

# Application of state-specific multireference Møller–Plesset perturbation theory to nonsinglet states

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We present molecular applications of a spin free size-extensive state-specific multireference perturbation theory (SS-MRPT), which is valid for model functions of arbitrary spin and generality. In addition to the singlet states, this method is equally capable to handle nonsinglet states. The formulation based on Rayleigh–Schrödinger approach works with a complete active space and treats each of the model space functions democratically. The method is capable of handling varying degrees of quasidegeneracy and of ensuring size consistency as a consequence of size extensivity. In this paper, we illustrate the effectiveness of the Møller–Plesset (MP) partitioning based spin free SS-MRPT [termed as SS-MRPT(MP)] in computations of energetics of the nonsinglet states of several chemically interesting and demanding molecular examples such as LiH, NH<sub>2</sub>, and CH<sub>3</sub>. The spectroscopic constants of <sup>3</sup>Σ<sup>-</sup> state of NH and OH<sup>+</sup> molecular systems and the ground <sup>1</sup>Σ<sub>g</sub><sup>+</sup> as well as excited <sup>3</sup>Σ<sub>u</sub><sup>+</sup> states of N<sub>2</sub> have been investigated and comparison with experimental and full configuration interaction values (wherever available) has also been provided. We have been able to demonstrate here that the SS-MRPT(MP) method is an intrinsically consistent and promising approach to compute reliable energies of nonsinglet states over different geometries. © 2009 American Institute of Physics. [DOI: 10.1063/1.3043364]

## I. INTRODUCTION

The effectiveness and wide applicability of single-reference (SR)-based methods<sup>1–3</sup> go down when one wishes to explore the computation of potential energy curve (PEC) along bond-breaking coordinates (i.e., computation of energy for a wide range of nuclear distortions) for both the ground and excited states as the SR situation exists only in a limited range of molecular geometries.<sup>4,5</sup> Not only that but also SR-based method fails to describe many chemically important situations such as transition states along a reaction coordinate, diradicals, etc. As results of this, a genuine multireference (MR) approach is a natural method of choice to overcome these difficulties. Unfortunately, the MR generalization of SR-based methods is not very straight forward and the resulting MR formalisms are not free from difficulties. The naive extension of the SR-based theories to deal with general MR situations is often fraught with the problem of choosing proper model functions. Despite the tremendous methodological developments, search for and development of an efficient and reliable MR method still remains one of the important frontier areas of quantum chemical research.<sup>4,5</sup>

The methodological difficulties associated with the computation of PEC originate from the MR character of the wave function in the dissociation region. Therefore, much research has been invested to develop a MR approach<sup>2,3,5–9</sup> which is able to compute electron correlation in a well balanced man-

ner over various geometries using the reference space containing all configurations needed for a proper zeroth-order description. Among the various MR-based methods, the MR perturbative theory (MRPT) is one of the widely used methods for nonempirical (*ab initio*) calculations of medium sized molecular systems. Despite the tremendous methodological developments, the search for an efficient and formally correct MRPT method remains a valuable task.<sup>10</sup> MRPT is based on the description of the zeroth-order wave function through the diagonalization of the electronic Hamiltonian in a properly chosen determinantal space [configuration state function (CSF) space, in general] and on the evaluation of the remaining correlation energy through perturbation theory. Several features of the MRPT method, viz. size extensivity and high-level accounting for the correlation effects, have contributed to the high popularity of MRPT in studies of the chemical and physical properties of molecules and clusters, including their energies, structures, and spectra. However, to limit the computational cost, most programs cannot evaluate the perturbation series beyond second order, which is only the first term in the correlation energy. Since the generalization of PT for a MR function is neither obvious nor unique, as it is for one SR, as a consequence there are many ways to set up the wave function, and hence numerous formulations of MRPT schemes have been elaborated. The classification of MRPT can be viewed on the basis of whether or not perturbative corrections are obtained from the eigenvalue problem of an effective Hamiltonian operator. The effective Hamiltonian based perturbation theory (multiroot MR theory)<sup>6</sup> based on a reference space spanned by a complete

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active space (CAS) is not free from “near-singularity” difficulty caused by very small or vanishing energy denominators which is sometimes called intruder states, even though this differs from the original definition.<sup>11,12</sup> This, however, has not stopped efforts toward the development of the multiroot MR methodology. To overcome these difficulties, there has been recent interest in developing state-specific/single root theories. It is evident from the literature that there has been so much work in MRPT methodology and applications over the last 20 years that lack of space does not permit mentioning many contributions here. Examples for MRPT without an effective Hamiltonian operator are (diagonalize then perturb) works of Davidson *et al.*,<sup>13–15</sup> Wolinski and Pulay,<sup>16</sup> Murphy and Messmer,<sup>17</sup> Andersson *et al.*,<sup>18,19</sup> Werner,<sup>20</sup> Dyall,<sup>21</sup> Hirao *et al.* [MR Møller–Plesset (MP) perturbation theory (MRMPPT)],<sup>22</sup> Rosta and Surján,<sup>23</sup> Angeli *et al.*,<sup>24</sup> and others. Examples for MRPT with an effective Hamiltonian operator are (perturb then diagonalize) works of Freed and co-workers,<sup>25</sup> Nakano *et al.* [multiconfiguration quasidegenerate perturbation theory (MCQDPT)],<sup>26</sup> Kozłowski and Davidson,<sup>27</sup> Zaitsevskii and Malrieu,<sup>28</sup> Angeli *et al.*,<sup>29</sup> Finley,<sup>30</sup> Mahapatra *et al.*,<sup>31–33</sup> etc. The various CAS-based perturbative methods can also differ in their choice of the mode of representing the reference function(s) relaxed or unrelaxed with respect to the coefficients. There are various pro- and contra issues for the different MRPTs, which shape their numerical performance. The MRPT of Mahapatra *et al.*<sup>31,32</sup> termed as SS-MRPT based on the CAS multiconfiguration (MC) reference wave function shows promise in its numerical performance. From the very mode of formulation of the SS-MRPT, it is clear that the combining coefficients are iteratively updated to the values that they should have in an exact state  $\psi$ . Hence, the SS-MRPT formulation provides a completely relaxed form of  $\psi$ . The SS-MRPT bypasses the intruder problem by focusing on only one specific state (as long as the state energy of interest is away from the energy of the virtual functions). Also, in this method all the reference determinants are treated on the same footing and is thus well suited to describe a wide range of molecular geometry possessing varying degrees of quasidegeneracy along with the presence of potential intruder states. The method is stable on the whole PEC if the reference wave function is appropriately chosen. Very recently, Chaudhuri *et al.*<sup>34</sup> proposed a computationally efficient version of MRMPPT (Ref. 22)/MCQDPT (Ref. 26) based on IVO-CASCI scheme<sup>35</sup> for describing PECs of the ground as well as excited states. Note that MRMPPT energy can also be calculated using the working equations of MCQDPT by setting the number of the states to 1. In passing we want to mention that the earlier configuration interaction with perturbation selection iteratively (CIPSI) method<sup>36</sup> can be viewed as a second-order perturbation correction to CI energies via diagrammatic techniques using multiconfigurational zeroth-order wave functions.

One of the important features of the SS-MRPT method over the currently popular perturbative methods starting from a CAS is that the SS-MRPT is intrinsically flexible in the sense that the method is able to handle relaxed (internally decontracted) coefficients of the reference function in addi-

tion to the unrelaxed (contracted) coefficient variety, and this feature can be utilized to explore the extent of accuracy gained if the coefficients are relaxed. At this point we want to mention the fact that if the method does not allow relaxation of MS coefficients during the computation of correlation effects, a correct description of the mixed electronic states (such as avoided crossings or mixed valence-Rydberg states) and of the PEC cannot be expected.<sup>26,37</sup> Nevertheless, the inaccuracy due to the relaxation effect of coefficients can also be taken care of within the unrelaxed variety by choosing a higher dimensional model space (MS), higher in dimension than that is chemically required. This often leads to the appearance of intruder states. For a detailed critique along this line, one may refer to Ref. 38. Note that the computational cost of decontracted formalism is higher than that of the corresponding contracted scheme. The second-order CAS perturbation theory (CASPT2) method,<sup>18,19</sup> MRMPPT,<sup>22</sup> and ( $n$ -electron valence state perturbation theory (NEVPT) approaches<sup>29</sup> are unrelaxed (contracted) in nature (these methods do not revise the content of the exact state  $\psi$  in the MS) and thus they may suffer from the internal contraction of the wave function in the reference space.

From the very mode of development, there are some common difficulties associated with most MRPT formulations such as size extensivity.<sup>39</sup> Although the CIPSI approach is numerically efficient, it lacks the formal requirement of strict separability. Other analogous methods suffer from similar defects. A redeeming feature of the CAS-based SS-MRPT(MP) is the size extensivity of the computed energies. The extensivity of the energy also implies correct separation into fragments generated from the active orbitals, and hence size consistency. The NEVPT is rigorously size extensive and size consistent.<sup>29</sup> A recent analysis<sup>40</sup> suggests that, while the various versions of the CASPT2 method are very close to being size consistent, the MRMPPT of Nakano *et al.* is not so,<sup>41</sup> and the extent and the magnitude of error due to the lack of size consistency is drastically modified by the mode of implementation of the perturbative scheme.

