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Quasiparticle Fock-space coupled-cluster theory — Source link

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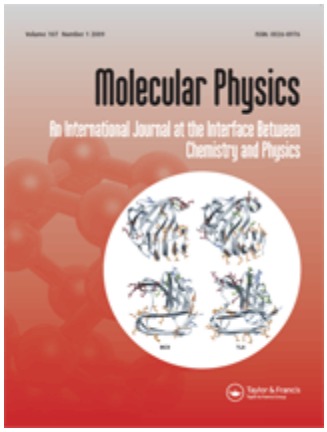

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RESEARCH ARTICLE

Quasiparticle Fock-Space Coupled-Cluster Theory

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The quasiparticle Fock-space coupled-cluster (QFSCC) theory, introduced by us in 1985, is described. This is a theory of many-electron systems which uses the second-quantization formalism based on the algebraic approximation: one chooses a finite spin-orbital basis, and builds a fermionic Fock space to represent all possible antisymmetric electronic states of a given system. The algebraic machinery is provided by the algebra of linear operators acting in the Fock space, generated by the fermion (creation and annihilation) operators. The Fock-space Hamiltonian operator then determines the systems stationary states and their energies.

Within the QFSCC theory, the Fock space and its operator algebra are subject to a unitary transformation which effectively changes electrons into some fermionic quasiparticles. A generalization of the coupled-cluster method is achieved by enforcing the principle of quasiparticle-number conservation. The emerging quasiparticle model of many-electron systems offers useful physical insights and computational effectiveness.

The QFSCC theory requires a substantial reformulation of the traditional second-quantization language, by making a full use of the algebraic properties of the Fock space and its operator algebra. In particular, the role of operators not conserving the number of electrons (or quasiparticles) is identified.

Keywords: many-electron systems, fermions, quasiparticles, Fock space, coupled-cluster method.

1. Introduction

In 1983, while working together in the Quantum Theory Project, we started a new theoretical project aimed at describing the electronic states of conducting (and possibly – superconducting) polymers. Our first paper was presented as a poster during the Sanibel Symposium in 1984, and subsequently it was published in the Symposium volume of the International Journal of Quantum Chemistry [1]. It was followed by a four-paper series [2–5] under the common title "Coupled-cluster method in Fock space," in which we introduced a new model of many-fermion systems – the quasiparticle model exploiting the algebraic properties of the fermionic Fock space, based on the coupled-cluster approach. The specialization of this theory to extended systems was discussed in [6]. In 1989 Maria Barysz joined the project, and we did some pilot applications of our Fock-space coupled-cluster (FSCC) theory to model π-electron systems [7]. In that paper we studied the ground-state energy

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and molecular (vertical) excitation energies (including ionization potentials, electron affinities, and singlet and triplet excitations), and compared the FSCC results with the full configuration-interaction (FCI) benchmark values.

It seems that the title of our quadrilogy [2–5] has popularized the name "Fock-space coupled-cluster method," which was then attributed *a posteriori* to the family of related coupled-cluster approaches [8]. However, our papers fostered a novel algebraic language which departed largely from the literature standards, e.g. those set forth by Paldus and Čížek [9]. That language, apparently, was too foreign to the practitioners of the coupled-cluster methodology to win wider popularity for our quasiparticle FSCC theory. We feel that now, given the time perspective, it is worthwhile to present a bird's eye view of its algebraic foundations.

2. Inspirations and motivations

Conducting polymers was a hot topic already in the eighties, long before the Nobel prize (2000) for Heeger, McDiarmid, and Shirakawa. In addition, there was a fascinating proposal (1964) by Little [10] of the so-called excitonic superconductivity in polymers of special architecture (a conducting backbone plus highly polarizable side groups). Essentially it was the electronic correlation which was the driving force for the superconductivity in the Little model, and the predicted transition temperature T_c was quite high. In 1983 we were fascinated by that model (it was before Bednorz and Müller started the high-T_c revolution in 1986 [11]), and we have been looking for a theoretical framework capable of handling the problem of electronic correlations in anisotropic metallic systems.

The quantum description of an extended electronic system requires numerical methods that fulfill the condition of extensivity. The coupled-cluster (CC) method [12–14] is thus a natural choice. In the (single-reference) CC method the ground-state N-electron wave function Ψ is represented by using the exponential Ansatz:

$$\Psi = \exp(\hat{T})\Phi \,, \qquad \hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_N \,, \tag{1}$$

where $\Phi = \Phi_{\rm HF}$ is the reference Slater determinant (the Hartree-Fock one in this case), and operators $\hat{T}_n$ generate n-tuple excitations from Φ. The (exact) wave function Ψ of Eq. (1) is not normalized, but fulfills the so-called *intermediate normalization condition*:

$$\langle \Phi | \Psi \rangle = 1 \,. \tag{2}$$

The success of the CC calculations for the homogeneous electron gas (see Emrich and Zabolitzky [15], and references therein) indicated that the CC method may be a proper tool also for conducting polymers. However, in the case of an extended system focusing on the ground-state is insufficient, and one needs to address also the (correlated) band-structure problem (e.g., in the spirit of Pantelides *et al.* [16]).This calls for a theoretical framework dealing simultaneously with a family of N-, $(N-1)$-, and $(N+1)$-electron states. Again, Emrich and Zabolitzky [15] gave some hint how the electronic-band spectrum could be calculated within the CC scheme; moreover, they proposed to use the Bogoliubov-Valatin transformation [17, 18], thus pawing the way into applications to supeconducting systems.

In a metallic system the shape of the Fermi surface may be sensitive to the correlation effects. In this respect the standard CC method based on the HF reference Slater determinant lacks the necessary flexibility. Our first step towards the CC method applicable to conducting polymers [1] was to optimize the reference Slater

determinant Φ along the line suggested by Chiles and Dykstra [19]: by transforming the orbitals occupied in Φ such that the single-excitation cluster operator vanishes, $\hat{T}_1 = \hat{0}$. The optimization of the orbitals is a self-consistent procedure leading to the Brueckner reference determinant, $\Phi = \Phi_{\rm B}$, that fulfills *the maximum overlap condition* with the exact wave function Ψ:

$$\langle \Phi_{\rm B} | \hat{Z} \Phi_{\rm B} \rangle = \text{maximum} \,, \qquad \hat{Z} = \frac{|\Psi\rangle\langle\Psi|}{\langle\Psi|\Psi\rangle} \,. \tag{3}$$

In [1] we showed that the Brueckner orbitals can be determined as eigenvectors of a one-electron operator which is a sum of the Fock operator and a correlation potential depending of the amplitudes of operators $\hat{T}_2$ and $\hat{T}_3$. We described in detail how this Brueckner-Hartree-Fock (BHF) method works in the case of a truncated cluster operator $\hat{T} = \hat{T}_2$, which allows for capturing the most essential electronic-correlation effects. Five years later Handy *et al.* [20] popularized that approach under the name of the Brueckner Doubles method (but instead of solving the BHF equations they performed orbital rotations using the amplitudes of operator $\hat{T}_1$).

Our next step was to look for a more general CC approach – a multireference one, that would allow for a simultaneous treatment of states with different numbers of electrons. We had the multireference CC method of Jeziorski and Monkhorst [21], but it was designed for an ensemble of states with the same electron number. There was also a family of multireference CC methods, proposed independently by Coester [22], Offermann *et al.* [23, 24], Mukherjee *et al.* [25], and Lindgren [26], which seemed more relevant for our purpose. However, the corresponding formalisms looked very different, and it was difficult to decide whether they are equivalent. We abandoned detailed analyses of these methods and, instead, took on a synthetic route: to build our own approach based on a general idea of quasiparticles. Another inspiration came from a series of papers by Kutzelnigg, opening with paper [27]: in these papers he emphasized the importance of the Fock-space view of many-electron systems – the view which necessarily implied a certain genealogy of states with different numbers of electrons. We also took advantage of a new algebraic tool – the contraction theorem – introduced by Harris *et al.* [28].

These are the origins of our quasiparticle model described in papers [2–5]. Below we present an overview of this model. The notation used is basically that of papers [2–7], with some modifications borrowed from [29].

3. Algebraic framework (I): Fock space

We consider a finite electronic system, e.g., a molecule within the Born-Oppenheimer approximation. Extended systems may be described by assuming the cyclic boundary conditions, and then studying the thermodynamic limit [6].

3.1. *Algebraic approximation and spin-orbital basis*

The algebraic approximation is assumed: we choose certain m_0-element orthonormal set of orbitals, from which the corresponding M-element ($M = 2m_0$) orthonormal set of spin orbitals is built (by applying a standard prescription). An ordered set of those spin orbitals reads as

$$(\phi_1, \phi_2, \ldots, \phi_M) \,. \tag{4}$$

This basis spans a complex vector space $\mathbb{V}^{(1)}$ of the dimension M, endowed with the scalar product denoted by $\langle\phi_a|\phi_b\rangle$.

3.2. *Index strings*

We shall consider finite ordered strings of indices, each index belonging to set $\{1, 2, \ldots, M\}$. A string of N indices (i.e., N indices arranged in a definite order) will be denoted by

$$X \equiv ij\cdots m \quad (n_X = N)\ , \tag{5}$$

where n_X stands for the number of indices in the string X (*the length* of X, in short). *The empty index string*, $n_X = 0$, will be symbolized by $X = 0$.

For $n_X \geq 2$, if any two indices in the index string X are the same, X is called *degenerate*, otherwise X is called *nondegenerate*. Index strings corresponding to $n_X = 0$ and $n_X = 1$ are of course nondegenerate. Two nondegenerate index strings X and Y of equal lengths are called *equivalent*, if one may be obtained by a *permutation* of the other. The parity of this permutation, $p(X, Y)$, calculated modulo 2, indicates two subcategories of equivalent index strings: X and Y may correspond either to $p(X, Y) = 0$ or to $p(X, Y) = 1$. The number of nondegenerate nonequivalent index strings of the length N is equal to $\binom{M}{N}$. The number of all the nondegenerate nonequivalent index strings (of the length $N = 0, 1, \ldots, M$) is equal to 2^M. Any nondegenerate index string X of the length M is equivalent to the index string $12\cdots M$, which will be called *the maximal ordered index string*.

3.3. *Determinantal wave functions*

The normalized Slater determinant built of spin orbitals $\phi_i\,,\ \phi_j\,,\ \ldots\,,\ \phi_m$ is denoted by $\phi_{ij\cdots m} \equiv \phi_X$, where the index string X is nondegenerate. The number of electrons corresponding to the wave function ϕ_X is $N \equiv n_X$. In the case of two nondegenerate and *equivalent* index strings X and Y ($n_X = n_Y \geq 2$) one finds that the corresponding Slater determinants are are *antisymmetric* with respect to permutations of the indices:

$$\phi_X = (-1)^{p(X,Y)}\phi_Y\ , \tag{6}$$

and for a degenerate string X one has $\phi_X = 0$. For $N = 1$, the corresponding Slater determinants are just spin orbitals of set (4), for $N = 0$ we assume that the corresponding wave function is a number: $\phi_0 = 1$. The set of functions

$$\{\phi_X\ :\ X \text{ nondegenerate and nonequivalent},\ n_X = N\}\ , \tag{7}$$

spans a complex vector space $\mathbb{V}^{(N)}$ of the dimension $\binom{M}{N}$; the corresponding scalar product is induced by the scalar product in $\mathbb{V}^{(1)}$. The basis set (7) is orthonormal with respect to this scalar product, provided that the spin-orbital basis set (4) is orthonormal.

3.4. *Electronic Hamiltonians*

There is a family on N-electron hamiltonians ($N = 0, 1, 2, \ldots, M$), which describes our electronic system:

$$\hat{H}^{(0)} = W \ , \qquad \hat{H}^{(1)} = W + \hat{h}(1) \ ,$$
$$\hat{H}^{(N)} = W + \sum_{n=1}^{N} \hat{h}(n) + \sum_{m<n}^{N} \hat{v}(m,n) \quad (\text{for } N = 2, 3, \ldots, M) \ , \tag{8}$$

where W is a constant term (e.g., representing the Coulombic repulsion of the atomic nuclei in the molecule), $\hat{h}(n)$ is the one-electron Hamiltonian (the kinetic energy plus the Coulombic attraction between the electron and the atomic nuclei) for electron n, and $\hat{v}(m,n)$ is the two-electron interaction term for electrons m and n.

3.5. *Full configuration-interaction expansions*

Within the algebraic approximation employing the spin-orbital basis (4), the eigenfunctions of Hamiltonians (8) are represented as the FCI expansions of the form:

$$\psi^{(N)} = \phi_X \, c^X = (n_X!)^{-1} \phi_{ij\cdots m} \, c^{ij\cdots m} \ , \tag{9}$$

where the expansion coefficients $c^X \equiv c^{ij\cdots m}$ are calculated by diagonalizing the Hamiltonian $\hat{H}^{(N)}$ within the vector space $\mathbb{V}^{(N)}$ (which is a formidable numerical challenge for $2 \ll N \ll M$). In the first equality in Eq. (9) we introduce *the Einstein summation convention for index strings*: it amounts to the implicit summation *restricted* to all nondegenerate nonequivalent index strings X of the length $n_X = N$. In the second equality in Eq. (9) we use the usual form of the Einstein summation convention: here we perform an implicit *unrestricted* summation over all indices $i, j, \ldots, m$. The use of the unrestricted index summation produces all possible strings X of the length $n_X = N$, including equivalent strings (the contribution from the degenerate strings is zero), and the redundant terms [see Eq. (6)] have to be counterbalanced by introducing the factor $(n_X!)^{-1}$. For consistence, it has been also assumed that coefficients $c^X \equiv c^{ij\cdots m}$ are *antisymmetric* with respect to permutations of the indices, compare Eq. (6):

$$c_X = (-1)^{p(X,Y)} c_Y \ , \tag{10}$$

and for a degenerate string X one has $c_X = 0$.

3.6. *Fermionic Fock space*

The fermionic Fock space $\mathbb{F} \equiv \mathbb{F}(M)$ is a complex vector space generated by the vector space $\mathbb{V}^{(1)}$ spanned by the spin-orbital basis (4). $\mathbb{F}$ is built as the following direct sum:

$$\mathbb{F} = \mathbb{V}^{(0)} \oplus \mathbb{V}^{(1)} \oplus \mathbb{V}^{(2)} \oplus \cdots \oplus \mathbb{V}^{(M)} \ ; \tag{11}$$

the general definition of vector spaces $\mathbb{V}^{(N)}$ is given in Sec. 3.3. Hence, the dimension of $\mathbb{F}$ is equal to 2^M. It is assumed that when $M \to \infty$, and the spin-orbital basis

(4) becomes *complete* in that limit, our Fock-space formalism becomes equivalent to the (nonrelativistic) electronic quantum-field theory.

A general Fock-space vector may be written as an ordered set of $M+1$ components:

$$\Psi = \left(\psi^{(0)},\, \psi^{(1)},\, \psi^{(2)},\, \ldots\,,\, \psi^{(M)}\right)\,, \tag{12}$$

where $\psi^{(N)} \in \mathbb{V}^{(N)}$, for $N = 0, 1, 2, \ldots, M$. Each wave function $\psi^{(N)}$ may be expressed as in Eq. (9). The scalar product in $\mathbb{F}$ is defined as

$$\langle \Psi_a | \Psi_b \rangle = \sum_{N=0}^{M} \langle \psi_a^{(N)} | \psi_b^{(N)} \rangle\,, \tag{13}$$

where $\langle \psi_a^{(N)} | \psi_b^{(N)} \rangle$ is the scalar product in $\mathbb{V}^{(N)}$.

