we assume that when $e_{[I][J]}(i_1 \cdots i_k)$ acts on a function ψ of N variables, then ψ is treated as a function of k variables $i_1 \cdots i_k$, all other variables being kept fixed. Otherwise $e_{[I][J]}\psi$ would vanish for $k \neq N$.

Still another, somewhat less explicit relation between the basis of Eq. (38) and the matric units of Eq. (20), has been studied in detail by Moshinsky and Quesne [36]. Using the states (26), $r = 0, 1, \ldots, 2n$ as a basis of the 2^{2n}-dimensional carrier space for the fundamental representation of $U(2^{2n})$, it is easy to see that the operators (38) yield "almost" the 2^{2n}-dimensional matric units. We note here that a convenient ordering of the states (26) can be achieved by interpreting their occupation number $m_1, \ldots, m_{2n}$, where $m_i = 0$, 1, as binary numbers $(m_1 \cdots m_{2n})_2$, as is the case in CAUGA [15, 28] (see also Sect. 7). For the present purposes, however, it is sufficient to consider groups of states $|[I_1, \ldots, I_r]\rangle$, having the same total occupancy $r = \sum_i m_i$. Assuming, thus, that the states (26) are ordered according to the increasing particle number, we find easily that the general matrix

representative $\|\langle[K]|e_{[J]}^{[I]}|[L]\rangle\|$, where $[I] = [I_1, \ldots, I_r]$, $[J] = [J_1, \ldots, J_{r'}]$, $[K] = [K_1, \ldots, K_p]$ and $[L] = [L_1, \ldots, L_{p'}]$, has the form [36]

$$
\begin{array}{c}
\begin{array}{ccc} p' < r' & p' = r' & p' > r' \end{array} \\
\begin{array}{c} p < r \\ p = r \\ p > r \end{array}
\left\|
\begin{array}{c|c|c}
\mathbf{0} & \mathbf{0} & \mathbf{0} \\
\hline
\mathbf{0} & \delta_{[I],[J]} & \mathbf{0} \\
\hline
\mathbf{0} & \mathbf{0} & f
\end{array}
\right\|,
\end{array}
\tag{41}
$$

where only the block f has a more complicated structure. We can thus achieve the desired result by projecting out the states with $p > r$ or $p' > r'$. This can be achieved using a standard projection operator [36]

$$
f_{r'} = \prod_{t=r'+1}^{2n} \left(\frac{\hat{N} - t}{r' - t} \right),
\tag{42}
$$

with $\hat{N}$ being the total number operator $\hat{N} = \sum_I N_I$. Thus, defining the new operators as

$$
\tilde{e}_{[J]}^{[I]} = e_{[J]}^{[I]} f_{r'},
\tag{43}
$$

we obtain the desired generators of $U(2^{2n})$. Note that we can write equivalently the desired projector as

$$
f_{r'} = \hat{1} - \sum_{t=r'+1}^{2n} |t\rangle\langle t| = \sum_{t=0}^{r'} |t\rangle\langle t|,
\tag{44}
$$

where $|t\rangle\langle t|$ is the projector onto the t-particle component of the carrier space,

$$
|t\rangle\langle t| = \sum_{[I]} |[I_1, \ldots, I_t]\rangle\langle[I_1, \ldots, I_t]|.
\tag{45}
$$

We then find easily that

$$
\begin{aligned}
\tilde{e}_{[J]}^{[I]} &= X_{I_1}^\dagger \cdots X_{I_r}^\dagger X_{J_{r'}} \cdots X_{J_1} \left(\sum_{t=0}^{r'} |t\rangle\langle t| \right) \\
&= X_{I_1}^\dagger \cdots X_{I_r}^\dagger X_{J_{r'}} \cdots X_{J_1} |r'\rangle\langle r'| \\
&= X_{I_1}^\dagger \cdots X_{I_r}^\dagger |0\rangle\langle 0| X_{J_{r'}} \cdots X_{J_1} \\
&= |[I]\rangle\langle[J]| = e_{[I][J]},
\end{aligned}
\tag{46}
$$

thus completing the "full circle" in investigating the relationship between the first and second quantization formulations. The above development clearly indicates the basic importance of Clifford algebras and related $U(2^{2n})$ or $U(2^n)$ groups for the general theory of $(2)n$-level fermion systems.

5. Orbital replacement operators

High-rank spinorbital replacement operators $e_{[J]}^{[I]}$ can also be defined recursively as implied by Eq. (36). This is particularly convenient for spin-free orbital analogues of $e_{[J]}^{[I]}$. Labelling orbitals with lower case Greek letters, we thus define

$$
E_{\mu\nu}^{\alpha\beta} = E_\mu^\alpha E_\nu^\beta - \delta_\mu^\beta E_\nu^\alpha,
\tag{47}
$$

$$
E_{\mu\nu\lambda}^{\alpha\beta\gamma} = E_{\mu\nu}^{\alpha\beta} E_\lambda^\gamma - \delta_\mu^\gamma E_{\lambda\nu}^{\alpha\beta} - \delta_\nu^\gamma E_{\mu\lambda}^{\alpha\beta}, \text{ etc.,}
\tag{48}
$$

where E^α_μ are $U(n)$ generators, Eq. (34). These operators will be referred to as *orbital replacement operators* or *E-operators* for short. While the rank-two operators (47) have often been used, since they naturally arise in the normal product form of two-particle operators [1, 3-5, 19, 32, 37], the generalization to higher orders was systematically employed only recently by Kutzelnigg [38], who calls them "excitation operators". Since the action of $E^{\alpha\beta\cdots}_{\mu\nu\cdots}$ replaces everywhere the orbitals μ, ν, ... by the orbitals α, β, ..., and since this replacement may also represent a de-excitation or a simple permutation of orbitals, we prefer the name "replacement operators". Even earlier exploitation of these operators is due to Hinze and Broad [39], who call them "spin-free reduced density operators". This name is justified by their close connection with spin-integrated reduced density matrices, discussed at the end of this section.