To extend the applicability of the method to new areas of chemistry, its strong and weak points should be known. We now discuss the issue of the cost of the method as a function of the size of the CAS and of the number of possible excitations. One objection of CAS-based MRPT (such as CASPT, MRMPPT, MCQDPT, SS-MRPT, etc.) formalisms is the exponential increase in the size of the MS when one increases the number of active orbitals. Among the CAS determinants, only a small percentage has a significant weight in the wave function, and a formalism based on a MR non-CAS wave function seems highly desirable from a computational point of view. Although recently much more attention is being focused on the various developments and subsequent implementations of SSMR-type methods, but the main criticism of the theories based on the wave operator of Jeziorski–Monkhorst type is its prohibitively increasing number of amplitudes, since the cluster operator is defined with respect to each reference determinant. In Jeziorski–Monkhorst ansatz-based SSMR method, more parameters are needed to be optimized for treating a single state only, and as a result of this, numerical implementation is not computa-

tionally cost effective. The criticism regarding the proliferation of cluster amplitudes in a theory using Jeziorski–Monkhorst ansatz is quite relevant. But this proliferation is shared by all such formalisms currently in use and not just confined to the SS-MRPT formalism only. Thus it is worthwhile to develop a MR theory which efficiently avoids the problem of intruders and is simultaneously computationally economical. The number of cluster amplitudes of the method considered can be reduced using a contracted description of the ansatz of the starting wave function as that of the contracted MR configuration interaction (MRCI) method such as positing the sensible approximation of equal amplitudes for all the one- and two-body inactive to virtual excitations. Since inactive excitations are numerous, such an assumption will lead to drastic reduction in the number of cluster amplitudes. This would amount to an “anonymous parentage for the inactive excitations” (API). Very recently, Pahari *et al.*<sup>32</sup> provided a version of SS-MRPT, termed as API-SSMRPT, which is very effective in drastically reducing the number of amplitudes without undue sacrifice in accuracy. The API-SSMRPT approach will open a possibility toward an accurate treatment for the states of arbitrary quasidegeneracy of small to large molecular systems since there is a drastic reduction in the number of cluster amplitudes in this approximation.

Another way to reduce the computational demand would be to work with a space of selected configurations instead of complete MS (CMS)(CAS). The choice of a CMS in a state-specific formalism is mainly dictated by the desire to achieve size extensivity. Not only that, in the study of chemical reaction mechanisms, CMS(CAS)-based method is a very useful approach and hence frequently used. However, CAS often generates far too many configurations and the size of the active space outgrows the capacity of present technology. Perturbation methods using a selected reference configuration space but retaining the advantages of the CAS-based PTs are necessary.<sup>41,42</sup>

The various CAS-based perturbative methods can also differ in their choice of the unperturbed Hamiltonian. It is well known that the performance of any perturbation theory is dependent on the choice of the zeroth-order Hamiltonian  $H_0$ . The zeroth-order Hamiltonian  $H_0$  of MRPT is often chosen to be of one-electron type so that it reduces to the Fock operator in the case of a SR space, but different choices based on a two-electron zeroth-order  $H_0$  are possible. A careful selection of the zeroth-order quantities can result in a size-consistent theory, such as that of Rosta and Surján,<sup>23</sup> Rassolov *et al.*,<sup>43</sup> or Angeli *et al.*<sup>24</sup> Heully *et al.*<sup>44,45</sup> also discussed a partitioning of the Hamiltonian where the size consistency is maintained. The original CASPT2 of Andersson *et al.*,<sup>18,19</sup> MRMPPT of Hirao *et al.*,<sup>22</sup> and MCQDPT of Nakano *et al.*<sup>26</sup> were formulated with the generalized Fock operator as the unperturbed Hamiltonian. Dyall<sup>21</sup> considered the entire active portion of  $H$  in  $H_0$  in his development of CASPT2.

In this paper, we consider MP version of SS-MRPT [termed as SS-MRPT(MP)] by considering zeroth-order Hamiltonian in such a way so as to try to mimic the MP procedures that have been found to be very effective in SR

perturbation expansion. MP-based perturbation method has undoubtedly been the most popular electron correlation approach in use over the last two decades. The tacit assumption behind chemical applications of MP theory is that the perturbation series is convergent. The second-order RS state-specific perturbation theory of Heully *et al.*<sup>45</sup> is conceptually the closest variant to the relaxed version of SS-MRPT(MP).

The explicitly spin free SS-MRPT was formulated more recently by Pahari *et al.*<sup>32</sup> via explicit symmetry adaptation of the wave function in terms of both spin and spatial symmetries using the spin-adapted generator state approach. In this formalism, the model functions are neither necessarily singlets nor single determinants. The model functions are, in the general formalism, genuine multideterminant CSFs. The detailed nature of the coupling scheme is not important so long as each CSF is generated with respect to some base CSF by excitation via spin free unitary generators. Among the properties of the spin free SS-MRPT approach, we can mention the following: (i) the spin adaptation of the SS-MRPT leads to an approach free from spin contamination for open-shell cases; (ii) using the spin free SS-MRPT method, one can calculate states with specific spin multiplicities at second-order level using a state-specific decontraction procedure.

In general, the problem of calculating open-shell singlet and triplet states is not a trivial task and the spin free SS-MRPT approach is capable to effectively deal with this for those states which have inherent MR character and inherent spin or spatial degeneracy. Viability of the SS-MRPT has already been demonstrated in some preliminary applications, where the target states are singlets.<sup>31–33</sup> *Ab initio* modeling of nonsinglet states, which are of central importance in chemistry, remains challenging, even though different sophisticated approaches have been developed. The goal of the present work is to extend the SS-MRPT approach of Mahapatra *et al.*<sup>31</sup> to calculate nonsinglet states of various interesting systems and to establish a general and stable avenue to compute the PEC of both ground as well as excited nonsinglet states. Even though in this investigation only small and pilot systems are considered, our investigations also aim at future works in the direction of describing the PEC of bigger systems with arbitrary complexity. In this paper, we observe from the general trend of the results obtained for the chemically interesting and theoretically “difficult” systems that the SS-MRPT(MP) is a potentially powerful, stable, and accurate method for computing PEC and spectroscopic constants of various nonsinglet ground and excited states which possess quasidegeneracy at some point on the PEC. We have explored the various choices of  $H_0$  in the MP-based SS-MRPT method. The performances of the SSMRPT(MP) method with various types of Fock operators are very similar for the systems studied by us in this article.

The organization of this paper is as follows. In Sec. II we would first describe the general formulation of the SS-MRPT. In Sec. III, we present numerical tests of the SS-MRPT(MP) method. Most of the tests were chosen from the literature to allow comparison of all the methods with SS-MRPT(MP). Finally, Sec. IV summarizes our presentation.

## II. THEORY

The SS-MRPT method has been described previously in length; we refer the reader to Refs. 31 and 32. In this section, we present a brief outline of the required working equations of the SS-MRPT method along with necessary notations and important aspects pertinent to the development of the working equations which would help to describe its structural features.

The SS-MRPT method can employ any set of reference configurations, assuming that the reference space is size consistent with respect to the dissociation process at hand. The reference function  $\psi_0$  is a combination of the MS functions (CSF)  $\phi_\mu$  spanning the CAS (equivalently called CMS),

$$\psi_0 = \sum_{\mu} c_{\mu} \phi_{\mu}. \quad (1)$$

Here  $c_{\mu}$ 's are the combining coefficients of the MS functions. Thus, the effect of the most relevant electronic interactions is taken into account. In the SS-MRPT, the combining coefficients are updated as a result of the inclusion of the virtual functions via the wave operators of Jeziorski–Monkhorst:<sup>8</sup>  $\Omega = \sum_{\mu} \exp(T^{\mu}) |\phi_{\mu}\rangle \langle \phi_{\mu}|$ . Such a cluster expansion ansatz was first used in the effective Hamiltonian context and has recently been exploited in the state-specific formulations as well.<sup>9</sup> Since the SS-MRPT theory uses the same ansatz as in Jeziorski–Monkhorst ansatz for the single root wave operator, it has more degrees of freedom than are needed to generate one root. At this point we want to mention the fact that the SS-MRPT (single root theory, avoids the intruders in a very effective manner) does not use the framework of the SU-based MRPT (a multiroot theory, plagued by intruders) at all.

In the SS-MRPT method, the cluster operator  $T^{\mu}$  acting on  $\phi_{\mu}$  creates a set of virtual functions  $\{\chi_l^{\mu}\}$ . It is possible that some virtual function  $\chi_l$  is generated *more than once* as a result of the excitation from various  $\phi_{\mu}$ 's by the action of various  $T^{\mu}$ . Thus, there is a *redundancy* in the cluster operators in that the same virtual function is reached from more than one MS function. In the SS-MRPT method, the redundancy is resolved via the use of appropriate sufficiency conditions which satisfy the twin target aims: (a) avoidance of intruders and (b) maintenance of extensivity. We present below, without a detailed derivation,<sup>31,32</sup> the form of the working equations for the cluster amplitudes and energy of the SS-MRPT method.

The cluster amplitude  $t_{\mu}^l$  of specific excitation between CSF  $\phi_{\mu}$  and the virtual function  $\chi_l^{\mu}$  can be written as

$$t_{\mu}^{l(1)} = \frac{H_{l\mu} + \sum_{\nu}^{\nu \neq \mu} \langle \chi_l^{\mu} | T^{\nu(1)} | \phi_{\nu} \rangle H_{\mu\nu} (c_{\nu} / c_{\mu})}{[(E_0 - H_{\mu\mu}) + (H_{\mu\mu}^0 - H_{ll}^0)]}, \quad (2)$$

where  $H_{l\mu} = \langle \chi_l | H | \phi_{\mu} \rangle$ ,  $H_{\mu\nu} = \langle \phi_{\mu} | H | \phi_{\nu} \rangle$ ,  $H_{\mu\mu}^0 = \langle \phi_{\mu} | H_0 | \phi_{\mu} \rangle$ ,  $H_{ll}^0 = \langle \chi_l | H_0 | \chi_l \rangle$ , and  $H_0$  is the zeroth-order Hamiltonian. Here,  $\langle \chi_l | T^{\mu(1)} | \phi_{\mu} \rangle$  is abbreviated as  $t_{\mu}^{l(1)}$  and  $E_0$  corresponds to the CAS energy. The same  $\chi_l^{\mu}$  can also be reached by the action of specific components of operator  $T^{\nu}$  on  $\phi_{\nu}$ , the corresponding cluster amplitudes are  $t_{\nu}^l$  (i.e.,  $\langle \chi_l | T^{\nu} | \phi_{\nu} \rangle$ ), and in this way  $t_{\nu}^l$  and  $t_{\mu}^l$  are coupled. Thus, some  $\chi_l^{\mu}$  are there which can be reached from the action of  $T^{\nu}$  on  $\phi_{\nu}$ . No cluster

amplitudes need to be stored in this formulation during computation. For the MP partitioning, the quantity  $(H_{\mu\mu}^0 - H_{ll}^0)$  would be the difference of the diagonal elements of  $f_{\mu}$  (a one-particle operator defined with respect to  $\phi_{\mu}$ ) containing the occupied and unoccupied orbitals of  $\phi_{\mu}$  involved in the excitation. The denominator in Eq. (2)  $[(E_0 - H_{\mu\mu}) + (H_{\mu\mu}^0 - H_{ll}^0)]$  is free from convergence difficulty. The difference  $(H_{\mu\mu}^0 - H_{\mu\mu})$  is usually of same sign and smaller than that of  $(E_0 - H_{ll}^0)$ . The term  $(E_0 - H_{ll}^0)$  is never small as long as the unperturbed energy is well separated from the energies of the virtual functions and this avoids intruders.