We now define a particular type of basis set in $\mathbb{F}$, which is called *the Fock basis*. It is related to the basis sets (7) corresponding to the $\mathbb{V}^{(N)}$ vector spaces. The elements of the Fock basis read

$$\begin{aligned}
\Phi_0 &= (\phi_0,\, 0,\, 0,\, \ldots\,,\, 0)\,, \\
\Phi_k &= (0,\, \phi_k,\, 0,\, \ldots\,,\, 0) \quad (k = 1, 2, \ldots, M)\,, \\
\Phi_{kl} &= (0,\, 0,\, \phi_{kl},\, \ldots\,,\, 0) \quad (k, l = 1, 2, \ldots, M;\; k < l)\,, \\
&\cdots \quad \cdots\,, \\
\Phi_{12\cdots M} &= (0,\, 0,\, 0,\, \ldots\,,\, \phi_{12\cdots M})\,,
\end{aligned} \tag{14}$$

where $\phi_0 = 1$, and the corresponding element of the Fock basis, Φ_0, is called the *physical vacuum*. It can be shown that the above basis set is orthonormal with respect to the scalar product (13), this property may be written as

$$\langle \Phi_X | \Phi_Y \rangle = \delta_{X,Y}\,, \tag{15}$$

where

$$\delta_{X,Y} = \delta^X{}_Y = \delta_X{}^Y = \delta^{X,Y} = \begin{cases} 0\,, & X \text{ or } Y \text{ degenerate, or } n_X \neq n_Y\,, \\ (-1)^{p(X,Y)}\,, & X, Y \text{ equivalent,} \end{cases} \tag{16}$$

is *the antisymmetric Kronecker delta*.

For $n_X = N$, each element Φ_X of the Fock basis (14) corresponds directly to some element ϕ_X of the basis set (7). Thus, the vector space $\mathbb{V}^{(N)}$ of N-electron wave functions corresponds to some *subspace* $\mathbb{F}^{(N)}$ of the Fock space, spanned by vectors Φ_X, $n_X = N$. One may thus introduce the following resolution of the Fock space into *a direct sum of its subspaces*:

$$\mathbb{F} = \mathbb{F}^{(0)} \oplus \mathbb{F}^{(1)} \oplus \mathbb{F}^{(2)} \oplus \cdots \oplus \mathbb{F}^{(M)}\,. \tag{17}$$

It will be also useful to consider a resolution

$$\mathbb{F} = \mathbb{F}^{(\mathrm{even})} \oplus \mathbb{F}^{(\mathrm{odd})}\,, \tag{18}$$

where the subspaces $\mathbb{F}^{(\mathrm{even})}$ and $\mathbb{F}^{(\mathrm{odd})}$ correspond to states with the even and odd number of electrons, respectively.

The general Fock-space vector (12) may be written as a linear combination of the Fock-basis vectors (14):

$$\begin{aligned}\Psi &= \Phi_X\, C^X \\ &= \Phi_0\, C^0 + \Phi_i\, C^i + \frac{1}{2}\,\Phi_{ij}\, C^{ij} + \,\cdots\, + (N!)^{-1}\,\Phi_{ij\cdots m}\, C^{ij\cdots m} + \,\cdots \\ &+ \Phi_{12\cdots M}\, C^{12\cdots M}\ , \end{aligned} \tag{19}$$

where we use a generalization of the notation introduced in Eq. (9): in the first equality in Eq. (19) we apply the Einstein summation convention for index strings, which is the implicit summation restricted to all nondegenerate nonequivalent index strings X of the length ranging from $n_X = 0$ to $n_X = M$. In the second equality in Eq. (19) we use the usual form of the Einstein summation convention: an implicit unrestricted summation over all indices.

A general remark applies: following papers [2–5], we make use of the assumption that the spin-orbital basis (4) is orthonormal. This property is inherited by the bases of the Slater determinants (7), and the Fock basis (14). It turns out in this case that it is just a matter of convenience whether a given index (or index string in general) is placed in the lower or in the upper position. Thus, one may write $\Phi_X \equiv \Phi^X$, $C_X \equiv C^X$, etc., and the only purpose for the particular choice is to satisfy the Einstein summation convention: $\Phi_X\, C^X \equiv \Phi^X\, C_X$. There is, however, a deeper sense in distinguishing between the lower and upper indices in the case of nonorthonormal bases, see the formalism described in [29]. Our orthonormal formalism is explicitly *covariant* with respect to the unitary transformations of the spin-orbital basis (4):

$$\phi_k \longrightarrow \phi'_k = \phi_l\, U^l{}_k\ , \tag{20}$$

where the unitary matrix $\boldsymbol{U} \in U(M)$, and $U(M)$ is the unitary group of the dimension M.

4. Algebraic framework (II): operators acting in Fock space

4.1. *Fermi-Dirac algebra*

Following [2], we use the name "Fermi-Dirac algebra" for the algebra of linear operators acting in the Fock space. This algebra, hereafter denoted by $\mathbb{A}_{\rm FD} \equiv \mathbb{A}_{\rm FD}(M)$, is generated by the so-called fermion operators, associated with the elements of the spin-orbital basis (4): the (fermion) creation operators $\{\hat{a}^k\}$, and the (fermion) annihilation operators operators $\{\hat{a}_k\}$, $k = 1, 2, \ldots, M$. We follow here the notation of Harris *et al.* [28]: the indices of the creation operators are fixed in the upper position, and the indices of the annihilation operators are fixed in the lower position, so *there is no freedom in raising and lowering of these indices*. In the formalism that uses a general nonorthogonal spin-orbital basis set [29], one restores that flexibility at the expense of introducing different symbols for the creation and annihilation operators. Let us add that the name "Fermi-Dirac algebra" appeals to the physical model which is associated with it – from the purely algebraic standpoint $\mathbb{A}_{\rm FD}$ turns out to be a kind of Clifford algebra.

The fermion operators may be defined by specifying their action on the elements

of the Fock basis (14):

$$\hat{a}^k \Phi^X = \Phi^Y \, \delta_Y{}^{Xk} = \Phi^{Xk} \, ,$$
$$\hat{a}_k \Phi_X = \Phi_Y \, \delta^{Yk}{}_X \, . \tag{21}$$

In particular, the annihilation operators fulfill *the vacuum annihilation condition*:

$$\hat{a}_k \Phi_0 = 0 \, , \quad k = 1, 2, \ldots, M \, . \tag{22}$$

The definitions in Eq. (21) employ the antisymmetrized Kronecker delta (16), and the Einstein summation convention of Eq. (19); they correspond to the same phase convention as used in [2]. It can be shown that the creation operator is the Hermitian conjugate of the corresponding annihilation operator:

$$\hat{a}^k = (\hat{a}_k)^\dagger \, . \tag{23}$$

The fermion operators defined in Eq. (21) fulfill the anticommutation rules:

$$\hat{a}_k \hat{a}_l + \hat{a}_l \hat{a}_k = \hat{a}^l \hat{a}^k + \hat{a}^k \hat{a}^l = \hat{0} \, ,$$
$$\hat{a}^k \hat{a}_l + \hat{a}_l \hat{a}^k = \delta^k{}_l \hat{1} \, , \tag{24}$$

where $\hat{0}$ and $\hat{1}$ are the zero and the unit operator in Fock space, respectively.

It is useful to introduce the products of the annihilation operators, and the analogous products of the creation operators:

$$\hat{a}_X \equiv \hat{a}_{ij\cdots m} = \hat{a}_i \hat{a}_j \cdots \hat{a}_m \, ,$$
$$\hat{a}^X \equiv \hat{a}^{ij\cdots m} \equiv (\hat{a}_X)^\dagger = \hat{a}^m \cdots \hat{a}^j \hat{a}^i \, ; \tag{25}$$

note *the reverse ordering* of the creation operators in the product $\hat{a}^X$, due to the relation (23). For completeness, we assume also that $\hat{a}^0 = \hat{a}_0 = \hat{1}$. One may use the products of the creation operators to generate the Fock basis (14) from the vacuum vector:

$$\Phi^X = \hat{a}^X \Phi_0 \, . \tag{26}$$

A product of the fermion operators, in which all the annihilation operators precede the creation ones, is called the *normal product* (of fermion operators). By using operators (25) as building blocks, one writes the normal products as

$$\hat{a}^X \hat{a}_Y \, . \tag{27}$$

For X and Y running (separately) through all the nondegenerate nonequivalent index strings of the length $N = 0, 1, \ldots, M$, one finds that there are exactly 2^{2M} different normal products of the form (27), which make a linearly-independent set of operators. This set may be chosen as a basis set in the *vector space* $\mathbb{A}_{\mathrm{FD}}$. Thus, the dimension of this vector space is 2^{2M}.

4.2. *Second-quantized representation of operators*

A general linear operator in $\mathbb{F}$ may be written as a linear combination of the normal products of fermion operators:

$$\hat{\Lambda} = \lambda_X{}^Y \, \hat{a}^X \hat{a}_Y \ , \tag{28}$$

where the Einstein summation convention of Eq. (19) is used. Such a representation of a linear operator is called the second-quantized representation. In Eq. (28), the (complex) linear coefficients $\lambda_X{}^Y$ are often referred to as *the amplitudes* of operator $\hat{\Lambda}$. When operator $\hat{\Lambda}$ is Hermitian with respect to the scalar product (13), one has $\lambda_Y{}^X = (\lambda_X{}^Y)^*$.

The matrix elements of operator $\hat{\Lambda}$ corresponding to the Fock basis (14) can be expressed by the λ-amplitudes and the elements of the antisymmetric Kronecker delta:

$$\Lambda_X{}^Y \equiv \langle \Phi_X | \hat{\Lambda} \Phi_Y \rangle = \delta_X{}^{X_1 X_2} \delta_{X_1}{}^{Y_1} \lambda_{X_2}{}^{Y_2} \delta_{Y_1 Y_2}{}^{Y} \ . \tag{29}$$

In the above equation one uses the Einstein summation convention of Eq. (19), the only nonzero contributions correspond to all possible partitions X_1, X_2 of string X, and all possible partitions Y_1, Y_2 of string Y; the resulting matrix element $\Lambda_X{}^Y$ is then *automatically antisymmetric* in strings X and Y. Eq. (29) establishes a linear one-to-one correspondence between the Λ-matrix elements and the λ-amplitudes of operator (28). When reversed, the correspondence (29) may be used to calculate the λ-amplitudes from the Λ-matrix elements.

The amplitudes $\lambda_X{}^Y$ and the matrix elements $\Lambda_X{}^Y$ are thus *complementary* sets of numbers that characterize a given linear operator $\hat{\Lambda}$. These sets depend on the particular choice of the Fock basis (14). Both sets may be viewed as consisting of tensor components of the valency (n_X, n_Y) with respect to the unitary transformations (20).

4.2.1. Particle-number operator

In the Fermi-Dirac algebra, in adddition to the "standard" operators $\hat{1}$ and $\hat{0}$, there is another unique operator – the particle-number operator:

$$\hat{N} = \delta_i{}^j \, \hat{a}^i \hat{a}_j \ . \tag{30}$$

The invariant subspaces of $\hat{N}$ are equal to subspaces $\mathbb{F}^{(N)}$, and correspond to the eigenvalues $N = 0, 1, 2, \ldots, M$. The particle-number operator is *invariant* with respect to the unitary transformations (20) corresponding to the $U(M)$ group.

4.2.2. Fock-space Hamiltonian

The family of electronic Hamiltonians (8), and the Fock basis (14), define the matrix of the Hamiltonian $\hat{H}$ that operates in the Fock space $\mathbb{F}$:

$$H_X{}^Y \equiv \langle \Phi_X | \hat{H} \Phi_Y \rangle = \begin{cases} \langle \phi_X | \hat{H}^{(N)} \phi_Y \rangle \ , & \text{for } n_X = n_Y = N \ , \\ 0 \ , & \text{for } n_X \neq n_Y \ . \end{cases} \tag{31}$$

The matrix elements $\langle \phi_X | \hat{H}^{(N)} \phi_Y \rangle$, corresponding to the basis of the determinantal functions (7), can be calculated by applying the well-known Slater-Condon rules. These matrix elements are expressed in terms of the constant W, and the one-electron integrals $h_i{}^k = \langle \phi_i | \hat{h} \phi_k \rangle$ and the two-electron integrals $v_{ij}{}^{kl} = \langle \phi_{ij} | \hat{v} \phi_{kl} \rangle$, corresponding to the spin-orbital basis (4).

By writing the matrix elements (31) in an explicit form, and by reverting the relationship provided by Eq. (29), one may now *derive* the amplitudes of the Fock-space Hamiltonian $\hat{H}$. The result is strikingly simple:

$$\hat{H} = W\hat{1} + h_i{}^j\,\hat{a}^i\hat{a}_j + \frac{1}{4}v_{ij}{}^{kl}\,\hat{a}^{ij}\hat{a}_{kl}\ . \tag{32}$$

As seen, the amplitudes of $\hat{H}$ are equal to parameters W, $h_i{}^k$, and $v_{ij}{}^{kl}$; the corresponding parts of $\hat{H}$ are called: the zero-electron, the one-electron, and the two-electron operator, respectively. Unlike in the case of a general operator (28), the number of the nonzero amplitudes of $\hat{H}$ is *extremely small*: $\mathcal{O}(M^4)$ compared to 2^{2M}. Actually, this number is also much smaller than the number of nonzero matrix elements (31), and even the number of the eigenvalues of $\hat{H}$ (equal to 2^M). The compactness of the representation provided by Eq. (32) is due to the absence of the n-electron interactions ($n > 2$) in the electronic Hamiltonians (8). One may say that the power of the Fock-space approach to many-electron systems derives from two factors: the built-in Pauli principle, and the simplicity of the Fock-space Hamiltonian.

The operators that commute with the particle-number operator (30) are called the electron-number conserving operators; Hamiltonian (32) belongs to this class. This gives rise to an important continuous symmetry of $\hat{H}$, governed by a unitary group $U(1)$ (in one dimension).

In the absence of the spin-orbit terms in in the electronic Hamiltonians (8), the Fock-space Hamiltonian $\hat{H}$ is *a spin scalar*: it commutes with the spin operators $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ (these are one-electron operators); hence, it commutes also with the spin-square operator $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$. The commutation with the spin operators corresponds to another continuous symmetry of $\hat{H}$ – the spin symmetry, described by the special unitary group $SU(2)$ (in two dimensions).

The Fock-space Hamiltonian $\hat{H}$ usually has also a discrete symmetry, corresponding to the time-reversal operation (represented by an *antiunitary* operator, see [29]). Discrete symmetry operations, corresponding to some point-group symmetry, may also be present.

4.2.3. Projection operators

The operators projecting onto the one-dimensional subspaces of the Fock space spanned by the members of the Fock basis (14) may be expressed as follows:

$$|\Phi_X\rangle\langle\Phi_X| = \hat{a}^X|\Phi_0\rangle\langle\Phi_0|\hat{a}_X\ , \tag{33}$$

where the projector onto the vacuum state Φ_0 can be written as

$$|\Phi_0\rangle\langle\Phi_0| = (M!)^{-1}(\hat{1} - \hat{N})(2\hat{1} - \hat{N})\cdots(M\hat{1} - \hat{N})\ . \tag{34}$$

The above operators, when written in the form corresponding to Eq. (28), apparently consist of very many terms (up to M-electron ones). Thus, the explicit use of projection operators within the second-quantization formalism should be avoided.

