Relationship between configuration interaction and coupled cluster approaches

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A variational principle for the linear coupled pair many-electron theory (L-CPMET) is given and its implications for the relationship between certain configuration interaction (CI) and coupled cluster approaches (CCA), and for the computational aspects of solving the algebraic systems occurring in CCA, are discussed. An exact relationship between the correlated energies and wave functions as obtained with the L-CPMET and with the CI limited to at most doubly excited configurations (D-CI) is derived and used to provide a new viewpoint on the origins of Davidson’s correction for unlinked cluster contributions in the D-CI energy. The results are illustrated on the CO molecule.

I. INTRODUCTION

The coupled cluster approach (CCA) to the many-electron correlation problem is based on the cluster expansion of the exact nonrelativistic electronic wave function. It was used for the first time in the nuclear many-Fermion correlation problem by Coester and Kümmel.1 The form of the CCA wave function guarantees the additivity of cluster components for noninteracting systems. However, in contrast to an ordinary configuration interaction (CI) linear expansion, the cluster expansion is not amenable to a variational approach. Even though the equations of the CCA are obtained by considering various moments of the Schrödinger equation, these are not associated with the usual variational principle of quantum mechanics and, consequently, the upper bound property for the energy is lost (cf., e.g., Ref. 2).

A general method of deriving the explicit form of the CCA equations was given by Čížek.3 He has also derived these equations for the most important case of pair clusters, thus formulating a coupled pair many-electron theory (CPMET).3 Presently, a number of reviews and derivations of the CPMET equations and of their applications are available.4-13 The orthogonally spin-adapted version of the CCA was also formulated14,15 and, very recently, this form of the CPMET equations was used by Chiles and Dykstra16 to obtain a computationally very promising SCEP (self-consistent electron pair) form17 of these equations (essentially, by transforming the virtual orbital part back into the atomic orbital basis). The most recent survey of the CCA and its applications to various molecular systems was given by Bartlett.18

The attractiveness of the CCA lies particularly in its size extensivity (cf., e.g., Ref. 11), which is especially important when studying various associative or dissociative processes. This is also the case for various perturbative approaches based on the Rayleigh–Schrödinger (RS) many-body perturbation theory (MBPT) (cf., e.g., Ref. 18). In fact, the special version of this approach, in which all the MBPT diagrams with at most doubly excited intermediate states are summed to all orders (the so-called DMBPT19), is equivalent to the linear version of the CPMET20 (the so-called L-CPMET). This approach yields correlation energies which are very close to the full CPMET correlation energies, unless the studied ground state is quasidegenerate, as, for example, in the case of the beryllium atom. In the latter case, the assumption of nondegeneracy represents too severe an approximation, and one should in fact use the CCA for a (nearly) degenerate ground state recently developed by Lindgren.13 The L-CPMET approach is also known as CEPA(0),20,21 since it involves no explicit coupling of pair clusters (all nonlinear terms in the CPMET approach are neglected).

Since the L-CPMET approach is closely related to perturbation theory, it is not surprising that one can associate with it a variational functional of the Hylleraas type (cf. Ref. 2, p. 187), as we shall show in this paper. This viewpoint suggests, in turn, a very simple and useful relationship between the L-CPMET and the corresponding variational approach, the doubly excited CI (referred to as D–CI). This relationship elucidates from a new viewpoint the often used Davidson corrections20-24 to the D–CI energies, and enables us to both improve upon this correction and to obtain the corresponding approximate wave function. It also suggests the suitability of certain numerical methods for solving the CCA equations by providing a better understanding of the relationship between variational and coupled cluster approaches in general.

II. BASIC FORMALISM

We briefly introduce the necessary notation and the basic formalism for the coupled cluster and variational CI approaches. We consider a nondegenerate ground state of an N-electron system described by the nonrelativistic electronic Hamiltonian $\hat{H}$. We designate the exact and the independent particle model (IPM) ground states by $|\psi_0\rangle$ and $|\Phi_0\rangle$, respectively. We shall use the time-independent Schrödinger equation in the normal product form (relative to the IPM ground state $|\Phi_0\rangle$ taken as the Fermi vacuum of the hole–particle
formalism (cf., e.g., Ref. 25)
\[ \hat{H}_N | \psi_0 \rangle = \Delta E | \psi_0 \rangle , \]  
where \( \Delta E \) is the correlation energy when we choose the restricted Hartree–Fock (RHF) solution for \( | \phi_0 \rangle \)
\[ \Delta E = E_0 - \langle \phi_0 | \hat{H} | \phi_0 \rangle , \]  
with \( E_0 \) being the lowest energy eigenvalue of the Hamiltonian \( \hat{H} \). Imposing the intermediate normalization condition on \( | \psi_0 \rangle \)
\[ \langle \psi_0 | \phi_0 \rangle = 1 , \]  
the correlation energy is also given by the asymmetric energy formula
\[ \Delta E = \langle \psi_0 | \hat{H}_N | \psi_0 \rangle . \]  

A. CI approach

In the variational CI approach, the exact state \( | \psi_0 \rangle \) is expanded through \( | \phi_0 \rangle \) by promoting one, two, three, etc. electrons from the spin-orbitals \( | B_j \rangle \) occupied in \( | \phi_0 \rangle \), into the virtual spin-orbitals \( | B^k \rangle \). Using the intermediate normalization [Eq. (3)] we can thus write
\[ | \psi_0 \rangle = (1 + \hat{C}) | \phi_0 \rangle , \]  
where \( \hat{C} \) is the sum of excitation operators \( \hat{C}_i \)
\[ \hat{C} = \sum_{i=1}^N \hat{C}_i . \]  
The \( i \)-th component \( \hat{C}_i \) of \( \hat{C} \) will thus generate from \( | \phi_0 \rangle \) an appropriate vector from the \( i \)-times excited subspace
\[ | \psi_0^{(i)} \rangle = \sum_i c_i^{(i)} | \phi_0^{(i)} \rangle , \]  
where \( | \phi_0^{(i)} \rangle \) is the \( i \)-times excited configuration state characterized by an ordered configuration \( I \)
\[ I = \{ B_1^1 B_2^2 \cdots B_i \} , \]  
obtained by promoting \( i \) electrons from the states \( | B_1 \rangle \), \( | B_2 \rangle \), ..., \( | B_i \rangle \) occupied in the reference IPM state \( | \phi_0 \rangle \) into the virtual states \( | B_1^1 \rangle \), \( | B_2^2 \rangle \), ..., \( | B_i^i \rangle \), respectively, while \( c_i^{(i)} \) designates the corresponding coefficient in the resulting CI wave function (5).

For a spin-independent Hamiltonian \( \hat{H} \), we can choose an appropriate coupling scheme and consider the expansion (7) in terms of orthonormal spin-adapted configurations. Our conclusions will hold equally for the spin-orbital formalism so that \( | \phi_0^{(i)} \rangle \) can, in the following, represent either an ordered spin-orbital configuration state with \( I \) given by Eq. (8) or an orthonormal spin-adapted configuration, in which case \( I \) designates appropriate orbital labels and spin coupling quantum numbers (cf., e.g., Refs. 14, 15, or 26).

