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Molecular applications of state-specific multireference perturbation theory to HF, H_2O, H_2S, C_2, and N_2 molecules

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In view of the initial success of the complete active space (CAS) based size-extensive state-specific multireference perturbation theory (SS-MRPT) [J. Phys. Chem. A **103**, 1822 (1999)] for relatively diverse yet simple chemically interesting systems, in this paper, we present the computation of the potential energy curves (PEC) of systems with arbitrary complexity and generality such as HF, H_2O, H_2S, C_2, and N_2 molecules. The ground states of such systems (and also low-lying singlet excited states of C_2) possess multireference character making the description of the state difficult with single-reference (SR) methods. In this paper, we have considered the Møller–Plesset (MP) partitioning scheme [SS-MRPT(MP)] method. The accuracy of energies generated via SS-MRPT(MP) method is tested through comparison with other available results. Comparison with FCI has also been provided wherever available. The accuracy of this method is also demonstrated through the calculations of NPE (nonparallelism error) and the computation of the spectroscopic constants of all the above mentioned systems. The quality of the computed spectroscopic constants is established through comparison with the corresponding experimental and FCI results. Our numerical investigations demonstrate that the SS-MRPT(MP) approach provides a balanced treatment of dynamical and non-dynamical correlations across the entire PECs of the systems considered. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2952666]

I. INTRODUCTION

In spite of a phenomenal success of the single-reference (SR)-based method[1] in treating the electron correlation in closed-shell and certain types of open-shell systems around equilibrium geometry, the effectiveness of the method goes down while describing dissociation, potential energy curve (PEC), "mixed electronic states," diradical species, etc., where a single-determinant description becomes completely inadequate [a (quasi)degeneracy situation]. The quasidegeneracy effect causes the electron correlation to be radically different at different nuclear geometries. Over the years, various SR-based approaches on how to treat such problems have been proposed.[2–4] An obvious physically more appealing solution to the problem is to replace the SR ansatz with a multireference (MR) one. Unfortunately, the generalization of single-reference coupled-cluster methods to the MR case is neither obvious nor unique. As a consequence, there are many ways to set up the wave function, the wave operator, and the excitation manifolds.[5] In calculation of PEC one has to deal with configurational degeneracy resulting from distorting the molecular system from its equilibrium geometry. It should be stated that the methods capable of reliable computation of the PEC still remain an active research area in contemporary quantum chemistry.[6] In recent time, the MR methods have emerged as the method of choice for computing PEC of small/moderate size molecules in a balanced manner.[7]

Among the various MR-based method, the multireference (MR) perturbation theory (MRPT) is widely and routinely used nowadays to compute PEC of various electronic states for systems of arbitrary generality and complexity. The MRPT based on Møller–Plesset (MP) partitioning scheme to treat dynamic correlation in a balanced manner starting from a MCSCF (multiconfiguration self-consistent field) or CASSCF (complete active space self-consistent field) reference function, is quite popular because of it being computationally cost effective with respect to the MRCI (multireference configuration interaction) method.[8] It is now well documented that the performance of MRPT based on effective Hamiltonian approach[9] goes down in the presence of intruder state problem.[10] Several attempts have been made in the last two decades to go beyond the effective Hamiltonian approach to bypass the difficulty of intruders. Although over the past decades, several multireference (MR) perturbative methods[11–21] have been developed, a method based on a truly multiconfigurational reference function generated via linear combination of several (reference degenerate/quasidegenerate) functions appears to be quite effective and promising to compute the state energies of a system of arbitrary complexity and size. The various complete active space (CAS)-based MR perturbative methods can differ in their choice of unperturbed Hamiltonian H_0, apart from the mode of representing the reference function as relaxed or unrelaxed

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with respect to the combining coefficients. Among them, two formalisms, CASPT2 (complete active space second order perturbation theory[14]) and MRMPPT (multireference Møller–Plesset perturbation theory[15]) have been extensively used. Both of them are based on a fixed linear combination of the model functions, i.e., they are of frozen coefficients variety (unrelaxed version). These methods differ in their choice of the zeroth-order unperturbed and virtual functions. Mukherjee *et al.* have suggested state-specific multireference PT (SS-MRPT) formalism using CAS,[22] which uses relaxed coefficients for the model functions, and which has been shown to be intruder free as well as size extensive in nature. The method has several attractive features for the study of chemical problems. The SS-MRPT emerged as a result of a physically appealing quasilinearization of a rigorously size-extensive state-specific multireference coupled-cluster formalism (SS-MRCC) developed by Mukherjee and co-workers[23,24] (MkMRCC), which provides quite accurate ground state energies for several systems with a strong multireference character. The SS-MRCC and SS-MRPT formulations are intruder-free as long as the state energy is energetically well separated from the virtual functions. The SS-MRPT method works with a CAS and treats each of the model space (MS) functions democratically. It thus has the twin advantage of being capable of handling varying degrees of quasidegeneracy, including real or avoided curve crossing, and of ensuring size consistency when localized orbitals are used as a consequence of size extensivity. This strategy is attractive in terms of the applicability to bigger systems. The SS-MRPT method is designed to bypass the intruder state problem in the presence of quasidegeneracy and avoided curve crossing. Thus this method is promising for calculations on electronic states that involve strong mixing between different zeroth-order contributions (e.g., real or avoided crossing). Very recently, Mukherjee and co-workers[25] have developed the spin-free version of the SS-MRPT and explored its efficacy in various single bond breaking situations where two active electrons are involved. In this paper, we scrutinized the performance of the SS-MRPT method by applying it to various molecular systems, which possess MR character and comparing the results with the values obtained using allied theories.

It is convenient at this stage to write working equations of the SS-MRPT [Rayleigh–Schrödinger (RS) based], which would help to discuss its structural features.

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

and

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

with $\tilde{H}_{\mu\nu}^{(2)} = H_{\mu\nu} + \Sigma_l H_{\mu l} t_{\nu}^{l(1)}$. Here, t_{μ}^{l} is the cluster amplitudes of specific excitation between CSF ϕ_{μ} to the virtual function χ_l. From the working equations [Eqs. (1) and (2)] for the SS-MRPT method, it is clear that the set $\{c_{\mu}\}$ and $\{T^{\mu}\}$ are coupled. Once the first order cluster amplitudes are obtained, the second order energy, $E^{(2)}$, is generated by the diagonalization of a pseudoeffective operator ($\tilde{H}$) (relaxed version) or by taking the expectation value of $\tilde{H}$ with the reference wave function Ψ_0 (unrelaxed version). In the case of the unrelaxed scheme, $E^{(2)} = \Sigma_{\mu\nu} c_{\mu}^{(0)} \tilde{H}_{\mu\nu}^{(2)} c_{\nu}^{(0)}$, where c_{μ}^{0} denotes the frozen model space coefficients. We will present, in this article, the results of the relaxed scheme.

From the above equation it is evident that the coupling terms [second term of the numerator in Eq. (1)] refer to the *same vacuum* and thus are not difficult to implement. A reduction of the coupling ensues if a diagonal unperturbed Hamiltonian is used, as in MP partition: This then restricts the dimension of the matrix for the linear equation to be solved merely to the dimension of the MS. In this paper, the unperturbed Hamiltonian in SS-MRPT has been chosen to be MP [and hence the name SS-MRPT(MP)].

