1822 *J. Phys. Chem. A* **1999,** *103,* 1822−1830

Molecular Applications of a Size-Consistent State-Specific Multireference Perturbation Theory with Relaxed Model-Space Coefficients

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Received: August 6, 1998; In Final Form: November 13, 1998

We explore in this paper the efficacy of the Rayleigh−Schrödinger (RS) and the Brillouin−Wigner (BW) perturbative counterparts of our recently developed multireference state-specific coupled-cluster formalism (SS-MRCC) with a complete active space (CAS). It is size-extensive and is designed to avoid intruders. The parent SS-MRCC method uses a sum-of-exponentials type of Ansatz for the wave operator. The redundancy inherent in such a choice is resolved by postulating suitable sufficiency conditions which at the same time ensure size-extensivity and size-consistency. The combining coefficients c_μ for ϕ_μ's are completely relaxed and are obtained by diagonalizing an effective operator in the model space, one root of which is the target eigenvalue of our interest. By invokation of a suitable partitioning of the Hamiltonian, very convenient perturbative versions of the formalism in both the RS and the BW forms are developed for the second-order energy. The unperturbed Hamiltonian is akin to the Epstein−Nesbet type when at least one of the orbitals is inactive and is the entire active portion of the Hamiltonian when all the orbitals involved are active. Illustrative numerical applications are presented for potential energy surfaces (PES) of a number of model and realistic systems where intruders exist and for molecules in their ground states with pronounced multireference character. Single reference MBPT and effective Hamiltonian-based multireference MBPT second-order results are also presented for comparisons. The results indicate the smooth performance of our state-specific perturbative formalisms in and around the region of intruders in the PES, indicating their suitability in bypassing intruders. In contrast, the effective Hamiltonian-based MBPT methods behave poorly in the regions of intruders.

I. Introduction

Attempts to develop methods capable of reliable computations of potential energy surfaces (PES) continue to remain an important area of activity in quantum chemistry. The methodological challenges such as ensuring size-consistency over a wide range of molecular geometries in a manifest manner, keeping a uniform quality of the wave function around the regions of real or avoided curve-crossings, and designing formulations which are tailored to bypass intruders seem not to be resolved completely as yet. Although the multireference CI (MRCI) methods have been widely used over the past two decades, the results are usually adjusted in a rather ad-hoc manner by invoking empirical size-extensivity corrections.[1] The multireference many-body perturbation theory (MR-MBPT) with a complete active space (CAS)[2,3] in the effective Hamiltonian framework ensures size-extensivity in an explicit fashion, but their practical utility remains limited in scope due to the ubiquitous intruder problem.[4] However, using various shift techniques, which characterize clever partitioning of the Hamiltonian, reasonable results have been obtained in many cases.[5] Such stratagems will not, however, work for nonperturbative approaches such as multireference coupled cluster methods where the full, rather than a partitioned, Hamiltonian figures. Thus, for the multireference coupled cluster methods using effective Hamiltonians,[6−8] the disadvantages stemming from intruders is serious indeed. It appeared at one time that working with incomplete model spaces[9−12] would resolve the intruder problem. While this is true for studies at a fixed molecular geometry, such as one needs in spectroscopy, there are still problems for potential energy surface (PES) studies since there are usually different intruders in the different regions of potential energy surfaces.

It seems now that the most promising approach to bypass intruders, yet at the same time retaining manifest size-extensivity, would be to start out with a multideterminant reference space but to target just the specific state of our interest. This has been the main thrust in some of the state-specific multireference perturbation theories in vogue today.[13−17] There have also been recent developments of a coupled cluster analogue of these methods.[18−19] All of them provide a contracted description of the reference function in the sense that the combining coefficients of the reference determinants in the CAS function are fixed at some preassigned values (usually from a variational optimization of the CAS function). This *unrelaxed description* of the coefficients might in some cases lead to poorer convergence of the above formalisms, particularly in the presence of intruders which tend to modify the coefficients drastically. An attractive alternative is to obtain the coefficients via the diagonalization of an effective operator (now called the intermediate Hamiltonian[20]) in the reference space. We may call such formalisms as using *relaxed* model-space coefficients. Such formulations have appeared recently in the literature.[20−24] We have invoked the coupled cluster Ansatz to represent the exact function as a cluster expansion around the multideterminant reference function.[19,25−28] We mention in particular our latest formulation, hereafter called the state-specific multireference coupled cluster (SS-MRCC) theory,[19,28] which treats all the reference determinants on the same footing and is thus

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10.1021/jp9832995 CCC: $18.00

potentially capable of describing electron correlation over a wide region of PES, where the relative importance of the reference determinants might change significantly. Preliminary applications of the method gave very encouraging results.[28] As a practical tool of being applicable to bigger molecules, where a full-fledged CC formulation would be computationally rather demanding, it seems worthwhile to explore the efficacy of the perturbative counterparts of the formalism. It turns out that the SS-MRCC theory is quite rich in its structure in that it subsumes in it size-consistent versions of both a Rayleigh−Schrödinger (RS) and a Brillouin−Wigner (BW) perturbation theory, depending on the expansion strategy. We develop and apply in this paper the first-order RS and BW perturbative expansion of the wave function of our SS-MRCC formalism, which provides the second-order energy. Henceforth, we shall refer to our state-specific size-consistent multireference formalism as the SS-MRPT method.

In section II, we present a brief resume of our SS-MRCC method. This serves both as an introduction of the essential ingredients of the approach and as a prelude to the perturbative formulations to follow. The RS and the BW versions of the perturbation theories are covered in section III. In section IV, we present the illustrative numerical applications, along with discussions. Section V contains the summarizing remarks.

II. A State-Specific Coupled-Cluster Theory with a Relaxed Reference Function: Brief Resume

We describe briefly here the essential aspects of the SS-MRCC formalism. We start with a set of reference determinants which ensure a proper dissociation of a molecular state into appropriate fragments. For detailed discussions leading to the formulation and the proof of its size-extensivity and size-consistency, we refer to our recent publications.[19,28]

Following the traditional convention of quasidegenerate many-body nomenclature, we term the doubly filled orbitals as inactive “core” orbitals, the partially filled occupied ones as active “valence” orbitals, and the virtual orbitals not contained in the reference function as inactive “particle” orbitals. We write the reference function ψ_0 as a combination of the reference determinants ϕ_μ spanning the CAS-space:

$$\psi_0 = \sum_\mu c_\mu \phi_\mu \tag{1}$$

The exact function ψ is written as a cluster expansion involving cluster operators T^μ exciting from corresponding ϕ_μ’s:

$$\psi = \sum_\mu \exp(T^\mu)\phi_\mu c_\mu \tag{2}$$

Each T^μ excites to all the virtual functions from ϕ_μ. Such a cluster expansion Ansatz was first used in the effective Hamiltonian context[8] and has recently been exploited in the state-specific formulations as well.[19,24,28] Since each ϕ_μ has different sets of active orbitals, any specific core-to-particle excitation would lead to a different virtual determinant from each ϕ_μ. This is however not so for excitations involving active orbitals. Thus, we would encounter redundancy of the cluster operators involving active orbitals. To determine all of them, we have to invoke suitable sufficiency conditions.