The basic equations of the variational approach may be simply obtained by projecting the Schrödinger equation (1) with \( | \psi_0 \rangle \) given by Eq. (5) onto the configuration states \( | \phi_0^{(i)} \rangle \) appearing linearly in \( | \psi_0 \rangle \) (cf., e.g., Ref. 2)
\[ \langle \phi_0^{(i)} | \hat{H}_N | \psi_0 \rangle = \Delta E \langle \phi_0^{(i)} | \psi_0 \rangle = \Delta E c_i^{(i)} . \]  
Since \( \hat{H}_N \) contains at most two-body operators, the left-hand side of Eq. (9) has the form
\[ \langle \phi_0^{(i)} | \hat{H}_N | \psi_0 \rangle = \sum_{j=i}^n \sum_j c_j^{(j)} H_j^{(i)} , \]  
where
\[ c_j^{(j)} = 0 , \text{ if } j < 0 ; \quad c_j^{(j)} = c_j^{(i)} = 1 \]  
and
\[ H_j^{(i)} = \langle \phi_0^{(i)} | \hat{H}_N | \phi_0^{(j)} \rangle . \]
Clearly,
\[ H_0^{(0)} = \langle \phi_0 | \hat{H}_N | \phi_0 \rangle = 0 . \]  
We thus obtain the well-known chain of CI equations (14) has the form [note that \( c_0^{(0)} = 1 \)]
\[ \sum_{j=i+1}^M \sum_j [ H_j^{(j)} - \Delta E c_j^{(j)} ] c_j^{(i)} = 0 , \]  
where
\[ c_i^{(i)} = c_i^{(0)} c_i . \]  
Considering, for the sake of simplicity, only the even-number-of-times excited configurations, the chain (14) has the form
\[ \sum_{j=i+2}^M \sum_j [ H_j^{(j)} - \Delta E c_j^{(j)} ] c_j^{(i)} = 0 , \]  
\[ \sum_{j=i+1}^M \sum_j \sum_k [ H_j^{(j)} c_j^{(j)} + \sum_j H_j^{(j)} c_j^{(j)} + \sum_j H_j^{(j)} c_j^{(j)} = \Delta E c_i^{(i)} , \]  
where the equation for each \( i > 0 \) represents a system of equations for all possible configurations \( I \). With some given finite set of (spin) orbital states, the full system (14) or (16) will yield the full–CI solution. To obtain a limited–CI approximation we decouple the above chain (14) or (16) at a certain excitation level \( i = m \) by neglecting all \( H_j^{(j)} \) matrix elements with \( j > m \). Thus, for example, the doubly-excited CI equations (D–CI) are obtained by neglecting all \( H_j^{(j)} \) matrix elements in the second Eq. (16), which gives
\[ \sum_j a_i^{(i)} c_i = E_D , \]
\[ a_i + \sum_j b_i^{(i)} c_i = E_D c_i , \]  
where we designated
\[ a_i = H_i^{(i)} , \quad b_i^{(i)} = H_i^{(i)} , \quad \text{and } c_i = c_i^{(i)} , \]  
with \( i, j = 1, \ldots, M \), where \( M \) is the number of biexcited configurations \( | \phi_0^{(j)} \rangle \), \( m = 2, E_D \) is the D–CI approximation to \( \Delta E \), Eq. (2), and \( a^* \) is the complex conjugate of \( a \). In matrix form we can write Eq. (17) as
\[ H C = E_D C , \]  
where
\[ H = \begin{bmatrix} 0 & a^t \\ a & b \end{bmatrix} \quad C = \begin{bmatrix} 1 \\ c \end{bmatrix}, \]  
\[ \text{with } a \text{ and } c \text{ being column matrices with } M \text{ entries } a_i \text{ and } c_j \text{, respectively, and } b \text{ is the } M \times M \text{ matrix with entries } b_{ij}. \]

**B. CC approach**

In the coupled cluster approach, the state \( |\psi_0\rangle \) is expanded through the same IPM configuration states \( |\phi_i^{(i)}\rangle \) as above, however, with the cluster expansion ansatz for the wave operator

\[ |\psi_0\rangle = \hat{\psi} |\phi_0\rangle, \]  
where again \( \hat{\psi} \) is the sum of the \( i \)-fold excitation operators \( \hat{T}_i \). Analogously to Eq. (7) we have that

\[ \hat{T}_i |\phi_0\rangle = \sum_i \hat{\psi}^{(i)} |\phi_i^{(i)}\rangle. \]  
The relationship between both excitation operators, or between the corresponding expansion coefficients in Eqs. (7) and (22), follows immediately from a comparison of both expansions [Eqs. (5) and (21)] (cf., e.g., Refs. 27 and 28) yielding

\[ \hat{C}_i = \sum_{i,j=1}^{\infty} (n_i) \hat{T}_j, \]  
where the sum extends over all partitions \( \phi_i \) of \( i \), i.e.,

\[ i = \sum_{j=1}^{\infty} (n_i), \quad 0 \leq n_i \leq i; \quad \hat{T}_j = 1. \]

The right-hand side of Eq. (23) contains one term consisting of a single factor \( \hat{T}_i \), which represents a connected \( i \)-times excited cluster component, while the remaining terms, involving products of at least two lower order components, represent disconnected \( i \)-times excited clusters. In the MBPT language, all the terms in the expansions (5) and (21), except for the Fermi vacuum component \( |\psi_0\rangle \), are represented by linked wave function type diagrams (i.e., the diagrams with at least one hole-particle pair of fermion lines in each disconnected part extending in the positive “time” direction). Furthermore, the term \( \hat{T}_i |\phi_0\rangle \) is represented by a connected diagram, while the product terms \( \hat{T}_i \hat{T}_j \hat{T}_k \cdots |\psi_0\rangle \) are represented by disconnected diagrams.

Assuming that \( \hat{T}_1 = 0 \) [which is exactly the case if Brueckner or maximum overlap (spin) orbitals are used], the first disconnected term appears in the quadruply excited component, namely,

\[ \hat{C}_1 = \hat{T}_1 = 0, \]
\[ \hat{C}_2 = \hat{T}_2 + \hat{T}_3, \]
\[ \hat{C}_3 = \hat{T}_4 + \frac{1}{2} \hat{T}_5. \]  
Since \( \hat{T}_1 \) is usually negligible\(^{29} \) relative to the corresponding disconnected component \( \hat{T}_2 \), the approximation \( \hat{T} \approx \hat{T}_2 \) represents, in most cases (i.e., when \( \hat{T}_3 \) is not very important, cf., e.g., Refs. 18 and 30), an excellent approximation.\(^{2} \)

With the coupled cluster ansatz [Eq. (21)] we can reduce the Schrödinger equation (1) to the following connected cluster form\(^{14,15} \):

\[ \left( \hat{\mathcal{H}}_{\text{CC}} \right)_C |\psi_0\rangle = \Delta E |\psi_0\rangle, \]  
where the subscript \( C \) indicates that only connected diagrams (or terms) are to be considered. The equations which determine various cluster components (i.e., the coefficients \( q^{(i)} \)) are again obtained\(^{14,15} \) by projecting Eq. (26) onto the configuration states \( |\phi_i^{(i)}\rangle \), i.e., by considering moments of Eq. (26) relative to the configuration states \( |\phi_i^{(i)}\rangle \), even though the resulting equations are not variational equations in the sense of providing an upper bound to the energy. In this approach, the energy is given by the projection of Eq. (26) onto the reference state \( |\psi_0\rangle \), i.e., by the asymmetric formula [Eq. (4)]

\[ \Delta E = \langle \phi_0 | \left( \hat{\mathcal{H}}_{\text{CC}} \right)_C |\psi_0\rangle, \]  
while the equations determining the cluster coefficients, which are obtained by projecting Eq. (26) onto the excited configurations

\[ \langle \phi_i^{(i)} | \left( \hat{\mathcal{H}}_{\text{CC}} \right)_C |\psi_0\rangle = 0 \]  
are energy independent.

