A state-specific multi-reference coupled-cluster approach with a cost-effective treatment of connected triples: implementation to geometry optimisation

Debi Banerjee, Monosij Mondal, Sudip Chattopadhyay & Uttam Sinha Mahapatra

Published online: 05 Feb 2016.

Submit your article to this journal ⤤

View related articles ⤤

View Crossmark data ⤤

Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

A state-specific multi-reference coupled-cluster approach with a cost-effective treatment of connected triples: implementation to geometry optimisation

Debi Banerjee[a], Monosij Mondal[b], Sudip Chattopadhyay[b] and Uttam Sinha Mahapatra[c]

[a]Department of Physics, Shibpur Dinobundhoo Institution (College), Howrah, India; [b]Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Howrah, India; [c]Department of Physics, Maulana Azad College, Kolkata, India

ABSTRACT

Recently, we have suggested an approximate state-specific multi-reference coupled-cluster (SS-MRCC) singles, doubles and triples method based on the CCSDT-1a+d approximation applied to the single-reference CC approach, in which the contribution of the connected triple excitations is iteratively treated. The method, abbreviated as SS-MRCCSDT-1a+d is intruder-free and fully size-extensive. It has been employed for geometry optimisations of various systems possessing quasi-degeneracy of varying degrees (like N_2H_2 and O_3) by invoking numerical gradient scheme. The method is also applied to CH_2 and square cyclobutadiene in their excited states. For all systems under study, the computed values are in good accordance with *state-of-the-art* theoretical estimates indicating that the method might be a promising candidate for an accurate treatment of geometrical parameters of states plagued by electronic degeneracy in a computationally tractable manner.
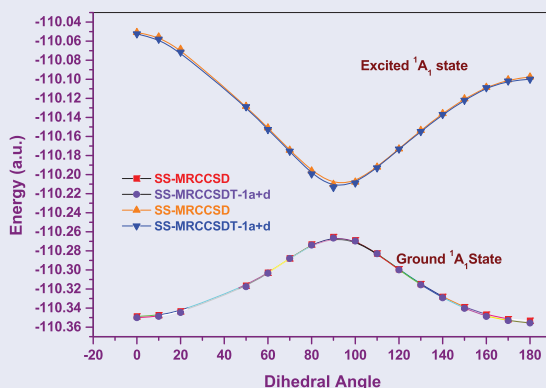
1. Introduction

The multi-reference (MR) coupled-cluster (MRCC) method is certainly one of the most successful approaches for the treatment of molecules with a strong quasi-degenerate character. In contrast to the MR configuration interaction (MRCI) approach, MRCC convalesces more correlation energy at a given level of truncation owing to the exponential parametrisation of the wave function. Despite the various successes of the MRCC model, development and implementation of MRCC formalisms remain an active domain of research in the realm of electronic structure theory [1,2]. Although there are several variants of genuine MRCC method according to the form of the wave operator Ansatz, in the present work, we will focus on the Jeziorski–Monkhorst MR generalisation of

the CC exponential Ansatz (usually termed as Hilbert space MRCC approach) [3]. Conventional effective Hamiltonian-based multi-root Hilbert space MRCC, say state-universal MRCC (SU-MRCC) [3,4] method yields energies of various states in a single calculation, and often suffers from several impediments such as the *intruder state problem* [5] leading to divergent behaviour of the cluster finding equations. The other objection that can occur in practical applications stems out from the multiplicity of the solutions (due to the nonlinear nature of the Bloch equation and the asymmetric treatment of the excitation manifolds associated with the different reference configurations in the Bloch wave operator) [6].

To overcome the intruder problem, one can exploit the intermediate Hamiltonian formalism [7].

CONTACT Sudip Chattopadhyay ✉ sudip@chem.iiests.ac.in; Uttam Sinha Mahapatra ✉ uttam.mahapatra@linuxmail.org

The state-specific parametrisation of MRCC wave function, where only one eigenvalue of the effective Hamiltonian is identical to the original Hamiltonian eigenvalue, avoids intruder problem in a very effective manner and has thus attracted a great attention in the last decade [8–16]. The state-specific or single-root MRCC approaches based on the Jeziorski–Monkhorst (JM) Ansatz [3] offer more optimisation parameters (cluster amplitudes) per state compared to the multi-state SU-MRCC methods. As the state-specific form of the JM Ansatz yields a redundant number of parameters, additional conditions are needed to obtain a unique solution to the Schrödinger equation of the target state and this leads to various formulations of state-specific MRCC, including Brillouin–Wigner MRCC approach (BW-MRCC) introduced by Hubač *et al.* and further developed in various directions by Pittner *et al.* [9,10,13], SS-MRCC formulations invented by Mahapatra *et al.* [11] and later developed by Evangelista *et al.* [17] who introduced the abbreviation MkCC, MRexpT approach due to Hanrath [14] and single-root MRCC (sr-MRCC) formalism of Mahapatra-Chattopadhyay [16]. The BW-MRCC and MRexp T methods are not size-extensive. The SS-MRCC method provides size-extensive energies, since all terms appearing in the energy and amplitude equations are connected in nature [1,11]. As shown by Mahapatra and Chattopadhyay [16], the sr-MRCC formalism is size-extensive, size-consistent, and recovers a high percentage of the correlation energy, even at the SD level. Moreover, due to structural flexibility, SS-MRCC (Mk-MRCC) and sr-MRCC methods can be implemented starting from an SRCC code, an advantage over the more complex MRexpT method [14]. It should be noted that the main objections of the JM Ansatz-based MRCC methods are the lack of invariance with respect to active orbital rotations (and the unfavourable scaling with the dimension of the active space which limits their applicability to small active spaces) [1]. SS-MRCC is thus size-consistent only when localised orbitals are used.

Previous studies in SRCC have shown that for achieving high accuracy, it is imperative to refine the description of dynamical correlation beyond the treatment of connected singles–doubles (i.e. one need to incorporate connected triples). It thus seems useful to study the performance of SS-MRCC method beyond the double excitation truncation of the cluster operator. Significant efforts have been made to include higher excitations in the BW-MRCC and SS-MRCC theories. The first development in this direction was published by Evangelista *et al.* [18] through an iterative inclusion of triples excitations in singles–doubles truncation scheme. Later, Pittner and co-workers [19,20] formulated a perturbative correction for the BW-MRCC and SS-MRCC (Mk-MRCC)

approach. In [20], they have also reported the development of an efficient implementation of the full-blown BW-MRCCSDT method. Although computational costs of full-blown CCSDT are too demanding, it can be used as a tool for benchmarking approximate methods. The underlying policy behind the development of Mk-MRCCSD(T) due to Pittner *et al.* [19,20] is to correct the matrix elements of the SS-MRCC-effective Hamiltonian using SR-CCSD(T) scheme. Evangelista *et al.* [21] proposed a systematic scheme for deriving perturbative triple corrections in SS-MRCCSD/Mk-MRCCSD method (termed as SS-MRCCSD(T)/Mk-MRCCSD(T)) through the development of a production level code. It is worth noting that the Mk-MRCC method with perturbative triples [22] has been suggested by neglecting the coupling terms in the triples amplitude equation, and thus often suffers from intruder state effects. In the Mk-MRCC(T) method of Evangelista *et al.* [23], the triples amplitude equation includes the linear coupling terms which requires to iterate the equation for the triple excitations. Note their amplitude equation includes a denominator shift and is thus insensitive to intruder states. The Mk-MRCCSD(T) formalism of Evangelista *et al.* can be viewed as a MR generalisation of the λ-CCSD(T) [24]. The progress on SU-MRCC with triples excitations achieved by (1) Balková and Bartlett [25], (2) Kowalski and Piecuch [26] and (3) Li and Paldus [27] should also be noted.

Block-correlated coupled-cluster (BCCC) method with a CASSCF (CAS-BCCC) reference function is an interesting variant of the intruder-free CC method, which was recently introduced by Li and co-workers [28]. Apart from its lack of core extensivity, the CAS-BCCC method offers many beneficial properties and shows a good numerical accuracy for ground-state and excited-state calculations. Several formalisms have also been suggested to incorporate MR ideas into the structure of the SRCC method including active-space or MR state-specific CC formulations of Adamowicz and co-workers [29] (for other concepts based on the idea of active-space CC; see [30]), reduced MRCC methods of Li and Paldus [31], method of moments of CC methods (MMCC) invoking MR perturbative/configuration interaction (CI) trial wave functions developed by Piecuch *et al.* [32], renormalised CC (CR-CC) approaches using the formalism of MMCC [33], tailored CC methods proposed by Bartlett and co-workers [34] and universal state-selective MR approach introduced by Kowalski [35]. These methods all seek to improve the behaviour of CCSD(T) without giving up its general structure.

Considering the advantages of SS-MRCC (*vide supra*), our group have been actively pursuing the development and application of SS-MRCC with perturbative

treatment of connected triples for SS-MRCCSD (termed as SS-MRCCSDT-1a+d) [36] analogous to the SR-based CCSDT-n-schemes. As the SS-MRCCSD with the SDT-1a+d correction is derived from the SS-MRCC method by truncation of the corresponding equations, the SS-MRCCSDT-1a+d equations are explicitly connected and the resulting triples correction is size-extensive. Although a series of iterative approximations denoted as SR-CCSDT-n ($n = 1 - 4$) [37] have been proposed due to lower computational scaling, a scheme with non-iterative inclusion of connected triples, say CCSD(T), often referred to as the 'gold standard', became very popular. At present, there is no general understanding as to which of the CCSDT-n methods is the best in terms of computational requirements and accuracy obtained for a given problem [37]. Consequently, a trial-and-error approach to test the applicability of a given CCSDT-n scheme is always worthwhile. Recently, we have implemented an approximate iterative CCSDT-n method (called as CCSDT-1a+d) [38] in which all diagonal terms in $\overline{VT_3}$ (diagonal terms) have been included in the T_3 determining equation, in addition to $\overline{VT_2}$. The CCSDT-1a+d method can be viewed as an attempt to treat the effects of triply excited determinants upon both single- and double-excitation operators on an equal footing. We emphasise at this point that at the CCSDT-1a+d level, important new $T_3 - T_3$ coupling terms appear due to the $\overline{VT_3}$ (diagonal terms). Therefore, CCSDT-1a and CCSDT-1a+d are (approximately) equivalent where $\overline{VT_3}$ (diagonal terms) are not significant. Illustrative applications presented in [36,38] demonstrate that the SDT-1a+d scheme is a promising approximation to the full SDT method over the entire bond-breaking process of alkaline-earth dimers, and isomerisation of cyclobutadiene. The superiority of the CCSDT-1a+d approach over other non-iterative treatments of triples in CC theory is evident when we examine the energy curve of the challenging Be_2 molecule. Thus, it offers a more useful avenue to treat electron correlation in the presence of configurational degeneracy than CCSDT-1a and CCSDT-1b while being less expensive than the full-blown CCSDT treatment. However, due to the iterative nature of the method, it is also computationally demanding with respect to the corresponding non-iterative analogue. The choice of SDT-1a+d truncation scheme represents a pragmatic compromise between the desire to achieve accuracy and the computational viability of the resulting method. The success of the CCSDT-1a+d scheme [38] in applications involving single bond breaking and biradical structures on singlet energy surfaces prompt the question of whether CCSDT-1a+d can be similarly effective within the framework of the SS-MRCC method (see [36]).

The goal of this communication is to examine the performance of the SS-MRCC method to calculations of equilibrium geometrical parameters of systems that are MR in nature through the inclusion of complete connected singles, doubles and partial triples (SDT-1a+d (entails the inclusion of off-diagonal Fock matrix elements)) [36] based numerical gradient scheme. Unlike the SR-based gradient approach, the SS-MRCCSDT-1a+d gradient treatment is more stable near transition states or at distorted geometries and, hence, can handle geometry optimisation of MR states more accurately. Although the numerical gradient scheme is inherently less efficient than the analytic one, it is more amenable from computational point of view. Although the gradient approach has already been well developed for the SR-based methods [39,40], much less is known about MR-based methods due to the greater complexity of the MR approaches compared to the SR one. In recent years, there has been increasing interest in the development of analytical derivatives for MR wave functions [41]. Using the string-based many-body formalism, analytic gradient formalism has been presented for active-space CC methods HF and MCSCF reference functions [42]. In 2007, Pittner and Šmydke [19] published a formulation of analytic gradients for the BW-MRCC (uncorrected and with iterative size-extensivity correction) and SU-MRCC methods (using Lagrange multipliers [39]) together with a pilot application within an FCI program. Very recently, Gauss and his co-workers [43] developed and implemented analytic gradients for the SS-MRCC method restricted to two closed-shell determinants and HF orbitals based on the Lagrangian formulation of Helgaker and Jørgensen formalism [39], later including orbital relaxation at the MCSCF rather than the HF level of theory. We hope BW-MRCC and Mk-MRCC gradient methods will provide various interesting chemical applications. For an overview of recent developments in this field, see also the review by Helgaker et al. [44].

