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Citation: *The Journal of Chemical Physics* **82**, 890 (1985); doi: 10.1063/1.448517

View online: <http://dx.doi.org/10.1063/1.448517>

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The coupled pair functional (CPF). A size consistent modification of the CI(SD) based on an energy functional

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(Received 30 July 1984; accepted 5 October 1984)

A modification of the CI(SD) energy functional is proposed which leads to size consistency through the use of partial normalization denominators. The method is derived from simple principles: correct description of separated two-electron systems and certain invariance requirements. This approach is connected to CEPA-1. The theoretical framework allows for a simple rationalization of connections between CI(SD), CEPA-1, and the linear version of CP-MET. As demonstrative applications we report comparisons with full CI calculations for BH, NH₃, H₂O, HF, and R_e, D_e for F₂, N₂, O₂, Cl₂, NO, and CO obtained for very large basis sets.

I. INTRODUCTION

CI treatments can—for virtually all cases of practical interest—only be carried out if the excitation level with respect to a reference space is restricted, e.g., to singles and doubles. This is simply a consequence of the prohibitive increase in computational work with increasing excitation level and the basis set size required. Any CI truncated below the full excitation level yields energies which do not scale properly with the system size, the familiar size consistency, or size extensivity problem.^{1,2} This shortcoming can be corrected at least in part by applying Davidson's or related correction procedures.²⁻⁵

Perturbation theoretical methods such as MBPT⁶ approaches avoid this deficiency from the very beginning, but one then faces problems due to the uncertain convergence behavior of perturbation expansions. The CI(SD) method can be modified to include higher excitations in an approximate way in order to achieve size consistency. This line is pursued in the electron pair approaches, e.g., Cizek's CP-MET⁷ or Meyer's CEPA.⁸⁻¹⁰ Most of the just mentioned alternatives to the CI are not related to an energy functional, i.e., the corresponding equations cannot be obtained through variation of a functional. The only exceptions are the linear version of Cizek's CP-MET,¹¹ a recent modification of CEPA-2 by Pulay¹²—both of which will be discussed briefly in this article—and the trivial case of second order perturbation theory. The idea of a CEPA-type functional has been briefly mentioned by Kutzelnigg^{9(b)} and by Meyer,^{8(c)} but has apparently never been used and no detailed investigation has been published to date.

In this article we propose, discuss, and apply a modification of the CI(SD) functional which accounts approximately for effects of higher excitations and is size extensive. The availability of an energy functional is of great importance. It opens the way to thorough theoretical investigations, since it is much easier to deal with a functional than to work with the equations defining, e.g., CP-MET, CEPA, or Davidson corrected CI. There are

further numerous practical and technical advantages. The computation of energy gradients—a problem of increasing interest^{13,14}—is greatly simplified in this case.¹² The definition of density matrices required for the computation of properties is now straightforward, as will be discussed in Sec. II E. This point is by no means trivial¹⁵ for methods which do not yield an explicit total wave function such as CP-MET, CEPA, Davidson corrected CI, and perturbation techniques. The availability of a functional also helps to save computation time: an error $\delta\psi$ in the wave function leads to an error proportional to $\langle\delta\psi|\delta\psi\rangle$ only in the energy, thus improving the convergence of any iterative procedure.

Our derivations rely on two basic principles only, a correct description of separated electron pairs on the "CI(SD) level" and certain invariance requirements with respect to unitary transformations of internal MO's. The method is (so far) restricted to the treatment of ground states of the corresponding symmetry which in addition can be sufficiently well described by a single reference wave function. Applications prove the present method to be remarkably stable with respect to near degeneracies, see Sec. IV.

II. CPF THEORY

A. Definitions and preliminary considerations

As a preparation for the subsequent considerations we discuss briefly some features of the size consistency problem of a CI(SD) for the single reference case. The CI(SD) wave function will be written as

$$\psi = \psi_0 + \sum_{Px} C_{Px} \psi_{Px}, \quad (1)$$

where ψ_0 denotes the normalized reference, x labels the external parts—i.e., $x = a$ for singles and $x = (a, b, p)$ for doubles with a, b denoting external MO's and p specifying their spin coupling if necessary—and P the internal parts of remaining CSFs. We will further use the abbreviations

$$\psi_P = \sum_x C_{Px} \psi_{Px}, \quad (2)$$

$$\psi_c = \sum_P \psi_P. \quad (3)$$

In the subsequent discussions we will use frequently MP⁶ perturbation theory to estimate various contributions to the energy and the wave function, i.e., we use

$$V = H - F, \quad (4)$$

the difference between H and the Fock operator as perturbation.

The CI(SD) correlation energy can then be written as

$$E_c(\text{SD}) = \frac{\langle \psi_0 + \psi_c | H - E_0 | \psi_0 + \psi_c \rangle}{1 + \langle \psi_c | \psi_c \rangle} \quad (5)$$

$$= \left\{ 2 \sum_P \langle \psi_0 | H - E_0 | \psi_P \rangle + \sum_{P,Q} \langle \psi_P | H - E_0 | \psi_Q \rangle \right\} / \left\{ 1 + \sum_P \langle \psi_P | \psi_P \rangle \right\},$$

$$E_0 = \langle \psi_0 | H | \psi_0 \rangle. \quad (6)$$

The size consistency problems of a CI(SD) are most easily explained if one expands the denominator in Eq. (5),

