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**Citation for published version (APA):**

Ruttink, P. J. A., Lenthe, van, J. H., Zwaans, R., & Groenenboom, G. C. (1991). Size consistent multireference single and double excitation configuration interaction calculations. The multireference coupled electron-pair approximation. *Journal of Chemical Physics*, 94(11), 7212-7220. <https://doi.org/10.1063/1.460204>

**DOI:**

[10.1063/1.460204](https://doi.org/10.1063/1.460204)

**Document status and date:**

Published: 01/01/1991

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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# Size consistent multireference single and double excitation configuration interaction calculations. The multireference coupled electron-pair approximation

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(Received 21 November 1990; accepted 22 February 1991)

A new size consistent extension to the multi reference configuration interaction method is described. The method termed multireference coupled electron pair approximation (MRCEPA) is akin to a multireference CEPA(0) approach, though nonlinear terms do receive separate attention. We show the performance of the approach in some model systems as well as in an application to calculation of ground and excited  $\pi\pi^*$  states of ethylene.

## I. INTRODUCTION

The coupled electron pair approximation (CEPA) method has the advantage over the method for configuration interaction with all single and double replacements (SDCI) that it yields size consistent results with only a slight increase in computational effort. Here, size consistency means that the energy of two subsystems is additive if the subsystems do not interact. It may be successfully applied to both closed<sup>1</sup> and open<sup>2</sup> shell systems, provided that a single configuration state function (CSF), e.g., the restricted Hartree-Fock determinant, is dominant in the correlated wave function. However, if there are low lying excitations (in case of multi-bond dissociation, open shell systems with high symmetry), more than one CSF is needed for a proper zeroth order description of the wave function.<sup>3,4</sup>

Fairly accurate results may be obtained using the multireference single double configuration interaction (MRSDCI) method. However, since any restricted CI calculation suffers from size consistency defects, an extension of the CEPA method to multiconfiguration (MC) reference sets is called for. In the following, a method is proposed, which includes size consistency corrections in MRSDCI calculations in a manner analogous to the CEPA(0) method, provided that the reference configuration set is complete in the active orbital space. Thus, our starting wave function is a second order CI function and the resulting function will accordingly be called the second order CEPA function.

In practice, our method amounts to shifting the diagonal  $H$ -matrix elements of the single and double excitations, as in the CI-type implementation of the CEPA method.<sup>5</sup> However, our method differs from the straightforward generalization of the CEPA(0) method to MC reference sets, which should be identical to the linearized version of the MC reference coupled cluster (CC) development.<sup>6-12</sup> Since the nonlinear terms in our modified MRSDCI equations are potentially important, they should receive proper attention when formulating size consistency corrections for wave functions based on a MC reference configuration set.

The results obtained by this method will be compared to results of the averaged coupled pair functional (ACPF) theory, as introduced recently by Gdanitz and Ahlrichs<sup>13</sup> and which may also be considered as a generalization of the CEPA (or CPF) philosophy to MC reference configuration sets.

In Sec. II, the method used for modifying the MRSDCI equations will be discussed. Applications to some model systems, including comparison with full CI and MRACPF<sup>13</sup> results, are reported in Sec. III and the method is applied to the calculation of ground and excited states of ethylene in Sec. IV. Finally, conclusions are drawn in Sec. V.

## II. THEORY

In this section the size consistency corrections for second order wave functions will be discussed in terms of the spin orbital formalism. Our reasoning is analogous to the derivation of the coupled pair approximation (CPA) equations by Hurley.<sup>14</sup>

### A. Wave functions

The second order wave function to be used is designated by

$$|\Psi_C\rangle = \sum_R c_R |R\rangle + \sum_I c_I |A_I\rangle, \quad (1)$$

where the reference configuration set  $\{|R\rangle\}$  is assumed to be complete within some (small) orbital subset (the active spin orbitals) and the set  $\{|A_I\rangle\}$  contains all single and double excitations with respect to any  $|R\rangle$ .

The size consistency corrections to be applied to the CI secular equations for this function will be calculated in the form of diagonal  $H$ -matrix element shifts. These shifts are calculated by assuming that the second order CEPA function may be approximated by the corresponding MC reference coupled cluster function<sup>6-8</sup> with internal contraction:<sup>15</sup>

$$|\Psi_{CC}\rangle = \exp(T)|0\rangle, \quad (2)$$

where the reference function  $|0\rangle$  is given by

$$|0\rangle = \sum_R c_R |R\rangle / \sqrt{\sum_R c_R^2}, \quad (3)$$

with the same coefficients  $c_R$  as in Eq. (1).  $T$  generates all single and double excitations with respect to any  $|R\rangle$ ,

$$T = \sum_{\mu} \sum_{\rho} t_{\mu\rho} \tau_{\mu\rho} + \sum_{\mu} \sum_{\nu} \sum_{\rho} \sum_{\sigma} t_{\mu\nu,\rho\sigma} \tau_{\mu\nu-\rho\sigma}, \quad (4)$$

where  $\tau$  is an excitation operator,  $t$  is the corresponding connected cluster amplitude,  $\mu$  and  $\nu$  are inactive or active spin orbital indices, and  $\rho$  and  $\sigma$  are active or external spin orbital indices. According to Eq. (3), the reference function  $|0\rangle$  is normalized. The excitation operators are defined such that they yield normalized excited functions  $\tau|0\rangle$ , i.e., we assume

$$\langle 0 | \tau^\dagger \tau | 0 \rangle = 1. \quad (5)$$

We do not need the explicit form of  $T$ , as given by Eq. (4). Instead, we define excitation classes as follows; The excitation class  $(k, \ell)$  contains all excitations with  $k$  holes in the inactive orbitals and  $\ell$  particles in the external orbitals. Since the number of electrons in the active orbitals is not fixed,  $k$  and  $\ell$  may differ from each other. Eq. (4) is thus equivalent to

$$T = \sum_k \sum_{\ell} T(k, \ell) \quad 0 \leq k, \ell \leq 2, \text{ except } k = \ell = 0. \quad (6)$$