2. Theory: A brief resumé

In SS-MRCC theory, the wave function for the target electronic state ψ is expressed by the JM [3] Ansatz and written as a linear combination of reference-specific exponential operators $\exp(T^\mu)$ acting on a set of reference functions $\{\phi_\mu\}$ (span a complete active (or model) space), where each term is weighted by a coefficient c_μ:

$$|\psi\rangle = \sum_\mu \exp(T^\mu)|\phi_\mu\rangle c_\mu. \tag{1}$$

All the parameters entering the wave function Ansatz equation (1) are optimised within the frame

of Schrödinger equation for a specific electronic state using the following equations (for the complete model space):

$$\langle\chi_l|\bar{H}_\mu|\phi_\mu\rangle c_\mu + \sum_\nu \langle\chi_l|\exp(-T^\mu)\exp(T^\nu)|\phi_\mu\rangle\tilde{H}_{\mu\nu}c_\nu$$
$$= 0 \ \forall \ l, \ \mu \tag{2}$$

It is important to note that T^μs have the property that at least one orbital involved in them must be inactive to maintain the intermediate normalisation condition. Here, the cluster operator, T^μ, induces excitations from ϕ_μ to the various virtual functions $\{\chi_l\}$ of the outer space. For SS-MRCCSD, $\{\chi_l\}$ are the singles and doubles reached from a given ϕ_μ. Note that when the JM Ansatz is invoked in the Schrödinger equation and projected on the excited functions generated by the cluster operators appearing in Equation (1), the number of conditions obtained is less than the number of unknowns appearing in the JM wave function. As Equation (2) is valid for each μ and l, the number of equations is proper if one uses as many $\{\chi_l\}$ corresponding to the given model function as there are number of unknowns in T^μ finding equations. As a result of this, supplementary conditions, the so-called *sufficiency conditions*, have to be imposed when solving the equations for cluster operators. Mahapatra *et al.* used physically motivated *sufficiency conditions* to construct Equation (2) starting from the JM-based Schrödinger equation.

In Equation (2), $\bar{H}_\mu$ is the reference-specific similarity-transformed Hamiltonian (which is non-Hermitian), defined as

$$\bar{H}_\mu = \exp(-T^\mu)H\exp(T^\mu). \tag{3}$$

The SS-MRCC energies are obtained by diagonalising the (non-symmetric) matrix, $\tilde{H}_{\mu\nu}$:

$$\sum_\nu \tilde{H}_{\mu\nu}c_\nu = Ec_\mu, \tag{4}$$

where the matrix elements of the effective operator $\tilde{H}_{\mu\nu}$ are defined as $\tilde{H}_{\mu\nu} = \langle\phi_\mu|\bar{H}_\nu|\phi_\nu\rangle$. Within the model space, the reference space coefficients, c_μ in Equation (2) and the energy of the target state can be obtained by diagonalisation of Equation (4). In SS-MRCC, all the variables $\{c_\mu, T^\mu\}$ are computed self-consistently. Equation (2) consists of two terms: the direct term (analogous to single-reference theory where computational cost scales linearly with the number of references) depending on cluster amplitudes of one particular reference and the couplings (the cost of which scales quadratically) that explicitly mix cluster amplitudes related to different

references. Assuming the completeness of the reference space, one can show that that the non-symmetric (effective) Hamiltonian and the cluster operators are connected in nature. As Equation (2) associates with the reference coefficients for the target state, the solution of it depends on the process of the diagonalisation of the effective Hamiltonian through Equation (4), which must be done in each iteration. The computational cost of the coupling terms in SS-MRCC (and in other JM-based MRCC methods) is much less than the direct terms. The SS-MRCC method is structurally flexible in the sense that it subsumes in it size-extensive versions of both SSMR perturbation theory [45] and SSMR coupled electron pair approximation [46] depending upon a suitable choice of quasi-linearized approximation strategy. Moreover, it is intrinsically flexible in the sense that it is constructed in a manner that it can relax the coefficients of the reference function, or keep the coefficients frozen if we so desire.

CCSD is the least elaborate truncation scheme which possesses most of the important features of correlation. After obtaining T_1 and T_2 using Equation (2), the equation for triples can be obtained using the scheme as discussed later.

We now delineate the derivation of the working equation for the triples by starting out with the following partitioning of the Hamiltonian operator, H: $H = H_{0\mu} + V_\mu$, where the terms in the Hamiltonian, respectively, represent the one- and two-electron contributions to the overall Hamiltonian with respect to ϕ_μ as the vacuum. The CCSDT-1a scheme retains only the connected composite of $\overline{H_{0\mu d}T_3^\mu}$ in the T_3 equation, with $\overline{H_{0\mu d}}$ being the diagonal part of the unperturbed Hamiltonian. Essentially, $\overline{H_{0\mu d}}$ is the diagonal of an effective Fock-like operator f_μ defined with respect to ϕ_μ as the vacuum:

$$\left\langle\chi_l|\overline{H_{0\mu d}T_3^\mu}|\phi_\mu\right\rangle + \left\langle\chi_l|\overline{VT_2^\mu}|\phi_\mu\right\rangle = 0. \tag{5}$$

In this development, we implement a simple approximation scheme, namely the CCSDT-1a+d, in addition to the well-documented CCSDT-1a. In the CCSDT-1a+d scheme, the central theme of the current work, we incorporate the entire share of contributions that stems out of $\overline{V_{\mu d}T_3^\mu}$, that is to say, the diagonal parts of the mono- and bi-electronic operators:

$$\left\langle\chi_l|\overline{H_{0\mu d}T_3^\mu}|\phi_\mu\right\rangle + \left\langle\chi_l|\overline{V_{\mu d}T_3^\mu}|\phi_\mu\right\rangle + \left\langle\chi_l|\overline{VT_2^\mu}|\phi_\mu\right\rangle = 0. \tag{6}$$

We then cast the triples (T_3) determining equations, Equations (5) and (6), for a triply excited function χ_l, with l being a composite index. Thus,

$$\langle\chi_l|\overline{H_{0\mu d}T_3^\mu}|\phi_\mu\rangle = (f_\mu(a,a) + f_\mu(b,b) + f_\mu(c,c)$$
$$- f_\mu(i,i) - f_\mu(j,j) - f_\mu(k,k))t_\mu^l, \tag{7}$$

where the orbitals a, b, c, ... represent the occupied set and i, j, k, ... are the unoccupied ones in ϕ_μ. Thus, in this notational scheme, $H_{\mu\mu} = \langle\phi_\mu|H|\phi_\mu\rangle$ and $H_{ll} = \langle\chi_l|H|\chi_l\rangle$, so that

$$\langle\chi_l|\overline{V_{\mu d}T_3^\mu}|\phi_\mu\rangle = (H_{\mu\mu} - H_{ll})t_\mu^l. \tag{8}$$

To proceed further, we express the cluster-amplitude-determining equations for the triply excited (with respect to ϕ_μ) function $|\chi_l\rangle$ in an attempt to generalise the CCSDT-1a scheme [47] in the shape of an explicitly connected cluster amplitude equation for SS-MRCC as follows:

$$\langle\chi_l|\overline{H_{0\mu d}T_3^\mu}|\phi_\mu\rangle c_\mu + \langle\chi_l|\overline{V_\mu T_2^\mu}|\phi_\mu\rangle c_\mu$$
$$+ \sum_\nu \langle\chi_l|T_3^\nu - T_3^\mu + T_2^\nu T_1^\nu + T_2^\mu T_1^\mu - T_2^\mu T_1^\nu$$
$$- T_1^\mu T_2^\nu + \cdots|\phi_\mu\rangle\tilde{H}_{\mu\nu}c_\nu = 0 \ \forall \ l, \ \mu. \tag{9}$$

In the CCSDT-1a+d variant, the corresponding equation reads as

$$\langle\chi_l|\overline{H_{0\mu d}T_3^\mu}|\phi_\mu\rangle c_\mu + \langle\chi_l|\overline{V_{\mu d}T_3^\mu}|\phi_\mu\rangle c_\mu$$
$$+ \langle\chi_l|\overline{V_\mu T_2^\mu}|\phi_\mu\rangle c_\mu + \sum_\nu \langle\chi_l|T_3^\nu - T_3^\mu + T_2^\nu T_1^\nu$$
$$+ T_2^\mu T_1^\mu - T_2^\mu T_1^\nu - T_1^\mu T_2^\nu + \cdots|\phi_\mu\rangle\tilde{H}_{\mu\nu}c_\nu = 0 \ \forall \ l, \ \mu. \tag{10}$$

The intruder avoidance of this equation becomes quite evident once we rewrite it in the following form (by invoking (4)):

$$(H_{ll} - H_{\mu\mu} + \overline{H}_{\mu\mu} - E)t_\mu^l c_\mu + \langle\chi_l|\overline{V T_2^\mu}|\phi_\mu\rangle c_\mu$$
$$+ \sum_\nu^{\nu\neq\mu} \langle\chi_l|T_3^\nu\rangle\tilde{H}_{\mu\nu}c_\nu + \sum_\nu \langle\chi_l|T_2^\nu T_1^\nu + T_2^\mu T_1^\mu$$
$$- T_2^\mu T_1^\nu - T_1^\mu T_2^\nu + \cdots|\phi_\mu\rangle\tilde{H}_{\mu\nu}c_\nu = 0 \ \forall \ l, \ \mu. \tag{11}$$

The merits of the above equation become quite obvious once we realise the fact that the gap $(\overline{H}_{\mu\mu} - E)$ is necessarily positive for the lowest energy state of interest of a particular space-spin symmetry so that the difference $(H_{ll} - H_{\mu\mu})$ gets widened up and thus allows for an effective avoidance of intruders even if some virtual functions become energetically proximate to one or some of the model space functions. It is noteworthy that this aspect

for the avoidance of intruder states can almost always be met for ground state (as this is a difference of an uncorrelated excited state energy and a correlated ground state energy), but is a much trickier issue for the computation of the excited states. In the case of the excited state(s), more iteration steps are required (which are application specific) to obtain convergence of the equations as compared to the ground state. Convergence of the iterative steps required is reasonably fast for all cases reported here. Such a manifest exploitation of the full capability to bypass intruder states introduces $(\overline{H}_{ll} - E)$ if we adopt a nonlinear expansion containing powers of cluster operator in the corresponding cluster amplitude finding equation. One major contribution arising from $\overline{f_\mu T_3^\mu}$ is omitted in the SS-MRCCSDT-1a+d (and SS-MRCCSDT-1a) scheme since its presence would have introduced a direct coupling between amplitudes of different ϕ_μ amounting to the storage of T_3^μ amplitudes. As the off-diagonal parts of the occupied–occupied and virtual–virtual blocks of the Fock matrices have been ignored, the storage of the triples amplitudes is no longer required for the SS-MRCCSDT-n methods considered here. Thus, the T_3 equations can be solved by simultaneously computing the T_3 amplitudes for all references within a loop over all orbital indices. Akin to the CCSDT-1a, the CCSDT-1a+d approximation too includes the effect of connected triples in the T_3 determining equation itself, and it does not pose any extra computational cost. In the SDT-1a type approximation, the triples amplitudes are determined via a Møller–Plesset type denominator, whereas, in the SDT-1a+d scheme, the denominator reflects the energy difference between two configurations. This is quite evident in the relative performance of the two schemes as we will envisage soon [36]. The CCSDT-1a+d bears a signature of the configurational degeneracy that becomes obvious from its numerical behaviour at the point of strong configurational degeneracy (for details, see [36]).

