

## Study of the Ground State Dissociation of Diatomic Molecular Systems Using State-Specific Multireference Perturbation Theory: A Brillouin–Wigner Scheme

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**Abstract:** The size-extensive second-order state-specific (or single root) multireference (MR) perturbation theory (SS-MRPT) in the Brillouin–Wigner (BW) form using Møller–Plesset perturbative evaluations of orders up to 2 [termed as SS-MRMPPT(BW)] presents a viable, as well as promising, approach to include both nondynamic and dynamic correlations in the study of the bond-stretching (in multireference/quasidegenerate situations) of molecular species with a manageable cost/accuracy ratio. It combines numerical stability in the presence of an intruder state problem with strict size consistency (when localized orbitals are used). In this paper, the SS-MRMPPT(BW) method has been shown to properly break the bonds (in the ground state) of several diatomic molecules (such as  $F_2$ ,  $Cl_2$  and  $Br_2$ , and BH) that have posed a severe challenge to any many-body theoretical approach due to the presence of quasidegeneracy of varying degrees in the ground state. A comparison of the resulting potentials with the various theoretical results reveals that the method represents a valuable tool that is capable of properly accounting even for very strong quasidegeneracies, while also performing well in nondegenerate situations. In this work, we have also calculated spectroscopic constants (such as equilibrium bond lengths, vibrational frequencies, and dissociation energies) of the ground state of these molecular systems. The SS-MRMPPT spectroscopic constants are compared with the most accurate available *ab initio* calculations and other theoretical estimates of previous works to calibrate the efficacy of the method. For the sake of completeness, we also compare the computed spectroscopic constants with the experimental observations. The accuracy of computed spectroscopic parameters appears to be rather consistent over a multitude of systems for various basis sets. The SS-MRMPPT enables quantitatively accurate and computationally affordable analysis of potential energy surfaces and spectroscopic constants of various multireference systems in the ground state. It is particularly visible for spectroscopic parameters and nonparallelism error (NPE) calculations. The calculations further reveal that the SS-MRMPPT(BW) method compared to its Rayleigh–Schrödinger counterpart [SS-MRMPPT(RS)] provides a more accurate and consistent solution for the whole dissociation path and spectroscopic constants.

### I. Introduction

Accurate quantum mechanical calculations of molecular electronic energy variations on potential energy surfaces (PESs) are essential in many contexts [such as equilibrium geometries, transition states, force constants, etc.]. The study of molecular electronic energies along bond breaking–making paths also provides key information needed in reaction kinetics and various spectroscopic processes. Thus, it is

worthwhile to try and calculate the PES at a level of accuracy that, hopefully, allows a comparison with experimental data (spectroscopic quantities).

The computation of a smooth PES requires a balanced treatment of dynamic and static correlation effects, and thus a genuine multireference (MR) formalism is warranted. Among the possible types of MR technologies available to compute the PES, we consider here MR-based perturbation theory (MRPT),<sup>1–17</sup> which is, in general, computationally cost-effective in describing dynamical correlation in the presence of electronic degeneracy. The conventional effective

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Hamiltonian MR approaches based on complete model space (CMS) suffer convergence difficulties once intruder states intervene while studying PES, which spoil the quality of the spectroscopic constants. To overcome this bottleneck, a state-specific multireference (SSMR) approach—targeting only the state of interest unencumbered by intruders—is an inherently useful strategy. Over the past few decades, many promising methods have emerged [for an overview, see ref 18]. Among the various intruder-free MRPT methods, multireference Møller–Plesset perturbation theory (MRMPPT),<sup>3</sup> complete active space perturbation theory (CASPT),<sup>5,6</sup> and second-order  $n$ -electron valence perturbation (NEVPT2) theory<sup>11</sup> approaches have been established as very efficient methods for computing the PES of any state (regardless of charge, spin, or symmetry) with satisfactory and consistent accuracy [see also ref 19]. The convergence of the MRPT with MP partitioning is not free from objections.<sup>20–23</sup> It must be admitted that CASPT2 can handle large active space leading to a satisfactory accuracy. However, it has two serious limitations which may invite inconsistent behavior of the method. One is a lack of strict size extensivity and the other, more importantly, is that it is occasionally subjected to the intruder state problem, causing divergences in the perturbation series.<sup>24,25</sup> MRMPPT<sup>3</sup> and MCQDPT<sup>4</sup> are also not rigorously size-extensive.<sup>24,25</sup> The main features of recently developed NEVPT2<sup>11</sup> theory are size consistency and the absence of intruder states. In our view, a state specific (or single root) MR method that is size-extensive as well as size-consistent is essential and crucial to getting correct results of dissociation PESs and associated spectroscopic parameters [see ref 26 regarding this aspect].

We also mention other developments in the context of MRPT methods which are able to deal with the PES. There have been significant contributions by Wolinski and Pulay,<sup>27</sup> Murphy and Messmer,<sup>28</sup> Dyall,<sup>29</sup> and most recently by Robinson and McDouall.<sup>30</sup> In this context, we also mention the development of multiconfiguration perturbation theory by Surján and his group.<sup>31</sup> Surján and Rosta<sup>32</sup> have investigated the MRPT using the APSG (antisymmetrized product of strongly orthogonal geminal) reference state. To increase the computational effectiveness, a number of groups<sup>30,33–35</sup> have investigated the possibility of avoiding the CASSCF step, by using orbitals obtained from simpler methods to define the active spaces for use in multireference perturbative treatments. The earlier CIPSI (Configuration Interaction with Perturbation Selection Iteratively) method<sup>36</sup> may be viewed as a forerunner of many of the more recent MR perturbation theories. This method can be viewed as a second order perturbation correction to CI energies via diagrammatic techniques using multiconfigurational zeroth order wave functions.

In recent times, Mukherjee and co-workers<sup>14,15,18</sup> have introduced a rather elegant size-extensive and size-consistent MRPT approach to tackle the intruder state problem [referred to as state specific second-order MRPT, SS-MRPT]. In SS-MRPT formulation, they used the Jeziorski–Monkhorst (JM) ansatz<sup>37</sup> in a state specific fashion. The SS-MRPT utilizes a multipartitioning strategy.<sup>10,38</sup> The SS-MRPT is quite rich in its structure in the sense that it can be viewed as versions

of both a Rayleigh–Schrödinger (RS) and a Brillouin–Wigner (BW) perturbation theory, depending on the expansion strategy [we use the nomenclature SS-MRPT(RS) and SS-MRPT(BW), respectively]. The SS-MRPT method has *all the attractive features* of the parent SS-MRCC method.<sup>39</sup> The SS-MRPT method obeys satisfactorily the logical and practical requirements of a good MRPT approach such as the following: (i) it is rigorously size-extensive and size-consistent (when localized orbitals are used); (ii) it is generally applicable to a wide class of problems within one framework, i.e., not dependent on specific choices of configurations; (iii) it bypasses the *intruder* state problem; (iv) it is efficient and cost-effective; (v) the model can properly treat dissociation of fragmentation problems (reactions) in a spin-pure way for closed as well as open shells (spin symmetry is essential to the proper description of bond breaking); (vi) there is flexibility of using the coefficients of reference functions in either a relaxed or an unrelaxed mode under the effect of the perturbation; (vii) it is able to calculate energies of similar quality in a wide domain of geometries. As the SS-MRPT method is designed to facilitate the relaxation of the reference function, it thus deals with the mixed-states problem characterized by large changes in the relative contributions of the coefficients of reference functions in an exact (correlated final) wave function compared to the zero-order function. The SS-MRPT approach is able to model any region of the PES of a molecular system (with closed-/open-shell and singlets/nonsinglets model functions) even when the traditional effective Hamiltonian based MR methods fail due to intruders.<sup>14,15,18,40</sup> More recently, a number of researchers have adapted the SS-MRPT approach to a production-level implementation;<sup>41</sup> hitherto the derivation has been formulated in terms of spin–orbitals. One of the main objections of the spin–orbital based formulation exists in the incorrect treatment of spin eigenstates. As a word of caution, it is important to note that the SS-MRPT method is useful as long as the target state energy is well separated from the virtual functions. This is generally true for the ground and low-lying states.<sup>40</sup> Our application in this paper is based on the problem of describing PESs of molecular systems in their ground states.

The main difficulty in CAS-based MR calculations arises from the use of CAS in constructing many-electron wave functions due the exponential increase of the size of the model space when one increases the number of active orbitals. The main relevant criticism of the theories based on the wave operator of the Jeziorski–Monkhorst type is its prohibitively increasing number of amplitudes as a function of the size of the model space, since the cluster operator is defined with respect to each reference determinant. The computational scaling, however, is not favorable if the number of the reference determinants is large. Beyond that, for each cluster operation (specific for the target state), one must solve a set of coupled equations which scales with the CAS size. In contrast, the ansatz for internally contracted methods is more compact. Despite the computational benefit of the internal contraction, internally contracted state-specific multireference formalisms may suffer due to internal contraction of the wave function in the reference space. In the

case of computation of the interaction between close lying states, or of weak crossings, some of the spurious effects induced by the internal contraction<sup>42</sup> may affect the stability and accuracy of this type of method. It is worth mentioning that CASPT2<sup>5,6</sup> can be implemented in terms of either internally contracted configurations, configuration state functions, or some combination of the two, whereas MRMPPT<sup>3</sup> is formulated in terms of configuration state functions. In this context, we can also mention the work on the reduced model space method in MRPT of Staroverov and Davidson.<sup>43</sup>

In order to corroborate the SS-MRPT with some applications, we have chosen to start with the implementation of its various variants. Instead of following an RS expansion based MP-type philosophy in SS-MRPT [named SS-MRMPPT(RS)], one may also use the BW-based MP-type [termed SS-MRMPPT(BW)] spirit while retaining the main advantages of size extensivity and size consistency rigorously in an intruder free way. Our multipartitioning scheme for RS and BW follows the ideas advanced by Mahapatra et al.<sup>14</sup> and Ghosh et al.,<sup>15</sup> respectively. There have been several numerical studies illustrating the ability and power of the SS-MRMPPT(RS) method to describe single, double, and triple bond breaking on singlet and nonsinglet PESs,<sup>14,40</sup> but little is known about the performance of the SS-MRMPPT(BW) approach in calculations of bond breaking in molecular species.<sup>14,15</sup> The pre-eminent success of the SS-MRMPPT(RS) method in treating electron correlation for many types of systems prompted us to apply the SS-MRMPPT(BW) scheme. The main goal of the present investigation and of the analysis is to examine the performance of the SS-MRMPPT(BW) method in the difficult quasi-degenerate situation arising from the bond stretching and to compare our results with other approaches, particularly those belonging to the general category of the MRMP method (such as CASPT2, MRMPPT, BWPT, etc). It would be very constructive if we are able to incorporate a comparative study of the results of the SS-MRMPPT method with respect to the other nonperturbative methods in each case. In this work, we also inspect explicitly the convergence issue with respect to the correlation treatment and the basis set for the SS-MRMPPT(BW) method along with its RS version. However, the application of the SS-MRMPPT(RS) is computationally less demanding than SS-MRMPPT(BW) at the cost of accuracy.

In this paper, we investigate the ground state of the X<sub>2</sub> [X = F, Cl, and Br] and BH molecules as our benchmark systems, as they are the prototype systems for a variety of spectroscopic and reaction dynamics studies. The importance of the X<sub>2</sub> systems as laser media, as well as their unusual behavior, provides motivation for trying to understand them better. The molecular dihalogens exhibit interesting yet only partially understood molecular properties, one being the apparent scrambling of the order in bond dissociation energies. As one descends along group VIIA of the periodic table, there should be an expected decrease from fluorine to iodine; curiously, the chlorine molecule has the highest bond dissociation energy. The traditional explanation lies in positing the fact that the fluorine atom has a very small size, with high electron density over it, resulting in molecular

fluorine being a stretched molecule (with a more than expected bond distance, as is envisaged in fact) owing to the high lone-pair–lone-pair repulsion. The fluorine molecule shows different electronic behavior in relation to chlorine and bromine molecules. It is already known that F<sub>2</sub> is unbound at the Hartree–Fock (HF) level. In contrast to fluorine, chlorine and bromine molecules are bound at the HF level. The situation dramatically changes for the CASSCF (Complete Active Space–Self Consistent Field) wave function. However, despite the improvement, the calculated bonding energy is still disappointingly small, as CASSCF does not treat the dynamic correlation, which is important for a correct description. Relying on the generalized valence bond method, recently Barbosa and Barcelos<sup>44</sup> have put forth an additional understanding of this phenomenon. It is now well-known that to compute the PES within “chemical accuracy”, sextuple excitations with respect to single-determinant reference functions are needed even for the single-bond (F–F) breaking of the F<sub>2</sub> molecule.<sup>45</sup> This is the main reason for the problems faced by the SR-based methods.

Along the ground state dissociating reaction path of X<sub>2</sub> and BH, the starting reference function changes multiconfigurational and encounters the perennial “intruder state problem”, which prompted us to undertake the present study of X<sub>2</sub> and BH dissociation. It is to be remembered that, when the “intruder state” makes a contribution to the target state, removing it from the perturbation expansion in the region of the singularity invites in a noticeable error in the computed perturbative energy in the context of an effective Hamiltonian-based approach(es). We have observed that the SS-MRMPPT formalism does not break down when generating a ground state dissociation energy surface for X<sub>2</sub> and BH. In this work, we also focus on the calculation of the spectroscopic constants through the computation of nonrelativistic PES for the dissociation of the X<sub>2</sub> molecule into two X atoms in the ground electronic state (belongs to the <sup>1</sup>Σ<sub>g</sub><sup>+</sup> representation) via the SS-MRMPPT(BW) [and also SS-MRMPPT(RS)] approach using various basis sets. We consider the same for the ground state of the BH molecule also. At this point, we want to state that the most detailed experimental information regarding energies along the entire reaction paths is available in diatomic molecules by virtue of their spectroscopic constants, and thus they furnish exacting tests for methods attempting to describe PESs. Actually, theoretical computation of vibrational frequencies has become almost “a must” for experimental spectroscopists these days, as it helps to interpret and assign experimental infrared or Raman spectra, especially in difficult and questionable cases. The SS-MRMPPT spectroscopic constants (evaluated by fitting the energy surfaces or curves to cubic polynomials) are found to be in reasonable agreement with the corresponding experimental values. In the present work, we calculate the dissociation energies as the difference in energy at an asymptotically large distance and the fitted energy minimum.

