

# Second-Order State-Specific Multireference Møller Plesset Perturbation Theory: Application to Energy Surfaces of Diimide, Ethylene, Butadiene, and Cyclobutadiene

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**Abstract:** The complete active space spin-free state-specific multireference Møller-Plesset perturbation theory (SS-MRMPPT) based on the Rayleigh-Schrödinger expansion has proved to be very successful in describing electronic states of model and real molecular systems with predictive accuracy. The SS-MRMPPT method (which deals with one state while using a multiconfigurational reference wave function) is designed to avoid intruder effects along with a balanced description of both dynamic and static correlations in a size-extensive manner, which allows us to produce accurate potential energy surfaces (PESs) with a correct shape in bond-breaking processes. The SS-MRMPPT method is size consistent when localized orbitals on each fragment are used. The intruder state(s) almost inevitably interfere when computing the PESs involving the breaking of genuine chemical bonds. In such situations, the traditional effective Hamiltonian formalism often goes down, so that no physically acceptable solution can be obtained. In this work, we continue our analysis of the SS-MRMPPT method for systems and phenomena that cannot be described either with the conventional single-reference approach or effective Hamiltonian-based traditional MR methods. In this article, we investigate whether the encouraging results we have obtained at the SS-MRMPPT level in the study of *cis-trans* isomerization of diimide ( $N_2H_2$ ), ethylene ( $C_2H_4$ ), and 1,3-butadiene ( $C_4H_6$ ) carry over to the study of chemical reactions. The energy surfaces of the double-bond flipping interconversion of the two equivalent ground and two lowest singlet state structures of cyclobutadiene have also been studied. All results have been discussed and assessed by comparing with other state-of-the-art calculations and corresponding experimental data whenever available.

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**Key words:** electron correlation; multireference perturbation theory; Rayleigh-Schrödinger expansion; state specific theory; energy surface; excited state; ionized state; barrier height; spectroscopic constants

## Introduction

It is now well recognized that the potential energy surfaces (PESs) play a central role in the theoretical description of molecular structures, properties, and reactivities. Along the PES, the correlation effects and the character of correlated wave functions change, which presents a challenge for approximate methods relying on error cancellation. A correct and balanced treatment of the interplay of dynamical (associated with the scattering of electrons at short distances) and nondynamical (associated with the overlap of near-degenerate atomic states) correlation effects is very crucial to get the correct PES.

In the study of PES over a wide range of reaction coordinates, the multireference formulation of perturbation theory (MRPT),

particularly in the version pioneered by Møller-Plesset (MP) is a very useful approach with low computational cost and hence frequently used.<sup>1</sup> There is extensive literature available on the problem of constructing MRPT methods of dynamic correlation on top of MR wave functions.<sup>2–4</sup> However, despite the progress of the MRPT achieved in the description of electronic states, there are still some problems associated with calculating the states that possess a strong MR character. The successful applicability to yield smooth PES via

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the traditional MRPT<sup>5</sup> approaches have been plagued by intruder states or intruder multiple solutions problems, occurring when some high-lying model functions come close in energy with some low-lying virtual functions at some point on a PES. Thus, they are not widely used among computational chemists. Although the use of incomplete model spaces or level shift technique reduces this danger, the situation becomes more complicated when these schemes have been admitted in the formulations. In view of these issues, much attention has been given to the so-called state-selective or state-specific (SS) MR approaches. In the past two decades, the interest in the development of SS methods for an accurate treatment of correlation effects within the MR framework has grown noticeably.<sup>6–12</sup> The MRPT-based SS approach permits performing calculations for one state at a time and provides a very efficient way of computing state energy *per se* and mapping PES of the target state. We should, however, mention the conceptually and very interesting second-order generalized van Vleck perturbation theory (GVVPT2) developed by Hoffmann and coworkers<sup>13</sup> using intermediate Hamiltonian strategy. It is distinct from both the usual SS-MRPTs and from state universal quasidegenerate perturbation theories (QDPT). It is a subspace-specific variant of MRPT and provides a way to consider more than one state at a time and is highly robust against intruders. Here, we also mention that the valence universal  $H^v$ -method by Chappard and Freed<sup>14</sup> alleviates the intruder state problem at second order simply by imposing a well-defined energy gap between the reference energies of the states corresponding to the model space and the states corresponding to the secondary space by forcing valence orbital degeneracy. However, small energy denominators or the equivalent effects transferred into the numerators appear again at the higher order realization of the method. Thus, sensitivity to intruder states is a central issue in perturbation theories and special attention needs to be paid. Although the CASPT2 and its various variants are now standard tools for many types of calculations, the CASPT technique is occasionally subjected to the intruder state problem and thus it is not always stable. In the GVVPT2 method, it is avoided by the collection of potential intruder states into the secondary model space. There are some common difficulties that most MRPT formulations are faced with; the fulfillment of the criterion of size consistency is one of the difficulties.<sup>15–17</sup> The various CASPT2,<sup>7</sup> MRMPPT,<sup>6</sup> and its multistate variant that is referred to as MCQDPT<sup>18</sup> methods by and large avoid the size-consistency error, but not rigorously. For avoiding the intruder state problem in Brillouin–Wigner (BW) multireference perturbation theory (BWPT), Hubač–Wilson and coworkers<sup>8,9</sup> paid the price of losing size extensivity. However, using a posteriori adjustment for lack of extensivity [based on a transition from a BW expansion to an expansion based on Rayleigh–Schrödinger (RS) perturbation theory] in second-order BW multireference perturbation theory, we arrive at a theory that can be seen to be size extensive. However, in general, this procedure does not ensure the removal of all the inextensive terms. Multiple iterations or the converged RS type of results will, however, unfortunately bring back the problem of potential intruders. We refer the interested reader to the original publications for further details.<sup>9</sup> The size extensivity is not manifested explicitly in GVVPT2<sup>13</sup> because of the explicit use of Hilbert space projectors. It should be noted that the size extensivity is not explicitly satisfied in the *p*-MCPT method.<sup>11</sup> Thus, the need to formulate multireference perturbative formalisms that can

generate a size-extensive and size-consistent expansion of energy yet avoiding intruders was very much warranted.

The formulation of complete active space (CAS)-based spin-free state-specific second-order multireference perturbation theory (SS-MRPT) proposed by Mukherjee and coworkers<sup>19,20</sup> is now recognized as a reliable and an efficient single root or SS-MRPT approach for studying real chemical problems with MR character. The basic features of SS-MRPT approach can be summarized as follows: (i) it is a genuine MR method that treats all references in the model space on an equal footing and hence is effective in the context of multireferential quantum chemical situations; (ii) it is devoid of the intruder state problem in a size-extensive manner; (iii) it is able to lead to size-consistent energies when a CAS as the model space and localized orbitals are used; and (iv) it is computationally cost effective. Hence, the SS-MRPT method<sup>19,20</sup> has enjoyed considerable success in the accurate prediction of energetics over the entire reaction path and calculations of spectroscopic constants of the system, which possess significant quasidegeneracy in addition to intruder effects (in small molecules) with a favorable trade-off between accuracy and low scaling (see Refs. 19–22). The SS-MRMPPT has been demonstrated to have theoretical and/or computational advantages over the currently widely used state-of-the-art MRPT methods.<sup>21</sup> The SS-MRMPPT method, however, is not invariant with respect to rotations of orbitals. Recently, the invariance property of the SS-MRPT method with respect to orbital rotations has been numerically tested by Mahapatra et al.<sup>23</sup> The accuracy and applicability of the SS-MRPT has been compared numerically on representative examples with other MRPT methods by Chaudhuri et al.<sup>24</sup> and Hoffmann et al.<sup>25</sup> They found significant difference in the performance of the MRPT methods if there is a swap in the dominant configuration in the reference function.

