ear response theory (e.g., Monkhorst, 1977; Mukherjee and Mukherjee, 1979; Emrich, 1981; Ghosh *et al.*, 1981,1982; Dalgaard and Monkhorst, 1983; Ghosh and Mukherjee, 1984; Sekino and Bartlett, 1984; Prasad *et al.*, 1985; Takahashi and Paldus, 1986; Salter *et al.*, 1987; Geertsen and Oddershede, 1986). These approaches may not be entirely satisfactory from a purely theoretical viewpoint, particularly when dealing with a group of quasidegenerate states but, on the other hand, may be preferable to genuine MR approaches in many practical applications when near degeneracy is not critical. We also mention here an extensive review of various developments in open shell CC formalism, particularly of the genuine MR approaches, recently published by Mukherjee and Pal (1989).

In my preceding lecture notes on CC theory (Paldus, 1992), written for the Bad Windsheim NATO ASI, an overview of the most basic features of the SR CC theory as well as a brief introduction to the fundamental equations of the MR theory were presented. This presentation emphasized the MBPT roots of the CC theory, providing an understanding of an intimate relationship between both approaches. For this as well as other reasons, it exploited primarily field theoretical diagrammatic techniques that facilitate an understanding of the connected cluster structure (and thus size extensivity) of the CC theory, the role and importance of the so-called exclusion principle violating (EPV) terms or diagrams, the relationship with finite-order MBPT, as well as other aspects of the CC formalism. These lecture notes (Paldus, 1992) also briefly addressed the direct (i.e., not finite field) approach to the calculation of other properties than the energy and were closed by a brief introduction to the MR formalism and basic equations employed in the open shell generalizations of the standard SR CC theory. In the following text we will thus assume that the reader is familiar with these developments and we recommend that he also consults other reviews on the subject (see above) as well as various monographs addressing this problem from different viewpoints (Hurley, 1976, Jørgensen and Simons, 1981; Lindgren and Morrison, 1982; Wilson, 1984; McWeeny, 1989; Harris *et al.*, 1992).

In contrast to the Bad Windsheim notes (Paldus, 1992), we shall emphasize here the algebraic version of the CC formalism, particularly the use of the so-called replacement operators (Paldus and Jeziorski, 1988) in deriving the explicit form of CC equations. This is not only done to achieve diversity and to cover different viewpoints, but also for the following reasons:

(i) The algebraic formulation is very important for a general and precise formulation of the MR formalism, as recently demonstrated in our rigorous account of the valence universal formalism (Jeziorski and Paldus, 1989), its relationship to the state universal methodology (see also Jankowski *et al.*, 1991b,1992) and derivation of corresponding cluster conditions.

(ii) Although the diagrammatic approach is extremely helpful and provides an invaluable insight [we quote as an illustration the so-called t'Hooft and Veltman "principle" stating that "the diagrams contain more truth than the underlying formalism" (Halzen and Martin, 1984)], its extension to the MR formalism is far from being straightforward.

(iii) The MR CC formalism leads generally to much more complex equations and algorithms than its SR counterpart. In fact, for certain types of open shells involving a number of unpaired electrons, or when relatively large model spaces are required, the complexity of the resulting formalism may call for the exploitation of symbol manipulation software such as MAPLE, MATHEMATICA or MACSYMA. The same holds even for some SR but multi-configurational methods mentioned earlier (cf., Janssen and Schaefer, 1991). In all these cases it is undoubtedly more straightforward to rely on an algebraic formulation.

We shall thus base our notes on an algebraic formalism, exploiting replacement operators from the universal enveloping algebra of U($n$). Although we wish to concentrate on MR approaches, it is important to start with a much simpler SR case (that is also relevant to state specific open shell approaches as indicated above) in order to familiarize the reader with basic features of the formalism employed. For the sake of simplicity we shall also forego all the aspects of this formalism that pertain to spin-adaptation or orthogonal spin-adaptation, even though the formalism may be relatively easily modified for this purpose (cf., Paldus and Jeziorski, 1988; Piecuch and Paldus 1989,1990,1992). We shall assume familiarity with the second quantization formalism (see, e.g., Paldus and Čížek, 1975; Paldus, 1981; Jørgensen and Simons, 1981; Lindgren and Morrison, 1982; Wilson, 1984; McWeeny, 1989; Gross *et al.*, 1991; Harris *et al.*, 1992) but will make every attempt to make the article self-contained as far as other algebraic formalism is concerned.

## 2. NOTATION AND BASIC FORMALISM

### 2.1. Second quantization

Before we turn our attention to CC theory, we first develop some useful algebra based on the second quantization formalism. Since we shall always work with semiempirical or *ab initio* model Hamiltonians, defined on an appropriate finite dimensional space, and employ molecular orbital (MO) formalism, we start by considering an $m$-dimensional one-electron space $\mathcal{V}_m$, spanned by $m$ orthonormal spin orbitals $|\mu\rangle$, $\mu = 1, 2, \ldots, m$; $m = 2n$. Invoking the second quantization formalism, we define creation ($X_\mu^\dagger$) and annihilation ($X_\mu$) operators, associated with our orthonormal spin orbital basis $\{|\mu\rangle\}$, that satisfy the following anticommutation relations

$$\{X_\mu^\dagger, X_\nu\} = \delta_\nu^\mu, \quad \{X_\mu^\dagger, X_\nu^\dagger\} = \{X_\mu, X_\nu\} = 0\,, \tag{1}$$

where $\delta_\nu^\mu$ designates the Kronecker delta symbol and braces indicate the anticommutator, $\{A, B\} = AB + BA$.

We recall that these operators are defined on an appropriate Fock space $\mathcal{F}$ that

can be built as a direct sum of tensor powers of our one-electron space $\mathcal{V}_m$, namely

$$\mathcal{F} = \bigoplus_{k=0}^{m} \mathcal{A}(\mathcal{V}_m^{\otimes k}) = \mathbb{C} + \mathcal{V}_m + \mathcal{A}(\mathcal{V}_m \otimes \mathcal{V}_m) + \cdots, \tag{2}$$

where $\mathcal{A}$ designates the antisymmetric component and $\mathbb{C}$ is the complex number field. Note that the finite dimensionality of $\mathcal{F}$ stems from the finite dimensionality of the one-electron space $\mathcal{V}_m$ employed (in the *ab initio* case, $m = \dim\mathcal{V}_m = 2n$ is given by the number $n$ of atomic orbitals (AO's) considered, i.e., by the size of the chosen AO basis; in the semiempirical case this dimension is given by the number of electrons or sites of the system, or corresponds to the so-called minimum basis set (MBS) of *ab initio* approaches) and Pauli principle (i.e., the antisymmetry of the states involved).

The one-dimensional zero-particle component of $\mathcal{F}$ is isomorphic with the underlying number field (here assumed to be the field of complex numbers $\mathbb{C}$) and is spanned by the true vacuum state $|0\rangle$ having the property

$$X_\mu|0\rangle = 0 \quad \text{or} \quad \langle 0|X_\mu^\dagger = 0\,, \qquad (\forall\mu)\,. \tag{3}$$

The basis of the $k$-particle component $\mathcal{W}_k = \mathcal{A}(\mathcal{V}_m^{\otimes k})$ may be chosen to consist of ordered configurations (equivalent to Slater determinants)

$$|\Phi_K\rangle \equiv X_{\mu_1}^\dagger X_{\mu_2}^\dagger \cdots X_{\mu_k}^\dagger|0\rangle, \quad (\mu_1 < \mu_2 < \cdots < \mu_k)\,, \tag{4}$$

where the subscript $K$ designates the index set $K \equiv \{\mu_1, \mu_2, \ldots, \mu_k\}$. We also recall that

$$\hat{n}_\lambda = X_\lambda^\dagger X_\lambda \tag{5}$$

defines the occupation number operator for the $\lambda$-th spin orbital,

$$\hat{n}_\lambda|\Phi_K\rangle = n_\lambda|\Phi_K\rangle\,, \tag{6}$$

the occupation number $n_\lambda$ being 0 or 1 depending on whether the spin orbital $|\lambda\rangle$ is occupied in $|\Phi_K\rangle$ or not, respectively. Clearly, $\hat{n}_\lambda$ is both Hermitian and idempotent,

$$n_\lambda^\dagger = n_\lambda, \quad n_\lambda^2 = n_\lambda\,. \tag{7}$$

The total electron number operator $\hat{N}$ is given by the sum of all spin orbital occupation number operators,

$$\hat{N} = \sum_\lambda \hat{n}_\lambda\,. \tag{8}$$

### 2.2. Unitary group and its universal enveloping algebra

It is well known that the off-diagonal generalization of the number operators (5) yields the one-body *replacement operators*,

$$e_\mu^\kappa = X_\kappa^\dagger X_\mu\,, \tag{9}$$

so called since they replace the $\mu$-th spin orbital by the $\kappa$-th spin orbital assuming that $n_\mu = 1$ in the state on which $e_\mu^\kappa$ acts, otherwise the state is annihilated. These



operators are known to possess a rich algebraic structure, namely that of a Lie algebra of the unitary group U($m$), since they satisfy the following commutation relations (Jordan, 1935; Moshinsky, 1966; Paldus 1974,1976,1988)

$$\left[e_\mu^\kappa, e_\nu^\lambda\right] = \delta_\mu^\lambda e_\nu^\kappa - \delta_\nu^\kappa e_\mu^\lambda\,, \tag{10}$$

as well as the Hermitian property

$$(e_\lambda^\kappa)^\dagger = e_\kappa^\lambda\,. \tag{11}$$

They may thus be regarded as the generators of the spin orbital *unitary group* U($m$) ≡ U($2n$).

This fact, along with the possibility to form spin-free [U($n$)] and orbit-free [U(2) or SU(2)] subalgebras of U($m$) ≡ U($2n$), and the well established representation theory of these subalgebras, form a basis of the so-called *unitary group approach* (UGA) to the many electron correlation problem (Paldus, 1974,1976,1988; Shavitt, 1988 and references therein). This approach enables an efficient spin-adaptation when dealing with spin-independent Hamiltonians, very effective generation and storage of $N$-electron configurations and calculation of requisite matrix elements (Sheppard, 1993). We shal not employ the full power of this approach in this text, but will restrict ourselves to spin orbital formalism. We shall see that already at the spin orbital level, the replacement operator algebra will provide us with a very useful machinery for the derivation of desired expressions, while being easily accessible to computer implementation.

As we just mentioned, and as may be easily verified, the one-body replacement operators (9) are closed with respect to the Lie product (or commutator product), eq. (10), and may thus be regarded as U($m$) generators. However, they are not closed with respect to an ordinary product, since

$$\begin{aligned} e_\mu^\kappa e_\nu^\lambda &= X_\kappa^\dagger X_\mu X_\lambda^\dagger X_\nu = X_\kappa^\dagger(\delta_\mu^\lambda - X_\lambda^\dagger X_\mu)X_\nu \\ &= X_\kappa^\dagger X_\lambda^\dagger X_\nu X_\mu + \delta_\mu^\lambda X_\kappa^\dagger X_\nu \\ &= e_{\mu\nu}^{\kappa\lambda} + \delta_\mu^\lambda e_\nu^\kappa\,, \end{aligned} \tag{12}$$

where we designated by $e_{\mu\nu}^{\kappa\lambda}$ the following two-body replacement operator

$$e_{\mu\nu}^{\kappa\lambda} = X_\kappa^\dagger X_\lambda^\dagger X_\nu X_\mu\,. \tag{13}$$

The algebraic structure and basic properties of replacement operators of both spin orbital and orbital types were explored in connection with the Clifford algebra UGA (Paldus and Sarma, 1985; Paldus *et al.*, 1987) and their usefulness in applications to CC theory was illustrated by deriving orthogonally spin-adapted form of pair cluster equations (Paldus and Jeziorski, 1988). In order to place this formalism into a more general context, we only mention here that the one-, two-, three-, etc. body

replacement operators, whose general definition will be given below, together with the identity operator $e$ that may be regarded as the zero-body operator, form a very convenient basis of the so-called universal enveloping algebra of U($m$). Let us only say that in contrast to the U($m$) Lie algebra, the *universal enveloping algebra* of U($m$) is an associative algebra, and that the basis $\{e, e^{\kappa}_{\mu}, e^{\kappa\lambda}_{\mu\nu}, \cdots\}$ is distinct from the well-known Poincaré-Birkhoff-Witt basis representing a standard basis for universal enveloping algebras, and possesses rather remarkable properties (see, e.g., Gould *et al.*, 1990).