3. Results and discussion

In the present section, the effectiveness of the SS-MRCCSDT-1a+d is demonstrated via computation of optimised molecular properties of spectroscopic interest of N_2H_2, O_3, CH_2 and square cyclobutadiene molecules. The small size of these systems has made them accessible to high-level electronic structure calculations for more than two decades and hence appear as popular benchmark systems. To judge the applicability of the SS-MRCCSDT-1a+d scheme, whenever possible, we compare its performance with that of results provided by previously published current generation methods in a variety of basis sets. If FCI data are not available for

the equilibrium structures, more appropriate reference points should be the most accurate available *ab initio* calculations, as experimental data include effects such as relativistic and non-adiabatic that are not taken into account in the present study. However, we have cited the experimental results here just as reference values so that one can judge whether our results are directed towards the experimental predictions or not. 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 freezing scheme of orbitals. Thereby, one can avoid, or at least attenuate, differences stemming out of the theoretical artifacts while comparing the results, nevertheless such a comparison in this context only represents the effectiveness of the method in a truly qualitative sense and is not intended for carrying any quantitative prediction whatsoever. For this reason, the quality of our comparison may not be appropriate. It should be noted that, in this article, our aim is 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-á-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.

Here, we have explored the capability of the SSMRCCSDT-1a+d approach to yield optimise geometrical parameters for the ground and first singlet-excited states. The computation of energy for the excited state at the SD or SDT-1a+d level of SS-MRCC method is done by converging (i.e. root-homing) on the higher root of the effective Hamiltonian. Although, the SS-MRCC has been suited to the calculation of the ground-state energy, as far as calculations for excited states are concerned, the possibility of convergence problems cannot be excluded. We also point out that root-homing scheme used here might seem to be useful for the kind of systems that have been dealt with in this work; however, the generality of the approach is lost in cases where the coefficients rapidly change sign, viz. 'mixed electronic states'. Here, it is worth noting that, for excited states, the problems of choosing the appropriate eigenvalue of the effective Hamiltonian from several eigenvalues is not an ambiguous matter in our SS-MRCC case as that of other single-root MRCC methods.

3.1.1 Diazene/diimide(N_2H_2)

As the first example, we consider the *cis–trans* isomerisation reaction of 1,2-diazene (N_2H_2) which has been

intensively studied by various *state-of-the-art ab initio* methods [48–56]. 1,2-Diazene, the simplest form of the azo-compounds, is a very useful candidate to stereospecifically reduce olefinic bonds. Azo compounds, containing –N=N– functional group, undergo a reversible *cis–trans* isomerisation either thermally or photochemically and act as powerful selective reducing agents and sources of free radicals which makes them potential systems for molecular switches or for optical data storage systems [57]. Regarding previous work on the energy surface of N_2H_2 (considering also reaction paths for diazene formation), the most detailed studies have been performed by Biczysko *et al.* [53]. Although different mechanisms have been proposed for this *cis–trans* isomerisation, the inversion process is the preferable path for the *cis–trans* isomerisation of diazene as demonstrated by Sokalski *et al.* [58]. A very recent study of Varandas and co-workers [53] reported rotational barrier heights of 54.96 kcal/mol and barrier heights of 51.07 kcal/mol for inversion using MRCI+Q/aug-cc-pVQZ along the MCSCF minimum energy pathway. However, the parametric 2-RDM (two-electron reduced density matrix) method with the *M* functional predicts that the rotational barrier for 1,2-diazene is lower than the inversional barrier by 3.1 kcal/mol in the extrapolated basis set limit (EBSL) [59]. The *M* parametric 2-RDM level of occupation number calculation predicts that the transition state in the rotational isomerisation is a strongly correlated system – a diradical – in agreement with MR methods. In fact, MR wave function methods support the rotational mechanism to be more energetically favourable, while SR methods suggest the inversional pathway to be more favourable [59]. With this knowledge in mind, the aim of the present study is to investigate the applicability of the SS-MRCCSDT-1a+d theory towards a correct description of energy curves of a strongly correlated rotational pathway (example of a rotation about a double bond) rather than a moderately correlated inversion pathway for the ground and excited states of the 1,2-diazene molecule (rigid rotation of the molecule).

The ground-state 1,2-diazene is dominated by a single configuration in the regions of local minima around *cis* and *trans* states. These configurations are $\phi_1 = 1a^2 1b^2 2a^2 2b^2 3a^2 3b^2 4a^2 4b^2$ for *cis* and $\phi_2 = 1a^2 1b^2 2a^2 2b^2 3a^2 3b^2 4a^2 5a^2$ for *trans* (as per the C_2 subgroup) As we can see, ϕ_1 and ϕ_2 differ by double excitation. In the region of the twisted geometries, both configurations are important and then we have a typical two-configuration closed-shell reference problem. Thus, the *cis–trans* isomerisation reaction of 1,2-diazene represents a typical two-state problem in which the contribution of the coefficients of reference configurations can change from 0 to 1 in a continuous manner and, in contrast to the
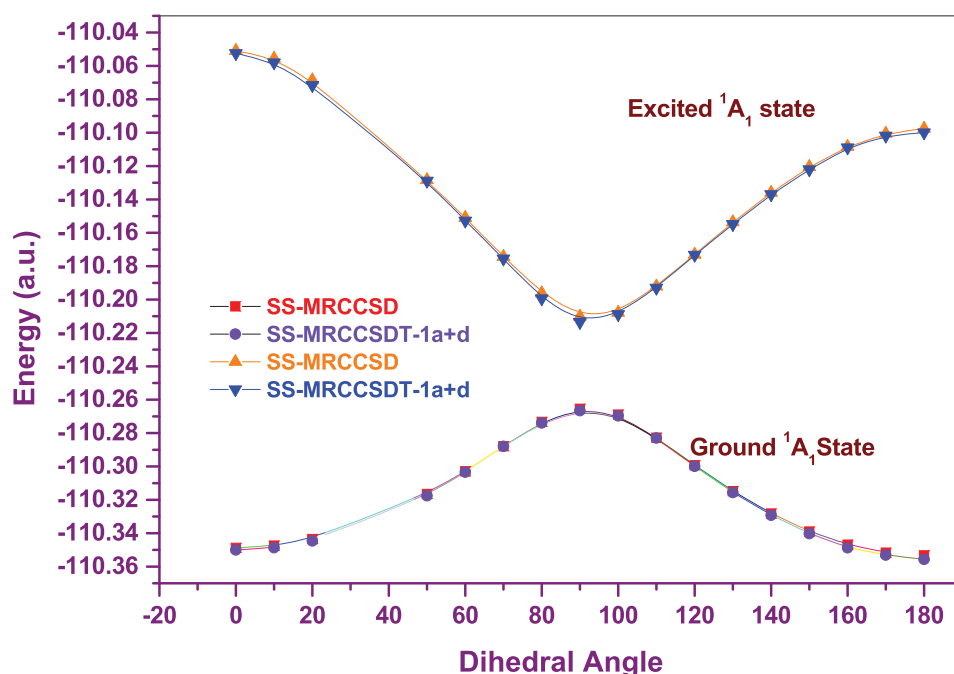
Figure 1. (Colour online). N_2H_2 torsional energy surfaces obtained with SS-MRCCSD and SS-MRCCSDT-1a+d methods for the ground and first biexcited states in cc-pVDZ basis set.

H4 models [60], it represents a real system. This shows that a method characterising the *cis/trans* isomerisation of 1,2-diazene must have a balanced description of both SR and MR states. It, therefore, can serve as a good probing ground for any electronic structure methodology tailored to treat quasi-degeneracies with varying degrees. In energy vs. dihedral angle plot, RHF-CCSD calculations show cusp around dihedral angle of 90° due to the configurational degeneracy, although the method provides a reliable description in the region from 0° to 70° [50]. It should be noted that a highly established current generation SRCC method, say CR-CCSD(T)$_\mathcal{L}$ (also known as CR-CC(2,3)) [33,61], also yields a pronounced cusp for a twisted conformation (about 90°) arising from an abrupt change in the Hartree–Fock reference determinant. However, as illustrated in several examples [33], the presence of the overlap-like denominator in the formula for the triples correction in CR-CC almost completely offsets the non-physical humps on energy surface produced by the CCSD(T) approach. Musiał *et al.* [56] demonstrated that the position of CCSD cusp also depends on the size of the basis sets. A correct curve should be smooth as it passes through the 90° point without a cusp. The sr-MRCCSD [16] as well as SU-MRCCSD and sr-BWMRCCSD [50] methods yield the correct shape of the rotational energy surface over the whole range of the dihedral angles without producing any cusp-like shape around the top of the barrier (i.e. transition region). All these facts indicate the clear benefit of using an MR-based method.

We employ a cc-pVDZ basis set and CASSCF(2,2) as the reference function. In ϕ_1 and ϕ_2, two active orbitals a and b belong to different symmetries, and hence the model space CAS(2,2) used in our applications is complete. The reaction paths connecting *trans*-1,2-diazene to the *cis*-1,2-diazene for the ground and first biexcited states are shown in Figure 1. As is apparent from the figure, the SS-MRCC method with both truncation schemes provides a very smooth and correct shape of the *cis–trans* isomerisation energy surface over the entire range of the dihedral angles for both the ground and excited states. The DIP-EOM-CCSDT′ method [62] can also provide the smooth cusp-free barrier surfaces of correct shapes for all dihedral angles [56] for these two states. The important thing is that the ground and biexcited $^1A_1$ SS-MRCC energy curves are completely cusp-free. We see that the lowest singlet-excited state, $^1A_1$ state PEC provided by the SS-MRCC approach, exhibits a very deep minimum around 90° similar to the DIP–EOM–CCSDT′. It is to be noted that in the close vicinity of 90°, switching of the ground and excited ^3B states occur. In the recent work due to Musiał *et al.* [56], it is seen that two states ^1A and ^3A show cusps in the vicinity of 100° in the EE–EOM–CCSD/cc-pVDZ level of calculations. Note that changing the dihedral angle near transition state in the parametric 2-RDM method with the M functional does not generate a cusp. From this fact, one can say that the parametric 2-RDM method with the M functional [59] has the ability to handle the configurational degeneracy of

Table 1. Equilibrium geometries for the ground state of 1,2-diazene (N_2H_2). Bond lengths and bond angles are given in Angstroms (Å) and degrees (°), respectively.

Conformers	Reference	Basis	Methods	R_{NN}	R_{NH}	∠ HNN
cis	Present work	cc-pVDZ	**SS-MRCCSD**	1.2510	1.0473	111.71
			SS-MRCCSDT-1a+d	1.2501	1.0410	111.52
	[53]	aug-cc-pVDZ	MRCI(12,10)	1.2597	1.0587	111.5
	[53]	aug-cc-pVTZ	MRCI(12,10)	1.2558	1.0481	111.6
	[51]	cc-pVDZ	CCSD(T)	1.2592	1.0501	111.48
	[51]	Best cal.	CCSD(T)	1.2456	1.0331	111.88
	[59]	aug-cc-pVDZ	M-2-RDM	1.2486	1.0360	111.93
			CR-CC(2,3)	1.2494	1.0348	111.83
trans	Present work	cc-pVDZ	**SS-MRCCSD**	1.2555	1.0423	105.35
	Present work		**SS-MRCCSDT-1a+d**	1.2560	1.0422	106.03
	[53]	aug-cc-pVTZ	MRCI(12,10)	1.2577	1.0426	105.9
	[53]	aug-cc-PVQZ	MRCI(12,10)	1.2563	1.0418	106.0
	[51]	cc-pVDZ	CCSD(T)	1.2643	1.0447	104.97
		Best cal.	CCSD(T)	1.2468	1.0281	106.17
	[55]	cc-pVDZ	MRSDCI	1.2655	1.0446	
			MRAQCC	1.2662	1.0453	
		cc-pVTZ	MRSDCI	1.2544	1.0306	
			MRAQCC	1.2556	1.0315	
		∞Z	MRAQCC	1.2487	1.0300	
	[59]	aug-cc-pVDZ	M-2-RDM	1.2486	1.0314	106.33
			CR-CC(2,3)	1.2495	1.0307	106.23
		Expt. [63]		1.2470	1.0300	106.3

ϕ_1 and ϕ_2 in the vicinity of the transition region and thus prevents an abrupt change in the rigid rotational energy curve.

