

## Comparison of CEPA and CP-MET Methods

S. Koch and W. Kutzelnigg

Lehrstuhl für Theoretische Chemie der Ruhr-Universität Bochum, D-4630 Bochum,  
Federal Republic of Germany

The known CEPA variants CEPA ( $\nu$ ) with  $\nu = 0, 1, 2, 3$  and two new ones with  $\nu = 4, 5$  are compared both formally and for various numerical examples with CP-MET. The main conclusions are: 1. In those situations where both CP-MET and the CEPA variants are justified (i.e. for "good" closed shell states) the correlation energies obtained with the 7 different schemes differ very little (by something like  $\pm 2\%$ ), with CEPA (1) closest to CP-MET (difference usually a fraction of 1%) and CEPA (4) nearly as close; this is rather insensitive to whether one uses canonical or localized orbitals. Even CEPA (3) is not too far from CP-MET, which confirms an earlier suggestion of Kelly. 2. In those cases where one of the 7 schemes fails (e.g. due to near degeneracy as in covalent molecules at large internuclear distances) the other 6 usually fail as well, though CEPA (0) is then somewhat poorer than the other schemes. Then no longer CEPA (1) but rather CEPA (3) is closest to CP-MET and then all schemes converge much better in a localized representation. 3. CEPA (2) usually leads to best agreement with experiment since it simulates to some extent triple substitutions. In none of the studied examples does CP-MET show a significant superiority as compared to the other schemes. Possible improvements to extend the domain of applicability of these methods are discussed.

**Key words:** Electron correlation – Coupled electron pair approximation (CEPA) – Coupled cluster (CC) – Coupled pair many electron theory (CP-MET) – Many-body perturbation theory (MBPT) – Møller-Plesset perturbation theory (MP-PT) – Near degeneracy.

### 1. Introduction

A method, called CP-MET (*c*oupled *p*air *m*any *e*lectron *t*heory) developed by Čížek [1] in 1966 for the treatment of electron correlation in atoms and molecules,

based on earlier work of Coester and Kümmel [2, 3] in nuclear theory, has been "discovered" for large-scale *ab initio* quantum chemical calculations only quite recently [4–6, 22, 23].

That this did not occur earlier must to some extent be ascribed to the fact that Čížek's paper was hard to read, and this not only because it was formulated in terms of diagrams at a time when diagram techniques were not yet as popular in theoretical chemistry as they are nowadays.

The apprehension of Čížek's method by people working with traditional quantum chemical methods such as CI [7] was made difficult by a difference in philosophy, so to say. The CI equations are easily explained to a beginner as eigenvalue equations of the matrix representation of the Hamiltonian in a basis of Slater determinants or of configuration state functions, although the real difficulties arise when it comes to expressing the matrix elements between configurations in terms of the integrals over the orbital basis [7]. However this second step, as formidable as it may be, can be regarded as "technical", one does not need to understand it in all details, in order to understand what CI is, unless one wants to write a CI program. In Čížek's method, however, the two analogous steps were mixed from the very beginning. There was no access to the theory for a reader who did not care about what in the field of CI would be regarded as technical details.

That a two step formulation analogous to that current for CI is also possible for CP-MET, and that what we regard as the physical essence of CP-MET can be written in two lines, became evident only later [8, 9] in spite of an earlier comparison of the traditional and the diagrammatic approaches to CP-MET [10], in which the main stress was put on demonstrating the superiority of the diagram technique.

If one cares less about differences in the original presentation, CP-MET and CI have, in fact, much in common and realizing this one can use the experience that has meanwhile been accumulated in the field of CI [7] to implement the CP-MET features into a traditional CI program.

CEPA, the "coupled electron pair approximation" [11, 12], has unlike CP-MET from the very beginning been developed in the context of large scale *ab initio* quantum chemistry in a rather pragmatic way. That CEPA and CP-MET were apart from their admitted common source in IEPA (the "independent electron pair approximation" [8], which is the same as Sinanoğlu's "many-electron theory" MET [13] or Nesbet's [14] two particle-Bethe-Goldstone theory) intimately related, became fully obvious only later [8, 9].

CEPA, or rather CEPA-PNO (PNO for pair natural orbitals) has been conceived [11] as a generalization of IEPA-PNO [15, 16]. Although PNO-CI [11] has been developed simultaneously as a variant of traditional CI (limited to double substitutions), which made the relation of CEPA to CI very clear, it had not been realized by the traditional CI people for quite a while that the basic ideas of CEPA can be easily implemented into any kind of CI program and are not limited to the use of PNO's. The "Davidson correction" to CI [17] was a step in the direction of

CEPA [18] though this was first not realized. This correction had in fact been studied earlier [15] and can even be traced further back [13]. The relations of the "Davidson correction" with earlier work and a generalization of it have been discussed by Davidson and Silver [19]. Nowadays the implementation [18, 20, 21] of CEPA into so-called "direct CI-methods" is a serious alternative to CEPA-PNO.

After it had been realized that CEPA and CP-MET differ by the presence of a few extra terms in CP-MET, Taylor et al. [22, 23] were the first to implement these CP-MET terms into the Karlsruhe CEPA-PNO program [12]. Taylor et al. had to face serious computer limitations and they were forced to use strongly truncated PNO expansions, which introduced a significant numerical noise into the results. Moreover their formulae [24] did not seem to be fully correct. After we had realized that it is nearly hopeless to derive these by hand we developed a computer program for their construction [4].

After Taylor et al. [22, 23] a few more CP-MET computer programs not based on PNO's for *ab initio* applications were developed, mainly by Bartlett and Purvis [5] and by Pople et al. [6] who introduced a new name (coupled cluster) and a new abbreviation (CC). The program used in the present paper has been coded independently [4]. An interesting variant of CP-MET has been presented by Nakatsuji and Hirao [25], some formal development was also carried out by the Harris-Monkhurst group [26, 27] and by Paldus [28].

The aim of the present paper is to compare CP-MET with various CEPA-variants [8]. The formal comparison (see also Refs. 8 and 17) will be given in Sect. 2 and numerical results will be discussed in Sect. 3. We also consider situations where both CEPA and CP-MET must fail, e.g. for potential curves at large distances of systems that dissociate into open shell states.

## 2. The Formal Relation Between CI, CEPA and CP-MET

In all three schemes we start from a reference function  $\Phi$  (e.g. a closed shell Slater determinant) and search for a wave operator  $W$  that transforms  $\Phi$  into an improved wave function  $\Psi$  (in intermediate normalization)

$$\Psi = W\Phi; \quad \langle \Phi | W | \Phi \rangle = \langle \Phi | \Phi \rangle = 1 \quad (1)$$

$W$  is expanded in a set of basis operators  $R_k$

$$W = 1 + \sum_k c_k R_k \quad (2)$$

where the  $R_k$  are usually single and double substitution (excitation) operators

$$R_i^a = a_a^+ a_i, \quad R_{ij}^{ab} = a_a^+ a_b^+ a_j a_i \quad (3)$$

from spin orbitals  $\psi_i$  occupied in  $\Phi$  to spin orbitals  $\psi_a$  unoccupied in  $\Phi$  (virtual). The  $\psi_p$  are supposed to form an orthonormal set.

The CI equations can be obtained by assuming that  $\Psi$  satisfies the Schrödinger equation

$$H\Psi = H\Phi + \sum_k c_k HR_k\Phi = E\Psi = E\Phi + E \sum_k c_k R_k\Phi \quad (4)$$

on multiplying it on the left by  $\langle\Phi|$  or by  $\langle\Phi|R_i^+$

$$\langle\Phi|H|\Phi\rangle + \sum_k c_k \langle\Phi|HR_k|\Phi\rangle = E \quad (5a)$$

$$\langle\Phi|R_i^+H|\Phi\rangle + \sum_k c_k \langle\Phi|R_i^+HR_k|\Phi\rangle = Ec_i. \quad (5b)$$

The CI equations are usually formulated for a  $\Psi$  normalized to unity, but this is a minor detail.