4.3. *Subalgebras of Fermi-Dirac algebra*

We now introduce some *subalgebras* of the Fermi-Dirac algebra: $\mathbb{A}_{\rm FD}^{(>)}$, $\mathbb{A}_{\rm FD}^{(<)}$, and $\mathbb{A}_{\rm FD}^{(=)}$, which are spanned (as *the vector spaces*) by the normal products (27) that

fulfill the conditions: $n_X > n_Y$, $n_X < n_Y$, and $n_X = n_Y$, respectively. The Fermi-Dirac algebra may be expressed as a direct sum:

$$\mathbb{A}_{\rm FD} = \mathbb{A}_{\rm FD}^{(>)} \oplus \mathbb{A}_{\rm FD}^{(=)} \oplus \mathbb{A}_{\rm FD}^{(<)} \, . \tag{35}$$

Algebra $\mathbb{A}_{\rm FD}^{(>)}$ is called *the excitation FD algebra*, and algebra $\mathbb{A}_{\rm FD}^{(<)}$ is called *the de-excitation FD algebra*, since the corresponding operators increase and decrease (respectively) the number of electrons (when acting on a Fock-space vector corresponding to a given number of electrons). Operators belonging to algebra $\mathbb{A}_{\rm FD}^{(=)}$ do not change the number of electrons – it is thus called *the electron-number conserving algebra*. All the operators that commute with the particle-number operator (30) belong to $\mathbb{A}_{\rm FD}^{(=)}$.

It is also useful to consider the following resolution of the vector space $\mathbb{A}_{\rm FD}$:

$$\mathbb{A}_{\rm FD} = \mathbb{A}_{\rm FD}^{(\rm even)} \oplus \mathbb{A}_{\rm FD}^{(\rm odd)} \, , \tag{36}$$

where $\mathbb{A}_{\rm FD}^{(\rm even)}$ and $\mathbb{A}_{\rm FD}^{(\rm odd)}$ are the vector subspaces, of the dimension 2^{2M-1} each, which are spanned by the normal products (27) that fulfill the conditions: $n_X + n_Y =$ even and $n_X + n_Y =$ odd, respectively. The vector space $\mathbb{A}_{\rm FD}^{(\rm even)}$ is a subalgebra of the Fermi-Dirac algebra, and it can be decomposed in a way analogous to that of Eq. (35):

$$\mathbb{A}_{\rm FD}^{(\rm even)} = \mathbb{A}_{\rm FD}^{(\rm even,>)} \oplus \mathbb{A}_{\rm FD}^{(=)} \oplus \mathbb{A}_{\rm FD}^{(\rm even,<)} \, , \tag{37}$$

where $\mathbb{A}_{\rm FD}^{(\rm even,>)}$ and $\mathbb{A}_{\rm FD}^{(\rm even,<)}$ are subalgebras of $\mathbb{A}_{\rm FD}^{(>)}$ and $\mathbb{A}_{\rm FD}^{(<)}$, respectively.

The excitation FD algebra $\mathbb{A}_{\rm FD}^{(>)}$ and the de-excitation FD algebra $\mathbb{A}_{\rm FD}^{(<)}$ (as well as their subalgebras) are *nilpotent algebras*: for any operator $\hat{C}$ belonging to $\mathbb{A}_{\rm FD}^{(>)}$ or $\mathbb{A}_{\rm FD}^{(<)}$ one has $\hat{C}^{M+1} = \hat{0}$. That property may be used for constructing some operator functions which are defined via infinite power series:

$$(\hat{1} + \hat{C})^{-1} = \hat{1} - \hat{C} + \hat{C}^2 - \ldots + \hat{C}^M \, , \tag{38}$$

$$\ln(\hat{1} + \hat{C}) = \hat{C} - \frac{1}{2}\hat{C}^2 + \frac{1}{3}\hat{C}^3 - \ldots - \frac{1}{M}\hat{C}^M \, , \tag{39}$$

$$\exp(\hat{C}) = \hat{1} + \hat{C} + \frac{1}{2!}\hat{C}^2 + \frac{1}{3!}\hat{C}^3 + \ldots + \frac{1}{M!}\hat{C}^M \tag{40}$$

where $M = 2m_0$. When $\hat{C}$ belongs to $\mathbb{A}_{\rm FD}^{(\rm even,>)}$ or $\mathbb{A}_{\rm FD}^{(\rm even,<)}$, one has $\hat{C}^{m_0+1} = \hat{0}$.

The above algebraic analysis of the Fermi-Dirac algebra seems of little use in applications to quantum chemistry: in fact, we need only those operators which belong to the electron-number conserving algebra $\mathbb{A}_{\rm FD}^{(=)}$. However, an analog of the resolution (37) will turn out to be of importance when *the quasiparticle representation* of the Fock space and the Fermi-Dirac algebra is introduced, see Sec. 5, Eq. (58). From now on we shall restrict our considerations to the operators that belong to algebra $\mathbb{A}_{\rm FD}^{(\rm even)}$, i.e., the operators of the form (28) built of the normal products (27) with the *even* number of fermion operators.

4.4. *Amplitude algebra and its diagrammatic representation*

When calculating a product of two operators, $\hat{C}\hat{D} = \hat{\Lambda}$, each written in the form given by Eq. (28), one has to consider the products of all pairs of terms. Then the contraction theorem [28] has to be applied, followed by assembling together the terms corresponding to the same normal product. That tedious and inefficient procedure may be reformulated such that the λ-amplitudes of operator $\hat{\Lambda}$ are *directly* expressed through the c-amplitudes of operator $\hat{C}$ and the d-amplitudes of operator $\hat{D}$. We write the result in the following form:

$$\lambda_X{}^Y = \delta_X{}^{X_1X_2} c_{X_1}{}^{Y_1Z} d_{ZX_2}{}^{Y_2} \delta_{Y_1Y_2}{}^Y \,, \tag{41}$$

where the rhs should be interpreted in the same spirit as the rhs of Eq. (29). Here we assume that operators $\hat{C}$, $\hat{D}$, and $\hat{\Lambda}$ belong to the algebra $\mathbb{A}_{\rm FD}^{\rm (even)}$ (in the general case an additional phase factor appears). Eq. (41) defines *the amplitude algebra* corresponding to the operator algebra $\mathbb{A}_{\rm FD}^{\rm (even)}$: it allows to calculate some *selected* amplitudes of the product operator directly from the amplitudes of the operator factors, bypassing the intermediate steps mentioned at the beginning of this section.

For the bookkeeping purposes, it is convenient to represent the algebraic expressions of the ampiltude algebra by diagrams. Our diagrams *do not correspond to operators*, but to *tensor quantities*: the operator amplitudes, see Fig. 1. The diagrammatic interpretation of Eq. (41) is given in Fig. 2. The diagrams depicted in

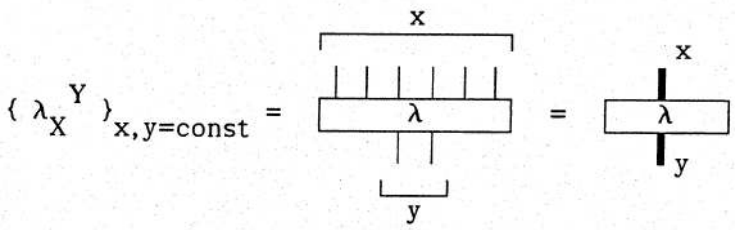

Figure 1. Diagrammatic representation of the λ-amplitudes of operator $\hat{\Lambda}$ of Eq. (28); $x \equiv n_X$, $y \equiv n_Y$. Note that *the set of upper lines* corresponds to *the lower index set* (X), and the *set of lower lines* corresponds to *the upper index set* (Y); no index symbols are indicated. Multiple (thin) lines corresponding to set X are collectively represented by a thick line labeled with x, the number of thin lines.

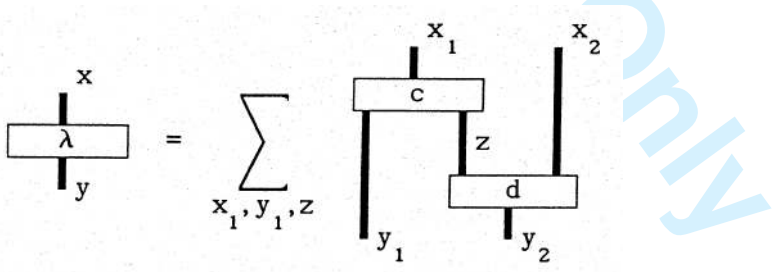

Figure 2. Diagrammatic representation of the amplitude algebra of Eq. (41); $x \equiv n_X$, $y \equiv n_Y$, etc. Conditions: $x_1 + x_2 = x$, $y_1 + y_2 = y$, $x_1, y_1, z = 0, 1, 2, \ldots, M$.

Figs. 1 and 2 are in fact closely related to the Hugenholtz diagrams: with "dots" expanded to boxes, and curved (or oblique) lines replaced by vertical, strictly parallel ones. This graphical language leads to very compact and readable diagrammatic equations, see papers [2–5, 7].

In Fig. 2, the rhs of the diagrammatic equation is a sum of diagrams. Within this sum, the diagrams corresponding to $z = 1, 2, \ldots$ are called *connected* diagrams, while those corresponding to $z = 0$ are called *disconnected* diagrams. The connected diagrams correspond to those terms in Eq. (41), in which there are *contractions* of indices belonging to the c- and d-amplitudes. Such contributions to a given λ-amplitude are called *the connected terms*; the remaining contributions are *the disconnected terms*. It is customary to extend this nomenclature to the whole operator $\hat{\Lambda} = \hat{C}\hat{D}$, and to speak of *the connected part*, and of *the disconnected part*, of $\hat{\Lambda}$. However, such a partition makes sense *only* if a given operator $\hat{\Lambda}$ is defined as a function of some other operators.

Like the Fermi-Dirac algebra, the corresponding amplitude algebra is associative. It is, however, useful to derive analogs of Eq. (41) for products of more than two operators (see [4]): such formulas become very handy when one is interested only in the *connected part* of a given operator-product amplitude.

4.5. *The Gauss factorization in Fermi-Dirac algebra*

Let $\hat{A}$ be a unitary operator in the Fermi-Dirac algebra $\mathbb{A}_{\rm FD}$, that diagonalizes a certain Hermitian operator $\hat{\Lambda}$ of the general form given in Eq. (28). The following *analog of the Gauss factorization* of $\hat{A}$ can be effected:

$$\hat{A} = (\hat{1} + \hat{C})(\hat{1} + \hat{D})\hat{B} \; , \tag{42}$$

where $\hat{C} \in \mathbb{A}_{\rm FD}^{(>)}$, $\hat{D} \in \mathbb{A}_{\rm FD}^{(<)}$, and $\hat{B} \in \mathbb{A}_{\rm FD}^{(=)}$. Operator $\hat{B}$ has to be nonsingular, and so are operators $\hat{1} + \hat{C}$ and $\hat{1} + \hat{D}$, see Eq. (38). There are several analogs of Eq. (42), differing in the permutation of the three factors (in general, with different $\hat{C}$, $\hat{D}$, and $\hat{B}$), but the form given here is the one which is employed in the QFSCC theory in Sec. 6. Let us note the following properties (which derive from *general* properties of the algebras, to which the respective operators belong): $\hat{C}\hat{B}, \hat{B}\hat{C} \in \mathbb{A}_{\rm FD}^{(>)}$, $\hat{D}\hat{B}, \hat{B}\hat{D} \in \mathbb{A}_{\rm FD}^{(<)}$, $\hat{C}^\dagger \in \mathbb{A}_{\rm FD}^{(<)}$, $\hat{D}^\dagger \in \mathbb{A}_{\rm FD}^{(>)}$.

5. Algebraic framework (III): quasiparticle representation

To arrive at *the quasiparticle representation* of vectors in the Fock space $\mathbb{F}$, and the operators in the Fermi-Dirac algebra $\mathbb{A}_{\rm FD}$, one employs a certain unitary operator $\hat{R} \in \mathbb{A}_{\rm FD}$ which is used to effect a transformation of the Fock basis (14), and the fermion operators (21).

5.1. *Quasiparticle representation in Fock space*

In our Fock space (see Sec. 3.6) we define a new (orthonormal) Fock basis

$$\{\underline{\Phi}_X \; : \; \text{nondegenerate and nonequivalent}, \; n_X = 0, 1, 2, \ldots, M\} \; , \tag{43}$$

by means of the transformation:

$$\Phi_X \longrightarrow \underline{\Phi}_X = \hat{R}\Phi_X \; . \tag{44}$$

The meaning of the index string $X \equiv ij\cdots m$ is now changed: the individual indices label *the quasiparticles* of the fermion nature (see Sec. 5.2), and the length of the

string, $n_X = N_q$, is the number of quasiparticles corresponding to the Fock-basis vector $\underline{\Phi}_X$. A new resolution of the Fock space, analogous to that of Eq. (17), emerges:

$$\mathbb{F} = \underline{\mathbb{F}}^{(0)} \oplus \underline{\mathbb{F}}^{(1)} \oplus \underline{\mathbb{F}}^{(2)} \oplus \cdots \oplus \underline{\mathbb{F}}^{(M)} \ , \tag{45}$$

where the subspace $\underline{\mathbb{F}}^{(N_q)}$ of the Fock space is spanned by vectors $\underline{\Phi}_X$, $n_X = N_q$. The Fock-space vector $\underline{\Phi}_0$ is called the *quasiparticle vacuum*.

A new representation of the general Fock-space vector (19) – the quasiparticle representation – now reads as

$$\Psi = \underline{\Phi}_X \, \underline{C}^X \ , \tag{46}$$

where the linear coefficients $\underline{C}^X$ correspond to the new Fock basis.

The subspace $\underline{\mathbb{F}}^{(1)}$, corresponding to the single-quasiparticle states, is invariant with respect to unitary transformations

$$\underline{\Phi}_k \longrightarrow \underline{\Phi}'_k = \underline{\Phi}_l \, \underline{U}^l{}_k \ , \tag{47}$$

where the unitary matrix $\underline{\boldsymbol{U}} \in \underline{U}(M)$, and $\underline{U}(M)$ is the unitary group of the dimension M [this group, and the one correspnding to Eq. (20), are different copies of the abstract unitary group $U(M)$]. It can be shown that our quasiparticle formalism is explicitly *covariant* with respect to the unitary transformations (47) of the the single-quasiparticle states. This covariance is not seen in the traditional approach [9, 14] to many-electron systems.

5.2. *Quasiparticle representation in Fermi-Dirac algebra*

We now use operator $\hat{R}$ to perform a similarity transformation of the fermion operators defined in Eqs. (21):

$$\begin{aligned} \hat{a}^k &\longrightarrow \underline{\hat{a}}^k = \hat{R} \, \hat{a}^k \hat{R}^\dagger \ , \\ \hat{a}_k &\longrightarrow \underline{\hat{a}}_k = \hat{R} \, \hat{a}_k \hat{R}^\dagger \ . \end{aligned} \tag{48}$$

The new *quasiparticle fermion operators*, $\underline{\hat{a}}^k$ and $\underline{\hat{a}}_k$, are *the quasiparticle creation and annihilation operators*, respectively.

The similarity transformation (48), generated by a unitary operator $\hat{R}$, is an isomorphism of the Fermi-Dirac algebra $\mathbb{A}_{\rm FD}$. Thus, the basic structural properties described in Sec. 4.1 are preserved:

(1) The quasiparticle annihilation operators fulfill the analog of condition (22):

$$\underline{\hat{a}}_k \underline{\Phi}_0 = 0 \ , \quad k = 1, 2, \ldots, M \ , \tag{49}$$

which is *the quasiparticle-vacuum annihilation condition*.