The first-quantized non-recursive definition of *E*-operators is also possible. For the *N*-electron layer $\mathscr{F}_N$ of the Fock space we can write

$$E^{\alpha_1\cdots\alpha_k}_{\mu_1\cdots\mu_k} \upharpoonright \mathscr{F}_N = 0 \quad \text{when } k > N,$$

and

$$E^{\alpha_1\cdots\alpha_k}_{\mu_1\cdots\mu_k} \upharpoonright \mathscr{F}_N = \sum_{i_1 \neq \cdots \neq i_k}^{N} \varepsilon^{\alpha_1\cdots\alpha_k}_{\mu_1\cdots\mu_k}(i_1 \cdots i_k) \quad \text{for } k \leq N, \tag{49}$$

where $\varepsilon^{\alpha_1\cdots\alpha_k}_{\mu_1\cdots\mu_k}$ is the *k*-electron integral operator with the kernel $\phi_{\alpha_1}(i_1) \cdots \phi_{\alpha_k}(i_k)\phi^*_{\mu_1}(i'_1) \cdots \phi^*_{\mu_k}(i'_k)$, ϕ_λ are the orthonormal orbitals on which the $U(n)$ transformations act, while $i_1 \cdots i_k$ designate the spatial coordinates of electrons $i_1, \ldots, i_k$. The operator $\varepsilon^{\alpha_1\cdots\alpha_k}_{\mu_1\cdots\mu_k}$ can also be viewed as the ket–bra operator of the form $|\phi_{\alpha_1} \cdots \phi_{\alpha_k}\rangle\langle\phi_{\mu_1} \cdots \phi_{\mu_k}|$. When $k = 2$ and $N \geq 2$, Eq. (49) simplifies to

$$E^{\alpha\beta}_{\mu\nu} \upharpoonright \mathscr{F}_N = \sum_{i<j}^{N} (|\phi_\alpha\phi_\beta\rangle\langle\phi_\mu\phi_\nu| + |\phi_\beta\phi_\alpha\rangle\langle\phi_\nu\phi_\mu|)(ij). \tag{50}$$

It should be noted that the definition (49) is actually more general than the recursive definition through (34), (47), (48), since it also applies to an arbitrary tensor space $V_n^{\otimes N}$ and not only to antisymmetric Fock spaces. The *E*-operators so defined span the algebra of bisymmetric operators discussed extensively in [40].

The *E*-operators may be easily symmetry adapted, since the symmetric group S_k acts naturally on a general operator $E^{\alpha_1\cdots\alpha_k}_{\mu_1\cdots\mu_k}$ as on any tensor. Since a simultaneous permutation of the lower and upper indices leaves these operators unchanged, e.g.

$$E^{\alpha\beta\gamma}_{\mu\nu\lambda} = E^{\beta\gamma\alpha}_{\nu\lambda\mu}, \tag{51}$$

it is immaterial whether S_k will act on the upper or lower indices.

For two-particle operators we simply obtain

$$^{[2]}E^{\alpha\beta}_{\mu\nu} \equiv {}^1E^{\alpha\beta}_{\mu\nu} = E^{\alpha\beta}_{\mu\nu} + E^{\beta\alpha}_{\mu\nu}, \tag{52}$$

$$^{[1^2]}E^{\alpha\beta}_{\mu\nu} \equiv {}^3E^{\alpha\beta}_{\mu\nu} = E^{\alpha\beta}_{\mu\nu} - E^{\beta\alpha}_{\mu\nu},$$

where we employ either the S_2 irrep symbol, or the corresponding spin multiplicity $(2S+1)$, to label the resulting symmetrized (or orthogonally spin-adapted) operators. In the following we shall employ the (anti)symmetrizer with respect to indices α and β,

$$^m\mathscr{S}_{\alpha\beta} = 1 + (2-m)\mathscr{P}_{\alpha\beta}, \tag{53}$$

where $\mathscr{P}_{\alpha\beta}$ permutes indices α and β, and $m = 1$ or 3. Equation (52) can then be re-written in the following compact way

$$^mE_{\mu\nu}^{\alpha\beta} = {}^m\mathscr{S}_{\alpha\beta}E_{\mu\nu}^{\alpha\beta}. \tag{54}$$

When a, b (r, s) designate the occupied (unoccupied) orbitals relative to a closed-shell determinant Φ_0, then the operators (54) acting on Φ_0 generate (unnormalized) particle–particle–hole–hole (pp–hh) coupled biexcited singlet configurations, whose advantages over other possible coupling schemes are well documented [41].

For three-particle operators, in addition to a symmetry adaptation with respect to S_3 [38], it is also useful to consider "partially" symmetrized operators. In this case, however, we must indicate precisely the indices involved, e.g.

$$^m\mathscr{S}_{\alpha\gamma}E_{\mu\nu\lambda}^{\alpha\beta\gamma} = {}^mE_{\mu\nu\lambda}^{\overline{\alpha\beta\gamma}}. \tag{55}$$

We shall conclude this section by listing some of the most useful properties of E-operators.

(i) The E-operators are "normal ordered" (cf. [42]) in a sense that $\langle E_{\mu\nu\cdots}^{\alpha\beta\cdots}\rangle = 0$, unless all the indices $\alpha\beta\cdots\mu\nu\cdots$ refer to the orbitals occupied in the reference state Φ_0, which defines the mean value $\langle\cdots\rangle$. The reader will note that the products of the $U(n)$ generators do not have this property. For example, $\langle E_r^a E_a^r\rangle = 2$ when a is doubly occupied and r is unoccupied in Φ_0. Loosely speaking we can say that $E_{\mu\nu\cdots}^{\alpha\beta\cdots}$ is a "normal ordered form" of the generator product $E_\mu^\alpha E_\nu^\beta \cdots$. The recursive definition, Eqs. (47), (48), providing the normal ordering, can be regarded as a special case of the spin-free Wick theorem discussed below.

(ii) The E-operators can be multiplied according to a Wick-type rule with all pairings having the phase $(+1)$ [38]. Thus, for instance

$$E_{\mu\nu}^{\alpha\beta}E_{\lambda\kappa}^{\gamma\delta} = E_{\mu\nu\lambda\kappa}^{\alpha\beta\gamma\delta} + \delta_\mu^\gamma E_{\lambda\nu\kappa}^{\alpha\beta\delta} + \delta_\nu^\gamma E_{\mu\lambda\kappa}^{\alpha\beta\delta}$$
$$+ \delta_\mu^\delta E_{\kappa\nu\lambda}^{\alpha\beta\gamma} + \delta_\nu^\delta E_{\mu\kappa\lambda}^{\alpha\beta\gamma} + \delta_{\mu\nu}^{\gamma\delta} E_{\lambda\kappa}^{\alpha\beta} + \delta_{\nu\mu}^{\gamma\delta} E_{\kappa\lambda}^{\alpha\beta}, \tag{56}$$

where $\delta_{\mu\nu\cdots}^{\alpha\beta\cdots}$ denotes the unit tensor $\delta_{\mu\nu\cdots}^{\alpha\beta\cdots} = \delta_\mu^\alpha\delta_\nu^\beta\cdots$. The four-particle term in Eq. (56) corresponds to the normal product, the three-particle terms to single pairings and the two-particle terms to double pairings. This Wick-type multiplication immediately yields all the commutators that appear every so often in many-body theory calculations. For example, we easily find that

$$[E_{\mu\nu}^{\alpha\beta}, E_\lambda^\gamma] = \delta_\nu^\gamma E_{\mu\lambda}^{\alpha\beta} + \delta_\mu^\gamma E_{\lambda\nu}^{\alpha\beta} - \delta_\lambda^\alpha E_{\nu\mu}^{\beta\gamma} - \delta_\lambda^\beta E_{\mu\nu}^{\alpha\gamma}. \tag{57}$$