The SS-MRPT method has many versions depending on the nature of partitioning of the zeroth order Hamiltonian and expansion of perturbation series. In this article, we apply the multipartitioning MP version<sup>2</sup> of SS-MRPT, which stems from state-specific multireference coupled-cluster (SS-MRCC) formalism<sup>26</sup> (developed with a CAS) using RS expansion strategy (henceforth termed as SS-MRMPPT). The SS-MRMPPT method considered here is a second-order approach. Although, at a given truncation level, SS-MRPT is usually less accurate than the parent CC method, nevertheless, SS-MRPT has the advantage that it is less expensive than the full-blown SS-MRCC one.<sup>26</sup>

In this work, we used the SS-MRMPPT method to study complete torsional PES in the ground state of  $N_2H_2$  (1,2-diimide),  $C_2H_4$ ,  $C_4H_6$ , as well as cyclobutadiene and compared its performance against the state-of-the-art calculations provided by single-reference and multireference methods to judge the quality of our results. To the best of our knowledge, several theoretical studies have been devoted to them. Rotations around the double bond in ethylene or rigid rotation of the  $N_2H_2$  molecule (which are forbidden according to the Woodward–Hoffmann rules) are an important class of phenomena (in which the crossing of occupied and unoccupied orbitals of different symmetries occurs) that should be treated by multireference methods. We show that the SS-MRMPPT approach not only generates a smooth torsional PES in the ground state for  $N_2H_2$ ,  $C_2H_4$ , and  $C_4H_6$  systems but also gives the correct morphology of potential surface which in turn provides barrier height that is close to the corresponding high-level theoretical results. The intrinsically

multireference automerization of cyclobutadiene between the two rectangular structures in ground and two lowest excited singlet states along the automerization path has also been studied with the SS-MRMPPT method. In this article, we examine two aspects: the overall quality of the torsional PES and the barrier height of the systems considered here. As is well known, the quality of the computed potential surfaces and barrier height critically depends on the quality of the basis set used. Unfortunately, there are no “black box” basis sets that would guarantee chemical accuracy for an arbitrary system over the whole range of geometries. Thus, in the following sections, we focus our attention on the SS-MRMPPT results and compare them with the other methods for different basis sets.

As a complete description of the derivation and formalism of the SS-MRMPPT method has been given previously,<sup>19,21</sup> in this article, we have not discussed theoretical development of the SS-MRMPPT method. In Results and Discussion, we applied this scheme to calculate the energy surface of  $N_2H_2$ ,  $C_2H_4$ , and  $C_4H_6$  along the rotational mode, and the potential surface along the rectangular inter conversion mode in cyclobutadiene. The results demonstrate satisfactory behavior of the present approach when compared with other methods. The summary and concluding remarks are given in the last section.

## Results and Discussion

In this section, the performance of the SS-MRMPPT method has been studied on several examples which demand multireference description. Here, we study the torsional PES of  $N_2H_2$ ,  $C_2H_4$ , 1,3-Butadiene, and automerization PES of cyclobutadiene. The automerization of cyclobutadiene represents a typical test system of multireference methods. Isomerization due to rigid rotation is an interesting topic in structural chemistry. Although theoretical investigations of rigid rotation isomerization are easy to carry out, they can be hampered by the fact that the process at transition state invokes multireference effects (as they are typically intermediate between two different bonding situations) that are difficult to handle quantum chemically with standard methods. During the computation of torsional PES, the wavefunction changes character from being well described by a single configuration to containing several configurations as the transition state is approached. These systems have been often used to investigate the performance of different methods with drastically changing wave function character. Thus, the torsional PES calculation is a good example for testing the performance and accuracy of the SS-MRMPPT scheme. It would be ideal to compare SS-MRMPPT versus FCI values to gauge the quantitative accuracy of the methodology. However, FCI calculations with moderate sized system and basis sets are intractable with current computational resources. As a direct comparison to experiment is not always possible, considerations of several previous theoretical results should be taken into account when calibrating electronic structure models. To assess the comparative performances of electronic structure methods from a perfectly quantitative standpoint, one needs to use the same basis, the same kind of orbitals, and the same geometry. Thereby, one can avoid, or at least attenuate, differences stemming out of the theoretical artifacts while comparing the results. A rigorous comparison of our results with other methods considered here, however, is difficult due to the use of different

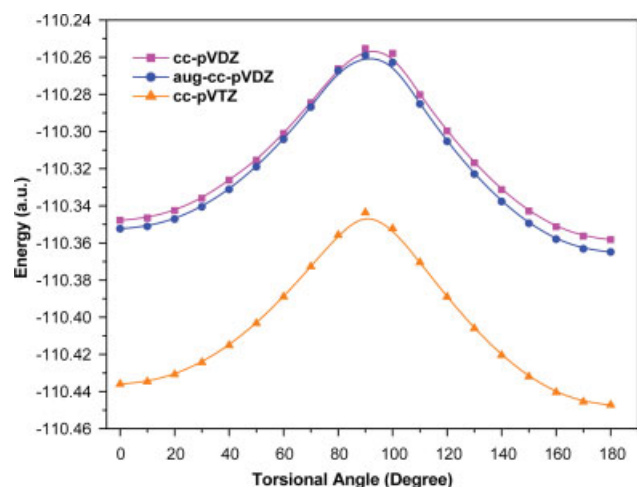
basis sets. For this reason, the quality of our comparison might not be appropriate. It should be noted that, in this article, our aim was not to look at our method only from the quantitative standpoint. Instead, we attempt to put forth the more qualitative aspect of the method in terms of its predictive power *vis-a-vis* other standard and established methods in routine use. In view of this, we have also collected the values provided by various methods with different basis and orbitals. To judge our results qualitatively, we also consider the results of various methods with different schemes just as a reference. In this article, we have also studied the barrier height [difference of the energy minima (stable conformer) and maxima (transition state) on the curves] and compared with experimental and previously published *ab initio* results to calibrate the present method. The procedure we have used involves running an initial mean-field calculation followed by SS-MRMPPT analysis. In this article, the reference space has been described by CAS(m, n) where “m” electrons are distributed among “n” active orbitals. The choice of chemically accurate and optimal CAS is an important aspect in correctly describing the energetics of molecules that may provide multiple reactions channels, and a different active space is needed for a reliable description of the energetics for each reaction channel. It is worthwhile to mention that the essence of the MR-based theory is to use as small an active space as possible.

The SS-MRMPPT program has been incorporated into the GAMESS(US)<sup>27</sup> program system and takes advantage of the procedures of the package. We freeze 1s orbitals on carbon in all correlated calculations unless stated otherwise.

### *cis-trans* Isomerization of Diimide ( $N_2H_2$ ) Molecule

The first application focuses on the rigid rotational reaction path and barrier height for  $N_2H_2$  molecule. Owing to its metastable nature, diimide is widely used as a reagent in stereospecific hydrogenation of double bond. The primary step in the process of such a reduction is the conversion of the stabler *trans*- $N_2H_2$  to the *cis*-conformer, which is believed to be the rate-limiting step of the reaction. This makes  $N_2H_2$  a system of widespread chemical interest. Besides, *cis-trans* isomerization of diimide ( $N_2H_2$ ) has been the issue of many experimental and theoretical investigations (see Refs. 28–30). References to most of the earlier theoretical works may be found in Ref. 28. The CASSCF calculations<sup>28</sup> predict three more transition states on the  $N_2H_2$  PES, in addition to the *trans-cis* and *trans-iso* isomerization processes. Recently, Varandas and coworkers<sup>31</sup> have published an article regarding *ab initio* calculations to determine the energy, geometry, and vibrational frequencies of all stationary points of the  $N_2H_2$  ground-state PES.

The rigid rotation of the  $N_2H_2$  system describes a two-dimensional MR problem in which the weights of reference functions change from 0 to 1 in a continuous manner. This rotation gives rise to a crossing of occupied and unoccupied orbitals of different symmetries. For the twisted configuration (with the dihedral angle  $\simeq 90^\circ$ ), the weights of both these configurations are equal owing to degeneracy. The ground-state configuration for the *cis*- (dihedral angle =  $0^\circ$ ) and *trans*- (dihedral angle =  $180^\circ$ ) conformers differ from one another by a double excitation. To get a qualitatively correct torsional PES for this rigid rotation, two closed shell-type configurations must be included in the reference space. In our calculations, we have used CAS(2,2) that is the smallest active



**Figure 1.** Rigid rotation (about the central N–N bond) potential energy surface for the  $N_2H_2$  molecule with SS-MRMPPT method. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

space that allows for a qualitatively correct treatment of torsional PES of  $N_2H_2$ . CAS(2,2) consists of two closed shell-type configurations and corresponds to the active orbital space spanned by two active orbitals (HOMO and LUMO). We use a fixed geometry for the molecule:  $r_{NN} = 1.2470 \text{ \AA}$ ,  $r_{NH} = 1.0300 \text{ \AA}$ , and  $\theta_{NNH} = 106.3^\circ$ . To illustrate the effect of basis sets on the  $N_2H_2$  PES computation, we have considered three types of basis sets, cc-pVDZ, cc-pVTZ, and aug-cc-pVDZ.<sup>32</sup> The SS-MRMPPT results for  $N_2H_2$  system given in the present work have been obtained by freezing N 1s core electrons.

