

# A Local Pair Natural Orbital-Based Multireference Mukherjee's Coupled Cluster Method

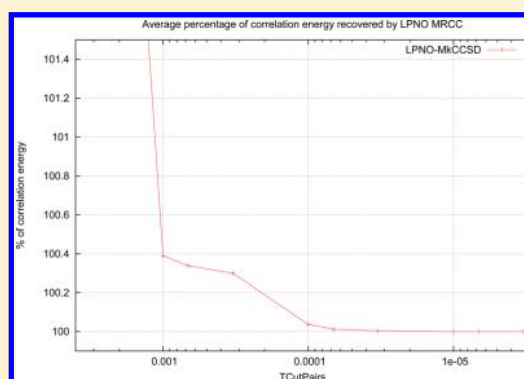
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**ABSTRACT:** This paper reports the development of a local variant of Mukherjee's state-specific multireference coupled cluster method based on the pair natural orbital approach (LPNO-MkCC). The current implementation is restricted to single and double excitations. The performance of the LPNO-MkCCSD method was tested on calculations of naphthylene isomers, tetramethyleneethane, and  $\beta$ -carotene molecules. The results show that 99.7–99.8% of correlation energy was recovered with respect to the MkCC method based on canonical orbitals. Moreover, the errors of relative energies between different isomers or along a potential energy curve (with respect to the canonical method) are below 0.4 kcal/mol, safely within the chemical accuracy. The computational efficiency of our implementation of LPNO-MkCCSD in the ORCA program allows calculation of the  $\beta$ -carotene molecule (96 atoms and 1984 basis functions) on a single CPU core.



## I. INTRODUCTION

The coupled cluster (CC) approach, introduced to quantum chemistry by Čížek,<sup>1</sup> is one of the most accurate ab initio methods for treatment of dynamical correlation. The advantages of this scheme include a compact description of the wave function, size-extensivity, and invariance toward orbital rotations together with a systematic hierarchy of approximations converging toward the full configuration interaction limit. The CCSD(T) method,<sup>2</sup> which includes connected single-, double-, and perturbative triple excitations, is often referred to as the gold standard of quantum chemistry.<sup>3</sup>

A disadvantage of traditional coupled cluster methods is the high associated computational cost, which prevents its application to larger systems. There are two basic strategies for addressing this problem: the large-scale parallelization of the code and orbital localization. Highly parallelized codes are becoming increasingly available that scale well up to tens of thousands of processors. However, parallelization itself is not sufficient to ensure that a given method will see large-scale chemical application. Methods like CCSD and CCSD(T) that feature  $O(n^6)$  and  $O(n^7)$  scaling, (with  $n$  being a measure of system size) lead to explosive computational cost and require extremely powerful supercomputers for application to even medium-sized molecules with a few dozen atoms. Clearly, such resources are not available to most computational chemists; hence, for the time being, such calculations remain refined to the area of pilot and benchmark studies.

By contrast, methods that introduce approximations in order to reduce the computational can be applied in a routine fashion and with restricted resources. However, in the design of low-order scaling methods, utmost attention must be devoted to ensuring that the results reliably closely resemble the results of the parent canonical electronic structure methods. There are currently a number of approaches that aim at linear scaling coupled cluster theory. Pioneering work in this field was reported early on by Pulay and Sæbø in the 1980s.<sup>4–7</sup> Their main idea was to use localized occupied orbitals and to span the virtual space by a set of redundant projected atomic orbitals (PAOs). In this basis, the matrices of one and two-electron integrals become sparse. This allows approximating or neglecting expensive terms based on the spatial distance of the participating orbitals, leading to  $O(n)$  scaling. The physical justification is the short-range character of electron correlation, which has a  $R^{-6}$  asymptote. Later, this approach has been greatly extended into the framework of (single-reference) coupled cluster theory by Werner, Schütz, and co-workers.<sup>8–14</sup> In this way, the coupled cluster calculations became available for extended systems and even enzyme active sites.<sup>15</sup>

The actual choice of localized orbitals is often not very critical, and several schemes available for localization.<sup>16,17</sup> However, how to most efficiently span the virtual

Received: April 9, 2015

Published: June 11, 2015

space in a local manner is more involved. In the local methods of Pulay, Werner, Schütz, and co-workers,<sup>8–10</sup> PAOs have been used. The PAOs are a priori localized but nonorthogonal. Each localized occupied orbital is assigned a domain of PAOs centered in its vicinity, while pairs are assigned pair domains. According to their real space distance, the pairs of occupied orbitals are treated at the highest level (strong pairs) or approximately (weak and distant pairs), or are neglected entirely (very distant pairs). Except for the neglected very distant pairs, the number of pairs as well as cluster amplitudes was shown to scale linearly with the size of the system for large systems. With careful program optimization, overall linear scaling can be reached.

There are many other local approaches, all of which have different strengths and weaknesses. We mention here the natural linear scaling method,<sup>18</sup> fragment molecular orbital method,<sup>19</sup> divide-and-conquer method,<sup>20</sup> atomic orbital-based CC,<sup>21</sup> cluster-in-molecule approach,<sup>22</sup> incremental scheme,<sup>23</sup> divide-expand-consolidate method,<sup>24</sup> and local completely renormalized coupled cluster method.<sup>25</sup>

A few years ago, we realized that pair natural orbitals (PNOs) offer unique advantages for spanning the virtual space in local correlation methods. Consequently, the LPNO-CCSD, LPNO-CEPA, and related methods were developed<sup>26–29</sup> and shown to be accurate, efficient, and robust. In PNO methods, each pair of (localized) occupied orbitals is assigned a separate set of natural orbitals. The expansion is truncated according to the occupation number of the natural orbitals, or a closely related criterion. PNOs were first used in the late 1960s, and in the early to mid 1970s, ingenious correlation methods were invented.<sup>30–38</sup> However, their full potential could be realized only much more recently in combination with local correlation approaches, modern hardware, and modern integral transformation technologies, foremost of which is the resolution of the identity (RI) or density fitting (DF) methodology.<sup>39</sup> In a nutshell, PNOs are as local or nonlocal as the physical situation requires (hence, they are self-adapting), and they provide the most compact description of the virtual space of the corresponding pair. In fact, giant reductions in the number of cluster amplitudes on the order of  $10^7$  can be achieved on the basis of PNOs.<sup>27</sup> PNOs are orthonormal within a given electron pair, are strictly orthogonal to all occupied orbitals, but are nonorthogonal if they belong to different electron pairs. However, as shown by Meyer, this slight nonorthogonality does not greatly complicate the formalism of a correlation method.<sup>32</sup> Furthermore, PNOs converge toward a very compact set as the basis set is approaching completion; hence, PNO-based methods do not involve the explosive computational cost upon basis set extension that canonical methods face. The PNO approach involves only a limited number of cutoff parameters:  $T_{\text{CutPairs}}$  for contributing electron pairs,  $T_{\text{CutPNO}}$  for the minimum occupation number of a PNO to be kept, and  $T_{\text{CutMKN}}$  for the local fitting domain. All of these cutoffs are based on energy or wave function criteria rather than on distances in real space. The advantages of this approach include high accuracy (as measured as the percentage of correlation energy relative to calculation with canonical orbitals), a smooth dependence of the error on the cutoff parameters, high compactness of the LPNO-based wave function, and black box character of the method, which is crucial for making the method widely applicable.