In the present implementation of the SS-MRPT theory, we have used the diagonal part of the following vacuum dependent Fock operator f_{μ} to define the zeroth-order Hamiltonian H_0:

$$f_{\mu} = \sum_{ij} \left[f_{\text{core}}^{ij} + \sum_{u} \left(V_{iu}^{ju} - \frac{1}{2} V_{iu}^{uj} \right) D_{uu}^{\mu} \right] \{E_i^j\}, \tag{3}$$

so that $H_{\mu}^{0} = \Sigma_i f_{\mu}^{ii} \{E_i^i\}$ and $H = H_{\mu}^{0} + V_{\mu}$, where u describes both a doubly occupied and a singly occupied active orbital in the CSF (configuration state function), ϕ_{μ}, and the D^{μ}'s are the one-particle density matrix elements in the CSF space labeled by the active orbitals. It is well known that the performance of any perturbation theory is dependent on the choice of zeroth-order Hamiltonian. A different choice of H_{μ}^{0} can be made,[25] and we plan to explore these other possibilities in the near future. The one-particle density matrix elements required in the construction of the CAS Hamiltonian matrix elements and in the subsequent second order pseudo effective operators $\tilde{H}$ calculation are computed first and stored in the fast memory. All the two- and three-body density matrix elements are computed on fly as and when they are needed during computation. Since, in our scheme, zeroth-order Hamiltonian H_0 is always diagonal (MP partitioning), thus $H_0^{\mu} = \Sigma_i f_{\mu}^{ii} \{E_i^i\}$. With this form of H_0, $(H_{\mu\mu}^{0} - H_{ll}^{0})$ is always a large value for converged mean field calculation. The term, $(E_0 - H_{\mu\mu})$ is usually a large quantity as long as the state of interest has no intruder. Thus, the denominators are robust to avoid intruders.

We must emphasize that with our choice of the unperturbed Hamiltonian, cluster amplitudes are coupled via frozen coefficient, only those amplitudes of the excitation inducing operators are coupled together, which share a common set of inactive orbital indices. This type of coupling is unique to all the MR-based theories in vogue. From the cluster amplitudes finding equation, Eq. (1), it is clear that the sum over ν appearing in the numerator is responsible for the coupling between the various t_{μ}^{l}'s (for all μ), which leads to a very efficient and cost effective computational scheme. In the SS-MRPT, a specific set of orbitals is associated for each type of excitation and consequently one can compute all the cluster amplitudes for various μ's using the same set of orbitals via Eq. (1). After calculating all such cluster amplitudes, the effective operator $\tilde{H}$ is computed and then diagonalized. It is noteworthy that in the RS-based SS-MRPT formalism, the zeroth-order coefficients c_μ^0's are used to evaluate the cluster operators in Eq. (1), but the coefficients are relaxed during the computation of $E^{(2)}$, since this is obtained by diagonalization via Eq. (2). It is now evident from the foregoing discussion that storing the cluster amplitudes is not required in the case of the SS-MRPT(MP) method: All the cluster amplitudes are computed on fly and their contributions to $\tilde{H}$ are incorporated after the calculation over of a particular t_μ^l's (for all μ), so the dimension of the cluster amplitude array is just equal to the dimension of the MS. Structurally, the SSMRPT(MP) method is very similar to the MRMP method of Hirao[15] (except the coupling term, which is mainly responsible for maintaining the size-extensivity of the SS-MRPT) and thus one can use the computational resource of MRMP method for the numerical applications of SS-MRPT(MP) method.

In this paper, we will present the numerical implementation of the spin-free SS-MRPT(MP) method[25] in general situations where more than two active orbitals and electrons are involved. The accuracy of this method is illustrated through calculations of the ground state energies of HF, H_2O, H_2S, C_2, and N_2 molecules. Two lowest singlet excited states of C_2 have also been investigated. These molecules show varying degrees of quasidegeneracy over a wide range of geometries. Hence, the computation of energies for various nuclear geometries of these systems serve as very useful and demanding test cases towards establishing the applicability and efficiency of the SS-MRPT(MP) method, which is designed to compute the state energy in an intruder free and size-extensive manner.

II. NUMERICAL APPLICATION

In this section we will discuss the numerical applications of the SS-MRPT(MP) method. The GAMESS (US) program package has been used to generate the CASSCF (and RHF) orbitals and one- and two-particle Hamiltonian integrals.

To judge the applicability of the SS-MRPT(MP) method towards bond breaking, we apply the method for the computation of PEC of HF, H_2O, H_2S, C_2, and N_2 to single bond, double bond, and triple bond breaking, respectively. To establish the applicability and generality of a method, results generated via double bond/triple breaking are more instructive than those for single bond breaking because of the corresponding increased difficulty of describing the systems. As already mentioned, the standard SR-based methods go down badly for multiple bond breaking reactions. The standard SR-based methods[1–4] are not able to provide an accurate description of dynamical correlation in the presence of the nondynamical correlation effects, which play a significant role in the case of computation of the PEC. This objection makes the conventional SR-based methods inapplicable to important areas of chemistry. MR-based methods[5] are indispensable in such cases. In order to test the applicability of the SS-MRPT(MP) method, in our numerical applications, we have plotted the SS-MRPT(MP) PEC along with FCI results. To address the quality of the computed PEC, we report the deviation of the computed energies $[\Delta E_{\text{method}}(R) = E_{\text{FCI}}(R) - E_{\text{method}}(R)]$ with respect to the corresponding FCI values (whenever available), which is more instructive. Another parameter to demonstrate the quality of the computed PEC is the nonparallelism error (NPE) with respect to FCI over a range of geometries. A diagnosis in terms of NPE is quite instructive and useful since it provides a measure of how well a method mimics the shape of the PEC of the exact FCI method (considered as a benchmark result). Thus, we also present the NPE value for each case. Usually, NPE is defined as the difference between the maximum and minimum errors along a PEC: $\text{NPE} = \max[\Delta E_{\text{method}}] - \min[\Delta E_{\text{method}}]$. To get a better feeling of the performance of our SS-MRPT(MP), the results of other *ab initio* methods [viz., CCSD, CCSD(T), CASPT2, etc.] have also been provided wherever available. One advantage of the present SS-MRPT(MP) approaches over CASPT2 methods is that the CASPT2 is approximately size consistent,[26] whereas the SS-MRPT(MP) being capable of handling varying degrees of quasidegeneracy in a size-extensive manner (and hence size consistent).[22] This issue is very important in terms of the applicability to bigger systems. Here, we want to mention the fact that the quality of results generated via MR-based PT strongly depends on the choice of active space. Thus, the choice of active space is very crucial to get results within desired accuracy.

We have also presented the values of various spectroscopic constants for the ground state calculated via Dunham analysis[27] of the PECs obtained. These include the equilibrium geometry r_e (Å), harmonic vibrational frequency ω_e (cm^{-1}), anharmonicity constant $\omega_e x_e$ (cm^{-1}), rotational constant B_e (cm^{-1}), and dissociation energy D_e. Although, moderate size basis sets are used in the study of the spectroscopic constants, it is worthwhile to compare the theoretical results with the corresponding experimental values.[28]

A. HF

Our first test case is the bond breaking of HF molecule. The computation of the ground state PEC of the HF molecule is a challenging problem for any many-body electronic structure theory due to an interplay of varying degree of dynamical and nondynamical correlations over the entire range of the PEC.[15,29–32] Hence, the computation of the ground PEC of HF molecule is a very good test case to demonstrate the potentiality of the SS-MRPT(MP) method.

We have used two sets of basis for which FCI results are available, viz., the DZ (Ref. 33) and 6-31G** (Refs. 34 and 35) in our calculations. We have also considered the cc-pVTZ.[36] In the cc-pVTZ basis, the FCI results are not available, hence we compare the performance of the SS-MRPT(MP) method with those of the experimental results through the computation of spectroscopic constants.[28] In our calculations of HF molecule, the MS is constructed by distributing two active electrons in 3σ and 4σ active orbitals. In our computation of correlated energies, we have used the canonical orbitals corresponding to the CASSCF calculation. In the case of HF molecule, we also present the calculations using RHF orbitals corresponding to the ground state configuration: $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$.

