The 'tailored' CCSD(T) description of the automerization of cyclobutadiene

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ARTICLE INFO

ABSTRACT

An alternative route to extend the CCSD(T) approach to multireference problems is presented. The well-known defect of the CCSD(T) model in describing the non-dynamic electron correlation effects is remedied by 'tailoring' the underlying coupled-cluster singles and doubles (CCSD) approach and applying the perturbative triples correction to it. The TCCSD(T) approach suggested in the paper has the same computational demands as the CCSD(T) method, though being mostly free from its drawbacks pertinent to multireference (quasidegenerate) situations. To test the approach we calculate the potential energy surface for the automerization of cyclobutadiene where the transition state exhibits a strong multireference character.

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1. Introduction

Since the pioneering works of Bartlett and co-workers [1,2] the perturbative-triples corrected CCSD method in its contemporary form CCSD(T) [3], derived by Raghavachari et al., has become the 'golden' standard in electronic structure theory along with its generalization to non-RHF cases [4]. It has been shown that the method is capable of providing the so-called chemical accuracy (~1 kcal/mol) in different quantum-chemical calculations where the non-dynamic electron correlation effects are sufficiently small. Being conceptually simple and computationally highly scalable [5,6], the CCSD(T) approach is an excellent model for treating the dynamic electron correlation in medium sized molecular systems. However a well-known failure of the method in describing multireference (MR) problems has spawned a series of works committed to extending the single-reference (SR) CCSD(T) model to quasidegenerate phenomena where the non-dynamic and/or static electron correlation effects are significant. Such approaches include the CCSD(TQ$_f$) method [7], where a perturbative factorized-quadruples correction is added, the ΛCCSD(T) approach [8,9], where the left-hand eigenvector is used to improve the energy obtained, the renormalized and completely-renormalized CCSD(T) and CCSD(TQ$_f$) approaches [10,11], where a renormalization procedure is applied to correct the final energy, and this is not a complete list. Although these approaches have extended the applicability of the perturbative (T) correction to moderately quasidegenerate situations, they still fail when strong non-dynamic electron correlation effects are present.

From the other side, there has been a 'boom' in multireference coupled-cluster (MRCC) methodology. The MRCC methods are well suited to describe non-dynamic electron correlation effects whereas the dynamic electron correlation often requires a more complete treatment than offered by MRCC. This is especially true when small active spaces are used in MRCC calculations. To improve the description of dynamic electron correlation effects some type of perturbative (T) correction has been adopted by different MRCC methods. A (T) correction has been added to the two-determinant state-universal (SU) 2D-MRCCSD method [12], general state-universal (SU) MRCCSD method [13], the state-specific Mukherjee MRCCSD approach [14], the Brillouin-Wigner MRCCSD method [15], and the single-reference based RMRCCSD method [16]. Despite the relative success of such combinations the resulting MRCC approaches (which employ a (T) correction) are, in general, more computationally demanding than the CCSD(T) method itself.

Apart from the aforementioned theoretical routes we attempt to extend the CCSD(T) model to MR problems in the simplest possible way to preserve the original computational demands of the approach. The idea of such a correction is similar to that of correcting the CCSD approach by 'tailoring' the most important cluster amplitudes [17]. As this method has only singly and doubly excited clusters, it is computationally equivalent to the CCSD approach itself. Considering the improvement over the standard CCSD method by applying the (T) correction, we might also anticipate such an improvement for the TCCSD(T) model. At the same time, 'tailoring' the CCSD(T) approach is expected to extend its applicability to MR problems. In the next section we discuss the details of the TCCSD(T) method and its interconnections with other formalisms. The method is used to study the potential energy surface (PES) for the automerization of cyclobutadiene. A correct description of the

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transition state of this transformation has been a challenging quasidegenerate problem for many years [12–14,18–20].