The advantages of the PNO approach have now been widely appreciated by a number of research groups, and exciting new

developments have been reported; for examples, see refs 40–46. Chemical applications of the methods are now rapidly emerging.<sup>47–52</sup> In fact, calculations on systems with over 600 atoms and 8800 basis functions have been reported.<sup>40–42</sup>

One drawback of the standard CC method that is not addressed by either localization or parallelization is that at a low truncation of the cluster operator it provides a poor description of nondynamical correlation. This is important for systems with quasidegenerate frontier orbitals, which are very common in chemistry, e.g., dissociation of molecules, transition states, diradicals, and transition-metal compounds. In the last decades, various approaches that address these issues were formulated and implemented. One group of these approaches are the Hilbert space methods, in which the reference function is treated at a multideterminantal level and each of these determinants is assigned its distinct cluster operator. The first progress in this direction was achieved by Jezierski and Monkhorst,<sup>53</sup> who introduced the aforementioned ansatz of the wave operator and formulated the state universal method (SU MRCC). The SU MRCC method was later developed by Kucharski and Bartlett<sup>54</sup> and Paldus et al.<sup>55,56</sup> However, the SU MRCC method was found to suffer from convergence difficulties, known as the intruder state problem. Another class of Hilbert space methods are the state-specific approaches (SS MRCC), where only one state is studied at a time. The first SS-MRCC approach based on the Brillouin–Wigner CC theory (MR BWCC) was introduced by Hubač et al.<sup>57–59</sup> and further developed by one of us and co-workers.<sup>60–72</sup> Thanks to their insensitivity toward the intruder state problem, the SS MRCC methods have lately become more popular than SU MRCC.<sup>73</sup>

Another SS MRCC approach that has been formulated by Mukherjee and co-workers<sup>74</sup> and further developed by Evangelista, Kállay, our group, and others<sup>72,75–88</sup> is known as Mukherjee's MR CC method (MkCC). It is presently the most commonly used one from Hilbert space SS MRCC approaches because of its rigorous size extensivity and insensitivity toward intruder states. Also, the structure of cluster amplitude equations is very similar to single-reference theory. Over the past decade, the development in this field was rather vivid and includes efficient evaluation of coupling terms,<sup>76</sup> the development of analytic gradients, inclusion of connected triples<sup>77,80</sup> and higher excitations<sup>79</sup> as well as automatically generated implementations,<sup>79</sup> the uncoupled approximation,<sup>89</sup> an internally contracted version,<sup>90</sup> massively parallel implementation,<sup>91–93</sup> an explicitly correlated version,<sup>94–96</sup> and calculations with localized active orbitals.<sup>97</sup> Other variants of the SS-MRCC methods have been developed,<sup>74,98–101</sup> and the relationship between various Hilbert space MRCC approaches has been systematically investigated by Kong.<sup>102</sup> A more recent important class of methods designed to treat the nondynamic correlation are internally contracted MRCC approaches.<sup>103–112</sup>

In this paper, the development of LPNO variants of MkCCSD and BWCCSD methods and their implementation in the ORCA program<sup>113</sup> is reported together with the numerical assessment of the method. The implementation is based on the open shell formulation of LPNO CCSD<sup>28</sup> in ORCA. The performance of the LPNO MRCC approaches is tested on three systems: naphthynes, tetramethyleneethane and  $\beta$ -carotene, which all have been studied previously by MkCC and BWCC (in canonical orbitals). Isomers of naphthynes are some of the largest molecules studied at MRCC, where the multireference character is strong and up to four reference configurations are required. The four isomers enable us also to

test the relative energy differences. TME is selected to test the performance of LPNO approaches along a potential energy curve corresponding to its torsion angle. Finally,  $\beta$ -carotene is the largest molecule studied at the MkCC level, and our calculations are aimed at showing the limits of applicability of LPNO approaches.

There is a valid question why we have chosen, for the time being, to implement the LPNO scheme rather than the superior, but more elaborate, domain local pair natural orbital (DLPNO) version.<sup>40</sup> There are two reasons. First, the UHF-based DLPNO code for general reference functions is still under development in ORCA, while it is available for LPNO.<sup>28</sup> Second, it is easier to proceed with LPNO, to identify and solve potential problems within this scheme, and to use the experience thus gained in later implementation of the DLPNO-MkCC method. However, as will be shown below, already the current implementation allows calculations that are far beyond reach with a canonical implementation of the method.

## II. THEORY

**A. Recapitulation of Hilbert Space MRCC Methods.** In this work we assume a complete model space spanned by  $M$  reference determinants  $\Phi_\mu$  obtained from all possible configurations of a given number of electrons in the active orbitals. Correspondingly, the orbital space is divided into three windows: the inactive orbitals occupied in all references, the external orbitals unoccupied in all the references, and the active orbitals with a different partial occupation in the various references. The reference function  $\Psi_\alpha^P$  is expressed as a linear combination of these references

$$|\Psi_\alpha^P\rangle = \sum_{\mu=1}^M C_\mu^\alpha |\Phi_\mu\rangle \quad (1)$$

where the expansion coefficients  $C_\mu^\alpha$  are not known a priori. The index  $\alpha$  corresponds to the electronic state studied.

The exact wave function  $\Psi_\alpha$  can be formally obtained using the wave operator  $\hat{\Omega}_\alpha$ , defined as

$$|\Psi_\alpha\rangle = \hat{\Omega}_\alpha |\Psi_\alpha^P\rangle \quad (2)$$

Furthermore, let us define the effective Hamiltonian  $H^{\text{eff}}$  as

$$\hat{H}^{\text{eff}} = \hat{P} \hat{H} \hat{\Omega}_\alpha \hat{P} \quad (3)$$

where  $\hat{P}$  is the projection operator onto the model space. The reference function  $\Psi_\alpha^P$  is thus an eigenfunction of the effective Hamiltonian, while the exact energy  $\mathcal{E}_\alpha$  is the corresponding eigenvalue

$$\hat{H}^{\text{eff}} |\Psi_\alpha^P\rangle = \mathcal{E}_\alpha |\Psi_\alpha^P\rangle \quad (4)$$

Within the model space, this equation can be rewritten in a matrix form as

$$\sum_\nu H_{\mu\nu}^{\text{eff}} C_\nu^\alpha = \mathcal{E}_\alpha C_\mu^\alpha \quad (5)$$

The wave operator is assumed in the form of a Jeziorski–Monkhorst ansatz<sup>53</sup>

$$\hat{\Omega}_\alpha = \sum_{\mu=1}^M e^{\hat{T}^{(\mu)}} |\Phi_\mu\rangle \langle \Phi_\mu| \quad (6)$$

where  $T^{(\mu)}$  is a cluster operator corresponding to the reference  $|\Phi_\mu\rangle$ . For simplicity, the index  $\alpha$  will be dropped in further text.