An alternative – and more convincing – way to the CI equations goes via the variation principle. One requires that the expectation value  $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$  is stationary with respect to variation of the  $c_k$  and gets the condition (5b), while the stationary energy is given by (5a).

The CI energy is “variational” i.e. it furnishes an upper bound to the true energy, but it is – for the operator basis  $R_k$  limited to single and double substitution operators – not “size consistent” (this name [6] is now commonly used, though it is somewhat misleading) – i.e. it has not the correct dependence on the number of electrons [15, 29–31].

Rayleigh–Schrödinger perturbation theory (but *not* Brillouin–Wigner perturbation theory), either starting from the bare nuclear Hamiltonian or, following Møller and Plesset [32], from the Hartree–Fock Hamiltonian, is “size consistent” but it has other drawbacks, the perturbation series may not converge at all or converge too slowly.

One can take care of the correct dependence on the particle number in the non-perturbative context, if one replaces the linear expansion (2) of the wave operator by the exponential form

$$W = \exp S = \exp \left\{ \sum_k d_k R_k \right\} \quad (6)$$

proposed by Coester and Kümmel [2, 3] (and suggested even earlier by Hugel-holtz [33] from an analysis of perturbation theory). For a review of applications of this ansatz in nuclear theory see Kümmel et al. [34].

Multiplying the Schrödinger equation

$$He^S\Phi = Ee^S\Phi$$

on the left by  $\langle\Phi|$  or by  $\langle\Phi|R_k^+$  leads to

$$\langle\Phi|He^S|\Phi\rangle = E\langle\Phi|e^S|\Phi\rangle \quad (7a)$$

$$\langle\Phi|R_k^+He^S|\Phi\rangle = E\langle\Phi|R_k^+e^S|\Phi\rangle. \quad (7b)$$

If  $\Phi$  is a closed shell Slater determinant and if the operator basis  $\{R_k\}$  contains only double substitution operators the power series expansion of  $e^S$  in (7) breaks off and one gets the CP-MET equations

$$\langle\Phi|H|\Phi\rangle + \langle\Phi|HS|\Phi\rangle = E \quad (8a)$$

$$\langle\Phi|R_k^+H|\Phi\rangle + \langle\Phi|R_k^+HS|\Phi\rangle + \frac{1}{2}\langle\Phi|R_k^+HS^2|\Phi\rangle = E\langle\Phi|R_k^+S|\Phi\rangle \quad (8b)$$

which can, in view of (6), also be written as

$$\langle\Phi|H|\Phi\rangle + \sum_k d_k \langle\Phi|HR_k|\Phi\rangle = E \quad (9a)$$

$$\langle\Phi|R_k^+H|\Phi\rangle + \sum_l d_l \langle\Phi|R_k^+HR_l|\Phi\rangle + \frac{1}{2} \sum_{l,m} d_l d_m \langle\Phi|R_k^+HR_lR_m|\Phi\rangle = Ed_k. \quad (9b)$$

If the basis contains single substitution operators as well, (8a) contains also a term in  $S^2$  and the expansion of (7b) goes up to  $O(S^4)$ .

While the CI equations (5) can also be obtained as stationarity conditions for the energy expectation value, this is not the case for the CP-MET equations (9). If one tries to make  $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$  stationary, one gets terribly complicated equations and nobody has so far bothered to solve them (for some attempts on these lines see however Ref. 35).

The energy  $E$  obtained from (9) is not an upper bound to the true energy and it is therefore hard to judge the quality of a CP-MET calculation from the accuracy of the energy.

There is a possibility to reconcile size consistency and variational stationarity, namely by using the unitary exponential ansatz [8, 36]

$$W = e^\sigma, \quad \sigma = -\sigma^\dagger. \quad (10)$$

A more detailed account of the theory [36] based on this ansatz will be published elsewhere.

The system (9) is non-linear; it can be solved iteratively, e.g. by neglecting the non-linear terms in the first iteration cycle.

Of course, if one neglects the bilinear terms in (9b) altogether one gets the CI system (5) which is not size consistent. One rather must substitute  $E$  in (9b) from (9a)

$$\begin{aligned} \langle\Phi|R_k^+H|\Phi\rangle + \sum_l d_l \langle\Phi|R_k^+HR_l|\Phi\rangle + \frac{1}{2} \sum_{l,m} d_l d_m \langle\Phi|R_k^+HR_lR_m|\Phi\rangle \\ = d_k \langle\Phi|H|\Phi\rangle + \sum_l d_k d_l \langle\Phi|HR_l|\Phi\rangle \end{aligned} \quad (11)$$

and ignore then all bilinear terms in order to get a zeroth-order approximation

$$\langle\Phi|R_k^+H|\Phi\rangle + \sum_l d_l \langle\Phi|R_k^+HR_l|\Phi\rangle = d_k \langle\Phi|H|\Phi\rangle \quad (12)$$

which is size consistent. Eqn. (12) (together with 9a) represents the “linear version” of CP-MET [1] and is now usually called CEPA (0) [8]. Eqn. (12) differs

from the CI equation (5b) by the replacement of the CI energy  $E$  by the "unperturbed" energy  $\langle\Phi|H|\Phi\rangle$ .

CEPA (0) looks very appealing since many other ways to solve the many body Schrödinger equation also lead to CEPA (0) as the first non-trivial approach. One gets there from the unitary ansatz (10) [8], as well as from perturbation theory if one searches for the optimum partition of the Hamiltonian  $H$  into an unperturbed  $H_0$  and a perturbation  $V$  [37]. (For still another way [18] see the end of this section.)

Unfortunately CEPA (0) is never exact, even not for a supersystem that consists of non-interacting two-electron systems, e.g. He atoms at pairwise infinite distance. However all CEPA-variants to be discussed below (except CEPA (5)) are exact in this special case (provided that single substitutions are included and that one uses localized MO's).

Even if one does not want to neglect all bilinear terms in (11), one realizes that many of these terms on the l.h.s. and the r.h.s. of (11) cancel, namely all those that can be represented by "unlinked diagrams" [8].

One can argue that the remaining (not cancelled) terms on the l.h.s. of (11) are small and of arbitrary sign, such that their net contribution may be negligible, and keep only the remaining terms on the r.h.s.

$$\langle\Phi|R_k^+H|\Phi\rangle + \sum_l d_l \langle\Phi|R_k^+HR_l|\Phi\rangle = d_k \langle\Phi|H|\Phi\rangle + \sum_l d_k d_l \langle\Phi|HR_l|\Phi\rangle_L \quad (13)$$

where the subscript  $L$  stands for linked. This explicitly means that only such terms are taken in the sum where the operators  $R_l$  and  $R_k$  have at least one index in common. (Paldus [28] points out that one should use the term "connected" rather than "linked" to be conform with the meaning of these terms in perturbation theory. He is probably right, but the tradition is in favour of "linked" and misunderstandings are hardly possible, since we are not in the framework of perturbation theory anyway.)

The approximation characterized by Eqn. (13) has been proposed by Kelly [38] in a slightly different context a few years before Čížek's presentation of CP-MET.

Let us, for the moment, refer to this as Kelly's approach. Kelly himself has never applied it, he became more interested in perturbation theory (MBPT) [39].

We have to point out a source of possible misunderstanding. In our nomenclature – because we argue in terms of particles only, i.e. we do not use the particle-hole formalism – there is only a *partial* cancellation of the terms on the r.h.s. of (11), in fact those terms on the r.h.s. that do not cancel are those taken care of in Kelly's approach (13). In an alternative formalism that is closely related to MBPT, nothing is left on the r.h.s. and the "Kelly terms" appear on the l.h.s. with negative sign as so-called EPV ("exclusion principle violating") terms. The argument is then, that EPV terms are usually quite large and must, at variance with "non-EPV" or "EPA" ("exclusion principle allowed") terms of the same order, not be neglected.