(2) The quasiparticle creation operator is the Hermitian conjugate of the corresponding quasiparticle annihilation operator:

$$\underline{\hat{a}}^k = (\underline{\hat{a}}_k)^\dagger \ . \tag{50}$$

(3) The anticommutation rules are fulfilled:

$$\hat{\underline{a}}_k\hat{\underline{a}}_l + \hat{\underline{a}}_l\hat{\underline{a}}_k = \hat{\underline{a}}^l\hat{\underline{a}}^k + \hat{\underline{a}}^k\hat{\underline{a}}^l = \hat{0}\ ,$$
$$\hat{\underline{a}}^k\hat{\underline{a}}_l + \hat{\underline{a}}_l\hat{\underline{a}}^k = \delta^k{}_l\hat{1}\ . \tag{51}$$

(4) The products of the quasiparticle annihilation operators, and the analogous products of the quasiparticle creation operators read as:

$$\hat{\underline{a}}_X \equiv \hat{\underline{a}}_{ij\cdots m} = \hat{R}\,\hat{a}_X\hat{R}^\dagger = \hat{\underline{a}}_i\hat{\underline{a}}_j\cdots\hat{\underline{a}}_m\ ,$$
$$\hat{\underline{a}}^X \equiv \hat{\underline{a}}^{ij\cdots m} \equiv (\hat{\underline{a}}_X)^\dagger = \hat{R}\,\hat{a}^X\hat{R}^\dagger = \hat{\underline{a}}^m\cdots\hat{\underline{a}}^j\hat{\underline{a}}^i\ . \tag{52}$$

In particular, we have $\hat{\underline{a}}^0 = \hat{\underline{a}}_0 = \hat{1}$.

(5) The products of the creation operators generate the Fock basis (43) from the quasiparticle-vacuum vector:

$$\underline{\Phi}^X = \hat{\underline{a}}^X\underline{\Phi}_0\ . \tag{53}$$

By using operators (52) as building blocks, one defines *the normal products of quasiparticle fermion operators* (or *the quasiparticle normal products*, in short):

$$\hat{\underline{a}}^X\hat{\underline{a}}_Y\ . \tag{54}$$

Again, for X and Y running (separately) through all the nondegenerate nonequivalent index strings of the length $N = 0, 1, \ldots, M$, one finds that there are exactly 2^{2M} different normal products of the form (54), which make a linearly-independent set of operators. This set becomes a new basis set in the vector space $\mathbb{A}_{\rm FD}$.

5.3. *Quasiparticle representation of operators (I)*

A general linear operator in $\mathbb{F}$, see Eq. (28), may be written as

$$\hat{\Lambda} = \underline{\lambda}_X{}^Y\,\hat{\underline{a}}^X\hat{\underline{a}}_Y\ , \tag{55}$$

where the quasiparticle normal products (54) are employed as the basis set in $\mathbb{A}_{\rm FD}$. In Eq. (55), the (complex) linear coefficients $\underline{\lambda}_X{}^Y$ are now referred to as *the quasiparticle amplitudes* of operator $\hat{\Lambda}$. As before, when operator $\hat{\Lambda}$ is Hermitian with respect to the scalar product (13), one has $\underline{\lambda}_Y{}^X = (\underline{\lambda}_X{}^Y)^*$.

The matrix elements of operator $\hat{\Lambda}$ corresponding to the Fock basis (43) will be called, in short, *the quasiparticle matrix elements* of this operator, and denoted by $\underline{\Lambda}_X{}^Y$. These matrix elements may be expressed by the $\underline{\lambda}$-amplitudes of Eq. (55) as in Eq. (29). Again, a linear one-to-one correspondence between the $\underline{\Lambda}$-matrix elements and the $\underline{\lambda}$-amplitudes is established.

The quasiparticle amplitudes $\underline{\lambda}_X{}^Y$ and the quasiparticle matrix elements $\underline{\Lambda}_X{}^Y$ are *complementary* sets of numbers that characterize a given linear operator $\hat{\Lambda}$ in the quasiparticle representation. Both sets may be viewed as consisting of tensor components of the valency (n_X, n_Y) with respect to the unitary transformations (47).

5.3.1. Quasiparticle-number operator

Once the quasiparticle representation is introduced to the Fermi-Dirac algebra, another unique operator (see Sec. 4.2.1) emerges: this is *the quasiparticle-number*

operator:

$$\hat{N}_q = \delta_i{}^j \, \hat{\underline{a}}^i \hat{\underline{a}}_j \ . \tag{56}$$

The invariant subspaces of $\hat{N}_q$ are equal to subspaces $\underline{\mathbb{F}}^{(N_q)}$, and correspond to the eigenvalues $N_q = 0, 1, 2, \ldots, M$. The quasiparticle-number operator is *invariant* with respect to the unitary transformations (47) corresponding to the $\underline{U}(M)$ group.

5.4. *Subalgebras of Fermi-Dirac algebra in quasiparticle representation*

By introducing the quasiparticle representation, one defines new subalgebras of the Fermi-Dirac algebra, analogous to those of Sec. 4.3: $\underline{\mathbb{A}}_{\rm FD}^{(>)}$, $\underline{\mathbb{A}}_{\rm FD}^{(<)}$, and $\underline{\mathbb{A}}_{\rm FD}^{(=)}$, which are spanned by the quasiparticle normal products (54) that fulfill the conditions: $n_X > n_Y$, $n_X < n_Y$, and $n_X = n_Y$, respectively. As the vector space, the Fermi-Dirac algebra may now be expressed as a direct sum:

$$\mathbb{A}_{\rm FD} = \underline{\mathbb{A}}_{\rm FD}^{(>)} \oplus \underline{\mathbb{A}}_{\rm FD}^{(=)} \oplus \underline{\mathbb{A}}_{\rm FD}^{(<)} \ . \tag{57}$$

Algebra $\underline{\mathbb{A}}_{\rm FD}^{(>)}$ is called *the quasiparticle excitation FD algebra*, and algebra $\underline{\mathbb{A}}_{\rm FD}^{(<)}$ is called *the quasiparticle de-excitation FD algebra*, since the corresponding operators increase and decrease (respectively) the number of quasiparticles (when acting on a Fock-space vector corresponding to a given number of quasiparticles). Operators belonging to algebra $\underline{\mathbb{A}}_{\rm FD}^{(=)}$ do not change the number of quasiparticles – it is thus called *the quasiparticle-number conserving algebra*. All the operators that commute with the quasiparticle-number operator (56) belong to $\underline{\mathbb{A}}_{\rm FD}^{(=)}$.

Another resolution of the vector space $\mathbb{A}_{\rm FD}$ may be given by an analog of Eq. (36), with $\underline{\mathbb{A}}_{\rm FD}^{(\rm even)}$ and $\underline{\mathbb{A}}_{\rm FD}^{(\rm odd)}$ being vector subspaces, of the dimension 2^{2M-1} each, which are spanned by the normal products (54) that fulfill the conditions: $n_X + n_Y =$ even and $n_X + n_Y =$ odd, respectively. The vector space $\underline{\mathbb{A}}_{\rm FD}^{(\rm even)}$ is a subalgebra of the Fermi-Dirac algebra, and one arrives at an analog of Eq. (37):

$$\underline{\mathbb{A}}_{\rm FD}^{(\rm even)} = \underline{\mathbb{A}}_{\rm FD}^{(\rm even,>)} \oplus \underline{\mathbb{A}}_{\rm FD}^{(=)} \oplus \underline{\mathbb{A}}_{\rm FD}^{(\rm even,<)} \ . \tag{58}$$

Algebras $\underline{\mathbb{A}}_{\rm FD}^{(>)}$ and $\underline{\mathbb{A}}_{\rm FD}^{(<)}$, as well as their respective subalgebras, $\underline{\mathbb{A}}_{\rm FD}^{(\rm even,>)}$ and $\underline{\mathbb{A}}_{\rm FD}^{(\rm even,<)}$, are nilpotent algebras, see Sec. 4.3. Therefore, analogs of Eqs. (38), (39), and (40) hold also for any operator $\hat{C}$ belonging to one of these algebras. From now on we shall restrict our considerations to the operators that belong to algebra $\underline{\mathbb{A}}_{\rm FD}^{(\rm even)}$, i.e., the operators of the form (55) built of the normal products (54) with the *even* number of the quasiparticle fermion operators. For any operator $\hat{\Lambda} \in \underline{\mathbb{A}}_{\rm FD}^{(\rm even)}$, written in the form of Eq. (55), one may find the following unique decomposition:

$$\hat{\Lambda} = \hat{\Lambda}^{(\rm even,>)} + \hat{\Lambda}^{(=)} + \hat{\Lambda}^{(\rm even,<)} \ , \tag{59}$$

where $\hat{\Lambda}^{(\rm even,>)} \in \underline{\mathbb{A}}_{\rm FD}^{(\rm even,>)}$, $\hat{\Lambda}^{(=)} \in \underline{\mathbb{A}}_{\rm FD}^{(=)}$, and $\hat{\Lambda}^{(\rm even,<)} \in \underline{\mathbb{A}}_{\rm FD}^{(\rm even,<)}$

5.5. *Special forms of quasiparticle transformation*

In order to obtain a manageable quasiparticle formalism, the form of the transformation operator $\hat{R}$ has to be considerably restricted. In particular, it seems that

$\hat{R}$ should not mix Fock-space vectors corresponding to even and odd numbers of electrons: thus $\hat{R} \in \mathbb{A}_{\rm FD}^{\rm (even)}$. In this case the resolution (18) of the Fock space is kept unchanged in the quasiparticle representation: $\underline{\mathbb{F}}^{\rm (even)} = \mathbb{F}^{\rm (even)}$ and $\underline{\mathbb{F}}^{\rm (odd)} = \mathbb{F}^{\rm (odd)}$. The same holds for the resolution (36) of the Fermi-Dirac algebra: $\underline{\mathbb{A}}_{\rm FD}^{\rm (even)} = \mathbb{A}_{\rm FD}^{\rm (even)}$ and $\underline{\mathbb{A}}_{\rm FD}^{\rm (odd)} = \mathbb{A}_{\rm FD}^{\rm (odd)}$. In addition, the forms of the quasiparticle fermion operators defined via transformation (48) should not be very complicated [i.e., approach the general form of the operator in Eq. (28)].

5.5.1. Bogoliubov-Valatin transformation

The above desiderata are fulfilled by the Bogoliubov-Valatin transformation [17, 18], generated by the $\hat{R}$ operator of the form

$$\hat{R}_{\rm BV} = \exp(i\hat{\Upsilon}) \,, \qquad \hat{\Upsilon} = \upsilon_i{}^j \, \hat{a}^i \hat{a}_j + \frac{1}{2} \upsilon_{ij}{}^0 \, \hat{a}^{ij} + \frac{1}{2} \upsilon_0{}^{ij} \hat{a}_{ij} \,, \tag{60}$$

where operator $\hat{\Upsilon}$ is Hermitian, and hence $\upsilon_j{}^i = (\upsilon_i{}^j)^*$ and $\upsilon_0{}^{ij} = (\upsilon_{ij}{}^0)^*$. Operators of the form (60) form a group isomorphic to $O(2M, \mathbb{R})$, the real orthogonal group in $2M$ dimensions. The corresponding transformations (48) may be written in the following form:

$$\begin{aligned} \underline{\hat{a}}^k &= \hat{a}^l \underline{K}_l{}^k + \hat{a}_l \underline{L}^{l,k} \,, \\ \underline{\hat{a}}_k &= \hat{a}_l (\underline{K}^l{}_k)^* + \hat{a}^l (\underline{L}_{l,k})^* \,, \end{aligned} \tag{61}$$

where, due to Eq. (50), one has $\underline{K}^l{}_k = \underline{K}_l{}^k$ and $\underline{L}_{l,k} = \underline{L}^{l,k}$; additional constraints come from the antcommutation conditions (51). The $\underline{K}$- and $\underline{L}$-parameters are functions of the υ-amplitudes of operator $\hat{\Upsilon}$; however, there is no need for the explicit use of these amplitudes in our further considerations. The quasiparticles corresponding to the fermion operators (61) are called the Bogoliubov quasiparticles.

It is useful to write down the reverse transformation with respect to that of Eqs. (61):

$$\begin{aligned} \hat{a}^k &= \underline{\hat{a}}^l K_l{}^k + \underline{\hat{a}}_l L^{l,k} \,, \\ \hat{a}_k &= \underline{\hat{a}}_l (K^l{}_k)^* + \underline{\hat{a}}^l (L_{l,k})^* \,, \end{aligned} \tag{62}$$

where $K^l{}_k = K_l{}^k$ and $L_{l,k} = L^{l,k}$; these parameters are functions of the $\underline{K}$- and $\underline{L}$-parameters of transformations (61). By inserting Eqs. (62) into Eq. (28), which provides a general form of an operator acting in the Fock space, one may now express the normal products of the fermion operators (27) through the normal products of the quasiparticle fermion operators (54); the necessary reordering of the quasiparticle creation and annihilation operators can be performed by means of the Wick theorem [9]. One then arrives at the quasiparticle representation of the operator, Eq. (28), with the $\underline{\lambda}$-amplitudes expressed as some linear functions of the original λ-amplitudes [these functions depend on the K- and L-parameters of transformations (62)].

5.5.2. Particle-hole transformation

The particle-hole (ph) transformation is a special case of the Bogoliubov-Valatin transformation (61). One uses a special form, denoted by $\hat{R}_{\rm ph}$, of the transformation

operator (60), such that

$$\underline{\Phi}_0 = \hat{R}_{\rm ph}\Phi_0 = \Phi_{12\cdots N} \ , \tag{63}$$

where $N = 2n_0$, and $\Phi_{12\cdots N}$ is an element of the Fock basis (14), corresponding to the determianatal function $\phi_{12\cdots N}$, built of the first N spinorbitals of the set (4). Interestingly, the transformation (44) becomes now simply *a permutation* of the Fock basis (14). Thus, the quasiparticle vacuum (63), and the remaining members of the Fock basis (43), are now eigenfunctions of the particle-number operator (30). The quasiparticle vacuum (63) is often referred to as *the Fermi vacuum*.

The ph transformations of the fermion operators are a special case of transformations (61) and read:

$$\begin{aligned} \underline{\hat{a}}^k &= \begin{cases} \hat{a}_k \ , & \text{for } k = 1,2,\ldots,N \ , \\ \hat{a}^k \ , & \text{for } k = N+1, N+2, \ldots, M \ , \end{cases} \\ \underline{\hat{a}}_k &= \begin{cases} \hat{a}^k \ , & \text{for } k = 1,2,\ldots,N \ , \\ \hat{a}_k \ , & \text{for } k = N+1, N+2, \ldots, M \ . \end{cases} \end{aligned} \tag{64}$$

The quasiparticles corresponding to indices $k = 1, 2, \ldots, N$ are called *holes*, while those corresponding to indices $k = N+1, N+2, \ldots, M$ are called *particles*.

5.5.3. Reference eigenstate and optimization of quasiparticle vacuum

The choice of a particular BV (or ph) transformation depends on a purely physical argument: the requirement that the quasiparticle vacuum $\underline{\Phi}_0$ provides an adequate approximation to some *reference eigenstate* of the Fock-space Hamiltonian $\hat{H}$, hereafter denoted by Ψ_0. The basic criteria for Ψ_0 are as follows: it should be the spin-singlet state, and correspond to *the lowest nondegenerate energy level* for the given value of $N = 2n_0$. Moreover, Ψ_0 should also be of some importance for the studied electronic system: most often it represents the ground state of the electrically neutral system (this works for the majority of molecules and solids). However, to meet the basic criteria, it is sometimes necessary to consider ionized systems: in calculations for the carbon atom, Ψ_0 should represent the ground state of C^{2+}; in calculations for the oxygen atom, Ψ_0 should represent the ground state of O^{2-}, etc.

