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Correlation Problems in Atomic and Molecular Systems. IV. Extended Coupled-Pair Many-Electron Theory and Its Application to the BH_3 Molecule

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The equations of the coupled-pair many-electron theory (CPMET) are extended to incorporate the effect of both unlinked and linked triexcited clusters. The minimal basis correlation energy of the BH_3 molecule in the ground state is calculated using the ordinary as well as extended CPMET in various degrees of approximation, and the relative importance of linked and unlinked triexcited clusters is studied. The results afford an unambiguous conclusion for closed-shell systems that, in contrast to the situation with tetraexcited states, unlinked triexcited clusters are negligible relative to the linked ones. It is shown that the extended CPMET reproduces the full configuration-interaction results to a very high degree of accuracy.

I. INTRODUCTION

The treatment of electronic correlation, in order to account for the inadequacies of the independent-particle model, has long ago been recognized as a central problem in atomic and molecular electronic structure calculations. Consequently this problem has been studied very extensively during the past two decades with various degrees of success. A rather extensive review of the past achievements may be found in Ref. 1 and in Sinanoğlu and Brueckner.[2] The need for a reliable, yet simple and feasible, treatment of the correlation problem is becoming even more acute, since calculations closely approaching the Hartree-Fock limit are becoming feasible for larger and larger atomic and molecular systems.

The methods for calculating correlation effects may be roughly divided into two basic categories, viz., variational and nonvariational, even though in some cases it may be difficult to draw this line unambiguously.

Perhaps the most commonly used variational method, which may, in principle, yield the exact result, is the method of configuration interaction (CI). The capabilities of this method have recently been extended considerably by improvements in analytical and computational techniques, such as the development of effective algorithms for finding eigenvalues and eigenvectors of large sparse matrices,[3] so that the handling of over 10^4 configurations is now feasible.[4] Unfortunately it is relatively difficult to implement various approximations and plausible physical assumptions in this method. Nevertheless, owing to its conceptual simplicity, and to the fact that in the limit it tends to the exact result, the CI method represents a basic "common denominator" for the comparison of other orbital theories.

Furthermore, for small or model systems, where full CI calculations are feasible, it enables one to obtain the exact result within the subspace of the N-electronic Fock space, spanned by a given set of basis functions. Such results are very useful from the methodical point of view, since they can serve as a convenient reference point for the testing of various approximate methods within the same subspace, and thus make it possible, at least in the first stage, to avoid very extensive and time-consuming computations. This is also one of the reasons why we have chosen the BH_3 molecule for our study, since the full CI treatment within the minimal Slater basis set has been carried out for this molecule by Pipano and Shavitt.[5]

The best-known nonvariational methods are various forms of perturbation theory. The most successful and systematic in this respect is the work of Kelly.[6]

Finally, there is a group of methods, which are neither variational nor perturbational, even though they may possess some features of both. These methods, introduced by Sinanoğlu[7(a)] and others, proved to be very promising; they are based on the cluster expansion of the exact wave function $|\Psi\rangle$, which may be conveniently expressed as

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle , \quad \langle\Phi_0|\Phi_0\rangle = \langle\Phi_0|\Psi\rangle = 1 . \tag{1}$$

Here $|\Phi_0\rangle$ represents the ground-state independent-particle model wave function, and a closed-shell $N=2n$ electronic system is implicitly assumed. The operator $\hat{T}$ has the form

$$\hat{T} = \sum_{i=1}^{N} \hat{T}_i , \tag{2}$$

where the i-particle excitation operator $\hat{T}_i$ represents all possible linked i-fold excitations, and may be conveniently written in the second quantized form

$$\hat{T}_i = (1/i\,!) \sum_{\substack{A_1'',\ldots,A_i'' \\ A_1',\ldots,A_i'}} \langle A_1'' A_2'' \cdots A_i'' |\hat{t}_i| A_1' A_2' \cdots A_i' \rangle \times \prod_{j=1}^{i} (\hat{X}^\dagger_{A_j''} \hat{X}_{A_j'}) , \tag{3}$$

where $\hat{X}^\dagger_A$ and $\hat{X}_A$ are the creation and annihilation operators defined on the complete set of spin orbitals $|A\rangle$. The spin orbitals occupied in $|\Phi_0\rangle$ are designated by singly primed capitals while unoccupied spin orbitals are labeled by doubly primed capitals. Notice that the operators $\hat{T}_i$ are nonlocal and have nonvanishing matrix elements between unoccupied and occupied states only. Considering a closed-shell system with a spin-independent Hamiltonian $\hat{H}$,

$$\hat{H} = \sum_i \hat{z}_i + \sum_{i<j} \hat{v}_{ij} , \tag{4}$$

a general spin orbital $\langle x|A\rangle$ may be written as a simple product of the orbital $\langle r|a\rangle$ and a pure spin function $\langle s|\eta_a\rangle$, i.e.,

$$|A\rangle = |a\rangle|\eta_a\rangle \tag{5}$$

or

$$\langle x|A\rangle = \langle r|a\rangle\langle s|\eta_a\rangle ,$$

where

$$x \equiv (r,s) \ \text{and} \ |\eta_a\rangle = |\tfrac{1}{2}\rangle \ \text{or} \ |-\tfrac{1}{2}\rangle . \tag{6}$$

Thus, the Hamiltonian may be expressed in the second quantized form as

$$\hat{H} = \sum_{a,b} \langle a|\hat{z}|b\rangle \sum_{\eta} \hat{X}^\dagger_{a\eta}\hat{X}_{b\eta} + \tfrac{1}{2} \sum_{a,b,c,d} \langle ab|\hat{v}|cd\rangle \sum_{\eta,\tau} \hat{X}^\dagger_{a\eta}\hat{X}^\dagger_{b\tau}\hat{X}_{d\tau}\hat{X}_{c\eta} , \tag{7}$$

since

$$\langle A|\hat{z}|B\rangle = \langle a|\hat{z}|b\rangle\langle\eta_a|\eta_b\rangle \tag{8a}$$

and

$$\langle AB|\hat{v}|CD\rangle = \langle ab|\hat{v}|cd\rangle\langle\eta_a|\eta_c\rangle\langle\eta_b|\eta_d\rangle , \tag{8b}$$

and

$$\hat{X}_A = \hat{X}_{a\eta} .$$

Assuming now that $|\Psi\rangle$ represents a pure singlet ground state of this closed-shell system, we find that the operator $\hat{T}$ in the expansion (1) is also spin independent, i.e., that

$$\langle A_1'' A_2'' \cdots A_i'' |\hat{t}_i| A_1' A_2' \cdots A_i' \rangle = \langle a_1'' a_2'' \cdots a_i'' |\hat{t}_i| a_1' a_2' \cdots a_i' \rangle \prod_{j=1}^{i} \langle \eta_j'' | \eta_j' \rangle , \tag{9}$$

where

$$|A_i''\rangle = |a_i''\rangle|\eta_i''\rangle \ \text{and} \ |A_i'\rangle = |a_i'\rangle|\eta_i'\rangle . \tag{10}$$

The relationship of the cluster expansion (1) to the CI expansion is very straightforward. Let us write the CI expansion of the exact wave function $|\Psi\rangle$ in the form

$$|\Psi\rangle = |\Phi_0\rangle + \sum_{i=1}^{N} \hat{C}_i|\Phi_0\rangle , \tag{11}$$

where $\hat{C}_i$ is an i-fold excitation operator, such that $\hat{C}_i|\Phi_0\rangle$ represents an appropriate linear combination of all possible i-fold excited configurations $|K_i\rangle$,

$$\hat{C}_i|\Phi_0\rangle = \sum_{K_i} a_{K_i}|K_i\rangle . \tag{12}$$

Then we immediately find that

$$\hat{C}_i = \hat{T}_i + \hat{Q}_i , \tag{13}$$

where

$$\begin{gathered} \hat{Q}_1 = 0, \quad \hat{Q}_2 = \tfrac{1}{2}\hat{T}_1^2, \quad \hat{Q}_3 = \hat{T}_1\hat{T}_2 + (1/3\,!)\hat{T}_1^3 , \\ \hat{Q}_4 = \hat{T}_1\hat{T}_3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + (1/4\,!)\hat{T}_1^4 + \tfrac{1}{2}\hat{T}_2^2, \ \text{etc.} \end{gathered} \tag{14}$$

Thus, the i-fold excited contribution (12), obtained by acting with $\hat{C}_i$ on the independent-particle single-determinantal wave function $|\Phi_0\rangle$, consists generally of two components. The first component, associated with $\hat{T}_i$, is usually referred to as a *linked* part (or, more appropriately, *connected* part), while the second component, given by $\hat{Q}_i$, is called an *unlinked* (*disconnected*) part.

The practical usefulness of the cluster expansion (1) in the theory of atomic and molecular electronic structure stems from the fact that the most important rôle in this expansion is played by the terms involving linked biexcited clusters $\hat{T}_2$. Indeed, if we use maximum overlap or "Brueckner orbitals" as the basis for the cluster expansion, we find that the monoexcited clusters $\hat{T}_1$ automatically vanish and, therefore, all unlinked clusters containing $\hat{T}_1$ also vanish. Even in the Hartree-Fock approximation we can expect the monoexcited clusters $\hat{T}_1$ to be negligible not only in view of the Brillouin theorem (which in general is not sufficient) but also from the $\hat{T}_1$ to all orders as discussed and calculated for some simple systems earlier.[7(b)]

Thus, neglecting $\hat{T}_1$, we find that the first nonnegligible unlinked terms appear in the tetraexcited states, for which we get

$$\hat{C}_4 = \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2 . \tag{15}$$

Sinanoğlu showed that the linked tetraexcited part ($\hat{T}_4$) is negligible in comparison with the unlinked part ($\frac{1}{2}\hat{T}_2^2$), at least for systems having a nonmetallic character.[7] Using the cluster expansion analysis of the full CI wave function for π-electronic model systems, we have shown[8] that this is also true for delocalized systems, unless they are so large that collective phenomena play an important rôle.[9]

Thus, neglecting $\hat{T}_4$ as well as the linked terms $\hat{T}_3$, $\hat{T}_5, \ldots, \hat{T}_N$, we obtain the wave function solely in terms of $\hat{T}_2$,

$$|\Psi\rangle \approx e^{\hat{T}_2}|\Phi_0\rangle . \tag{16}$$

This is the wave function which was used by Sinanoğlu. Applying the variational principle to this wave function he obtained a system of equations for the $\hat{T}_2$ matrix elements. In the derivation of this system of equations he neglected all terms which couple $\hat{T}_2$ matrix elements corresponding to different hole pairs; owing to this approximation the method is no longer variational. In this way a set of systems of equations is obtained (one system for each hole pair), which is very convenient for numerical calculations and which may be referred to as Sinanoğlu's decoupled-pair many-electron theory[7] (DPMET).

A systematic method for the calculation of the components of the cluster expansion of the exact wave function has recently been formulated in Papers I and II of the present series.[10] This method, which, too, is nonvariational, may be conveniently formulated using the second quantization formalism, Wick's theorem, and Feynman-like diagrams. The general method, which in principle allows a determination of the exact wave function, has been specialized for practical purposes for the case (16), when the operator $\hat{T}$ is approximated by $\hat{T}_2$. This yields the generalization of Sinanoğlu's DPMET in which the coupling of pairs is fully taken into account. Indeed, one can derive the same theory, which is referred to as the coupled-pair many-electron theory (CPMET), by decoupling the chain of CI equations by neglecting linked tetraexcited clusters, as shown in Paper III.[11] This method of derivation clearly shows the great advantage of the diagrammatical technique in this case. It is felt that this approach is more practical for proceeding beyond the DPMET than another generalization, the hierarchy of many-particle equations, referred to by Nesbet[12] as "Bethe-Goldstone equations."