It can also be shown that the Wick-type rule holds for symmetry-adapted operators. For example, we can write

$$
{}^m E^{\alpha\beta}_{\mu\nu} E^{\gamma\delta}_{\lambda\kappa} = {}^m E^{\overline{\alpha\beta}\gamma\delta}_{\mu\nu\lambda\kappa} + \delta^{\gamma}_{\mu} {}^m E^{\overline{\alpha\beta}\delta}_{\lambda\nu\kappa} + \delta^{\gamma}_{\nu} {}^m E^{\overline{\alpha\beta}\delta}_{\mu\lambda\kappa}
$$
$$
+ \delta^{\delta}_{\mu} {}^m E^{\overline{\alpha\beta}\gamma}_{\kappa\nu\lambda} + \delta^{\delta}_{\nu} {}^m E^{\overline{\alpha\beta}\gamma}_{\mu\kappa\lambda} + \delta^{\gamma\delta}_{\mu\nu} {}^m E^{\alpha\beta}_{\lambda\kappa} + \delta^{\gamma\delta}_{\nu\mu} {}^m E^{\alpha\beta}_{\kappa\lambda}, \tag{58}
$$

where the symmetrized operators are defined analogously to Eq. (55).

(iii) The symmetry-adapted operators that correspond to Young diagrams with more than two columns must vanish in view of the Pauli principle [this property is valid only for the Fock-space definition, Eqs. (34), (47), (48) and not for the general definition if Eq. (49)]. In other words, the E-operators can form bases for at most two-column irreps of the symmetric group. A simple example of this property is the identity

$$
E^{\alpha\beta\gamma}_{\mu\nu\lambda} + E^{\beta\alpha\gamma}_{\mu\nu\lambda} + E^{\alpha\gamma\beta}_{\mu\nu\lambda} + E^{\gamma\beta\alpha}_{\mu\nu\lambda} + E^{\gamma\alpha\beta}_{\mu\nu\lambda} + E^{\beta\gamma\alpha}_{\mu\nu\lambda} = 0, \tag{59}
$$

which shows that for a given selection of three occupied and three virtual orbitals we can have at most five independent triexcited singlet configurations or clusters [43]. Obviously, fewer independent configurations arise when some of the orbitals are identical. Thus, assuming that $\nu = \lambda$, we obtain using Eq. (51) that

$$
E^{\alpha\beta\gamma}_{\mu\nu\nu} + E^{\beta\gamma\alpha}_{\mu\nu\nu} + E^{\gamma\alpha\beta}_{\mu\nu\nu} = 0, \tag{60}
$$

obtaining two independent triexcited singlets. If, in addition $\beta = \gamma$, we have

$$
E^{\alpha\beta\beta}_{\mu\nu\nu} + 2E^{\beta\alpha\beta}_{\mu\nu\nu} = 0, \tag{61}
$$

and only one configuration results.

(iv) The expectation values of E-operators of rank k provide the elements of the spin-integrated kth order reduced density matrix [44]. For a closed shell reference state, such a density matrix is easily obtained by symmetrizing the unit tensor $\delta^{\alpha_1\cdots\alpha_k}_{\mu_1\cdots\mu_k}$ with the operators from the center of the group algebra of S_k. For $k = 2$ and $k = 3$, Eqs. (47) and (48) give (assuming that all the indices pertain now to occupied orbitals)

$$
\langle E^{\alpha\beta}_{\mu\nu} \rangle = (4 - 2\mathscr{P}_{\alpha\beta})\delta^{\alpha\beta}_{\mu\nu} = ({}^1\mathscr{S}_{\alpha\beta} + 3\,{}^3\mathscr{S}_{\alpha\beta})\delta^{\alpha\beta}_{\mu\nu}, \tag{62}
$$

$$
\langle E^{\alpha\beta\gamma}_{\mu\nu\lambda} \rangle = (8 - 4\mathscr{C}^{\{12\}} + 2\mathscr{C}^{\{3\}})\delta^{\alpha\beta\gamma}_{\mu\nu\lambda} = (2\mathscr{S}^{[21]} + 4S^{[1^3]})\delta^{\alpha\beta\gamma}_{\mu\nu\lambda}, \tag{63}
$$

where $\mathscr{C}^{[\lambda]}$ are the class sum operators for the permutation group of k indices (either $\alpha\beta\gamma\cdots$ or $\mu\nu\kappa\cdots$) and $\mathscr{S}^{[\lambda]}$ are the "character operators" (character projectors), providing an alternative basis for the center of the corresponding group algebra. The precise definition of $\mathscr{S}^{[\lambda]}$ is

$$
\mathscr{S}^{[\lambda]} = \sum_{\{\mu\}} \chi^{[\lambda]}\{\mu\} \mathscr{C}^{\{\mu\}}, \tag{64}
$$

where the summation extends over all classes $\{\mu\}$ of S_k and $\chi^{[\lambda]}\{\mu\}$ is the character of a class $\{\mu\}$ in the irrep $[\lambda]$. For $k = 2$, $\mathscr{S}^{[2]}$ and $\mathscr{S}^{[1^2]}$ reduce to ${}^1\mathscr{S}_{\alpha\beta}$ and ${}^3\mathscr{S}_{\alpha\beta}$, respectively. For $k = 3$, the explicit forms for the class sum and character operators

are: $\mathscr{C}^{\{12\}} = \mathscr{P}_{\alpha\beta} + \mathscr{P}_{\beta\gamma} + \mathscr{P}_{\alpha\gamma}$, $\mathscr{C}^{\{3\}} = \mathscr{P}_{\alpha\beta\gamma} + \mathscr{P}_{\beta\alpha\gamma}$, $\mathscr{S}^{[21]} = 2 - \mathscr{C}^{\{3\}}$ and $\mathscr{S}^{[1^3]} = 1 - \mathscr{C}^{\{12\}} + \mathscr{C}^{\{3\}}$. In the general case (for an arbitrary k) we find that

$$\langle E_{\nu_1 \cdots \nu_k}^{\alpha_1 \cdots \alpha_k} \rangle = (-1)^k \sum_{\{\mu\}} (-2)^{n^{\{\mu\}}} \mathscr{C}^{\{\mu\}} \delta_{\nu_1 \cdots \nu_k}^{\alpha_1 \cdots \alpha_k}, \tag{65}$$

where the summation extends over all classes of S_k and $n^{\{\mu\}}$ is the total number of cycles in the class $\{\mu\}$ or, equivalently,

$$\langle E_{\nu_1 \cdots \nu_k}^{\alpha_1 \cdots \alpha_k} \rangle = \sum_{[\lambda]} m^{[\lambda]} \mathscr{S}^{[\lambda]} \delta_{\nu_1 \cdots \nu_k}^{\alpha_1 \cdots \alpha_k}, \tag{66}$$

where the summation is over all two-column irreps of S_k and $m^{[\lambda]}$ is the spin multiplicity associated with the representation $[\lambda]$, i.e. $m^{[\lambda]} = b + 1$ for $[\lambda] = [2^a 1^b]$.