Chlorine and bromine introduce a new level of complexity to our computational methods because they are so large. Chlorine and bromine have 17 and 35 electrons, respectively,



and taking into consideration every electron for these atoms costs a great deal computationally. Also, the core electrons have quite high energy so that there is the possibility of relativistic effects on the core electrons. In systems containing heavy atoms, such as chlorine or bromine, relativistic effects and spin-orbit coupling cannot be neglected (in some cases even in the first-order perturbative treatment) to get correct results. Since the ground state ( $^1\Sigma_g^+$ ) has zero angular and spin momentum, it is not subject to spin-orbit splitting; however, relativistic effects play an important role. These relativistic effects are not taken into consideration under standard levels of theory. In our calculations presented in this paper, the inner-shell electron correlation and relativistic effects have been disregarded. In our remaining discussion, we will mainly focus on the analysis of the basis set and a balanced treatment of dynamical as well as nondynamical correlation effects, the key to a successful description of molecular PESs involving bond making and breaking.

The SS-MRMPPT(BW) approach has been shown to work slightly better and be consistent in comparison to the SS-MRMPPT(RS). It is important to note that the convergence of the correlation energy with basis set size of the SS-MRMPPT(BW) is better than the RS counterpart, as it should be. A close observation of the numerical performance of the SS-MRMPPT methods exhibits that the overall performance of SS-MRMPPT(BW) is better and more consistent over its RS counterpart. This paper is not to advocate replacement of the SS-MRMPPT(RS) approach with the SS-MRMPPT(BW) one; rather, it is to throw light on the role of the scheme of perturbative expansion in the treatment of the coupling term maintaining size extensivity. The SS-MRPT method is generalizable to SS-MRENPT in RS and BW expansion. In this context, we remark that the SS-MRENPT approach is endowed with size extensivity and size consistency properties in contrast to the traditional MRPT method with EN partition. In the present work, the SS-MRENPT with RS and BW expansion has been applied to investigate the  $F_2$  system. The results of the SS-MRPT with an EN partition are not too good. The ground state PESs of  $F_2$  via SS-MRMPPT have already been published by Mahapatra et al.<sup>14</sup> with the EN-type partitioning scheme (using RHF orbitals). However, that work was based on relatively small basis sets. We have used sequences of the correlation-consistent cc-pVXZ basis sets (with spherical components) of Dunning in calculations described in this paper. The basis sets used in this paper were taken from ref 46.

Before embarking on the numerical performance of the SS-MRPT method, we first discuss in section II some salient methodological aspects of the SS-MRPT method, which are pertinent for numerical discussion. The numerical results are presented and discussed in section III. A summary and outlook is given in section IV.

## II. Brief Résumé of Theory and Discussion

Before presenting the results of the present work, we shall give a brief introduction of the SS-MRPT theory. It is not our purpose here to describe the detailed derivation of the SS-MRPT method starting from the mother theory, the SS-MRCC formalism. Such details can be found elsewhere.<sup>14,18,39</sup>

Considerable theoretical and computational progress has been achieved for a companion perturbation theory (SS-MRPT) for state-specific multireference coupled cluster methods of Mukherjee and co-workers.<sup>18,39,41</sup> The formal development of SS-MRPT has been based on the JM ansatz. In the JM ansatz, the wave function has the form

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

where the combining coefficients of the model space (MS) functions  $c_{\mu}$ 's are a priori unknown. The reference function  $\psi_0$  is a combination of the MS function (configuration state functions, CSF)  $\phi_{\mu}$ , called the complete model space (CMS):

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

Here, the cluster operator,  $T^{\mu}$ , acting on  $\phi_{\mu}$  creates a set of virtual functions,  $\{\chi^{\mu}\}$ . Every CSF is associated with its own cluster excitation operator to take care of differential correlation and dynamical correlation effects, instead of applying one universal operator to the whole reference function. This makes the approach based on this ansatz the method of choice for computing the state energies *per se*. Inserting the ansatz into the Schrödinger equation yields<sup>37</sup>

$$(H - E) \sum_{\mu} \exp(T^{\mu})|\phi_{\mu}\rangle c_{\mu} = 0$$

If all the parameters are independent, there is redundancy in the ansatz in the sense that some excited CSFs can be reached in multiple ways by the linear excitation of some reference CSFs. Thus, the use of the JM ansatz in a state specific fashion introduces an inherent redundancy problem. Mukherjee and co-workers tackled the obstacle and solved the amplitude equations by using some physically motivated sufficiency conditions.<sup>39</sup> The SSMR approach of Mukherjee and co-workers explicitly contains the eigenvector coefficients in contrast to both state-universal<sup>37</sup> and Brillouin-Wigner based methods.<sup>12</sup> In recent years, BW methods have been applied to the many-electron systems in a state specific formulation. For all practical purposes, actual perturbative computations require the truncation of the perturbative expansion, and this truncation is only meaningful if the perturbation series either converges rapidly or at least converges rapidly in an asymptotic sense. The general problem of spin-adaptation using the JM ansatz based MR methods is quite a nontrivial and a rather involved exercise.<sup>47</sup> The spin-adaptation of the SS-MRPT method has been achieved (i) by invoking suitable spin-free unitary generators to define the cluster operators and (ii) by considering the entire portion of the highest closed-shell component,  $\phi_{0\mu}$ , of a model function  $\phi_{\mu}$  as the vacuum to define all the excitations on  $\phi_{\mu}$  in normal order [see ref 18 for the spin-free development of SS-MRPT in detail]. In the SS-MRPT development, intermediate normalization is used, making the introduction of a complete active space essential (the amplitudes corresponding to the internal excitations are set to zero). It is also worth mentioning that the assumption of a complete model space enables proving the connectivity of

the cluster operator making the method scale correctly with the number of electrons (size-extensive). This is an important and nontrivial result. It should be noted that, because of the lack of invariance of the SS-MRPT with respect to active orbitals, strict size consistency can be demonstrated only for localized orbitals (which would also be the case for the analogous perturbation theory).

To discuss the structural features of cluster finding equations of the SS-MRPT approach, we recall the following quasi-linearized form of the parent SS-MRCC theory:<sup>39</sup>

$$\begin{aligned} &\langle \chi_l^\mu | H | \phi_\mu \rangle c_\mu + \left[ \sum_m \langle \chi_l^\mu | H | \chi_m \rangle - \langle \phi_\mu | H | \phi_\mu \rangle \delta_{lm} \right] \langle \chi_m^\mu | T^\mu | \phi_\mu \rangle c_\mu - \\ &\left[ \sum_v \langle \chi_l^\mu | T^\mu | \phi_\mu \rangle \varepsilon \right] c_\mu + \left[ \sum_v \langle \chi_l^\mu | T^\nu | \phi_\mu \rangle \tilde{H}_{\mu\nu} \right] c_\nu = 0 \quad \forall l, \mu \end{aligned} \quad (2)$$

Here,  $\{\chi_l^\mu\}$  (for all  $\mu$ ) are the set of virtual functions spanning the space complementary to the space of  $\psi_0$ ,  $\tilde{H}_{\mu\nu} = \langle \phi_\mu | H | \phi_\nu \rangle + \langle \phi_\mu | \overline{HT}^\nu | \phi_\nu \rangle$ . In the development of SS-MRPT, one can treat  $\varepsilon$  a dependent from our choice of  $\tilde{H}_{\mu\nu}$ , depending on the RS or BW mode of formulation, but not on a specific partitioning strategy. For the RS version, one can choose  $\tilde{H}_{\mu\nu}$  as  $H_{\mu\nu}$ , while the second order effective pseudo-operator  $\tilde{H}_{\mu\nu}^{(2)}$  can be chosen for the BW scheme. The partitioning of  $H$  affects the second and third terms of eq 2. Thus, from the very mode of development of the SS-MRPT method, one can observe that the formalism provides a completely independent treatment of the size-extensivity correction term and partitioning of the total Hamiltonian. Hence, one can consider several schemes for the development of the MRPT-like approach from the parent SS-MRCC theory.

For actual applications, the form of the working equations for the first-order cluster amplitudes can be written as

$$t_\mu^{(1)} = \frac{H_{l\mu}}{[E_0 - H_{ll}]} + \frac{\sum_{\nu \neq \mu} \langle \chi_l^\mu | T^{\nu(1)} | \phi_\mu \rangle H_{\mu\nu} (c_\nu^0 / c_\mu^0)}{[E_0 - H_{ll}]} \quad (3)$$

for RS, and

$$t_\mu^{(1)} = \frac{H_{l\mu}}{[E - H_{ll}]} + \frac{\sum_{\nu \neq \mu} \langle \chi_l^\mu | T^{\nu(1)} | \phi_\mu \rangle \tilde{H}_{\mu\nu} (c_\nu / c_\mu)}{[E - H_{ll}]} \quad (4)$$

for BW. The dependence of denominators on the unknown exact energy eigenvalue  $E$  is one of the distinguishing features of Brillouin–Wigner methods. This property is responsible for the existence of a natural gap that may lead to a rapid convergence of perturbation series. Here,  $H_{l\mu} = \langle \chi_l^\mu | H | \phi_\mu \rangle$ , and  $H_{ll} = \langle \chi_l^\mu | H | \chi_l^\mu \rangle$ .  $\chi_l^\mu$  stands for a general (mono/bi)-excited function from the  $\phi_\mu$ .  $H_0$  is the zeroth-order Hamiltonian. In practice, however, for a given MR reference wave function, the MRPT energy depends on the definition of the zero order Hamiltonian. Different variants of MRPT deviate from each other in the selection of these quantities.

As in the SS-MRPT method, the partitioning of  $H$  and the treatment of the size-extensivity correction term are independent, and we can even choose  $\mathbf{H}_0$  to be a one-particle operator, as that for a truly MP theory. In SS-MRPT, the

zeroth-order Hamiltonian,  $\mathbf{H}_0$ , is different for different CSFs,  $\phi_\mu$  or  $\psi_0$  [henceforth, we refer to  $\mathbf{H}_0$  for  $\phi_\mu$  as  $H_{0\mu}$ ]. In our MP partition, we choose  $H_{0\mu}$  to be a sum of the Fock operators for the function  $\phi_\mu$ . This will correspond to a multipartitioning MP perturbation theory analogous to what was originally advocated by Malrieu and co-workers.<sup>10</sup> Our SS-MRPT thus utilizes a multipartitioning strategy. We can also envision using an EN type of partition for  $H$ . In both the choices,  $H_{0\mu}$  is a diagonal operator, and this lends a simpler structure to the SS-MRPT. The SS-MRPT uses the best traits of the multipartitioning strategy as well as of a rigorously size-extensive formulation.

In the cluster amplitude finding equation of the SS-MRPT [see eqs 3 and 4], two sets of terms are present: (i) the first term, called the “direct” term [analogous to the SR part for each  $\phi_\mu$ , thus preserving the structure of SR perturbation theory], and (ii) the second part, called the “coupling” term, which is mainly responsible for the twin goals of the formulation: alleviate intruders (which are ubiquitous in a traditional effective Hamiltonian based MR approach) and maintenance of rigorous size extensivity. This plays an important role in the wave function being size-consistent with localized molecular orbitals. It is worth mentioning that the reliability of a computational approach as applied to large systems and chemical reactions depends critically on its ability to maintain the size consistency of calculated properties. Hence, the coupling term(s) have physically and numerically distinct contributions to the electron correlation problem for MR situations. This distinction is the primary feature of the SS-MRPT. The working equations of the SU- and SS-based MRPT methods differ in the form of the coupling terms. However, a repeated solution of essentially the same set of equations for each state is required in the case of SS-based methods, whereas in the conventional SU approach, all states are considered simultaneously.

We note that eqs 3 and 4 involve the coefficients  $c_\mu^0/c_\mu$  explicitly indicating that the cluster amplitudes depend on them. In contrast, coefficients do not appear(s) in the cluster amplitude equation of pure state universal theory. The coefficients and the required energy of the target state are generated by diagonalizing an effective operator (non-Hermitian)  $\tilde{H}_{\mu\nu}^{(2)}$  defined in CAS (or CMS):

$$\sum_\nu \tilde{H}_{\mu\nu}^{(2)} c_\nu = E^{(2)} c_\mu \quad (5)$$

Once the cluster amplitudes,  $t_\mu^{(1)}$ , are determined using the reference coefficient, the reference function can be updated by diagonalization of the matrix  $\tilde{H}_{\mu\nu}^{(2)}$ , and thus a self-consistent procedure is obtained. The number of unknowns in this formalism is exactly the same as in the corresponding SUMR-based theory. As the theory is state specific, only one eigenvalue corresponding to the target state represents the exact energy, while the remaining eigenvalue(s) have no physical meaning. That is, if the number of linearly independent functions in the CAS (i.e., Hilbert space) is  $N$ , only one root is meaningful (represents the exact intruder free energy); the rest of the roots are extraneous, which is the principal difference with the state-universal-based method(s). It should be emphasized that the strict separability of

the matrix elements of the effective Hamiltonian ensures the separability of its eigenvalues and eigenvectors provided that complete model spaces and localized orbitals are used. Very recently, Evangelista et al.<sup>41</sup> observed that localizing the orbitals to maintain rigorous size consistency of the method does not affect the accuracy of the results obtained.

Equations 3, 4, and 5 are the working expressions used in this work for the evaluation of cluster operators and energy in the perturbative framework. The sets  $\{T^q\}$  and  $\{c_\mu\}$  are coupled through eqs 4 and 5 in the case of BW. From the working equations, it is evident that the  $c_\mu$ 's are updated iteratively for the BW case, whereas  $c_\mu^0$  is used for RS scheme to evaluate the cluster amplitudes and  $\tilde{H}$ . In the RS case, model space combination coefficients get relaxed during the computation of energy when this is obtained by diagonalization. The CAS energy,  $E_0$  and coefficients (unrelaxed) for the reference functions,  $c_\mu^0$ 's are obtained by diagonalizing the matrix of  $H_{\mu\nu}$ . Thus, for the RS theory,  $E_0$  (CAS energy) appears in the denominator, while in BW, the target state energy appears. It should be noted that all the variables  $[c_\mu, T^q]$  are determined self-consistently for the BW case. Thus, the computation of the SS-MRPT energy requires knowledge of first-order cluster amplitudes which can be obtained via an iterative procedure because of the presence of coupling terms. There are several provisions about how to perform iterations of the cluster equations in the SS-MRPT method.<sup>14</sup> Consideration of different solution techniques of the first order equations is an important aspect. Very recently, Evangelista et al.<sup>41</sup> demonstrated that the iterative solution of the SS-MRPT amplitude equations is not a bottleneck issue. The perturbative energy for the RS scheme is a (up to) second-order quantity, whereas for the BW expansion, this is pseudo-second-order in nature [the energy is no longer rigorously second order] as the amplitude finding equations for BW are not truly first-order due to the presence of explicit  $\tilde{H}_{\mu\nu}$  in an amplitude equation, eq 4. In eq 5, there is a choice: one can use it to compute the energy either as an expectation value with respect to the unrelaxed (or frozen) function or by diagonalization in the relaxed form. It should be noted that, in SS-MRPT(RS), the effect of relaxation of the coefficient is somewhat different compared to the traditional MR-MBPT. The effect of large mixing of reference functions and consequent relaxation cannot be estimated fully by SS-MRPT(RS), because frozen  $c_\mu$ 's figure in the amplitude finding equation. SS-MRMPPT(RS) can be regarded as an approximation to the SS-MRMPPT(BW) method. But, we expect that the SS-MRPT(BW) scheme takes this relaxation fully.