In the case of the BV quasiparticle representation of Sec. 5.5.1, the $\underline{K}$- and $\underline{L}$-parameters may be optimized within the Hartree-Fock-Bogoliubov procedure, in which $\underline{\Phi}_0 \equiv \Phi_{\rm HFB}$ is determined from the variational condition:

$$\langle \Phi_{\rm HFB} | \hat{H} \Phi_{\rm HFB} \rangle = \ \text{minimum} \ , \tag{65}$$

subject to the constraint

$$\langle \Phi_{\rm HFB} | \hat{N} \Phi_{\rm HFB} \rangle = N \ . \tag{66}$$

However, the resulting BV quasiparticle vacuum $\Phi_{\rm HFB}$ *is not*, in general, an eigenfunction of $\hat{N}$. Alternatively, one may invoke the maximum-overlap condition (3), with $\Psi \equiv \Psi_0$, and optimize the Brueckner-Bogoliubov quasiparticle vacuum, $\underline{\Phi}_0 \equiv \Phi_{\rm BB}$.

In the case of the ph quasiparticle representation of Sec. 5.5.2, it is understood that the spinorbitals occupied in the Slater determinant $\phi_{12\cdots N}$ are somehow optimized *before* the ph transformation corresponding to Eqs. (63) and (64) is performed. The Hartee-Fock procedure, leading to $\underline{\Phi}_0 \equiv \Phi_{\rm HF}$ is a standard, but one

may also employ the maximum-overlap condition (3), with $\Psi \equiv \Psi_0$.

5.5.4. *Symmetry breaking*

Our Fock-space Hamiltonian (32) commutes with the particle-number operator (30), and it is hereafter assumed that it commutes also with the spin operators, see Sec. 4.2.2. With the time-reversal symmetry present, and possibly some point-group symmetry as well, one arrives at a fairly rich symmetry group of the Hamiltonian, $\mathbb{G}_H$ (however, this is not the *full symmetry group* of $\hat{H}$, see Sec. 6.1). By design (see Sec. 5.5.3), our reference eigenstate Ψ_0 is nondegenerate, and hence belongs to a one-dimensional irreducible representation of $\mathbb{G}_H$.

The optimization of the BV quasiparticle vacuum, Eq. (63), either within the Hartree-Fock, or maximum-overlap procedure, may lead to *symmetry-broken solutions* with respect to some symmetry operations of $\mathbb{G}_H$. The resulting *symmetry-broken quasiparticle vacuum* may be of physical importance in applications to extended systems [6]. The symmetry-breaking is reflected in the properties of the corresponding quasiparticles: for example, the Bogoliubov quasiparticles may have an indefinite electric charge, see Sec. 5.6.1; however, even in this case a spin-adapted BV formalism is possible.

The requirement that the particle-number symmetry is kept, necessarily restricts one's considerations to the ph transformation of Sec. 5.5.2. It is important to note that only in this case, with the quasiparticle vacuum of the form (63), the full symmetry of the reference eigenstate Ψ_0 can be recovered. In Sec. 6.4.2 we shall point out that only in this case it is possible to arrive at the Fock-space coupled-cluster formalism which is fully symmetry-adapted with respect to $\mathbb{G}_H$.

5.6. *Quasiparticle representation of operators (II)*

We now write down some important operators in the Bogoliubov-Valatin quasiparticle representation introduced in Sec. 5.5.1. Istead of the particle-number operator (30), it will be useful to consider a closely related operator, *the pseudocharge operator* [2]:

$$\hat{Q} = \hat{N} - N\hat{1} \,, \tag{67}$$

which "measures" the number of electrons relative to the electron content $N = 2n_0$ in the reference eigenstate Ψ_0. Assume that our electronic system is electrically neutral in the Ψ_0 state. Then each eigenvalue of operator (67), multiplied by $-e$ (where e is the elementary charge), represents the net electric charge of the corresponding eigenstate.

5.6.1. *Pseudocharge operator in quasiparticle representation*

In the BV quasiparticle representation the pseudocharge operator (67) assumes the following general form

$$\hat{Q} = {q_i}^j \, \underline{\hat{a}}^i \underline{\hat{a}}_j + \frac{1}{2} {q_{ij}}^0 \, \underline{\hat{a}}^{ij} + \frac{1}{2} {q_0}^{ij} \underline{\hat{a}}_{ij} \,, \tag{68}$$

where *the quasiparticle amplitudes* of $\hat{Q}$ fulfill the conditions ${q_j}^i = ({q_i}^j)^*$ and ${q_0}^{ij} = ({q_{ij}}^0)^*$; these amplitudes are functions of the K- and L-parameters of transformations (62). Condition (66) is assumed. For simpler notation, the quasiparticle amplitudes (here: the q-amplitudes) are not underlined – we shall stick to this convention if no ambiguity arise.

In the ph quasiparticle representation of Sec. 5.5.2, the general form of Eq. (68) simplifies to

$$\hat{Q} = q_i \delta_i{}^j \, \hat{\underline{a}}^i \hat{\underline{a}}_j \, , \tag{69}$$

where $q_i = -1$ for holes ($i = 1, 2, \ldots, N$), and $q_i = 1$ for particles ($i = N+1, N+2, \ldots, M$). Parameters q_i are new quantum numbers – pseudocharges, characterizing the quasiparticles (particles and holes).

Let us note that, in the BV quasiparticle representation, the pseudocharge operator (68) *does not commute* with the quasiparticle-number operator (56). Therefore, the Bogoliubov quasiparticles lack a definite pseudocharge (and, hence, a definite electric charge). This is to be contrasted with the ph quasiparticle representation: here the pseudocharge operator (69) commutes with $\hat{N}_q$.

5.6.2. Fock-space Hamiltonian in quasiparticle representation

The Fock-space Hamiltonian (32) written in the BV quasiparticle representation reads:

$$\begin{aligned} \hat{H} = {} & \eta_0{}^0 \hat{1} + \eta_i{}^j \, \hat{\underline{a}}^i \hat{\underline{a}}_j + \frac{1}{2} \eta_{ij}{}^0 \, \hat{\underline{a}}^{ij} + \frac{1}{2} \eta_0{}^{ij} \hat{\underline{a}}_{ij} \\ & + \frac{1}{4} \eta_{ij}{}^{kl} \, \hat{\underline{a}}^{ij} \hat{\underline{a}}_{kl} + \frac{1}{6} \eta_{ijk}{}^l \, \hat{\underline{a}}^{ijk} \hat{\underline{a}}_l + \frac{1}{6} \eta_i{}^{jkl} \, \hat{\underline{a}}^i \hat{\underline{a}}_{jkl} \\ & + \frac{1}{24} \eta_{ijkl}{}^0 \, \hat{\underline{a}}^{ijkl} + \frac{1}{24} \eta_0{}^{ijkl} \hat{\underline{a}}_{ijkl} \, , \end{aligned} \tag{70}$$

where the quasiparticle amplitudes of $\hat{H}$ fulfill the conditions: $\eta_j{}^i = (\eta_i{}^j)^*$, $\eta_0{}^{ij} = (\eta_{ij}{}^0)^*$, $\eta_{kl}{}^{ij} = (\eta_{ij}{}^{kl})^*$, $\eta_l{}^{ijk} = (\eta_{ijk}{}^l)^*$, and $\eta_0{}^{ijkl} = (\eta_{ijkl}{}^0)^*$. These amplitudes are linear functions of the amplitudes of operator (32), and (nonlinear) functions of the K- and L-parameters of transformations (62).

Some η- amplitudes of Hamiltonian $\hat{H}$ have special meaning: in particular, $\eta_0{}^0 = \langle \underline{\Phi}_0 | \hat{H} \underline{\Phi}_0 \rangle$. When $\underline{\Phi}_0 = \Phi_{\rm HFB}$, see conditions (65) and (66), one finds that $\eta_0{}^{ij} = \eta_{ij}{}^0 = 0$; this is a generalization of the Hylleraas theorem. It is convenient to perform a unitary transformation (47) of the single-quasiparticle states such that $\eta_i{}^j = \varepsilon_i \delta_i{}^j$; then parameters ε_i, $i = 1, 2, \ldots, M$, become *approximate* energies of the Bogoliubov quasiparticles; their physical interpretation provide an extension of the Koopmans theorem. Of course, the above properties are kept also in the case of the ph quasiparticle representation.

It is seen that, in the BV quasiparticle representation, the Fock-space Hamiltonian (70) *does not commute* with the quasiparticle-number operator (56). This observation is crucial for the construction of the Fock-space coupled-cluster theory in Sec. 6. In the ph quasiparticle representation, the form of the Fock-space Hamiltonian is essentially the same as that of Eq. (70), only the corresponding expressions for the η-amplitudes become simpler, see Eqs. (32) in [2]. Thus, the problem of noncommutation with the quasiparticle-number operator persists also in the case of the ph quasiparticle representation.

The commutation of the Fock-space Hamiltonian with the particle-number operator [or, equivalently, with the pseudocharge operator (67)] is a different story: these operators commute *independently* of the representation. However, within the BV (or even ph) quasiparticle representation, this property *is not self-evident.*

In the traditional particle-hole second-quantization formalism [9, 14], the central role is played by the so-called *normal product of fermion operators with respect to*

the Fermi vacuum. But instead of the *explicit*, "static" construction of Eq. (54), corresponding to the quasiparticle fermion operators defined in Eq. (64), one introduces there an *implicit*, "dynamical" definition of the normal product, employing the original fermion operators (21). Witin that approach one defines the so-called *normal-ordered Hamiltonian* [14], which is equivalent to our Eq. (70), but looks very similar to the untransformed form of Eq. (32). At this point the classical approach and the present one enter the diverging paths.

6. Quasiparticle Fock-space coupled-cluster theory

The departing point for the QFSCC theory is the following observation: finding the spectrum of the Fock-space Hamiltonian (32) for a small number of electrons, $N = 0, 1$ or 2, is very simple – but this part of the spectrum is usually of little interest. On the other hand, the spectrum of of the Fock-space Hamiltonian (70), corresponding to a small number of quasiparticles, $N_q = 0, 1$ or 2, is most interesting – but Hamiltonian (70) does not commute with the quasiparticle-number operator (56), and thus has to be diagonalized in the whole Fock space. This problem could be circumvented by performing a similarity transformation of the Fock Hamiltonian (70), and finding the transformed hamiltonian that commutes with the quasiparticle-number operator (56).

Below we shall employ the quasiparticle representation corresponding to a general BV quasiparticle transformation of Sec. 5.5.1. This allows for a most compact and transparent presentation of the basic ideas of the QFSCC theory. However, it is the (more specific) ph transformation of Sec. 5.5.2, which is a standard in the treatment of the electronic states in molecules. Therefore, we shall occasionally discuss some consequences of working within the ph representation.

6.1. *Principle of quasiparticle-number conservation*

We are looking for a nonsingular operator $\hat{\Omega} \in \underline{\mathbb{A}}^{(\mathrm{even})}_{\mathrm{FD}} = \mathbb{A}^{(\mathrm{even})}_{\mathrm{FD}}$ (hereafter called *the wave operator*) to perform a similarity transformation of the Fock-space Hamiltonian written in the form given in Eq. (70). The transformed operator, hereafter called *the quasiparticle Fock-space Hamiltonian*,

$$\hat{G} = \hat{\Omega}^{-1} \hat{H} \hat{\Omega} \, , \tag{71}$$

is required to commute with the quasiparticle-number operator (56):

$$[\hat{G}, \hat{N}_q] \equiv \hat{G}\hat{N}_q - \hat{N}_q \hat{G} = \hat{0} \, . \tag{72}$$

The above equations state *the principle of quasiparticle-number conservation*, which is the governing principle of the QFSCC theory. It is allowed that the wave operator $\hat{\Omega}$ is not unitary. Because of a basic algebraic property of similarity transformation, the energy spectra of $\hat{G}$ and $\hat{H}$ are the same.

Eq. (72) may be backtransformed to give

$$\hat{H}\hat{N}'_q - \hat{N}'_q \hat{H} = \hat{0} \, , \tag{73}$$

where $\hat{N}'_q = \hat{\Omega}\hat{N}_q\hat{\Omega}^{-1}$. We see that operator $\hat{N}'_q$ is a *constant of motion* for the Fock-space Hamiltonian, and corresponds to a continuous symmetry, governed by

a unitary group $U'(1)$, which is a copy of the group $U(1)$ associated with the particle-number operator (30), see Sec. 4.2.2.

The symmetry operators associated with operator $\hat{N}'_q$ *do not belong* to $\mathbb{G}_H$, the symmetry group of the Fock-space Hamiltonian $\hat{H}$, see Sec. 5.5.4. However, $\mathbb{G}_H$ is only a ("very small") subgroup of the full symmetry group of $\hat{H}$. In the simple case of a Hermitian Fock-space operator (28) with nondegenerate eigenvalues, the corresponding full symmetry group is as big as $\bigotimes U(1)_n$, $n = 1, 2. \ldots, 2^M$. Thus, the algebraic construction based on Eqs. (71) and (72) effectively recovers one of the "hidden" U(1)-symmetries of Hamiltonian $\hat{H}$.

6.2. *Quasiparticle Fock-space Hamiltonian*

By design, the quasiparticle Fock-space Hamiltonian belongs to the quasiparticle-number conserving subalgebra $\underline{\mathbb{A}}^{(=)}_{\rm FD}$, and reads as

$$\hat{G} = {g_0}^0\,\hat{1} + {g_i}^j\,\hat{\underline{a}}^i\hat{\underline{a}}_j + \frac{1}{(2!)^2}\,{g_{ij}}^{kl}\,\hat{\underline{a}}^{ij}\hat{\underline{a}}_{kl} + \frac{1}{(3!)^2}\,{g_{ijk}}^{lmn}\,\hat{\underline{a}}^{ijk}\hat{\underline{a}}_{lmn} + \ldots\,, \qquad (74)$$

where, in principle, arbitrary N_q-quasiparticle terms appear, up to $N_q = M$. However, in practice one is interested only in the eigenvalues of $\hat{G}$ corresponding to $N_q = 0, 1$ and 2; in such a case the first three terms on the rhs of Eq. (74) suffice. The quadratic matrices $\{{g_i}^j\}$ and $\{{g_{ij}}^{kl}\}$ are non-Hermitian in general (since the wave operator $\hat{\Omega}$ is not unitary). Parameter ${g_0}^0$ is equal to E_0, the eigenvalue of $\hat{H}$ corresponding to the reference eigenstate Ψ_0.

6.2.1. Calculation of excitation spectrum

By diagonalizing the shifted quasiparticle Fock-space Hamiltonian, $\hat{G} - {g_0}^0\,\hat{1}$, in the subspaces $\underline{\mathbb{F}}^{(N_q)}$ [see Eq. (45)], $N_q > 0$, one arrives at the *excitation spectrum* with respect to the reference-state energy $E_0 = {g_0}^0$. To this end, one has to build matrices $\boldsymbol{G'}^{(N_q)}$, with matrix elements

$${G'_X}^Y = \langle \underline{\Phi}_X | (\hat{G} - {g_0}^0\,\hat{1}) \underline{\Phi}_Y \rangle\,, \quad (n_X = n_Y = N_q)\,, \qquad (75)$$

which can be calculated by applying formula (29). Since these matrices are non-Hermitian, an appropriate diagonalization routine should be used, see, e.g., Hirao and Nakatsuji [30].

Each subspace $\underline{\mathbb{F}}^{(N_q)}$ represents the so-called "N_q-quasiparticle sector", corresponding to N_q quasiparticles. In the case of $N_q > 1$, Hamiltonian $\hat{G}$ accounts for the interactions among quasiparticles; this is reflected in the calculated excitation spectrum.