(v) In various applications we often encounter density matrices which are symmetrized with respect to some indices. In order to see how to perform such a symmetrization, we first consider $\langle {}^m E_{\mu\nu}^{\alpha\beta} \rangle$. Using the first Eq. (62) and the fact that

$$ {}^m\mathscr{S}_{\alpha\beta} \mathscr{P}_{\alpha\beta} = (2 - m)\,{}^m\mathscr{S}_{\alpha\beta}, \tag{67}$$

we obtain

$$\langle {}^m E_{\mu\nu}^{\alpha\beta} \rangle = {}^m S_{\alpha\beta}[4 - 2(2 - m)]\delta_{\mu\nu}^{\alpha\beta} = 2m\,{}^m\mathscr{S}_{\alpha\beta}\delta_{\mu\nu}^{\alpha\beta}. \tag{68}$$

Analogously, writing $\mathscr{C}^{\{3\}}$ as $\mathscr{P}_{\alpha\beta}(\mathscr{P}_{\beta\gamma} + \mathscr{P}_{\alpha\gamma})$ and replacing $\mathscr{P}_{\alpha\beta}$ by $(2 - m)$ in view of Eq. (67), we can easily symmetrize ${}^m E_{\mu\nu\kappa}^{\alpha\beta\gamma}$ [cf. Eq. (55)]:

$$\langle {}^m E_{\mu\nu\lambda}^{\overline{\alpha\beta}\gamma} \rangle = 2m\,{}^m\mathscr{S}_{\alpha\beta}(2 - \mathscr{P}_{\alpha\gamma} - \mathscr{P}_{\beta\gamma})\delta_{\mu\nu\lambda}^{\overline{\alpha\beta}\gamma}. \tag{69}$$

A straightforward generalization for the four-particle case gives

$$\langle {}^m E_{\mu\nu\lambda\kappa}^{\overline{\alpha\beta}\gamma\delta} \rangle = 2m\,{}^m\mathscr{S}_{\alpha\beta}[4 - 2(\mathscr{P}_{\alpha\gamma} + \mathscr{P}_{\alpha\delta} + \mathscr{P}_{\beta\gamma} + \mathscr{P}_{\beta\delta} + \mathscr{P}_{\gamma\delta})$$
$$+ \mathscr{P}_{\alpha\gamma\delta} + \mathscr{P}_{\alpha\delta\gamma} + \mathscr{P}_{\beta\gamma\delta} + \mathscr{P}_{\beta\delta\gamma} + \mathscr{P}_{\alpha\gamma}\mathscr{P}_{\beta\delta} + \mathscr{P}_{\alpha\delta}\mathscr{P}_{\beta\gamma}]\delta_{\mu\nu\lambda\kappa}^{\overline{\alpha\beta}\gamma\delta}. \tag{70}$$

This result can be further symmetrized in additional indices following the same technique.

6. Application to the coupled-cluster theory

The set of operators ${}^m E_{ab}^{rs}$, where a, b (r, s) designate the occupied (unoccupied) orbitals in a closed shell reference determinant Φ_0, forms a natural basis for the expansion of the pair-cluster operator T_2 in the orthogonally spin-adapted coupled-pair theory [45, 46]. To simplify the notation, we assume in this section that an unrestricted summation is carried out over all those indices (not necessarily repeated), which appear only on the right hand side of our equations but not on the left hand side. Thus, we can write that

$$T_2 = \tfrac{1}{8}\,{}^m t_{rs}^{ab}\,{}^m E_{ab}^{rs}, \tag{71}$$

where the implicit summation over m extends over only two values of m, namely $m = 1$ and $m = 3$. The cluster amplitudes ${}^m t_{rs}^{ab}$ are simply related to the unnormalized amplitudes $\langle a^1 a^2 | \hat{\tau}_2 | a_1 a_2 \rangle_S$ of [45] by

$$ {}^m t_{rs}^{ab} = (2 - m)m^{-1/2}\langle rs | \hat{\tau}_2 | ab \rangle_{(m-1)/2}. \tag{72}$$

They may also be related to the geminals $\tau_{\alpha\beta}^m(r_1, r_2)$ of the first-quantized coupled-cluster theory [35] via the overlap integral

$$^m t_{rs}^{ab} = \langle \phi_r \phi_s | \tau_{ab}^m \rangle, \tag{73}$$

where ϕ_r, ϕ_s designate a pair of virtual orbitals. The amplitudes $^m t_{rs}^{ab}$ are assumed to have the following symmetry properties

$$^m t_{rs}^{ab} = {}^m t_{sr}^{ba} = (2-m){}^m t_{rs}^{ba} = (2-m){}^m t_{sr}^{ab}, \tag{74}$$

which guarantee that the number of independent coefficients in (71) is the same as the number of doubly excited singlet configurations.

We shall now illustrate how the E-operators of Sect. 5 can be used to evaluate, in a rather straightforward and selfcontained way, the quadratic part $^m Q_{rs}^{ab}$ of the orthogonally spin-adapted coupled-pair equations. This quadratic part can be defined as [32, 35].

$$^m Q_{rs}^{ab} = \frac{1}{2m} \langle {}^m E_{rs}^{ab}[[H, T_2], T_2] \rangle, \tag{75}$$

where $\langle \cdots \rangle$ denotes the expectation value with respect to the reference state Φ_0 and the factor $1/m$ is introduced for convenience. Writing the Hamiltonian H as $H = \frac{1}{2} v_{\lambda\kappa}^{\mu\nu} E_{\mu\nu}^{\lambda\kappa}$ and T_2 as $T_2 = \frac{1}{4} {}^{m'} t_{pp'}^{cc'} E_{cc'}^{pp'}$, exploiting the symmetry properties of the cluster amplitudes $^{m'} t_{pp'}^{cc'}$, Eq. (74), and of the two electron integrals $v_{\lambda\kappa}^{\mu\nu} = \langle \phi_\lambda \phi_\kappa | r_{12}^{-1} | \phi_\mu \phi_\nu \rangle$, and using Eq. (56), we can expand the inner commutator in (75) as

$$[H, T_2] = \frac{1}{2} v_{\lambda\kappa}^{\mu p} {}^{m'} t_{pp'}^{cc'} E_{\mu cc'}^{\lambda\kappa p'} + \frac{1}{4} v_{\lambda\kappa}^{pp'} {}^{m'} t_{pp'}^{cc'} E_{cc'}^{\lambda\kappa}$$

$$- \frac{1}{2} v_{\lambda c}^{\mu\nu} {}^{m'} t_{pp'}^{cc'} E_{\mu\nu c'}^{\lambda pp'} - \frac{1}{4} v_{cc'}^{\mu\nu} {}^{m'} t_{pp'}^{cc'} E_{\mu\nu}^{pp'}. \tag{76}$$