In our implementation, the occupied orbital window is set to include all active and inactive orbitals, whereas the virtual orbital window consists of all active and external orbitals, as shown in Figure 1. The cluster operators are defined within this

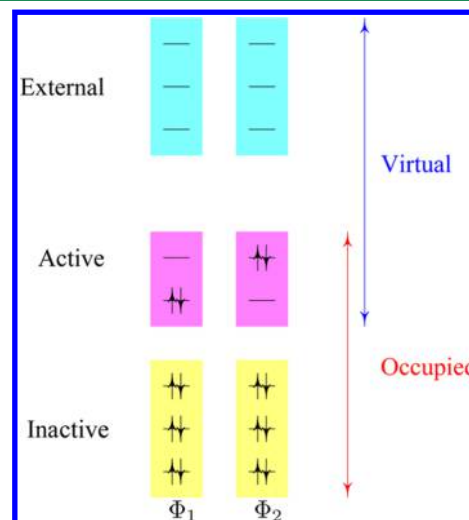


Figure 1. Orbital layout.

scheme. In this way, a common set of integrals is used, although it is redundant in the sense that integrals with active indices are included more than once. However, because the number of active orbitals is rather limited in Hilbert space approaches, this is a minor issue. Similarly, the cluster operator  $T^{(\mu)}$  includes “invalid” excitations—i.e. excitations from a virtual active (wrt.  $\Phi_\mu$ ) and/or to an occupied active (wrt.  $\Phi_\mu$ ) orbital, where the corresponding amplitudes have to be explicitly zeroed.

**B. LPNO Approach for MRCC.** For the extension of the LPNO approach to multireference problems, the setup of PNOs is a delicate issue. For several reasons, foremost of which include computational cost of the integral transformation step, the storage of PNO-related quantities, and the simplicity of the coupling terms in the cluster equations, it is useful to have one common set of PNOs for all references. This means the PNOs need to be optimized for all the references in order to obtain a balanced treatment. We thus generate a common set of PNOs by diagonalization of density matrix averaged over references.

The active orbitals have to be the same for all references and also independent of the pair index  $ij$ ; however, for coding purposes it is highly beneficial to have a common framework for all virtual indices, both active and external ones. To achieve this, the active orbitals are formally included among the PNOs, but they are kept unchanged; they are also formally included into the occupied orbital window. The occupied and virtual orbital windows thus overlap, but the amplitudes of all excitations, which are not allowed with respect to a particular reference determinant as Fermi vacuum, are set to zero.

The algorithm for determining the PNOs can be divided into several steps. First, the inactive orbitals are localized using the Foster–Boys localization.<sup>114</sup>

Second, for each occupied pair  $ij$  of inactive and/or active orbitals and for each reference  $\mu$ , the MP2 amplitudes are calculated from exchange integrals  $K_{ij}^{ab}$  and diagonal Fock matrix elements  $f_{pp}$  as

$$t_{ij}^{ab}(\mu) = \frac{K_{ij}^{ab}}{f_{aa}(\mu) + f_{bb}(\mu) - f_{ii}(\mu) - f_{jj}(\mu)} \quad (7)$$

While in the single-reference method the canonical virtual basis is employed here and the Fock matrix is diagonal with  $f_{aa}$  and  $f_{bb}$  becoming orbital energies, in the multireference case this no longer holds. While in conventional MkCC cluster amplitudes at the MP2 level are used only as the initial guess for the cluster amplitude equation, here they are used to construct PNOs, and this in principle could lead to lower accuracy. However, Liakos et al.<sup>115</sup> have recently investigated this effect and found out that the accuracy of the final results is not affected.

If the corresponding pair MP2 energy is greater than the  $T_{\text{CutPairs}}$  cutoff parameter for any of the references, the pair is kept. Otherwise, the pair is neglected and only its MP2 energies are stored for each reference.

If the pair  $ij$  is kept, a pair density matrix is constructed for each of the reference configurations

$$D^{ij}(\mu) = \tilde{T}^{ij+}(\mu)T^{ij}(\mu) + \tilde{T}^{ij}(\mu)T^{ij+}(\mu) \quad (8)$$

where  $T^{ij}(\mu)$  is a matrix of amplitudes  $t_{ij}^{ab}(\mu)$  of the  $ij$  pair, and  $\tilde{T}^{ij}(\mu)$  is (for closed shell RHF case) defined as

$$\tilde{T}^{ij}(\mu) = \frac{1}{1 + \delta_{ij}}(4 T^{ij}(\mu) - 2 T^{ji}(\mu)) \quad (9)$$

Subsequently, common pair density matrices  $D^{ij}$  are obtained as an average of  $D^{ij}(\mu)$  over all references. The choice of the weights for this averaging is not unique; one can use constant weight or reference-dependent weights. The natural choice may appear to be the square of CASSCF coefficient for each reference. However, we have decided to choose the former possibility

$$D^{ij} = \frac{1}{M} \sum_{\mu} D^{ij}(\mu) \quad (10)$$

In this way, it is ensured that the PNOs are well-suited for all references. In particular, the incorporation of dynamic correlation may change the information content of the active space in the sense that a weak reference may gain significant weight under the influence of dynamic correlation. It is then important that the PNO space allows for this weight to develop naturally over the course of the calculation. This would be suppressed by a weighting of the densities with the CASSCF coefficients.

To keep the active orbitals the same for all pairs and at the same time to include them formally among virtual orbitals, off-diagonal blocks of the density matrix involving active orbital indices have to be zeroed out. The diagonalization of  $D^{ij}$  matrices

$$D^{ij}d_a^{ij} = \bar{n}_a^{ij}d_a^{ij} \quad (11)$$

thus formally yields PNOs with active indices equal to the original active orbitals (up to a sign), while they are treated on an equal footing with “true” PNOs. This construction greatly simplifies the code development. As usual, only PNOs with occupation number  $\bar{n}_a^{ij}$  greater than  $T_{\text{CutPNO}}$  are included into the CC calculation. The energy of the neglected PNOs, calculated as the difference between pair energy in MO basis and truncated PNO basis, are stored and added as a correction at the end of the calculation as in the single-reference case.<sup>26</sup>

Once the PNOs have been obtained, the integrals are transformed to the PNO basis as in the single-reference case.

