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Correlation problems in atomic and molecular systems. VI. Coupled-cluster approach to open-shell systems

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A new approach to the *direct* determination of excitation energies and various attachment or detachment energies, such as electron affinities and ionization potentials, is presented. It is based on the coupled-cluster ansatz for the trial wave function, generalized to the open-shell excited or ionized states in a way which enables a variation principle to be used, assuming that the closed-shell ground-state coupled-cluster wave function is known. The conditions for the applicability of this approach are discussed, and the basic formalism is derived. A technique enabling a systematic elimination of disconnected clusters in a general open-shell case is presented and used. An example pertaining to ionization processes is worked out in some detail. Finally, the relationship of the presented approach to configuration-interaction and perturbative Green's-function approaches is briefly outlined.

I. INTRODUCTION

Recently there has been a renewed interest in the exploitation of the cluster expansion ansatz for the calculation of correlated nonrelativistic wave functions. The explicit equations for the connected cluster components,[1-4] based on the cluster ansatz first introduced in nuclear physics,[5] have been rederived in several different ways,[6-10] and the spin-adapted form of the theory was given.[11] A new method for the calculation of properties with the cluster wave function was formulated[12] and the conditions of solvability of the coupled-cluster equations were examined.[13]

A particularly interesting application of this approach to both the three-[14] and two-dimensional[15] electron gas was achieved by Freeman, and various applications to nuclear,[16-18] atomic,[19,20] molecular,[4,19,21] solid state,[22] and extended weakly interacting systems[23] have been carried out or are currently in progress.

Further, an interesting approach, termed variational localized-site cluster expansion, was formulated and applied to various systems by Klein *et al.*[24]

Several approaches appeared recently[25,26] enabling an exploitation of the coupled-cluster ansatz for open shells. In this paper we present another possible approach[27] to the open-shell problem. This approach is completely general, even though it should be particularly useful for open-shell systems or states, in which the bulk of the correlation effects is reasonably well described by the corresponding closed-shell coupled-cluster wave function. Indeed, should the transition to the open-shell system or state (i.e., particle attachment or detachment, excitation, etc.) be a true many-body rather than basically a few-body transition (in other words, should it lead to an extensive reconstruction of the wave function), the presented method can be expected to be rather inefficient.

A particularly attractive feature of the presented approach is the elimination of the reference-state contribution, thus enabling a *direct* calculation of the pertinent energy differences as in some other many-body approaches (cf., for example, the Green's function approach[28]). In this connection, the presented "multistep" technique, which enables the elimination of the disconnected cluster components, is of interest in a broader context than is the scope of this paper.

We first summarize the main features of the closed-shell theory in Sec. II. In Sec. III we discuss the possibilities of extending the coupled-cluster theory to open shells and formulate the cluster ansatz for the wave function used in this paper. In Sec. IV we eliminate the reference-state contribution as well as the disconnected components and formulate the basic equations of our approach. An example of a specific application of this theory for the determination of the ionization potentials or electron affinities is briefly outlined in Sec. V. Finally, the applicability of the present approach as well as its relationship to other theories is discussed in Sec. VI.

A more detailed form of these equations, enabling the calculation of ionization potentials, electron affinities, and excitation energies of closed-shell systems, as well as the results of various model calculations, will be the subject of a subsequent paper.[29]

II. SUMMARY OF THE CLOSED-SHELL THEORY

The most essential characteristic of the coupled-cluster approach is the use of the exponential expansion for the exact nonrelativistic wave function $|\Psi\rangle$,

$$|\Psi\rangle = \exp(\hat{T})|\Phi_0\rangle\,, \quad \langle\Psi|\Phi_0\rangle = \langle\Phi_0|\Phi_0\rangle = 1\,, \tag{1}$$

where $|\Phi_0\rangle$ is the closed-shell independent-particle model (single determinant) reference state, and

$$\hat{T} = \sum_i \hat{T}_i\,, \tag{2}$$

where[30]

$$\hat{T}_i = (i!)^{-2} \sum_{A^1,\ldots,A^i} \sum_{A_1,\ldots,A_i} \langle A^1 \ldots A^i|\hat{t}_i|A_1 \ldots A_i\rangle_A \times \prod_{j=1}^{i} (\hat{X}^\dagger_{A^j} \hat{X}_{A_j})\,, \tag{3}$$

represents the i-particle component of the operator $\hat{T}$. Thus the exact wave function is determined by the (antisymmetrized) t_i matrix elements, defining the $\hat{T}_i$ operators, Eq. (3). These matrix elements are determined by solving the pertinent system of (nonlinear) algebraic equations, which are obtained by substituting the cluster expansion, Eq. (1), into the time-independent Schrödinger equation. The individual equations of this algebraic system represent in fact the projections of the Schrödinger equation onto the appropriate one-dimensional subspaces, defined by the independent-particle model configuration states (cf., for example, Ref. 11). The detailed structure of these equations depends, of course, on the approximations made regarding various components of the operator $\hat{T}$.

The explicit form of these equations may be most conveniently derived using the diagrammatic technique,[1,2] based on the time-independent Wick's theorem (cf., for example, Ref. 32). In this approach the i-particle component of the operator $\hat{T}$ is represented by the T_i skeletons and diagrams[33] (cf., for example, Figs. 4–6 of Ref. 2 or Figs. 1 and 11 of Ref. 11). Assuming that the Hamiltonian $\hat{H}$ contains only one- and two-particle terms $\hat{Z}$ and $\hat{V}$, respectively, which are represented by the usual H diagrams (skeletons) (cf., for example, Fig. 2 of Ref. 2), one obtains the desired system of equations by equating to zero all connected diagrams, which have the same external (noncontracted) lines, and which result from one H and an arbitrary number of T_i $(i = 1, 2, 3, \ldots)$ diagrams.

In this way the chain of mutually coupled equations for the T_i components, which is equivalent to the exact Schrödinger equation, may be obtained (cf., also, the nondiagrammatic formulation of this problem given in Ref. 3). For practical applications, this system is then decoupled by making plausible physical assumptions concerning the T_i components.

In the simplest approximation $\hat{T} \approx \hat{T}_2$, at most two T_2 vertices can appear in any connected diagram having two-particle and two-hole external lines, yielding thus the nonlinear algebraic system of equations[1,2] of the so-called "coupled-pair many-electron theory" (CPMET).