2. Theory

The TCCSD(T) approach is based on the 'tailored' CCSD method [17] instead of the regular CCSD approach. A multireference problem under consideration is approximately split into two separate problems: (1) description of the non-dynamic (and/or static) electron correlation effects, and (2) description of the dynamic electron correlation effects. Providing that we have a particular determinant as the *Fermi vacuum*, the orbital space is divided into four parts: inactive occupied orbitals (inactive holes), active occupied orbitals (active holes), active virtual orbitals (active particles), inactive virtual orbitals (inactive particles). This is one of the standard classifications of orbitals in multireference theories (see Figure 1). Determinants obtained by all possible electronic excitations among the active orbitals (together with the determinant which defines the Fermi vacuum) span the so-called *reference space* (S_R) with a corresponding projector $\hat{P}$. Other excited determinants, limited to singles and doubles from any of the reference determinants, span the *external space* (S_E) with a corresponding projector $\hat{Q}$. By $\hat{Q}_2$ we will label a projector associated with a manifold of determinants from S_E that are single and double excitations from the Fermi-vacuum determinant. In particular, $\hat{Q}\hat{Q}_2\hat{Q} = Q_2$ (in SR theories, limited to single and double excitations, $\hat{Q} = \hat{Q}_2$). The projector associated with the Fermi-vacuum determinant will be designated as $\hat{P}_0$ (in SR theories $\hat{P} = \hat{P}_0$). An assumption is made that the reference space must be sufficiently complete to provide a qualitative zero-order description of the problem under consideration (non-dynamic electron correlation). The rest of the dynamic electron correlation is accounted for using the orthogonal complement to S_R and the power of the CC formalism. The division of excitations into 'internal' and 'external' is a rather standard concept [21,22].

In the TCCSD(T) model the non-dynamic electron correlation is accounted for by doing a Full CI calculation within the reference space only [17]. That is, we search for the eigenvectors of the normal-ordered Hamiltonian [23], $\hat{H}_N$, exclusively in the reference space S_R:

$$\hat{H}_N|C^{(n)}\rangle = E^{(n)}|C^{(n)}\rangle, \quad |C^{(n)}\rangle \in S_R, \tag{1}$$

where $|C^{(n)}\rangle$ is an nth eigenvector with an $E^{(n)}$ eigenvalue. One needs to select an electronic state of interest from the eigenset obtained. The corresponding active-space Full CI vector contains the major part of the information about the non-dynamic electron correlation
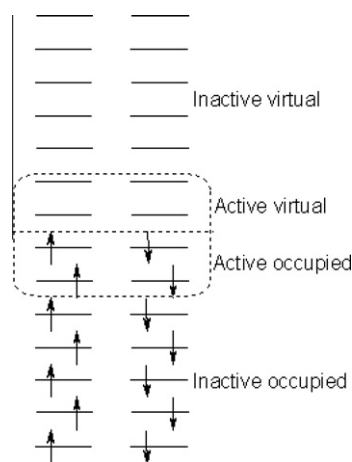

Figure 1. Orbital classification in multireference methods.

pertinent to the considered electronic state. Then intermediate normalization is applied to the chosen CI vector $|C^{(n)}\rangle$:

$$|C^{(n)}\rangle \rightarrow |0\rangle + \sum_{\substack{A_1 \\ I_1}} C_{I_1}^{A_1}|_{I_1}^{A_1}\rangle + \sum_{\substack{A_1 < A_2 \\ I_1 < I_2}} C_{I_1 I_2}^{A_1 A_2}|_{I_1 I_2}^{A_1 A_2}\rangle + \cdots$$
$$+ \sum_{\substack{A_1 < A_2 < \cdots < A_M \\ I_1 < I_2 < \cdots < I_M}} C_{I_1 I_2 \cdots I_M}^{A_1 A_2 \cdots A_M}|_{I_1 I_2 \cdots I_M}^{A_1 A_2 \cdots A_M}\rangle, \tag{2}$$

where $|0\rangle$ is the Fermi-vacuum determinant, $|_{I_1 I_2 \cdots I_k}^{A_1 A_2 \cdots A_k}\rangle$ is a k-fold excited determinant with respect to the Fermi vacuum, $C_{I_1 I_2 \cdots I_k}^{A_1 A_2 \cdots A_k}$ is the corresponding CI coefficient, and M is the maximal excitation rank in the reference space. Here I_k designates active holes, A_k – active particles. Small roman letters i_k/a_k will designate inactive holes/particles, respectively; small italic letters i_k/a_k will designate simply holes/particles, respectively. The weight of the Fermi-vacuum determinant in (2) is scaled to unity, appropriately modifying other coefficients of $|C^{(n)}\rangle$. We should note that due to the intermediate normalization, $\langle 0|C^{(n)}\rangle = 1$, it is important for the Fermi-vacuum determinant $|0\rangle$ to be the top-weighted one in the $|C^{(n)}\rangle$ expansion (2). Otherwise one should redefine it to be so.