We thus generalize the two-body replacement operators (13) and define a general $r$-body replacement operator

$$e^{\kappa_1\kappa_2\cdots\kappa_r}_{\lambda_1\lambda_2\cdots\lambda_r} = X^{\dagger}_{\kappa_1} X^{\dagger}_{\kappa_2} \cdots X^{\dagger}_{\kappa_r} X_{\lambda_r} \cdots X_{\lambda_2} X_{\lambda_1} \,. \tag{14}$$

Clearly, when employing a finite dimensional one-particle space $\mathcal{V}_m$, the higher than $m$-body replacement operators will vanish.

We next investigate some basic properties of these operators and of the universal enveloping algebra they span.

### 2.3. Algebra of replacement operators

We first observe that in view of the anticommutation properties of creation and annihilation operators, Eq. (1), the replacement operators (14) are invariant with respect to any simultaneous permutation of their upper and lower indices, and change at most their phase when the subscripts or the superscripts are permuted among themselves, i.e.

$$e^{\kappa_1\kappa_2\cdots\kappa_r}_{\lambda_1\lambda_2\cdots\lambda_r} = e^{\kappa_{p_1}\kappa_{p_2}\cdots\kappa_{p_r}}_{\lambda_{p_1}\lambda_{p_2}\cdots\lambda_{p_r}} = (-1)^p e^{\kappa_1\kappa_2\cdots\kappa_r}_{\lambda_{p_1}\lambda_{p_2}\cdots\lambda_{p_r}} \,, \tag{15}$$

where $p$ designates the parity of the permutation $P$, $P : i \to p_i (i = 1, \ldots, r)$. For example, in the two-body case, we have that

$$e^{\kappa\lambda}_{\mu\nu} = e^{\lambda\kappa}_{\nu\mu} = -e^{\kappa\lambda}_{\nu\mu} = -e^{\lambda\kappa}_{\mu\nu} \,. \tag{16}$$

In order to avoid multiple subscripts it will often be useful to introduce the following simplified notation by designating

$$e^{\kappa_1\kappa_2\cdots\kappa_r}_{\mu_1\mu_2\cdots\mu_r} = e^{12\cdots r}_{12\cdots r}, \; e^{\lambda_1\lambda_2\cdots\lambda_s}_{\nu_1\nu_2\cdots\nu_s} = e^{1'2'\cdots s'}_{1'2'\cdots s'}, \text{etc.} \tag{17}$$

Thus, for example, the basic commutation property for U($n$) generators, Eq. (10), will take the following form in this notation

$$\left[e^1_1, e^{1'}_{1'}\right] = \delta^{1'}_1 e^1_{1'} - \delta^1_{1'} e^{1'}_1 \,, \tag{10'}$$

or

$$\left[e^1_1, e^2_2\right] = \delta^2_1 e^1_2 - \delta^1_2 e^2_1 \,. \tag{10''}$$

Equivalently, Eq. (15) will now read as

$$e^{12\cdots r}_{12\cdots r} = e^{p_1p_2\cdots p_r}_{p_1p_2\cdots p_r} = (-1)^p e^{1\;2\cdots\;r}_{p_1p_2\cdots p_r} \,. \tag{15'}$$



This notation not only avoids multiple subscripts, but also highlights the symmetry properties of our relationships.

To verify that the replacement operators provide a basis of the universal enveloping algebra of U($m$) and to derive an equivalent recursive definition for them, we investigate general products of these operators. Clearly, just as the product of two one-body operators yields a two-body operator, Eq. (12), the product of a two-body and a one-body operator should yield a three-body operator. Indeed,

$$\begin{aligned} e^{12}_{12}e^{1'}_{1'} &\equiv e^{\kappa_1\kappa_2}_{\mu_1\mu_2}e^{\lambda}_{\nu} = X^{\dagger}_{\kappa_1}X^{\dagger}_{\kappa_2}X_{\mu_2}X_{\mu_1}X^{\dagger}_{\lambda}X_{\nu} \\ &= X^{\dagger}_{\kappa_1}X^{\dagger}_{\kappa_2}X_{\mu_2}(\delta^{\lambda}_{\mu_1} - X^{\dagger}_{\lambda}X_{\mu_1})X_{\nu} \\ &= X^{\dagger}_{\kappa_1}X^{\dagger}_{\kappa_2}(\delta^{\lambda}_{\mu_2} - X^{\dagger}_{\lambda}X_{\mu_2})X_{\nu}X_{\mu_1} + \delta^{\lambda}_{\mu_1}X^{\dagger}_{\kappa_1}X^{\dagger}_{\kappa_2}X_{\mu_2}X_{\nu} \\ &= X^{\dagger}_{\kappa_1}X^{\dagger}_{\kappa_2}X^{\dagger}_{\lambda}X_{\nu}X_{\mu_2}X_{\mu_1} + \delta^{\lambda}_{\mu_1}X^{\dagger}_{\kappa_1}X^{\dagger}_{\kappa_2}X_{\mu_2}X_{\nu} + \delta^{\lambda}_{\mu_2}X^{\dagger}_{\kappa_1}X^{\dagger}_{\kappa_2}X_{\nu}X_{\mu_1} \\ &= e^{121'}_{121'} + \delta^{1'}_1 e^{12}_{12} + \delta^{1'}_2 e^{12}_{11'} \,, \end{aligned} \tag{18a}$$

and, similarly,

$$\begin{aligned} e^{1'}_{1}e^{12}_{12} &= e^{1'12}_{1'12} + \delta^1_1 e^{1'2}_{12} + \delta^2_1 e^{11'}_{12} \\ &= e^{121'}_{121'} + \delta^1_1 e^{1'2}_{12} + \delta^2_1 e^{11'}_{12} \,. \end{aligned} \tag{18b}$$

In general,

$$e^{12\cdots k}_{12\cdots k}e^{1'}_{1'} = e^{12\cdots k1'}_{12\cdots k1'} + \sum_{i=1}^{k} \delta^{1'}_i e^{12\cdots i\cdots k}_{12\cdots 1'\cdots k} \,, \tag{19}$$

and similarly for $e^{1'}_{1}e^{12\cdots k}_{12\cdots k}$.

We can thus define the higher order replacement operators recursively, namely

$$e^{12\cdots k(k+1)}_{12\cdots k(k+1)} = e^{12\cdots k}_{12\cdots k}e^{k+1}_{k+1} - \sum_{i=1}^{k} \delta^{k+1}_i e^{12\cdots i\cdots k}_{12\cdots(k+1)\cdots k} \,, \tag{20}$$

or, specifically

$$\begin{aligned} e^{\kappa\lambda}_{\mu\nu} &= e^{\kappa}_{\mu}e^{\lambda}_{\nu} - \delta^{\lambda}_{\mu}e^{\kappa}_{\nu} \,, \\ e^{\kappa\lambda\rho}_{\mu\nu\tau} &= e^{\kappa\lambda}_{\mu\nu}e^{\rho}_{\tau} - \delta^{\rho}_{\mu}e^{\kappa\lambda}_{\tau\nu} - \delta^{\rho}_{\nu}e^{\kappa\lambda}_{\mu\tau} \\ &= e^{\kappa}_{\mu}e^{\lambda\rho}_{\nu\tau} - \delta^{\lambda}_{\mu}e^{\kappa\rho}_{\nu\tau} - \delta^{\rho}_{\mu}e^{\lambda\kappa}_{\nu\tau}, \text{ etc.} \end{aligned} \tag{21}$$

Thus, we always contract the superscripts on the right with the subscripts on the left: the contracted terms are added when multiplying replacement operators and subtracted when 'decomposing' them into a product of two lower-order operators.

This simple rule extends to products of two replacement operators of an arbitrary order. Thus, for example, for the product of two two-body operators we get

$$\begin{aligned} e^{\lambda\kappa}_{\mu\nu}e^{\lambda'\kappa'}_{\mu'\nu'} &= e^{\lambda\kappa\lambda'\kappa'}_{\mu\nu\mu'\nu'} + \delta^{\lambda'}_{\mu}e^{\lambda\kappa\kappa'}_{\mu'\nu\nu'} + \delta^{\lambda'}_{\nu}e^{\lambda\kappa\kappa'}_{\mu\mu'\nu'} + \delta^{\kappa'}_{\mu}e^{\lambda\kappa\lambda'}_{\nu\nu'\mu'} + \delta^{\kappa'}_{\nu}e^{\lambda\kappa\lambda'}_{\mu\nu'\mu'} \\ &+ \delta^{\lambda'\kappa'}_{\mu\nu}e^{\lambda\kappa}_{\mu'\nu'} + \delta^{\lambda'\kappa'}_{\nu\mu}e^{\lambda\kappa}_{\nu'\mu'} \,, \end{aligned} \tag{22}$$

where

$$\delta^{\lambda\kappa\cdots}_{\mu\nu\cdots} = \delta^{\lambda}_{\mu}\delta^{\kappa}_{\nu}\cdots \tag{23}$$

defines a generalized Kronecker symbol. We thus see that a general rule is to form the highest order replacement operator by merging the index sets of both operators forming the product, while including at the same time all the lower order replacement operators that result from all possible contractions of the superscripts on right hand side operator with the subscripts on left hand side operator. The reader who is familiar with the second quantization formalism will recognize the parallel with the time-independent Wick's theorem (see, e.g., Paldus and Čížek, 1975 or Paldus, 1981). Indeed, the replacement operators represent the normal product form of the creation and annihilation operators involved (with respect to the true vacuum state $|0\rangle$), while the contracted terms correspond to standard contractions of the MBPT formalism. Since all contractions vanish except those between an annihilator and a creator, these contractions involve only the subscripts on the left (annihilators) and superscripts on the right (creators). Following the above rules, the resulting normal products (represented by the replacement operators) are automatically in the 'canonical' form that requires no phase adjustment.