It is worth mentioning that the resulting system of equations, which has to be solved, does not contain explicitly the calculated correlation energy $\Delta\epsilon$. This energy is in fact given by projection of the Schrödinger equation on the ground-state determinant $|\Phi_0\rangle$, i.e., by the sum of diagrams containing no external lines. Even in the general case, the energy expression involves at most T_2 components. Thus, after solving a given algebraic system of equations, the correlation energy $\Delta\epsilon$ is calculated using a simple formula, which is linear in the t_2-matrix elements.[1,2]

For a spin-independent Hamiltonian $\hat{H}$, one can assume the spin independence of the operator $\hat{T}$ and derive simple rules for obtaining the pertinent spin-free equations (factor of 2 for each closed loop of oriented lines rule). This is particularly easy to implement in the case of singly and doubly excited clusters, since the number of linearly independent singlets and the number of distinct t_i-matrix elements is the same. This is not true for higher than doubly excited clusters, where special considerations are necessary.[4] However the most appropriate way of handling the spin symmetry of the Hamiltonian considered is to use the graphical methods of spin algebras[11] (cf. also, Refs. 31 and 35).

An explicit form of the equations determining the t_i-matrix elements in various approximations may be found in Ref. 4. The spin adapted form of the CPMET is given in Ref. 11.

III. CLUSTER ANSATZ FOR THE OPEN-SHELL CASE

There are several possible ways to extend the cluster ansatz, Eq. (1), which is suitable for closed-shell systems with spin-independent Hamiltonians, to the open-shell case. In order to appropriately exploit the spin-independent character of the forces considered (and derive the spin-free theory), as well as the hole-particle formalism and the corresponding diagrammatic technique, it is essential that the reference state $|\Phi_0\rangle$ is a single antisymmetrized product of single-particle states. Moreover, the open-shell states in which we are primarily interested are those associated with various excited or ionized states of molecules, having closed-shell ground states.

As long as these excitations or ionizations only involve directly one or two valence electrons, it is reasonable to assume that the majority of the pair (or higher cluster) correlations will not be drastically changed. Thus it will be more convenient to start from the correlated ground (or new reference) state $|\Psi\rangle$ and calculate the changes with respect to this state, rather than to introduce again all the correlation into the uncorrelated independent-particle model reference state as we must have done for the ground state $|\Psi\rangle$. Clearly, this assumption and, consequently, the whole formalism based on it, may not be particularly advantageous for more general open-shell systems, which may not be simply related to some closed-shell system, and where the other alternative, closely paralleling the closed-shell ground-state formalism, might be equally justified.

Nevertheless, we shall restrict our considerations here to the states, which may be efficiently described in terms of the correlated closed-shell state $|\Psi\rangle$ as follows:

$$|\Psi_\Gamma\rangle = \hat{W}_\Gamma |\Psi\rangle = \hat{W}_\Gamma \exp(\hat{T}) |\Phi_0\rangle . \tag{4}$$

Here, the operator $\hat{W}_\Gamma$ has a double purpose: first, to form an appropriate open-shell state from $|\Psi\rangle$ (or $|\Phi_0\rangle$)[36] and, second, to describe the changes in the correlation in this new state relative to $|\Psi\rangle$.

Thus, in general,

$$\hat{W}_\Gamma = \sum_{i=1}^{m} \hat{W}_i^{(\Gamma)} , \tag{5}$$

where the $\hat{W}_1^{(\Gamma)}$ term yields an appropriate zero (or first) order wave function of the open-shell system considered when acting on $|\Phi_0\rangle$.[36] The subsequent terms $W_i^{(\Gamma)}$; $i = 2, 3, \ldots$, containing i more creation-annihilation operator pairs than $\hat{W}_1^{(\Gamma)}$, describe the changes in the correlation relative to the "reference" state $|\Psi\rangle$. In order to simplify our notation, we shall drop the superscript (Γ), specifying a given open-shell state, whenever confusion cannot arise.

Thus, for example, for a mononegative (or a monopositive) ion of a closed-shell system we can write

$$\hat{W}_{i+1} = [i!(i+1)!]^{-1} \sum_{A} \sum_{A^1,\ldots,A^i} \sum_{A_1,\ldots,A_i} \langle A; A^1 \ldots A^i | \hat{w}_{i+1} | (A); A_1 \ldots A_i \rangle_A \times \prod_{j=1}^{i} (\hat{X}^\dagger_{A^j} \hat{X}_{A_j}) \hat{M}_A , \quad i = 0, 1, \ldots , \tag{6}$$

where

$$\langle A; A^1 \ldots A^i | \hat{w}_{i+1} | (A); A_1 \ldots A_i \rangle_A = \langle A^0; A^1 \ldots A^i | \hat{w}_{i+1} | A_1 \ldots A_i \rangle_A , \tag{7}$$

$$\hat{M}_A = \hat{X}^\dagger_{A^0}$$

for the mononegative ion (electron attachment) and

$$\langle A; A^1 \ldots A^i | \hat{w}_{i+1} | (A); A_1 \ldots A_i \rangle_A = \langle A^1 \ldots A^i | \hat{w}_{i+1} | A_0; A_1 \ldots A_i \rangle_A , \tag{8}$$

$$\hat{M}_A = \hat{X}_{A_0}$$

for the monopositive ion (ionization).

Similarly, for the excited states of closed-shell systems we can write

$$\hat{W}_i = (i!)^{-2} \sum_{A^1,\ldots,A^i} \sum_{A_1,\ldots,A_i} \langle A^1 \ldots A^i | \hat{w}_i | A_1 \ldots A_i \rangle_A \times \prod_{j=1}^{m} (\hat{X}^\dagger_{A^j} \hat{X}_{A_j}), \quad i \geqslant 1 . \tag{9}$$

When $|\Psi\rangle$ and $|\Psi_\Gamma\rangle$ represent the exact eigenstates, they must be orthogonal. However, even when $|\Psi\rangle$ is only approximate, $|\Psi_\Gamma\rangle$ will be in most cases automatically orthogonal to the ground state $|\Psi\rangle$: this will be the case whenever $\hat{W}_\Gamma$ is not a particle number conserving operator [as in the case of Eqs. (5)–(8)], or when the symmetry species of the excited state $|\Psi_\Gamma\rangle$ is different from that of the corresponding ground state $|\Psi\rangle$. In case that $|\Psi_\Gamma\rangle$ is not automatically orthogonal to $|\Psi\rangle$, one can of course orthogonalize it by projecting out the $|\Psi\rangle$ component from $|\Psi_\Gamma\rangle$. In fact, as shown in the Appendix, this is equivalent to using $|\Psi_\Gamma\rangle$ as defined by Eq. (4) and assuming in all subsequent derivations its orthogonality to $|\Psi\rangle$.