The next important step is a similarity transformation of the normal-ordered Hamiltonian, $\hat{H}_N$:

$$\hat{H}_N^{ND} = e^{-\hat{T}_1 - \hat{T}_2}\hat{H}_N e^{\hat{T}_1 + \hat{T}_2} = \left(\hat{H}_N e^{\hat{T}_1 + \hat{T}_2}\right)_C, \tag{3}$$

where superscript ND stands for 'non-dynamic', subscript $_C$ means 'connected diagrams only', and $\hat{T}_1 = \sum_{\substack{A_1 \\ I_1}} T_{I_1}^{A_1}\hat{A}_1^+\hat{I}_1$, $\hat{T}_2 = \frac{1}{4}\sum_{\substack{A_1 A_2 \\ I_1 I_2}} T_{I_1 I_2}^{A_1 A_2}\hat{A}_1^+\hat{A}_2^+\hat{I}_2\hat{I}_1$ are the cluster operators called 'internal' because they are defined within the reference space S_R only. The amplitudes, $T_{I_1}^{A_1}$ and $T_{I_1 I_2}^{A_1 A_2}$, come from the active-space Full CI decomposition (2) according to the well-known conversion procedure:

$$T_{I_1}^{A_1} = C_{I_1}^{A_1}, \tag{4}$$
$$T_{I_1 I_2}^{A_1 A_2} = C_{I_1 I_2}^{A_1 A_2} - (T_{I_1}^{A_1} T_{I_2}^{A_2} - T_{I_1}^{A_2} T_{I_2}^{A_1}). \tag{5}$$

In such a way the original renormalized $|C^{(n)}\rangle$ vector (2) is approximated by an exponential-form vector:

$$|C^{(n)}\rangle \approx e^{\hat{T}_1 + \hat{T}_2}|0\rangle. \tag{6}$$

The similarity transformation (3) serves to '*hide*' *the non-dynamic electron correlation* into the Hamiltonian $\hat{H}_N^{ND}$. Then the dynamic electron correlation can be treated separately. In the original TCCSD approach [17] this is accomplished by including in the exponential ansatz all external (and semi-internal) singly and doubly excited clusters which correspond to the projector $\hat{Q}_2$. We go further and add the perturbative triples (T) correction which is highly efficient in accounting for the dynamic electron correlation. In the same time accounting for higher (triple) connected clusters makes the excitation space more symmetrical and balanced with respect to reference determinants, thus reducing the overestimated role played by the Fermi-vacuum determinant. This is a different strategy than one used in genuine MRCC methods where the excitation space is sufficiently complete from the beginning whereas the (T) correction serves to get the residue of the dynamic electron correlation. In the case of the TCCSD(T) method the perturbative triples correction is expected to play a much more important role because it directly brings into play the effects of important higher excitations absent in the parental TCCSD ansatz.

Having constructed the similarity-transformed Hamiltonian, $\hat{H}_N^{ND}$, one can proceed to solving the TCCSD equations [17]:

$$\forall \langle X| = \langle X|Q_2 : \langle X|e^{-\hat{t}_1-\hat{t}_2}\widehat{H}_N^{ND}e^{\hat{t}_1+\hat{t}_2}|0\rangle = 0,$$
$$E_{CC} = \langle 0|e^{-\hat{t}_1-\hat{t}_2}\widehat{H}_N^{ND}e^{\hat{t}_1+\hat{t}_2}|0\rangle, \tag{7}$$

where $\langle X|$ is an excited determinant from the conjugate external space, S_E, $\widehat{X}$ being the corresponding excitation operator, E_{CC} is the correlation energy, $\hat{t}_1 = \sum_{a_1 \atop i_1} t_{i_1}^{a_1}\hat{a}_1^+\hat{i}_1, \hat{t}_2 = \frac{1}{2!2!}\sum_{a_1,a_2 \atop i_1,i_2} t_{i_1 i_2}^{a_1 a_2}\hat{a}_1^+\hat{a}_2^+\hat{i}_2\hat{i}_1$ are the *external cluster operators* (completely active amplitudes are excluded by definition). These external amplitudes, $t_{i_1}^{a_1}$ and $t_{i_1 i_2}^{a_1 a_2}$, whose indices cannot contain all active labels, are to be determined. Eq. (7) are connected because the Hamiltonian $\widehat{H}_N^{ND}$ is built using only connected diagrams due to Eq. (3):

$$\forall \langle X| = \langle X|\widehat{Q}_2 : \langle X|\left(\widehat{H}_N^{ND}e^{\hat{t}_1+\hat{t}_2}\right)_C|0\rangle = 0,$$
$$E_{CC} = \langle 0|\left(\widehat{H}_N^{ND}e^{\hat{t}_1+\hat{t}_2}\right)_C|0\rangle. \tag{8}$$

Because $\hat{t}_k$ and $\widehat{T}_k$ operators commute one can use the regular CCSD solver keeping the internal amplitudes fixed on their CASFCI values (Eqs. (4) and (5)).