To represent more compactly the multicontracted terms, we define antisymmetrized Kronecker symbol

$$\Delta^{\lambda_1\lambda_2\cdots\lambda_r}_{\mu_1\mu_2\cdots\mu_r} \equiv \Delta^{12\cdots r}_{12\cdots r} = \sum_{P\in S_r}(-1)^p \delta^{1\ 2\ \cdots\ r}_{p_1p_2\cdots p_r}\,, \tag{24}$$

the sum extending over all permutations $P : i \to p_i\,(i = 1,\ldots,r)$ of the symmetric group $S_r$. Thus, the last two terms on the right hand side of Eq. (22) may be represented by a single term, namely

$$\delta^{\lambda'\kappa'}_{\mu\nu}e^{\lambda\kappa}_{\mu'\nu'} + \delta^{\lambda'\kappa'}_{\nu\mu}e^{\lambda\kappa}_{\nu'\mu'} = \left(\delta^{\lambda'\kappa'}_{\mu\nu} - \delta^{\lambda'\kappa'}_{\nu\mu}\right)e^{\lambda\kappa}_{\mu'\nu'} = \Delta^{\lambda'\kappa'}_{\mu\nu}e^{\lambda\kappa}_{\mu'\nu'}\,. \tag{25}$$

We also note that the following decomposition holds

$$\Delta^{12\cdots i\,1'\ \ 2'\cdots\ \ j'}_{12\cdots i(i+1)(i+2)\cdots(i+j)} = \sum_{[P]}(-1)^p \Delta^{1\ 2\cdots\ i}_{p_1p_2\cdots p_i}\Delta^{1'\ 2'\cdots\ j'}_{p_{i+1}p_{i+2}\cdots p_{i+j}}\,, \tag{26}$$

where the sum extends over all coset representatives $[P]$ for the subgroup chain $S_{i+j} \supset S_i \otimes S_j$, with $P : i \to p_i\,(i = 1,\ldots,i+j)$, $P \in S_{i+j}$. Thus, for example

$$\Delta^{1234}_{1234} = \Delta^{12}_{12}\Delta^{34}_{34} + \Delta^{12}_{34}\Delta^{34}_{12} + \Delta^{12}_{14}\Delta^{34}_{23} + \Delta^{12}_{23}\Delta^{34}_{14} - \Delta^{12}_{13}\Delta^{34}_{24} - \Delta^{12}_{24}\Delta^{34}_{13}\,. \tag{27}$$

Using this notation, we can now write for the general product of two replacement



operators

$$\begin{aligned} e^{12\cdots r}_{12\cdots r}e^{1'2'\cdots s'}_{1'2'\cdots s'} &= e^{12\cdots r1'2'\cdots s'}_{12\cdots r1'1'\cdots s'} \\ &+ \sum_{i=1}^{s}\sum_{j=1}^{r}\delta^{i'}_{j}e^{12\cdots j\cdots r1'2'\cdots(i-1)'(i+1)'\cdots s'}_{12\cdots i'\cdots r1'2'\cdots(i-1)'(i+1)'\cdots s'} \\ &+ \sum_{i<j=1}^{s}\sum_{k<\ell=1}^{r}\Delta^{i'j'}_{k\ell}e^{12\cdots k\cdots\ell\cdots r1'\cdots(i-1)'(i+1)'\cdots(j-1)'(j+1)'\cdots s'}_{12\cdots i'\cdots j'\cdots r1'\cdots(i-1)'(i+1)'\cdots(j-1)'(j+1)'\cdots s'} \\ &+ \cdots \\ &+ \sum_{k_1<k_2<\cdots<k_s=1}^{r}\Delta^{1'2'\cdots s'}_{k_1k_2\cdots k_s}e^{1\cdots k_1\cdots k_2\cdots k_s\cdots r}_{1\cdots 1'\cdots 2'\cdots s'\cdots r}\,, \end{aligned} \tag{28}$$

with the last maximally contracted term corresponding to the case $s < r$. Clearly, when $s = r$, there is only one maximally contracted term $\Delta^{1'2'\cdots r'}_{1\ 2\ \cdots\ r}e^{1\ 2\ \cdots\ r}_{1'2'\cdots r'}$, while for $s > r$ this term takes the form

$$\sum_{i_1<i_2<\cdots<i_r=1}^{s}\Delta^{i_1i_2'\cdots i_r'}_{1\ 2\ \cdots\ r}e^{1'\cdots 1\cdots\ 2\cdots\cdots\ r\cdots\ s'}_{1'\cdots i_1'\cdots i_2'\cdots\cdots i_r'\cdots s'}\,. \tag{28'}$$

With the help of this rule we can now easily evaluate commutators of replacement operators, thus generalizing the one-body or generator commutation relations (10). Thus, for example, Eqs. (18) imply that

$$\left[e^{12}_{12},e^{1'}_{1'}\right] = \delta^{1'}_{1}e^{12}_{1'2} + \delta^{1'}_{2}e^{12}_{11'} - \delta^{1}_{1'}e^{1'2}_{12} - \delta^{2}_{1'}e^{11'}_{12}\,, \tag{29}$$

while Eq. (22) gives

$$\begin{aligned} \left[e^{12}_{12},e^{1'2'}_{1'2'}\right] &= \sum_{i,j=1}^{2}(-1)^{i+j+1}\left(\delta^{i'}_{j}e^{1\ 2\ \bar{\imath}'}_{1'2'j} - \delta^{i}_{j'}e^{1'\ 2'\ \bar{\imath}}_{1\ 2\ j'}\right) \\ &+\Delta^{1'2'}_{12}e^{12}_{1'2'} - \Delta^{12}_{1'2'}e^{1'2'}_{12}\,, \end{aligned} \tag{30}$$

where $\bar{\imath} = 3 - i$, $(i = 1,2)$. In the general case, the uncontracted terms cancel out and only contracted terms remain: those corresponding to the left operator subscripts and the right operator superscripts appear with the positive sign, while those obtained by contracting the left operator superscripts with the right operator subscripts are subtracted.

### 2.4. Orbital replacement operators

Although, for the sake of simplicity, we restrict ourselves in these notes to spin nonadapted formalism, we shall at least briefly indicate the most basic modifications that lead to the corresponding spin-free or even orthogonally spin-adapted formalism. For this purpose we assume that the spin orbital space $\mathcal{V}_m \equiv \mathcal{V}_{2n}$ is expressed as a tensor product of an orbital space $\mathcal{O}_n$ and a two-dimensional spin space $\mathcal{S}_2$,

$\mathcal{V}_{2n} = \mathcal{O}_n \otimes \mathcal{S}_2$. We further assume that our spin orbitals $|\kappa\rangle$ are expressed as monomials consisting of the orbital part $|k\rangle$ and the spin part $|\sigma\rangle$,

$$|\kappa\rangle \equiv |k\sigma\rangle = |k\rangle \otimes |\sigma\rangle, \quad (k = 1, \ldots, n; \sigma = \pm\tfrac{1}{2} \text{ or } \sigma = \pm). \tag{31}$$

The creation and annihilation operators are then similarly indexed as, e.g., $X^\dagger_\kappa = X^\dagger_{k\sigma}$, etc., as are the U($2n$) generators,

$$E^{k\sigma}_{l\sigma'} = X^\dagger_{k\sigma} X_{l\sigma'} . \tag{32}$$

We then define the orbital U($n$) generators as a partial trace over the spin part of spin orbital generators,

$$E^k_l = \sum_\sigma e^{k\sigma}_{l\sigma} = e^{k+}_{l+} + e^{k-}_{l-} . \tag{33}$$

It is easily seen that they indeed satisfy the same commutation relations as the spin orbital generators (Moshinsky, 1966; Paldus, 1974,1976,1988), namely

$$\left[E^k_l, E^m_n\right] = \delta^m_l E^k_n - \delta^k_n E^m_l .$$

We can then similarly define the higher order orbital replacement operators by the recursion relations (Kutzelnigg, 1985; Paldus and Jeziorski, 1988)

$$\begin{aligned} E^{ik}_{jl} &= E^i_j E^k_l - \delta^k_j E^i_l , \\ E^{ikm}_{jln} &= E^{ik}_{jl} E^m_n - \delta^m_j E^{ik}_{nl} - \delta^m_l E^{ik}_{jn} , \text{etc.} \end{aligned} \tag{35}$$

It is obvious that they possess the same algebraic structure as the spin orbital ones. However, in contrast to the spin orbital case, these replacement operators do not necessarily yield orthogonal states when acting on some reference configuration. They may be, however, orthogonally spin-adapted with respect to some chosen coupling scheme. Thus, for example, in the two-body case, we arrive to the particle-particle–hole-hole (*pp-hh*) coupled states (Čížek, 1966b; Paldus, 1977; Paldus *et al.*, 1977; Paldus and Jeziorski, 1988) by taking appropriate symmetric and antisymmetric linear combinations, i.e.

$${}^m E^{ik}_{jl} = {}^m S_{jl} E^{ik}_{jl} , \quad (m = 1, 3) \tag{36}$$

where

$${}^m S_{jl} = e + (2 - m)(j, l) , \tag{37}$$

the latter symbol $(j, l)$ designating the transposition $j \leftrightarrow l$. The operator with $m = 1$ corresponds to the singlet intermediate coupling of particles and holes, and the corresponding symmetizer ${}^1S_{jl}$ represents in fact the projector associated with the totally symmetric irreducible representation [2] of $S_2$. On the other hand, ${}^3S_{jl}$ is associated with the totally antisymmetric two box irrep [$1^2$] and produces doubly excited states with triplet coupled particles and holes. Clearly, if either $j = l$ or $i = k$, this second state vanishes.



In the general case of $k$-body orbital replacement operators, we may simply employ the representation theory for $S_k$ in order to obtain orthogonally spin-adapted states associated with the genealogical coupling scheme (Kutzelnigg, 1985). However, other ways of symmetrization may prove to be useful in special cases (Paldus and Jeziorski, 1988).

### 2.5 Summary of basic properties of replacement operators

For the purposes of future reference we now summarize the basic properties of spin orbital replacement operators that will be useful to us in the following developments. For other interesting properties of these operators we refer the reader to the original literature (Koutecký and Laforgue, 1977; Kutzelnigg, 1985; Paldus and Jeziorski, 1988; Jeziorski and Paldus, 1989; Gould *et al.* 1990). Although we restrict ourselves to the spin orbital formalism, we note that all the properties listed below hold for the orbital replacement operators as well.

(i) Invariance with respect to any simultaneous permutation of upper and lower indices or any even permutation of either lower or upper indices. Phase change if either subscripts or superscripts undergo an odd permutation:

$$e^{\lambda_1 \cdots \lambda_r}_{\mu_1 \cdots \mu_r} \equiv e^{12 \cdots r}_{12 \cdots r} = e^{p_1 p_2 \cdots p_r}_{p_1 p_2 \cdots p_r} = (-1)^{p+q} e^{p_1 p_2 \cdots p_r}_{q_1 q_2 \cdots q_r} , \tag{38}$$

where $p$ and $q$ designate the parity of permutations $P : i \to p_i$ and $Q : i \to q_i$, $i = 1, \ldots, r$.

(ii) The symmetry property (i) implies that $e^{\lambda_1 \cdots \lambda_r}_{\mu_1 \cdots \mu_r}$ vanishes if either $\lambda_i = \lambda_j$ or $\mu_i = \mu_j$ for some $i, j = 1, \ldots r$.

(iii) The sum of replacement operators over all permutations of lower (upper) indices vanishes,

$$\sum_{P \in S_r} e^{1\ 2\ \cdots\ r}_{p_1 p_2 \cdots p_r} = 0 . \tag{39}$$

This follows immediately from the property (i) and the fact that $S_r$ contains equal numbers of even and odd permutations. This seemingly selfevident identity, that also holds for orbital replacement operators (Paldus and Jeziorski, 1988), seems to be equivalent to Green's polynomial identities (Green, 1971), a definitely nontrivial result (Gould *et al.*, 1990).