From now on we assume that the indices a, b, c, c', d, $d'(r, s, p, p', q, q')$ label exclusively the occupied (virtual) orbitals, the indices λ, κ, μ, ν range over all orbitals and m, m', m'', designating the multiplicity, equal to 1 or 3. Using once again Eq. (56) (and its appropriate generalization) to evaluate the outer commutator in (75), and realizing that most of the resulting pairings give a vanishing contribution to $^m Q_{rs}^{ab}$, we find that

$$^m Q_{rs}^{ab} = {}^m Q_{rs}^{ab}(123) + {}^m Q_{rs}^{ab}(45) \tag{77}$$

where

$$^m Q_{rs}^{ab}(123) = \frac{1}{8m} v_{\lambda\kappa}^{qp} {}^{m'} t_{pp'}^{cc'} {}^{m''} t_{qq'}^{dd'} \langle {}^m E_{rs}^{ab} E_{dcc'd'}^{\lambda\kappa p'q'} \rangle, \tag{78}$$

and

$$^m Q_{rs}^{ab}(45) = -\frac{1}{8m} v_{dd'}^{pp'} {}^{m'} t_{pp'}^{cc'} {}^{m''} t_{qq'}^{dd'} \langle {}^m E_{rs}^{ab} E_{cc'}^{qq'} \rangle$$

$$- \frac{1}{4m} v_{\lambda d}^{pp'} {}^{m'} t_{pp'}^{cc'} {}^{m''} t_{qq'}^{dd'} \langle {}^m E_{ab}^{rs} E_{cc'd'}^{\lambda qq'} \rangle. \tag{79}$$

In Eq. (77) we have employed the partitioning of $^mQ_{rs}^{ab}$ into the sum of the contributions from the hard-to-compute diagrams (diagrams 1, 2, and 3 of [47]) and from easily "factorizable" diagrams (diagrams 4 and 5 of [47]), discussed in detail in [47] and [48] and often exploited in practical calculations [35, 47-51]. A deeper physical meaning of an approximate cancellation of the first three diagrams has been elucidated in [52].

The evaluation of the first term in Eq. (79), which we denote by $^mA_{rs}^{ab}$, is straightforward if we use Eq. (58) and note that both possible double pairings give an identical contribution. Using, further, Eq. (68), we obtain

$$
\begin{aligned}
^mA_{rs}^{ab} &= -\frac{1}{4m}\, v_{dd'}^{pp'}\,^{m'}t_{pp'}^{cc'}\,^{m''}t_{rs}^{dd'}\langle^mE_{cc'}^{ab}\rangle \\
&= -\tfrac{1}{2}\,^m\mathcal{S}_{ab}v_{dd'}^{pp'}\,^{m'}t_{pp'}^{ab}\,^{m''}t_{rs}^{dd'} \\
&= -v_{dd'}^{pp'}\,^mt_{pp'}^{ab}\,^mt_{rs}^{dd'}.
\end{aligned}
\tag{80}
$$

In arriving at the last equality we employed the fact that $^m\mathcal{S}_{ab}\,^{m'}t_{pp'}^{ab} = 2\delta_{mm'}\,^mt_{pp'}^{ab}$ and that m'' must equal m since otherwise $^{m''}t_{rs}^{dd'}$ and $v_{dd'}^{pp'}\,^mt_{pp'}^{ab}$ would have a different symmetry under the interchange of d and d', so that the sum over d and d' would vanish.

After combining the two terms resulting from the pairings of qq' with rs, the second term in (79), denoted by $^mB_{rs}^{ab}$, takes the form

$$
\begin{aligned}
^mB_{rs}^{ab} &= -\frac{1}{4m}\, v_{\lambda d}^{pp'}\,^{m'}t_{pp'}^{cc'}\,^m\mathcal{S}_{rs}\,^{m''}t_{rs}^{dd'}\langle^mE_{c'd'c}^{\overline{ab}\lambda}\rangle \\
&= -\frac{1}{4m}\, v_{\lambda d}^{pp'}\,^{m'}t_{pp'}^{cc'}\,^mt_{rs}^{dd'}\,^{m''}\mathcal{S}_{cc'}\langle^mE_{c'd'c}^{\overline{ab}\lambda}\rangle.
\end{aligned}
\tag{81}
$$

In obtaining the second equality we used the fact that $^m\mathcal{S}_{rs}\,^{m''}t_{rs}^{dd'} = 2\delta_{mm''}\,^mt_{rs}^{dd'}$ and that we can symmetrize the last factor in cc' (since $^{m'}t_{pp'}^{cc'}$ has already a definite symmetry in c and c'). To proceed further, we employ the identity

$$
^{m'}\mathcal{S}_{cc'}\langle^mE_{c'd'c}^{\overline{ab}\lambda}\rangle = 2m\,^m\mathcal{S}_{ab}\,^{m'}\mathcal{S}_{cc'}(m'\delta_{c'd'c-}^{ab\lambda} - \delta_{mm'}\,\delta_{c'd'c}^{a\lambda b}),
\tag{82}
$$

obtained by additional symmetrization of (69). Inserting (82) into (81) and replacing $^{m'}\mathcal{S}_{cc'}$ by 2 (since $^{m'}t_{pp'}^{cc'}$ has already a definite symmetry in cc') we finally obtain

$$
^mQ_{rs}^{ab}(45) = -m'\,^m\mathcal{S}_{ab}v_{cd}^{pp'}\,^{m'}t_{pp'}^{ca}\,^mt_{rs}^{db} + v_{dd'}^{pp'}\,^mt_{pp'}^{ab}\,^mt_{rs}^{dd'},
\tag{83}
$$

where the first and second terms correspond to diagrams 4 and 5 of [47], respectively.

