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Normal order and extended Wick theorem for a multiconfiguration reference wave function

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A generalization of normal ordering and of Wick's theorem with respect to an arbitrary reference function Φ as some generalized ''physical vacuum'' is formulated in a different (but essentially equivalent) way than that suggested previously by one of the present authors. Guiding principles are that normal order operators with respect to any reference state must be expressible as linear combinations of those with respect to the genuine vacuum, that the vacuum expectation value of a normal order operator must vanish (with respect to the vacuum to which it is in normal order), and that the well-known formalism for a single Slater determinant as physical vacuum must be contained as a special case. The derivation is largely based on the concepts of ''Quantum Chemistry in Fock space,'' which means that particle-number-conserving operators (excitation operators) play a central role. Nevertheless, the contraction rules in the frame of a generalized Wick theorem are derived, that hold for non-particle-number-conserving operators as well. The contraction rules are formulated and illustrated in terms of diagrams. The contractions involve the ''residual n-particle density matrices'' λ, which are the irreducible (non-factorizable) parts of the conventional n-particle density matrices γ, in the sense of a cumulant expansion for the density. A spinfree formulation is presented as well. The expression of the Hamiltonian in normal order with respect to a multiconfiguration reference function leads to a natural definition of a generalized Fock operator. MC-SCF-theory is easily worked out in this context. The paper concludes with a discussion of the excited configurations and the first-order interacting space, that underlies a perturbative coupled cluster type correction to the MCSCF function for an arbitrary reference function, and with general implications of the new formalism, that is related to ''internally contracted multireference configuration interaction.'' The present generalization of normal ordering is not only valid for arbitrary reference functions, but also if the reference state is an ensemble state.
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I. INTRODUCTION

If one formulates many-body perturbation theory[1] or related non-perturbative methods in Fock space, one has to evaluate expectation values with respect to a reference function Φ, of products of fermion creation and annihilation operators $a_p^\dagger$ and a_q. For this purpose a recipe is useful that is usually referred to as Wick's theorem.[2] It states that any product of fermion operators is equal to their *normal product* plus all possible normal-ordered *contractions*, and it contains a sign rule. An operator product is in normal order if all creation operators are to the left of all annihilation operators. The vacuum expectation value of a normal ordered operator vanishes. Strictly speaking, Wick's theorem is a direct consequence of the anticommutation relations of the fermion operators, and hardly merits the name *theorem*, even if admittedly the situation was slightly less trivial in the original context[2] where time-dependent operators and time-ordered products were involved.

A significant simplification is achieved if the reference function Φ is a closed-shell single Slater determinant, that can be interpreted as a *physical vacuum*, such that with a reinterpretation of creation operators for occupied one-particle states as *hole annihilation* operators and the analogous definition of *hole creation* operators a redefinition of normal order *with respect* to Φ is possible. The main message of Wick's theorem *in the particle-hole sense* is then, that physical observables, which are expectation values with respect to the physical vacuum Φ become the sums of all possible *full contractions*.

In a more modern formulation of many-body theory, referred to as Quantum Chemistry in Fock space,[3,4] the central quantities are no longer the basic creation and annihilation operators $a^p = a_p^\dagger$ and a_q, but rather the so called excitation operators like a_p^q or a_{pq}^{rs} written in a generalized tensor notation.

$$a_p^q = a^q a_p\,; \quad a_{pq}^{rs} = a^r a^s a_q a_p\,. \tag{1a}$$

If only spinfree operators are involved, it is convenient to replace the excitation operators (1a) by their spin-independent counterparts

$$E_P^Q = a_{P\alpha}^{Q\alpha} + a_{P\beta}^{Q\beta}\,;$$

$$E_{PQ}^{RS} = a_{P\alpha Q\alpha}^{R\alpha S\alpha} + a_{P\alpha Q\beta}^{R\alpha S\beta} + a_{P\beta Q\alpha}^{R\beta S\alpha} + a_{P\beta Q\beta}^{R\beta S\beta}\,. \tag{1b}$$

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Capital (cap.) letters as labels refer to spin-free orbitals, and lower case (l.c.) letters to spin-orbitals.

The excitation operators in Eqs. (1a) and (1b) are in normal order (with respect to the genuine vacuum), and products of them can be expanded as sums of excitation operators, like

$$a_q^p a_{su}^{rt} = a_{qsu}^{prt} + \delta_q^r a_{su}^{pt} + \delta_q^t a_{su}^{rp}, \tag{2a}$$

$$E_Q^P E_{SU}^{RT} = E_{QSU}^{PRT} + \delta_Q^R E_{SU}^{PT} + \delta_Q^T E_{SU}^{RP}. \tag{2b}$$

The contraction rules, of which Eqs. (2a) and (2b) are examples, can be regarded as an extension of Wick's theorem.[3,4]

In the same tensor notation, excitation operators $\tilde{a}$ or $\tilde{E}$ in normal order with respect to the physical vacuum Φ can be defined,[4,5] such that again expectation values with respect to the physical vacuum are obtained as the sum of all full contractions. The wave function Φ, regarded as physical vacuum, is a single Slater determinant wave function. In the absence of spin-dependent operators for an even number of electrons, Φ will usually be chosen as a closed-shell Slater determinant with doubly occupied orbitals.

For the $\tilde{a}$ or $\tilde{E}$ operators the extended Wick theorem Eqs. (2a) and (2b) is replaced by

$$\begin{aligned} \tilde{a}_q^p \tilde{a}_{su}^{rt} = {} & \tilde{a}_{qsu}^{prt} + \delta_q^r n_q a_{su}^{pt} + \delta_q^t n_q \tilde{a}_{su}^{rp} - \delta_s^p (1-n_p) \tilde{a}_{qu}^{rt} \\ & - \delta_u^p (1-n_p) \tilde{a}_{sq}^{rt} + (\delta_s^p \delta_q^r \tilde{a}_u^t - \delta_s^p \delta_q^t \tilde{a}_u^r - \delta_u^p \delta_q^r \tilde{a}_s^t \\ & + \delta_u^p \delta_q^t \tilde{a}_s^r) n_p (1-n_q), \end{aligned} \tag{3}$$

where n_p (=0 or 1) is the occupation number of the spin-orbital ψ_p in Φ. One can in Eq. (3) replace the $\tilde{a}$ by the $\tilde{E}$ and l.c. by cap. letters, n_P (= 0, 1, or 2) is then the occupation number of the spinfree orbital φ_P in the closed-shell determinant Φ.

As powerful as the concept of normal ordering with respect to a reference function Φ is, it has so far only been applicable to the special case that Φ is a (preferentially closed-shell state) single Slater determinant. There are open-shell states describably to zeroth order by a single Slater determinant. To define such a determinant as physical vacuum is possible, but not very advantageous.

The many-body formalism has been applied to open-shell states, for which the zeroth order wave function is *not* a closed-shell Slater determinant and can hence not be used as physical vacuum. It has become customary to introduce an auxiliary wave function, usually for a smaller number of particles, i.e., the closed-shell-part of Φ and to use normal order and Wick theorem with respect to this auxiliary function.[6,7] Approaches of this type have been quite popular, but are less powerful than the theory for closed-shell states, since the energy is no longer formally a vacuum expectation value.

For what follows it is convenient to define *basic operators*. A basic operator with respect to the genuine vacuum is a normal order product of creation and annihilation operators. The particle-number-conserving operators (3) are a subset of that of the basic operators. These are classified according to their *excitation rank* as single excitation, double excitation, etc. operators or alternatively as one-particle, two particle operators, etc. Non-particle-number-conserving operators have a creation rank (the number of upper labels), and annihilation rank (the number of lower labels), and an *effective creation rank*, which is the difference of the two.

One of the present authors[8–10] has recently proposed a generalization of normal ordering and of the corresponding Wick theorem for a multideterminantal state as the physical vacuum. Once one has realized that such a generalization must exist,[8,9] there are several ways to arrive at it. Obviously some properties and theorems have to survive in the general case. These are

(a) Any product of basic operators can be formulated as a linear combination of their normal product (which is a basic operator as well, with respective creation and annihilation ranks added), and *contractions*, which are normal order operators of the same effective creation rank, but different (lower) excitation ranks. This expansion can be referred to as generalized Wick's theorem.

(b) For a particle-number-conserving product of basic operators, the Wick expansion can also contain a full contraction, which is a simple number. *Normal order* does *not* apply to the full contraction.

(c) The vacuum expectation value of any basic operator and of normal order operators in general, vanishes.

(d) The effective creation rank of an operator is independent of the reference to the genuine or a different vacuum. In particular particle-number-conserving operators are so, independently of the reference. (This excludes reference states without fixed particle number like that created by the Bogoliubov transformation.)

It follows from (a) to (d) that the vacuum expectation value $\langle \Phi | \Omega | \Phi \rangle$ of an operator Ω must be its fully contracted part, which vanishes for Ω not particle-number-conserving, and is a simple number for Ω particle-number conserving, and equal to a density matrix element for Ω a basic operator. This indicates both the privileged role of particle number-conserving (excitation) operators and gives a hint that density matrix element will play a role. It is further obvious that excitation operators in normal order with respect to any physical vacuum must be expandable in terms of excitation operators in normal order with respect to the genuine vacuum, of the same and lower excitation rank. This must also hold conversely.

We shall show here that from these premises and the guiding principle that the known normal ordering which respect to a closed-shell vacuum must appear as a special case, we automatically come to a normal ordering and an extended Wick theorem for arbitrary reference wave functions. Although we first consider only particle-number-conserving joperators, the generalization to arbitrary operators does not present difficulties.

We thus open a new route, alternative to that described previously.[10] There the notion of the new normal ordering was arrived at by defining it in such a way that the expectation values of the normal ordered products are zero with respect to Φ and that fermion creation/annihilation operators anticommute under the new normal ordering. The new nor-

mal products turned out to be some unitary transforms of ordinary normal products defined with respect to any one single determinant contained in Φ. The extension of Wick's theorem then follows as an algebraic identity. A way to develop coupled cluster theory starting from a multideterminant Φ was also suggested.[8,10]

The present and the former approaches discussed above are complementary and lead ultimately to the same working expression for the Wick's expansion. The present approach is particularly suited to practical applications in multireference many-body theory. It is easily modified to a spinfree formalism. It directly allows one to write the Hamiltonian in normal order form with respect to a multiconfiguration reference function in terms of either spindependent or spinfree operators and to express energies of multiconfiguration states as vacuum expectation values. We also think that the present approach has some advantages from a didactical point of view, and we have stressed didactics more than is customary in an original paper.

We shall start (Sec. II) by recapitulating the traditional concepts of normal ordering and Wick's theorem, and their extension to Quantum Chemistry in Fock space, including the spinfree theory. We analyze the traditional particle hole formalism in terms of a single Slater determinant reference function (Sec. III). We then generalize this formalism to allow that the one-electron basis is not the direct sum of the basis sets for occupied and unoccupied spin-orbitals (Sec. IV). This necessarily introduces density matrix elements in the formulation of normal order operators and of the generalized Wick theorem.

We shall find a formulation that allows the direct generalization to arbitrary reference states (Sec. V) which, interestingly enough, is also applicable to an ensemble state as reference. We then derive the corresponding generalized Wick theorem (Sec. VI) and give a simple rationalization of the new contraction rules together with their Hugenholtz-type diagrammatic representation (Sec. VII). We discuss commutators of operators (Sec. VIII) and a spinfree formalism (Sec. IX). The multiple contractions are determined by residual density matrix elements, which are non-zero only for all labels referring to active spin-orbitals. We formulate MC-SCF-theory in the new notation (Sec. X). We finally discuss excited configurations in the new formalism (Sec. XI) and make concluding remarks (Sec. XII).

Application to many-body perturbation and coupled-cluster theory for multiconfiguration reference functions will be the subject of forthcoming papers.

II. NORMAL ORDERING AND WICK'S THEOREM WITH RESPECT TO THE GENUINE VACUUM

Let ψ_p be an orthonormal set of spin-orbitals and a^p as well as a_p the corresponding creation and annihilation operators.[3,4] (Conventionally these operators are written as $a_q^\dagger$ and a_p respectively, but this notation is not recommended in the present context, in which a tensor notation[3,4] is imperative). A product of fermion operators (a^p or a_p) is said to be in ''normal order,'' if all creation operators appear left to all annihilation operators; e.g.,

$$a^p a^q a_r a_s a_t \tag{4}$$

is in normal order. A product that is not in normal order can, by repeated application of the anticommutation relations for fermion operators

$$[a^p,a_q]_+=\delta_q^p;\quad [a^p,a^q]_+=0;\quad [a_p,a_q]_+=0 \tag{5}$$

be expanded into a sum of normal-ordered operators, e.g.,

$$a^p a_q a^r a_s = a^p(\delta_q^r - a^r a_q)a_s = \delta_q^r a^p a_s - a^p a^r a_q a_s\,, \tag{6a}$$

$$\begin{aligned} a_q a^p a^r a_s &= \delta_q^p a^r a_s - a^p a_q a^r a_s \\ &= \delta_q^p a^r a_s - \delta_q^r a^p a_s + a^p a^r a_q a_s\,. \end{aligned} \tag{6b}$$

This expansion is called *Wick's theorem*.[2] It can be phrased in the following form: An arbitrary product of fermion operators is equal to the corresponding normal product plus all possible contractions. In Eqs. (6a) and (6b) $a^p a^r a_q a_s$ is the normal product and $\delta_q^r a^p a_s$ or $\delta_q^p a^r a_s$ are contractions. There can be multiple contractions as the double contractions $\delta_s^p\delta_q^r$ and $\delta_q^p\delta_s^r$ in

$$\begin{aligned} a_q a_s a^p a^r &= a^p a^r a_q a_s - \delta_s^p a^r a_q + \delta_q^p a^r a_s + \delta_s^r a^p a_q \\ &\quad - \delta_q^r a^p a_s + \delta_s^p\delta_q^r - \delta_q^p\delta_s^r\,. \end{aligned} \tag{6c}$$

In applying Wick's theorem an obvious *sign rule* has to be observed. The *vacuum expectation* value of any normal order operator vanishes, e.g.,

$$\langle 0|a^p a^r a_q a_s|0\rangle = 0. \tag{7a}$$

The vacuum expectation value of a product of operators is hence equal to the sum of all full contractions, e.g.,

$$\langle 0|a_q a_s a^p a^r|0\rangle = \delta_s^p\delta_q^r - \delta_q^p\delta_s^r\,. \tag{7b}$$

Particularly important are products of the same number of creation and annihilation operators. Such products are *particle-number-conserving*, i.e., application of such a product on an n-fermion wave function transforms it to another n-fermion wave function. For *particle-number-conserving operators in normal order* a compact notation is possible,[3,4] e.g.,

$$a_q^p = a^p a_q\,; a_{rs}^{pq} = a^p a^q a_s a_r = a_{sr}^{qp}\,. \tag{8}$$

A product of such normal order operators can be expanded into a sum of normal order operators, e.g.,

$$a_q^p a_s^r = a_{qs}^{pr} + \delta_q^r a_s^p\,, \tag{9a}$$

$$\begin{aligned} a_{rs}^{pq} a_{vw}^{tu} &= a_{rsvw}^{pqtu} + \delta_r^t a_{vsw}^{pqu} + \delta_r^u a_{wsv}^{pqt} + \delta_s^t a_{rvw}^{pqu} + \delta_s^u a_{rwv}^{pqt} \\ &\quad + \delta_r^t\delta_s^u a_{vw}^{pq} + \delta_s^t\delta_r^u a_{wv}^{pq}\,. \end{aligned} \tag{9b}$$

Equations (9a) and (9b) represents what has been called *generalized Wick's theorem*.[3,4] For this theorem *no* sign rule has to be observed, but the pairing of the upper to the lower indices has to be kept. If one contracts, e.g., t with r in the 2^{nd} term in Eq. (9b), the *remaining partners* of the con-

tracted spin orbitals (here p and v) become paired (i.e., are above each other). Contractions always go *from upper right to lower left* in the formula.