(iv) The mean value of a replacement operator $e^{1 \cdots r}_{1 \cdots r}$, Eq. (38), in a given reference state $|\Phi\rangle$ vanishes, i.e.,

$$\langle e^{12 \cdots r}_{12 \cdots r} \rangle \equiv \langle \Phi | e^{\lambda_1 \cdots \lambda_r}_{\mu_1 \cdots \mu_r} | \Phi \rangle = 0 , \tag{40}$$

unless all the labels $\lambda_1, \ldots, \lambda_r$ and $\mu_1, \ldots, \mu_r$ belong to spin orbitals *occupied* in $|\Phi\rangle$, in which case

$$\langle e^{12 \cdots r}_{12 \cdots r} \rangle = \Delta^{12 \cdots r}_{12 \cdots r} . \tag{41}$$

Thus, $\langle e^{12\cdots r}_{12\cdots r}\rangle = (-1)^p$ where $p$ is the parity of the permutation $P : \lambda_i \rightarrow \mu_i\,(i = 1, \ldots r)$, and $n_{\lambda i} = n_{\mu i} = 1\,(i = 1, \ldots, r)$ for $|\Phi\rangle$. Clearly, this property is another reflection of the fact that the replacement operators possess the normal order property. It must be emphasized, however, that analogous result does not hold for products of replacement operators, e.g.

$$\langle e^{\alpha}_{\rho} e^{\rho}_{\alpha}\rangle \neq 0 \tag{42}$$

even when $n_\alpha = 1$ but $n_\rho = 0$ in $|\Phi\rangle$.

(v) For the product rule, Eq. (28), and the corresponding rule for the Lie product (commutator) of replacement operators, Eqs. (29), (30), we refer to Section 2.3.

### 2.6. Hamiltonian

We shall consider systems described by the model Hamiltonians, involving at most two-body interactions, of the form

$$H = Z + V = \sum_{\kappa,\mu} z^{\kappa}_{\mu} e^{\mu}_{\kappa} + \tfrac{1}{4} \sum_{\kappa,\lambda,\mu,\nu} v^{\kappa\lambda}_{\mu\nu} e^{\mu\nu}_{\kappa\lambda}\,, \tag{43}$$

where

$$z^{\kappa}_{\mu} = \langle \mu|\hat{z}|\kappa\rangle\,, \tag{44}$$

$$v^{\kappa\lambda}_{\mu\nu} = \langle \mu\nu|\hat{v}|\kappa\lambda\rangle_{\mathcal{A}} = \langle \mu\nu|\hat{v}|\kappa\lambda\rangle - \langle \mu\nu|\hat{v}|\lambda\kappa\rangle\,, \tag{45}$$

represent one- and two-electron integrals in a chosen orthonormal MO basis. Note that the antisymmetrized form of two-electron integrals is employed, so that again

$$v^{\kappa\lambda}_{\mu\nu} = v^{\lambda\kappa}_{\nu\mu} = -v^{\kappa\lambda}_{\nu\mu} = -v^{\lambda\kappa}_{\mu\nu}\,. \tag{46}$$

Using Einstein summation convention — that will always be assumed unless confusion should arise — we thus have

$$H = z^{\kappa}_{\mu} e^{\mu}_{\kappa} + \tfrac{1}{4} v^{\kappa\lambda}_{\mu\nu} e^{\mu\nu}_{\kappa\lambda}\,. \tag{47}$$

Using non-antisymmetrized two-electron integrals we have for the two-electron component (no Einstein convention)

$$V = \tfrac{1}{2} \sum_{\mu,\nu,\kappa,\lambda} \langle \mu\nu|\hat{v}|\kappa\lambda\rangle e^{\mu\nu}_{\kappa\lambda}\,, \tag{48}$$

since

$$\sum_{\mu,\nu,\kappa,\lambda} \langle \mu\nu|\hat{v}|\kappa\lambda\rangle e^{\mu\nu}_{\kappa\lambda} = \sum_{\mu,\nu,\kappa,\lambda} \langle \mu\nu|\hat{v}|\lambda\kappa\rangle e^{\mu\nu}_{\lambda\kappa} = -\sum_{\mu,\nu,\kappa,\lambda} \langle \mu\nu|v|\lambda\kappa\rangle e^{\mu\nu}_{\kappa\lambda}\,. \tag{49}$$

In most molecular applications one considers a spin independent Hamiltonian (see, e.g., Paldus, 1988)

$$H = Z + V = \sum_{i,k} \langle i|\hat{z}|k\rangle E^{i}_{k} + \tfrac{1}{2} \sum_{i,j,k,\ell} \langle ij|\hat{v}|k\ell\rangle E^{ij}_{k\ell}\,, \tag{50}$$



where the orbital replacement operators of Section 2.4 are employed. The resulting spin invariance of $H$,

$$\left[H, S^2\right] = \left[H, S_z\right] = 0\,, \tag{51}$$

where $S^2$ and $S_z$ represent total spin operators, can dramatically simplify the problem and may be conveniently exploited using UGA orbital formalism (cf., Paldus, 1988) or graphical methods of spin algebras (Jucys *et al.*, 1960; Jucys and Bandzaitis, 1977; El Baz and Castel, 1972; Lindgren and Morrison, 1982; Paldus, 1977; Wilson, 1984).

## 3. SINGLE REFERENCE CC FORMALISM

Before we address the MR CC formalism, we consider in this section the standard SR version of CC theory. This will enable us to illustrate the *modus operandi* of an algebraic approach, based on the replacement operator algebra, on a relatively simple case, while deriving at the same time basic CC equations that are employed in both RHF or UHF based approaches and whose spin-adaptation can yield basic equations for the closed shell as well as simple open shell cases, as long as the state considered can be reasonably well described by a SR configuration wave function.

### 3.1. General CC equations

As we explained in some detail earlier (Section 3.5 of Paldus, 1992), the *wave operator* $W$ that transforms the independent particle model (IPM) wave function $|\Phi\rangle$, describing the nondegenerate ground state of some $N$-electron system, into the exact wave function $|\Psi\rangle$,

$$|\Psi\rangle = W|\Phi\rangle\,, \tag{52}$$

can be expressed as an exponential of the so-called *cluster operator* $T$,

$$W = e^{T} \equiv \exp(T)\,, \tag{53}$$

that represents the *connected* component of the exact wave function in the MBPT sense (i.e., when $|\Psi\rangle$ is expressed in the perturbation theoretic form, $T|\Phi\rangle$ represents the connected component of $|\Psi\rangle$).

The use of this cluster expansion form for the exact wave function, Eqs. (52) and (53), is referred to as the *exponential* or *cluster ansatz* for $|\Psi\rangle$. The precise form of the cluster operator $T$ (i.e., the actual values of its various cluster components) depends, of course, on the choice of the IPM reference wave function $|\Phi\rangle$ and on the MO basis employed. In most practical implementations of the theory, one employs the HF (or SCF) MO wave function for $|\Phi\rangle$, representing "the best" SR wave function in the sense of variational principle (i.e., yielding the lowest upper bound to the exact energy $E$ within the manifold of single antisymmetrized product wave functions considered). In theoretical considerations, one often invokes Brueckner MO's, forming "the best" SR wave function $|\Psi^{(B)}\rangle$ in the sense of maximizing the overlap with the exact wave function, since in this case the mono-excited component entirely vanishes. However, any SR (i.e. single antisymmetrized product, Eq. (4), or single Slater determinant)

wave function $|\Phi\rangle$ may be used as our reference. For example, it may be convenient to employ localized MO's rather than canonical SCF MO's in some applications. Note that we shall always assume $|\Phi\rangle$ to be normalized to 1, i.e. $\langle\Phi|\Phi\rangle = 1$, while the so-called intermediate normalization

$$\langle\Phi|\Psi\rangle = 1\,, \tag{54}$$

will be used for the exact wave function $|\Psi\rangle$, as implied by the form of $W$, Eq. (53).

The cluster operator $T$ will thus involve, in general, the one-body ($T_1$), two-body ($T_2$), etc., up to the $N$-body ($T_N$) components,

$$T = \sum_{i=1}^{N} T_i\,, \tag{55}$$

where $N$ is the total electron number. Only when the Brueckner wave function $|\Phi^{(B)}\rangle$ is used as a reference, $T_1$ clusters are entirely absent from $T$. Expanding formally $\exp(T)$ on the right hand side of Eq. (52) into a power series in $T$ and collecting terms of the same excitation order, we arrive at the full configuration interaction (FCI) expansion for $|\Psi\rangle$,

$$|\Psi\rangle = \sum_{i=0}^{N} C_i|\Phi\rangle\,, \tag{56}$$

with $C_0 = 1$ in view of the intermediate normalization employed and $C_i|\Phi\rangle$ representing the $i$-times excited component of $|\Psi\rangle$, so that

$$C_i = T_i + \sum_{\mathcal{P}_i}\prod_{j=1}^{p}(n_j!)^{-1}T_j^{n_j}\,, \tag{57}$$

the sum extending over all nontrivial partitions $\mathcal{P}_i$ of $i$, $i = \sum_{j=1}^{p} jn_j$, $1 \le n_j \le i$, $2 \le p < i$. The first term of the right hand side of Eq. (57), $T_i$, represents the $i$-body *connected* cluster component, while the remaining terms embody the corresponding *disconnected* $i$-body clusters.

The basic CC equations that determine the cluster operators $T_i$ may be arrived at by substituting the cluster expansion for $|\Psi\rangle$, Eqs. (52), (53), into the time independent Schrödinger equation

$$H|\Psi\rangle = E|\Psi\rangle\,, \tag{58}$$

and premultiplying with the inverse of the wave operator $W^{-1} = \exp(-T)$, yielding

$$e^{-T}He^{T}|\Phi\rangle = E|\Phi\rangle\,. \tag{59}$$

Projecting now onto the reference configuration $|\Phi\rangle$ gives the energy expression

$$E = \langle\Phi|e^{-T}He^{T}|\Phi\rangle \equiv \langle e^{-T}He^{T}\rangle\,, \tag{60}$$

while the projection onto the excited state manifold that spans the orthogonal complement to Span$\{|\Phi\rangle\}$ produces the energy independent CC equations

$$\langle\Phi_i^{(k)}|e^{-T}He^{T}|\Phi\rangle = 0\,. \tag{61}$$



Here we assume that the relevant $N$-electron space $\mathcal{W}_N$ (i.e., the $N$-electron component $\mathcal{A}(\mathcal{V}_m^{\otimes N})$ of the Fock space $\mathcal{F}$) is partitioned (graded) by the excitation order ($k$) relative to a chosen reference configuration $|\Phi\rangle$,

$$\mathcal{W}_N = \bigoplus_{k=0}^{N}\mathcal{W}_N^{(k)}\,, \tag{62}$$

where $\mathcal{W}_N^{(0)} = \text{Span}\{|\Phi\rangle\}$ represents the one-dimensional SR space spanned by the reference configuration $|\Phi\rangle \equiv |\Phi_{K_0}\rangle$, while $\mathcal{W}_N^{(k)} = \text{Span}\{|\Phi_i^{(k)}\rangle : i = 1,\dots M\}$ with $i$ enumerating all those $N$-electron ordered configurations (4), whose index set $K = \{\mu_1\mu_2\cdots\mu_N\}$ differs from that characterizing the reference configuration $|\Phi\rangle \equiv |\Phi_{K_0}\rangle$ in $k$ spin orbital labels, i.e. $|K \cap K_0| = N - k$, $|L|$ designating the cardinality of the set $L$.