ψ satisfies the Schrödinger equation with the eigenvalue E:

$$H\psi = H\sum_\mu \exp(T^\mu)\phi_\mu c_\mu = E\psi \tag{3}$$

To generate the equations determining the cluster amplitudes as well as the energy and the coefficients, it is convenient to rewrite $H\exp(T^\mu)$ for each μ in eq 3 in normal order taking each ϕ_μ as the vacuum. Using Wick’s theorem, we then find

$$H\exp(T^\mu) = \{\overline{H\exp(T^\mu)}\exp(T^\mu)\}_\mu = \exp(T^\mu)\{\overline{H\exp(T^\mu)}\}_\mu \tag{4}$$

The connected entity $\bar{H}_\mu \equiv \{\overline{H\exp(T^\mu)}\}_\mu$ denotes all terms obtained by joining the operators in H with those of T^μ. The notation $\{\cdots\}_\mu$ signifies that the operator inside the brace has been written in normal order with respect to ϕ_μ as the vacuum. Since T^μ has only hole-particle excitations of various ranks, the entire factor $\exp(T^\mu)$ can be taken out of the second equality of eq 4 from the left, leading to the right side of eq 4.

The coefficients c_μ for a CAS-CI or a CAS-SCF based ψ can be determined by rewriting each term in the sum on the right side of eq 3 in normal order with respect to the corresponding ϕ_μ, using eq 4 and projecting onto the reference determinants:

$$\sum_\nu \langle\phi_\mu|H\exp(T^\nu)|\phi_\nu\rangle c_\nu = \sum_\nu \langle\phi_\mu|\{\overline{H\exp(T^\nu)}\exp(T^\nu)\}_\nu|\phi_\nu\rangle c_\nu = \sum_\nu \langle\phi_\mu|\overline{\{H\exp(T^\nu)\}_\nu}|\phi_\nu\rangle c_\nu \equiv \sum_\nu \langle\phi_\mu|\bar{H}_\nu|\phi_\nu\rangle c_\nu = Ec_\mu \tag{5}$$

Since our model space is a CAS, the uncontracted operators in T^ν in the second equality of eq 5 always lead to excitations out of the model space, and this is why we have the simplification leading to the third equality of eq 5.

From now on, we shall denote the matrix-element $\langle\phi_\mu|\bar{H}_\nu|\phi_\nu\rangle$ by the symbol $\tilde{H}_{\mu\nu}$. $\tilde{H}_{\mu\nu}$ is clearly a connected term if the operator T^ν is connected. Using eq 5, the equation determining the eigenvalue E is given by

$$\sum_\nu \tilde{H}_{\mu\nu} c_\nu = Ec_\mu \tag{6}$$

For determining the cluster amplitudes, we again start from eq 3 and obtain

$$\sum_\mu \exp(T^\mu)Q\bar{H}_\mu|\phi_\mu\rangle c_\mu + \sum_{\mu\nu}\exp(T^\mu)|\phi_\nu\rangle\tilde{H}_{\nu\mu}c_\mu = E\sum_\mu \exp(T^\mu)|\phi_\mu\rangle c_\mu \tag{7}$$

where Q is the projector onto the virtual space spanned by the set $\{\chi_l\}$ and the sum $\sum_\nu|\phi_\nu\rangle\langle\phi_\nu|$ is the projector P onto the space of reference determinants. Due to the presence of linearly dependent cluster amplitudes, eq 7 would generate an insufficient number of equations for determining all the cluster amplitudes. We have proposed recently[19,28] a set of sufficiency conditions which lead in a natural manner to a manifestly size-extensive formalism.

In order to arrive at these equations, we first *interchange the dummy indices* μ and ν in the second term on the left side of eq 7. We next note that, instead of using the traditional form of the resolution of identity, we can invoke a completely equivalent expression of the form

$$I = \exp(T^\mu)[Q+P]\exp(-T^\mu) \equiv \bar{Q}_\mu + \bar{P}_\mu \tag{8}$$

Using this new resolution of identity, we can write the rearranged eq 7 as

$$\sum_{\mu}[\bar{Q}_{\mu} + \bar{P}_{\mu}] \exp(T^{\mu})Q\bar{H}_{\mu}|\phi_{\mu}\rangle c_{\mu} + \sum_{\mu\nu}[\bar{Q}_{\mu} + \bar{P}_{\mu}] \exp(T^{\nu}) \times |\phi_{\mu}\rangle\tilde{H}_{\mu\nu}c_{\nu} = E\sum_{\mu}[\bar{Q}_{\mu} + \bar{P}_{\mu}] \exp(T^{\mu})|\phi_{\mu}\rangle c_{\mu} \quad (9)$$

We now posit the *sufficiency conditions* that the terms in eq 9 containing $\bar{Q}_{\mu}$ for each μ are equal:

$$\bar{Q}_{\mu} \exp(T^{\mu})\bar{H}_{\mu}|\phi_{\mu}\rangle c_{\mu} + \sum_{\nu}\bar{Q}_{\mu} \exp(T^{\nu})|\phi_{\mu}\rangle\tilde{H}_{\mu\nu}c_{\nu} = \bar{Q}_{\mu} \exp(T^{\mu})|\phi_{\mu}\rangle \quad (10)$$

The right side of eq 10, however, vanishes, since Q annihilates fuctions of the model space:

$$\bar{Q}_{\mu} \exp(T^{\mu})|\phi_{\mu}\rangle = \exp(T^{\mu})Q|\phi_{\mu}\rangle = 0 \quad (11)$$

Using the expression of $\bar{Q}_{\mu}$, and the linear independence of each function χ_l constituting Q, we deduce that

$$\langle\chi_l|\bar{H}_{\mu}|\phi_{\mu}\rangle c_{\mu} + \sum_{\nu}\langle\chi_l|\exp(-T^{\mu}) \exp(T^{\nu})|\phi_{\mu}\rangle\tilde{H}_{\mu\nu}c_{\nu} = 0 \ \forall\ l, \mu \quad (12)$$

The above set leading to eq 12 are our stipulated working equations for determining the cluster amplitudes of T^{μ}. It is straightforward to verify that the remaining part of eq 9, containing P, would also be equal and would generate eq 6, which indicates the consistency of our sufficiency conditions vis-a-vis eq 7. Let us note that in solving the equations for the cluster amplitudes, eq 12, the knowledge of the coefficients c_{μ}'s is required. The two sets are thus coupled. At the end, we obtain both the cluster amplitudes and the relaxed coefficients from the diagonalization, eq 6.