As the name already suggests, the CPMET is useful whenever the interaction between pairs is of significant importance. The additional advantage of the CPMET is that it is invariant with respect to a unitary transformation of the occupied orbitals and, separately, of the unoccupied orbitals. Moreover, the CPMET represents a convenient basis for a comparison of various existing theories of correlation effects.[9,10] These advantages are obtained, however, at the cost of the more complicated structure of this theory.

As already mentioned, the importance of the unlinked tetraexcited clusters and the negligibility of the linked ones seem to be reasonably well established. Also, the highly excited clusters $\hat{T}_i$, $i \geq 5$, may safely be disregarded since they appear only in states having very high excitation energies. On the other hand, the negligibility of the linked triexcited terms has never been justified, and represents, so far, a purely heuristic assumption. This problem is particularly important in view of recent extensive CI studies for a number of molecules,[5,13] which show that in certain cases the triexcited states may play quite an important rôle, even though a smaller rôle than the tetraexcited states.

Therefore, in this paper, we examine the rôle of the triexcited clusters in the correlation energy calculations. For the sake of completeness we also consider monoexcited clusters and the rôle of unlinked clusters containing $\hat{T}_1$, particularly the unlinked triexcited clusters $\hat{T}_1\hat{T}_2$. This may be done straightforwardly within the framework of the CPMET, adding the appropriate terms and equations to include the monoexcited clusters. Next, we study the effect of linked triexcited clusters by extending the CPMET to include the most important contributions of this type. This method is referred to as the extended CPMET (i.e., ECPMET). After formulating the appropriate systems of equations we apply them to the minimum Slater basis set model of the BH_3 molecule. This molecule seems to be very appropriate for this kind of study since the triexcited states play a relatively important rôle in this case as compared with other molecules studied by extensive CI calculations.[4,13]

On the basis of the study of the relative importance of linked and unlinked triexcited states, a practical version of ECPMET, which includes only terms expected to give significant contribution to the correlation energy, is outlined, and it is shown that this method reproduces the full CI results to a high degree of accuracy while being significantly less challenging computationally.

II. COUPLED-PAIR MANY-ELECTRON THEORY

We first recall the simplest (and most important) form of CPMET for closed-shell systems, which results when all but doubly excited linked clusters are neglected, so that

$$\hat{T} \approx \hat{T}_2 , \tag{17}$$

and which we shall term the *A approximation*. The pertinent nonlinear system of equations for the matrix elements of the operator $\hat{T}_2$ may be schematically written as follows:

$$v_i + \lambda_i^A = 0 , \tag{18}$$

where

$$\lambda_i^A = \sum_{j=1}^{M_2} c_{ij}^{2(2)} t_j^{(2)} + \sum_{\substack{j,k=1 \\ (j \leq k)}}^{M_2} d_{ijk}^{2(2,2)} t_j^{(2)} t_k^{(2)} . \tag{19}$$

Here we designate the unknown $\hat{t}_2$ matrix elements $\langle a_r'' a_s'' | \hat{t}_2 | a_t' a_u' \rangle$ and the corresponding (known) $\hat{v}$ matrix elements $\langle a_r'' a_s'' | \hat{v} | a_t' a_u' \rangle$ simply by $t_i^{(2)}$ and v_i, $i = 1, \ldots, M_2$, respectively, a_r'', a_s'' being arbitrary virtual orbitals and a_t', a_u' arbitrary occupied orbitals of the chosen independent-particle model used as a starting approximation. The number M_2 of $t_i^{(2)}$ matrix elements is the same as the number of distinct biexcited singlet configurations in the CI problem. In fact, there exists a simple relationship[8] between the $\hat{t}_2$ matrix elements and the corresponding biexcited state coefficients in the CI expansion of the exact wave function. The superscripts p and (q) of the linear coefficients $c_{ij}^{p(q)}$ specify that these terms arise from the interaction of p- and q-fold excited linked clusters (i and j, respectively) and, similarly, the coefficients $d_{ijk}^{p(q,r)}$ of the nonlinear terms originate in the interaction of mutually unlinked q- and r-fold excited linked clusters j and k [i.e., $(q+r)$-fold excited unlinked clusters in $\hat{T}_q \hat{T}_r$] with the p-fold excited linked cluster i in $\hat{T}_p$.

In the simple case of the A approximation, only biexcited linked clusters appear, so that $p = q = r = 2$ throughout.

The simplest way to obtain the analytical expressions for the coefficients is to draw appropriate R diagrams,[10] and to assign to them the corresponding algebraic expressions in accordance with the rules formulated in Paper I. The explicit form of Eq. (18) was given in previous papers of this series.[10,11] The explicit expressions for the linear and nonlinear coefficients c and d, respectively, which appear in the general form of Eqs. (18) and (19) are summarized briefly in Appendix A.

Let us now determine how the system of equations (18) is modified when we explicitly consider the monoexcited clusters $\hat{T}_1$ (and the corresponding unlinked terms in which they appear) in addition to the linked biexcited clusters $\hat{T}_2$. In particular, we are interested in including the unlinked triexcited clusters, which always contain $\hat{T}_1$ terms, as seen from Eq. (14).

First we observe that, assuming at most two-particle interactions, the linked clusters $\hat{T}_p$ will couple with linked clusters $\hat{T}_{p+k}$, $k = -1, 0, 1, 2$, yielding the linear terms of the theory. For nonlinear terms, we observe that the unlinked clusters $\hat{T}_p \hat{T}_q$ will couple with the linked clusters $\hat{T}_{(p+q-k)}$, $k = 0, 1, 2$. Conversely, the equations for the linked clusters $\hat{T}_p$ will generally contain unlinked clusters of the types $\hat{T}_q \hat{T}_{(p-q+k)}$, $k = 0, 1, 2$ and $q = 1, 2, \ldots$. Here, from the outset, we neglect unlinked terms which would lead to higher than quadratic nonlinear terms in the unknown $\hat{t}$-matrix elements.

Thus we find that $\hat{T}_1$ matrix elements, $t_i^{(1)}$, will generally be coupled with $\frac{1}{2}\hat{T}_1^2$ and $\hat{T}_1 \hat{T}_2$ clusters, while $\hat{T}_2$ matrix elements, $t_i^{(2)}$, will couple with $\hat{T}_1 \hat{T}_2$, $\hat{T}_1 \hat{T}_3$, and $\frac{1}{2}\hat{T}_1^2$ clusters in addition to the $\frac{1}{2}\hat{T}_2^2$ clusters already considered in the A approximation above. Finally, we shall be neglecting the cubic terms $(1/3!)\hat{T}_1^3$, which indeed may be safely disregarded as will be apparent from our results.

In principle, it is not difficult to consider all the unlinked terms just listed. However, their importance will vary significantly. In order to get a very rough idea, at least, of the importance of these individual nonlinear terms relative to the linear ones, we can examine the lowest order of perturbation theory (based on the independent-particle wave function as the zero-order function) in which these terms may appear. This is shown schematically in Table I, which indicates that the most important unlinked terms after $(1/2!)\hat{T}_2^2$ should be the $\hat{T}_1 \hat{T}_2$ triexcited terms.

Thus, the first approximation beyond the A approximation $\hat{T} \approx \hat{T}_2$ is obtained by considering the $\hat{T}_1$ clusters in linear terms only (B approximation), i.e., all terms which appear for the first time in the first two orders of the perturbation theory. In other words, the B approximation corresponds to a consideration of the $\hat{T}_1$ terms in addition to the $\hat{T}_2$ and $(1/2!)\hat{T}_2^2$ terms of the A approximation, and of the direct coupling between all these types of clusters. (We must not forget, however, that in the iterative solution of the corresponding nonlinear system of equations all other unlinked types of clusters containing $\hat{T}_1$ and $\hat{T}_2$ are generated in higher orders of perturbation theory, even though they are not treated properly.)

In the next approximation (C approximation), we consider explicitly the unlinked triexcited clusters of the type $\hat{T}_1 \hat{T}_2$, which lead to nonlinear terms involving $t_i^{(1)}$ and $t_i^{(2)}$ matrix elements, so that monoexcited clusters still appear only linearly in these terms.[14] As Table I indicates, in this approximation all terms which appear for the first time in the first three orders of perturbation theory are properly accounted for.

Designating the pertinent spinless $\hat{T}_1$ matrix elements [cf. Eq. (9)] $\langle a_k'' | \hat{t}_1 | a_l' \rangle$ simply as $t_i^{(1)}$, $i = 1, 2, \ldots, M_1$, the corresponding system of $(M_1 + M_2)$ equations for approximations B and C may

TABLE I. Lowest order of perturbation theory (LOPT) in which various linked and unlinked clusters first appear (cf. also Ref. 6). Among the linked clusters only $\hat{T}_1$ and $\hat{T}_2$ are considered, and all unlinked clusters which are coupled with these through quadratic terms of the pertinent system of equations are given in the right-hand side of the table.

Linked clusters	LOPT	Unlinked clusters (coupled quadratically with the linked ones)	LOPT
$\hat{T}_1$	2	$\hat{T}_1\hat{T}_2$	3
		$\frac{1}{2}\hat{T}_1^2$	4
$\hat{T}_2$	1	$\frac{1}{2}\hat{T}_2^2$	2
		$\hat{T}_1\hat{T}_2$	3
		$\frac{1}{2}\hat{T}_1^2$	4
		$(\hat{T}_1\hat{T}_3)$	4

be written schematically as follows:

$$\begin{aligned} &f_i+\kappa_i^A+\kappa_i^B+\kappa_i^C=0\ , \quad i=1,\ \ldots\ ,M_1 \\ &v_i+\lambda_i^A+\lambda_i^B+\lambda_i^C=0\ , \quad i=1,\ \ldots\ ,M_2 \end{aligned} \tag{20}$$

where $\kappa_i^A=0$, λ_i^A is given by (19) and, further,

$$\begin{aligned} \kappa_i^B &= \sum_{j=1}^{M_1} c_{ij}^{1(1)} t_j^{(1)} + \sum_{j=1}^{M_2} c_{ij}^{1(2)} t_j^{(2)}\ , \\ \kappa_i^C &= \sum_{j=1}^{M_1}\sum_{k=1}^{M_2} d_{ijk}^{1(1,2)} t_j^{(1)} t_k^{(2)}\ , \\ \lambda_i^B &= \sum_{j=1}^{M_1} c_{ij}^{2(1)} t_j^{(1)}\ , \\ \lambda_i^C &= \sum_{j=1}^{M_1}\sum_{k=1}^{M_2} d_{ijk}^{2(1,2)} t_j^{(1)} t_k^{(2)}\ . \end{aligned} \tag{21}$$

The symbol f_i designates the matrix element $\langle a_k'' | \hat{f} | a_i' \rangle$ of the $\hat{f}$ operator, which is defined as

$$\langle a | \hat{f} | b \rangle = \langle a | \hat{z} | b \rangle + \sum_{c'} \langle ac' | \hat{v} | bc' \rangle_A\ , \tag{22}$$

where

$$\langle ab | \hat{v} | cd \rangle_A = 2\langle ab | \hat{v} | cd \rangle - \langle ab | \hat{v} | dc \rangle\ , \tag{23}$$

and which corresponds to the matrix element $t_i^{(1)} \equiv \langle a_k'' | \hat{t}_1 | a_i' \rangle$. Again, there is the same number of $t_i^{(1)}$, $i=1,\ldots,M_1$ matrix elements as there are singlet monoexcited configurations in the CI expansion, and a simple relationship exists between the CI monoexcited coefficients and the corresponding $t_i^{(1)}$ matrix elements. When the Hartree-Fock basis is used, all the f_i terms in the first equation (20) vanish in view of the Brillouin theorem.