We can write CI, CEPA (0) and Kelly's approach in one common set of equations

$$\langle\Phi|H|\Phi\rangle + \sum_k d_k \langle\Phi|HR_k|\Phi\rangle = E \quad (14a)$$

$$\langle\Phi|R_k^+H|\Phi\rangle + \sum_l \langle\Phi|R_k^+HR_l|\Phi\rangle d_l = W_k d_k \quad (14b)$$

with  $W_k = E$  in the case of CI,  $W_k = \langle\Phi|H|\Phi\rangle$  for CEPA-0 and

$$W_k^{(K)} = \langle\Phi|H|\Phi\rangle + \sum_l d_l \langle\Phi|HR_l|\Phi\rangle_L \quad (15)$$

with  $K$  for Kelly (where  $L$  means: linked to  $k$ ). One can also write

$$W = \langle\Phi|H|\Phi\rangle + \Delta W. \quad (16)$$

The energy shift  $\Delta W$  is then 0 for CEPA (0), equal to the total correlation energy

$$\Delta E = E - \langle\Phi|H|\Phi\rangle = \sum_l d_l \langle\Phi|HR_l|\Phi\rangle \quad (17)$$

for CI, and the sum of all contributions to  $\Delta E$  which are linked to  $R_k$ , for Kelly.

One can suggest alternative energy shifts by the following arguments.

If one pair of electrons characterized by the occupied spin orbitals  $\psi_i$  and  $\psi_j$  is independent of the rest of the system, the energy shift to be taken for all double substitutions from this pair is just the correlation energy

$$\varepsilon_{ij} = \sum_{a \leq b} d_{ij}^{ab} \langle\Phi|HR_{ij}^{ab}|\Phi\rangle \quad (18)$$

of this pair ( $d_{ij}^{ab}$  and  $R_{ij}^{ab}$  in (18) have an obvious meaning, see Eqn. 3).

So the simplest modification of CEPA (0), that leads to the exact result for a supersystem consisting of non-interacting pairs, consists in choosing the IEPA energy shift [13–16]

$$W_{ij} = \langle\Phi|H|\Phi\rangle + \varepsilon_{ij} \quad (19)$$

for all  $R_{ij}^{ab}$ . This is the recipe of the standard CEPA version [11, 12] that has later been called CEPA (2) [40].

Kelly's approach, as it is formulated in Eqn. (13), has a different energy shift for each substitution operator  $R_{ij}^{ab}$ . One can however interpret "linked" with respect to the occupied orbitals (holes)  $\psi_i$  and  $\psi_j$  only and get thus a slightly modified scheme, called CEPA (3), which is essentially Kelly's scheme but with a common  $W_{ij}$  for every pair.

CEPA (1) is somewhat in between CEPA (2) and CEPA (3). Meyer [11, 40] was led to CEPA (1) in searching for a scheme that is, in a special case, invariant with respect to a unitary transformation from localized to canonical orbitals. Neither CEPA (2) nor CEPA (3) have this invariance property. The best justification of CEPA (1) is probably a heuristic one, the energy shift of CEPA (2) is "too small", that of CEPA (3) "too large", so CEPA (1) should be a good compromise (see however Sect. 3).

Before the variants CEPA (1) and CEPA (2), originally written CEPA-1 and CEPA-2, were proposed [40] the notation CEPA (1) had been used in a different meaning [12] that has not been taken up since.

As to the inclusion of single substitutions in CEPA see Ahlrichs [18].

In a previous review [8] the definition of these various CEPA-variants was, for simplicity's sake, given on spin-orbital level.

In practice, one does, however, not want to use pairs of spin-orbitals, but rather spin-irreducible pairs. For closed-shell states three types of pairs have to be considered:  $II$ ,  $^sIJ$  and  $^tIJ$  which are defined in terms of the (spin free) orbitals  $\phi_I$  and  $\phi_J$  and where the superscripts  $s$  and  $t$  mean that  $\phi_I$  and  $\phi_J$  are coupled to a singlet or a triplet. One can then eliminate spin and interpret "linked" and "unlinked" in terms of orbitals rather than spin orbitals. The expressions for the energy shifts  $\Delta W_k$  get thus somewhat more complicated, but the computation is of course, much simplified. The energy shifts are collected in Table 1 (see also Ref. 9).

Two new variants are included.

In CEPA (4) all interorbital contributions  $\varepsilon_{IJ}$  to the energy shift are neglected except the particular  $^s\varepsilon_{IJ}$  and  $^t\varepsilon_{IJ}$  for the pair  $IJ$  that one considers. For intraorbital pairs the energy shift is the same as in CEPA (2), but for interorbital pairs it contains  $\varepsilon_{II} + \varepsilon_{JJ}$ , i.e. for these there is a larger shift. This is better justified than the choice of CEPA (2) unless one argues that the formally too small shifts in CEPA (2) simulate the effect of triple substitutions.

CEPA (5) is finally the analogon to CEPA (3) that is obtained if one does not start from the Coester-Kümmel  $e^S$ -ansatz, but from the unitary ansatz (10) up to 3<sup>rd</sup> order in  $\sigma$ , if one neglects the unlinked terms but keeps the EPV terms.

**Table 1.** Energy shifts for various CEPA-variants

	$\Delta W(II)$	$\Delta W(^sIJ)$	$\Delta W(^tIJ)$
CEPA (0)	0	0	0
CEPA (2)	$\varepsilon_{II}$	$^s\varepsilon_{IJ}$	$^t\varepsilon_{IJ}$
CEPA (1)	$\varepsilon_{II} + \frac{1}{2} \sum_{K(\neq I)} (^s\varepsilon_{IK} + ^t\varepsilon_{IK})$	$\frac{1}{2}(\varepsilon_{II} + \varepsilon_{JJ} + ^s\varepsilon_{IJ} + ^t\varepsilon_{IJ} + \frac{1}{2} \sum_{K(\neq I, J)} (^s\varepsilon_{IK} + ^t\varepsilon_{IK} + ^s\varepsilon_{JK} + ^t\varepsilon_{JK}))$	as $W(^tIJ)$
CEPA (3)	$\varepsilon_{II} + \sum_{K(\neq I)} (^s\varepsilon_{IK} + ^t\varepsilon_{IK})$	$\varepsilon_{II} + \varepsilon_{JJ} + \frac{1}{2} ^s\varepsilon_{IJ} + \frac{5}{6} ^t\varepsilon_{IJ} + \frac{1}{2} \sum_{K(\neq I, J)} (^s\varepsilon_{IK} + ^t\varepsilon_{IK} + ^s\varepsilon_{JK} + ^t\varepsilon_{JK})$	$\varepsilon_{II} + \varepsilon_{JJ} + \frac{5}{6} ^s\varepsilon_{IJ} + \frac{13}{18} ^t\varepsilon_{IJ} + \frac{1}{2} \sum_{K(\neq I, J)} (^s\varepsilon_{IK} + ^t\varepsilon_{IK} + ^s\varepsilon_{JK} + ^t\varepsilon_{JK})$
CEPA (4)	$\varepsilon_{II}$	$\varepsilon_{II} + \varepsilon_{JJ} + \frac{1}{2} ^s\varepsilon_{IJ} + \frac{5}{6} ^t\varepsilon_{IJ}$	$\varepsilon_{II} + \varepsilon_{JJ} + \frac{5}{6} ^s\varepsilon_{IJ} + \frac{13}{18} ^t\varepsilon_{IJ}$
CEPA (5)	see text		

The energy shifts in CEPA (5) are  $\frac{4}{3}$  of those of CEPA (3), but in CEPA (5) Eqn. (14) is replaced by

$$\langle \Phi | H | \Phi \rangle + \frac{4}{3} \sum_k d_k \langle \Phi | H R_k | \Phi \rangle + \frac{1}{3} \sum_{k,l} d_k^* \{ \langle \Phi | R_k^+ H R_l | \Phi \rangle - \langle \Phi | H | \Phi \rangle \delta_{kl} \} d_l = E \quad (20a)$$

$$\langle \Phi | R_k^+ H | \Phi \rangle \left\{ 1 - \frac{2}{3} \sum_l |d_l|^2 \right\} + \sum_l \langle \Phi | R_k^+ H R_l | \Phi \rangle d_l = W_k d_k. \quad (20b)$$

CP-MET differs from CEPA (3) by the presence of various nonlinear terms. We have implemented them in the PNO formalism. The formal expressions are too lengthy to be given here, but they are available on request.

