PHYSICAL REVIEW A VOLUME 24, NUMBER 4 OCTOBER 1981

Coupled-cluster method for multideterminantal reference states

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(Received 27 April 1981)

A general coupled-cluster method valid for arbitrary multideterminantal reference states is formulated. The resulting cluster expansion for the wave function is a generalization of that introduced by Silverstone and Sinanoğlu and applied by Sinanoğlu and collaborators. The connected nature of the cluster operators and the effective interaction is proven in the case when the reference space is *complete*, i.e., is invariant under unitary transformations of partly occupied orbitals. For incomplete reference spaces the disconnected terms appearing in the effective interaction are properly generated by the coupled-cluster theory. Approximate schemes for solving coupled-cluster equations are proposed and their relation with perturbation theory is briefly discussed.

I. INTRODUCTION

It is well known that the formal solution to the closed-shell correlation problem can be obtained by using the complete configuration-interaction method. In this method the N-electron wave function Ψ is written in the form

$$\Psi=(1+C_1+C_2+\cdots+C_N)\Phi\ , \tag{1}$$

where C_n, $n=1,2,\ldots,N$, is a linear combination of all possible operators creating n-tuple excitations out of a closed-shell determinant Φ. The linear coefficients in C_n are determined from the variation principle which leads to the following equations for the operator $C=C_1+C_2\cdots+C_N$ and the energy E:

$$E=\langle\Phi\,|\,H(1+C)\Phi\rangle\ , \tag{2}$$

$$\langle\Phi^*\,|\,(H-E)(1+C)\Phi\rangle=0\ , \tag{3}$$

where Φ^* runs over all excited determinants. If the orbital basis set used to construct Φ and the excited determinants Φ^* were complete (i.e., infinite) then E would be the exact energy of the system. When this basis set is finite then Eqs. (2) and (3) may still provide us with a reasonable approximation to the exact energy provided that the dimension of the basis is large enough. Unfortunately, for such orbital basis sets and for systems with more than a few electrons, the number of variables in the system of algebraic equations (2) and (3) becomes enormous and these equations cannot be handled in practice. Some further approximations are clearly necessary, the simplest one consisting in limiting C to single and double excitations only. It is known, however, that such an approximation, albeit satisfactory for small N, becomes increasingly poorer with growing N.[1–3] This is due to the fact that the approximate energy is not size consistent.[4–6] For extended systems this would lead to correlation energies which are not proportional to N.[6,7] Addition of C_3 and C_4 does not help and, in general, there is no easy way of simplifying Eqs. (2) and (3) without losing the size-consistency property.

A general, formally appealing, and computationally practical solution to this problem is given by the coupled-cluster method.[8–10] If the wave function Ψ is written as[11]

$$\Psi=e^T\Phi\ , \tag{4}$$

where $T=\ln(1+C)$, then the equations for T

$$\langle\Phi^*\,|\,e^{-T}He^T\Phi\rangle=0 \tag{5}$$

can be simplified by arbitrary truncations of T without losing the size consistency of the resulting approximate energy

$$E=\langle\Phi|e^{-T}He^{T}\Phi\rangle\ . \tag{6}$$

In atomic and molecular physics the importance of using (4) was first recognized by Sinanoğlu,[12] while the explicit equations from which T can be calculated in practice were first derived by Čižek.[9] In fact, Eqs. (5) and (6) form a basis for almost all size-consistent approximate methods of studying correlation effects in closed-shell systems.[6,10,13,14] Because of the great success of these method in nuclear,[15] atomic,[16–19] molecular,[1–3,5,6,20–24] and electron-gas[25,26] applications, there has been considerable interest recently in generalizing Eqs. (5) and (6) to treat open-shell problems. The straightforward approach to write the open-shell wave function in the form of Eq. (4) with Φ being an open-shell determinant from a suitable degenerate reference space is possible[27] but leads to very complicated equations and correlation energies which are generally not invariant under the choice of Φ. The situation simplifies considerably when Φ is determined uniquely by symmetry or if Ψ is closely related to some closed-shell state Ψ_0. In the latter case one may write

$$\Psi=We^{T}\Phi\ , \tag{7}$$

where T is fixed by $\Psi_0=e^{T}\Phi$ and W is determined either from the Schrödinger equation[28] or by using the variation principle.[29] The open-shell coupled-cluster theory based on Eq. (7) is relatively simple since the same commutative operator algebra of particle-hole creation operators as in the closed-shell case can be utilized. However, the validity of the ansatz (7) is severely limited to situations in which a transition from Ψ_0 to Ψ does not lead to an extensive reconstruction of the wave function.[29] Moreover, since the operator W does contain disconnected terms, special care is needed to obtain size-consistent results.

A completely general, explicitly connected open-shell coupled-cluster theory has been proposed by Mukherjee *et al.*[30,31] in a series of papers started in 1975. These authors considered the wave operator U transforming a chosen multideterminantal reference space $\mathcal{M}_0$ onto the functional manifold spanned by the exact solutions of the Schrödinger equation. They assume that this operator can be represented in the exponential form

$$U=e^{T}P\ , \tag{8}$$

where P is the orthogonal projection on $\mathcal{M}_0$ and T is given by the second-quantized expression

$$T=t_r^{\alpha}a^{r}a_{\alpha}+\left[\frac{1}{2!}\right]^2 t_{rs}^{\alpha\beta}a^{r}a^{s}a_{\beta}a_{\alpha}+\cdots\ . \tag{9}$$

In Eq. (9) a^{κ} and a_{κ}, $\kappa=r,s,\alpha,\beta$, are the usual fermion creation and annihilation operators, $a^{\kappa}=a_{\kappa}^{\dagger}$, defined for the spin-orbital basis χ_{κ} used to construct the determinants of $\mathcal{M}_0$. The Einstein convention is employed in (9) and throughout the text, implying summation over repeated lower and upper indices. It is also assumed that the indices $\alpha,\beta,\ldots$ run over core and valence spin-orbitals, $r,s,\ldots$ over virtual and valence spin-orbitals, and the coefficients $t_{rs\ldots}^{\alpha\beta\cdots}$ are antisymmetric in their upper and lower indices. The terms carrying valence labels only are excluded from the summation. The core, valence, and virtual spin-orbitals are, by definition, occupied in all, some and none of the reference determinants, respectively. Equation (8) represents a reasonable generalization of Eq. (4). However, two new very important elements appear. Firstly, the operator algebra in which T is represented is not commutative since the valence particles can be created as well as annihilated in Eq. (9). Secondly, in sharp contrast to the closed-shell case, the operator T *is not* uniquely defined by Eqs. (8) and (9). To see this we note that if X is given by Eq. (9), with $t_r^{\alpha},t_{rs}^{\alpha\beta},\ldots$ replaced by $x_r^{\alpha}, x_{rs}^{\alpha\beta},\ldots$, then XP is not changed by the transformations like

$$\begin{aligned} x_r^{\alpha}&\rightarrow x_r^{\alpha}+mc_r^{\alpha}\ ,\\ x_{ri}^{\alpha i}&\rightarrow x_{ri}^{\alpha i}-c_r^{\alpha}\ , \end{aligned} \tag{10}$$

where i runs over all valence spin-orbitals, m is the number of valence electrons, and c_r^{α} are arbitrary constants. Thus, the equation $U=(1+X)P$ has infinitely many solutions for X. Since all X are nilpotent, the operators $T=\ln(1+X)$ exist and provide us with infinitely many solutions to the equation (8). In particular, the partitioning of T into one, two, and higher many-body components is not defined by Eq. (8) alone. We see that some additional conditions should be imposed on T to make it well defined. In their third paper[31] Mukherjee *et al.* must have realized that difficulty since they assumed that T must also satisfy

$$U^{(k)}=e^{T}P^{(k)},\quad k=0,1,2,\ldots,m-1 \tag{11}$$

where $P^{(k)}$ and $U^{(k)}$ are the appropriate projector and wave operator for the ionized system involving

only k valence electrons.[32] This means that T applies not only to all states from $\mathcal{M}_0$ but also to all singly, doubly, . . . , etc., ionized states that can be obtained from $\mathcal{M}_0$. It can be verified that Eqs. (8), (9), and (11) define T uniquely.