As the notation of individual terms in Eqs. (20) suggests, the terms with superscripts A and B are considered in the B approximation, while all terms must be considered in the C approximation. The two sets of equations for $i=1,\ \ldots\ ,M_1$ and $i=1,\ldots,M_2$ are mutually coupled in both the B and C approximations.

The explicit expressions for the coefficients $c_{ij}^{p(q)}$ and $d_{ijk}^{p(q,r)}$ in terms of the matrix elements of the one- and two-particle parts of the Hamiltonian (4) or (7), are obtained most easily by drawing the appropriate R diagrams, as shown in Appendix A.

Considering the monoexcited clusters in addition to the linked biexcited ones, the correlation energy $\Delta\epsilon$ will be given not only by the diagrams corresponding to the skeletons of Figs. 1(a) and 1(b), as in the A approximation, but also by the diagrams corresponding to the skeletons of Figs. 1(c) and 1(d). We can, therefore, write

$$\Delta\epsilon = \Delta\epsilon^A + \Delta\epsilon^B\ , \tag{24}$$

where

$$\Delta\epsilon^A = \sum_{a_1'',a_2'',a_1',a_2'} \langle a_1' a_2' | \hat{v} | a_1'' a_2'' \rangle_A \langle a_1'' a_2'' | \hat{t}_2 | a_1' a_2' \rangle\ , \tag{25}$$

and

$$\Delta\epsilon^B = \sum_{a_1'',a_2'',a_1',a_2'} \langle a_1' a_2' | \hat{v} | a_1'' a_2'' \rangle_A \times \langle a_1'' | \hat{t}_1 | a_1' \rangle \langle a_2'' | \hat{t}_1 | a_2' \rangle\ . \tag{26}$$

Obviously, monoexcited clusters will contribute to the correlation energy not only through the second term $\Delta\epsilon^B$ but also through $\Delta\epsilon^A$ owing to their interaction with the biexcited clusters. In fact, we shall see later on that the direct contribution of the monoexcited clusters $\Delta\epsilon^B$ is negligible in comparison to their contribution through $\Delta\epsilon^A$, resulting from their effect on the $\hat{t}_2$ matrix elements by their interaction with the biexcited clusters $\hat{T}_2$.

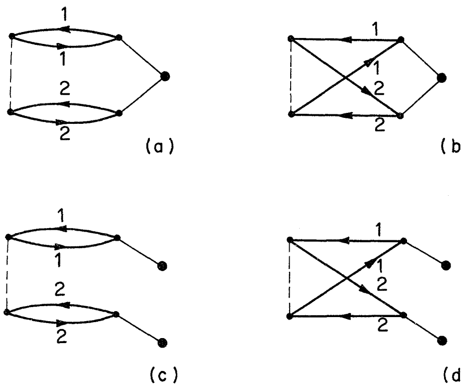

FIG. 1. R skeletons corresponding to the correlation energy of the ground state described by the wave function in the cluster expansion form (1).

Finally, we should mention that the spatial symmetry of the system (atom or molecule) may be easily exploited to reduce the system of equations (18) or (20) to the same extent as in the corresponding CI method. This is simply achieved by observing that the operator $\hat{T}$ of (1) is invariant with respect to any symmetry operation which leaves the Hamiltonian invariant. Thus the numbers M_1 and M_2 of unknown $t_i^{(1)}$ and $t_i^{(2)}$ matrix elements in the $M_1 + M_2$ equations (18) or (20) is the same as the number of symmetry adapted singlet monoexcited and biexcited configurations, respectively, in the CI method.

III. EXTENDED CPMET

It was shown in Sec. II how monoexcited and unlinked triexcited clusters can be incorporated into the CPMET. In fact, neither the complexity nor the order of the problem is significantly increased by these extensions, since the number of monoexcited states is generally much smaller than the number of biexcited states, particularly for larger systems.

On the other hand, the treatment of the linked part of the triexcited states is much more involved, since it requires additional equations for the determination of the $\hat{t}_3$ matrix elements $\langle a_i'' a_j'' a_k'' | \hat{t}_3 | a_l' a_m' a_n' \rangle$, in addition to the $\hat{t}_1$ and $\hat{t}_2$ matrix elements previously considered. Obviously, the number M_3 of these matrix elements, which we shall generally designate $t_i^{(3)}$, $i = 1, 2, \ldots, M_3$, is considerably larger than the number of $\hat{t}_2$ matrix elements M_2.

In view of the negligibility of the linked tetraexcited clusters contribution in comparison with that of the unlinked tetraexcited terms, which seems to be well established (excepting the case of large systems in which collective phenomena play an important rôle[9]), one might ask whether a similar situation would not apply for the triexcited clusters as well, making an extension of the CPMET to include linked triexcited clusters unnecessary. Moreover, since the triexcited states are generally less important than the tetraexcited ones in the correlation energy calculations,[4,5,13] the assumption that linked triexcited clusters are quite negligible might seem rather plausible.

However, even a very crude estimate of the rôle of linked versus unlinked clusters, based on the lowest order of perturbation theory in which the pertinent contribution appears for the first time, shows that this rôle is reversed in triexcited as compared to tetraexcited clusters. While for the tetraexcited states the linked contribution first occurs in the third order of perturbation and the unlinked terms begin contributing in the second order,[6] we find that the reverse is true for the triexcited clusters, where *unlinked* states first contribute in the third order and *linked* terms already contribute in the second order. The typical diagrams illustrating this fact are shown in Fig. 2(a)–2(d).

In any case, only actual calculations can verify the relative importance or unimportance of the linked triexcited clusters. In such calculations, consideration of all the terms which are coupled with the linked triexcited states, while not difficult in principle, would present serious problems from the computational point of view, particularly for large systems. We must not forget, however, that all the triexcited clusters (both linked and unlinked) represent only a rather small correction to the correlation energy (at most a few percent) and the pertinent nonlinear terms, which represent rather highly excited states, may be safely neglected.

Thus it may be concluded that only linear terms need be considered in the equations for the linked triexcited clusters, such terms accounting for the direct coupling of these clusters to the biexcited and monoexcited states. The pertinent system of equations (D approximation) will have the following general form:

$$\begin{aligned}
f_i + \kappa_i^A + \kappa_i^B + (\kappa_i^C) + \kappa_i^D &= 0, \qquad i = 1, \ldots, M_1 \\
v_i + \lambda_i^A + \lambda_i^B + (\lambda_i^C) + \lambda_i^D &= 0, \qquad i = 1, \ldots, M_2 \qquad (27) \\
(\mu_i^A + \mu_i^B + \mu_i^C) + \mu_i^D &= 0, \qquad i = 1, \ldots, M_3
\end{aligned}$$

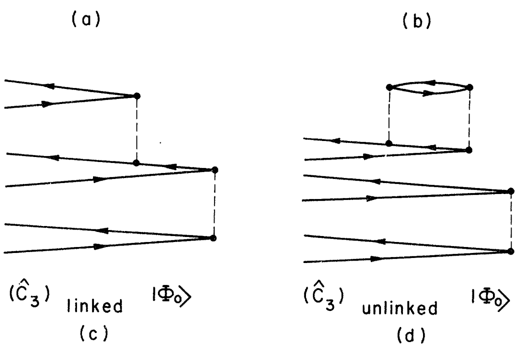

FIG. 2. Illustration of the typical diagrams of the Goldstone perturbation theory, corresponding to the linked and unlinked triexcited and tetraexcited clusters of the exact wave function of the closed-shell ground state. The diagrams with the lowest possible order of perturbation theory are shown.

where

$$\mu_i^A = \mu_i^B = \mu_i^C \equiv 0$$

and

$$\kappa_i^D = \sum_{j=1}^{M_3} c_{ij}^{1(3)} t_j^{(3)} \,,$$

$$\lambda_i^D = \sum_{j=1}^{M_3} c_{ij}^{2(3)} t_j^{(3)} \,, \tag{28}$$

$$\mu_i^D = \sum_{j=1}^{M_3} c_{ij}^{3(3)} t_j^{(3)} + \sum_{j=1}^{M_2} c_{ij}^{3(2)} t_j^{(2)} \,,$$

all other terms having been defined in (19) and (21). The terms (κ_i^C) and (λ_i^C) were inserted in parentheses in order to indicate that they may be omitted if we do not wish to consider the unlinked triexcited clusters (μ_i^C vanishes in any case). Thus by neglecting the C terms we would consider the effect of linked triexcited clusters only (D' approximation). Further, it may be expected that the coupling of the monoexcited and triexcited clusters, described by the term κ_i^D, would be of secondary importance. (Notice that there is no coupling of triexcited to monoexcited states in the term μ_i^D.) We shall, thus, also consider the approximation in which the κ_i^D term is neglected, and will refer to it as the D'' approximation. Finally, considering only the linked biexcited and triexcited clusters in the system of equations (27), neglecting all terms containing $t_i^{(1)}$ matrix elements, we obtain the D''' approximation.

In all these cases the incorporation of linked triexcited clusters goes beyond the pair description in terms of linked clusters, and consequently we term all the D-type approximations *extended* CPMET (i.e., ECPMET).

The explicit form of the D terms (28) in the system of equations (27) is given in Appendix B. In contrast to previous approximations involving only $\hat{t}_2$ and $\hat{t}_1$ matrix elements, the appropriate treatment of $\hat{t}_3$ matrix elements (characterizing the ECPMET) requires a slightly more sophisticated approach. In the case of monoexcited and biexcited clusters the number of different spin-free $\hat{t}$ matrix elements corresponding to a given orbital configuration exactly equals the number of independent spin-adapted singlet configurations. On the other hand we find that in the triexcited case we generally have one additional $\hat{t}_3$ matrix element for each orbital configuration, as compared with the number of independent singlets. Thus, in the most general case, in which all occupied a_1', a_2', a_3' and all unoccupied a_1'', a_2'', a_3'' orbitals in a given triexcited configuration are different, we have *five* linearly independent singlets in the CI procedure, while in view of the fact that the $\hat{T}$ operator is spin independent, we have *six* different $\hat{t}_3$ matrix elements, say

$$\langle a_1'' a_2'' a_3'' | \hat{t}_3 | a_{i_1}' a_{i_2}' a_{i_3}' \rangle \,, \tag{29}$$

where i_1, i_2, i_3 may be any of the $3! = 6$ permutations of the integers 1, 2, and 3.

Similarly, when two of the orbitals (either occupied or unoccupied) are identical, there are *two*[15] CI singlets, while in the cluster expansion we must consider *three* $\hat{t}_3$ matrix elements. For example, when $a_1'' = a_2'' = a''$ we have to consider only the identical and two cyclic permutations in (29), i.e., i_1, i_2, $i_3 = 1, 2, 3$; $2, 3, 1$ and $3, 1, 2$. Finally, when both two occupied and two unoccupied orbitals are identical, we have only *one* singlet but *two* $\hat{t}_3$ matrix elements, say $\langle a''a''b'' | \hat{t}_3 | a'a'b' \rangle$ and $\langle a''a''b'' | \hat{t}_3 | a'b'a' \rangle$. Thus, in this last case, there are twice as many $\hat{t}_3$ matrix elements as there are singlet configurations in the CI method, while in the most favorable case there are six $\hat{t}_3$ matrix elements for each five CI singlets. Obviously, for large molecular systems having no symmetry, the ratio of the number of $\hat{t}_3$ and CI matrix elements will approach the value $\frac{6}{5}$ (from above), while for small and highly symmetric molecules this ratio approaches the factor of 2 (from below).