An explicit form of these equations is best obtained through the use of diagrammatic techniques (cf., e.g., Refs. 3, 14, 15, 25, and 26). One sees immediately from Eq. (27) that \( \Delta E \) depends at most on the first two components \( \hat{T}_1 \) and \( \hat{T}_2 \). Assuming that \( \hat{T} \approx \hat{T}_2 \), only the linear term survives, so that the CPMET correlation energy \( E_{CP} \) is given by

\[ E_{CP} = \langle \phi_0 | \hat{\mathcal{H}}_{\text{CC}} \hat{T}_2 |\psi_0\rangle. \]  
We also find that the system (28) decouples automatically, obtaining

\[ \langle \phi_i^{(i)} | \hat{\mathcal{H}}_{\text{CC}} |\psi_0\rangle = 0 \]  
or, more explicitly,

\[ a_l + \sum_{j=1}^{\infty} b_j |l_j| = \sum_{j=K}^{\infty} d_{l_j}, \]  
where \( a_l \) and \( b_j \) are given again by Eq. (18), \( t_j = t_j^{(j)} \), and \( d_{l_j} \) represents the connected part of the matrix element between the doubly excited configuration \( |\phi_i^{(i)}\rangle \) and the quadruply excited configuration consisting of double excitations given by the configurations \( J \) and \( K \). For an explicit form of these coefficients see Ref. 3, or in the orthogonally spin-adapted case Ref. 14.

Designating the column matrix of \( t_l \) coefficients as \( t \), we can also write Eq. (29) as

\[ E_{CP} = a^t t. \]  
Neglecting the nonlinear terms in the CPMET Eq. (31), we obtain the corresponding L-CPMET equations

\[ a + b t_L = 0, \]
\[ E_L = a^t L a = a^t b^{-1} a, \]  
where the subscript \( L \) indicates the linear approximation, and where we have assumed that \( b \) is nonsingular in the last equation.

Let us mention, finally, that the same simple rela-
tionship between the D-CI matrix $H$ [Eq. (20)] and the corresponding L-CPMET equations [Eqs. (33) and (34)] holds even when both mono- and biexcited configurations are considered and an RHF reference state is used (cf., e.g., Ref. 15). However, this is not the case when also triexcited configurations are taken into account [cf., diagram 7(c) of Ref. 15]. We thus assume in the following that $H$ [Eq. (20)] and the corresponding CCA equations involve either doubly excited configurations (D-CI) or both singly and doubly excited configurations (sometimes referred to as the SD-CI), even though we shall always use the D-CI matrix $H$ [Eq. (20)] for simplicity's sake.

III. COMPARISON OF VARIATIONAL AND COUPLED CLUSTER APPROACHES

We now briefly outline the relationship between the variational limited CI approaches and the corresponding CCA's in order to understand better the derivations and the discussion in the subsequent sections. We shall, in particular, examine the simplest CCA, namely the L-CPMET and the corresponding D-CI approach.

Both D-CI and L-CPMET exploit the same information about the system considered as given by the D-CI matrix $H$ [Eq. (20)] or, equivalently, by its submatrices $a$ and $b$ with matrix elements defined by Eq. (18). It should be noted that $b$ in Eq. (33) need not be Hermitian, since we can multiply each equation of this linear system by an arbitrary nonvanishing scalar. This is, in fact, the case in the usual formulation of the variational limited CI approaches and the corresponding L-CPMET equations (cf., e.g., Refs. 3, 14, and 15), where renormalized coefficients $\tilde{\gamma}$ are often used. However, it is very easy to make a transition from these unnormalized $t$-matrix elements or coefficients to the normalized ones, as is shown in Refs. 14 and 15, so that the assumption that the matrices $a$ and $b$ are identical in the D-CI problem [Eq. (19)] and in the CPMET [Eq. (33)] problems represents no restriction on the generality of our considerations.

In order to see the conditions for the breakdown of the L-CPMET approach in more physical terms, as well as to clarify the relationship of this method with both variational and perturbative approaches, it is convenient to transform the D-CI matrix $H$ [Eq. (20)] to a form in which its doubly excited part is diagonal (cf. Refs. 31 and 32). Consider, thus, a unitarily equivalent matrix

$$
\tilde{H} = V^H H V ,
$$

where $V$ has the same block structure as $H$ [Eq. (20)]

$$
V = \begin{bmatrix} 1 & 0 \\ 0 & V \end{bmatrix} ,
$$

and where $V$ is the unitary matrix which diagonalizes $b$

$$
bv = v\beta ,
$$

with

$$
\beta = [\beta_I] .
$$

Thus,

$$
\tilde{H} = \begin{bmatrix} 0 & \alpha^T \\ \alpha & \beta \end{bmatrix} ,
$$

where

$$
\alpha = v^T a .
$$

The transformation $V$ thus introduces a new basis in the doubly excited subspace.

Clearly, $\tilde{H}$ [Eq. (39)] has the same eigenvalues as the original D-CI matrix $H$, Eq. (20). It is easy to see that, also, the corresponding L-CPMET problem

$$
a + \beta \tau = 0 ,
$$

yields the same energy as the original problem [Eqs. (33) and (34)]

$$
\tilde{E}_L = \alpha^T \tau = -\alpha^T \beta^{-1} \alpha = -a^T b^{-1} a = E_L ,
$$

since Eq. (37) implies that

$$
v\beta^{-1} v^T = b^T ,
$$

assuming $b$ is regular. In fact, the L-CPMET correlation energy [Eq. (42)] can be written in the form

$$
E_L = -\sum_{I=1}^M |\alpha_I|^2 / \beta_I ,
$$

which shows immediately that $E_L$ will have a singularity if $\beta_I = 0$ for some $I$.

In a well-behaved problem, the matrix $b$ will be diagonally dominant and positive definite. Only when some of the doubly excited configurations will be quasidegenerate with the reference RHF state can we expect the lowest eigenvalue of $b$ to be very small or even negative. We have investigated the behavior of the L-CPMET approximation in such quasidegenerate cases elsewhere.

Using the canonical form (39) of the D-CI matrix, we can also write the corresponding secular problem in a simple form. Expanding the associated secular determinant about the first row or column, or using simply the partitioning technique, we obtain

$$
E_D = -\sum_{I=1}^M |\alpha_I|^2 / (\beta_I - E_D) ,
$$

the well known formula of the escalator diagonalization method.

Equations (44) and (45) also indicate a connection with corresponding perturbative approaches. Solving the L-CPMET equations (33) iteratively, using basically an algorithm due to Jacobi, we see immediately that we obtain an equivalent result to the DMBPT. In fact, partitioning properly the diagonal terms, we can go continuously from an Epstein–Nesbet type perturbation theory to the Möller–Plesset type (cf. Ref. 32). Moreover, when the canonical form (39) is used, we obtain the desired L-CPMET or DMBPT energy already in the second order of Rayleigh–Schrödinger perturbation theory (RSPT), as Eq. (44) indicates. On the other hand, the D-CI energy can be obtained from the corresponding second order Brillouin–Wigner perturbation theory (BWPT), as follows from Eq. (45). It is well...
known that the RSPT is size extensive while BWPT is not, which is consistent with the characteristics of the D-CI and L-CPMET approaches.

The size extensivity of the L-CPMET (or, in fact, of the CCA in general) follows immediately from the cluster ansatz [Eq. (21)] which transforms multiplicative structures into additive ones, and which leads to the cancellation of all disconnected clusters, Eq. (26). In order to see this cancellation in more detail, let us consider the appropriate moments of the Schrödinger equation associated with the D-CI and L-CPMET cases.