A different way of circumventing the problem of an ill-defined T has been chosen by Coester[33] and by Offermann, Ey and Kümmel.[34] These authors represented the Bloch wave operator[35,36] in the form

$$U=e^{S^{(0)}}e^{S^{(1)}}\cdots e^{S^{(m-1)}}(1+S^{(m)})P\ , \tag{12}$$

where $S^{(k)}$ are defined recursively by[34]

$$U^{(0)}=e^{S^{(0)}}P^{(0)} \tag{13}$$

and

$$U^{(k)}=e^{S^{(0)}}e^{S^{(1)}}\cdots e^{S^{(k-1)}}(1+S^{(k)})P^{(k)}\ , \tag{14}$$

for $k>0$. The operators $S^{(k)}$ are well defined since it is assumed that each term in the second-quantized expression for $S^{(k)}$ contains *exactly* k operators annihilating valence particles. It is interesting that the ansatz (12), although completely general, can be obtained from Eq. (8) if one assumes that

$$T=S^{(0)}+S^{(1)}+\cdots+S^{(m)}$$

and neglects both higher powers of $S^{(m)}$ and noncommutativity of $S^{(k)}$ operators.

Still another formulation of the open-shell coupled-cluster theory has been given by Lindgren.[37] He assumed that

$$U=\{e^{S}\}P\ , \tag{15}$$

where U is the Bloch wave operator, S is of the form of Eq. (9), and the curly brackets denote the normal product defined with respect to a certain reference or "vacuum" determinant apparently belonging to $\mathcal{M}_0$. The ansatz (15) does not define S properly since Lindgren's $\Omega=\{e^{S}\}$, satisfying $U=\Omega P$, is not defined uniquely by U and P [cf. the discussion around Eq. (10)]. It is not clear from Lindgren's work how he made S a well-defined operator, and, in particular, how he partitioned S into one, two, and higher many-body components. Using the normal ordering in the ansatz (15) leads to additional problems. The whole theory *is not* invariant under the arbitrary choice of a vacuum determinant and, moreover, the use of powerful Lie algebraic techniques[10] in developing coupled-cluster equations is not possible. The development of the theory relies then heavily on somewhat vague, graphical arguments.

All the general approaches discussed above share two common features: (i) the cluster operators T, $S^{(k)}$, or S are expanded in a noncommutative operator algebra, and (ii) these operators are ill defined unless we assume that they are universal in the sense that they represent also the wave operators for singly, doubly, etc., ionized states.[31]

In this paper we present another approach to the general multideterminantal coupled-cluster theory. In this approach the cluster operators are represented with commutative algebras and are uniquely defined by the N-electron wave operator U only. The coupled-cluster equations are derived using simple Lie-algebraic methods without involving any diagrammatic representation. They consist of the "direct part," which is the same as in the closed-shell theory, and a coupling term characteristic of the open-shell case. The coupling term generates the "folded" or "backwards" diagrams of the open-shell many-body perturbation theory.[38] Our method is independent of the partitioning $H=H_0+V$, but the connection with perturbation theory is as straightforward as in the closed-shell case. Both degenerate and quasidegenerate situations can be treated without any changes in the basic equations. In a particular case, our cluster ansatz leads to the cluster expansion for the open-shell wave function which has the same form as that proposed by Silverstone and Sinanoğlu[39] and used by Sinanoğlu and collaborators.[40]

The plan of this paper is as follows. In Sec. II we present a general derivation of the coupled-cluster ansatz and the basic equations for cluster operators. In Sec. III the connectedness of the cluster operators in the case of a "complete" reference space is proven. In Sec. IV an important case of an incomplete reference space is considered. It is shown, that, if necessary, our theory can generate disconnected contributions to the effective Hamiltonian. Section V contains a discussion of possible approximation schemes.

II. COUPLED-CLUSTER METHOD FOR A COMPLETE REFERENCE SPACE

Let us consider a set of N-electron Slater determinants Φ_μ, $\mu=1,2,\ldots,M$, constructed from $K+L$ orthonormal spin-orbitals χ_α in such a way that the first K spin-orbitals referred to as the core spin-orbitals are occupied in all Φ_μ and the last L, referred to as valence spin-orbitals, are occupied only in some of the Φ_μ. We assume that all distributions of $N-K$ "valence electrons" among L valence orbitals are allowed. This means that $M=L![(N-K)!(L-N+K)!]^{-1}$. The reference

space $\mathcal{M}_o$ spanned by all Φ_μ functions is then *complete*, i.e., is invariant under unitary transformations of valence orbitals. The requirement of the completeness of $\mathcal{M}_0$ in the above sense is essential but not indispensable, and we shall show later that it can be relaxed at the expense of admitting disconnected contributions to the effective Hamiltonian. The projection operators on $\mathcal{M}_0$ and on its orthogonal complement $\mathcal{M}_0^{\perp}$ are denoted by P and Q, respectively. We obviously have

$$P=\sum_\mu P_\mu \ , \tag{16}$$

where $P_\mu=|\Phi_\mu\rangle\langle\Phi_\mu|$. In Eq. (16) and in the ensuing text the summation indices μ, ν, λ range from 1 to M.

We assume that the orbitals χ_α are chosen in such a way that by diagonalizing the Hamiltonian H in $\mathcal{M}_0$ we obtain a reasonable zeroth-order approximation to some M exact eigenfunctions Ψ_μ and eigenvalues E_μ of H. This means that $\mathcal{M}_0$ is a reasonable zeroth-order approximation to the exact manifold $\mathcal{M}$ spanned by exact solutions to the Schrödinger equation

$$(H-E_\mu)\Psi_\mu=0 \ . \tag{17}$$

The coupled-cluster theory outlined in this section is aimed at providing a systematic way of improving this zeroth-order approximation by describing the electron correlation using two-, three-, and higher-electron cluster functions. The convergence of the resulting approximation scheme depends on the quality of the initial $\mathcal{M}_0$ but for the derivation of the basic formalism it is sufficient to assure only that no function from $\mathcal{M}$ is orthogonal to all of Φ_μ, i.e., that all functions

$$\tilde{\Phi}_\mu=P\Psi_\mu \tag{18}$$

are linearly independent. This means that P generates a one-to-one mapping from $\mathcal{M}$ to $\mathcal{M}_0$. The inverse of this mapping, acting from $\mathcal{M}_0$ to $\mathcal{M}$, will be denoted by U. We extend the domain of this mapping to the whole Hilbert space by requiring that U is a linear operator acting as zero on $\mathcal{M}_0^{\perp}$. More precisely, U is defined by

$$U\tilde{\Phi}_\mu=\Psi_\mu \tag{19}$$

and

$$UP=U \ . \tag{20}$$

Using Eqs. (19) and (20), it is easy to check that

$$PU=P \ , \tag{21}$$

$$U^2=U \ , \tag{22}$$

$$U\Psi_\mu=\Psi_\mu \ . \tag{23}$$

Equations (22) and (23) show that U is essentially a (nonorthogonal) projection on the exact manifold $\mathcal{M}$. This projection, usually referred to as the wave operator, has been introduced by Bloch[35] in the context of perturbation theory in which case it has a much simpler structure[41] than the usual orthogonal projection considered by Kato.[42] Using Eqs. (19), (20), (17), and (23) it is easy to see that

$$HU=UHU \ , \tag{24}$$

which is the basic equation from which U can be determined. Once U is known, Ψ_μ and E_μ can be obtained either by diagonalizing H in $\mathcal{M}$, which is now spanned by the functions

$$\tilde{\Psi}_\mu=U\Phi_\mu \tag{25}$$

or, simpler yet, by diagonalizing the effective Hamiltonian

$$H^{\text{eff}}=PHU \tag{26}$$

within the reference space $\mathcal{M}_0$:

$$H^{\text{eff}}\tilde{\Phi}_\mu=E_\mu\tilde{\Phi}_\mu \ . \tag{27}$$

To apply Eqs. (24), (26), and (27) in a many-body context, it is necessary to guess a suitable second-quantized representation for U. Since U can be written as

$$U=\sum_\mu |\tilde{\Psi}_\mu\rangle\langle\Phi_\mu| \ , \tag{28}$$

and since each $\tilde{\Psi}_\mu$ can be uniquely expanded in terms of single, double, etc., excitations from Φ_μ it is not difficult to see that U can be uniquely represented in the form

$$U=\sum_\mu (1+F^\mu)P_\mu \ , \tag{29}$$

where F^μ belongs to the commutative algebra τ_μ generated by those operators of the form $a^r a_\alpha$ for which α labels a spin-orbital occupied in Φ_μ and r labels a spin-orbital vacant in Φ_μ. F^μ can be thus expanded as

$$F^\mu=f_r^\alpha(\mu)a^r a_\alpha+\left[\frac{1}{2!}\right]^2 f_{rs}^{\alpha\beta}(\mu)a^r a^s a_\beta a_\alpha+\cdots \ , \tag{30}$$

where the coefficients $f_{rs\ldots}^{\alpha\beta\ldots}(\mu)$ are totally antisymmetric in α, β, . . . and r,s, . . . separately, and are nonzero only if χ_α, χ_β, . . . are occupied

and $\chi_r, \chi_s, \ldots$ are empty in Φ_μ. Because of the intermediate normalization

$$\langle \Phi_\mu | \tilde{\Psi}_\nu \rangle = \delta_{\mu\nu} \tag{31}$$

and the completeness of $\mathcal{M}_0$ all coefficients $f_{rs\ldots}^{\alpha\beta\ldots}(\mu)$ carrying valence labels only are equal to zero. In formula (30) and throughout the text the indices $\alpha,\beta,\alpha_1,\alpha_2, \ldots$ are used to label core and valence spin-orbitals and the indices $r,s,r_1,r_2, \ldots$ to label valence and virtual orbitals. In the following, the letters ρ,σ,τ will always label virtual orbitals, i,j,k,l— valence orbitals, and b,c,d—core orbitals only. The indices κ,ξ,ω,η will run over all single-particle states. It should be emphasized that all equations in this section are invariant under separate unitary transformations of core, valence, and virtual orbitals. Thus, these orbitals need not be specified in more detail now.