We also use the corresponding projection operators  $P(k, \ell)$  and the projection operators  $P_0$ ,  $P_a$ , and  $P_b$  defined by:

$$P_0 = P(0, 0),$$

$$P_a = \sum_k \sum_{\ell} P(k, \ell),$$

$$0 \leq k, \ell \leq 2, \text{ except } k = \ell = 0$$

$$P_b = \sum_k \sum_{\ell} P(k, \ell),$$

$$k > 2 \text{ or } \ell > 2. \quad (7)$$

Thus,  $P_0$  projects to the reference configuration space,  $P_a$  projects to the interacting space of the reference configurations spanned by the set  $\{|A_i\rangle\}$  and  $P_b$  projects to the space spanned by all higher excitations. In practice,  $P_b$  may be considered to project to the interacting space of the set  $\{|A_i\rangle\}$ .

In the following, we assume that the second order CEPA function may be written as

$$|\Psi_C\rangle = (P_0 + P_a)|\Psi_{CC}\rangle = [1 + P_a \exp(T)]|0\rangle \quad (8)$$

This function will be used for calculating the size consistency corrections to be applied to the second order SDCI function in order to obtain the second order CEPA function.

## B. The diagonal $H$ -matrix element shift

The coupled cluster function is assumed to satisfy the following equations

$$\langle 0 | (H - E) \exp(T) | 0 \rangle = 0, \quad (9)$$

$$\langle 0 | \tau^\dagger (H - E) \exp(T) | 0 \rangle = 0 \text{ for each } \tau. \quad (10)$$

Since the higher excitations in  $\Psi_{CC}$  (viz. that part of  $\Psi_{CC}$

which is given by  $P_b \Psi_{CC}$ ) do not interact with any reference configuration  $|R\rangle$ , Eq. (9) is identical to the first secular equation for the corresponding CI problem:

$$E = \langle 0 | H | 0 \rangle + \langle 0 | HT | 0 \rangle = E_0 + E_{\text{corr}}. \quad (11)$$

Using Eqs. (2), (7), and (8), Eq. (10) may be rewritten as

$$\langle 0 | \tau^\dagger (H - E) | \Psi_C \rangle + \langle 0 | \tau^\dagger H P_b \exp(T) | 0 \rangle = 0. \quad (12)$$

The second term in Eq. (12), which is missing in the secular equations for the SDCI function, will be used to obtain the size-consistency corrections wanted. To this end we note that Eq. (12) may be rewritten as:

$$\langle 0 | \tau^\dagger (H + \Delta H_\tau - E) | \Psi_C \rangle = 0, \quad (13)$$

provided that the diagonal shift  $\Delta H_\tau$  is given by

$$\Delta H_\tau = \langle 0 | \tau^\dagger H P_b \exp(T) | 0 \rangle / \langle 0 | \tau^\dagger | \Psi_C \rangle. \quad (14)$$

In the following, Eqs. (13) and (14) will be taken as the set of equations to be satisfied by the second order CEPA function  $\Psi_C$ . These equations lead to a pseudo eigenvalue problem since the shifts  $\Delta H_\tau$  depend on the connected cluster amplitudes in  $T$ , or, equivalently, on the configuration coefficients  $c_i$  in  $\Psi_C$ .

Note that the coefficients  $c_i$  in Eq. (1) are not identical to the connected cluster amplitudes  $t$  in Eq. (4) since the  $c_i$  will contain contributions from disconnected clusters.<sup>16,17</sup>

In the following, Eq. (14) is simplified using two approximations which are analogous to the approximations used in the CEPA(0) method.

## C. The direct term approximation

This approximation was introduced by Kelly and Sessler<sup>18</sup> and Kelly.<sup>19</sup> In our formalism it takes the following form. In the expansion of  $\exp(T)|0\rangle$  in Eq. (14), only those terms are retained which contain  $\tau$ . The selection of terms thus depends on the excitation  $\tau$  for which the shift is being calculated. In order to determine which terms in  $\exp(T)|0\rangle$  contain the excitation  $\tau|0\rangle$  and also which terms belong to the interacting space of  $\tau|0\rangle$ , we divide the excitation operators in  $T$  in two groups. The first group  $T_\tau$  contains  $\tau$  and all excitation operators  $\tau'$  which only contain spin orbital indices which are also present in  $\tau$ . The complement of  $T_\tau$  is denoted by  $T_\tau^c$ . It contains all other excitation operators. Assuming that all excitation operators mutually commute, we then have

$$\exp(T)|0\rangle = \exp(T_\tau^c) \exp(T_\tau)|0\rangle. \quad (15)$$

The direct term approximation is obtained by projecting the second factor in Eq. (15) to  $\tau|0\rangle$ , after projection by  $P_b$  [cf. Eq. (14)]. This yields

$$P_b \exp(T)|0\rangle \approx P_b \exp(T_\tau^c) \tau|0\rangle \times \langle 0 | \tau^\dagger \exp(T_\tau) | 0 \rangle. \quad (16)$$

Because of the Pauli exclusion principle, we have  $\tau' \tau | 0 \rangle = 0$ . Therefore,  $T_\tau^c$  in Eq. (15) may be replaced by  $T$ . Moreover, since all excitation operators in  $T_\tau^c$  generate excitations which are orthogonal to  $\tau|0\rangle$ ,  $T_\tau$  in Eq. (16) may also be replaced by  $T$ . Therefore, we have

$$P_b \exp(T)|0\rangle \approx P_b \exp(T) \tau|0\rangle \langle 0 | \tau^\dagger \exp(T) | 0 \rangle. \quad (17)$$

Further, we have from Eqs. (2), (4), and (8)

$$\langle 0 | \tau^\dagger \exp(T) | 0 \rangle = \langle 0 | \tau^\dagger | \Psi_C \rangle. \quad (18)$$

By substituting Eqs. (17) and (18) into Eq. (14) we then find

$$\Delta H_\tau = \langle 0 | \tau^\dagger H P_b \exp(T) \tau | 0 \rangle, \quad (19)$$

for the diagonal  $H$ -matrix element shift. This is equivalent to taking only the first term in Eq. (47) in the evaluation of Eq. (49) of Ref. 4.