The operator $\hat{W}$ may now be represented diagrammatically in a similar way as the operator $\hat{T}$: In order to distinguish between the diagrams and skeletons associated with $\hat{T}_i$ and $\hat{W}_i$ operators [particularly in the excitation case, Eq. (9)], we now use the square-shaped apex for the W terms. Thus, for example, the W skeletons and W diagrams associated with the $\hat{W}_1$ and $\hat{W}_2$ operators for the monopositive ion (ionization) case [Eqs. (6) and (8)] are shown in Fig. 1. Similarly, those corresponding to $\hat{W}_1$ and $\hat{W}_2$ operators for the excitation case [Eq. (9)] are shown in Fig. 2. We can thus use the same diagrammatic formalism, based on the time-independent Wick's theorem, as in earlier considerations.[1,2,4,11,32,34]

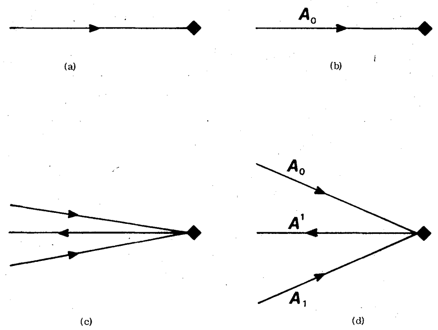

FIG. 1. Example of W-skeletons (a) and (c) and W-diagrams (b) and (d) pertaining to the ionization processes. The skeleton (a) and the corresponding diagrams (b) describe the zero-order term $\hat{W}_1$, while the skeleton (c) and diagrams (d) express the first-order term $\hat{W}_2$, Eqs. (6) and (8).

IV. DERIVATION OF BASIC EQUATIONS

In the case of the closed-shell ground state, the t_i-matrix elements enter the trial ket $|\Psi\rangle$, Eqs. (1)–(3), in a highly nonlinear manner. In contrast, the open-shell trial ket $|\Psi_\Gamma\rangle$, Eq. (4), is linear in the matrix elements of the operator $\hat{W}_\Gamma$. Thus we can use the Ritz variational method to determine the operator $\hat{W}_\Gamma$. This assumes, of course, that the highly nonlinear terms in the t_i-matrix elements, which appear in the energy mean value expression, are sufficiently small and can be neglected.

Moreover, we shall see that the ansatz for $|\Psi_\Gamma\rangle$, Eq. (4), enables us to determine *directly* the energy differences (i.e., excitation energies, ionization potentials, electron affinities, etc.) rather than the absolute energies of the given open-shell states. Unless a complete reconstruction of the wave function occurs, the former (i.e., direct) approach is much more effective than the latter one, since it does not require a recalculation of the correlation effects, which are not essentially changed in the excitation or ionization process considered. It should also be clear that, in any approximate calculation, the resulting values for these energy differences will not be equal to the difference of the variationally determined individual state energies, since the operator $\hat{T}$ and, thus, the reference closed-shell ground state, is determined nonvariationally. However, since there is no variational principle for the energy differences, we feel that the use of different treatments for the ground (or reference) state and for the pertinent excited or ionized states (i.e., nonvariational versus variational) is of little importance, particularly when both the ground-state energy and the pertinent energy difference are determined with a sufficiently high accuracy.

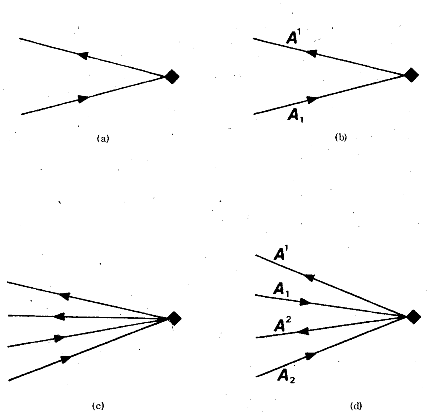

FIG. 2. Example of W-skeletons (a) and (c) and W-diagrams (b) and (d) pertaining to the excitation processes. The skeleton (a) and the corresponding diagrams (b) represent the term $\hat{W}_1$, while (c) and (d) represent the term $\hat{W}_2$, Eq. (9).

A. Energy difference evaluation

We first derive an expression for the energy difference ΔE_Γ,

$$\Delta E_\Gamma = \langle \Psi_\Gamma | \hat{H}_N | \Psi_\Gamma \rangle \langle \Psi_\Gamma | \Psi_\Gamma \rangle^{-1} - \langle \Psi | \hat{H}_N | \Psi \rangle \langle \Psi | \Psi \rangle^{-1} , \qquad (10)$$

between the energies of the open-shell state $|\Psi_\Gamma\rangle$ and a corresponding reference state $|\Psi\rangle$. Using our cluster ansatz we can write

$$\begin{aligned}\Delta E_\Gamma = {} & \langle \Phi_0 | \exp(\hat{T}^\dagger) \hat{W}_\Gamma^\dagger \hat{H}_N \hat{W}_\Gamma \exp(\hat{T}) | \Phi_0 \rangle \\ & \times \langle \Phi_0 | \exp(\hat{T}^\dagger) \hat{W}_\Gamma^\dagger \hat{W}_\Gamma \exp(\hat{T}) | \Phi_0 \rangle^{-1} \\ & - \langle \Phi_0 | \exp(\hat{T}^\dagger) \hat{H}_N \exp(\hat{T}) | \Phi_0 \rangle \\ & \times \langle \Phi_0 | \exp(\hat{T}^\dagger) \exp(\hat{T}) | \Phi_0 \rangle^{-1} , \end{aligned} \qquad (11)$$

and evaluate both the numerators and the denominators using the diagrammatic technique.

Let us recall that $\exp(\hat{T})|\Phi_0\rangle$ is represented by all possible M diagrams,[1,2] each of which consists of none, one, two, etc., T diagrams. Similarly, the Hermitian conjugate quantities are represented by corresponding conjugate diagrams and skeletons[2,32] ($\overline{T}$, $\overline{M}$, and $\overline{W}$ diagrams and skeletons).

Thus the Fermi vacuum mean values appearing in Eq. (10) or (11) are given by all possible fully contracted (i.e., vacuum) connected and disconnected diagrams containing appropriate $\overline{M}$, $\overline{W}$, H, W, and M diagrams as indicated in Table I.

Finally, since all our operators are in the N-product form, no diagrams with internal lines originating and ending on the same vertex (supervertex) can appear (elimination of Hartree-Fock diagrams; cf., for example, Ref. 32).

B. Elimination of disconnected terms

We next show how to eliminate the disconnected (sometimes referred to in this context incorrectly as "unlinked"[37]) terms from the energy expression (10) or (11). In contrast to a similar cancellation, which occurs in the derivation of the closed-shell equations or in the Goldstone perturbation theory, this elimination requires several steps in the present case.

In order to demonstrate this cancellation, we shall schematically represent the sum of all possible *connected and disconnected* vacuum diagrams (skeletons), formed from a given set of constituting diagrams (skeletons), by enclosing this set in a *dashed* rectangle, while the sum of all possible *connected* vacuum diagrams is indicated by enclosing the pertinent set of constituting diagrams in a *solid* rectangle.