We note that Eq. (2) involves the coefficients  $c_{\mu}$  explicitly, indicating that the cluster amplitudes depend on them, as is expected of a state-specific formalism. The above equation, Eq. (2), is a coupled equation(s) involving the cluster amplitudes and MS coefficients. In the SS-MRPT(MP) formalism, the coefficients and the energy of the target state are obtained by diagonalizing an effective operator  $\tilde{H}_{\mu\nu}^{(2)}$  defined over CAS/CMS,

$$\sum_{\nu} \tilde{H}_{\mu\nu}^{(2)} c_{\nu}^{(2)} = E^{(2)} c_{\mu}^{(2)}, \quad (3)$$

with  $\tilde{H}_{\mu\nu}^{(2)} = H_{\mu\nu} + \sum_l H_{\mu l} t_{\nu}^{l(1)}$ . Here,  $E^{(2)}$  is the desired eigenvalue up to the second order. We also note that the sets  $c_{\mu}$  and  $T^{\mu}$  are coupled through Eqs. (2) and (3). The combining coefficients  $c_{\mu}$  can be determined either from (i) a CASCI or CASSCF calculation (the unrelaxed description) or (ii) by updating the coefficients to the values they should have in the presence of the virtual functions (the relaxed description) via Eq. (3), that is, MS coefficients are revised during the incorporation of the effect of the dynamical correlation. The diagonalization of the effective Hamiltonian produces [using Eq. (3)] a revised function in the reference space. To get unrelaxed energy results (akin to CASPT2 or MRMPPT), one can use  $E^{(2)} = \sum_{\mu, \nu} c_{\mu}^0 \tilde{H}_{\mu\nu}^{(2)} c_{\nu}^0$ , where  $c_{\mu}^0$  stands for the unrelaxed (contracted) coefficients of the reference functions. In the case of large CAS, the unrelaxed method has computational merits as compared with the relaxed one, diagonalization of large matrix is not necessary.

From the structural form of the working equation, one can say that when the coefficient for a reference determinant is accidentally close to zero, the cluster amplitudes could become artificially large, which might affect the computed energy. This could happen in the relatively large CAS expansion, since the expansion includes determinants unnecessary for the state of interest. But this will not happen for the SS-MRPT case. If one can write the code as  $(c_{\nu} / c_{\mu})$  and say  $c_{\mu}$  is very small and the value of  $c_{\nu}$  is reasonably large, then one might think of encountering the problem of divergence. But in the formalism of SS-MRPT, if  $c_{\mu}$  is very small then we observe that the value of  $\langle \chi_l | T^{\mu} | \phi_{\mu} \rangle$  should also be very small. As in any reference function ( $\psi_0$ ), if the contribution of some of its component function ( $\phi_{\mu}$ ) is very small, then the back coupling from other components ( $\phi_{\nu}$ ) in the cluster finding equation should not be large, at least not larger than the zero-order value, i.e.,  $\langle \chi_l | T^{\nu} | \phi_{\nu} \rangle H_{\mu\nu} c_{\nu}$  will be as small as  $c_{\mu}$ .

From the very mode of development of the SS-MRPT(MP) theory, it is quite clear that for a situation where reference function ( $\psi_0$ ) contains only one CSF (SR configuration case), the term ( $E_0 - H_{\mu\mu}$ ) of Eq. (2) is zero. The term ( $H_{\mu\mu}^0 - H_{\mu\mu}^0$ ) provides orbital energy difference and then the cluster finding equation, Eq. (2), reduces to that of the traditional SRMPPT case. Note that in the presence of the term ( $E_0 - H_{\mu\mu}$ ) in MR situation, the dynamical correlation in the back drop of nondynamical correlation is evaluated. In passing, we want to mention the fact that the term ( $E_0 - H_{\mu\mu}$ ) in the SS-MRPT(MP) theory is mainly responsible to maintain the size extensivity and intruder-free nature of the formalism. Note that this term is zero for SR case and it arises to incorporate the nondynamical correlation effects.

In the SS-MRPT, the reference, the zeroth-order wave function is first determined, and the perturbation calculation is done with those wave functions used as reference based on RS scheme. As the SS-MRPT method is based on RS-perturbative scheme, the zeroth-order coefficients  $c_\mu^0$ 's are used to evaluate the cluster operators in Eq. (2).

The SS-MRPT(MP) method is computationally very economical as (i) the method is second-order RS-based perturbation theory, (ii) the zeroth-order Hamiltonian is of MP type, and (iii) the coupling terms [Eq. (2)] are defined with respect to the *same vacuum* and are thus easy to implement numerically.

The spin adaptation of the SS-MRPT for states of arbitrary spins is rather nontrivial and requires quite an extensive formal development. In spin free SS-MRPT method, spin free unitary generators are used to define the cluster operators. An interesting sidelight of the SS-MRPT is that once the CSFs with a given set of orbital occupancy are defined, the working equations for the cluster amplitudes are *independent of the spin eigenvalue(s)*, and we do not need to know the transition density matrix elements at all. Once the cluster amplitudes are found, the effective operator  $\tilde{H}^{(2)}$  for the various spin values can be constructed separately and the corresponding perturbed energies are obtained on diagonalization.

In the spin free SS-MRPT, the entire portion of the highest closed-shell component of a model function  $\phi_\mu$  is defined as the vacuum  $\phi_{0\mu}$  to represent all the excitations on  $\phi_\mu$  in normal order. The holes in  $\phi_{0\mu}$  include not only the doubly occupied inactive orbitals but also doubly occupied active orbitals of  $\phi_\mu$ . The use of the entire portion  $\phi_{0\mu}$  of the highest closed-shell component of  $\phi_\mu$  as the vacuum to define all the excitations on  $\phi_\mu$  in normal order is rather powerful and offers a simple yet convenient access not only to define the various excitation operators but also to simplify the resulting working equations in the spin free formulation. With respect to  $\phi_{0\mu}$  the holes are denoted by the labels  $i, j, \dots$ , and the particle orbitals are denoted as  $a, b, \dots$ . The particle orbitals are totally unoccupied in  $\phi_\mu$ , or are necessarily active orbitals which are singly occupied in  $\phi_\mu$ , denoted by  $u, v, \dots$ .

In the first-order perturbation theory, the particle rank of the perturbation is at most 2, the possible excitation operators entering the various cluster operators can be classified as follows.

### One-body:

- (1) hole  $\rightarrow$  particle ( $h \rightarrow p$ ):  $t_i^{\mu a} \{E_i^a\}$ ,  

$$\left(E_i^a = \sum_{\sigma=\alpha,\beta} E_{i\sigma}^{a\sigma}\right).$$
- (2) hole  $\rightarrow$  valence ( $h \rightarrow v$ ):  $t_i^{\mu u} \{E_i^u\}$ .
- (3) valence  $\rightarrow$  particle ( $v \rightarrow p$ ):  $t_u^{\mu a} \{E_{iu}^a\}$ .

### Two-body:

- (4)  $2h \rightarrow 2p$ :  $t_{ij}^{\mu ab} \{E_{ij}^{ab}\}$ .
- (5)  $h, v \rightarrow 2p$ :  $t_{iu}^{\mu ab} \{E_{iu}^{ab}\}$ .
- (6)  $2h \rightarrow p, v$ :  $t_{ij}^{\mu au} \{E_{ij}^{au}\}$ .
- (7)  $2v \rightarrow 2p$ :  $t_{uv}^{\mu ab} \{E_{uv}^{ab}\}$ .
- (8)  $h, v \rightarrow p, v$ :  $t_{iu}^{\mu av} \{E_{iu}^{av}\}$  ( $u \neq v$ ) and  $t_{iu}^{\mu va} \{E_{iu}^{va}\}$ .
- (9)  $2v \rightarrow p, v$ :  $t_{uv}^{\mu wa} \{E_{uv}^{wa}\}$ .
- (10)  $2h \rightarrow 2v$ :  $t_{ij}^{\mu uv} \{E_{ij}^{uv}\}$ .
- (11)  $h, v \rightarrow 2v$ :  $t_{iu}^{\mu wx} \{E_{iu}^{wx}\}$ .

In all the excitation classes above, the operators  $E$  in curly brackets denote the normal ordering with respect to  $\phi_{0\mu}$ , and the ‘‘local’’ holes, valence, and particles are all defined with respect to this vacuum. The orbitals appearing in the above equations are all space orbitals. For the diagonal one-particle operators considered as  $H_0$  in this paper, the cluster amplitudes of particular classes are decoupled from other classes in the first-order perturbation.

The most important aspect we want to demonstrate is how accurate is SS-MRPT(MP) for the computation of energies of nonsinglet states? Obviously, only practical calculations can demonstrate the utility of the method for general use in the calculations on the ground and excited states with arbitrary spin. We decided to test the methods on examples where full configuration interaction (FCI) or other high-level calculations are available.

## III. NUMERICAL APPLICATION

In this part, results from some calculations are presented in order to illustrate how the method, introduced above, can be utilized in the actual calculations. The performances of SS-MRPT(MP) method in the case of singlet states with MR character are well tested.<sup>31–33</sup> Further calculations of the relaxed variant of SS-MRPT(MP) have been carried out for the singlet, doublet, and triplet states in this communication. Although we do discuss the calculations on singlet state(s), our principal thrust here is to explore the efficacy and viability of the SS-MRPT(MP) method in the context of nonsinglet states.