6.2.2. Few-quasiparticle sectors

Within a general BV quasiparticle representation, not only Hamiltonian $\hat{H}$, but also Hamiltonian $\hat{G}$ commute with the pseudocharge operator (67). However, in the case of $\hat{G}$ that property is achieved only when the wave operator $\hat{\Omega}$ is *exact*, i.e., the commutation relation (72) is exactly fulfilled. In the ph representation, Hamiltonians $\hat{H}$ and $\hat{G}$ commute with the pseudocharge operator (67) at any level of approximation. Hence, for $N_q = np + nh$ the number of particles np, and the number of holes nh, are *separately* conserved. In this case each N_q-quasiparticle sector corresponding to the subspace $\underline{\mathbb{F}}^{(N_q)}$ splits into several (np, nh)-sectors corresponding to subspaces $\underline{\mathbb{F}}^{(np,nh)}$; these (np, nh)-sectors are invariant subspaces of

Hamiltonian $\hat{G}$). In the spin-adapted case each subspace $\underline{\mathbb{F}}^{(np,nh)}$ splits further into spin-adapted invariant subspaces ${}^{2S+1}_{M_S}\underline{\mathbb{F}}^{(np,nh)}$, where $2S+1$ is the spin multiplicity ($S = 0, 1/2, 1, 3/2, \ldots, N_q/2$), and M_S is an eigenvalue of the $\hat{S}_z$ operator ($M_S = S, S-1, \ldots, -S$).

For the 0-quasiparticle sector, the corresponding subspace $\underline{\mathbb{F}}^{(0)} = {}^{1}_{0}\underline{\mathbb{F}}^{(0p,0h)}$ is one-dimensional. For the 1-quasiparticle sector one has

$$\underline{\mathbb{F}}^{(1)} = \underline{\mathbb{F}}^{(0p,1h)} \oplus \underline{\mathbb{F}}^{(1p,0h)} \,, \tag{76}$$

where, for example,

$$\underline{\mathbb{F}}^{(0p,1h)} = {}^{2}_{1/2}\underline{\mathbb{F}}^{(0p,1h)} \oplus {}^{2}_{-1/2}\underline{\mathbb{F}}^{(0p,1h)} \,. \tag{77}$$

The corresponding excitation energies are: ionization potentials [for the $(0p,1h)$-sector], and electron affinities [for the $(1p,0h)$-sector]. The respective excited states are spin doublets, and hence are doubly degenerate (because of spin).

For the 2-quasiparticle sector one finds that

$$\underline{\mathbb{F}}^{(2)} = \underline{\mathbb{F}}^{(0p,2h)} \oplus \underline{\mathbb{F}}^{(1p,1h)} \oplus \underline{\mathbb{F}}^{(2p,0h)} \,, \tag{78}$$

where, for example,

$$\underline{\mathbb{F}}^{(1p,1h)} = {}^{1}_{0}\underline{\mathbb{F}}^{(1p,1h)} \oplus {}^{3}_{1}\underline{\mathbb{F}}^{(1p,1h)} \oplus {}^{3}_{0}\underline{\mathbb{F}}^{(1p,1h)} \oplus {}^{3}_{-1}\underline{\mathbb{F}}^{(1p,1h)} \,. \tag{79}$$

The corresponding excitation energies are: double ionization potentials [for the $(0p,2h)$-sector], "energies of single excitations" [for the $(1p,1h)$-sector], and double electron affinities [for the $(2p,0h)$-sector]. The respective excited states are spin singlets (nondegenerate), or spin triplets (triply degenerate).

6.3. *Wave operator*

The Fock-space Hamiltonian $\hat{H}$ belongs to the particle-number conserving subalgebra $\mathbb{A}^{(=)}_{\rm FD} \in \mathbb{A}^{(\rm even)}_{\rm FD}$ $(= \underline{\mathbb{A}}^{(\rm even)}_{\rm FD})$. From the resolution (58), the following resolution may be derived

$$\mathbb{A}^{(=)}_{\rm FD} = \underline{\mathbb{A}}'^{(\rm even,>)}_{\rm FD} \oplus \underline{\mathbb{A}}'^{(=)}_{\rm FD} \oplus \underline{\mathbb{A}}'^{(\rm even,<)}_{\rm FD} \,, \tag{80}$$

where $\underline{\mathbb{A}}'^{(\rm even,>)}_{\rm FD} = \underline{\mathbb{A}}^{(\rm even,>)}_{\rm FD} \cap \mathbb{A}^{(=)}_{\rm FD}$, $\underline{\mathbb{A}}'^{(=)}_{\rm FD} = \underline{\mathbb{A}}^{(=)}_{\rm FD} \cap \mathbb{A}^{(=)}_{\rm FD}$, and $\underline{\mathbb{A}}'^{(\rm even,<)}_{\rm FD} = \underline{\mathbb{A}}^{(\rm even,<)}_{\rm FD} \cap \mathbb{A}^{(=)}_{\rm FD}$ are subalgebras of $\mathbb{A}^{(=)}_{\rm FD}$ (since the intersection of two subalgebras of a given algebra is a subalgebra as well). With an analog of the decomposition (59) applied to $\hat{H}$, one now seeks the wave operator $\hat{\Omega}$ which would eliminate the excitation and the de-excitation components of the transformed operator (71), in order to arrive at the commutation condition (72).

In the ph quasiparticle representation, Sec. 5.5.2, the particle-number symmetry is preserved, so $\hat{\Omega} \in \mathbb{A}^{(=)}_{\rm FD}$ at any level of approximation. Thus, in this case the resolution (80) applies also to $\hat{\Omega}$. On the other hand, in the general BV representation, Sec. 5.5.1, approximate $\hat{\Omega}$ may have (presumably small) components belonging to subalgebras $\mathbb{A}^{(\rm even,>)}_{\rm FD}$ and $\mathbb{A}^{(\rm even,<)}_{\rm FD}$. In this case one has to rely on the resolution (58) – in our further discussion we shall employ this more general approach.

6.3.1. The Gauss representation

Let $\hat{A} \in \mathbb{A}_{\rm FD}^{\rm (even)}$ $(= \underline{\mathbb{A}}_{\rm FD}^{\rm (even)})$ be a unitary operator that diagonalizes the Fock-space Hamiltonian (70). The Gauss factorization (42) may now be applied to operator $\hat{A}$, where operators $\hat{C}$, $\hat{B}$, and $\hat{D}$ now correspond to the resolution given in Eq. (58). By eliminating a quasiparticle-number conserving factor $\hat{B}$, one finds that the wave operator may be written in the following *Gauss representation*:

$$\hat{\Omega} = \hat{\Omega}_{\rm ex} \hat{\Omega}_{\rm dx} \, , \tag{81}$$

where

$$\hat{\Omega}_{\rm ex} = \hat{1} + \hat{C} \, , \qquad \hat{\Omega}_{\rm dx} = \hat{1} + \hat{D} \, . \tag{82}$$

In the above definition, $\hat{C} \in \underline{\mathbb{A}}_{\rm FD}^{\rm (even,>)}$, $\hat{D} \in \underline{\mathbb{A}}_{\rm FD}^{\rm (even,<)}$, and $\hat{\Omega}_{\rm ex}$ and $\hat{\Omega}_{\rm dx}$ will be referred to as the *excitation wave operator* and the *de-excitation wave operator*, respectively. The similarity transformation (71) is thus performed in two steps: After the first similarity transformation, the *auxiliary quasiparticle Fock-space Hamiltonian* is obtained:

$$\hat{\Gamma} = \hat{\Omega}_{\rm ex}^{-1} \hat{H} \, \hat{\Omega}_{\rm ex} = (\hat{1} + \hat{C})^{-1} \hat{H} \, (\hat{1} + \hat{C}) \, . \tag{83}$$

In the quasiparticle representation given by Eq. (55), operator (83) reads as

$$\hat{\Gamma} = \gamma_X{}^Y \, \hat{\underline{a}}^X \hat{\underline{a}}_Y \, . \tag{84}$$

After the second similarity transformation, one arrives at the proper quasiparticle Fock-space Hamiltonian:

$$\hat{G} = \hat{\Omega}_{\rm dx}^{-1} \hat{\Gamma} \, \hat{\Omega}_{\rm dx} = (\hat{1} + \hat{D})^{-1} \hat{\Gamma} \, (\hat{1} + \hat{D}) \, . \tag{85}$$

Operators $(\hat{1} + \hat{C})^{-1} = \hat{1} + \hat{C}'$ and $(\hat{1} + \hat{D})^{-1} = \hat{1} + \hat{D}'$ may be expressed by means of the expansion (38), and one finds that $\hat{C}' \in \underline{\mathbb{A}}_{\rm FD}^{\rm (even,>)}$, $\hat{D}' \in \underline{\mathbb{A}}_{\rm FD}^{\rm (even,<)}$.

After the second similarity transformation, the decomposition (59) of Hamiltonian $\hat{G}$ should give:

$$\hat{G}^{\rm (even,>)} = \hat{0} \, , \quad \hat{G}^{(=)} = \hat{G} \, , \quad \hat{G}^{\rm (even,<)} = \hat{0} \, . \tag{86}$$

One may now backtransform Eq. (85) to obtain

$$\hat{\Gamma} = (\hat{1} + \hat{D}) \, \hat{G} \, (\hat{1} + \hat{D})^{-1} = (\hat{1} + \hat{D}) \, \hat{G} \, (\hat{1} + \hat{D}') \, . \tag{87}$$

After using the algebraic properties of operators which are listed at the end of Sec 4.5, one calculates the difference

$$\hat{\Gamma} - \hat{G} = \hat{D}\hat{G} + \hat{G}\hat{D}' + \hat{D}\hat{G}\hat{D}' = \hat{\Gamma}^{\rm (even,<)} \, , \tag{88}$$

where $\hat{\Gamma}^{\rm (even,<)}$ corresponds to the decomposition (59) of Hamiltonian $\hat{\Gamma}$. Because of Eq. (86), one immediately finds that

$$\hat{\Gamma}^{\rm (even,>)} = \hat{G}^{\rm (even,>)} = \hat{0} \, , \tag{89}$$

and

$$\hat{\Gamma}^{(=)} = \hat{G}^{(=)} = \hat{G} \; . \tag{90}$$

Eq. (89) has to be fulfilled after the first similarity transformation (83); this is *the basic condition that determines the operator* $\hat{C}$. Let us note that the number of the c-amplitudes of operator $\hat{C}$ (written in the quasiparticle representation) is equal to the number of (vanishing) γ-amplitudes of operator $\hat{\Gamma}$: the number of unknowns equals the number of equations (conditions).

Eq. (90) brings an important message: the quasiparticle Fock-space Hamiltonian $\hat{G}$ is *instantly* obtained from the auxiliary quasiparticle Fock-space Hamiltonian $\hat{\Gamma}$. Thus, as far as only the spectrum of the Fock Hamiltonian $\hat{H}$ is of interest, there is no need to perform the second similarity transformation (85), and to determine the operator $\hat{D}$. However, without that operator the knowledge of the eigenfunctions of $\hat{H}$ is incomplete. In particular, one needs $\hat{D}$ (or its equivalent, see Sec. 6.3.4) to calculate expectation values and transition moments, see Sec. 6.4.1. It is the third equality in Eq. (86) that provides the condition from which $\hat{D}$ can be determined.

6.3.2. Representation of wave functions

The full similarity operator (81) is needed to determine the eigenfunctions of the Fock Hamiltonian $\hat{H}$. With the help of this operator, and the Fock basis (43), we define a set of *auxiliary wave functions*,

$$\underline{\Psi}_X = \hat{\Omega}\underline{\Phi}_X \; , \tag{91}$$

which may be used for representing the true eigenfunctions of the Fock Hamiltonian $\hat{H}$:

$$\Psi_X = \underline{\Psi}_Y {B^Y}_X \; , \quad (n_X = n_Y = N_q) \; , \tag{92}$$

for $N_q = 1, 2, \ldots, M$. The coefficients ${B^Y}_X$ are calculated by diagonalizing the quasiparticle Fock-space Hamiltonian $\hat{G}$ within an invariant subspace $\underline{\mathbb{F}}^{(N_q)}$, see Sec. 6.2.1: they correspond to the right eigenvectors of the matrix defined in Eq. (75). However, neither the auxiliary wave functions (91), nor the true eigenfunctions (92) are normalized; the intermediate normalization condition, see Eq. (2), is also not fulfilled in general, except for $X = 0$ (see below).

For $X = 0$, one may put ${B^0}_0 = 1$, and thus $\Psi_0 = \underline{\Psi}_0$. Some further simplifications are also possible:

$$\Psi_0 = \hat{\Omega}\underline{\Phi}_0 = \hat{\Omega}_{\rm ex}\underline{\Phi}_0 = (\hat{1} + \hat{C})\underline{\Phi}_0 \; , \tag{93}$$

since $\hat{\Omega}_{\rm dx}\underline{\Phi}_0 = (\hat{1} + \hat{D})\underline{\Phi}_0 = \underline{\Phi}_0$. Thus, operator $\hat{\Omega}_{\rm ex}$ alone is sufficient to determine the (unnormalized) reference eigenfunction Ψ_0. It is seen from Eq. (93), that in this case the intermediate normalization condition is fulfilled: $\langle \underline{\Phi}_0 | \Psi_0 \rangle = 1$.

6.3.3. Exponential Ansatz

The Gauss representation of the wave operator given in Eqs. (81) and (82) is not useful in practice, since it does not lead to a size-extensive (or size-consistent) formalism: For instance, the γ-amplitudes of operator $\hat{\Gamma}$ calculated by means of the similarity transformation (83), are not *purely* connected functions of the η-amplitudes of operator $\hat{H}$, and the c-amplitudes of operator $\hat{C}$ (see further discussion in this Section).

By applying an analog of Eq. (39), corresponding to the quasiparticle representation, one may define new operators:

$$\hat{\Theta} = \ln(\hat{1} + \hat{C}) \, , \qquad \hat{\Xi} = \ln(\hat{1} + \hat{D}) \, , \tag{94}$$

where $\hat{\Theta} \in \underline{\mathbb{A}}_{\rm FD}^{({\rm even},>)}$, $\hat{\Xi} \in \underline{\mathbb{A}}_{\rm FD}^{({\rm even},<)}$. Now, with the help of an analog of Eq. (40), one may define *an exponential representation* of the wave operators of Eq. (82):

$$\hat{\Omega}_{\rm ex} = \exp(\hat{\Theta}) \, , \qquad \hat{\Omega}_{\rm dx} = \exp(\hat{\Xi}) \, . \tag{95}$$

The above representation is a generalization of the exponential Ansatz which is the cornerstone of the single-reference CC method [12–14]. One may now write the similarity transformation (83) in the form of the (finite) *commutator expansion*:

$$\begin{aligned} \hat{\Gamma} &= \exp(-\hat{\Theta}) \, \hat{H} \exp(\hat{\Theta}) \\ &= \hat{H} + [\hat{H}, \hat{\Theta}] + \frac{1}{2!}[[\hat{H}, \hat{\Theta}], \hat{\Theta}] + \frac{1}{3!}[[[\hat{H}, \hat{\Theta}], \hat{\Theta}], \hat{\Theta}] + \ldots \, . \end{aligned} \tag{96}$$

Thanks to the algebraic properties of commutators involving operators belonging to the Fermi-Dirac subalgebra $\underline{\mathbb{A}}_{\rm FD}^{({\rm even})}$ $(= \mathbb{A}_{\rm FD}^{({\rm even})})$, see [28], each term in the expansion (96) may be represented by sum of diagrams of the purely connected character, see Fig. 2 and the discussion at the end of Sec. 4.4. This means that the γ-amplitudes of operator $\hat{\Gamma}$ are *connected functions* of the η-amplitudes of operator $\hat{H}$, and the θ-amplitudes of operator $\hat{\Theta}$.