In the D-CI case, Eq. (9) can be written in the form

$$
\langle \psi_1^{(i)} | (\hat{H}_d - E_0) (1 + \hat{C}_0) | \psi_0 \rangle = 0 ,
$$

while the corresponding L-CPMET equations follow from Eq. (26):

$$
\langle \psi_1^{(i)} | [\hat{H}_d (1 + \hat{T}_2)]_L - E_L | \psi_0 \rangle = 0 ,
$$

where $i \leq 2$. The basic difference between these two systems of equations lies in the presence of the term $\langle \psi_1^{(i)} | E_0 \hat{C}_1 | \psi_0 \rangle = E_0 \phi_1^{(i)}$ in the D-CI system (46). This term corresponds to the unlinked diagrams in the perturbation theory approach, and is therefore responsible for the size inconsistency of the D-CI approach. In the L-CPMET (or CPMET) approach, these unlinked terms have been canceled by the unlinked (and thus disconnected) component $\langle \psi_1^{(i)} | [\hat{H}_d \phi_1^{(j)}]_L | \psi_0 \rangle$. This cancellation is implicit in the connected cluster form of the Schrödinger equation, Eq. (26).

It should be noted, however, that the canceled term $\langle \psi_1^{(i)} | E_0 \hat{C}_1 | \psi_0 \rangle$ contains both the EPV (exclusion principle violating) and the non-EPV components since the summations over the (spin) orbital labels in each factor are independent. From this viewpoint, the L-CPMET “overcorrects” the D-CI result and the EPV terms are reintroduced through certain nonlinear EPV connected terms in the CPMET approach. The most important terms in this respect are those represented by diagrams which can be separated over one or two hole lines: these terms play the most important role when going from the L-CPMET to the CPMET approach (cf. Refs. 31, 34, and 35) and form the basis of various CEPAs, $k \neq 0$, approaches (cf. Refs. 31 and 34).

In this respect, it is interesting to compare the D-CI and the L-CPMET approaches for the case of two-electron systems. Clearly, the D-CI approach yields the exact energy within the model space considered, while the L-CPMET does not. This is due to the fact that the latter approach includes a correction for the unlinked tetraexcited clusters [which is implicit in the connected form given by Eq. (26), as explained above]. However, all tetraexcited components are unphysical in this case, and thus of the EPV type. These terms would be subsequently cancelled by the nonlinear CPMET terms, which are also always of the EPV type in the two-electron case considered, and the D-CI result would be restored. Clearly, the CPMET, or its simple version the L-CPMET, are designed for many-electron rather than two-electron systems, for which the number of non-EPV unlinked type contributions will be much larger than the number of similar EPV type terms.

Therefore, the corrections for the unlinked tetraexcited terms, present in the D-CI approach, will be much more important than the overcorrection due to the inclusion of the EPV terms, which are necessary to achieve the factorization, and which are corrected for when the proper “coupling” of pair clusters is considered in the CPMET approach.

IV. HYLLERAAS-TYPE FUNCTIONAL FOR THE L-CPMET

Since the L-CPMET can be regarded as a special case of perturbation theory as explained above, it is worthwhile to look for the Hylleraas-type functional (cf. Ref. 2, p. 187) whose optimization yields an equivalent result. Such a functional must clearly contain the same information about the system as contained in the D-CI matrix $H$, Eq. (20). Such a functional might thus provide, at least in principle, a useful insight into the relationships of CI and CC approaches.

We recall that in the D-CI approach the correlation energy is given by the minimum of the following Rayleigh quotient

$$
F_D(\mathbf{Y}) = \mathbf{Y}^\dagger \mathbf{H} \mathbf{Y} / (\mathbf{Y}^\dagger \mathbf{Y}) ,
$$

where $\mathbf{H}$ is the D-CI matrix (20) (with the diagonal entries relative to the reference RHF state energy) and $\mathbf{Y}$ is an arbitrary trial vector. Since we wish to relate this variational approach with the L-CPMET approach, we shall use an intermediate normalization for $\mathbf{Y}$ and write

$$
\mathbf{Y}_L = \begin{bmatrix} 1 \\ \mathbf{x} \end{bmatrix} ,
$$

without restricting generality in any way.

The minimum condition for $F_D(\mathbf{Y})$ [Eq. (48)] is given by the eigenvalue equation

$$
\mathbf{H} \mathbf{U} = \mathbf{U} \Lambda ,
$$

where $\Lambda$ is diagonal

$$
\Lambda = [\lambda_i \delta_{ij}] ,
$$

with the lowest eigenvalue $\lambda_0$ giving the minimum of $F_D(\mathbf{Y})$, which defines the desired correlation energy $E_D$

$$
E_D = \min F_D(\mathbf{Y}) = F_D(\mathbf{Y}(\hat{\epsilon})) = \lambda_0 ,
$$

$$
\mathbf{Y}(\hat{\epsilon}) - \mathbf{u}_0 ,
$$

and $\mathbf{U}$ is a unitary matrix whose $i$th column $\mathbf{u}_i$ represents an eigenvector of $H$, which is associated with an eigenvalue $\lambda_i$.

Recalling elementary properties of the diagonal form of a Hermitian matrix, we can write

$$
H = \mathbf{U} \Lambda \mathbf{U}^\dagger
$$

or, equivalently, in terms of matrix elements

$$
H_{ij} = \sum_k \lambda_k n_{ik} n_{jk}^* ,
$$

where we designated the matrix elements of $H$ and $\mathbf{U}$ by

After recalling these elementary facts, let us consider the problem outlined at the outset. Just as in perturbation theory, we can construct the desired Hylleraas functionals in each order by inspection; it is easy to see that the L-CPMET equations (33) are obtained as a condition for an extremum of the functional

$$F_L(Y_L) = f_L(x) = Y_L^T H Y_L,$$  

with $Y_L$ given by Eq. (49). Using an explicit form of the D-CI matrix $H$ [Eq. (20)] we obtain the following quadratic function:

$$f_L(x) = \begin{bmatrix} x^T \end{bmatrix}^T \begin{bmatrix} 0 & a \\ a & b \end{bmatrix} \begin{bmatrix} x^T \end{bmatrix} = x^T a + a^T x + x^T b x,$$  

so that the conditions for an extremum of $f_L(x)$ become

$$a + bx = 0.$$  

The conditions are identical with the L-CPMET equations (33) when we identify the unknowns $x$ and $t_L$.

The necessary and sufficient condition for an existence of a unique extremum is the definiteness of the matrix $b$. In this case, $b^{-1}$ exists and we can easily verify that the L-CPMET energy $E_L$, as given by Eq. (34), can be obtained as an extremal value of the functionals (57) or (58),

$$E_L = \frac{x^T a + a^T x + x^T b x}{1 + x^2},$$

so that the solutions of the system (59). Both functionals (48) and (57) represent clearly special cases of the same general functional $G$, given by the quadratic form

$$G(X) = X^T H X.$$  

Indeed, we have

$$G_D(Y) = G(X) = G(Y_D),$$

when

$$X = Y_D = Y (Y^T Y)^{-1/2} = Y / ||Y||,$$  

and

$$G_L(Y_L) = f_L(x) = G(X) = G(Y_L),$$

when

$$X = Y_L = \begin{bmatrix} 1 \\ x \end{bmatrix}.$$  

This formulation provides an interesting geometrical viewpoint on the two approaches considered. Both the D-CI and the L-CPMET energies can be regarded as the extrema of the same functional but under different constraints: the trial vectors are restricted to the unit sphere $||X|| = 1$ in the D-CI case, and to the tangent plane $x_0 = 1$ to this sphere, at the point corresponding to the reference RHF state in the L-CPMET case.