$$E_c(\text{SD}) = \langle \psi_0 + \psi_c | H - E_0 | \psi_0 + \psi_c \rangle \times (1 - \langle \psi_c | \psi_c \rangle) + O(V^6), \quad (7)$$

where $O(V^6)$ denotes a deviation of sixth order in V , and notes that the term ΔE ,

$$\Delta E = -\langle \psi_0 + \psi_c | H - E_0 | \psi_0 + \psi_c \rangle \langle \psi_c | \psi_c \rangle \quad (8)$$

is to a large extent cancelled by contributions of higher excitations.²⁻¹⁰

The Davidson correction³ provides a simple and quite popular remedy to this deficiency. Various modifications of the Davidson correction have been proposed,²⁻⁵ which yield the corrected correlation energy \tilde{E}_c up to deviations in sixth order:

$$\tilde{E}_c = \langle \psi_0 + \psi_c | H - E_0 | \psi_0 + \psi_c \rangle + O(V^6). \quad (9)$$

The term $O(V^6)$ is actually not present in the modification proposed by Siegbahn.⁵

The relationship (9) for \tilde{E}_c suffers from two basic shortcomings. First, \tilde{E}_c is evaluated with ψ_c as determined by a CI(SD). One thereby underestimates the cluster corrections, as is easily verified for simple models such as He_n , where both $E_c(\text{SD})$ and \tilde{E}_c increase like \sqrt{n} .¹⁶

Second, Eq. (9) tends to overshoot the contributions of higher excitations. This is due to the fact that higher excitations do not cancel Eq. (8) completely, as is obvious for the two-electron case where no correction should be made. This is especially due to the contribution of terms

$$\langle \psi_0 + \psi_P | H - E_0 | \psi_0 + \psi_P \rangle \langle \psi_P | \psi_P \rangle \quad (10)$$

in Eq. (8) which are clearly not cancelled by higher excitations. The first of the just mentioned problems could be solved by a direct minimization of the functional

$$F_c[\psi_c] = \langle \psi_0 + \psi_c | H - E_0 | \psi_0 + \psi_c \rangle, \quad (11)$$

with respect to variations of ψ_c . This is identical with Cizek's linear version of CP-MET.^{7,11} In order to avoid the second problem one clearly has to keep at least a "partial normalization denominator" if one wants to preserve a simple CI(SD)-like method.

B. The coupled pair functional

The foregoing discussion suggests to determine E_c and ψ_c through minimization of a functional which includes only a partial normalization

$$F_d[\psi_c] = 2 \sum_P \frac{\langle \psi_0 | H - E_0 | \psi_P \rangle}{N_P} + \sum_{P,Q} \frac{\langle \psi_P | H - E_0 | \psi_Q \rangle}{M_P M_Q}, \quad (12)$$

$$N_P = 1 + \sum_Q T_{PQ} \langle \psi_Q | \psi_Q \rangle, \quad (13)$$

$$T_{PQ} = T_{QP}, \quad (14)$$

$$M_P = \sqrt{N_P}. \quad (15)$$

The crucial quantities are the "topological factors" T_{PQ} which determine the partial normalization denominators N_P . Two limiting choices are obvious:

$$T_{PQ} = 1 \rightsquigarrow N_P = 1 + \langle \psi_c | \psi_c \rangle, \quad (16)$$

which leads to the CI(SD), i.e., the functional (5), or

$$T_{PQ} = 0 \rightsquigarrow N_P = 1, \quad (17)$$

which leads to the linear version of the CP-MET, compare Eq. (11).

For the case under consideration—a single reference and inclusion of all singles and doubles which interact with the reference—one may write $P = (ijp)$ for doubles and $P = i$ for singles, where p labels the different spin couplings if necessary. This nomenclature is self-evident for closed shell cases. For open shell states it implies a special spin coupling of singles. $P = i$ is understood to label the CSFs which have vanishing interaction with ψ_0 by means of the Brillouin theorem. The singles—from i —which in addition involve a spin flip of a singly occupied MO j are indexed as $P = (ijp)$, since the corresponding CSFs are double replacements on the spin orbit level. An analogous route is pursued for the fully internal excitations.

If n_i denotes the occupation of the i th orbital in the reference, we put

$$T_{PQ} = \frac{\delta_{ik} + \delta_{il}}{2n_i} + \frac{\delta_{jk} + \delta_{jl}}{2n_j} \quad (18)$$

for $P = (ijp)$, $Q = (klq)$. This formula also covers singles if we formally equate $P = i$ with $P = ii$ for this purpose.

Let us consider a few typical cases to justify the choice made for T_{PQ} .

(i) Separated closed shell electron pairs, i.e., two-electron systems at mutually infinite distances. Starting

from localized occupied orbitals it is easy to write down a functional of the form (12) which yields the correct correlation energy on the CI(SD) level

$$F_c = 2 \sum_P \frac{\langle \psi_0 | H - E_0 | \psi_P \rangle}{N_P} + \sum_P \frac{\langle \psi_P | H - E_0 | \psi_P \rangle}{N_P}, \quad (19)$$

$$N_i = N_{ii} = 1 + \langle \psi_i | \psi_i \rangle + \langle \psi_{ii} | \psi_{ii} \rangle. \quad (20)$$

Here one has to consider only the cases $P = i$ and $P = ii$, since the remaining ψ_P vanish. F_c from Eqs. (19) and (20) clearly is a special case of Eqs. (12)–(15). In other words, this trivial model leads to the requirement $T_{PQ} = 1$ for $P = Q = ii$, and $T_{PQ} = 0$ for $(P, Q) = (ii, jj)$, $i \neq j$, and analogously for the singles as indicated in connection with Eq. (18).

