Comparison of low-order multireference many-body perturbation theories

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Tests have been made to benchmark and assess the relative accuracies of low-order multireference perturbation theories as compared to coupled cluster (CC) and full configuration interaction (FCI) methods. Test calculations include the ground and some excited states of the Be, H_2, BeH_2, CH_2, and SiH_2 systems. Comparisons with FCI and CC calculations show that in most cases the effective valence shell Hamiltonian (H^v) method is more accurate than other low-order multireference perturbation theories, although none of the perturbative methods is as accurate as the CC approximations. We also briefly discuss some of the basic differences among the multireference perturbation theories considered in this work. © *2005 American Institute of Physics.*
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I. INTRODUCTION

The most natural method for treating quasidegenerate electronic states is to apply some type of multireference (MR) formalism, such as the MR configuration interaction (CI) approach, MR coupled cluster (CC) methods, or MR perturbation theory (PT). MR-based approaches have the advantage over their single-reference counterparts in providing the flexibility needed to describe important molecular characteristics, such as bond breaking pathways, excited states, and transition states, within a few-body truncation scheme. For this reason, considerable effort has been devoted for more than two decades to formulate MR methods for both ground and excited electronic states. Ideally, these approaches should have most or all of the following characteristics: (i) size extensivity and size consistency, (ii) applicability to both closed- and open-shell systems, (iii) ability to accommodate all kinds of multidimensional reference spaces for different states, geometries, etc., (iv) low computer cost and high accuracy, (v) uniform accuracy in regions of real and/or avoided curve-crossings and in nondegenerate regimes, and (vi) rapid convergence.

Extensive studies over the past two decades have demonstrated that the state-of-the-art finite-order multireference many-body perturbation theory (MR-MBPT) methods, such

as the complete active space perturbation theory (CASPT),[1] multireference Møller–Plesset perturbation theory (MR-MP),[2,3] state-selective quasidegenerate perturbation theory,[4] quasidegenerate perturbation theory with multiconfigurational self-consistent field reference functions (CASPT2),[5] n-electron valence space perturbation theory (NEVPT),[6,7] state-specific multireference perturbation theory (SS-MRPT),[8,9] multiconfiguration perturbation theory (MCPT),[11–13] multideterminant state perturbation theory (MDSPT),[14] the intermediate Hamiltonian (IH) method,[15] and the effective valence shell Hamiltonian method (H^v),[16] are all capable of providing reasonable results for quasidegenerate and open-shell atomic and molecular systems, including larger systems. This should be contrasted with the infinite-order many-body methods based on CC theory[17–20] that offer very high accuracies, but are typically limited to smaller systems, although significant progress has been achieved recently in extending the applicability of CC methods and CC computer programs to larger many-electron systems containing dozens of light atoms (see, e.g., Ref. 21) or several transition metal atoms (see, e.g., Ref. 22). The choice of method usually involves a trade off between accuracy and computational cost as well as a concern for the ease of use of various computer programs. In addition, for systems involving quasidegenerate and/or open-shell electronic states, it is important to consider the ability of a given method to describe the relevant nondynamic correlation. By design, all MR-MBPT methods are capable of representing nondynamic correlation very well. The popular single-reference CC approaches, such as CCSD(T) (CC method with singles, doubles, and noniterative triples),[23] which accurately describe high-order dynamic correlation effects, may fail when large contributions from nondynamic correlation are

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present,[24–26] although the recently formulated completely renormalized (CR) extensions of the CCSD(T) method, such as the CR-CCSD(T) approach, behave quite well in quaside-generate cases involving bond breaking.[24–28] Genuine multi-reference CC (MR-CC) methods,[29,30] which are based on the concept of multidimensional model spaces and the general-ized Bloch equation, fare very well in quasidegenerate cases, but they may suffer from problems due to single or multiple intruder state solutions.[30–32] The state-selective or state-specific (SS) MR-CC approaches, such as the Brillouin–Wigner MR-CC theory,[33–37] the SS MR-CC approach of Mahapatra *et al.*,[38,39] and the active-space CC methods of Adamowicz, Piecuch, Bartlett, and their collaborators,[40–52] are much better in this regard, although their accuracy varies from very high to sometimes comparable to or worse than the accuracy of single-reference CC calculations (see, e.g., Ref. 30 for an overview).