Thus, for example, the numerator $\langle \Psi | \hat{H}_N | \Psi \rangle$ of the second term in Eq. (10), given by the sum of all connected and disconnected vacuum diagrams formed from one $\bar{M}$, one M, and one H diagram (cf. Table I), is represented by the left-hand side of the schematic equation shown in Fig. 3.

Separating, now, in each diagram appearing on the left-hand side of the equation in Fig. 3 the connected part containing the H vertex (supervertex) from the rest of the diagram, and realizing that no single component ($\bar{M}$, H, or M) can yield a fully contracted (i.e., vacuum) diagram, since it is in the N-product form,[1,32] we can factor the sum of diagrams, representing $\langle \Psi | \hat{H}_N | \Psi \rangle$, as indicated on the right-hand side of the equation in Fig. 3.[38]

Let us stress that each M (or $\bar{M}$) diagram contains none, one, two, etc., T (or $\bar{T}$) diagrams. Thus, for each connected diagram containing an H (super)vertex we can always find all possible connected and disconnected diagrams containing an arbitrary $\bar{M}$ and M diagram (i.e., containing an arbitrary number of $\bar{T}$ and T diagrams for which all $\bar{T}$ supervertices possess the same number of external lines as all the T supervertices so that the fully contracted diagrams can be formed). Consequently, the sum of all diagrams, which equals $\langle \Psi | \hat{H}_N | \Psi \rangle$, factorizes as schematically indicated by a juxtaposition[38] of the two rectangles on the right-hand side of the equation in Fig. 3. In the algebraic notation this equation takes the form

$$\langle \Psi | \hat{H}_N | \Psi \rangle = \langle \Psi | \hat{H}_N | \Psi \rangle_{\mathrm{C}} \langle \Psi | \Psi \rangle , \tag{12}$$

where $\langle \Psi | \hat{H}_N | \Psi \rangle_{\mathrm{C}}$ designates the *connected component* of $\langle \Psi | \hat{H}_N | \Psi \rangle$, given by the sum of all connected vacuum diagrams, each containing one $\bar{M}$, one H, and one M diagram.

TABLE I. Composition of resulting diagrams representing the individual terms appearing in the energy difference ΔE_Γ, Eq. (10) or (11).

Term	Number of constituting diagrams of type $\bar{M}$ and M	$\bar{W}$ and W	H
$\langle \Psi_\Gamma \| \hat{H}_N \| \Psi_\Gamma \rangle$	1	1	1
$\langle \Psi_\Gamma \| \Psi_\Gamma \rangle$	1	1	0
$\langle \Psi \| \hat{H}_N \| \Psi \rangle$	1	0	1
$\langle \Psi \| \Psi \rangle$	1	0	0

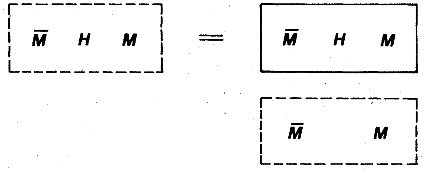

FIG. 3. Schematic representation of the factorization of the matrix element $\langle \Psi | \hat{H}_N | \Psi \rangle$ into the connected part, represented by the heavy-line rectangle, and the connected plus disconnected part (dashed rectangles). The algebraic form of this equation is given by Eq. (12). See text for more details.

We thus find that the second term in Eq. (10) or (11) yields

$$\langle \Psi | \hat{H}_N | \Psi \rangle \langle \Psi | \Psi \rangle^{-1} = \langle \Psi | \hat{H}_N | \Psi \rangle_{\mathrm{C}} . \tag{13}$$

Similarly, the sum of all diagrams representing the numerator $\langle \Psi_\Gamma | \hat{H}_N | \Psi_\Gamma \rangle$ of the first term on the right-hand side of Eq. (10) or (11) may be factored as shown schematically in Fig. 4(a). We note immediately that the dashed rectangles in terms (ii) and (iii) of Fig. 4(a) represent the overlaps $\langle \Psi | \Psi_\Gamma \rangle$ and $\langle \Psi_\Gamma | \Psi \rangle$, respectively. Thus, assuming the orthogonality of $|\Psi\rangle$ and $|\Psi_\Gamma\rangle$, the second and third terms on the right-hand side of the equation in Fig. 4(a) vanish. As shown in the

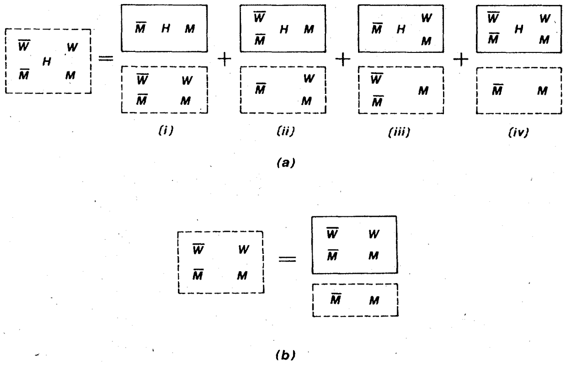

FIG. 4. Schematic representation of the factorization into the connected (heavy rectangles) and connected plus disconnected (dashed rectangles) components for the matrix elements $\langle \Psi_\Gamma | \hat{H}_N | \Psi_\Gamma \rangle$ (a) and $\langle \Psi_\Gamma | \Psi_\Gamma \rangle$ (b).

Appendix, this orthogonality assumption does not restrict the generality of our considerations.

In the algebraic form we can write the factorization shown in Fig. 4(a) as follows:

$$\langle\Psi_\Gamma|\hat{H}_N|\Psi_\Gamma\rangle = \langle\Psi|\hat{H}_N|\Psi\rangle_{\mathcal{C}}\langle\Psi_\Gamma|\Psi_\Gamma\rangle + \langle\Psi_\Gamma|\hat{H}_N|\Psi_\Gamma\rangle_{\mathcal{C}}\langle\Psi|\Psi\rangle\,, \tag{14}$$

so that the first term in Eq. (10) or (11) yields

$$\langle\Psi_\Gamma|\hat{H}_N|\Psi_\Gamma\rangle\,\langle\Psi_\Gamma|\Psi_\Gamma\rangle^{-1} = \langle\Psi|\hat{H}_N|\Psi\rangle_{\mathcal{C}} + \langle\Psi_\Gamma|\hat{H}_N|\Psi_\Gamma\rangle_{\mathcal{C}} \times\langle\Psi|\Psi\rangle\,\langle\Psi_\Gamma|\Psi_\Gamma\rangle^{-1}\,. \tag{15}$$

Consequently, the desired energy difference ΔE_Γ, Eq. (10), is given by the second term on the right-hand side of Eq. (15) in view of Eq. (13).