The f coefficients can be determined directly from Eq. (24). Inserting (29) into (24), multiplying by Φ_μ from the right, and projecting against a basis set in $\mathcal{M}_0^\perp$ one obtains

$$\langle \Phi^* | H(1+F^\mu)\Phi_\mu \rangle = \sum_\nu \langle \Phi^* | F^\nu \Phi_\nu \rangle \langle \Phi_\nu | H(1+F^\mu)\Phi^\mu \rangle , \tag{32}$$

where Φ^* runs over all determinants of the form

$$\Phi_{\alpha_1\cdots\alpha_n}^{r_1\cdots r_n}(\mu) = a^{r_1}\cdots a^{r_n} a_{\alpha_n}\cdots a_{\alpha_1}\Phi_\mu, \qquad n=1,2,\ldots,N \tag{33}$$

except those carrying valence labels only. When the F^μ operators are represented with Eq. (30), then Eq. (32) reduces to a system of coupled quadratic equations for the f coefficients. Assuming that $H=H_0+\zeta V$, where H_0 is a sum of one-electron operators, and solving this system of equations perturbatively around $\zeta=0$, it is easy to show that the second-order f coefficients contain disconnected contributions, i.e., contain terms which can be represented as products of two factors having no common indices. Graphically, such terms would be illustrated by disconnected diagrams. Consequently, there is a lot of cancellation of these disconnected terms in the evaluation of the matrix elements of H^{eff}. Equation (32) is equivalent to the complete CI calculations for all states in $\mathcal{M}$, and hence cannot be solved exactly. Moreover, the disconnected nature of F makes it very difficult to devise a sensible scheme to solve it in an approximate way. For example, neglecting the quadratic part of Eq. (32) or truncating F^μ to the one- and two-body part $F_1^\mu + F_2^\mu$ only would lead to a disconnected perturbation expansion for the matrix elements of H^{eff} and, consequently, to not-size-consistent energies. This difficulty may be overcome in exactly the same way as in the closed-shell theory, i.e., by reformulating the whole many-body theory such that only the logarithm of $1+F^\mu$ appears. Defining

$$T^\mu = \ln(1+F^\mu) = \sum_{m=1}^{N} \frac{(-1)^{m-1}}{m}(F^\mu)^m , \tag{34}$$

where the logarithm series is finite since all elements of τ_μ are nilpotent, we can replace Eq. (29) by

$$U = \sum_\mu e^{T^\mu} P_\mu . \tag{35}$$

Because of Eq. (34), T^μ takes on the same form as F^μ. In particular,

$$T^\mu = T_1^\mu + T_2^\mu + \cdots + T_N^\mu , \tag{36}$$

where

$$T_n^\mu = \left[\frac{1}{n!}\right]^2 t_{r_1\cdots r_n}^{\alpha_1\cdots\alpha_n}(\mu) a^{r_1}\cdots a^{r_n} a_{\alpha_n}\cdots a_{\alpha_1} . \tag{37}$$

Similarly, as in the case of the f coefficients, the t coefficients are antisymmetric and nonzero only if $\alpha_1,\ldots,\alpha_n$ label occupied and $r_1,\ldots,r_n$ unoccupied orbitals in Φ_μ. As a consequence of Eq. (31), a t coefficient is zero if all its indices correspond to valence orbitals. Since the relation between F^μ and T^μ is the same as in the closed-shell theory, the relation between cluster functions generated by F^μ and cluster functions generated by T^μ is the same, except for antisymmetrization, as the relation between moments and cumulants in the probability theory.[43]

The cluster ansatz (35) for U leads to the following cluster expansion for the exact wave function:

$$\Psi_\nu = \sum_\mu c_{\nu\mu} e^{T^\mu}\Phi_\mu , \tag{38}$$

where the coefficients $c_{\nu\mu}$ are obtained by diagonalizing the effective Hamiltonian H^{eff} of Eq. (26). In a particular case when the set of core orbitals is empty, $K=0, L=N$, the above expansion has the same form as the cluster expansion for the open-shell wave function proposed by Silverstone and Sinanoğlu.[39] It should be stressed, however, that the expansion (38) makes sense only if it applies simultaneously to all $\bar{M}$ wave functions from the exact manifold $\mathcal{M}$. Since the number of all t coefficients in (38) is about M times greater than the

dimension of the total N-electron Hilbert space, the T^{μ} operators and consequently the cluster functions generated by them cannot be uniquely determined from the knowledge of only one function Ψ_{ν}. Westhaus and Sinanoğlu[44] made an attempt to solve this problem in the case of a simpler linear cluster expansion for Ψ_{ν}. It is easy to see, however, that the action of their "model operator" Ω on the basic determinants D_L is not defined by their Eq. (36). Their cluster functions f remain then completely arbitrary. Sinanoğlu and collaborators[39,40] overcome this difficulty by introducing the "anonymous parentage" approximation, i.e., by assuming that T^{μ} is independent of μ.

The system of coupled equations for the cluster operators T^{μ} or the t coefficients can be derived easily by inserting Eq. (35) into Eq. (24), multiplying by Φ_{μ} from the right, by $e^{-T^{\mu}}$ from the left, and projecting against all functions from $\mathcal{M}_0^{\perp}$. The result is

$$\langle \Phi_{\alpha_1 \cdots \alpha_n}^{r_1 \cdots r_n}(\mu) \mid e^{-T^{\mu}} H e^{T^{\mu}} \Phi_{\mu} \rangle = \sum_{\lambda \neq \mu} H_{\lambda\mu}^{\text{eff}} \langle \Phi_{\alpha_1 \cdots \alpha_n}^{r_1 \cdots r_n}(\mu) \mid e^{-T^{\mu}} e^{T^{\lambda}} \Phi_{\lambda} \rangle , \quad (39)$$

where

$$H_{\nu\mu}^{\text{eff}} = \langle \Phi_{\nu} \mid e^{-T^{\mu}} H e^{T^{\mu}} \Phi_{\mu} \rangle \quad (40)$$

and $\Phi_{\alpha_1 \cdots \alpha_n}^{r_1 \cdots r_n}(\mu)$, $n = 1,2,\ldots,N$ are all determinants of the form of Eq. (33). In deriving Eq. (40) we made use of the fact that

$$(T^{\mu})^{\dagger} \Phi_{\nu} = 0 . \quad (41)$$

This is true only if the manifold $\mathcal{M}_0$ is complete. In such a case each term in (37) contains at least one core orbital annihilation operator or virtual orbital creation operator which makes Eq. (41) hold for each μ and ν.

When the cluster operators T^{μ} are represented by Eqs. (36) and (37), then Eqs. (39) and (40) reduce to a system of coupled nonlinear algebraic equations for the t coefficients. This system of equations is equivalent to complete CI calculations for all M states from $\mathcal{M}$ and, hence, is potentially exact. As we shall show in Sec. III, the virtue in using Eqs. (39) and (40) versus Eq. (32) lies in the fact that Eqs. (39) and (40) can be easily simplified by neglecting nonlinear terms and higher many-particle operators in (36) without introducing any disconnected contribution to H^{eff}, i.e., without making the approximate energy not size consistent.