Using the well known operator identity (see, e.g., Theorem 3, Section 3.2 of Louisell, 1964)

$$e^{-A}Be^{A} = \sum_{n=0}^{\infty}(n!)^{-1}[\cdots[[B,\underbrace{A],A],\cdots,A}_{n}]\,, \tag{63}$$

we can rewrite the energy expression (60) as

$$\begin{aligned} E &= \langle H + [H,T] + \tfrac{1}{2}[[H,T],T]\rangle \\ &= \langle H\rangle + \langle[H,T_1+T_2]\rangle + \tfrac{1}{2}\langle[[H,T_1],T_1]\rangle\,, \end{aligned} \tag{64}$$

since $H$ contains at most two-body terms, so that at most two-body cluster operators (producing two-particle – two-hole states in $\mathcal{W}_N^{(2)}$) can contribute (see also explicit evaluation of these terms in Section 3.2). Moreover, if the HF MO's are employed, $E - \langle H\rangle \equiv \Delta E$ represents the correlation energy, and

$$\Delta E \equiv E - \langle H\rangle = \langle[H,T_1]\rangle + \langle[V,T_2]\rangle + \tfrac{1}{2}\langle[[V,T_1],T_1]\rangle\,. \tag{65}$$

Similarly, for the CC equations (61) at most four-fold commutators from the expansion (63) will survive when $B = H$ contains at most two-body interactions, so that the general form of these equations takes the form

$$\langle\Phi_i^{(k)}|H + [H,T] + \tfrac{1}{2}[[H,T],T] + \tfrac{1}{3!}[[[H,T],T],T] + \tfrac{1}{4!}[[[[H,T],T],T],T]|\Phi\rangle = 0\,. \tag{66}$$

### 3.2. Replacement operator algebra representation

The representation of the Hamiltonian $H$ in terms of the replacement operators was given in Section 2.6. In order to apply the algebraic formalism outlined in Section 2, we have to provide a similar representation for cluster operators $T_i$. This is easily done using the second quantized representation for $T_i$'s. To simplify our notation and avoid multiple indices as much as possible, we introduce the following labeling convention for the spin orbitals $|\mu\rangle$: Spin orbitals that are occupied in the reference configuration $|\Phi\rangle$ will be designated by the letters from the beginning of the Latin alphabet, i.e., $a, b, c$, etc., (and called hole or occupied spin orbitals), while those not

occupied in $|\Phi\rangle$ (particle, excited, unoccupied or virtual spin orbitals) by the letters from the end of the alphabet, i.e. $r, s, t$, etc. The generic spin orbitals (i.e., either occupied or not) will be labelled by the lower case letters of the Greek alphabet, as before. When an arbitrary number of spin orbitals is involved, we attach to these labels numerical subscripts. Thus, we can represent the $i$-body cluster operator as follows

$$\begin{aligned} T_i &= (i!)^{-2} \sum_{r_1,\cdots,r_i} \sum_{a_1,\cdots,a_i} \langle r_1 \cdots r_i | t_i | a_1 \cdots a_i \rangle_{\mathcal{A}} X^\dagger_{r_1} \cdots X^\dagger_{r_i} X_{a_i} \cdots X_{a_1} \\ &= (i!)^{-2} t^{a_1 a_2 \cdots a_i}_{r_1 r_2 \cdots r_i} e^{r_1 r_2 \cdots r_i}_{a_1 a_2 \cdots a_i} , \end{aligned} \tag{67}$$

where in the last equation we again employ the Einstein summation convention. The antisymmetrized cluster amplitudes are labelled accordingly, i.e.

$$t^{a_1 a_2 \cdots a_i}_{r_1 r_2 \cdots r_i} \equiv \langle r_1 r_2 \cdots r_i | t_i | a_1 a_2 \cdots a_i \rangle_{\mathcal{A}} = \sum_{P \in S_i} (-1)^p \langle r_1 r_2 \cdots r_i | t_i | a_{p_1} a_{p_2} \cdots a_{p_i} \rangle , \tag{68}$$

the sum extending over all permutations $P : j \to p_j, (j = 1, \ldots, i)$. Thus, these amplitudes possess the same antisymmetry properties as the replacement operators themselves, Eqs. (15) and (38), or the two-electron integrals $v^{\kappa\lambda}_{\mu\nu}$, Eq. (46).

Specifically, the one- and two-body cluster operators take the form

$$T_1 = t^a_r e^r_a , \tag{69}$$

$$T_2 = \tfrac{1}{4} t^{ab}_{rs} e^{rs}_{ab} , \tag{70}$$

and

$$t^{ab}_{rs} = t^{ba}_{sr} = -t^{ab}_{sr} = -t^{ba}_{rs} . \tag{71}$$

Since the particle $(r, s, \cdots)$ and hole $(a, b, \cdots)$ labels are always distinct, we see that any two replacement operators arising from cluster operators commute, i.e.

$$\left[ e^{rs\cdots}_{ab\cdots}, e^{tu\cdots}_{cd\cdots} \right] = 0 , \tag{72}$$

so that generally

$$[T_i, T_j] = 0 \tag{73}$$

for any $i$ and $j$. For the same reason we also have that

$$e^{r_1 r_2 \cdots r_k}_{a_1 a_2 \cdots a_k} = \prod_{i=1}^{k} e^{r_i}_{a_i} . \tag{74}$$

It is also useful to realize that annihilation condition, Eq. (3), implies the following property for the reference configuration $|\Phi\rangle$ (in this context often called a Fermi vacuum in contrast to the true or physical vacuum $|0\rangle$)

$$X^\dagger_a |\Phi\rangle = X_r |\Phi\rangle = 0 , \tag{75}$$



as well as the corresponding Hermitian conjugate relationships. We thus also have that

$$e^a_r |\Phi\rangle = e^{ab}_{rs} |\Phi\rangle = \cdots = 0 , \tag{76}$$

and

$$\langle \Phi | e^r_a = \langle \Phi | e^{rs}_{ab} = \cdots = 0 , \tag{77}$$

as well as

$$T^\dagger_i |\Phi\rangle = 0 \quad \text{and} \quad \langle \Phi | T_i = 0 . \tag{78}$$

In view of these relationships, we can thus write the CC expression for the energy, Eq. (65), in the form

$$\Delta E = \langle H T_1 \rangle + \langle V T_2 \rangle + \tfrac{1}{2} \langle V T_1^2 \rangle . \tag{79}$$

Next, a general $k$-times excited configuration from $\mathcal{W}^{(k)}_N$ can be represented in the form

$$|\Phi^{(k)}_i\rangle \equiv |\Phi^{r_1 r_2 \cdots r_k}_{a_1 a_2 \cdots a_k}\rangle = e^{r_1 r_2 \cdots r_k}_{a_1 a_2 \cdots a_k} |\Phi\rangle , \tag{80}$$

and its dual by

$$\langle \Phi^{(k)}_i | \equiv \langle \Phi^{r_1 r_2 \cdots r_k}_{a_1 a_2 \cdots a_k} | = \langle \Phi | e^{a_1 a_2 \cdots a_k}_{r_1 r_2 \cdots r_k} . \tag{81}$$

Note also that, e.g.

$$T_2 |\Phi\rangle = \tfrac{1}{4} t^{ab}_{rs} e^{rs}_{ab} |\Phi\rangle = \tfrac{1}{4} t^{ab}_{rs} |\Phi^{rs}_{ab}\rangle , \tag{82}$$

and similarly for $T_i |\Phi\rangle$.

Let us, finally, derive the general explicit expression for the energy, Eq. (79), in terms of one- and two-body cluster components and integrals. Using Eqs. (47), (69) and (70) we can write

$$\langle H T_1 \rangle = z^\kappa_\mu t^a_r \langle e^\mu_\kappa e^r_a \rangle + \tfrac{1}{4} v^{\kappa\lambda}_{\mu\nu} t^a_r \langle e^{\mu\nu}_{\kappa\lambda} e^r_a \rangle , \tag{83a}$$

$$\langle V T_2 \rangle = \tfrac{1}{16} v^{\kappa\lambda}_{\mu\nu} t^{ab}_{rs} \langle e^{\mu\nu}_{\kappa\lambda} e^{rs}_{ab} \rangle , \tag{83b}$$

$$\tfrac{1}{2} \langle V T_1^2 \rangle = \tfrac{1}{8} v^{\kappa\lambda}_{\mu\nu} t^a_r t^b_s \langle e^{\mu\nu}_{\kappa\lambda} e^r_a e^s_b \rangle . \tag{83c}$$

Using the $N$-product form for the replacement operator products, Eq. (28), and property (iv), Eq. (40), we see immediately that only maximally contracted terms can contribute, so that

$$\langle Z T_1 \rangle = z^\kappa_\mu t^a_r \delta^r_\kappa \langle e^\mu_a \rangle = z^\kappa_\mu t^a_r \delta^r_\kappa \delta^\mu_a = z^r_a t^a_r , \tag{84a$_1$}$$

$$\begin{aligned} \langle V T_1 \rangle &= \tfrac{1}{4} v^{\kappa\lambda}_{\mu\nu} t^a_r \left( \delta^r_\kappa \langle e^{\mu\nu}_{a\lambda} \rangle + \delta^r_\lambda \langle e^{\mu\nu}_{\kappa a} \rangle \right) \\ &= \tfrac{1}{4} (v^{rb}_{cd} \Delta^{cd}_{ab} + v^{br}_{cd} \Delta^{cd}_{ba}) t^a_r = v^{rb}_{ab} t^a_r , \end{aligned} \tag{84a$_2$}$$

$$\langle V T_2 \rangle = \tfrac{1}{16} v^{\kappa\lambda}_{\mu\nu} t^{ab}_{rs} \Delta^{rs}_{\kappa\lambda} \langle e^{\mu\nu}_{ab} \rangle = \tfrac{1}{8} v^{rs}_{\mu\nu} t^{ab}_{rs} \Delta^{\mu\nu}_{ab} = \tfrac{1}{4} v^{rs}_{ab} t^{ab}_{rs} , \tag{84b}$$

$$\tfrac{1}{2} \langle V T_1^2 \rangle = \tfrac{1}{8} v^{\kappa\lambda}_{\mu\nu} t^a_r t^b_s \langle e^{\mu\nu}_{\kappa\lambda} e^{rs}_{ab} \rangle = \tfrac{1}{2} v^{rs}_{ab} t^a_r t^b_s . \tag{84c}$$

Thus, altogether

$$\Delta E = f_a^r t_r^a + \tfrac{1}{4} v_{ab}^{rs}(t_{rs}^{ab} + 2t_r^a t_s^b)\,, \tag{85}$$

where

$$f_a^r = z_a^r + v_{ac}^{rc}\,, \tag{86}$$

or, generally

$$\langle \mu|f|\nu\rangle = \langle \mu|z|\nu\rangle + \sum_c (\langle \mu c|v|\nu c\rangle - \langle \mu c|v|c\nu\rangle)\,, \tag{87}$$

the summation extending over the occupied orbitals as our notation indicates. Clearly, when canonical HF MO's are employed, then

$$\langle \mu|f|\nu\rangle \equiv f_\nu^\mu = \varepsilon_\mu \delta_{\mu\nu}\,, \tag{88}$$

$\varepsilon_\mu$'s representing the orbital energies. Since, however, $r \neq a$, we see that the one-body contribution represented by the first term on the right hand side of (85) vanishes. Similarly, if Brueckner orbitals are employed ($T_1 = 0$), or if $T_1$ clusters are neglected, we have that

$$\Delta E^{(\text{pair})} = \tfrac{1}{4} v_{ab}^{rs} t_{rs}^{ab}\,. \tag{89}$$

Finally, note that in the diagrammatic representation (cf., e.g., Paldus, 1992) the three energy terms on the right hand side of (85) are represented by the three diagrams shown in Fig. 1.