We present the full torsional PES for  $N_2H_2$  as a function of the dihedral angle (reaction coordinate) in Figure 1, with all other degrees of freedom frozen at the geometry considered here. In fact, Figure 1 describes the reaction path connecting *trans*- $N_2H_2$  to the *cis* one. Inspection of the figure leads to various important conclusions. Although SS-MRMPPT/cc-pVDZ and SS-MRMPPT/aug-cc-pVDZ surfaces are quite close to each other, the difference between the two PESs with the PES obtained via SS-MRMPPT/cc-pVTZ scheme is noticeable on the scale shown in the Figure 1 that exhibits dependence on the basis sets used. Figure 1 displays that the torsional potential surface at  $90^\circ$  is shifted toward higher values of torsional angle with increase in the flexibility of the basis sets used. As shown in Figure 1, the morphology of SS-MRMPPT PES is very similar to the PES obtained via single-root MRBWCCSD method (see Fig. 1 in Ref. 33). We note that SS-MRMPPT yields a smooth and correct shape of the potential surface along the entire spectrum of torsional coordinates including nondegenerate zones as that of the full-blown single root MRBWCCSD. This is due to the fact that the SS-MRMPPT (and also MRBWCC one) method is able to switch itself from a nondegenerate to a quasidegenerate situation in a continuous manner, thus providing smooth energy surfaces. It is evident that at dihedral angle  $\simeq 90^\circ$ , there is no unphysical cusp for the SS-MRMPPT method similar to the single root BWMRCCSD scheme as it should be. In the work of Hubač and coworkers,<sup>33</sup> we found that the CCSD treatment fails completely to describe the transition state [twisted conformation

(about  $90^\circ$ )]. From the present calculations of Chaudhuri et al.,<sup>30</sup> it has been observed that the computationally demanding CCSD and/or CR-CC(2,3) approaches are not able to produce smooth torsional PESs for *cis-trans* conversions of  $N_2H_2$  as they exhibit a cusp near the transition state. Therefore, well-established single-reference-based methods are not capable of describing the PES even qualitatively because of an incorrect account of the nondynamical electron correlation at transition geometries. It should be noted that the CR-CC(2,3) method represents a very efficient alternative to the CCSD(T) scheme<sup>34</sup> to yield very good potentials for geometries with highly stretched bonds (see Ref. 35). In contrast to our SS-MRPT, the SU-MRCCSD method diverges in the nondegenerate region (around  $0^\circ$  and  $180^\circ$ ), in spite of yielding the correct shape of the barrier PES almost throughout the entire spectrum of torsional coordinates (see Ref. 33). This is attributed to the deficiency of the reference function in the sense that intruder effects are prominent in the nondegenerate regions. As the SU-MRCC theory treats more than one state at a time, any imbalance in the treatment of electron correlation in one state due to potential intruders may spoil the convergence behavior of the working equations of other states. Since the full-blown SU-MRCCSD suffers from this pitfall, its perturbative counterpart would definitely inherit the same problem. Thus, it is clear that for an accurate treatment of the torsional PES of  $N_2H_2$ , a SS multireference-based method is needed. According to Figure 1, we have observed that the SS-MRMPPT approach does not face this problem and gives the correct shape of the ground-state potential surface. The present calculation clearly demonstrates the strength of the SS-MRMPPT method.

The accuracy of the computed SS-MRMPPT potential surface may further be assessed by computing the barrier height. SS-MRMPPT relative energies of *trans* with respect to the *cis* and *transition state* of  $N_2H_2$  have been displayed in Table 1. There are several theoretical results (with different basis sets) that may serve for calibration purposes. As mentioned previously, our ambition is not to illustrate the comparison from quantitative point of view, but to compare the consistency of our SS-MRMPPT method with the previously reported standard single-reference and MR methods. The accuracy of the calculations of the present work have been assessed by comparing with the best theoretical results reported by Varandas and coworkers,<sup>31</sup> which describe the most extensive studies of stationary points on the global PES of  $N_2H_2$  studied till

**Table 1.** Barrier Height (kcal/mol) with respect to *trans*- $N_2H_2$ .

Basis	Method	TS- $N_2H_2$	<i>cis</i> - $N_2H_2$
cc-pVDZ	SS-MRPT	64.58	6.55
cc-pVTZ	SS-MRPT	64.24	6.98
aug-cc-pVDZ	SS-MRPT	66.44	7.84
aug-cc-pVQZ	MCSSCF <sup>a</sup>	61.03	4.60
aug-cc-pVQZ	MRCI <sup>a</sup>	56.39	5.03
aug-cc-pVQZ	MRCI+Q <sup>a</sup>	54.96	5.05
aug-cc-pVQZ	CASSCF <sup>a</sup>	62.93	6.68
cc-pVQZ	CCSD(T) <sup>a</sup>	–	5.21
6-31G*	G2M(MP2) <sup>a</sup>	48.86	4.81
aug-cc-pVTZ	IVO-MRMP <sup>b</sup>	48.45	5.87

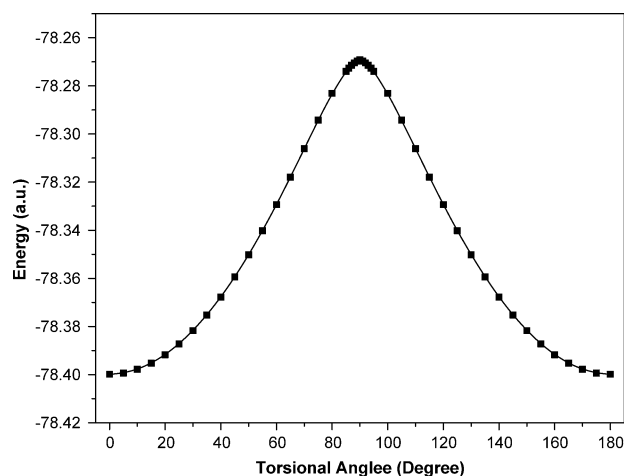
<sup>a</sup>Ref. 31.

<sup>b</sup>Ref. 30 with CAS(12,12).

date. In the table, we also include the result reported by Martin and Taylor<sup>29</sup> obtained at the level of the coupled-cluster, CCSD(T) method, with extrapolation to the basis set limit and inclusion of inner-shell correlation effects and anharmonicity in the zero-point energy. We have also considered the IVO-MRMP<sup>30</sup> results. From an inspection of Table 1, we find a good overall agreement between the results computed via SS-MRMPPT and previously published highly sophisticated theoretical results. Our results are satisfactorily close to the results of computationally highly expensive methods. At this point it should be noted that the CAS used in these methods by Varandas and coworkers is the full valence CAS that involves 12 correlated electrons distributed over 10 active orbitals (10,12) in contrast to our CAS(2,2). Note that the computational cost involved in the combined CAS(8,8)/(10,12) calculations is an order of magnitude higher than that of CAS(2,2) calculations. Nevertheless, the computationally full-blown MRCC methods are quite demanding in comparison with the MRPT methods. Results provided by the SS-MRMPPT method are not dramatically different for different choices of basis sets. Keeping these observations in mind, our SS-MRMPPT method is very effective to compute stationary points on N<sub>2</sub>H<sub>2</sub> PES without altering the active space. This aspect is quite important to calculate relevant energetics reliably when chemistry in polyatomic systems is considered.