When $N = K$ (closed-shell case) the manifold $\mathcal{M}_0$ is one dimensional and the right-hand side of Eq. (39) vanishes. Equation (39) reduces then to the well-known equations of the closed-shell coupled-cluster theory. The left-hand side of Eq. (39) is of the same form as in the closed-shell case and can be expanded using the techniques of Refs. 10 and 45. The right-hand side of Eq. (39) is characteristic of the multideterminantal reference state (open-shell) theory. It takes account of the coupling of T^{μ} operators with different μ, and, after perturbation expansion, leads to the so-called folded or backwards diagrams.[38] It should be mentioned, however, that for certain types of open-shell configurations this coupling may vanish due to symmetry. This takes place when $\mathcal{M}_0$ contains only one determinant corresponding to a given set of good quantum numbers. Such open-shell configurations have been recently considered from the point of view of diagrammatic perturbation theory by the Czechoslovak school.[46]

To end this section we would like to emphasize that for general open-shell configurations all basic determinants are treated in Eqs. (39) and (40) on an equal footing and neither of them is chosen as a distinguished vacuum state.

III. CONNECTEDNESS PROPERTY

In this section we shall show that the perturbation expansion for T^{μ} operators contains only connected terms. This means that only connected diagrams would appear if a diagrammatic representation for this expansion were invoked. The connectedness of T^{μ} guarantees the connectedness of the matrix elements of H^{eff} since $e^{-T^{\mu}} H e^{T^{\mu}}$ can be expanded as

$$e^{-T^{\mu}} H e^{T^{\mu}} = H + [H,T^{\mu}] + \frac{1}{2!}[[H,T^{\mu}],T^{\mu}] + \cdots , \quad (42)$$

and the commutator of two second-quantized operators may contain only connected terms. Analogously, the left-hand side of Eq. (39) is connected if T^{μ} is connected. Unfortunately, the coupling term on the right-hand side of Eq. (39) is not manifestly connected and, hence, the connectedness of T^{μ} requires a special proof.

To define the desired connected perturbation expansion for T^{μ} we have to partition H into a one-electron unperturbed operator H_0 and a perturbation V,

$$H = H_0 + V , \quad (43)$$

where

$$H_0=\epsilon_\kappa a^\kappa a_\kappa \ , \tag{44}$$

and V is expressed via antisymmetrized matrix elements of a two-body interaction V,

$$V=\tfrac{1}{4}v_{\kappa\omega}^{\xi\eta}a^\kappa a^\omega a_\eta a_\xi \ . \tag{45}$$

Equation (44) means that Φ_μ, $\mu=1,\ldots,M$ and all determinants of Eq. (33) are eigenfunctions of H_0. We assumed for simplicity that V is due to a two-body interaction only. If V also contained a one-particle screening, its effect could be included by appropriately redefining $v_{\kappa\omega}^{\xi\eta}$. To exclude a possibility of vanishing denominators we assume also that the energies of the core, valence, and virtual orbitals are such that the spectra of H_0 in $\mathcal{M}_0$ and $\mathcal{M}_0^\perp$ do not have common points. We do not have to assume that all valence orbitals have the same energy or that H_0 is degenerate in $\mathcal{M}_0$. This makes our method applicable to quasidegenerate problems or to systems with more than one open shell.

Inserting Eq. (43) into Eq. (39) one obtains

$$[(\epsilon_{r_1}+\cdots+\epsilon_{r_n})-(\epsilon_{\alpha_1}+\cdots+\epsilon_{\alpha_n})]t_{r_1\cdots r_n}^{\alpha_1\cdots\alpha_n}(\mu)+\langle\Phi_{\alpha_1\cdots\alpha_n}^{r_1\cdots r_n}(\mu)\,|\,e^{-T^\mu}Ve^{T^\mu}\Phi_\mu\rangle$$
$$=\sum_{\lambda\neq\mu}V_{\lambda\mu}^{\mathrm{eff}}\langle\Phi_{\alpha_1\cdots\alpha_n}^{r_1\cdots r_n}(\mu)\,|\,e^{-T^\mu}e^{T^\lambda}\Phi_\lambda\rangle \ , \tag{46}$$

where

$$V_{\nu\mu}^{\mathrm{eff}}=\langle\Phi_\nu\,|\,e^{-T^\mu}Ve^{T^\mu}\Phi_\mu\rangle \tag{47}$$

are the matrix elements of the effective interaction operator $V^{\mathrm{eff}}=PVU$. To derive Eq. (46) one has to make use of the fact that[45]

$$[H_0,T_n^\mu]=\left[\frac{1}{n!}\right]^2[(\epsilon_{r_1}+\cdots+\epsilon_{r_n})-(\epsilon_{\alpha_1}+\cdots+\epsilon_{\alpha_n})]t_{r_1\cdots r_n}^{\alpha_1\cdots\alpha_n}(\mu)a^{r_1}\cdots a^{r_n}a_{\alpha_n}\cdots a_{\alpha_1} \tag{48}$$

and

$$t_{r_1\cdots r_n}^{\alpha_1\cdots\alpha_n}(\mu)=\langle\Phi_{\alpha_1\cdots\alpha_n}^{r_1\cdots r_n}(\mu)\,|\,T^\mu\Phi_\mu\rangle \ . \tag{49}$$

The double and higher commutators with H_0 vanish since $[H_0,T^\mu]\in\tau_\mu$. Formula (47) shows that, if T^μ are connected, the matrix elements of V^{eff} have to be connected as well. For off-diagonal elements, however, a somewhat stronger result holds. If we assume that Φ_ν is obtained from Φ_μ replacing the spin-orbitals $\chi_i,\chi_j,\ldots$ by the spin-orbitals $\chi_k,\chi_l,\ldots$, i.e., $\Phi_\nu=\Omega_\mu^\nu\Phi_\mu$, where

$$\Omega_\mu^\nu=a^k a^l\cdots a_j a_i \ , \tag{50}$$

then for $\mu\neq\nu$ Eq. (47) can be rewritten as

$$V_{\nu\mu}^{\mathrm{eff}}=-\langle\Phi_\mu\,|\,[e^{-T^\mu}Ve^{T^\mu},a^i a^j\cdots a_l a_k]\Phi_\mu\rangle \ . \tag{51}$$

This shows that if T^μ are connected then the off-diagonal elements of V^{eff} are not only connected, but also each term in the connected expansion for $V_{\nu\mu}^{\mathrm{eff}}$ must contain *all* the indices $i,j,\ldots$ and $k,l,\ldots$. We shall say that $V_{\nu\mu}^{\mathrm{eff}}$ is connected with all valence spin-orbitals which distinguish Φ_ν and Φ_μ, i.e., which are occupied in Φ_ν and vacant in Φ_μ or vice versa. This property of $V_{\nu\mu}^{\mathrm{eff}}$ plays an important role in the proof of the connectedness of the coupling term in the right-hand side of Eq. (46).

Now, multiplying each of the equations (46) by

$$[(\epsilon_{r_1}+\cdots+\epsilon_{r_n})-(\epsilon_{\alpha_1}+\cdots+\epsilon_{\alpha_n})]^{-1}a^{r_1}\cdots a^{r_n}a_{\alpha_n}\cdots a_{\alpha_1}$$

and summing over all sets of indices $r_1\cdots r_n$ and $\alpha_1\cdots\alpha_n$ one obtains

$$T^\mu=\mathscr{R}^\mu(e^{-T^\mu}Ve^{T^\mu})-\sum_{\lambda\neq\mu}V_{\lambda\mu}^{\mathrm{eff}}\mathscr{R}^\mu(e^{-T^\mu}e^{T^\lambda}\Omega_\mu^\lambda) \ , \tag{52}$$

where Ω_μ^λ is defined as the only operator from τ_μ satisfying $\Phi_\lambda=\Omega_\mu^\lambda\Phi_\mu$, and

$$\mathscr{R}^\mu=\mathscr{R}_1^\mu+\mathscr{R}_2^\mu+\cdots+\mathscr{R}_N^\mu \tag{53}$$

is a superoperator playing the role of the reduced resolvent. For an arbitrary operator A the action of $\mathscr{R}_n^\mu$ is defined precisely as

$$\mathscr{R}_n^\mu(A)=\left[\frac{1}{n!}\right]^2\frac{\langle\Phi_\mu|a^{\alpha_1}\cdots a^{\alpha_n}a_{r_n}\cdots a_{r_1}QA\Phi_\mu\rangle}{\epsilon_{\alpha_1}+\cdots+\epsilon_{\alpha_n}-(\epsilon_{r_1}+\cdots+\epsilon_{r_n})}a^{r_1}\cdots a^{r_n}a_{\alpha_n}\cdots a_{\alpha_1}\,. \tag{54}$$

The projector $Q=1-P$ appears here in order to remove all terms corresponding to the excitations into the reference space, i.e., all terms carrying valence indices only. It may be shown that $X=\mathscr{R}^\mu(A)$ is the only operator from τ_μ satisfying the commutator equation $[X,H_0]=A$ and the condition $X\Phi_\mu\in\mathscr{M}_0^\perp$.