Working equations clearly offer the solution to the *intruder state problems* for low-lying electronic states as long as  $E_0/E$  is well separated from the external space. This is a convenient aspect of applying the SS-MRPT method to PES, illustrated in the next section. It is noteworthy that, if the contribution of an intruder state is significant, then the "shifting technique to avoid the intruder" will not correct the situation rigorously, and a substantial error in the perturbation energy may be expected. In such situations, one may expand the reference space to include the intruder state. It is well-known that in most cases the effect of intruder states becomes more

pronounced away from equilibrium region, and successful treatment of this aspect improves the accuracy of predicted energies.

The development of IMS-based SSMR theory<sup>18</sup> may have the potential to avoid or at least to attenuate the instability of the theory when the virtual determinants do not remain reasonably well-separated in energy from the state energy. To attenuate the computational cost of the CAS-based SS-MRPT method, one can use the IMS-based SS-MRPT scheme. Another way to reduce the computational demand would be to work with a contracted description of the ansatz of the starting wave function as that in the case of the contracted MRCI method.<sup>18</sup>

It should be underlined that mere elimination of small denominators is not sufficient to ensure the convergence of cluster finding equations [eqs 3 and 4] because of the explicit presence of  $c_\mu$  in it. In the development of the SS-MRPT amplitude finding equations, we have assumed that all the elements of the eigenvector  $c_\mu$  are nonzero, which allows us to divide the  $\mu$ th cluster equation by  $c_\mu$ . The working equation is prone to numerical instability owing to the presence of the coefficients  $c_\mu$  (or  $c_\mu^0$ ) in the denominator, and the paucity of these makes the terms explode. This is an unwarranted situation. This issue is completely different from the conventional intruder effect (related to the vanishing energy difference in the denominator of the cluster finding equations, leading to convergence difficulties). If the reference coefficients go to zero (nearly vanishing), the value of  $\langle\chi_\mu^i|T^{v(1)}|\phi_\mu\rangle\tilde{H}_{\mu\nu}c_\nu/[\langle\chi_\mu^i|T^{v(1)}|\phi_\mu\rangle H_{\mu\nu}c_\nu^0]$  becomes small, akin to the values of the coefficients  $c_\mu$ . 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 in the cluster finding equation should not be large, at least not larger than the zero-order value; i.e.,  $\langle\chi_\mu^i|T^v|\phi_\mu\rangle H_{\mu\nu}c_\nu$  will be as small as  $c_\mu$ . Consequently, the problem of divergence is alleviated. Practical calculations show that SS-MRPT method has good convergence properties even for molecules far away from their equilibrium geometries. In our present applications, we have observed that the amplitude finding equations do not suffer from numerical instability even when all coefficients ( $c_\mu$ ) have been included. But still, the appearance of  $c_\mu$  in the denominator invites a threat for the calculations of excited states. Recently, a numerically more robust approach has been suggested and implemented by Evangelista et al.<sup>41,48</sup> Explicit discussion of this issue has appeared in the recent paper of Engels-Putzka and Hanrath.<sup>49</sup> In this paper, they devised a technique which is very effective in drastically reducing the numerical instability of amplitude finding equations without an undue sacrifice in accuracy. In passing, we should mention that the cluster finding equations in the SUMR<sup>37</sup> and BWMR<sup>12,50</sup> approaches have no  $c_\mu$  coefficient in the denominator and are free from such difficulties.

In this article, we have considered MP type partitionings. In our numerical application, we used the following definition of the Fock operator in the case of SS-MRMPPT:

$$f_\mu = \sum_{ij} \left[ f_{\text{core}}^{ij} + \sum_u \left( v_{iu}^{ju} - \frac{1}{2} v_{iu}^{ij} \right) D_{uu}^\mu \right] \{E_i\} \quad (6)$$



Here,  $u$  represents both a doubly occupied and a singly occupied active orbital in  $\phi_\mu$ , and  $D^\mu$ 's are the densities labeled by the active orbitals. Since our  $H_0$  is always diagonal for MP scheme, the zeroth-order Hamiltonian operator is  $H_0^\mu = \sum_i f_{ii}^\mu \{E_i^\mu\}$ . Thus,  $H_0$  is built on one-particle operators; i.e., it is monoelectronic in nature. The use of diagonal zero-order operators ensures the maximum computational simplicity of the scheme, which can attenuate computational cost in rather complicated situations. For the sake of comparison, results of the EN partition (appropriately generalized in the context of multipartitioning<sup>10</sup>) have also been presented.

This discussion will remain incomplete if we do not discuss the characteristic features of the SS-MRPT with respect to the multireference state specific Brillouin–Wigner second-order perturbation theory (BWPT) of Hubač and co-workers.<sup>12</sup> In this part, we will analyze qualitatively the structural kinship and scaling (size-extensivity) property of these two methods. Theoretical derivations and detailed discussions of further aspects of these approaches are given elsewhere.<sup>12,14</sup> A complete active space is employed as a reference for both the perturbation theory studies. Here, we want to state that both the BWPT of Hubač and co-workers<sup>12</sup> and the SS-MRPT developed by Mukherjee and co-workers<sup>14</sup> are based on the “diagonalize then perturb” philosophy.

In the state-specific Brillouin–Wigner PT of Hubač and co-workers,<sup>12</sup> working equations are obtained by introducing the SS wave operator in the BW form of the Bloch equation. The equations that determine the amplitudes of the wave operator are coupled only through the exact energy of the target state (the price paid is the lack of size extensivity of the method), a computational advantage emphasized by Hubač and co-workers. Thus, in BWPT, the amplitude equations naturally decouple for each reference and do not contain expansion coefficients for the reference wave function. On the other hand, the development of the SS-MRPT formalism of Mukherjee and co-workers involves inserting the state-specific JM wave operator into the expansion for the exact wave function and using the physically motivated sufficiency condition discover cluster finding equations. As a result of this, in contrast to the BWPT, the amplitudes of the SS-MRPT for reference  $\mu$  are dependent on the amplitudes of the entire model space through the renormalization (or coupling) terms. We recall that, in the SS-MRPT formalism, the renormalization terms have been exploited to attain the twin goals of ensuring size extensivity and avoiding intruders. Although both the theories of Mukherjee and co-workers and of Hubač and his group use sufficiency conditions, it is worth noticing the difference in the sufficiency conditions of BWPT and SS-MRPT. In contrast to the BWPT approach, the SS-MRPT(BW) method explicitly contains the eigenvector coefficients. This reference coefficient weighing originates from the sufficiency condition used.

To make some comment on the formulation of BWPT proposed by Hubač and co-workers,<sup>12</sup> we have written the perturbative equations with the same  $\mathbf{H}_0$  used by us and with the energy parameter unexpanded. Their amplitude equations, in place of the coupling term, contain the target energy  $E$  itself, multiplied by certain expressions containing just the

amplitudes of the  $\mathbf{T}^\mu$ . The coupling of the various  $t^\mu$ 's with different  $\mu$ 's is thus implicit, appearing via  $E$ , since  $E$  involves all the cluster operators with different  $\mu$ 's. The equation for the first order cluster operator in our terminology is

$$\langle \chi_l^\mu | H | \phi_\mu \rangle + \langle \chi_l^\mu | H_0 T^{\mu(1)} | \phi_\mu \rangle = E \langle \chi_l^\mu | T^{\mu(1)} | \phi_\mu \rangle \quad (7)$$

Using the multipartitioning expression<sup>10</sup> of  $H$  we get

$$\langle \chi_l^\mu | H | \phi_\mu \rangle + (H_{ll} - E) \langle \chi_l^\mu | T^{\mu(1)} | \phi_\mu \rangle + \sum_{m \neq l} \langle \chi_l^\mu | [H_0]_\mu | \chi_m^\mu \rangle \langle \chi_m^\mu | T^{\mu(1)} | \phi_\mu \rangle = 0 \quad (8)$$

A strong objection to the choice of sufficiency conditions used by Hubač and co-workers to yield amplitude equations is that BWPT is not rigorously size-extensive due to the presence of disconnected terms stemming from  $E \langle \chi_l | T^{\mu(1)} | \phi_\mu \rangle$ . There are no counter terms to cancel this disconnected contribution. The remaining terms of this equation are connected in nature. Attempts to restore size extensivity in the formalism of BWPT attempt to do so by way of expanding the target energy  $E$  in terms of an unperturbed RS-like energy  $E_0$ . The size-extensivity correction in this way does not necessarily improve the quality of results with respect to the nonextensive parent theory.<sup>51</sup> It has been observed that the intruders would not show up if the inextensivity correction is incorporated by one iteration only. However, in general, this procedure does not ensure the removal of all the inextensive terms. Multiple iterations or the converged RS type of results will, however, unfortunately bring back the problem of potential intruders. In spite of that, recent calculations have shown that this approach produces very promising results in some difficult quasi-degenerate situations. On the other hand, SS-MRPT(BW) is both size-extensive and size-consistent (when localized orbitals are used). The cluster amplitudes in the BW series are generally obtained in the SS-MRPT theory by using BW-type denominators but are corrected for size inextensivity with counter terms originating from coupling terms; such counter terms are inherently absent in the BWPT approach.<sup>12</sup> In SS-MRPT(BW), there is an extra term  $\sum_r \langle \chi_l | T^{\mu(1)} | \phi_\mu \rangle H_{lr} (c_r/c_\mu)$  which cancels the disconnected term; as a result, the final cluster finding equation is manifestly connected. Hence, the amplitude finding equations in SS-MRPT involve an explicit coupling between the cluster operators for all the  $\mu$ 's as demanded by the rigorous requirement of size extensivity. Proving the extensivity and consistency of both cluster amplitudes and the energy  $E$  of SS-MRPT is a rather involved exercise, and we refer to the original papers for details.<sup>14,15</sup>

The above-mentioned, nice formal properties provide a unique niche for the SS-MRPT approach that has opened the possibility toward accurate treatment for the electronic states, especially when investigating large systems that are computationally intractable for the more robust electron correlation methods. The SS-MRPT method resolves the contradiction between the conditions for a reliable as well as good convergence and those for asymptotic separability in the context of the MRPT approach.<sup>10</sup> The goodness of

the SS-MRPT method in different partition and expansion schemes will be examined by way of example calculations in the next section, where we shall illustrate the accuracy of the SS-MRPT method for a number of homonuclear diatomic halogen and BH molecules. The performances of the SS-MRMPPT(RS) and SS-MRMPPT(BW) methods based on the same CAS have been compared. To validate our numerical implementation, we tested our results against independent numerical results available in the literature. The remainder of this paper consists of discussion of our numerical applications.

### III. Numerical Applications: Dissociation PES of Molecular Systems

In the present paper, we deal with the dissociation of single bond systems. Despite their geometric simplicity, the electronic structure of these molecules provides a difficult challenge for MRPT. We have organized the sequence of the presentation of our numerical results in two parts: (A) dissociation of  $X_2$  [ $X = F, Cl, \text{ and } Br$ ] systems and (B) the calculation of the ground state PES of the astrophysically important BH molecule in order to show the applicability of the SS-MRPT approach to an open-shell case. In this paper, we have also investigated the effects of orbital rotation on the total SS-MRMPPT energy.

In the approach pursued here, the recovery of correlation is perceived as a two-stage process. The procedure we used involved running an initial CASSCF calculation followed by SS-MRMP analysis. The SS-MRPT correction ensures (provides the second order energy in the full active space) a proper treatment of the dynamic electron correlation in the wave function. All current calculations use CASSCF for the description of the reference state because it is size-consistent and correctly describes the static correlation. CASSCF wave functions are especially useful for exploring the details of PES. In the CASSCF method, the active electrons are distributed in all possible ways over the active orbitals with a given space-spin symmetry of the state considered. The active space provided by the user of the CASSCF software represents a key point to obtain accurate theoretical predictions, once the dynamic correlation has subsequently been taken into account, for instance, at the SS-MRPT level. In our CASSCF calculations for electronic states of the  $X_2$  and BH systems, two electrons were active, and the active space included two orbitals [denoted as CAS (2,2)] for each internuclear distance. In our calculations of the BH system, we also used the same CAS, termed CAS(val), as the one reported in ref 52, and thereby the performance of the various SS-MRMPPT variants can be assessed by comparing our results with the results reported in ref 52 of Sherrill and co-workers. The choice of the active space stemmed from the electron configuration of the ground state of the molecules. In order of increasing severity, our tests include the homonuclear diatomic molecules  $F_2$ ,  $Cl_2$ , and  $Br_2$ . The single bonding in  $X_2$  is basically a chemical reaction that involves one bonding orbital(s) and the corresponding higher-lying antibonding orbital. CAS(2,2) is thus the smallest active space that allows for a qualitatively correct treatment of the bond breaking since, in the dissociation region, both bonding

and antibonding orbitals become quasi-degenerate nonbonding orbitals. On the other hand, the larger reference space provides improved first order energies and smaller overall perturbation corrections. Not only that, increasing size of the reference space enhances the diagonal perturbation matrix elements. It might be expected that the perturbation series displays slow convergence with the larger reference spaces in comparison to the smaller one. It is always desirable to use as accurate a description of the unperturbed state as possible. In this computational method, the full reaction coordinate is computed at the CASSCF level of theory [using GAMESS(US) quantum-chemistry software]. For the perturbation calculations, mono- and bielectronic integrals are calculated by the GAMESS(US) program package.

**A. Ground State PES of Homonuclear Dihalogen Molecules  $X_2$ .** Theoretical studies on ground electronic states along the dissociation path of  $X_2$  are very challenging as it possesses quasi-degeneracy at some point on the reaction path and there are potential intruders at some other points in the PES. This is the main reason (to our knowledge) for the inapplicability of state-universal MRCC theory to generate spectroscopic constants of  $X_2$ . Thus, these systems are appropriate to test the efficacy of any state-specific MR-based theory. Therefore, in order to obtain a PES accurate enough in the whole range of the reaction path, computation of both nondynamical and dynamical electron correlation in a sophisticated and intruder free manner is very much essential.