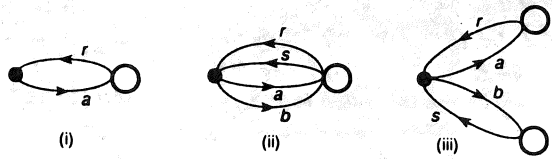


**Fig. 1.** Hugenholtz diagrams representing the CC energy, Eq. (85).

### 3.3. Explicit CCD equations

We shall consider the most basic CC approach, in which only pair clusters are retained, in order to illustrate the replacement operator based technique. We thus set

$$T = T_2, \quad T_1 = T_3 = T_4 = \cdots = 0\,, \tag{90}$$

so that

$$|\Psi\rangle \approx \exp(T_2)|\Phi\rangle\,. \tag{91}$$

Once the pair cluster amplitudes $t_{rs}^{ab}$ that determine $T_2$, Eq. (70), are known, the CCD energy can be easily calculated using Eq. (89). We will thus derive the explicit form of CCD equations for these cluster amplitudes, starting from the general CC equations (66). To obtain the correct number of equations, as well as for other reasons (see, e.g., Paldus, 1992), we shall project onto the manifold of biexcited states $|\Phi_{ab}^{rs}\rangle$, as also suggested by Eq. (82).•) This immediately implies that at most double commutators



can survive, since even the maximally contracted terms arising from the triple and quadruple commutators in (66) will have virtual labels and thus yield the vanishing result in view of property (iv), Eq. (40). Thus, the relevant form of general CC equations (66) in the basic CCD case is as follows

$$\langle \Phi_{ab}^{rs}|H + [H,T_2] + \tfrac{1}{2}[[H,T_2],T_2]|\Phi\rangle = 0\,, \tag{92}$$

with $H$ given by Eq. (43) or (47) and $T_2$ by Eq. (70). Note that while it is convenient to employ unrestricted summations, as in Eq. (70), the number of independent pair clusters is much smaller in view of their symmetry properties, Eq. (71), so that in fact (no Einstein summation convention used here)

$$T_2 = \sum_{a<b} \sum_{r<s} t_{rs}^{ab} e_{ab}^{rs}\,. \tag{93}$$

General CCD equations (92) represent, clearly, a nonlinear algebraic system of equations for the unknown pair cluster amplitudes $t_{rs}^{ab}$, involving an absolute, a linear and a quadratic term, that we shall designate as $A_{ab}^{rs}$, $L_{ab}^{rs}$ and $Q_{ab}^{rs}$, respectively. Thus, we write schematically CCD equations as

$$A_{ab}^{rs} + L_{ab}^{rs} + Q_{ab}^{rs} = 0\,, \tag{94}$$

with

$$A_{ab}^{rs} = \langle e_{rs}^{ab} H\rangle\,, \tag{95}$$

$$L_{ab}^{rs} = \langle e_{rs}^{ab}[H,T_2]\rangle\,, \tag{96}$$

and

$$Q_{ab}^{rs} = \tfrac{1}{2}\langle e_{rs}^{ab}[[H,T_2],T_2]\rangle\,. \tag{97}$$

#### 3.3.1. *Linear CCD equations*

In the first approximation, we may neglect the quadratic term, obtaining the linear approximation to CCD equations, usually designated as the L-CCD approximation,

$$A_{ab}^{rs} + L_{ab}^{rs} = 0\,. \tag{98}$$

The explicit form of the absolute term $A_{ab}^{rs}$, Eq. (95), is easily obtained, since

$$A_{ab}^{rs} = \langle e_{rs}^{ab} Z\rangle + \langle e_{rs}^{ab} V\rangle = z_\mu^\nu \langle e_{rs}^{ab} e_\nu^\mu\rangle + \tfrac{1}{4} v_{\mu\nu}^{\kappa\lambda}\langle e_{rs}^{ab} e_{\kappa\lambda}^{\mu\nu}\rangle\,, \tag{99}$$

The first term clearly vanishes, since the virtual spin orbital labels cannot be contracted away. For the same reasons only fully contracted term can survive in the second term, so that

$$A_{ab}^{rs} = \tfrac{1}{4} v_{\mu\nu}^{\kappa\lambda} \Delta_{rs}^{\mu\nu} \langle e_{\kappa\lambda}^{ab}\rangle = \tfrac{1}{4} v_{\mu\nu}^{\kappa\lambda} \Delta_{rs}^{\mu\nu} \Delta_{\kappa\lambda}^{ab} = v_{rs}^{ab}\,. \tag{100}$$

•) Concerning the possibilities to project onto different, eventually larger, subspaces than those spanned by the repalcement operators associated with the cluster components considered, see Jankowski *et al.*, 1991a.

Note, that

$$w^{\kappa\lambda}_{\mu\nu}\Delta^{\mu\nu}_{rs} = w^{\kappa\lambda}_{\mu\nu}(\delta^{\mu\nu}_{rs} - \delta^{\mu\nu}_{sr}) = w^{\kappa\lambda}_{rs} - w^{\kappa\lambda}_{sr} = 2w^{\kappa\lambda}_{rs}\,, \tag{101}$$

and, similarly

$$w^{\kappa\lambda\rho}_{\mu\nu\tau}\Delta^{\mu\nu\tau}_{rst} = 3!w^{\kappa\lambda\rho}_{rst}\,, \quad \text{etc.}\,, \tag{102}$$

assuming that the quantities $w^{\kappa\lambda\ldots}_{\mu\nu\ldots}$ are fully antisymmetric in its indices as are the replacement operators, Eq. (15) or (38).

To derive the explicit form of the linear term $L^{rs}_{ab}$, Eq. (96), it will be useful to find first the required commutators,

$$[H, T_2] = [Z, T_2] + [V, T_2]\,. \tag{103}$$

Thus, relying on the basic rules for the algebra of replacement operators, we find

$$\begin{aligned}[Z, T_2] &= \tfrac{1}{4}z^{\nu}_{\mu}t^{cd}_{uv}\,[e^{\mu}_{\nu}, e^{uv}_{cd}] \\ &= \tfrac{1}{4}z^{\nu}_{\mu}t^{cd}_{uv}\,(\delta^{u}_{\nu}e^{\mu v}_{cd} + \delta^{v}_{\nu}e^{u\mu}_{cd} - \delta^{\mu}_{c}e^{uv}_{\nu d} - \delta^{\mu}_{d}e^{uv}_{c\nu}) \\ &= \tfrac{1}{2}t^{cd}_{uv}\left(z^{u}_{\mu}e^{\mu v}_{cd} - z^{\nu}_{c}e^{uv}_{\nu d}\right)\,,\end{aligned} \tag{104}$$

since $t^{cd}_{uv}z^{v}_{\mu}e^{u\mu}_{cd} = t^{cd}_{vu}z^{v}_{\mu}e^{\mu u}_{cd} = t^{cd}_{uv}z^{u}_{\mu}e^{\mu v}_{cd}$, etc. Similarly

$$\begin{aligned}[V, T_2] &= \tfrac{1}{16}v^{\kappa\lambda}_{\mu\nu}t^{cd}_{uv}\,[e^{\mu\nu}_{\kappa\lambda}, e^{uv}_{cd}] \\ &= \tfrac{1}{4}t^{cd}_{uv}\left(v^{u\lambda}_{\mu\nu}e^{\mu\nu v}_{c\lambda d} - v^{\kappa\lambda}_{c\mu}e^{u\mu v}_{\kappa\lambda d}\right) + \tfrac{1}{8}t^{cd}_{uv}\left(v^{uv}_{\mu\nu}e^{\mu\nu}_{cd} - v^{\mu\nu}_{cd}e^{uv}_{\mu\nu}\right)\,.\end{aligned} \tag{105}$$

Writing now

$$L^{rs}_{ab} = (L_1)^{rs}_{ab} + (L_2)^{rs}_{ab} = \langle e^{ab}_{rs}[Z, T_2]\rangle + \langle e^{ab}_{rs}[V, T_2]\rangle\,, \tag{106}$$

we first evaluate the first term

$$(L_1)^{rs}_{ab} = \langle e^{ab}_{rs}[Z, T_2]\rangle = \tfrac{1}{2}t^{cd}_{uv}\left(z^{u}_{\mu}\langle e^{ab}_{rs}e^{\mu v}_{cd}\rangle - z^{\nu}_{c}\langle e^{ab}_{rs}e^{uv}_{\nu d}\rangle\right)\,, \tag{107}$$

where we used Eq. (104). Since again only fully contracted terms can contribute (since otherwise virtual labels remain and the reference state mean value vanishes in view of property (iv), Eq. (40)), we get

$$\begin{aligned}(L_1)^{rs}_{ab} &= \tfrac{1}{2}t^{cd}_{uv}\left(z^{u}_{\mu}\Delta^{\mu v}_{rs}\Delta^{ab}_{cd} - z^{\nu}_{c}\Delta^{uv}_{rs}\Delta^{ab}_{\nu d}\right) \\ &= t^{cd}_{uv}z^{u}_{\mu}\Delta^{\mu v}_{rs} - t^{cd}_{rs}z^{\nu}_{c}\Delta^{ab}_{\nu d} \\ &= z^{u}_{r}t^{ab}_{us} + z^{u}_{s}t^{ab}_{ru} - z^{a}_{c}t^{cb}_{rs} - z^{b}_{c}t^{ac}_{rs}\,,\end{aligned} \tag{108}$$

or

$$(L_1)^{rs}_{ab} = \mathcal{A}_{rs}z^{u}_{r}t^{ab}_{us} - \mathcal{A}_{ab}z^{a}_{c}t^{cb}_{rs}\,, \tag{108'}$$

where

$$\mathcal{A}_{\mu\nu} = e - (\mu, \nu) \tag{109}$$



is the antisymmetrizer in $\mu$ and $\nu$ [note that $\mathcal{A}_{\mu\nu} = {}^3S_{\mu\nu}$, Eq. (37)].