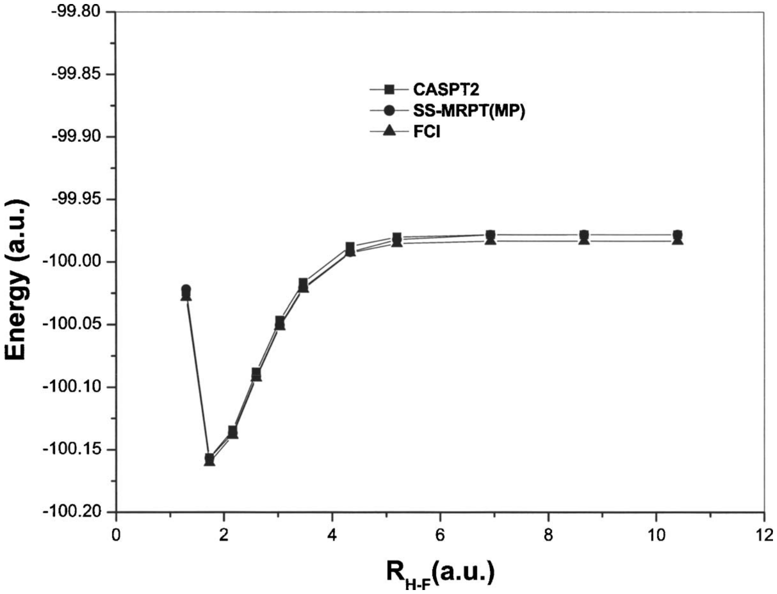

FIG. 1. PEC of the ground state of the HF molecule using CASSCF orbitals and DZ basis.

In Fig. 1, we have presented the PEC for HF molecule in DZ basis, which is clearly shown to mimic the CASPT2 and FCI PEC.[32] We have plotted in Fig. 2 the energy differences for SS-MRPT(MP) and CASPT2 (Ref. 32) with respect to the FCI values.[32] There are no significant deviations as compared to the FCI results[32] in the general trend of the result. From our results, it is clear that with respect to the FCI values, the SS-MRPT(MP) method exhibits a maximum and a minimum deviation of the order of 0.3 and 4.3 kcal/mol, respectively. On the other hand, the corresponding values for CASPT2 are 2.5 and 3.5 kcal/mol, respectively. The NPE for the state obtained via SS-MRPT(MP) method is within 4 kcal/mol and the error is less uniform than in the CASPT2 results. The SS-MRPT(MP) results are closer to FCI in the range of 2–6 a.u.. In another set of calculation, we have used RHF orbitals corresponding to the configuration, $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$, using DZ basis. In Fig. 3, we have plotted the deviation (ΔE) of the SS-MRPT(MP) energies with respect to the FCI values along with corresponding CASCI values using DZ basis and RHF orbitals. In Fig. 3, the corresponding deviation to CASCI is shifted by 100 mH towards FCI for the sake of better representation. The corresponding energy values along with CCSD are given in Table I. Although the deviation, ΔE for CCSD is small for shorter bond distances, the values increases with increase in bond length. On the other hand, the ΔE for SS-MRPT(MP) method is more consistent in comparison to CCSD one and also the deviation is quite small at elongated bond length in comparison to the CCSD values. The NPE of SS-MRPT(MP) and CCSD with RHF orbitals are 1.2 and 6.8 kcal/mol, respectively.

To demonstrate the sensitivity of the results generated via SS-MRPT method with respect to the size and nature of basis sets, we have also presented the calculations using the standard split-valence polarized double-zeta basis sets 6-31G**.[34,35] For this basis set, the FCI values [also MP2, CASPT2, CCSD and CCSD(T) results] are available.[34,35]

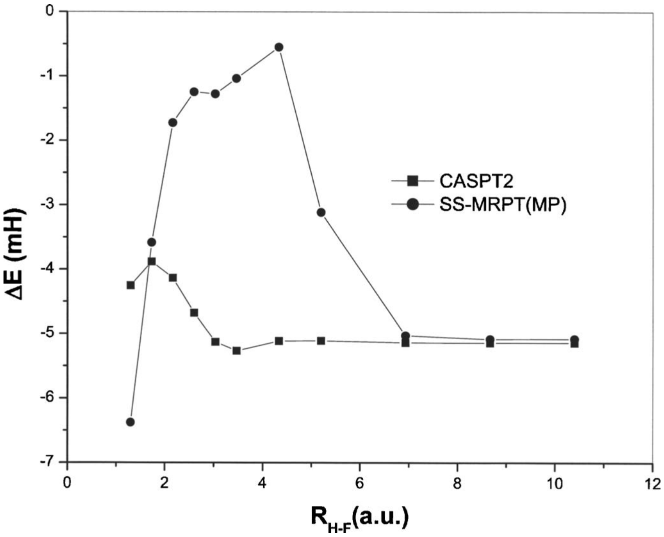

FIG. 2. Deviation of energies of the ground state of the HF molecule from the FCI values using DZ basis and CASSCF orbitals.

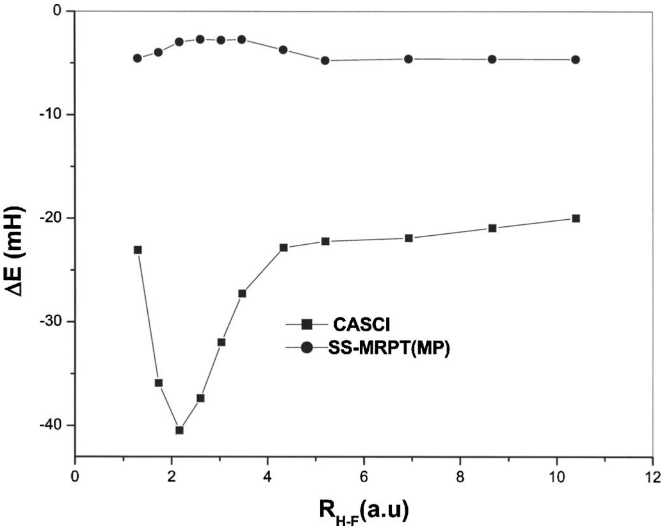

FIG. 3. Deviation of energies of the ground state of the HF molecule from the FCI values using DZ basis and RHF orbitals [ΔE corresponding to CASCI is shifted by 100 mH towards FCI].

TABLE I. Deviation ($-\Delta E$ in mH) of ground state energies of HF molecule from FCI values using RHF orbitals and DZ basis.

R (a.u.)	RHF	CASCI	SSMRPT(MP)	CCSD
1.299	123.23	123.06	4.56	1.35
1.733	138.43	135.90	3.97	1.63
2.166	152.67	140.45	2.97	2.18
2.599	167.86	137.37	2.71	3.05
3.032	185.51	131.97	2.78	4.32
3.466	206.48	127.26	2.72	6.05
4.332	255.15	122.82	3.71	9.70
5.198	299.39	122.21	4.75	11.60
6.931	352.44	121.89	4.59	12.27
8.664	375.354	120.92	4.61	12.29
10.397	387.29	119.96	4.63	12.28

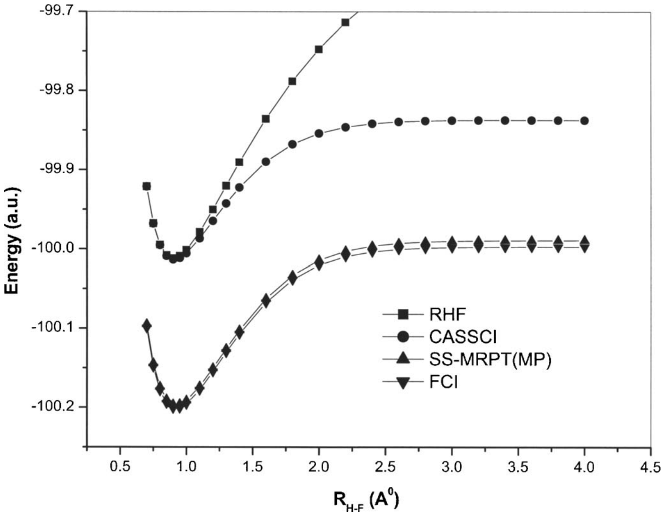

FIG. 5. PEC of the ground state of the HF molecule using 6-31G** basis and RHF orbitals.