It should be noted that this generalized Wick theorem holds in the same form for boson operators as for fermion operators. One can also introduce spinfree particle number conserving operators, such as

$$E_Q^P = a_{Q\alpha}^{P\alpha} + a_{Q\beta}^{P\beta}, \tag{10a}$$

$$E_{RS}^{PQ} = a_{R\alpha S\alpha}^{P\alpha Q\alpha} + a_{R\alpha S\beta}^{P\alpha Q\beta} + a_{R\beta S\alpha}^{P\beta Q\alpha} + a_{R\beta S\beta}^{P\beta Q\beta}, \tag{10b}$$

which are also spin-conserving. For these operators the generalized Wick theorem holds in the same form as Eq. (9a), e.g.,

$$E_Q^P E_S^R = E_{QS}^{PR} + \delta_Q^R E_S^P. \tag{11}$$

Both the a and the E-operators are invariant with respect to a simultaneous permutation of upper and lower indices, e.g.,

$$a_{rs}^{pq} = a_{sr}^{qp}; E_{RS}^{PQ} = E_{SR}^{QP}. \tag{12}$$

For the a-operators there is also a simple relation with respect to permutation of *either* lower *or* upper indices, e.g.,

$$a_{rs}^{pq} = -a_{rs}^{qp} = -a_{sr}^{pq}. \tag{13}$$

This rule has no counterpart for the E-operators. Use of this rule should therefore be avoided if one wants to derive relations that hold both for the a and the E operators.

III. NORMAL ORDER AND WICK'S THEOREM WITH RESPECT TO A SINGLE SLATER DETERMINANT REFERENCE FUNCTION

Let Φ be a single Slater determinant, in which the spin orbitals $\{\psi_i; (i=1,..n)\}$ are occupied, and let the occupied ψ_i together with the unoccupied $\{\psi_a; (a>n)\}$ form an orthonormal set of basis functions ψ_p. This Φ is often called the *physical vacuum*. Note the difference between the labels $i,j,k\ldots$ and a,b,c for occupied and unoccupied spin-orbitals, respectively.

We rename a^i as a *hole annihilation operator* and a_i as a *hole creation operator*. Hence a_a and a^i are annihilation operators in the *particle-hole sense* (or with respect to Φ) or *quasiparticle annihilation operators*, analogously a^a and a_i are creation operators with respect to Φ or *quasiparticle creation operators*. The conventional definition—in our notation—of a normal order product in the particle-hole sense—or with respect to Φ—is then, that all quasiparticle creation operators are left to all quasiparticle annihilation operators. So

$$a^a a_i a_j a_b a^j a_c \tag{14}$$

is in normal order with respect to Φ, which implies in particular that

$$\langle \Phi | a^a a_i a_j a_b a^j a_a | \Phi \rangle = 0. \tag{15}$$

Conventionally our a_i and a^i are written as $b_i^\dagger$ and b_i, in order to indicate that $b_i^\dagger$ is a quasiparticle creation operator. Then Eq. (14) would read $a_a^\dagger b_i^\dagger b_j^\dagger a_b b_j a_c$ and make directly obvious that this is a normal product with respect to Φ, but this notation would be inappropriate for our purposes.

Arbitrary products of fermion operators in the particle-hole sense can again be expanded as sums of operators in normal order with respect to Φ. Wick's theorem states again that an arbitrary product is equal to the normal product plus all contractions, now with respect to Φ. A simple example is

$$\begin{aligned} a_a a^i a^b a_j &= -a_a a^b a_i a^j \\ &= -\delta_a^b a^i a_j + a^b a_a a^i a_j - \delta_a^b \delta_j^i \\ &\quad + \delta_a^b a_j a^i + \delta_a^j a^b a_a - a^b a_a a_j a^i \\ &= -\delta_a^b \delta_j^i + \delta_a^b a_j a^i + \delta_a^j a^b a_a + a^b a_j a_a a^i. \end{aligned} \tag{16}$$

The counterpart of the particle-number-conserving operators of Sec. II are now the *charge-conserving* operators. (Both particle-number-conserving and charge conserving mean an effective creation rank 0.) A product of fermion operators is charge-conserving if the number of particle creation plus hole annihilation operators is equal to that of particle annihilation plus hole creation operators. It is simpler to observe that for a charge-conserving operator the number of upper labels must agree with that of lower labels. Again a compact formulation of these operators is possible. We characterize them with a tilde, e.g.,

$$\tilde{a}_{kl}^{ij} = a_k a_l a^j a^i, \tag{17a}$$

$$\tilde{a}_{bl}^{aj} = -a^a a_l a^j a_b. \tag{17b}$$

The sign convention will become obvious later.

One can establish a simple relation between normal products with respect to Φ and with respect to the genuine vacuum $|0>$. In fact one can start from the $\tilde{a}$ operators defined by Eqs. (17a) or (17b) and expand them using Wick's theorem with respect to $|0>$, i.e.,

$$\tilde{a}_k^i = -a_k a^i = -\delta_k^i + a_k^i, \tag{18a}$$

$$\begin{aligned} \tilde{a}_{kl}^{ij} &= a_k(\delta_l^j - a^j a_l) a^i \\ &= \delta_l^j(\delta_k^i - a^i a_k) - (\delta_k^j - a^j a_k)(\delta_l^i - a^i a_l) \\ &= \delta_l^j \delta_k^i - \delta_l^j a_k^i - \delta_k^i \delta_l^i + \delta_k^j a_l^i + \delta_l^i a_k^j - \delta_k^i a_l^j + a^j a^i a_k a_l \\ &= a_{kl}^{ij} - \delta_k^i a_l^j - \delta_l^j a_k^i + \delta_l^i a_k^j + \delta_k^j a_l^i + \delta_k^i \delta_l^j - \delta_l^i \delta_k^j, \end{aligned} \tag{18b}$$

$$\tilde{a}_{bl}^{aj} = -\delta_l^j a_b^a + a^a a^j a_l a_b = -\delta_l^j a_b^a + a_{bl}^{aj}. \tag{18c}$$

The generalization of Eqs. (18a) to (18c) to arbitrary (particle or hole) labels is[4,5]

$$\tilde{a}_q^p = a_q^p - \delta_q^p n_p, \tag{19a}$$

$$\begin{aligned} \tilde{a}_{rs}^{pq} &= a_{rs}^{pq} - \delta_r^p n_p a_s^q - \delta_s^q n_q a_r^p + \delta_s^p n_p a_r^q \\ &\quad + \delta_r^q n_q a_s^p + \delta_{rs}^{pq} n_p n_q, \end{aligned} \tag{19b}$$

$$\begin{aligned}\widetilde{a}^{pqr}_{stu} &= a^{pqr}_{stu} - \delta^p_s n_p a^{qr}_{tu} + \delta^q_s n_q a^{pt}_{ru} + \delta^r_s n_r q^{qp}_{tu} + \delta^p_t n_p a^{qr}_{su} \\ &- \delta^q_t n_q a^{pr}_{su} + \delta^r_t n_r a^{pq}_{su} + \delta^p_u n_p a^{qr}_{ts} + \delta^q_u n_q a^{pr}_{st} - \delta^r_u n_r a^{pq}_{st} \\ &+ n_p n_q \delta^{pq}_{st} a^r_u + n_p n_r \delta^{pr}_{su} a^q_t + n_q n_r \delta^{qr}_{tu} a^p_s - n_p n_q \delta^{pq}_{su} a^r_t \\ &- n_p n_q \delta^{pq}_{ut} a^r_s - n_p n_r \delta^{pr}_{st} a^q_u - n_p n_r \delta^{pr}_{tu} a^q_s - n_q n_r \delta^{qr}_{ts} a^p_u \\ &- n_q n_r \delta^{qr}_{su} a^p_t - n_p n_q n_r \delta^{pqr}_{stu} . \end{aligned} \tag{19c}$$

$$n_p = 1 \text{ for } \psi_p \text{ occupied in } \Phi;$$

$$n_p = 0 \text{ for } \psi_p \text{ unoccupied in } \Phi, \tag{20a}$$

$$\delta^{pq}_{rs} = \delta^p_r \delta^q_s - \delta^p_s \delta^q_r ;$$

$$\begin{aligned}\delta^{pqr}_{stu} &= \delta^p_s \delta^q_t \delta^r_u + \delta^p_t \delta^q_u \delta^r_s + \delta^p_u \delta^q_s \delta^r_t \\ &- \delta^p_t \delta^q_s \delta^r_u - \delta^p_u \delta^q_t \delta^r_s - \delta^p_s \delta^q_u \delta^r_t . \end{aligned} \tag{20b}$$

One can forget the original definition of Eqs. (17a), (17b) and use Eqs. (19a) to (19c) as the definition of the $\widetilde{a}$ operators. The generalization to higher orders is straightforward. With increasing rank more types of contractions appears.

For products of $\widetilde{a}$ operators there is again a *generalized Wick theorem* like Eqs. (9a) and (9b), but in addition to particle contractions we also have hole contractions and combined contractions, e.g.,[4,5]

$$\widetilde{a}^p_q \widetilde{a}^r_s = \widetilde{a}^{pr}_{qs} + \delta^r_q (1-n_q) \widetilde{a}^p_s - \delta^p_s n_p \widetilde{a}^r_q + \delta^r_q \delta^p_s n_p (1-n_q), \tag{21a}$$

$$\begin{aligned}\widetilde{a}^p_q \widetilde{a}^{rs}_{tu} &= \widetilde{a}^{prs}_{qtu} + \delta^r_q (1-n_q) \widetilde{a}^{ps}_{tu} + \delta^s_q (1-n_q) \widetilde{a}^{rp}_{tu} - \delta^p_t n_p \widetilde{a}^{rs}_{qu} \\ &- \delta^p_u n_p \widetilde{a}^{rs}_{tq} + \delta^r_q (1-n_q) \delta^p_t n_p \widetilde{a}^s_u - \delta^r_q (1-n_q) \delta^p_u n_u a^s_t \\ &- \delta^s_q (1-n_p) \delta^p_t n_p \widetilde{a}^r_u + \delta^s_q (1-n_q) \delta^p_u n_p \widetilde{a}^r_t . \end{aligned} \tag{21b}$$

As in Eqs. (9a) and (9b) particle contractions go from upper right to lower left, but only if $n_q = 0$, while hole contractions go from lower right to upper left, namely if $n_p = 1$. There is a sign rule, according to which there is a factor (-1) for each hole contraction and another factor (-1) for each *closed loop*, as e.g., $\delta^r_q \delta^p_s$ in Eq. (21a) or $\delta^r_q \delta^p_t$ in Eq. (21b).

For the product $\widetilde{a}^{pr}_{qs} \widetilde{a}^{tv}_{uw}$ the number of terms in the generalized Wick expansion is already so large that we rather give only one example of each type of contraction, with the number of contractions of this type in parenthesis

product: $\widetilde{a}^{pr}_{qs} \widetilde{a}^{\ tv}_{uw}$, (22a)

normal product: $\widetilde{a}^{prtv}_{qsuw}$, (22b)

single-particle contraction(4): $\delta^t_q (1-n_t) \widetilde{a}^{prv}_{usw}$, (22c)

single-hole contraction(4): $\delta^p_u n_p \widetilde{a}^{\ trv}_{qsw}$, (22d)

double-particle contraction (2):

$$\delta^t_q \delta^v_s (1-n_q)(1-n_s) \widetilde{a}^{pr}_{uw}, \tag{22e}$$

single-particle-single-hole contraction (16):

$$\delta^t_q (1-n_q) \delta^p_u n_p \widetilde{a}^{rv}_{sw}, \tag{22f}$$

double-particle-single-hole contraction (8):

$$\delta^t_q \delta^v_s (1-n_q)(1-n_s) \delta^p_u n_p \widetilde{a}^r_w , \tag{22g}$$

single-particle-double-hole contraction (8):

$$\delta^t_q (1-n_q) \delta^p_u n_p \delta^r_w n_q \widetilde{a}^v_s , \tag{22h}$$

double-particle-double-hole contraction (4):

$$\delta^t_q \delta^v_s (1-n_q)(1-n_s) \delta^p_u \delta^r_w n_p n_r . \tag{22i}$$

The sign rule is as explained before, i.e., there is a factor (-1) for each hole contraction and an additional factor (-1) for each closed loop. Otherwise, pairings have to be kept.

For the $\widetilde{E}$ operators defined in analogy to Eqs. (10a) and (10b) as[4,5]

$$\widetilde{E}^P_Q = \widetilde{a}^{P\alpha}_{Q\alpha} + \widetilde{a}^{P\beta}_{Q\beta}, \tag{23a}$$

$$\widetilde{E}^{PQ}_{RS} = \widetilde{a}^{P\alpha Q\alpha}_{R\alpha S\alpha} + \widetilde{a}^{R\alpha Q\beta}_{R\alpha S\beta} + \widetilde{a}^{P\beta Q\alpha}_{R\beta S\beta} + \widetilde{a}^{P\beta S\beta}_{R\beta S\beta}, \tag{23b}$$

the contraction rules are the same as for the $\widetilde{a}$ operators, but there is a factor (-2) for each closed loop. For the contraction rules outlined in this section a diagrammatic illustration has been given.[3,4] We can't go into details, but we point out that the diagrams introduced in Sec. VII reduce to the former ones[3,4] for a single-Slater determinant reference state.

IV. GENERALIZATION OF THE PARTICLE-HOLE FORMALISM

In this section, we still consider normal ordering with respect to a single Slater determinant Φ, but unlike in the preceding section, we shall no longer assume that the orthonormal one-particle basis $\{\psi_p\}$, in terms of which a_p and a^p are defined, can be divided into subsets of orbitals occupied and unoccupied in Φ. This case is thus more general in that both ψ_i and ψ_a are now some linear combinations of ψ_p's. Then the traditional formulation of a normal order product with respect to Φ can no longer be used. However, the definitions (19a) to (19c) can easily be generalized.