Before investigating the properties of  $Cl_2$  and  $Br_2$ , we consider the demanding example of  $F_2$ , which is well-known to have multireference character in its equilibrium description. The fluorine molecule is one of the most widely studied and still one of the most difficult diatomic molecules in terms of obtaining a correct dissociation behavior. Almost any new single or multiconfiguration reference approach to the correlation energy has been long-since checked for the computation of the lowest state of the  $F_2$  molecule as a simple multireference system that is difficult to solve.<sup>14,26,45,53–60</sup>

A proper description of the reference wave function of equilibrium and the entire reaction coordinate including dissociated  $X_2$  requires a linear combination of two closed-shell determinants:  $(core)\sigma_g^2$  and  $(core)\sigma_u^2$  in the  $D_{2h}$  point group. As the stretching of the  $X_2$  bond increases, the contribution from the second determinant to the total CASSCF(2,2) wave function increases significantly. Needless to say, the SR-based method noticeably underestimates the second determinant contribution. Recent papers by Pittner et al.<sup>26</sup> and Evangelista et al.<sup>48</sup> provide a nice summary of the performance of various many-body methods applied to the  $F_2$  problem. A comprehensive tabulation of spectroscopic constants of  $F_2$  obtained from different perturbation theory have been found in a paper by Rosta and Surjan.<sup>59</sup> The dissociation energy of  $F_2$  has been determined by Yang et al.<sup>61</sup> using ion-pair dissociation imaging. In very recent articles, Bartlett and Musial<sup>62</sup> have given a detailed discussion of the performance of a new hierarchy of SR-based coupled-cluster methods,  $nCC$  for the  $F_2$  bond-breaking process. Very recently, Evangelista et al.<sup>48</sup> published a nice paper regarding the performance of various MRCC methods to calculate the dissociation energy of  $F_2$  in considerable



detail. It should be emphasized here that the most extensive application at the production level of SS-MRCC theory by Mukherjee and co-workers<sup>39</sup> beyond double excitation was carried out by Evangelista et al.<sup>48</sup> [termed by them as Mk-MRCC]. They provide a benchmark for other high-accuracy calculations of the  $F_2$  dissociation surface. In this paper,<sup>48</sup> they stated that the low accuracy of MR-BWCCSD theory to describe the dissociation reaction of  $F_2$  in comparison to the Mk-MRCCSD is due to the size inextensivity of BWCC method. Recently, Ruedenberg and co-workers<sup>63</sup> established the nonrelativistic PES taking into account electron correlations only in the valence shell, while to get very accurate results, one must also include the effects of relativity. The spectroscopic results of Evangelista et al.<sup>48</sup> along with the present work allow an assessment of effectiveness of the SS-MRMPPT in comparison to the computationally demanding parent, full-blown SS-MRCC (Mk-MRCC) method. It is evident from the above discussion that  $F_2$  provides a unique testing ground for different theoretical approaches to the study of PESs. Because the  $F_2$  system is small enough for the application of very large basis sets close to the limit, we have done a series of calculations for the system to get a definite answer to the performance of the SS-MRMPPT with the RS and BW scheme. The results for  $F_2$  have been obtained with a variety of basis sets. The perturbation series converges safely if diffuse basis functions are added to the basis set. It is worth mentioning that, in our numerical application, we have not observed any unphysical kink (or barrier) in the  $F_2$  dissociation PES, but Mášik et al.<sup>57</sup> have observed that there is an unphysical barrier in the CASPT2 dissociation surfaces near  $R(FF) = 3 \text{ \AA}$ .

For our computations on the  $F_2$  system, let us first consider the frozen-core calculations using the DZP+basis<sup>54</sup> [which is the standard Huzinaga–Dunning DZ set with the most diffuse p function uncontracted and augmented by six Cartesian d functions ( $\alpha_d(F) = 1.580$ )] where we have various theoretical results<sup>26,45,53–60</sup> for comparison. Spectroscopic constants of  $F_2$  at various levels of theory are available in the literature for this basis. Hence, we have performed our calculations using this basis to demonstrate the efficacy of the SS-MRPT for different partitions and expansion schemes. The spectroscopic properties (equilibrium bond length and dissociation energy) derived from our PESs are reported in Table 1 for the  $F_2$  molecule using the DZP+ basis. The fluorine 1s core orbitals have been kept frozen (uncorrelated) in our calculations. Comparisons are presented with other multireference perturbation calculations focusing only on the relative performance of the methods of Hirao (MRMPPT),<sup>3</sup> Roos and co-workers (CASPT2),<sup>5</sup> and the APSG (antisymmetrized product of strongly orthogonal geminals) PT of Surján and co-workers.<sup>59</sup> For the sake of comparison, we have also summarized the results of spin-flip and MR-CISD methods.<sup>58</sup> For a balanced comparison, we also report in Table 1 the best nonrelativistic, valence-correlated, CBS results from Bytautas et al.<sup>63</sup> The FCI result is not available at this level, and the results from Bytautas et al. have been taken as a reference. The results in the table show the ability of both versions of SS-MRMPPT to reproduce the established theoretical values well. The results

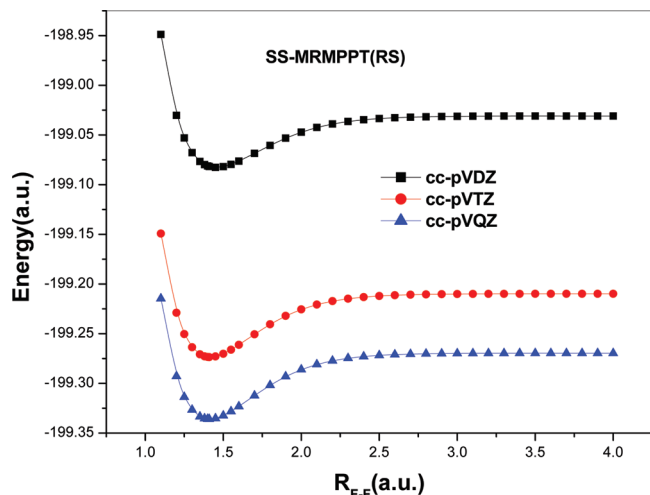
**Table 1.** Spectroscopic Constants for the Electronic Ground State of  $F_2$  Molecule Using DZP+ Basis Sets

method	$R_e$ (Å)	$D_e$ (eV)
CASSCF	1.5107	0.63
SS-MRMPPT(RS)	1.4330	1.42
SS-MRMPPT(BW)	1.4321	1.35
GVB <sup>a</sup>	1.512	0.453
APSG <sup>a</sup>	1.501	0.486
MRMPPT2 <sup>a</sup>	1.4254	1.440
GVB1H1PT <sup>a</sup>	1.445	1.025
GVB1H2PT <sup>a</sup>	1.420	1.180
APSG1H1PT <sup>a</sup>	1.447	1.026
APSG1H2PT <sup>a</sup>	1.423	1.274
MRCISD10 <sup>b</sup>	1.435	1.222
MRLCCM10 <sup>b</sup>	1.439	1.221
MRCISD32 <sup>b</sup>	1.436	1.275
MRLCCM32 <sup>b</sup>	1.439	1.257
CASPT2 <sup>c</sup>	1.442	1.275
MRMBPT(2) <sup>c</sup>		
simple averaging	1.374	2.348
double averaging	1.377	2.196
SF-SCF <sup>d</sup>	1.567	0.28
SF-CIS(D) <sup>d</sup>	1.429	1.14
SF-OD <sup>d</sup>	1.437	1.24
VOO-CCD(2) <sup>d</sup>	1.417	1.51
MR-CISD <sup>d</sup>	1.435	1.22
best <i>ab initio</i> <sup>e</sup>	1.4148	1.70
experiment	1.412	1.66

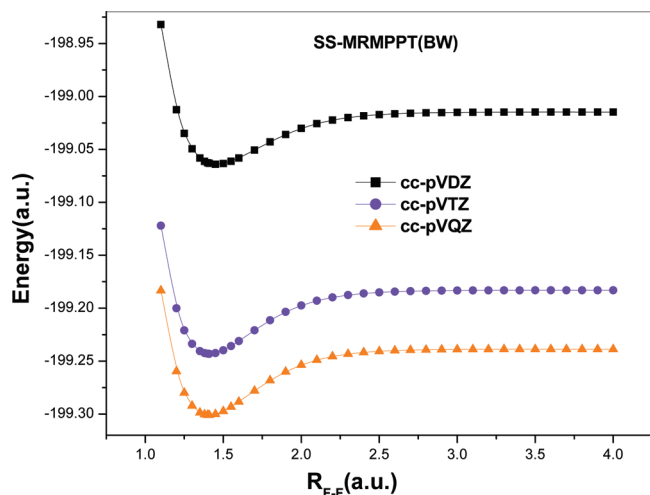
<sup>a</sup> Ref 59. <sup>b</sup> Ref 54. <sup>c</sup> Ref 57. <sup>d</sup> Ref 58. <sup>e</sup> Ref 63 (2,2) CAS has been used in our works.

from the CASSCF, GVB (generalized valence bond), and APSG (represents an independent electron-pair model) calculations compare well with spin-flip-SCF (SF-SCF). Although incorporation of the dynamical correlation in the SF-SCF method improves the results, the SS-MRMPPT represents a somewhat better description for the spectroscopic constants than SF-SCF based correlated methods [such as SF-CIS(D), SF-OD, and so on]. From the table, it is abundantly clear that the agreement of the SS-MRMPPT results with state-of-the-art *ab initio* results of Bytautas et al.<sup>63</sup> (and also the experimental ones) is definitely better than for CASPT2, GVB+HPT, and APSG+HPT and is of the same quality as the MRMPPT of Hirao.<sup>3</sup> It seems therefore reasonable to say in this case that SS-MRMPPT is not only a useful MRPT approach but also a strong competitor to other well established MRPT methods such as CASPT2, MRMPPT, and so on. A major advantage of the computed SS-MRMPPT energy is that it is rigorously size-extensive in nature in contrast to the MRMPPT and CASPT2. It may be of interest to note that Rintelman et al. investigated extensively the size extensivity problem of MRMPPT and CASPT2 with the  $F_2$  molecule using a series of basis sets. To illustrate that this high accuracy of the SS-MRMPPT in predicting spectroscopic constants is not an accident, we re-evaluate the same using various correlation-consistent basis sets.

The DZP+basis is too small to illustrate a sensible comparison of the computed spectroscopic data with the corresponding experimental results. Actually, in the case of  $F_2$ , the use of a basis set up to quadruple- $\zeta$  quality is sensible (in accordance with the literature) in order to demonstrate the effect of the basis set and to compare the calculated results with the experimental data. In Figures 1 and 2, we

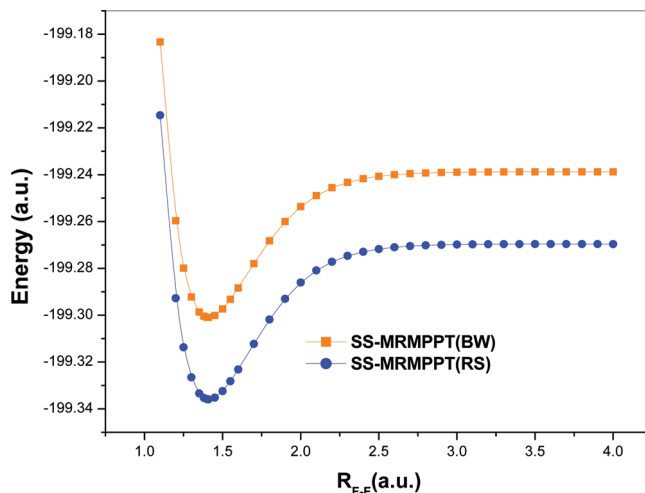


**Figure 1.** Potential energy surfaces for the  $F_2$  molecule with the SS-MRMPPT(RS) method in different cc-pVXZ basis sets.



**Figure 2.** Potential energy surfaces for the  $F_2$  molecule with the SS-MRMPPT(BW) method in different cc-pVXZ basis sets.

draw the SS-MRMPPT PESs for  $F_2$  using a different correlation consistent basis sets. From the PESs, it can be seen that a qualitatively balanced description is obtained by SS-MRMPPT approaches for various basis sets. From our computations, we have observed that the SS-MRMPPT(BW) potential surfaces are situated above the SS-MRMPPT(RS) surfaces at all geometries for all basis sets considered here [see Figure 3]. As the traditional full configuration interaction (FCI) and the high level PES calculations are not available for these basis sets, comparison of SS-MRMPPT methods is made with the spectroscopic parameters of high level methods reported in the literature, and thereby one can envision the correct description of bond breaking. Table 2 contains the spectroscopic constants for  $F_2$  in various cc-pVXZ basis sets with different SS-MRPT methods using EN and MP partition schemes. These basis sets would be expected to describe, for example, the anion character of the  $F^+F^-$  charge transfer components of the wave function with more flexibility. It is interesting to compare our results with the Mk-MRMP2 results of Evangelista et al.<sup>41</sup> In Table 2,



**Figure 3.** Potential energy surfaces for the  $F_2$  molecule with the SS-MRMPPT(RS) and SS-MRMPPT(BW) methods in the cc-pVQZ basis set.

we present results of the CASSCF and CCSD as well as CCSDT for comparison. Further, we tabulate a variety of state selective equation of motion coupled cluster based methods of Nooijen.<sup>55</sup> Results of auxiliary-field quantum Monte Carlo method (AFQMC) calculations, which yields spin-contamination-free results within a Hilbert space, of Purwanto et al.<sup>60</sup> have also been reported in Table 2. BW-MRCCSD results and the rather recent results from the Mk-MRCC method of Evangelista et al.<sup>48</sup> are also given in the same table to calibrate the quality of our results because the Mk-MRCC method serves as a benchmark. In fact, methods such as Mk-MRCC and BW-MRCC provide useful results for our understanding of the electronic structure of molecules despite their high computational cost. Due to this high numerical cost, applications of such methods remain constrained to relatively small systems in contrast to the corresponding MRPT part. We observed that SS-MRMPPT and Mk-MRPT2 methods are of comparable accuracy. Here, we recall once more that, in the Mk-MRPT2 computation, Evangelista et al. used unrelaxed description, and we have already discussed the importance of the issue of relaxed variants. Table 2 displays that the performance of the SS-MRMPPT is better than the CCSD and various EOM-CC methods. It is found that, even though only a single bond is broken in the dissociation considered here, nonetheless, sextuple excitations with respect to single-determinant reference functions are required to recover the binding energy with a “chemical accuracy”. This view is supported by the fact that dissociation energy and vibrational frequency provided by CCSD are not as good as the other methods reported in the table. Recently, Purwanto et al.<sup>60</sup> observed that, in the case of  $F_2$  with the cc-pVXZ basis, the RCCSD(T) method breaks down in the dissociation limit. On the other hand, the PES provided by UCCSD(T) is correct in the dissociation limit, but the shape of the surface near the equilibrium distance is distorted in nature, which invites significant error in the intermediate geometries. From the table, we have observed that the SS-MRMPPT results for each basis set are comparable to those obtained with the AFQMC method. Here, it is important to note that the