In our applications, we have considered various examples of chemically important situations for nonsinglet states where the accurate description of nondynamical and dynamical correlations is essential. In this paper, we have presented the initial applications of SS-MRPT(MP) method to energies of nonsinglet states of LiH (single-bond stretching up to dissociation limit), NH<sub>2</sub> (symmetrical stretching of two bonds), and CH<sub>3</sub> (symmetrical stretching of three bonds) systems for which an exact treatment of electron correlation is readily accessible via FCI. We have presented the values of various spectroscopic constants of the ground state,  $^3\Sigma^-$  of

NH and OH<sup>+</sup> systems calculated using a Dunham analysis<sup>46</sup> of the PEC computed via SS-MRPT(MP) along with the corresponding FCI values for comparison. These include the equilibrium geometry  $R_e(\text{\AA})$  and harmonic vibrational frequency  $\omega_e(\text{cm}^{-1})$ . We have also reported dissociation energy  $D_e(\text{eV})$ . We have also calculated the same for the ground  $^1\Sigma_g^+$  and excited  $^3\Sigma_u^+$  states of N<sub>2</sub> molecule using different basis sets and partitioning schemes.

These systems have been a subject of many tests of various spin-adapted theoretical methods. Here, we have reported only results of the relaxed version of SS-MRPT method. For all the systems, we compare our results with the FCI values. In addition to the FCI method, we also present results of  $H_v^{\text{third}}$  method<sup>47</sup> and other methods whenever available by means of which one can illustrate the usefulness and versatility of the SS-MRPT(MP) method. At this point, it is pertinent to mention the fact that the  $H_v^{\text{third}}$  method is computationally more demanding than the SS-MRPT(MP) method (with respect to the computer time, memory, and disk requirements of the implementation). Of course, desirable methods are those with high accuracy and low computational cost, but one usually cannot achieve both at the same time. To elucidate the difficulties associated with the SR-based approach, we have also reported the results of various SR-based methods in some cases. In this paper, instead of state energy, we have reported the deviation (error) of the computed energies [ $\Delta E_{\text{method}}(R) = E_{\text{method}}(R) - E_{\text{FCI}}(R)$ ] with respect to the corresponding FCI values which is more instructive. To measure the quality of results, we also report the nonparallelism errors (NPEs) defined as the difference between the maximal and minimal deviations from FCI values within a given range of geometry. By calculating NPE it is possible to see how parallel the PECs are to FCI.

The performance of the MRPT methods depends not only on the quality of the reference wave function but also on the quality of the treatment of correlation in the reference state. As we have already emphasized that crucial to the good performance of MRPT is the choice of the unperturbed Hamiltonian  $H_0$ . A (quasi-) one-electron MP-type Hamiltonian is usually preferred over a many-electron one (such as Epstein–Nesbet, Dyall,<sup>21</sup> etc). In designing the zeroth-order Hamiltonian  $H_0$  for the perturbation treatment of the dynamical correlation energy, a compromise has to be made for simplicity of the first-order equation and fast convergence of the perturbation expansion. It is important that  $H_0$  have a simple structure, otherwise the whole idea of a computationally efficient second-order PT is lost. In this vein, in our implementation of SS-MRPT we have considered that the  $H_0$  is equivalent to the MP Hamiltonian in the limit of a closed-shell reference state, i.e.,  $H_0$  is based on one-particle operators.

In SS-MRPT(MP) method, we choose  $H_{0\mu}$  to be a sum of the diagonal elements of Fock operator for the function  $\phi_\mu$ . This corresponds to a multipartitioning MP perturbation theory.<sup>38</sup> In this paper, we want to demonstrate to what extent the state energies and spectroscopic constants of the SS-MRPT(MP) method are sensitive to the nature of  $H_0$ . We consider the following two Fock operators:

$$f_\mu = \sum_{ij} \left[ f_{\text{core}}^{ij} + \sum_u \left( V_{iu}^{ju} - \frac{1}{2} V_{iu}^{uj} \right) D_{uu}^\mu \right] \{E_i^j\}, \quad (4)$$

with this choice for the Fock operator, the  $H_0$  for MP partitioning is  $\sum_{ij} f_{\text{core}}^{ij} \{E_i^j\}$  and the corresponding SS-MRPT(MP) is called as SS-MRPT(MP)[I], and

$$\tilde{f}_\mu = \sum_{ij} \left[ f_{0\mu}^{ij} + \sum_{u_s} V_{iu_s}^{ju_s} \right] \{E_i^j\}, \quad (5)$$

with this choice for the Fock operator, the  $H_0$  for MP partitioning is  $\sum_{ij} \tilde{f}_{\mu}^{ij} \{E_i^j\}$ , and then SS-MRPT(MP) is termed as SS-MRPT(MP)[II].  $f_{0\mu}$  is the Fock operator for  $\phi_{0\mu}$ . Here,  $u$  describes both a doubly occupied and a singly occupied ( $u_s$ ) active orbital in  $\phi_\mu$ , and the  $D^{\mu}$ 's are the one-particle density matrix elements in the CSF space labeled by the active orbitals where  $i, j, u, \dots$ , refers to spatial orbitals. The  $D^{\mu}$ 's are computed first and stored in the first memory which are used in the construction of the reference space Hamiltonian matrix elements and second-order pseudoeffective operators  $\tilde{H}$ . All other density matrix elements (say two and three bodies) are computed on the fly during computation. It is worth mentioning that the choice of an inappropriate MS may lead to convergence difficulties when solving the working equations. Within a given basis set, extension of the size of the CAS does not necessarily improve the energy because a CAS expansion tends to invite the intruder state problem. The performance of the SS-MRPT(MP)[I] is very similar to the SS-MRPT(MP)[II] for the LiH, NH, and OH<sup>+</sup> systems, and thus we have reported only SS-MRPT(MP)[I] results.

As we have already mentioned, in order to describe bond breaking, diradicals, and other electronic structure problems where SR theory fails, a reliable description of nondynamical correlation is essential as a starting point. The use of a multiconfigurational expansion as the zeroth-order (reference) wave function is necessary for such applications. Several solutions to the nondynamical correlation problem have been suggested.<sup>48,49</sup> Most commonly, the MCSCF reference function is chosen to be a CASSCF wave function. A usual strategy to deal with quasidegenerate systems is to describe the zeroth-order wave function through a CASSCF calculation to take into account the statical correlation and to improve the result by employing second-order perturbation theory to recover the dynamical correlation of the electrons. A CASSCF reference function is obtained by partitioning the molecular orbitals into doubly occupied core and (occupied or vacant) active orbitals and optimizing the expansion coefficients of all configuration functions generated by all possible arrangements of the “active” electrons among the active orbitals. Note that the CASSCF wave function incorporates all nondynamical correlation when the full valence active space is considered. The CASSCF also allows the possibility of size-consistent energy and wave function. This method is a computationally affordable mean-field approach for small sized systems. In this paper, for all calculations we used CASSCF orbitals as CASSCF wave function is a good zeroth-order approximation to the state of interest. In this paper, the GAMESS(U.S.) program system was used to compute the reference function and one as well as two particle integrals. All

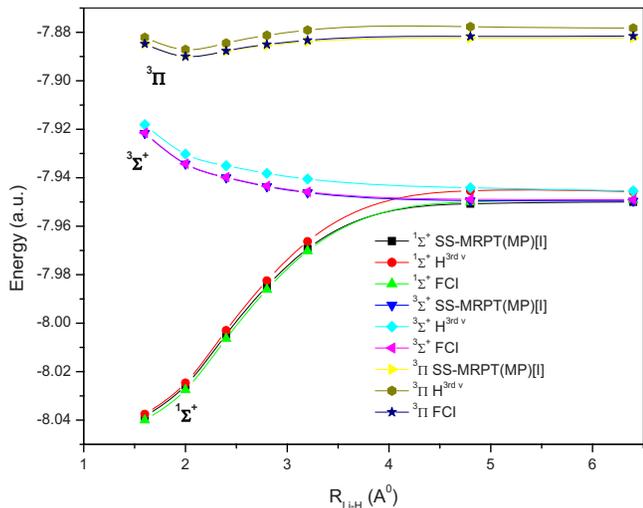


FIG. 1. (Color online) Plot of low-lying electronic states ( $X^1\Sigma^+$  and  $1^3\Sigma^+$  and  $1^3\Pi$ ) of LiH molecule using cc-pVTZ basis.

CASSCF calculations have been carried out using the GAMESS(U.S.) which we have interfaced to the SS-MRPT(MP) program.

### A. LiH

As a first application, we have studied the energies of the ground state,  $X^1\Sigma^+$  and two low-lying nonsinglet states,  $3\Sigma^+$  and  $3\Pi$  of LiH to assess the amount of correlation energy recovered in the MR perturbation approach, SS-MRPT(MP). The study of energies of different states of LiH molecule over the wide range of nuclear distortions is usually considered as a calibration technique to establish the applicability of MR-based correlation approaches since this molecule exhibits significant and various degrees of nondynamical correlation over the entire PEC.<sup>50,51</sup> Calculations are performed using cc-pVTZ (Dunning's correlation consistent valence triple zeta) basis set<sup>52</sup> for which the FCI results are available over a wide range of geometries (up to  $4R_e$ ). FCI energies using this basis for different states can be found in Ref. 52. We have used the same scheme as Ref. 52. The ground state of this system is dominated by the  $\phi_1=1\sigma^22\sigma^2$  configuration at equilibrium; the configurations  $\phi_2=1\sigma^23\sigma^2$  and  $\phi_3=1\sigma^22\sigma3\sigma$  both become important when the Li-H bond is stretched. The last CSF is an open-shell function. The triplet  $\Sigma$  and  $\Pi$  states are essentially singly excited states arising out of  $2\sigma\rightarrow3\sigma$  and  $2\sigma\rightarrow2\pi$  transitions, respectively.

In Fig. 1, we present the PEC of the ground and low-lying nonsinglet states of LiH generated via SS-MRPT(MP)[I] method using cc-pVTZ basis. The figure makes it clear that the SS-MRPT(MP)[I] reproduces the same pattern as that of the FCI one, and the SS-MRPT(MP) curve is in close proximity to FCI compared to the  $H_v^{\text{third}}$  method. The figure indicates that the low-lying states including the ground state generated via SS-MRPT(MP)[I] method are very smooth, which is evident from their corresponding NPE values.

Table I depicts the energy differences of the SS-MRPT(MP)[I] method with respect to the FCI values for the  $X^1\Sigma^+$ ,  $3\Sigma^+$ , and  $3\Pi$  states. In the table, we have also reported

TABLE I. Energy differences (mH) with respect to FCI [ $\Delta E_{\text{method}}(R) = E_{\text{method}}(R) - E_{\text{FCI}}(R)$ ] for various methods for LiH using cc-pVTZ basis (Ref. 52).