In this part we have analyzed the performance of the SS-MRPT(MP) method with respect to the FCI along with MP2, CASPT2, CCSD, CCSD(T), and CASCI values for bond breaking reactions in the HF molecule. The ground state PECs using CASSCF and RHF orbitals for the HF system in a 6-31G** basis are given in Figs. 4 and 5, respectively. From the figures, it is observed that all of the methods reproduce qualitatively the correct shape of the ground state PEC as that of the FCI one except the RHF scheme. In Fig. 6, we have plotted the deviation of SS-MRPT results using CASSCF orbitals from FCI along with CASPT2 and CASSCF results; the CASSCF curve is shifted by 120 mH towards FCI for clarity of comparison between these methods. In Fig. 7, we have also plotted the same in the case of RHF orbitals. Additionally, we have reported results of MP2, CCSD, and CCSD(T) in the same figure. To get a better feeling, we have also quoted the relative errors with respect to the FCI values in Table II. From Fig. 7 and Table II, we can say that the performance of CCSD/CCSD(T) is very poor at large distances and the MP2 energies diverge with increasing bond length as expected. This poor performance is due to the inapplicability of SR-based theory in cases of strong near degeneracies, which occur at large bond distances. It is important to mention the fact that the performance of CCSD is better than the CCSD(T) method. Sherill and co-workers[34,35] showed that the unrestricted RHF-based results of SR methods are much better and match FCI very closely around equilibrium and near dissociation. For CASCI the minimum and maximum deviations are approximately 160 and 190 mH, whereas the corresponding values for SS-MRPT(MP) are 4.50 and 8.3 mH, while those for deviations for CCSD are 2.54 and 22.80 mH, respectively. The NPE of CASCI is approximately 18.6 kcal/mol and of the SS-MRPT is 2.5 kcal/mol with RHF orbitals. The CASSCF method shows an NPE of 18 kcal/mol. The NPE of SS-MRPT(MP) using CASSCF orbital goes down to 2.8 kcal/mol, whereas the corresponding value for CASPT2 is 2.8 kcal/mol. From the work of Abrams and Sheriil,[34] in the case of HF system, it is observed that the maximum and minimum errors with respect to the FCI for the SOCI method (a variant of MR-CISD approach) is 9.20 and 4.08 mH, respectively. The NPE

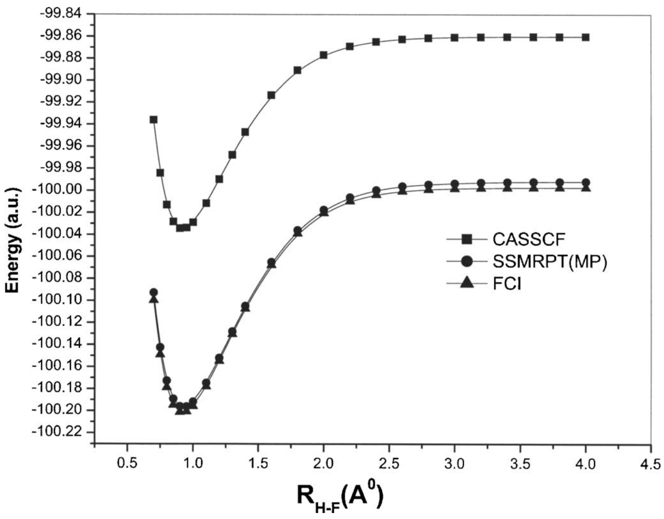

FIG. 4. PEC of the ground state of the HF molecule using 6-31G** basis and CASSCF orbitals.

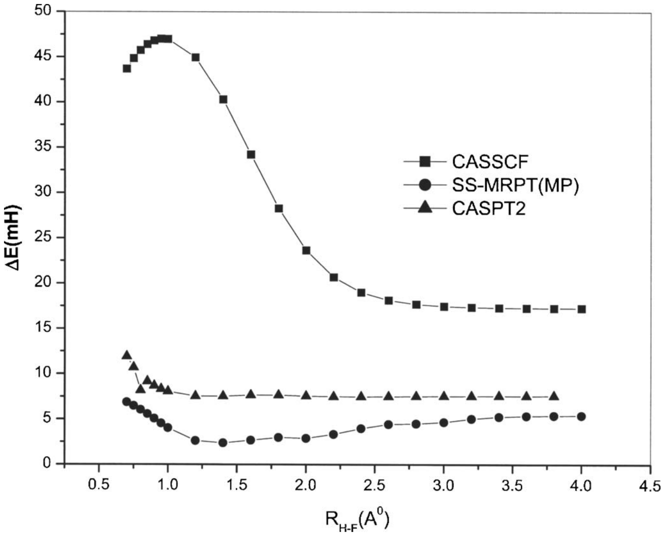

FIG. 6. Deviation of energies of the ground state of the HF molecule from the FCI values using 6-31G** basis and CASSCF orbitals [ΔE corresponding to CASSCF is shifted by 120 mH towards FCI].

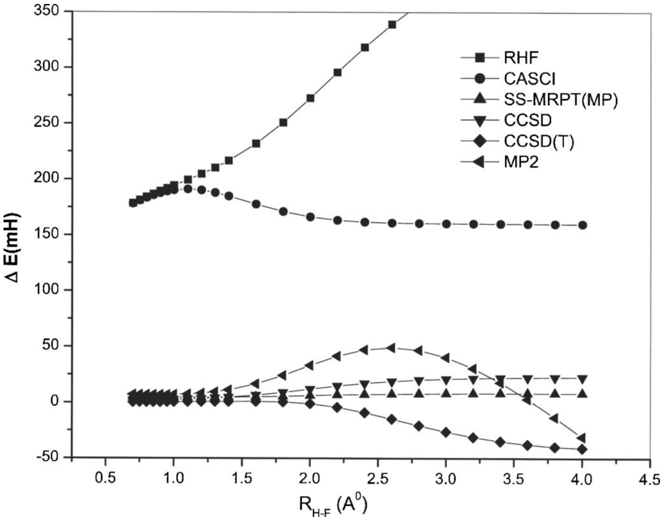

FIG. 7. Deviation of energies of the ground state of the HF molecule from the FCI values using 6-31G** basis and RHF orbitals.

of SOCI method are 3.20 kcal/mol, which is higher than the corresponding values of CASPT2 and SS-MRPT(MP) methods. From Table II it is evident that the errors obtained for CASPT2 along the PEC with respect to FCI is opposite to that of SS-MRPT(MP). It has been observed by Abrams and Sheriil[34] that the error versus FCI for CISD[TQ] (second order MR-CISD approach) over the PEC is the opposite of CASPT2. At this point, we want to mention that the MS used in CASPT2 and SOCI calculations is (8e-/3011), i.e., eight active electrons and five active orbitals[34] whereas our MS is constructed by two active electrons and two active orbitals (2e-/2000) [where the notation indicates, number of active electrons/number of active orbitals per irreducible representation of the largest Abelian subgroup)]. Thus, the dimension of MS used in CASPT2 and SOCI calculations is larger than ours. From Table II, it is evident that the NPE for both the methods, SS-MRPT(MP) and CASPT2, is identical although the MS used in CASPT2 is larger than that of SS-MRPT(MP).

Our calculations show that the errors of results generated via SS-MRPT(MP) approach with respect to the FCI values are small over a wide range of nuclear geometries for the very challenging HF system using a small active space. As we have already mentioned, the FCI values are not available for the cc-pVTZ basis, hence, it is quite constructive to compute the spectroscopic constants instead of presenting PEC and comparing them with the experimental values.[28] In Table III, we present the calculations of spectroscopic constants of the HF molecule using cc-pVTZ basis along with the experimental values. From the table (Table III), it is clear that the quality of the spectroscopic constants computed via the SS-MRPT(MP) method is encouraging with respect to the experimental results. Thus, we may conclude that the SS-MRPT(MP) method based on CASSCF reference function provides a qualitatively correct description of the ground state PEC of the HF molecule.

B. H_2O

Our next example is the computation of the ground state PEC for the totally symmetric stretching mode of the H_2O molecule because of its MR character and benchmark FCI

TABLE II. Deviation ($-\Delta E$ in mH) of ground state energies of HF molecule from FCI values using RHF orbitals (except CASPT2) and 6-31G** basis. [Basis: 6-31G** and the CCSD, CCSD(T), MP2, CASPT2, and FCI results have been taken from Refs. 34 and 35. CAS: ($2e^-$/2000) for SS-MRPT(MP) and ($8e^-$/3011) for CASPT2.]