Of course, the $\hat{t}_3$ matrix elements corresponding to a given orbital configuration do not all have to be considered as independent variables. Indeed, we can always eliminate one of the $\hat{t}_3$ matrix elements and thus reduce the system of nonlinear equations (27) (and the corresponding number of the unknown $\hat{t}_3$ matrix elements) so that its order equals the order of the corresponding CI problem with linearly independent, symmetry adapted configurations.

The detailed procedure for reducing the system of equations (27) to the size of the corresponding CI problem is described in Appendix C, and only a brief discussion will be given here. We note that all $\hat{t}_3$ matrix elements may be considered on an equal footing, and that in the original system (27) we have as many equations as matrix elements. As shown in Appendix C, we may ignore the linear-dependence relationship between different matrix elements and solve the original system (27) as it is, which does indeed yield the correct relationships between the linearly-dependent elements automatically. On the other hand, the reduction described in Appendix C can be carried out very easily and lowers the order of the problem significantly, particularly for small highly symmetric molecules like BH_3.

IV. APPLICATION TO BH_3 MOLECULE

The different CPMET and ECPMET procedures described in this paper have been applied to a minimal basis calculation for the ground state of the BH_3 molecule. Configuration-interaction calculations

TABLE II. CI results for the correlation energy E_{cor} of the BH_3 molecule using the minimal Slater basis set of Pipano and Shavitt (Refs. 5 and 16). (These results are for D_{3h} symmetry with a bond length of $R_{BH} = 2.3$ bohr.)

Excitations included	Problem order	$-E_{cor}$ (a.u.)
0 + 2	22	0.047 150
0 + 1 + 2	25	0.047 180
0 + 2 + 4	88	0.048 050
0 + 1 + 2 + 4	91	0.048 081
0 + 2 + 3 + 4	128	0.048 442
0 + 1 + 2 + 3 + 4	131	0.048 481
full CI	196	0.048 491

for this case, including full CI (196 configurations), had been carried out by Pipano and Shavitt,[5] but for the present study these were repeated using more accurate integral values[16]; the same integrals and the same self-consistent-field (SCF) starting approximation were then used in the (E)CPMET calculations. The CI results, showing correlation energies E_{cor} relative to the SCF energy for different selections of excitation levels [appropriate for comparison with different (E)CPMET approximations], are presented in Table II. The problem order (i.e., number of configurations) for each calculation is also given.

Though the total contribution of triexcited states in this example is only 0.8% of the full CI correlation energy, this is probably a higher relative contribution than in bigger molecules,[4] and thus BH_3 should be an appropriate system for the study of the relative importance of linked versus unlinked triexcited clusters.

The CPMET and ECPMET results are shown in Table III. In addition to the A, B, and C approximations of CPMET, three versions of ECPMET (the D approximation) are shown. The D' approximation neglects the unlinked triexcited clusters [the C terms, enclosed in parentheses in (27)], since these have already been shown to be negligible in the C approximation calculations. In the D'' approximation the terms coupling triexcited with monoexcited states [κ_i^p in (27)] are also neglected, while in D''' the monoexcited states are left out altogether, thus also eliminating any unlinked triexcited contribution, leaving only linked biexcited and triexcited clusters and unlinked tetraexcited contributions. The computed correlation energy E_{cor} and the order of the system of equations are given in Table III for each of these cases.

The Newton-Raphson method was used to solve the nonlinear system of equations of both CPMET and ECPMET, and was found to converge very rapidly (results accurate to eight decimal places were generally obtained in 2–3 iterations). It should be noted that the nonlinearity appears in the biexcited part of the problem (in the λ_i^A term) only, while the triexcited equations, though coupled to the biexcited part, are strictly linear. In fact, the additional computational effort involved in extending CPMET to include linked triexcited clusters is about the same as that required for dealing with the unlinked tetraexcited contribution. In a few cases, both the reduced and unreduced systems of the ECPMET equations were solved, yielding identical results. This can be taken as a useful test of the correctness of the computational procedures and programs.

Details of the numerical and computational aspects of the (E)CPMET equations will be described elsewhere.

V. DISCUSSION

A comparison of the (E)CPMET results with those of CI leads to a number of useful conclusions:

First, the assumption that linked tetraexcited clusters are of negligible importance is easily reconfirmed. Thus the A approximation, in which only the unlinked part of the tetraexcited clusters is accounted for, gives a correlation energy almost identical to that obtained by the 0 + 2 + 4 excitation CI, in which linked and unlinked contributions are lumped together.

Second, as may be expected, the effect of including monoexcited states is very small. Moreover, in both CI and (E)CPMET this effect is approximately additive, independently of which other excitations (in addition to the biexcited states) are included, and accounts for $3\text{–}4 \times 10^{-5}$ a.u., or less than 0.1% of the total computed correlation energy. A detailed analysis shows that the contribution of monoexcited states is entirely due to their interaction with the linked biexcited clusters, so that the correlation energy is given entirely by the diagrams in Figs. 1(a) and 1(b), while the direct monoexcited contribution, represented by the diagrams in Figs. 1(c) and 1(d), is extremely small (5×10^{-8} a.u., three orders of magnitude less than the indirect effect through biexcited states).

TABLE III. The (E)CPMET results for the correlation energy E_{cor} of the BH_3 molecule using a minimum Slater basis set.

Approximation	Clusters included	Problem order	$-E_{cor}$ (a.u.)
A	$2_L + 4_U$	21	0.048 048
B	$1_L + 2_L + 4_U$	24	0.048 081
C	$1_L + 2_L + 3_U + 4_U$	24	0.048 079
D'''	$2_L + 3_L + 4_U$	61	0.048 450
D''	$(1_L) + 2_L + 3_L + 4_U$	64	0.048 489
D'	$1_L + 2_L + 3_L + 4_U$	64	0.048 490

Finally, the prediction on the relative importance of linked and unlinked triexcited clusters, based on the lowest order of perturbation in which each type of term appears, is easily confirmed. The C and D' approximations of (E)CPMET account for unlinked and linked triexcited states, respectively, and a comparison of the C result with that of the B approximation shows that the effect of the unlinked terms is negligible. On the other hand, the D' result agrees quite well with the $0+1+2+3+4$ excitation CI calculation (or with full CI, for that matter), in which both linked and unlinked contributions are lumped together. (Since the contribution of unlinked triexcited clusters is so small it is probably safe to assume that the total triexcited contribution, if desired, can be obtained by adding together the energy increments of approximations C and D', relative to B, instead of having to perform the more laborious D approximation calculation.) Thus we conclude that, at least as far as the calculation of the correlation energy is concerned, the relative importance of linked and unlinked terms is completely reversed for triexcited clusters compared with tetraexcited ones: *The rôle of the unlinked triexcited clusters is negligible in comparison with the linked triexcited terms.*[17]

In comparing the CI and (E)CPMET results it should not be forgotten that the nonlinear terms [which are always included in (E)CPMET] account not only for the unlinked tetraexcited clusters in the wave function, but, once the nonlinear system has been solved, also include the effect of the unlinked hexaexcited, octaexcited, etc., clusters. Thus it is more appropriate to compare the results of the D' approximation, in which all important clusters are considered, with the full CI result, rather than with the result of the $0+1+2+3+4$ CI calculation, even though the appropriate energy differences here are very small indeed.

Before concluding this discussion, let us briefly consider the advantages and disadvantages of the (E)CPMET and CI procedures. The main advantage of the CI method lies in its variational nature, thus ensuring that the energy obtained represents an upper bound. This property is clearly lost in (E)CPMET, but is seems reasonable to assume that this property is not so important when the method used is accurate enough to reproduce the variational (CI) correlation energy within a few percent (or even a fraction of 1%).

In both CI and (E)CPMET we have to solve a nonlinear problem in order to obtain the correlation energy: In the former method this is the well-known eigenvalue problem, while in the latter case this is an algebraic system of nonlinear equations. As already mentioned, the nonlinearity of this system is not strong, and the first-order Newton-Raphson iteration procedure yields very rapid convergence. Furthermore, the order of the (E)CPMET problem is generally significantly lower than the order of the corresponding CI problem, as a comparison of Tables II and III shows. In any case, in both the CI and (E)CPMET procedures the critical step, as far as computing effort is concerned, is not the solution of the nonlinear problem but rather the calculation of all the coefficients in the system of equations. In this respect (E)CPMET is clearly more advantageous, unless a perturbational approach to the CI problem[18] is undertaken, but in such an approach the variational character of CI is also lost. Further, in this approach it is rather difficult to apply the physically reasonable and systematic simplifications used in CPMET.

VI. CONCLUSIONS

In summary we can conclude that the extension of CPMET to incorporate the linked part of the triexcited clusters yields a very good approximation for the calculation of the ground-state correlation energy of closed-shell systems. This is due to the fact that in contrast to the case of tetraexcited states, where unlinked clusters play the dominant rôle, the reverse is true for the triexcited clusters. The actual calculations of the correlation energy of the BH_3 molecule within the minimal Slater-type orbital basis set indicate that the ECPMET reproduces the full CI result to very high accuracy (an error of 0.0025%). It is most likely that this surprisingly high accuracy is fortuitous, and in other cases, particularly for larger atomic and molecular systems and extensive enough basis sets which yield a true Hartree-Fock limit, a much larger error may result; but the accuracy of the proposed method will still be most satisfactory even if the error in the correlation energy is larger by two or three orders of magnitude than in the present case.

ACKNOWLEDGMENTS

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APPENDIX A: EXPLICIT FORM OF CPMET EQUATIONS

The system of Eqs. (18) or (20) may be written explicitly as follows

$$\langle 1'' | \hat{f} | 1' \rangle + \sum_{X \in \mathcal{S}} \kappa^X(1'', 1') = 0 \,,$$

$$\langle 1''2'' | \hat{v} | 1'2' \rangle + \sum_{X \in \mathcal{S}} [\lambda^X(1'', 1'; 2'', 2') \qquad \text{(A1)}$$

$$+ \lambda^X(2'', 2'; 1'', 1')] = 0 \,,$$

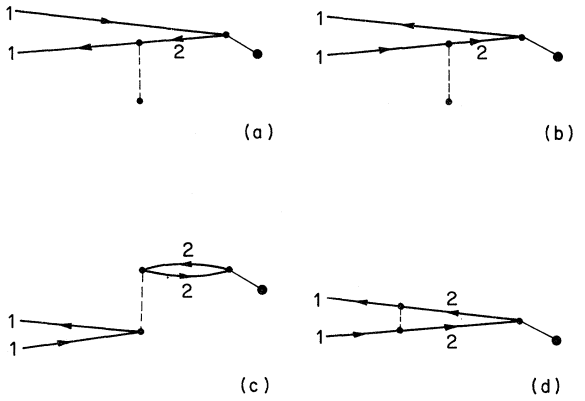

FIG. 3. R skeletons yielding $c^{1(1)}$ coefficients.