**Table 2.** Spectroscopic Constants for the Electronic Ground State of F<sub>2</sub> Molecule Using Different cc-pVXZ Basis

basis	method	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
cc-pVDZ	CASSCF	1.5309	575	
	SS-MRMPPT(RS)	1.4546	809	1.40
	SS-MRMPPT(BW)	1.4557	795	1.34
	SS-MRENPT(RS)	1.4342	887	2.15
	SS-MRENPT(BW)	1.4365	865	1.89
	Mk-MRPT2 <sup>a</sup>	1.4454	815	1.29
	CCSD <sup>b</sup>	1.432	885	0.96
	CCSDT <sup>b</sup>	1.4577	787	1.18
	BW-MRCCSD <sup>b</sup>	1.4469	821	1.63
	Mk-MRCCSD <sup>b</sup>	1.4548	793	1.37
	AFQMC <sup>c</sup>	1.467	725	1.29
	RCCSD(T) <sup>c</sup>	1.4751	785	1.18
	UCCSD(T) <sup>c</sup>	1.4428	853	1.14
	LSDA <sup>c</sup>	1.3970	1026	3.45
	B3LYP <sup>c</sup>	1.4097	1033	1.64
cc-pVTZ	CASSCF	1.4696	699	0.72
	SS-MRMPPT(RS)	1.4151	918	1.71
	SS-MRMPPT(BW)	1.4134	917	1.62
	SS-MRENPT(RS)	1.4001	1017	2.63
	SS-MRENPT(BW)	1.3984	987	2.26
	Mk-MRPT2 <sup>a</sup>	1.4055	955	1.61
	CCSD <sup>b</sup>	1.3946	1012	1.22
	CCSDT <sup>b</sup>	1.4154	923	1.50
	BW-MRCCSD <sup>b</sup>	1.4060	953	2.03
	Mk-MRCCSD <sup>b</sup>	1.4127	925	1.71
	AFQMC <sup>c</sup>	1.411	928	1.70
	RCCSD(T) <sup>c</sup>	1.4131	926	
	UCCSD(T) <sup>c</sup>	1.3987	1022	1.49
	LSDA <sup>c</sup>	1.3863	1065	3.49
	B3LYP <sup>c</sup>	1.3957	1072	1.65
	DIP-STEOM-CCSD[2-] <sup>d</sup>	1.4353	834	
cc-pVQZ	DIP-EOM-CCSD[2-] <sup>d</sup>	1.4249	811	
	CSS-EOM-CCSD[B] <sup>d</sup>	1.4173	901	
	RSS-EOM-CCSD[B] <sup>d</sup>	1.4126	927	
	CASSCF	1.4688	696	0.72
	SS-MRMPPT(RS)	1.4120	931	1.80
	SS-MRMPPT(BW)	1.4094	921	1.69
	SS-MRENPT(RS)	1.3994	1016	2.71
	SS-MRENPT(BW)	1.3962	988	2.31
	Mk-MRPT2 <sup>a</sup>	1.4023	958	1.68
	CCSD <sup>b</sup>	1.3906	1016	1.29
	CCSDT <sup>b</sup>	1.4124	925	1.58
	BW-MRCCSD <sup>b</sup>	1.4024	955	2.12
	Mk-MRCCSD <sup>b</sup>	1.4093	926	1.79
	AFQMC <sup>c</sup>	1.411	912	1.77
	RCCSD(T) <sup>c</sup>	1.4108	929	
	UCCSD(T) <sup>c</sup>	1.3946	1036	1.567
	LSDA <sup>c</sup>	1.3856	1062	3.47
	B3LYP <sup>c</sup>	1.3944	1109	1.63
	best <i>ab initio</i> <sup>e</sup>	1.4148	920	1.70
	experiment	1.412	916.64	1.66

<sup>a</sup> Ref 41. <sup>b</sup> Ref 48 [for symmetry-adapted natural orbitals]. <sup>c</sup> Ref 60. <sup>d</sup> Ref 55. <sup>e</sup> Ref 63. Experiment: ref 86 (2,2) CAS has been used in our works.

CAS(10,12) has been used in the AFQMC method, whereas in our calculation we have used CAS(2,2). Computationally, the SS-MRPT method is less demanding than the AFQMC one. The values of spectroscopic constants of the SS-MRMPPT in Table 2 are in better agreement with the highly accurate available *ab initio* calculation<sup>63</sup> (and also experiment) than those of the LSDA and B3LYP methods. It should be noted that the shapes of the LSDA and B3LYP PESs are not correct in the intermediate region of UCCSD(T) in contrast to the SS-MRMPPT one. As seen in Table 2, the errors in the computed spectroscopic constants are usually

large for several of the methods for the cc-pVDZ basis relative to that of the other basis. It is important to realize, however, that the poor performance of various methods for cc-pVDZ basis is not in its inability to describe charge transfer components of the wave function, but rather it is an inflexibility of the valence region itself. It has been found that, in order to obtain good results, the use of quite large and proper atomic orbital basis sets is clearly desirable. Analyzing the results in Table 2, we find that the calculated spectroscopic constants of the ground state via different variants of SS-MRPT agree reasonably well with the corresponding experimental values. Our spectroscopic constants agree quite well with the previously calculated theoretical values. In general, the SS-MRMPPT provides superior results (for the spectroscopic constants of F<sub>2</sub>) relative to the BW-MRCC methods reported by Evangelista et al.<sup>48</sup> The present calculations of F<sub>2</sub> produce almost the same equilibrium distance, vibrational frequency, and dissociation energy as those reported in Mk-MRCC. In other words, the SS-MRPT results are competitive with the Mk-MRCC to deliver accurate energetics for the dissociation of F<sub>2</sub> but at lesser cost in the calculation. It is worth noting that the SS-MRPT method is computationally cost effective for realistic applications, and it is able to achieve a similar level of accuracy as the Mk-MRCC method for the treatment of the dynamical correlation and can thus serve as a reference for calibration of more approximate approaches. Table 2 clearly displays that the various SS-MRMPPT results do not differ significantly in the general trends for a given partitioning. In this work, we have also listed in Table 3 the comparative performance of the various methods reported by Shepard et al.<sup>64</sup> for the sake of comparison. Our observations are that the SS-MRMPPT results generate spectroscopic properties that are better than the best single-reference MP methods summarized in this study (MP3, MP4). From Tables 2 and 3, we have observed, in general, our current multireference calculations via SS-MRMPPT methods predict  $R_e$  values with an accuracy competitive to, or better than, the MR-SDCI and MR-AQCC methods, despite the fact that the MR-AQCC method is computationally costly. In contrast to the SS-MRMPPT method, the calculated  $R_e$  values using the MR-CISD and MR-AQCC methods tend to be smooth and monotonic with basis set improvement. From Tables 2 and 3, as far as the prediction of spectroscopic constants is concerned, we note that the general performance of the SS-MRMPPT is better than its EN counterpart. Being a symmetrical system, it is well known that the EN partition meets with particular difficulties in the description of the dissociative part of the PES<sup>65</sup> with a delocalized basis of molecular orbitals, as unphysical Coulombic terms and other artifacts appear in the interaction energy of the fragments. In particular, we want to mention that Angeli et al.<sup>66</sup> also observed the defects of the EN partition with respect to dissociation in the case of F<sub>2</sub> even in the case of CAS containing 78 432 determinants [e.g., Figure 1 of ref 66]. Our numerical experience with the EN partitioning is mingled. Very satisfactory results with EN for correlation energies have been obtained in some cases,<sup>18</sup> while in other cases, an overestimation of low-order contributions and very



**Table 3.** Equilibrium Bond Length for the Electronic Ground State of F<sub>2</sub> Molecule Using Different cc-pVXZ Basis<sup>a</sup>

basis	MP2	MP3	MP4	MRSDCI	MRAQCC	SS-MRMPPT(RS)	SS-MRMPPT(BW)
cc-pVDZ	1.4239	1.4168	1.4504	1.4652	1.4620	1.4546	1.4557
cc-pVTZ	1.3958	1.3837	1.4151	1.4191	1.4184	1.4151	1.4134
cc-pVQZ	1.3275	1.3812	1.4149	1.4153	1.4153	1.4120	1.4094

<sup>a</sup> Results are taken from: ref 64.**Table 4.** Spectroscopic Constants for the Electronic Ground State of F<sub>2</sub> Molecule Using cc-pVQZ Basis for Various NEVPT2 along with the SS-MRMPPT Method

method	$R_e$ (Å)	$D_e$ (eV)
SS-MRMPPT(RS)	1.4120	1.80
SS-MRMPPT(BW)	1.4094	1.69
NEVPT2 <sup>a</sup>	1.3960	1.717
PCNEVPT2 <sup>a</sup>	1.3960	1.720
NEVPT3 <sup>a</sup>	1.4171	1.390
FDD-MR(C)/NEVPT2 <sup>a</sup>	1.4050	1.751
FDD-MR(C)/NEVPT3 <sup>a</sup>	1.4200	1.395
MP-EN <sup>a</sup>	1.4108	1.77
(SC) <sup>2</sup> SDCI <sup>a</sup>	1.4129	1.59
MRCI <sup>a</sup>	1.4119	1.62
8-ref CASSCF <sup>b</sup>	1.4076	1.64
8-ref CI <sup>b</sup>	1.4076	1.66
best <i>ab initio</i> <sup>c</sup>	1.4148	1.70
experiment	1.412	1.66

<sup>a</sup> Ref 42. <sup>b</sup> Ref 67. <sup>c</sup> Ref 63, (2,2) CAS has been used in our works.

slow convergence have been reported. However, more extensive analysis of several systems is required before one can assume this to be a general conclusion. Work towards this direction is in progress in our laboratory. All of this underlines the importance of a detailed study of the partitioning problem in SS-MRPT, just as with that of the other MRPT. This paper illustrates the considerations that are necessary when choosing a zeroth-order Hamiltonian for the MRPT method. Inspecting Table 2, one observes that in the case of the F<sub>2</sub> molecule with the cc-pVTZ basis, the SS-MRMPPT method yields accurate predictions of the equilibrium distance, vibrational frequency, and dissociation energy.

For the sake of completeness of our comparative study, in Table 4, we have also presented the SS-MRMPPT results along with another well studied internally contracted state-specific MRPT method, variants of the NEVPT2 method<sup>42</sup> which also confirm what is said for the potentiality of the SS-MRMPPT scheme. In a paper by Angeli et al.,<sup>42</sup> various active spaces have been considered. In this table, a selection of the previously published theoretical values of Lourderaj et al.<sup>67</sup> has also been reported. From Table 4, it is observed that the SS-MRMPPT describes the ground state spectroscopic properties to a reasonable accuracy in comparison with the various NEVPT2 schemes, MRCI, (SD)<sup>2</sup>SDCI, and MP-EN methods, and with respect to the experiments. In some cases, the agreement of the SS-MRMPPT results with highly accurate *ab initio* results<sup>63</sup> is acceptably closer than that for other methods reported in the table. The comparative demonstration in Table 4 clearly illustrates again the efficacy and reliability of the SS-MRMPPT method to predict the spectroscopic properties.

It is interesting to compare our findings with the recently introduced method of correlation energy extrapolation by

**Table 5.** Spectroscopic Constants for the Electronic Ground State of F<sub>2</sub> Molecule<sup>a</sup>

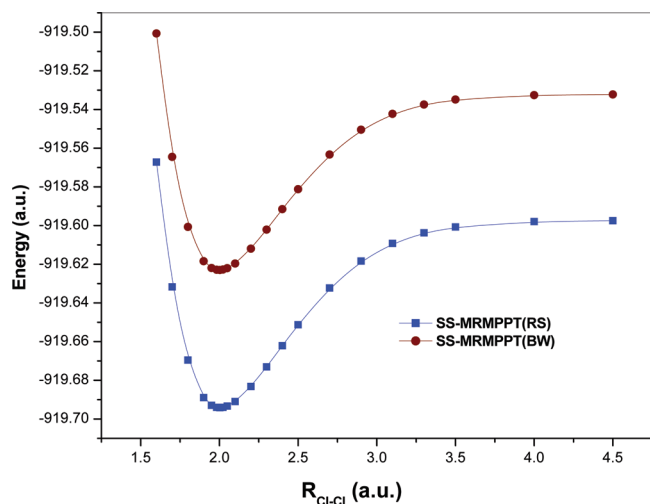
method	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
SS-MRMPPT(RS)	1.4120	931	1.80
SS-MRMPPT(BW)	1.4094	921	1.69
CEEIS	1.4135	915	1.66
CC-5/R12	1.4122	918.9	
ic-MRCI+Q	1.4105	916.9	1.59
ic-MRCI		899.7	1.49
CASPT3	1.4091	920.0	1.47
(mv)td-2	1.4118	915.2	1.59
4R RMR CCSD(T)	1.416	911.2	
experiment	1.412	916.64	1.66

<sup>a</sup> Various theoretical results are taken from ref 63 [for a detailed discussion, see Tables X and XI of ref 63]. (2,2) CAS has been used in our works.