Having obtained the external amplitudes, $t_{i_1}^{a_1}$ and $t_{i_1 i_2}^{a_1 a_2}$, one can proceed to the final step and determine the perturbative triples (T) energy correction. The important restriction here is that the (T) correction is based upon solely the external cluster amplitudes, $t_{i_1}^{a_1}$ and $t_{i_1 i_2}^{a_1 a_2}$. This is consistent with one of the purposes of the perturbative triples correction, namely, an efficient account of the dynamic electron correlation. Hence the following energy correction terms, expressed diagrammatically as [1–3,24]

$$\tag{9}$$
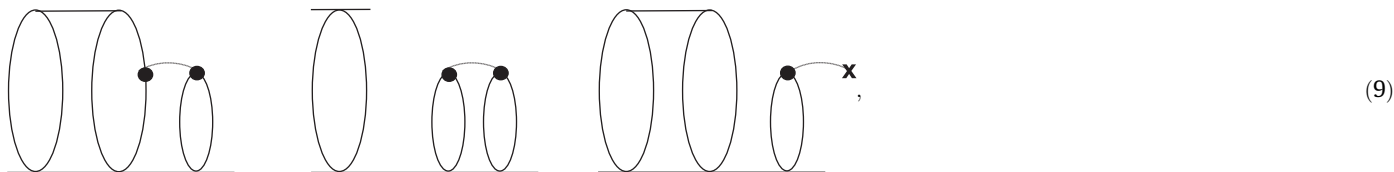
involve only external *t*-amplitudes (at least one index must be inactive).

According to the nomenclature of Li and Paldus the TCCSD(T) method suggested belongs to the so-called 'externally corrected' CC approaches [25] (the word 'externally' here has nothing to do with the external space S_E). In such approaches the information about the non-dynamic electron correlation is 'grabbed' from an external (usually not CC) calculation. Then the CC theory is employed for the dynamic electron correlation. One of the most successful externally corrected schemes is the RMRCCSD method of Paldus and Li [26], although other approaches exist [27]. In the RMRCCSD method a MRCI calculation is used to obtain values of higher-than-doubly excited clusters (triples and quadruples). Then the CCSD equations are solved in the presence of these higher-excited clusters that improve the values of the singly and doubly excited amplitudes and in turn the energy. Alternatively, the TCCSD approach does not deal with higher-excited clusters. Instead one insists on the correct structure of the reference part (2) of the total wavefunction. However the reference part is still approximated using only singly and doubly excited amplitudes (Eq. (6)) whose values are 'frozen'. Hence the TCCSD approach has the same computational cost as the CCSD method, the TCCSD(T) approach being of same cost as CCSD(T). Moreover there is an important consequence of having the reference part of the wavefunction frozen. Apart from other externally corrected approaches the TCCSD/TCCSD(T) methods can equally access excited electronic states of the same symmetry because the reference *T*-

amplitudes are frozen and characterize the electronic state of interest. In other words freezing the reference part of the wavefunction prevents a collapse to the ground electronic state. However there can still be some complications connected with the non-linear nature of the coupled cluster equations. The application of the TCCSD(T) scheme to excited states is under investigation. Let us also note that because of the use of solely connected diagrams and Full CI quantities for the reference part the TCCSD/TCCSD(T) methods are size-extensive.

One can also introduce an alternative method which utilizes the entire reference space explicitly. In such a scheme the approximation (6) would include up to 4-fold excited clusters from S_R (because this is the maximal excitation level which can show up in the CCSD equations):

$$|C^{(n)}\rangle \approx e^{\widehat{T}_1+\widehat{T}_2+\widehat{T}_3+\widehat{T}_4}|0\rangle, \tag{10}$$

where all $\widehat{T}$-operators act solely within the active space. This would correct the values of triples and quadruples from S_R which are approximated by cluster products in the TCCSD scheme (Eq. (6)), although both approaches are still 'unrelaxed'. Such an approach is somewhat closer to the RMRCCSD method [26], though the key difference, namely freezing the entire reference wavefunction part, still allows accessing both the ground and excited electronic states, preventing a collapse to the ground state. Relaxation of the reference-space amplitudes in such an approach would give an asymmetric (approximate) variant of the general SRMRCC method [28].