(ii) n identical separated closed shell pairs, e.g., He_n . Starting again from localized occupied orbitals, the functional (19) now simply reads

$$F_c = \langle \psi_0 + \psi(S) + \psi(D) | H - E_0 | \psi_0 + \psi(S) + \psi(D) \rangle / N, \quad (21)$$

where, in an obvious notation,

$$\psi(S) = \sum_i \psi_i, \quad (22)$$

$$\psi(D) = \sum_i \psi_{ii} + \sum_{i < j} \psi_{ij1}, \quad (23)$$

$$N = 1 + \langle \psi_i | \psi_i \rangle + \langle \psi_{ii} | \psi_{ii} \rangle. \quad (24)$$

The label $ij1$ in Eq. (23) denotes the pair function with singlet coupled holes and particles, the corresponding term clearly vanishes in a localized description. It is desirable in this case that Eq. (21) is invariant with respect to a unitary transformation of occupied orbitals. Such a transformation induces a unitary transformation in the space of singly and doubly excited CSFs which leaves $\psi(S)$ and $\psi(D)$ invariant. Invariance of F_c [Eq. (21)] thus requires the N_P constructed according to Eq. (13), Eq. (18) to be identical to N from Eq. (24). This is proved by exhausting all possible cases. Unfortunately, we cannot offer a simple two line proof for this simple and basic statement. To be more explicit, unitary invariance requires to put $T_{PQ} = 0.5$ for $(P, Q) = (ii, ij1)$, $(ij1, ij1)$, and $T_{PQ} = 0.25$ for $(P, Q) = (ij1, jk1)$. These considerations are very similar to those of Meyer⁸ who considered a special transformation—from localized to completely delocalized orbitals—to achieve unitary invariance of CEPA-1 for this case.

Let us summarize the present state of affairs. We have required a correct description of separated pairs in a localized description and unitary invariance for identical pairs. This then determines T_{PQ} uniquely for all singles and all singlet pairs—for the closed shell case $n_i = 2$, of course.

(iii) Separated triplet pairs. Let us label the occupied orbitals of the i th pair by i and i' . Proceeding again as above it is obvious that the functional (19) accounts for higher excitations in a correct way if

$$N_{ii'-1} = N_i = N_{i'} = 1 + \langle \psi_i | \psi_i \rangle + \langle \psi_{i'} | \psi_{i'} \rangle + \langle \psi_{ii'-1} | \psi_{ii'-1} \rangle. \quad (25)$$

This is not reproduced correctly by Eqs. (12)–(15), and (18), which give $N_{ii'-1}$ as required but yield

$$N_i = 1 + \langle \psi_i | \psi_i \rangle + \langle \psi_{ii'-1} | \psi_{ii'-1} \rangle, \quad (26)$$

and similarly for $N_{i'}$. However, the fact that $\langle \psi_{i'} | \psi_{i'} \rangle$ is missing in Eq. (26) affects F_c only in eighth order in V . This almost meaningless deficiency does not justify—in our opinion—to deviate from the simple formula (18). It can again be shown that F_c [Eq. (12)] is invariant with respect to a unitary transformation of the occupied orbitals i and/or i' . This requirement actually fixes T_{PQ} for triplet pairs: $T_{PQ} = 1$ for $P = Q$, and $T_{PQ} = 0.5$ for semijoint pairs such as $(P, Q) = (ii' - 1, ij' - 1)$, in the case $n_i = 1$.

(iv) Let us finally consider a system $A \cdots B \cdots C$ of noninteracting subsystems A, B, C . The functional F_c [Eq. (12)] is size extensive if the occupied orbitals are localized on the respective subsystems

$$F_c(A \cdots B \cdots C) = F_c(A) + F_c(B) + F_c(C) \quad (27)$$

in an obvious shorthand notation. This follows from the fact that $T_{PQ} = 0$ for disjoint P, Q — $(P, Q) = (i, j)$, (ii, jj) , $(ij \pm 1, kl \pm 1)$ —and that $\psi_{ijp} = 0$ if i and j refer to orbitals on different subsystems. For identical subsystems it can furthermore be proved that F_c is invariant with respect to unitary transformations of corresponding orbitals. To give an example, for Ne_n at large interatomic distances one can subject the $1s$ AOs to a transformation U , the $2s$ AOs to a transformation V , etc., without affecting F_c . This feature is of practical importance in the treatment of intermolecular interactions where MOs may be localized or delocalized depending on the actual symmetry and intermolecular distance.

The model considerations presented above fixed the T_{PQ} only for the respective special cases. To give an example, for closed shell systems one could in fact multiply the T_{PQ} , where P and/or Q denote triplet pairs, by an arbitrary real number without destroying size extensivity or invariance properties. However, if one aims at a simple and generally applicable formula, then Eq. (18) appears to be the simplest choice which describes the limiting cases (i)–(iii) as correctly as possible. A further comment on the present choice for T_{PQ} will be made in Sec. III where we discuss the connections of the present method with CEPA approaches.

Let us finally comment on the term $\langle \psi_P | H - E_0 | \psi_Q \rangle / (M_P M_Q)$ occurring in Eq. (12). For separated pairs only the case $P = Q$ occurs, and all considerations sketched above do not fix the denominator in a unique way for $P \neq Q$. Any other averaging, e.g., $0.5(N_P + N_Q)$ instead of $M_P M_Q$, would have also been possible. The actual choice of the denominator affects F_c only in fifth order in V for $P \neq Q$ (the corresponding contribution for $P = Q$ enters in fourth order), and we have, therefore, made in Eq. (12) what appeared a simple and reasonable choice to us.