The optimised geometries of the *trans*-1,2-diazene and *cis*-1,2-diazene provided by our SS-MRCC calculations are shown in Table 1. The geometries optimised by the other advanced methods are also included for the sake of comparison. It is perhaps worth mentioning that only for *trans*-1,2-diazene experimental geometric data are available [63]. Data assembled in the table indicate that the performance of the SS-MRCCSDT-1a+d numerical gradient approach is very satisfactory for the geometrical isomers of N_2H_2 molecule. For both *cis* and *trans* isomers, the ground-state geometrical parameters like bond length and angle are of comparable quality as the standard high-level CC schemes. It has been shown that geometries of *cis*

and *trans* configurations calculated at SS-MRCCSD and SS-MRCCSDT-1a+d levels agree well with the current generation theoretical estimates such as MRCI, MRCI+Q, MRAQCC and M-2-RDM. For the sake of completeness, we have also mentioned the experimental values for *trans* structure, keeping in mind the question of the size of an adequate basis set.

The accuracy of the calculations of the present work may further be assessed by comparing with the results of the relative energy gaps and barrier height of the *cis–trans* isomers. In Table 2, we have assembled the relative energies of the *cis* and *trans* isomers and the barrier height provided by the SS-MRCC calculations with SD and SDT-1a+d truncation schemes along with the other results obtained with established CI and CC methods. It is worth pointing out that predicting accurate barrier heights for

Table 2. Relative stability and barrier height (kcal/mol) with respect to *trans*-N_2H_2.

Reference	Basis	Method	TS-N_2H_2	*cis*-N_2H_2
Present work	cc-pVDZ	**SS-MRCCSDT-1a+d**	54.33	4.54
Present work	cc-pVDZ	**SS-MRCCSD**	55.13	2.84
Ref. 56	cc-pVDZ	DIP-EOM-CCSDT'	63.6	6.4
Ref. 56	cc-pVTZ	DIP-EOM-CCSDT'	64.8	7.7
Ref. 53	aug-cc-pVQZ	MRCI	56.39	5.03
Ref. 53	aug-cc-pVQZ	MRCI+Q	54.96	5.05
Ref. 53	cc-pVQZ	CCSD(T)	–	5.21
Ref. 59	aug-cc-pVDZ	2-RDM	51.52	
		CR-CCSD(T)	63.65	
	EBSL	2-RDM	50.73	
		CCSD(T)	62.64	
		CR-CCSD(T)	60.04	

chemical reactions is a challenge in quantum chemistry as the transition states usually have pronounced MR character. A comparison with the experimental estimates is not possible as we do not have reliable reference data. We observe significant deviations across methods for the strongly correlated rotational energy barrier. Table 2 clearly indicates that the quality of SS-MRCCSDT-1a+d results are acceptably good and very close to the previously published *stae-of-the-art* results. Both SS-MRCCSD and SS-MRCCSDT-1a+d methods yield a consistent set of data. The table indicates that the *trans* form is more stable and the *cis* is higher only by 3 kcal/mol. After incorporating corrections due to connected triples, this difference is enhanced to 5 kcal/mol. The SS-MRCCSDT-1a+d rotational barrier energy of 54 kcal/mol using the cc-pVDZ basis is similar to that previously calculated by Biczysko *et al.* using MRCI + Q/augcc-pVQZ [53], while the CC methods such as CCSD(T) and CR-CC(2,3) [33] provide slightly higher rotational barriers of 60.04 and 62.64 kcal/mol in the EBSL, respectively (see [59] for details). At the DIP–EOM–CCSDT′ level, the barrier heights are 63.6 kcal/mol with cc-pVDZ basis and 64.8 kcal/mol for the cc-pVTZ one. The DIP–EOM–CCSDT′ calculations (due to Musiał *et al.* [56]) provide a consistent set of values with the energy of the *cis* configuration being higher by 6.4 and 7.7 kcal/mol, respectively, for the double- and triple-zeta basis sets. The barrier heights obtained by the SS-MRCCSDT-1a+d with CASSCF orbitals are also similar for the calculations with the *M* parametric 2-RDM method [59].

From the above discussion, it is found that the SS-MRCCSDT-1a+d method provides a balanced description of both single- and MR correlations in the rotational barrier between *cis* and *trans* 1,2-diazene.

3.1.2. Ozone (O₃)

For years, various investigations [12,64–76] on the accurate description of optimised geometry of ozone molecule by well-established advanced theoretical methods have indicated that an accurate estimation of its optimised geometrical parameters in the ground state needs a correct and balanced description of both static and dynamic correlations by the use of an MR and excitations beyond doubles in the cluster operator. The ground state of O_3 has significant MR character (a prototype singlet with appreciable biradical character) even in its equilibrium description. A very good assemble of the methods used to study the ozone can be found in a recent paper by Hino *et al.* [77]. It has also been illustrated that ground state of ozone poses a challenge for the well-established equation of motion (EOMCC) approach [73]. Note that the ground as well as excited states of ozone can be properly addressed by MRCI methods [78]. Bartlett and co-workers [67] have

demonstrated that the CCSD[T] model fails to yield accurate results for O_3. Pabst *et al.* [79] have also illustrated the failure of the CC2 method for optimisation of the ground-state geometry of ozone as the CC2 method predicts a barrierless, exothermic and symmetric dissociation of O_3 to three oxygen atoms. Ozone is an extreme example for the collapse of CC2-like methods, although CC2 is a very useful model. Pabst *et al.* [79] also argue that the SRCC calculation with either iterative or perturbative triple excitations including terms up to fifth order leads to accurate results. It should be noted that reasonable accuracy can be achieved via the tailored CCSD method by exploiting a large active space consisting of 12 electrons in nine active orbitals [77]. Therefore, caution must be paid whenever SRCC models are applied to systems with strong biradical character. Hence, O_3 serves as a valuable benchmark for the performance of the MRCC methods. All these facts provide a strong motivation to study this system with our recently developed SS-MRCCSDT-1a+d code.

We choose a CAS(2,2) (consisting of $[core\cdots]4b_2^2 6a_2^1 1a_2^2$ and $[core\cdots]4b_2^2 6a_2^1 2b_1^2$ configurations) for assessing the performance of our present calculations. In order to judge results of our method in comparison to those obtained by the advanced methods, we performed our calculations with the often-used DZP basis set. Bartlett and co-workers [67] observed that the effect of basis sets on bond angle is negligibly small in the context of the CCSDT model. The three 1s orbitals of oxygen have been kept frozen in our correlation treatment. The calculated optimised bond lengths and bond angles are given in Table 3 along with the results of various advanced theoretical methods and experiment [80]. The table highlights the importance of considering the MR model to treat the ground-state optimised structure of ozone. We found that SS-MRCCSD and Mk-MRCCSD [21,23] greatly improve the O–O bond length and the ∠ O–O–O in ozone with respect to CCSD. Table 3 clearly indicates that SS-MRCC/cc-pVDZ with different truncations geometrical parameters are in good agreement with the Mk-MRCCSD(T)/cc-pVTZ values. For cc-pVDZ, all of the calculated properties using SS-MRCCSDT-1a+d (and SS-MRCCSD) are reasonably closer to the CCSDTQ and ic-MRCCSDT D [75] values with deviations of 0.011 for R_{O-O} and 0.2 for ∠O–O–O. The agreement of our SS-MRCC results with the values provided by ic-MRCCSDt D calculations [75] using cc-pVDZ basis is also noticeable. The encouraging results displayed in Table 3 strengthen our belief that highly accurate computations of molecular geometry for the ground-state ozone are possible with numerical gradient SSMRCC method using a CAS(2,2) in connection with perturbative triples via SDT-1a+d scheme [38].

Table 3. Results of equilibrium geometries for the ground state of O_3 molecule, using the methods described in the text. Bond lengths (R_e) and bond angles ($\angle$O–O–O) are given in Angstroms (Å) and degree(°), respectively.

Reference	Basis	Methods	R_{O-O}	$\angle$O–O–O
Present work	DZP	**SS-MRCCSD**	1.2807	116.0
		SS-MRCCSDT-1a+d	1.2811	116.4
	cc-pVDZ	**SS-MRCCSD**	1.2801	116.1
		SS-MRCCSDT-1a+d	1.2800	116.5
Ref. 69	DZP	TCSCF CISD	1.271	116.2
		CISD[TQ]	1.281	116.7
		SRCCSD(T)	1.287	116.8
		SRCCSDT	1.286	116.
		2R-RMR CCSD	1.276	116.5
		3R-RMR CCSD	1.277	116.7
Ref. 67	DZP	CCSDT-1a	1.295	116.6
		CCSDT-1b	1.292	116.6
		CCSDT-1c	1.294	116.8
		CC3	1.293	116.8
		CCSDT-2	1.283	116.8
		CCSDT-3	1.285	116.9
		CCSDT	1.286	116.7
		CCSD(TQf)	1.290	116.6
		CCSDT-3(Q_f)	1.290	116.6
Ref. 68		B-CCD(T)	1.288	116.8
		CI-SD[TQ]	1.281	116.7
Ref. 66	DZP	MRCI	1.261	116.5
		MR-ACPF	1.315	115.8
		MR-AQCC	1.292	116.1
		MR-AQCC-v	1.286	116.2
Ref. 70	DZP	TR-BWCCSD	1.297	116.2
	cc-pVTZ	TR-BWCCSD	1.280	116.3
		CCSDT (Q_f)	1.279	116.6
Ref. [21,23]	cc-pVTZ	Mk-MRCCSD(T)	1.2897	116.1
	cc-pV5Z	Mk-MRCCSD(T)	1.2814	116.3
Ref. 74	cc-pCV5Z	icMR-CISD+QD	1.2700	116.84
		icMR-AQCC	1.2709	116.84
		icMR-AQCC+RMVD	1.2714	116.84
Ref. 72	cc-pVDZ	ic-MR-CISD/CAS(18,12)	1.291	116.2
	cc-pV5Z		1.271	116.9
Ref. 75	cc-pVQZ	ic-MRCCSD	1.273	116.9
	cc-pVDZ	ic-MRCCSDT D	1.291	116.3
	cc-pVDZ	ic-MRCCSDt D	1.281	116.3
	cc-pVDZ	CCSDT	1.283	116.5
	cc-pVDZ	CCSDTQ	1.291	116.3
Ref. 80		Experiment	1.273	116.8

TR: Two-reference.

3.1.3. $\widetilde{a}\,^1A_1$ and $\widetilde{c}\,^1A_1$ methylene, CH_2

We now investigate methylene (CH_2) in the excited states, $\widetilde{a}\,^1A_1$ (1^1A_1) and $\widetilde{c}\,^1A_1$ (2^1A_1), which are said to have diradical character [19,20,55,81–93] and are therefore more challenging to calculate. To the best of our knowledge, although $\widetilde{a}$ state has been carefully studied by various experiments [94] and computational methods, the $\widetilde{c}$ excited state is not well addressed. The $\widetilde{a}\,^1A_1$ and $\widetilde{c}\,^1A_1$ excited states are closed-shell singlet and may be described by the admixture two-configuration wave functions (C_{2v} symmetry): (1) $\phi_1 = (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(2b_1)^0$, and (2) $\phi_2 = (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^0(2b_1)^2$. The first excited state, $\widetilde{a}\,^1A_1$, may be appropriately presented by $C_1(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(2b_1)^0 + C_2(1a_1)^2(2a_1)^2 \times (1b_2)^2(3a_1)^0(2b_1)^2$, and the fourth excited

state, $\widetilde{c}\,^1A_1$, may be correctly presented by $C_1(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^0(2b_1)^2 + C_2(1a_1)^2(2a_1)^2 \times (1b_2)^2(3a_1)^2(2b_1)^0$. Note that the CI coefficients $C_1 + C_2$ ($|C_1| > |C_2|$) for the $\widetilde{a}\,^1A_1$ state have opposite signs and the coefficients for the $\widetilde{c}\,^1A_1$ state have the same sign. The $\widetilde{c}\,^1A_1$ state can be viewed as a doubly excited state with respect to the $\widetilde{a}\,^1A_1$ state. In light of this, both $^1A_1$ states of CH_2 can serve as benchmarks for our SSMRCCSDT-1a+d method. Previous studies indicate, in general, methods such as FCI, MRCI and spin-flip (SF) or MRCC are all capable of describing the low-lying excited states of CH_2. A more comprehensive review of previous works in this context can be found in [95].