Method	$R$			
	(Li-H)/Å	$X^1\Sigma^+$	$1^3\Sigma^+$	$1^3\Pi$
SS-MRPT(MP)[I]	1.6	1.587	-0.151	0.093
	2.0	1.801	-0.060	0.133
	2.4	1.722	-0.146	-0.122
	2.8	1.408	-0.233	-0.380
	3.2	0.872	-0.303	-0.544
	4.8	-0.782	-0.501	-0.758
$H_v^{\text{third}}$	1.6	-2.476	3.365	2.655
	2.0	-2.880	4.018	2.834
	2.4	-3.374	4.775	3.216
	2.8	-3.673	5.198	3.763
	3.2	-3.892	5.308	4.213
	4.8	-4.589	4.751	3.978
GMS-SUMCCSD (3R SU-CCSD)	1.6	-3.383	3.663	3.267
	2.0	0.103	0.093	0.151
	2.4	0.098	0.112	0.091
	2.8	0.107	0.147	0.058
	3.2	0.124	0.274	0.043
	4.8	0.146	0.196	0.038
	6.4	0.236	0.195	0.034
	6.4	0.256	0.277	0.034

the values of these triplet states generated via  $H_v^{\text{third}}$  (Ref. 47) and GMS-SUMRCCSD (3R SU-CCSD) (Ref. 52) methods. First, one notices that the third-order perturbation theory,  $H_v^{\text{third}}$ , is slightly worse than the second-order theory, SS-MRPT(MP)[I], since the deviation of SS-MRPT(MP)[I] from FCI is small as compared to the  $H_v^{\text{third}}$  one. We finally note that NPEs in the case of SS-MRPT(MP)[I] for the  $X^1\Sigma^+$ ,  $3\Sigma^+$ , and  $3\Pi$  states are 1.62, 0.36, and 0.54 kcal/mol, respectively, whereas the corresponding values for  $H_v^{\text{third}}$  are 1.32, 1.21, and 0.97 kcal/mol, respectively. The nonsinglet state energies computed via SS-MRPT(MP)[I] method are of a better quality than the computationally expensive  $H_v^{\text{third}}$  method (in vein of their NPE and deviation from FCI results). Table I also demonstrates that the pattern of PEC of LiH provided by SS-MRPT(MP)[I] is in agreement with the full-blown coupled cluster method, GMS-SUMRCCSD (3R SU-CCSD), which is computationally very expensive and more sophisticated in comparison to the SS-MRPT(MP)[I] and  $H_v^{\text{third}}$  methods. The results in Table I show that the GMS-SUMRCCSD method performs well throughout and the NPE values for the  $X^1\Sigma^+$ ,  $3\Sigma^+$ , and  $3\Pi$  states are 0.158, 0.184, and 0.117 kcal/mol (see Tables V and VII in Ref. 52). Table I indicates that the SS-MRPT(MP)[I] method generates very accurate PEC of LiH using cc-pVTZ basis for low-lying nonsinglet states,  $3\Sigma^+$  and  $3\Pi$ . The energies for the  $3\Sigma^+$  and  $3\Pi$  states computed by SS-MRPT(MP)[I] method are of almost identical quality as the 3R SU-MRCCSD ones (from the point of  $\Delta$  and NPE values). This is due to the fact that these states are free from the effect of ubiquitous intruder as there is no strong interference from other important configurations.

TABLE II. Energy differences (mH) with respect to FCI [ $\Delta E_{\text{method}}(R) = E_{\text{method}}(R) - E_{\text{FCI}}(R)$ ] for various methods for nonsinglet states of  $\text{NH}_2$  using DZP basis (Ref. 49). [Note:  $\text{N}\cdots\text{H}_2$  corresponds to the ground state H–H bond length and N–H bond at about  $2.0R_{\text{eq}}$ .]

Method	$R$ ( $\text{\AA}$ )	${}^2B_1$	${}^2A_1$
SCF	$R_{\text{eq}}$	169.612	165.570
	$1.5R_{\text{eq}}$	217.796	196.167
	$2.0R_{\text{eq}}$	316.805	258.087
	$\text{N}\cdots\text{H}_2$	155.616	165.656
CASSCF	$R_{\text{eq}}$	121.87	127.642
	$1.5R_{\text{eq}}$	107.089	118.054
	$2.0R_{\text{eq}}$	94.464	102.363
	$\text{N}\cdots\text{H}_2$	114.01	114.621
SDCI <sup>a</sup>	$R_{\text{eq}}$	9.003	8.482
	$1.5R_{\text{eq}}$	23.472	18.097
	$2.0R_{\text{eq}}$	69.157	48.673
	$\text{N}\cdots\text{H}_2$	13.292	22.295
SDCI+Q <sup>a</sup>	$R_{\text{eq}}$	0.572	0.618
	$1.5R_{\text{eq}}$	1.584	2.403
	$2.0R_{\text{eq}}$	9.026	6.886
	$\text{N}\cdots\text{H}_2$	2.440	9.222
SS-MRPT(MP) [I]	$R_{\text{eq}}$	12.400	12.172
	$1.5R_{\text{eq}}$	8.3590	10.534
	$2.0R_{\text{eq}}$	10.044	12.523
	$\text{N}\cdots\text{H}_2$	14.010	17.231
SS-MRPT(MP) [II]	$R_{\text{eq}}$	5.172	7.47
	$1.5R_{\text{eq}}$	0.82	6.44
	$2.0R_{\text{eq}}$	3.78	10.45
	$\text{N}\cdots\text{H}_2$	3.76	11.01
$H_v^{\text{third}}$	$R_{\text{eq}}$	14.771	-19.456
	$1.5R_{\text{eq}}$	0.171	-1.604
	$2.0R_{\text{eq}}$	5.635	7.681
	$\text{N}\cdots\text{H}_2$	10.029	10.202
MRCI <sup>a</sup>	$R_{\text{eq}}$	3.466	3.329
	$1.5R_{\text{eq}}$	2.279	3.935
	$2.0R_{\text{eq}}$	1.501	2.267
	$\text{N}\cdots\text{H}_2$	3.375	3.165

<sup>a</sup>Reference 49.

## B. $\text{NH}_2$

In our next example, we have studied the energy of nonsinglet states,  ${}^2B_1$  and  ${}^2A_1$ , of  $\text{NH}_2$  system for which an exact treatment of electron correlation is readily accessible via FCI and for which previous *ab initio* results have been reported. To enable one to compare with FCI results of Bauschlicher *et al.*,<sup>53</sup> we have used the same basis and scheme as in Ref. 53. The geometries used for  ${}^2B_1$  and  ${}^2A_1$  are given explicitly in Ref. 53. In a number of applications, we find the basis sets of the DZP quality quite sufficient to obtain useful and systematically reliable results. In our applications, we have used all the configurations emerging out of the distribution of seven electrons in six active orbitals to construct our required CAS. The leading configuration for  ${}^2B_1$  state is  $1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^1$  at all geometries. For the  ${}^2A_1$  state, the main contribution is from the configuration corresponding to  $3a_1 \rightarrow 1b_1$  excitation relative to the  ${}^2B_1$  configuration at all the geometries reported here except the last one which corresponds to  $1b_1 \rightarrow 4a_1$  excitation.

In Table II, we have summarized the results of SS-

MRPT(MP)[I],  $H_v^{\text{third}}$ , and other available methods in terms of the corresponding deviation from FCI values  $\Delta E$ . From the results shown in Table II, one can see that the SCF zeroth-order function becomes an increasingly poor zeroth-order description of the system compared to the CASSCF one as the NH bonds are stretched for both the states. The error of total energy in the case of CASSCF is small in comparison to the SCF and decreases slightly with increase in stretching of NH bonds. The results of Table II demonstrate that the inclusion of dynamical correlation effect reduces the error of the CASSCF/SCF energy with respect to the FCI value. The table describes that the performance of the SR-based methods such as SDCI (Ref. 53) increasingly deteriorates as the bond length is increased for both the states, as it should be. The deviation from FCI values increases more rapidly for  ${}^2A_1$  state than the other one. Thus, the SR-based method is not suitable to compute the energy in the dissociation region. The CASSCF gives a PEC which is more parallel to FCI in comparison to the SDCI. We can see that the performance of the SS-MRPT(MP)[I] method is not very close to the FCI, while the error of the SS-MRPT(MP)[I] has the same sign at all geometries. It is not yet clear what features of the method lead to such a deviation. However, since in chemistry, we are primarily interested in getting PEC parallel to the exact one, the absolute error is less important. In this case, the error with respect to the FCI ( $\Delta E$ ) of SS-MRPT(MP)[I] for both the states is large in comparison to the MRCI and SDCI+Q methods, but the NPE is small in comparison to the SDCI+Q one. In spite of yielding a large deviation from FCI values at various geometries, the NPE for  ${}^2B_1$  and  ${}^2A_1$  in the case of SS-MRPT(MP)[I] are 3.54 and 4.20 kcal/mol, respectively. Note that the NPE is small. There is a significant NPE in the case of  $H_v^{\text{third}}$  method (the NPEs of  ${}^2B_1$  and  ${}^2A_1$  states are 9.37 and 11.19 kcal/mol, respectively). Thus, the NPE in the case of the SS-MRPT(MP)[I] approach is smaller than that of the  $H_v^{\text{third}}$  one as in the case of LiH system. We have already mentioned that the SS-MRPT(MP)[I] method is computationally cost effective in comparison to the  $H_v^{\text{third}}$  method. The NPEs of  ${}^2B_1$  state for SDCI, SDCI+Q, and MRCI (Ref. 53) are 37.72, 5.30, and 1.23 kcal/mol, respectively, whereas for  ${}^2A_1$  state, these are 25.20, 5.40, and 1.05 kcal/mol, respectively. From Table II we observe that the energy deviations from the FCI of the SS-MRPT(MP)[I] are worse than those obtained from MRCI method. Again the NPE of the SS-MRPT(MP)[I] is less than the SDCI+Q method. As the NPE of SS-MRPT(MP)[I] method is reasonably small and encouraging, we may say that the performance of the SS-MRPT(MP)[I] method for the computation of doublet states of  $\text{NH}_2$  is promising.