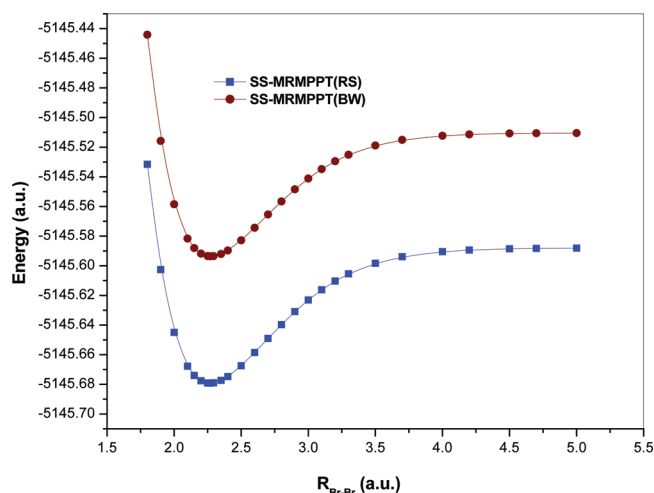
intrinsic scaling (CEEIS).<sup>63</sup> Table 5 compares the spectroscopic constants relating to the F<sub>2</sub> molecule that are obtained from the CEEIS method of Ruedenberg and co-workers<sup>63</sup> and various sources reported by them in addition to our SS-MRMPPT/cc-pVQZ method. Comparing the results, we find that SS-MRMPPT(RS) and SS-MRMPPT(BW) are both accurate and of comparable accuracy with CEEIS. In this context, it should be kept in mind that the present SS-MRMPPT calculations do not incorporate the correction due to core–electron correlations and relativity effects (including spin–orbit coupling) in contrast to the CEEIS. These incorporations significantly improve the overall quality of the PES and hence can considerably change the values of the spectroscopic constants.<sup>63,68</sup>

Here, we also want to mention that (2,2)MR-MP2 calculations done by Barbosa and Barcelos<sup>44</sup> with an aug-cc-pVTZ basis set have given values  $R_e = 1.428$  Å,  $\omega_e = 888$  cm<sup>-1</sup>, and  $D_e = 1.59$  eV. Malrieu et al.<sup>69</sup> have performed (SC)<sup>2</sup>SDCI calculations of F<sub>2</sub> with a basis set of 5s4p3d2f1g quality and reported  $R_e = 1.389$  Å,  $\omega_e = 1004.2$  cm<sup>-1</sup>, and  $D_e = 3.05$ . In the same paper, Malrieu et al. reported the corresponding values for the (MR-SDCI + Q) method as 1.417, 930, and 1.658, respectively.

Very recently, Zhang et al.<sup>70</sup> have implemented the idea of a locally contracted configuration interaction of singles and doubles (by introducing a coupled-electron pair approximation, CEPA-3) including the leading part of the triples and quadruples in the evaluation of equilibrium bond lengths ( $A^0$ ) and harmonic frequencies (cm<sup>-1</sup>) of the F<sub>2</sub> molecule with the TZVP basis set. The results obtained therefrom reveal that the bond length and the frequency respectively vary as (i) LC-CEPA-3, 1.380 and 1052.6; (ii) LC-CEPA-3+TQ/col/line, 1.416 and 911.5; and (iii) LC-CEPA-3+TQ/explicit, 1.415 and 907.8. Our overall observation is that the SS-MRMPPT approach is very competitive in accuracy with the theoretical results of Zhang et al.<sup>70</sup> as well in the case of the F<sub>2</sub> system.



**Figure 4.** Potential energy surfaces for the  $\text{Cl}_2$  molecule with the SS-MRMPPT(RS) and SS-MRMPPT(BW) methods in the cc-pVQZ basis set.



**Figure 5.** Potential energy surfaces for the  $\text{Br}_2$  molecule with the SS-MRMPPT(RS) and SS-MRMPPT(BW) methods in the cc-pVQZ basis set.

Several comparisons of the results of the SS-MRMPPT with respect to the different theoretical calculations including the most accurate available *ab initio* calculations in the context of  $\text{F}_2$  molecule have shown that the method is a very useful companion perturbation theory to the parent full blown SS-MRCC(Mk-MRCC) one and can be used to study larger multireference systems, for which SS-MRCC is generally not applicable. It is justified to use the SS-MRMPPT formalism as an effective and acceptable compromise between the computational demands and accuracy, and this we propose to adapt in our next applications (say,  $\text{Cl}_2$  and  $\text{Br}_2$ ).

The general properties followed by  $\text{Cl}_2$  and  $\text{Br}_2$  molecules are very close to each other and can be discussed together. In Figures 4 and 5, we draw the potential surfaces calculated by the SS-MRMPPT methods for  $\text{Cl}_2$  and  $\text{Br}_2$  using cc-pVQZ basis sets to display the pattern of the computed PESs. The spectroscopic properties using computed PESs at each level of SS-MRMPPT calculation for these molecules along with the experimental results are presented in Tables 6 and 7. The

**Table 6.** Spectroscopic Constants for the Electronic Ground State of the  $\text{Cl}_2$  Molecule

Basis	Method	$R_e$ (Å)	$\omega_e$ ( $\text{cm}^{-1}$ )	$D_e$ (eV)
cc-pVDZ	CASSCF	2.0628	468	1.42
	SS-MRMPPT(RS)	2.0367	543	2.02
cc-pVTZ	SS-MRMPPT(BW)	2.0366	543	1.94
	CASSCF	2.0368	504	1.69
cc-pVQZ	SS-MRMPPT(RS)	2.0085	574	2.51
	SS-MRMPPT(BW)	2.0054	563	2.37
TZVP	CASSCF	2.0337	504	1.71
	SS-MRMPPT(RS)	2.0020	584	2.63
TZVP	SS-MRMPPT(BW)	1.9991	565	2.47
TZVP	LC-CEPA-3 <sup>a</sup>	1.989	585.8	
	LC-CEPA-3+TQ/col/line <sup>a</sup>	2.016	533.9	
	LC-CEPA-3+TQ/explicit <sup>a</sup>	2.013	539.1	
	CCSD <sup>a</sup>	2.003	559.0	
	CCSD(T) <sup>a</sup>	2.011	543.1	
	experiment	1.988	564.9	2.475

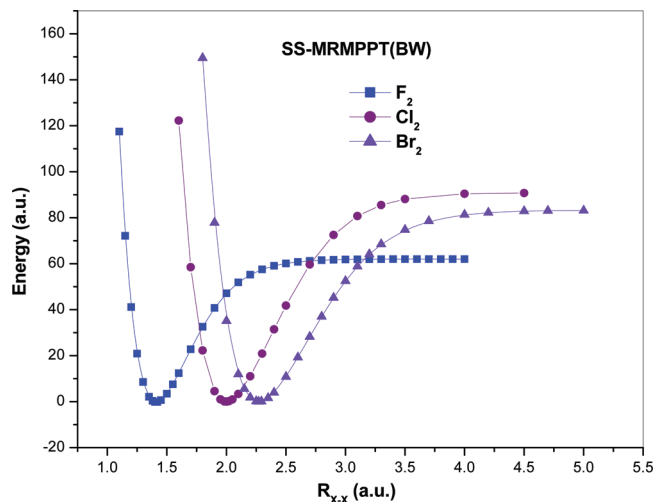
<sup>a</sup> Ref 70. Experiment: ref 86 (2,2) CAS has been used in our works.

**Table 7.** Spectroscopic Constants for the Electronic Ground State of the  $\text{Br}_2$  Molecule Using Different cc-pVXZ Bases<sup>a</sup>

basis	method	$R_e$ (Å)	$\omega_e$ ( $\text{cm}^{-1}$ )	$D_e$ (eV)
cc-pVTZ	CASSCF	2.3408	294	1.48
	SS-MRMPPT(RS)	2.2854	326	2.33
cc-pVQZ	SS-MRMPPT(BW)	2.2892	328	2.18
	CASSCF	2.3371	294	1.50
cc-pV5Z	SS-MRMPPT(RS)	2.2684	336	2.47
	SS-MRMPPT(BW)	2.2739	334	2.25
cc-pV5Z	CASSCF	2.3371	293	1.50
	SS-MRMPPT(RS)	2.2720	331	2.47
cc-pV5Z	SS-MRMPPT(BW)	2.2786	327	2.20
	experiment	2.283	323.2	1.971

<sup>a</sup> Experiment: ref 86; (2,2) CAS has been used in our works.

calculations documented in Tables 6 and 7 have been done with the exclusion of the He core correlation for  $\text{Cl}_2$  and  $\text{Br}_2$ . To judge the performance of the SS-MRMPPT methods for the  $\text{Cl}_2$  system, we analyze our results vis-a-vis the values obtained from the CCSD, CCSD(T) LC-CEPA-3, and LC-CEPA-3+TQ methods.<sup>70</sup> Table 6 clearly demonstrates that our method yields equilibrium bond lengths and harmonic frequencies that are quite akin to those obtained from LC-CEPA-3 for  $\text{Cl}_2$  molecule. Although LC-CEPA-3+TQ equilibrium bond lengths are similar to CCSD and CCSD(T), the average absolute deviation relative to experimental equilibrium bond lengths is a little larger than that of our results with the cc-pVQZ basis. We have obtained consistently quantitative descriptions for  $\text{Cl}_2$  and  $\text{Br}_2$  molecules along the wide range of bonding coordinates and thereby got encouraging spectroscopic constants with good accuracy. Comparing the experimental results, we see once again that the SS-MRMPPT method yields an accurate description of the spectroscopic parameters. All of the calculated bond lengths for  $\text{Br}_2$  are slightly longer than the experimental result, and the reverse is true for  $\text{Cl}_2$ . For both the systems, the SS-MRMPPT calculations overshoot the vibrational frequency. We have observed that the spectroscopic constants for  $\text{Cl}_2$  and  $\text{Br}_2$  systems obtained from SS-MRMPPT with a good basis are chemically accurate. For both these diatomic systems, the performance of SS-MRMPPT(BW) is slightly better than the RS scheme as that in the case of the  $\text{F}_2$ . In



**Figure 6.** Potential energy surfaces for the  $X_2$  [ $X = \text{F}, \text{Cl}$ , and  $\text{Br}$ ] molecules with the SS-MRMPPT(BW) method in the cc-pVQZ basis set.

the more complex system,  $\text{Br}_2$ , we have a less satisfactory performance of the SS-MRMPPT method. While the calculated results shown here are not free from approximation, and thus not exact, it is nonetheless significant that, of all  $X_2$ ,  $\text{Br}_2$  shows the largest discrepancy between our calculation and the experimental data. The cause of this discrepancy is not clear. We ascribe the unsatisfactory result of the SS-MRMPPT for  $\text{Br}_2$  (i) to the increased number of electrons [implying a rather large CAS] and (ii) to the absence of the relativistic effects in the formalism. Actually, in  $\text{F}_2$ ,  $\text{Cl}_2$ , and  $\text{Br}_2$ , the active orbitals mainly consist of atomic p, d, and f orbitals, respectively. To increase the accuracy, one can suggest the inclusion of appropriate sets of orbitals in the active space. However, the resulting dimension of the CAS space would make the corresponding numerical calculations most impractical, especially for  $\text{Cl}_2$  and  $\text{Br}_2$ . Recent studies at the MRCI level<sup>63</sup> demonstrate the importance of the flexibility of the reference space in the description of PESs in the case of the  $\text{F}_2$  molecule. We have already mentioned that the incorporation of the relativistic effect is very important for the numerical accuracy of the SS-MRMPPT method for large systems. This is also true for other nonrelativistic methods. For  $\text{Cl}_2$  and  $\text{Br}_2$  calculations, using a rather large CAS cannot even provide a qualitatively acceptable form of the PES due to the strong importance of the dynamical correlation of the inner electrons along with relativistic effects. In our opinion, in order to get a quantitative agreement of the spectroscopic constants with the corresponding experimental data, inclusion of these effects is inevitable. It is noteworthy that, in order to make contact with physical reality, using large basis sets and extrapolations to the complete basis set (CBS) limit is essential, though we have not explored this aspect in the current paper. A good deal of quantitative information has been learned about  $\text{Cl}_2$  and  $\text{Br}_2$  from this study, but a considerable amount of additional theoretical research should be performed in order to understand the molecular species better.

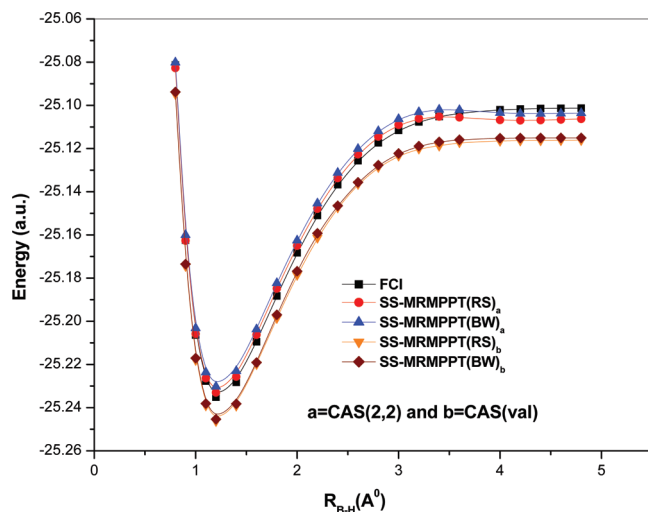
The calculated values of the dissociation energy exhibit the trend  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2$  [see also Figure 6], as also observed experimentally. This is usually explained by enhanced Pauli

repulsion between the occupied  $p(\pi)$  orbitals, which is particularly strong in  $\text{F}_2$  because it has the shortest bond of the dihalogens. The plots shown in Figure 6 need special mention at this juncture. Here, we have plotted the potential energy surfaces for the  $X_2$  system ( $X = \text{F}, \text{Cl}, \text{Br}$ ), and for a clear presentation we have subtracted out the energy value at the equilibrium internuclear distance for the concerned system in an attempt to emphasize the actual trend in the data. It is quite evident that the computed equilibrium bond distances via SS-MRMPPT(BW) and SS-MRMPPT(RS) agree well with the experimental trend for the  $X_2$  systems, that is,  $R_{\text{eq}}(\text{F}-\text{F}) > R_{\text{eq}}(\text{Cl}-\text{Cl}) > R_{\text{eq}}(\text{Br}-\text{Br})$ .

**B. Ground State PES of BH Molecule.** In this subsection, we consider the dissociation of the diatomic boron hydride (BH) molecule, where the presence of an open-shell model function(s) is necessary for the accurate description of nondynamical correlation. The accurate computation of the ground-state ( $X^1\Sigma^+$ ) PES of the BH molecule is a “touchstone” for many ab initio methods.<sup>18,52,71–81</sup> The ground state reaction path of the BH system shows varying degrees of quasi-degeneracy with a rather physical nature and hence is appropriate to test the efficacy of the different multireference many-body methods. Thus, for this molecule, the use of the spin-free SS-MRPT method in studying PES seems to be justified. It is well documented that MP2, MP3, and MP4 schemes of the SR-based method cannot lead to a correct dissociation limit.<sup>64</sup> Kowalski and Piecuch<sup>76</sup> observed that the quality of the results of the CCSD[T], CCSD(T), and CCSD(TQ<sub>f</sub>) methods is not as good at larger bond distances. They have demonstrated that the renormalized CC methods<sup>82</sup> are able to remove the failures of the traditional SRCC methods at a larger internuclear bond separation. Al-Saidi et al.<sup>81</sup> also observed the failure of RCCSD(T) with the cc-pVXZ basis to describe the BH molecule for larger bond lengths. They observed that AFQMC/cc-pVDZ results are in very good agreement with FCI energies and exhibit uniform behavior across the entire PES. Dutta and Sherrill<sup>75</sup> also showed that the performance of MP2 and CCSD(T) goes down with very large errors in the bond breaking region [the computed PES has an unphysical shape in the intermediate bond breaking region]. This arises from the inapplicability of SR-based theory in cases of strong degeneracies as occurring at large bond distances. Dutta and Sherrill<sup>75</sup> summarized that methods on the basis of the UHF reference exhibiting significantly better performance for BH molecule than the RHF reference. In our calculation, we have used the CASSCF reference, as it is able to dissociate BH in a correct manner.