The second term $(L_2)^{rs}_{ab}$ we split again into the two parts arising from the two terms on the right hand side of Eq. (105), i.e.

$$(L_2)^{rs}_{ab} = \langle e^{ab}_{rs}[V, T_2]\rangle = B^{rs}_{ab} + C^{rs}_{ab}\,, \tag{110}$$

where

$$B^{rs}_{ab} = \tfrac{1}{4}t^{cd}_{uv}\left(v^{u\lambda}_{\mu\nu}\langle e^{ab}_{rs}e^{\mu\nu v}_{c\lambda d}\rangle - v^{\kappa\lambda}_{c\mu}\langle e^{ab}_{rs}e^{u\mu v}_{\kappa\lambda d}\rangle\right)\,, \tag{111}$$

and

$$C^{rs}_{ab} = \tfrac{1}{8}t^{cd}_{uv}\left(v^{uv}_{\mu\nu}\langle e^{ab}_{rs}e^{\mu\nu}_{cd}\rangle - v^{\mu\nu}_{cd}\langle e^{ab}_{rs}e^{uv}_{\mu\nu}\rangle\right)\,. \tag{112}$$

Evaluating again mean values of the replacement operator products, e.g., $\langle e^{ab}_{rs}e^{\mu\nu v}_{c\lambda d}\rangle$, we realize that the virtual labels $r, s$ and $v$ must be contracted away for the resulting mean value not to vanish. Writing down the nonvanishing terms, we get

$$\langle e^{ab}_{rs}e^{\mu\nu v}_{c\lambda d}\rangle = \Delta^{\mu v}_{rs}\langle e^{ab\nu}_{c\lambda}\rangle + \Delta^{\nu v}_{rs}\langle e^{ab\mu}_{\lambda dc}\rangle\,, \tag{113}$$

and, similarly,

$$\langle e^{ab}_{rs}e^{u\mu v}_{\kappa\lambda d}\rangle = \Delta^{uv}_{rs}\langle e^{ab\mu}_{\kappa d\lambda}\rangle\,. \tag{114}$$

The generic labels $\kappa$, $\lambda$, $\mu$ and $\nu$ appearing inside the mean values can run only over occupied orbitals. Since they invariably represent the summation labels, we replace them by $e$, $f$, $g$, etc. in accordance with our labelling convention for spin orbitals. Substituting, thus, the results (113) and (114) into our expression for $B^{rs}_{ab}$, Eq. (111), we get

$$\begin{aligned}B^{rs}_{ab} &= \tfrac{1}{4}t^{cd}_{uv}[v^{u\lambda}_{\mu\nu}(\Delta^{\mu v}_{rs}\langle e^{ab\nu}_{cd\lambda}\rangle + \Delta^{\nu v}_{rs}\langle e^{ab\mu}_{\lambda dc}\rangle) + v^{\kappa\lambda}_{c\mu}\Delta^{uv}_{rs}\langle e^{ab\mu}_{\kappa\lambda d}\rangle] \\ &= \tfrac{1}{2}\mathcal{A}_{rs}t^{cd}_{us}v^{uf}_{re}\Delta^{abe}_{cdf} + \tfrac{1}{2}t^{cd}_{rs}v^{fg}_{ce}\Delta^{abe}_{fgd}\,.\end{aligned} \tag{115}$$

Recalling the property (26), specifically in our case that

$$\Delta^{abe}_{cdf} = \Delta^{ab}_{cd}\delta^{e}_{f} + \mathcal{A}_{ab}\Delta^{be}_{cd}\delta^{a}_{f}\,, \tag{116}$$

and similarly for $\Delta^{abe}_{fgd}$, we get

$$\begin{aligned}B^{rs}_{ab} &= \mathcal{A}_{rs}(t^{ab}_{us}v^{ue}_{re} + \mathcal{A}_{ab}t^{be}_{us}v^{ua}_{re}) + t^{ce}_{rs}v^{ab}_{ce} + \mathcal{A}_{ab}t^{cb}_{rs}v^{ea}_{ce} \\ &= \mathcal{A}_{rs}v^{uc}_{re}t^{eb}_{us} - \mathcal{A}_{ab}v^{ad}_{cd}t^{cb}_{rs} + v^{ab}_{cd}t^{cd}_{rs} + \mathcal{A}_{rs}\mathcal{A}_{ab}v^{au}_{rc}t^{bc}_{su}\,.\end{aligned} \tag{117}$$

Finally, for the $C^{rs}_{ab}$, Eq. (112), we get easily that

$$C^{rs}_{ab} = \tfrac{1}{8}t^{cd}_{uv}(v^{uv}_{\mu\nu}\Delta^{\mu\nu}_{rs}\Delta^{ab}_{cd} - v^{\mu\nu}_{cd}\Delta^{uv}_{rs}\Delta^{ab}_{\mu\nu}) = \tfrac{1}{2}(v^{uv}_{rs}t^{ab}_{uv} - v^{ab}_{cd}t^{cd}_{rs})\,. \tag{118}$$

Realizing that the first two terms on the right hand side of (117) may be grouped together with the corresponding terms in $(L_1)^{rs}_{ab}$, Eq. (108), using the HF-like one-electron operator $f^{\mu}_{\nu}$, Eqs. (86), (87), we can express the final result as follows

$$L^{rs}_{ab} = \mathcal{A}_{rs}f^{u}_{r}t^{ab}_{us} - \mathcal{A}_{ab}f^{a}_{c}t^{cb}_{rs} + \tfrac{1}{2}(v^{ab}_{cd}t^{cd}_{rs} + v^{uv}_{rs}t^{ab}_{uv}) + \mathcal{A}_{rs}\mathcal{A}_{ab}v^{au}_{rc}t^{bc}_{su}\,. \tag{119}$$

The individual terms in this expression may be easily identified with their corresponding diagrammatic representation shown in Fig. 2.

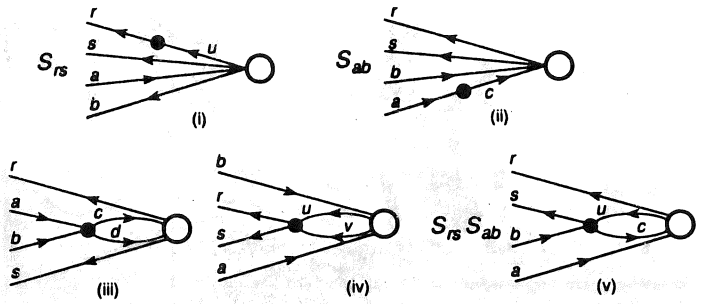


**Fig. 2.** Hugenholtz diagrams representing the linear part of CCD equations. Note that symmetrizers in the diagrammatic form correspond to antisymmetrizers in the algebraic form (Piecuch and Paldus 1989,1990,1992). Note also that the symmetry of these diagrams immediately implies the numerical factors in the algebraic form.

**3.3.2.** *Full CCD equations*

To obtain full CCD equations, we only have to add the nonlinear (quadratic or bilinear) term $Q^{rs}_{ab}$, Eq. (97), to the L-CCD equations (98), (100) and (119). To evaluate this term, we again consider separately the contributions from the one- and two-electron components of the Hamiltonian,

$$Q^{rs}_{ab} = (Q_1)^{rs}_{ab} + (Q_2)^{rs}_{ab} . \tag{120}$$

We easily find that the one-electron part vanishes. Indeed,

$$\begin{aligned}(Q_1)^{rs}_{ab} &= \tfrac{1}{2}\langle e^{ab}_{rs}[[Z,T_2],T_2]\rangle \\ &= \tfrac{1}{16} t^{cd}_{uv} t^{ef}_{tw} \left( z^u_\mu \langle e^{ab}_{rs}[e^{\mu v}_{cd}, e^{tw}_{ef}]\rangle - z^v_e \langle e^{ab}_{rs}[e^{uv}_{\nu d}, e^{tw}_{ef}]\rangle \right) ,\end{aligned} \tag{121}$$

where we employed Eq. (104) for the commutator $[Z,T_2]$. Realizing that

$$\langle e^{ab}_{rs}[e^{\mu v}_{cd}, e^{tw}_{ef}]\rangle = -\delta^\mu_e \langle e^{ab}_{rs} e^{tvw}_{cdf}\rangle - \delta^\mu_f \langle e^{ab}_{rs} e^{wvt}_{cde}\rangle = 0 , \tag{122}$$

and, similarly,

$$\langle e^{ab}_{rs}[e^{uv}_{\nu d}, e^{tw}_{ef}]\rangle = \delta^t_\nu \langle e^{ab}_{rs} e^{uvw}_{edf}\rangle + \delta^w_\nu \langle e^{ab}_{rs} e^{uvt}_{fde}\rangle = 0 , \tag{123}$$

since the virtual spin orbital labels cannot be fully contracted out, we see that

$$(Q_1)^{rs}_{ab} = 0 , \tag{124}$$

so that

$$Q^{rs}_{ab} = (Q_2)^{rs}_{ab} = \tfrac{1}{2}\langle e^{ab}_{rs}[[V,T_2],T_2]\rangle . \tag{125}$$

Using expression (105) for the commutator $[V,T_2]$, we can write for the required double commutator appearing on the right hand side of (125) the following explicit



expression

$$\begin{aligned} Q \equiv\ & 1\ddot{6}[[V,T_2],T_2] \\ =\ & t^{cd}_{uv} t^{ef}_{tw} \Big( v^{u\lambda}_{\mu\nu}[e^{\mu\nu w}_{c\lambda d}, e^{tw}_{ef}] - v^{\kappa\lambda}_{c\mu}[e^{u\mu v}_{\kappa\lambda d}, e^{tw}_{ef}] + \tfrac{1}{2} v^{uv}_{\mu\nu}[e^{\mu\nu}_{cd}, e^{tw}_{ef}] - \tfrac{1}{2} v^{\mu\nu}_{cd}[e^{uv}_{\mu\nu}, e^{tw}_{ef}] \Big) \\ =\ & t^{cd}_{uv} t^{ef}_{tw} \Big[ v^{u\lambda}_{\mu\nu} \Big( \delta^t_\lambda e^{\mu\nu vw}_{cedf} + \delta^w_\lambda e^{\mu\nu vt}_{cfde} - \delta^\mu_e e^{tvvw}_{c\lambda df} - \delta^\mu_f e^{wvvt}_{c\lambda de} - \delta^v_e e^{\mu tvw}_{c\lambda df} - \delta^v_f e^{\mu wvt}_{c\lambda de} - \Delta^{\mu\nu}_{ef} e^{tvw}_{c\lambda d} \Big) \\ & + v^{\kappa\lambda}_{c\mu} \Big( \delta^\mu_e e^{utvw}_{\kappa\lambda df} + \delta^\mu_f e^{uwvt}_{\kappa\lambda de} - \delta^t_\kappa e^{uvvw}_{e\lambda df} - \delta^t_\lambda e^{uvvw}_{\kappa edf} - \delta^w_\kappa e^{uvvt}_{f\lambda de} - \delta^w_\lambda e^{uvvt}_{\kappa fde} - \Delta^{tw}_{\kappa\lambda} e^{uvv}_{efd} \Big) \\ & - \tfrac{1}{2} v^{uv}_{\mu\nu} \Big( \delta^\mu_e e^{tvw}_{cdf} + \delta^\mu_f e^{wvt}_{cde} + \delta^v_e e^{utw}_{cdf} + \delta^v_f e^{wvt}_{cde} + \Delta^{\mu\nu}_{ef} e^{tw}_{cd} \Big) \\ & - \tfrac{1}{2} v^{\mu\nu}_{cd} \Big( \delta^t_\nu e^{uvw}_{evf} + \delta^t_\nu e^{uvw}_{\mu ef} + \delta^w_\mu e^{uvt}_{fve} + \delta^w_\nu e^{uvt}_{fve} + \Delta^{tw}_{\mu\nu} e^{uv}_{ef} \Big) \Big] . \end{aligned} \tag{126}$$

Now, again, evaluating the mean value $\langle e^{ab}_{rs} Q\rangle$, only those terms from $Q$ can contribute that have at most two virtual labels as superscripts (and may thus be contracted with the $r$ and $s$ labels from $e^{ab}_{rs}$), so that, e.g.

$$\langle e^{ab}_{rs} e^{tvwv}_{\dots}\rangle = \langle e^{ab}_{rs} e^{tvw}_{\dots}\rangle = \langle e^{ab}_{rs} t^{tuv}\rangle = \cdots = \langle e^{ab}_{rs} e^{tuvw}_{\dots}\rangle = 0 . \tag{127}$$