We should emphasize here that the interchange of the dummy indices μ and ν in the second term of the left side of eq 7 is essential to arrive at a size-extensive formulation. Invoking a similar sufficiency condition for each μ in the parent expression, eq 7, leads to a size-inextensive theory, which is related structurally to some other recent attempts.[24,29] The proof for connectedness of the cluster amplitudes from eq 12 hinges essentially on completeness of the active space and the connectedness of the composite $\sum_{\nu}\langle\chi_l|\exp(-T^{\mu}) \exp(T^{\nu})|\phi_{\mu}\rangle\tilde{H}_{\mu\nu}c_{\nu}/c_{\mu}$. For details the reader is referred to our recent papers,[19,28,30] where these aspects are discussed at length.

Since the reference determinants span a CAS, it also follows that the energy obtained as the eigenvalue of eq 6 is also size-extensive. The extensivity of the energy also implies correct separation into fragments generated from the active orbitals and, hence, size-consistency.

III. Emergence of RS and BW State-Specific Perturbation Theories with Relaxed Coefficients

For the perturbative formulations up to the first order in cluster operators, it is convenient to rewrite our SS-MRCC equation, eq 12, in the following quasilinearized form:

$$[\langle\chi_l|H|\phi_{\mu}\rangle + \sum_{m}(\langle\chi_l|H|\chi_m\rangle - \langle\phi_{\mu}|\bar{H}_{\mu}|\phi_{\mu}\rangle\delta_{lm})\langle\chi_m|T^{\mu}|\phi_{\mu}\rangle + \cdots]c_{\mu} + \sum_{\nu}\langle\chi_l|[T^{\nu} - T^{\mu}] + \cdots|\phi_{\mu}\rangle\tilde{H}_{\mu\nu}c_{\nu} \equiv [\langle\chi_l|H|\phi_{\mu}\rangle + (\sum_{m} \langle\chi_l|H|\chi_m\rangle - \langle\phi_{\mu}|\bar{H}_{\mu}|\phi_{\mu}\rangle\delta_{lm})\langle\chi_m|T^{\mu}|\phi_{\mu}\rangle + \cdots]c_{\mu} + \sum_{\nu}\langle\chi_l|T^{\nu} + \cdots|\phi_{\mu}\rangle\tilde{H}_{\mu\nu}c_{\nu} - E\langle\chi_l|T^{\mu}|\phi_{\mu}\rangle c_{\mu} = 0 \ \forall\ l, \mu \quad (13)$$

Starting from the above equation, we now generate appropriate RS and BW perturbative expansions in a systematic manner. To achieve this, we first partition the Hamiltonian into an unperturbed component H_0 and a perturbation V. We then expand each cluster operator T^{μ} appearing explicitly in the equation above as a power series in V. In the RS development, we also expand E as a power series. However, for the BW formulation, we leave E unexpanded. The treatment of the terms $\langle\phi_{\mu}|\bar{H}_{\mu}|\phi_{\mu}\rangle$ in eq 13 needs some special care. For the RS theory, we expand $\langle\phi_{\mu}|\bar{H}_{\mu}|\phi_{\mu}\rangle$ again as a power series. For the BW case, however, we leave it unexpanded just as for E.

Denoting by $T^{\mu(n)}$ the cluster operator T^{μ} at order n and collecting all terms of order n, we then obtain the formal expressions of the state-specific RS or BW multireference perturbation theory (SS-MRPT) of order n. In particular, the cluster amplitudes at the first order for the RS expansion are obtained from

$$[\langle\chi_l|H|\phi_{\mu}\rangle + \sum_{m}(\langle\chi_l|H_0|\chi_m\rangle - \langle\phi_{\mu}|[H_0]_{\mu}|\phi_{\mu}\rangle\delta_{lm}) \times \langle\chi_m|T^{\mu(1)}|\phi_{\mu}\rangle]c_{\mu} + \sum_{\nu}\langle\chi_l|T^{\nu(1)}|\phi_{\mu}\rangle[H_0]_{\mu\nu}c_{\nu} - E_0\langle\chi_l|T^{\mu(1)}|\phi_{\mu}\rangle c_{\mu} = 0 \ \forall\ l, \mu \quad (14)$$

All the quantities in eq 14 are expressed using ϕ_{μ} as the vacuum. The corresponding BW version takes the following form:

$$[\langle\chi_l|H|\phi_{\mu}\rangle + \sum_{m}(\langle\chi_l|H_0|\chi_m\rangle - \langle\phi_{\mu}|\bar{H}_{\mu}|\phi_{\mu}\rangle\delta_{lm}) \times \langle\chi_m|T^{\mu(1)}|\phi_{\mu}\rangle]c_{\mu} + \sum_{\nu}\langle\chi_l|T^{\nu(1)}|\phi_{\mu}\rangle\tilde{H}_{\mu\nu}c_{\nu} - E\langle\chi_l|T^{\mu(1)}|\phi_{\mu}\rangle c_{\mu} = 0 \ \forall\ l, \mu \quad (15)$$

We note at this point that there is a coupling of the different T^{μ} operators for various μ's via the term $\sum_{\nu}\langle\chi_l|T^{\nu(1)} - T^{\mu(1)}|\phi_{\mu}\rangle[H_0]_{\mu\nu}c_{\nu}$, where the coupling essentially stems from the off-diagonal terms $[H_0]_{\mu\nu}c_{\nu}$ with $\nu \neq \mu$. Since a significant contribution of the nondynamical correlation effects comes from off-diagonal terms coupling determinants which are doubly excited with respect to one another, it is imperative that we include at least the portion of the two-body terms in H_0 which can couple the ϕ's which are doubly excited with respect to one another. Such two-body terms in H_0 have previously been considered by others as well.[16,17]

It thus warrants that we include in our H_0 all two-body terms which scatters electrons from all pairs of active orbitals to all pairs, same or different. In order to precisely define our H_0, it would be convenient to rewrite H in normal order with respect to the core as the vacuum:

$$H = E_c + \sum_{ij}\langle i|f_c|j\rangle\{a_i^{\dagger}a_j\}_c + {}^1\!/_2\sum_{ijkl}\langle ij|kl\rangle\{a_i^{\dagger}\, a_j^{\dagger}a_l a_k\}_c \quad (16)$$

Here the symbols i, j, etc., run over the one particle basis for description and E_c is the expectation value $\langle 0|H|0\rangle$ with respect to the core function $|0\rangle$ and f_c is the core Fock-like one-body operator. We now define our H_0 as a sum of E_c, the core Fock operator f_c, all the diagonal ladder operators of the two-body term of eq 16 which has at least one inactive orbital, and the entire active portion of the two-body term. This choice for H_0 is like the Epstein−Nesbet (EN) partitioning for all determinants having at least one inactive orbital, but it differs from EN in that $H_{0\mu\nu}$ coincides with just the matrix-element $H_{\mu\nu}$. This choice of H_0 is the same as the one introduced by Dyall.[17]

With this H_0, our working equation for $T^{\mu(1)}$ in the RS expansion may be written as

$$H_{l\mu}c_\mu^0 + (H_{ll} - E_0)t_\mu^{l(1)}\, c_\mu^0 + \sideset{}{'}\sum_{m,l\neq m} H_{lm}t_\mu^{m(1)}c_\mu + \sum_{\nu}^{\nu\neq\mu} \langle\chi_l|T^{\nu(1)}|\phi_\mu\rangle H_{\mu\nu}c_\nu^0 = 0 \quad (17)$$

where $\langle\chi_l|T^{\mu(1)}|\phi_\mu\rangle$ is abbreviated as $t_\mu^{l(1)}$. The prime in the sum above restricts the sum to χ_m's differing from χ_l only in the active orbitals. This is a consequence of our choice of H_0. E_0 and c_μ^0's are obtained by diagonalizing the matrix of $H_{\mu\nu}$.