C. Variational equations

Variation of the functional F_c [Eqs. (12)–(14)], with respect to the parameters C_{Px} [Eq. (1)], is straightforward and yields

$$\left\langle \psi_{Px} | H - E_0 - A_P | \psi_0 + M_P \sum_Q \frac{\psi_Q}{M_Q} \right\rangle = 0, \quad (28)$$

where

$$A_P = \sum_Q \frac{N_P}{N_Q} T_{PQ} \epsilon_Q, \quad (29)$$

$$\epsilon_P = \frac{2 \langle \psi_0 | H - E_0 | \psi_P \rangle}{N_P} + \sum_Q \frac{\langle \psi_Q | H - E_0 | \psi_P \rangle}{M_Q M_P}. \quad (30)$$

The ϵ_P constitute a decomposition of the total correlation energy into contributions corresponding to the respective P , since

$$F_c = \sum_P \epsilon_P. \quad (31)$$

In order to see some general features of the present method let us express ϵ_P and F_c in terms of the correlation function obtained as a solution of Eqs. (28)–(30). Multiplying Eq. (28) with C_{Px} and summing over x one gets after simple rearrangements using Eqs. (2), (13), (14), (28), and (29):

$$\epsilon_P = \langle \psi_0 | H - E_0 | \psi_P \rangle + \sum_Q T_{PQ} \left[\frac{N_P}{N_Q} \epsilon_Q \langle \psi_P | \psi_P \rangle - \epsilon_P \langle \psi_Q | \psi_Q \rangle \right], \quad (32)$$

$$E_c = F_c[\psi_c] = \sum_P \langle \psi_0 | H - E_0 | \psi_P \rangle + \sum_{PQ} T_{PQ} \frac{N_P - N_Q}{N_Q} \epsilon_Q \langle \psi_P | \psi_P \rangle. \quad (33)$$

Since $\epsilon_P = O(V^2)$, $N_P = 1 + O(V^2)$, $A_P = O(V^2)$, it follows immediately that the ψ_P depend on the choice of T_{PQ} in terms proportional to V^3 :

$$\psi_\lambda(T) - \psi_\lambda(T') = O(|T - T'| * V^3) \quad (34)$$

and consequently,

$$\epsilon_P(T) - \epsilon_P(T') = O(|T - T'| * V^4), \quad (35)$$

$$E_c(T) - E_c(T') = O(|T - T'| * V^4). \quad (36)$$

This is expected, of course, since cluster corrections enter the energy in fourth order. From Eqs. (32) and (33) we then get

$$\epsilon_P = \langle \psi_0 | H - E_0 | \psi_P \rangle + O(V^4), \quad (37)$$

$$E_c = \langle \psi_0 | H - E_0 | \psi_c \rangle + O(V^6). \quad (38)$$

The present method does not lead to the usual transition energy formula, but the deviation—the second term on the right-hand side of Eq. (33)—starts in sixth order in V . The individual terms furthermore cancel to some extent at least, and do so exactly for special cases, e.g., for separated pairs.

In connection with the variational equation let us comment briefly on the variation principle. F_c is not bounded from below by the lowest eigenvalue of H . This is shown by a rather extreme application, see Sec. IV, where the coefficient of the reference in the full CI is only 0.76. However, it is easily shown that F_c is at least bounded from below by some real number M ,

$$F_c[\psi_c] \geq M, \quad M > -\infty. \quad (39)$$

For a proof we define

$$\tilde{\psi}_c = \sum_P \frac{\psi_P}{M_P} \quad (40)$$

and write

$$F_c = 2 \sum_P \frac{\langle \psi_0 | H - E_0 | \psi_P \rangle}{N_P} + \langle \tilde{\psi}_c | H - E_0 | \tilde{\psi}_c \rangle. \quad (41)$$

Since $\|\psi_P\|/N_P \leq \|\psi_P\|/M_P \leq 1/\sqrt{T_{PP}} \leq \sqrt{2}$, and since $H - E_0$ is bounded from below, the relationship (39) follows directly from Eq. (41). Although Eq. (39) is probably of little practical help, one may hope that, since F cannot collapse to $-\infty$, the present functional is also quite stable in the critical case of near degeneracies.

By virtue of the functional formulation it is tempting to apply the present method to the treatment of excited states of the same symmetry as the ground state. However, our method depends crucially on the fact that the state under consideration can be described by a single reference wave function in zeroth order. This condition is usually not met—and even SCF treatments are not straightforward. Our efforts to understand the theoretical implications have been without success so far but it appears worthwhile to find out by test calculations.