The equations for the θ-amplitudes of operator $\hat{\Theta}$, corresponding to the condition (89), may now be written symbolically as

$$\gamma_X{}^Y \left(\theta_{X'}{}^{Y'} \right) = 0 \, , \quad (n_X > n_Y \, , \, n_{X'} > n_{Y'}) \, , \tag{97}$$

and the number of unknowns (the θ-amplitudes) is equal to the number of equations. These equations are linear in the η-amplitudes of operator $\hat{H}$, and nonlinear in the θ-amplitudes of operator $\hat{\Theta}$. These are *the coupled-cluster excitation equations*, corresponding to the exponential Ansatz for the excitation wave operator.

Once the CC equations (97) are solved, yielding the amplitudes $\theta_{X'}{}^{Y'}$, one may use the condition (90) to determine the g-amplitudes of the quasiparticle Fock-space Hamiltonian (74):

$$g_X{}^Y = \gamma_X{}^Y \left(\theta_{X'}{}^{Y'} \right) \, , \quad (n_X = n_Y \, , \, n_{X'} > n_{Y'}) \, . \tag{98}$$

Then the excitation spectrum of our many-electron system can be calculated, as described in Sec. 6.2.1.

One may apply an analog of Eq. (96) to rewrite Eq. (85), with the de-excitation wave operator expressed within the exponential Ansatz given in the second of Eqs. (95). The g-amplitudes of operator $\hat{G}$ are now connected functions of the γ-amplitudes of operator $\hat{\Gamma}$, and the ξ-amplitudes of operator $\hat{\Xi}$. The CC equations for the ξ-amplitudes of operator $\hat{\Xi}$, corresponding to the third condition in (86), may now be written symbolically as

$$g_X{}^Y \left(\xi_{X'}{}^{Y'} \right) = 0 \, , \quad (n_X < n_Y \, , \, n_{X'} < n_{Y'}) \, ; \tag{99}$$

again, the number of unknowns (the ξ-amplitudes) is equal to the number of equations. These equations are linear in the γ-amplitudes of operator $\hat{\Gamma}$, and nonlinear in the ξ-amplitudes of operator $\hat{\Xi}$. These are *the coupled-cluster de-excitation equations*, corresponding to the exponential Ansatz for the de-excitation wave operator.

In the exponential Ansatz of Eq. (1), the *additive* separability of the cluster operator $\hat{T}$ ensures the *multiplicative* separability of the wave function Ψ. This is the basis for the proof that the CC formalism is size-extensive (or size-consistent). The connected character of the equations from which the amplitudes of $\hat{T}$ are determined appears to be *a necessary condition* for these properties to hold. As seen, the exponential Ansatz of Eqs. (95) leads to the equations (97) and (99) for the amplitudes of operators defined in Eqs. (94), that are *connected* functions of the respective amplitudes. Thus, the necessary condition for the size-consistency of the QFSCC formalism is met.

6.3.4. The Lindgren-Jeziorski-Paldus exponential Ansatz

Eqs. (97) and (99) are highly nonlinear equations for the unknown amplitudes; a closer inspection of these equations indicates that this is due to "connections" among the unknown amlitudes. Moreover, it turns out that Eqs. (97) are not directly compatible with the CC equations corresponding to the single-reference CC method, see Eq. (1), despite that the (unnormalized) reference eigenfunction may now be expressed as $\Psi_0 = \exp(\hat{\Theta})\underline{\Phi}_0$, see Eqs. (93) and (95).

Already in the first paper [2] we realized that it is possible to circumvent the problem of inter-amplitude connections in Eqs. (97): this could be done by introducing certain *connected functions* ${\tau_X}^Y(\theta_{X'}{}^{Y'})$, such that the amplitudes of the operator $\hat{C} = \exp(\hat{\Theta}) - \hat{1}$ became purely disconnected functions of parameters ${\tau_X}^Y$ (except for the linear term). The underlying idea was to replace in Eqs. (97) the unknown θ-amplitudes by the τ-parameters as unknowns. This construction happened to be equivalent to the so-called *normal exponential Ansatz* invented by Lindgren [26]. That fact was duly recognized in paper [4], where we rewrote the Lindgren exponential in an elegant algebraic form proposed by Jeziorski and Paldus [31].

In paper [31], Jeziorski and Paldus introduced *a new operator product* in the Fermi-Dirac subalgebra $\underline{\mathbb{A}}_{\rm FD}^{\rm (even)}$, which is defined for the quasiparticle normal products (54) belonging to $\underline{\mathbb{A}}_{\rm FD}^{\rm (even)}$. This *asterisk product*, denoted by $*$, operates as follows:

$$(\hat{\underline{a}}^{X_1}\hat{\underline{a}}_{Y_1}) * (\hat{\underline{a}}^{X_2}\hat{\underline{a}}_{Y_2}) := \hat{\underline{a}}^{X_1X_2}\hat{\underline{a}}_{Y_1Y_2} \ . \tag{100}$$

Hence, from the point of view of the contraction theorem [28], it is a "contractionless" product. In addition, the corresponding asterisk-product algebra $\underline{\mathbb{A}}_{\rm FD}^{\rm (even)}$ is commutative. It should be stressed that the asterisk product is here defined only for operators expressed in the quasiparticle representation, see Eq. (55), and for different quasiparticle representations different asterisk products are obtained. It should be noted that the Jeziorski-Paldus construction of the asterisk product works for the general BV quasiparticle representation, see Sec. 5.5.1, while the original Lidgren proposal is limited to the ph quasiparticle reprezentation of Sec. 5.5.2.

We now introduce an operator $\hat{T} \in \underline{\mathbb{A}}_{\rm FD}^{\rm (even,>)}$, of the form

$$\hat{T} = {\tau_X}^Y \, \hat{\underline{a}}^X \hat{\underline{a}}_Y \ , \quad (n_X > n_Y) \ , \tag{101}$$

and use it to define *the Lindgren-Jeziorski-Paldus (LJP) exponential*:

$$\exp*(\hat{T}) := \hat{1} + \hat{T} + \frac{1}{2!}\hat{T}*\hat{T} + \frac{1}{3!}\hat{T}*\hat{T}*\hat{T} + \ldots \; ; \tag{102}$$

the above series terminates after the (m_0+1)th term, as in Eq. (40). This new form of the operator exponential is now used to express the excitation wave operator of Eq. (95):

$$\hat{\Omega}_{\rm ex} = \exp(\hat{\Theta}) = \exp*(\hat{T}) \; . \tag{103}$$

The operator $\hat{T}$ of Eq. (101) will be called *the excitation cluster operator*. The relations between operators $\hat{\Theta}$ and $\hat{T}$ are summarized below:

$$\hat{\Theta} = \ln[\exp*(\hat{T})] \; , \qquad \hat{T} = \ln*[\exp(\hat{\Theta})] \; , \tag{104}$$

where the standard operator-logarithm function ln is defined in Eq. (39), and the asterisk operator-logarithm function $\ln*$ is defined in an analogy to the LJP exponential of Eq. (40). A careful analysis of the relations (104), involving the so-called operator cumulants [31], reveals that the τ-amplitudes of operator $\hat{T}$ are purely connected functions of the θ-amplitudes of operator $\hat{\Theta}$, and vice versa.

It is now useful to rewrite Eq. (83) in a form which avoids the explicit use of operator $\hat{\Omega}_{\rm ex}^{-1}$:

$$\hat{\Gamma} = \hat{H}\,\hat{\Omega}_{\rm ex} - (\hat{\Omega}_{\rm ex} - \hat{1})\,\hat{\Gamma} \; . \tag{105}$$

When $\hat{\Omega}_{\rm ex} = \exp(\hat{\Theta})$, we know from the commutator expansion of Eq. (96) that the γ-amplitudes of operator $\hat{\Gamma}$ are purely connected functions of the θ-amplitudes of operator $\hat{\Theta}$ and the η-amplitudes of operator $\hat{H}$. Therefore: all the disconnected terms at the rhs of Eq. (105) exactly cancel. When $\hat{\Omega}_{\rm ex} = \exp*(\hat{T})$ is substituted in Eq. (105), the cancellation of the disconnected contributions should hold as well (since the τ-amplitudes of operator $\hat{T}$ are purely connected functions of the θ-amplitudes of operator $\hat{\Theta}$). Thus, one may rewrite Eq. (105) in the following symbolic form

$$\hat{\Gamma} = \left\{ \hat{H}\, \exp*(\hat{T}) - [\exp*(\hat{T}) - \hat{1}]\,\hat{\Gamma} \right\}_{\rm connected} \; , \tag{106}$$

which indicates that only the connected terms should be taken into account. The above formula is the basis for deriving the coupled-cluster (CC) equations which are discussed in the next Section (a slightly different, but equivalent, route to the CC equations was chosen in paper [2]).

An analogous construction may be applied also to the de-excitation wave operator of Eq. (95): in the first step one introduces an operator $\hat{S} \in \underline{\mathbb{A}}_{\rm FD}^{({\rm even},<)}$, of the form

$$\hat{S} = \sigma_X{}^Y \, \hat{\underline{a}}^X \hat{\underline{a}}_Y \; , \quad (n_X < n_Y) \; , \tag{107}$$

and builds an analog of the Lindgren-Jeziorski-Paldus (LJP) exponential of Eq. (102). However, this time it is advantageous to use the following construction involving *the inverse* of the de-excitation wave operator of Eq. (95):

$$\hat{\Omega}_{\rm dx}^{-1} = \exp(-\hat{\Xi}) = \exp*(\hat{S}) \; . \tag{108}$$

The operator $\hat{S}$ of Eq. (107) will be called *the de-excitation cluster operator*. In order to arrive at the more manageable form of conditions (99), we shall use an analog of Eq. (106), adapted to the representation given in Eq. (108):

$$\hat{G} = \left\{ \exp*(\hat{S})\, \hat{\Gamma} - \hat{G}\, [\exp*(\hat{S}) - \hat{1}] \right\}_{\text{connected}} . \tag{109}$$

The above formula (but not in an explicit form) was behind some of the derivations in paper [4]).

6.4. *Quasiparticle coupled-cluster equations*

Our goal is to find analogs of Eqs. (97) and (98) corresponding to the LJP exponential Ansatz for the excitation wave operator, given in Eqs. (102) and (103). To this end one uses the representation (106) of the operator $\hat{\Gamma}$, with only the connected terms taken into account. The presence of $\hat{\Gamma}$ at the rhs of Eq. (106) gives rise to some entanglement, but it is easily resolved in practice. Eqs. (97) now read as

$$\gamma_X{}^Y \left(\tau_{X'}{}^{Y'} \right) = 0 , \quad (n_X > n_Y \ , \ n_{X'} > n_{Y'}) , \tag{110}$$

and the number of unknowns (the τ-amplitudes) is equal to the number of equations. These equations are linear in the η-amplitudes of operator $\hat{H}$, and nonlinear in the τ-amplitudes of operator $\hat{T}$. However, at this point there is a big difference with respect to Eqs. (97): due to the lack of contractions among the τ-amplitudes, each connected contribution to the γ-amplitudes is due to contractions between a given η-amplitude and a few τ-amplitudes. Since the η-amplitudes have at most four indices, the lhs of Eq. (110) is a polynomial (in the unknown τ-amplitudes) of the fourth degree (at most). Eqs. (110) are called *the coupled-cluster excitation (CCex) equations*, corresponding to the LJP exponential Ansatz for the excitation wave operator.

The g-amplitudes of the quasiparticle Fock-space Hamiltonian (74) are obtained by means of the following analogs of Eqs. (98):

$$g_X{}^Y = \gamma_X{}^Y \left(\tau_{X'}{}^{Y'} \right) , \quad (n_X = n_Y \ , \ n_{X'} > n_{Y'}) . \tag{111}$$

It turns out that in the above equations the γ-amplitudes are polynomials of at most second degree.

It should be added that now Eq. (93) can be written in the form of $\underline{\Psi}_0 = \exp*(\hat{T})\underline{\Phi}_0$, and it becomes equivalent to Eq. (1) (for $\underline{\Phi}_0 \equiv \Phi$ and $\underline{\Psi}_0 \equiv \Psi$). This property holds *despite that* the forms of the operator $\hat{T}$ are different in these equations: it turns out that the part of operator (101) corresponding to $Y = 0$ is the same as the whole operator $\hat{T}$ of Eq. (1).

The derivation of the explicit form of Eqs. (110) and (111) can be done most easily by applying the diagrammatic representation of the amplitude algebra, see Sec. 4.4. A few most important diagrammatic equations corresponding to Eqs. (110) and (111) are presented in paper [2].

The analog of Eqs. (99), corresponding to the LJP exponential Ansatz for the de-excitation wave operator, given in Eq. (108), can be derived by using the representation (109) of the operator $\hat{G}$, with only the connected terms taken into

account:

$$g_X{}^Y \left(\sigma_{X'}{}^{Y'} \right) = 0 \, , \quad (n_X < n_Y \, , \; n_{X'} < n_{Y'}) \, ; \tag{112}$$

as before, the number of unknowns (the σ-amplitudes) is equal to the number of equations. These equations are linear in the γ-amplitudes of operator $\hat{\Gamma}$, and nonlinear in the σ-amplitudes of operator $\hat{S}$. However, it can be shown [4] that there is a general decoupling scheme which reveals a very important property: Eqs. (112) are equivalent to *linear equations* for the unknown σ-amplitudes. Eqs. (112) are called *the coupled-cluster de-excitation (CCdx) equations*, corresponding to the LJP exponential Ansatz for the de-excitation wave operator.

6.4.1. Expectation values and transition moments

It should be stressed that one may single out a relatively small subset of the CCex equations (110), and approximately decouple it from the rest of these equations, see Sec. 6.5.1. The calculated τ-amplitudes are then fed into Eqs. (111), and a subset of the g-amplitudes is calculated. This allows one to determine the ground-state energy $g_0{}^0 = E_0$, and a part of the excitation spectrum, see Sec. 6.2.1. When (a subset of) the CCdx equations (112) is solved in addition to that, one can determine the eigenfunctions of the Fock-space Hamiltonian $\hat{H}$, corresponding to the ground state and to the calculated excitation spectrum, see Sec. 6.3.2. The normalization of these wave functions is not an easy task, however (they are of an FCI complexity). Despite of that, as shown in [5], the unnormalized wave function of the form given in Eq. (92) may be used for calculating expectation values and transition moments of various operators; to this end, one may obtain [5] *the density matrices* and *the transition matrices* corresponding to the eigenfunctions (92). The necessary formulas can be derived by using the diagrammatic language employed in the derivation of the CC equations (110), (111), and (112). Applications of this approach may be found in the papers by Barysz et al. [32, 33].

6.4.2. Symmetry adaptation of QFSCC theory

As indicated in Sec. 5.5.4, our optimized quasiparticle vacuum $\underline{\Phi}_0$ may correspond to broken symmetry with respect to the symmetry group of the Fock-space Hamiltonian, $\mathbb{G}_H$. We shall say that $\underline{\Phi}_0$ *retains* the symmetry of a *subgroup* $\mathbb{G}'_H \subset \mathbb{G}_H$, if it belongs to a one-dimensional representation of $\mathbb{G}'_H$. There is a very important theorem [1, 2] which applies to the QFSCC theory: in such a case the wave operator $\hat{\Omega}$, as well as all the related operators, including the CC operators $\hat{T}$ and $\hat{S}$, and the quasiparticle Fock-space Hamiltonians $\hat{\Gamma}$ and $\hat{G}$, *commute* with the symmetry operators belonging to $\mathbb{G}'_H$.