Applying a one-electron transformation, the a^p_q or a^{pq}_{qs} operators remain formally invariant, while expressions like $n_p \delta^p_q$ are changed to density matrix elements

$$\delta^p_q n_p \Rightarrow \langle \Phi | a^p_q | \Phi \rangle = \gamma^p_q , \tag{24a}$$

$$n_p n_q \delta^{pq}_{rs} \Rightarrow \langle \Phi | a^{pq}_{rs} | \Phi \rangle = \gamma^{pq}_{rs} . \tag{24b}$$

These density matrix elements are diagonal only in a specific (natural) basis $\{\psi_i, \psi_a\}$, not in a more general basis $\{\psi_p\}$. Hence, we must replace Eqs. (19a) to (19c) by

$$\widetilde{a}^p_q = a^p_q - \gamma^p_q , \tag{25a}$$

$$\widetilde{a}^{pq}_{rs} = a^{pq}_{rs} - \gamma^p_r a^q_s - \gamma^q_s a^p_r + \gamma^p_s a^q_r + \gamma^q_r a^p_s + \gamma^{pq}_{rs} , \tag{25b}$$

$$\begin{aligned}\widetilde{a}^{pqr}_{stu} &= a^{pqr}_{stu} - \gamma^p_s a^{qr}_{tu} + \gamma^q_s a^{pr}_{tu} + \gamma^r_s a^{qp}_{tu} + \gamma^p_t a^{qr}_{su} - \gamma^q_t a^{pr}_{su} \\ &+ \gamma^r_t a^{pq}_{su} + \gamma^p_u a^{qr}_{ts} + \gamma^q_u a^{pr}_{st} + \gamma^r_u a^{pq}_{st} + \gamma^{pq}_{st} a^r_u \\ &+ \gamma^{pr}_{su} a^q_t + \gamma^{qr}_{tu} a^p_s - \gamma^{pq}_{su} a^r_t - \gamma^{pq}_{ut} a^r_s - \gamma^{pr}_{st} a^q_u \\ &- \gamma^{pr}_{tu} a^q_s - \gamma^{qr}_{ts} a^p_u - \gamma^{qr}_{su} a^p_t - \gamma^{pqr}_{stu} . \end{aligned} \tag{25c}$$

It is easily checked that

$$\langle\Phi|\tilde{a}^p_q|\Phi\rangle=\langle\Phi|a^p_q|\Phi\rangle-\gamma^p_q=0, \tag{26a}$$

$$\langle\Phi|\tilde{a}^{pq}_{rs}|\Phi\rangle=\gamma^{pq}_{rs}-2\,\gamma^p_r\gamma^q_s+2\,\gamma^p_s\gamma^q_r+\gamma^{pq}_{rs}=0, \tag{26b}$$

i.e., that expectation values of $\tilde{a}$ operators with respect to Φ vanish.

One can invert Eqs. (25a) to (25c) to

$$a^p_q=\tilde{a}^p_q+\gamma^p_q, \tag{27a}$$

$$\begin{aligned}a^{pq}_{rs}&=\tilde{a}^{pq}_{rs}+\gamma^p_r(\tilde{a}^q_s+\gamma^q_s)+\gamma^q_s(\tilde{a}^p_r+\gamma^p_r)\\&\quad-\gamma^p_s(\tilde{a}^q_r+\gamma^q_r)-\gamma^q_r(\tilde{a}^p_s+\gamma^p_s)-\gamma^{pq}_{rs}\\&=\tilde{a}^{pq}_{rs}+\gamma^p_r\tilde{a}^q_s+\gamma^q_s\tilde{a}^p_r-\gamma^p_s\tilde{a}^q_r-\gamma^q_r\tilde{a}^p_s+\gamma^{pq}_{rs},\end{aligned} \tag{27b}$$

$$\begin{aligned}a^{pqr}_{stu}&=\tilde{a}^{pqr}_{stu}+\gamma^p_s\tilde{a}^{qr}_{tu}-\gamma^q_s\tilde{a}^{pr}_{tu}-\gamma^r_s\tilde{a}^{qp}_{tu}-\gamma^p_t\tilde{a}^{qr}_{su}+\gamma^q_t\tilde{a}^{pr}_{su}\\&\quad-\gamma^r_t\tilde{a}^{pq}_{su}-\gamma^p_u\tilde{a}^{qr}_{ts}-\gamma^q_u\tilde{a}^{pr}_{st}+\gamma^r_u\tilde{a}^{pq}_{st}+\gamma^{pq}_{st}\tilde{a}^r_u\\&\quad+\gamma^{pr}_{su}\tilde{a}^q_t+\gamma^{qr}_{tu}\tilde{a}^p_s-\gamma^{pq}_{su}\tilde{a}^r_t-\gamma^{pq}_{ut}\tilde{a}^r_s-\gamma^{pr}_{st}\tilde{a}^q_u\\&\quad-\gamma^{pr}_{tu}\tilde{a}^q_s-\gamma^{qr}_{ts}\tilde{a}^p_u-\gamma^{qr}_{su}\tilde{a}^p_t+\gamma^{pqr}_{stu}.\end{aligned} \tag{27c}$$

Equations (27a) to (27c) are, of course, a manifestation of Wick's theorem with respect to Φ, applied to a^q_p or a^{pq}_{rs}, which are not in normal order with respect to Φ (see also Sec. VII).

For the formulation of the generalized Wick theorem (21a) and (21b) in the present context, it is convenient to define the matrix element η^p_q of the ''one-hole density matrix''

$$\eta^p_q=\delta^p_q-\gamma^p_q=\langle\Phi|\,\delta^p_q-a^p_q|\Phi\rangle=\langle\Phi|a_q a^p|\Phi\rangle, \tag{28}$$

one then gets instead of Eqs. (21a) and (21b)

$$\tilde{a}^p_q\tilde{a}^r_s=\tilde{a}^{pr}_{qs}+\eta^r_q\tilde{a}^p_s-\gamma^p_s\tilde{a}^r_q+\eta^r_q\gamma^p_s, \tag{29}$$

$$\begin{aligned}\tilde{a}^p_q\tilde{a}^{rs}_{tu}&=\tilde{a}^{prs}_{qtu}+\eta^r_q\tilde{a}^{ps}_{tu}+\eta^s_q\tilde{a}^{rp}_{tu}-\gamma^p_t\tilde{a}^{rs}_{qu}-\gamma^p_u\tilde{a}^{rs}_{tq}\\&\quad+\gamma^p_t\eta^r_q\tilde{a}^s_u-\gamma^p_t\eta^s_q\tilde{a}^r_u-\gamma^p_u\eta^r_q\tilde{a}^s_t+\gamma^p_u\eta^s_q\tilde{a}^r_t.\end{aligned} \tag{30}$$

Density matrix elements of this type as well as hole density matrix elements have also been used in the context of ''internally contracted CI.''[16,17]

V. NORMAL ORDERING WITH RESPECT TO AN ARBITRARY REFERENCE FUNCTION

The formalism of the previous section only refers marginally to the fact that the reference function Φ is a single Slater determinant, and is therefore an appropriate starting point for a generalization to an arbitrary reference function. The assumption that Φ is a single Slater determinant is still implicit in relations like

$$\gamma^{pq}_{rs}=\gamma^p_r\gamma^q_s-\gamma^p_s\gamma^q_r \tag{31}$$

that we have used in Sec. IV, e.g., in Eq. (26b), but which are no longer valid in the general case. So we must avoid imposing relations of this type.

Our general premises outlined in Sec. I require that for a general reference function $\tilde{a}^p_q$ is a linear combination of a^p_q and a constant, that $\tilde{a}^{pq}_{rs}$ is a linear combination of a^{pq}_{rs}, of a^p_r,a^p_s,a^q_r,a^q_s and a constant, and so forth. The relations (25a) to (25c) are of this form, and so are the relations (27a) to (27c), so we may tentatively use either of these sets as definition of the normal ordered operators with respect to arbitrary reference functions. We note that Eqs. (27a) to (27c) are equivalent to Eqs. (25a) to (25c) only if Φ is a single Slater determinant, since in the last reformulation in Eqs. (27a) to (27c) use has been made of (31). Choosing Eqs. (25a) to (25c) for the generalized definition of $\tilde{a}^{pq}_{rs}$ we are led to

$$\langle\Phi|\tilde{a}^{pq}_{rs}|\Phi\rangle=\gamma^{pq}_{rs}-2\,\gamma^p_r\gamma^q_s+2\,\gamma^p_s\gamma^q_r+\gamma^{pq}_{rs}. \tag{32}$$

This should vanish, since we must require that the expectation value of a normal order operator vanishes for the wave function with respect to which the operator is in normal order. This is the other of our premises. However Eq. (32) vanishes only if (31) holds, i.e., if Φ is a single Slater determinant. This can hence not be the searched-for generalized definition of normal ordering.

Let us now rather consider Eqs. (27a) to (27c),which satisfy our first premise as well,and choose Φ as an arbitrary function. We get

$$\langle\Phi|a^p_q|\Phi\rangle=\gamma^p_q=\langle\Phi|\tilde{a}^q_p|\Phi\rangle+\gamma^p_q;\Rightarrow\langle\Phi|\tilde{a}^q_p|\Phi\rangle=0, \tag{33a}$$

$$\langle\Phi|a^{pq}_{rs}|\Phi\rangle=\gamma^{pq}_{rs}=\langle\Phi|\tilde{a}^{pq}_{rs}|\Phi\rangle+\gamma^{pq}_{rs};\Rightarrow\langle\Phi|\tilde{a}^{pq}_{rs}|\Phi\rangle=0, \tag{33b}$$

$$\langle\Phi|\tilde{a}^{pqr}_{stu}|\Phi\rangle=0. \tag{33c}$$

Now we have achieved that the expectation values with respect to Φ of normal-order operators do, in fact vanish.

The general (recursive) definition of normal-order operators is hence in Eqs. (27a) to (27c). In order to give these equations in a more compact form we introduce the entity $\Sigma(-1)^p A^{p_1p_2\cdots p_k}_{q_1q_2\cdots q_k}B^{p_{k+1}\cdots p_n}_{q_{k+1}\cdots q_n}$ defining the sum over all partitions of both the n upper labels p_i and the n lower labels q_i into respective subsets of k and $n-k$ labels, keeping the original pairing of the p_i and q_i as much as possible, with appropriate sign factors, namely (-1) for each permutation of a pair $(p_j,q_j;p_l,q_l)$ to $(p_j,q_l;p_l,q_j)$. An illustration is

$$\begin{aligned}\Sigma(-1)^p\gamma^p_q a^{rt}_{su}&=\gamma^p_q a^{rt}_{su}+\gamma^r_s a^{pt}_{qu}+\gamma^t_u a^{pr}_{qs}-\gamma^p_s a^{rt}_{qu}-\gamma^p_u a^{rt}_{sq}\\&\quad-\gamma^r_q a^{pt}_{su}-\gamma^r_u a^{pt}_{qs}-\gamma^t_q a^{rp}_{su}-\gamma^t_u a^{pr}_{qs}.\end{aligned} \tag{34}$$

Note that p for *parity* in $(-1)^p$ has nothing to do with the same symbol used for one of the labels. With this definition and solving for $\tilde{a}$ Eqs. (27a) to (27c) become

$$\tilde{a}^p_q=a^p_q-\gamma^p_q, \tag{35a}$$

$$\tilde{a}^{pr}_{qs}=a^{pr}_{qs}-\Sigma(-1)^p\gamma^p_q\tilde{a}^r_s-\gamma^{pr}_{qs}, \tag{35b}$$

$$\tilde{a}^{prt}_{qsu}=a^{prt}_{qsu}-\Sigma(-1)^p\gamma^p_q\tilde{a}^{rt}_{su}-\Sigma(-1)^p\gamma^{pr}_{qs}\tilde{a}^{\ t}_{\ u}-\gamma^{prt}_{qsu}, \tag{35c}$$

$$\tilde{a}^{prtv}_{qsuw} = a^{prtv}_{qsuw} - \Sigma(-1)^p \gamma^p_q \tilde{a}^{rtv}_{suw} - \Sigma(-1)^p \gamma^{pr}_{qs} \tilde{a}^{\ tv}_{uw} - \Sigma(-1)^p \gamma^{prt}_{qsu} \tilde{a}^{v}_{w} - \gamma^{prtv}_{qsuw}. \tag{35d}$$

Thus we have achieved fulfillment of the requirements that for Φ a single Slater determinant the former definition is retrieved and that for an arbitrary Φ expectation values of normal-order operator vanish.

We make an interesting observation. The wave function Φ, with respect to which we define normal ordering, enters the definition of the normal-order operators only via the reduced density matrices associated with Φ. This makes a further generalization almost trivial, namely normal ordering with respect to an ensemble state. Operators in normal order with respect to an ensemble, characterized by an n-particle density matrix

$$\gamma^{(n)} = \sum_k n_k |\Phi_k\rangle\langle\Phi_k| \tag{36}$$

have a vanishing ensemble expectation value and obey the same contraction rules as derived here, with appropriately defined residual reduced density matrices.

VI. THE GENERALIZED WICK THEOREM WITH RESPECT TO ARBITRARY REFERENCE FUNCTIONS

We regard Eqs. (35a) to (35d) as the definition of the charge-conserving basic operators in normal order with respect to an arbitrary reference function Φ. From these definitions one gets directly the decomposition of products of normal order operators to sums of normal-order operators, i.e., the multiconfiguration generalization of the generalized Wick's theorem. The simplest example is

$$\begin{aligned}\tilde{a}^p_q \tilde{a}^r_s &= (a^p_q - \gamma^p_q)(a^r_s - \gamma^r_s) \\ &= a^{pr}_{qs} + \delta^r_q a^p_s - \gamma^p_q a^r_s - a^p_q \gamma^r_s + \gamma^p_q \gamma^r_s \\ &= a^{pr}_{qs} + \delta^r_q (\tilde{a}^p_s + \gamma^p_s) - \gamma^p_q (\tilde{a}^r_s + \gamma^r_s) - (\tilde{a}^p_q + \gamma^p_q)\gamma^r_s + \gamma^p_q \gamma^r_s \\ &= \tilde{a}^{pr}_{qs} + \eta^r_q \tilde{a}^p_s - \gamma^p_s \tilde{a}^r_q + \eta^r_q \gamma^p_s + \gamma^{pr}_{qs} - \gamma^p_q \gamma^r_s + \gamma^r_q \gamma^p_s ,\end{aligned} \tag{37}$$

where the contraction rule (9a) as well as the definitions (24a) and (24b)of $\gamma^p_q, \gamma^{pq}_{rs}$ and (28) for η^p_q have been used. We further define the *residual density matrix element* λ^{pr}_{qs} – in the sense of a cumulant expansion – as

$$\lambda^{pr}_{qs} = \gamma^{pr}_{qs} - \gamma^p_q \gamma^r_s + \gamma^p_s \gamma^r_q , \tag{38}$$

such that Eq. (37) can be written in a more compact form as

$$\tilde{a}^p_q \tilde{a}^r_s = \tilde{a}^{pr}_{qs} + \eta^r_q \tilde{a}^p_s - \gamma^p_s \tilde{a}^r_q + \gamma^p_s \eta^r_q + \lambda^{pr}_{qs} . \tag{39}$$

We note that λ^{pr}_{qs} vanishes if Φ is a single Slater determinant. In this case Eq. (39) reduces to Eq. (29). For a multideterminantal Φ, we can always divide our one-particle basis into occupied spin-orbitals (label $i,j,k\ldots; n_i = 1$) active spin-orbitals (label $x,y,z,\ldots; 0 < n_x < 1$) and virtual spin-orbitals (label $a,b,c\ldots; n_a = 0$). Then λ^{pr}_{qs} vanishes unless all labels refer to active spin-orbitals, i.e., only $\lambda^{xy}_{uv} \neq 0$.

In analogy to Eq. (38) we define residual three and four-particle density matrix elements

$$\lambda^{prt}_{qsu} = \gamma^{prt}_{qsu} - \Sigma(-1)^p \gamma^p_q \lambda^{rt}_{su} - \det\{\gamma^p_q \gamma^r_s \gamma^t_u\}, \tag{40a}$$

$$\lambda^{prtv}_{qsuw} = \gamma^{prtv}_{qsuw} - \Sigma(-1)^p \gamma^p_q \lambda^{rtv}_{suw} - \tfrac{1}{2}\Sigma(-1)^p \lambda^{pr}_{qs} \lambda^{tv}_{uw} - \Sigma(-1)^p \gamma^p_q \gamma^r_s \lambda^{tv}_{uw} - \det\{\gamma^p_q \gamma^r_s \gamma^t_u \gamma^v_w\}, \tag{40b}$$

which are related to a cumulant expansion of the reduced density matrices, with $\det\{\ldots\}$ the sum of all permutations of the lower labels with a sign factor corresponding to the parity of the permutations, e.g.,

$$\det\{\gamma^p_q \gamma^r_s\} = \gamma^p_q \gamma^r_s - \gamma^p_s \gamma^r_q \tag{41}$$

and with the sum over three factors the generalization of Eqs. (35a) to (35d) for a partition into 3 subsets.