D. Solution of CPF equations

Any direct CI(SD) procedure is easily modified to solve Eq. (38). For this purpose it is convenient to define the modified “CI vector”

$$\tilde{C}_{Px} = C_{Px}/M_P. \quad (42)$$

The expressions for the residual vector

$$\sigma_{Px} = \langle \psi_{Px} | H - E_0 | \psi_0 \rangle / M_P + \sum_{Qy} \langle \psi_{Px} | H - E_0 | \psi_{Qy} \rangle \tilde{C}_{Qy},$$

and for ϵ_P [Eq. (30)],

$$\epsilon_P = \sum_x \tilde{C}_{Px} \left[\frac{\langle \psi_0 | H - E_0 | \psi_{Px} \rangle}{M_P} + \sigma_{Px} \right] \quad (43)$$

then require only a modification of the processing of integrals contributing to $\langle \psi_0 | H - E_0 | \psi_{Px} \rangle$, which is trivial. We then update the C_{Px} with the aid of the usual first order procedure

$$C_{Px} \rightarrow C_{Px} - \left[\frac{\sigma_{Px} - A_P \tilde{C}_{Px}}{H_{Px,Px} - E_0 - A_P + \Delta} \right] M_P, \quad (44)$$

where Δ is a level shift parameter.¹⁷ In order to accelerate convergence we further apply Pulay's DIIS method,¹⁸

which is roughly equivalent to the Davidson procedure¹⁹ for a CI. In connection with the DIIS technique we recommend $\Delta = 0.3$ a.u. from our present experience.

The just described modifications have been added to the Columbus MR CI(SD) program package²⁰ and are running on the SIEMENS S7880 and the CYBER 205 installed at the University of Karlsruhe.

A single CPF iteration requires the same computational effort as a CI(SD) iteration since the evaluation of the residual vector is virtually the same. The present procedure converges the energy to 10^{-6} a.u. in six cycles for well behaved cases like N_2 , O_2 , F_2 . However, 10–15 iterations may be necessary for critical cases such as the A' and A'' states of NSF^+ . Here it usually helps to increase Δ , see Eq. (44), to 0.5.

E. First order density matrix

One of the advantages of a method based on an energy functional is that it is easy to give the explicit expressions for the corresponding n -particle density matrices, and we will do so for the one-particle density matrix γ . The latter is conveniently—and in a unique way—defined by means of perturbation theory in considering

$$H(\lambda) = H + \lambda g \quad (45)$$

and the requirement that

$$\left(\frac{\partial E}{\partial \lambda} \right)_{\lambda=0} = \left\{ \frac{\partial}{\partial \lambda} E_0 + \frac{\partial}{\partial \lambda} F_c[\psi_c, H(\lambda)] \right\}_{\lambda=0} = \text{tr } \gamma g \quad (46)$$

holds for arbitrary (fixed) ψ_0 , ψ_c and one-particle operator g . The corresponding analysis is straightforward for the present functional F_c [Eq. (12)] and yields

$$\gamma = \gamma_0(1 - a) + \tilde{\gamma}, \quad (47)$$

where γ_0 is the one-particle density matrix of ψ_0 , and

$$\tilde{\gamma}_{rs} = 2 \sum_{Px} \frac{\gamma_{rs}^{0,Px} C_{Px}}{N_P} + \sum_{Px} \sum_{Qy} \gamma_{rs}^{Px,Qy} \frac{C_{Px} C_{Qy}}{M_P M_Q}, \quad (48)$$

$$a = \sum_P \frac{\langle \psi_P | \psi_P \rangle}{N_P} = \text{tr } \tilde{\gamma} / \text{tr } \gamma_0. \quad (49)$$

The $\gamma_{rs}^{Px,Qy}$ denote here the first order (transition) density matrix elements between CSFs ψ_{Px} and ψ_{Qy} with respect to (spin) orbitals r and s . From Eq. (47) it follows, of course,

$$\text{tr } \gamma = \text{number of electrons}. \quad (50)$$

III. CONNECTIONS WITH OTHER METHODS

The present method is closely connected to Meyer's⁸ CEPA-1. This is obvious if one writes the CEPA-1 equations in the present nomenclature,^{8,10}

$$\langle \psi_{Px} | H - E_0 - A_P | \psi_0 + \sum_Q \psi_Q \rangle = 0, \quad (51)$$

$$A_P = \sum_Q T_{PQ} \epsilon_Q, \quad (52)$$

$$\epsilon_P = \langle \psi_P | H - E_0 | \psi_0 \rangle, \quad E_c = \sum_P \epsilon_P, \quad (53)$$

and compares with Eqs. (28)–(30), and (37). For the present choice of T_{PQ} , Eq. (52) has the same structure as the CEPA-1 energy shift for the closed shell case if only double substitutions are considered^{8,10} (the treatment of singles appears to be different in different existing CEPA programs). Using the same T_{PQ} in Eq. (52) and in Eqs. (28)–(30) one finds agreement up to and including third order in the correlation functions ψ_P and fourth order for E_c . We have used the Karlsruhe CEPA program¹⁰ to compare with the present method, and obtained deviations of the order of 10^{-5} a.u. in the correlation energy for H_2O and HF for TZP basis sets. Since the basis sets are not identical (the existing CEPA program was based on Gaussian lobe functions), this discrepancy may at least in part be due to basis set problems.

It has been pointed out that CEPA-1 is closely related to CP-MET or CCSD^{8–10,21–23} (which includes the singles in addition to the doubles considered in CP-MET). It is therefore expected that the present method should yield results similar to CP-MET or CCSD as will be demonstrated by the applications reported in the next section. Since CEPA methods and their connection to many body perturbation theory have been discussed in various reviews^{9,10} we need not go into further details here. We only mention that CEPA methods are often discussed in starting from a spin orbit description.^{8–10,21,22} The transition to singlet or triplet pairs then requires some averaging to determine the shifts A_P —or the T_{PQ} in the present nomenclature—as discussed in detail by Hurley.²¹ The present proposal for T_{PQ} [Eqs. (38)–(41)] then corresponds to an averaging (with equal weights) over all spin orbit pairs which differ only in spins. We were actually led by this idea in our attempt to summarize the results obtained for T_{PQ} in special cases which resulted in the final equation (18). Our prescription differs from those discussed by Hurley,²¹ which appears inevitable if one wants to preserve unitary invariance at least for the most important cases as discussed in Sec. II B.