Equation (52) is a convenient starting point for deriving the perturbation expansion of T^μ. When V is parametrized as $V\to\zeta V$ then T^μ and $V_{\nu\mu}^{\rm eff}$ become functions of the variable ζ and these quantities can be expanded as

$$T^\mu=\sum_{m=1}^{\infty}\zeta^m\overset{(m)}{T}{}^\mu,\quad V_{\nu\mu}^{\rm eff}=\sum_{m=1}^{\infty}\zeta^m\overset{(m)}{V}{}_{\nu\mu}^{\rm eff}\,. \tag{55}$$

Inserting (55) into (52) and comparing coefficients at the same power of ζ we obtain recursive formulas for $T^{(m)\mu}$ and $V_{\nu\mu}^{(m)\rm eff}$. For $m=1$, 2, and 3 these formulas can be written in the following form:

$$\overset{(1)}{V}{}_{\nu\mu}^{\rm eff}=\langle\Phi_\nu|V\Phi_\mu\rangle\,, \tag{56}$$

$$\overset{(1)}{T}{}^\mu=\mathscr{R}^\mu(V)\,, \tag{57}$$

$$\overset{(2)}{V}{}_{\nu\mu}^{\rm eff}=\langle\Phi_\nu|[V,\overset{(1)}{T}{}^\mu]\Phi_\mu\rangle\,, \tag{58}$$

$$\overset{(2)}{T}{}^\mu=\mathscr{R}^\mu([V,\overset{(1)}{T}{}^\mu])-\sum_{\lambda\neq\mu}V_{\lambda\mu}\mathscr{R}^\mu((\overset{(1)}{T}{}^\lambda-\overset{(1)}{T}{}^\mu)\Omega_\mu^\lambda)\,, \tag{59}$$

$$\overset{(3)}{V}{}_{\nu\mu}^{\rm eff}=\langle\Phi_\nu|[V,\overset{(2)}{T}{}^\mu]\Phi_\mu\rangle+\tfrac{1}{2}\langle\Phi_\nu|[[V,\overset{(1)}{T}{}^\mu],\overset{(1)}{T}{}^\mu]\Phi_\mu\rangle\,, \tag{60}$$

and

$$\begin{aligned}\overset{(3)}{T}{}^\mu=&\mathscr{R}^\mu([V,\overset{(2)}{T}{}^\mu])+\tfrac{1}{2}\mathscr{R}^\mu([[V,\overset{(1)}{T}{}^\mu],\overset{(1)}{T}{}^\mu])-\sum_{\lambda\neq\mu}[\overset{(2)}{V}{}_{\lambda\mu}^{\rm eff}\mathscr{R}^\mu((\overset{(1)}{T}{}^\lambda-\overset{(1)}{T}{}^\mu)\Omega_\mu^\lambda)\\&+V_{\lambda\mu}\mathscr{R}^\mu(\{(\overset{(2)}{T}{}^\lambda-\overset{(2)}{T}{}^\mu)+\tfrac{1}{2}(\overset{(1)}{T}{}^\lambda-\overset{(1)}{T}{}^\mu)^2+\tfrac{1}{2}[\overset{(1)}{T}{}^\lambda,\overset{(1)}{T}{}^\mu]\}\Omega_\mu^\lambda)]\,.\end{aligned} \tag{61}$$

Let us examine in more detail the expressions for $T^{(1)\mu}$, $T^{(2)\mu}$, and $T^{(3)\mu}$. Using Eqs. (57) and (54) one obtains

$$\begin{aligned}\overset{(1)}{T}{}^\mu=&\frac{\langle\Phi_\mu|a^\alpha a_r QV\Phi_\mu\rangle}{\epsilon_\alpha-\epsilon_r}a^r a_\alpha\\&+\frac{1}{4}\frac{\langle\Phi_\mu|a^\alpha a^\beta a_s a_r QV\Phi_\mu\rangle}{\epsilon_\alpha+\epsilon_\beta-\epsilon_r-\epsilon_s}a^r a^s a_\beta a_\alpha\,,\end{aligned} \tag{62}$$

which shows that $T^{(1)\mu}$ is trivially connected. Assume now that $\Phi_\lambda=a^k a_i\Phi_\mu$. It is not difficult to see that the expression for $T^{(1)\mu}$ must be exactly the same as for $T^{(1)\lambda}$ except that the index i is everywhere replaced by k and vice versa. It must be so since the transposition $i\leftrightarrow k$ transforms Φ_μ into Φ_λ without changing the range of summations in Eq. (62). Symbolically, one may write

$$\overset{(1)}{T}{}^\lambda=\mathscr{P}_{ik}\overset{(1)}{T}{}^\mu\,, \tag{63}$$

where $\mathscr{P}_{ik}$ performs the transposition $i\leftrightarrow k$. One might also say that diagrams for $T^{(1)\lambda}$ could be obtained from diagrams for $T^{(1)\mu}$ by interchanging everywhere the valence line labels i and k. The relation (63) shows that all terms in $T^{(1)\lambda}$ and $T^{(1)\mu}$ which carry neither the label i nor the label k must be identical. Therefore, in calculating the difference $T^{(1)\lambda}-T^{(1)\mu}$, the only surviving terms are those carrying i, k, or both of these indices. Since $V_{\lambda\mu}$ depends on both i and k, the product $V_{\lambda\mu}(T^{(1)\lambda}-T^{(1)\mu})$ must be connected via these valence indices. Analogously, one may show that if Φ_λ is obtained from Φ_μ by a double or higher substitution, $\Omega_\mu^\lambda=a^k a^l\cdots a_j a_i$, then

$T^{(1)\lambda}=\mathscr{P}_{ik}\mathscr{P}_{jl}\cdots T^{(1)\mu}$ and $V_{\lambda\mu}$ is connected with $T^{(1)\lambda}-T^{(1)\mu}$ via at least one of the valence indices $i,j,\ldots$ and $k,l,\ldots$. Since the summation in Eq. (59) does not contain the diagonal term it is clear that $T^{(2)\mu}$ is connected. In view of Eq. (60) $V_{\nu\mu}^{(3)\text{eff}}$ must be connected as well.

To prove the connectedness of $T^{(3)\mu}$ it is enough to verify that $[T^{(1)\lambda},T^{(1)\mu}]$ and $T^{(2)\lambda}-T^{(2)\mu}$ are connected with $V_{\lambda\mu}$. For the commutator $[T^{(1)\lambda},T^{(1)\mu}]$ it must be so since the contraction[45] between $T^{(1)\lambda}$ and $T^{(1)\mu}$ can only be performed via valence indices which distinguish Φ_λ and Φ_μ. For example, if $\Omega_\mu^\lambda=a^k a_i$ then all terms in $T^{(1)\lambda}$ and $T^{(1)\mu}$ containing neither k nor i commute and do not contribute to $[T^{(1)\lambda},T^{(1)\mu}]$. To show that $T^{(2)\lambda}-T^{(2)\mu}$ is connected with $V_{\lambda\mu}$ we write $T^{(2)\mu}$ explicitly in the form

$$T^{(2)\mu}=T_1^{(2)\mu}+T_2^{(2)\mu}+T_3^{(2)\mu}, \tag{64}$$

where

$$T_n^{(2)\mu}=\left[\frac{1}{n!}\right]^2\frac{a^{r_1}\cdots a^{r_n}a_{\alpha_n}\cdots a_{\alpha_1}}{\epsilon_{\alpha_1}+\cdots+\epsilon_{\alpha_n}-(\epsilon_{r_1}+\cdots+\epsilon_{r_n})}$$
$$\times\left\{\langle\Phi_\mu|a^{\alpha_1}\cdots a^{\alpha_n}a_{r_n}\cdots a_{r_1}Q[V,T_1^{(1)\mu}]\Phi_\mu\rangle-\sum_\nu\langle\Phi_\mu|a^{\alpha_1}\cdots a^{\alpha_n}a_{r_n}\cdots a_{r_1}Q(T_1^{(1)\nu}-T_1^{(1)\mu})\Phi_\nu\rangle\langle\Phi_\nu|V\Phi_\mu\rangle\right\} \tag{65}$$

If $T^{(1)\lambda}$ is related to $T^{(1)\mu}$ via Eq. (63) and if $\mathscr{M}_0$ is complete (making the ν summation invariant under the unitary transformation $\chi_k\to\chi_i,\chi_i\to\chi_k$), then it is easy to see that the expression for $T^{(2)\lambda}$ can also be obtained from the expression for $T^{(2)\mu}$ by interchanging the indices i and k, i.e., $T^{(2)\lambda}=\mathscr{P}_{ik}T^{(2)\mu}$. The same argument as in the first order leads now to the conclusion that $T^{(2)\lambda}-T^{(2)\mu}$ must be connected with $V_{\lambda\mu}$. Thus, $T^{(3)\mu}$ and, as a consequence, $V_{\nu\mu}^{(4)\text{eff}}$ are shown to be connected.