#### Study of Torsional Energy Surface of Ethylene (C<sub>2</sub>H<sub>4</sub>)

The next system investigated in this article is ethylene, the simplest olefinic hydrocarbon, as its torsional barrier is still a issue of controversy. There have been extensive experimental<sup>36,37</sup> and theoretical studies on the C<sub>2</sub>H<sub>4</sub> system.<sup>25,38–43</sup> Several authors have studied the torsional energy surface of C<sub>2</sub>H<sub>4</sub> as an example of a true two-configuration MR problem. In spite of its very simple electronic structure, it exhibits some very interesting phenomena such as transition state and diradical. It is to be remarked that ethylene at 90° (the  $\pi$ -bond is broken and the  $\pi$  and  $\pi^*$ -orbitals become degenerate) can be considered as a simple diradical transition state. In view of this, the torsional potential surface of ethylene is a classical example of interplay of nondynamical and dynamical correlation effects. Thus, an accurate description of torsional barrier of the ethylene molecule needs a truly MR description that is based on a reference space which is able to provide an adequate, size-consistent, zero-order description. Various SR-based methods such as SCF, MP2, CCSD, and restricted DFT (BLYP and B3LYP) exhibit a cusp at 90° and this artifact has been corrected at the TCSCF level that yields a smooth surface around the barrier (see Ref. 41 for details). Krylov et al.<sup>41</sup> have found that CCSD(T) torsional PES also has a small cusp. Recently, Chaudhuri et al.<sup>30</sup> observed that the CR-CC(2,3) also exhibits a cusp for 90° as it is based on the single configuration. Thus, one may conclude that to get the correct shape of the torsional PES, inclusion of nondynamical correlation in an accurate manner is very crucial. Consequently, it provides a good probing ground for testing the efficacy of different methods in their capability to describe degeneracy ranging from quasidegeneracy in its transition configuration to the nondegenerate *cis/trans* configuration. Recently, Hoffmann et al.<sup>25</sup> have published a comparative study of SS-MRPT, GVVPT, and MCPT methods through the investigation of torsional PES of ethylene using CAS(2,2) and DZP basis. However, various benchmark studies of ethylene clearly illustrate

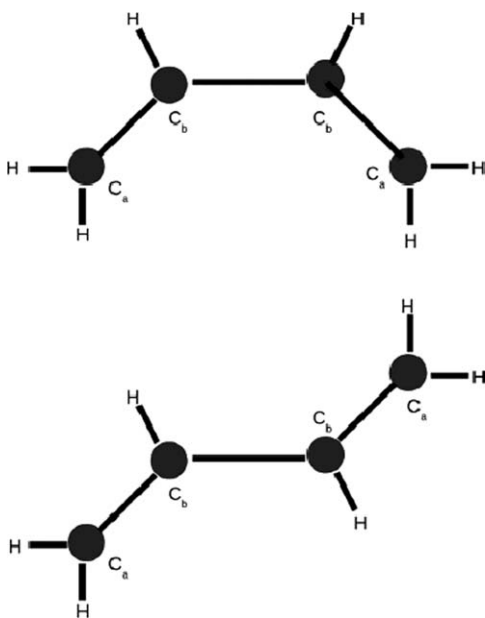


**Figure 2.** Rigid rotation (about the central C–C bond) potential energy surface for the C<sub>2</sub>H<sub>4</sub> molecule with SS-MRMPPT method.

that even FCI does not yield correct agreement with experimental data when used in conjunction with a small orbital basis set, for example, DZP. In the present contribution, we use CAS(2,2) [the active space consists of two orbitals ( $\pi$  and  $\pi^*$ ) and two electrons] and cc-pVTZ basis.<sup>32</sup> Thus, the calculation with this basis set is much more reliable than the DZP one. In this article, in addition to the complete torsional PES, we also compute barrier height. In our present calculation, the CH and CC bond lengths were fixed at the following values:  $R_{CC} = 1.3313 \text{ \AA}$ ,  $R_{CH} = 1.0720 \text{ \AA}$ , while the angle  $\angle HCH$  was fixed at the value of 121.48°. It should be noted that Hoffmann et al.<sup>25</sup> did not report the value of barrier height for internal rotation for ethylene molecule for which experimental value is available. In passing, we also mention that Pittner et al.<sup>43</sup> have presented a theoretical investigation of ethylene using their MR-BWCC method.

Figure 2 displays the profile of the required PES calculated at SS-MRMPPT level of theory as a function of the dihedral angle between two CH<sub>2</sub> groups. The figure clearly depicts the fact that the SS-MRMPPT surface is smooth and does not exhibit an unphysical cusp at twisted position even with smallest possible active space. Our SS-MRMPPT enjoys the advantage of describing the correct shape of torsional PES in C<sub>2</sub>H<sub>4</sub> as it has enough flexibility to treat the  $\pi^2$  and  $\pi^{*2}$  configuration on an equal footing and uses a unique active space throughout the entire energy profile. The morphology of the SS-MRMPPT torsional PES is very similar with TCSCF-CISD and VOO-CCD of Krylov and coworkers.<sup>41</sup> As that of Figure 3 of Ref. 42, the shape of the torsional surfaces provided by the SS-MRMPPT as well as MROPT(2) and MRCI+Q are very similar. It is worth noting that MCPT<sup>25</sup> torsional surface has a cusp, which is not there with the GVVPT2 method. This observation illustrates the fact that the MCPT2 theory is not a suitable one if there is a change in the dominant configuration in the zeroth order function.

Because of the unavailability of FCI for cc-pVTZ basis to judge the quality of the SS-MRMPPT torsional PES, we also evaluate the barrier height (energy difference between the *trans* and twisted conformers) and compared it with those obtained by standard theoretical methods and experimental results. We have already mentioned that



**Figure 3.** Structure of 1,3-butadiene (*cis* and *trans*).

the same basis set, the same set of orbitals, and same geometry should be used in all calculations to avoid, or at least attenuate to a considerable extent, the differences that originate from the theoretical artifacts while comparing the results. Here, we have assembled the results of different methods for different basis sets just as a matter of reference. The results of barrier height obtained by SS-MRMPPT and other methods along with the corresponding experimental value are given in Table 2. Perusal of the presented data shows that the energy barrier spans a small range depending on the method used, and a synchronized treatment of both dynamical and nondynamical correlation effects is very crucial to get the correct order barrier to rotation. The barrier to rotation for RHF and UHF methods are grossly overestimated and underestimated, respectively, because they completely lack the second important configuration. As far as barrier heights are concerned, although calculations done via CASSCF provide a smooth and correct shaped surface, it overestimates the barrier. SF-based DFT, OO-CCD, and VOO-CCD calculations also overestimate the barrier height. Comparing with the experimental barrier height, one can see that the SS-MRMPPT, MRMP/EN, and VOO-CCD values are only slightly overestimated in comparison with other methods. According to the table, the SS-MRMPPT appears to provide predictions of barrier height in quantitative agreement to those of the values of LDA, BP86, and FT97 published by Filatov and Shaik<sup>40</sup> as well as VOO-CCD/DZP and MRDCI results of Krylov et al.<sup>41</sup> It is interesting to note that the barrier height obtained via SS-MRMPPT method closely resembles the MRMP(2)/(3) and MREN(2)/(3) results (shown in Table 2) presented by Hirao and coworkers.<sup>42</sup> As shown in Table 2, the BP86, FT97, VOO-CCD/DZP, MRMP(2)/(3), MREN(2)/(3), and MRDCI results agree reasonably well with experimental results. The correspondence of the SS-MRMPPT result to experiment is also very good for this system, which implies a good performance of the SS-MRMPPT approach. Comparing the results obtained with the

other methods, we can draw conclusions similar to that in case of  $N_2H_2$ , that is, the torsional PES and barrier height of  $C_2H_4$  molecule obtained via SS-MRMPPT is good in a general sense.

#### Study of Internal Rotation Energy Surface of 1,3-Butadiene ( $C_4H_6$ )

Going a little further to a more complicated and chemically interesting example, we look at the calculation of the full torsional potential surface (due to the rotation around the central bond of the butadiene skeleton) of butadiene and of the implied barrier height to test the performance of the SS-MRMPPT method (Fig. 3). As the smallest conjugated polyene, the electronic structure of the ground state of 1,3-butadiene has received a great deal of experimental and theoretical attention.<sup>44–46</sup> Most theoretical studies have focused attention primarily on the planar and twisted minima, and less so on the surface connecting them. At the twisted position(s) (i.e., transition geometries), both reference configurations [ $(\pi)^2$  and  $(\pi^*)^2$ ] are exactly degenerate and have the same weight in the resulting wave functions. Moreover, the ground and the lowest triplet state states are nearly isoenergetic at the twisted configuration. Thus, to find a balanced description of the surface, both nondynamical and dynamical correlations need to be taken care. Thus, the molecule represents an excellent probing ground for testing the efficiency of SS-MRMPPT and various MR-based approaches in their ability to account for quasidegeneracy. In butadiene, twisting about the terminal  $C=C$  bonds does not by itself produce isomerization; however, this motion is used by butadiene as a first step toward

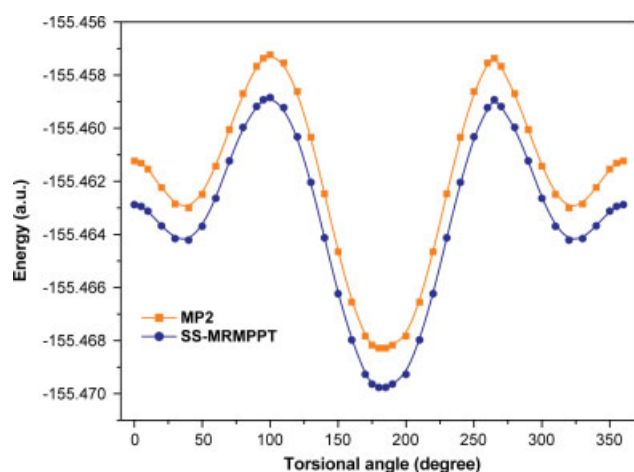
**Table 2.** Barrier Height (kcal/mol) of Internal Rotation for Ethylene.