One of the drawbacks of 'unrelaxed' externally corrected schemes is that usually they do not reproduce the Full CI results in the limit unless the 'unrelaxed' (frozen) variables come from that Full CI. However if the corresponding approximate 'unrelaxed' quantities are reasonable this should not constitute a serious problem. In other words, the TCCSD/TCCSD(T) approaches should give accurate results when the reference coefficients (2) from the active-space-only Full CI calculation (*CASFCI*) do not differ significantly from those coming from the general Full CI calculation (*FCI*):

$$\langle C_{CASFCI}^{(n)}|C_{FCI}^{(n)}\rangle \approx 1, \tag{11}$$

where normalization to unity is applied to both vectors.

Therefore apart from the systematically convergent hierarchical methods, like CCSD, CCSDT, CCSDTQ, *etc.*, the 'externally corrected' approaches depend upon the quality of this external correction that is supposed to hide the effects of higher excitations into the lower ones (the final method relies on the correction-supplying method).

Potential disadvantage of the TCCSD approach is a noticeable orbital dependence because of the 'unrelaxed' nature of the reference [17]. Apparently it is crucial to properly select the active orbitals. Beside that, ozone molecule calculations, for example, favored CASSCF orbitals [29], although, in general, other orbital sets can be considered as well.

The TCCSD ansatz is also symmetry-broken as would be a SRCC based model. Because the TCCSD ansatz does not involve higher than double clusters, the exponential approximation, $e^{T_1+T_2}|0\rangle$, of

the true reference vector $|C^{(n)}\rangle$ (see Eq. (2)) can, in general, lead to noticeable symmetry contaminations, when the condition

$$\langle C^{(n)}|e^{\widehat{T}_1+\widehat{T}_2}|0\rangle \approx 1 \tag{12}$$

does not hold (both vectors are assumed to be normalized to unity). This is especially true when an open shell determinant is used as the Fermi-vacuum determinant, $|0\rangle$. Even if the energy is accurate enough, the corresponding wavefunction can, in principle, be rather poor in terms of molecular symmetry properties (spin and spatial). However it should still be essentially better than the CCSD wave function obtained for the same system (except for purely SR situations).

All the above considerations show that 'tailoring' is an effective patch to the CCSD and CCSD(T) models. Despite the formal drawbacks, the TCCSD(T) method can provide electronic energies of genuine MRCC quality as we demonstrate in the next section for the automerization of cyclobutadiene.

3. Numerical results

Recently noticeable attention has been paid to an adequate description of the automerization (see Figure 2) of cyclobutadiene [12–14,18–20] that has been a challenge for both theoretical and experimental chemists for a long time. The transition state of this transformation (geometrical square) has a pronounced multireference character (exact quasidegeneracy) making its description challenging for electronic structure methods. This is due to the existence of two equivalent configurations of double C–C bonds. The reference determinants fit the minimal (2,2) active space containing HOMO, LUMO and 2 electrons. In transition state calculations standard SRCC methods significantly underestimate the importance of the doubly excited reference determinant. This is the case where a MRCC formalism is required.

Another problem, pointed out by Paldus and Li [13], is connected with the use of restricted Hartree–Fock orbitals for the transition state description. This often results into an unphysical cusp in the PES if the underlying method is not sufficiently accurate (a similar example is ethylene twisted to 90% [30]). Those authors built a two-dimensional approximation to the PES of the cyclobutadiene automerization using a variety of SRCC and MRCC methods. In their work the sum of two C–C bond lengths was fixed at $2 \cdot 1.4668$ Å, while the C–H bond length was 1.079 Å ($\angle HCC = 135°$).

In our work the restriction on C–C bond lengths is relaxed adding one more degree of freedom, while the C–H bond length and H–C–C angles are kept the same. We calculate a 3-D PES in the standard spherical cc-pVDZ basis set (see Figure 3). The transition state as well as the minimum regions are then refined in the standard cc-pVTZ basis set. The calculations are done with the
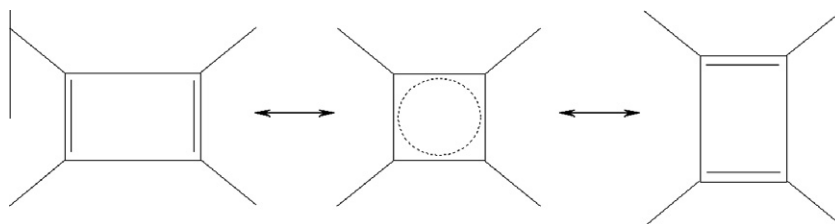