One so far has not succeeded to derive the CEPA or CP-MET equations from an energy functional, except for the rather simple case of Cizek's linear version of CP-MET¹¹ (also often called CEPA-0), which is certainly not bounded from below in general, see Eq. (11). Based on previous attempts¹⁰ (which were halfway successful at best) Pulay has recently proposed the functional,¹² see Eqs. (2) and (3),

$$F = \langle \psi_0 + \psi_c | H - E_0 | \psi_0 + \psi_c \rangle + 2/3 \sum_P \langle \psi_P | \psi_P \rangle \langle \psi_P | H | \psi_0 \rangle, \quad (54)$$

which upon variation with respect to ψ_c leads to CEPA-2 like equations. As a consequence of the third power dependence on the ψ_P this functional actually assumes for any system all real numbers between $\pm\infty$ (and complete variation always results in $\|\psi_c\| = \infty$, $E = -\infty$). Only extensive applications can demonstrate the merits and limitations of this proposal.

IV. DEMONSTRATIVE APPLICATIONS

Comparison with full CI results provides the best test for the present method. Thanks to the remarkable progress achieved by Handy and Schaefer *et al.*,^{24,25} these are available for BH, NH₃, H₂O, and HF. In Table I we compare the full CI results with those obtained by the present method and other related techniques—related in the sense that they are also designed to be size consistent.^{26,27} The results are visualized in Fig. 1. In a comparison of the corresponding results one should keep in mind the differences in computational work required by the respective methods. The SD MBPT (2) calculations certainly require the least effort. CI(SD), CPF, and CCSD should be roughly comparable. Since the CCSD equations are more involved and more strongly coupled, this method could be somewhat slower than a CI(SD). Fourth order calculation involving triple excitations and the SAC methods^{27,28} appear to require much more computation time than CI(SD)-type calculations. The evaluation of Davidson's correction is very fast, of course.

A short look at Table I reveals that the Davidson-corrected CI(SD) results are in the mean closest to the full CI for BH, NH₃, H₂O, and HF. We have mentioned in Sec. II that even inclusion of this correction does not lead to size consistency and is bound to fail for sufficiently large systems. This conclusion can be tested in computations of (HF)₂ and (HF)₃ for sufficiently large intermolecular distances, say 100 a.u. The full CI energy of (HF)₂ is then simply twice—for (HF)₃ three times—the energy of HF. Our theoretical conclusions are in fact confirmed by the results: the deviations between the full CI and the corrected CI(SD) increase strongly from HF (1.3 mH) to (HF)₂ (6.3 mH) and (HF)₃ (16 mH). This leads to spurious "dimerization" and "trimerization" energies of 3.7 and 12.1 mH. The CPF method is strictly size extensive, in agreement with the considerations presented in Sec. II.

The deviations between any of the other methods and the full CI are almost the same in the average, except

for the SD MBPT (2), which is less accurate. The present CPF, the CCSD and the SAC (versions A and B) results are remarkably close—deviations of ≤ 1 mH in the correlation energy—except for the extreme case of H₂O with a symmetric stretch to $2R_e$. Here one finds a more pronounced scatter among the results and poorer agreement with full CI—with the remarkable exception of SAC-B, which deviates only 4 mH from full CI—but all these methods were not developed for this case and would normally not be applied to it. It should be noted that the CPF energy is below the full CI result and thus violates the variation principle only for this rather extreme case. The SDTQ MBPT (4) results are very close to full CI for HF and H₂O (R_e) (deviations of 0.5 and 1 mH), but not much is gained with respect to the CPF for the other cases. Although the SDTQ MBPT (4) results are remarkably stable with respect to "near degeneracy effects," the corresponding problems are reflected by the deviations from full CI for BH (5 mH) and H₂O ($2 R_e$) (16 mH). In the authors' not unbiased opinion this comparison indicates an advantage of the CPF and CCSD over the other methods considered, at least as far as the "price performance" ratio is concerned. One should keep in mind that only rather small basis sets are used in the calculations compiled in Table I. They recover roughly 40%–60% of the corresponding total correlation energies for NH₃, H₂O, and HF. Since only a small number of electrons is correlated—at most ten, in H₂O—all results should be considered with some care. For a further assessment of the usefulness of the present CPF method we have to resort to comparisons with experimental results. Although this is what the method is designed for, one then has to cope with the usual basis set problems and possible uncertainties in experimental results. We have been using the CPF since the summer of 1983. In Table II we list D_e (obtained as the difference between molecular and atomic energies) and R_e for those cases where the use of sufficiently large basis sets allows to assess the reliability of the new method.²⁹

TABLE I. Comparison of computed correlation energies from full CI treatments with approximate methods.^a