R (angs)	RHF	CASCI	SSMRPT	CASPT2	CCSD	CCSD(T)	MP2
0.700	178.51	178.330	4.831	11.912	2.177	0.284	7.192
0.750	181.376	181.039	4.844	10.698	2.254	0.316	7.112
0.800	184.128	183.522	4.854	9.819	2.339	0.351	7.040
0.850	186.782	185.737	4.867	9.168	2.435	0.388	6.984
0.900	189.361	187.637	4.883	8.688	2.541	0.426	6.957
0.950	191.887	189.172	4.915	8.328	2.659	0.466	6.973
1.000	194.386	190.266	4.561	8.056	2.794	0.507	7.046
1.200	204.653	190.191	4.465	7.540	3.536	0.680	8.169
1.400	216.722	184.860	4.657	7.543	4.719	0.853	11.173
1.600	232.020	177.753	5.068	7.666	6.524	0.901	16.561
1.800	250.967	171.190	5.578	7.659	9.022	0.452	24.250
2.000	272.872	166.371	6.208	7.561	11.957	−1.117	33.203
2.200	296.068	163.460	6.869	7.494	14.821	−4.311	41.523
2.400	318.633	161.940	7.290	7.484	17.210	−9.067	47.267
2.600	339.220	161.195	7.575	7.501	19.005	−14.790	49.193
2.800	357.234	160.815	7.832	7.521	20.276	−20.728	46.877
3.000	372.579	160.603	8.004	7.537	21.153	−26.270	40.506
3.200	385.411	160.469	8.107	7.551	21.753	−31.035	30.621
3.400	396.011	160.368	8.176	7.565	22.164	−34.845	17.907
3.600	404.703	160.268	8.222	7.556	22.444	−37.679	3.045
3.800	411.813	160.155	8.248	7.576	22.634	−39.627	−13.353
4.000	417.646	160.026	8.258	7.579	22.761	−40.843	−30.787

TABLE III. Spectroscopic constants of the ground state of various molecules. Experiment: Ref. 28.

System	Method	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	D_e (eV)
HF	SS-MRPT (MP)	0.9220	3915.07	84.60	20.568	6.01
cc-pVTZ basis	Experiment	0.9171	4138.52	90.07	20.939	$\leqslant$6.40
C_2 ($X\,^1\Sigma_g^+$)	SS-MRPT(MP)	1.2586	1833.66	13.46	1.7608	5.88
6-31G* basis	FCI	1.2530	1853.85	13.13	1.7766	5.86
	Experiment	1.2422	1855.63	13.3	1.8205	6.33
N_2	SS-MRPT	1.0954	2401.26	18.82	1.9927	8.887
cc-pVTZ basis	8R-RMRCCSD	1.1011	2364.40	13.91	1.9856	
	Experiment	1.0977	2358.54	14.31	1.9982	9.905

results being available for comparison. This is a very often used model to test the performance of both SR and MR methods.[37,38] Simultaneous stretching of both OH distances has been calculated at the FCI level by Li *et al.*[37] using a 6-31G basis. In our calculations for H_2O molecule we have employed the same basis and scheme as used by Li *et al.*[37] Although the basis set is small (and hence FCI are available), we can use it to make several interesting observations to establish the applicability of the SS-MRPT(MP) method. In our calculation we have considered (6×6) CAS: Six electrons are distributed in $1b_1, 3a_1, 1b_2, 4a_1, 2b_2, 2b_1$. We have calculated the ground state energies via SS-MRPT(MP) method at three different points along the symmetric dissociation PEC since the FCI values are available at three geometries studied. The results are presented in Table IV. As seen from the table, the error with respect to the FCI values increases with increase in the OH-bond stretching in the case of CCSD and CCSD(T), whereas in the case of SS-MRPT(MP), the deviation is minimum at $1.5R_e$ and maximum at R_e (R_e stands for equilibrium distance). The deviation changes sign in the case of CCSD(T) method. The NPE for CCSD is 5.4 kcal/mol, whereas those for CASSCF and SS-MRPT(MP) method are 2.0 and 0.8 kcal/mol, respectively. On analyzing the NPE, we come to the conclusion that the SS-MRPT(MP) method shows promise in its numerical performance.

C. H_2S

For another chemically interesting example, we next look at the bond breaking of hydrogen sulfide, H_2S. In recent times, many workers[39–42] have done extensive studies on the computation of PEC of H_2S molecule due to asymmetric stretching (the HSH bond angle fixed at the ground state equilibrium value,[42] the energy is computed along asymmetric stretches). There exist different extents of quasidegeneracy in the internuclear separation as the bond is stretched asymmetrically. We have computed the PEC of the ground state of the system via asymmetric stretching (single bond breaking).

The photoexcitation-dissociation process of hydrogen sulfide, H_2S, has been widely studied from both theoretical and experimental points of view.[39–42] It is pertinent to mention the fact that the ground state of the system possesses a pronounced MR character even at equilibrium position. In our calculation, we focus on the computation of the PEC and the corresponding dissociation energy of the ground state using the experimental equilibrium geometry.[42] The computation of the ground state PEC is performed using cc-pVDZ and cc-pVTZ basis.[36] Hydrogen sulfide belongs to the point group C_{2v} at its equilibrium position, which is maintained for symmetric stretch and angle bending motions. However, this symmetry is destroyed in the case of asymmetric stretch motions (the two SH bond lengths are unequal) and then the molecule belongs to the point group C_s. In our calculations, six active electrons are distributed in five active orbitals (6×5) in all possible ways to construct the MS or reference space. In Fig. 8, we have plotted the PEC of H_2S using the above mentioned basis sets. From the figure it is clear that the PEC generated via SS-MRPT(MP) is very smooth and the effect of the size of the basis set is strong. Since FCI results are not available to check the quality of the computed PEC, we have calculated the dissociation energy and compared it primarily to the experimental value. Our calculated value is 82.5 kcal/mol using cc-pVTZ basis, whereas the corresponding experimental value is 89.9 kcal/mol.[40] The use of larger active space may improve the value. Our good results using SS-MRPT(MP) method bolster the point that the method is promising to compute the PEC. Using the same MS as ours, Freed *et al.*[40] obtained the dissociation energy value as 81.3 kcal/mol via their third order H_v method, which is computationally more expensive than the SS-MRPT(MP) method.

TABLE IV. Deviation ($-\Delta E$ in mH) of ground state energies (with respect to FCI) for the totally symmetric stretching modes of H_2O using 6-31G basis set. CCSD, CCSD(T), and FCI values have been taken from Ref. 17.

R (Å)		SS-MRPT	CCSD	CCSD(T)	FCI
R_e	48.577	7.425	1.464	0.512	−76.120 097
$1.5R_e$	51.735	6.103	5.410	1.066	−75.991 930
$2R_e$	51.653	6.710	10.138	−5.586	−75.880 468

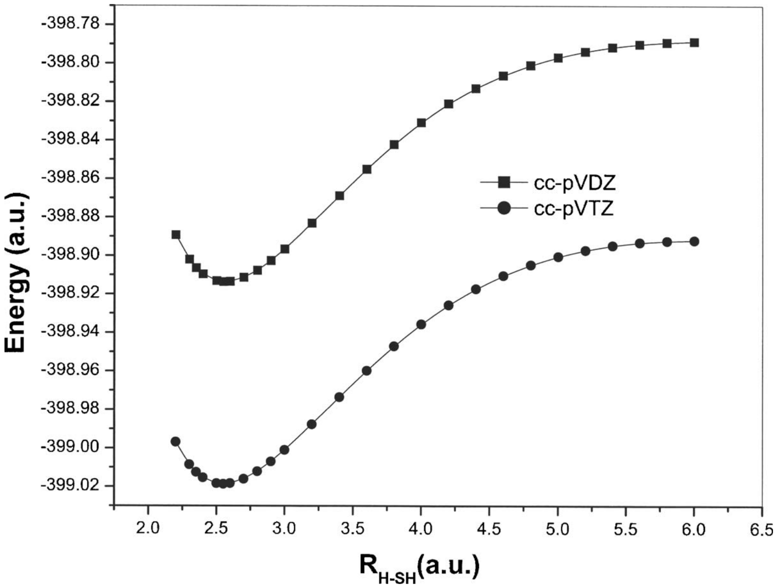

FIG. 8. PEC of the ground state of the H_2S molecule using cc-pVDZ and cc-pVTZ basis sets.