Finally, the denominator $\langle\Psi_\Gamma|\Psi_\Gamma\rangle$ may be factored as indicated in Fig. 4(b), yielding

$$\langle\Psi_\Gamma|\Psi_\Gamma\rangle = \langle\Psi_\Gamma|\Psi_\Gamma\rangle_{\mathcal{C}}\langle\Psi|\Psi\rangle\,, \tag{16}$$

so that we obtain the desired result

$$\Delta E_\Gamma = \langle\Psi_\Gamma|\hat{H}_N|\Psi_\Gamma\rangle_{\mathcal{C}}\langle\Psi_\Gamma|\Psi_\Gamma\rangle_{\mathcal{C}}^{-1}\,. \tag{17}$$

We next note that both the numerator and the denominator in this expression may be written as bilinear Hermitian forms in terms of the $\hat{W}$ matrix elements,

$$\Delta E_\Gamma = \sum_{ij} H_{ij}w_i w_j \Big/ \sum_{ij} S_{ij}w_i w_j\,, \tag{18}$$

where w_i designate the pertinent $\hat{W}$ matrix elements arranged in some definite order.

The corresponding expressions for the H_{ij} or S_{ij} matrix elements are then simply obtained as a sum of all *connected* diagrams formed from the pertinent W diagrams, representing the matrix elements w_i and w_j involved, arbitrary $\overline{M}$ and M diagrams, given by the approximation considered, and one H diagram or an empty diagram in between, respectively.

We present an example of this procedure in Sec. V.

C. Basic equations

Having determined the pertinent H_{ij} and S_{ij} matrix elements in terms of the one- and two-particle integrals, defining our model Hamiltonian in the chosen (atomic or molecular orbital) basis, and in terms of the t_i-matrix elements determined from the reference-(ground-) state calculation, it is straightforward to calculate the desired energy differences $\Delta E_\Gamma = E_\Gamma - E$ (note that reference-state energy E is fixed and is only used as a convenient energy zero) and the corresponding w_i matrix elements from the pertinent eigenvalue problem

$$\sum_j (H_{ij} - \Delta E_\Gamma S_{ij})w_j = 0\,. \tag{19}$$

For spin-independent Hamiltonians one can, of course, eliminate the explicit spin dependence and obtain a spin-free formalism. This is most conveniently done[11] by exploiting the graphical methods of spin algebras[39,40] (cf. also Refs. 31 and 35).

V. EXAMPLE

In order to illustrate the above outlined general procedure, let us consider an example involving ionization[41] of a closed-shell system. For the sake of simplicity let us restrict ourselves to a simple approximation, in which all but the $\hat{T}_2$ component of the $\hat{T}$ operator vanish and, for the ion, consider only the first term $\hat{W}_1$ in the $\hat{W}$ operator.

Thus, in order to obtain the matrix elements H_{ij} we must construct all the connected diagrams involving one $\overline{W}_1$, one H (i.e., F or V), and one W_1 diagram and an arbitrary number of $\overline{T}_2$ and T_2 diagrams. In fact, one can construct connected diagrams of this type having an arbitrarily large number of $\overline{T}_2$ and T_2 diagrams. We see easily that such diagrams exist as long as the difference between the number of oriented lines in the $\overline{W}$ and $\overline{M}$ diagrams on the one hand, and the W and M diagrams on the other hand, lies between -4 and $+4$. It seems reasonable to assume that diagrams containing a large number of $\overline{T}_2$ and/or T_2 components will be relatively unimportant, since they correspond to high-order terms in the perturbation theory approach (cf. Sec. VI, Table II). Assume, thus, that we can restrict our considerations to at most one $\overline{T}_2$ and one T_2 diagram.

Then, the diagrams yielding H_{ij}'s in the approximation just mentioned may be classified into three types, namely, those containing (i) no T_2 ($\overline{T}_2$) diagram, (ii) one T_2 (or $\overline{T}_2$) diagram, and (iii) both T_2 and $\overline{T}_2$ diagrams. These diagrams are easily constructed and are shown (in the Hugenholtz form) in Fig. 5. In the same way the overlap diagrams may be obtained.[42]

A more detailed description of important particular cases will be given in a subsequent paper[29] describing an application of this theory to certain model systems.

VI. DISCUSSION

The usefulness of the exponential ansatz for the correlated wave function of closed-shell systems stems from two basic facts: (i) the negligibility of the connected tetraexcited clusters as compared with the disconnected ones (symbolically $T_4 \ll \frac{1}{2}T_2^2$); and (ii) a transformation of the multiplicative

TABLE II. Classification of various connected and disconnected clusters according to the lowest order of the perturbation theory in which they contribute.

	Closed shell		Open shell	
Order	Connected	Disconnected	Connected	Disconnected
0	...	...	W_1	...
1	T_2	...	W_2	W_1T_2
2	T_1, T_3	T_2^2	W_3	$W_1T_1, W_1T_2^2, W_1T_3$ W_2T_2
3	T_4	T_1T_2, T_2T_3, T_2^3	W_4	$W_1T_1T_2, W_1T_2T_3, W_1T_2^3$ W_1T_4 $W_2T_1, W_2T_3, W_2T_2^2$ W_3T_2
4	T_5	T_1^2, T_1T_3, T_3^2 T_2T_4, T_2^4 $T_1T_2^2, T_3T_2^2$	W_5	$W_1T_1T_3, W_1T_2T_4, W_1T_1^2$ $W_1T_5, W_1T_3^2, W_1T_2^4$ $W_1T_1T_2^2, W_1T_3T_2^2$ $W_2T_1T_2, W_2T_2T_3, W_2T_2^3$ $W_3T_1, W_3T_3, W_3T_2^2$ W_4T_2

structure for the noninteracting wave-function components into an additive one (cf. also Ref. 43).

The first property enables a physically sensible truncation of the chain of coupled equations (cf., for example, Refs. 1, 3, and 19), which are equivalent to the Schrödinger equation, while the second property automatically guarantees the "size consistency"[44,45] of the formalism.

In the open-shell case, our basic ansatz [Eq. (4)] assumes that the pair (or higher cluster) correlations in the closed-shell (correlated) reference state $|\Psi\rangle$ are not drastically modified by a creation (an annihilation) or an excitation of a few "quasiparticles" in this reference state, as already mentioned. In other words, it assumes that the pairs (clusters) and their interactions in the closed-shell part of the open-shell state (system) considered are not significantly altered by the introduction of the open-shell part.