To compute PES, for this molecule, we have employed two different basis sets, namely, 6-31G\*\* and cc-pVQZ, which enables a comparison with the exact FCI results.<sup>52,80</sup> In both cases, we employed a CAS(2,2) [(core) $\sigma^2$ , (core) $\sigma^{*2}$ , and (core) $\sigma\sigma^*$ ]. As already mentioned, we also present the calculations performed on the BH molecule employing the same CAS scheme [CAS(val)] and basis as used by Sherrill and co-workers<sup>52</sup> for a comparison with the literature data of various previous calculations. The larger the space, the larger is the amount of the nondynamical correlation introduced. Calculations with a second active space, CAS-



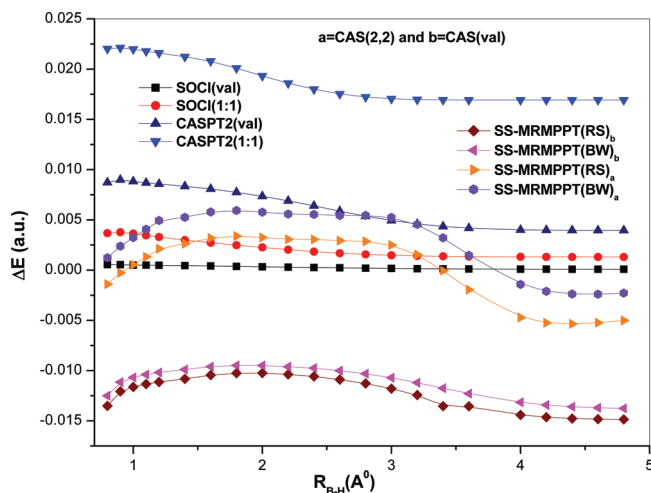


**Figure 7.** Potential energy surfaces for the BH molecule in the cc-pVQZ basis set.

(val), have been performed in order to see whether this active space could give a more balanced treatment of the correlation effect for the target state. As CAS contains open-shell CSF, it is desirable to apply a proper spin-adapted state-specific theory to compute a completely accurate PES. The use of the cc-pVXZ basis set in our present calculations of spectroscopic constants is due to the possibility of direct comparison with calculations by other methods including the FCI one. Sherrill and co-workers<sup>78,79</sup> have provided several spectroscopic constants for the ground state of BH using different types of basis sets including the cc-pVXZ via FCI method.

Dissociation PESs for the BH molecule for the cc-pVQZ basis via the CASPT2, SOCI, and FCI methods have been reported by Abrams and Sherrill.<sup>52</sup> The PES obtained by the SS-MRMPPT method along with FCI are displayed in Figure 7. As far as the shape of the resulting PES is concerned, it is observed that the SS-MRMPPT/CAS(val) also produces a qualitatively correct PES, just as that of the FCI one. Therefore, we feel encouraged to investigate the PES using the larger reference space, CAS(val), and we are interested to see whether an increase of the reference space improves the results. Here, we want to mention that the quality of the SS-MRMPPT/CAS(val) PES is slightly better than the CASPT2(val) as far as NPE is concerned.

We now focus our attention to the error graph with respect to the corresponding FCI values. In Figure 8, we have plotted the corresponding graph along with previously published results using CASPT2 and SOCI methods.<sup>52</sup> In terms of these deviations, it has been observed that the CASPT2(1:1) performs much poorer than the methods considered here. The errors of SS-MRMPPT with respect to the FCI are modest, and overall SS-MRMPPT does quite well in the case of BH. Although SS-MRMPPT/CAS(2,2) values are more close to the FCI in comparison to the SS-MRMPPT/CAS(val), the errors for the former change sign in contrast to the latter one. In other words, a larger fluctuation for SS-MRMPPT/CAS(2,2) is observed relative to that for the SS-MRMPPT/CAS(val). Not only is the value of error an important issue, equally important is the requirement of the generated PES



**Figure 8.** Plots of the errors versus FCI as a function of bond length using the cc-pVQZ basis set.

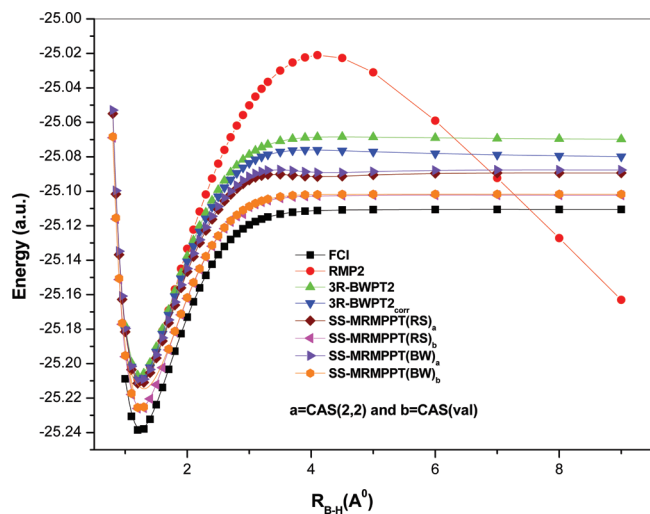
**Table 8.** Nonparallelity Error (NPE) in kcal/mol for BH Using Various Basis Sets<sup>a</sup>

basis	method	NPE
cc-pVQZ	CASSCF(val)	9.25
	SS-MRMPPT(RS)/CAS(val)	2.86
	SS-MRMPPT(BW)/CAS(val)	2.65
	SOCI(val)	0.29
	SOCI(1:1)	1.54
	CASPT2(val)	3.16
6-31G**	CASPT2(1:1)	3.26
	SS-MRMPPT(RS)/CAS(2,2)	4.82
	SS-MRMPPT(BW)/CAS(2,2)	4.76
	SS-MRMPPT(RS)/CAS(val)	2.89
	SS-MRMPPT(BW)/CAS(val)	2.68
	3R-BWPT2	7.38
	3R-BWPT2 <sub>corr</sub>	4.83
	BWCCSD	7.16

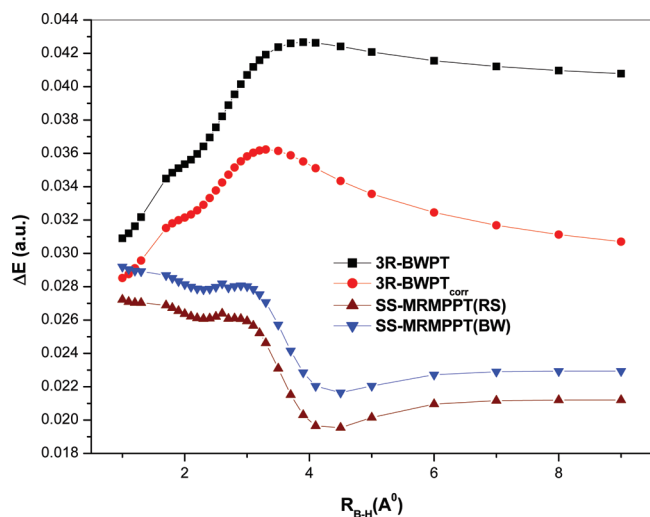
<sup>a</sup> SOCI and CASPT2 values have been taken from ref 52. BWPT and BWCC values have been taken from ref 80.

to be parallel to the corresponding FCI one. The deviation of SS-MRMPPT/CAS(val) from FCI is comparable with that of CASPT2(val). For better clarity, in Table 8, we also summarized the nonparallelity errors (NPE). For a given set of calculations in a dissociative surface, the NPE is defined as the difference between the maximal and minimal deviations from the exact FCI PES. The NPE for SS-MRMPPT approaches are very modest. In terms of the NPE (indicating the quality of the overall shape of the PES), we observe that the SS-MRMPPT/CAS(val) PES is marginally better than the CASPT2 method.

Recently, Paap et al.<sup>80</sup> have published applications of multireference state specific second-order Brillouin–Wigner perturbation theory (BWPT2) to the bond breaking process in the ground state of the BH molecule using the 6-311G\*\* basis. It is thus instructive to examine the performance of SS-MRMPPT(BW) using the same basis set. The results of the BWPT2 method are then used to access the performance of the calculations based on the SS-MRMPPT method. In Figures 9 and 10, we have summarized results for the 6-311G\*\* basis as a function of the nuclear separation. Also, as expected, the RMP2<sup>80</sup> is seen to perform reasonably well at smaller internuclear separations but becomes increasingly



**Figure 9.** Potential energy surfaces for the BH molecule in the 6-311G\*\* basis set.



**Figure 10.** Plots of the errors versus FCI as a function of bond length using the 6-311G\*\* basis set [CAS(2,2) has been used in SS-MRMPPT calculations].

poor (diverging in nature) as one goes over to large nuclear separations (owing to the poor quality of the RHF wave function in describing bond breaking), indicating the necessity of a multireference description. Figure 10 illustrates that the BWPT2 energies are in less agreement with FCI than the SS-MRMPPT with CAS(2,2) and CAS(val). In the 6-311G\*\* basis, SS-MRMPPT with CAS(val) gives a better overall accuracy and a more uniform behavior than SS-MRMPPT/CAS(2,2) in mapping the PES. This is also evident from the NPE values. The NPE values calculated for various methods using the 6-311G\*\* basis are set out in Table 8. Inspecting the results listed in Figures 9 and 10 as well as the NPE values in Table 8, we can draw the conclusion that the PESs have been generated reasonably well by the SS-MRMPPT method. Considering the overall performance (in the context of NPE and spectroscopic constants) in the entire studied region of geometries for various basis sets, the SS-MRMPPT/CAS(val) scheme gives very satisfactory results with the small NPE.

In our numerical work, we thus observed that SS-MRMPPT produces a smooth and consistent behavior across the entire PES between the equilibrium and the dissociation limit in BH bond breaking for various cc-pVXZ bases, suggesting it may be used with confidence to calculate various spectroscopic constants. In Table 9, the SS-MRMPPT results are gathered and compared with those computed in the most recent theoretical studies; the experimental data are also reported. Using recent theoretical results, we have summarized spectroscopic constants calculated by CCSD(T) and FCI (acts as benchmark) values for the various cc-pVXZ basis sets of Sherrill and co-workers<sup>79</sup> in the same table. We have also included the results for various basis sets employing different methods considered here which can provide a measure of the effects due to basis set choice (i.e., which level of basis set is required to obtain a given accuracy). The choice of an appropriate basis set is especially intricate in studies on electronic states of a molecule. In order to examine the accuracy of the spectroscopic values at different levels of correlated theory, we also tabulated the coupled cluster results of Martin et al.<sup>73</sup> and Larsen et al.<sup>77</sup> with different basis sets to display the effectiveness of the SS-MRMPPT method, as a scheme, to provide spectroscopic properties. They have demonstrated the convergence aspect of spectroscopic constants of BH with respect to contracted and uncontracted basis sets. They have also illustrated that the correction due to the nonadiabatic effect is much more important in predicting spectroscopic constants accurately than that of basis set errors in the case of BH. In this context, we mention the recent work of Sherrill and coworkers.<sup>78,79</sup>

From the tabulation of data in Table 9, we observed that for each basis set the performance of the SS-MRMPPT methods in both the perturbative schemes is very close to the results of CCSD(T) and FCI for Sherrill and co-workers.<sup>78,79</sup> Here, we should recall that the SS-MRMPPT method is computationally quite less demanding compared to the significant computational cost of the CC-based methods. The works of Abrams and Sherrill<sup>78</sup> via the FCI/DZP-NO(5Z) scheme provide very sound estimations of the ground state dissociation energy, vibrational frequency, equilibrium internuclear distance, and some other measurable quantities. As we have seen for the BH molecular system, SS-MRMPPT can also compete with the precision of the other well established sophisticated *ab initio* methods. At this point, we want to discuss the accuracy of the SS-MRMPPT method to yield dissociation energy,  $D_e$ . Our best theoretical value for  $D_e$  is 3.57 eV, obtained by SS-MRMPPT(RS)/cc-pVTZ. Bauschlicher et al.<sup>74</sup> determined a  $D_e$  of 3.65 eV using (4e-/9) orbital complete active space multireference configuration interaction wave functions. A more accurate  $D_e$  value was computed by Curtiss and Pople<sup>72</sup> through QCISD(T) calculations. The most recent calculation by Miliordos and Mavridis<sup>83</sup> provides a value for  $D_e$  of 3.53 eV. Our works thus provide very sound estimations of the ground state dissociation energy of BH. As far as the computational cost is concerned, the overall agreement of the SS-MRMPPT  $D_e$  with accurate high-level theoretical methods is very good, giving general support to the reliability of the present SS-MRMPPT results. From a comparative study of various

**Table 9.** Spectroscopic Constants for the Electronic Ground State of BH Molecule Using Different cc-pVXZ Bases<sup>a</sup>

basis	method	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
cc-pVDZ	CASSCF	1.2672 (1.2665)	2269 (2277)	3.25 (3.12)
	SS-MRMPPT(RS)	1.2582 (1.2552)	2310 (2347)	3.35 (3.28)
	SS-MRMPPT(BW)	1.2581 (1.2554)	2310 (2346)	3.34 (3.28)
	CCSD(T) <sup>b</sup>	1.2558	2342.65	
	FCI <sup>b</sup>	1.2560	2340.72	3.44
cc-pVTZ	CASSCF	1.2512 (1.2504)	2275 (2278)	3.36 (3.18)
	SS-MRMPPT(RS)	1.2296 (1.2267)	2348 (2372)	3.54 (3.48)
	SS-MRMPPT(BW)	1.2299 (1.2273)	2355 (2378)	3.54 (3.45)
	CCSD(T) <sup>b</sup>	1.2354	2350.84	
	FCI <sup>b</sup>	1.2356	2348.71	
cc-pVQZ	CASSCF	1.2498 (1.2242)	2270 (2392)	3.37 (3.06)
	SS-MRMPPT(RS)	1.2317 (1.2227)	2349 (2395)	3.55 (3.46)
	SS-MRMPPT(BW)	1.2314 (1.2222)	2354 (2377)	3.55 (3.46)
	CCSD(T) <sup>b</sup>	1.2333	2358.91	
	FCI <sup>b</sup>	1.2335	2356.78	
	FCI/cc-pV 5Z <sup>b</sup>	1.23285	2358.21	
	FCI/cc-pCVDZ <sup>b</sup>	1.25434	2340.12	
	FCI/cc-pCVTZ <sup>b</sup>	1.23339	2355.26	
	FCI/cc-pCVDZ <sup>c</sup>		2340.1	
	FCI/aug-cc-pCVDZ <sup>c</sup>		2320.8	
	MRCI <sup>d</sup>	1.2301	2358	3.68
	MRCI+Q <sup>d</sup>	1.2301	2359	3.68
	RCCSD(T) <sup>d</sup>	1.2296	2361	3.68
	RCCSDT <sup>d</sup>	1.2304		3.68
	FCI/DZP <sup>e</sup>	1.2491	2339	3.48
	FCI/DZP-NO <sup>e</sup>	1.2362	2354	3.57
	FCI/DZP-NO(5Z) <sup>e</sup>	1.2362	2350	3.57
	FCI/631G <sup>**e</sup>	1.2344	2388	3.61
	FCI/WMR-ANO <sup>e</sup>	1.2675	2309	3.47
	ref 71	1.2338	2254	3.65
	exp (ref 87)	1.23217	2366.73	
	experiment	1.2324	2367	3.57

<sup>a</sup> The values in parentheses describe the values using CAS(2,2). <sup>b</sup> Ref 79. <sup>c</sup> Ref 73. <sup>d</sup> Ref 83. <sup>e</sup> Ref 78, experiment: ref 86.

spectroscopic properties, we have found that SS-MRMPPT is a reliable tool to achieve quantitative accuracy for calculating various spectroscopic properties of BH via the computation of intermolecular interaction energies over all geometries including those near the dissociation limit, as with that of X<sub>2</sub> systems.