D. C_2

In our next example, we consider the computation of PECs of some low-lying states including the ground state ($X\ ^1\Sigma_g^+$, $B\ ^1\Delta_g$, and $B'\ ^1\Sigma_g^+$) of the C_2 molecule (containing double bond). The study of these electronic states helps to explain various interstellar chemical phenomena and combustion reactions involving the C_2 molecule. Thus, this system has been studied intensely by several theoretical chemists.[43–47] One of the interesting features of this system is that the low-lying electronic states are energetically very close even at equilibrium geometry. The quasidegeneracies or near degeneracies between the various low-lying states change very rapidly due to elongation/contraction of the bond with respect to the equilibrium value. It is now well documented[43–45,47] that the performances of SR-based methods and their different variants to compute the PEC of the ground as well as low-lying singlet excited states go down in the case of C_2 molecule due to the presence of various degrees of quasidegeneracies over the entire potential surfaces. Hence, to compute the PECs, a true MR-based method is necessary for this system. These near degeneracies in C_2 and failures[43–45,47] of various full-blown single-reference coupled-cluster methods make this system an excellent interesting example to establish the utility of any MR-based method.[43–47] As we have already mentioned, the SR-based methods have an inherent limitation for treating quasidegeneracy that they are obliged to treat the nondynamical correlation attendant upon the quasidegeneracy via higher-body cluster operators. Thus, the PEC calculations of the above mentioned states of C_2 are good examples to test the performance and accuracy of the SS-MRPT(MP) scheme, which is designed to handle electronic quasidegeneracies and bond breaking phenomena. In this article, we compare the above mentioned three PECs of C_2 generated by the SS-MRPT(MP) theory with those from the FCI and other correlated treatments.

In a recent paper, Abrams and Sherill[44] presented full configuration interaction potential energy curves for the various low-lying states of C_2 using 6-31G* basis [polarized double-zeta basis] and demonstrated that the ground state spectroscopic constants computed using this basis appear quite promising compared to the DZP type basis sets. For comparison with FCI values, we have also used the same basis[45] in our SS-MRPT(MP) calculation, which allows us to carefully examine the reliability and quality of results generated via SS-MRPT(MP) method for PECs of the ground as well as the above stated low-lying singlet excited states. In our calculations, six active electrons are distributed in $2\sigma_u$, $1\pi_u$, $3\sigma_g$, $1\pi_g$, and $3\sigma_u$ orbitals. The lowest two core orbitals are kept frozen and all six Cartesian *d*-type polarization functions are used in our calculations.

One does not encounter any problem while constructing the reference function using CASSCF for the ground state, $X\ ^1\Sigma_g^+$ around equilibrium. However, it is quite difficult to construct the reference function for the $X\ ^1\Sigma_g^+$ and other singlet excited states $B'\ ^1\Sigma_g^+$ and $B\ ^1\Delta_g$ as we elongate the bond. The $B\ ^1\Delta_g$ state remains energetically above the $X\ ^1\Sigma_g^+$ and $B'\ ^1\Sigma_g^+$ states around $R=1.0$ Å, then it crosses $B'\ ^1\Sigma_g^+$ and lies in between $X\ ^1\Sigma_g^+$ and $B'\ ^1\Sigma_g^+$ states up to $R=1.7$ Å and becomes energetically lowest after this crossing point and asymptotically approaches the state $X\ ^1\Sigma_g^+$ at larger distances. Thus, we have employed state-average (SA) CASSCF method to construct the reference function and hence we compute all the three states through the construction of the model functions and the zeroth-order Hamiltonian H_0 using these orbitals generated via state-averaged scheme using equal weights. In all cases, we started with the core Hamiltonian and generated the guess orbitals in the example of the C_2 molecule as the orbitals will be least biased to any of the above mentioned three states. The SA-CASSCF scheme is not free from objection, still a democratic averaging makes the generation of orbital technically advantageous without losing much accuracy. Although, there is no mixing between $B\ ^1\Delta_g$ and $^1\Sigma_g^+$ states in the SA-CASSCF calculation, very recently Sherill and Piecuch[45] reported that it is technically easier to perform the computations using

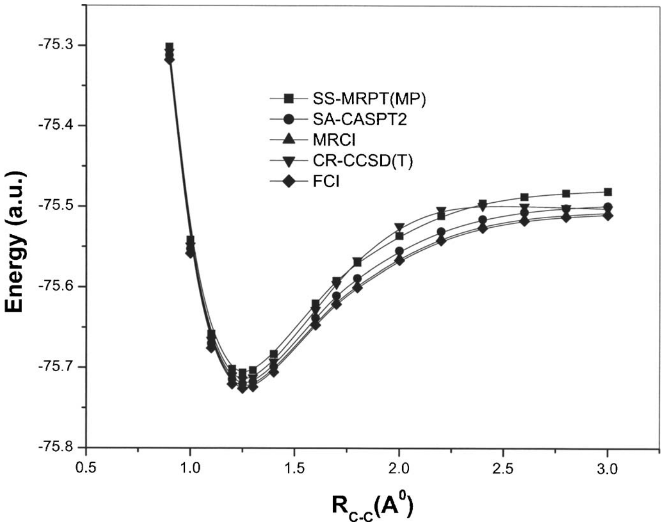

FIG. 9. PEC of the ground state ($X\,^1\Sigma_g^+$) of the C_2 molecule.

CASSCF orbitals averaged over all three states: $X\,^1\Sigma_g^+$, $B\,^1\Delta_g$, and $B'\,^1\Sigma_g^+$ without losing much accuracy. For a detail discussion, see Ref. 45.

In Figs. 9–11, we have presented the state energies computed using SS-MRPT(MP) method along with the corresponding SA-CASPT2, MRCI [this is a kind of complete limit for multireference configuration interaction with singles and doubles (MR-CISD)], CR-CCSD(T), and FCI results of Sherill and Piecuch[45] for $X\,^1\Sigma_g^+$, $B\,^1\Delta_g$, and $B'\,^1\Sigma_g^+$ states, respectively. Comparing with FCI PECs, from the figures it is observed that the shape of FCI PECs are reproduced by SS-MRPT(MP) methods and the curves remain reasonably parallel with the FCI ones. The crossing between $X\,^1\Sigma_g^+$ and $B\,^1\Delta_g$ occurs at a distance $R \sim 1.7$ Å in good agreement with FCI results. The closest approach of two $X\,^1\Sigma_g^+$ and $B'\,^1\Sigma_g^+$ states occur at $R=1.7$ Å and the energy separation between them is ~ 10 kcal/mol In Fig. 12, the energy differences are plotted with respect to the FCI values. From the small fluctuations of computed energies with respect to the FCI values seen in the figure, it is clear that for a wide range of geometries the SS-MRPT(MP) method performs very well and can be used as a reasonably good approach to calculate PECs of C_2 molecule. From Fig. 12 we observe that the deviation from FCI is smaller for the ground state than for the other two excited states. The corresponding deviations for the $B\,^1\Sigma_g^+$ state is slightly higher than the $B\,^1\Delta_g$ state. For $X\,^1\Sigma_g^+$ state, the NPE is 8.8 kcal/mol. For the $B\,^1\Delta_g$ state, the NPE goes down to 5.0 kcal/mol and on the other hand, NPE for the $B\,^1\Sigma_g^+$ state is 8.2 kcal/mol. The present calculations clearly demonstrate that the ground and excited states are well represented by the SS-MRPT(MP) method with a SA-CASSCF reference function. From our numerical experiment using SS-MRPT(MP) method, it is observed that the state energies of $B\,^1\Sigma_g^+$ is highly sensitive with respect to the values of MS coefficients than the other two states. At this point, it is pertinent to mention the fact that the model space in the case of SA-CASPT2 and MRCI calculations,[45] in contrast to our scheme, is constructed by distributing eight active electrons in the $2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$, $1\pi_g$, and $3\sigma_u$