**C. Cluster Equations for LPNO-MkCCSD.** The LPNO-MkCCSD cluster equations for monoexcited amplitudes are formally identical to the canonical method

$$\langle \Phi(\mu)_i^a | e^{-T(\mu)} H e^{T(\mu)} | \Phi(\mu) \rangle C_{\mu}^{\alpha} + \sum_{\nu \neq \mu} H_{\mu\nu}^{\text{eff}} C_{\nu}^{\alpha} \langle \Phi(\mu)_i^a | e^{-T(\mu)} e^{T(\nu)} | \Phi(\mu) \rangle = 0 \quad (12)$$

For double excitations, PNO indices replace the virtual indices  $a, b$

$$\langle \Phi(\mu)_{ij}^{\bar{a}_i \bar{b}_j} | e^{-T(\mu)} H e^{T(\mu)} | \Phi(\mu) \rangle C_{\mu}^{\alpha} + \sum_{\nu \neq \mu} H_{\mu\nu}^{\text{eff}} C_{\nu}^{\alpha} \langle \Phi(\mu)_{ij}^{\bar{a}_i \bar{b}_j} | e^{-T(\mu)} e^{T(\nu)} | \Phi(\mu) \rangle = 0 \quad (13)$$

Similarly to the canonical method, the “direct” terms  $\langle \Phi(\mu)_i^a | e^{-T(\mu)} H e^{T(\mu)} | \Phi(\mu) \rangle$  and  $\langle \Phi(\mu)_{ij}^{\bar{a}_i \bar{b}_j} | e^{-T(\mu)} H e^{T(\mu)} | \Phi(\mu) \rangle$  are identical to single-reference residual calculated using the amplitudes for the  $\mu$ th reference. However, the actual working equations of the LPNO method differ considerably from the canonical ones; detailed expressions can be found in refs 27 and 28. Compared with LPNO-CCSD, the use of overlapping orbital windows requires small changes in the implementation for terms calculated in the AO basis.

The coupling terms in the  $T_1$  cluster equations are identical to canonical MkCC because the singles are defined in the canonical MO basis.

$$\langle \langle \Phi(\mu)_i^a | e^{-T(\mu)} e^{T(\nu)} | \Phi(\mu) \rangle \rangle = \Delta t_i^a(\nu/\mu, \mu) \quad (14)$$

where

$$\Delta t_{i\dots}^a(\nu/\mu, \mu) = t_{i\dots}^a(\nu/\mu) - t_{i\dots}^a(\mu) \quad (15)$$

and  $t_{i\dots}^a(\mu)$  is the cluster amplitude corresponding to the  $\mu$ th reference. The amplitude  $t_{i\dots}^a(\nu/\mu)$  is equal to the corresponding amplitude for the  $\nu$ th reference if orbitals  $i\dots$  are all occupied and orbitals  $a\dots$  all unoccupied for both  $\Phi_{\mu}$  and  $\Phi_{\nu}$  or zero otherwise.

The coupling terms in the  $T_2$  equation can be expressed in the PNO basis as

$$\langle \langle \Phi(\mu)_{ij}^{\bar{a}_i \bar{b}_j} | e^{-T(\mu)} e^{T(\nu)} | \Phi(\mu) \rangle \rangle = \Delta t_{ij}^{\bar{a}_i \bar{b}_j}(\nu/\mu, \mu) + \frac{1}{2} P(ij) P(ab) \Delta t_i^{\bar{a}_i}(\nu/\mu, \mu) \Delta t_j^{\bar{b}_j}(\nu/\mu, \mu) \quad (16)$$

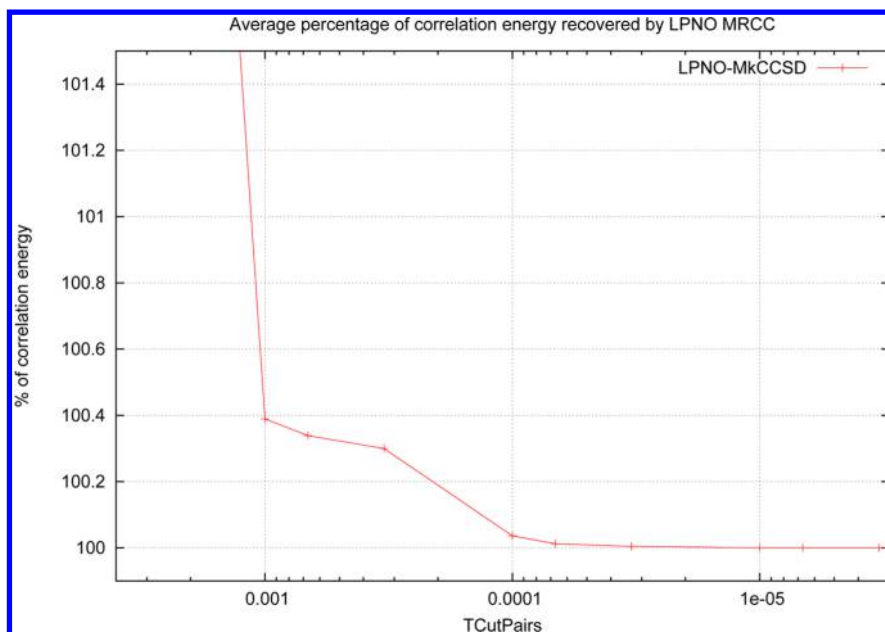
where the  $T_1$  amplitudes with PNO virtual index  $t_i^{\bar{a}_i}(\mu)$  are obtained by transforming the  $T_1$  amplitudes  $t_i^a(\mu)$  to the PNO basis of the corresponding  $ij$  pair.

The matrix elements of the effective Hamiltonian are formally identical to the canonical MRCC method

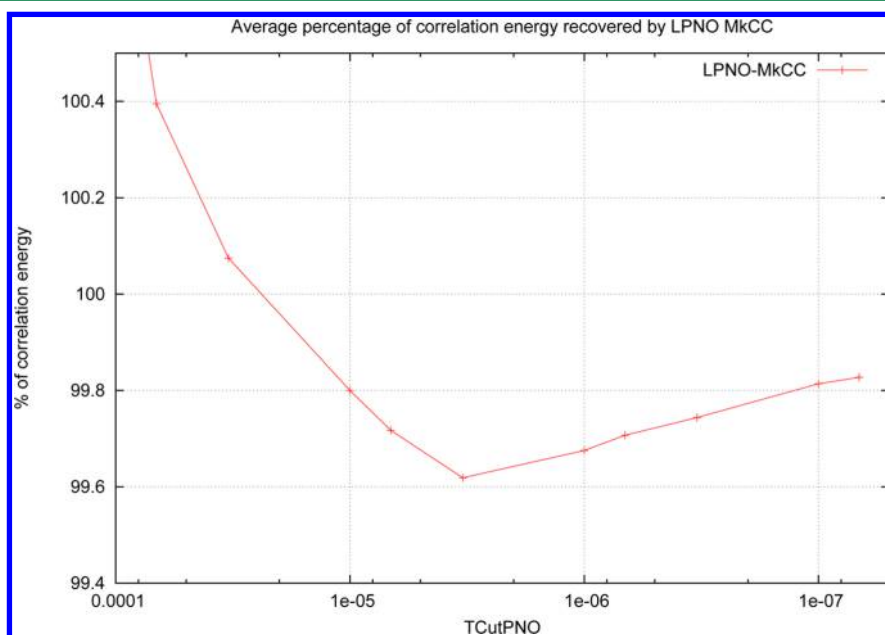
$$H_{\mu\nu}^{\text{eff}} = \langle \Phi(\mu) | \hat{H}^{\text{eff}} | \Phi_{\nu} \rangle = \langle \Phi(\mu) | \hat{H} | \Phi(\mu) \rangle \delta_{\mu\nu} + \langle \Phi(\mu) | \hat{H}_N(\nu) e^{\hat{T}(\nu)} | \Phi_{\nu} \rangle_C \quad (17)$$

For the diagonal elements, they can be interpreted as energy of the  $\mu$ th reference using the routines to calculate correlation energy from the single-reference code, along with the perturbative correction for neglected pairs and PNOs. The off-diagonal elements, for references that differ by up to a double excitation, can be picked up from the  $T_1$  and  $T_2$





**Figure 2.** Average percentage of correlation energy of TME as a function of  $T_{\text{CutPairs}}$ .



**Figure 3.** Average percentage of correlation energy of TME as a function of  $T_{\text{CutPNO}}$ . Calculated in cc-pVTZ basis set.

amplitude equation residuals corresponding to the respective internal amplitude.