#### D. $H$ -matrix element equivalence

In the spin orbital formalism, the matrix element between a double and a quadruple excitation is either zero or it is equal to the matrix element between the reference determinant and (another) double excitation.<sup>16,17</sup> If the quadruple excitation  $|Q\rangle$  is doubly excited with respect to the double excitation  $|D\rangle = \tau|0\rangle$ , we have

$$|Q\rangle = \tau'|D\rangle = \tau'\tau|0\rangle \quad (20)$$

and in this case the interaction  $H$ -matrix elements are related by

$$\begin{aligned} \langle D | H | Q \rangle &= \langle 0 | \tau^\dagger H \tau' \tau | 0 \rangle \\ &= \langle 0 | H \tau' | 0 \rangle = \langle 0 | H | D' \rangle, \end{aligned} \quad (21)$$

where we have assumed that  $\tau$  and  $\tau'$  do not have orbital indices in common. In the CEPA method, this relation is used in order to avoid the explicit calculation of matrix elements involving quadruple excitations. In the CEPA(0) variant we use the approximation<sup>9,10</sup>

$$\langle D | H T | D \rangle = \langle 0 | \tau^\dagger H T \tau | 0 \rangle \approx \langle 0 | H T | 0 \rangle \quad \text{for any } \tau. \quad (22)$$

In the case of a single determinant reference function, the configurations in  $P_b \exp(T) \tau | 0 \rangle$  interacting with  $\tau | 0 \rangle$  consist of the quadruple excitations  $T \tau | 0 \rangle$ . Therefore, we have

$$\langle 0 | \tau^\dagger H P_b \exp(T) \tau | 0 \rangle = \langle 0 | \tau^\dagger H T \tau | 0 \rangle. \quad (23)$$

For the diagonal shift we thus have for the single reference CEPA(0) variant

$$\Delta H_\tau = \langle 0 | H T | 0 \rangle. \quad (24)$$

For a MC reference set, we now consider the analogous relation

$$\langle R | \tau^\dagger H P_b \exp(T) \tau | S \rangle = \langle R | H T | S \rangle. \quad (25)$$

Using Eq. (25) directly leads again to Eq. (24) for the diagonal shift, i.e., we then use Eq. (24) with Eq. (3). This would be the linearized version of the multi reference coupled cluster method in its simplest form.

Equation (25) only holds for those terms  $\tau'$  in  $T$  which satisfy the following three conditions:

- (i) The corresponding  $H$ -matrix element contains only 2-electron contributions, since in this case the matrix element only depends on the orbital replacements relating the two configurations.
- (ii)  $T$  and  $\tau$  have no orbital indices in common.
- (iii)  $\tau'\tau|0\rangle$  belongs to excitation class  $(k, \ell)$  with  $k > 2$  or  $\ell > 2$ .

The first two conditions also apply in the case of a single determinant reference function; The third condition is then

automatically satisfied. According to (i), Eq. (25) may not be used for the single excitation terms in  $T$ . Because of the generalized Brillouin theorem<sup>20</sup> the shift contribution  $\langle 0 | H \tau_1 | 0 \rangle$  vanishes if the multiconfiguration self-consistent-field (MCSCF) values for the reference coefficients  $c_R$  are used. These shift contributions may thus be expected to be small. Moreover, the invariance with respect to transformations among the active orbitals can only be preserved by not distinguishing between the single and double excitations. Therefore, no attempts will be made to include corrections to Eq. (25) for the single excitation terms.

In analogy to the CEPA(0) method, the second condition will also be ignored in the present formalism.

Because of these approximations the shifts will only depend on the excitation class of  $\tau$ . Using condition (iii) and Eqs. (7) and (25), we then have for any excitation operator  $\tau(k, \ell)$  belonging to the excitation class  $(k, \ell)$  the following shift:

$$\begin{aligned} \Delta H(k, \ell) &= \langle 0 | \tau^\dagger(k, \ell) H P_b \exp(T) \tau(k, \ell) | 0 \rangle \\ &= \langle 0 | \tau^\dagger(k, \ell) H \sum_{k'} \sum_{\ell'} [\exp(T)]_{k', \ell'} \tau(k, \ell) | 0 \rangle \\ &= \langle 0 | H \sum_{k'} \sum_{\ell'} [\exp(T)]_{k', \ell'} | 0 \rangle \\ &= \langle 0 | H \sum_{k'} \sum_{\ell'} P(k', \ell') | \Psi_C \rangle, \end{aligned} \quad (26)$$

where  $k' > 2 - k$  or  $\ell' > 2 - \ell$ .

The restrictions on  $k$  and  $\ell$  follow from the second line of Eq. (26) [ $k + k' > 2$  or  $\ell + \ell' > 2$ , because of the projection with  $P_b$ , cf. Eq. (7)]. The result is, that only those excitation classes  $(k', \ell')$  contribute to the shift, that are complementary to  $(k, \ell)$  in the sense that the excitations  $\tau(k + k', \ell + \ell')$  do not belong to the interacting space of the reference set. This is the essential difference with the single reference determinant result of Eq. (24). The reason for excluding the excitations with  $k + k' \leq 2$  or  $\ell + \ell' \leq 2$  is that they are already included in the MRSDCI configuration set, so their interaction matrix element already appears in the CI matrix. This argument only holds exactly if the reference set is complete with respect to the active orbital occupations.