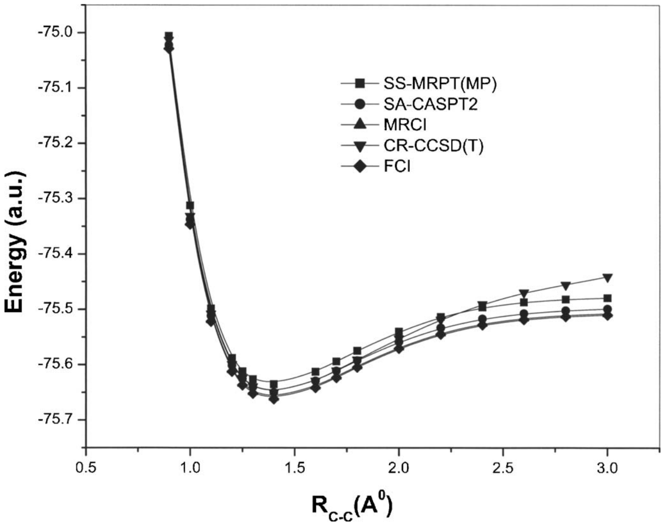

FIG. 10. PEC of the lowest delta state ($B\,^1\Delta_g$) of the C_2 molecule.

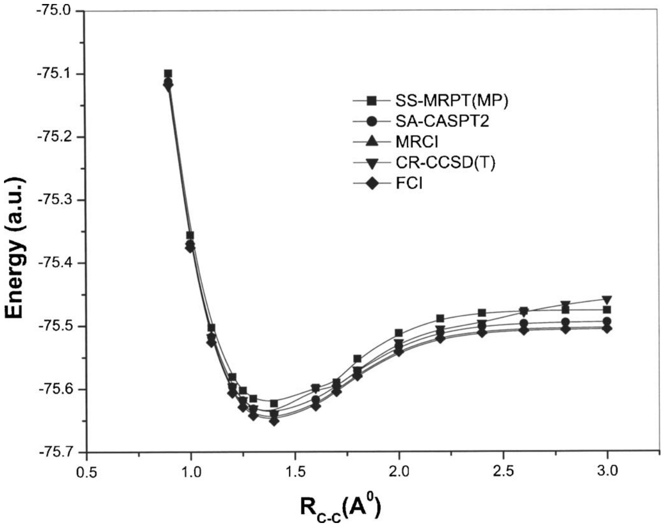

FIG. 11. PEC of the lowest singlet excited sigma state ($B'\,^1\Sigma_g^+$) of the C_2 molecule.

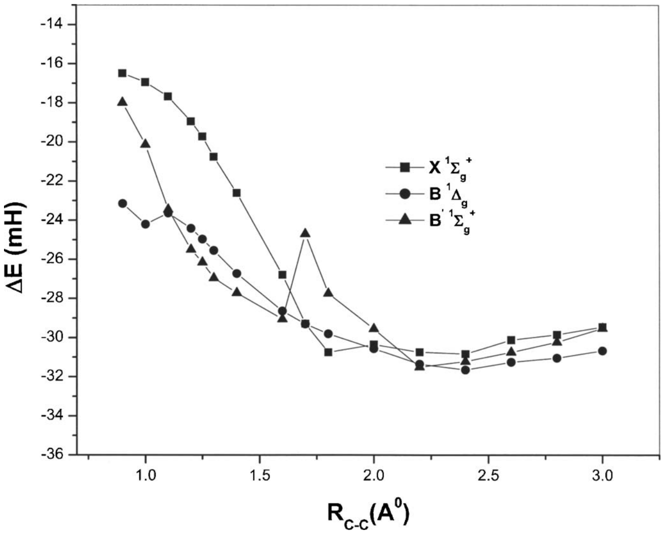

FIG. 12. Deviation of energies of the $X\,^1\Sigma_g^+$, $B\,^1\Delta_g$, and $B'\,^1\Sigma_g^+$ states of the C_2 molecule from the corresponding FCI values.

orbitals. The doubly occupied $2\sigma_g$ orbital generally remains inactive to construct the MS in our calculations. The number of model space CSF in our calculations is 80 whereas in the latter case this is 264. Here, we want to state the fact that Sherrill and Piecuch[45] observed that the NPE of SA-CASPT2 method for $X\,^1\Sigma_g^+$, $B\,^1\Delta_g$, and $B'\,^1\Sigma_g^+$ are 8.1, 7.3, and 6.3 kcal/mol respectively, with the same MS as is used in our calculations. The NPE is comparable to the SA-CASPT2 value with the identical size of MS.

Since the computed ground state PEC with the SS-MRPT(MP) method is very smooth and close to the FCI values, it prompted us to calculate the various spectroscopic constants (for the ground state) using the PEC. Several authors have applied various *ab initio* methods to compute the ground state spectroscopic constants of this molecule.[44,48] In Table III we have presented the various spectroscopic constants generated via PEC for the SS-MRPT(MP) method along with FCI values for the ground state. From the table we may conclude that the performance of the SS-MRPT(MP) to calculate the ground state spectroscopic constants is quite satisfactory. From the numerical applications of the SS-MRPT(MP) method to the C_2 system, we observed that the performance of the method is promising.

E. N_2

We present a study of the bond breaking process of the N_2 molecule. In any examination of bond breaking, one must consider the case of N_2. A correct and balanced treatment of the interplay of dynamical and nondynamical correlation effects is crucial for N_2 molecule containing a triple bond, since the pronounced multireference character of N_2 molecule even around the equilibrium geometry is well known.[49–53] For this reason, we apply the SS-MRPT(MP) method to compute the PEC of the ground state of the N_2 molecule and the quality of the computed PEC is assessed by computing the ground state spectroscopic constants that can be directly compared to experimental values. Laidig and co-workers[49] first pointed out that the traditional SR-based methods are not able to produce the ground state PEC of the N_2 molecule.

We employ the cc-pVTZ basis set[36] to generate the ground $^1\Sigma_g^+$ state potential energy curve of N_2. The same basis set was employed by Li and Paldus[51] in their 8R-RMRCCSD calculations. In this basis, the FCI results are not available, hence we compare the performance of the SS-MRPT(MP) method with that of 8R-RMRCCSD. The active space used in our calculations comprises three bonding molecular orbitals (σ, π_x, π_y) and three antibonding molecular orbitals $(\sigma^*, \pi_x^*, \pi_y^*)$. This is the minimal set of active orbitals and six active electrons that is required to study the PEC of triply bonded systems like N_2.[51] With this choice of active orbital and active electrons 32 CSF's are generated, which constitute the reference function.

In Fig. 13, we have presented the ground state PEC generated by SS-MRPT(MP) method for N_2 molecule using cc-pVTZ basis. For the sake of comparison of the potentiality of the SS-MRPT(MP) approach to other available sophisticated method(s), we have also included the results of 8R-RMRCCSD in the figure. The energies obtained from 8R-RMRCCSD and SSMRPT(MP) are very close. We observe that in the bond-breaking geometries, the PEC becomes almost parallel to the R axis and remains parallel to the 8R-RMRCCSD curve, which clearly demonstrates that in spite of a large change of the model coefficients with R in a complex way through the PEC, the extent of dynamical correlation included via SSMRPT(MP) makes the PEC not less parallel at least than 8R-RMRCCSD PEC. In Fig. 14, we have plotted the energy differences between SS-MRPT(MP) and 8R-RMRCCSD methods. From the figures it is quite clear that the performance of SS-MRPT(MP) method is very close in proximity to the full-blown 8R-RMRCCSD results. However, it is important to mention the fact that the 8R-RMRCCSD is computationally much more demanding than SS-MRPT(MP) method.