**V. MODEL EXAMPLE**

Before we discuss the implications of the above given functionals we wish to illustrate them in more detail on the simplest possible example: a two-electron, two-level model system with only one doubly excited configuration. This system will be described by the following D-CI matrix:

$$H_1 = \begin{bmatrix} 0 & a \\ a & b \end{bmatrix},$$

which we assume to be real in order to simplify our notation as much as possible. In this case, the general functional (61) is given by the following quadratic form in two variables:

$$G_1(X) = G_1 \left( \begin{bmatrix} x_0 \\ x_1 \end{bmatrix} \right) = \begin{bmatrix} 0 & a \\ a & b \end{bmatrix} \begin{bmatrix} x_0 \\ x_1 \end{bmatrix} = x_0 (2a x_0 + b x_1) + x_1 (2b x_0 + a x_1).$$

When restricting the variables $x_0 = y_0^2$, $x_1 = y_1^2$ to the unit circle

$$y_0^2 + y_1^2 = 1,$$  

we obtain the D-CI functional

$$F_D(Y) = G(Y_D) = G_1 \left( \begin{bmatrix} \cos \beta \\ \sin \beta \end{bmatrix} \right) = \sin \beta (2a \cos \beta + b \sin \beta)$$

$$= a \sin 2\beta + \frac{1}{2} b (1 - \cos 2\beta) = \frac{1}{2} \left[ 1 - (1 + \tan^2 2\beta)^{-1/2} \right],$$  

assuming $|\beta| < \pi/4$,

$$= \frac{\tan \beta}{1 + \tan^2 \beta},$$

where we have set

$$x_0 = y_0^2 = \cos \beta = y_0 (y_0^2 + y_1^2)^{-1/2},$$  

$$x_1 = y_1^2 = \sin \beta = y_1 (y_0^2 + y_1^2)^{-1/2}.$$  

Similarly, setting $x_0 = y_0^2 = 1$ and $x_1 = y_1^2 = x$, following Eq. (49), we obtain the L-CPMET functional

$$f_L(x) = G_L \left( \begin{bmatrix} 1 \\ x \end{bmatrix} \right) = x (2a + b x).$$

Both sets of variational parameters are related as follows:

$$x = \frac{x_1}{x_0} = \frac{y_1}{y_0} = \frac{y_0}{y_0^2} = \tan \beta,$$  

and

$$y_0^2 = \cos \beta = (1 + x^2)^{-1/2},$$  

$$y_1^2 = \sin \beta = x (1 + x^2)^{-1/2},$$

so that we can also write the above functionals in the following equivalent forms:

$$F_L = f_L(x) = G_L (\beta) = \tan \beta (2a + b \tan \beta),$$

and

$$F_D = G_D (\beta) = x (2a + b x) / (1 + x^2),$$

$$= F_L (\tan \beta) / (1 + \tan^2 \beta).$$
FIG. 1. Relationship of D-CI and L-CPMET variational parameters in a simple two-dimensional model case. The relationship given by Eq. (82), which connects extremal values of variational parameters, is shown below the $x_2$ axis, since $x_2^{\text{L}} = -a/b < 0$, assuming that $a, b > 0$. The points marked by full circles indicate the absolute minimum of the functional $G_0(X)$ [Eq. (67)] on the unit circle and on its tangent at $x_0 = 1$, representing D-CI and L-CPMET solutions, respectively.

The relationship between various variational parameters used above is illustrated in Fig. 1.

Thus, while in the D-CI approach we are searching for a minimum of the functional (67) along the unit circle (68) (cf. Fig. 1), in the L-CPMET approach, we search for the minimum of the same functional along the tangent at unity ($x_0 = 1$, $x_1 = 0$), which corresponds to the RHF reference state used. Since the functional (67), or (61) in general, is a homogeneous quadratic form, we have for any scalar $k$

\[ G(kX) = k^2 G(X) . \]  

(74)

We can also see immediately that both functionals (73a) and (73b) have the same nodes, at least in the physically relevant interval $-\pi/2 < \beta < \pi/2$.

The extremum of $f_2(\beta)$ will occur for $x = x_2^{\text{L}}$ given by the condition

\[ \left. \frac{df_2(\beta)}{dx} \right|_{x=x_2^{\text{L}}} = 2(a + bx) |_{x=x_2^{\text{L}}} = 0 , \]  

(75)

which is equivalent to the corresponding L-CPMET equation [Eq. (33) or (59)] for $x_2^{\text{L}}$

\[ a + bx_2^{\text{L}} = 0 , \]  

(76)

so that

\[ x_2^{\text{L}} = \tan \beta_2^{\text{L}} = -a/b , \quad -\pi/2 < \beta_2^{\text{L}} < \pi/2 , \]  

(77)

and

\[ E_L = ax_2^{\text{L}} = f_2(x_2^{\text{L}}) = -a^2/b = -b \tan^2 \beta_2^{\text{L}} = g_2(\beta_2^{\text{L}}) . \]  

(78)

Similarly, the extremum of $F_2(Y) = g_2(\beta)$ occurs at

\[ \beta = \beta_2^{\text{D}} , \]  

given by the condition

\[ \left. \frac{dg_2(\beta)}{d\beta} \right|_{\beta=\beta_2^{\text{D}}} = 2a \cos 2\beta + b \sin 2\beta |_{\beta=\beta_2^{\text{D}}} = 0 , \]  

(79)

which yields

\[ \tan 2\beta_2^{\text{D}} = -2a/b , \]  

(80)

so that we find immediately from the last Eq. (69) that

\[ E_D = g_2(\beta_2^{\text{D}}) = \frac{1}{2} 

| 1 - [1 + (2a/b)^2]^{1/2} \]  

(81)

which is clearly identical with the lowest eigenvalue of $H_1$ [Eq. (66)] assuming that $b > 0$.

The relationship between both extremal parameter values follows immediately from Eqs. (77) and (80), yielding (cf., also, Fig. 1)

\[ \tan 2\beta_2^{\text{D}} = 2 \tan \beta_2^{\text{L}} \]  

(82)

or

\[ \tan \beta_2^{\text{D}} = \tan \beta_2^{\text{L}} \left( 1 - \tan^2 \beta_2^{\text{L}} \right)^{-1} . \]  

(83)

Geometrically, the L-CPMET extremum occurs when the gradient of $G_0(X)$ [Eq. (67)] is perpendicular to the line $x_0 = 1$, while the D-CI minimum occurs when the gradient is normal to the unit circle, Eq. (68).

The above simple model may be easily extended by considering $N$ noninteracting systems of this kind, in which case the D-CI matrix [Eq. (20)] has the form

\[ H_N = \begin{bmatrix} 0 & a^T \\ a & b_1 \end{bmatrix} , \quad a^T = a\Phi_N , \quad b_1 = b1 , \]  

(84)

where

\[ J. Chem. Phys., Vol. 76, No. 5, 1 March 1982\]
\[ \phi_0 = \begin{bmatrix} 1 & 1 & \ldots & 1 \end{bmatrix}^T. \]  
(85)

This model has been often employed\textsuperscript{11,18,21,31-39} to examine the size extensivity of the D-CI approach. This was done by comparing the D-CI energies with the exact one given by \( NE_D \). We shall thus only concentrate on a comparison of the D-CI and the L-CPMET energies for this model, which are relevant to this paper.