Methods	Barrier height
SS-MRPTPT/cc-pVTZ	69.99
RHF/DZP <sup>a</sup>	109.77
UHF/DZP <sup>a</sup>	49.58
SF-BLYP/DZP <sup>a</sup>	90.16
SF-B3LYP/DZP <sup>a</sup>	86.24
SF-5050/DZP <sup>a</sup>	80.25
CASSCF/DZP <sup>a</sup>	78.40
R-OD/DZP <sup>a</sup>	90.17
U-OD/DZP <sup>a</sup>	72.64
R-VOD/DZP <sup>a</sup>	86.24
U-VOD/DZP <sup>a</sup>	72.41
VOO-CCD/DZP <sup>a</sup>	67.34
MRDCI/DZP <sup>a</sup>	62.72
LDA/TZ2P <sup>b</sup>	73.9
BP86/TZ2P <sup>b</sup>	67.1
FT97/TZ2P <sup>b</sup>	69.2
MRCI/cc-pVQZ <sup>c</sup>	67.9
MRCI+Q/cc-pVQZ <sup>c</sup>	67.0
MREN(2)/cc-pVQZ <sup>c</sup>	72.4
MREN(3)/cc-pVQZ <sup>c</sup>	65.5
MRMP(2)/cc-pVQZ <sup>c</sup>	65.0
MRMP(3)/cc-pVQZ <sup>c</sup>	65.8
MROPT(2)/cc-pVQZ <sup>c</sup>	65.6
Experiment	64.57, 59.72

<sup>a</sup>Ref. 41.

<sup>b</sup>Ref. 40.

<sup>c</sup>Ref. 42 and experiment in Ref. 36.



**Figure 4.** Rigid rotation (about the central C–C–C–C) potential energy surfaces for the  $C_4H_6$  molecule with SS-MRMPPT and single reference MP2 methods. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

*cis-trans* isomerization, as intersystem crossing produces ground-state molecules with substantial internal energy that can be used to overcome the barrier to isomerization. As that of  $C_2H_4$ , it exhibits a wide range of chemically interesting features such as transition states and diradicals. In the literature,<sup>45</sup> there is a large range of theoretical estimates of the barrier height available depending on the method considered, implying that the problem is not settled as yet. The results from the previously published theory predicts that the *trans* conformer is the most stable conformer in butadiene although the conformational preference of butadiene can be controlled by the placement of a suitable substituent. A full discussion can be found in Ref. 45.

Here, we use the active space consisting of two orbitals and two electrons, termed as CAS(2,2). The basis set is Dunning's correlation consistent cc-pVDZ basis set.<sup>32</sup> We use a fixed geometry for the molecule; i.e., remaining internal coordinates are fixed at the values, the bond lengths:  $C_aC_b = 1.4703 \text{ \AA}$ ,  $C_bC_c = 1.3287 \text{ \AA}$ ,  $CH = 1.0790 \text{ \AA}$ , and bond angles:  $\angle CCC = 123.93^\circ$  and  $\angle CCH = 121.59^\circ$ . Figure 4 shows a graph of the calculated energy versus dihedral angle ( $a - b - a - b$ ) for butadiene at the SS-MRMPPT level as obtained with cc-pVDZ basis using the RHF orbitals. We have also generated results using the SR-based MP2 technique. The shapes of the curves are apparently similar to the MP2/6-311\*\* one.<sup>45</sup> The figure clearly displays that the SS-MRMPPT and MP2 energy changes smoothly from one configuration geometry to another. There are no cusps at the transitions points. We can thus conclude that the SS-MRMPPT method perform well even in nondegenerate situations. The SS-MRMPPT figure also depicts a substantial energy difference between the *trans* and the *cis* conformers of butadiene (3.32 kcal/mol).

As a further test of the intrinsic robustness of our SS-MRMPPT formalism, we turn our attention to computations of the barrier height for the butadiene isomerization, yielding the results listed in Table 3. We should also mention, at least in passing, an accurate determination of the barrier height was not the aim of this study. Our result has also been compared with those available in the literature. The barrier height has been calculated by finding the difference

**Table 3.** Barrier Height (kcal/mol) for Butadiene.

Methods	Barrier height
SS-MRPTPT/cc-pVDZ	6.64
MP2/cc-pVDZ	6.42
MP2/6-311G <sup>***a</sup>	5.75
Observed <sup>b</sup>	7.16

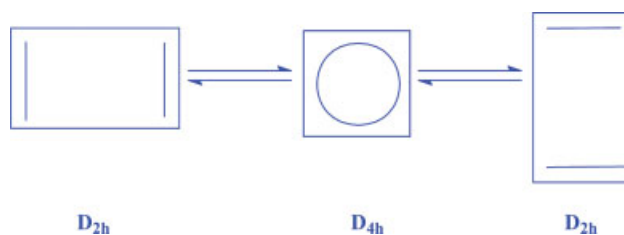
<sup>a</sup>Ref. 45.

<sup>b</sup>Ref. 46.

in the energy between the *trans* and the  $90^\circ$  dihedral angle conformer. There is a 6.64 kcal/mol barrier for interconversion of the two structures, *cis* and *trans* at the level of SS-MRMPPT/cc-pVDZ which is satisfactorily close to the observed value of 7.16 kcal/mol.<sup>46</sup> Thus, the  $\sim 6$  kcal/mol energy barrier separating the two conformers should represent a hindrance to their interconversion. We note that the SS-MRMPPT result for the barrier height is very close in proximity to those obtained at the MP2/6-311\*\* one<sup>45</sup> level (5.75 kcal/mol). Good correspondence of the performance of the single reference MP2 (which is devoid of nondynamical correlation) with the calculated barrier height of butadiene via SS-MRMPPT method confirms that the SS-MRMPPT method not only performs in situations posing nondegeneracies but also in the cases that bear pronounced quasi or strong degeneracy.

#### Automerization Potential of Cyclobutadiene

For a final illustration of robustness of the SS-MRMPPT method, we consider the study of bond-flipping automerization (which can be classified as second order in terms of the Jahn-Teller distortion) potential of cyclobutadiene involving interconversion of two equivalent  $D_{2h}$  structures via transition through square structure  $D_{4h}$  (Fig. 5), which continues to be a challenge for electronic structure methods. In the automerization barrier in cyclobutadiene, the transition structure has a diradical character. Cyclobutadiene is an example of an antiaromatic system, with two carbon-carbon single bonds and two double bonds. The experimental structure of cyclobutadiene is not available; however, there are many theoretical calculations. This highly reactive and short-lived system has been studied theoretically using various methods with different levels of sophistication.<sup>13,47–55</sup> The ground state of cyclobutadiene is found to be a closed shell singlet. It is well known that the lowest square singlet geometry actually represents the transition state for the isomerization reaction yielding two equivalent rectangular structures



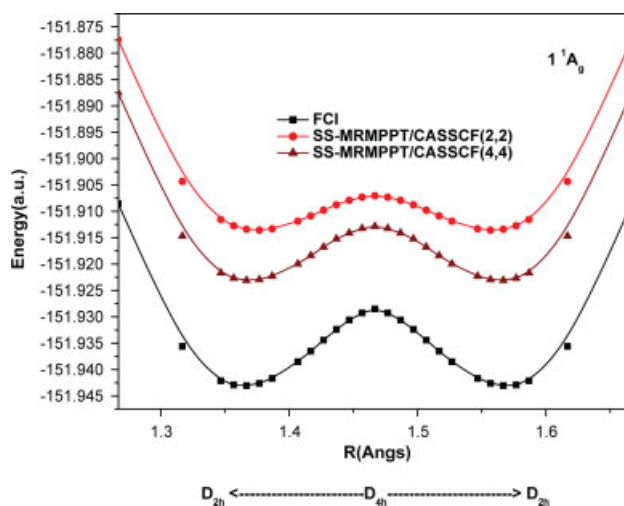
**Figure 5.** Automerization reaction of cyclobutadiene in the ground state (two resonance structures for cyclobutadiene). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of  $D_{2h}$  symmetry. At the square geometry, being an open shell system, the highest occupied molecular orbital is a pair of degenerate  $e_g$  orbitals housing two electrons. This degeneracy is lifted by a rectangular distortion. Consequently, the treatment of the square structure calls for a multiconfigurational method, whereas for the investigation of rectangular ground state, a single reference approach may be useful. Despite the fact that degeneracy is lifted by rectangular distortions, the ground state is still considerably multiconfigurational. Hence, in the automerization potential of cyclobutadiene, the degree of degeneracy can be varied continuously from a non-degenerate situation to a highly degenerate one. Thus, it can serve as a benchmark and testing ground for different theoretical models. The satisfactory and consistent performance of SS-MRMPPT over the entire automerization path of cyclobutadiene is a stringent test of the formulation. A high level of theoretical model is required for a proper description of cyclobutadiene as high degeneracy in the  $\pi$  system, along with strong dynamical  $\pi$ - $\sigma$  and  $\sigma$ - $\sigma$  correlation, requires a balanced and accurate treatment of all electrons. This can be achieved via SS-MRMPPT method.