The corresponding BW expression is given by

$$H_{l\mu}c_\mu + (H_{ll} - E)t_\mu^{l(1)}c_\mu + \sideset{}{'}\sum_{m,l\neq m} H_{lm}t_\mu^{m(1)}c_\mu + \sum_{\nu}^{\nu\neq\mu} \langle\chi_l|T^{\nu(1)}|\phi_\mu\rangle \tilde{H}_{\mu\nu}c_\nu = 0 \quad (18)$$

The pseudoeffective operator $\tilde{H}^{(2)}$ up to second order in both cases is given by

$$\tilde{H}_{\mu\nu}^{(2)} = \sum_l H_{\mu l}t_\nu^{l(1)} + H_{\mu\nu} \quad (19)$$

$\tilde{H}^{(2)}$ on diagonalization provides us the respective second-order energy $E^{(2)}$:

$$\sum_\nu \tilde{H}_{\mu\nu}^{(2)}\, c_\nu^{(2)} = E^{(2)}\, c_\mu^{(2)} \quad (20)$$

Equations 17−20 are our final working expressions for the evaluation of cluster operators and energy.

To get a better insight regarding the avoidance of intruders, we rewrite eqs 17 and 18 as[30]

$$t_\mu^{l(1)} = \frac{H_{l\mu}}{E_0 - H_{ll}} + \frac{\sum_{\nu}^{\nu\neq\mu} \langle\chi_l|T^{\nu(1)}|\phi_\mu\rangle H_{\mu\nu}\frac{c_\nu}{c_\mu} + \sideset{}{'}\sum_{m,l\neq m} H_{lm}t_\mu^{m(1)}}{E_0 - H_{ll}} \quad (21)$$

for the RS version and

$$t_\mu^{l(1)} = \frac{H_{l\mu}}{E - H_{ll}} + \frac{\sum_{\nu}^{\nu\neq\mu} \langle\chi_l|T^{\nu(1)}|\phi_\mu\rangle \tilde{H}_{\mu\nu}\frac{c_\nu}{c_\mu} + \sideset{}{'}\sum_{m,l\neq m} H_{lm}t_\mu^{m(1)}}{E - H_{ll}} \quad (22)$$

for the BW version. For a more detailed discussion, we refer to one of our forthcoming papers.[30]

So long as the state energy E_0 or E remains well-separated from the virtual functions, the denominators in both cases remain reasonable and this avoids intruders. This holds true even if some of the $H_{\mu\mu}$'s are close to H_{ll}.

In the preliminary applications of our perturbative formalisms, the term $\sum_m' H_{lm}t_\mu^{m(1)}$ is zero by symmetry (see Section IV). Thus, the equations used by us in this paper are

$$t_\mu^{l(1)} = \frac{H_{l\mu}}{E_0 - H_{ll}} + \frac{\sum_{\nu}^{\nu\neq\mu} \langle\chi_l|T^{\nu(1)}|\phi_\mu\rangle H_{\mu\nu}\frac{c_\nu}{c_\mu}}{E_0 - H_{ll}} \quad (23)$$

for the RS version and

$$t_\mu^{l(1)} = \frac{H_{l\mu}}{E - H_{ll}} + \frac{\sum_{\nu}^{\nu\neq\mu} \langle\chi_l|T^{\nu(1)}|\phi_\mu\rangle H_{\mu\nu}\frac{c_\nu}{c_\mu}}{E - H_{ll}} \quad (24)$$

for the BW version. This does not affect the extensivity of our formalisms. The results, described in the next section, indicate that this neglect does not significantly affect the quality of the calculations either.

IV. Molecular Applications

Algorithmic Considerations. We note that there are couplings between the various T-amplitudes in the perturbation equations, as are evident from eqs 23 and 24. But these are not too many: only those components of T^ν's with $\nu \neq \mu$ can couple which can cause excitations to χ_l by their action on ϕ_μ. Their effects can be included in an iterative manner. We start a loop for a μ. Equations 21 and 22 are then solved by using the previously computed values of T^ν's for other ν's. For the RS case, the values of the energy E_0 and the zeroth-order coefficients are obtained by diagonalizing the matrix of $H_{\mu\nu}$, and they are fixed in the iterative updating of the cluster amplitudes. Only after the convergence of the cluster amplitudes is reached, do we diagonalize the matrix of $\tilde{H}_{\mu\nu}^{(2)}$ to get both the second-order energy and the relaxed coefficients at the second order. A typical feature of the formalism up to second order of energy in the RS formulation is then the use of the zeroth-order coefficients $c_\mu^{(0)}$ to compute the cluster operators and $\tilde{H}$, *but allow the coefficients to relax* while computing $E^{(2)}$, since this is obtained by diagonalization. For the BW case, however, we update the cluster amplitudes, the energy E, and the coefficients. We have found that a fast convergence is reached by converging the cluster amplitudes first in an inner loop while keeping the coefficients and E fixed, and update E and the coefficients in an outer loop after the convergence of the cluster amplitudes in the current inner loop is reached. In the updating of E and the coefficients, eq 20 is used.

Results and Discussions. We have applied both the RS and the BW versions of our SS-MRPT method to test their relative efficacies. Most of the systems chosen by us display the essential features of quasidegeneracy and/or avoided crossings. The model problems H_4 and H_8 serve as good testing grounds for the present formalism. The reaction path of the BeH_2 model system, widely studied by various workers, also serves as another very good test case for our theory. We have carried out a very detailed calculation for the ground-state PES of the Li_2 molecule with a rather small basis, for which we could do the full CI results for comparison. A larger basis set calculation for this molecule has also been carried out, for which we could perform only the CISDTQ calculations for a similar comparison. The other PES studied by us that of the F_2 molecule. As a spin-off from our SS-MRPT, we can also study molecules of pronounced multireference character, and we have applied it to molecules CH_2 and C_2 in their ground state. For most of the systems studied, we also provide results from the single reference MBPT and the effective Hamiltonian-based multireference MBPT (MR-

TABLE 1: Comparison of the Second-Order Ground-State Energies of the P4 Model with the FCI Results[a]