Moreover, it assumes the importance of the higher-order disconnected clusters as compared to the connected ones. Thus, for example, the triexcited component of the low-lying excited states is assumed to be reasonably well representable by the disconnected clusters of the W_1T_2 type, making thus the consideration of the connected W_3 clusters unnecessary. (Note that in the closed-shell ground state the importance of the connected and disconnected triexcited clusters is just reversed.[4]) Should the higher-excited connected clusters prove to be essential in a given open-shell state, the formalism offered here would become impractical, since a large number of diagrams would have to be considered (in fact, any presently known formalism becomes computationally very difficult in such a case). This also applies to the higher powers of t_i-matrix elements as mentioned earlier (cf. Sec. V).

The higher-excited connected clusters were indeed found to be small as compared with the disconnected ones in the cluster analysis of the full CI wave functions for several low-lying excited states of the PPP model of benzene.[27,29]

Moreover, in estimating the importance of various clusters we can again be guided by the lowest order of perturbation theory in which a given component contributes for the first time. We have summarized this information in Table II for both closed and open-shell low-order clusters. We recall, for example, that in the closed-shell case[4] the disconnected T_2^2 terms appear already in the second order of perturbation theory, while the connected tetraexcited term T_4 appears for the first time in the third order (cf. Table II). Likewise, the connected T_3 component appears in the second order while the most important disconnected component T_1T_2 appears only in the third order (cf. Fig. 2 of Ref. 4). Our case study of the BH_3 molecule[4] showed clearly that indeed the T_4 and T_1T_2 clusters (third-order appearance) were completely negligible with respect to the $\frac{1}{2}T_2^2$ and T_3 clusters (second-order appearance).[46]

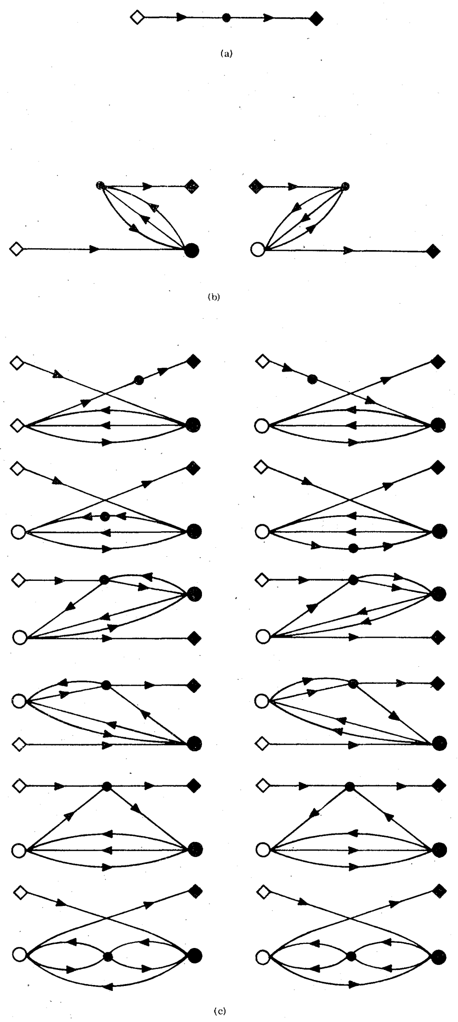

FIG. 5. Hugenholtz skeletons (diagrams) determining the H_{ij} matrix elements in Eqs. (18) and (19) for the ionization potential calculation in the approximation considering the zero-order terms in T_2 clusters (a), the first-order terms in T_2 or $\bar{T}_2$ (b), and bilinear terms in T_2 and $\bar{T}_2$ (c).

In the open-shell case we find that the W_1T_2 clusters appear already in the first order, while the W_3 clusters appear only in the second order.

In the closed-shell case by far the most important terms are, of course, the T_2 clusters. The next important contribution is due to the disconnected $\frac{1}{2}T_2^2$ clusters followed by T_3 and T_1 clusters (usually in this order, depending, of course, on the one-electron basis used). Thus the clusters, which contribute to the first two nonvanishing orders of the perturbation theory, yield a very good description of the correlation effects.[4,19-21]

For the open-shell case, the connected terms contribute already in the zeroth order so that, correspondingly, the disconnected clusters contribute already in the first order (cf. Table II). However, it is hoped that the clusters, which contribute in the first two nonvanishing orders of perturbation theory, should give again a reasonable description of the open-shell states involved. The pertinent clusters to be considered in this case are W_1, W_2, and W_1T_2 clusters. For the excitation energy calculations, these contributions require that 28 diagrams be considered, while the terms appearing in the next order of perturbation theory (i.e., clusters W_3, W_1T_1, $W_1T_2^2$, W_1T_3, and W_2T_2; cf. Table II) would require an additional 328 diagrams. However, the number of diagrams required increases much less drastically for the ionization potential or electron affinity calculations.

It is worth noting that by restricting ourselves to the $\hat{W}_1$ terms only, our problem reduces to a simple CI problem within the set of zero-order configurations (for example, in the case of excitation energy calculations, to the CI involving monoexcited configurations). Consequently, the presented approach may also be regarded as a "renormalized" CI calculation, in which the higher-excited configurations are represented by disconnected clusters. For example, triexcited configurations are represented by the W_1T_2 clusters. Since we are not interested in the energies of the highly excited states, but only in their effect on the low-lying states, their approximate representation by the disconnected components (involving, moreover, the ground-state pair clusters) should be satisfactory.

In a similar way we can easily see the relationship of the presented formalism with the Green's-function approach. This is particularly simple using the diagrammatic representation in both cases. The pertinent Green's-function formalism up to and including the third order of the perturbation theory was presented earlier.[28,47] To find the corresponding perturbation theory diagrams, which are accounted for in the coupled-cluster approach, we simply replace the T_i vertices by an appropriate set of perturbation theory diagrams, which in turn are simply obtained by iterating the basic coupled-cluster equations in the diagrammatic form (cf., for example, Refs. 2 and 11). Similarly, the W_0 vertices are replaced by appropriate open lines, characterizing the Green's-function diagrams, and the necessary number of interaction vertices (as follows from Table II). For the basic open-shell vertices shown in Figs. 1 and 2 these replacements are schematically illustrated in Fig. 6.

Thus each diagram of our coupled-cluster approach corresponds to a certain subset of the diagrams for the perturbative Green's-function

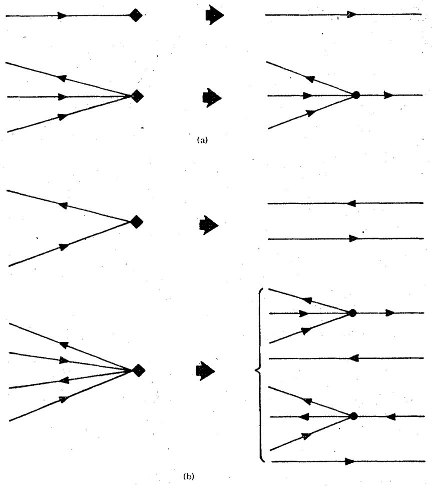

FIG. 6. Schematic representation of the relationship between the present theory and perturbative Green's-function approach. The indicated replacements yield the corresponding diagrams (skeletons) for the latter approach.

approach.[28] We easily find that, except for the time orderings of interaction vertices, we recover in this way all the third-order diagrams of the Green's-function approach[28] when using the diagrams shown in Fig. 5.