In an inductive generalization of this argument to higher orders no new elements appear. Due to the Campbell-Baker-Hausdorff formula[47]

$$\ln(e^{-T^\mu}e^{T^\lambda})=T^\lambda-T^\mu+\tfrac{1}{2}[T^\lambda,T^\mu]+\tfrac{1}{12}[[T^\lambda,T^\mu],T^\mu]-\tfrac{1}{12}[[T^\lambda,T^\mu],T^\lambda]+\cdots . \tag{66}$$

$e^{-T^\mu}e^{T^\lambda}$ can be expressed as a polynomial in $T^\lambda-T^\mu$ and in commutators. The commutators are both explicitly connected and connected with $V_{\lambda\mu}^{\text{eff}}$. The difference $T^\lambda-T^\mu$ is connected with $V_{\lambda\mu}^{\text{eff}}$ because the relation (63) can easily be generalized by induction to arbitrarily higher order. Using the diagrammatic language one might say that, if $\Omega_\mu^\lambda=a^k a^l\cdots a_j a_i$, then the diagrams for T^λ can be obtained from the diagrams for T^μ by the following relabeling of the valence lines $i,k,j,l,\ldots\to k,i,l,j,\ldots$. In forming the difference $T^\lambda-T^\mu$ diagrams containing neither of these labels cancel out. This completes our proof of the connected nature of the perturbation expansions for T^μ and for the matrix elements of V^{eff}. The fact that the latter do not contain any disconnected terms has been observed for the first time by Brandow[38] and is usually referred to as the linked valence theorem.[34]

It is worthwhile to add here that the connectedness of T^μ operators guarantees the connected nature of all cluster functions entering the cluster expansion for open-shell wave function given by Eq. (38).

IV. COUPLED-CLUSTER METHOD FOR AN INCOMPLETE REFERENCE SPACE

If the valence spin-orbitals χ_i, $i=1,2,\ldots,L$, are not degenerate the spectrum of H_0 within the complete model space $\mathscr{M}_0$ consists of several energy levels distributed usually over a broad energy range. Under the influence of the perturbation ζV these energy levels split and evolve as complex curves $E_\mu(\zeta)$ defined by Eq. (17) in which H is replaced by $H_0+\zeta V$. Any branching of these curves among themselves does not affect the convergence of the perturbation expansion for V^{eff}. The convergence breaks down, however, when for $|\zeta|\le 1$ one of $E_\mu(\zeta)$ merges with the continuum or branches with a state not evolving from $\mathscr{M}_0$.[41,42] Such an external state destroying the convergence of the series (55) is usually referred to as an intruder state.[48] A likelihood of merging with the continuum or branching with an intruder state is considerably reduced by removing highly excited states from $\mathscr{M}_0$, i.e., by limiting $\mathscr{M}_0$ to one or very few suitably chosen eigenspaces of H_0. The simplest example of such a situation is given by the two

open shells built up from $1s$ and $2s$ spin-orbitals for the helium atom. The complete reference space consists then of six determinants corresponding to three configurations: $1s^2$, $1s\,2s$, and $2s^2$. Since the $2s^2$ state of He is autoionizing, the perturbation series for V^{eff} cannot be convergent in this case. After removing the $2s^2$ determinant from $\mathcal{M}_0$ the merging with the continuum does not occur and the perturbation expansion for V^{eff} may be expected to converge. We can also reject the $1s^2$ determinant and keep only four $1s\,2s$ determinants. The resulting incomplete reference space then becomes exactly degenerate. It should be emphasized that the problems of intruder states, noticed for the first time in nuclear physics, is equally severe in molecular quantum theory.[49] The well-known difficulties in constructing a satisfactorily convergent perturbation expansion for molecular interaction energies may be viewed as being also due to the appearance of intruder states.[50,51]

A diagrammatic many-body perturbation theory for an incomplete model space has been recently given by Hose and Kaldor.[52] Below we present a purely algebraic approach based on coupled-cluster ideas.

Let $\mathcal{M}_0$ now be an incomplete reference space spanned by M functions Φ_μ, $\mu=1,2,\ldots,M$. $\mathcal{M}_0$ can be extended to a complete reference space $\mathcal{M}_c$ by adding all determinants corresponding to missing occupancies of valence orbitals. The orthogonal complements of $\mathcal{M}_0$ and $\mathcal{M}_c$ will be denoted by $\mathcal{M}_0^\perp$ and $\mathcal{M}_c^\perp$. The projection operators on $\mathcal{M}_0$, $\mathcal{M}_c$, $\mathcal{M}_0^\perp$, and $\mathcal{M}_c^\perp$ will be denoted by P, P_c, Q, and Q_c, respectively. The wave operator U is defined by Eqs. (18)–(20) and maps $\mathcal{M}_0$ on the manifold $\mathcal{M}$ spanned by the exact solutions Ψ_μ, $\mu=1,2,\ldots,M$, to the Schrödinger equation (17). To derive a cluster expansion for U we have to examine the structure of the τ_μ algebras in some more detail. First we note that the bilinear form $B(T_1,T_2)=\langle T_1\Phi_\mu \mid T_2\Phi_\mu\rangle$ is a positive definite scalar product in τ_μ. Let $\mathcal{C}_\mu$ now be the subalgebra of τ_μ generated by all operators of the form $a^i a_j$, i.e., all operators carrying valence labels only. It can easily be shown that the orthogonal complement $\mathcal{C}_\mu^\perp$ is not only a subalgebra but also an ideal in τ_μ. We shall also consider the linear manifold $\tau_\mu^0 \subset \tau_\mu$ spanned by all operators producing excitations within $\mathcal{M}_0$. The incompleteness of $\mathcal{M}_0$ means that τ_μ^0 and $\mathcal{C}_\mu \ominus \tau_\mu^0$ are not closed under the multiplication operation, i.e., are not subalgebras of τ_μ.

The wave operator U can now be uniquely represented in the form

$$U=\sum_\mu (1+G^\mu+F^\mu)P_\mu \,, \tag{67}$$

where $G^\mu \in \mathcal{C}_\mu \ominus \tau_\mu^0$ and $F^\mu \in \mathcal{C}_\mu^\perp$. It is seen that G^μ and F^μ produce excitations into $\mathcal{M}_c \ominus \mathcal{M}_0$ and $\mathcal{M}_c^\perp$, respectively. If $\mathcal{M}_0$ were complete, G^μ would vanish and (67) would reduce to (29). In full analogy with Eq. (35) each term in Eq. (67) can be represented as $\exp(X^\mu)P_\mu$, where $X^\mu=\ln(1+G^\mu+F^\mu)$. However, since $\mathcal{C}_\mu \ominus \tau_\mu^0$ is not a subalgebra of τ_μ the expansion of the logarithm produces terms belonging to τ_μ^0 and, consequently, X^μ must be written as

$$X^\mu=W^\mu+S^\mu+T^\mu \,, \tag{68}$$

where $W^\mu \in \tau_\mu^0$, $S^\mu \in \mathcal{C}_\mu \ominus \tau_\mu^0$, and $T^\mu \in \mathcal{C}_\mu^\perp$. Thus, as a result of the incompleteness of $\mathcal{M}_0$ the cluster operators X^μ contain a component producing excitations within the reference space. Moreover, this component has a purely *disconnected* character, i.e., consists of disconnected terms only. To prove this we note that

$$\mathcal{P}_0^\mu(e^{W^\mu+S^\mu}-1)=0 \,, \tag{69}$$

where $\mathcal{P}_0^\mu$ is the superoperator of the orthogonal projection on τ_μ^0 [the operator T^μ does not enter Eq. (69) since $\mathcal{C}_\mu^\perp$ is an ideal in τ_μ]. Expressing W^μ and S^μ in terms of one-, two-, and higher many-particle operators

$$\begin{aligned} W^\mu &= W_1^\mu + W_2^\mu + \cdots \,, \\ S^\mu &= S_1^\mu + S_2^\mu + \cdots \,, \end{aligned} \tag{70}$$

and using Eq. (69) one obtains

$$W_1^\mu = 0 \,, \tag{71}$$

$$W_2^\mu = -\tfrac{1}{2}\mathcal{P}_0^\mu(S_1^\mu S_1^\mu) \,, \tag{72}$$

$$W_3^\mu = -\mathcal{P}_0^\mu(S_1^\mu S_2^\mu)+\tfrac{1}{2}\mathcal{P}_0^\mu[S_1^\mu \mathcal{P}_0(S_1^\mu S_1^\mu)] - \tfrac{1}{6}\mathcal{P}_0^\mu(S_1^\mu S_1^\mu S_1^\mu) \,. \tag{73}$$