Ignoring condition (ii) implies the introduction of the so-called exclusion principle violating (EPV) terms.<sup>14</sup> Further refinements are possible if the EPV terms are considered in more detail. This, however, spoils for example, the invariance under transformations within the various orbital subsets. Note that the unsatisfactory behavior of the CEPA(0) method in cases of near degeneracy will not carry over to the multi configuration reference case, provided all configurations which are dominant in the wave function are included in the reference set.

#### E. The relation between $\Delta H(k, \ell)$ and the correlation energy

Equation (9) may be used to calculate the energy of  $\Psi_C$ . The reference energy is given by

$$E_0 = \langle 0 | H | 0 \rangle. \quad (27)$$

Using the projection operators of Eq. (7), we have

$$E = \langle 0|H|\Psi_C\rangle = E_0 + \langle 0|HP_a|\Psi_C\rangle = \sum_k \sum_{\ell} E(k,\ell), \quad (28)$$

where

$$E(k,\ell) = \langle 0|HP(k,\ell)|\Psi_C\rangle. \quad (29)$$

The shift  $\Delta H(k,\ell)$  may thus be expressed in terms of the correlation energy contributions per excitation class

$$\Delta H(k,\ell) = \sum_{k'} \sum_{\ell'} E_{k'\ell'} \quad (k' > 2 - k \text{ or } \ell' > 2 - \ell). \quad (30)$$

Using Eq. (30) in Eq. (12) we see that the only difference with the CEPA(0) method is that the shifts depend on the excitation class of the configuration at hand. If our method is applied in the case of a single determinant closed shell reference function with only the double excitations, it is identical to the CEPA(0) method, since then we have only one excitation class, i.e.,  $k = \ell = 2$  and thus

$$\Delta H(2,2) = E(2,2) = E - E_0. \quad (31)$$

Equation (11) then, reduces to

$$\langle 0|\tau^\dagger(2,2)(H - E_0)|\Psi_C\rangle = 0 \quad (32)$$

and this equation is linear in the coefficients of the double excitations in  $\Psi_C$  as in the CEPA(0) method.<sup>11,12</sup> However, if we use Eq. (26), we have to deal with a nonlinear problem, resulting in a pseudo-eigenvalue problem which has to be solved iteratively. This may be done efficiently by using the Davidson diagonalization method (cf. Ref. 21). The diagonal element shifts then only have the effect of slightly slowing down convergence compared to a normal MRSDCI calculation.

## F. The spin-adapted formalism

The approximations made in the previous section for a wave function based on spin orbitals may equally well be used in a spin adapted formalism, although it is not quite clear whether they will have the same effect. This is particularly true for the shift contributions of the single excitations if the reference set contains open shell configurations.

The  $H$ -matrix element equivalence relation Eq. (25) is based on the assumption that the matrix elements do not contain contributions from the 1-electron part of  $H$ . However, if  $|S\rangle$  is singly excited with respect to  $|R\rangle$ , the Coulomb integral contributions ( $\mu\nu/\rho\rho$ ) to the left hand side of Eq. (25) depend on the orbital indices in  $\tau$  and therefore Eq. (25) does not hold for these terms.

In the spin orbital formalism, these terms may be avoided by discarding all single excitation contributions to  $E(k,\ell)$  in Eq. (24). For a single configuration reference function this problem is also avoided if SCF orbitals are used, because these orbitals satisfy the Brillouin theorem. In the MC reference case, however, the single excitation contributions may be numerically important because of the relaxation of the reference configuration coefficients in the second order CEPA function with respect to their complete active space self-consistent-field (CASSCF) coefficients.

Therefore, treating the single excitations [ $(k,\ell)$  with  $k = 1$  or  $\ell = 1$ ] in the same way as the other classes intro-

duces an error in the shift, which may be expected to increase with the relaxation of the reference configurations in the MRCEPA calculation. The advantage of this procedure is that the CEPA shifts are easily implemented in a direct MRSDCI program,<sup>22</sup> using the spin-adapted formalism. Also, the invariance to transformations within the inactive, active, and external orbital sets, respectively, is retained.<sup>23</sup>

## III. TEST CALCULATIONS

MRCEPA has been tested for three different test cases. The results have been compared with SCF, CASSCF, Davidson corrected and uncorrected MRSDCI results, MRACPF,<sup>13</sup> and full CI.<sup>24,25</sup>

The Davidson correction to the MRSDCI,<sup>26</sup> uses the following multireference version of this formula:<sup>27,28</sup>

$$\Delta E = (E_{\text{MRSDCI}} - E_{\text{MCSCF}})(1 - c_0^2); \quad (33)$$

$$c_0^2 = \langle \Psi_{\text{MRSDCI}} | \Psi_{\text{MCSCF}} \rangle.$$

All calculations are done with the GAMESS<sup>29-31</sup> and ATMOL<sup>32,33</sup> program packages. The Werner and Knowles second order MCSCF program<sup>34</sup> as included in the ATMOL package is used for the CASSCF calculations.

The MRCEPA, as derived above, assumes that a complete active space, even without space or spin symmetry restrictions, is used as a reference configuration set. This requirement does not have to be strictly met. The absence of symmetry restrictions though, is imperative to obtain size consistency regardless of spin-coupling, e.g., in  $O_2$ . In the test calculations on  $He_2$ ,  $O_2$ ,  $H_2O$ , and  $BeH_2$  consequently, no such restrictions were employed. For the  $H_2O$  calculations results for a  $C_{2v}$  restricted CAS reference set are shown to illustrate the rather insensitiveness of MRCEPA to the actual reference configuration set used. In the calculations on ethylene the reference configurations were all screened on symmetry.