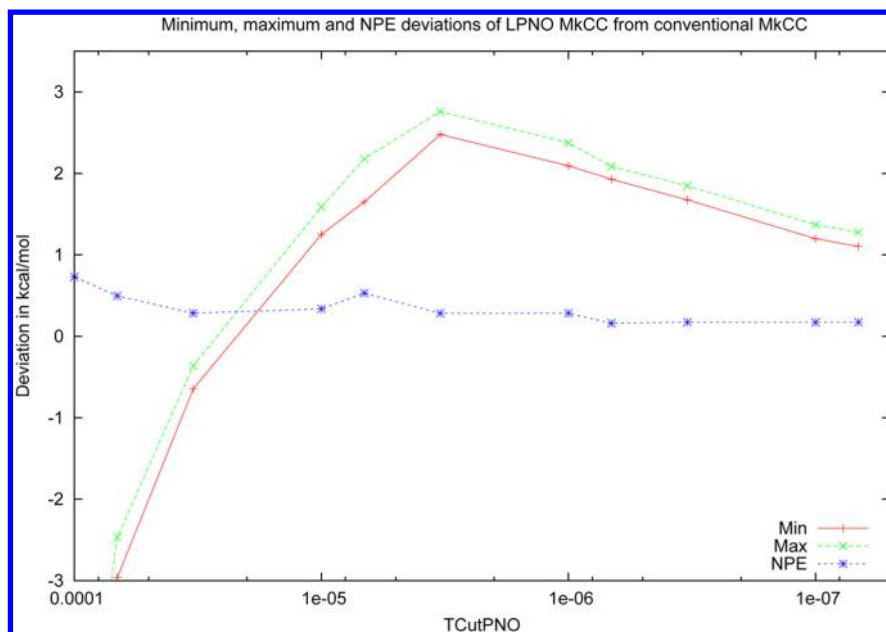
The obtained PNOs are recanonicalized to obtain orbital energies for the denominators in cluster equations. This represents a potential problem because again the orbitals are not canonical with respect to all references. In practice, we make recanonicalize the orbitals with respect to one of the references. This relies on the fact that the residuals, which are converged to zero, are constructed from molecular orbital representation of the Fock matrix, and the diagonal Fock matrix elements in PNO basis are used only for denominators. It was verified that the results of both LPNO-MkCCSD and LPNO-BWCCSD are independent of these denominators as long as the cluster equations are converged.

### III. RESULTS AND DISCUSSION

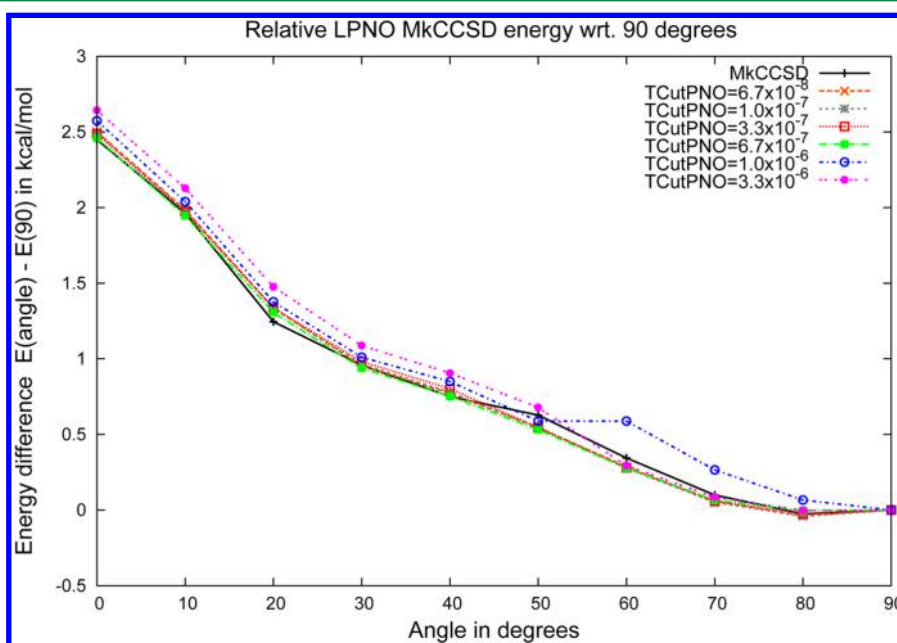
In all our calculations, the PNO cutoffs were left at their default values identical to the single-reference method, unless otherwise noted.  $T_{\text{CutMKN}}$  was left at 0.001 throughout. 1s orbitals on non-hydrogen atoms were excluded from correlation treatment.

**A. Tetramethyleneethane.** The calculations of tetramethyleneethane (TME) by LPNO-MkCCSD method were performed in the cc-pVTZ basis set.<sup>116</sup> The model space consisted of two references: HOMO<sup>2</sup> LUMO<sup>0</sup> and HOMO<sup>0</sup> LUMO<sup>2</sup> built from the canonical HF orbitals. The geometries were taken from ref 83. The dihedral angle was varied between 0° and 90° with a step of 10°.

First, the dependence of the LPNO MRCC energies on the remaining two cutoff parameters,  $T_{\text{CutPNO}}$  and  $T_{\text{CutPairs}}$ , was



**Figure 4.** Minimum and maximum deviations and nonparallelity error of LPNO-MkCCSD of tetramethylethane with respect to canonical MkCCSD as a function of  $T_{\text{CutPNO}}$ . Calculated in cc-pVTZ basis set.



**Figure 5.** Relative energies of TME with respect to 90° conformer as a function of the torsion angle. Calculated in cc-pVTZ basis set.

tested. In these tests, only one parameter was varied while the other one was kept fixed to the default value used in the single-reference LPNO CCSD ( $3.33 \times 10^{-7}$  for  $T_{\text{CutPNO}}$ ,  $1 \times 10^{-4}$  for  $T_{\text{CutPairs}}$ ).

Figure 2 shows the dependence of the fraction of correlation energy recovered by LPNO-MkCCSD on the  $T_{\text{CutPairs}}$  parameter. As the reference, the calculation with  $T_{\text{CutPairs}} = 0$  is used. The results show that the energy remains constant for up to  $T_{\text{CutPairs}} = 6.7 \times 10^{-6}$ . For higher values, the fraction starts to increase because of overestimation by the perturbative correction. There is a significant increase near  $T_{\text{CutPairs}} = 3.3 \times 10^{-4}$  to ca. 100.3% and another at  $3.3 \times 10^{-3}$  to 106.1%. At the default value, the fraction is on average 100.04%.