The λ matrices may also be called the *irreducible* (non factorizable) parts of the respective γ matrices in analogy to the similar quantities in propagator theory. However, this notation would be somewhat confusing since the γ-matrices are already referred to as *reduced* density matrices (density matrices of reduced particle rank). The term *reduced* would then have to be used in two different meanings in the same context. The λ-matrices play a central role in the present theory. Note that for an N-body system all γ matrices up to rank N have to be considered, while the λ-matrices become increasingly less important for high particle rank, such that truncation of the λ matrices at a given particle rank much smaller than N will often be justified. The λ^{pq}_{rs} matrix describes pair correlation, the λ^{pqr}_{stu} matrix genuine (irreducible, connected) three-particle correlations, etc.

For the contraction rules, we then get Eq. (39) and

$$\tilde{a}^p_q \tilde{a}^{rs}_{tu} = \tilde{a}^{prs}_{qtu} + \eta^r_q \tilde{a}^{ps}_{tu} + \eta^s_q \tilde{a}^{pr}_{ut} - \gamma^p_t \tilde{a}^{rs}_{qu} - \gamma^p_u \tilde{a}^{rs}_{tq} + \{\eta^r_q \gamma^p_t + \lambda^{pr}_{qt}\}\tilde{a}^s_u - \{\eta^r_q \gamma^p_u + \lambda^{pr}_{qu}\}\tilde{a}^s_t - \{\eta^s_q \gamma^p_t + \lambda^{ps}_{qt}\}\tilde{a}^r_u + \{\eta^s_q \gamma^p_u + \lambda^{ps}_{qu}\}\tilde{a}^r_t - \lambda^{rs}_{tq}\tilde{a}^p_u - \lambda^{rs}_{qu}\tilde{a}^p_t - \lambda^{pr}_{ut}\tilde{a}^s_q - \lambda^{ps}_{tu}\tilde{a}^r_q + \eta^r_q \lambda^{ps}_{tu} + \eta^s_q \lambda^{pr}_{ut} - \gamma^p_t \lambda^{rs}_{qu} - \gamma^p_u \lambda^{rs}_{tq} + \lambda^{prs}_{qtu} , \tag{42a}$$

$$\tilde{a}^p_q \tilde{a}^r_s \tilde{a}^t_u = \tilde{a}^{prt}_{qsu} + \eta^r_q \tilde{a}^{pt}_{su} + \eta^t_q \tilde{a}^{pr}_{us} + \eta^t_s \tilde{a}^{pr}_{qu} - \gamma^p_s \tilde{a}^{rt}_{qu} - \gamma^p_u \tilde{a}^{rt}_{sq} - \gamma^r_u \tilde{a}^{pt}_{qs} + \{\eta^r_q \gamma^p_s + \lambda^{pr}_{qs}\}\tilde{a}^{\ t}_u + \{\eta^t_q \gamma^p_u + \lambda^{pt}_{qu}\}\tilde{a}^r_s + \{\eta^t_s \gamma^r_u + \lambda^{rt}_{su}\}\tilde{a}^p_q - \{\eta^r_q \gamma^p_u + \lambda^{pr}_{qu}\}\tilde{a}^t_s - \{\eta^t_s \gamma^p_u + \lambda^{pt}_{su}\}\tilde{a}^r_q - \{\eta^t_q \gamma^r_u + \lambda^{rt}_{qu}\}\tilde{a}^p_s + \{\gamma^p_s \gamma^r_u - \lambda^{pr}_{us}\}\tilde{a}^{\ t}_q + \{\eta^r_q \eta^t_s - \lambda^{rt}_{sq}\}\tilde{a}^p_u - \{\eta^t_q \gamma^p_s + \lambda^{pt}_{qs}\}\tilde{a}^r_u + \eta^r_q \eta^t_s \gamma^p_u - \eta^t_q \gamma^p_s \gamma^r_u + \eta^t_s \lambda^{pr}_{qu} - \gamma^r_u \lambda^{pt}_{qs} + \eta^t_q \lambda^{pr}_{us} - \gamma^p_u \lambda^{rt}_{sq} + \eta^r_q \lambda^{pt}_{su} - \gamma^p_s \lambda^{rt}_{qu} + \lambda^{prt}_{qsu} . \tag{42b}$$

In comparing Eqs. (42a) with (30) we see that there are extra terms involving λ^{pr}_{qt} and λ^{prs}_{qtu}. While the normal product and the single contractions are the same in Eqs. (30) and (42a), there are additional double contractions as well as a triple contraction in Eq. (42a).

The expression of $\tilde{a}^{pr}_{qs}\tilde{a}^{tv}_{uw}$ is already so lengthy, that we are not giving it explicitly. We are only documenting prototypes of the various contractions. This can be compared with Eqs. (22a) to (22i) . To simplify the notation we introduce the two-hole density matrix with elements:

$$\eta^{pr}_{qs} = \eta^{p}_{q}\eta^{r}_{s} - \eta^{p}_{s}\eta^{r}_{q} + \lambda^{pr}_{qs}. \tag{43}$$

Then we have (the number in parenthesis indicates the number of equivalent terms of the respective type)

product: $\tilde{a}^{pr}_{qs}\tilde{a}^{tv}_{uw}$, (44a)

normal product: $\tilde{a}^{prtv}_{qsuw}$, (44b)

single-particle contractions(4): $\eta^{t}_{q}\tilde{a}^{prv}_{usw}$, (44c)

single-hole contractions(4): $-\gamma^{p}_{u}\tilde{a}^{rtv}_{sqw}$, (44d)

double-particle contraction (1):

$$(\eta^{t}_{q}\eta^{v}_{s} - \eta^{t}_{s}\eta^{v}_{q} + \lambda^{tv}_{qs})\tilde{a}^{pr}_{uw} = \eta^{tv}_{qs}\tilde{a}^{pr}_{uw}, \tag{44e}$$

double-hole contraction (1):

$$(\gamma^{p}_{u}\gamma^{r}_{w} - \gamma^{p}_{w}\gamma^{r}_{u} + \lambda^{pr}_{uw})\tilde{a}^{tv}_{qs} = \gamma^{pr}_{uw}\tilde{a}^{tv}_{qs}, \tag{44f}$$

single-particle-single-hole contractions (16):

$$(\eta^{v}_{s}\gamma^{r}_{w} + \lambda^{rv}_{sw})\tilde{a}^{pt}_{qu}, \tag{44g}$$

further double contractions (16):

$$-\lambda^{rv}_{uw}\tilde{a}^{pt}_{qs}, -\lambda^{rv}_{sq}\tilde{a}^{pt}_{wu}, -\lambda^{tv}_{sw}\tilde{a}^{pr}_{qu}, -\lambda^{pr}_{ws}\tilde{a}^{tv}_{uq} \tag{44h}$$

double-particle-single-hole contractions (4):

$$\{\eta^{tv}_{qs}\gamma^{r}_{w} - \eta^{v}_{q}\lambda^{rt}_{sw} + \eta^{v}_{s}\lambda^{rt}_{qw} - \eta^{t}_{s}\lambda^{rv}_{qw} + \eta^{t}_{q}\lambda^{rv}_{sw} - \lambda^{rtv}_{sqw}\}\tilde{a}^{\ p}_{u}, \tag{44i}$$

double-hole-single particle contractions (4):

$$\{-\eta^{v}_{s}\gamma^{pr}_{uw} - \gamma^{r}_{w}\lambda^{pv}_{su} + \gamma^{r}_{u}\lambda^{pv}_{sw} + \gamma^{p}_{w}\lambda^{rv}_{su} - \gamma^{p}_{u}\lambda^{rv}_{sw} - \lambda^{prv}_{usw}\}\tilde{a}^{\ t}_{q}, \tag{44j}$$

further triple contractions (4,4):

$$\{\eta^{t}_{s}\lambda^{rv}_{uw} + \eta^{v}_{s}\lambda^{rt}_{wu} - \gamma^{r}_{w}\lambda^{tv}_{us} - \gamma^{r}_{u}\lambda^{tv}_{sw} + \lambda^{rtv}_{suw}\}\tilde{a}^{p}_{q}, \tag{44k}$$

$$:\{\eta^{v}_{s}\lambda^{pr}_{qw} + \eta^{v}_{q}\lambda^{pr}_{ws} - \gamma^{r}_{w}\lambda^{pv}_{qs} - \gamma^{p}_{w}\tilde{\gamma}^{rv}_{sq} + \lambda^{prv}_{qsw}\}\tilde{a}^{\ t}_{u} \tag{44l}$$

full contractions:

$$\begin{aligned}
&\lambda^{prtv}_{qsuw} + \eta^{v}_{s}\lambda^{prt}_{qwu} + \gamma^{v}_{q}\lambda^{prt}_{wsu} + \eta^{t}_{s}\lambda^{prv}_{quw} + \eta^{t}_{q}\lambda^{prv}_{usw} - \gamma^{r}_{u}\lambda^{ptv}_{qsw} - \gamma^{r}_{w}\lambda^{ptv}_{qus} - \gamma^{p}_{u}\lambda^{rtv}_{sqw} - \gamma^{p}_{w}\lambda^{rtv}_{suq} + \eta^{tv}_{qs}\gamma^{pr}_{uw} + \eta^{v}_{s}\gamma^{r}_{w}\lambda^{pt}_{qu} - \eta^{v}_{s}\gamma^{r}_{u}\lambda^{pt}_{qw} \\
&- \eta^{v}_{q}\gamma^{r}_{w}\lambda^{pt}_{su} + \eta^{v}_{q}\gamma^{r}_{u}\lambda^{pt}_{sw} - \eta^{t}_{s}\gamma^{r}_{w}\lambda^{pv}_{qu} + \eta^{t}_{s}\gamma^{r}_{u}\lambda^{pv}_{qw} + \eta^{t}_{q}\gamma^{r}_{w}\lambda^{pv}_{su} - \eta^{t}_{q}\gamma^{r}_{u}\lambda^{pv}_{sw} - \eta^{v}_{s}\gamma^{p}_{w}\lambda^{rt}_{qu} + \eta^{v}_{s}\gamma^{p}_{u}\lambda^{rt}_{qw} + \eta^{v}_{q}\gamma^{p}_{w}\lambda^{rt}_{su} - \eta^{v}_{q}\gamma^{p}_{u}\lambda^{rt}_{sw} \\
&+ \eta^{t}_{s}\gamma^{p}_{w}\lambda^{rv}_{qu} - \eta^{t}_{s}\gamma^{p}_{u}\lambda^{rv}_{qw} - \eta^{t}_{q}\gamma^{p}_{w}\lambda^{rv}_{su} + \eta^{t}_{q}\gamma^{p}_{u}\lambda^{rv}_{sw} + \lambda^{rv}_{sw}\lambda^{pt}_{qu} - \lambda^{rv}_{su}\lambda^{pt}_{qw} - \lambda^{rv}_{qw}\lambda^{pt}_{su} + \lambda^{rv}_{qu}\lambda^{pt}_{sw} - \lambda^{rt}_{sw}\lambda^{pv}_{qu} + \lambda^{rt}_{su}\lambda^{pv}_{qw} + \lambda^{rt}_{qw}\lambda^{pv}_{su} \\
&- \lambda^{rt}_{qu}\lambda^{pv}_{sw} - \lambda^{pv}_{uw}\lambda^{rt}_{sq} - \lambda^{pv}_{qs}\lambda^{rt}_{wu} - \lambda^{pt}_{wu}\lambda^{rv}_{sq} - \lambda^{pt}_{qs}\lambda^{rv}_{uw} - \lambda^{pr}_{ws}\lambda^{tv}_{uq} - \lambda^{pr}_{us}\lambda^{tv}_{qw} - \lambda^{pr}_{qw}\lambda^{tv}_{us} - \lambda^{pr}_{qu}\lambda^{tv}_{sw},
\end{aligned} \tag{44m}$$

VII. CONTRACTION RULES AND GRAPHICAL REPRESENTATION

The results of the last section look, at first glance, rather complicated. However, they can be cast into some rather simple rules. These rules are best illustrated with the aid of diagrams.

Diagrams are built up from *operator vertices* (symbolized as dots), *fermion lines* (lines with arrows) and *contraction points* (small open circles or squares). A basic n-particle operator in normal order with respect to Φ is described by a vertex with *n ingoing lines* (arrows towards the vertex) corresponding to *lower* and *n outgoing lines* (arrows off the vertex) corresponding to *upper labels*. The order of operators in the formula from left to right is translated to an order of the vertices from bottom to top in the diagrams. It is irrelevant whether free (open-ended) fermion lines go up or down, it only matters whether they *enter or leave a vertex*. Of course, the logical, i.e., vertical order of the vertices matters as well. A vertex may be thought to be multiplied by a matrix element of an operator, which carries then the same labels, just upper ones exchanged with lower ones.

The formation of a *normal product* is indicated by joining the vertices with a broken line, making it formally a single vertex. A *contraction* involves the same number of ingoing and outgoing fermion lines at a *contraction point*. There are single contractions, which involve a density matrix element $-\gamma^{q}_{p}$ for downgoing and a hole-density matrix element η^{q}_{p} for upgoing contractions. Whether a contraction is upgoing or downgoing depends on the order of the vertices between which the contraction takes place. *Self-contractions* entering and leaving the same vertex are excluded. Of course, multiple single contractions between two vertices are possible.

There are further genuine multiple contractions involving residual density matrix elements λ^{rs}_{pq} or λ^{stu}_{pqr}, etc. Multiple contractions can contain partial *self-contractions* of lines from the same vertex. *Pure* self-contractions involving only one vertex and one density matrix element don't occur.

On Fig. 1 we give a graphical illustration of the contraction rule (39) between two one-particle operators, on Fig. 2

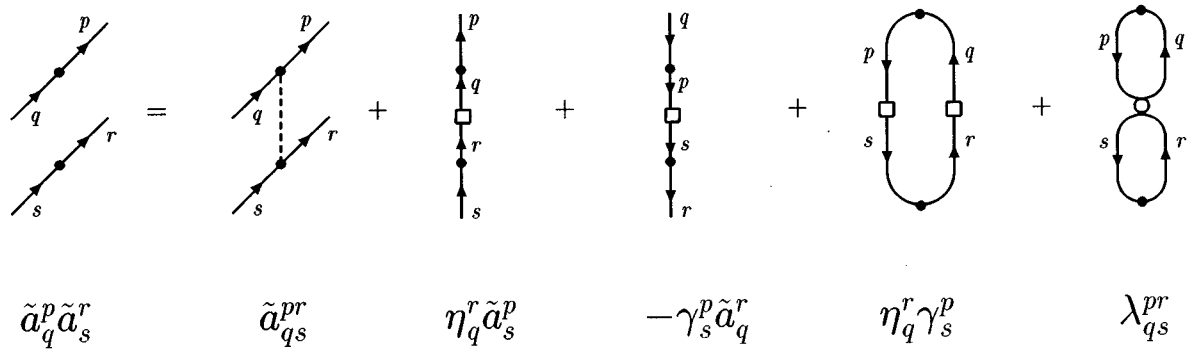

FIG. 1. Graphical illustration of Eq. (39).

for the contraction rule (42a) between a one particle and a two-particle operator, on Fig. 3 for the contraction rules (42b) between three one-particle operators and on Fig. 4 for the contraction rule (44a) to (44m) between two two-particle operators. In Figs. 1 and 2 we explicitly indicate the labels to make a comparison with the analytic formulas obvious.