### A. Size consistency of $He_2$ and $O_2$

The size consistency of the MRCEPA results is illustrated by calculations on the He dimer using a  $(14s,2p) = [6s,2p]$  basis<sup>35</sup> and on two oxygen atoms using a  $(9s,5p) = [4s,2p]$  double zeta basis.<sup>36</sup> For He, the reference wave function was CAS in the Hartree-Fock 1s and 2s orbitals of each atom. The oxygen atoms were described by single-configuration Hartree-Fock wave functions and the dimers employ the corresponding proper dissociation function. Table I shows the energies of the monomers and of the dimers at large distance and the size-consistency errors calculated from these numbers. The singlet and quintet couplings for the oxygen atoms yield identical results.

The results in Table I nicely illustrate that the MRCEPA method yields size-consistent results to within the convergence criterion ( $3 \times 10^{-5}$ ) used. Note that, unlike in CI, the accuracy of the MRCEPA energy is only linear in the accuracy of the CI coefficients.

### B. $H_2O$

The test calculations involve the cleavage of both OH bonds at a constant angle in the water molecule. Geometry

TABLE I. Size consistency tests: energies in hartree, size consistency error ( $\Delta$ ) in  $\mu$ hartree.

He <sub>2</sub>	Monomer	Dimer	$\Delta$
SCF	-2.861 679 1	-5.723 358 2	0.0
MRSDCI	-2.899 719 5	-5.798 892 9	546.1
MRSDCI Dav.	-2.900 004 0	-5.799 994 0	14.0
MRCEPA	-2.900 001 8	-5.800 003 5	0.1
O <sub>2</sub>			
(MC)SCF	-74.802 100 15	-149.604 200 30	0.0
MRSDCI	-74.857 013 69	-149.711 901 91	2125.5
MRSDCI Dav.	-74.858 134 87	-149.716 023 22	246.5
MRCEPA	-74.858 175 60	-149.716 354 25	3.1

and basis set were chosen according to Gdanitz and Ahlrichs.<sup>13</sup> The  $1s$  orbital was frozen on the SCF level, so the MRCEPA results can be compared with full CI results from Bauschlicher and Taylor<sup>25</sup> and MRACPF. Two sets of calculations are reported, featuring different sizes for the active space, that defines the CAS reference space for the MRCEPA and MRACPF calculations. In Table II, the CAS space consists of the  $3a_1, 4a_1, 1b_1$ , and  $2b_1$  orbitals. This active space, which is the minimal space required for proper dissociation, yields 12 symmetry allowed CSF's. For the calculations reported in Table III, the active space is extended to the  $3a_1, 4a_1, 1b_1, 1b_2, 2b_1$  and  $2b_2$  orbitals, yielding a total of 55 symmetry allowed CSF's in the reference space. The equilibrium OH bond length  $R_{eq}$  is 1.889 726 bohr, the HOH angle is fixed at 104.5°. The calculations are performed for the three internuclear distances used previously.<sup>25</sup> The calculations employing only the symmetry allowed reference configurations are denoted by a suffix "sym".

The energy difference with full CI is small for all calculations beyond the MCSCF level, though both MRCEPA and MRACPF are an order of magnitude better than straight MRSDCI. The quality of the MRCEPA method seems to follow the quality of the reference wave function, getting better for larger distances and larger reference wave functions. The MRACPF method does not show such regular behavior.

TABLE II. Energy differences with full CI in mhartree for H<sub>2</sub>O with a 12 CSF reference (see text).

Geometry	$1.0R_{eq}$	$1.5R_{eq}$	$2.0R_{eq}$
Full CI energy (hartree)	-76.256 62	-76.071 41	-75.952 27
MCSCF	161.90	146.62	128.59
MRSDCI	4.81	4.29	3.62
MRSDCI Dav.	-1.61	-1.87	-1.15
MRCEPA	-1.15	-1.10	-0.74
MRACPF	-0.12	-0.22	0.18
MRSDCI <sub>sym</sub>	4.96	4.51	3.75
MRSDCI Dav <sub>sym</sub>	-1.43	-1.60	-1.00
MRCEPA <sub>sym</sub>	-0.97	-0.84	-0.59

TABLE III. Energy differences with full CI in mhartree for H<sub>2</sub>O with a 55 CSF reference (see text).

Geometry	$1.0R_{eq}$	$1.5R_{eq}$	$2.0R_{eq}$
Full CI energy (hartree)	-76.256 62	-76.071 41	-75.952 27
MCSCF	126.74	118.26	112.39
MRSDCI	2.30	1.72	1.54
MRSDCI Dav.	-1.45	-1.93	-1.75
MRCEPA	-0.85	-0.73	-0.61
MRACPF	-0.40	-0.79	-0.78
MRSDCI <sub>sym</sub>	2.50	2.04	1.79
MRSDCI Dav <sub>sym</sub>	-1.21	-1.57	-1.48
MRCEPA <sub>sym</sub>	-0.62	-0.39	-0.34

The symmetry restricted and complete reference functions yield quite comparable results.

### C. BeH<sub>2</sub>

The last comparison with Full CI and MRACPF concerns the  $C_{2v}$  insertion reaction of H<sub>2</sub> with Be. Geometry and basis set are taken from Laidig and Bartlett.<sup>37</sup> The CAS space in the first set of calculations (1) consists of the  $1b_2$  and the  $3a_1$  orbitals (cf. Ref. 13), which provides proper dissociation to Be and H<sub>2</sub>. Since no allowance is made for the near degeneracy in Be itself, the MRCEPA wave function may be expected to be of rather meager quality. Therefore, we also performed a calculation correlating the Be atom better, extending the active space to  $\{2a_1, 3a_1, 1b_2, 2b_2\}$  yielding a CAS space of 12 symmetry adapted CSF's. The results for this CAS space are labeled large. The results are given in Table IV.

The comparison shows that in this case, the MRCEPA and the normal and the corrected MRSDCI values are less good than the ones of MRACPF.<sup>13</sup> For the large CAS space, the MRCEPA is better, but the MRSDCI itself is even closer to the full CI. This suggests an overcorrection of the unlinked cluster contributions in this case.

TABLE IV. Be/H<sub>2</sub> energy differences with full CI energy in mhartree.