The dependence of average percentage of correlation energy recovered on the  $T_{\text{CutPNO}}$  is shown in Figure 3. The graph shows a very smooth, slowly changing curve. The trend here is similar to what has been reported for LPNO-CCSD. At the lowest level ( $6.7 \times 10^{-8}$ ), approximately 99.82% of the correlation energy is recovered, compared with 99.74% at the default value of cutoff. At very high levels of  $T_{\text{CutPNO}}$ ,  $10^{-4}$  to  $10^{-5}$ , more than 100% of correlation is recovered because of the overshooting of the perturbative correction for the neglected pairs and PNOs.<sup>27</sup>

However, these are only averaged percentages, and variation of the performance along the rotational barrier needs to be studied. In Figure 4, the minimum and maximum deviations are shown, as well as the nonparallelity error (NPE, defined as the

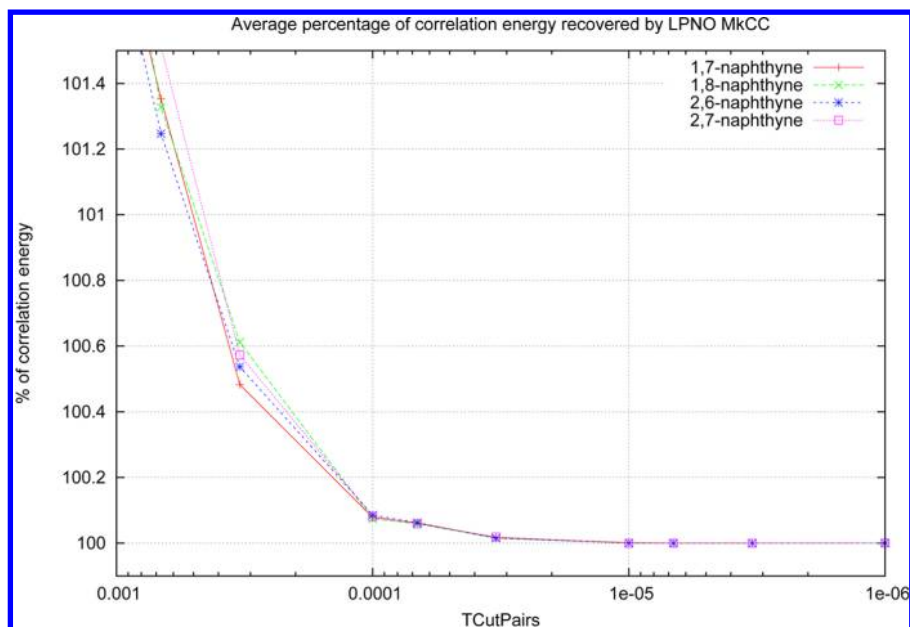


Figure 6. Percentage of correlation energy of naphthylenes as a function of  $T_{\text{CutPairs}}$ . Calculated in cc-pVTZ basis set.

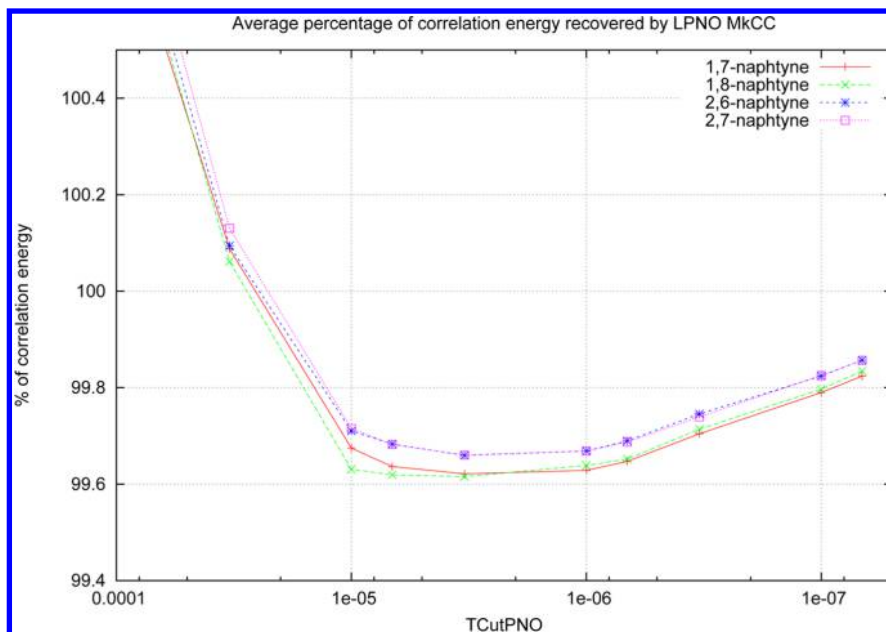


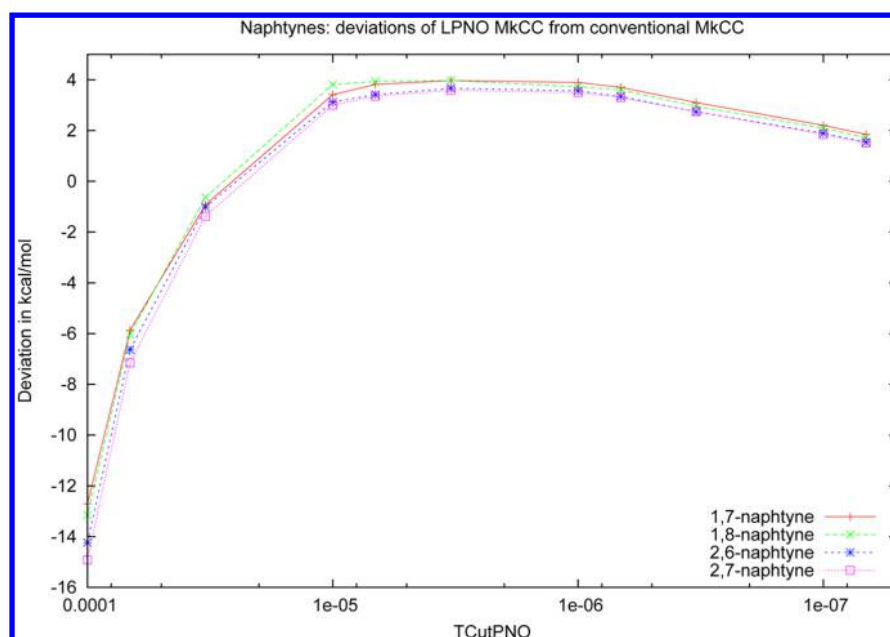
Figure 7. Percentage of correlation energy of naphthylenes as a function of  $T_{\text{CutPNO}}$ . Calculated in cc-pVTZ basis set.

difference between maximum and minimum deviation along the potential curve). The results are again highly satisfactory, with NPE converging smoothly to about 0.2 kcal/mol.