As mentioned earlier, we also provide the calculation of the barrier height for the bond-flipping automerization of cyclobutadiene via SS-MRMPPT method. The barrier height for the automerization of cyclobutadiene can be defined as the energetical difference between the  ${}^1B_{1g}$  square geometry (transition state,  $D_{4h}$ ) and the  ${}^1A_g$  rectangular geometry of cyclobutadiene ( $D_{2h}$ ). The results presented in the article of Li and Paldus<sup>54</sup> demonstrate that RMR-CCSD,<sup>56</sup> CCSD(T), and CR-CC(2,3) exhibit singular behavior in the vicinity of the transition state (diradicaloid state) geometry, although these are generally very promising in overcoming the shortcomings of the standard SRCC method in the presence of quasidegeneracy. Another interesting observation is that when one uses the two-configurational MCSCF orbitals *in lieu* of the RHF ones, the performance of RMRCC improves. Thus, to study automerization potential and barrier of cyclobutadiene, it is necessary to use a highly sophisticated MR-based method. Highly sophisticated data available (such as RMRCC, SUMRCC, MRB-WCC, SS-MRCC, and SS-EOM-CEPA)<sup>53,54</sup> for this problem have been cited in the literature, which motivated us to consider this system as a test case.

In our present calculations, two lowest singlet states [ $2{}^1A_{1g}$  and  $1{}^1B_{1g}$ ], apart from the ground state ( $1{}^1A_{1g}$ ), have been considered and briefly discussed. In our calculation, we have used CAS(4,4) that was constructed within the  $\pi$  electron orbital manifold, which includes four electrons placed in two  $\pi$  and two  $\pi^*$  orbitals. We also used CAS(2,2) to examine the effect of the size of the CAS. We use the SS-MRMPPT method for computing automerization potential using the same geometrical scheme as that of Li and Paldus.<sup>54</sup> One C-C bond length is labelled by  $R1 = R$  and the other one is given by  $R2 = 2 \times 1.4668 - R$  (all bond-length values are in angstroms). In our calculations, the automerization pathway is defined (as that of Li and Paldus<sup>54</sup>) by the shorter bond length  $R$  (Å) of a rectangular conformation, keeping the sum of the shorter and longer bond lengths equal to twice the equilibrium bond length of a square conformation (1.4668 Å).

To assess the influence of basis set on the SS-MRMPPT procedure, we carried out calculations on the reaction set using the STO-3G and cc-pVDZ basis sets.<sup>32</sup> The four core 1s and 2s carbon orbitals were kept frozen in our first set of calculations with STO-3G



**Figure 6.** SS-MRMPPT/CASSCF(2,2) and SS-MRMPPT/CASSCF(2,2) potential energy surfaces with STO-3G basis set for the automerization reaction of cyclobutadiene in the ground state ( $1{}^1A_{1g}$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

basis. It should be mentioned that FCI data are available for the STO-3G basis set with this scheme.<sup>54</sup> These FCI values can be used to assess the performance of our SS-MRMPPT method. In our second set of calculations with the same basis set, 1s core orbital of each carbon was kept frozen. For STO-3G basis set, molecular orbitals are taken from the restricted Hartree-Fock (RHF) and CASSCF calculations. The four core 1s carbon orbitals have also been kept frozen in the SS-MRMPPT calculations with cc-pVDZ basis. These basis sets have been used for comparison with earlier studies using various methods.<sup>48–55</sup>

Figure 6 describes the SS-MRMPPT PES with CASSCF(2,2) and CASSCF(4,4) using STO-3G basis set for the automerization reaction of cyclobutadiene in the ground state ( $1{}^1A_{1g}$ ): reaction path connecting two rectangular structures via the intermediate square structure. This PES has been plotted by linear interpolation of the selected internal coordinates,  $R$  (Å).<sup>54</sup> We also plotted the corresponding FCI surface<sup>54</sup> in the same figure as it can serve as a benchmark for comparison with all other approximate methods. It is evident that the difference between the two SS-MRMPPT PESs is not too small to be visible on the scale shown in Figure 6. The SS-MRMPPT/CASSCF(4,4) energies are always lower than the SS-MRMPPT/CASSCF(2,2) ones over the entire reaction coordinates. On the whole, the SS-MRMPPT/CASSCF(4,4) and SS-MRMPPT/CASSCF(2,2) potentials are roughly parallel. It is interesting to note that the shape of the SS-MRMPPT PES for automerization reaction of cyclobutadiene in the  $1{}^1A_{1g}$  state is similar to the corresponding FCI one.<sup>54</sup> It is also observed that the shape of the PESs obtained at SS-MRMPPT level are indeed virtually the same as those at the level of spin restricted open-shell Kohn–Sham-based CI (ROKS+CI),<sup>40</sup> multireference average quadratic coupled cluster (MR-AQCC),<sup>52</sup> and SS-MRCCSD<sup>54</sup> (SS-MRCC of Mukherjee and coworkers<sup>26</sup>) theories. We observe that the SS-MRMPPT PESs are situated above the FCI one. The SS-MRMPPT/CASSCF(4,4)



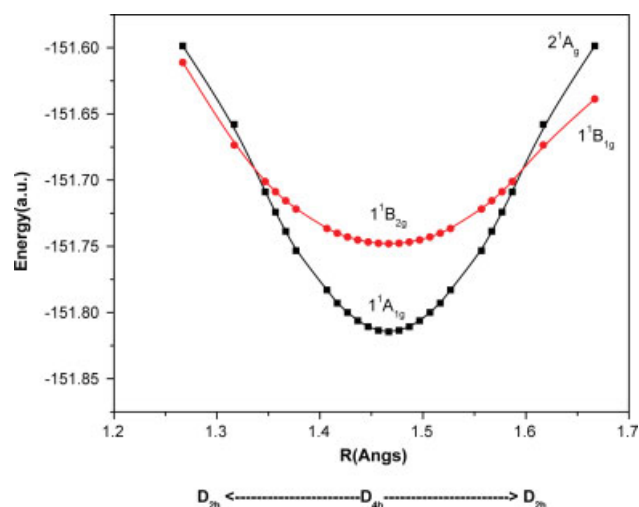
lies in between the SS-MRMPPT/CASSCF(2,2) and FCI values. Figure 6 clearly shows that both the SS-MRMPPT surfaces are not quite close to the FCI one. However, the performance of the SS-MRMPPT method is apparently quite promising when considering the errors relative to the FCI values. For an easy overall assessment of the quality of the estimated PES and to compare the performance of the different methods, we use the quantity called the nonparallelity error (NPE), which is the difference between the maximal and minimal deviations of the total energy obtained in the calculations of the PES with the particular method from the FCI results. The NPE value is a very useful diagnostic that measures the smoothness of the error with respect to the FCI surface. Table 4 reports the NPE values of the SS-MRMPPT and other methods for the ground state. The NPE value indicates that the SS-MRMPPT method provides a PES that is satisfactorily parallel to the FCI one even though the resultant surface deviates noticeably from that obtained with the FCI one. In the entire range of reaction coordinates considered, the NPE of SS-MRMPPT/CASSCF(4,4) is 3.38 kcal/mol. As measured by the NPE index of Table 4, SS-MRMPPT and SU-MRCCSD are quite competitive. As far as the perturbative method is concerned, the NPE of SS-MRMPPT is rather small.