As in the other cases mentioned above, the two active orbitals a and b involved in the two model functions belong to different symmetries. Thus, the model space CAS(2,2) is complete. CASSCF(2,2) type of reference wave functions have been used in the present work. For both $\widetilde{a}\,^1A_1$ CH_2 and $\widetilde{c}\,^1A_1$ CH_2, we have used DZP and TZ2P basis sets [96] as full CI calculations with these basis sets have already been published [84,95]. We have used the schemes as used in [84,95] for DZP and TZ2P basis sets. In the case of $\widetilde{a}\,^1A_1$ CH_2 state, we also consider cc-pVTZ basis set where only 1s orbital was frozen for which a comparison with other MRCC treatments such as BW-MRCCSDT and Mk-MRCCSDT data is available.

Selected optimised geometrical parameters for the $\widetilde{a}\,^1A_1$ CH_2 are assembled in Table 4. The results of Mk-MRCC and BW-MRCC as well as of the single-reference CC method are also incorporated for comparison. Table 4 illustrates that SS-MRCCSDT-1a+d values with CAS(2,2) and different basis sets accord with the equilibrium structure yielded by the *state-of-the-art ab initio* calculations. For DZP basis, the inclusion of connected triples perturbatically leads to a decrease of the bond length and valence angle by 0.0069 Å and 0.07°. For cc-PVTZ basis set, the table represents a decrease of bond length by 0.0007 Å and an increase of the valence angle by 0.66° due to inclusion of connected triples. For TZ2P basis, values assembled in the table represent an increase of the bond length by 0.0028 Å and of valence angle by 0.36 ° due to inclusion of connected triples. It should be noted that Pittner and co-workers [19,20] found that the use of a larger basis set and connected triples generally leads to a decrease of the bond length and increase of the valence angle at their MRCC level of calculations. For cc-PVTZ basis set, overall, a very good agreement has been found between SS-MRCCSDT-1a+d and the full-blown BW-MRCCSDT as well as Mk-MRCCSDT values as differences between full MR-CCSDT and SS-MRCCSDT-1a+d method with approximate inclusion of connected triples are acceptably small. The TZ2P SS-MRCCSDT-1a+d results appear to be in reasonable agreement with

Table 4. Results of equilibrium geometries for the $\widetilde{a}^1 A_1$ excited state of CH_2 system. Bond lengths and bond angles are given in Angstroms (Å) and degrees (°), respectively.

Ref.	Basis	Methods	R_{C-H}	$\measuredangle$ HCH
Present works	DZP	**SS-MRCCSD**	1.1178	102.12
		SS-MRCCSDT-1a+d	1.1109	102.05
	TZ2P	**SS-MRCCSD**	1.1053	102.20
		SS-MRCCSDT-1a+d	1.1081	101.84
	cc-pVTZ	**SS-MRCCSD**	1.1110	101.78
		SS-MRCCSDT-1a+d	1.1103	101.12
Ref. [84,95]	DZP	CCSD(T)	1.1199	101.28
		CCSDT	1.1199	101.42
		FCI	1.1199	101.44
	TZ2P	CCSD(T)	1.1089	101.72
		CCSDT	1.1088	101.86
		FCI	1.1089	101.89
	ANO	MRCI	1.1112	101.95
	est. complete basis	CMRCI	1.1061	102.23
	est. complete basis	RCCSD(T)	1.1058	102.23
Ref. 85	cc-pVDZ	SRCCSD	1.127	100.4
		2R-RMR-CCSD	1.127	100.8
		3R-RMR-CCSD	1.127	100.7
	cc-pVTZ	SRCCSD	1.109	101.6
		2R-RMR-CCSD	1.108	101.9
		3R-RMR-CCSD	1.108	101.9
Ref. [19,20]	6-31G	BW-MRCCSD	1.129	103.7
	6-31G* fzc	BW-MRCCSD	1.116	102.0
	6-31G	SU-MRCCSD	1.129	103.7
	6-31G* fzc	SU-MRCCSD	1.116	102.0
	6-31G	FCI	1.130	103.6
	6-31G* fzc	FCI	1.118	101.8
Ref. [19,20]	cc-pVTZ	Mk-MRCCSDT	1.110	101.90
		BWMRCCSDT	1.110	101.79
	cc-pV5Z	BWMRCCSDT-1 n.c.	1.1077	102.18
		BWMR CCSDT-1 a.c.	1.1066	102.48
Ref. 90	aug-cc-pCV6Z	MRACPF	1.1107	101.7
	aug-cc-pCV6Z	MRCI	1.1190	101.6
Ref. 91	aug-cc-pCVQZ	IC-MR-ACPF	1.1069	102.31
Ref. 92	aug-cc-pVQZ	IC-MRCISD+Q	1.1102	102.0
Ref. 94		Experiment	1.107	102.4

the larger basis set (aug-cc-pCV6Z) MRACPF and MRCI geometries of Kerkines *et al.* [90]. Although the basis set effect is still significant, the closer agreement between SSMRCCSDT-1a+d (SSMRCCSD) and experiment [94] is meaningful. It is also noticed that the values provided by SS-MRCCSDT-1a+d/TZP method are very close to the FCI/TZ2P results [82,84] differing by an order of 10^{-3} Åfor the bond length and 0.5° for the bond angle. The predicted SSMRCCSDT-1a+d geometries for $\widetilde{a}\,^1A_1$ CH_2 agree quite well with the IC-MR-ACPF/aug-cc-pCVQZ level of calculations [91]. The equilibrium CH distance and the ∠HCH of the $\widetilde{a}\,^1A_1$ CH_2 state also agree well with the available IC-MRCI/aug-cc-pVQZ values with the Davidson correction [92].

Next, we focus on the $\widetilde{c}\,^1A_1$ CH_2 which is theoretically more challenging than $\widetilde{a}$ as it is the second root of its spatial and spin symmetry ($^1A_1$) and, therefore, more difficult to describe than the lowest state of a given symmetry and earlier calculations show that $\widetilde{c}$ state requires a proper MR description. Theoretical investigation of states

not the lowest of their symmetry are usually difficult. The barrier to linearity is so small that one cannot definitively determine if the $\widetilde{c}$ state of CH_2 is linear or bent and it might be difficult to establish the shape of the potential from the experiment. In the near past, Schaefer III-Sherrill and co-workers have examined the structures and vibrational frequencies of the four lowest electronic states of methylene using DZP and TZ2P basis sets and FCI, along with the various approximate CI and CC treatments [95]. The internally contracted MRCC (IC-MRCI) calculations of Bauschlicher [97] yields very flat bending energy surface for the $\widetilde{c}$ state. As per values reported in [97], the energy gap between the linear and bent structures is only about 0.03 kcal/mol at the MRCI level of theory and they argue in favour of quasi-linear structure for the $\widetilde{c}$ state. Results of Bauschlicher [97] indicate that the changeover from CASSCF to MRCI calculations indicates the fact that improving the correlation treatment favours the linear form. Initially, Bauschlicher and Yarkony [98] argued that the bent structure at the

Table 5 Results of equilibrium geometries for the $(\widetilde{c}\,^1A_1)$ excited state of CH_2 system. Bond lengths and bond angles are given in Angstroms (Å) and degrees (°), respectively.

Ref.	Basis	Methods	R_{C-H}	$\sphericalangle$ HCH
Present works	DZP	**SS-MRCCSD**	1.0738	168.76
		SS-MRCCSDT-1a+d	1.0744	169.53
	TZ2P	**SS-MRCCSD**	1.0660	170.51
		SS-MRCCSDT-1a+d	1.0683	169.54
Ref. [84,95]	DZP	TCSCF-CISD	1.0719	170.00
		FCI	1.0749	169.68
	TZ2P	TCSCF	1.0556	176.20
		FCI	1.0678	170.08
	TZ3P(2f,2d)+2diff	TCSCF-CISD	1.064	171.6
Ref. 97	aug-ccpV5Z	ICMRCI	1.068	171.9
Ref. 91	aug-cc-pCVQZ	IC-MR-ACPF	1.0671	171.89
Ref. 92	aug-cc-pVQZ	IC-MRCISD+Q	1.0679	172.0

TCSCF-CISD/DZP level of calculation may be due to artifactual symmetry breaking of the wave function. Schaefer III-Sherrill and co-workers [95] encountered a barrier of 0.07 kcal/mol to linearity of extremely flat bending potential surface at the FCI/TZ2P level of theory, which should be free of symmetry-breaking problems. They argued that improvements in the basis set or in the treatment of the electron correlation from a TC-SCF calculation to a TCSCF-based CISD/CISDTQ/FCI calculation tended to decrease the angle. Bunker et al. [83] found that the $\widetilde{c}\,^1A_1$ CH_2 is bent, but the theoretical energy difference between the linear and bent geometries is only about 0.03 kcal/mol at the TCSCF-CISD/TZ3P(2f ,2d) + diff level, and later reported a value of 0.02 kcal/mol. It may be interesting to note that the question of whether the $\widetilde{c}\,^1A_1$ state is linear or bent is not addressed here. It is evident from the current literature of electronic structure theory that the bent configuration is lower in energy [82–84,91,92].

The equilibrium geometries for $\widetilde{c}\,^1A_1$ CH_2 obtained by our SS-MRCC methods are collected in Table 5. At this point, it is worth noting that there is no experimental determination of the $\widetilde{c}$ state structure. In agreement with previous works [95], the $\widetilde{c}\,^1A_1$ state remains bent at the SS-MRCC level of calculations with both SD and SDT-1a+d truncations. From the table, one can see that the geometrical parameters in the current SS-MRCCSDT-1a+d work are in good agreement with FCI results reported by Schaefer III-Sherrill and co-workers [95]. The SS-MRCCSDT-1a+d values are in closer agreement to the FCI values than those of the SS-MRCCSD level of calculations. For instance, the deviation between FCI and SS-MRCCSDT-1a+d for bond length (Å) and angle (°) are 0.0066 and 0.14, respectively. The corresponding deviations for the SS-MRCCSD method are 0.0089 and 0.83 respectively. Our SS-MRCCSDT-1a+d calculations also confirm the prediction of the TCSCF-CISD/TZ3P(2f,2d)

+ 2 diff level of calculation of Yamaguchi et al. [95]. The predicted equilibrium geometrical parameters for the $\widetilde{c}\,^1A_1$ state also agree quite well with IC-MRCI study with aug-ccpV5Z basis [97]. Similarly, SS-MRCCSDT-1a+d structures of the $\widetilde{c}\,^1A_1$ state are in good agreement with the IC-MR-ACPF/aug-cc-pCVQZ equilibrium geometry by Flores and Gdanitz [91]. Our calculated results are in good agreement with the IC-MRCI+Q/aug-cc-pVQZ values [92], reflecting the accuracy of our SS-MRCCSDT-1a+d gradient approach. With the improvements in the treatment of the electron correlation, the SS-MRCC bond length and angle of the $\widetilde{c}\,^1A_1$ state increase. The inclusion of triples clearly leads to improved agreement between our calculated and observed values for both these states.

It is found in the present study that the two low-lying states of $^1A_1$ CH_2 all have bent structures in accordance with the previous study [84]. At the SS-MRCCSDT-1a+d/DZP level of theory, the bond lengths (in Å) of the two excited singlet states are in the order: $\widetilde{a}\,^1A_1$ (1.1109) > $\widetilde{c}\,^1A_1$ (1.0744) which is consistent with the FCI/DZP results of Schaefer III-Sherrill and co-workers: $\widetilde{a}\,^1A_1$ (1.1199) > $\widetilde{c}\,^1A_1$ (1.0749). Note that with the same basis set, the bond angles of the two states are in the reverse order of the bond lengths. The predicted ordering of the bond angles (°) for the two closed-shell singlet obtained by SS-MRCCSDT-1a+d/DZP method [$\widetilde{a}\,^1A_1$ (102.05) < $\widetilde{c}\,^1A_1$ (169.53)] is also consistent with the values obtained by FCI/DZP calculations [$\widetilde{a}\,^1A_1$ (101.44) < $\widetilde{c}\,^1A_1$ (169.68)]. The same observation has also been found at the level of SS-MRCC and FCI theories when the relatively small DZP basis set is replaced by the more flexible TZ2P basis set [95]. The present SS-MRCC results in combination with the previous FCI estimates for the $\widetilde{c}\,^1A_1$ state may be helpful in calibrating methods meant to describe excited electronic states. Tables 4 and 5 indicate that better agreement between the theoretical treatments, and experiment can be achieved via the complete

Table 6. Optimised geometrical parameters of the square (transition structure) cyclobutadiene in its ground (S_0, 1^1B_{1g}) and first singlet-excited (S_1, 1^1A_{1g}) states. Bond lengths are given in Å.