Contraction with a small open square means a contraction factor η^p_q for an upgoing line (particle contraction) or $-\gamma^p_q$ for a downgoing line (hole contraction). Contraction with a small open circle involves as contraction factor a residual density matrix element λ^{pv}_{qs} ,λ^{qrt}_{qsu} etc. depending on the (same) number of ingoing and outgoing lines.

There is a sign rule for the expressions symbolized by the diagrams. A factor (-1) arises (a) for any down-going *single* contraction, (b) for any closed loop, including those in partial self-contractions, (c) for any residual density matrix elements of odd particle rank e.g. λ^{pqv}_{stu}, (d) for any odd permutation of the original pairing of external lines.

Our diagrams are Hugenholtz[11] like (H) with point vertices and contraction points, while one may as well use Goldstone-like[12] (G) diagrams with line vertices and contraction lines (both horizontal), on which paring between entering and leaving fermion lines is manifest. There are many more G diagrams than H diagrams, since to each H diagram

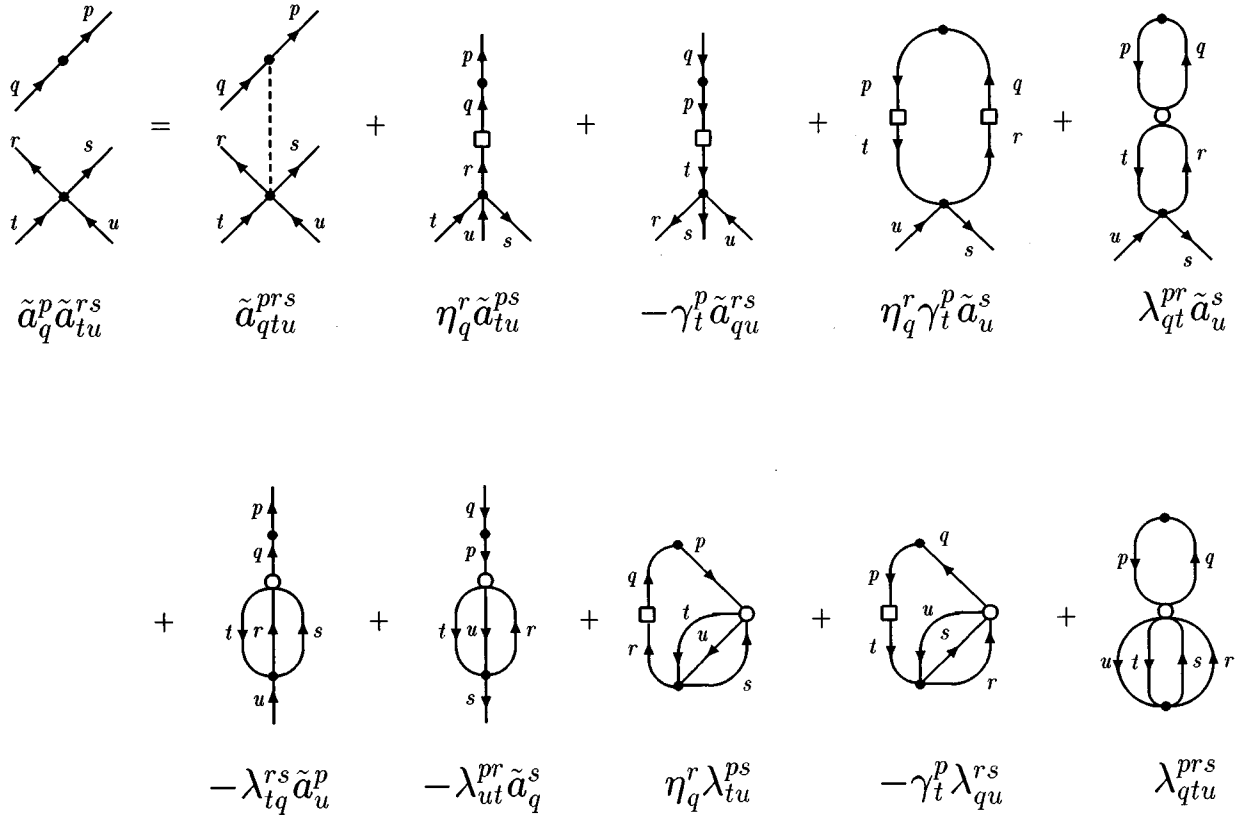

FIG. 2. Graphical illustration of Eq. (42a).

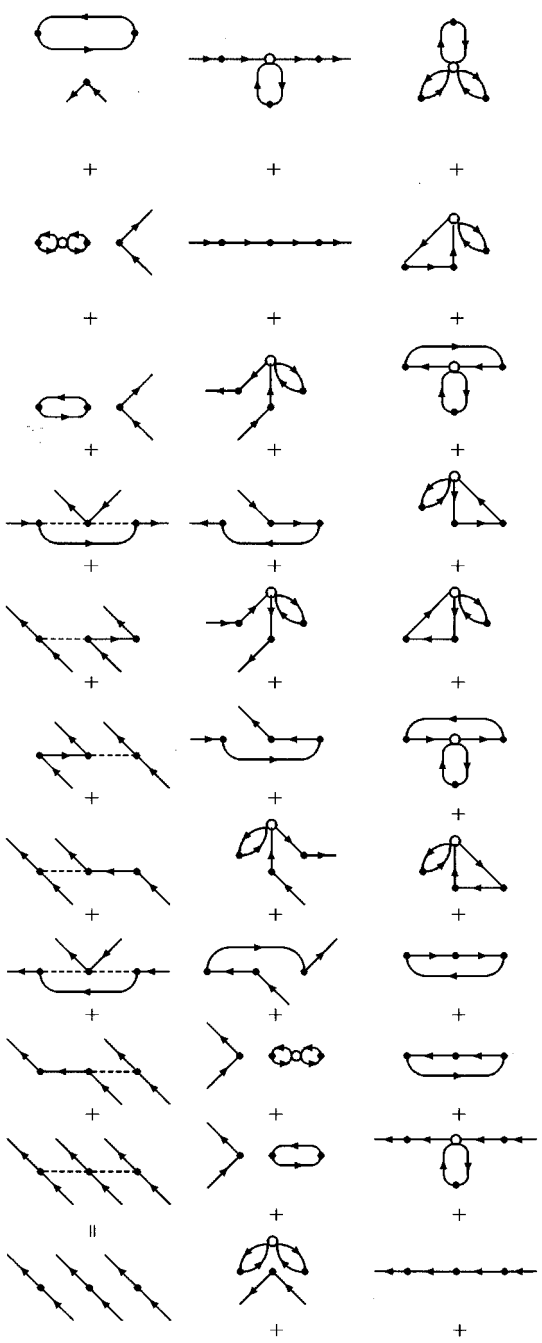

FIG. 3. Graphical illustration, turned by 90°, of Eq. (42b).

there are as many G diagrams as there are distinguishable permutations at the vertices or contraction points.

In order to count closed loops (which is important for the sign rule), G diagrams are the more convenient. Otherwise, one has to do this from the formula corresponding to the diagram, being aware that one H diagram can represent several formulas with different sign factors.

In a forthcoming paper we shall introduce G diagrams to represent the spinfree formalism (see Sec. IX), because there they are indispensable. To introduce G diagrams in the present context might create confusion, because the G diagrams that one could define now, would be incompatible with those used in the spinfree context, except for singlet reference states.

From the graphical representations of the contribution in Figs. 1 to 4 one can extract the general contraction rules which are collected on Figs. 5 and 6.

The contractions are much simplified if one chooses the fermion operators *for natural spin orbitals*, which diagonalize the one-particle density matrix such that

$$\gamma_q^p = \delta_q^p n_p; \quad \eta_q^p = \delta_q^p (1-n_p); \quad 0 \leqslant n_p \leqslant 1. \tag{45}$$

For this choice single contractions are only possible between identical labels.

Note that the natural spin orbitals have pure α and β spin , if the reference state is an eigenstate of S_z with $M_s = 0$.[13] To simplify the diagrams, we assume, starting with Fig. 3 that Eq. (45) is satisfied, and symbolize single contractions just by a line without a small rectangular box as in Figs. 1 or 2. An upgoing contraction line then means a factor $1-n_p$ and a downgoing line a factor $-n_p$. If Eq. (45) does not hold, the γ and η elements must be inserted into the respective contractions.

For contractions, as they are symbolized on Fig. 5, only the lines involved in the contraction matter. Either vertex can, in addition, have an arbitrary number of external (uncontracted) lines. These may, of course, contract with a third vertex as on Fig. 3. For simplicity we have written in Fig. 5 one extra external line on each vertex, without marking it by an arrow.

On Fig. 5 the first two diagrams represent single contractions, the remaining 10 diagrams double contractions. The number of possible contractions increases rapidly with the degree of contraction. In order to be able to depict compactly all 3-fold and 4-fold contractions, we group contractions with the same topology, but different directions of the arrows to *skeletons*.[1,14] The skeletons are conceptually related to Feynman diagrams without specification of time-ordering, though the present context is, of course, time-independent. From a skeleton one gets the corresponding diagrams by taking all possible consistent choices of the directions of arrows.

The two single-contraction diagrams (a^1) and (a^2) on Fig. 5 correspond to one skeleton (a) on Fig. 6, the 10 double contractions (b_1^1) to (b_4^2) on Fig. 5 are represented by the 4 skeletons (b_1) to (b_4) on Fig. 6. We have, on Fig. 6, 9 skeletons for triple contractions, and 20 skeletons for quadruple contractions.

The diagrams with point vertices used in this section allow an interesting generalization. As already mentioned, the actual contraction is independent of the remaining external lines. This means that these rules are not limited to contractions between *particle number conserving* operators (with the same name number of ingoing and outgoing lines) but that they hold for vertices which are arbitrary products of creation and annihilation operators in normal order. Hence although we have started from particle-number-conserving operators we have found rules that hold for arbitrary normal order-operators. Thus our formulation has the same status of the algebraic identity derived via a different route,[8–10] which

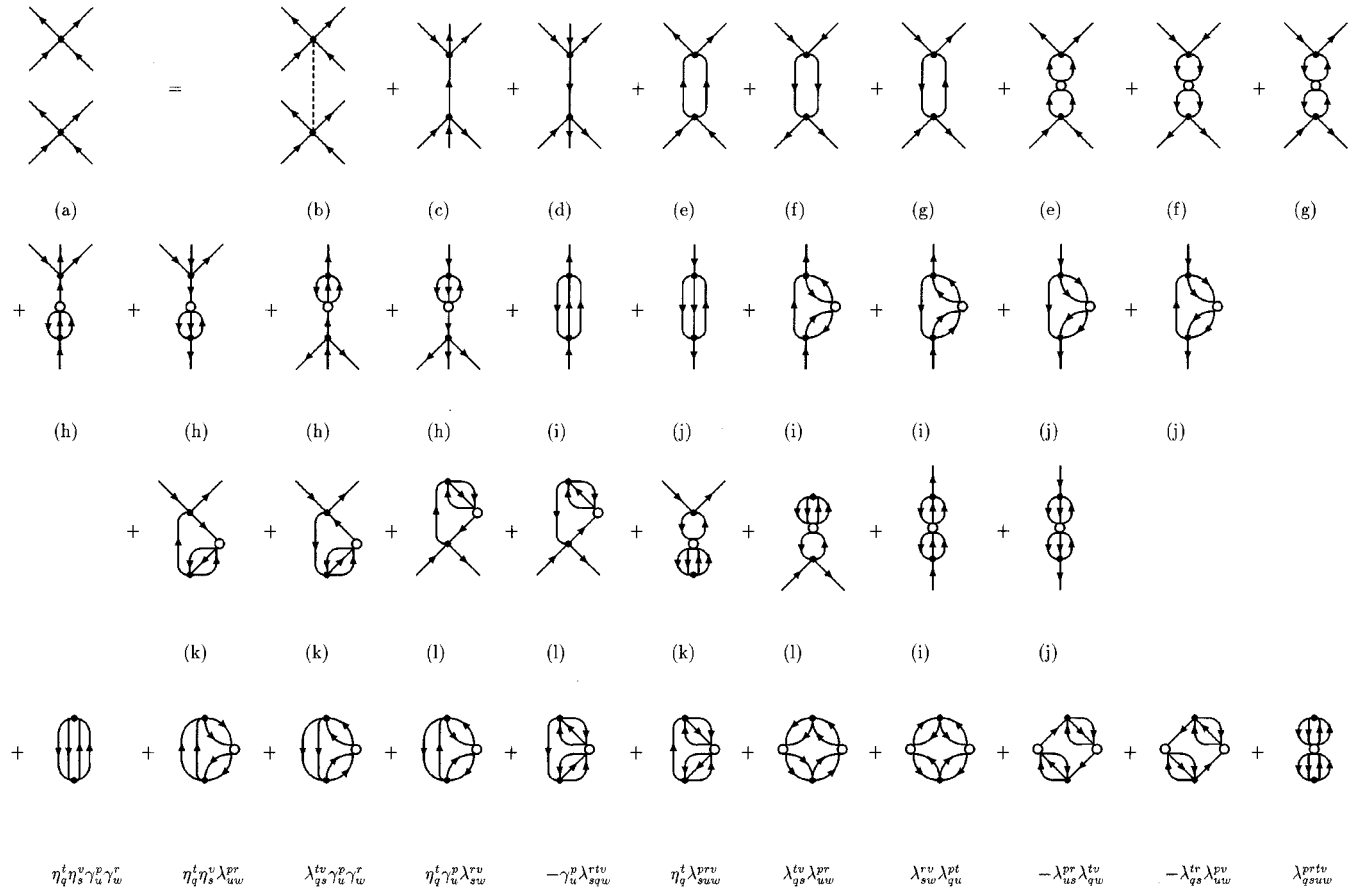

FIG. 4. Graphical illustration of Eqs. (44a) to (44m). Captions like (e) under a diagram refer to respective expressions in Eq. (44a), etc., i.e. Eq. (44e). Note that expressions like Eq. (44e) contain in general more than one type of diagram. The same caption, e.g., (e) occurs hence usually more then once. For the fully contracted diagrams represented by Eq. (44m) explicit expressions for the diagrams are given.

was valid for both particle number conserving and nonconserving operators. We illustrate this generality to rederive Eq. (35b) in terms of the present contraction rules. In fact Eq. (35b) is the recursive definition of $\tilde{a}_{qs}^{pr}$ from which we started, but if we solve it for a_{qs}^{pr}

$$a_{qs}^{pr}=\tilde{a}_{qs}^{pr}-\Sigma\,\gamma_q^p\tilde{a}_s^r-\gamma_{qs}^{pr} \tag{46}$$

it can be regarded as the Wick expansion with respect to Φ of the operator $a_{qs}^{pr}=a^r a^p a_q a_s=\tilde{a}^r\tilde{a}^p\tilde{a}_q\tilde{a}_s$ which is *not* in normal order with respect to Φ. This decomposition, done in terms of our contraction rules is illustrated on Fig. 7. One sees that single contractions can here only involve downgoing lines. These represent the sum on the r.h.s. of Eq. (46). In order to establish the identity of Eq. (46) and Fig. 7 one must note that the sum of all full contractions is, in view of Eq. (38) the density matrix element $\gamma_{qs}^{pr}=\lambda_{qs}^{pr}+\gamma_q^p\gamma_s^r-\gamma_s^p\gamma_q^r$.