To study the effect of choice of one-electron  $H_0$  on the performance of SS-MRPT, we have also included the results using another mono-electronic  $H_0 = \sum_{\mu\tilde{\mu}} \tilde{f}_{\mu}^{ii} \{E_i^i\}$  partition scheme in Table II. From the table, it is evident that as we move from  $H_0 = \sum_{\mu} f_{\mu}^{ii} \{E_i^i\}$  to  $H_0 = \sum_{\mu\tilde{\mu}} \tilde{f}_{\mu}^{ii} \{E_i^i\}$ , we observe the improvement of the quality of the result(s) generated via the SS-MRPT(MP) method. From the Table II, we notice that the deviations of the SS-MRPT(MP)[II] scheme from the corre-

TABLE III. Energy differences (mH) with respect to FCI [ $\Delta E_{\text{method}}(R) = E_{\text{method}}(R) - E_{\text{FCI}}(R)$ ] for various methods for the ground state,  ${}^2B_1$  ( $C_{2v}$  symmetry label) of planar  $\text{CH}_3$  radical.

$R$ (a.u.)	$R_e$	$1.5R_e$	$2.0R_e$
SCF	154.70	198.91	290.12
CASSCF	96.42	73.74	65.13
CASPT2D <sup>a</sup>	14.2	7.9	5.4
CASPT2N <sup>a</sup>	12.5	7.9	5.8
SDCI <sup>b</sup>	8.38	23.22	70.65
SDCI+Q <sup>b</sup>	0.11	2.03	15.99
MCPF <sup>b</sup>	1.96	5.40	19.24
MRCI <sup>b</sup>	2.09	1.16	0.68
SS-MRPT(MP)[I]	12.8	9.1	11.4
SS-MRPT(MP)[II]	9.2	0.6	2.8

<sup>a</sup>Reference 19.

<sup>b</sup>Reference 54.

sponding FCI values are lower than the SS-MRPT(MP)[I] ones for both the states,  ${}^2B_1$  and  ${}^2A_1$ . The NPEs of the SS-MRPT(MP)[II] for  ${}^2B_1$  and  ${}^2A_1$  states are 2.73 and 1.80 kcal/mol, respectively. This study motivated us to further investigate the applicability of the  $H_0 = \sum_{\mu} \tilde{f}_{\mu}^{ii}$  scheme for molecular systems with arbitrary spin of the target states. Work toward this direction is in progress in our laboratory using different types of orbitals.

At this point we want to say that the  $\Delta E$  results of  ${}^2A_1$  state of  $\text{NH}_2$  generated via SS-MRPT(MP) presented above are not good as that of the other cases although the NPE is small. One probable reason for such a deviation is that the active off-diagonal part of Fock operator in the zeroth-order Hamiltonian has not been considered in this paper. Note that the inclusion of off-diagonal elements will introduce couplings between the different types of excitation classes (see Sec. II).

### C. $\text{CH}_3$ radical

Our next case concerns the  $\text{CH}_3$  radical. We consider the energies of the ground state (doublet state) of planar  $\text{CH}_3$  radical due to symmetrical stretching of three single CH bonds. The simultaneous dissociation of three CH bonds in planar  $\text{CH}_3$  radical is a typical triple-bond breaking model and thus has been used to calibrate the potentiality of various *ab initio* approaches. This example, although simple, occurs in many organic reactions. In 1987, Bauschlicher and Taylor<sup>54</sup> performed FCI benchmark calculations on the symmetrically stretched planar  $\text{CH}_3$  radical. The planar ground state of  $\text{CH}_3$  radical is of  $D_{3h}$  symmetry. The largest Abelian subgroup of  $D_{3h}$  ( $C_{2v}$ ) is used for computational purposes. In this paper, we have computed the energies of the ground state,  ${}^2B_1$  [ $1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^1$ ], over different geometries including equilibrium point using the same basis and scheme as in the corresponding FCI benchmark papers of Bauschlicher and Taylor.<sup>54</sup> We have used ( $7 \times 7$ ) CAS (seven active electrons are distributed over seven active orbitals such as four  $a_1$ , one  $b_1$ ,  $b_2$ ,  $a_2$  symmetry) in CASSCF calculations. For this system, we compare the performance of the SS-MRPT(MP) method against FCI results. In Table III, we

have summarized the deviation (error)  $\Delta E$  of SS-MRPT(MP) results with respect to the FCI ones. To judge the quality of results, the SS-MRPT(MP) values are compared with those of SR-based methods, MRCI and MCPF, taken from the literature.<sup>54</sup> As in the other cases, the performances of the SR-based CI methods go down as one moves away from the equilibrium geometry. SR-based truncated CI methods are not generally reliable for dissociation processes because a truncated CI wave function is not size extensive as we have already mentioned in Sec. I. The NPE values of CASSCF and SCF methods are 19.62 and 84.90 kcal/mol, respectively. It can be seen from Table III that the  $\Delta E$  (and also NPE) values for CASSCF method are smaller than those of the corresponding SCF values over different distances which indicates that MR-based mean-field reference function is a better choice than the SR-based mean-field one. The table shows that the  $\Delta E$  values for CASSCF method decrease as the bond length increases, whereas for SCF, the corresponding values increase which indicate that the SR wave function becomes worse as a starting zeroth-order function. This makes clear the fact that the ground state of  $\text{CH}_3$  radical possesses different extents of MR nature over various geometries which is expected. Although CASSCF is in better agreement with the FCI than SCF, the  $\Delta E$  values for CASSCF are quite large, it grossly underestimates the energy and thus inclusion of dynamical correlation in CASSCF improves the results. Thus, for a qualitatively correct description of the ground state of the  $\text{CH}_3$  radical over a wide range of geometries, both nondynamical and dynamical correlations are crucial. Hence, this radical is a very challenging case of bond breaking for very strong nondynamical and dynamical correlation effects. Table III makes it clear that the error in total energy (with respect to the FCI) is reduced remarkably for different bond distances compared to the CASSCF by subsequent calculations of dynamical correlation. From the table, we observe that the results of the MRCI method are in better agreement with the corresponding FCI values than those of other methods reported in the table. The results in Table III show that the deviation of MCPF method from FCI increases with symmetrical stretching of CH bond as in the SR-based methods. From the table we have observed that the  $\Delta E$  values for SS-MRPT(MP)[II] are lower than that of the SS-MRPT(MP)[I]. The table demonstrates that the SS-MRPT(MP) method mimics the behavior of FCI method, and its error against the FCI,  $\Delta E$ , is small as that of the CASPT2 method. The encouraging observation is that the performance of the SS-MRPT(MP) is good even at substantially distorted geometries and is almost similar to the CASPT2 one. Note that the error in total energy of the SS-MRPT(MP) and CASPT2 methods is large at equilibrium distance than that at the other bond distances. The  $\Delta E$  for MRCI method is large at equilibrium distance as in the case of the SS-MRPT(MP) method and the value decreases with bond length. The NPEs of SS-MRPT(MP)[I] and SS-MRPT(MP)[II] are 2.32 and 5.39 kcal/mol, respectively. Although a switch over from  $f_{\mu}$  operator to  $\tilde{f}_{\mu}$  reduces the deviation from the corresponding FCI values, the NPEs are slightly small for the SS-MRPT(MP)[I] scheme in comparison to the SS-MRPT(MP)[II]. Results of the SS-MRPT(MP)

methods are not dramatically different for different choices of  $H_0$  in the case of SS-MRPT(MP) for  $\text{CH}_3$  values. The trend of the results (NPE and  $\Delta E$ ) indicates that all the variants of SS-MRPT(MP) do rather well. The NPEs for CASPT2D, CASPT2N, MRCI, and MCPF are 5.52, 4.20, 0.88, and 10.83 kcal/mol, respectively. It should be noted that although the error in total energy in SS-MRPT(MP) and CASPT2 methods is almost similar, the NPE of the SS-MRPT(MP)[I] method is slightly better compared to the CASPT2 one. However, the NPE of CASPT2 is close in proximity to the SS-MRPT(MP)[II]. For chemical applications, not only the absolute error in the energy along the bond distances is important but also NPEs are vital. In passing we want to mention that the various CASPT2 versions by and large avoid the size-consistency error, but not rigorously so. From the point of  $\Delta E$  and NPE values, SS-MRPT(MP) method yields fairly reliable energies close to those of FCI (and MRCI) ones which illustrate that the SS-MRPT(MP) method does indeed more or less accurately recover the dynamical correlation energy for  $\text{CH}_3$  radical over the different bond distances even for symmetrically highly stretched three CH bonds.

The preliminary applications of the SS-MRPT(MP) method to compute PEC of nonsinglet states indicate that it is very efficient and is not plagued by intruders even in rather difficult cases. It also provides quite accurate values of state energies for chemically interesting systems where intruders are present at some regions of the PEC and there is quasidegeneracy at some other region. Its success to compute PEC has prompted us to study the spectroscopic properties, which we present in Sec. IV. In order of increasing severity, our tests include the  $^3\Sigma^-$  ground states of NH and  $\text{OH}^+$  systems and the ground  $^1\Sigma_g^+$  and excited  $^3\Sigma_u^+$  states of  $\text{N}_2$  molecule.

#### D. Spectroscopic constants

This part embodies a description and the consequent analysis of the spectroscopic constants of the  $^3\Sigma^-$  ground states of NH and  $\text{OH}^+$  systems and the ground  $^1\Sigma_g^+$  and excited  $^3\Sigma_u^+$  states of  $\text{N}_2$  derived from our computed PEC generated via homolytic rupture of a chemical bond using SS-MRPT(MP) method. Test calculations of various spectroscopic constants on a few chemically interesting molecular systems (involve single- and triple-bond dissociations) of realistic size have been performed in order to show the usefulness of the SS-MRPT(MP) method. Although comparison with experiment is the ultimate goal to test the potentiality of a theoretical method, useful insight can be obtained by comparison with results of FCI. Hence along with experimental results, comparison with FCI has also been provided wherever available.

