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A multi-configuration reference CEPA method based on pair natural orbitals*

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Summary. A multi-reference CI scheme is proposed which is aiming at a considerable reduction of the generally very large number of configurations of CI expansions in multi-configuration reference cases. This reduction is achieved by combining the idea of internal contraction, the concept of pair natural orbitals (PNO's) and CEPA (coupled electron pair) type approximations for the contributions of higher than double excitations. This latter estimate leads to size consistent results and also permits to employ reference wavefunctions that contain only the dominantly occupied configurations of the considered system. Applications to two test cases, the lowest states (^3P, ^1D and ^1S) of the carbon atom and the symmetry forbidden C_{2v} insertion reaction of Be and H_2, show that our method is able to truncate CI expansions to lengths of no more than 10^3–10^4 without losing more than 1–2% of the correlation energy. The calculated excitation energies and energy barriers agree with the full CI results in the respective basis within about 1 kcal/mol. Thus the MC-CEPA-PNO method presents a very efficient way to obtain "chemical accuracy" in CI-calculations for molecular systems.

Key words: Coupled electron pair approximation (CEPA) – Multi-reference configuration interaction – Pair natural orbitals (PNOs)

1 Introduction

Electron correlation can be divided into non-dynamic correlation (attributable to degeneracies, quasi-degeneracies, curve crossings etc.) and dynamic correlation. The former is generally taken care of by a multi-configuration-SCF (MCSCF) wavefunction – in most cases the Complete Active Space SCF (CASSCF) is used – with a comparatively short expansion length. If one wants to incorporate dynamic correlation effects on top of a CASSCF calculation by means of a CI-type expansion in terms of virtual SCF orbitals, the number of configurations becomes extremely large (often 10^5–10^7), in particular if one is aiming at size-consistent

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* Dedicated to Prof. Dr. W. Kutzelnigg on the occasion of his 60th birthday

** *Present address*: Institut für Physikalische Chemie, Universität Basel, Klingelbergstr. 80, CH-4056 Basel, Switzerland results and is forced to include also higher than double excitations. The progress of modern computer technology as well as the development of efficient quantum chemical program codes has made CI-calculations with expansion lengths in the order of 10^6 to 10^7 feasible, and even longer expansion lengths up to 10^9 seem possible.

In this paper we present an alternative approach. By using a) the idea of internal contraction [1, 2, 3], b) pair natural orbitals (PNO's) for all single and double excitations into the virtual space [4, 5, 2] and c) a CEPA-type approximation to the full coupled cluster equations [6, 7] (which avoids the explicit inclusion of higher than double excitations) we can truncate the CI-expansion length to no more than 10^3–10^4 configurations even for multi-configuration reference wavefunctions without losing more than about 1–2% of the total correlation energy. (We prefer to interpret the abbreviation PNO as "pair natural orbital" instead of the original term "pseudo-natural orbital" [8, 2, 6] since the latter is much less specific.)

The present approach is a generalization of the PNO-CEPA single-reference method originally proposed by Meyer [9, 6]. It is partly based on the programs of Ahlrichs et al. [10] for the closed-shell case and Staemmler and Jaquet [11] for the single-reference open-shell case. The determination of the PNO's follows closely the method given in [5], while the construction of the CI matrix elements uses a semidirect way.

A PNO expansion of multi-configuration reference CI wavefunctions has already been described by Taylor [12]. Contrary to our semidirect, internally contracted approach, Taylor presented an indirect, uncontracted method that necessitates to setup the complete CI-matrix between all configurations that have nonvanishing interaction matrix elements with any reference configuration. The advantage of our method is the reduced effort in four index transformation steps and a further decrease of the number of configurations that have to be considered, but our configurations have a more complicated structure than those in Taylor's approach.

2 Outline of the method

2.1 *Excitation operators*

We want to solve the N-electron Schrödinger equation:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \tag{1}$$

where the wavefunction Ψ describes one specific state of the molecule under consideration. We start from a multi-reference wavefunction Ψ_0 which has been obtained e.g. by a CASSCF calculation. Such a wavefunction is generally size consistent as is a RHF-wavefunction, but this is not a necessary condition for our method.

A fully correlated size consistent wavefunction can be generated from Ψ_0 by means of the exponential ansatz first proposed by Coester and Kümmel [13, 14, 15]:

$$\Psi = \exp\left(\sum_i c_i \hat{E}_i\right)\Psi_0 \tag{2}$$

$$= \left(1 + \sum_i c_i \hat{E}_i + \tfrac{1}{2}\sum_{i,j} c_i c_j \hat{E}_i \hat{E}_j + \dots\right)\Psi_0. \tag{3}$$

Generally the $\hat{E}_i$ are the excitation operators which generate singly, doubly, triply etc. excited configurations. In the following we will restrict our treatment to $\hat{E}_i$-operators describing single and double excitations.

They are constructed as follows: We start from the usual creation and annihilation operators $\eta_p^\dagger$, η_p and $\bar{\eta}_p^\dagger$, $\bar{\eta}_p$ for spin orbitals φ_p, $\bar{\varphi}_p$ and build spin-free primitive excitation operators (indicated by the lower case letter $\hat{e}$):

$$\hat{e}_{pq} = \frac{1}{\sqrt{2(1 + \delta_{pq})}}(\eta_p^\dagger \eta_q + \bar{\eta}_p^\dagger \bar{\eta}_q) \tag{4}$$

$$\hat{e}_{pq,rs} = \sqrt{\frac{1}{2(1 + \delta_{pq})} \cdot \frac{(1 + \delta_{pr})(1 + \delta_{qs})}{(1 + \delta_{pr}\delta_{qs})^2}}\,(\eta_p^\dagger \hat{e}_{rs} \eta_q + \bar{\eta}_p^\dagger \hat{e}_{rs} \bar{\eta}_q) \tag{5}$$

for single and double excitations. Instead of the $\hat{e}_{pq,rs}$ of Eq. (5) for the doubles, we generally use spin-adapted operators for singlet double excitations:

$$\hat{e}^S_{pq,rs} = \frac{1 + \delta_{pr}\delta_{qs}}{(1 + \delta_{pr})(1 + \delta_{qs})}(\hat{e}_{pq,rs} + \hat{e}_{rq,ps}), \tag{6}$$

and triplet double excitations:

$$\hat{e}^T_{pq,rs} = \frac{2}{\sqrt{6}}(\hat{e}_{pq,rs} - \hat{e}_{rq,ps}) \tag{7}$$

[7, 16].