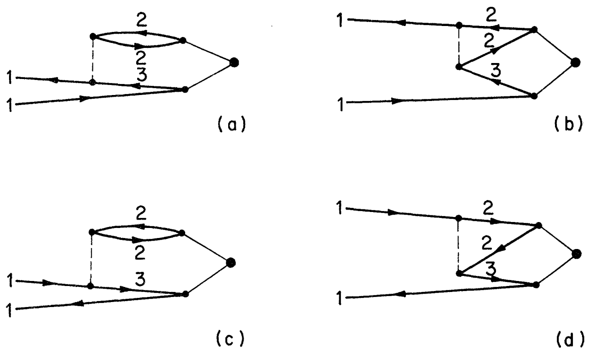

FIG. 4. R skeletons yielding $c^{1(2)}$ coefficients.

where we use the notational convention in which $i'' \equiv d_i''$ and $i' \equiv d_i'$, so that

$$\langle 1'' | \hat{f} | 1' \rangle \equiv \langle d_1'' | \hat{f} | d_1' \rangle \text{ , etc.,} \tag{A2}$$

and the set $\mathcal{S}$ contains A for the A approximation, A and B for the B approximation and, finally, all A, B, and C for the C approximation. Further, d_1'' and d_1' in the first Eq. (A1) correspond to all possible[19] singlet monoexcited states

$$\left| \begin{matrix} d_1'' \\ d_1' \end{matrix} \right\rangle$$

and in the second Eq. (A1), d_1'', d_2'', d_1', and d_2' correspond to all possible[19] singlet biexcited states

$$\left| \begin{matrix} d_1'' & d_2'' \\ d_1' & d_2' \end{matrix} \right\rangle .$$

When $d_1' \neq d_2'$ and $d_1'' \neq d_2''$ we have two singlet states and correspondingly two $\hat{t}_2$ matrix elements $\langle d_1''d_2'' | \hat{t}_2 | d_1'd_2' \rangle$ and $\langle d_1''d_2'' | \hat{t}_2 | d_2'd_1' \rangle$. Here we distinguish the occupied and the unoccupied orbitals by singly and doubly primed letters, respectively. For Hartree-Fock orbitals we obviously have $\langle 1'' | \hat{f} | 1' \rangle = 0$.

To obtain the explicit expressions for λ^X in terms of the $\hat{f}$, $\hat{v}$, $\hat{t}_1$, and $\hat{t}_2$ matrix elements, it is simply necessary to draw the appropriate R skeletons and assign to them the appropriate algebraic expressions.[10] The pertinent skeletons for the A approximation have been given earlier,[10] while those for the B and C approximations are shown in Figs. 3–7. The explicit expressions for the coefficients κ^X and λ^X of (A1) are listed for individual approximations in the following.

A Approximation

We have to consider only the second system of Eqs. (A1), so that

$$\kappa^A(1'' ; 1') \equiv 0 , \tag{A3}$$

while

$$\lambda^A(1'', 1' ; 2'', 2') = \sum_{3'',4'',3',4'} \{ \langle 1'', 2'' ; 1', 2' | c^{2(2)} | 3'', 4'' ; 3', 4' \rangle \langle 3''4'' | \hat{t}_2 | 3'4' \rangle$$
$$+ \sum_{5'',6'',5',6'} \langle 1'', 2'' ; 1', 2' | d^{2(2,2)} | 3'', 4'' ; 3', 4' : 5'', 6'' ; 5', 6' \rangle \langle 3''4'' | \hat{t}_2 | 3'4' \rangle \langle 5''6'' | \hat{t}_2 | 5'6' \rangle \} . \tag{A4}$$

The skeletons determining the linear coefficients $c^{2(2)}$ and the nonlinear coefficients $d^{2(2,2)}$ are shown in Figs. 7 and 8, respectively, of Paper I. From these figures we immediately get the expressions for the above coefficients:

$$\langle 1'', 2'' ; 1', 2' | c^{2(2)} | 3'', 4'' ; 3', 4' \rangle = (\langle 1'' | \hat{f} | 3'' \rangle \langle 3' | 1' \rangle - \langle 3' | f | 1' \rangle \langle 1'' | 3'' \rangle) \langle 2'' | 4'' \rangle \langle 4' | 2' \rangle$$
$$+ (\langle 1''3' | \hat{v} | 1'3'' \rangle_A \langle 2'' | 4'' \rangle - \langle 1''3' | \hat{v} | 1'4'' \rangle \langle 2'' | 3'' \rangle) \langle 4' | 2' \rangle - \langle 2''3' | \hat{v} | 4''1' \rangle \langle 1'' | 3'' \rangle \langle 4' | 2' \rangle + \tfrac{1}{2} \langle 1''2'' | \hat{v} | 3''4'' \rangle$$
$$\times \langle 3' | 1' \rangle \langle 4' | 2' \rangle + \tfrac{1}{2} \langle 3'4' | \hat{v} | 1'2' \rangle \langle 1'' | 3'' \rangle \langle 2'' | 4'' \rangle \tag{A5}$$

and

$$\langle 1'', 2''; 1', 2' | d^{2(2,2)} | 3'', 4''; 3', 4' : 5'', 6''; 5', 6' \rangle = \langle 3'5' | \hat{v} | 3''5'' \rangle_A \Delta(4'', 6''; 4', 6')$$
$$- \langle 3'6' | \hat{v} | 4''6'' \rangle_A \Delta(3'', 5''; 4', 5') - \langle 3'5' | \hat{v} | 3''4'' \rangle_A \Delta(5'', 6''; 4', 6')$$
$$- \langle 3'4' | \hat{v} | 3''6'' \rangle_A \Delta(4'', 5''; 6', 5') + \tfrac{1}{2} \langle 3'5' | \hat{v} | 4''6'' \rangle \Delta(3'', 5''; 4', 6')$$
$$+ \tfrac{1}{2} \langle 3'5' | \hat{v} | 6''4'' \rangle \Delta(3'', 5''; 6', 4') + \tfrac{1}{2} \langle 3'4' | \hat{v} | 5''6'' \rangle \Delta(3'', 4''; 5', 6'), \qquad \text{(A6)}$$

where

$$\Delta(i'', j''; k', l') = \langle 1'' | i'' \rangle \langle 2'' | j'' \rangle \langle k' | 1' \rangle \langle l' | 2' \rangle \qquad \text{(A7)}$$

and $\langle ij | \hat{v} | kl \rangle_A$ is defined in (23).

The system of equations for the A approximation given earlier[10,11] is clearly obtained from (A1), (A5), and (A6) by carrying out the summations over the δ symbols $\langle i | j \rangle = \delta_{ij}$. Thus, in the second term on the right-hand side of (A4) one has quadruple summations, while in the first term there are at most double summations. The form in which the δ functions have been summed over is more useful for practical calculations, while the form given here allows a more compact notation and also shows clearly the structure of the CPMET system of equations.

B Approximation

In addition to the λ^A terms given above, we have to consider the following B terms, for which we can write

$$\kappa^B(1''; 1') = \sum_{2'', 2'} \langle 1''; 1' | c^{1(1)} | 2''; 2' \rangle \langle 2'' | \hat{t}_1 | 2' \rangle$$
$$+ \sum_{2'', 3'', 2', 3'} \langle 1''; 1' | c^{1(2)} | 2'', 3''; 2', 3' \rangle \times \langle 2''3'' | \hat{t}_2 | 2'3' \rangle \qquad \text{(A8)}$$

and

$$\lambda^B(1'', 1'; 2'', 2') = \sum_{3'', 3'} \langle 1'', 2''; 1', 2' | c^{2(1)} | 3''; 3' \rangle \times \langle 3'' | \hat{t}_1 | 3' \rangle . \qquad \text{(A9)}$$

The pertinent $c^{1(1)}$, $c^{1(2)}$, and $c^{2(1)}$ coefficients may be determined easily from the skeletons shown in Figs. 3, 4, and 5, respectively, yielding

$$\langle 1''; 1' | c^{1(1)} | 2''; 2' \rangle = \langle 1'' | \hat{f} | 2'' \rangle \langle 1' | 2' \rangle - \langle 2' | \hat{f} | 1' \rangle \langle 2'' | 1'' \rangle + \langle 1''2' | \hat{v} | 1'2'' \rangle_A, \qquad \text{(A10)}$$

$$\langle 1''; 1' | c^{1(2)} | 2'', 3''; 2', 3' \rangle = \langle 1''2' | \hat{v} | 3''2'' \rangle_A \langle 1' | 3' \rangle - \langle 3'2' | \hat{v} | 1'2'' \rangle_A \langle 3'' | 1'' \rangle , \qquad \text{(A11)}$$

and

$$\langle 1'', 2''; 1', 2' | c^{2(1)} | 3''; 3' \rangle = \langle 1''2'' | \hat{v} | 3''2' \rangle \langle 1' | 3' \rangle - \langle 3'2'' | \hat{v} | 1'2' \rangle \langle 3'' | 1'' \rangle . \qquad \text{(A12)}$$

C Approximation

The additional terms κ^C and λ^C in Eqs. (A1) have the form

$$\kappa^C(1''; 1') = \sum_{\substack{2'', 3'', 4'' \\ 2', 3', 4'}} \langle 1''; 1' | d^{1(1,2)} | 2''; 2' : 3'', 4''; 3', 4' \rangle \langle 2'' | \hat{t}_1 | 2' \rangle \langle 3''4'' | \hat{t}_2 | 3'4' \rangle , \qquad \text{(A13)}$$

$$\lambda^C(1'', 1'; 2'', 2') = \sum_{\substack{3'', 4'', 5'' \\ 3', 4', 5'}} \langle 1'', 2''; 1', 2' | d^{2(1,2)} | 3''; 3' : 4'', 5''; 4', 5' \rangle \langle 3'' | \hat{t}_1 | 3' \rangle \langle 4''5'' | \hat{t}_2 | 4'5' \rangle \qquad \text{(A14)}$$

The pertinent nonlinear coefficients $d^{1(1,2)}$ and $d^{2(1,2)}$, representing the unlinked triexcited clusters, are easily determined from the skeletons shown in Figs. 6 and 7, respectively. Thus

$$\langle 1''; 1' | d^{1(1,2)} | 2'', 3'', 4''; 2', 3', 4' \rangle = (2 \langle 2'3' | \hat{v} | 2''3'' \rangle_A \langle 1' | 4' \rangle$$
$$- \langle 3'4' | \hat{v} | 3''2'' \rangle_A \langle 1' | 2' \rangle) \langle 4'' | 1'' \rangle - (\langle 2'4' | \hat{v} | 2''3'' \rangle_A \langle 4'' | 1'' \rangle$$
$$+ \langle 2'4' | \hat{v} | 3''4'' \rangle_A \langle 2'' | 1'' \rangle) \langle 1' | 3' \rangle \qquad \text{(A15)}$$

and

$$\begin{aligned}\langle 1'', 2''; 1', 2' | d^{2(1,2)} | 3'', 4'', 5''; 3', 4', 5'\rangle &= (\langle 1''3' | \hat{v} | 4''3''\rangle_A \langle 4' | 1'\rangle - \langle 4'3' | \hat{v} | 1'3''\rangle_A \langle 1'' | 4''\rangle \\ &+ \langle 1''4' | \hat{v} | 3''4''\rangle_A \langle 3' | 1'\rangle - \langle 3'4' | \hat{v} | 1'4''\rangle_A \langle 1'' | 3''\rangle)\langle 2'' | 5''\rangle\langle 5' | 2'\rangle \\ &+ (\langle 3'4' | \hat{v} | 1'5''\rangle\langle 2'' | 4''\rangle - \langle 2''3' | \hat{v} | 5''4''\rangle\langle 4' | 1'\rangle)\langle 1'' | 3''\rangle\langle 5' | 2'\rangle \\ &- \langle 1''4' | \hat{v} | 3''5''\rangle\langle 4'' | 2''\rangle\langle 3' | 1'\rangle\langle 5' | 2'\rangle + \langle 3'5' | \hat{v} | 4''2'\rangle\langle 1'' | 3''\rangle\langle 4' | 1'\rangle\langle 2'' | 5''\rangle \\ &+ (\langle 4'5' | \hat{v} | 3''2'\rangle\langle 2'' | 5''\rangle - \langle 2''4' | \hat{v} | 5''3''\rangle\langle 5' | 2'\rangle)\langle 1'' | 4''\rangle\langle 3' | 1'\rangle . \end{aligned} \tag{A16}$$

APPENDIX B: EXPLICIT FORM OF EXTENDED CPMET EQUATIONS

The nonlinear system of Eqs. (27) of ECPMET (implicitly including the approximations $A-D$ as well as additional approximations D', D'', D''' obtained by neglecting certain interactions and clusters as indicated in the main text) may be written in the following explicit form, using the same conventions as in Appendix A:

$$\begin{gathered}\langle 1'' | \hat{f} | 1'\rangle + \sum_{X \in \mathcal{S}} \kappa^X(1''; 1') = 0 , \\ \langle 1''2'' | \hat{v} | 1'2'\rangle + \sum_{X \in \mathcal{S}} \sum_{P_2} \lambda^X(p_1'', p_1'; p_2'', p_2') = 0 , \\ \sum_{X \in \mathcal{S}} \sum_{P_3} \mu^X(p_1'', p_1'; p_2'', p_2'; p_3'', p_3') = 0 ,\end{gathered} \tag{B1}$$

where again the set $\mathcal{S}$ contains an appropriate subset of indices A, B, C, or D yielding the desired approximation, and the last summation in the second and third equations extends over all permutations of the symmetric groups S_2 and S_3, respectively, so that

$$P_2 = \begin{pmatrix} 1 & 2 \\ p_1 & p_2 \end{pmatrix} \text{ and } P_3 = \begin{pmatrix} 1 & 2 & 3 \\ p_1 & p_2 & p_3 \end{pmatrix} \tag{B2}$$

for both singly and doubly primed indices simultaneously.