	BH	NH ₃	H ₂ O (R_e)	H ₂ O ($1.5 R_e$)	H ₂ O ($2 R_e$)	HF	(HF) ₂	(HF) ₃
CI(SD) ^b	0.097 16	0.119 64	0.140 17	0.188 61	0.249 64	0.190 52	0.366 66	0.531 50
D.c. ^{b,c}	0.104 14	0.125 29	0.146 08	0.208 34	0.309 69	0.198 38	0.393 09	0.583 10
SD MBPT(4) ^d	0.097 87	0.123 43	0.144 86	0.201 10	0.289 83	0.198 17
SDTQ MBPT(4) ^d	0.097 31	0.124 76	0.147 04	0.204 87	0.293 69	0.200 12
CCSD ^d	0.100 57	0.124 97	0.146 24	0.205 40	0.300 73	0.196 82
SAC-A ^e	0.100 54	0.125 03	0.146 42	0.205 11	0.295 24	0.197 21
SAC-B ^e	0.100 61	0.124 98	0.146 34	0.205 80	0.306 28	0.197 01
CPF ^f	0.101 53	0.124 17	0.145 02	0.205 81	0.318 76	0.196 66	0.393 32	0.589 98
Full CI ^g	0.102 37	0.126 68	0.148 03	0.210 99	0.310 07	0.199 68	0.399 35	0.599 03

^a The entries give the negative correlation energies in hartrees. Basis sets, molecular geometries, and number of frozen orbitals are as in Ref. 25. (HF)₂ and (HF)₃ calculated at an intermolecular distance of 100 a.u., see the text.

^b Reference 29 and present work.

^c CI(SD) plus Davidson correction, abbreviated D.c.

^d From Ref. 26.

^e From Ref. 27.

^f Present work.

^g From Ref. 25.

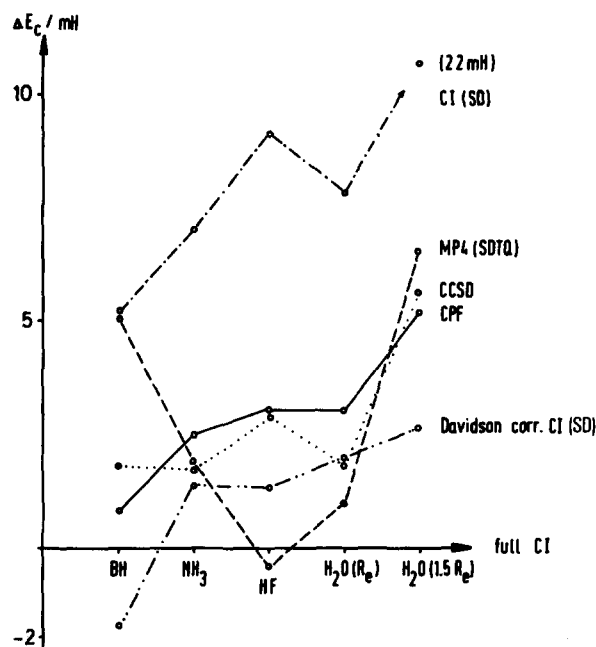


FIG. 1. Deviation of correlation energies computed by CI(SD) (---), MP4 (---), CCSD (···), Davidson corrected CI(SD) (-·-·-), and CPF (—) methods from full CI results.

In the calculations we have used basis sets including up to $3d$, $3f$, and $1g$ function per atom. The results for D_e and R_e are still not converged. The first g set on F lowers the total energy of F_2 by 13 mH and the contribution of $2g$ and $1h$ can be reliably estimated to be 4 and 7 mH.²⁹ A further basis set extension will affect the computed D_e by still a few kcal/mol as estimated in Table II. The CPF as well as CI(SD) results show a

consistent trend: We have always found an increase of D_e and a decrease of R_e on basis set extension. From trends observed we expect the following relationship between complete basis set CPF results and experiment: the computed R_e will probably be slightly too short (e.g., ≈ 0.013 a.u. for F_2) and D_e probably too small by a few kcal/mol.

In order to rationalize these findings let us recall that the CPF method can (at best) account for contributions of unlinked triples, quadruples, etc. This technique does in no way include effects of linked triples and quadruples. This then leaves us with the following error sources to explain deviations between experiment and CPF.

(i) The CPF does not account for effects of unlinked terms in an exact way. Although we have no clear cut evidence that this causes major problems, this may account for errors of a few kcal/mol in D_e .

(ii) The contributions of linked triples and quadruples—the latter probably to a lesser extent—could contribute in the order of a few kcal/mole to D_e (the total contributions of triples is ≈ 13 kcal/mol for F_2 ³⁰). Inclusion of these terms should further increase R_e as is indicated by their increasing contribution to E for increasing R .³⁰

(iii) Only valence shell correlation was included in the present work. We expect core valence contributions to increase D_e , their influence on R_e is probably small. Pilot calculations for N_2 (using basis A, see Table II, augmented by additional $2d$, $1f$ to describe core-core and core-valence effects) yield an increase of D_e by 0.7 kcal/mol, indicating a total effect of ≈ 1 kcal/mol for complete basis sets.

TABLE II. Comparison of diatomic bond distances R_e (a.u.) and dissociation energies D_e (kcal/mol) as computed by means of CI(SD), CPF, and MP4 (Ref. 31) methods with experiment.^a

Method		CI(SD) A	CPF A	CPF B	CPF limit ^b	Exp ^c	MP4 ^d
CO	D_e	233	246	250	253 ± 2	259	260
	R_e	2.115	2.131	2.12 ^e	...	2.132	...
N ₂	D_e	193	209	214	218 ± 2	228	224
	R_e	2.056	2.073	2.068	...	2.074	...
NO	D_e	119	136	140	143 ± 2	153	149
	R_e	2.146	2.173	2.175 ^e	...	2.175	...
O ₂	D_e	88.4	105	109	112 ± 2	120	120
	R_e	2.240	2.272	2.269	...	2.282	...
F ₂	D_e	10.6	30.8	32.9	34.5 ± 1	38.2	36.9
	R_e	2.594 ^e	2.672	2.656	...	2.668	...
Cl ₂	D_e	32.4	48.9	52.4	55 ± 1	58.2	...
	R_e	3.760 ^f	3.797	3.778	...	3.760	...