For single-configuration closed-shell reference wavefunctions Ψ_0, only operators $\hat{e}_{pq}$ with p occupied and q virtual and $\hat{e}_{pq,rs}$ with $q \leqslant s$ occupied and p, r virtual are needed to generate all possible singly and doubly excited configurations. Furthermore, the excited configurations are orthogonal to each other and normalized, i.e.

$$\Psi_i = \hat{E}_i \Psi_0 \tag{8}$$

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \tag{9}$$

$\hat{E}_i$ and $\hat{E}_j$ being any of the operators of Eqs. (4) and (5). This means, the primitive $\hat{e}$-operators form already an orthonormal, and in particular linear independent set of excitation operators and need not be further modified.

For multi-configuration reference wavefunctions, one needs single excitations from inactive to active, inactive to virtual and active to virtual orbitals (all of them satisfying Brillouin's theorem if one starts from a CASSCF reference wavefunction Ψ_0) and double excitations of internal, semiinternal and external nature [17, 7]. The configurations generated by the application of the corresponding primitive $\hat{e}$-operators (4, 5) to Ψ_0 are generally no longer orthonormal nor linear independent. For instance, excitations from different active orbitals into the space of the virtual orbitals might lead to the same excited configuration. We generate an orthonormal set of independent excitation operators $\hat{E}_i$ (uppercase letters) satisfying Eq. (9) by a Löwdin orthogonalization of the primitive $\hat{e}$ operators, i.e. by diagonalizing the overlap matrix:

$$S_{ij} = (\hat{e}_i \Psi_0 | \hat{e}_j \Psi_0) \tag{10}$$

and discarding all linear combinations belonging to eigenvalues of S below a given threshold.

The Löwdin orthogonalization of the primitive $\hat{e}$ operators has been chosen to ensure that the final set of orthogonal $\hat{E}$ operators is independent of the more or less arbitrary order of the $\hat{e}$ operators before orthogonalization. Of course, since orbitals belonging to different subspaces (inactive, active, virtual) are already orthogonal to each other, configurations $\hat{e}_i\Psi_0$ with different numbers of electrons in these different subspaces are orthogonal, and the overlap matrix (10) consists of several rather small blocks. On the other hand, the use of pair natural orbitals and the MCCEPA or ACPF approximations for the higher excited configurations has the consequence that the final correlation energy is not completely independent of the way of orthogonalizing the primitive $\hat{e}$ operators. In particular, the size consistency of our approach is slightly violated in cases in which a molecule dissociates in two subsystems each of which contains unpaired electrons.

In the case of semiinternal double excitations, we first generate the corresponding singly excited configurations – i.e. those which are coupled to Ψ_0 by a one-electron matrix element – by the application of $\hat{e}_{pq}$. In the second step, the full set of singles and doubles is generated and Schmidt orthogonalized to the singles. By this procedure, we are able to clearly distinguish between singles and semiinternal doubles. If we start from a CASSCF reference wavefunction Ψ_0, the Brillouin conditions are satisfied and the singles do not contribute in second order to the energy. However, this is no prerequisite of our method; a multi-configuration wavefunction Ψ_0 without variationally optimized orbitals can as well be used as reference.

Our way of generating singly and doubly excited configurations corresponds exactly to the "internal contraction" used by Werner and coworkers [3, 16] and first proposed by Meyer [2] in the context of spin-adapted excitation operators. By this procedure one obtains the "direct interacting space" [1], i.e. the full set of those excited configurations coupled directly to Ψ_0 by one- or two-electron matrix elements. Just this set of configurations has also been incorporated in our previous programs for closed-shell [10] and simple open-shell [11] cases. Our experience as well as that of Werner and of many other authors for multi-reference wavefunctions has shown that this choice yields excellent results even with comparatively small CI expansion lengths.

2.2 *MCCEPA equations*

The ansatz (3) together with the orthognormality relation of Eq. (9) implies the intermediate normalization:

$$\langle \Psi_0 | \Psi \rangle = 1. \tag{11}$$

If we insert the ansatz (3) into the Schrödinger equation (1) and project with Ψ_0 we get:

$$\langle \Psi_0 | \hat{H} | \Psi \rangle = \langle \Psi_0 | E | \Psi \rangle = E \tag{12}$$

or written explicitly:

$$E = \langle \Psi_0 | \hat{H} | \left(1 + \sum_i c_i \hat{E}_i + \tfrac{1}{2} \sum_{i,j} c_i c_j \hat{E}_i \hat{E}_j + \cdots \right) \Psi_0 \rangle. \tag{13}$$

If one is allowed to neglect all terms beyond those linear in the coefficients c_i, the total energy can be written as:

$$E = \langle \Psi_0 | \hat{H} | \left(1 + \sum_i c_i \hat{E}_i\right) \Psi_0 \rangle$$

$$= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \sum_i c_i \langle \Psi_0 | \hat{H} | \hat{E}_i \Psi_0 \rangle$$

$$= E_0 + \sum_i \varepsilon_i \tag{14}$$

with

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \tag{15}$$

$$\varepsilon_i = c_i \langle \Psi_0 | \hat{H} | \hat{E}_i \Psi_0 \rangle. \tag{16}$$

In the case of a closed-shell single reference SCF wavefunction Ψ_0 the neglect of higher order terms in Eq. (13) is a good approximation since a) singly excited configurations satisfy the Brillouin theorem such that products of coefficients $c_i c_j$ are very small and b) the products of doubly excited configurations are quadruply excited and do not interact with Ψ_0. For more general reference wavefunctions Ψ_0, the neglect of the nonlinear terms in Eq. (13) is less justified, the approximation thus introduced depends on the choice of the excitation operators $\hat{E}_i$. Nevertheless, we neglect these terms as we avoid to treat higher than double excitations explicitly in our approximation.