CEPA and CP-MET are also related to perturbation theory (PT) (for a recent comparison see Ahlrichs [18], who made the important statement, that all existing MBPT schemes are either identical to or approximations to one of the CEPA variants). The "Møller-Plesset perturbation theory" (MP-PT) used by Pople et al. [41] which is formulated purely analytically, and the diagrammatic "many-body-perturbation theory" (MBPT) used by Robb [42], Silver et al. [43] and others [44-46] are completely identical, except of course for different computer implementation and for analysis and interpretation.

We assume that the Hartree-Fock ground state  $\Phi$  is always the reference function.

Then MBPT (2), i.e. 2<sup>nd</sup> order PT, is of "IEPA-type", in other words to 2<sup>nd</sup> order in PT the pairs behave as independent. Couplings between the pairs show first up to 3<sup>rd</sup> order. To 2<sup>nd</sup> order IEPA and the exact solution agree. IEPA can be obtained by summing a special class of diagrams, namely all independent pair-like diagrams (mainly the so-called "ladder diagrams") to infinite order [47].

PT to 3<sup>rd</sup> order is of "CEPA-type", i.e. to 3<sup>rd</sup> order in the perturbation parameter of MP-PT the exact solution, all CEPA-variants and CP-MET agree. A certain procedure that takes care of all diagrams of 3<sup>rd</sup> order and sums other similar diagrams to infinite order [46, 48] leads in fact to CEPA (0) [18].

Differences between the various CEPA-schemes and CP-MET first show up in 4<sup>th</sup> order of PT [18].

However, none of these schemes (not even CP-MET) agrees with the exact solution to 4<sup>th</sup> order. In 4<sup>th</sup> order PT contributions show up that are not expressible through electron pairs (or single substitutions), but which require electron triples. These terms are rather complicated and most applications of 4<sup>th</sup> order PT are limited to so-called SDQ-MBPT (4), (S for single, D for double, Q for quadruple substitutions, where the latter are actually pairs of double substitutions).

SDQ-MBPT (4) is identical with the perturbation expansion up to 4<sup>th</sup> order of CP-MET, while full 4<sup>th</sup> order MBPT contains terms that are not included in CP-MET. But conversely full 4<sup>th</sup> order MBPT does not contain certain terms that are taken care of by CP-MET, namely terms of 5<sup>th</sup> and higher orders. It has been

pointed out previously [5, 6] that in many practical cases the results of SDQ-MBPT (4) are very close to those of CP-MET, which indicates that in those cases 5<sup>th</sup> and higher orders are not important, but there is no reason to believe that this is always so.

Anyway the lowest non-trivial order in perturbation theory to which CP-MET and the CEPA variants can be compared is the 4<sup>th</sup> order. The 4<sup>th</sup> order version of CEPA (0) is D-MBPT (4), in which only double substitutions are taken care of, while the 4<sup>th</sup> order version of CP-MET namely SDQ-MBPT (4) has already been mentioned.

The 4<sup>th</sup> order approximations of the other CEPA variants can also be defined. Zingales and Ahlrichs [21] have performed a numerical comparison of various CEPA variants and CP-MET on 4<sup>th</sup> order level using also data from Bartlett and Purvis. We are comparing these data with our  $\infty$  order results in Tables 3 to 5.

### 3. Problems of Near Degeneracy

The determination of the CEPA or CP-MET coefficients leads to solutions of systems of the type

$$\sum_l (H_{kl} - W_k \delta_{kl}) d_l = h_k \quad (21)$$

with

$$H_{kl} = \langle \Phi | R_k^\dagger H R_l | \Phi \rangle; h_l = \langle \Phi | H R_l | \Phi \rangle. \quad (22)$$

If  $W_k$  is constant as in CEPA (0), the system (21) is linear, otherwise an iterative solution through a chain of linear systems is necessary.

Of course, the solution of the linear system is only possible if the matrix  $\{H_{kl} - W_k \delta_{kl}\}$  is non-singular, for CEPA (0) if  $H_{kl}$ , i.e. the matrix representation of the Hamiltonian in the space of configurations doubly (and singly) excited with respect to  $\Phi$ , has no eigenvalue equal to  $W_k = E_0 = \langle \Phi | H | \Phi \rangle$ .

If  $\Phi$  is an approximation to a non-degenerate ground state one can expect that all eigenvalues of  $\{H_{kl}\}$  are higher than  $E_0$  i.e. that in CEPA (0) no singularity occurs, and *a fortiori* not in CP-MET or the other CEPA-variants, where in view of the negative energy shifts  $W_k < E_0$ .

If  $\Phi$  is degenerate with some other (doubly substituted) configuration  $\Phi'$ , such that  $\langle \Phi | H | \Phi' \rangle \neq 0$ , the matrix  $\{H_{kl} - E_0 \delta_{kl}\}$  may become singular, but the energy shift of the other schemes (which lowers  $E_0$  to  $W_k$ , but does not lower  $E' = \langle \Phi' | H | \Phi' \rangle$ ) will usually make the other schemes well-behaved. Nevertheless, the results will not be very reliable in any case, since it is without doubt a poor approximation to include all (singly and) doubly substituted configurations with respect to  $\Phi$  but not also with respect to  $\Phi'$ .

More interesting are situations where no  $\Phi'$  is exactly degenerate with  $\Phi$ , but where  $\Phi'$  has an energy  $E'$  only slightly above  $E_0$  (so-called near-degeneracy).

$|E' - E_0|$  is smaller than or of the same order as the various energy shifts, large differences between the various CEPA-variants are to be expected, and especially CEPA (0) should overestimate the expansion coefficient of  $\Phi'$ .

Large differences between the CEPA variants are hence a warning, and an indication of near-degeneracy.

One can argue that there should be "exact" energy shifts, which are usually not known, but which lead to the exact coefficients of singly and doubly substituted configurations and hence to the exact correlation energy

$$\Delta E = \sum_k d_k^* h_k \quad (23)$$

(in the same basis of course).

An alternative expression for  $\Delta E$  is

$$\Delta E = \sum_{k,l} d_k^* (H_{kl} - W_k \delta_{kl}) d_l. \quad (24)$$

One can conclude from this expression and its stationarity with respect to variations of the  $d_k$ , that differences in the  $W_k$  affect  $\Delta E$  basically as

$$\delta W_k |d_k|^2. \quad (25)$$

If all coefficients are small ( $d_k \ll 1$ : "dynamical correlation"), different energy shifts have little effect on  $\Delta E$ , while for large coefficients ("non-dynamical correlation"),  $\Delta E$  depends sensitively on the energy shift. However, let us stress this again: a more sophisticated treatment of correlation is then necessary and even CP-MET is not good enough (except, of course, for the trivial case of a two-electron system, or for "effective two electron systems" as the Be atom, where even IEPA is exact).