In the same way, starting by postulating the contraction rules, we can construct the basic normal order operators of any excitation and creation rank with respect to the multiconfiguration wave function.

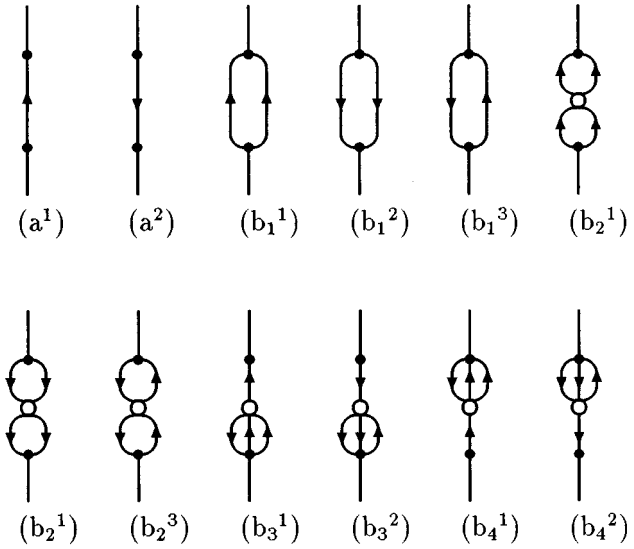

FIG. 5. Single and double contractions between two vertices. The external single lines (without arrows) can mean any combination of an arbitrary number of ingoing and outgoing lines.

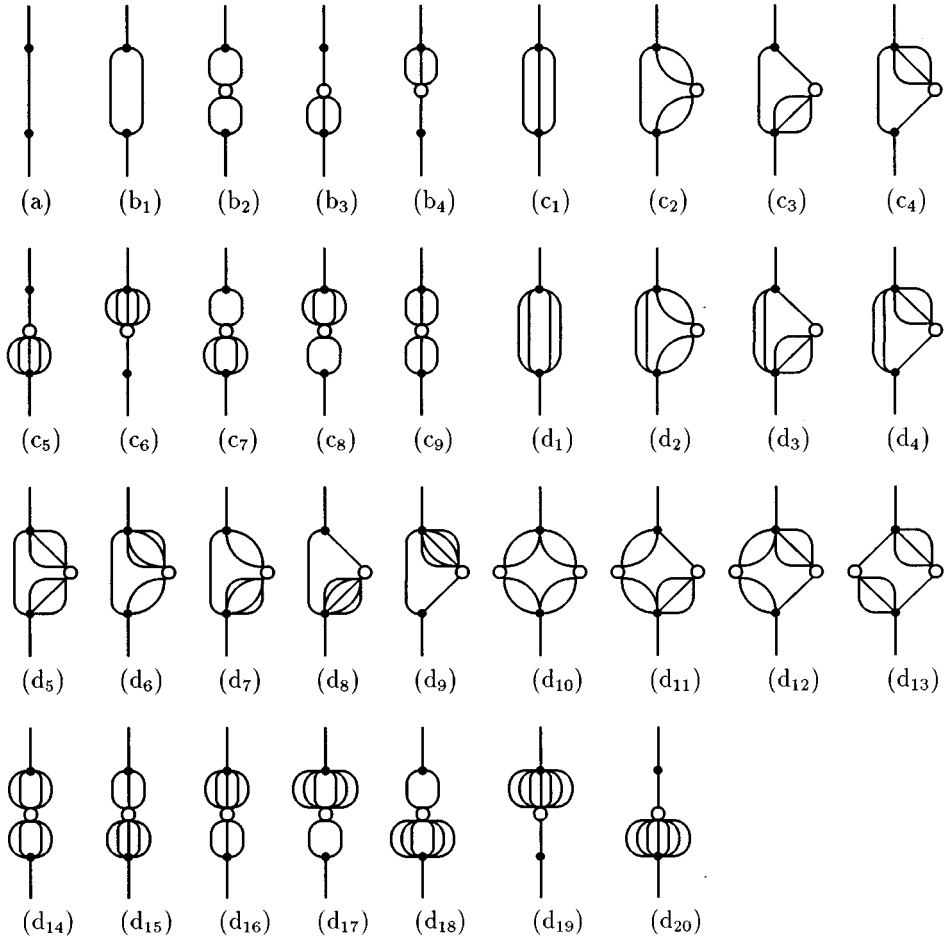

FIG. 6. Skeletons (i.e., diagrams without arrows on internal lines) of single, double, and triple contractions between two vertices.

To close this section we note that for a single Slater determinant reference function all multiple contractions involving the λ-elements vanish (these only contribute if all lines entering or leaving a λ-element correspond to active orbitals). Then only diagrams with line contractions survive and we retrieve the conventional Hugenholtz diagrams.

The diagrams that we have used correspond to the standard convention in many-body theory. Nevertheless some authors prefer diagrams where the logical order of the vertices is from right to left (just as in the formula) rather than from bottom to top. This convention means to turn our diagrams by 90^o to the left.

VIII. COMMUTATORS

One is also interested in commutators between $\tilde{a}$ operators. One obtains

$$[\tilde{a}^p_q,\tilde{a}^r_s]=\delta^r_q\tilde{a}^p_s-\delta^p_s\tilde{a}^r_q+\delta^r_q\gamma^p_s-\gamma^r_q\delta^p_s, \tag{47}$$

$$[[\tilde{a}^p_q,\tilde{a}^r_s],\tilde{a}^t_u]=\delta^r_q\delta^t_s\tilde{a}^p_u-\delta^r_q\delta^p_u\tilde{a}^t_s+\delta^p_s\delta^r_u\tilde{a}^t_q-\delta^p_s\delta^t_q\tilde{a}^r_u+\delta^r_q(\delta^t_s\gamma^p_u-\delta^p_u\gamma^t_s)+\delta^p_s(\delta^r_u\gamma^t_q-\delta^t_q\gamma^r_u), \tag{48}$$

$$\begin{aligned}[][\tilde{a}^{pr}_{qs},\tilde{a}^t_u]=&\delta^t_q\tilde{a}^{pr}_{us}+\delta^t_s\tilde{a}^{pr}_{qu}-\delta^p_u\tilde{a}^{tr}_{qs}-\delta^r_u\tilde{a}^{pt}_{qs}+(\delta^t_q\gamma^p_u-\delta^p_u\gamma^t_q)\tilde{a}^r_s\\&+(\delta^r_u\gamma^t_q-\delta^t_q\gamma^r_u)\tilde{a}^p_s+(\delta^p_u\gamma^t_s-\delta^t_s\gamma^p_u)\tilde{a}^r_q\\&+(\delta^t_s\gamma^r_u-\delta^r_u\gamma^t_s)\tilde{a}^p_q+\delta^t_s\lambda^{pr}_{qu}+\delta^t_q\lambda^{pr}_{us}\\&-\delta^r_u\lambda^{pt}_{qs}-\delta^p_u\lambda^{tr}_{qs},\end{aligned} \tag{49}$$

$$\begin{aligned}[][\tilde{a}^p_q,\tilde{a}^{rs}_{tu}]=&\delta^r_q\tilde{a}^{ps}_{tu}+\delta^s_q\tilde{a}^{rp}_{tu}-\delta^p_t\tilde{a}^{rs}_{qu}-\delta^p_u\tilde{a}^{rs}_{tq}\\&+(\eta^r_q\gamma^p_t-\gamma^r_q\eta^p_t)\tilde{a}^s_u-(\eta^r_q\gamma^p_u-\eta^p_u\gamma^r_q)\tilde{a}^s_t\\&+(\eta^s_q\gamma^p_u-\eta^p_u\gamma^s_q)\tilde{a}^r_t-(\eta^s_q\gamma^p_t-\eta^p_t\gamma^s_q)\tilde{a}^r_u\\&+\delta^r_q\lambda^{ps}_{tu}+\delta^s_q\lambda^{rp}_{tu}-\delta^p_t\lambda^{rs}_{qu}-\delta^p_u\lambda^{rs}_{tq}.\end{aligned} \tag{50}$$

We shall need expressions like

$$\langle\Phi|[\tilde{A},\tilde{a}^t_u]|\Phi\rangle;\quad\langle\Phi|[[\tilde{A},\tilde{a}^t_u],\tilde{a}^v_w]|\Phi\rangle, \tag{51}$$

$$\tilde{A}=\tilde{f}=f^q_p\tilde{a}^p_q\quad\text{or}\quad\tilde{A}=\tilde{g}=\tfrac{1}{2}g^{qs}_{pr}\tilde{a}^{pr}_{qs}=\tfrac{1}{4}\overline{g^{qs}_{pr}}\tilde{a}^{pr}_{qs};$$

$$\overline{g^{qs}_{pr}}=g^{qs}_{pr}-g^{sq}_{pr}. \tag{52}$$

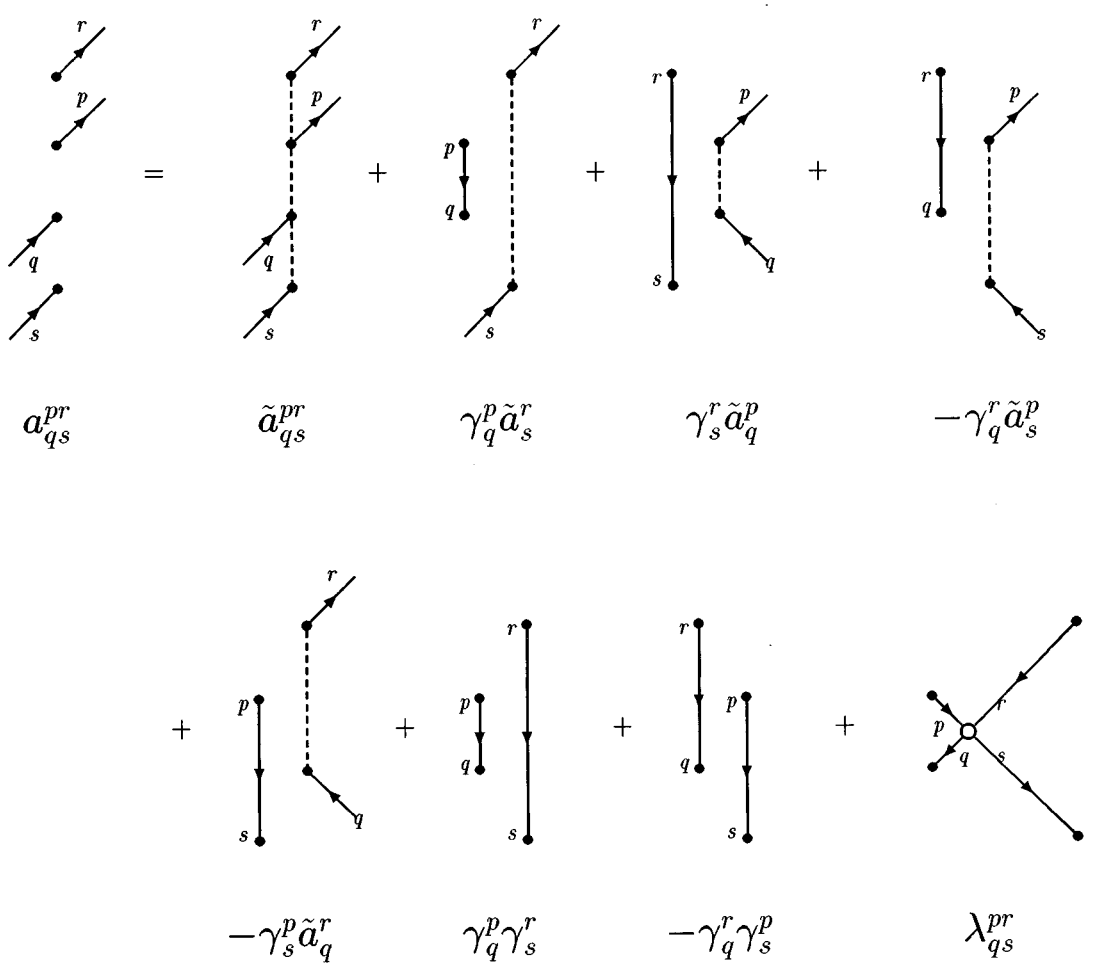

FIG. 7. Graphical illustration of Eq. (46).

The results are

$$\langle\Phi|[\tilde{f},\tilde{a}^{\ t}_u]|\Phi\rangle = f^t_p\gamma^p_u - f^q_u\gamma^t_q, \tag{53a}$$

$$\langle\Phi|[[\tilde{f},\tilde{a}^{\ t}_u],\tilde{a}^v_w]|\Phi\rangle = \delta^t_w f^q_u\gamma^v_q + \delta^v_u f^t_p\gamma^p_w - f^t_w\gamma^v_u - f^v_u\gamma^t_w, \tag{53b}$$

$$\langle\Phi|[\tilde{g},\tilde{a}^{\ t}_u]|\Phi\rangle = \tfrac{1}{2}\,\overline{g^{qt}_{pr}}\lambda^{pr}_{qu} - \tfrac{1}{2}\,\overline{g^{qs}_{pu}}\lambda^{pt}_{qs}, \tag{54a}$$

$$\begin{aligned}\langle\Phi|[\tilde{g},\tilde{a}^{\ t}_u],\tilde{a}^v_w]|\Phi\rangle &= \tfrac{1}{2}\,\delta^v_u\{\overline{g^{qt}_{pr}}\gamma^{pr}_{qw} + \overline{g^{qs}_{wp}}(\gamma^p_q\gamma^t_s - \gamma^p_s\gamma^t_q)\}\\ &+ \tfrac{1}{2}\,\delta^t_w\{\overline{g^{qs}_{pu}}\gamma^{pv}_{qs} + \overline{g^{vq}_{pr}}(\gamma^p_q\gamma^r_u - \gamma^p_u\gamma^r_q)\} + \tfrac{1}{2}\overline{g^{qs}_{uw}}\gamma^{tv}_{qs}\\ &+ \tfrac{1}{2}\overline{g^{tv}_{pr}}\gamma^{pr}_{uw} + \overline{g^{qt}_{wp}}(\lambda^{pv}_{qu} - \gamma^p_u\gamma^v_q) + \overline{g^{qv}_{up}}(\lambda^{pt}_{qw} - \gamma^p_w\gamma^t_q).\end{aligned} \tag{54b}$$

We can compare this with the analogous expression in terms of the a instead the $\tilde{a}$ operators.

$$\langle\Phi|[f,a^t_u]|\Phi\rangle = f^t_p\gamma^p_u - f^q_u\gamma^t_q, \tag{55}$$

$$\langle\Phi|[[f,a^t_u],a^v_w]|\Phi\rangle = \delta^t_w f^q_u\gamma^v_q + \delta^v_u f^t_p\gamma^p_w - f^t_w\gamma^v_u - f^v_u\gamma^t_w, \tag{56}$$

$$\langle\Phi|[g,a^t_u]|\Phi\rangle = \tfrac{1}{2}\overline{g^{tq}_{pr}}\gamma^{pr}_{uq} - \tfrac{1}{2}\overline{g^{qs}_{up}}\gamma^{tp}_{qs}, \tag{57a}$$

$$\begin{aligned}\langle\Phi|[[g,a^t_u],a^v_w]|\Phi\rangle &= \tfrac{1}{2}\,\delta^t_w\overline{g^{qs}_{pu}}\gamma^{pv}_{qs} + \tfrac{1}{2}\,\delta^v_u\overline{g^{qt}_{pr}}\gamma^{pr}_{qw}\\ &+ \tfrac{1}{2}\overline{g^{qs}_{uw}}\gamma^{tv}_{qs} + \tfrac{1}{2}\overline{g^{tv}_{pr}}\gamma^{pr}_{uw} + \overline{g^{qt}_{wp}}\gamma^{pv}_{qu}\\ &+ \overline{g^{qv}_{up}}\gamma^{pt}_{qw}.\end{aligned} \tag{57b}$$

Since a^p_q differs from $\tilde{a}^p_q$ only in a constant, commutators involving only $\tilde{a}^p_q$ are invariant with respect to the replacement $\hat{a}^p_q \rightarrow a^p_q$. The change from $\tilde{a}^{pr}_{qs}$ to a^{pr}_{qs} does, however, makes a difference.