It remains to consider $^mQ_{rs}^{ab}(123)$. Since r and s can only be paired with p' and q' or with q' and p', and since both pairings yield the same result, we can write

$$
^mQ_{rs}^{ab}(123) = \frac{1}{16m}\, v_{\lambda\kappa}^{qp}\,^{m'}t_{pr}^{cc'}\,^{m''}t_{qs}^{dd'}\,^{m'}\mathcal{S}_{cc'}\,^{m''}\mathcal{S}_{dd'}\langle^mE_{c'd'dc}^{\overline{ab}\lambda\kappa}\rangle,
\tag{84}
$$

where we have chosen to symmetrize the four-particle density matrix in cc' and dd' and to divide the whole expression by 4. The explicit expression for the required symmetrized four-particle density matrix is

$$
{}^{m'}\mathscr{S}_{cc'}\,{}^{m''}\mathscr{S}_{dd'}\langle{}^{m}E^{\overline{ab}\lambda\kappa}_{c'd'dc}\rangle
$$

$$
= 2m\,{}^{m''}\mathscr{S}_{dd'}\,{}^{m'}\mathscr{S}_{cc'}\,{}^{m}\mathscr{S}_{ab}\{m'm''\delta^{ab\lambda\kappa}_{c'd'dc}+[2(2-m'')\delta_{mm'}-m']\delta^{ab\kappa\lambda}_{c'd'dc}
$$

$$
-m'\delta_{mm'}\delta^{\lambda ba\kappa}_{c'd'dc}-m''\delta_{mm'}\delta^{a\kappa\lambda b}_{c'd'dc}\}. \tag{85}
$$

This result can be obtained by further symmetrization of Eq. (70). Actually, such a symmetrization is quite simple since, due to the presence of ${}^{m'}\mathscr{S}_{cc'}\,{}^{m''}\mathscr{S}_{dd'}$, all the terms which differ by permutations of c and c' or d and d' can be collected together and represented by a single term. Inserting (85) into (84) and replacing ${}^{m'}\mathscr{S}_{cc'}\,{}^{m''}\mathscr{S}_{dd'}$ by the factor of 4, we get

$$
{}^{m}Q^{ab}_{rs}(123)=-m'\,{}^{m}\mathscr{S}_{rs}v^{pq}_{cc'}\,{}^{m'}t^{cc'}_{pr}\,{}^{m}t^{ab}_{qs}+\tfrac{1}{2}{}^{m}\mathscr{S}_{ab}\{m'm''v^{pq}_{cd}
$$

$$
+[2-m'-m''+(2-m)(2-m')(2-m'')]v^{qp}_{cd}\}\,{}^{m'}t^{ca}_{pr}\,{}^{m''}t^{db}_{qs}, \tag{86}
$$

where we replaced $2\delta_{mm'}$ by $1+(2-m)(2-m')$ to obtain a more symmetric expression. The first term on the right hand side of Eq. (86) originates from the last two terms of Eq. (85) and corrresponds to the diagram 3 of [47].

Using Eqs. (72) and (73) one may verify that our expression for ${}^{m}Q^{ab}_{rs}$ is fully equivalent to the expressions derived in [45], [35] or [50]. Similar technique can be used to find the explicit form of the linear part $m^{-1}\langle{}^{m}E^{ab}_{rs}[H,T_2]\rangle$ of the coupled-pair equations. The derivation is then somewhat simpler since the four-particle density matrix does not appear. This approach is particularly convenient in cases when the standard diagrammatic technique may not readily apply, such as in various multi-configuration approaches. For example, we found the present method very useful in deriving the explicit form of the spin-adapted multireference linear coupled-cluster equations, which include connected semi-internal three- and four-particle cluster operators [53].

7. Clifford algebra unitary group approach

We have seen in Sect. 3 that Clifford algebras appear naturally in the description of many-fermion systems. The 2^n basis elements of the Clifford algebra C_n can be related with orbital occupancies of spin-free antisymmetrized states (Slater determinants), Eq. (26). These simple "building blocks" can be conveniently numbered and used to obtain fully spin-adapted CAUGA [28]. In this section we wish to draw attention to the possibility of using only partially spin-adapted bases in CI calculations exploiting the CAUGA scheme. Let us briefly summarize the basic tenets of CAUGA.

Interpreting the occupation numbers $m_1, m_2, \ldots, m_n$ of the basic building blocks (antisymmetrized states) (26) as binary integers $(m_1 m_2 \cdots m_n)_2$, $m_i = 0, 1$, we can conveniently label them by single integer index p [15, 28]

$$
p \equiv p_{\{m_i\}} = 2^n - (m_1 m_2 \cdots m_n)_2. \tag{87}
$$

The matric basis of $U(2^n)$ is now defined by Eq. (29) with $[I]$ and $[J]$ interpreted as ordered sets of orbital rather than spinorbital indices. Replacing $[I]$ and $[J]$ by corresponding orbital occupancies, we can label each $U(2^n)$ generator by a pair of indices p and q defined by Eq. (87). Henceforth, these generators will be denoted by E_{pq}. As discussed in Sect. 4, the $U(n)$ generators, Eq. (33), can be expressed through the $U(2^n)$ generators using Eq. (39) (cf. also [28, 29]). Employing the labeling of Eq. (87) and designating the $U(n)$ generators by Λ_{ij}, we obtain [29, 15, 28]

$$\Lambda_{ii} = \sum_{p=1}^{2^n} m_i^p E_{pp}, \tag{88}$$

where m_i^p are occupancies of the pth building block, and

$$\Lambda_{ij} = (-1)^{j-i+1} \sum_{p,q,r} (-1)^{S_2(q)} E_{p+\tau,p+\tau'}, \tag{89}$$

where

$$\tau \equiv \tau_{ij}(r, q), \qquad \tau' \equiv \tau_{ji}(q, r),$$

$$\tau_{kl}(u, v) = 2^{n-l}(2^{l-k+1}u + 2v + 1),$$

with

$$p = 1, 2, \ldots, 2^{n-j}$$

$$q = 0, 1, \ldots, (2^{j-i-1} - 1),$$

$$r = 0, 1, \ldots, (2^{i-1} - 1),$$

and $S_2(q)$ designating the digital sum of q_2 (the binary representation of q). Thus, all raising and lowering generators Λ_{ij} of $U(n)$ are given as linear combinations of 2^{n-2} $U(2^n)$ generators E_{pq} with simple coefficients ± 1 (all elementary generators have coefficients $+1$). For example, the representation of $U(5)$ raising generators is shown in Table 1 (see [15] for a graphical representation of a simple