To further illustrate the use of the formalism, we calculate the PES of the two lowest singlet states. We have deliberately chosen the excited root while we diagonalize the matrix of the dressed Hamiltonian  $\tilde{H}$  to generate the excited state. Calculation of the relative ordering of the lowest singlet electronic states of cyclobutadiene and representing the PESs for the rectangular distortion paths presents a real challenge for a method capable of quantitatively treating both the nondynamic and dynamic correlation effects. The PES of low-lying excited states might be useful in understanding the reactivity of cyclobutadiene together with its inherent high angular strain. In Figure 7, we summarize the PESs of the two lowest excited singlet states against the automerization reaction coordinate obtained by the SS-MRMPPT/STO-3G. An interesting feature of our present results is the agreement between the shape of SS-MRMPPT/STO-3G energy surfaces for the singlet excited states and the corresponding MRCCSD of Balková and Bartlet<sup>48</sup> and MR-AQCC of Eckert-Maksić et al.<sup>52</sup> It is interesting to note that the extent of variation of energies as a function of the rectangular reaction coordinate provided by the SS-MRMPPT, MR-AQCC, and MRCCSD methods are identical in nature. It is worth noting that in contrast to the SS-MRMPPT method, MR-AQCC and MRCCSD methods are capable of optimizing the structural parameters of the ground and excited states on an equal footing. One must keep in mind that both the MRCCSD and MR-AQCC methods suffer from

**Table 4.** Nonparallelism Error (NPE) for the Automerization PES of Cyclobutadiene as Obtained with Various Methods and STO-3G Basis Set.

Methods	NPE (kcal/mol)
SS-MRMPPT/CASSCF(4,4)	3.38
SU-CCSD <sup>a</sup>	2.468
Mk-MRCCSD <sup>a</sup>	1.068
RMCCSD <sup>a</sup>	1.588
RMCCSD(T) <sup>a</sup>	0.455

<sup>a</sup>Ref. 54.



**Figure 7.** Energy variation along the automerization path of cyclobutadiene for the two lowest excited states. The excited states  $1^1B_{1g}$  and  $2^1A_g$  have a planar equilibrium square structure of  $D_{4h}$  symmetry [ $1^1B_{2g}$  and  $1^1A_{1g}$ , respectively] just like the transition state for the double-bond flipping interconversion reaction between two equivalent ground-state singlet isomers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

intruder state effects. The presence of a typical aromatic character associated with the systems concerned makes the two lowest singlet states genuinely interesting. It is a notable feature of this system that the square geometry gets stabilized at the cost of destabilization of the rectangular geometry. The decrease in the antiaromaticity and even to some extent the onset of an enhancement of the aromatic nature in a coupled manner induce a steep stabilization of the two states on traversing from the rectangular to the square geometry. The transition state regime shows a higher stability of the singlet  $A_g$  state *vis-a-vis* the singlet  $B_g$  state. The energy order is just the opposite in the rectangular zone.

As a further test of the robustness of the formalism, we also compute the automerization barrier. A large number of theoretically estimated barriers of the two rectangular structures are available for this system in the literature.<sup>48–55</sup> Although the experimental structure of cyclobutadiene is not reported till now as per our knowledge, there is a host of experimental observations<sup>57</sup> for automerization barrier height. The energy barriers obtained by the SS-MRMPPT procedure alongwith earlier theoretical and experimental results are given in Table 5. To strengthen this comparison, we also listed the results of various DFT methods of Filatov and Shaik.<sup>40</sup> A low barrier is compatible with the rapid equilibration of the two geometrical isomers. The presented data in the table clearly depict that the energy barrier spans a wide range depending on the basis set and method used. Hence, we have also assembled the SS-MRMPPT barrier height for various basis sets, indicating automerization barrier has a strong basis set dependency. As in the case of other methods (MR-BWCC and Mk-MRCC), we also observed that the energy barrier increases with the flexibility of the basis set. This finding is also in harmony with a pronounced dependence of the dynamic electron correlation on the quality of the basis set in contrast to its nondynamic counterpart.

Table 5. Automerization Barrier (kcal/mol) of Cyclobutadiene.

Basis	Methods	Barrier	
STO-3G	SS-MRMPPT/CASSCF(2,2) <sup>a</sup>	3.82	
	SS-MRMPPT/CAS(2,2)/RHF <sup>a</sup>	4.05	
	SS-MRMPPT/CASSCF(4,4) <sup>a</sup>	6.35	
	FCI/MCSCF <sup>a,b</sup>	12.53	
	FCI/RHF <sup>a,b</sup>	12.29	
	SS-MRMPPT/CASSCF(2,2) <sup>c</sup>	4.04	
	SS-MRMPPT/CASSCF(4,4) <sup>c</sup>	6.90	
	cc-pVDZ	SS-MRMPPT/CASSCF(4,4) <sup>c</sup>	9.85
		CCSD <sup>b</sup>	21.2
		SUCCSD <sup>b</sup>	7.0
RMRCCSD <sup>b</sup>		10.4	
CCSD(T) <sup>b</sup>		15.7	
SUCCSD(T) <sup>b</sup>		4.8	
RMRCCSD(T) <sup>b</sup>		7.2	
SUCCSD/MCSCF <sup>b</sup>		7.2	
Mk-MRCCSD/MCSCF <sup>b</sup>		7.9	
RMRCCSD/MCSCF <sup>b</sup>		9.5	
SU-MRCCSD(T)/MCSCF <sup>b</sup>		5.7	
RMRCCSD(T)/MCSCF <sup>b</sup>		5.9	
CCSDT <sup>d</sup>		6.4	
2D-MRCCSD(T) <sup>b</sup>		6.6	
BWMRCCSDn.c. <sup>d</sup>		9.8	
BWMRCCSDa.c. <sup>d</sup>		6.5	
BWMRCCSD(T)n.c. <sup>d</sup>		10.0	
BWMRCCSD(T)a.c. <sup>d</sup>		6.1	
Mk-MRCCSD <sup>d</sup>		7.8	
Mk-MRCCSD(T) <sup>d</sup>		7.8	
MR-CISD/SS-CASSCF <sup>e</sup>		7.3	
MR-CISD+Q/SS-CASSCF <sup>e</sup>		7.6	
MR-AQCC/SS-CASSCF <sup>e</sup>		7.7	
MR-CISD/SA-2-CASSCF <sup>e</sup>		6.5	
MR-CISD+Q/SA-2-CASSCF <sup>e</sup>		7.2	
MR-AQCC/SA-2-CASSCF <sup>e</sup>		7.3	
GVB <sup>f</sup>		10.94	
GVB+CS <sup>f</sup>		5.30	
cc-pVTZ		SS-MRMPPT/CASSCF(4,4) <sup>c</sup>	10.71
		MR BWCCSD i.c. <sup>d</sup>	7.4
	MR MkCCSD <sup>d</sup>	9.1	
	MR BWCCSD(T)n.c. <sup>d</sup>	11.3	
	MR BWCCSD(T)a.c. <sup>d</sup>	7.0	
	MR BWCCSD(T)i.c. <sup>d</sup>	6.8	
(3s2p1d/2s)	MR MkCCSD(T) <sup>d</sup>	8.9	
	SCF <sup>g</sup>	30.6	
	CCSD <sup>g</sup>	19.8	
	CCSD(T) <sup>g</sup>	14.6	
	CCSDT-1b <sup>g</sup>	9.4	
	CCSDT <sup>g</sup>	6.4	
TZ2P	MRCCSD <sup>g</sup>	5.8	
	LDA <sup>h</sup>	14.3	
	BLYP <sup>h</sup>	13.3	
	BP86 <sup>h</sup>	11.4	
	FT97 <sup>h</sup>	11.9	
cc-pVDZ	SS-EOM-CEPA[+2]/MCSCF <sup>i</sup>	8.5	
cc-pVTZ	SS-EOM-CEPA[+2]/MCSCF <sup>i</sup>	9.6	
cc-pVDZ	SS-EOM-CEPA[+2]/Brueckner <sup>i</sup>	8.6	

(continued)

Table 5. (Continued)

Basis	Methods	Barrier
cc-pVTZ	SS-EOM-CEPA[+2]/Brueckner <sup>i</sup>	9.8
	Experiment	1.6–10
	ZPVE	–2.5

<sup>a</sup>Freezing 1s and 2s orbitals on each carbon atom.<sup>b</sup>Ref. 54.<sup>c</sup>Four 1s carbon orbitals frozen.<sup>d</sup>Ref. 53.<sup>e</sup>Ref. 52.<sup>f</sup>Ref. 51.<sup>g</sup>Ref. 50.<sup>h</sup>Ref. 40.<sup>i</sup>Three body terms in transformed Hamiltonian included: Ref. 55; Experiment: Ref. 57 ZPVE: Ref. 52.