R (au)	SCF (au)	SR-MBPT	MR-MBPT	SS-MRPT RS	SS-MRPT BW	FCI (au)
2.0	−1.944 133	−116.078	−0.902	1.467	6.419	−2.074 481
2.2	−1.998 014	−1.458	−0.744	0.755	5.363	−2.102 335
2.4	−2.039 775	0.283	0.133	1.025	5.363	−2.136 637
2.6	−2.072 157	1.186	1.036	1.576	5.374	−2.164 970
2.8	−2.097 241	1.937	1.917	2.167	5.678	−2.187 172
3.0	−2.116 620	2.59	2.779	2.726	6.041	−2.204 309
3.2	−2.131 526	3.159	3.646	3.228	6.398	−2.217 427
3.4	−2.142 924	3.659	4.566	3.677	7.029	−2.227 391
3.6	−2.151 583	4.109	5.612	4.082	7.029	−2.234 898
3.8	−2.158 119	4.521	6.887	4.455	7.575	−2.240 506
4.0	−2.163 026	4.878	8.525	4.775	7.801	−2.244 633

[a] H−H bond length = 2.0 au. Basis: dzv+a p function (exponent = 1.0). All energy entries except for SCF are differences with respect to the FCI values, in 10^{-3} au (mH).

MBPT) derived from the state-universal MRCC theory[8] for the sake of comparison. The latter in particular is chosen for comparison because (1) it uses the same Ansatz for the wave operator and (2) we want to assess how it performs vis-a-vis our state-specific formulation in the regions of intruders. To indicate the relative performance of the various methods, we have shown in the tables the *energy differences* with respect to the best CI results (FCI in most cases). Thus the entries for each method in the tables correspond to $E_{\text{method}} - E_{\text{CI}}$.

(a) H_4 Model Systems. The H_4 models have been widely studied by many workers[31] in various geometrical arrangements. Presently, we have carried out the calculations for the trapezoidal (H4) and rectangular (P4) geometeries. These models are examined extensively, mainly due to two reasons: (1) The degree of degeneracy can be varied continuously from a nondegenerate situation to a highly degenerate one by the variation of a single parameter defining their geometry. (2) The simplicity of the system makes a full CI calculation very easy.

(i) P4 Model. In the rectangular geometry, the distance of approach of the two H_2 molecules, *R* is varied from the square geometry, for which a complete configurational degeneracy occurs, and then gradually elongated to the rectangular geometry. The H−H distance in each H_2 molecule is kept fixed at the stretched bond length of 2.0 au to enhance the effect of quasidegeneracy which occurs at $R = 2.0$ au. The basis used for the study is a dzv+p(expnt=1.0) from the GAMESS library.

The lowest energy determinant corresponds to the configuration $\phi_1 = 1a_1^2\,1b_2^2$ in the C_{2v} symmetry, and this becomes quasidegenerate with the determinant $\phi_2 = 1a_1^2\,2a_1^2$ at $R = 2.0$ au. As *R* is increased, the quasidegeneracy fades away. We have taken these two configurations, ϕ_1 and ϕ_2, in our model space and since $2a_1$ and $1b_2$ are of different symmetery, the model space is complete. The configuration ϕ_1 has been chosen as the Hartree−Fock function.

In Table 1 we give the results for the ground-state difference energy for the molecule with respect to the FCI values. We have also listed for comparison the SCF and the differences of the single-reference based MBPT (SR-MBPT), the effective Hamiltonian-based MR-MBPT with respect to the FCI values. As is expected, around the degenerate region, the single reference results from SR-MBPT are quite inferior compared to the FCI values which warrants a truly multireference calculation. As can be seen from the table, the RS results are somewhat better than the BW values throughout.

(ii) H4 Model. This model has been first introduced by Jankowski and Paldus[32] and later studied in detail using the state-universal and valence-universal coupled cluster methodology by Paldus *et al.*[33] In this geometry again the bond length for each H_2 is taken to be 2.0 au, and they are kept in an isoceles trapezoidal position with the shorter end-to-end distance between them fixed at 2.0 au. We start out with the geometry wherein the two hydrogen molecules are placed parallel to each other, making a square configuration. This is then deformed continuously in a symmetric manner by widening the angle so that the two H_2 molecules make progressively obtuse angles with the line joining those two end points which are 2.0 au apart. The various configurations are specified uniquely by an angle ϕ, which is the difference of the actual obtuse angle and $\pi/2$. Following ref 34, we specify the configurations by a parameter $\phi = \alpha\pi$. Thus by varying α from 0 to 0.5, we go from a square configuration to a linear one. The basis used in our calculation is of DZ quality[35] with a Cartesian p function with an exponent 0.9.

TABLE 2: Comparison of the Second-Order Ground-State Energies of the H4 Model with the FCI Results[a]

α	SCF (au)	SR-MBPT	MR-MBPT	SS-MRPT RS	SS-MRPT BW	FCI (au)
0.00	−1.931 750	−295.652	−2.784	−0.369	4.044	−2.063 112
0.01	−1.951 444	−25.026	−2.878	−0.572	3.849	−2.069 401
0.02	−1.969 599	−10.280	−2.924	−0.890	3.508	−2.079 470
0.10	−2.069 109	−2.390	−2.979	−1.103	2.387	−2.160 115
0.25	−2.133 651	−1.599	−91.649	−0.962	1.579	−2.217 381
0.40	−2.148 427	−1.490	5.604	−0.923	1.390	−2.230 887
0.50	−2.150 367	−1.428	5.051	−0.854	1.427	−2.232 700

[a] H−H bond length = 2.0 au. Basis: dz+a p function. All energy entries except for SCF are differences with respect to the FCI values, in 10^{-3} au (mH).

The lowest energy determinant corresponds to the configuration $\phi_1 = 1a_1^2\,1b_2^2$ in the C_{2v} symmetry, and this becomes quasidegenerate with the determinant $\phi_2 = 1a_1^2\,2a_1^2$ at $\alpha = 0$. For intermediate values of α (in the range of 0.25), there are intruders affecting ϕ_2. In Table 2 we present the SCF, the difference energies for the single-reference based MBPT (SR-MBPT), and the effective Hamiltonian-based MR-MBPT together with our SS-MRPT(BW) and SS-MRPT(RS) with respect to the FCI values. For the SR-MBPT, ϕ_1 is taken as the reference determinant. As is evident from the table the SR-MBPT results are quite poor for low values of α. This is due to the near degeneracy of ϕ_2 with ϕ_1 at low values of α at this configuration. Both SS-MRPT (RS) and MR-MBPT work well around these geometries, though the former works much better. The MR-MBPT results are poorer midway at about $\alpha = 0.25$, clearly reflecting the presence of intruders. The present state-specific calculations are uniformly good, the RS version being generally better than the BW version. Also, as can be seen from Tables 1 and 2, the P4 model does not suffer as much from intruders as for the H4 model. In both these models, the SS-MRPT works very well.