The above equations demonstrate that W^μ contains exclusively disconnected terms. If X^μ operators are determined from Eqs. (24) and (69), then the disconnected terms in W^μ produce disconnected terms in S^μ, T^μ, and in $V_{\nu\mu}^{\text{eff}}$. Moreover, since $(X^\mu)^\dagger \Phi_\nu$ is generally nonvanishing for $\mu \neq \nu$, the off-diagonal matrix elements of V^{eff} cannot be expressed via commutators only. This produces some additional disconnected terms appearing for the first time in $V_{\nu\mu}^{(2)\text{eff}}$. Nevertheless, the disconnected terms represent only a small fraction of all

terms contributing to S^μ, T^μ, or $V_{\nu\mu}^{\text{eff}}$ and it would be desirable to have a theory which could produce the connected terms directly without performing complicated cancellations. Such a theory could be based on Eqs. (68)–(73) but we found it practically more convenient to start with the following ansatz:

$$U=\sum_\mu (1+G^\mu)e^{T^\mu}P_\mu \ , \tag{74}$$

where $G^\mu \in \mathscr{C}_\mu \ominus \tau_\mu^0$ and $T^\mu \in \mathscr{C}_\mu^\perp$. This form of U is entirely general since G^μ is the same as in Eq. (67) and $\Gamma^\mu=\ln[1+(1+G^\mu)^{-1}F^\mu]$. The nonexponential part of (74) will produce disconnected terms which must anyway appear in V^{eff}. It is interesting that (74) results directly from Eqs. (69)–(72) if $\mathscr{M}_0$ is the exact degenerate manifold spanned by the four determinants obtained by a single excitation from a doubly-occupied orbital ϕ_i to an unoccupied nondegenerate orbital ϕ_k. In this case $S^\mu=S\{^\mu$ and, consequently, $\mathscr{P}_0^\mu(S\{^\mu S\{^\mu) = S\{^\mu S\{^\mu$. The cluster operator X^μ now takes the form

$$X^\mu=-\tfrac{1}{2}S\{^\mu S\{^\mu+S\{^\mu+T^\mu=\ln(1+S\{^\mu)+T^\mu \ , \tag{75}$$

and $\exp(X^\mu)$ reduces to $(1+S^\mu)\exp(T^\mu)$.

General equations for G^μ and T^μ can be derived in essentially the same way as Eqs. (52) and (47). Inserting (74) into (24), applying Eqs. (42)–(44), and making use of the fact that $\mathscr{C}_\mu$ is a subalgebra and $\mathscr{C}_\mu^\perp$ an ideal in τ_μ, one obtains

$$G^\mu=\mathscr{R}_0^\mu(e^{-T^\mu}Ve^{T^\mu}(1+G^\mu)) - \sum_\lambda \mathscr{R}_0^\mu(e^{-T^\mu}e^{T^\lambda}(1+G^\lambda)\Omega_\mu^\lambda V_{\lambda\mu}^{\text{eff}} \ , \tag{76}$$

$$T^\mu=\mathscr{R}^\mu((1+G^\mu)^{-1}e^{-T^\mu}Ve^{T^\mu}(1+G^\mu)) - \sum_{\lambda\neq\mu} \mathscr{R}^\mu((1+G^\mu)^{-1}e^{-T^\mu}e^{T^\lambda}(1+G^\lambda)\Omega_\mu^\lambda)V_{\lambda\mu}^{\text{eff}} \ , \tag{77}$$

and

$$V_{\nu\mu}^{\text{eff}}=\langle \Phi_\nu \mid e^{-T^\mu}Ve^{T^\mu}(1+G^\mu)\Phi_\mu\rangle \ , \tag{78}$$

where $\mathscr{R}_0^\mu$ and $\mathscr{R}^\mu$ are superoperators playing the role of the reduced resolvent and defined by Eqs. (53) and (54), except that Q must now be replaced by P_c-P and Q_c, respectively. It should be noted that $V_{\nu\mu}^{\text{eff}}$ cannot be expressed solely via commutators since $(G^\mu)^\dagger\Phi_\nu$ is not generally equal to zero. Equations (76)–(78) are written in such a form that the perturbation expansion of G^μ, T^μ, and $V_{\nu\mu}^{\text{eff}}$ is straightforward.

When $\mathscr{M}_0$ is complete, $G^\mu=0$ and Eqs. (77) and (78) reduce to Eqs. (52) and (47), respectively. Thus, all automatic cancellations of disconnected terms characteristic of Eqs. (52) and (47) are also taken into account in Eqs. (76)–(78). The disconnected terms, due to G^μ, appear for the first time in off-diagonal matrix elements of $V^{(2)\text{eff}}$. The operators $G^{(2)\mu}$ and $T^{(2)\mu}$ contain also, in general, disconnected terms. One may ask if V^{eff} can be entirely connected for some incomplete reference spaces. This is probably the case if $\mathscr{M}_0$ is exactly degenerate and if the degeneracy of valence spin-orbitals is not accidental. Additional cancellations of disconnected terms are then possible due to (i) equality of certain energy denominators, and (ii) symmetry relations between the integrals $v_{\kappa\omega}^{\xi\theta}$. It can easily be shown that due to (i) the disconnected terms in $V_{\nu\mu}^{(2)\text{eff}}$ cancel out and $V_{\nu\mu}^{(2)\text{eff}}$ becomes entirely connected for any exactly degenerate $\mathscr{M}_0$. In general, however, (i) is not sufficient to eliminate disconnected terms from $V_{\nu\mu}^{(3)\text{eff}}$ and one must invoke (ii) to perform further cancellations. This can be illustrated by the following example. Let $\mathscr{M}_0$ consist of four degenerate triplet ($S=1, M_S=1$) determinants $\Phi_1=a^1a^4\Phi_0$ $\Phi_2=a^2a^3\Phi_0$, $\Phi_3=a^1a^3\Phi_0$, and $\Phi_4=a^2a^4\Phi_0$ built of a core state Φ_0 and a set of four valence spin-orbitals with spins up and energies $\epsilon_1=\epsilon_2$ and $\epsilon_3=\epsilon_4$. It is easy to see then that $G^\mu=G\{^\mu$ and that $V_{21}^{(3)\text{eff}}$ contains the following contribution originating from $\langle\Phi_2 \mid VG^{(2)1}\Phi_1\rangle$:

$$\frac{1}{(\epsilon_1-\epsilon_3)^2}v_{3b}^{1b}v_{2c}^{4c}(v_{1d}^{1d}+v_{4d}^{4d}-v_{2d}^{2d}-v_{3d}^{3d}) \ , \tag{79}$$

where the summation over core spin-orbitals is implicit. This expression is evidently disconnected and enters $V_{21}^{(3)\text{eff}}$ unless the degeneracy of valence orbitals is not accidental and the integrals in parentheses cancel each other by symmetry. The above example shows that a demonstration of the connectedness of $V_{\nu\mu}^{\text{eff}}$ for an exactly degenerate incomplete $\mathscr{M}_0$ is generally not simple and requires a consideration of symmetries underlying the existing degeneracy. This observation seems to be in disagreement with the conclusion reached by Hose and Kaldor[52] who constructed a diagrammatic expansion for the Bloch wave operator U and the effective interaction $V^{\text{eff}}=PVU$.

It should be added here that the Bloch V^{eff} is only one of many effective interactions proposed in the literature.[53] These effective interactions may be viewed as various[54] methods to make the Bloch V^{eff} Hermitian, and may lead in some cases to less

disconnected expansions. To the authors' knowledge, however, for a general quasidegenerate incomplete reference space the disconnected terms cannot be entirely removed from the effective interaction.