From the entries of Table 5, which collects the database reference values for the barrier heights, one can argue that a balanced treatment of both dynamic and nondynamic correlation is a prerequisite to obtain accurate results in agreement with those from experiment. Regardless of the comparison with experiment, there is a striking difference between the MR-BWCCSD(T)<sub>nc</sub> [MR-BWCCSD<sub>nc</sub>] and MR-BWCCSD(T)<sub>ac</sub> [MR-BWCCSD<sub>ac</sub>] results for the same basis in contrast to Mk-MRCC schemes. It is important to note that the (MR-BWCCSD<sub>nc</sub>) suffers from size-extensive error while (MR-BWCCSD<sub>ac</sub>) often rather overshoots correction of this error.<sup>43,53</sup> Thus, a comparison with respect to the state-of-the-art Mk-MRCC method is more appropriate in this context. In the present case, we also consider the calculations of the barrier height for the bond-flipping automerization of cyclobutadiene by using the multireference average quadratic coupled cluster (MR-AQCC) method (which is capable of optimizing the structural parameters of the ground, transition, and excited states on an equal footing) due to Eckert-Maksić et al.<sup>52</sup> as a benchmark. The main advantage of the MR-AQCC method is the combination of multireference and approximate size-extensivity effects, which allow for a balanced description of the nondynamic and dynamic electron correlations.

As mentioned by Schmidt and Gordon,<sup>58</sup> the MCSCF tends to overstabilize the transition square structure. The MCSCF internal rotation barrier of Nakamura et al.<sup>59</sup> is only 2.5 kcal/mol. It is important to note that experimentally, the energy barrier for automerization of cyclobutadiene is predicted to be in the range of 1.6–10 kcal/mol. We first concentrate on results obtained with STO-3G basis. The STO-3G basis along with the scheme of Li and Paldus<sup>54</sup> gives a value of 4.05 kcal/mol and 3.82 kcal/mol for the SS-MRMPPT/CAS(2,2) with RHF and CASSCF orbitals, respectively, and 6.35 kcal/mol in the case of SS-MRMPPT/CASSCF(4,4) approach confirming the modest influence of the size of the reference space. Our second set of calculations with STO-3G basis set (four 1s carbon orbitals frozen) demonstrates that the inclusion of correlation of 2s electrons of each carbon atom clearly has an effect on the SS-MRMPPT energy values and consequently the predicted barrier height. The corresponding FCI value is in the range 12.5–12.3 kcal/mol. The reason for this large discrepancy is not clear to us. It is important to note that the estimated barrier height with TZ2P basis set at the level of spin-restricted open-shell Kohn–Sham (ROKS) method studied by Filatov and Shaik<sup>40</sup> is now close to the standard MR-based correlated methods such as

Mk-MRCCSD, MR-BWCCSD, RMRCCSD, and so on. The table indicates that the CCSD and CCSD(T) values with cc-pVDZ basis are clearly slightly high when compared with experimental results, whereas the SS-MRMPPT/cc-pVDZ value is satisfactorily close to the experimental result. The computation of automerization barrier for the SS-MRMPPT method with cc-pVDZ basis set yields a value of 9.85 kcal/mol, which lies satisfactorily close to the values of the calculations of RMRCCSD/MCSCF, MR-BWCCSD<sub>nc</sub>, and MR-BWCCSD(T)<sub>nc</sub> methods. SS-MRPT/cc-pVTZ value compares rather well with the MR-BWCCSD(T)<sub>nc</sub> one in comparison with the other scheme mentioned in the table for the cc-pVTZ basis. The SS-MRMPPT barrier to rotation in cyclobutadiene is also in reasonable agreement with the computationally expensive SS-EOM-CEPA method.<sup>55</sup> Again, our result with cc-pVDZ basis is nearly close to the values with the MR-CISD+Q/cc-pVDZ, MR-AQCC/cc-pVDZ, and RMRCC/cc-pVDZ automerization barriers. The table demonstrates that the results of calculations with GVB+CS are closer to our results than the GVB choice for the cc-pVDZ basis. Again, the value obtained at the SS-MRMPPT/cc-pVDZ level lies very close to the results of full-blown Mk-MRCC/cc-pVDZ and MR-BWCC/cc-pVDZ (with and without size-extensivity correction) methods. It should be re-emphasized that the Mk-MRCC, MRB-WMRCC, RMRCC, and MR-AQCC methods are computationally demanding even for medium-to large-sized systems, indicating the clear benefit of using SS-MRMPPT approach. We think that this potential benefit of the SS-MRMPPT variant with respect to the full-blown Mk-MRCCSD may be quite relevant in future applications. Here, we re-emphasize that at a given truncation level, many-body perturbation theory is usually less accurate than CC. We find a very good overall agreement between the computed barrier via SS-MRMPPT method and experimental barrier height as that of the other established MRCC methods. It is found that the SS-MRMPPT/cc-pVDZ barrier height for CAS(2,2) and CAS(4,4) reference space for CASSCF orbitals lie in the middle of the range of the experimental values (1.6–10 kcal/mol).<sup>57</sup> According to the data in Table 5, it is evident that the automerization barrier is rather sensitive to the basis sets and the theoretical method used. Here, we mention that there is a large scatter of the experimental and theoretical estimates of the barrier automerization of cyclobutadiene in the literature that should be rectified by using the state-of-the-art methodology and computations.

In the above discussion, the goodness of the SS-MRMPPT has been verified once more. We also observed that when the nondynamical contribution to the correlation energy plays a chemically important role, the balanced treatment of dynamical correlation in association with the nondynamical correlation yields results very close to the correct ones. We can summarize this section by stating that at least for the small molecular systems tested in this work and in our previous works, the SS-MRMPPT approach is capable of providing results of satisfactory quality at a fraction of the computer effort.

## Conclusions

In this article, we have applied SS-MRPT that is based on RS expansion and uses MP partitioning (SS-MRMPPT) to generate torsional PESs of the ground state of N<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>4</sub>H<sub>6</sub> systems. Energy variation along the automerization path of cyclobutadiene for the

ground state and the two lowest singlet excited states provided by the SS-MRMPPT method have also been considered and briefly discussed. The main advantage of the SS-MRMPPT method is the combination of multireference and size-extensivity effects, which allows for a balanced description of both nondynamical and dynamical electron correlation effects. In this article, we have also addressed the issue of barrier height and the influence of dynamical and nondynamical correlations on these quantities. We compared our results with experiments, where available, and with previous calculations performed by sophisticated SR- and MR-based methods with different basis sets. Here, it is worth mentioning that identical geometries, basis sets, and orbitals have to be used in all comparisons to minimize artifactual differences when comparing the results. In view of this, previously reported results have been used to calibrate our results qualitatively. Generally, we observe a satisfactory agreement of our results with the different theories considered here.

The SS-MRMPPT method gives the correct shape of the ground as well as lowest singlet excited states PES almost over the whole range of the reaction coordinates for the cyclobutadiene system, and SS-MRMPPT surfaces are favorably similar to those obtained by other state-of-the-art methodologies and computations. This study illustrates that unlike the CCSD and its variants (such as renormalized CC method, e.g., CR-CC<sup>35</sup>), the SS-MRMPPT provides smooth and reliable ground-state PESs for the N<sub>2</sub>H<sub>2</sub> system. Here, it is important to mention the fact that the complete renormalized CC methods (CR-CC) can be regarded as a new generation of noniterative single-reference CC approaches that are designed to improve the results of the CCSD(T) and CCSD(TQ) calculations in the bond-breaking/biradical regions of molecular potential energy surfaces (see Ref. 60). We also observed that with the SS-MRMPPT method, even a very small active space restores the correct qualitative behavior across the entire energy surface, as we have found in our earlier calculations for other systems. The dependence of our results on the reference size has also been addressed in this article. It is noteworthy that the effect of CAS size is not significant. In this work, we also observed that the inclusion of more extended basis sets did not significantly change the energy barrier. It should be noted that the SS-MRMPPT method appears as a valuable formalism that is capable to properly account for the full potential surface without facing the problem of cusp at the barrier top (strong quasidegeneracies), while also performing well at other points in nondegenerate situations.

Overall, in comparing our calculations with the benchmark results, we found that reliable results were obtained with a variety of orbitals and reference space that indicates the efficacy of the SS-MRMPPT method.

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