(b) H_8 Model System. This model system studied is a sort of extension of the simple H_4 model. It too bears the essential features of the H_4 system but is bigger. As shown in Figure 1 the model comprises of eight hydrogen atoms arranged in a distorted octagonal arrangement. The four pairs of hydrogen atoms are kept at a fixed internuclear separation of 2.0 au. The pairs (5,6) and (7,8) are in fixed positions while the other two pairs are moved parallely as shown in the figure. The geometry of the model is determined simply by the distance α between the side of the regular octagon and the line indicating the internuclear separation of the moved H_2 unit. Here too the degeneracy can be varied continuously by the variation of a single parameter α as shown in Figure 1; also a FCI calculation is feasible for this system, making useful comparisons possible.

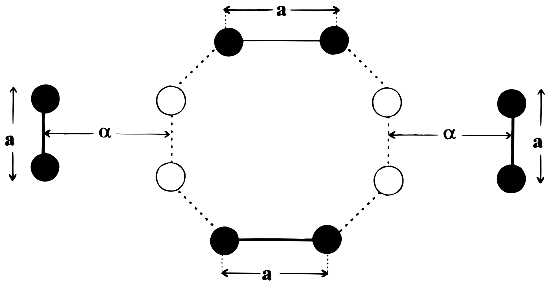

Figure 1. Geometrical arrangement of the four H_2 molecules in the H_8 model problem.

TABLE 3: Comparison of the Second-Order Ground-State Energies of H_8 with the FCI Results[a]

				SS-MRPT		
α	SCF (au)	SR-MBPT	MR-MBPT	RS	BW	FCI (au)
0.0001	−4.065 562	18.068	8.017	11.372	21.736	−4.204 803
0.001	−4.065 828	18.225	8.041	11.402	21.746	−4.204 886
0.003	−4.066 418	18.543	8.095	11.467	21.767	−4.205 075
0.01	−4.068 474	19.375	8.281	11.684	21.832	−4.205 769
0.03	−4.074 276	20.257	8.797	12.212	21.939	−4.208 036
0.06	−4.082 780	19.867	9.495	12.747	21.922	−4.212 169
0.08	−4.088 316	19.286	9.895	12.962	21.838	−4.215 336
0.10	−4.093 745	18.685	10.242	13.101	21.73	−4.218 763

[a] H−H bond length = 2.0 au. Basis and geometry: ref 36. All energy entries except for SCF are differences with respect to the FCI values, in 10^{-3} au (mH).

For the present study we have used the basis as suggested by Jankowski *et al.*[36] The parameter α is varied over a wide range of values going from 0.0001 to 0.10. We have given in Table 3 the SCF energy and the differences of our present SS-MRPT results both in the RS and BW schemes together with the differences of the SR-MBPT, MR-MBPT with respect to the FCI values. Here again, the RS values are closer to the FCI results.

(c) BeH_2 Model System. In this model system we study the C_{2v} insertion reaction of Be in H_2 to form the BeH_2 molecule. This system is interesting in that, at some distance of approach R of the H_2 molecule to Be, there is a crossing of two configurations. We take these two configurations as our model space functions. The relative importance of the model space functions vary greatly with R, so that only a state-specific function treating all the model space functions on the same footing is expected to work well. This system has the additional interesting feature that one or the other model function encounters intruders at small and large values of R, although the ground state itself remains rather well separated from the virtual states.

The system has usually been studied at specific points of the sample path as given by Purvis *et al.*[37] We too have followed the same sampling points on the reaction path. The arrangements of Be and the two H-atoms for the various H−H distances and R for all the sample points are shown in Figure 2. In Table 4 we list the SCF, the differences of the single reference-based SR-MBPT, the traditional effective Hamiltonian-based MRPT, our present SS-MRPT(RS), and SS-MRPT(BW) with respect to the full CI values for nine sample points denoted by A−I.

At geometries A−D the dominant configuration is $1a_1^2\,2a_1^2\,1b_2^2$, which in our study has been taken as ϕ_1. However, at other geometries, e.g. E−I, the determinant $1a_1^2\,2a_1^3\,3a_1^2$ is seen to have a lower energy as compared to the previous ϕ_1, resulting in an avoided crossing (between E and F). This latter configuration is treated as ϕ_2. At geometry E both these functions are seen to be equally important. Purvis *et al.*[37] have used two different reference determinants on both sides of the avoided crossing, depending on which is the dominant configuration. However, we have started with the Hartree−Fock function corresponding to the configuration $1a_1^2\,2a_1^2\,1b_2^2$ and have used it over the entire range of geometries studied here. Again since the two active orbitals are of different symmetries, they form a complete model space. Even though ϕ_1 is not the dominant function beyond sample point D, nevertheless, we have still used this configuration as our Hartree−Fock function to generate the orbitals at all distances. The success over the entire range of geometries is a stringent test of our formulation.

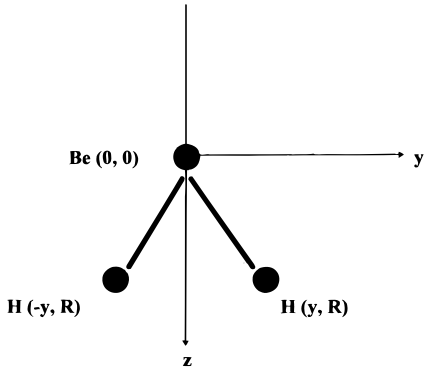

Figure 2. Geometrical arrangement of C_{2v} insertion of Be in H_2.

At the point A, the MR-MBPT diverges since there is an intruder in this region perturbing ϕ_2. Its performance gets vastly improved in the regions of quasidegeneracy involving avoided crossing. The situation worsens again around the point I, where there is again an intruder—but this time perturbing ϕ_1. The results for the SR-MBPT requires some explanation. Since ϕ_1 beyond point D is higher in energy than that of ϕ_2, the SR-MBPT generates the excited function beyond D, and these, rather than the lowest energy results, are shown in the table. The SR-MBPT works well before the point F is reached, since up to this point the function ϕ_1 is energetically well-separated from other functions. Around the point F, we have the avoided crossing of the two lowest states, and ϕ_2 acts as the intruder for ϕ_1. Beyond this point, the performance remains consistently poor, since at geometries G, H, and I ϕ_1 approaches a virtual function acting as an intruder. In contrast, the SS-MRPT results are consistently good, showing smooth behavior for all the sample points, indicating the efficacy of the methods to obviate intruders. Again, it is seen that the RS values are closer to the FCI results.

(d) Li_2 Potential Energy Surface. The study of the Li_2 PES is another natural choice for testing the efficacy of any theory which is designed to bypass intruders. This system, though rather small, has an entire range of low-lying excited states acting as intruders at various distances. The functions $\phi_1 = 1\sigma_g^2\,1\sigma_u^2\,2\sigma_g^2$ and $\phi_2 = 1\sigma_g^2\,1\sigma_u^2\,2\sigma_u^2$ comprise the two reference determinants that make up our active space and are the functions needed to describe the bond-breaking.