##### 1. Ground state $^3\Sigma^-$ of the NH and $\text{OH}^+$ systems

As a first test we have chosen to calculate the spectroscopic constants of the  $^3\Sigma^-$  ground state of the NH and  $\text{OH}^+$  systems. In this context, we mention that recently Abrams and Sherrill<sup>55</sup> compared a host of standard polarized double-zeta basis sets for use in FCI benchmark computations for calculating spectroscopic constants of the ground state of NH

TABLE IV. Spectroscopic constants for  $^3\Sigma^-$  of NH and  $\text{OH}^+$  using 6-31G\*\* (Ref. 56).  $R_e$  in Å,  $D_e$  in eV, and other quantities in  $\text{cm}^{-1}$ .  $\Delta E(R_e) = [E_{\text{method}}(R_e) - E_{\text{FCI}}(R_e)]$ . Experiment: Reference 57.

System	$R_e$	$\omega_e$	$D_e$	$\Delta E$ (mH)
(a) NH				
SS-MRPT(MP)[I]	1.0461	3199	3.25	6.08
FCI	1.0442	3267	3.18	( $R_e=1.0442$ )
Experiment	1.0362	3282	3.68	
(b) $\text{OH}^+$				
SS-MRPT(MP)[I]	1.0301	2998	4.92	2.96
FCI	1.0323	3161	4.80	( $R_e=1.0323$ )
Experiment	1.0289	3113	5.29	

and  $\text{OH}^+$  systems. For the molecules considered here, they have demonstrated the performance of 6-31G\*\* basis to be better on an average for the various *ab initio* methods. One might expect that FCI, representing the complete treatment of electron correlation for a given basis set, might require even larger basis sets. However, the FCI spectroscopic constants obtained by Abrams and Sherrill<sup>55</sup> using 6-31G\*\* basis<sup>56</sup> are generally in good agreement with experiment. Consequently, in our applications to compute the spectroscopic constants of  $^3\Sigma^-$  states of NH and  $\text{OH}^+$ , we have used the same basis.<sup>56</sup> For comparison with FCI values of Abrams and Sherrill,<sup>55</sup> in the present study we used the same scheme as used by Abrams and Sherrill. In our computation, we have used  $C_{2v}$  point group and four electrons six active orbitals ( $a_1b_1b_2a_1b_1b_2$ ), ( $4 \times 6$ ) CAS for both NH and  $\text{OH}^+$  systems in our CASSCF calculations.

In Ref. 55, the single point FCI energy is reported. The deviation of the SS-MRPT(MP) energy from the FCI,  $\Delta E$ , is shown in the last column of Table IV. At  $R=1.0442$  Å distance, in the case of NH, the  $\Delta E$  is 6.08 mH, whereas the  $\Delta E$  value for  $\text{OH}^+$  is just 2.96 mH at  $R=1.0323$  Å. Thus, we have observed in these systems that the error  $\Delta E$  is also small.

Different spectroscopic constants and dissociation energies of the  $^3\Sigma^-$  ground states of NH and  $\text{OH}^+$  systems derived from our computed PEC generated via SS-MRPT(MP)[I] method are presented in Table IV. From the table it is clear that the SS-MRPT(MP)[I] spectroscopic constants of  $^3\Sigma^-$  state for both NH and  $\text{OH}^+$  systems are overall in good agreement with both the corresponding FCI and the experimental values. Table IV shows that the SS-MRPT(MP)[I] method provides accurate predictions of equilibrium bond length of both the systems. The  $R_e$  value of SS-MRPT(MP)[I] method is very close to the FCI value. Both FCI and SS-MRPT(MP)[I] methods overestimate the bond length with respect to the experimental value. Here, we find that the SS-MRPT(MP)[I] harmonic vibrational frequency in both the systems underestimates FCI values, whereas FCI and SS-MRPT(MP)[I] both overestimate the experimental one.<sup>57</sup> It is observed from literature<sup>55</sup> that most quantum chemical methods generally overestimate harmonic vibrational frequencies. The correct prediction of dissociation energy  $D_e$  is a challenging task for any quantum me-

TABLE V. Total state energies (a.u.) and the deviation from FCI values (mH) for ground  $^1\Sigma_g^+$  state of  $N_2$  using DZP basis (Ref. 19).

Distance (a.u.)	2.05	2.10	2.15	2.50	3.00	4.00	50.00
FCI	-109.146 91	-109.150 64	-109.150 49	-109.087 32	-108.957 53	-108.842 21	-108.829 52
FCI-CASSCF	55.61	55.90	56.14	57.08	57.12	48.10	40.74
FCI-CASPT2N	4.88	4.91	4.94	4.87	3.65	0.83	.26
FCI-SSMRPT(MP)[I]	6.4	6.34	6.6	7.13	7.14	7.89	7.77
FCI-SSMRPT(MP)[II]	6.14	6.20	6.26	6.33	4.89	5.03	4.19

chanical method. The value of  $D_e$  is highly sensitive to the size and nature of basis sets. From Table IV we observe that the  $D_e$  values computed via SS-MRPT(MP)[I] for both the systems are very close to the FCI values. The SS-MRPT(MP)[I] and FCI results underestimate the experimental  $D_e$  value. The most probable reason for this is the nature of basis sets. The polarized double-zeta basis sets are not proper for a correct description of the dynamical correlation over the entire PEC.<sup>55</sup> At the end we may say that the results show that the SS-MRPT(MP)[I] method works very well to generate various spectroscopic constants despite our use of the conceptually minimal choice of the MS which bolsters our belief that the method has the potential to yield reasonably good spectroscopic constants.

## 2. $^1\Sigma_g^+$ ground and $^3\Sigma_u^+$ excited state of $N_2$ molecule

We next consider  $N_2$  molecule. The  $N_2$  molecule is a paradigm system in the sense that this molecule poses serious challenge to any theory where both nondynamical and dynamical correlations are important in varying degrees along the PEC. Thus, this system provides a nontrivial test case for any MR-based method due to the difficulties in properly describing the dissociation process for a triple bond. We have considered the computation of spectroscopic constants of ground  $^1\Sigma_g^+$  and excited  $^3\Sigma_u^+$  states of  $N_2$  extracted from the corresponding PEC generated via SS-MRPT(MP) method. For  $N_2$  system, the study of  $^3\Sigma_u^+$  excited state is an interesting numerical test case to judge the applicability of a MP-based MRPT method, as for this system CASPT2 show irregularities due to intruder states in the excited state.<sup>24,58</sup> In order to get good quality PEC and correct trend of spectroscopic constants for this system, both nondynamical and dynamical correlations have to be computed in a balanced manner at a sufficiently high level using balanced basis sets. In our CASSCF calculation, for this system, the CAS used contains six active electrons and six active orbitals ( $6e, 6v$ ). After performing the CASSCF calculation, during perturbative treatment at second order to compute dynamical correlation via SS-MRPT(MP) the  $1s$  electrons are kept frozen. For the ground state of this system, we have already published<sup>33</sup> results of state energies with the SS-MRPT(MP)[I] method, and we have used the same basis as the one reported in Ref. 19. For this basis (DZP), FCI values are known. For the sake of completeness, we summarize the comparative performance of the SS-MRPT(MP)[II] method *vis-à-vis* the SS-MRPT(MP)[I] one in Table V using the same basis, DZP.<sup>19</sup> We can remark that in the case of the spectroscopic constants of the ground state of  $N_2$ , the SS-MRPT(MP)[II] results are

much improved with respect to SS-MRPT(MP)[I] method as one moves toward the region of dissociation. As we have already mentioned that the correlation energy at the dissociation limit is dominated not by the short-range dynamical correlation of the electrons, but rather by contributions of the nondynamical correlation. Thus, the SS-MRPT(MP)[II] is slightly better than SS-MRPT(MP)[I] to treat the dynamical and nondynamical correlations in a balanced manner. At shorter distance, the performances of the two SS-MRPT(MP) variants are almost identical in the case of DZP basis. To test the quality of the perturbed wave function generated via SS-MRPT(MP) method, we study the spectroscopic constants extracted from the computed PEC. The spectroscopic properties derived from our PEC using DZP basis are reported in Table VI. Table VI reports results of CASPT2 and FCI together with our two different SS-MRPT(MP) calculations. From the table, we notice that the performances of the two SS-MRPT(MP) schemes are very close to the CASPT2 one to yield equilibrium bond length  $R_e$  with respect to the FCI value. The results of the two SS-MRPT(MP) schemes are hardly distinguishable from those of CASPT2. The CASPT2 provides slightly better value for  $\omega_e$  in comparison to both the SS-MRPT(MP) schemes. On the other hand, the table shows that both the SS-MRPT(MP) approaches give better dissociation energies than even the CASPT2 method. For this basis set, the SS-MRPT(MP)[II]  $D_e$  is closer to FCI value among the various methods reported in the table. As is apparent from Table VI, the overall performance of the SS-MRPT(MP) for both the partitions is very close to one another and closer to the experimental and FCI values.

In our next set of application to compute the ground state spectroscopic constants, we have considered Dunning's correlation consistent valence zeta basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ.<sup>56</sup> The spectroscopic constants computed using SS-MRPT(MP) method using different correlation consistent basis sets are set out in Table VI. For these basis sets, we have only reported the results of SS-MRPT(MP)[I] scheme. We have considered cc-pVDZ basis as FCI and MRMPPT results are available.<sup>59</sup> The results of CCSD and CC3<sup>60</sup> are also incorporated in the table for the sake of comparison. These values are collected from Ref. 59. In the case of cc-pVDZ basis, the agreement of our computed spectroscopic constants via SS-MRPT(MP)[I] method with the corresponding FCI values is quite good in comparison to the MRMPPT method. Furthermore, note that the SS-MRPT(MP)[I] method gives better dissociation energies than even computationally expensive full-blown CCSD and CC3 (except in the case of  $\omega_e$ ) methods. Note that the accuracy of

TABLE VI. Spectroscopic constants for the ground  $^1\Sigma_g^+$  and excited  $^3\Sigma_u^+$  states of  $N_2$  using different basis sets (Ref. 56).  $R_e$  in Å,  $D_e$  in eV, and other quantities in  $\text{cm}^{-1}$ . Experiment: 57; CAS: (6e, 6v) for SS-MRPT(MP) and MRMPPT; CAS: (10e, 8v) for various NEVPT.