In view of the symmetry of this model, we have that
\[ X^T = [x_1 \, x_2 \, \ldots \, x_N], \quad x_j^2 = x_j \phi_0, \]  
(86)

with \( x_0 = 1 \), \( x_1 = x \) in the L-CPMET case, and \( \|X\| = \|Y_D\| = 1 \) in the D-CI case, so that
\[ x_0 = y_0^2 = \cos \beta, \quad x_1 = y_1^2 = N^{-1/2} \sin \beta. \]  
(87)

The general functional [Eq. (61)] is now simply a multiple of the corresponding functional \( G_1 \) [Eq. (67)] for one isolated system
\[ G_0(X) = NG_1 \left( \begin{array}{c} x_0 \\ x_1 \end{array} \right). \]  
(88)

Correspondingly, the L-CPMET functional [Eqs. (57) and (58)] is also additive
\[ f^{(N)}_L(x) = NF_L(x) = NG_1 \left( \begin{array}{c} 1 \\ x \end{array} \right), \]  
(89)

while the D-CI functional will depend nonlinearly on the particle number \( N \)
\[ F^{(N)}_D(Y) = NG_1 \left( \begin{array}{c} \cos \beta \\ N^{-1/2} \sin \beta \end{array} \right). \]  
(90)

We also note that the Hamiltonian matrix \( H_r \) [Eq. (84)] is automatically in the canonical form (39) used in Sec. III, so that
\[ E_L^{(N)} = NE_L = -N a^2 / b, \]  
(91)

while the D-CI energy \( E_D^{(N)} \) is given by Eq. (45), which in this case becomes
\[ E_D^{(N)} = -N - a^2 / b - E_D^{(N)} \]  
(92)

so that
\[ E_D^{(N)} = \frac{1}{2} b \left[ 1 - \left( 1 + N (2a/b)^2 \right)^{1/2} \right], \]  
(93)

which is also easily seen to minimize \( F_D^{(N)}, \) Eq. (90).

This result also nicely illustrates the size extensivity of the L-CPMET procedure, in contrast to the D-CI method. Expanding the D-CI energy \( E_D^{(N)} \) [Eq. (93)] about the L-CPMET value \( E_L^{(N)} \) [Eq. (91)], we obtain
\[ E_D^{(N)} = -N (a^2 / b) \left[ 1 - N (a/b)^2 + 2 N^2 (a/b)^4 - 5 N^3 (a/b)^6 \right. \]  
\[ + 14 N^4 (a/b)^8 - \ldots \]  
\[ = E_L^{(N)} \left[ 1 - N (a/b)^2 + 2 N^2 (a/b)^4 - 5 N^3 (a/b)^6 \right. \]  
\[ + 14 N^4 (a/b)^8 - \ldots \]. \]  
(94)

The reason behind this very different behavior of the D-CI and the L-CPMET (and CPMET) approaches may be easily understood from the geometrical properties of the variational spaces characterizing them. As we have seen above, the variational space in the D-CI approach is compact, namely a unit sphere in the \((M + 1)\)-dimensional Euclidean space, while in the L-CPMET case, the variational space is a linear space given by the tangent hyperplane to the unit sphere just mentioned, at the point characterizing the RHF reference state (cf., also, the above example). Thus, if one would regard the D-CI variational space as a Lie group, then the corresponding L-CPMET variational space is given by the corresponding Lie algebra. Consequently, the independent systems behave additively in the linear L-CPMET space, so that this approach is size extensive, while this is not the case for the D-CI space, which has a multiplicative rather than additive structure. The additive character of the L-CPMET space will be preserved in the CPMET approach, even though the respective functional will be given by a form which is higher than quadratic.

This viewpoint nicely illustrates the basic incompatibility between the requirements of size extensivity and the upper bound property, as warranted by the use of the variational principle, as long as the trial functions are selected from the subspaces characterized by a rather limited excitation level.

VI. RELATIONSHIP BETWEEN THE D-CI AND THE L-CPMET APPROACHES

A. Exact relationship

We shall exploit the fact that both approaches and the corresponding functionals are closely related and that they are defined through the same matrix representative of the Hamiltonian, as a comparison of Eqs. (48) and (57) indicates. To obtain the desired relationship, we thus could express the L-CPMET functional (57) in terms of the D-CI eigenvalues and eigenvectors by substituting for \( H \), using Eq. (54), and then attempt to find an extremum of this functional explicitly. Indeed, this procedure would yield a system of linear equations which can be easily solved in terms of \( \lambda_i, u_i \), and \( \eta_1 \). Substituting this solution into the L-CPMET energy expression [Eq. (60)] we would obtain the L-CPMET energy in terms of the variational energies \( \lambda_i \) and corresponding eigenvectors. Even though this procedure is not difficult to carry out, it is a bit laborious, and one can simply obtain the same result directly using the fact that the L-CPMET equations are related with the D-CI matrix as Eqs. (20) and (33) indicate.

Assume, thus, that none of the eigenvalues \( \lambda_i \) of \( H \) [Eq. (20)] vanishes, so that \( H \) is invertible. Since \( H^{-1} \) must also be Hermitian, we can write it in the same block structure as the matrix \( H \), namely,
\[ H^{-1} = \begin{bmatrix} p & q^T \\ q & r \end{bmatrix}, \]  
(95)

with \( r \) Hermitian
\[ r^T = r. \]  
(96)

The condition that \( H^{-1} \) [Eq. (95)] is the inverse of \( H \) [Eq. (20)] implies the following conditions for the component blocks of \( H^{-1} \):

\[ \begin{array}{c}
\end{array} \]
An explicit form of these conditions for the first column is clearly
\[
a^i q = 1 ,
\]
\[
ap + b q = 0 .
\]
Since $p$ is a nonzero scalar, this last equation is in fact identical with the L-CPMET system [Eq. (59)] when we set
\[
x_q = t_q = p^{-1} q .
\]
We thus find for the L-CPMET energy that
\[
E_L = a^i x_q = p^{-1} a^i q = p^{-1} ,
\]
where we have used Eq. (98) in the last step. Knowing the eigenvectors $u_i$ and the corresponding eigenvalues $\lambda_i$ of $H$ [Eq. (50)] we can write for the elements of $H^{-1}$
\[
(H^{-1})_{ij} = \sum_k \lambda_k \lambda_k^{-1} u_{ik} u_{jk} ,
\]
so that, in the special case needed, we have
\[
p = (H^{-1})_{00} = \sum_k \lambda_k^{-1} |u_{0k}|^2 .
\]
We thus find that
\[
E_L = \left[ \sum_k |u_{0k}|^2 / \lambda_k \right]^{-1} .
\]
Furthermore, using again Eq. (100),
\[
x_q = t_q = [x_q] ,
\]
and Eq. (102) for $q$
\[
q_i = (H^{-1})_{0i} = \sum_k u_{0k} u_{ik} / \lambda_k ,
\]
we find easily the components $x_i$, where $x_i$ and $q_i$ are components of $x$ and $q$ column vectors, respectively,
\[
q = \{ q_i \} ,
\]
\[
x_q = t_q = [x_q] , \quad i = 1, \ldots, M ,
\]
and $M$ designates the number of doubly excited configurations considered.

We can thus summarize
\[
E_D = \lambda_0 ,
\]
\[
E_L = \left( \sum_{j=0}^M \kappa_j \right)^{-1} ,
\]
and
\[
x_i = \sum_{j=0}^M \left( u_{ij} / u_{0i} \right) \kappa_j \sum_{k=0}^M \kappa_j,
\]
where
\[
\kappa_j = |u_{0j}|^2 / \lambda_j .
\]
Finally, we also note that with identifications given by Eqs. (100) and (101), the system of linear equations (98) and (99) is equivalent to the L-CPMET problem. This fact could be exploited in finding actual L-CPMET solutions when a D-CI matrix is available in either an implicit or an explicit form.