A model study in which near degeneracy situations were simulated, was recently performed by Jankowski and Paldus [49].

### 4. Basis Sets

The basis sets were chosen so as to make possible a direct comparison with previous results.

For  $BH_3$  a minimal basis was chosen similar to that used by Taylor et al. [22]. The other basis sets are usually of "double-zeta + polarization" quality, and are explained in Table 2. They allow a direct comparison with previous calculations. For Be and  $Be_2$  a larger basis was used.

### 5. Discussion of the Numerical Results

On Table 3 the results for the  $BH_3$  molecule for two basis sets are presented.

To facilitate the comparison of the various methods, for each basis set the CP-MET energies were arbitrarily used as reference values (100%). (This does

Table 2. Basis sets used

BH <sub>3</sub>	(a) minimal STO(21/1) simulated by fully contracted Gaussians (10 for 1s <sub>B</sub> , 4 for 2s <sub>B</sub> , 5 for 2p <sub>B</sub> , 10 for 1s <sub>H</sub> ) after Huzinaga [64] (b) DZ + P: (951/51) Huzinaga basis contracted to (531/31) with $\eta_d(B) = 0.61$ ; $\eta_p(H) = 0.65$
H <sub>2</sub> O	(951/51) contracted to (531/31) with $\eta_d(O) = 1.25$ , $\eta_p(H) = 0.75$
HCN	(951/951/31) contracted to (531/531/31) with $\eta_d(C) = 0.7$ , $\eta_d(N) = 0.95$ , $\eta_p(H) = 0.8$
N <sub>2</sub>	(951) contracted to (531); $\eta_d = 0.95$
F <sub>2</sub>	(951) contracted to (531); $\eta_d = 1.4$
Be and Be <sub>2</sub>	(10 + 1, 5, 2) contracted to (8, 3, 2) with 10s from Huzinaga [64], additional s with $\eta_s = 0.015$ ; $\eta_p = 3.0$ , 1.0, 0.316, 0.12, 0.04 (the first three contracted with coefficients 0.02662, 0.07353, 0.40988) $\eta_d = 0.35$ , 0.12

contracted are always the first (steepest) functions

not necessarily mean that we regard CP-MET as the best possible method. Full CI in the same basis (if available) would have been a better reference.)

For BH<sub>3</sub> the various methods don't differ much. CI (with double excitations) differs from CP-MET by only 2% (small basis) to 3% (large basis).

Keeping in mind that the various schemes don't differ much, one realizes nevertheless that CEPA (1), CEPA (4) and CEPA (3) are very close to CP-MET (deviations < 1%) with CEPA (3) somewhat too small in absolute value (0.4% in the small and 0.6% in the large basis) while both CEPA (1) and CEPA (4) are too large by roughly the same amount.

That the results in the canonical and the localized representation are not exactly the same is due to approximations in the determination of the PNO's such that the space spanned by them is not exactly the same. (In the "direct" method of Ahlrichs and Zitz [21] where PNO's are avoided, CI and CEPA (0) are exactly invariant with respect to a change from localized to canonical representation, CEPA (1) is very close to invariant, while CEPA (2) changes slightly with the representation.) In the present study, scaling CP-MET to 100%, one sees that CEPA (1) and CEPA (0) (which should be exactly invariant, as should be CP-MET) and CEPA (1) (which is supposed to be approximately invariant) have practically the same value in the two representations, while CEPA (2), CEPA (3) and CEPA (4) show differences of a few tenths of a percent.

It is noteworthy that Kelly's idea that the bilinear EPA (= non EPV) terms should be negligible, is confirmed, in the sense that in practically all cases studied here their contribution to the correlation energy lies between 0 and 3%. These terms just make the difference between CEPA (3) and CP-MET.

Table 3. BH<sub>3</sub>,  $r(BH) = 2.3 a_0$ , negative valence shell correlation energy of CP-MET in mh (milli hartree) and in % of the CP-MET results for the other schemes

Basis	can./loc.	Ref.	CP-MET = 100%	CEPA (0)	CEPA (2)	CEPA (1)	CEPA (4)	CEPA (3)	CEPA (5)	CI-D
min.	can.	22	48.428	101.3	100.7			99.6		98.1
min.	loc.	22	48.295	101.3	100.6			99.6		98.1
min.	can.	this work	47.669	101.3	100.7	100.2	100.3	99.6	99.0	98.2
min.	loc.	this work	47.579	101.3	100.4	100.2	100.2	100.0	99.5	98.1
(421/21)	can.	5	116.90	100.8						
(421/21)	can. <sup>a</sup>	18	117.21	102.6	101.8	100.6		99.4		97.0
(531/31)	can.	this work	119.33	102.7	101.8	100.6	100.9	99.4	98.1	97.0
(531/31)	loc.	this work	119.21	102.6	101.3	100.6	100.6	99.8		97.0

<sup>a</sup> Fourth-order perturbation theory.



The numerical value of the correlation energy depends, of course, on the basis, on whether 4<sup>th</sup> order or  $\infty$  order values are taken and on whether or not a PNO expansion is used. However the percentage values are rather insensitive to these variations (unless one wants to compare (DZ+P) basis with minimal basis calculations).

In Table 4 the analogous results for H<sub>2</sub>O are collected. The trends are very much the same. Here the difference between CI and CP-MET amounts to 4–6%, but CEPA (0) differs from CP-MET by only ~1.5%. CEPA (1) is closest to CP-MET, CEPA (2) is not bad either, but CEPA (3) is somewhat too small ("error" ~1.5%). Again we confirm within a few tenths of a percent the relations found by Zirz and Ahlrichs [21].

In the example of HCN (Table 5) that has also been studied by Taylor et al. [23] CP-MET and CI differ by 7% and CEPA (0) is off by 2–3%. Again CEPA (1) is closest to 100%, followed by CEPA (4) (too large), CEPA (3) (too small) and CEPA (2) (too large).

Especially illustrative is a study of N<sub>2</sub> at various internuclear distances (Table 6). Close to the equilibrium distance (2.074 a<sub>0</sub>) the percentage values are, as one might have guessed, nearly the same as those of HCN at its equilibrium distance. For larger internuclear separation the pattern changes, however. The deviations from 100% increase considerably, as is e.g. seen in the column CI. CEPA (1) is closest to 100% for the two shorter distances, but deviates significantly and unsystematically from CP-MET for larger distances; on the whole it is rather CEPA (3) which parallels CP-MET best. Illustrative is the quantity called "norm of the correlation function". It is defined as

$$N_c = \sqrt{\sum_{i < j} \sum_{a < b} |d_{ij}^{ab}|^2} \quad (26)$$

and is a measure of the overlap  $S$  of the reference Slater determinant with the correlated wave function

$$S = (1 + N_c^2)^{-1/2}. \quad (27)$$

For  $R = 2.074 a_0$ ,  $N_c$  is roughly 0.33 for all schemes and  $S \approx 0.95$ ; at  $R = 2.5 a_0$   $S \approx 0.93$  although differences between the various schemes become apparent; at  $R = 3.25 a_0$ ,  $N_c$  becomes larger than 1 – and hence  $S$  smaller than  $1/\sqrt{2}$  for CEPA (2), i.e.  $\Phi$  does no longer dominate the wave function, while CEPA (0) diverges.  $N_c$  is always smallest for CI, next comes CEPA (5) and then CP-MET and CEPA (3).

At  $R = 4 a_0$  only CI, CEPA (1), CEPA (3) and CEPA (4) converge.

For the potential curves of N<sub>2</sub> and F<sub>2</sub> only the results from a calculation in the localized representation are reported. For canonical orbitals the results are pretty much the same near the equilibrium distances, but for larger distances (where the results are poor anyway) the calculations in the canonical representation show much poorer convergence behaviour.