Figure 2. The automerization of cyclobutadiene. The left and right structures correspond to the degenerate minima. The structure in the middle corresponds to the 'multireference' transition state.
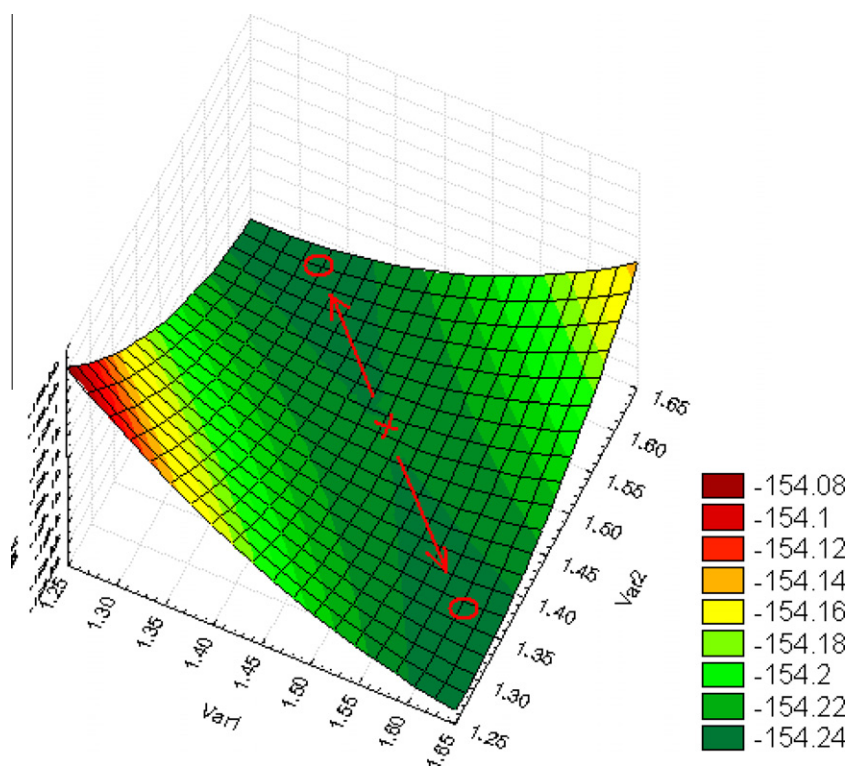

Figure 3. The potential energy surface for the automerization of cyclobutadiene calculated with the TCCSD(T) method in the spherical cc-pVDZ basis set (frozen core).

ACES III computer package [5]. The RHF orbitals are used and the core is frozen in all calculations. Though we employed the RHF orbitals the calculated PES does not contain 'sharply' visible cusps reflecting the correctness of the TCCSD(T) model. The PES is used to localize the minima and the transition state. These extreme points are determined by polynomial fitting of the corresponding PES regions. The corresponding pseudo-extreme geometries are:

- Minimum (rectangle): $R1_{C-C} = 1.37$ Å; $R2_{C-C} = 1.575$ Å(cc-pVDZ);$R1_{C-C} = 1.35$ Å; $R2_{C-C} = 1.58$ Å (cc-pVTZ).
- Transition state (square): $R_{C-C} = 1.47$ Å (cc-pVDZ); $R_{C-C} = 1.46$ Å (cc-pVTZ).

The automerization barrier height is estimated using cc-pVDZ and cc-pVTZ basis sets. The peculiarity of the barrier height calculation is that the barrier value is so small that any approximation can noticeably affect it (like bond length freezing, basis set, method, *etc.*). Though we put one more degree of freedom into consideration, the C–H bond length and H–C–C angle are still frozen. This makes comparison of the barrier height, obtained with different methods and different approximations to geometry, somewhat less rigorous. But it still permits a facile comparison of different methods. Thus, our aim is to achieve agreement of the TCCSD(T) value with a range of the most accurate MRCC results available for the problem. The experimental value of the automerization barrier is believed to lie within the range of 1.6–10 kcal/mol [31].

Table 1 illustrates the results. One can see that the TCCSD(T) method significantly reduces the original CCSD(T) barrier height, the TCCSD(T) value being similar to the SUCCSD(T) one. Actually the absolute energies obtained with TCCSD(T) and SUCCSD(T) are also very similar (see Table 2). The latter approach is a genuine multi-state MRCC method with perturbative triples correction. As

Table 1
Automerization barrier heights in kcal/mol calculated with different methods in the spherical cc-pVDZ and cc-VTZ basis sets (geometry optimization does not necessarily correspond to the final *ab initio* level presented).