State	Basis	Method	$R_e$	$\omega_e$	$D_e$
$^1\Sigma_g^+$	DZP	SS-MRPT(MP)[I]	1.1225	2313	8.777
		SS-MRPT(MP)[II]	1.1229	2308.6	8.694
		CASPT2 <sup>a</sup>	1.1227	2341	8.622
		FCI <sup>a</sup>	1.1231	2342	8.748
	cc-pVDZ	SS-MRPT(MP)[I]	1.1202	2299.4	8.58
		MRMPPT <sup>b</sup>	1.1212	2275	8.37
		CCSD <sup>b</sup>	1.1128	2409	
		CC3 <sup>b</sup>	1.1195	2331	
		FCI <sup>b</sup>	1.1201	2323	8.74
		Experiment	1.098	2358.6	9.906
	cc-pVTZ	SS-MRPT(MP)[I]	1.1050	2313.6	9.196
	cc-pVQZ	SS-MRPT(MP)[I]	1.1013	2330.8	9.438
		CASPT2 <sup>c</sup>	1.1023	2332.6	9.37
		CASPT3 <sup>c</sup>	1.1011	2350.7	9.59
		SC-NEVPT2 <sup>c</sup>	1.1027	2332.6	9.649
		PC-NEVPT2 <sup>c</sup>	1.1023	2336.0	9.744
		SC-NEVPT3 <sup>c</sup>	1.1029	2331.6	9.536
Experiment		1.098	2358.6	9.906	
$^3\Sigma_u^+$	cc-pVTZ	SS-MRPT(MP)[I]	1.2999	1429.9	3.077
		SS-MRPT(MP)[I]	1.2932	1504.6	3.403
	cc-pVQZ	SS-MRPT(MP)[I]	1.2932	1504.6	3.403
		Experiment	1.287	1460.6	3.686

<sup>a</sup>Reference 19.

<sup>b</sup>Reference 59.

<sup>c</sup>Third entry of Ref. 29.

the  $\omega_e$  value computed via CC3 method is quite good. Thus, for cc-pVDZ basis set, the accuracy of the SS-MRPT(MP)[I] method to compute various spectroscopic constants is good when compared to the FCI results or the experimental values.

Our next analysis concerns the cc-pVTZ/cc-pVQZ basis. For the ground state, the spectroscopic properties calculated via various perturbation theories such as CASPT2, CASPT3, NEVPT2, and NEVPT3 using cc-pVQZ basis [see Ref. 29 (third entry)] are set out in Table VI to demonstrate the potentiality and generality of the SS-MRPT(MP)[I] method. Note that the active space used by Angeli *et al.* [see Ref. 29 (third entry)] in their CASSCF calculation contains ten valence electrons distributed over eight valence orbitals (10e, 8v) which is larger than ours (6e, 6v). From the inspection of Table VI, it is clear that the equilibrium distance  $R_e$  for the ground state is well described by the SS-MRPT(MP)[I] method as that by the other methods reported in the table. In the case of the ground state, the performance of the SS-MRPT(MP)[I] method to compute the harmonic frequency  $\omega_e$  is also good as is evident from the analysis of the comparison of the results of the SS-MRPT(MP)[I] method with other methods and experimental value quoted in Table VI. For the harmonic frequency  $\omega_e$  we notice an improvement in the SS-MRPT(MP) result when the size of basis set is increased as that notice in the case of the  $R_e$  value. As far as the prediction of dissociation energy of the ground  $^1\Sigma_g^+$  is concerned, the computed dissociation energy by the SS-MRPT(MP) method for different basis sets is close to the value of other available methods and the experimental value.

From the table it is also evident that the quality of dissociation energy obtained from SS-MRPT(MP)[I] is improved with increase in the size of basis sets.

For the excited state we have used two different basis sets (cc-pVTZ and cc-pVQZ)<sup>56</sup> to compute the spectroscopic constants. For this state ( $^3\Sigma_u^+$ ), as FCI values for these basis sets are not available, although we have not studied the performance of the SS-MRPT(MP)[I] up to the basis set saturation limit, we have tabulated the corresponding experimental values for the sake of comparison and demonstration of the applicability of the method. The calculations of the PEC for the excited triplet state  $^3\Sigma_u^+$  of  $N_2$  using the SS-MRPT(MP)[I] method for both basis sets do not show any hint of intruder state problem (does not exhibit any discontinuity in the PEC). Such a conclusion is borne out from the inspection of the spectroscopic constants of the SS-MRPT(MP)[I] method. As that for the ground state, the spectroscopic constants such as  $R_e$ ,  $\omega_e$ , and  $D_e$  are also well predicted by the SS-MRPT(MP)[I] PEC for the  $^3\Sigma_u^+$  excited state since the SS-MRPT(MP)[I] results show satisfactory agreement with experimental values. Comparison with experimental data indicates that the values of the various spectroscopic constants improve with the increase in size of the basis set. Thus, for both the states, ground as well as excited, we have observed a reasonable agreement of SS-MRPT(MP)[I] results for the spectroscopic constants with experiment and other well established methods (whenever available). Finally, we may say that the performance of the SS-MRPT(MP)[I] shows convergence behavior with respect to the size of basis set for the ground  $^1\Sigma_g^+$  as well as  $^3\Sigma_u^+$  excited states of  $N_2$  molecule. The present calculation dem-

onstrates that the spectroscopic constants of the nonsinglet excite state are well described by the SS-MRPT(MP)[I] method as that of the singlet ground state even in the case of nontrivial  $N_2$  system. From Table VI, we observe that generally the SS-MRPT(MP) method tends to overestimate the spectroscopic constants for the experimental values as do the other reported methods.

From the foregoing discussion it is now evident that the overall accuracy of the suite of the SS-MPR(MP) schemes to yield spectroscopic constants such as the equilibrium bond distance, harmonic frequency, and dissociation energy is quite satisfactory for the systems reported by us in this paper. At the end of this section we want to say that the SS-MRPT(MP) approach is designed to treat correlations rather accurately, and we envisage that a future large-scale application should start with a relatively optimal CAS, dictated mainly by the demand of providing a conceptually minimal but qualitatively correct description, followed by a perturbative expansion (up to second order) around the model functions spanning the CAS.

#### IV. CONCLUSION AND SUMMARIZING REMARKS

The main purpose of the present work is to describe and ascertain the convergence trend of the SS-MRPT using two different MP partitioning schemes (diagonal  $H_0$ ) at the level of second-order perturbation to compute the total energies over various geometries including dissociation limit and various spectroscopic constants for nonsinglet states of small sized chemically interesting molecules, and we have observed through a few numerical examples that this appears to be actually the case. For different choices of diagonal  $H_0$ , we have observed that the results obtained by the SS-MRPT(MP) method are not dramatically different. In this paper, we have tried to demonstrate the potentiality of a state-specific MR second-order perturbation method, SS-MRPT(MP), based on a CASSCF reference function to compute the energies of nonsinglet states using some chemically interesting systems for which the exact FCI results are available in the literature so that we can calibrate the quality of the results. In our previous paper,<sup>33</sup> we had been able to show that the SS-MRPT(MP) method is quite promising in applications to break the single, double, and triple-bonded systems in the singlet state with pronounced quasidegenerate nature. The work presented here is the first step in an attempt to describe the PEC of nonsinglet states by means of SS-MRPT(MP) method. From our numerical comparison with FCI values and other well established methods, we have observed that the performance of SS-MRPT(MP) method to calculate the energy of nonsinglet electronic states is fairly accurate. To give a better idea of the efficiency of the SS-MRPT(MP) method, we have also quoted NPEs which show that the errors are reasonably small in the case of SS-MRPT(MP) method.

The description of results and corresponding discussion shows that the performance of the SS-MRPT(MP) method is not identical for all the systems studied here. This is also true for the other methods (CASPT2, MRCI, SDCI, SDCI+Q) reported in this paper. Since different approximations are in-

involved in different methods reported in this paper, the selection of the most appropriate method strongly depends on the kind of molecule under study and the property that we are interested in. The SS-MRPT(MP) energies for the systems we have studied are qualitatively correct giving a particularly good description of correlations. In most of the cases, the results of the SS-MRPT(MP) method are close to the FCI ones and the errors  $\Delta E$  of the SS-MRPT(MP) are small over the different geometries. In some cases, the errors of SS-MRPT(MP) method are slightly large, but we have observed that the NPEs are not appreciable. The computed spectroscopic constants for the nonsinglet states via SS-MRPT(MP) method are also in good agreement with FCI as well as experimental values. From our findings we can say that the SS-MRPT(MP) method is capable of providing consistent and promising results for the different nonsinglet states of the systems considered here at the different geometries in an intruder-free manner as in the case of the singlet states<sup>33</sup> and thus deserves our attention not only for its applicability but also for its generality.

In most of the cases, although the performance of SS-MRPT method to compute the dynamical correlation (with respect to the FCI and other effective and established methods) is very encouraging, calculations using different basis sets are needed to get better information about the efficacy of the SS-MRPT(MP) method to handle the same. The credibility of our results will be further supported if relatively small basis set dependence of the results is observed. We plan to explore investigations of basis set convergence in near future. We also investigated the performance of the SS-MRPT(MP) method to yield the spectroscopic constants extracted from the PEC computed by the SS-MRPT(MP) method and assessed them with respect to the FCI and experimental results. Our numerical results demonstrate that the performance of the SS-MRPT(MP) method to compute spectroscopic constants and dissociation energy is more or less close to FCI and experimental values.

Although MP-based perturbation theory is one of the most widely used methods to address the correlation problem in quantum chemistry, bielectronic  $H_0$  also offers a very useful scheme for a balance treatment between the zeroth-order wave function and the outer space. Thus, it is very useful to compare the results of different partitions to establish the applicability and potentiality of the SS-MRPT method. Pilot applications of the SS-MRPT(MP) method using Epstein-Nesbet-type partitioning (a diagonal bielectronic zeroth-order hamiltonian) have been published in Ref. 32. Applications of the SS-MRPT approach using different partitioning schemes are underway.

As a general conclusion we state that the SS-MRPT(MP) method proves to be a reliable tool for predicting the energies and various spectroscopic constants of nonsinglet states in an intruder-free and size-extensive manner. We are not now in a position to argue that SS-MRPT(MP) is a superior method for general use but it is certainly a potential one. For such a claim, more extensive applications of the method are called for.

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