B. Approximate relationships

Let us now examine some simplifications and applications of the derived relationships [Eqs. (109) and (110)] between the D-CI and the L-CPMET approaches. In turn this analysis will enable us to see in a new light the very often employed simple approximations which correct the D-CI results for the size inconsistency due to the unlinked terms, particularly the well known Davidson correction.\(^20\)

We first note that the coefficients $\kappa_j$ [Eq. (111)] are given by the ratio of the probability factor $|u_{0j}|^2$, representing the weight of the RHF reference configuration in the $j$th D-CI state $j \geq 0$, and the $j$th D-CI energy eigenvalue $\lambda_j$. Except in quasidegenerate cases, the RHF reference configuration gives clearly the largest contribution to the D-CI ground state. We can thus assume that
\[
|u_{00}|^2 \gg |u_{0j}|^2 , \quad j > 0 .
\]
We also assume that the D-CI eigenstates are ordered according to their energies
\[
\lambda_j < \lambda_{j+1} , \quad j \geq 0 ,
\]
and, if no quasidegeneracy is present, that there is a large energy gap between the ground state and the excited D-CI states, namely,
\[
\lambda_0 < \lambda_j , \quad j > 0 .
\]
Then
\[
|\kappa_0| = |u_{00}|^2 / |\lambda_0| \gg |u_{0j}|^2 / |\lambda_j| = |\kappa_j| , \quad j > 0 ,
\]
so that retaining only the first term in the sum on the right-hand side of Eq. (109) will yield a very good approximation $E_L^{(0)}$ to $E_L$. Thus,
\[
E_L^{(0)} = \lambda_0 + \lambda_0 \left( 1 - |u_{00}|^2 - 1 \right)
\]
\[
= E_D + E_D \left( 1 - |u_{00}|^2 / |u_{00}|^2 \right).
\]
This is exactly the approximation derived by Siegbahn,\(^23\) who used a perturbation theory estimate for the unlinked cluster contribution [cf. also, Eq. (V') of Ref. 21 and Eq. (24) of Ref. 24]. In fact, this approximation is implicitly contained in the paper by Bartlett and Shavitt\(^22\) [when Eq. (20) of Ref. 22 is solved exactly for $S$, rather than expanded to the first order in $S$], who first showed explicitly the origin of this correction. When also $|u_{00}|^2 = 1$, the approximation (117) is very close to the well known Davidson correction\(^20\)
\[
E_L^{(0)} = E_D + E_D \left( 1 - |u_{00}|^2 \right).
\]
Thus, both the original\(^20\) and renormalized\(^21-24\) Davidson corrections can also be regarded as the first approximation to the L-CPMET energy based on the D-CI results.

Using higher than the ground state D-CI eigenvalues and eigenvectors (or, more precisely, the reference state components of these eigenvectors), we can improve the approximation to $E_L$, which in the absence...
of quasidegeneracy is always very close to the full CPMET result. In fact, the L-CPMET approach yields often better energies, and corresponding properties derived from the potential energy hypersurface near equilibrium geometry, than the CPMET approach (e.g., Ref. 40), since it overestimates the correction due to the unlinked tetraexcited clusters, and this overestimate is in the same direction and of roughly the same magnitude as the correction to CPMET due to the connected triexcited clusters. Thus, employing other than the ground state D-CI eigenvalues \( \lambda_j \) \((j>0)\) and the corresponding weights of the RHF ground state \( |\psi_{0}\rangle \), the relationship (109) enables one to introduce further systematic corrections to D-CI. With increasing \( \lambda_j \), the terms \( \kappa_j \) [Eq. (111)] will generally decrease (though not monotonically), so that using a few terms in the relationships (109) and (110) might yield a result which is very close to the L-CPMET one. We illustrate this behavior on an example in Sec. VIII.

Another very simple improvement may be obtained using an Unsöld-type approximation. Thus, assuming that

\[
\lambda_j = \tilde{\lambda} \quad j > 0 ,
\]

(119)

where \( \tilde{\lambda} \) is the average doubly excited state energy

\[
\tilde{\lambda} = \text{Tr}(b)/M , \quad \text{Tr}(b) = \sum_{K=1}^{\infty} b_{KK} ,
\]

(120)

and \( M \) is the number of doubly excited states used, we obtain

\[
E_L^{(U)} = \left[ |\psi_0\rangle \langle \psi_0| / \lambda_0 + (1 - |\psi_0\rangle \langle \psi_0| / \tilde{\lambda}^{-1} \right] .
\]

(121)

We note that \( E_L^{(U)} \) will tend to \( E_L^{(0)} \) as the basis set used is extended since, in this case, \( \tilde{\lambda} \rightarrow \infty \). Obviously, in this case, the assumption (120) is not valid and it should be replaced by a more realistic way of obtaining \( \tilde{\lambda} \).

Finally, we observe that the various approximate energies discussed above will be generally ordered as follows:

\[
E_L < E_L^{(U)} < E_L^{(0)} < E_L^{(P)} < E_D .
\]

(122)

VII. COMPUTATIONAL IMPLICATIONS FOR THE SOLUTION OF CCA EQUATIONS

We outline briefly the implications of the above given results for the appropriateness of various numerical algorithms for the solution of algebraic systems of equations arising in the CCA.

For the L-CPMET approach, which may be regarded as the first approximation to the CPMET, the problem is equivalent to that of finding an appropriate stationary point of the Hermitian quadratic function \( f_L(x) \), Eq. (58). This is most easily seen if we redefine the function \( f_L(x) \) in terms of the new variable \( z \)

\[
z = v^T (x - x_0) ,
\]

(123)

with \( v \) defined by Eq. (37) and \( x_0 \) is the solution of the system (59). Substituting \( x \) from Eq. (123), i.e.,

\[
x = x_0 + vz ,
\]

(124)

we find easily that

\[
\tilde{f}_L(z) = f_L(x) = z^T \beta z + f_L(x_0)
\]

(125)

or, explicitly

\[
\tilde{f}_L(z) = E_L + \sum_{K=1}^{M} \beta_K |z_K|^2 .
\]

(126)

Considering, for simplicity, the most often occurring case of a real D-CI matrix so that both the \( a \) and \( b \) submatrices of \( H \) are real and \( b \) is symmetric, we see immediately that \( f_L(x) \) is a quadratic function with gradient \( g \)

\[
g(x) = 2(bx + a) ,
\]

(127)

and with the Hessian \( h \)

\[
h = 2b .
\]

(128)

We also see immediately from Eq. (126) that \( z = 0 \) or \( x = x_0 \) is a unique minimum point (or a strong global minimizer) of \( f_L(x) = f_L(x) \) when \( \beta_K > 0 \) for all \( K \), i.e., when \( b \) is positive definite. This is usually the case unless the RHF ground state is quasidegenerate [cf. the text following Eq. (44)].

Thus, when \( b \) is positive definite the solution of the L-CPMET equations is equivalent to the problem of minimization of the functional \( f_L(x) \), suggesting the use of conjugate direction methods. Recently, these techniques for solving linear algebraic systems have been extensively studied, particularly in connection with large sparse systems.

It is well known that the convergence of the conjugate gradient method, as measured by the number of iterations which are required to lower the error of the initial approximation \( x^{(0)} \) by a prescribed factor, is proportional to the square root of the spectral condition number \( \kappa(b) \) of the coefficient matrix \( b \). The error is measured in the so called energy norm so that one minimizes the value of the functional \( f_L(x) \) rather than the distance \( ||x - x_0|| \). The spectral condition number is defined as the ratio of the largest and the smallest eigenvalue of \( b \)

\[
\kappa(b) = \beta_\infty / \beta_1 .
\]

(129)

Thus, the more clustered the eigenvalues of \( b \) are, the faster is the convergence of the conjugate gradient method.