State	References	Basis	Method	R_{CC}	R_{C-H}
Ground state	Present work	STO-3G	**SS-MRCCSD**	1.4763	1.1044
		STO-3G	**SS-MRCCSDT-1a+d**	1.4676	1.0823
	Ref. 25	[3s2p1d/ls]	MRCCSD	1.4477	1.1016
	Ref. [103]	cc-pVDZ	MRAQCC/SA-4-CASSCF	1.461	1.092
	Ref. [101]	cc-pVTZ(mixed)	EOM-SF-CCSD	1.440	1.080
Excited state	Present work	STO-3G	SS-MRCCSD	1.4764	1.1052
		STO-3G	SS-MRCCSDT-1a+d	1.4871	1.1054
	Ref. 25	[3s2p1d/ls]	MRCCSD	1.4608	1.1019
	Ref. [103]	cc-pVDZ	MRAQCC/SA-4-CASSCF	1.461	1.092
	Ref. [101]	cc-pVTZ(mixed)	EOM-SF-CCSD	1.427	1.080
	Ref. [107]	6-31G(d)	FORS/MCSCF	1.4464	1.0699

basis set estimates of the more complete treatments of electron correlation.

3.1.4. Transition state geometry of Cyclobutadiene (D_{4h} symmetric CBD)

We finally consider the first singlet-excited state of cyclobutadiene (CBD) in its square conformation with D_{4h} symmetry. We mention this system here to illustrate the type of predictive power the SS-MRCCSDT-1a+D method may have in investigations on reaction mechanisms involving biradical transition state(s). The square structure has been recognised as the transition state in the automerisation of CBD (Rectangular(CBD)→ Square(CBD)→ Rectangular(CBD) in the ground state). This prototypical anti-aromatic (due to its four π-electrons), highly strained and short-lived system has been a challenge for both experimental [99] and theoretical [20,22,25,36,100–107] chemists since many decades. Theoretical study of the square CBD (a disjoint biradical) in the ground and excited states has been of great interest for over a century due to recurring questions of its anti-aromatic vs. aromatic character, geometry, electronic structure and reactivity. The e_g^2 configuration of the square D_{4h} symmetric CBD yields four states: $^3A_{2g}$, $^1B_{1g}$, $^1B_{2g}$ and $^1A_{1g}$. It should be noted that independent of the density functional used, the triplet $^3A_{2g}$ is the ground state of the square CBD, with the lowest singlet ^1B_1g excited state being 4 kcal/mol above the ground state [108]. This state ordering is opposite to the results of the wave-function-based calculations, which yield a singlet $^1B_{1g}$ ground state [25,101,103]. In fact, the energy of the lowest triplet state, $^3A_{2g}$, is fairly close to that of the ground-state singlet, $^1B_{1g}$, and their relative ordering is highly sensitive with respect to the level of treatment of the correlation energy. It has been argued by Eckert-Maksić et al. [103] that the rapid interconversion of two structures $^1B_{1g}$ CBD and $^3A_{2g}$ CBD indicate that the lowest triplet state might play a vital role in the chemical

reactivity of CBD. Here, we have focused on the ground (S_0) $^1B_{1g}$ and the first singlet (S_1) $^1A_{1g}$ states. The challenges originate in the MR character of the ground (S_0) and excited (S_1) electronic states of the D_{4h} symmetric CBD which emerge from the (quasi)degeneracy in the π system and hence a reliable theoretical description of both states requires MR methods. The degree of orbital quasi-degeneracy as well as the nature of the low-lying excited states of CBD depends strongly on nuclear positions (see Figure 2 in [103]). Thus, the estimation of optimised geometries of both states along with their energy gap represents an excellent probing ground for testing the efficiency of the method designed to handle quasi-degeneracies like SS-MRCC. Note that the CBD adopts a rhombic (D_{2h}structure in its S_1 state rather than square one, D_{4h}) in the full-optimised reaction space MR-AQCC/SA-4-CASSCF [103] and MRCC [25] level of calculations as a result of pseudo-Jahn–Teller distortions (see Figure 3 in [103]). In S_1 state of CBD, the preference of the rhombic conformation emerges from the energy lowering of the nuclear electron attractive term of σ-electrons and the kinetic term of π electrons.

In our calculations, we have used the same model and basis set as reported by Li and Paldus [104]. In the present work, the eight 1s carbon electrons have been kept frozen in the SS-MRCC calculations rather than 16 (1s and 2s electrons) on carbon atoms [104]. A two-dimensional reference space, CAS(2,2), is used. The optimised geometrical parameters of the states considered are depicted in Table 6. It should be noted that the geometry of D_{4h} symmetric CBD in its ground state (S_0) has already been published by Mahapatra and Chattopadhyay [36] using the same freezing scheme of Li and Paldus. Here, we primarily focus on the excited S_1 state and the energy difference of spectroscopic interest. Our SS-MRCC study clearly indicates that the predicted CC and CH bond lengths increase during the excitation from $S_0 \rightarrow S_1$ (with assumed square structure). However, the CC and CH

Table 7. Energy differences (in kcal/mol) between 1^1B_{1g} and 1^1A_{1g} states in the square conformation of cyclobutadiene (D_{4h} symmetry).

References	Basis	Method	ΔE
Present work	STO-3G	**SS-MRCCSDT-1a+d**	49.4
Ref. [101]	cc-pVTZ	EOM-SF-CCSD	41.8
Ref. [103]	cc-pVDZ	MRAQCC/SA-4-CASSCF	32.6
	cc-pVTZ	MRAQCC/SA-4-CASSCF	31.5
Ref. 25	[3s2p1d/ls]	MRCCSD	52.8
	[3s2p1d/ls]	MRCCSD(T)	52.6

bond distances of the ground sate differ very little from the excited states in the transition state structure. It is wroth noting that MR-AQCC/SS-CASSCF/ccpVDZ level of theory [103] gives virtually the same structural parameters for both these states, differing only at higher decimals and hence neglected. The calculated bond lengths using our SS-MRCC methods are also in good accord with the values of FORS/MCSCF/6-31G(d) calculations [107]. Note that the geometries yielded in the MR-CCSD and EOM-SF-CCSD/cc-pVTZ (mixed) calculations reported in the table are very close to the geometries obtained by our present work.

Table 7 summarises some of the theoretical results for the excitation energies of D_{4h} CBD at the S_0 and S_1 equilibrium geometries. Estimation of excitation energies of CBD has been serving as a useful probing ground for any method designed to handle quasi-degeneracies. Note that there is a large scatter of the theoretically predicted values for the energy gap between 1^1B_{1g} and 1^1A_{1g} in the literature depending on the level of calculations implemented, implying that the problem is not settled as yet. The SS-MRCCSDT-1a+d (SS-MRCCSD) energy difference between the optimised ground and excited states for the square conformation of CBD is about 49 (48) kcal/mol. This value does not include the zero-point vibrational energy. Our estimated values are very close to ∼ 53 kcal/mol obtained by Balkova and Bartlett with the MR-CCSD and MR-CCSD(T) methods in the (3s2p1d/ls) basis confirming the effectiveness of our present scheme.

From the above analysis, it is evident that the accurate agreement between SS-MRCSDT-1a+d with *state-of-art* level of *ab initio* calculations and FCI whenever available (and also with the experiment) is not fortuitous which strengthens our belief that highly accurate computations of molecular properties for MR systems are possible with our present SS-MRCC scheme using a CAS(2,2) in connection with perturbative triples correction. It is to be noted that the inclusion of connected triples approximately via SDT-1a+d [38] scheme at SS-MRCCSD level does not significantly change the overall description. Here, we observe that the SS-MRCCSDT-1a+d method yields results very close to the full-blown MR-CCSDT one. However, the satisfactory performance

of our SDT-1a+d scheme to incorporate connected triples correction within the framework of MRCC model is promising for further development. To reduce the computational cost, one can employ the SDT-1a+d scheme for triples equations in a non-iterative manner.

In this work, only a pilot implementation is described, which is not efficient in general. The gradient for SS-MRCC can be implemented efficiently by exploiting techniques well known from the standard CC-based gradient method, which will be a subject of the following work. We should mention that it would be useful to develop an analytic approach which would certainly be less expensive than the numerical gradient procedure since the gradient method is based on numerical rather than analytical differentiation. This fact inspires us to develop the analytical gradient to make the method truly useful. Work in this direction is in progress. We will also examine the performance of the SS-MRCC method with SDT-1a+d approximation to treat open-shell states in the future work.

We conclude this part by addressing the relationship of the present SS-MRCCSDT-1a+d approach with the CR-CC method (in which one corrects the standard CCSD energy for the effects of triply and other higher-than-doubly excited clusters) of Piecuch *et al.* [33] which bears a close kinship with our present approach where they distinguish between approximation *A*, which uses Møller–Plesset denominators only, and approximation *D*, which uses the Epstein–Nesbet partitioning which is similar to what we do, when we switch from CCSDT-1a to CCSDT-1a+d. They demonstrated that approximation *D* is always superior (more accurate) compared to variant *A*, especially for an accurate description of single bond breaking (i.e. energy surfaces) involving diradicals. In both CR-CC(2,3) and our CCSDT1-a+d schemes, the correction is fully size-extensive. Although the CR-CCSD(T) method improves the asymptotic behaviour of CCSD(T), the method is not size-extensive. In our CCSDT-1a+d method, we have used bare Hamiltonian for the corrections whereas CR-CC(2,3) method requires the entire effective Hamiltonian matrix, which is not as readily available as the bare Hamiltonian itself. It is important to note that the CR-CC(2,3) includes the triples, but connected quadruples are neglected in it. In CCSDT-1a+d method, there is also no quadruple terms. At this juncture, it is worth stressing that owing to their efficiency, the CR-CC method and related approaches have recently been implemented in widely used quantum-chemical packages.

4. Conclusion

The SS-MRCC method belonging to the group of single-root Hilbert space methods, eliminates the intruder

state problem. As the SS-MRCCSDT-1a+d equations have emerged from the fully connected SS-MRCC equations, the working equations for SS-MRCCSDT-1a+d are connected and hence SS-MRCCSDT-1a+d provides size-extensive energy. CCSDT-1a+d is a new perturbative correction to single-reference CCSD. We found that the partial inclusion of connected triples to SS-MRCCSD using CCSDT-1a+d scheme (just by taking certain terms in the linearised equation for triples) has significant effect on the correlation treatment. The resulting method has been abbreviated as SS-MRCCSDT-1a+d. One of the important features of the resulting SS-MRCCSDT-1a+d method is that it does not require storage of the triples amplitudes. Although less rigorous than the full-blown SS-MRCCSDT, triples correction via SDT-1a+d scheme (just by considering certain terms in the linearised triples equation) is useful due to its lower computational cost and its applicability to larger systems. SS-MRCCSDT-1a+d can be viewed as a good compromise between accuracy and the computational cost.