Geometry	$G1$	$G2$	$G3$
Full CI energy (hartree)	-15.622 88	-15.602 92	-15.624 96
MCSCF	53.31	64.35	66.68
MRSDCI	0.78	1.91	3.05
MRSDCI Dav.	-2.57	-5.02	-4.02
MRCEPA	-1.65	-2.55	-5.88
MRACPF	-0.90	-0.90	-0.53
MRLCCM	-2.62	-2.40	-5.50
MCSCF large	9.06	15.97	23.66
MRSDCI large	0.04	0.08	0.18
MRSDCI Dav. large	-0.11	-0.66	-1.07
MRCEPA large	-0.06	-0.41	-1.16

## IV. APPLICATION TO ETHYLENE

### A. Introduction

To investigate the behavior of the MRCEPA in a practical application, we applied the method to the ground state ( $N$ ) and the  $V^1(\pi, \pi^*)$  state of ethylene in its planar and twisted conformation. The resulting potential energy surfaces will be used in a calculation of the UV absorption spectrum of the system.<sup>38</sup> We performed calculations with different numbers of reference configurations and compared the result with those of the MCSCF and MRSDCI approaches. Ethylene provides an interesting test problem because obtaining a proper description of its  $V \leftarrow N$  transition has been a major challenge for many years of theoretical studies.

The first problem encountered is the calculation of the vertical transition energy. Diffuse functions must be included in the basis set to account for the diffuse character of the  $V$  state, but at the SCF level this results in a vertical transition energy which is too low, while the state becomes very diffuse and so the oscillator strength becomes too small.<sup>39,40</sup> These results can be improved by a SDCI calculation, but several studies have shown that for a good description of the  $V$  state, a MRSDCI calculation is needed<sup>41-43</sup> and that the inclusion of higher order excitations, e.g., by using the Davidson size consistency correction, does have a significant effect on the calculated vertical transition energy. Recently, it was shown by R. J. Cave<sup>44</sup> that size inconsistency of CI calculations can also have a significant effect on the calculated molecular properties of the  $V$  state of ethylene.

The most important geometry change in ethylene upon excitation to the  $V$  state is the relaxation to a  $90^\circ$  twisted conformation, so we included this geometry in our test calculations.

### B. Method

For the calculations on the planar conformation (symmetry  $D_{2h}$ ) we used the experimental ground state geometry reported by Kuchitsu:<sup>45</sup>  $R(\text{C}-\text{C}) = 1.330 \text{ \AA}$ ,  $R(\text{C}-\text{H}) = 1.076 \text{ \AA}$ ,  $\alpha(\text{C}-\text{C}-\text{H}) = 121.7^\circ$ . This geometry is also used in other theoretical studies, but it is slightly different from the "standard" geometry of Herzberg<sup>46</sup>:  $R(\text{C}-\text{C}) = 1.339 \text{ \AA}$ ,  $R(\text{C}-\text{H}) = 1.086 \text{ \AA}$  and  $\alpha(\text{C}-\text{C}-\text{H}) = 121.2^\circ$ . These differences are not relevant in this study, since we will not compare with experimental data. For the twisted conformation, these parameters are left unchanged, except for the C-C torsion angle which is put to  $89.9^\circ$ , forcing the symmetry point group to  $D_2$  (a torsion angle of  $90^\circ$  would give a  $D_{2d}$  symmetry which is reduced to  $C_{2v}$  by our CI program, causing the  $V$  state to be of  $A_1$  symmetry).

To define the symmetry labels for the planar conformation, we use the following axis assignments: The  $z$  axis is taken to be along the C-C bond and the  $x$  axis is perpendicular to the plane of the molecule. For the twisted conformation we use the same choice for the  $z$  axis. This causes the  $B_2$  and  $B_3$  representation in  $D_2$  to correlate with the twofold degenerate  $E$  representation in  $D_{2d}$ .

The  $AO$  basis set employed is the triple-zeta basis set due to Dunning<sup>47</sup> with a  $(5s) = \rangle[3s]$  contraction for hydrogen

TABLE V. Summary of the active orbital spaces (CAS), the number of reference configurations ( $N_{\text{ref}}$ ) and the total number of configurations ( $N_{\text{conf}}$ ) for the calculations on the ground ( $N$ ) and  $V^1(\pi, \pi^*)$  state.

State	Method	CAS	$N_{\text{ref}}$	$N_{\text{conf}}$	
				Planar	Twisted
$V$	$A'$	$\pi, \pi^*$	1	22 121	38 739
	$B'$	$\pi, \pi^*, 2\pi, 2\pi^*$	4	78 950	129 976
	$C'$	$\pi, \pi^*, \sigma, \sigma^*$	4	83 298	146 800
	$D'$	$\pi, \pi^*, 2\pi, 2\pi^*, \sigma, \sigma^*$	13	294 950	507 702
$N$	$A$	$\pi, \pi^*$	2	19 525	34 465
	$B$	$\pi, \pi^*, 2\pi, 2\pi^*$	6	74 142	123 468
	$C$	$\pi, \pi^*, \sigma, \sigma^*$	7	105 674	184 612
	$D$	$\pi, \pi^*, 2\pi, 2\pi^*, \sigma, \sigma^*$	19	310 236	533 280

and a  $(10s, 6p) = \rangle[5s, 3p]$  contraction for carbon, augmented with polarization functions on the carbon and the hydrogen<sup>48</sup> and a set of diffuse  $s$  and  $p$  functions (exponent  $0.02 \text{ bohr}^{-2}$ ) on each carbon atom, giving a total number of 72 functions.