The A through C terms κ and λ have been given in Appendix A, while

$$\mu^X(1'', 1'; 2'', 2'; 3'', 3') \equiv 0 \text{ for } X = A,\ B, \text{ and } C. \tag{B3}$$

The D terms, responsible for the linked triexcited clusters, have the following general form:

$$\kappa^D(1''; 1') = \sum_{\substack{2'',3'',4'' \\ 2',3',4'}} \langle 1''; 1' | c^{1(3)} | 2'', 3'', 4''; 2', 3', 4'\rangle\langle 2''3''4'' | \hat{t}_3 | 2'3'4'\rangle , \tag{B4}$$

$$\lambda^D(1'', 1'; 2'', 2') = \sum_{\substack{3'',4'',5'' \\ 3',4',5'}} \langle 1'', 2''; 1', 2' | c^{2(3)} | 3'', 4'', 5''; 3', 4', 5'\rangle\langle 3''4''5'' | \hat{t}_3 | 3'4'5'\rangle , \tag{B5}$$

and

$$\begin{aligned}\mu^D(1'', 1'; 2'', 2'; 3'', 3') &= \sum_{\substack{4'',5'' \\ 4',5'}} \langle 1'', 2'', 3''; 1', 2', 3' | c^{3(2)} | 4'', 5''; 4', 5'\rangle\langle 4''5'' | \hat{t}_2 | 4'5'\rangle \\ &+ \sum_{\substack{4'',5'',6'' \\ 4',5',6'}} \langle 1'', 2'', 3''; 1', 2', 3' | c^{3(3)} | 4'', 5'', 6''; 4', 5', 6'\rangle\langle 4''5''6'' | \hat{t}_3 | 4'5'6'\rangle .\end{aligned} \tag{B6}$$

The explicit form of the coefficients $c^{1(3)}$, $c^{2(3)}$, $c^{3(2)}$, and $c^{3(3)}$ is again most easily determined by drawing the appropriate R skeletons and the correponding R diagrams. Notice, also, that there are no terms of the $c^{3(1)}$ type.

The R skeletons for the coefficients $c^{1(3)}$ are shown in Fig. 8 and yield

$$\langle 1''; 1' | c^{1(3)} | 2'', 3'', 4''; 2', 3', 4'\rangle = (\langle 2'3' | \hat{v} | 2''3''\rangle_A \langle 1'' | 4''\rangle - \langle 2'3' | \hat{v} | 2''4''\rangle_A \langle 1'' | 3''\rangle)\langle 4' | 1'\rangle . \tag{B7}$$

Similarly, the skeletons determining the $c^{2(3)}$ terms are shown in Fig. 9, yielding

$$\langle 1'', 2''; 1', 2' | c^{2(3)} | 3'', 4'', 5''; 3', 4', 5'\rangle = (\langle 1''3' | \hat{v} | 4''3''\rangle_A \langle 4' | 1'\rangle$$

$$- \langle 3'4' | \hat{v} | 3''1' \rangle_A \langle 1'' | 4'' \rangle) \langle 2'' | 5'' \rangle \langle 5' | 2' \rangle$$

$$+ (\langle 3'4' | \hat{v} | 1'5'' \rangle \langle 1'' | 3'' \rangle - \langle 1''4' | \hat{v} | 3''5'' \rangle \langle 3' | 1' \rangle) \langle 2'' | 4'' \rangle \langle 5' | 2' \rangle \, . \tag{B8}$$

The coefficients $c^{3(2)}$ and $c^{3(3)}$ which enter the μ^D terms are obtained from the skeletons shown in Figs. 10 and 11, respectively, giving

$$\langle 1'', 2'', 3''; 1', 2', 3' | c^{3(2)} | 4'', 5''; 4', 5' \rangle = (\langle 1''2'' | \hat{v} | 1'4'' \rangle \langle 4' | 2' \rangle - \langle 1''4' | \hat{v} | 1'2' \rangle \langle 2'' | 4'' \rangle) \langle 5' | 3' \rangle \langle 3'' | 5'' \rangle \tag{B9}$$

and

$$\langle 1'', 2'', 3''; 1', 2', 3' | c^{3(3)} | 4'', 5'', 6''; 4', 5', 6' \rangle = \langle 6' | 3' \rangle \langle 3'' | 6'' \rangle [(\langle 1'' | \hat{f} | 4'' \rangle \langle 4' | 1' \rangle - \langle 4' | \hat{f} | 1' \rangle \langle 1'' | 4'' \rangle$$

$$+ \langle 1''4' | \hat{v} | 1'4'' \rangle_A) \langle 5' | 2' \rangle \langle 2'' | 5'' \rangle + \langle 1''2'' | \hat{v} | 4''5'' \rangle \langle 4' | 1' \rangle \langle 2'' | 5'' \rangle + \langle 4'5' | \hat{v} | 1'2' \rangle \langle 5' | 2' \rangle \langle 1'' | 4'' \rangle$$

$$- (\langle 2''4' | \hat{v} | 5''1' \rangle \langle 5' | 2' \rangle + \langle 2''4' | \hat{v} | 2'5'' \rangle \langle 5' | 1' \rangle) \langle 1'' | 4'' \rangle] \, . \tag{B10}$$

Notice that in the κ^D terms there are quadruple summations, in the λ^D terms triple summations and, finally, in the μ^D term, there are at most double summations. Again, for the numerical calculations it is best to carry out the summations over the δ symbols $\langle i | j \rangle = \delta_{ij}$ first and thus reduce the final number of summations as much as possible. This results in a less compact and less transparent form of these equations, which is, nevertheless, more suitable for effective computer programming.

APPENDIX C: REDUCTION OF ECPMET SYSTEM OF EQUATIONS

In this appendix we show that by choosing the appropriate supplementary conditions a larger ECPMET system of equations, comprising all the different orbital $\hat{t}_3$ matrix elements, yields a linearly independent *bona fide* system of equations, which may be reduced, if desired, to a smaller system involving only the orbital $\hat{t}_3$ matrix elements corresponding to the linearly independent configurations. To do so we must recall, at least very briefly, how the system of equations of the ECPMET is obtained in the first place.

Let us start with the Schrödinger equation for a general closed-shell N electronic system ($N = 2n$), with a Hamiltonian $\hat{H}$, which we can write in the form

$$(\hat{Q} - \Delta\epsilon) | \Psi \rangle = 0 \, , \tag{C1}$$

where

$$\hat{Q} = \hat{H} - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \tag{C2}$$

and

$$\Delta\epsilon = E - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \tag{C3}$$

represent the Hamiltonian in the normal product form and the correlation energy, respectively, and

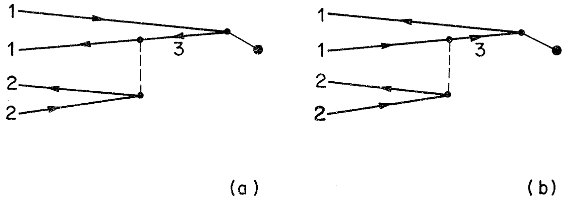

FIG. 5. R skeletons yielding $c^{2(1)}$ coefficients.

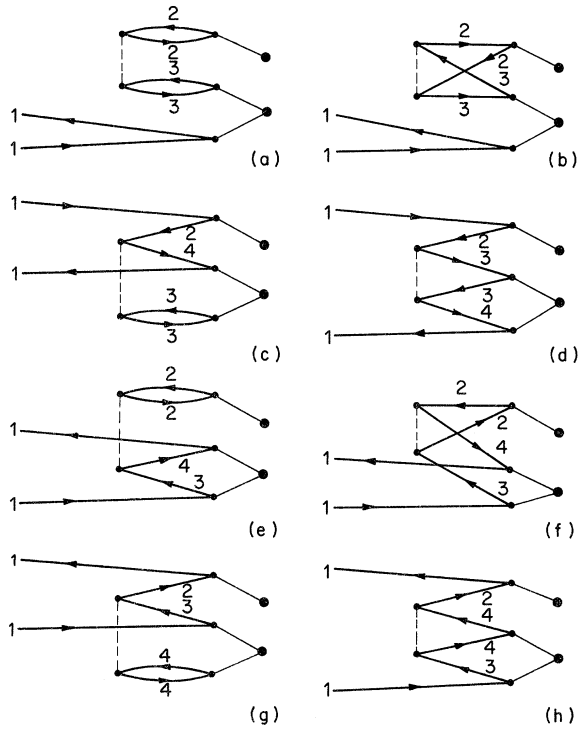

FIG. 6. R skeletons yielding $d^{1(1,2)}$ coefficients.

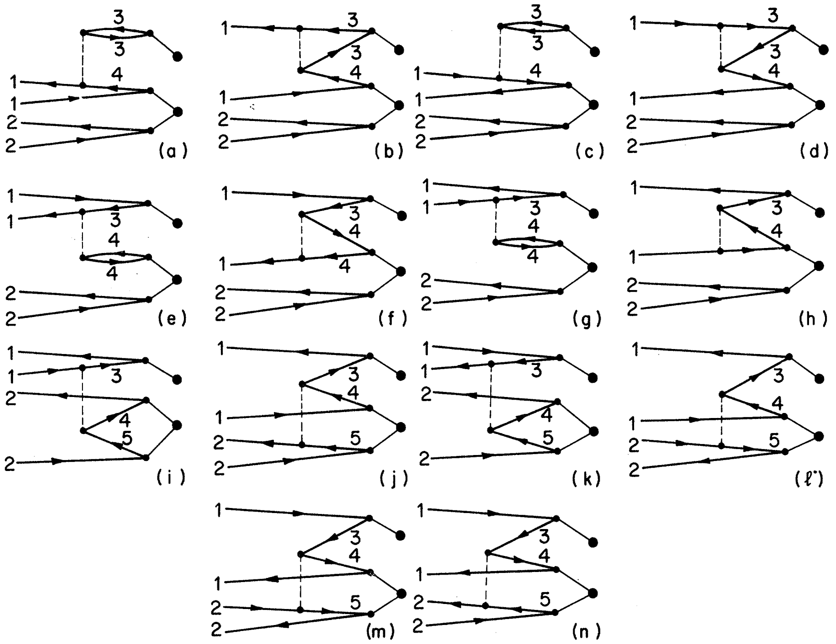

FIG. 7. R skeletons yielding $d^{2(1,2)}$ coefficients.