The equations for the determination of the coefficients (or amplitudes) c_i in Eq. (3) are obtained by projecting the Schrödinger equation with the excited configuration $\Psi_i = \hat{E}_i \Psi_0$:

$$\langle \hat{E}_i \Psi_0 | \hat{H} | \Psi \rangle = \langle \hat{E}_i \Psi_0 | E | \Psi \rangle = E \langle \hat{E}_i \Psi_0 | \Psi \rangle. \tag{17}$$

Inserting the explicit form of Eq. (3) and shifting all nonlinear terms to the r.h.s. one gets:

$$\langle \hat{E}_i \Psi_0 | \hat{H} | \left(1 + \sum_j c_j \hat{E}_j\right) \Psi_0 \rangle = E \langle \hat{E}_i \Psi_0 | \left(1 + \sum_j c_j \hat{E}_j + \tfrac{1}{2} \sum_{j,k} c_j c_k \hat{E}_j \hat{E}_k + \cdots \right) \Psi_0 \rangle$$

$$- \langle \hat{E}_i \Psi_0 | \hat{H} | \left(\tfrac{1}{2} \sum_{j,k} c_j c_k \hat{E}_j \hat{E}_k + \cdots \right) \Psi_0 \rangle. \tag{18}$$

The l.h.s. contains only linear terms, i.e. those terms that are needed for a conventional SD-CI (singles and doubles CI) on top of Ψ_0. The r.h.s. contains all additional nonlinear terms.

The full solution of Eq. (18) without any approximation corresponds to the full MC-coupled cluster method and requires the inclusion of all nonlinear terms and the evaluation of the corresponding matrix elements. We construct an approximate solution with the following assumptions:

i) We first neglect all nonlinear terms in the first part of the r.h.s. of Eq. (18). This leads to:

$$E \langle \hat{E}_i \Psi_0 | \left(1 + \sum_j c_j \hat{E}_j + \tfrac{1}{2} \sum_{j,k} c_j c_k \hat{E}_j \hat{E}_k + \cdots \right) \Psi_0 \rangle$$

$$= c_i E \tag{19}$$

$$\approx c_i E_0 + c_i \sum_j c_j \langle \Psi_0 | \hat{H} | \hat{E}_j \Psi_0 \rangle$$

because of the orthogonality of Eq. (9) of the excited configurations. In the last step the approximation of Eq. (14) was used.

ii) We take only the bilinear term in the second part of the r.h.s. of Eq. (18). These terms contain many complicated matrix elements. The most important of them are those in which one of the indices j or k is equal to i [7]. If we neglect all other contributions to the double sum we get:

$$\begin{aligned}
&\langle \hat{E}_i \Psi_0 | \hat{H} | \Big(\tfrac{1}{2} \sum_{j,k} c_j c_k \hat{E}_j \hat{E}_k \Big) \Psi_0 \rangle \\
&\qquad \approx \tfrac{1}{2} \langle \hat{E}_i \Psi_0 | \hat{H} | \Big\{ c_i c_i \hat{E}_i \hat{E}_i + c_i \sum_{j(\neq i)} c_j (\hat{E}_j \hat{E}_i + \hat{E}_i \hat{E}_j) \Big\} \Psi_0 \rangle \qquad (20) \\
&\qquad = c_i \langle \hat{E}_i \Psi_0 | \hat{H} | \sum_j \frac{1}{2(1+\delta_{ij})} c_j (\hat{E}_j \hat{E}_i + \hat{E}_i \hat{E}_j) \Psi_0 \rangle . \qquad (21)
\end{aligned}$$

After these two simplifications Eq. (18) for the amplitudes c_i reads:

$$\begin{aligned}
\langle \hat{E}_i \Psi_0 | \hat{H} | \Big(1 + \sum_j c_j \hat{E}_j \Big) \Psi_0 \rangle = c_i \Big\{ E_0 + \sum_j c_j \big[\langle \Psi_0 | \hat{H} | \hat{E}_j \Psi_0 \rangle \qquad (22) \\
- \tfrac{1}{2} (1+\delta_{ij})^{-1} (\langle \hat{E}_i \Psi_0 | \hat{H} | \hat{E}_i \hat{E}_j \Psi_0 \rangle + \langle \hat{E}_i \Psi_0 | \hat{H} | \hat{E}_j \hat{E}_i \Psi_0 \rangle) \big] \Big\} .
\end{aligned}$$

Now, many terms in the square bracket on the r.h.s. of Eq. (22) cancel exactly or to a large extent and need not be calculated or may be approximated. In particular, if $\hat{E}_i$ and $\hat{E}_j$ are disjoint excitations – from different occupied orbitals into different virtual orbitals – one has:

$$\langle \Psi_0 | \hat{H} | \hat{E}_j \Psi_0 \rangle = \langle \hat{E}_i \Psi_0 | \hat{H} | \hat{E}_i \hat{E}_j \Psi_0 \rangle = \langle \hat{E}_i \Psi_0 | \hat{H} | \hat{E}_j \hat{E}_i \Psi_0 \rangle \qquad (23)$$

and the corresponding contributions in Eq. (22) vanish.