Table 1. Example of a general representation of the $U(n)$ generators Λ_{ij} in terms of the $U(2^n)$ generators E_{pq}, $\Lambda_{ij} = \sum_k \pm E_{pq}$ for $n = 5$. Only the relevant indices are listed and the sign of each term on the right hand side is indicated as $\pm(\ )$. Only raising generators are listed

ij	$\pm E_{pq}$ represented by $\pm p,q$							
12	9,17	10,18	11,19	12,20	13,21	14,22	15,23	16,24
23	5,9	6,10	7,11	8,12	21,25	22,26	23,27	24,28
34	3,5	4,6	11,13	12,14	19,21	20,22	27,29	28,30
45	2,3	6,7	10,11	14,15	18,19	22,23	26,27	30,31
13	−5,17	−6,18	−7,19	−8,20	13,25	14,26	15,27	16,28
24	−3,9	−4,10	7,13	8,14	−19,25	−20,26	23,29	24,30
35	−2,5	4,7	−10,13	12,15	−18,21	20,23	−26,29	28,31
14	3,17	4,18	−7,21	−8,22	−11,25	−12,26	15,29	16,30
25	2,9	−4,11	−6,13	8,15	18,25	−20,27	−22,29	24,31
15	−2,17	4,19	6,21	−8,23	10,25	−12,27	−14,29	16,31

structure of this relationship). However, for a given $U(n)$ irrep $\Gamma(a, b, c)$,

$$a = \tfrac{1}{2}N - S, \qquad b = 2S, \qquad c = n - a - b, \tag{90}$$

which pertains to an n-level model of an N-electron system with total spin S, we only need $\binom{n-2}{a-1} + \binom{n-2}{c-1}$ terms if $b \neq 0$ and $\binom{n-2}{a-1}$ terms if $b = 0$ [15], so that only a fraction of the total number of terms appearing in the general expression (89) is neded for each particular multiplet.

The spin-adapted states may in turn be represented as linear combinations of two-box Weyl tableaux $U(2^n)$ states, since it can be shown that any $U(n)$ irrep with at most k columns is contained at least once in the totally symmetric k-box representation of $U(2^n)$ [54]. For example, a subduction of the two-box representation [2] of $U(2^6) \equiv U(64)$ of dimension 2080 to $U(6)$ gives

$$[2] \downarrow U(6) = \sum_{k=0}^{6} [2^k] + \sum_{k=0}^{5} [2^k 1] + \sum_{k=0}^{4} [2^k 1^2]$$

$$+ 2 \sum_{k=0}^{3} [2^k 1^3] + 3 \left(\sum_{k=0}^{2} [2^k 1^4] + [1^5] + [21^5] + [1^6] \right), \tag{91}$$

where $[2^0] \equiv [0]$, $[2^0 1^k] \equiv [1^k]$, etc. The simplest way to obtain this expansion is to decompose the one-box representation as $[0] + [1] + [1^2] + \cdots + [1^6]$ and then calculate all possible inner direct products using the Littlewood-Richardson rules [55] while discarding all the irreps that enter the antisymmetric part of $[1] \boxtimes [1]$. Equation (91) indicates that the frequencies of irreps that correspond to singlets, triplets and doublets are equal to unity. In general, these frequencies only depend on the spin S and are equal to S for S odd, to $(S + \tfrac{1}{2})$, for S fractional, and to $(S + 1)$ for S even.

Thus, in the many-electron case we only need to consider the symmetric two-box states, which we shall represent for simplicity as follows

$$[p|q] = \boxed{\,p\,|\,q\,}\rangle. \tag{92}$$

For example, the highest weight state in any irrep $\Gamma(a, b, c)$ of $U(n)$ is represented by $[2^c | 2^{b+c}]$.

One of the advantages of CAUGA is the fact that it is not dependent on any specific coupling scheme, even though the most natural coupling is that characterizing the VB-type Rumer states. However, one can just as easily construct the Gel'fand–Tsetlin states of UGA if desired [15, 28]. For any chosen coupling scheme the action of the $U(n)$ generators Λ_{ij} reduces simply to the action of E_{pq}'s on the two-box tableaux states (92), which is very simple indeed. Defining the unnormalized states $(p|q)$ as

$$(p|q) = (1 + \delta_{pq})^{1/2} [p|q], \tag{93}$$

we get that

$$E_{ij}(p|q) = \delta_{jp}(i|q) + \delta_{jq}(i|p).$$ (94)

In other words, the operator replaces the index j by the index i and only if the double occupancy is created or destroyed, we must include an extra factor of $\sqrt{2}$. The double occupancy of our two-box tableau can only occur when $b = S = 0$.

It is worth noting that any set of the basic two-box states (92) forms an orthonormal system. This observation suggests a particularly simple practical implementation of CAUGA employing a suitably chosen subset of the two-box states as a CI basis. Clearly, if we wish to accomplish a full CI, we choose the smallest possible set of two-box states, which span the carrier space for a given irrep $\Gamma(a, b, c)$ of $U(n)$. Usually, this set will also span additional carrier spaces for one or more other irreps of $U(n)$. However, as implied by the decomposition shown in Eq. (91), the additional representations which mix in will be usually low dimensional irreps with high spin multiplicity, so that the dimension increase should be only a moderate one. This dimensionality excess should be well compensated by the simplicity, and thus the resulting efficiency, in the calculation of the matrix representative of the Hamiltonian.

We thus consider a possibility to employ directly the two-box tableau states (92) as a CI basis, since the higher spin-multiplicity states will be automatically eliminated by the diagonalization procedure. A very similar approach has already been implemented in a vector processing environment [56].

The number of two-box tableaux that must be generally considered for a given irrep $\Gamma(a, b, c)$ of $U(n)$ is easily seen to be equal to $\binom{n}{a}\binom{n}{c}$ for $b \neq 0$ and to $\frac{1}{2}\binom{n}{a}\left[\binom{n}{a} + 1\right]$ when $b = 0$, since the corresponding states carry the (generally reducible) direct product representation $[1^{a+b}] \boxtimes [1^a]$, the dimension of $[1^m]$ being $\binom{n}{m}$. Equivalently, they are given by the number of possible combinations of 0's and 1's in a binary representation of the highest weight state indices 2^c and 2^{b+c}. The structure of this two-box basis is best apparent from its graphical representation given in Figs. 7 and 8 of [15]: If we represent the states (92) on a rectangular grid of $2^n \times 2^n$ points, then the states that are associated with the same orbital occupancies, and whose linear combinations will yield fully spin-adapted states (for the connection with Gel'fand–Tsetlin and Rumer bases see [15, 28]), are lying on the same co-diagonal (cf. Fig. 8 of [15]). The number of such state is given by the Young–Yamanouchi genealogical spin branching diagram values $f(N, S)$, (see, e.g. [20], Chap. 1). The relevant labels are most easily generated by permuting zero and unit entries in binary strings representing the highest weight state labels 2^c and 2^{b+c}, Eq. (87). Thus, for example, for $N = n = 5$ and $S = \frac{1}{2}$ we need the irrep $\Gamma(2, 1, 2)$ whose highest weight state is $[4|8]$. The possible integers labeling other states

are thus

4: 11100		8: 11000	
6: 11010		12: 10100	
7: 11001		14: 10010	
10: 10110		15: 10001	
11: 10101	and	20: 01100	
13: 10011		22: 01010	
18: 01110		23: 01001	
19: 01101		26: 00110	
21: 01011		27: 00101	
25: 00111		29: 00011,	

$$(95)$$

since in this case $\binom{5}{2} = \binom{5}{3} = 10$. We thus have 10^2 two-box tableaux to represent 75 states of $\Gamma(2, 1, 2)$, as follows from the dimension formula [12]

$$\dim \Gamma(a, b, c) = \frac{b+1}{n+1} \binom{n+1}{a} \binom{n+1}{c}. \tag{96}$$

Obviously, the largest boost in the dimension will result from the states having the largest number of open shells.