For both geometries and both states a series of calculations with different sets of configurations is done. First, we do a CASSCF calculation for four different sets of active orbitals. Those CAS functions constitute the reference space for the subsequent MRSDCI and MRCEPA calculations. So the orbitals entering the MRSDCI and MRCEPA calculations are optimized for each state separately in a CASSCF calculations for the reference configurations. The SCF ground state configuration is, for the planar geometry ( $D_{2h}$ )

$$1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u}^2$$

and for the twisted geometry ( $D_2$ )

$$2^{-1/2} 1a_1^2 1b_1^2 2a_1^2 2b_1^2 1b_2^2 1b_3^2 3a_1^2 (2b_3^2 + 2b_2^2).$$

The active orbital spaces are summarized in Table V. The smallest set ( $A$ ) consists of just the  $\pi(1b_{3u}/2b_3)$  and  $\pi^*(1b_{2g}/2b_2)$  orbitals. ( $B$ ) has an additional pair of orbitals of  $\pi$  and  $\pi^*$  symmetry, while ( $C$ ) has an additional  $\sigma(3a_g/3a_1)/\sigma^*(3b_{1u}/3b_1)$  pair. The largest set ( $D$ ) has both the additional  $\pi/\pi^*$  and  $\sigma/\sigma^*$  orbitals. The number of electrons in the active space is two for ( $A$ ) and ( $B$ ) and four for ( $C$ ) and ( $D$ ).

In the MRSDCI and MRCEPA calculations, all single and double excitations relative to the reference configurations are included, but the two lowest  $\sigma$  orbitals and their complements are kept doubly occupied and unoccupied, respectively. The resulting numbers of configurations are given in Table V.

### C. Results and discussion

The results of all the calculations, for the planar and the twisted geometries on the  $N$  and the  $V$  states with the four different sets of reference configurations are given in Table VI.

First, we will show how the results depend on the choice of the reference set. For this purpose, we plot in Fig. 1 the

TABLE VI(A). The energies<sup>a</sup> for the ground (*N*) and *V*<sup>1</sup> ( $\pi, \pi^*$ ) state of ethylene at the planar geometry.

State	Method <sup>b</sup>	CASSCF	MRSDCI	MRSDCI + Q <sup>c</sup>	MRCEPA
<i>V</i>	<i>A'</i>	-77.788 956	-78.048 851	-78.072 631	-78.105 601
	<i>B'</i>	-77.789 848	-78.052 931	-78.083 973	-78.088 006
	<i>C'</i>	-77.803 410	-78.057 360	-78.080 918	-78.103 483
	<i>D'</i>	-77.819 459	-78.061 782	-78.089 629	-78.090 364
<i>N</i>	<i>A</i>	-78.088 898	-78.360 411	-78.383 378	-78.387 806
	<i>B</i>	-78.091 346	-78.362 727	-78.385 928	-78.389 365
	<i>C</i>	-78.114 552	-78.365 828	-78.385 731	-78.389 008
	<i>D</i>	-78.120 212	-78.368 371	-78.388 118	-78.390 216
(B) For the twisted geometry					
<i>V</i>	<i>A'</i>	-77.840 353	-78.137 756	-78.167 029	-78.175 100
	<i>B'</i>	-77.847 814	-78.141 044	-78.169 999	-78.175 682
	<i>C'</i>	-77.861 986	-78.144 131	-78.171 392	-78.175 839
	<i>D'</i>	-77.875 360	-78.148 174	-78.174 576	-78.176 394
<i>N</i>	<i>A</i>	-77.968 708	-78.241 862	-78.265 962	-78.271 938
	<i>B</i>	-77.969 383	-78.243 034	-78.267 464	-78.272 423
	<i>C</i>	-77.983 954	-78.245 970	-78.268 852	-78.272 646
	<i>D</i>	-77.993 097	-78.248 223	-78.270 489	-78.272 600

<sup>a</sup>) In atomic units.

<sup>b</sup>) See Table V.

<sup>c</sup>) The Davidson corrected MRSDCI.

energy of the CASSCF, MRSDCI, and MRCEPA calculations for method (*A*), (*B*), and (*C*) (see Table V) relative to the energy of the corresponding calculation with the largest number of configurations (*D*). This is done for both states and both geometries.

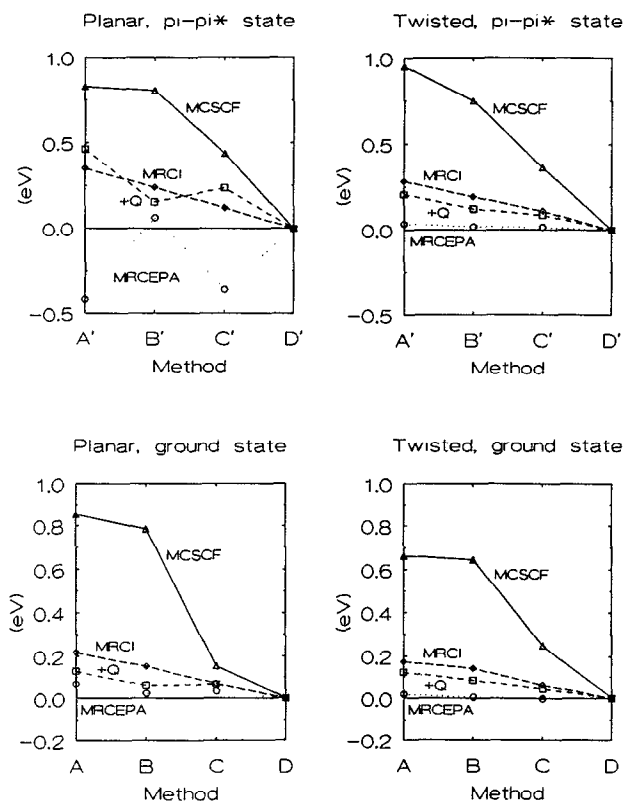


FIG. 1. Relative energies calculated for the reference sets of Table V.

First, we note that the CASSCF and the MRSDCI energies are decreasing as a function of the number of configurations, which is to be expected because of the variational character of these methods. Strictly speaking, this argument is not valid for comparing (*B*) and (*C*), because (*C*) does not include all configurations of (*B*), but it is correct for the series *A*-*B*-*D* and *A*-*C*-*D*.