At the equilibrium geometry,[38] there are intruders which mix strongly with the function ϕ_2, since the active orbital $2\sigma_u$ orbital lies much higher than the other active $2\sigma_g$ orbital in this geometry. At the distances R around 5 and 9 au, there are avoided crossings of the higher excited functions with ϕ_2. Only a rather accurate theory would thus be able to give a very smooth behavior at around this point. Beyond $R = 11.0$ au the two model functions become prominently quasidegenerate.

As mentioned earlier, we have carried out detailed calculations using a small basis of DZ[35] quality and further with a somewhat larger basis (6-311G**) from the GAMESS library.

TABLE 4: Comparison of the Second-Order Ground-State Energies of BeH_2 with the FCI Results[a]

geometry	coordinates (y, R) in (au)	SCF (au)	SR-MBPT	MR-MBPT	SS-MRPT		FCI (au)
					RS	BW	
A	(2.54, 0.00)	−15.741 664	2.27	divergent	2.568	3.388	−15.779 172
B	(2.08, 1.00)	−15.699 566	1.794	3.072	1.994	2.772	−15.737 224
C	(1.62, 2.00)	−15.628 440	4.119	4.343	4.152	5.445	−15.674 818
D	(1.39, 2.50)	−15.562 676	7.016	5.675	6.547	9.053	−15.622 883
E	(1.275, 2.75)	−15.521 188	17.105	6.011	11.97	17.147	−15.602 919
F	(1.16, 3.00)	−15.477 278	114.927	0.189	5.662	23.743	−15.624 481
G	(0.93, 3.50)	−15.401 953	228.265	0.208	7.231	19.881	−15.693 194
H	(0.70, 4.00)	−15.360 226	329.646	6.608	0.576	10.666	−15.736 688
I	(0.70, 6.00)	−15.325 420	125.164	59.573	2.432	7.311	−15.760 878

[a] Basis and geometry: ref 37. All energy entries except for SCF are differences with respect to the FCI values, in 10^{-3} au (mH).

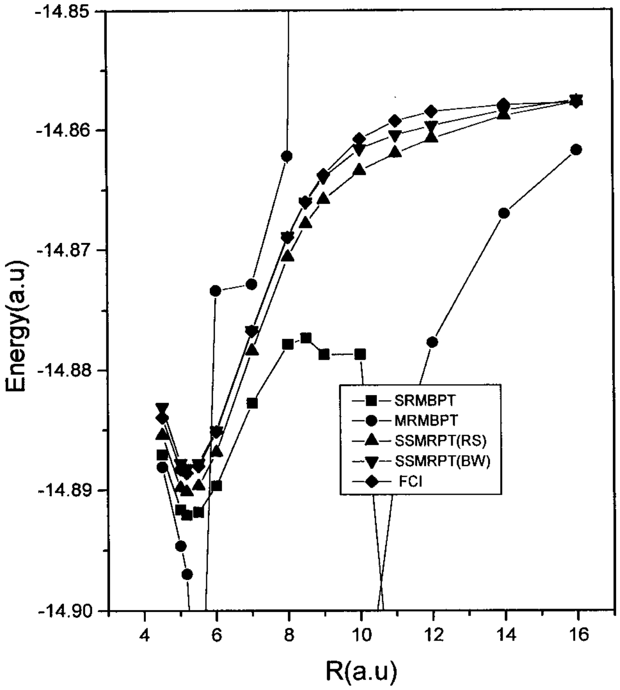

Figure 3. PES of Li_2 using DZ basis.

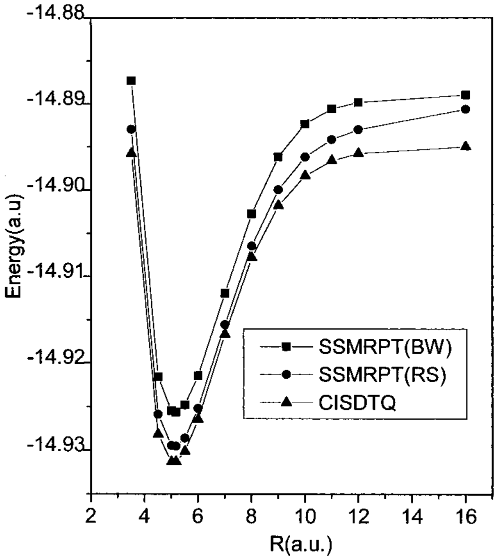

Figure 4. PES of Li_2 using 6-311G** basis.

TABLE 5: Spectroscopic Constants of Li_2 in the Ground State using SS-MRPT

method	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	$\beta\omega_e$ (cm^{-1})
SS-MRPT(RS)[a]	2.723	0.874	362.3479	4.657
SS-MRPT(BW)[a]	2.727	0.840	375.123	5.195
FCI[a]	2.716	0.872	376	5.01
SS-MRPT(RS)[b]	2.635	1.100	353.166	3.513
SS-MRPT(BW)[b]	2.635	1.064	357.763	3.729
CISDTQ[b]	2.599	1.051	364.226	3.912
exptl results[c]	2.670	1.056	351	2.59

[a] Reference 35. [b] Basis: 6-311G** and a Cartesian d function (=0.2). [c] Reference 39.

For the DZ basis we have compared our results obtained by SS-MRPT(RS) and SS-MRPT(BW) methods with those from the single reference based SR-MBPT, the MR-MBPT, and the FCI calculations.

As can be seen clearly from the plots given in Figure 3, the single reference theory starting with ϕ_1 diverges at large values of R since its reference function ϕ_1 encounters an intruder in ϕ_2. More interesting is the MR-MBPT plot, which shows a discontinuity in the range of $R \approx 5-6$ au and also at $R \approx 8-10$ au, clearly indicating its breakdown in the presence of intruders. However, the state-specific plots are considerably better at all ranges of R. As expected, the results from the MR-MBPT at large values of R are also good, although they are not quite as accurate as our SS-MRPT results. For the larger basis we have only carried out the SS-MRPT(RS) and SS-MRPT(BW) calculations and compared with a CISDTQ calculation since we could not perform a FCI with this basis. In Figure 4 we have given a plot of the PES of the molecule in these three cases. The figure shows the close comparison with the CISDTQ curve.

For this system we have also evaluated the spectroscopic constants by fitting a Morse potential to our computed ground state PES. We have thus obtained the dissociation energy D_e, the equilibrium bond-distance R_e, the harmonic vibrational frequency ω_e, and the anharmonicity constant $\beta\omega_e$. In Table 5 we present these values for the DZ and 6-311G** bases together with the FCI and CISDTQ values as applicable. The experimental values are listed alongwith for comparison.[39]

(e) F_2 Potential Energy Surface. Another interesting and often studied system is the F_2 molecule. Though the F−F bond is rather weak, giving a very low dissociation energy, nevertheless this single bond is highly correlated making its study rather interesting. We have scanned the PES of the system over a wide range of internuclear separations using a DZ + P basis.[40] We have also carried out calculations for this system with the single reference based SR-MBPT and the MR-MBPT. In Figure 5 we give the plots of the PES for the SR-MBPT, MR-MBPT, and our SS-MRPT calculations. The performance of the single reference theory is quite poor at large R as can be seen from the figure. The MR-MBPT plot is seen to have an erratic behavior around $R = 5$ au because of intruders. In contrast, our SS-MRPT plots are seen to behave quite smoothly.