To estimate, in general, the relative increase in the dimensionality of the CI problem, we take the ratio of the number of two-box tableaux and of the dimension of $\Gamma(a, b, c)$ which gives (assuming $b \neq 0$)

$$f \equiv \binom{n}{a} \binom{n}{c} \Big/ \dim \Gamma(a, b, c) = \frac{(n+1-a)(n+1-c)}{(b+1)(n+1)}$$

$$= \frac{\frac{1}{2}N + S + 1}{2S+1} \cdot \frac{n+1-\frac{1}{2}N+S}{n+1}. \tag{97}$$

We can similarly consider the case when $b = 0$ so that generally

$$\lim_{n \to \infty} f = \frac{\frac{1}{2}N + S + 1}{2S+1} \cdot \frac{1}{1 + \delta_{S,0}}. \tag{98}$$

To get a better idea of the possible boost in the dimension when two-box tableaux are used directly as a basis, we present some typical cases in Table 2. When considering, for example, only singly and doubly excited configurations from a given set of reference configurations, this factor will be at most as large as for $N = 4$ and $n \to \infty$, so that the dimension boost will not exceed 50% for the singlets and 33% for the triplets.

To conclude, we would like to stress once again the simplicity of the relevant algebra in calculating the matrix elements of $U(n)$ generators or of their various products in the two-box tableaux basis. This algebra is particularly simple for non-singlet states since in this case no double occupancies of two-box tableaux are possible, so that all the matrix elements are either 0 or 1. Moreover, the integers labeling these tableaux separate naturally into the two disjoint sets, say

Table 2. Relative dimensionality increase f, Eqs. (97), (98), for typical values of n, N and S

n	N	S	f
4	4	0	21/20
		1	16/15
6	6	0	210/175
		1	225/189
		2	36/35
12	6	0	24310/15730
		1	32670/23166
		2	9504/8580
∞	6	0	2
		1	5/3
		2	6/5
∞	10	0	3
		1	7/3
		2	8/5
∞	N	0	$\frac{1}{2}(\frac{1}{2}N+1)$
		1	$\frac{1}{3}(\frac{1}{2}N+2)$
		2	$\frac{1}{5}(\frac{1}{2}N+3)$

Ω_1 and Ω_2 [cf. example (95)] and all the generators E_{pq} interchange only the integers within each set Ω_i, so that for each set Ω_i we can consider a different effective representation of Λ_{ij} in terms of E_{pq} (cf. Table 1). In the above example of $\Gamma(2, 1, 2)$ we see that out of the eight possible E_{pq} operators we only need the 2nd, 3rd and 5th for Ω_1 and the 4th, 6th and 7th for Ω_2.

Moreover, the action of any Λ_{ij} on an arbitrary two-box tableau can be easily computed directly using the following simple algorithm [valid for the irreps with $b \neq 0$ or, generally, when the renormalized states, Eq. (93), are used]: Consider $\Lambda_{ij}[r|s]$ (or $\Lambda_{ij}(r|s)$ if $b=0$). Using a complementary binary representation of $(r-1)$ and $(s-1)$, change 0 and 1 in positions i and j into 1 and 0, respectively, in each binary representative $(r-1)_2$ and (separately) $(s-1)_2$, if possible, and attach the sign $(-1)^k$, where k is the number of 1's between the ith and jth positions. Otherwise, matrix element vanishes. Using again the above example, we thus have

$$\Lambda_{12}[18|22] = \Lambda_{12}[\mathbf{0}1110|\mathbf{0}1010]$$

$$= [\mathbf{1}0110|01010] + [01110|\mathbf{1}0010]$$

$$= [10|22] + [18|14], \tag{99}$$

where the binary digits being interchanged are printed in bold face. Likewise,

$$\Lambda_{13}[18|22] = \Lambda_{13}[\mathbf{0}1\mathbf{1}10|01010]$$

$$= (-1)^1[\mathbf{1}1\mathbf{0}10|01010] = -[6|22], \tag{100}$$

etc., as may be easily verified using Table 1 and Eq. (94). Clearly, this process may be easily repeated as many times as necessary when products of generators

must be considered. In fact, the rules illustrated by Eqs. (99) and (100) have a very simple first quantization interpretation, since each box of the Weyl tableau defining CAUGA states, Eq. (92), can be viewed as a Slater determinant. Thus, denoting the orbitals transformed by $U(5)$ as ϕ_i, $i = 1, \ldots, 5$ and the orbital determinants as $|\phi_1 \phi_2 \cdots \phi_k|$, we can write Eq. (99) also in the form

$$
\begin{aligned}
\Lambda_{12}[18\,|\,22] &= \Lambda_{12}(|\phi_2 \phi_3 \phi_4| \otimes |\phi_2 \phi_4|) \\
&= (\Lambda_{12}|\phi_2 \phi_3 \phi_4|) \otimes |\phi_2 \phi_4| + |\phi_2 \phi_3 \phi_4| \otimes (\Lambda_{12}|\phi_2 \phi_4|) \\
&= |\phi_1 \phi_3 \phi_4| \otimes |\phi_2 \phi_4| + |\phi_2 \phi_3 \phi_4| \otimes |\phi_1 \phi_4| \\
&= [10\,|\,22] + [18\,|\,14].
\end{aligned}
\tag{101}
$$

The possibility to write the two-box quasi-spin-adapted configurations (92) as direct products of two Slater determinants is implied by the fact that they carry the representation $[1^{a+b}] \boxtimes [1^a]$, as noted earlier.

We note, finally, that our binary representation also gives immediately the weight generator matrix elements (i.e., the orbital occupancies) when we add both binary numbers in $[p\,|\,q]$ digitwise. For example, considering again the state $[18\,|\,22] = [01110\,|\,01010]$, the digitwise sum gives the occupancies (02120).

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