IX. SPINFREE FORMALISM

Often one deals with spin-independent operators, which means, e.g., that

$$\hat{h} = h^p_q a^q_p;\quad h^p_q = h^{P\alpha}_{Q\alpha} = h^{P\beta}_{Q\beta} = h^P_Q;\quad h^{P\alpha}_{Q\beta} = h^{P\beta}_{Q\alpha} = 0, \tag{58a}$$

$$\hat{g} = \tfrac{1}{2}g^{pr}_{qs}a^{qs}_{pr};\quad g^{pr}_{qs} = g^{P\alpha P\alpha}_{Q\alpha S\alpha} = g^{P\alpha R\beta}_{Q\alpha S\beta} = \ldots = g^{PR}_{QS};$$
$$g^{P\alpha R\alpha}_{Q\beta R\beta} = \ldots = 0, \tag{58b}$$

$$h_q^p=\langle\varphi_q|\hat{h}|\varphi_p\rangle;$$

$$g_{qs}^{pr}=\langle\varphi_q(1)\varphi_s(2)|\hat{g}(1,2)|\varphi_p(1)\varphi_r(2)\rangle, \tag{58c}$$

i.e., that matrix elements of the operators are spin-independent for like spin of the two electrons and zero for different spin of the two electrons. In this case one can sum the a operators over spin and define the E operators as in Eqs. (10a) and (10b) and rewrite Eqs. (58a) to (58c) as

$$\hat{h}=h_Q^P E_P^Q; \quad \hat{g}=\tfrac{1}{2}g_{QS}^{PR}E_{PR}^{QS} \tag{59}$$

and the sums in Eq. (59) only go over labels P,Q,R,S of spinfree orbitals.

Note that the E_Q^P operators only span a subset of the algebra spanned by the a_q^p operators. One can span the full algebra if one considers additional operators of the type

$$a_{Q\beta}^{P\alpha};\ a_{Q\alpha}^{P\beta};\ a_{Q\alpha}^{P\alpha}-a_{Q\beta}^{P\beta}, \tag{60}$$

but these are not required if one only considers spin-conserving operators.

The E operators are in normal order with respect to the *genuine* vacuum, while the $\tilde{E}$ operators in normal order with respect to a single Slater determinant closed shell reference state[4,5] are given in Eqs. (23a) and (23b). We now want to define the $\tilde{E}$ operators in normal order with respect to an *arbitrary reference function* Φ.

The first guess for this definition is to take directly Eqs.(23a) and (23b). This works for the one-particle operators

$$\tilde{E}_Q^P=\tilde{a}_{Q\alpha}^{P\alpha}+\tilde{a}_{Q\beta}^{P\beta}=a_{Q\alpha}^{P\alpha}-\gamma_{Q\alpha}^{P\alpha}+a_{Q\beta}^{P\beta}-\gamma_{Q\beta}^{P\beta}=E_Q^P-\Gamma_Q^P, \tag{61}$$

where Γ_Q^P is the spinfree one-particle density matrix

$$\Gamma_Q^P=\gamma_{Q\alpha}^{P\alpha}+\gamma_{Q\beta}^{P\beta}=\langle\Phi|E_Q^P|\Phi\rangle. \tag{62}$$

Let us try the same recipe with Eq. (23b) and construct, using Eq. (35b), the following operator:

$$\begin{aligned}&\tilde{a}_{Q\alpha S\alpha}^{P\alpha R\alpha}+\tilde{a}_{Q\alpha S\beta}^{P\alpha R\beta}+\tilde{a}_{Q\beta S\alpha}^{P\beta R\alpha}+\tilde{a}_{Q\beta S\beta}^{P\beta R\beta}\\&=a_{Q\alpha S\alpha}^{P\alpha R\alpha}-\Sigma(-1)^p\gamma_{Q\alpha}^{P\alpha}\tilde{a}_{S\alpha}^{R\alpha}-\gamma_{Q\alpha S\alpha}^{P\alpha R\alpha}\\&\quad+\text{terms with different spin}\\&=E_{QS}^{PR}-\Gamma_Q^P\tilde{E}_S^R-\Gamma_S^RE_Q^P+\gamma_{S\alpha}^{P\alpha}\tilde{a}_{Q\alpha}^{R\alpha}+\gamma_{S\beta}^{P\alpha}\tilde{a}_{Q\alpha}^{R\beta}+\gamma_{S\alpha}^{P\beta}\tilde{a}_{Q\beta}^{R\alpha}\\&\quad+\gamma_{S\beta}^{P\beta}\tilde{a}_{Q\beta}^{R\beta}+(P,S\ \text{exchanged with}\ R,Q)-\Gamma_{QS}^{PR}.\end{aligned} \tag{63}$$

If Φ is an eigenfunction of S_z with arbitrary M_s, the $\gamma_{S\alpha}^{P\beta}$ vanish. If, moreover, $M_s=0$, then $\gamma_{S\alpha}^{P\alpha}=\gamma_{S\beta}^{P\beta}$, and the operator (63) is spin-conserving. In the more general case we can project out the spin-conserving part of Eq. (63), and get

$$\tilde{E}_{QS}^{PR}=E_{QS}^{PR}-\Gamma_Q^P\tilde{E}_S^R-\Gamma_S^R\tilde{E}_Q^P+\tfrac{1}{2}\Gamma_S^P\tilde{E}_Q^R+\tfrac{1}{2}\Gamma_Q^R\tilde{E}_S^P-\Gamma_{QS}^{PR} \tag{64}$$

and we can use this as the definition of $\tilde{E}_{QS}^{PR}$. This is a spin-conserving operator and it fulfills the requirements for a normal-order operator, namely (a) that the *vacuum expectation value* with respect to Φ vanishes and (b) that it reduces to the known definition for a single determinant reference. We can hence give the counterpart of Eqs.(35a) to (35d) for the general spin-conserving normal order excitation operators.

$$\tilde{E}_Q^P=E_Q^P-\Gamma_Q^P, \tag{65a}$$

$$\tilde{E}_{QS}^{PR}=E_{QS}^{PR}-\Sigma(-\tfrac{1}{2})^p\Gamma_Q^P\tilde{E}_S^R-\Gamma_{QS}^{PR}, \tag{65b}$$

$$\begin{aligned}\tilde{E}_{QSU}^{PRT}=&E_{QSU}^{PRT}-\Sigma(-\tfrac{1}{2})^p\Gamma_Q^P\tilde{E}_{SU}^{RS}\\&-\Sigma(-\tfrac{1}{2})^p\Gamma_{QS}^{PR}\tilde{E}_U^T-\Gamma_{QSU}^{PRT}.\end{aligned} \tag{65c}$$

The factor $(-1/2)^p$ means that there is a factor $-\frac{1}{2}$ for every permutation that violates the original pairing of upper and lower labels.

Although the definition (65a) to (65c) is perfectly legitimate, one may wonder what it means physically. The spinfree formulation can easily be rationalized in terms of normal ordering for an ensemble. Suppose $\{\Phi_{M_S},M_S=S,S-1,\ldots S\}$ is a set of wave functions with total spin quantum number $S\neq 0$. Then one can define the M_S-averaged ensemble

$$\gamma^{(n)}=\frac{1}{2S+1}\sum_{M_S=-S}^{S}|\Phi_{M_S}\rangle\langle\Phi_{M_S}| \tag{66}$$

and consider normal ordering with respect to this. All expectation values of spinfree operators like the Hamiltonian are independent of M_S and hence the same for the ensemble as for any M_S. The $\tilde{E}$ operators defined in this section correspond to this spin-averaging. Of course, in atomic theory, one can think of an analogous averaging over angular momentum.

One can now derive the contraction rules for the $\tilde{E}$ operators, e.g.,

$$\begin{aligned}\tilde{E}_Q^P\tilde{E}_S^R=&\tilde{E}_{QS}^{PR}+(\delta_Q^R-\tfrac{1}{2}\Gamma_Q^R)\tilde{E}_S^P\\&-\tfrac{1}{2}\Gamma_S^P\tilde{E}_Q^R+(\delta_Q^R-\tfrac{1}{2}\Gamma_Q^R)\Gamma_S^P+\Lambda_{QS}^{PR}\end{aligned} \tag{67}$$

with

$$\Lambda_{QS}^{PR}=\Gamma_{QS}^{PR}-\Gamma_Q^P\Gamma_S^R+\tfrac{1}{2}\Gamma_S^P\Gamma_Q^R. \tag{68}$$

This resembles very much Eqs. (39) and (38) except for the factor $\frac{1}{2}$ for each pairing violation.

The contraction rules for the $\tilde{E}$ operator resemble those for the $\tilde{a}$ operators with spin-orbital labels, except for the additional factors $(1/2)^p$. If Φ is a closed-shell single Slater determinant, the factors $n_P\Gamma_Q^P$ are equal to 2, and the total factor is the product of factors 2 for each closed loop.

The graphical representation of the $\tilde{E}$ operators and the Γ matrices can be achieved in terms of Goldstone type diagrams with line vertices. Details will be given in a forthcoming paper.

X. MC-SCF THEORY

Let the many-electron Hamiltonian

$$H = h^p_q a^q_p + \tfrac{1}{2} g^{rs}_{pq} a^{pq}_{rs} \tag{69}$$

be given in normal order with respect to the genuine vacuum. We use again the spin-orbital formulation, which is formally easier, although for computation the spinfree formalism is preferable. We want to express H in terms of the $\widetilde{a}$ operators, which are in normal order with respect to the multiconfiguration wave function Φ.

$$\begin{aligned} H &= h^p_q(\widetilde{a}^q_p + \gamma^q_p) \\ &\quad + \tfrac{1}{2} g^{rs}_{pq}(\widetilde{a}^{pq}_{rs} + \gamma^p_r \widetilde{a}^q_s + \gamma^q_s \widetilde{a}^p_r - \gamma^q_r \widetilde{a}^p_s + \gamma^p_s \widetilde{a}^q_r + \gamma^{pq}_{rs}) \\ &= \{h^p_q \gamma^q_p + \tfrac{1}{2} g^{rs}_{pq} \gamma^{pq}_{rs}\} \\ &\quad + \{h^p_q + \tfrac{1}{2} g^{rp}_{sq} \gamma^s_r + \tfrac{1}{2} g^{pr}_{qs} \gamma^s_r - \tfrac{1}{2} g^{pr}_{sq} \gamma^s_r - \tfrac{1}{2} g^{rp}_{qs} \gamma^s_r\} \widetilde{a}^q_p \\ &\quad + \tfrac{1}{2} g^{rs}_{pq} \widetilde{a}^{pq}_{rs} \\ &= E_0 + f^p_q \widetilde{a}^q_p + \tfrac{1}{2} g^{rs}_{pq} \widetilde{a}^{pq}_{rs}, \end{aligned} \tag{70}$$

$$E_0 = h^p_q \gamma^p_q + \tfrac{1}{2} g^{rs}_{pq} \gamma^{pq}_{rs} = \langle \Phi | H | \Phi \rangle, \tag{71a}$$

$$f^p_q = h^p_q + \overline{g}^{rp}_{sq} \gamma^s_r, \tag{71b}$$

$$\overline{g}^{rp}_{sq} = g^{rp}_{sq} - g^{pr}_{sq}. \tag{71c}$$

We recognize E_0 as the reference energy and $f^p_q \widetilde{a}^q_p$ as a generalized Fock operator. Let us note the natural emergence of the generalized Fock operator as the one-body component of H in normal order. The stationarity condition of MC-SCF theory for $\langle \Phi | H | \Phi \rangle$ is conventionally formulated[15] as

$$\begin{aligned} 0 &= \langle \Phi | [H, a^t_u] | \Phi \rangle \\ &= h^p_q \langle \Phi | [a^q_p, a^t_u] | \Phi \rangle + \tfrac{1}{2} g^{rs}_{pq} \langle \Phi | [a^{pq}_{rs}, a^t_u] | \Phi \rangle \\ &= h^t_q \gamma^q_u - h^p_u \gamma^t_p + \tfrac{1}{2} \overline{g}^{tq}_{rs} \gamma^{rs}_{uq} - \tfrac{1}{2} \overline{g}^{pq}_{su} \gamma^{st}_{pq}, \end{aligned} \tag{72}$$

where we have used Eqs. (55) and (57a).

Alternatively we can start from H in terms of the $\widetilde{a}$ operators as in Eq. (70) and note that commutators with respect to $\widetilde{a}^t_u$ are the same as those with respect to a^t_u

$$\begin{aligned} 0 &= \langle \Phi | [H, \widetilde{a}^t_u] | \Phi \rangle \\ &= f^p_q \langle \Phi | [\widetilde{a}^q_p, \widetilde{a}^t_u] | \Phi \rangle + \tfrac{1}{2} g^{pq}_{rs} \langle \Phi | [\widetilde{a}^{rs}_{pq}, \widetilde{a}^t_u] | \Phi \rangle \\ &= f^p_q \{\delta^t_p \gamma^q_u - \gamma^q_u \gamma^t_p\} \\ &\quad + \tfrac{1}{2} g^{pq}_{rs} \{\delta^t_p \lambda^{rs}_{uq} + \delta^t_q \lambda^{rs}_{pu} - \delta^r_u \lambda^{ts}_{pq} - \delta^s_u \lambda^{rt}_{pq}\} \\ &= f^t_q \gamma^q_u - f^p_u \gamma^t_p + \tfrac{1}{2} \overline{g}^{tq}_{rs} \lambda^{rs}_{uq} - \tfrac{1}{2} \overline{g}^{pq}_{us} \lambda^{ts}_{pq}. \end{aligned} \tag{73}$$

The result is based on Eqs. (53a) and (54a).

The results (72) and (73) are, of course, equivalent, i.e., the basic equations of MC-SCF theory remain the same in the new formalism. Nevertheless, Eq. (73) is the more convenient, since it contains λ instead of γ. While γ has matrix elements for all labels, λ is nonvanishing only if all of its labels refer to active orbitals. Of course, one could have arrived at Eq. (73) from Eq. (72) by simply using Eq. (38), but one would hardly have had a motivation for doing so. Anyway, at this point, the advantages of the new formalism are not yet obvious. This changes when we go beyond MC-SCF theory.