$|\Phi_0\rangle$ is the independent-particle wave function of the ground state. Considering the cluster expansion (1) of the exact wave function $|\Psi\rangle$ and using the diagrammatical technique, the Schrödinger equation (C1) may be rewritten in the form

$$e^{\hat T}\hat P\,|\Phi_0\rangle = 0\ , \tag{C4}$$

where

$$\hat P = \sum_{r\in\Delta} w_R(r) \sum_{\rho} \hat D_R(r,\rho) - \Delta\epsilon\ , \tag{C5}$$

as shown in Paper I. Indeed, Eq. (C4) is identical to Eq. (51) of Paper I. Let us recall that $w_R(r)$ is the weight of the rth resulting (R) skeleton, while $\hat D_R(r,\rho)$ is the operator assigned to the corresponding R diagram. Here ρ designates the set of spin orbitals which label the oriented lines of the given R diagram; this set is conveniently subdivided into the two subsets, ρ_1 and ρ_2, $\rho \equiv (\rho_1, \rho_2)$, consisting of spin orbitals which label the external and the internal oriented lines, respectively. The first subset ρ_1 contains $2j$ elements, assuming the R diagram has j open paths, and is generally written in the form

$$\rho_1 \equiv (A_1'', A_1'; A_2'', A_2'; \cdots ; A_i'', A_i'; \cdots ; A_j'', A_j')\ , \tag{C6}$$

where each pair of indices A_i'' and A_i', separated from other pairs by semicolons, labels the outgoing and the ingoing external oriented lines, respec-

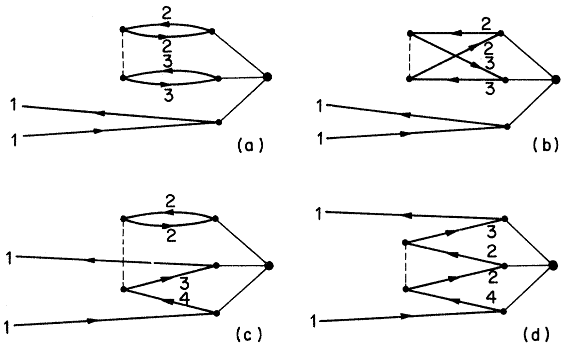

FIG. 8. R skeletons yielding $c^{1(3)}$ coefficients.

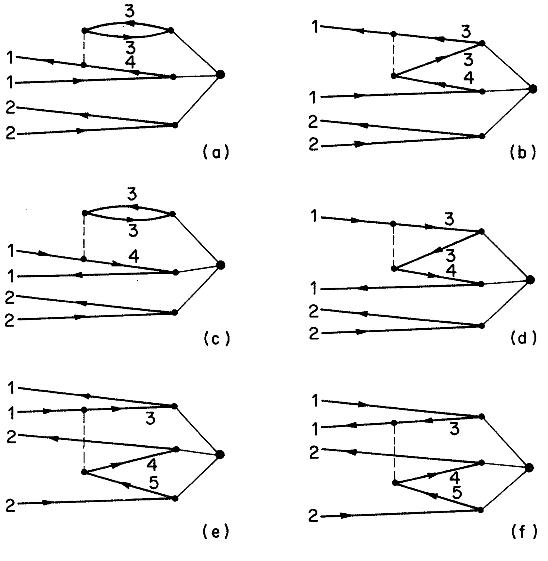

FIG. 9. R skeletons yielding $c^{2(3)}$ coefficients.

tively, of the ith open oriented path. Finally, the first summation in (C5) extends over all connected R skeletons.

The operator $\hat{P}$ defined by (C5) may be written in a general second quantitized form as follows:

$$\hat{P}=\sum_{j=0}^{N} \hat{P}_j, \tag{C7}$$

where

$$\hat{P}_0=\sum_{r\in\Delta_0} w_R(r)\sum_{\rho_2} d_R(r,\rho_2)-\Delta\epsilon \tag{C8}$$

is a c number in which the first summation extends over all vacuum connected R skeletons (i.e., over the connected R skeletons having no open oriented paths), while for $j\neq 0$ we can write

$$\hat{P}_j=\frac{1}{j!}\sum_{\substack{A_1''\cdots A_j''\\ A_1'\cdots A_j'}} \langle A_1''\cdots A_j''|\hat{p}_j|A_1'\cdots A_j'\rangle \prod_{i=1}^{j}(\hat{X}^\dagger_{A_i''}\hat{X}_{A_i'}), \tag{C9}$$

where

$$\langle A_1''\cdots A_j''|\hat{p}_j|A_1'\cdots A_j'\rangle=\sum_{r\in\Delta_j} w_R(r)\sum_{\rho_1\in\theta}\sum_{\rho_2} d_R(r,\rho_1,\rho_2). \tag{C10}$$

The first summation in (C10) extends over all connected R skeletons having j open oriented paths, and the second summation extends over all R diagrams for which

$$\rho_1=(A_{i_1}'',A_{i_1}';A_{i_2}'',A_{i_2}';\ldots;A_{i_j}'',A_{i_j}'), \tag{C11}$$

where i_1, i_2, ..., i_j is some permutation of the integers 1, 2, ..., j. Finally, $d_R(r,\rho)$ is the scalar quantity assigned to the rth R diagram carrying spin orbital labels $\rho\equiv(\rho_1,\rho_2)$, which is related to the above-mentioned operator $\hat{D}_R(r,\rho)$ (assigned to the same R diagram) by

$$\hat{D}_R(r,\rho_1,\rho_2)=d_R(r,\rho_1,\rho_2)\prod_{i=1}^{j}(\hat{X}^\dagger_{A_i''}\hat{X}_{A_i'}), \tag{C12}$$

assuming that ρ_1 is given by (C6).

We now see that in order to satisfy (C4) we must have

$$\hat{P}_j|\Phi_0\rangle=0 \tag{C13}$$

for every j. Clearly for $j=0$ we must set

$$\hat{P}_0=0, \tag{C14}$$

which yields the formula for the correlation energy in terms of the $\hat{t}_1$ and $\hat{t}_2$ matrix elements [cf. skeletons of Fig. 1 and the corresponding (orbital) expressions (24)–(26)], while Eqs. (C13) for $j\neq 0$ yield the (E)CPMET system of equations for the $\hat{t}_k$ matrix elements.

If we require all the matrix elements (C10), $j\neq 0$, to vanish, i.e.,

$$\langle A_1''\cdots A_j''|\hat{p}_j|A_1'\cdots A_j'\rangle=0, \tag{C15}$$

then obviously Eqs. (C13) are also satisfied. In other words, Eqs. (C15) represent the sufficient conditions for the validity of (C13). In fact, Eqs. (C15) are equivalent to Eqs. (53) of Paper I. However, Eqs. (C15) are necessary conditions for the validity of (C13) only when all the N-electronic configurations

$$\prod_{i=1}^{j}(\hat{X}^\dagger_{A_i''}\hat{X}_{A_i'})|\Phi_0\rangle \tag{C16}$$

appearing on the right-hand side of (C13) are linearly independent (of course, all $j!$ terms which differ by *the same* permutation of the occupied and of the unoccupied (spin) orbitals are considered as one term). This is indeed the case for the monoexcited states. However, for $j\geq 2$ the various states

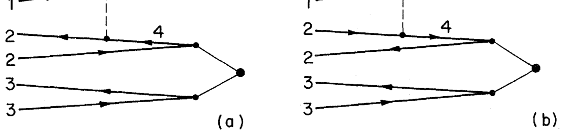

FIG. 10. R skeletons yielding $c^{3(2)}$ coefficients.

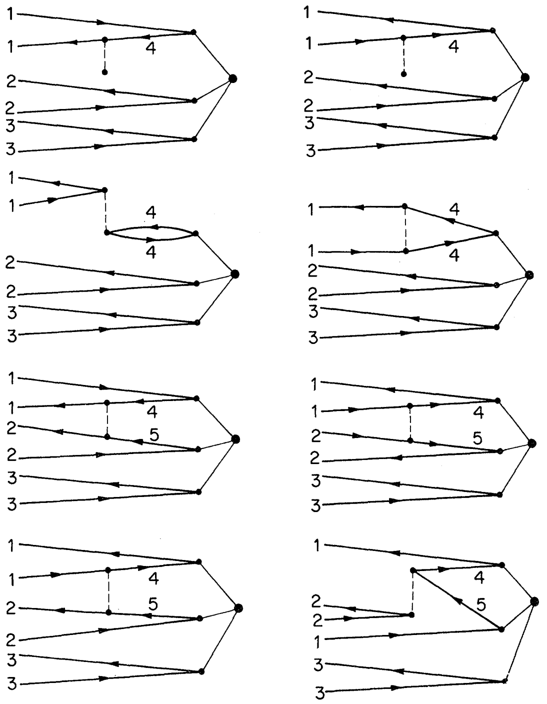

FIG. 11. R skeletons yielding $c^{3(3)}$ coefficients.

(C16) which differ only by the permutation of, say, occupied orbitals, keeping the unoccupied ones in a fixed order, are linearly dependent. In fact, all these states are identical up to the phase factor (± 1), so that the necessary and sufficient condition for (C13) to be satisfied is that for each distinct orbital set we have

$$\sum_{P\in S_j} (-1)^p \langle A_1'' \cdots A_j'' | \hat{p}_j | A_{p_1}' \cdots A_{p_j}' \rangle = 0 \, , \quad \text{(C17)}$$

the summation extending over all permutations of, say, the occupied orbital set, and p designating the parity of the corresponding permutation

$$P = \begin{pmatrix} 1 & \cdots & j \\ p_1 & \cdots & p_j \end{pmatrix} . \quad \text{(C18)}$$

The expression on the left-hand side of Eq. (C17) is easily recognized as the antisymmetrized $\hat{p}_j$-matrix element,

$$\langle A_1'' \cdots A_j'' | \hat{p}_j | A_1' \cdots A_j' \rangle_A = \sum_{P\in S_j} (-1)^p \langle A_1'' \cdots A_j'' | \hat{p}_j | A_{p_1}' \cdots A_{p_j}' \rangle \, . \quad \text{(C19)}$$

These antisymmetrized matrix elements are in fact the appropriate elements to use in the spin orbital case. Indeed, using these elements we can write the operator $\hat{P}_j$ given by (C9) as

$$P_j = \sum_{\substack{A_1'' < A_2'' < \cdots < A_j'' \\ A_1' < A_2' < \cdots < A_j'}} \langle A_1'' \cdots A_j'' | \hat{p}_j | A_1' \cdots A_j' \rangle_A \times \prod_{i=1}^{j} (\hat{X}_{A_i''}^{\dagger} \hat{X}_{A_i'}) \, , \quad \text{(C20)}$$

where the summation extends over *ordered* spin orbital configurations. In this case all the states (C16) on the right-hand side of $\hat{P}_j | \Phi_0 \rangle$ are linearly independent, immediately yielding the necessary as well as sufficient condition (C17), i.e.,

$$\langle A_1'' \cdots A_j'' | \hat{p}_j | A_1' \cdots A_j' \rangle_A = 0 \, . \quad \text{(C21)}$$

Now consider the form of (E)CPMET in which the explicit spin dependence has been eliminated. This form may be achieved by the use of the facts that $|\Psi\rangle$ represents the singlet ground state of a closed-shell electronic system and that $\hat{H}$ is spin independent. We shall see that in this case we face an analogous, yet slightly more complex, situation as in the spin orbital case.