The efficacy of the SS-MRCCSDT-1a+d method to yield optimised geometrical parameters has been tested on the ground state of N_2H_2 and O_3 exhibiting MR character using numerically oriented static response approach. In addition to $\tilde{a}\,^1A_1$ CH_2, we have reported optimised geometries for the lowest $\tilde{c}\,^1A_1$ of CH_2 which features a very flat bending potential. Our aim has also been to verify the applicability of the SS-MRCCSDT-1a+d gradient method for the estimation of the optimised geometries of ground and excited states of square conformation of CBD with D_{4h} symmetry. The computed results are compared with other advanced *ab initio* methods and with experimental data whenever available. The results obtained for these systems employing CAS(2,2) in our numerical gradient scheme are very encouraging as our estimates are in good agreement with the results obtained with advanced SRCC and MRCC calculations. Apart from its lack of orbital invariancy, the gradient scheme for the SS-MRCCSDT-1a+d method offers many beneficial properties and shows a good numerical accuracy for ground-state and excited-state calculations. The triple correction in the SS-MRCC calculation using SDT-1a+d scheme is seen to match fairly well with the predicted FCI values whenever available. The results presented in the present work reiterate the importance of the triples effect. As the full-blown SS-MRCCSDT method is computationally demanding, the SS-MRCCSDT-1a+d method seems to be a promising tool only for benchmark treatment of systems where the intricate interplay of dynamic correlation and quasi-degeneracy plays an important role, while the SS-MRCCSDT-1a+d approach can be employed for application calculations. One will only be able to convincingly conclude once robust codes

to compute analytical gradients are developed for the SS-MRCSDT-1a+d, which could tackle molecules of arbitrary complexity with extensive basis sets.

Acknowledgments

Disclosure statement

Funding

References

[1] J. Paldus, in *Methods in Computational Molecular Physics, NATO ASI Series B: Physics*, edited by S. Wilson and G.H.F. Diercksen (Plenum, New York, 1992), Vol. 293, 99–194, P. Čársky, J. Paldus, and J. Pittner, editors, *Recent Progress in Coupled Cluster Methods:Theory and Applications* (Springer, Berlin, 2010); D.I. Lyakh, M. Musial, V.F. Lotrich, and R.J. Bartlett, *Chem. Rev.* **112**, 182 (2012).
[2] E. Prochnow, M.E. Harding, and J. Gauss, J. Chem. Theory Comput. **6**, 2339 (2010); O. Demel, J. Pittner, and F. Neese, J. Chem. Theory Comput. **11**, 3104 (2015).
[3] B. Jeziorski and H.J. Monkhorst, Phys. Rev. A **24**, 1668 (1981).
[4] B. Jeziorski and J. Paldus, J. Chem. Phys. **90**, 2714 (1989); P. Piecuch and J. Paldus, Theor. Chim. Acta **83**, 69 (1992); J. Chem. Phys. **101**, 5875 (1994). B. Jeziorski, Mol. Phys. **108**, 3043 (2010).
[5] T.A. Schucan and H.A. Weidenmüller, Ann. Phys. (N.Y.) **73**, 108 (1972); G. Hose and U. Kaldor, J. Phys. B **12**, 3827 (1979); P. Piecuch and J. Paldus, Phys. Rev. A **49**, 3479 (1993); J.P. Finley, R.K. Chaudhuri, and K. Freed, J. Chem. Phys. **103**, 4990 (1995); J. Paldus and X. Li, Adv. Chem. Phys. **110**, 1 (1999).
[6] K. Kowalski and P. Piecuch, Phys. Rev. A **61**, 052506 (2000); Int. J. Quantum Chem. **80**, 757 (2000).
[7] J.-P. Malrieu, P. Durand, and J.-P. Daudey, J. Phys. A **18**, 809 (1985); D. Mukhopadhyay, B. Datta, and D. Mukherjee, Chem. Phys. Lett. **197**, 236 (1992); L. Meissner, *ibid.* **255**, 244 (1996).
[8] J.-L. Heully and J.-P. Malrieu, Chem. Phys. Lett. **199** 545, (1992); J. Meller, J.P. Malrieu, and J.L. Heully, *ibid.* **244**, 440 (1995); J.-L. Heully and J.-P. Malrieu, J. Mol. Struct. THEOCHEM **768**, 53 (2006).
[9] J. Mášik and I. Hubač, in *Quantum Systems in Chemistry and Physics: Trends in Methods and Applications*, edited by R. McWeeny et al. (KA, Dordrecht, 1997); J. Mášik, I. Hubač, and P. Mach, J. Chem. Phys. **108**, 6571 (1998).

[10] I. Hubač and S. Wilson, in *Brillouin- Wigner Methods for Many-Body Systems;* and references therein, edited by J. Maruani and S. Wilson (Springer, Amsterdam, 2010).

[11] U.S. Mahapatra, B. Datta, B. Bandyopadhyay, and D. Mukherjee, Adv. Quantum Chem. **30**, 163 (1998); U.S. Mahapatra, B. Datta, and D. Mukherjee, Mol. Phys. **94**, 157 (1998); J. Chem. Phys. **110**, 6171 (1999).

[12] J. Pittner, P. Nachtigall, P. Čársky, J. Mášik, and I. Hubač, J. Chem. Phys. **110**, 10275 (1999); I. Hubač, J. Prittner, and P. Čársky, *ibid*. **112**, 8779 (2000).

[13] J. Prittner, J. Chem. Phys. **118**, 10876 (2003).

[14] M. Hanrath, J. Chem. Phys. **123**, 084102 (2005); M. Hanrath, in *Recent Progress in Coupled Cluster Methods:Theory and Applications*, edited by P. Čársky, J. Paldus, and J. Pittner (Springer, Berlin, 2010).

[15] L. Kong, Int. J. Quantum Chem. **109**, 441 (2009).

[16] U.S. Mahapatra and S. Chattopadhyay, J. Chem. Phys. **134**, 044113 (2011).

[17] F.A. Evangelista, W.D. Allen, and H.F. Schaefer III, J. Chem. Phys. **125**, 154113 (2006); *ibid*. **127**, 024102 (2007).

[18] F.A. Evangelista, A.C. Simmonett, W.D. Allen, H.F. Schaefer III, and J. Gauss, J. Chem. Phys. **128**, 124104 (2008).

[19] J. Pittner and J. Šmydke, J. Chem. Phys. **127** 114103 (2007).

[20] O. Demel and J. Pittner, J. Chem. Phys. **128**, 104108 (2008); K. Bhaskaran-Nair, O. Demel, and J. Pittner, *ibid*. **132**, 154105 (2010); O. Demel, K. Bhaskaran-Nair, and J. Pittner, *ibid*. **133**, 134106 (2010).

[21] F.A. Evangelista, E. Prochnow, J. Gauss, and H.F. Schaefer III, J. Chem. Phys. **132**, 074107 (2010).

[22] K. Bhaskaran-Nair, O. Demel, and J. Pittner, J. Chem. Phys. **129**, 184105 (2008).

[23] F.A. Evangelista, W.D. Allen, and H.F. Schaefer III, J. Chem. Phys. **127**, 024102 (2007).

[24] J.F. Stanton, Chem. Phys. Lett. **281**, 130 (1997); T.D. Crawford and J.F. Stanton, Int. J. Quantum Chem. **70**, 601 (1998); A.G. Taube and R.J. Bartlett, J. Chem. Phys. **128**, 044110 (2008).

[25] A. Balková and R.J. Bartlett, J. Chem. Phys. **101**, 8972 (1994).

[26] K. Kowalski and P. Piecuch, Mol. Phys. **102**, 2425 (2004).

[27] X. Li and J. Paldus, J. Chem. Phys. **124**, 034112 (2006).

[28] T. Fang and S. Li, J. Chem. Phys. **127**, 204108 (2007); J. Shen, T. Fang, and S. Li, in *Progress in Theoretical Chemistry and Physics Frontiers in Quantum Systems in Chemistry Physics*, *Vol. 19*, edited by P. Piecuch, S. Wilson, P.J. Grout, J. Maruani, G. Delgado-Barrio (Springer, Berlin, 2009), pp. 241–255; T. Fang, J. Shen, and S. Li, in *Recent Progress in Coupled Cluster Methods: Theory and Applications*, edited by P. Čársky, J. Paldus, and J. Pittner (Springer, Berlin, 2010).

[29] L. Adamowicz, P. Piecuch, and K.B. Ghose, Mol. Phys. **94**, 225 (1998); N. Oliphant and L. Adamowicz, J. Chem. Phys. **94**, 1229 (1991); N. Oliphant and L. Adamowicz, Int. Rev. Phys. Chem. **12**, 339 (1993); P. Piecuch, N. Oliphant, and L. Adamowicz, J. Chem. Phys. **99**, 1875 (1993); V.V. Ivanov, D.I. Lyakh, and L. Adamowicz, Phys. Chem. Chem. Phys. **11**, 2355 (2009).

[30] P. Piecuch, S.A. Kucharski, and R.J. Bartlett, J. Chem. Phys. **110**, 6103 (1999); P. Piecuch, Mol. Phys. **108**, 2987 (2010); J. Shen and P. Piecuch, Chem. Phys. **401**, 180 (2012); J. Shen and P. Piecuch, J. Chem. Theory Comput. **8**, 4968 (2012).

[31] X.Z. Li and J. Paldus, J. Chem. Phys. **107**, 6257 (1997); X.Z. Li and J. Paldus, *ibid*. **108**, 637 (1998); X.Z. Li and J. Paldus, Mol. Phys. **98**, 1185 (2000).

[32] M. D. Lodriguito, K. Kowalski, M. Włoch, and P. Piecuch, J. Mol. Struct. THEOCHEM **771**, 89 (2006).

[33] P. Piecuch and M. Włoch, J. Chem. Phys. **123**, 224105 (2005); P. Piecuch, M. Włoch, J.R. Gour, and A. Kinal, Chem. Phys. Lett. **418**, 467 (2006); M. Włoch, M.D. Lodriguito, P. Piecuch, and J.R. Gour, Mol. Phys. **104**, 2149 (2006); M. Włoch, J.R. Gour, and P. Piecuch, J. Phys. Chem. A **111**, 11359 (2007); W. Li and P. Piecuch, J. Phys. Chem. A, **114**, 6721 (2010).

[34] T. Kinoshita, O. Hino, and R.J. Bartlett, J. Chem. Phys. **123**, 074106 (2005); A. Melnichuk and R.J. Bartlett, *ibid*. **137**, 214103 (2012).

[35] K. Kowalski, J. Chem. Phys. **134**, 194107 (2011); J. Brabec, H.J.J. van Dam, J. Pittner, and K. Kowalski, *ibid*. **136**, 124102 (2012).

[36] U.S. Mahapatra and S. Chattopadhyay, J. Comp. Chem. **33**, 1285 (2012).

[37] Y.S. Lee and R.J. Bartlett, J. Chem. Phys. **80**, 4371 (1984); Y.S. Lee, S.A. Kucharski, and R.J. Bartlett, *ibid*. **81**, 5906 (1984); G.E. Scuseria and H.F. Schaeffer, Chem. Phys. Lett. **152**, 382 (1988); G.E. Scuseria, A.C. Scheiner, T.J. Lee, J.E. Rice, and H.F. Schaeffer, J. Chem. Phys. **86**, 2881 (1987); J. Noga, R.J. Bartlett, and M. Urban, Chem. Phys. Lett. **134**, 126 (1987); J. Noga and R.J. Bartlett, J. Chem. Phys. **86**, 7041 (1987); Y. He, Z. He, and D. Cremer, Theor. Chem. Acc. **105**, 182 (2001).

[38] U.S. Mahapatra and S. Chattopadhyay, Mol. Phys. **110**, 75 (2012).

[39] T. Helgaker and P. Jørgensen, Adv. Quantum Chem. **19**, 183 (1988).

[40] P. Pulay and W. Meyer, J. Mol. Spectrosc. **40**, 59 (1971); Y. Yamaguchim, Y. Osamura, J.D. Goddard, and H.F. Schaefer III, in *A New Dimension in Quantum Chemistry* (Oxford University Press, New York, 1994); M. Kállay and P.R. Surján, J. Chem. Phys. **115**, 2945 (2001).

[41] S. Pal, Phys. Rev. A **39**, 39 (1991); N. Vaval, R. Roy, and S. Pal, Phys. Rev. A **49**, 1623 (1994); P.G. Szalay, and R.J. Bartlett, J. Chem. Phys. **101**, 4936 (1994); P.G. Szalay, Int. J. Quantum Chem. **55**, 151 (1995); J.E. Stevens, R.K. Chaudhuri, and K.F. Freed, J. Chem. Phys. **105**, 8754 (1996); H. Nakano, K. Hirao, and M.S. Gordon, *ibid*. **108**, 5660 (1998); H. Lischka, R. Shepard, R.M. Pitzer, I. Shavitt, M. Dallos, T. Müller, P.G. Szalay, M. Seth, G.S. Kedziora, S. Yabushita, and Z.Y. Zhang, Phys. Chem. Chem. Phys. **3**, 664 (2001); T.J. Dudley, Y.G. Khait, and M.R. Hoffmann, *ibid*. **119**, 651 (2003); P. Celani and H.-J. Werner, *ibid*. **119**, 5044 (2003); Y.G. Khait, D. Theis, and M.R. Hoffmann, Mol. Phys. **108**, 2703 (2010).