Of course, because of the Pauli principle one has:

$$| \hat{E}_i \hat{E}_i \Psi_0 \rangle = 0 \qquad (24)$$

if $\hat{E}_i$ describes a double excitation from a doubly occupied orbital. In the majority of cases, one observes:

$$| \langle \Psi_0 | \hat{H} | \hat{E}_j \Psi_0 \rangle | \geqslant | \langle \hat{E}_i \Psi_0 | \hat{H} | \hat{E}_i \hat{E}_j \Psi_0 \rangle | \qquad (25)$$

since the excitation operators $\hat{E}_i$ and $\hat{E}_j$ can contain excitations from the same occupied orbitals and/or into the same virtual orbitals which because of Eq. (24) will render the norm of $|\hat{E}_i \hat{E}_j \Psi_0\rangle$ smaller than 1. Excitations of this type occur already in the closed-shell case, but are more frequent and more complicated in MC-reference cases.

After some experimentation we found that:

$$\langle \hat{E}_i \Psi_0 | \hat{H} | \hat{E}_i \hat{E}_j \Psi_0 \rangle \approx \langle \Psi_0 | \hat{H} | \hat{E}_j \Psi_0 \rangle \langle \hat{E}_i \hat{E}_j \Psi_0 | \hat{E}_i \hat{E}_j \Psi_0 \rangle \qquad (26)$$

and

$$\langle \hat{E}_i \Psi_0 | \hat{H} | \hat{E}_j \hat{E}_i \Psi_0 \rangle \approx \langle \Psi_0 | \hat{H} | \hat{E}_j \Psi_0 \rangle \langle \hat{E}_j \hat{E}_i \Psi_0 | \hat{E}_j \hat{E}_i \Psi_0 \rangle \qquad (27)$$

are the best approximations to the matrix elements which are needed in addition to those already calculated for the SD-CI (l.h.s. of Eq. (18)). Equations (26) and (27) are obvious consistent with the inequality of Eq. (25) and contain Eqs. (23) and (24) as special cases. For the closed-shell case it is easy to verify that Eqs. (26) and (27) are correct for all double excitations but become approximations as soon as single excitations are included. Since in Eqs. (26) and (27) only normalization integrals have to be calculated the additional effort beyond that already necessary for the SD-CI is very small.

Using Eqs. (26) and (27) we obtain our final equation for the MCCEPA amplitudes c_i:

$$\langle \hat{E}_i\Psi_0|\hat{H}|\left(1+\sum_j c_j\hat{E}_j\right)\Psi_0\rangle = c_i\left[E_0+\sum_j \varepsilon_j d_{ij}\right] \tag{28}$$

with

$$d_{ij} = 1-\tfrac{1}{2}(1+\delta_{ij})^{-1}(\langle \hat{E}_i\hat{E}_j\Psi_0|\hat{E}_i\hat{E}_j\Psi_0\rangle + \langle \hat{E}_j\hat{E}_i\Psi_0|\hat{E}_j\hat{E}_i\Psi_0\rangle) \tag{29}$$

where apparently the "CEPA corrections" d_{ij} do not depend on the amplitudes c_i.

The MCCEPA coefficients d_{ij} may become negative as the norm of $\hat{E}_i\hat{E}_j\Psi_0$ can become greater than one if $\hat{E}_j$ describes an excitation in partially filled orbitals and $\hat{E}_i$ an excitation out of these orbitals. As these negative coefficients spoil the convergence of the CI-iterations and as these coefficients are approximate anyway we set them to zero in this case.

Of course, the MCCEPA Eqs. (28) and (29) constitute only an approximation to the full multi-reference coupled cluster equations, the effect of the different approximations (e.g. Eqs. (25), (26) and (27)) cannot be easily estimated. They are essentially the same as those used in single-reference CEPA schemes and their accuracy can only be judged in comparison with SD-CI and full CI calculations.

2.3 Size consistency and connection with other CEPA variants

Several different approximate coupled cluster schemes have been proposed in the literature for the closed-shell (for reviews see [7, 18]) or simple open-shell cases [9, 11], but in recent years also for multi-reference cases [19, 20, 21, 22]. In all of them it is tried to simplify the full coupled cluster equations (18) using approximations that do not violate the size-consistency.

The conventional CI with singles and doubles on top of the MC reference (SD-CI) is obtained if one truncates the ansatz (3) after the linear terms. In this case, the r.h.s. of Eqs. (18), (22) and (28) simply read c_iE, E being the total energy, and the cancellation between the two terms on the r.h.s. of Eq. (18) cannot occur since the second term containing the bilinear contributions has not been included at all. The SD-CI wavefunction is not size consistent, neither in the single-reference nor in the multi-reference case.

The simplest approximation to the full coupled cluster equation is the one called CEPA-0 [18, 23] or linearized Coupled Cluster approximation (LCCA) [24]. One starts from Eq. (22), allows for all cancellations derived from Eq. (23) in order to preserve the size consistency and neglects all further matrix elements on the r.h.s. of Eq. (22) which survive. This leads to Eq. (28) with:

$$d_{ij} = 0. \tag{30}$$

The CEPA-0 scheme is certainly size consistent, but generally overestimates correlation energies, since too many coupling elements are neglected.

The CEPA-2 approximation originally proposed by Meyer [6] and applied in our single-reference CEPA program [10, 11] is also a special case of Eq. (28) if one chooses:

$$d_{ij} = \delta_{ij}, \tag{31}$$

where i and j refer now to pairs, i.e. to the sum of all excitations from a given pair of occupied orbitals into the virtual space. This recipe could not be generalized to the multi-reference case since the definition and identification of electron pairs is hardly possible in multi-reference cases, in particular not for excitations from the active space.

Our cluster correction of Eq. (29) is closely related to the formulae proposed by Kelly and Sessler [25, 26], for a single-determinant closed-shell reference wavefunction the two approximations are identical.