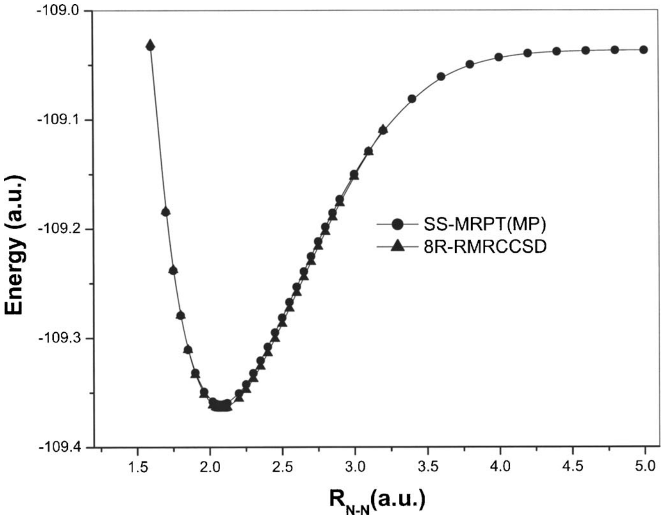

FIG. 13. PEC of the ground state of the N_2 molecule using cc-pVTZ basis.

To check the extent of NPE, we take another basis where the FCI energy values are known. For this reason, we have

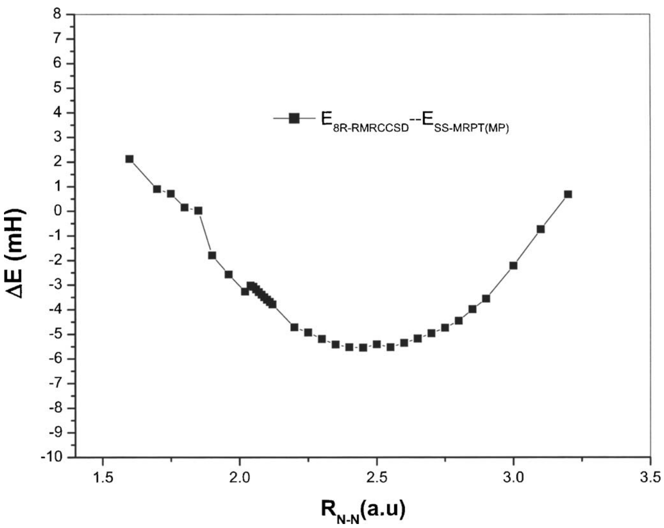

FIG. 14. Deviation of the ground state energies of the N_2 molecule from the 8R-RMRCCSD values using cc-pVTZ basis.

TABLE V. Deviation ($-\Delta E$ in mH) of ground state energies of N_2 from FCI values using DZP basis. MRCI, CASPT2, and FCI results have been taken from Ref. 53.

R (a.u.)	CASSCF[a]	SSMRPT (MP)[a]	SS-MRPT[b]	MRCI	CASPT2
2.05	55.3	5.1	6.4	1.0	4.88
2.10	55.4	5.1	6.34	0.72	4.91
2.15	50.6	5.6	6.6	0.73	4.94
2.50	56.1	5.9	7.13	0.76	4.87
3.00	56.2	6.9	7.14	0.8	3.65
4.00	48.0	8.2	7.89	0.65	0.83
50.00	40.7	7.7	7.77	0.5	0.26

[a] Cartesian *d* function.
[b] Spherical *d* function.

used the DZP basis[53] so that our computed results can be compared directly to their FCI results. The MS chosen is the same as used with ccpvTZ calculation. For this basis set, we have performed two sets of calculations: (i) Basis with a cartesian *d* function and (ii) basis with a spherical *d* function. In Table V we have tabulated the deviation of results of SS-MRPT(MP), MRCI, and CASPT2 from the corresponding FCI values. From the table (Table V), we see that the minimum and maximum errors of the SS-MRPT(MP) method are 3.0 kcal/mol (near equilibrium) and 5.0 kcal/mol (as we approach the bond breaking region), respectively, for cartesian *d* function. Therefore, NPE is only 2 kcal/mol, which is rather small. In the case of spherical *d* functions, the NPE is within 1 kcal/mol. The NPE for MRCI is 0.3 kcal/mol. Although the deviation from FCI is small in the case of CASPT2 in comparison to the SS-MRPT(MP) method, the NPE is 2.9 kcal/mol.

Due to the smooth and satisfactory nature of the computed PEC via SS-MRPT(MP) approach, spectroscopic constants are also computed and presented in Table III as well as compared to the corresponding 8R-RMRCCSD and the experimental results. From the table, we may conclude that the spectroscopic constants generated via SS-MRPT(MP) method are very close to the corresponding values of the 8R-RMRCCSD method and experimental values and we may conclude that the quality of the PEC computed via SS-MRPT(MP) approach is quite good.

From the above mentioned numerical applications on chemically interesting and challenging systems such as HF, H_2O, H_2S, C_2, and N_2, the energies computed via SS-MRPT(MP) approach appear to be reliable for the state(s) and geometries considered. Hence, from these test applications we may expect the SS-MRPT(MP) method to be a promising theoretical tool for quantitatively describing the ground state PEC of small and medium-sized molecules. The deviation of results of SS-MRPT(MP) approach from FCI for various systems is quite modest over large nuclear geometries. The small NPEs for these systems establish the fact that the quality of SS-MRPT(MP) PEC is reliable [zero NPE means a complete match to the shape of the FCI curve]. Hence, the SS-MRPT(MP) method is very promising to incorporate the dynamical and nondynamical effects in a balanced manner. The spectroscopic constants calculated using the PEC generated via SS-MRPT(MP) are quite encouraging with respect to the FCI/experimental values. Thus, the present work bolsters our belief that SS-MRPT(MP) is capable of producing reliable and uniformly accurate energies even for such challenging systems as C_2 and N_2, and therefore, can be used to model the bond breaking/making reactions.

III. SUMMARIZING REMARKS

This paper embodies the application of an explicitly spin-free complete active space (CAS) based state-specific multireference perturbation theory, SS-MRPT(MP). The theory is size extensive as well as gives size-consistent energy when localized orbitals are used and is designed to handle the potential energy curves (PECs) involving bond breaking in an intruder free manner. We have applied this method to study the PECs for very difficult molecules such as HF, H_2O, H_2S, N_2, and C_2 thereby demonstrating the fact that the SS-MRPT(MP) is very effective to compute the PEC of electronic states possessing a pronounced MR character. To establish the quality of results generated using SS-MRPT(MP) method, comparisons with FCI and other highly sophisticated electronic structure theories have also been provided wherever available. Two "diagnostics parameters" such as energy difference with respect to the FCI (ΔE) and NPE are used to quantify the performance of the method. The NPE is satisfactory in all the example studied here except the HF system using DZ basis with CASSCF orbitals. The combined ΔE and NPE results indicate that the SS-MRPT(MP) method is quite effective to compute the PEC of different molecular systems containing degeneracies to different extents over the whole range of PECs. The ground state spectroscopic constants are also extracted from the corresponding PECs, and are compared with the corresponding experimental or FCI results. We have shown the reliability and accuracy of the equilibrium bond lengths, dissociation energies, and harmonic vibrational frequencies of the systems studied here computed using the PEC generated via SS-MRPT(MP) method. Numerical applications in this article indicate that the SS-MRPT(MP) method is robust and does not go down for systems with varying degrees of nondynamical correlation.

At the end, we should say more test cases are needed to make a firm judgement on the prospects of the method. We hope that the SS-MRPT(MP) will open an avenue for accurate treatment of dynamical and nondynamical correlation effects for small to large molecular systems having states with pronounced near degeneracies in the near future. Thus, further developments and wide chemical applications of this method are quite desirable. In the near future, we wish to explore the performance of the SS-MRPT method using various partitioning schemes and different types of orbitals.

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