Method	cc-pVDZ, kcal/mol	cc-pVTZ, kcal/mol
CCSD	21.0	23.2
CCSD(T)	15.8	18.3
CR-CCSD(T)	18.3	–
ΛCCSD(T)	16.8	19.2
TCCSD	9.4	12.9
TCCSD(T)	4.6	7.0
2D-MRCCSD(T)[a]	6.6	–
SUCCSD(T)[b]	4.8	5.9
BWCCSD(T)(a.c.)[c]	6.1	7.0
BWCCSD(T)(i.c.)[c]	5.7	6.8
MkCCSD(T)[c]	7.8	8.9
RMRCCSD(T)[b]	7.2	9.5
SUCCSD[b]	7.0	8.7
BWCCSD(a.c.)[c]	6.5	7.6
BWCCSD(i.c.)[c]	6.2	7.4
MkCCSD[c]	7.8	9.1
RMRCCSD[b]	10.4	13.0
MRCISD[d]	7.3	8.4
MRCISD + Q[d]	7.6	8.8
MRAQCC[d]	7.7	8.9
DIP-EOM-CCSD	8.3	10.7
SS-EOM-CCSD[+2][e]	8.3	9.5
Experimental range	1.6–10[f]	

[a] Taken from Ref. [12] where a split-valence [3s2p1d/1s] basis set was used. The method is equivalent to SUCCSD, being an early application.
[b] Taken from Ref. [13].
[c] Taken from Ref. [14].
[d] Taken from Ref. [20].
[e] Taken from Ref. [19].
[f] Taken from Ref. [31].

Table 2
Electronic energies calculated with different (T)-corrected methods in the cc-pVDZ basis set. The values in parentheses are the deviations from the SUCCSD(T) values in mH. Geometries used in the SUCCSD(T) calculations are only slightly different from those used in other calculations (only 0.003 Å). Only significant energy digits are shown.

Method	Energy of the minimum, H/(mH)	Energy of the transition state, H/(mH)
SUCCSD(T)	−154.246/(0)	−154.238/(0)
TCCSD(T)	−154.244/(2)	−154.237/(1)
CCSD(T)	−154.242/(4)	−154.217/(21)
ΛCCSD(T)	−154.241/(5)	−154.214/(24)
CR-CCSD(T)	−154.235/(11)	−154.206/(32)

expected the TCCSD(T) results differ noticeably from the TCCSD values showing the significance of the (T) correction for externally corrected schemes. Actually the difference in absolute energy values is much more pronounced. One can notice that the perturbative (T) correction is less significant for genuine MRCC methods being almost negligible for the MkCCSD (Mukherjee MRCCSD method [32,33]). The value of 7.0 kcal/mol obtained with the TCCSD(T) approach falls in the middle of the experimental range (the zero-point vibrational energy correction would make it smaller). Other corrected single reference CCSD(T) approaches, like CR-CCSD(T) or ΛCCSD(T), do not improve upon the original CCSD(T) value. In particular, the tendency of ΛCCSD(T) to give the quasi-upper-bound description, usually useful for bond-breaking, works against the method in the current case. The double-ionization DIP-EOMCCSD method (CCSD for the ground state, up to $R_{i_1 i_2 i_3}^{a_1}$ term for excited states) is a potential approach to tackle multireference problems with the EOMCC formalism. Its results and generalization will be published elsewhere [30].

It is also interesting to compare the absolute energies given by (T)-corrected methods for the minimum and transition state. Table 2 provides these values calculated in the cc-VDZ basis set. The genuine MRCC SUCCSD(T) values taken from Ref. [13] are believed to be of the best quality (these values are estimated from Figure 3 of Ref. [13]). While the minimum energies are reproduced more-less satisfactory by all methods shown, the transition state description is absolutely not acceptable for the CCSD(T), ΛCCSD(T) and CR-CCSD(T) methods. One can see that the corresponding energy errors have the same magnitude as the calculated barrier height value itself, the error difference between the minimum and transition state calculations being of the same order. At the same time the TCCSD(T) energies are very close and perfectly 'parallel' to the SUCCSD(T) results (2 and 1 mH errors).