The most widely used cluster correction for multi-reference wavefunctions is the pragmatic ACPF approach of Gdanitz and Ahlrichs [23]. This uses an energy functional:

$$F_c = \frac{\langle (1 + \sum_i c_i \hat{E}_i)\Psi_0 | \hat{H} - E_0 | (1 + \sum_i c_i \hat{E}_i)\Psi_0 \rangle}{1 + \sum_i^a c_i^2 + \frac{2}{n_{el}} \sum_i^e c_i^2} \tag{32}$$

where the sum Σ_i^a contains all internal excitations, i.e. those with the same occupation of the orbitals outside the active space, and Σ_i^e contains all remaining excitations. It is well known that this approach is nearly size consistent and yields correlation energies which are rather close to the full CI results.

To enable comparisons of different correlation methods, we included the (PNO-)CI, ACPF and CEPA-0 variants in our MCCEPA program. A comprehensive presentation of the results of these methods is given in the third section of this article.

2.4 Computational details

For all external and semiinternal excitations pair natural orbitals (PNO's) [2] have been used in order to reduce the CI expansion length. The most dramatic reduction is achieved by a truncation of the PNO expansion for each individual pair after a given threshold, for instance 10^{-7} H. In particular, the expansion lengths for weakly occupied pairs, those with small coefficients in the reference wavefunction, are very short.

The calculation of the off-diagonal CI matrix elements follows a semidirect strategy: The rather complicated matrix elements between configurations belonging to different pairs – i.e. excitations $\hat{E}_i$ and $\hat{E}_j$ from different pairs of occupied orbitals – which involve non-orthogonal PNO's are performed once and stored on peripheral storage after the determination of the PNO's and before the CI iterations. Since the total number of configurations is comparatively small (10^3–10^4) the storage of the CI matrix requires generally no more peripheral storage than the two-electron integrals. The matrix elements between external configurations belonging to the same pair which need two-electron integrals with four external indices are constructed directly as proposed by Ahlrichs and Driessler [5] and Meyer and coworkers [27, 28]: Instead of calculating and storing the necessary

K-operators over PNO's φ_a before the CI iterations they are recalculated in each iteration n for the total density from the original atomic integrals. This can be written schematically as:

$$\sum_a c_a^{(n)} K_a = \sum_a c_a^{(n)} K(D_a) = K\left(\sum_a c_a^{(n)} D_a\right), \tag{33}$$

where D denotes the density for which K is evaluated. Similarly also non-diagonal matrix elements that include three external indices can be evaluated as shown e.g. in [3]. In order to accelerate the convergence behaviour of the CI iterations Pulay's DIIS method [29, 30] is applied.

Since the determination of the PNO's is a rather fast step, the most time-consuming parts of the whole program are a) the calculation of the parts of the CI-matrix with up to two external indices which is approximately proportional to $N^3 \cdot N_c^3 \cdot N_{CSF}^2$ but has to be performed only once and b) the calculation of the CI-matrix parts with 3 and 4 external indices which goes as $N^4 \cdot N_c^2$ and has to be performed in every iteration (N being the number of functions, N_c the number of occupied orbitals to be correlated and N_{CSF} the number of configurations in the reference). The factor in front of $N^3 \cdot N_c^3 \cdot N_{CSF}^2$ depends also on the ratio of the average number of PNO's per pair (N_{PNO}^{av}) and N. Of course the time necessary for the evaluation of the off-diagonal CI-blocks increases rapidly with the number of the configurations in the reference; however it turned out that one can neglect configurations with coefficients smaller than about 0.05–0.08 from the reference without loosing a significant amount of accuracy. In this way, N_{CSF} can be kept very small in most cases.

As an alternative to the direct calculation of the CI-matrix parts with 3 and 4 external indices in every iteration, they could be calculated once and processed like the rest of the CI-matrix as has been done in most prior applications of PNO's [6, 10, 2, 11, 12]. However, this needs $N_{PNO}^{av} \cdot N^4 \cdot N_c^2$ computational steps and is thus preferable only if N_{PNO}^{av} is smaller than the number of CI iterations. Typically for small molecules with $N \approx 100$ we need less than 10 iterations to reach converged energies, whereas N_{PNO}^{av} uses to be 20–30. Nevertheless, a construction and diagonalization of the full CI matrix can be advisable for excited states in order to guarantee the orthogonality to lower states of the same symmetry. Similar arguments apply to extended systems where many double excitations (those from remote orbitals) can be described with only a few PNO's. For such cases it is most efficient to use a hybrid of the two alternatives by constructing all CI-matrix elements for double excitations with few PNO's and using the semidirect method for the others.

3 Results of test calculations

We have checked the accuracy of our MCCEPA-method by performing test calculations that span the typical domain of MR-CI applications: Accurate calculation of excitation energies and the proper description of potential energy surfaces in regions where bond breaking and/or bond forming occurs. We have chosen one example of each of these applications: The three lowest electronic states (^3P, ^1D and ^1S) of the carbon atom and the C_{2v} insertion reaction of Be and H_2 [19].