Table 4. H<sub>2</sub>O, experimental geometry, negative valence shell correlation energy of CP-MET in mh and in % of CP-MET for the other schemes

Basis	can./loc.	Ref.	CP-MET	CEPA (0)	CEPA (2)	CEPA (1)	CEPA (4)	CEPA (3)	CEPA (5)	CI-D
(542/31)	can. <sup>a</sup>	5	286.21	101.6						96.3
(531/31)	can. <sup>b</sup>	18	220.87	101.3	100.5	99.4		98.3		95.5
(531/31)	can.	this paper	224.15	101.5	101.0	100.0	100.3	98.8	97.7	96.1
(531/31)	loc.	this paper	222.69	101.3	100.9	99.9	99.7	98.8	97.7	96.1

<sup>a</sup> Including the K shell of O.

<sup>b</sup> Fourth-order perturbation theory.

Table 5. HCN experimental geometry ( $r_{CH} = 2.014 a_0$ ,  $r_{CN} = 2.179 a_0$ ), negative valence shell correlation energy of CP-MET in mh, for the other schemes in % of CP-MET

Basis	can./loc.	Ref.	CP-MET	CEPA (0)	CEPA (2)	CEPA (1)	CEPA (4)	CEPA (3)	CEPA (5)	CI-D
(31/531/531)	loc.	22	292.50		103.1			99.6		93.7
(21/421/421)	can.	5	290.17	101.9						
(21/421/421)	can. <sup>a</sup>	18	297.28	102.1	101.3	99.4		97.4		91.8
(31/531/531)	can.	this paper	300.20	103.2	102.4	100.5	101.2	98.6	96.8	92.9
(31/531/531)	loc.	this paper	300.75	103.2	102.4	100.5	101.2	98.7	97.0	92.9

<sup>a</sup> Fourth-order perturbation theory.



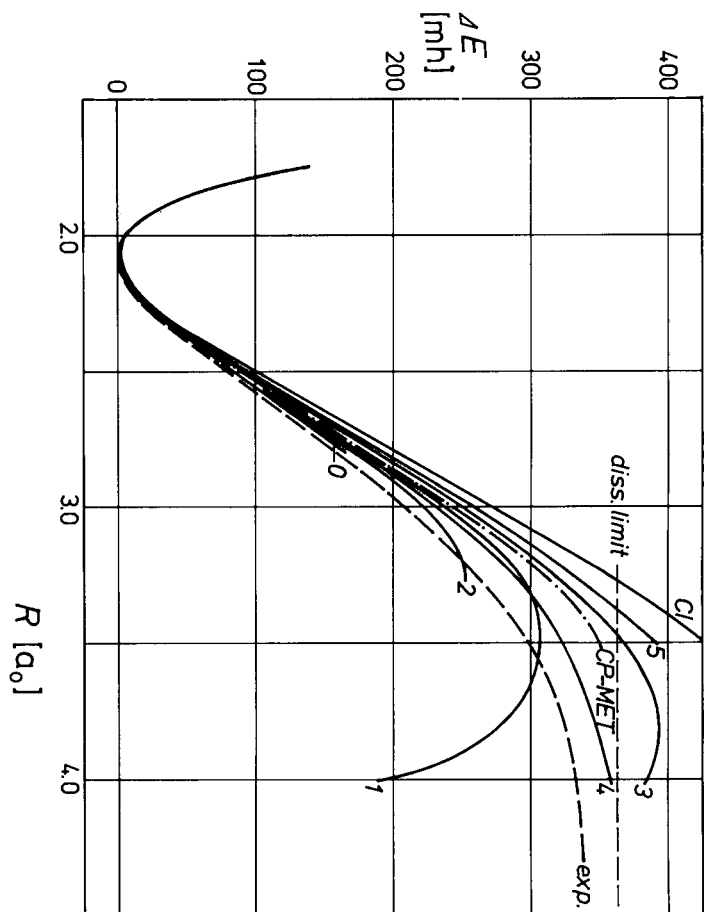
**Table 6.**  $N_2$  at various internuclear distances (basis 951), negative SCF-energy in h, negative valence shell correlation energy of CP-MET in mh, for the other schemes in % of CP-MET (resp. of CEPA (3) in the last line)

$R(a_0)$	SCF	CP-MET	CEPA (0)	CEPA (2)	CEPA (1)	CEPA (4)	CEPA (3)	CEPA (5)	CI-D	$-E_{\text{corr}}/N_e$
1.8	108.90599	292.89 0.29	102.3 0.30	101.8 0.30	100.5 0.29	100.9 0.30	99.2 0.29	97.9 0.28	94.5 0.27	
2.074	108.96639	317.26 0.33	102.8 0.34	102.1 0.34	100.5 0.33	101.0 0.33	98.9 0.32	97.3 0.31	93.3 0.30	
2.5	108.83440	361.96 0.39	104.3 0.42	103.1 0.42	95.7 0.40	101.5 0.41	98.3 0.38	96.1 0.36	91.1 0.35	
2.8	108.70270	396.49 0.45	107.1 0.55	104.8 0.52	101.1 0.48	102.3 0.49	97.9 0.44	95.2 0.41	89.2 0.38	
3.25	108.51918	453.35 0.59	div.	114.3 1.24	104.4 0.78	105.6 0.80	97.7 0.62	93.5 0.53	85.5 0.44	
3.5	108.43197	500.96 0.83	div.	div.	108.7 1.33	106.2 1.15	96.1 0.81	90.3 0.70	80.8 0.47	
4.0	108.28908	div.	div.	div.	131.7 3.81	105.2 1.93	606.97 =100% 1.69	div.	71.8 0.57	

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**Fig. 1.** Potential curves for the  $N_2$  ground state in CP-MET, SD-CI and CEPA variants compared with the experimental one

On Fig. 1 the potential curves obtained from the various schemes are compared with the experimental curve. It can be seen that near the equilibrium geometry all curves are quite good and that for large distances all curves become poor. On the whole the CEPA (2) curve agrees best with experiment, while the equilibrium distance and the force constant are best obtained from CEPA (0) (see Table 8). This result should not be overinterpreted. Here no single substitutions are included and we have seen elsewhere [50] that these have a nonnegligible effect on the force constants (in lowering them) and that CEPA (2) including single substitutions gives currently excellent agreement with experiment. With singles the CEPA (0) values probably become somewhat too small.

In fact Zirz and Ahlrichs (private communication) found with a slightly larger basis ((10, 6, 2) in the contraction [6, 4, 2]) and inclusion of single substitutions force constants for  $N_2$  roughly 1.5 units smaller than ours, such that CEPA (2) reproduces the experimental value almost exactly.

The analogous results for  $F_2$  are collected on Table 7 and illustrated on Fig. 2. Here all schemes except CEPA (0) converge up to  $7 a_0$  (and probably for even larger distances) provided that one uses the localized representation (in the canonic one or the  $\sigma$ - $\pi$ -separation divergences occur earlier).