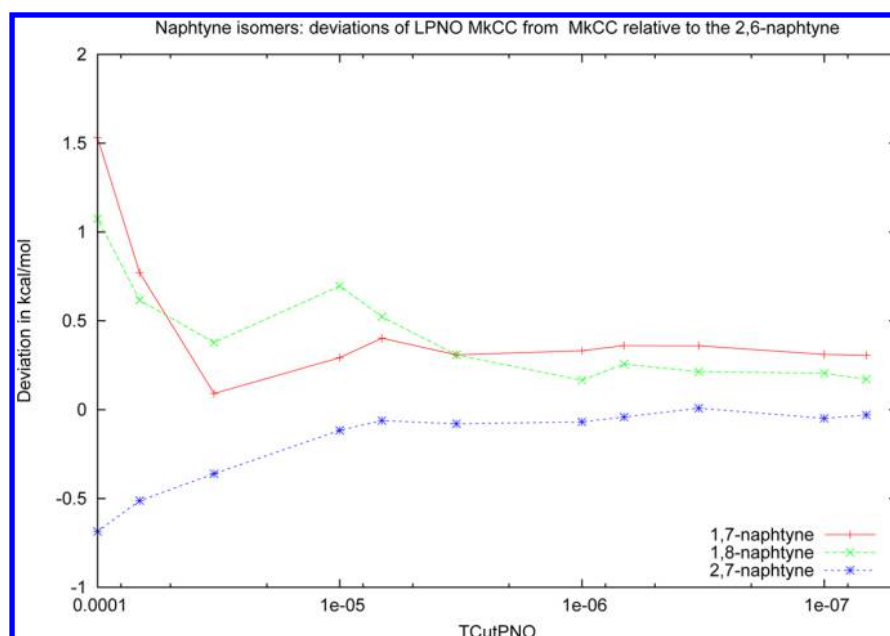
Although the absolute energies of the canonical MRCC method are not fully recovered by the LPNO version, the situation is much better for the relative energies, which are chemically relevant. Figure 5 shows the relative energies of TME with respect to its 90° twisted conformation. Clearly, even for larger cutoff values, the errors in relative energies are well below 0.5 kcal/mol along the whole curve.

Because the MkCC method is not invariant with respect to rotations of active orbitals and previous study<sup>97</sup> found a superior performance with localized active orbitals, we have performed analogous calculations in localized active orbitals for the TME molecule. There was no significant impact of the

orbital localization on the efficiency of the calculation in terms of the number of required PNO pairs (decrease from 31 to 32 to 28–30 at the default  $T_{\text{CutPNO}}$ ); however, we had to use four reference configurations, making the calculation more expensive. The percentage of correlation energy (with respect to canonical calculation with the same localized active orbitals) is 99.7–99.8% along the twist angle curve, which is comparable to 99.8% for canonical active orbitals. The results are significantly more dependent on the twist angle (0.1% versus 0.01%), which might be due to the somewhat inadequate weighting of reference configurations in this case; here, 4 references including open shell determinants had to be used and two of them have small weight in the wave function, while constant weighting is used in the density matrix calculation for PNOs. Another effect could be the contributions of discarded PNOs to



**Figure 8.** Deviations of LPNO-MkCCSD energies of naphthynes from canonical MkCCSD as a function of  $T_{\text{CutPNO}}$ . Calculated in cc-pVTZ basis set.



**Figure 9.** Deviations of energy differences between 2,6-naphthylene and the remaining three isomers from canonical MkCCSD as a function of  $T_{\text{CutPNO}}$ . Calculated in cc-pVTZ basis set.

off-diagonal elements of effective Hamiltonian (which is presently not implemented), because in the localized active orbitals the absolute values of the off-diagonal elements are much smaller (by 2 orders of magnitude) and the neglected portion thus becomes relatively more important. We plan a detailed investigation of these effects in a future work.

Because the BWCCSD has been found to provide a good description of this system as well, LPNO-BWCC was also employed. The results are similar to those of LPNO-MkCC. At the LPNO-BWCC level, slightly more correlation was recovered (99.79%) and the NPE error with respect to canonical BWCC was approximately 0.1 kcal/mol. Using the a posteriori corrected LPNO-BWCC, the performance was

somewhat worse: 99.69% of correlation energy was obtained using default cutoffs, and the NPE was 0.3 kcal/mol.

**B. Isomers of Naphthynes.** Four isomers, 1,7-naphthylene, 1,8-naphthylene, 2,6-naphthylene, and 2,7-naphthylene, were studied at the LPNO-MkCCSD level in the cc-pVTZ basis set.<sup>116</sup> The geometries for single-point calculations, as well as results of canonical MkCCSD were obtained from ref 117. A CAS(2,2) active space was used for all the isomers. However, because of symmetry, all four references are needed only for 1,7-naphthylene, whereas just two references are required for the other three isomers.

First we investigated the percentage of correlation energy recovered as a function of the cutoff parameters. The setup was the same as in the case of TME. Figures 6 and 7 show the



fraction of correlation energy recovered by LPNO-MkCCSD as a function of  $T_{\text{CutPairs}}$  and  $T_{\text{CutPNO}}$ , respectively. For the  $T_{\text{CutPairs}}$  dependence, the results again show very small deviations from 100% up to the default  $T_{\text{CutPairs}}$  value of  $10^{-4}$ . The somewhat larger percentage at the default value, 100.08%, than in the case of TME corresponds to the larger size of the molecule. For larger values of the cutoff, the percentage increases significantly. The differences between the four isomers are rather small. As far as the  $T_{\text{CutPNO}}$  dependence is concerned, the curves have the typical shape with a minimum near  $T_{\text{CutPNO}} = 6.7 \times 10^{-6}$  and strong overestimation for very large values of the cutoff. At the default  $T_{\text{CutPNO}}$  value, 99.70–99.75% of correlation is recovered. The dependence is again very smooth for all four isomers.

In Figure 8, the deviations of total energies from canonical MkCCSD are presented. The deviations of the energy differences between 2,6-naphthylene and the three remaining isomers are presented in Figure 9. For all three isomers, the deviation is well below chemical accuracy: 0.4 kcal/mol for 1,7-naphthylene, 0.2 kcal/mol for 1,8-naphthylene, and less than 0.1 kcal/mol for 2,7-naphthylene. Furthermore, the dependence of the deviation on  $T_{\text{CutPNO}}$  is smooth and slow, and almost the same differences are obtained for  $T_{\text{CutPNO}}$  of  $10^{-6}$  or lower.

The four-reference character of 1,7-naphthylene represents also a test of the convergence of LPNO-MkCCSD. MkCC method can exhibit convergence problems when some of the  $C_\mu$  coefficients are small. In this case, the  $C_\mu$  coefficients for the monoexcited references are in the region of 0.05–0.09, which is high enough to have a considerable effect on energy but low enough to cause the convergence issues. The canonical MkCCSD calculations from ref 117 required more than 100 iterations to reach convergence of  $10^{-6}$  for the residuals scaled by  $C_\mu$ . Using LPNO-MkCCSD, we were able to converge the scaled residuals to  $10^{-7}$  in less than 25 iterations for all the values of  $T_{\text{CutPNO}}$ . The explanation is the dramatic reduction of the number of cluster amplitudes, yielding easier convergence.