Since the two main approximations in our method are the CEPA-type treatment of the unlinked cluster contributions and the use of PNO's, the aim of the

Table 1. Full CI energy (in H) and deviations from it (in mH) for the lowest states of C. The energies of ACPF, MCCEPA and CEPA-0 have been corrected for PNO errors

State[a]	Basis	CASSCF[b]	PNO-error	SD-CI[c]	ACPF	MCCEPA	CEPA-0	Full CI
^3P small	DZ1D	78.346	0.091	1.643	− 0.170	1.039	− 2.194	− 37.731406
	TZ1D	83.392	0.218	1.996	− 0.054	1.322	− 2.359	− 37.768608
	TZ2D1F	94.226	0.870	2.750	0.305	1.905	− 2.473	− 37.779461
	QZ1D	84.646	0.281	2.077	− 0.029	1.373	− 2.401	− 37.772751
	QZ2D1F	95.445	0.932	2.812	0.310	1.936	− 2.535	− 37.783570
	QZ3D2F1G	98.123	1.124	3.008	0.431	2.101	− 2.505	− 37.786266
^3P big	DZ1D	60.166	0.131	0.368	− 0.484	− 0.194	− 1.393	− 37.731406
	TZ1D	64.243	0.245	0.676	− 0.305	0.055	− 1.358	− 37.768608
	TZ2D1F	75.095	0.932	0.967	− 0.321	0.093	− 1.719	− 37.779461
	QZ1D	65.402	0.297	0.745	− 0.279	0.084	− 1.380	− 37.772751
	QZ2D1F	76.220	0.995	1.018	− 0.313	0.102	− 1.761	− 37.783570
	QZ3D2F1G	78.902	1.161	1.115	− 0.273	0.167	− 1.788	− 37.786266
^1D small	DZ1D	81.473	0.127	2.095	0.240	1.296	− 1.830	− 37.675517
	TZ1D	87.205	0.246	2.586	0.415	1.655	− 2.032	− 37.715016
	TZ2D1F	100.363	0.923	3.397	0.775	2.212	− 2.208	− 37.730473
	QZ1D	88.479	0.315	2.673	0.449	1.713	− 2.062	− 37.719288
	QZ2D1F	101.647	0.995	3.529	0.860	2.320	− 2.180	− 37.734741
	QZ3D2F1G	105.389	1.260	3.751	0.981	2.483	− 2.179	− 37.738943
^1D big	DZ1D	63.202	0.197	0.332	− 0.565	− 0.214	− 1.520	− 37.675517
	TZ1D	67.875	0.306	0.751	− 0.334	0.138	− 1.501	− 37.715016
	TZ2D1F	81.080	0.971	1.081	− 0.381	0.240	− 1.973	− 37.730473
	QZ1D	69.032	0.369	0.822	− 0.302	0.191	− 1.513	− 37.719288
	QZ2D1F	82.248	1.040	1.205	− 0.292	0.349	− 1.924	− 37.734741
	QZ3D2F1G	85.994	1.316	1.315	− 0.266	0.415	− 1.995	− 37.738943

^1S small	DZ1D	113.154	2.456	0.420	− 0.701	− 2.706	− 11.130	− 37.619946
	TZ1D	119.553	2.719	1.188	− 0.495	− 2.236	− 11.662	− 37.664909
	TZ2D1F	132.406	3.721	1.512	− 0.538	− 2.377	− 12.668	− 37.677762
	QZ1D	121.073	2.984	1.350	− 0.469	− 2.149	− 11.754	− 37.670071
	QZ2D1F	133.740	3.965	1.656	− 0.525	− 2.279	− 12.747	− 37.682738
	QZ3D2F1G	137.873	4.841	1.772	− 0.462	− 2.169	− 12.647	− 37.686871
^1S big	DZ1D	49.084	0.135	0.179	− 0.320	− 0.069	− 0.840	− 37.619946
	TZ1D	58.275	0.470	0.888	0.087	0.394	− 0.769	− 37.664909
	TZ2D1F	71.128	0.477	1.131	0.056	0.528	− 1.106	− 37.677762
	QZ1D	60.275	0.633	1.036	0.163	0.489	− 0.778	− 37.670071
	QZ2D1F	72.942	0.615	1.261	0.116	0.606	− 1.130	− 37.682738
	QZ3D2F1G	77.075	0.666	1.353	0.133	0.675	− 1.200	− 37.686871

[a] Small ($1s^22s^22p^2$) and big ($1s^22s^22p^2 + 1s^22p^4$) reference

[b] This is the correlation energy of the respective reference

[c] Conventional SD-CI using virtual orbitals instead of PNO's

present test calculations is to check how large the corresponding errors in the total correlation energy are and how they depend on the size of the basis set and the choice of the reference wavefunction Ψ_0.

The quality of the MCCEPA approximation was tested by comparison with full CI in the same basis set. PNO-CI (i.e. SD-CI using PNO's instead of virtual orbitals), ACPF and CEPA-0 calculations were performed, and for some states also single-reference CEPA-2 calculations [11], but the latter results are not documented here. This comparison yields an idea of how much of the correlation energy which is missing after SD-CI is covered by the different approximations to full CI.

The effect of using PNO's is tested by performing conventional SD-CI calculations (with virtual orbitals) and comparing these results with our PNO-CI energies. As the amount of correlation energy that is lost due to the PNO expansion is only in the magnitude of a few percent we assume that it does not change very much when another correlation method instead of SD-CI is employed. Therefore we corrected for the PNO errors of the MCCEPA, ACPF and CEPA-0 method by adding the PNO-CI errors to the corresponding energies.

3.1 The ^3P, ^1D and ^1S states of the carbon atom

We have chosen this example for our first test calculations as it allows a rigorous treatment with rather large basis sets even at the full CI level. On the other hand, we can as well compare the calculated excitation energies directly with experiment in order to check whether chemical accuracy ($\approx$ 1 kcal/mol) can be reached. Thus this system can serve both as a model system and a real system.

The three lowest states of C show several typical features which are often encountered in the treatment of excited states: States of different spin multiplicity or of different electronic structure (closed shell versus open shell) have to be treated with the same accuracy. The near degeneracy of the 2*s* and 2*p* orbitals might require different reference wavefunctions for different states. The energies of the states might be affected differently by the improvement of the basis set.

The three states of C considered here can be described in first order starting from a $1s^2 2s^2 2p^2$ reference configuration. Due to the 2*s*, 2*p* near degeneracy the $1s^2 2p^4$ configuration is expected to have a rather small excitation energy and it might be necessary to include it into the reference wavefunction. Therefore, our calculations for the three states have been performed both starting from the $1s^2 2s^2 2p^2$ configuration (small reference) and $1s^2 2s^2 2p^2 + 1s^2 2p^4$ (big reference). In all calculations the reference wavefunctions Ψ_0 were CASSCF wavefunctions for the respective state.