We now discuss the aspect of the effect of orbital rotation on the SS-MRMPPT energy from a numerical point of view for the BH system. Whether or not a method is invariant depends on the ansatz and the amplitude equations. It is now well documented that there are serious difficulties in making JM-ansatz based methods orbital invariant with respect to active space rotation, although they are invariant with respect to rotations in core orbital space and inactive virtual orbital space.<sup>41,84</sup> This is a very relevant and important issue. If a molecule has degenerate representations at a high symmetry point, then it may happen very easily that the orbitals change very rapidly as a function of minor geometrical distortions. If the electronic structure method is sensitive to such rotations (for example, if the results depend on the precise definitions of the orbitals at the high symmetry point), then one can expect to obtain poor results. In our numerical analysis, we have observed that the change in SS-MRMPPT energy due to the active–active rotation is not negligible, and the change for SS-MRMPPT(BW) is less than its RS counterpart [see Table 10]. Our results indicate that the change in energy due to virtual–virtual rotations is much smaller than that of the active–active one. On the other hand, the effect of occupied–occupied orbital(s) rotations exhibits a

**Table 10.** Numerical Test of the Change in Energy (a.u.) of SS-MRMPPT/CAS(2,2) with Respect to the Orbital Rotations (about  $\pi/4$ ), Performed on the Ground State of the BH Molecule for the Equilibrium Bond Length in the cc-pVQZ Basis<sup>a</sup>

rotation	SS-MRMPPT(RS)	SS-MRMPPT(BW)
no rotation	–25.214396	–25.212309
A–A rotation	–25.220023	–25.214260
V–V rotation	–25.214455	–25.212350

<sup>a</sup> A–A, active–active; V–V, virtual–virtual.

very small influence. Thus, the resulting effective Hamiltonians,  $\tilde{H}_{\mu\nu}^{(2)}$ , of SS-MRMPPT method 5 are not invariant with respect to orbital rotations within active subspace, and therefore, to ensure reproducibility of the energies, the orbitals should be specified unambiguously.

Our study explores several general trends of MR-based methods. Figures of PESs show that the SS-MRPT procedure is able to yield a qualitatively balanced description for the equilibrium region as well as the dissociation zone of the X<sub>2</sub> and BH molecule, and the computed dissociation PESs are completely exempt from any “intruder state” problem. Our work in this paper shows that the performance of the SS-MRMPPT(BW/RS) methods to compute the spectroscopic constants of different chemical systems with varying degrees of MR character is quite satisfactory. Applications to a number of state energies and comparison with benchmark FCI results (when available) show a uniform behavior of the SS-MRMPPT formalism. We see that SS-MRMPPT recovers most of the binding energy of the X<sub>2</sub> and BH



molecules. This fact is more significant if one considers the dimension of CAS we have used. The agreement of the SS-MRMPPT spectroscopic constants with the previously published theoretical calculations is reasonably good. The accuracy of the results appears to be encouraging, taking into account the low computational cost. We have illustrated that the method gives geometries, frequency, and dissociation energies which are at least as accurate as the corresponding results obtained with the Mk-MRCC method and more reliable than the CCSDT method for  $X_2$  systems where the wave function has a strong MR character in their ground state.

From the foregoing analysis we have noticed that the two methods, SS-MRMPPT(RS) and SS-MRMPPT(BW), are also chemically accurate relative to each other. However, the performance of SS-MRMPPT(BW) is generally better than that of its RS cousin, although the RS scheme is computationally less expensive than its BW counterpart. Further work is required to assess more fully the accuracy of the SS-MRMPPT(BW) method; however, our initial results validate the accuracy of the theory vis-à-vis the experiment and other theoretical methods. Very good agreement with the experiment is observed for  $F_2$ ,  $Cl_2$ , and BH molecules using the SS-MRMPPT technique, while a relatively less satisfactory agreement is observed for  $Br_2$ . As a whole, the above numerical analysis reveals that the SS-MRMPPT is a useful method, with an extremely reasonable performance/cost ratio.

We now discuss the effect of basis set size. As is well-known, the choice of basis used for calculations of spectroscopic constants is very crucial, especially in the determination of bond dissociation energy. A closer inspection of the comparison of the computed spectroscopic constants for the various basis sets gives us an optimistic view of the expected accuracy of the individual orbital basis sets and of the infinite basis set extrapolation limit. The spectroscopic constants summarized in the tables display the necessity and utility of using large basis sets in analyzing and demonstrating intrinsic errors associated with theoretical methods. The SS-MRMPPT calculations have been performed for  $X_2$  with different basis sets using the same active space to examine the basis set effect on the quality of spectroscopic constants. The systematic exploration of various basis sets permits an assessment of the reliability of our results. Although the shape of the surface is similar for all the basis sets, there are important quantitative changes of PESs as the basis set is increased [see Figures 1 and 2]. From the tables, one notes that the variation of basis sets has a substantial effect on spectroscopic constants (which looks rather unsystematic at first glance), as it should be. From the tables of  $F_2$ , the change of spectroscopic constants appears slightly less systematic when compared to the Mk-MRCC approach. This is also true for other systems. We hope to investigate the issue more deeply in the future. However, the aforementioned findings encourage us to make the comment that the numerical accuracy of the SS-MRMPPT method is appreciably good, and the method is capable of incorporating most of the essential correlation that has been left out by the mean-field method(s). It should be noted that our calculations have not

been corrected for basis-set superposition errors (BSSE) point-by-point using the counterpoise technique. Such a correction reduces an artificial bias toward dissociation energies and bond lengths, particularly for weakly bound species, such as those investigated in this work. It is worth noting, in the dissociation PES calculations of  $F_2$ , that the contributions due to innercore electron (1s) correlation and relativistic effects (which have been excluded from the correlation treatment in the present study) to the dissociation of the molecule have been estimated to be less than 1 kcal/mol.<sup>26,85</sup> The basis set superposition error in the case of the  $F_2$  molecule is about the same in magnitude but opposite in sign. So one can expect the cancellation of these effects for the computation of the dissociation PES of  $F_2$  [see ref 85]. Nevertheless, incorporation of relativistic effects to chemical processes is not only desirable but also essential for the level of “spectroscopic accuracy” or “chemical accuracy” even for  $X_2$  and BH diatomics. Considering the pros and cons of the SS-MRPT approach, we think that further improvements are needed. However, it should also be pointed out that the corrections due to the core correlation, nonadiabatic correction, basis saturations, and relativistic(s) effects are not always necessarily negligible compared to the intrinsic errors in the methods considered.

#### IV. Conclusion

This paper is a continuation of our preceding studies<sup>40</sup> on the numerical applications of the SS-MRPT method, drawing on a previous work of Mukherjee and co-workers.<sup>14</sup> The SS-MRPT method, which is based on a multiconfiguration reference state, can provide increased accuracy for treating potential energy surfaces far from equilibrium, certain types of excited states, and the mapping of complete reaction paths. The SS-MRMPPT method includes nondynamical and dynamical correlation effects in a balanced way in the electronic wave function of closed-shell and open-shell states and performs satisfactorily at low numerical expenses (the only problem seems to be a rapidly increasing cost of CASSCF with the increasing size of the active space). For large systems, SS-MRPT is usually the method of choice instead of SS-MRCC (can only be applied to relatively small electron systems because of their high computational cost) as the former gives a manageable accuracy/cost ratio for dealing with multiconfigurational problems.

A characteristic application of SS-MRPT is to describe bond dissociation processes in rather complicated cases with a satisfactory accuracy. The SS-MRMPPT in RS and BW variants is endowed with the desirable properties of strict separability and *absence of intruder states*. The SS-MRPT can handle the lowest energy state regardless of charge or spin symmetry with reasonable and consistent accuracy, supporting our use of this method as a “standard” for treating small- to medium-sized systems. As the validity of the SS-MRMPPT(RS) has already been illustrated in a large number of earlier publications,<sup>40</sup> this work focuses on establishing the efficacy of the SS-MRMPPT(BW) method. We have included the results of SS-MRPT, using Møller–Plesset (MP) as well as Epstein–Nesbet (EN) partitions with respect to

the RS and BW expansion. In order to show that our results are not spoiled by intruder state effects that are not related to the partitioning, intruder containing molecules and reference spaces have been investigated here.

In this work, we performed SS-MRMPPT calculations using complete active space: keeping the active space as small as possible for computing the nondynamical correlation (i.e., proper dissociation). The aim of the present investigation is to calibrate the adequacy of the SS-MRPT approach through the computation of the reaction paths of singlet ground states of  $X_2$  [ $X = F, Cl, \text{ and } Br$ ] and BH for Dunning's correlation-consistent double-, triple-, and quadruple- $\zeta$  basis sets. As recognized in several studies, along the dissociating reaction path of  $X_2$  and BH, the zeroth-order reference function changes multiconfigurationaly, and hence the bond breaking involved is difficult to handle computationally. Therefore, the dissociation of  $X_2$  and BH molecular systems is a demanding test case used traditionally to benchmark new computational methods. In order to display the performance of the SS-MRMPPT method, the potential energy surface obtained using the SS-MRPT method (without changing the size of the CAS) is used to calculate the spectroscopic constants. The accuracy of the computed SS-MRMPPT spectroscopic constants is assessed by comparing them with the corresponding accurate and established theoretical and experimental results (whenever available). In general, agreement between the SS-MRMPPT and experiment is significantly better than that with its EN counterpart for the systems studied by us in this paper. With the example applications presented here, it seems that it may not be fair at this stage to conclude definitively about the relative performance of SS-MRMPPT and SS-MRENPT methods. More exhaustive calculations, in particular for the SS-MRENPT, are needed to come to a definitive conclusion, which is on the way. In the present work, the applicability of the SS-MRMPPT(BW) method to  $X_2$  and BH systems is documented in detail. In the case of  $F_2$  system, we consider results from full-blown Mk-MRCC (parent SS-MRCC theory) and BW-MRCC calculations for a comparison reported recently which establishes the fact that the SS-MRMPPT method provides a convenient way (considering the rather low computational effort) to generate an accurate potential energy surface involving bond breaking to provide spectroscopic constants of good quality for the ground state of  $F_2$ . It has been demonstrated that the SS-MRMPPT(BW) along with its RS counterpart provide very good results for single bond breaking over the entire reaction pathways, eliminating the failures of the conventional MRPT methods in those multireference situations. It is to be remarked that our SS-MRMPPT results for the RS and BW expansion produce spectroscopic properties close to each other even in the smallest CAS space. The foregoing numerical analysis of the SS-MRMPPT(RS) and SS-MRMPPT(BW) results demonstrates clearly that the BW values are better as compared to the RS values, as is seen in the NPE value. The different spectroscopic constants that we have computed too point to this. Our numerical results also confirm that the orbital rotation effect on the energy is less in the case of SS-MRMPPT(BW) in comparison to its RS counterpart.

Thus, the SS-MRMPPT(BW) method can be considered as a very effective perturbative companion of the state-specific multireference coupled cluster method of Mukherjee and co-workers.

The issue that merits separate discussion at this juncture is the extent of relaxation of the reference coefficients in SS-MRMPPT. The effect of large mixing of reference functions and consequent relaxation cannot be estimated fully by SS-MRMPPT(RS), while the SS-MRPT(BW) scheme takes this relaxation fully during the computation of cluster amplitudes and energy. Here it should be mentioned that, if the computational model does not allow relaxation of the coefficients of the reference configurations in the correlation treatment, a correct description of the potential energy surfaces where the orbitals change very rapidly as a function of minor geometrical distortions (as in the case of weakly avoided crossings) cannot be expected. We plan to explore this issue in the near future by considering systems that pose such complexities.

A source of error in our SS-MRPT results (especially in the context of  $Br_2$ ) is the exclusion of the relativistic effects. Additionally, a proper and good description of the electronic structure of the  $X_2$  must involve an improvement of construction of the zero-order wave function. Our findings demonstrate that the SS-MRPT approach can indeed accommodate most of the effects responsible for binding in the  $F_2$ ,  $Cl_2$ ,  $Br_2$ , and BH molecules. This paper presents an effort toward the ongoing research to produce the accurate spectroscopic parameters for  $F_2$ ,  $Cl_2$ ,  $Br_2$ , and BH which one can use in a variety of spectroscopic and chemical applications. The present results should prove useful in the calibration of new theoretical methods for bond breaking. In order to achieve chemical accuracy for our computed spectroscopic constants with respect to the experimental findings, incorporation of relativistic effects is an inevitable issue. Our observations suggest that the SS-MRMPPT is a very reasonable and useful variant of MRPT with comparable strengths, and the corresponding wave function has sufficient flexibility to model the large changes in electronic structure that can occur during chemical reactions. As a final remark, we can say that the success of the method ensures that a great deal of additional work on the SS-MRPT programs is to be expected in the days to come.

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