Here again we evaluate the spectroscopic constants and give the results in Table 6, along with the experimental results.[39]

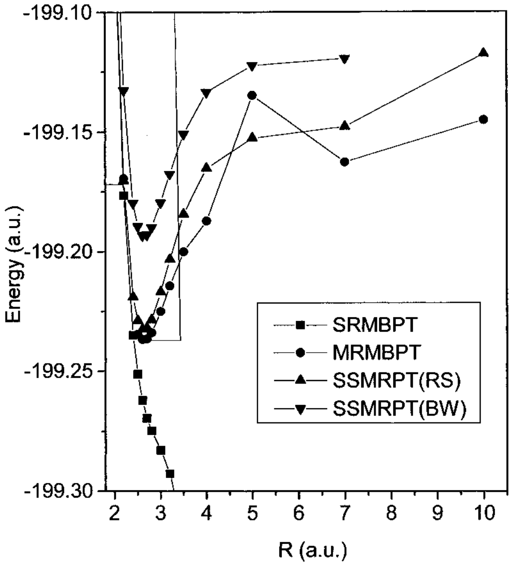

Figure 5. PES of F_2.

TABLE 6: Spectroscopic Constants of F_2 in the Ground State using SS-MRPT

method	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	$\beta\omega_e$ (cm^{-1})
SS-MRPT(RS)[a]	1.385	2.336	985.476	12.888
SS-MRPT(BW)[a]	1.391	2.043	941.452	13.447
exptl results[b]	1.411	1.659	917	11.2

[a] Basis: ref 40. [b] Reference 39.

(f) Molecules with Pronounced Multireference Character: CH_2 and C_2. We have also studied one specific state of each of the molecules CH_2 and C_2 which have a pronounced multireference character. The effect of correlation is rather high for these two states. We have done the calculations only at specific geometeries. These studies are carried out to discern to what extent the SS-MRPT provides quantitative description of the ground-state energy.

For the excited singlet state of the CH_2 molecule, we have used the same basis and geometery as employed by Bauschlischer and Taylor[41] in their treatment. The calculations have also been compared with the full CI results. Here we have considered the two configurations $1a_1^2\,2a_1^2\,1b_2^2\,3a_1^2$ and $1a_1^2\,2a_1^2\,1b_2^2\,1b_1^2$ in our active space. Again, the two active orbitals belong to different symmetries, and our model space is complete. Here too we have done the Hartree–Fock, single reference based SR-MBPT, and the MR-MBPT calculations, to illustrate the relative performances of the various methods. We list the SCF and the difference energy values in Table 7, with respect to the FCI values.

The singlet ground state of the C_2 molecule was also studied by us using the DZ basis of Huzinaga and Dunning as reported by Nakatsuji[42] and also with a larger DZP basis, as used by Watts and Bartlett,[43] at the equilibrium bond distance of 2.348 au. We have done two calculations with the first basis. In one, we have kept the two core orbitals and the top nine virtual orbitals as frozen—this scheme being the same as used by Nakatsuji.[42] In the other, we have kept the two core and the top two orbitals as frozen. The FCI results shown in the table corresponds to the respective values using the same orbital-freezing schemes. For the calculations using the second basis, we have kept the two core and the top two virtual orbitals as frozen. Since we could not compute the FCI energies in this scheme, we cite the CCSD(T) results with the same basis as given by Watts and Bartlett. In Table 7 we have presented the results of our calculations where we have once again listed the SCF and the differences of the SR-MBPT and MR-MBPT with respect to the CI values. FCI values with the first basis are quoted, while only the CCSD(T) values with the larger basis were available.

All the results presented indicate excellent performance of these size-consistent second-order perturbation methods. In general, the RS version seems to work better.

V. Concluding Remarks

We have presented in this paper the perturbative counterparts of our recently developed state-specific multireference CC (SS-MRCC) theory based on a CAS. In this formulation, all the model space determinants are treated on the same footing. The model space coefficients in this formalism are flexible, not constrained to some preassigned values. Both the components of the cluster operators and the coefficients are determined self-consistently by solving the SS-MRCC equations. We have shown the emergence of the first-order equation for the wave function and the generation of the second-order energy in both RS and BW form, depending on our expansion scheme. In the RS version of the state-specific multireference perturbation theory (SS-MRPT), the zeroth-order energy E_0 is obtained by diagonalizing the matrix of H in the model space. The zeroth-order coefficients are also obtained at this stage. In the solution for the first-order cluster amplitudes, E_0 and the coefficients are kept fixed. Only after the convergence for the cluster amplitudes is reached, do we relax the coefficients by way of diagonalizing the second-order matrix of the effective operator, which provides both the second-order energy and the relaxed coefficients at that order. For the BW version of the SS-MRPT, the energy parameter E and the coefficients as well as the first-order cluster amplitudes are self-consistently determined. We have presented illustrative aplications of the PES for a number of model and real systems where the presence of intruders is quite prominent. We have also applied our formalism to molecules CH_2 and C_2, which have pronounced multireference character at the equilibrium geometry. For comparisons, we have also presented results from the single reference MBPT, the

TABLE 7: Comparison of Second-Order Ground-State Energies with FCI Values for Molecules CH_2 and C_2 (All Entries in au)

system	SCF (au)	SR-MBPT	MR-MBPT	SS-MRPT		FCI (au)
				RS	BW	
CH_2[a]	−39.031 552	−4.369	−6.393	−4.751	4.179	−39.027 183
C_2[b]	−75.664 985	−138.692	−13.899	−13.081	3.294	−75.526 293
C_2[c]	−75.831 443	−189.695	2.914	−49.054	1.308	−75.641 748
C_2[d]	−75.605 558	123.68	−203.166	−58.201	6.721	−75.729 238[e]

[a] Basis, geometry, and FCI: ref 41. [b] Basis: ref 42 (freezing as per ref 42. [c] Basis: ref 42. [d] Basis: ref 43. [e] CCSD(T) results reported in ref 43. Two core and two highest orbitals are kept frozen in the bases in footnotes *c* and *d*. All energy entries except for SCF are differences with respect to the FCI values, in 10^{-3} au (mH).

multireference MBPT based on effective Hamiltonians, and the FCI (or a CISDTQ). Our results clearly indicate that the SS-MRPT performs smoothly across the regions of avoided crossings or in the presence of intruders, while the SR-MBPT or the MR-MBPT performs rather poorly in the various regions of the PES.

Acknowledgment. The authors wish to thank the University Grants Commission (New Delhi) for financial support. This paper is dedicated to Chanchal K. Majumdar on the happy occasion of his 60th birthday. D.M. thanks the S.N. Bose Center for Basic Sciences for conferring on him an honorary Professorship.

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