Table 7.  $F_2$  at various internuclear distances (basis 951), negative SCF-energy in h, negative valence shell correlation energy of CP-MET in mh, for the other schemes in % of CP-MET

$R(a_0)$	SCF	CP-MET	CEPA (0)	CEPA (2)	CEPA (1)	CEPA (4)	CEPA (3)	CEPA (5)	CI-D	$-E_{corr}$ $N_c$
2.3	198.72095	406.34 0.28	101.4 0.29	101.1 0.28	100.2 0.28	100.5 0.28	99.2 0.28	98.3 0.27	94.3 0.26	
2.68	198.73324	424.41 0.31	102.3 0.33	101.8 0.32	100.5 0.32	101.0 0.32	99.3 0.31	98.2 0.30	93.6 0.29	
3.0	198.69985	440.14 0.35	103.9 0.38	102.8 0.37	101.1 0.36	101.8 0.37	99.6 0.35	98.1 0.33	92.9 0.31	
3.5	198.63278	467.52 0.42	108.6 0.53	105.0 0.48	102.3 0.45	103.6 0.47	100.0 0.43	98.0 0.39	91.6 0.36	
4.0	198.57259	496.75 0.50	119.1 0.82	107.6 0.61	103.7 0.56	105.6 0.59	100.5 0.52	97.9 0.45	90.3 0.42	
5.0	198.48966	551.14 0.64	182.1 2.3	110.9 0.83	105.6 0.74	108.1 0.80	101.3 0.68	97.6 0.64	88.2 0.51	
6.0	198.44407	590.21 0.73	div.	111.5 0.93	106.0 0.85	108.6 0.91	101.5 0.78	97.5 0.61	87.3 0.57	
7.0	198.41949	613.72 0.78	div.	111.2 0.97	105.9 0.89	108.5 0.95	101.6 0.82	97.5 0.64	87.0 0.61	

Table 8. Equilibrium distance ( $r_e$ ) in  $a_0$ , force constant ( $k_e$ ) in mdyne/Å, harmonic vibration frequency ( $\omega_e$ ) and anharmonicity ( $\omega_e x_e$ ) in  $\text{cm}^{-1}$ , minimum energy ( $E_{\min}$ ) in hartree for  $N_2$  and  $F_2$  in different approximations (partially localized:  $\sigma$ - $\pi$ -separation)

		$r_e$	$k_e$	$\omega_e$	$\omega_e x_e$	$-E_{\min}$
$N_2$	CI-D	2.061	26.4	2529	14.3	109.26388
	CEPA (0)	2.082	23.8	2402	17.5	109.29525
	CEPA (2)	2.079	24.2	2421	16.5	109.29275
	CEPA (1)	2.075	24.8	2450	15.9	109.28694
	CEPA (3)	2.071	25.2	2474	15.3	109.28133
	CEPA (4)	2.077	24.5	2437	16.1	109.28915
	CEPA (5)	2.068	26.1	2516	n.d.	109.27612
	CP-MET	2.074	24.8	2452	15.3	109.28543
	exp. <sup>a</sup>	2.074	22.92	2358.6	14.324	
$F_2$	CI-D	2.604	6.74	1097	8.71	199.13566
	CEPA (0)	2.678	4.74	921	16.38	199.17276
	CEPA (2)	2.666	5.15	959	12.97	199.17062
	CEPA (1)	2.651	5.57	998	10.84	199.16538
	CEPA (3)	2.639	5.89	1026	9.93	199.16026
	CEPA (4)	2.658	5.36	979	11.65	199.16752
	CEPA (5)	2.630	6.13	1047	9.43	199.15525
	CP-MET	2.634	6.06	1041	9.53	199.16279
	exp. <sup>a</sup>	2.668	4.70	916.6	11.236	

<sup>a</sup> Ref. 65.

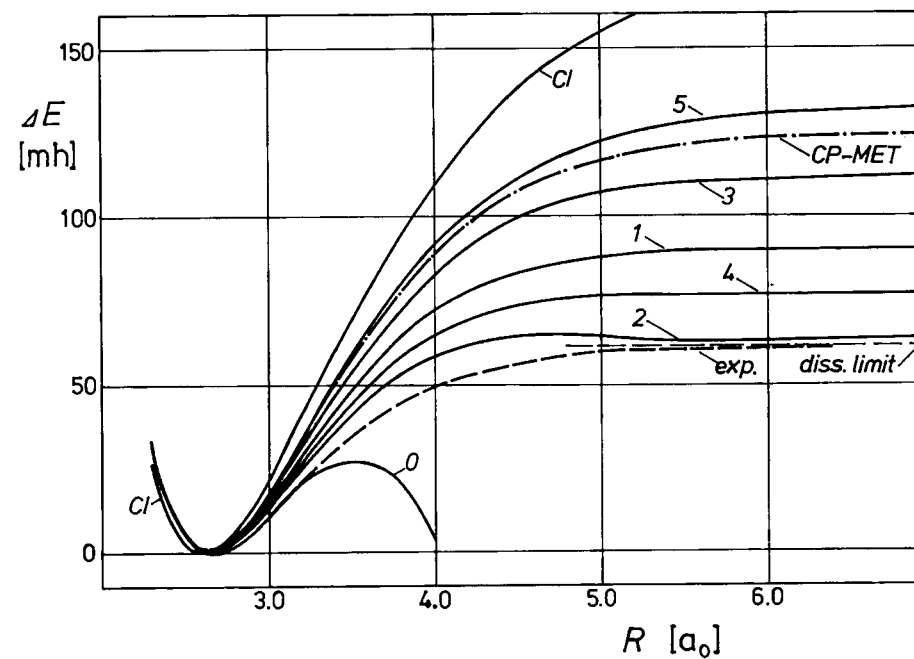


Fig. 2. As Fig. 1 but for  $F_2$

To be frank, all schemes become unreliable for the dissociation of a single or multiple bond as long as one starts from a single Slater determinant as reference function. It is also of minor importance that CEPA (2) is, on the whole, closest to experiment (probably because it simulates to some extent the inclusion of triple substitutions) and that CEPA (3) is closest to CP-MET (since CP-MET itself is not better than any other scheme, except D-CI). One may note that CP-MET seems to lie always above the experimental curve, as if it were an upper bound (which it strictly cannot be).

One may regard the dissociation of a covalent bond as a case of near degeneracy. Two other examples of near degeneracy are realized for the Be atom (where the configuration  $1s^2 2s^2$  is near to degeneracy with  $1s^2 2p^2$ ) and the  $\text{Be}_2$  molecule.

The results for the Be atom are collected in Table 9. As it is characteristic for the case of near degeneracy (see Sect. 3) one notes a large difference between CEPA (0) and other schemes ( $\sim 8\%$  deviation) while these agree rather well among each other.

$\text{Be}_2$  is a very "tough" molecule for the theoretician. Several recent calculations [51–55] have led to rather strange conclusions. There has mainly been a controversy whether this molecule has a "van der Waals" minimum near  $8 a_0$  or a "chemical" minimum near  $5 a_0$ , or both. We do not want to settle this controversy, but rather contribute to the explanation why this controversy occurs.  $\text{Be}_2$  is for all internuclear distances a closed shell system, so the right dissociation does not pose a problem.

We have performed various CEPA and CP-MET calculations both at  $R = 40 a_0 (\sim \infty)$  and at  $R = 5 a_0$  and collected the results in Table 10. The variation of the correlation energy between the different schemes is about as expected. The rather large differences between the canonical and the localized representation are in part an artifact of the PNO approximation and an indication that one should go beyond it. The change in the correlation energy between  $R \sim \infty$  and  $R = 5 a_0$  varies in the different scheme between  $-3$  and  $-10$  mh. The SCF repulsion at  $R = 5 a_0$  is  $8.60$  mh and one realizes that the net effect of SCF repulsion and change of the correlation energy is attractive for some schemes (e.g. CEPA (0) or CEPA (2) canonical) and repulsive for other schemes.