In contrast, the MRCEPA results are almost independent of the number of configurations, except for the *V* state of the planar geometry. In this case, the MRCEPA calculations based on a reference space which contains only one configuration of the  $\pi$ - $\pi^*$  type (*A'* and *C'*) gives energies which are far lower than any reasonable full CI estimate. These results suggest that increasing the reference space hardly affects the MRCEPA result as soon as the most important configurations are included in the reference space. So, for the description of the *V*<sup>1</sup>( $\pi, \pi^*$ ) state at the planar geometry it is essential to include at least two orbitals of  $\pi^*$  symmetry in the reference space. This observation is consistent with the conclusions of several other CI studies.<sup>41-43</sup> The omission of an important reference configuration in a MRCEPA calculation can be identified *a posteriori* by the inspection of the MRCEPA vector: One or more configurations not included in the reference space gain a large coefficient, while the sum of the squares of the coefficients of the reference configurations

$$\tilde{c}_0^2 = \sum_{i \in \text{ref}} c_i^2 \quad (34)$$

is much smaller than unity. This was also observed by Bauschlicher *et al.*<sup>49</sup> in MRACPF calculations. It is, of course, not possible to give rock-solid criteria, but for the aforementioned calculations (*A'*) and (*C'*) we find  $\tilde{c}_0^2 = 0.38$  and  $0.50$ , respectively, while in all other MRCEPA calculations  $\tilde{c}_0^2$  varies between  $0.83$  and  $0.90$ .

The Davidson corrected values are less dependent on



TABLE VII. The vertical excitation energies in eV.

Geometry	Method	CASSCF	MRSDCI	MRSDCI + Q	MRCEPA
Planar	<i>A</i>	8.16	8.48	8.46	7.68
	<i>B</i>	8.20	8.43	8.22	8.20
	<i>C</i>	8.47	8.39	8.29	7.77
	<i>D</i>	8.18	8.34	8.12	8.16
Twisted	<i>A</i>	3.49	2.83	2.69	2.63
	<i>B</i>	3.31	2.78	2.65	2.63
	<i>C</i>	3.32	2.77	2.65	2.63
	<i>D</i>	3.20	2.72	2.61	2.62

the reference set than the MRSDCI results, if the calculations (*A'*) and (*C'*) for the *V* state at the planar geometry are discarded, but the results are not as constant as for the MRCEPA. Furthermore, it would have been difficult to discard the results (*A'*) and (*C'*) by inspection of the MRSDCI vector.

Generally, one is interested in relative energies, rather than in absolute values, so we extracted from Table VI the vertical transition energies at both geometries (Table VII) and the difference between the energies of the twisted and the planar geometry, i.e., the torsion barrier in both states (Table VIII).

Although we lack full CI data to compare with, we can draw some interesting conclusions from Tables VII and VIII. Considering the vertical transition energy of the planar geometry we first note that we should discard the MRCEPA results of methods (*A'*) and (*C'*) because of reasons mentioned above. The remaining MRCEPA values (8.20 and 8.16 eV) are, respectively, 0.23 and 0.18 eV lower than the corresponding MRSDCI values. Comparable size-consistency effects on the vertical transition energy of ethylene have been found before. For example, Cave<sup>44</sup> reports the values 8.35 and 8.17 eV, respectively, for a two reference CI and a quasidegenerate variational perturbation theory (QDVPT)<sup>50,51</sup> calculation (they use the same geometry but a different basis set). The Davidson-corrected results show the same trend but have a larger spread.

For the vertical transition energy at the twisted geometry, the favorable behavior of the MRCEPA is evident; It gives almost constant values. For the larger reference spaces,

the MRSDCI and particularly the Davidson corrected values tend to the same results.

From Table VIII it is clear that the size-consistency effects for the torsion barriers is rather small: Both the MRCEPA and the Davidson correction give a lowering of 0–2 kcal/mol, except again for the calculations (*A'*) and (*C'*) for the *V* state.

## V. CONCLUSION

We have given the theory for a multi reference CEPA approach. It shows in test calculations to compare well with full CI. The resulting potential curves are seen to converge to the full CI result as the reference configuration set is increased.

We have demonstrated by a series of calculations on the ground and  $V^1(\pi, \pi^*)$  state on the planar and twisted conformation of ethylene, that the MRCEPA energy depends on the set of reference configurations in a very favorable way: If the most important configurations are contained in the CAS space which constitutes the reference space, a result is obtained which hardly changes upon increasing the reference set. The omission of an important reference configuration can easily be identified by inspection of the CEPA vector: The contributions of the reference configurations to the CEPA vector ( $\tilde{c}_0^2$ ) are then far from unity.

The calculation of the torsion barriers and the vertical transition energies in ethylene suggest that the MRCEPA is a promising tool for the calculation of both ground and excited state potential energy surfaces.

TABLE VIII. The torsion barriers in kcal/mole.

State	Method	CASSCF	MRSDCI	MRSDCI + Q	MRCEPA
<i>V</i>	<i>A'</i>	– 32.3	– 55.8	– 59.2	– 43.6
	<i>B'</i>	– 36.4	– 55.3	– 54.0	– 55.0
	<i>C'</i>	– 36.8	– 54.4	– 56.8	– 45.4
	<i>D'</i>	– 35.1	– 54.2	– 53.3	– 54.0
<i>N</i>	<i>A</i>	75.4	74.4	73.7	72.7
	<i>B</i>	76.5	75.1	74.3	73.4
	<i>C</i>	82.0	75.2	73.3	73.0
	<i>D</i>	79.8	75.4	73.8	73.8

## ACKNOWLEDGMENTS

The CYBER 205 computer time was financed by the Foundation SURF from the National Fund Supercomputers (NFS). We thank the SARA supercomputer advisers for support.

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