The convergence characteristics as represented by the spectral condition number \( \kappa(b) \) can be improved by a so-called preconditioning. Generally, a preconditioning is achieved through a transformation of the unknowns

\[
y = E^T x ,
\]

(130)

where the preconditioning matrix \( C \)

\[
C = EE^T ,
\]

(131)

is a positive definite matrix and \( E^T \) designates the transpose of \( E \). For simplicity, we assume that \( b \) is a positive definite real symmetric matrix. Since

\[
x^T bx = y^T by ,
\]

(132)

with

\[
\tilde{b} = E^{-1} b E^{-T} ,
\]

(133)

the system (33) or (59) becomes
\[ \tilde{a} + b \tilde{a} = 0, \quad (134) \]

where
\[ \tilde{a} = E^{-1}a. \quad (135) \]

Since, further, \( \tilde{b} \) is similar (with similarity transformation \( E^T \)) to \( C^{-1}b \), it has the same eigenvalues as \( C^{-1}b \). Thus, choosing an appropriate preconditioning matrix \( C \), the spectral condition number of \( b \) can be lower than that of \( b \) and a faster convergence can be achieved for the system (134).

Since the transformation (130) must be performed at least once when using the preconditioning, it is of practical importance that \( E \) or \( C \) is so chosen that the system (130) can be easily solved. It is thus usually assumed that \( E \) is a sparse lower triangular matrix. Assuming that \( b \) is diagonally dominant, so that its eigenvalues lie not very far away from the diagonal entries of \( b \), we can apply the following simple diagonal preconditioning matrix
\[ C = b^{d1} = ee^T, \quad (136) \]

where \( b^{d1} \) designates the diagonal part of \( b \), so that
\[ e = [(b_{ij})^{1/2}]_{ij}. \quad (137) \]

Assuming that the off-diagonal matrix elements are small compared to 1, the majority of the eigenvalues of \( \tilde{b} \) should be clustered around one.

We have programmed the conjugate gradient method using the algorithm and the code as given by Axelsson and Barker.\textsuperscript{42} This program will be referred to as the CG (conjugate gradient) program. We have also written the preconditioned version using the simple preconditioning matrix (136). This version is referred to as the PCG (preconditioned CG) program.

For comparison we also programmed and used a very recently proposed approach by Purvis and Bartlett, called the reduced linear equation (RLE) method.\textsuperscript{43} This method is very similar to that proposed earlier by Pople \textit{et al.}\textsuperscript{44} In fact, both these approaches can be shown to fall into the category of conjugate gradient algorithms.\textsuperscript{41,42} Moreover, since the RLE space is built up as a span of the iterants of the usual Jacobi algorithm
\[ x^{(m+1)} = - (b^{d1})^{-1} [a + (b - b^{d1})x^{(m)}], \quad (138) \]

the RLE procedure should perform similarly as the mentioned PCG method. This indeed turns out to be the case and the work on a detailed elucidation of this relationship is in progress.

It should also be noted that the basic computational step in all the algorithms based on the steepest descent or conjugate gradient methods (with or without preconditioning) is that of forming the matrix product \( bc^{(n)} \) of a sparse coefficient matrix \( b \) with some vector \( c^{(n)} \) characterizing the \( n \)th iteration. This is precisely the same step which is required in most modern diagonalization algorithms for large sparse matrices. Moreover, this step is also amenable to a so-called direct approach, and may be handled in the same fashion as in the corresponding direct D-CI approach.\textsuperscript{45} This enables one to exploit considerable computational experience. We would also like to note that a very close similarity of algorithms which can be employed to obtain the D-CI and DMBPT solutions has been both noted and exploited by Blomberg and Siegbahn.\textsuperscript{46} Furthermore, a suitable variant of Newton's method or the so-called self-correcting conjugate gradient algorithm\textsuperscript{47} should provide solutions for the general large scale CPMET or ECPMET approaches, which are based on higher than quadratic functionals.

### VIII. NUMERICAL EXAMPLE

In this section we will illustrate the theory of the previous sections by some results on the CO molecule.

An RHF solution for CO is obtained at the experimental internuclear distance of 2.132 a.u., using the ATML03 suite of programs.\textsuperscript{48} The basis of 58 atomic orbitals used is the same as the one employed by Amos and consists of a set of (11, 6, 3/5, 4, 2) contracted Gaussians on each nucleus. The SCF energy of \(-112.78098\) a.u. obtained with this basis lies 0.01 a.u. above the HF limit of Ref. 50.

In the ensuing L-CPMET and CI calculations, we keep the lowest two molecular orbitals (the core MO's) doubly occupied. Apart from this restriction, all possible single and double excitations from the RHF reference state are included. Using the spatial symmetry group \( C_{2v} \) one obtains 7272 spin-projected states, which in our case are symmetrically orthogonalized spin bonded functions.\textsuperscript{49}

Before considering the 7272-dimensional L-CPMET and CI problems, we first examine the usefulness of the relationship (109). To study how rapidly the sum in this equation approaches the exact L-CPMET energy, we need all eigenvectors and eigenvalues of the D-CI matrix \( H \). In order to obtain these, we have to truncate our...
basis of singly and doubly excited configurations. To that end, we have examined separately the interaction of each of the 7271 configurations with the RHF ground configuration, and selected those which produced an energy lowering of more than $3 \times 10^4$ a.u. In this manner, a 225-dimensional D-CI matrix $H$ was obtained and subsequently completely diagonalized.

In order to investigate the "convergence" of the sum in Eq. (109), we define

$$E_L^{(n)} = \left( \sum_{j=0}^{n} \kappa_j \right)^{-1},$$

(139)

where $\kappa_j$ has been defined in Eq. (111). The values of $E_L^{(n)}$ as a function of $n$ are given in Table I, together with the corresponding eigenvalues $\lambda_n$ of $H$ [cf. Eq. (50)]. Recall that $\lambda_0$ gives the D-CI correlation energy, Eq. (108). Note also that $E_L^{(225)}$ gives the renormalized Davidson correction, as shown by Eq. (117), and that $E_L^{(n)}$ with $n = 224$ gives the exact L-CPMET energy for this model. The different approximations to the L-CPMET energy $E_L$, which were introduced in Sec. VI B, are summarized in Table II. Note that they satisfy the inequalities (122).

The main conclusion which can be drawn from this model calculation is that the Davidson corrections account for the major part of the difference between the D-CI and the L-CPMET energies. We observe that the approximants (139) following $E_L^{(225)}$ approach very slowly the L-CPMET energy $E_L$. This is due to an irregular distribution of the ground state components $\eta_0$ as a function of $j$, which causes $\kappa_j$ not to decrease monotonically, although $\lambda_j$ and $E_L^{(n)}$ are monotonic. The Unsld-type approximation is not far from the exact result in this case.

Since the $E_L^{(n)}$ values [Eq. (139)] approached $E_L$ very slowly in the model 225-dimensional case, we consider only the eigenvector with the lowest eigenvalue in the full 7272-dimensional case. The energy corrections which can be derived from this lowest eigenstate are given in the last column of Table II. The L-CPMET energy $E_L$ is obtained in this case using the PCG program, as outlined in Sec. VII, and, alternatively, using the RLE method of Purvis and Bartlett. Starting with the zero vector, one needs seven iterations for a seven digit accuracy.

We find again that the Davidson $E_L^{(225)}$ and renormalized Davidson $E_L^{(225)}$ corrections for the unlinked clusters bring the D-CI result close to the L-CPMET energy $E_L$. The Unsld-type approximation $E_L^{(22)}$ is again closest to $E_L$, as predicted by the inequalities (122). However, the difference between $E_L^{(22)}$ and $E_L^{(225)}$ energies is small, due to the fact that $\kappa$ is large ($\kappa = 9.203$ 18 a.u.). It is also worthwhile to note that the relative importance of the correction for unlinked clusters as given by the L-CPMET approach is significantly larger for the 7272-dimensional model (namely, 8.9% of the D-CI energy) than for the 225-dimensional case (5.1%).

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