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APPENDIX A: ORTHOGONALITY CONDITION

We will show that we can always assume in our derivations that the state $|\Psi_\Gamma\rangle$, as defined by Eq. (4), is orthogonal to $|\Psi\rangle$.

Indeed, suppose that this is not the case, so that

$$\langle\Psi|\Psi_\Gamma\rangle = \langle\Psi|\hat{W}_\Gamma|\Psi\rangle \neq 0 . \tag{A1}$$

In such a case, we can remove the reference-(ground-) state component from $|\Psi_\Gamma\rangle$. Designating, thus, the orthogonalized state as $|\Psi'_\Gamma\rangle$,

$$|\Psi'_\Gamma\rangle = \hat{W}'_\Gamma|\Psi\rangle , \tag{A2}$$

where[48]

$$\hat{W}'_\Gamma = \lambda_\Gamma + \hat{W}_\Gamma , \tag{A3}$$

we find that $\langle\Psi'_\Gamma|\Psi\rangle = 0$ if

$$\lambda_\Gamma = -\langle\Psi|\Psi_\Gamma\rangle_{\mathcal{C}} , \tag{A4}$$

the subscript $\mathcal{C}$ designating again the connected component (cf. Sec. IV B), since

$$\langle\Psi|\hat{W}_\Gamma|\Psi\rangle = \langle\Psi|\Psi\rangle\langle\Psi|\hat{W}_\Gamma|\Psi\rangle_{\mathcal{C}} = \langle\Psi|\Psi\rangle\langle\Psi|\Psi_\Gamma\rangle_{\mathcal{C}} . \tag{A5}$$

We now calculate the energy mean value E_Γ,

$$E_\Gamma \equiv \langle\Psi'_\Gamma|\hat{H}_N|\Psi'_\Gamma\rangle\langle\Psi'_\Gamma|\Psi'_\Gamma\rangle^{-1} . \tag{A6}$$

Using the same technique as explained in Sec. IV B (cf. Figs. 3 and 4), we find

$$\langle\Psi'_\Gamma|\hat{H}_N|\Psi'_\Gamma\rangle = \langle\Psi|\hat{H}_N|\Psi\rangle_{\mathcal{C}}\langle\Psi|\Psi\rangle\,\mathcal{S} + \langle\Psi|\Psi\rangle\,\mathcal{H} \tag{A7}$$

and

$$\langle\Psi'_\Gamma|\Psi'_\Gamma\rangle = \langle\Psi|\Psi\rangle\,\mathcal{S} , \tag{A8}$$

where

$$\begin{aligned}\mathcal{H} = {} & \langle\Psi_\Gamma|\hat{H}_N|\Psi_\Gamma\rangle_{\mathcal{C}} \\ & + 2\mathrm{Re}\{\langle\Psi_\Gamma|\hat{H}_N|\Psi\rangle_{\mathcal{C}}(\lambda_\Gamma + \langle\Psi|\Psi_\Gamma\rangle_{\mathcal{C}})\} ,\end{aligned} \tag{A9}$$

and

$$\mathcal{S} = |\lambda + \langle\Psi|\Psi_\Gamma\rangle_{\mathcal{C}}|^2 + \langle\Psi_\Gamma|\Psi_\Gamma\rangle_{\mathcal{C}} . \tag{A10}$$

We thus get for the desired mean value, Eq. (A6),

$$E_\Gamma = \langle\Psi|H_N|\Psi\rangle_{\mathcal{C}} + \mathcal{H}/\mathcal{S} . \tag{A11}$$

The first term on the right-hand side gives the energy of the reference state E in view of Eq. (13).

Thus for the energy difference $\Delta E_\Gamma \equiv E_\Gamma - E$ we find

$$\Delta E_\Gamma = \mathcal{H}/\mathcal{S}. \tag{A12}$$

Substituting for λ_Γ from Eq. (A4) we get

$$\mathcal{H} = \langle\Psi_\Gamma|\hat{H}_N|\Psi_\Gamma\rangle_{\mathcal{C}} \tag{A13}$$

and

$$\mathcal{S} = \langle\Psi_\Gamma|\Psi_\Gamma\rangle_{\mathcal{C}} , \tag{A14}$$

so that finally

$$\Delta E_\Gamma = \langle\Psi_\Gamma|\hat{H}_N|\Psi_\Gamma\rangle_{\mathcal{C}}\langle\Psi_\Gamma|\Psi_\Gamma\rangle_{\mathcal{C}}^{-1} . \tag{A15}$$

This is, however, the same expression as Eq. (17) and our assertion is proved.

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[1] J. Čížek, J. Chem. Phys. 45, 4256 (1966) (paper I).

[2] J. Čížek, Adv. Chem. Phys. 14, 35 (1969) (paper II).

[3] J. Čížek and J. Paldus, Int. J. Quantum Chem. 5, 359 (1971) (paper III).

[4] J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A 5, 50 (1972) (paper IV).

[5] F. Coester, Nucl. Phys. 7, 421 (1958); F. Coester and H. Kümmel, Nucl. Phys. 17, 477 (1960); H. Kümmel, in *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic, New York, 1962), p. 265; J. da Providencia, Nucl. Phys. 61, 87 (1965).

[6] H. Kümmel, Nucl. Phys. A 176, 205 (1971); H. Kümmel and K. H. Lührmann, Nucl. Phys. A 191, 525 (1972); K. H. Lührmann and H. Kümmel, Nucl. Phys. A 194, 225 (1972).

[7] F. E. Harris, in *Electrons in Finite and Infinite Structures* (Proceedings of the NATO ASI in Gent, Belgium), edited by P. Phariseau and L. Scheire (Plenum, New York, 1977), p. 274.

[8] A. C. Hurley, *Electron Correlation in Small Molecules* (Academic, New York, 1977).

[9] P. Grange and J. Richert, The Correlated Many-Body Wave Function of Nuclear Systems (Laboratoire de Physique Nucléaire Théorique, Centre de Récherches Nucléaires de Strasbourg, France) (unpublished).

[10] B. H. Brandow, Adv. Quantum Chem. 10, 187 (1977).

[11] J. Paldus, J. Chem. Phys. 67, 303 (1977) (paper V).