CP-MET	61.060	mh
CEPA (0)	108.46	%
CEPA (2)	100.33	%
CEPA (1)	100.16	%
CEPA (4)	100.31	%
CEPA (3)	99.99	%
CEPA (5)	98.06	%
CI-D	97.97	%

**Table 9.** Be atom ground state ( $E_{\text{SCF}} = -14.572831$  h). Negative correlation energy for CP-MET (including  $K$  shell) in mh and for the other variants in % of CP-MET (canonical representation)

**Table 10.** Negative valence shell correlation energies  $-E_{\text{corr}}$  of  $\text{Be}_2$  at  $R = 40 a_0$  and lowerings  $\Delta E_{\text{corr}}$  of the valence shell correlation energy from  $40 a_0$  to  $5 a_0$  in mh in the canonical and the localized representation.

$$E_{\text{SCF}}(R = 40 a_0) = -29.14566 \text{ h}$$

$$\Delta E_{\text{SCF}} = E_{\text{SCF}}(R = 5 a_0) - E_{\text{SCF}}(R = 40 a_0) = 8.60 \text{ mh}$$

	can.		loc.	
	$-E_{\text{corr}}(R = 40 a_0)$	$\Delta E_{\text{corr}}$	$E_{\text{corr}}(R = 40 a_0)$	$\Delta E_{\text{corr}}$
CP-MET	94.82	5.06	90.27	3.54
CEPA (0)	109.26	9.74	100.31	6.20
CEPA (2)	101.12	9.25	90.27	7.69
CEPA (1)	97.12	7.36	90.27	5.52
CEPA (4)	97.22	7.43	90.27	5.66
CEPA (3)	92.94	6.80	90.27	3.62
CEPA (5)	89.56	6.70	87.99	3.23
CI-D	89.65	6.61	83.38	5.11

The crux is that the SCF interaction varies very little with distance, much less than the energy for a typical closed-shell repulsion does [56] and that therefore an extremely high accuracy of the correlation energy is necessary in order to obtain a qualitatively correct potential curve. The CEPA or CP-MET level is obviously not enough since it is uncertain to within a few mh. Unless one is able to obtain the correlation energy with an accuracy of a few tenth of a mh one has no chance to locate the minimum of  $\text{Be}_2$ .

The last example that we want to discuss is the BH molecule (Table 11). For its ground state a full CI calculation had been performed by van der Velde [57] and we could hence compare this with our various schemes in the same basis. We note that CEPA (2) and CEPA (4) are closest to "full CI" and that CP-MET misses about 2% of the "full CI" energy.

## 6. Conclusions

1. The numerical results obtained from CP-MET and from CEPA are even closer than one might have anticipated. On the whole (including a wider range of internuclear separations) the CP-MET and CEPA (3) correlation energies differ by about 1–2%. This confirms Kelly's conjecture [38] that the non-linear non-EPV terms are relatively unimportant.

That this holds both in the canonical and the localized representation (though slightly better in the localized one) is an indication that this result is not limited to molecules with well-localizable bonds. The authors have often met the prejudice that CEPA is limited to systems with localizable electrons. This is not true, since

**Table 11.** BH at  $R = 2.336$  (basis from Ref. 57), negative valence shell correlation energies in mh (canonical representation)

	this work <sup>a</sup>	<sup>b</sup>
CI-D	68.3	69.4
CEPA (5)	68.5	69.7 <sup>c</sup>
CEPA (3)	69.7	70.9
CEPA (1)	70.9	72.0
CEPA (4)	71.0	72.2 <sup>c</sup>
CEPA (2)	72.0	73.3
CEPA (0)	74.0	75.5
CP-MET	70.4	70.8 <sup>d</sup>
CC-SD	—	71.6 <sup>c</sup>
CI (full)	—	72.7

<sup>a</sup> Only doubles ( $E_{\text{SCF}} = -25.1055$  h).

<sup>b</sup> With singles and doubles from Ref. 18 ( $E_{\text{SCF}} = -25.1056$  h).

<sup>c</sup> This work corrected for contribution of singles (ca. 0.8 mh) and estimated PNO-deficiency (ca. 0.4 mh).

<sup>d</sup> Corrected for PNO-deficiency only.

one can perfectly use the canonical representation. An advantage of the localized representation is that more off-diagonal blocks vanish practically and that the computer time goes with a smaller power of the number of electrons.

2. If one limits the comparison to near-equilibrium geometries, CEPA (1) and CEPA (4) are closest to CP-MET, while CEPA (2) yields a somewhat larger (in absolute value) correlation energy. If one compares physical properties with "exact" (experimental) ones, CEPA (2) is often better than other CEPA-variants. One can understand this because the CEPA (2) energy shift, although it looks incorrect for inter-pairs, simulates in a way important triple substitutions [11, 58]. In the case of  $\text{Be}_2$  for large internuclear separation where triple substitutions play an extremely important role, they are almost exactly simulated by CEPA (2) [59].

Zirz and Ahlrichs [21] gave some evidence that the exact results are generally bracketed by CEPA (1) and CEPA (2), this even for BH where a strong dynamical correlation is present.

3. The various CEPA-variants lead to very close results if the "norm of the correlation function"  $N_c$  is small, i.e. if the correlated wave function  $\Psi$  is mainly determined by a single Slater determinant  $\Phi$  and "dynamical correlation". In this case even CEPA (0) seems to be good enough.

4. Significant differences, mainly between CEPA (0) and the other CEPA-variants occur if  $\Phi$  is near-degenerate with some other configuration, i.e. if "non-dynamical" correlation effects occur and lead to a large norm of the correlation function. This is always the case if one wants to dissociate a covalent bond. If  $N_c$  becomes too large all CEPA variants and CP-MET fail, but CEPA (2)

appears to be the best choice of all variants. In order to get reliable potential curves one ought to start from a multi-configurational reference function.

5. An essential question is: "does it pay to implement the additional CP-MET terms into a CEPA program and use them routinely?" The programming effort has been considerable but this has only to be done once and does no longer count. The overall computer time (including the integral evaluation and the SCF time), in the examples studied was roughly 130% of that of a CEPA calculations with the same basis. This again may seem not exceedingly more. Quite critical is the extra demand of peripheral storage, which is a bottleneck at our computer and limits the size of molecules to be treated. Anyway the additional effort may be regarded as tolerable and it may even be reduced if one does not base the method on the PNO expansion. However, the advantages of CP-MET in all cases studied by us have turned out to be minimal. Either both CP-MET and CEPA yield acceptable results (namely for "good" closed shell molecules) or both fail (namely if the wave function is not dominated by a single Slater determinant) and then one has to look for an improved method anyway. There may be cases (a referee suggested that molecules with delocalized  $\pi$ -systems might fall in this class) where CP-MET is really superior to CEPA, but we are doubtful about this.

One can, of course, regard CEPA as an approximation to CP-MET and conclude from this that CP-MET should be *a priori* better. But even CP-MET is not the final truth and an approximation itself and the CEPA variants can also be justified without referring to CP-MET.

We conclude that we do not see any stringent reasons to prefer CP-MET over CEPA in "normal" situations (where to be precise we choose CEPA (2)). When CEPA becomes critical one should go one step further anyway.

6. One of the most interesting questions is of course which is the practicable next step in a hierarchy of increased sophistication. Let us, to this end, first recall the drawbacks of both CP-MET and CEPA:

- These methods are non-variational, they do not provide upper bounds to the energy.
- Only double substitutions are accounted for, although the inclusion of single substitutions is no serious problem – and they often turn out to be quite important [50].
- The reference function is limited to a single configuration state usually, even to a closed-shell Slater determinant, but the generalization to arbitrary single configuration states is straightforward both on CEPA [11, 60] and CP-MET level [61].
- The calculated quantities are total energies although what one is really interested in are in many cases rather energy differences.
- The wave operator in the intermediately normalized form is not separable [62]. This is usually not recognized, because it only applies to a universal

(multistate) wave operator, not when one just wants to apply it to a ground state.

The drawbacks (a), (d) and (e) (of which only (a) is usually regarded as serious) can be overcome by using the unitary wave operator, the theory of which will be outlined in a separate paper [62].

To overcome drawback (b) one has to include triple substitutions, which has already been done in some special cases [63] and which is quite current in nuclear physics [34].

In principle drawback (c) can be avoided if one starts from a multiconfiguration reference function. One must probably find a scheme that combines all these improvements.

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