^a Basis sets used in the present work are denoted as A: (10, 6, 2, 1)/[6, 4, 2, 1] except for Cl: (11, 7, 2, 1)/[7, 4, 2, 1], and B: (10, 6, 3, 2, 1)/[6, 4, 3, 2, 1] except for F: (11, 7, 3, 3, 1)/[7, 5, 3, 3, 1] and Cl: (11, 7, 2, 1, 1)/[7, 4, 2, 1, 1]. Only valence shells were correlated.

^b Extrapolation to the complete basis set limit.

^c Experimental values as evaluated by Binkley and Frisch (Ref. 31).

^d MP4 results from Binkley and Frisch using a 6-3111G (3d) (1f) basis (Ref. 31).

^e CI(SD) result for basis B: $R_e = 2.579$ a.u.

^f CI(SD) result for basis B: $R_e = 3.744$ a.u.

^g Not optimized.

Although the contributions of the three mentioned effects will differ from case to case, we expect them to be of about the same importance. It is encouraging that the present method yields a consistent pattern: D_e is always predicted too low, even if extrapolated to a complete basis. This is reasonable since triple excitations and core-core as well as core-valence correlation effects should increase D_e .

In Table II we have also listed the MP4 results of Binkley and Frisch.³¹ These authors employed a 6-3111 G(3d)(1f) basis which is roughly comparable to our small basis set A. The agreement of these MP4 results for D_e with experiment is impressive indeed. However, by virtue of the present results this is to some extent due to a cancellation of basis saturation effects with higher order contributions of the perturbation expansion. Additional calculations for N₂ yield the following results: the second f and the first g set increase D_e by 1 and 3 kcal/mol, respectively. Further basis set extension (beyond 10s, 6p, 3d, 2f, 1g) should add 3 kcal/mol, at least, core-valence and core-core terms about 1 kcal, which adds up to 8 kcal/mol. Similar relationships may be expected for the other molecules listed in Table II, except for F₂ and Cl₂ where these effects are smaller. This indicates that complete basis set MP4 calculations overshoot D_e , especially for CO and O₂ by the same amount as the CPF results are too low.

Although the CPF results are not exact deviations from experiment are small and consistent and show none of the erratic features of the CI(SD) method. This is especially encouraging with respect to D_e which is often difficult to compute since one compares here atomic and molecular states with different electronic structure and errors do not cancel as, e.g., for intramolecular rearrangements.

V. SUMMARY

We have developed a size extensive modification of the CI(SD) energy functional in using partial denominators as defined in Eqs. (12)–(15), and (18). For this purpose we introduced the topological factors T_{PQ} which were determined from the requirements of a correct description of a system of separated electron pairs and invariance with respect to a unitary transformation of equivalent orbitals of identical subsystems. These features suggest that the CPF method accounts in a reliable approximation for effects due to higher excitations as far as the coefficients of the corresponding CSFs are essentially products of singly and/or doubly excited terms. In the parlance of MBPT these correspond basically to the unlinked terms. The CPF then should miss essentially effects of linked triples and quadruples and should be close to the CCSD technique⁶ and to CEPA-1.⁸ These suggestions are in fact confirmed by the comparisons discussed in Sec. IV.

Application of CPF method for CO, N₂, NO, O₂, F₂, and Cl₂ show a marked improvement of computed R_e and D_e over the CI(SD), which requires the same computational labor. These shortcomings of a CI(SD) are

often not rectified by MR-CI(SD) calculations if only a few more references are included. We often found it more economic to perform a large basis set CPF instead of a smaller basis set MR-CI(SD) calculation. MR-CI studies are indispensable, of course, for a reliable description of the total hypersurface including the dissociation channels. This has been convincingly demonstrated by Buenker, Peyerimhoff *et al.*,³² and by Brown, Shavitt, and Shepard³³ in their comparison with full CI results for water.²⁵ However, such studies can at present hardly be carried out routinely for even small molecules as SF₂, NSF, SPCl, HNSO, etc., in using basis sets which include up to f AOs (which is required if one aims for errors less than 0.04 a_0 in computed R_e values). The single reference CPF leads here to around 100 000 CSFs and the corresponding computations—typically 10 to 20 min CPU time on the CYBER 205 for a total run—can be performed routinely.

ACKNOWLEDGMENTS

Discussions with V. Staemmler, Bochum, on the subtleties of open shell CEPA methods have been of great help for this work. We are grateful to F. B. Brown, H. Lischka, R. Pitzer, I. Shavitt, and R. Shepard for making the COLUMBUS set of computer programs available to us. H. Lischka, Vienna, M. Schindler, Bochum, R. Becherer, H. J. Böhm, and H. Schiffer, all from Karlsruhe, have made significant contributions to help converting the programs for the CYBER 205. We thank K. Jankowski for valuable discussions. It is a pleasure to acknowledge the excellent service provided by the "Rechenzentrum der Universität Karlsruhe." This work was supported in part by the DFG and the "Fonds der Chemischen Industrie."

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