**C.  $\beta$ -Carotene.** The calculations of  $\beta$ -carotene (Figure 10) are primarily motivated to test the limits of applicability of our

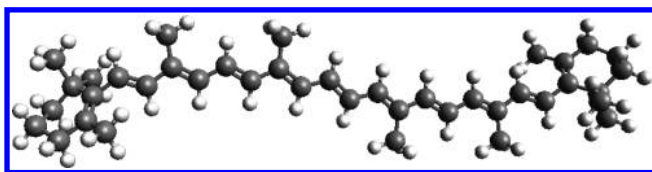


Figure 10.  $\beta$ -Carotene.

LPNO-MkCC implementation. Results of canonical MRCC methods are available in the 6-31G basis set; however, these calculations (performed using NWCHEM<sup>118</sup> in CAS(4,4) model

space with 20 symmetry allowed references) required a supercomputer with tens of thousands of cores.<sup>91,93,117,119,120</sup>

For LPNO-MkCC, we used the same geometry as in the previous calculations. Apart from 6-31G as before, cc-pVDZ and cc-pVTZ were also employed. 6-31G and cc-pVDZ calculations were performed on a single core with only 6 GB of memory; for cc-pVTZ, the memory was extended to 17.5 GB. However, the model space in these calculations was reduced to the two symmetry-allowed references from a CAS(2,2) space, which was primarily motivated by the fact that so far the expressions for effective Hamiltonian matrix elements for mutually tri- and tetra-excited references are not implemented in ORCA.

The LPNO-MkCC energies are listed in Table 1. The calculation in 6-31G basis required less than 1 day of CPU time; the cc-pVDZ calculation required approximately 4 days. The difference between cc-pVDZ and 6-31G energies is ca. 2.5 hartree for total energy and 2 hartree for correlation energy. In light of this finding and also based on the experience from previous test systems, it is clear that the error caused by the LPNO treatment is orders of magnitude smaller than the basis set error for total energies and only very close to the basis set limit will it start to be comparable. In both cases, approximately 20 iterations were needed to converge the cluster amplitudes to  $10^{-7}$ .

To test the limits of applicability further, we performed also a calculation in cc-pVTZ basis set (1984 basis functions). Again, one CPU was used, but the memory was extended to 17.5 GBytes and the RIJCOSX approximation was used for SCF. The calculation took approximately 4 weeks to converge to  $10^{-5}$ , with half of the time corresponding to generation of PNOs and PNO transformation and half to 14 iterations of cluster equations. Although the average number of PNOs per pair is increased only to 29, the computational cost of the  $O(n^4)$  and  $O(n^5)$  steps becomes dominant. As a result, we conclude that this system size is on the limit of applicability of the method and a DLPNO treatment would be greatly beneficial here.

For comparison, we include also results of LPNO-BWCCSD with and without a posteriori correction. There is a significant discrepancy between the multireference character obtained by the different MRCC approaches. At the LPNO-MkCCSD level, the  $C_\mu$  coefficient is 0.145 for 6-31G and 0.130 for cc-pVDZ basis set, which is high enough to rationalize a multireference treatment. In contrast, at BWCCSD the multireference character is negligible and the use of a multireference method is not justified. The a posteriori correction increases the multireference character considerably, but it still lies below the MkCC level. It is also rather untypical that the a posteriori corrected LPNO-BWCCSD energy lies above LPNO-

Table 1. Results of LPNO-MRCC Calculation of  $\beta$ -Carotene

method	basis	total energy (hartree)	correlation energy (hartree)	$C_\mu$ coefficients	$N_{\text{KeptPairs}}/N_{\text{Pairs}}$	$N_{\text{PNO}}$ per pair
LPNO-MkCCSD	6-31G	−1550.55955	−3.95268	−0.9890 0.1455	2889/23653	14
LPNO-BWCCSD	6-31G	−1550.55464	−3.94776	−0.9998 0.0168	2889/23653	14
LPNO-BWCCSD ap <sup>a</sup>	6-31G	−1550.55744	−3.95057	−0.99675 0.0806	2889/23653	14
LPNO-MkCCSD	cc-pVDZ	−1553.16235	−5.84463	−0.9915 0.1299	3197/23653	21
LPNO-BWCCSD	cc-pVDZ	−1553.15851	−5.84079	−0.99996 0.0089	3197/23653	21
LPNO-BWCCSD ap <sup>a</sup>	cc-pVDZ	−1553.16052	−5.84280	−0.9979 0.0655	3197/23653	21
LPNO-MkCCSD	cc-pVTZ	−1554.61441	−6.90932	−0.9999 0.04679	3393/23653	29

<sup>a</sup>A posteriori corrected LPNO-BWCCSD.

MkCCSD. From this we conclude that LPNO-BWCCSD is not suitable for systems of this size because of its lack of size-extensivity, which is not adequately corrected by the a posteriori correction. The USS correction<sup>70–72</sup> might be able to recover the missing correlation energy more accurately, and its implementation in the LPNO-BWCCSD scheme is envisioned in the future.

It has to be acknowledged that the carotene molecule is not a typical multireference system, and the system was chosen only to demonstrate the limits of applicability of the LPNO methods. The CAS(2,2) model space here is too small for a quantitative application study. This becomes apparent when excitation energies (i.e., energy differences between the four electronic states within CAS(2,2) space) for the system are calculated. The LPNO-MkCCSD results in the cc-pVDZ basis are approximately 2.0, 3.4 and 4.6 eV; the first transition is significantly lower than the experimental value (2.61 eV).<sup>121</sup>

#### IV. CONCLUSIONS

We report the development of a local variant of Mukherjee's state-specific multireference coupled cluster method based on the pair natural orbital approach. The method has been implemented in the ORCA program, presently with restriction to single and double excitations. The Brillouin–Wigner SS MRCC method has been implemented as well.

We performed a numerical assessment of the LPNO-MkCCSD method on naphthylene isomers, tetramethylethane, and  $\beta$ -carotene molecules, where comparison with corresponding canonical MRCC results was possible. The results show that 99.7–99.8% of correlation energy was recovered with respect to the canonical MkCC method using the default cutoff parameters from single-reference LPNO-CCSD. Moreover, the errors of relative energies between different naphthylene isomers or along a potential energy curve of TME (with respect to the canonical method) are below 0.4 kcal/mol, i.e., safely within chemical accuracy, and they change very slowly with the cutoff parameters. The computational efficiency of our implementation of LPNO-MkCCSD in the ORCA program allows calculation of the  $\beta$ -carotene molecule (96 atoms and 1984 basis functions) on a single CPU core. In contrast, previous calculations of this system at the MRCC level were performed on supercomputers and only in 6-31G (472 basis functions).

The results are encouraging both for future chemical applications and for further development of the method, including a DLPNO generalization of the scheme.

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##### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was supported by the Czech Science Foundation (projects 208/11/2222 and 15-00058Y). F.N. gratefully acknowledges the Max Planck society, the RESOLV cluster of excellence (university of Bochum), and the DFG priority program SPP 1601 for financial support of this work. The collaboration was also supported by the DAAD/14/14 project. We thank Dr. Karol Kowalski and Dr. Jiří Brabec for providing

us with the results of canonical MRCC calculations and Dr. Frank Wennmohs for technical assistance with the ORCA program.

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