We used cartesian Gaussian basis functions with exponents taken from Huzinaga's tables [31]. We took the 7*s*3*p*, 9*s*5*p* and 11*s*7*p* basis sets contracted to 4*s*2*p*, 6*s*3*p* and 8*s*4*p*, respectively. These basis sets will be denoted by DZ, TZ and QZ. The exponents of the polarization functions were taken from Dunning [32]. Only pure *d*, *f* and *g* components of the corresponding polarization functions were included in the basis set.

Table 1 shows the calculated correlation energies of the different states compared to full CI energies. In all cases the deviations of the different methods from full CI decrease when the reference wavefunction is enlarged from the small to the big reference space. This is especially true for the ^1S state where the $1s^22p^4$ configuration has a weight of about 8% in the reference wavefunction and is responsible for about 63 mH of the correlation energy which is approximately half of the correlation energy of this state with the small reference. For the ^1D and ^3P states these weights amount to only about 2% and 19 mH which is about 20% of the corresponding small reference correlation energy. Obviously the small reference is no more acceptable for the ^1S state whereas it is a reasonable choice for the two other states. This is reflected by the PNO-errors and also by the deviations of the MCCEPA and CEPA-0 methods from full CI.

The calculated energies (Table 1) show the typical behaviour of the different correlation approximations. SD-CI consistently yields too low correlation energies since higher excitations are completely missing. CEPA-0 overestimates the correlation energy by about the same amount by which CI underestimates it as long as reasonable reference functions are chosen. Whenever the reference function is too small (small reference for ^1S) CEPA-0 yields unreliable low energies.

The ACPF and MCCEPA energies are much closer to the full CI results. Whereas ACPF has a tendency to overestimate the cluster corrections MCCEPA generally underestimates them. In most cases ACPF seems to be in slightly better agreement with full CI than MCCEPA. This is especially true for the ^1S state with the small reference wavefunction. But this might be an artifact due to the large PNO error in this case. We have also performed some calculations with the old CEPA-2 version for comparisons, the results were in between MCCEPA and CEPA-0, also overestimating the cluster corrections.

The PNO errors are generally below 1 mH, i.e. between 0.5 and 1.5% of the respective correlation energies. Table 1 shows that they increase with increasing basis set, but are very similar for the three states. The only exception is the ^1S state with the small reference, where the PNO errors are as large as 3–5%. (It should be noted that we have slightly overestimated the PNO errors since the configuration space in the CI program is slightly larger than that in our current MCCEPA program that was used for calculating the PNO-CI energies.) We can conclude that the loss in energy due to the use of PNO's is in the order of 1% [5] provided that the reference function is chosen reasonably.

In Table 2 we present the calculated term energies for the ^1D and ^1S states of the C-atom. Obviously the deviations from the full CI results are quite large and unsystematic for the CASSCF reference wavefunction, but considerably improved for all four methods of including correlation effects. There seems to be no substantial difference in the accuracy between the four methods, but the MCCEPA results show the most consistent behaviour. Again, the ^1S state is quite poorly described with the small reference. Since the PNO errors are similar for these states, they cancel to a large extent for the energy differences.

For all basis sets except for the largest one (QZ3D2F1G) the errors in our approximations (MCCEPA, PNO's) are considerably smaller than the errors due to the limited basis. That means that for MCCEPA-PNO calculations on medium-sized molecular systems with typical basis sets of say TZ2D1F quality the atomic basis is still the source of the largest errors in a MCCEPA treatment. On the other hand, if we reach "chemical accuracy" of 1 kcal/mol $\approx$ 350 cm^{-1} with our largest basis set, about half of this error has to be attributed to the MCCEPA and PNO approximations.

Table 2. Calculated term energies for the ^1D and ^1S states of C, in cm^{-1}, for full CI and deviations from the full CI result for the other methods. (ACPF, MCCEPA and CEPA-0 values are corrected for the PNO error)

States	Basis	CASSCF	PNO-error	SD-CI	ACPF	MCCEPA	CEPA-0	Full CI
^3P–^1D small	DZ1D	686.2	7.9	99.2	90.0	56.4	79.9	12266.2
	TZ1D	836.9	6.2	129.5	103.0	73.1	71.6	11762.1
	TZ2D1F	1347.0	11.5	142.0	103.2	67.4	58.0	10751.6
	QZ1D	841.4	7.6	130.8	105.1	74.5	74.3	11733.8
	QZ2D1F	1361.2	13.9	157.4	120.7	84.3	77.8	10716.7
	QZ3D2F1G	1594.7	29.8	163.1	120.7	83.9	71.4	10386.2
^3P–^1D big	DZ1D	666.2	14.5	– 7.9	– 17.8	– 4.3	– 27.9	12266.2
	TZ1D	797.1	13.5	16.5	– 6.3	18.2	– 31.4	11762.1
	TZ2D1F	1313.5	8.5	25.0	– 13.2	32.3	– 55.7	10751.6
	QZ1D	796.6	15.8	16.9	– 5.0	23.4	– 29.2	11733.8
	QZ2D1F	1323.0	9.9	41.0	4.7	54.2	– 35.7	10716.7
	QZ3D2F1G	1556.6	34.0	43.9	1.6	54.5	– 45.6	10386.2
	exp.[a]							10164.
^3P–^1S small	DZ1D	7639.5	519.0	– 268.4	– 116.5	– 821.9	– 1961.2	24462.6
	TZ1D	7936.4	548.9	– 177.3	– 96.8	– 780.8	– 2041.7	22759.3
	TZ2D1F	8379.6	625.7	– 271.7	– 185.0	– 939.7	– 2237.6	22320.4
	QZ1D	7994.8	593.2	– 159.6	– 96.6	– 773.0	– 2052.9	22535.7
	QZ2D1F	8404.6	665.7	– 253.7	– 183.3	– 925.1	– 2241.3	22130.1
	QZ3D2F1G	8724.0	815.8	– 271.3	– 196.2	– 937.2	– 2226.0	21814.7
^3P–^1S big	DZ1D	– 2432.3	0.8	– 41.5	36.1	27.5	121.3	24462.6
	TZ1D	– 1310.0	49.5	46.5	86.1	74.4	129.2	22759.3
	TZ2D1F	– 870.8	– 100.0	36.0	82.6	95.6	134.6	22320.4
	QZ1D	– 1125.4	73.7	63.9	97.0	88.9	132.2	22535.7
	QZ2D1F	– 719.5	– 83.4	53.3	94.2	110.6	138.7	22130.1
	QZ3D2F1G	– 401.0	– 108.6	52.2	89.1	111.5	128.9	21814.7
	exp.[a]							21618.