Let us now look at the Hessean of the Hamiltonian

$$H^{tv}_{uw} = \langle \Phi | [[H, a^t_u], a^v_w] | \Phi \rangle = \langle \Phi | [[H, \widetilde{a}^t_u], \widetilde{a}^v_w] | \Phi \rangle. \tag{74}$$

Starting from Eqs. (56) and (57b) we get

$$\begin{aligned} H^{tv}_{uw} &= \delta^t_w (h^q_u \gamma^v_q + \tfrac{1}{2} \overline{g}^{qs}_{pu} \gamma^{pr}_{qs}) \\ &\quad - h^t_w \gamma^v_u + \tfrac{1}{2} \overline{g}^{qs}_{uw} \gamma^{tv}_{qs} + \delta^v_u (h^t_p \gamma^p_w + \tfrac{1}{2} \overline{g}^{qt}_{pr} \gamma^{pr}_{qw}) \\ &\quad - h^v_u \gamma^t_w - \tfrac{1}{2} \overline{g}^{tv}_{pr} \gamma^{pr}_{uw} \overline{g}^{qt}_{wp} \gamma^{pv}_{qu} + \overline{g}^{qv}_{up} \gamma^{pt}_{qw}, \end{aligned} \tag{75}$$

while by means of Eqs. (53b) and (54b) we arrive at

$$\begin{aligned} H^{tv}_{uw} &= \delta^t_w (f^q_u + \tfrac{1}{2} \overline{g}^{qs}_{pu} \gamma^{pv}_{qs} + \overline{g}^{vq}_{pr} \gamma^p_q \gamma^r_u) \\ &\quad - f^t_w \gamma^v_u + \delta^v_u (f^t_p + \tfrac{1}{2} \overline{g}^{qt}_{pr} \gamma^{pr}_{qw} + \overline{g}^{qs}_{wp} \gamma^p_q \gamma^t_s) \\ &\quad - f^v_u \gamma^t_w + \tfrac{1}{2} \overline{g}^{qs}_{uw} \gamma^{tv}_{qs} + \tfrac{1}{2} \overline{g}^{tv}_{pr} \gamma^{pr}_{uw} + \overline{g}^{qt}_{wp} (\lambda^{pr}_{qu} - \gamma^p_u \gamma^r_q) \\ &\quad + \overline{g}^{qv}_{up} (\lambda^{pt}_{qw} - \gamma^p_w \gamma^t_q). \end{aligned} \tag{76}$$

The equivalence of the two expressions can be checked without difficulty.

XI. EXCITED CONFIGURATIONS

In the theory based on a *single-Slater determinant* reference function Φ, one improves Φ towards an eigenfunction of the many-electron Hamiltonian H by admixing excited configurations

$$\Phi^a_i = a^a_i \Phi, \quad \Phi^{ab}_{ij} = a^{ab}_{ij} \Phi, \text{ etc.} \tag{77}$$

In Eq. (77) it makes no difference whether we use a^a_i and a^{ab}_{ij} or $\widetilde{a}^a_i$ and $\widetilde{a}^{ab}_{ij}$. It is better to use the spin-conserving exited configurations

$$\Phi^A_I = E^A_I \Phi; \quad \Phi^{AB}_{IJ} = E^{AB}_{IJ} \Phi, \text{ etc.} \tag{78}$$

It is even recommended to replace the doubly excited configurations by their symmetrized counterparts

$$\Phi^{+AB}_{IJ} = E^{+AB}_{IJ} \Phi; \quad \overline{\Phi}^{AB}_{IJ} = \overline{E}^{AB}_{IJ} \Phi, \tag{79a}$$

$$E^{+AB}_{IJ} = N^+ (E^{AB}_{IJ} + E^{BA}_{IJ}); \quad \overline{E}^{AB}_{IJ} = N^- (E^{AB}_{IJ} - E^{BA}_{IJ}) \tag{79b}$$

with N^+ and N^- normalization factors. Note that for $I = J$ and/or $A = B$ different expressions have to be used, which complicates the bookkeeping somewhat.

For a *multideterminant* reference function

$$\Phi = \sum_\mu c_\mu \phi_\mu, \tag{80}$$

we switch again to excitations on spin-orbital level. Here three new aspects arise. While for a single determinant reference function there are only two classes of spin orbitals, namely, occupied ψ_i and unoccupied ψ_a, we have now three classes, including the active (partially occupied) orbitals ψ_x. Accordingly there are many more types of excitations, since one can excite from ψ_i to ψ_x and ψ_a and from ψ_x to ψ_a and even from ψ_x to ψ_y. Further there are two possibilities to define excited wave functions, either one excites from the individual configurations ϕ_μ contained in Φ, as given by Eq. (80), e.g.,

$$\phi_i^a(\mu)=a_i^a\phi_\mu, \quad \text{etc.}, \tag{81}$$

or one can excite the entire Φ

$$\Phi_i^a=a_i^a\Phi, \quad \text{etc.} \tag{82}$$

For the latter choice one refers to an *internally contracted* scheme.[16,17] If one takes all possible excitations, the two choices (81) and (82) must be equivalent. Since the number of n-electron basis functions is much larger for the choice (81), there must be considerable linear dependencies between these functions. If one wants to take full advantage of the formalism developed in this paper, one is practically obliged to use the internally contracted excitations (82).

Actually Eq. (82) corresponds to *conventional* internally contracted excitations. In the context of this paper it is much more natural to choose *normal-order internally contracted* excitations of the general type

$$\tilde{a}_p^q\Phi; \quad \tilde{a}_{pr}^{qs}\Phi, \quad \text{etc.} \tag{83}$$

These types have been used in Refs. 8–10 as well. A first difference between the conventional and normal order excitations is seen, if one considers the overlap with the reference function Φ.

$$\langle\Phi|a_p^q\Phi\rangle=\gamma_p^q; \quad \langle\Phi|a_{pr}^{qs}\Phi\rangle=\gamma_{pr}^{qs}, \tag{84a}$$

$$\langle\Phi|\tilde{a}_p^q\Phi\rangle=0, \quad \langle\Phi|\tilde{a}_{pr}^{qs}\Phi\rangle=0. \tag{84b}$$

The normal-order excitations are always orthogonal to Φ, while this holds for the conventional ones only if the corresponding density matrix elements vanish. Since

$$\gamma_i^a=0; \quad \gamma_i^x=0; \quad \gamma_x^a=0, \quad \text{etc.}, \tag{85}$$

the only nonvanishing overlap integrals of the conventional excitations with Φ are

$$\langle\Phi|a_x^y\Phi\rangle=\gamma_x^y; \quad \langle\Phi|a_{xz}^{yu}\Phi\rangle=\gamma_{xz}^{yu}. \tag{86}$$

Let us now consider the overlap integrals between different excited configurations

$$\langle a_p^q\Phi|a_r^s\Phi\rangle=\langle\Phi|a_q^p a_r^s|\Phi\rangle=\gamma_{qr}^{ps}+\delta_q^s\gamma_r^p, \tag{87a}$$

$$\langle\tilde{a}_p^q\Phi|\tilde{a}_r^s\Phi\rangle=\langle\Phi|\tilde{a}_q^p\tilde{a}_r^s|\Phi\rangle=\eta_q^s\gamma_r^p+\lambda_{qr}^{ps}, \tag{87b}$$

if we choose the ψ_p as natural spin orbitals, and assume $p\neq q, s\neq r$, then in either case all single excitations are orthogonal to each other except those where all four label refer to active orbitals.

More interesting is the overlap between singly and doubly excited configurations. We exclude the case that all 6 labels refer to active orbitals. Then

$$\langle\tilde{a}_p^q\Phi|\tilde{a}_{tu}^{rs}\Phi\rangle=\eta_q^r\lambda_{tu}^{ps}+\eta_q^s\lambda_{ut}^{pr}-\gamma_t^p\lambda_{qu}^{rs}-\gamma_u^p\lambda_{tq}^{rs}. \tag{88}$$

If we take the special case $p=i, q=a$, then the overlap vanishes. In particular $\tilde{a}_i^a\Phi$ is orthogonal to $\tilde{a}_{ix}^{ay}\Phi$. The corresponding conventional excitations are nonorthogonal

$$\begin{aligned}\langle a_i^a\Phi|a_{ix}^{ay}\Phi\rangle&=\langle\Phi|a_a^i a_{ix}^{ay}|\Phi\rangle\\&=\langle\Phi|a_{aix}^{iay}+a_{ix}^{iy}-a_{ax}^{ay}+a_x^y|\Phi\rangle=\gamma_x^y.\end{aligned} \tag{89}$$

Normal order external single excitations $\tilde{a}_i^a\Phi$ are orthogonal to normal-order single excitations *with spectator* like $\tilde{a}_{ix}^{ax}\Phi$. The corresponding conventional excitations are not. Unfortunately, excitations like $\tilde{a}_i^x\Phi$ or $\tilde{a}_x^a\Phi$ are not orthogonal to $\tilde{a}_{iy}^{xz}\Phi$ or $a_{xy}^{az}\Phi$, respectively. But in these overlaps higher body λ's rather than γ's appear whose importance goes down faster with the particle rank.

Anyhow there are more orthogonality relations for the normal-order than for the conventional excitations. Since in order to take advantage of the generalized Wick theorem we need to take normal order excitations, we assume henceforth that these are taken.

We can classify normal-order internally contracted excited configurations in the following way:

$$\begin{aligned}&(a)\ \text{external:} && \tilde{a}_i^a\Phi;\tilde{a}_{ij}^{ab}\Phi;\tilde{a}_{ijk}^{abc}\Phi, \ \text{etc.}\\&(b)\ \text{internal:} && \tilde{a}_x^y\Phi;\tilde{a}_{xy}^{zu}\Phi, \ \text{etc.}\\&(c)\ \text{mixed (external/internal):} && \tilde{a}_{ix}^{ay}\Phi;\tilde{a}_{ijx}^{aby}\Phi;\tilde{a}_{ixy}^{azu}\Phi, \ \text{etc.}\\&(d)\ \text{semiinternal (+):} && \tilde{a}_i^x\Phi;\tilde{a}_{ix}^{yz}\Phi;\tilde{a}_{ij}^{xy}\Phi, \ \text{etc.}\\&(e)\ \text{semiinternal (-):} && \tilde{a}_x^a\Phi;\tilde{a}_{xy}^{az}\Phi;\tilde{a}_{xy}^{ab}\Phi, \ \text{etc.}\end{aligned} \tag{90}$$

Excitations of types (a), (b), (c) don't change the number of active electrons, those of type (d) increase it (hence +) those of type (d) reduce it (hence −).

An important concept in going beyond a given reference function is that of the *first order interacting space*. This consists of all excited configurations that have a nonvanishing matrix of the Hamiltonian with the reference function. In closed-shell single reference theory the interacting space consists simply of the functions $a_{ij}^{ab}\Phi$. In the multireference-case the situation is more complicated.

We first note that all those functions do not belong to the first-order interacting space, in which three or more labels refer to either fully occupied or fully unoccupied states, such as $\tilde{a}_{ijk}^{abx}\Phi, \tilde{a}_{ijx}^{abc}\Phi$. By virtue of the Brillouin theorem the following excitations can be excluded: $\tilde{a}_i^a\Phi$. For a CAS-SCF reference, that we shall always suppose to be chosen, all excitations among active orbital can be omitted, because they can improve the reference function only indirectly, i.e., $\tilde{a}_x^y\Phi$; $\tilde{a}_{xy}^{zu}\Phi$, etc. One can further eliminate all fully external double excitations with spectator such as $\tilde{a}_{ijx}^{aby}\Phi$; $a_{ijxz}^{abyu}\Phi$. Note that the corresponding conventional excitations would

not have vanishing matrix element of H with Φ and would hence have to be included in the first-order interacting space.

The first-order interacting space consists hence of the following excitations [compare them with Eq. (90)]

$$\begin{aligned}
&(a)\ \text{external:}\quad \widetilde{a}_{ij}^{ab}\Phi,\\
&(b)\ \text{internal:}\quad \text{none},\\
&(c)\ \text{mixed:}\quad a_{ix}^{ay}\Phi,\ a_{ixy}^{azu}\Phi,\ a_{ixyz}^{auvw}\Phi\ \text{etc.},\\
&(d)\ \text{semiinternal}\,(+)\text{:}\quad \text{all as in Eq. (90)},\\
&(e)\ \text{semiinternal}\,(-)\text{:}\quad \text{all as in Eq. (90)}.
\end{aligned}\tag{91}$$

In principle the internal rank in mixed excitations can go up to the number of active electrons. However there are linear dependencies and it is important to choose a most convenient non-redundant set. For two active electrons (assuming no symmetry) one can, e.g., choose the set

$$a_{ixy}^{axy}\Phi;\quad x<y \tag{92a}$$

with x and y going over all active orbitals, such that the operators a_{xy}^{xy} project to the various Slater determinants contained in Φ. A better choice is

$$a_i^a\Phi, a_{ix}^{ay}\Phi;\quad 1<x\leqslant y. \tag{92b}$$

A similar but slightly more complicated situation arises for the two types of semiinternal excitations (d) and (e).

If one wants to go beyond the first-order interacting space one will add the external single excitations as well as the fully internal excitations, in order to improve the reference functions in the presence of the leading excitations. One will also have to consider triple excitations as in the closed-shell case. Details will be outlined in a forthcoming paper.

XII. CONCLUDING REMARKS

After it had been realized that a generalization of normal ordering to arbitrary reference functions must be possible[8–10] there were several ways to arrive at this generalization. One way[8–10] is based on the observation that any arbitrary wave function can be obtained from a single Slater determinant by means of a unitary Fock space operator. Then accordingly transformed creation and annihilation operators play the role of the original operators with respect to the Slater determinant, especially as far as anticommutation relations are concerned.

The way chosen here starts from recognizing certain properties that normal-order operators have to satisfy, and uses the guiding principle that for a single Slater determinant the well-known particle-hole formalism must appear as a special case.

Our derivation is largely based on the use of particle-number-conserving operators and their properties. These operators are fully sufficient for the formulation of a many-body theory. Nevertheless, we arrived at contraction rules which constitute a generalized Wick theorem, that holds for non-particle-number-conserving operators as well, and which agree with those obtained on the other route,[8–10] which was not limited to particle-number-conserving operators.

We hesitate to call our multiconfiguration reference wave function a ''physical vacuum,'' since it does not share all properties that one usually associates with this concept (e.g., no quasiparticles occupied), but in some sense it is a generalization of the single Slater determinant as physical ''vacuum.''

The present formalism is particularly suited for spinfree operators, where the elimination of spin is perfectly straightforward, even if this has not been fully worked out in the present paper.

Although at some intermediate steps complicated formulas arose (some of them could only be manipulated using MATHEMATICA), the formalism of generalized normal ordering appears to be quite manageable. In view of this it is rather astonishing that such a generalization has not been tried earlier.

The main power of this formalism lies in the fact that a fully separable and hence connected cluster expansion is possible in a state-specific theory without the need to introduce valence-universality.

A further advantage of our formalism is that residual rather than full density matrix elements of higher particle rank appear. Since the former become increasingly less important for increasing particle rank, approximations become possible, in which λ elements beyond a given particle rank are systematically neglected. This is somewhat analogous to ignoring excitation operators beyond a given particle rank in coupled-cluster theory, and is at least size consistent. In special cases higher-order λ elements may even vanish exactly. For a GVB wave function there are, e.g., no λ elements beyond particle rank 2.

In forthcoming papers (a) the spinfree formulation will be elaborated in more detail, (b) MBPT and CC-theory based on multireference wave functions will be formulated.

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