4. Conclusions

The applicability of the CCSD(T) approach to MR problems has been extended by 'tailoring' the underlying CCSD approach. The extension provides reciprocal gains: CCSD(T) benefits from TCCSD and TCCSD benefits from the perturbative triples correction (T). In particular, the (T) correction brings noticeable relaxation effects to the 'unrelaxed' TCCSD approach by more complete accounting for both the dynamic and non-dynamic electron correlation. Despite some formal drawbacks the resulting TCCSD(T) method is believed to be capable of describing MR problems at the cost of CCSD(T). In particular, the barrier height of the automerization of cyclobutadiene calculated with the TCCSD(T) method agrees with the results obtained by genuine MRCC methods, demonstrating significant improvement over the CCSD(T) value. For this particular calculation the TCCSD(T) model essentially outperforms other corrected SR-(T) approaches. The TCCSD(T) value is also better than the

TCCSD one reflecting the importance of the perturbative (T) correction for the TCCSD approach.

Therefore 'tailoring' of the CCSD(T) approach presents a convenient way to extend the applicability of SR methods to MR problems. More extensive numerical studies are to be presented in the future.

Acknowledgements

References

[1] Y.S. Lee, S.A. Kucharski, R.J. Bartlett, J. Chem. Phys. 81 (1984) 5906.
[2] M. Urban, J. Noga, S.J. Cole, R.J. Bartlett, J. Chem. Phys. 83 (1985) 4041.
[3] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
[4] J.D. Watts, J. Gauss, R.J. Bartlett, J. Chem. Phys. 98 (1993) 8718.
[5] V. Lotrich et al., J. Chem. Phys. 128 (2008) 194104.
[6] T. Janowski, P. Pulay, J. Chem. Theory Comput. 4 (2008) 1585.
[7] S.A. Kucharski, R.J. Bartlett, J. Chem. Phys. 108 (1998) 9221.
[8] S.A. Kucharski, R.J. Bartlett, J. Chem. Phys. 108 (1998) 5243.
[9] A.G. Taube, R.J. Bartlett, J. Chem. Phys. 128 (2008) 044110.
[10] K. Kowalski, P. Piecuch, J. Chem. Phys. 113 (2000) 18.
[11] K. Kowalski, P. Piecuch, J. Chem. Phys. 113 (2000) 5644.
[12] A. Balkova, R.J. Bartlett, J. Chem. Phys. 101 (1994) 8972.
[13] X. Li, J. Paldus, J. Chem. Phys. 131 (2009) 114103.
[14] K. Bhaskaran-Nair, O. Demel, J. Pittner, J. Chem. Phys. 129 (2008) 184105.
[15] O. Demel, J. Pittner, J. Chem. Phys. 124 (2006) 144112.
[16] X. Li, J. Paldus, J. Chem. Phys. 124 (2006) 174101.
[17] T. Kinoshita, O. Hino, R.J. Bartlett, J. Chem. Phys. 123 (2005) 074106.
[18] P. Čársky, R.J. Bartlett, G. Fitzgerald, J. Noga, V. Špirko, J. Chem. Phys. 89 (1988) 3008.
[19] O. Demel, K.R. Shamasundar, L. Kong, M. Nooijen, J. Phys. Chem. A 112 (2008) 11895.
[20] M. Eckert-Maksic, M. Vazdar, M. Barbatti, H. Lischka, Z.B. Maksic, J. Chem. Phys. 125 (2006) 064310.
[21] P. Piecuch, N. Oliphant, L. Adamowicz, J. Chem. Phys. 99 (1993) 1875.
[22] P. Piecuch, S.A. Kucharski, R.J. Bartlett, J. Chem. Phys. 110 (1999) 6103.
[23] R.J. Bartlett, M. Musiał, Rev. Mod. Phys. 79 (2007) 291.
[24] S.A. Kucharski, R.J. Bartlett, J. Chem. Phys. 108 (1998) 5243.
[25] J. Paldus, X. Li, Collect. Czech. Chem. Commun. 68 (2003) 554.
[26] X. Li, J. Paldus, J. Chem. Phys. 107 (1997) 6257.
[27] P. Piecuch, R. Toboła, J. Paldus, Phys. Rev. A 54 (1996) 1210.
[28] D.I. Lyakh, V.V. Ivanov, L. Adamowicz, J. Chem. Phys. 122 (2005) 024108.
[29] O. Hino, T. Kinoshita, G. Kin-Lic Chan, R.J. Bartlett, J. Chem. Phys. 124 (2006) 114311.
[30] M. Musiał, A. Perera, R. J. Bartlett, submitted for publication.
[31] D.W. Whitman, B.K. Carpenter, J. Am. Chem. Soc. 104 (1982) 6473.
[32] U.S. Mahapatra, B. Datta, D. Mukherjee, J. Chem. Phys. 110 (1999) 6171.
[33] F.A. Evangelista, W.D. Allen, H.F. Schaefer III, J. Chem. Phys. 127 (2007) 024102.