In the case of the continuous symmetries, the above-listed operators commute with the Hermitian generators $\hat{Q}_{\rm cs}$ of the respective symmetries, for instance,

$$[\hat{T}, \hat{Q}_{\rm cs}] = [\hat{S}, \hat{Q}_{\rm cs}] = \hat{0} \, . \tag{113}$$

Specifically:

(1) If the ph quasiparticle representation of Sec. (5.5.2) is chosen, the conditons (113) hold for $\hat{Q}_{\rm cs} = \hat{Q}$, the pseudocharge operator of Eqs. (67) and (69).
(2) If, in addition, $\underline{\Phi}_0$ is at least of the unrestricted Hartree-Fock (UHF) quality, the conditons (113) hold for $\hat{Q}_{\rm cs} = \hat{S}_z$, the spin operator for z-projection of the total spin, see Sec. 4.2.2.
(3) If $\underline{\Phi}_0$ corresponds to the restricted Hartree-Fock (RHF) wave function for the closed shell, the conditons (113) hold also for $\hat{Q}_{\rm cs} = \hat{S}_x$ and $\hat{Q}_{\rm cs} = \hat{S}_y$ (how-

ever, if one of these conditions is fulfilled, the other one follows automatically). At this point the QFSCC theory is spin adapted..

One may now use the appropriate commutation conditions (113) for the *symmetry adaptation* of the amplitudes of operators $\hat{T}$ and $\hat{S}$ (and $\hat{\Gamma}$ and $\hat{G}$ as well); the discrete symmetries of $\mathbb{G}'_H$ may be handled accordingly. Such a procedure is quite straightforward: some amplitudes of operators $\hat{T}$, $\hat{S}$, $\hat{\Gamma}$ and $\hat{G}$ have to vanish identically, and some are related by symmetry to other amplitudes. At this point, it is often advantageous to define a set of *unique symmetry-adapted amplitudes*. This approach results in a tremendous simplifications in the CC equations (110), (111), and (112), and does not require advanced group-theoretical tools. By arriving at the symmetry-adapted quasiparticle Fock-space Hamiltonian (74), one may take advantage of the symmetry-splitting of the $\underline{\mathbb{F}}^{(N_q)}$ subspaces, discussed in Sec. 6.2.2.

In dealing with a particular set of equations (110), (111), or (112), it is strongly advocated to follow a step-by-step procedure:
(i) derive the necessary diagrammatic equations for the general BV quasiparticles (this provides *the most compact* diagrammatic representation possible!),
(ii) "translate" each diagram into the corresponding algebraic expressions by using the general rules of papers [2] and [4],
(iii) in the obtained algebraic equations, express the general amplitudes through the symmetry-adapted ones.
In practice the above procedure may be carried out "manually", and gives a full control over the obtained symmetry-adapted equations.

6.5. *Practical aspects*

Our paper with Maria Barysz [7] provided a test of the QFSCC *method* (within the ph representation) at the so-called CCD level, which is the simplest meaningful level of the theory. In that paper we discussed also the emerging challenge: the problem of the so-called intruder states, which may be traced to the existence of multiple solutions to the (nonlinear) CC equations. Fortunately, during last 20 years a great progress has been made in the theory and the practice of the FSCC approach originating from the papers [22–26]: in particular, in taming the intruder states. Below, we use the modern perspective to discuss a few practical aspects of the QFSCC method.

6.5.1. CCSDT level

In the single-reference CC method, see Eq. (1), the so-called CCSDT level of theory corresponds to the approximation $\hat{T} \approx \hat{T}_1 + \hat{T}_2 + \hat{T}_3$; thus, S stands for the single, D for the double, and T – for the triple excitations from the reference Slater determinant [34, 35]. In the *computational* FSCC method, the CCSDT level of theory is currently the state of the art [36–44]: this corresponds to the CC operator $\hat{T}$ of Eq. (101) being truncated such that only the τ-amplitudes with $n_X + n_Y = 2$ (S), $n_X + n_Y = 4$ (D), and $n_X + n_Y = 6$ (T) are retained.

We now write down Eqs. (110) and (111) in a more explicit form, compatible with the CCSDT level of theory. A natural stratification of these equations, corresponding to $Y = N_q$ (where N_q is the number of quasiparticles of the sector $\underline{\mathbb{F}}^{(N_q)}$, see Sec. 6.2.2), emerge:

(1) The vacuum sector, $N_q = 0$. The CCex-SDT equations read symbolically as (the primes to indices of the τ-amplitudes are suppressed for better read-

ability):

$$\gamma_{ij}{}^{0}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0},\tau_{ijklmn}{}^{0}) = 0\ ,$$
$$\gamma_{ijkl}{}^{0}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0},\tau_{ijklmn}{}^{0}) = 0\ ,$$
$$\gamma_{ijklm}{}^{0}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0},\tau_{ijklmn}{}^{0}) = 0\ , \qquad (114)$$

and the corresponding g-amplitude is simply

$$g_{0}{}^{0} = \gamma_{0}{}^{0}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0})$$
$$= \eta_{0}{}^{0} + \frac{1}{2}\eta_{0}{}^{ij}\tau_{ij}{}^{0} + \frac{1}{8}\eta_{0}{}^{ijkl}\tau_{ij}{}^{0}\tau_{kl}{}^{0} + \frac{1}{24}\eta_{0}{}^{ijkl}\tau_{ijkl}{}^{0}\ . \qquad (115)$$

The equations for the vacuum sector are *completely decoupled* from the rest of the CCex equations, and are identical to the CC equations corresponding to the single-reference Ansatz, see Eq. (1).

(2) The 1-quasiparticle sector, $N_q = 1$. The CCex-SDT equations:

$$\gamma_{ijk}{}^{l}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0},\tau_{ijklmn}{}^{0},\tau_{ijk}{}^{l},\tau_{ijklm}{}^{n};\ \gamma_{i}{}^{j}) = 0\ ,$$
$$\gamma_{ijklm}{}^{n}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0},\tau_{ijklmn}{}^{0},\tau_{ijk}{}^{l},\tau_{ijklm}{}^{n};\ \gamma_{i}{}^{j}) = 0\ , \qquad (116)$$

and the corresponding g-amplitudes:

$$g_{i}{}^{j} = \gamma_{i}{}^{j}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0},\tau_{ijk}{}^{l},\tau_{ijklm}{}^{n})\ . \qquad (117)$$

The equations for the 1-quasiparticle sector are *completely decoupled* from the CCex equations corresponding to $N_q \geq 2$, but their solutions depend on the τ-amplitudes of the vacuum sector. The dependence of Eqs. (116) on the $\gamma_{i}{}^{j}$-amplitudes is explicitly indicated. This depndence has interesting implication: while Eqs. (116) are apparently *linear* in the amplitudes $\tau_{ijk}{}^{l}$ and $\tau_{ijklm}{}^{n}$, they become *quadratic* when the (linear) dependence on these amplitudes of the amplitudes $\gamma_{i}{}^{j}$ is taken into account.

(3) The 2-quasiparticle sector, $N_q = 2$. The CCex-SDT equations:

$$\gamma_{ijkl}{}^{mn}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0},\tau_{ijklmn}{}^{0},\tau_{ijk}{}^{l},\tau_{ijklm}{}^{n},\tau_{ijkl}{}^{mn};\ \gamma_{i}{}^{j},\gamma_{ij}{}^{kl}) = 0\ , \qquad (118)$$

and the corresponding g-amplitudes:

$$g_{ij}{}^{kl} = \gamma_{ij}{}^{kl}(\tau_{ij}{}^{0},\tau_{ijkl}{}^{0},\tau_{ijk}{}^{l},\tau_{ijklm}{}^{n},\tau_{ijkl}{}^{mn})\ . \qquad (119)$$

The equations for the 2-quasiparticle sector are *completely decoupled* from the CCex equations corresponding to $N_q \geq 3$, but their solutions depend on the τ-amplitudes of the preceding sectors. The dependence of Eqs. (118) on the amplitudes $\gamma_{i}{}^{j}$ and $\gamma_{ij}{}^{kl}$ is explicitly indicated. Again, Eqs. (118) are apparently *linear* in the amplitudes $\tau_{ijkl}{}^{mn}$, but they become *quadratic*, for similar reason as discussed in the case of the 1-quasiparticle sector.

An important observation follows: the CC equations (110), (111), and (112), and the CCSDT equations of the present section in particular, are explicitly covariant with respect to the unitary transformations of Eq. (47).

6.5.2. *BHF approach*

When the Brueckner (maximum-overlap) optimization of the quasiparticle vacuum $\underline{\Phi}_0$ is undertaken, see Eqs. (3) and Sec. 5.5.3, *the necessary condition* for the maximum reads as

$$\tau_{ij}{}^{0} = 0 \, . \tag{120}$$

The above condition may be imposed while solving the CCex equations (110) for the vacuum sector, to this effect one may use the BHF procedure described in papers [1] and [3]. The optimization of $\underline{\Phi}_0$ which employs the condition (120) has several advantages:
(i) At a given approximation level (e.g., the CCSDT one), it should provide *the best* representation of the reference eigenstate through Eq. (1). The focus on the "quality" of the calculated ground-state energy, Eq. (115), may be misleading in this respect, since the value of $g_0{}^0$ lacks the property of being the upper-bound to the exact E_0.
(ii) A great simplification of Eqs. (114), (116), and (118) is achieved: the saving in the number of included diagrams is substantial.
(iii) The degree of nonlinearity in Eqs. (114) is reduced: they are at most *quadratic* in the corresponding τ-amplitudes.

6.5.3. *Active quasiparticles*

In the atomic and molecular applications of the FSCC method one has to face a broad spectrum of the quasiparticle energies. In the ph quasiparticle representation, Sec. 5.5.2, the holes corresponding to the core orbitals, and the particles corresponding to high empty orbitals, are often of little interest, but due to their high energies they may contribute to the intruder-state problem. As a solution, in the FSCC method one often considers only the quasiparticles with relatively low energies: they become the so-called *active* (or *valence*) quasiparticles (active holes and particles within the ph representation). The purpose is to arrive at the quasiparticle Fock-space Hamiltonian (74) which depends on the active quasiparticles only. It can be shown that this can be achieved by introducing relatively small modifications of the CCex equations of Sec. 6.5.1:

(1) The vacuum sector, $N_q = 0$. Eqs. (114) and (115) are left unchanged.
(2) The 1-quasiparticle sector, $N_q = 1$. Let us consider M_a ($< M$) active quasiparticles. One has to introduce new $\tau_{i''}{}^{j'}$ amplitudes, which are responsible for a decoupling of the states corresponding to the active $(i', j', \ldots = 1, 2, \ldots, M_a)$ and inactive $(i'', j'', \ldots = M_a + 1, M_a + 2, \ldots, M)$ quasiparticles; indices $i, j, \ldots = 1, 2, \ldots, M$ enumerate general quasiparticles (active or inactive). The decoupling conditions, of the form $\gamma_{i''}{}^{j'} = 0$, constitute the CCex equations for the $\tau_{i''}{}^{j'}$ amplitudes [these equations derive from Eqs. (117)]. The $\tau_{i''}{}^{j'}$ amplitudes become *additional* variables in Eqs. (116), now of the form $\gamma_{ijk}{}^{l'} = 0$ and $\gamma_{ijklm}{}^{n'} = 0$, and in Eqs. (117), now of the form $g_{i''}{}^{j'} = \gamma_{i''}{}^{j'}$.
(3) The 2-quasiparticle sector, $N_q = 2$. One introduces additional $\tau_{i''j}{}^{k'l'}$ amplitudes, corresponding to the decoupling conditions of the form $\gamma_{i''j}{}^{k'l'} = 0$ [these equations derive from Eqs. (119)]. The $\tau_{i''}{}^{j'}$ amplitudes from the 1-quasiparticle sector, and the $\tau_{i''j}{}^{k'l'}$ amplitudes, become *additional* variables in Eqs. (118), now of the form $\gamma_{ijk}{}^{l'm'} = 0$, and in Eqs. (119), now of the form $g_{i'j'}{}^{k'l'} = \gamma_{i'j'}{}^{k'l'}$.

As a rule: by introducing the active quasiparticles, one increases the number of different kinds of unknowns (the τ-amplitudes), and the number of different types

of the CC equations. However, the overall number of (nonzero) unknowns and equations may be considerably reduced.

6.5.4. Factorization of CC equations

While implementing the single-reference CC metod at the CCSDTQ level, Kucharski and Bartlett [45, 46] introduced a very useful tool for handling the corresponding diagrammatic equations. They found that these equations can be, step by step, *factorized* by introducing certain *diagram intermediates*. This leads to an effective linearization of the CC equations. This factorization technique is currently a standard in the FSCCSDT method developed in Bartlett's group [36–44]. Needless to say, this technique may be applied also to the CCex-SDT equations of Sec. 6.5.1.

6.5.5. Intruder states in 1-quasiparticle sector

As numerical experience indicates, the active-quasiparticle approach of Sec. 6.5.3 is insufficient to fully cure the intruder-state problem. In the 1-quasiparticle sector, see Sec. 6.5.1, the practical solution [36–38] involves using the equation-of-motion (EOM) approach, which can be shown to be (formally, but not computationally!) equivalent to directly solving Eqs. (116).

6.5.6. Intruder states in 2-quasiparticle sector

In the case of the 2-quasiparticle sector, see Sec. 6.5.1, the EOM method is not equivalent to directly solving Eqs. (118). However, Meissner [47, 48] adpted the so-called intermediate-Hamiltonian (IH) technique to cope with the intruder states within the FSCCSD method. This technique has been recently implemented also at the CCSDT level by Musiał and Bartlett [40–44].

The QFSCC theory described in the present paper should be augumented to absorb the developments mentioned in Secs. 6.5.3 – 6.5.6. However, that seems to be only a technical matter.

7. Concluding remarks

The QFSCC theory is a completely general, comprehensive approach to many-electron systems. It builds a consistent physical model: the quasiparticle model of many-electron systems, which is based on the quasiparticle representation of the fermionic Fock space and the corresponding Fermi-Dirac algebra of operators. Moreover, it provides a new, general and flexible, algebraic and diagrammatic language which is effective in deriving a necessary system of equations for calculating system's properties: the excitation spectrum, and the expectation values and transition moments (with the purpose of approaching the FCI values).

The QFSCC theory may be considered a generalization of the single-reference CC theory [12, 13]: it builds a *hierarchy* of states, corresponding to different numbers of electrons, which stem from a certain reference eigenstate Ψ_0 of the Fock-space Hamiltonian (by assumption: a nondegenerate, closed-shell one). As a computational tool, the QFSCC method can be formulated such that it becomes equivalent to the FSCC methods, see the corresponding references in the recent review by Bartlett and Musiał [14]. However, the algebraic QFSCC methodology offers considerable simplifications in deriving the basic FSCC equations – in the QFSCC approach there is no need for: handling incomplete model spaces and the corresponding projectors, imposing the subsystem-embedding conditions, relaxing the intermediate normalization of the wave functions, explicit working with various op-

erators and their commutators, dealing with the proliferating Brandow diagrams, resorting to a computer-assisted generation of the working CC equations, etc.

The quasiparticle model of many-electron systems offered by the QFSCC theory is not of a universal utility, however. Its *hierarchical structure* has to be confronted with a strictly *egalitarian structure* of the multireference CC Ansatz of Jeziorski and Monkhorst [21]. The latter approach is indispensable for treating strongly coupled, quasidegenerate states, with the same number of electrons (as, e.g., in weakly interacting open-shell systems, corresponding to breaking of chemical bonds).

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