[a] Ref. [42].

3.2 Be + H_2 reaction

The C_{2v} reaction of Be and H_2 has been introduced by Purvis and Bartlett [33] and used by many other authors [19, 20, 21, 23] as a benchmark test for multi-configuration correlation methods. It represents the simplest prototype of a symmetry forbidden insertion reaction; the dominant electronic configuration being $2a_1^2 3a_1^2$ for the reactants Be + H_2 and $2a_1^2 1b_1^2$ for the product BeH_2.

Our test calculations have been performed with a reference wavefunction Ψ_0 containing just these two configurations and the same basis set as employed by Purvis and Bartlett [33]. In addition to the three geometries (G1, G2 and G3) in the vicinity of the transition state that were proposed in the literature we also considered two reasonable geometries for the reactants Be + H_2 and the product (linear symmetric BeH_2).

Table 3 shows that the behaviour of the different correlation methods follows more or less the same pattern as for the lowest states of the C-atom: SCF and CASSCF have rather large errors and considerably overestimate the barrier. SD-CI does not include enough correlation while CEPA-0 overestimates it, thus SD-CI yields a still too high barrier and CEPA-0 a too low barrier (compared to full CI). Again the ACPF and MCCEPA results are rather close to full CI with MCCEPA slightly more consistent than ACPF. The PNO error amounts to 1–2% of the total correlation energy, this comparatively large error can be further

Table 3. Be + H_2 C_{2v} insertion: Full CI results and deviations from it

	Products	G1	G2	G3	Reactants
r_{Be-H_2}	0.00	2.50	2.75	3.00	100.00[a]
r_{H-H}	5.10	2.78	2.55	2.32	1.40[a]
SCF	37.26	59.88	81.29	88.28	64.99[b]
CASSCF	36.97	53.00	63.95	66.44	49.97
Full CI	− 15.779044	− 15.622599	− 15.602591	− 15.624731	− 15.762848
SD-CI	0.56	0.79	1.90	3.01	1.58
MCCEPA	0.29	0.20	0.15	0.54	− 0.02
ACPF	0.11	− 0.59	− 0.56	− 0.03	− 0.00
CEPA-0	− 0.51	− 2.45	5.78[c]	− 4.47	− 1.91
PNO-error	− 0.21	− 1.35	− 1.23	− 0.96	− 0.05
SCF		60.20	80.23	88.49[d]	
MCSCF		53.31	64.35	66.68[d]	
MRSDCI		0.78	1.91	3.05[d]	
MRCEPA		− 1.68	− 2.55	− 5.88[d]	
MRACPF		− 0.90	− 0.90	− 0.53[e]	
MRLCCM		− 2.62	− 2.40	− 5.50[f]	

[a] In a.u.

[b] This work. Energy difference to full CI in mH. The energies differ slightly from those given in the literature [33] since in our calculations Gaussian lobe functions have been employed instead of cartesian Gaussians.

[c] Saddle point with respect to variation of Ψ compare to Ref. [23] (Table 1, footnote[c]).

[d] Ref. [20]

[e] Ref. [23]

[f] Ref. [19]

reduced if a larger reference wavefunction is used. The results of other authors, which are included for comparison confirm our observations. It should be noted that both the MRLCCM method of Laidig and Bartlett [19] and the MRCEPA method of Ruttink et al. [20] correspond to the CEPA-0 approximation.

4 Conclusions

The test calculations presented in the previous section show that our MC-CEPA-PNO method is a simple and efficient way to achieve chemical accuracy in multi-reference CI calculations for molecular systems. We obtained similar results for several larger systems that have been investigated recently, e.g. excited states of N_2^{2+} [34], F^{3+} [35], O_2^+ [36] and NiO_6^{10-} [37], potential energy surfaces for the reaction of NO with a Ni-cluster [38], of FNO [39] and BrHO [40] and magnetic properties of oxygen-bridged transition-metal complexes [41]. The main reasons are:

i) The MCCEPA and the ACPF estimates of the cluster corrections lead to energies which are very close to the full CI limits and in all cases much superior to the MC-SD-CI results (underestimating the true correlation energy) and CEPA-0 results (overestimating it). The additional numerical effort (i.e. beyond MC-SD-CI) for obtaining these estimates are small (MCCEPA) or even negligible (ACPF). Furthermore, the MCCEPA and ACPF results are quite reliable even for a comparatively small reference wavefunction.

ii) The use of pair natural orbitals reduces the CI expansion length. The corresponding loss in correlation energy amounts to about 1%, depending on the size of the reference space and the basis set.

iii) The semidirect way of constructing off-diagonal CI matrix elements and the short CI expansion length enable the use of the MC-CEPA-PNO program on small workstations even for rather large basis sets (150–200 basis functions). A small version of the program can already be used on a MICRO-VAX or PC.

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