[12] H. J. Monkhorst, Int. J. Quantum Chem. Suppl. 11, 421 (1977).

[13] T. P. Zivković and H. J. Monkhorst, Analytic Connection between Configuration-Interaction and Coupled-Cluster Solutions (Univ. of Utah) (unpublished).

[14] D. L. Freeman, Phys. Rev. B 15, 5512 (1977).

[15] D. L. Freeman, The Correlation Energy of the Two-Dimensional Electron Gas at Intermediate Densities (Univ. of Rhode Island) (unpublished).

[16] H. Kümmel, K. H. Lührmann, and J. G. Zabolitzky, Rep. Prog. Phys. (to be published).

[17] J. da Providência and C. M. Shakin, Phys. Rev. C 4, 1560 (1971); C 5, 53 (1972).

[18] J. G. Zabolitzky, Nucl. Phys. A 228, 272, 285 (1974); H. Kümmel and J. G. Zabolitzky, Phys. Rev. C 7, 547 (1973).

[19] J. Paldus and J. Čížek, in *Energy, Structure and Reactivity*, edited by D. W. Smith and W. B. McRae (Wiley, New York, 1973), p. 198.

[20] J. Paldus, B. G. Adams, and J. Čížek (unpublished).

[21] P. R. Taylor, G. B. Bacskay, N. S. Hush, and A. C. Hurley, Chem. Phys. Lett. 41, 444 (1976). These authors failed to notice our earlier and more thorough work (Ref. 4) concerning the same system.

[22] F. E. Harris and H. J. Monkhorst (private communication).

[23] J. Čížek, J. Ladik, and S. Suhai (private communication).

[24] D. J. Klein, J. Chem. Phys. 64, 4868 (1976), Mol. Phys. 31, 783, 811 (1976); D. J. Klein and M. A. García-Bach, J. Chem. Phys. 64, 4873 (1976); Mol. Phys. 31, 797 (1976).

[25] D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Mol. Phys. 30, 1861 (1975); 33, 955 (1977).

[26] R. Offermann, H. Kümmel, and E. Ey, Degenerate Many-Fermion Theory in exp *S*-Form I. General Formalism (Ruhr University, Bochum) (unpublished); R. Offermann, II. Comparison with Perturbation Theory (Ruhr University, Bochum) (unpublished).

[27] M. Saute, Docteur ès Sciences Thesis (University of Rheims, 1976).

[28] J. Paldus and J. Čížek, J. Chem. Phys. 60, 149 (1974), L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. 36, 205 (1977), and references therein.

[29] M. Saute (unpublished).

[30] We exploit here the convention by which the hole and particle states are labeled by subscripts and superscripts, respectively, a general state having then no labels (cf. Ref. 31).

[31] J. Paldus, B. G. Adams, and J. Čížek, Int. J. Quantum Chem. 11, 813, (1977).

[32] J. Paldus and J. Čížek, Adv. Quantum Chem. 9, 105 (1975).

[33] Let us recall (Refs. 1 and 2) that the skeletons, which are obtained by stripping off the free (Ref. 32) (i.e., summation) labels from the diagrams, are very convenient for the topological considerations determining the correct combinatorial factors involved. For the derivation of explicit algebraic expressions associated with diagrams, one can use either the Goldstone type diagrams (Ref. 1) or, better yet, one Goldstone version (any) for each Hugenholtz diagram (Refs. 2 and 11). These are sometimes referred to as Brandow (Ref. 34) diagrams (cf., for example, Appendix A of Ref. 11). The latter may also be conveniently coupled with the angular momentum diagrams when the spin-adapted form is desired (Ref. 11). In this paper we shall only use Hugenholtz diagrams, which are best suited for general considerations and afford the most economical representation. Moreover, it is straightforward to convert them into the Goldstone or Brandow diagrams.

[34] B. H. Brandow, Rev. Mod. Phys. 39, 771 (1967).

[35] B. G. Adams, J. Paldus, and J. Čížek, Int. J. Quantum Chem. 11, 849 (1977).

[36] Note that in the particle-hole formalism, using $|\Phi_0\rangle$ as the reference state, both $\hat{W}_\Gamma$ and $\exp(\hat{T})$ will be expressible as linear combinations of the products of creation operators only. Moreover, each term of $\exp(\hat{T})$ contains an even number of the creation operators with respect to $|\Phi_0\rangle$ [cf. Eq. (3)]. Thus $\hat{W}_\Gamma$ commutes with $\exp(\hat{T})$.

[37] Cf., for example, footnote 26 of Ref. 11.

[38] Following strictly our convention we should also enclose the two rectangles on the right-hand side of the equation in Fig. 3 in another dashed rectangle. In order to simplify our symbolic equations we will agree to delete these overall dashed rectangles enclosing the individual (necessarily disconnected) factors.

[39] A. P. Jucys, I. B. Levinson, and V. V. Vanagas, *Mathematical Apparatus of the Theory of Angular Momentum* (Institute of Physics and Mathematics of the Academy of Sciences of the Lithuanian S. S. R., Mintis, Vilnius, 1960), in Russian. English translations: (Israel Program for Scientific Translations, Jerusalem, 1962) and (Gordon and

Breach, New York, 1964); A. P. Jucys and A. A. Bandzaitis, *The Theory of Angular Momentum in Quantum Mechanics* (Institute of Physics and Mathematics of the Academy of Sciences of the Lithuanian S. S. R., Mintis, Vilnius, 1964), in Russian.

[40] E. El Baz and B. Castel, *Graphical Methods of Spin Algebras in Atomic, Nuclear and Particle Physics* (Dekker, New York, 1972).

[41] Note that the case involving an electron attachment (electron affinity calculation) is simply obtained by reversing the orientation of lines (time reversal).

[42] One can obtain these diagrams by eliminating the interaction (H) vertices from the diagrams of Fig. 5 and by excluding the equivalent diagrams from those so obtained.

[43] H. Primas, in *Modern Quantum Chemistry*, edited by O. Sinanoğlu (Academic, New York, 1965), Vol. II, p. 45.

[44] This very appropriate term was recently introduced by Pople (Ref. 45).

[45] J. A. Pople, R. Seeger, and R. Krishnan, Int. J. Quantum Chem. Suppl. 11, 149 (1977).

[46] Of course, it would be highly desirable to carry out a similar study for a number of other molecules, especially those containing several heavy atoms, and for larger than minimal basis sets, in order to determine the limits of accuracy for various truncated cluster expansions.

[47] This formulation pertained to the calculation of the excitation energies. The corresponding formalism for the ionization potentials and electron affinities is simply obtained from this more general formalism by deleting all but the self-energy diagrams (for more details, cf. Ref. 32).

[48] The scalar operators are simply designated by the appropriate scalar multiplying the identity operator.