V. APPROXIMATION SCHEMES

The equations (47) and (52), or (76) and (77), form a system of extraordinarily complicated, highly nonlinear algebraic equations for the t coefficients. They can be applied in practice only if one simplifies them in some sensible way. Three kinds of simplifications are particularly natural and suggest themselves. Firstly, one can calculate V^{eff} perturbatively through some low order in ζV and improve the results using a suitable Padé approximant.[55] Secondly, one may neglect higher powers of T^{μ} and keep only linear or possibly also quadratic terms in T^{μ}. This leads to the linear and the quadratic coupled-cluster methods. Thirdly, we may truncate the second-quantized expression for T^{μ} neglecting higher many-particle operators in Eq. (36). Obviously, these three kinds of approximations are interrelated and, particularly the last two, should be applied simultaneously. In the following discussion we shall assume for simplicity that the reference space $\mathcal{M}_0$ is complete. The effective interaction through the third order is given then by Eqs. (56)–(60). These equations can further be expanded in terms of spin-orbitals using the technique described in detail in Ref. 56. If for $0 \le \zeta \le 1$ the states from $\mathcal{M}$ are well separated energetically from the rest of the spectrum, the perturbation theory is expected to converge fast and the third-order treatment should be accurate enough. The example of the C^{2+} ion shows that the convergence may be much better than in the closed-shell case and even $V + V^{(2)\text{eff}}$ may give quite reasonable results.[57] This is due to the fact that the $2s^2$-$2p^2$ quasidegeneracy spoiling the convergence in the closed-shell case is not harmful in two-open-shell calculations. When for $0 \le \zeta \le 1$ the states from $\mathcal{M}$ are not well separated energetically from the rest of the spectrum, the order by order treatment is not expected to be convergent and some nonperturbative approach must be found. Such an approach can be obtained by linearizing Eq. (52). The resulting linear approximation to Eq. (52) is

$$T^{\mu} = \mathcal{R}^{\mu}(V) + \mathcal{R}^{\mu}([V,T^{\mu}]) - \sum_{\lambda \neq \mu} V_{\lambda\mu} \mathcal{R}^{\mu}((T^{\lambda} - T^{\mu})\Omega_{\mu}^{\lambda}) \, . \tag{80}$$

If V^{eff} is now calculated from the formula

$$V_{\nu\mu}^{\text{eff}} = V_{\nu\mu} + \langle \Phi_{\nu} | \{ [V,T^{\mu}] + \tfrac{1}{2}[[V,T^{\mu}],T^{\mu}] \} \Phi_{\mu} \rangle \, , \tag{81}$$

then it is easy to check that the energies calculated from Eqs. (80) and (81) differ from the exact energies by terms of the fourth order in ζV. Solving Eqs. (80) and (81) may also be interpreted as a summation of certain classes of diagrams up to infinite order in ζV. The linear coupled-cluster theory is known to be accurate in the closed-shell case[3] except when a considered state is quasidegenerate.[17,23] When this quasidegeneracy is taken into account by a proper choice of the reference space then the linear coupled-cluster method is expected to be quite accurate also for closed-shell states. When the accuracy of Eqs. (80) and (81) is not sufficient, the quadratic term

$$\begin{aligned} &\tfrac{1}{2}\mathcal{R}^{\mu}([[V,T^{\mu}],T^{\mu}]) \\ &\quad - \tfrac{1}{2} \sum_{\lambda \neq \mu} V_{\lambda\mu} \mathcal{R}^{\mu}(\{ (T^{\lambda} - T^{\mu})^2 + [T^{\lambda},T^{\mu}] \} \Omega_{\mu}^{\lambda}) \\ &\quad - \sum_{\lambda \neq \mu} \langle \Phi_{\lambda} | [V,T^{\mu}] \Phi_{\mu} \rangle \mathcal{R}^{\mu}((T^{\lambda} - T^{\mu})\Omega_{\mu}^{\lambda}) \end{aligned} \tag{82}$$

must be added to (80) and the effective interaction should be calculated from Eq. (47) expanded through terms cubic in T^{μ}. It can easily be checked that the energies obtained from such a quadratic coupled-cluster theory have an error of the fifth order in ζV. Obviously, the linear or quadratic coupled-cluster equations cannot be solved exactly since T^{μ} satisfying Eq. (80) contains all n-body contributions up to $n = N$. Further approximations involving a truncation of the second-quantized expression for T^{μ} are clearly necessary. Such a truncation is, however, not as obvious as in the closed-shell case since now there is no unambiguous relation between the cluster size and the multiplicity of the excitation produced by a cluster operator. For example, only the operators of the form $a^{\rho}a^{\sigma}a_{\beta}a_{\alpha}$ produce genuine double excitations. The operators of the form $a^{\sigma}a^{i}a_{j}a_{\alpha}$ produce single excitations from $\mathcal{M}_0$ and the operators $a^{k}a^{l}a_{j}a_{i}$ do not produce excitations at all. The set of single excitations from $\mathcal{M}_0$ is defined as a subset of functions from $\mathcal{M}_0^{\perp}$ that can be obtained by replacing a single spin-orbital in one of the Φ_{μ} functions. The linear space spanned by all these single excitations will be denoted by $\mathcal{M}_1$. The subspace of double excitations $\mathcal{M}_2$ is defined analogously as a subspace

of $\mathcal{M}_0^{\perp}\ominus\mathcal{M}_1$ spanned by all determinants that can be obtained by double substitutions from the determinants of $\mathcal{M}_0$. The triple and higher excitation subspaces $\mathcal{M}_3$, $\mathcal{M}_4$, etc., are defined recursively in the same way. The n-body part of T^{μ} can now be decomposed as

$$T_n^{\mu}={}_1T_n^{\mu}+{}_2T_n^{\mu}+\cdots+{}_nT_n^{\mu}\ , \tag{83}$$

where ${}_mT_n^{\mu}$ produces m-fold excitations, i.e., ${}_mT_n^{\mu}\Phi_{\mu}\in\mathcal{M}_m$. It should be remarked here that also in the coupled-cluster theories of Mukherjee *et al.*,[30] of Offermann *et al.*,[34] and of Lindgren[37] the n-body part of cluster operators produces all excitations up to the n-tuple ones. Because of the computational convenience each ${}_mT_n^{\mu}$ can be further divided into internal, all-external and partly external (semi-internal) components.[39,40] The excitation produced by $a^{r_1}\cdots a^{r_n}a_{a_m}\cdots a_{a_1}$ is internal if $r_1,\ldots,r_n$ are exclusively valence labels, is all-external if $r_1,\ldots,r_n$ are exclusively virtual labels, and is partly external if the set $r_1,\ldots,r_n$ is a mixture of valence and virtual labels. For example, in the two-body case $a^ia^ja_ca_b$ is internal, $a^pa^qa_{\beta}a_{\alpha}$ is external, and $a^qa^ia_ca_b$ is a partly external (semi-internal) component of ${}_2T_2^{\mu}$. The all-external excitations are most difficult to take into account because their number is the greatest.

By inspecting Eqs. (56)–(61) it is easy to see that

$$T^{\mu}=\overset{(1)}{T}{}_1^{\mu}+\overset{(1)}{T}{}_2^{\mu},\quad T^{\mu}=\overset{(2)}{T}{}_1^{\mu}+\overset{(2)}{T}{}_2^{\mu}+\overset{(2)}{T}{}_3^{\mu}\ ,$$

but $T^{(3)\mu}$ contains also a five-body contribution. This five-body contribution produces, however, only triple excitations and, in general, one can show that $T^{(n)\mu}$ may produce only up to $(n+1)$-tuple excitations.

Using Eqs. (56)–(61) it is easy to prove that the linear coupled-cluster method is accurate through the second order in ζV if T^{μ} is assumed to consist of only one- and two-body operators. To obtain a method accurate through the third order one must add the three-body single and double excitations, i.e., assume that

$$T^{\mu}={}_1T_1^{\mu}+{}_1T_2^{\mu}+{}_1T_3^{\mu}+{}_2T_2^{\mu}+{}_2T_3^{\mu}\ . \tag{84}$$

It is seen that all-external three-body operators do not appear in Eq. (84). Thus, the number of linear coefficients present in (84) increases only quadratically with the dimension of the virtual space and calculations based on Eq. (84), and (80) should be feasible in practice.

Another significant simplification of the coupled-cluster equations is obtained if one assumes that the coefficients $t_{rs\ldots}^{\alpha\beta\ldots}(\mu)$ are independent of μ for some or for all values of the indices $\alpha,r,\beta,s,\ldots$ ("anonymous parentage" approximation). This approximation is a drastic one, however, since, in general, the resulting energy is not accurate even through the second order in ζV. An approximate coupled-cluster method based on a variant of the anonymous parentage approximation combined with the complete neglect of the internal and semi-internal excitations has been recently considered in the literature[58] and applied.[59]

ACKNOWLEDGMENTS

The authors are indebted to Dr. Baird Brandow, to Professor Frank Harris, and to Professor Herman Kümmel for critically reading and commenting on the manuscript. One of them (B. J.) wishes to thank Professor Jiři Čižek and Professor Joseph Paldus for stimulating discussions during this author's visit to Waterloo. This work was supported in part by NSF Grant No. CHE 79006129 and by the Polish Academy of Sciences within the project MR-I.9.

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