Let us first recall that for the spin-independent Hamiltonian and the singlet closed-shell ground state, the operator $\hat{T}$ is spin independent in the sense of Eq. (9). This means that the z-component of spin is conserved along each oriented path of our diagrams. It is not difficult to realize that in the same spin-independent closed-shell case the operator $\hat{P}$, Eq. (C5), is also spin independent in the same sense, so that we can write

$$\langle A_1'' \cdots A_j'' | \hat{p}_j | A_1' \cdots A_j' \rangle = \langle a_1'' \cdots a_j'' | \hat{p}_j | a_1' \cdots a_j' \rangle \prod_{i=1}^{j} \langle \eta_i'' | \eta_i' \rangle \, . \quad \text{(C22)}$$

The matrix element $\langle a_1'' \cdots a_j'' | \hat{p}_j | a_1' \cdots a_j' \rangle$ is determined by the same R diagram as the matrix element $\langle A_1'' \cdots A_j'' | \hat{p}_j | A_1' \cdots A_j' \rangle$: We have only to replace the spin orbital indices with the corresponding orbital indices and to assign a factor of 2 to each closed loop of oriented lines. Using the relationship (C22) we can rewrite the expression for $\hat{P}_j$ given by (C9) in the form

$$\hat{P}_j = \frac{1}{j!} \sum_{\substack{a_1'' \cdots a_j'' \\ a_1' \cdots a_j'}} \langle a_1'' \cdots a_j'' | \hat{p}_j | a_1' \cdots a_j' \rangle \prod_{i=1}^{j} \hat{\Gamma}(a_i'', a_i') \, , \quad \text{(C23)}$$

where we have designated

$$\hat{\Gamma}(a_i'', a_i') = \sum_{\eta_i} \hat{X}_{a_i''\eta_i}^{\dagger} \hat{X}_{a_i'\eta_i} \, . \quad \text{(C24)}$$

We now find that, just as in the spinorbital case, a sufficient condition for the vanishing of $\hat{P}_j | \Phi_0 \rangle$ is that all orbital $\hat{p}_j$ matrix elements vanish, while this is a necessary condition only if all states

$$\prod_{i=1}^{j} \hat{\Gamma}(a_i'', a_i') | \Phi_0 \rangle \quad \text{(C25)}$$

are linearly independent.

For the monoexcited and biexcited configurations we indeed find all the pertinent states (C25) to be linearly independent, so that the corresponding system of equations for the $\hat{t}_1$ and $\hat{t}_2$ orbital matrix elements is simply obtained by equating the $\hat{p}_j$ orbital matrix elements to zero. However, for the triexcited case, the states (C25) are no longer linearly independent, and we find that for each given set of orbitals a_i'', a_i', $i = 1, 2, 3$, there is one linearly dependent state. In other words, one constraint among these states exists, namely,

$$\sum_{P\in S_3} \prod_{i=1}^{3} \Gamma(a_i'', a_{p_i}') | \Phi_0 \rangle = 0 \, , \quad \text{(C26)}$$

where the summation extends over all permutations of, say, the occupied orbital set. Thus, in view of this linear dependence, the necessary condition that $\hat{P}_j | \Phi_0 \rangle$ shall vanish is that for each distinct orbital set a_i'', a_i', $i = 1, 2, 3$, we should have

$$\langle a_1'' a_2'' a_3'' | \hat{p}_3 | a_{p_1}' a_{p_2}' a_{p_3}' \rangle = \alpha \, , \quad \text{(C27)}$$

where p_1, p_2, p_3 represent an arbitrary permutation of the integers 1, 2, 3 and α is a completely arbitrary constant, which is, of course, the same for all permutations p_1, p_2, p_3 of each distinct orbital set a_i'', a_i', $i = 1, 2, 3$. This yields as many distinct equations as there are various $\hat{t}_3$ matrix elements [i.e., we have six $\hat{t}_3$ matrix elements and six equations (C27) for each orbital configuration a_i'', a_i', $i = 1, 2, 3$, in which all the orbitals are different; three if two occupied or two unoccupied orbitals are identical, and only two if both two occupied and two unoccupied orbitals are identical, as discussed in the main text].

Since for a given orbital configuration the constants α are identical, we can select one of Eqs. (C27), say the one corresponding to the permutation r_1, r_2, r_3 of the occupied orbitals, and subtract this equation from the remaining Eqs. (C27) corresponding to the same orbital configuration, obtaining, generally, the following system of equations:

$$\langle a_1''a_2''a_3'' | \hat{p}_3 | a_{p_1}'a_{p_2}'a_{p_3}' \rangle - \langle a_1''a_2''a_3'' | \hat{p}_3 | a_{r_1}'a_{r_2}'a_{r_3}' \rangle = 0. \tag{C28}$$

This system contains one less equation for each distinct orbital set than the system (C27), since p_1, p_2, p_3 must now differ from r_1, r_2, r_3 (in this order). Thus, for each distinct set of orbitals a_i'', a_i', $i = 1, 2, 3$, we now have one more unknown matrix element $\langle a_1''a_2''a_3'' | \hat{t}_3 | a_{p_1}'a_{p_2}'a_{p_3}' \rangle$ than the number of corresponding Eqs. (C28).

Observe now, however, that applying the same reasoning, based on the linear dependency (C26), to the expression $\hat{T}_3 | \Phi_0 \rangle$ rather than to the $\hat{P}_3 | \Phi_0 \rangle$, we find that the expression $\hat{T}_3 | \Phi_0 \rangle$ is invariant with respect to the following substitution

$$\langle a_1''a_2''a_3'' | \hat{t}_3 | a_{p_1}'a_{p_2}'a_{p_3}' \rangle \rightarrow \langle a_1''a_2''a_3'' | \hat{t}_3 | a_{p_1}'a_{p_2}'a_{p_3}' \rangle + \beta \,, \tag{C29}$$

where β is an arbitrary constant, which is the same for all permutations p_1, p_2, p_3 of the given orbital set a_i'', a_i', $i = 1, 2, 3$.

In view of this arbitrariness of β, two alternative courses of action are now open to us.

(i) For each distinct orbital set we can choose β in such a way that the constants α in (C27) will vanish. This will lead to the larger system of the ECPMET equations mentioned earlier. This set is clearly linearly independent, since owing to (C29) we can choose one of the $\hat{t}_3$ matrix elements, corresponding to a given orbital set, arbitrarily and we have chosen it in such a way that α in (C27) vanishes, in which case we have to consider all distinct $\hat{t}_3$ matrix elements in these equations on an equal footing.

(ii) For each distinct orbital set we can choose β in (C29) to be equal and opposite in sign to the $\hat{t}_3$ matrix element corresponding to the same permutation r_1, r_2, r_3 which had been selected to obtain the system of Eqs. (C28). This, of course, is equivalent to setting

$$\langle a_1''a_2''a_3'' | \hat{t}_3 | a_{r_1}'a_{r_2}'a_{r_3}' \rangle = 0 \tag{C30}$$

in the system of Eqs. (C28), thus obtaining the same number of unknowns as there are equations; this number is the same as the number of CI linearly independent singlet triexcited configurations. Thus, (C28) together with (C30) represent the desired reduced system of the ECPMET.

In conclusion it should be noted that this reduction procedure for the linked triexcited clusters may easily be generalized to an arbitrary case. Indeed, in the case of tetraexcited and higher-excited states there will be a number of relationships of the type (C26) expressing the linear dependency among the states (C25), $j \geq 3$. Obviously, the number of equations and of unknowns may be reduced in a similar, even though formally somewhat more complicated, way as above, by the number of available independent relationships of the type (C26) corresponding to each distinct orbital set.

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[14] We have also performed calculations which include the unlinked part of the biexcited clusters $\frac{1}{2}\hat{T}_1^2$. These calculations prove the complete negligibility of these terms, since their inclusion does not change the results obtained with the C approximation (up to eight decimal places, at least). Clearly, the cubic terms $(1/3!)\hat{T}_1^3$ will give an even smaller effect and may be safely disregarded. This result is also indicated by considering the lowest order of perturbation theory in which these terms will appear.

[15] The number of linearly independent singlets, and of corresponding $\hat{t}_3$ matrix elements, may be smaller than this maximum in some cases because of spatial symmetry requirements. In any event it can be shown that there always is one more $\hat{t}_3$ matrix element than the corresponding number of linearly independent CI singlets.

[16] The atomic orbital integrals were recomputed (to an accuracy of better than 10^{-6} a.u.) using R. M. Stevens' program [Program 161, Quantum Chemistry Program Exchange, Indiana University, 1970 (unpublished)]. Errors of up to 0.7×10^{-4} a.u. were found in the original integrals used in Ref. 5. The CI results were recomputed using programs written by A. Pipano (unpublished).

[17] Actually the smallness of unlinked triexcited clusters is understandable in terms of the smallness of $\hat{T}_1$, i.e., "the effect of correlation on orbitals", Ref. 7(b).

[18] Z. Gershgorn and I. Shavitt, Intern. J. Quantum Chem. 2, 751 (1968).

[19] When exploiting the space symmetry, the number of $\hat{t}_1$ and $\hat{t}_2$ matrix elements and, correspondingly, of Eqs. (A1) is reduced by the same number as the order of CI including monoexcited and biexcited states.

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Electron Binding Energies, X-Ray Spectra, and L-Shell Fluorescence Yields in Curium ($Z=96$)

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The Cm K x-ray spectrum from the decay of ^{249}Cf and the Cm L x-ray, internal conversion, and γ-ray spectra associated with the 42.9-keV $E2$ transition in the α decay of ^{250}Cf were measured at high resolution. From these data accurate values for the binding energies of K, L_1, L_2, L_3, M_1, M_2, M_3, M_4, M_5, N_1, N_2, N_3, N_4, N_5, O_2, O_3, O_4, and P_3 electrons in Cm were obtained. Values were derived also for the L-subshell fluorescence yields in Cm: $\omega_1=0.28\pm0.06$, $\omega_2=0.55\pm0.02$, and $\omega_3=0.63\pm0.02$.

INTRODUCTION

The experimental determination of accurate values for the energies of atomic electron levels provides information with which theoretical calculations of atomic structure may be compared, and, as a practical matter, these values make available energy reference standards for β- and γ-ray spectroscopy. Further, the x-ray spectra of trans-fermium elements could provide a means for their identification, and Carlson, Nestor, Malik, and Tucker[1] were thus prompted to calculate electron binding energies for Z values from 96 to 120. They used relativistic Hartree-Fock-Slater finite-nuclear-size wave functions and made small corrections to these results by extrapolating experiment-calculation energy differences known at lower Z values. It is of interest to compare these binding energies as far as possible with measured values. For $Z>95$ experimental electron-binding-energy information is limited; K through M_3, N_1, and O_1 measurements have been made in berkelium[2] ($Z=97$); and recently measurements for K through M_3, N_1, N_2, N_3, and $O_{2,3}$ have been published[3] for californium ($Z=98$). Experimental information on binding-energy differences is available for elements of $96\leq Z\leq 100$ from very accurate measurements of K x-ray spectra.[4] There are presented in this paper measurements made on radiations of ^{246}Cm and ^{245}Cm from which electron binding energies and L-subshell fluorescence yields in curium ($Z=96$) have been derived.

EXPERIMENTAL METHODS

About 17% of the α decay of 13-yr ^{250}Cf produces the 42.9-keV first-excited state of ^{246}Cm, which decays by a highly converted pure $E2$ transition.[5] Measurements of the energies of the internal-conversion-electron lines and the unconverted γ ray