[42] M. Kállay, J. Gauss, and P.G. Szalay, J. Chem. Phys. **119**, 2991 (2003).

[43] E. Prochnow, F.A. Evangelista, H.F. Schaefer III, W.D. Allen, and J. Gauss, J. Chem. Phys. **131**, 064109 (2009); T.-C. Jagau, E. Prochnow, F.A. Evangelista, and J. Gauss, J. Chem. Phys. **132**, 144110 (2010).

[44] T. Helgaker, S. Coriani, P. Jørgensen, K. Kristensen, J. Olsen, and K. Ruud, Chem. Rev. **112**, 543 (2012).

[45] U.S. Mahapatra, B. Datta, and D. Mukherjee, J. Phys. Chem. A **103**, 1822 (1999); U.S. Mahapatra, S. Chattopadhyay, and R.K. Chaudhuri, J. Chem. Phys. **129** 024108(1–13) (2008); *ibid.* **130** 014101(1–15) (2009).

[46] S. Chattopadhyay, D. Pahari, U.S. Mahapatra, and D. Mukherjee, J. Chem. Phys. **120**, 968 (2004); S. Chattopadhyay and U.S. Mahapatra, J. Phys. Chem. A **108**, 11664 (2004).

[47] I. Shavitt and R.J. Bartlett, *Many-Body Methods in Chemistry and Physics: Many-Body Perturbation Theory and Coupled-Cluster Methods* (Cambridge Press, New York, 2009).

[48] H.J.A. Jensen, P. Jorgensen, and T. Helgaker, J. Chem. Phys. **85**, 3917 (1986).

[49] D. Whitelegg and R.G. Wooley, J. Mol. Struct. THEOCHEM **209**, 23 (1990); K. Kim, I. Shavitt, and J.E. Del Bene, J. Chem. Phys. **96**, 7573 (1992).

[50] P. Mach, J. Mášik, J. Urban, and I. Hubač, I. Mol. Phys. **94**, 173 (1998).

[51] J.M.L. Martin and P.R. Taylor, Mol. Phys. **96**, 681 (1999).

[52] D.Y. Hwang and A.M. Mebel, J. Phys. Chem. A **107**, 2865 (2003).

[53] M. Biczysko, L.A. Poveda, and A.J.C. Varandas, Chem. Phys. Lett. **424**, 46 (2006).

[54] R.K. Chaudhuri, K.F. Freed, S. Chattopadhyay, and U. Sinha Mahapatra, J. Chem. Phys. **128**, 144304 (2008).

[55] R. Shepard, G.S. Kedziora, H. Lischka, I. Shavitt, T. Müller, P.G. Szalay, M. Kállay, and M. Seth, Chem. Phys. **37**, 349 (2008).

[56] M. Musiał, Ł. Lupa, K. Szopa, and S.A. Kucharski, Struct. Chem. **23**, 1377 (2012).

[57] H. Fliegl, A. Kohn, C. Hattig, and R. Ahlrichs, J. Am. Chem. Soc. **125**, 9821 (2003); S. Loudwig and H. Bayley, J. Am. Chem. Soc. **128**, 12404 (2006); P. Gorostiza and E.Y. Isacoff, Science **322**, 395 (2008).

[58] W.A. Sokalski, R.W. Gora, W. Bartkowiak, P. Kobylinski, J. Sworakowski, A. Chyla, and J. Leszczynski, J. Chem. Phys. **114**, 5504 (2001).

[59] A.M. Sand, C.A. Schwerdtfeger, and D.A. Mazziotti, J. Chem. Phys. **136**, 034112 (2012).

[60] P. Piecuch and J. Paldus, J. Chem. Phys. **101**, 5875 (1994); P. Piecuch and J. Paldus, J. Phys. Chem. **99**, 15354 (1995).

[61] In CR-CC(2,3), Piecuch et al. [33] reformulated CR-CCSD(T) method in terms of the left eigenstates $\langle \phi | \mathcal{L}$ of the similarity-transformed Hamiltonian of CC theory.

[62] In the DIP-EOM-CCSDT′ method, the ground state has been treated CCSD model and the DIP part is as in the full CCSDT one which usually gives results of comparable quality as the full DIP–EOM–CCSDT (double ionisation potential equation-of-motion coupled-cluster singles–doubles with full inclusion of the connected triple excitations) model but with lower scaling.

[63] J. Damaison, F. Hegelund, and H. Burger, J. Mol. Struct.THEOCHEM **413**, 447 (1997).

[64] T.J. Dudley, Y.G. Khait, and M.R. Hoffmann, J. Chem. Phys. **119**, 651 (2003).

[65] T. Tsuneda, H. Nakano, and K. Hirao, J. Chem. Phys. **103**, 6520 (1995).

[66] L. Füsti-Molnár and P.G. Szalay, J. Phys. Chem. **100**, 6288 (1996).

[67] J.D. Watts, J.F. Stanton, and R.J. Bartlett, Chem. Phys. Lett. **178**, 471 (1991); J.D. Watts and R.J. Bartlett, J. Chem. Phys. **108**, 2511 (1998); S.A. Kucharski and R.J. Bartlett, *ibid*. **110**, 8233 (1999).

[68] M.L. Leininger and H.F. Schaefer III, J. Chem. Phys. **107**, 9059 (1997).

[69] X. Li and J. Paldus, J. Chem. Phys. **110**, 2844 (1999).

[70] I. Hubač, J. Pittner, and P. Čársky, J. Chem. Phys. **112**, 8779 (2000).

[71] I. Ljubić and A. Sabljić, J. Phys. Chem. A **106**, 4745 (2002); Chem. Phys. Lett. **214**, 385 (2004).

[72] T. Müller, S.S. Xantheas, H. Dachsel, R.J. Harrison, J. Nieplocha, R. Shepard, G.S. Kedziora, and H. Lischka, Chem. Phys. Lett. **293**, 72 (1998).

[73] M. Musiał, S.A. Kucharski, P. Zerzucha, T. Kus, and R.J. Bartlett, J. Chem. Phys. **131**, 194104 (2009); K. Kowalski and M. Valiev, Int. J. Quantum Chem. **108**, 2178 (2008).

[74] F. Holka, P.G. Szalay, T. Müller, and V.G. Tyuterev, J. Phys. Chem. A **114**, 927 (2010).

[75] M. Hanauer and A. Köhn, J. Chem. Phys. 134, 204111 (2011).

[76] K. Bhaskaran-Nair and K. Kowalski, J. Chem. Phys. **137**, 216101 (2012); S. Banik, L. Ravichandran, J. Brabec, I. Hubač, K. Kowalski, and J. Pittner, *ibid*. **142**, 114106 (2015).

[77] O. Hino, T. Kinoshita, G.K.L. Chan, and R.J. Bartlett, J. Chem. Phys. **124**, 114311 (2006).

[78] A. Banichevich and S.D. Peyerimhoff, Chem. Phys. **174**, 93 (1993); A. Banichevich and S.D. Peyerimhoff, *ibid*. **178**, 155 (1993).

[79] M. Pabst, A. Köhn, J. Gauss, and J.F. Stanton, Chem. Phys. Lett. **495**, 135 (2010).

[80] V.G. Tyuterev, S. Tashkun, P. Jensen, A. Barbe, and T. Cours, J. Mol. Spectrosc. **198**, 57 (1999).

[81] K. Kowalski and P. Piecuch, Chem. Phys. Lett. **334**, 89 (2001).

[82] H.F. Schaefer, Science **231**, 1100 (1986).

[83] P.R. Bunker, P. Jensen, Y. Yamaguchi, and H.F. Schaefer III, J. Mol. Spectrosc. **179**, 263 (1996); P. R. Bunker, P. Jensen, Y. Yamaguchi, and H.F. Schaefer III, J. Phys. Chem. **100**, 18088 (1996).

[84] C.D. Sherrill, T.J. Van Huis, Y. Yamaguchi, and H.F. Schaefer, J. Mol. Struct. THEOCHEM **400**, 139 (1997).

[85] X. Li and J. Paldus, Collect. Czech. Chem. Commun. **63**, 1381 (1998); X. Li and J. Paldus, J. Chem. Phys. **110**, 2844 (1999).

[86] V.N. Staroverov and E.R. Davidson, Chem. Phys. Lett. **296**, 435 (1998).

[87] P.G. Szalay, T. Müller, and H. Lischka, Phys. Chem. Chem. Phys. **2**, 2067 (2000); A.G. Csaszar, M.L. Leininger, and V. Szalay, J. Chem. Phys. **118**, 10631 (2003).

[88] A.I. Krylov and C.D. Sherrill, J. Chem. Phys. **116**, 3190 (2002).

[89] O. Demel, J. Pittner, P. Čársky, and I. Hubač, J. Phys. Chem. A **108**, 3125 (2004).

[90] I.S.K. Kerkines, P. Čársky, and A. Mavridis, J. Phys. Chem. A **109**, 10148 (2005).

[91] J.R. Flores and R.J. Gdanitz, J. Chem. Phys. **123**, 144316 (2005).

[92] X. Liu, W. Bian, X. Zhao, and X. Tao, J. Chem. Phys. **125**, 074306 (2006).

[93] N.B. Amor, D. Maynau, J.-P. Malrieu, and A. Monari, J. Chem. Phys. **129**, 064112 (2008).

[94] H. Petek, D.J. Nesbitt, D.C. Darwin, P.R. Ogilby, C.B. Moore, and D.A. Ramsay, J. Chem. Phys. **91**, 6566 (1989).

[95] Y. Yamaguchi, C.D. Sherrill, and H.F. Schaefer III, J. Phys. Chem. **100**, 7911 (1996); C.D. Sherrill, M.L. Leininger, T.J. Van Huis, and H.F. Schaefer III, *ibid*. **108**, 1040 (1998).

[96] D. Feller, J. Comput. Chem. **17**, 1571 (1996); K.L. Schuchardt, B.T. Didier, T. Elsethagen, L. Sun, V. Guru-moorthi, J. Chase, J. Li, and T.L. Windus, J. Chem. Inf. Model. **47**, 1045 (2007). See www.emsl.pnl.gov/forms/basisform.html.

[97] C.W. Bauschlicher, Theor. Chem. Acc. **96**, 11 (1997).

[98] C.W. Bauschlicher and D.R. Yarkony, J. Chem. Phys. **69**, 3875 (1978).

[99] G. Maier, Angew Chem. Int. Ed. Engl. **120**, 3 09 (1974); M. Eckert- Maksić and Z.B. Maksić, in *The Chemistry of Cyclobutanes*, Vol. 16, edited by Z. Rappoport and J.F. Liebman (Wiley, Chichester, 2005).

[100] D.I. Lyakh, V.F. Lotrich, and R.J. Bartlett, Chem. Phys. Lett. **166**, 501 (2011).

[101] S.V. Levchenko and A.I. Krylov, J. Chem. Phys. **120**, 175 (2004); S.V. Levchenko, T. Wang, and A. I. Krylov, *ibid*. **122**, 224106 (2005).

[102] J. C. Sancho-García, J. Pittner, P. Čársky, and I. Hubač, J. Chem. Phys. **112**, 8785 (2000).

[103] M. Eckert-Maksić, M. Vazdar, M. Barbatti, H. Lischka, and Z.B. Maksić, J. Chem. Phys. **125**, 064310 (2006).

[104] X. Li and J. Paldus, J. Chem. Phys. **131**, 114103 (2009).

[105] T. Saito, S. Nishihara, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura, and K. Yamaguchi, Chem. Phys. Lett. **498**, 253 (2010).

[106] J.L. Menke, E.V. Patterson, and R.J. McMahon, J. Phys. Chem. A. **114**, 6431 (2010).

[107] S. Koseki and A. Toyota, J. Phys. Chem. A. **101**, 5712 (1997).

[108] M. Filatov and S. Shaik, J. Chem. Phys. **110**, 116 (1999).