Thus,

$$\begin{aligned} 32 Q^{rs}_{ab} &= 16\langle e^{ab}_{rs}[[V,T_2],T_2]\rangle = \langle e^{ab}_{rs} Q\rangle \\ &= t^{cd}_{uv} t^{ef}_{tw} \Big[ v^{u\lambda}_{\mu\nu} \Big( \delta^t_\lambda \langle e^{ab}_{rs} e^{\mu vvw}_{cedf}\rangle + \delta^w_\lambda \langle e^{ab}_{rs} e^{\mu vvt}_{cfde}\rangle \Big) - v^{\kappa\lambda}_{c\mu} \Delta^{tw}_{\kappa\lambda} \langle e^{ab}_{rs} e^{uvv}_{efd}\rangle \\ &\quad - \tfrac{1}{2} v^{uv}_{\mu\nu} \Big( \delta^\mu_e \langle e^{ab}_{rs} e^{tvw}_{cdf}\rangle + \delta^\mu_f \langle e^{ab}_{rs} e^{wvt}_{cde}\rangle + \delta^v_e \langle e^{ab}_{rs} e^{\mu tw}_{cdf}\rangle \\ &\quad + \delta^v_f \langle e^{ab}_{rs} e^{\mu wt}_{cde}\rangle + \Delta^{\mu\nu}_{ef} \langle e^{ab}_{rs} e^{tw}_{cd}\rangle \Big) - \tfrac{1}{2} v^{\mu\nu}_{cd} \Delta^{tw}_{\mu\nu} e^{uv}_{ef} \Big] \end{aligned} \tag{128}$$

$$\begin{aligned} &= t^{cd}_{uv} t^{ef}_{tw} \Big( \mathcal{A}_{tw} v^{ut}_{\mu\nu} \langle e^{ab}_{rs} e^{\mu vvw}_{cedf}\rangle - 2 v^{tw}_{c\mu} \langle e^{ab}_{rs} e^{uv\mu}_{edf}\rangle \\ &\quad - \big[ v^{uv}_{e\mu} \langle e^{ab}_{rs} e^{\mu tw}_{dcf}\rangle + v^{uv}_{f\mu} \langle e^{ab}_{rs} e^{\mu tw}_{dec}\rangle \big] - v^{uv}_{ef} \langle e^{ab}_{rs} e^{tw}_{cd}\rangle - v^{tw}_{cd} \langle e^{ab}_{rs} e^{uv}_{ef}\rangle \Big) \\ &= 2^5 (D^{rs}_{ab} + E^{rs}_{ab} + F^{rs}_{ab} + G^{rs}_{ab} + H^{rs}_{ab}) , \end{aligned}$$

where

$$2^5 D^{rs}_{ab} = t^{cd}_{uv} t^{ef}_{tw} \mathcal{A}_{tw} v^{ut}_{\mu\nu} \langle e^{ab}_{rs} e^{\mu vvw}_{cedf}\rangle = t^{cd}_{uv} t^{ef}_{tw} \mathcal{A}_{tw} v^{ut}_{\mu\nu} \Delta^{vw}_{rs} \langle e^{\mu vab}_{cedf}\rangle = 2\mathcal{A}_{rs} t^{cd}_{ur} t^{ef}_{ts} v^{ut}_{gh} \Delta^{ghab}_{cedf} , \tag{129}$$

$$2^4 E^{rs}_{ab} = -t^{cd}_{uv} t^{ef}_{tw} v^{tw}_{c\mu} \Delta^{uv}_{rs} \Delta^{ab\mu}_{edf} = -2 t^{cd}_{rs} t^{ef}_{tw} v^{tw}_{cg} \Delta^{abg}_{edf} , \tag{130}$$

$$\begin{aligned} 2^5 F^{rs}_{ab} &= -t^{cd}_{uv} t^{ef}_{tw} \mathcal{A}_{ef} v^{uv}_{eg} \Delta^{tw}_{rs} \Delta^{gab}_{dcf} = -2 t^{cd}_{uv} t^{ef}_{rs} \mathcal{A}_{ef} v^{uv}_{eg} \Delta^{gab}_{dcf} \\ &= 2^2 t^{cd}_{uv} t^{ef}_{rs} v^{uv}_{eg} \Delta^{gab}_{cdf} = 2^2 t^{cd}_{uv} t^{cf}_{rs} v^{uv}_{cg} \Delta^{abg}_{edf} = 2^5 E^{rs}_{ab} , \end{aligned} \tag{131}$$

$$2^5 G^{rs}_{ab} = -t^{cd}_{uv} t^{ef}_{tw} v^{uv}_{ef} \Delta^{tw}_{rs} \Delta^{ab}_{cd} = -2^2 t^{ab}_{uv} t^{ef}_{ts} v^{uv}_{ef} , \tag{132}$$

$$2^5 H^{rs}_{ab} = -t^{cd}_{uv} t^{ef}_{tw} v^{tw}_{cd} \Delta^{uv}_{rs} \Delta^{ab}_{ef} = -2^2 t^{cd}_{rs} t^{ab}_{tw} v^{tw}_{cd} = 2^5 G^{rs}_{ab} . \tag{133}$$

We recall that all the spin orbital labels on $\Delta$ symbols (that arise from the mean value of a replacement operator) must be hole labels, as reflected in the above used notation. Using now identity (27) for $\Delta^{ghab}_{cdef}$ and similar ones [see Eq. (26) for the general case] for $\Delta^{abg}_{cdf}$ and $\Delta^{gab}_{cdf}$ [see, e.g., Eq. (116)], and gathering together identical terms, we get, finally

$$\begin{aligned} D^{rs}_{ab} &= \tfrac{1}{2} \mathcal{A}_{rs} \left[ \mathcal{A}_{ab} t^{ac}_{ur} t^{bd}_{vs} + t^{ab}_{vr} t^{cd}_{us} \right] v^{uv}_{cd} \\ &= \mathcal{A}_{rs} \left( t^{ac}_{ru} t^{bd}_{sv} + \tfrac{1}{2} t^{ab}_{rv} t^{cd}_{su} \right) v^{uv}_{cd} , \end{aligned} \tag{134}$$

$$\begin{aligned} E^{rs}_{ab} &= \tfrac{1}{4} \left( \mathcal{A}_{ab} t^{ca}_{rs} t^{bg}_{tw} + t^{cg}_{rs} t^{ab}_{tw} \right) v^{tw}_{cg} = \tfrac{1}{4} \left( t^{ab}_{uv} t^{cd}_{rs} + \mathcal{A}_{ab} t^{bc}_{rs} t^{ad}_{uv} \right) v^{uv}_{cd} \\ &= \tfrac{1}{4} \left( t^{ab}_{uv} t^{cd}_{rs} + \mathcal{A}_{ab} t^{ad}_{rs} t^{bc}_{uv} \right) v^{uv}_{cd} = F^{rs}_{ab} , \end{aligned} \tag{135}$$

$$G^{rs}_{ab} = -\tfrac{1}{8} t^{ab}_{uv} t^{cd}_{rs} v^{uv}_{cd} = H^{rs}_{ab} . \tag{136}$$

Since the last two terms ($G^{rs}_{ab} = H^{rs}_{ab}$) partially cancel the first term in $E^{rs}_{ab} = F^{rs}_{ab}$, we get finally

$$Q^{rs}_{ab} = \left[ \mathcal{A}_{rs} \left( t^{ac}_{ru} t^{bd}_{sv} + \tfrac{1}{2} t^{ab}_{rv} t^{cd}_{su} \right) + \tfrac{1}{2} \mathcal{A}_{ab} t^{ad}_{rs} t^{bc}_{uv} + \tfrac{1}{4} t^{ab}_{uv} t^{cd}_{rs} \right] v^{uv}_{cd} . \tag{137}$$

The diagrammatic representation of the resulting four nonlinear terms constituting $Q^{rs}_{ab}$ is shown in Fig. 3. We note again that to antisymmetrizers $\mathcal{A}_{ij}$ in Eq. (137) correspond symmetrizers $\mathcal{S}_{ij}$ in the diagrammatic representation shown in Fig. 3 (similarly as for Fig. 2), which interchange the hole $(a, b)$ or the particle $(r, s)$ labels on nonequivalent fermionic lines (see also Piecuch and Paldus, 1989). Clearly, this interchange corresponds to the corresponding interchange of labels on the biexcited state $|\Phi^{rs}_{ab}\rangle$ onto which we project, thus resulting in a sign change. Note also that in the first diagram (term) the $\mathcal{S}_{rs}(\mathcal{A}_{rs})$ operator may be replaced by the $\mathcal{S}_{ab}(\mathcal{A}_{ab})$ operator. The numerical factors $(1, \frac{1}{2}, \frac{1}{2}, \frac{1}{4})$ are again given by the number of equivalent summation lines in these diagrams. For details of diagrammatic representation we refer the reader to Bad Windsheim lecture notes (Paldus, 1992), where also more details concerning the higher approaches involving $T_1$ and $T_3$ clusters, CCSD and CCSDT methods, respectively, as well as concerning the calculation of other properties than energy, may be found. We also refer the reader to other reviews and descriptions of SR CC theories given earlier (in particular, see Bartlett, 1981, 1989, where also actual applications are described).



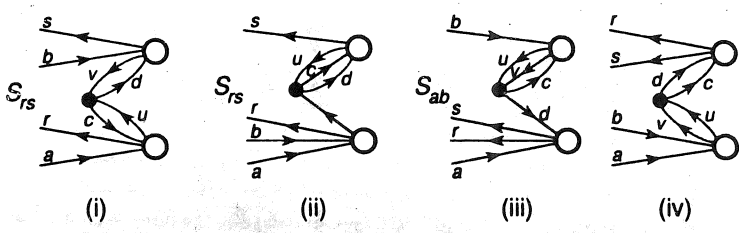


**Fig. 3.** Hugenholtz diagrams representing the nonlinear part of CCD equations. See also caption to Fig. 2.

## 4. MULTI-REFERENCE CC FORMALISM

As already pointed out, an extension of the SR cluster ansatz to the multi-reference (MR) situations is essential for a proper description of general open-shell systems or even nearly generate closed-shell ones. Although the SR formalism works remarkably well even if quite severe quasidegeneracy is encountered (cf., e.g., Jankowski and Paldus, 1980; Paldus *et al.*, 1988), and its range of applicability may be further extended by considering connected higher excited clusters, namely $T_3$ or even $T_4$ (Bartlett *et al.*, 1989, 1990; Kucharski and Bartlett, 1989; Noga *et al.*, 1989; Lee and Taylor, 1989; Lee *et al.*, 1990; Lee and Scuseria, 1990; Rendell *et al.*, 1990; Scuseria and Lee, 1990; Watts *et al.*, 1990; Oliphant and Adamowicz, 1991; Lee and Rendell, 1991; Lee and Rice, 1991; Rendell *et al.*, 1991; Rice *et al.*, 1991; for an approximate account of $T_4$ clusters, see e.g., Paldus *et al.*, 1984; Takahashi and Paldus, 1985; Piecuch *et al.*, 1990), an appropriate treatment of general open-shell and quasidegenerate situations requires the MR formalism, particularly when one wishes to explore entire potential energy surfaces for a group of strongly interacting states at certain geometries.

The difficulties that one encounters in extending the SR coupled cluster ansatz to the MR case have been already briefly alluded to in the Introduction. For greater detail concerning the historical developments we refer to earlier reviews (Lindgren and Mukherjee, 1987; Mukherjee and Pal, 1989; Paldus, 1992). Here we hope to present a concise yet very basic introduction to the MR formalism and the open-shell generalizations of the standard exponential cluster ansatz (Jeziorski and Paldus, 1989). We again refer the reader to Chapter 5 of our earlier exposition (Paldus, 1992) concerning the most basic concepts and theory of the MR formalism, in particular the derivation of the so-called *Bloch equation* and the related *effective Hamiltonian formalism*. These topics will be only briefly reviewed here for the sake of completeness and to introduce the required notation. We will then concentrate on the basics of the Fock space and Hilbert space MR formalisms for the complete model spaces. For the problems concerning incomplete model spaces we refer the reader to the original literature (Brandow 1967, 1977; Hose and Kaldor, 1979, 1980, 1982; Jeziorski and