A useful guide through the vast array of many-body methods is provided by benchmarking their performance for "difficult" systems that are small enough for comparisons with full configuration interaction (FCI) calculations. In this paper, we compare the performance of different MR-MBPT methods with the FCI and CC calculations for a few different systems of increasing complexity, namely, H_2, Be, BeH_2, CH_2, and SiH_2.

Among the above systems, the Be atom has served as a widely used benchmark case for testing *ab initio* methods and for comparing the efficiency of various quantum chemi-cal methods. While having only four electrons, the Be atom is a "difficult" system, since the near $1s^22s^2$-$1s^22p^2$ degen-eracy and the existence of a true $1s^22s3s$ intruder state intro-duce severe divergence problems in many types of perturba-tive calculations.[53] The accurate determination of singlet-triplet splittings ($^1A_1$–$^3B_1$) for CH_2 and SiH_2 is also nontrivial, since it requires the precise and well balanced incorporation of electron correlation effects and an accurate description of the ground and excited states of different sym-metries. The H_2 and BeH_2 systems offer the opportunity for considering the performance as a function of nuclear geom-etry and varying degree of configurational quasidegeneracy.

While the quality of predictions from multireference per-turbation theory methods may critically depend on the choice of reference space, the comparisons here employ only a minimal complete active space (CAS) as the reference space. This choice is made, in part, because the methods vary in the flexibility for choosing reference spaces. Illustrations of the dependence on reference space are described elsewhere for several of the methods considered here.[54]

Section II summarizes the basic formalism used to define all multireference perturbation theory methods, and a brief description of the specific MR-MBPT approaches used in this work is presented in Sec. III. A comparison of various multireference perturbation theory calculations with the cor-responding FCI and CC results is discussed in Sec. IV. Con-clusions are provided in Sec. V.

II. THEORETICAL BACKGROUND

The most extensively used low-order multireference per-turbation theory methods can broadly be classified as either

"perturb then diagonalize" or "diagonalize then perturb" ap-proaches. The starting point for all these methods is the de-composition of the exact Hamiltonian H into the zeroth-order Hamiltonian $H^{(0)}$ and the perturbation V,

$$H = H^{(0)} + V, \tag{1}$$

where $H^{(0)}$ is often constructed as a sum of one-electron Fock-like operators. The full many-electron Hilbert space of dimension N is then partitioned into a reference space $\mathcal{M}_0$ (also called the active or model space) of dimension $M \ll N$, defined by the projector P, and its orthogonal complement $\mathcal{M}_0^\perp$ associated with the projector $Q = 1 - P$. Once the active space $\mathcal{M}_0$ is defined, a wave operator Ω is introduced that satisfies

$$|\Psi_i\rangle = \Omega|\Psi_i^{(0)}\rangle, \quad i = 1, \dots, M, \tag{2}$$

where $|\Psi_i^{(0)}\rangle$ and $|\Psi_i\rangle$ are the *unperturbed* and *the exact* (FCI) wave functions of the ith eigenstate of the Hamil-tonian, respectively. The wave operator Ω, which formally represents the mapping of the reference space $\mathcal{M}_0$ onto the target space $\mathcal{M}$ spanned by the M eigenstates $|\Psi_i\rangle$, has the properties,

$$\Omega P = \Omega, \quad P\Omega = P, \quad \Omega^2 = \Omega. \tag{3}$$

With the aid of the wave operator Ω, the Schrödinger equation for the M eigenstates of the Hamiltonian correlating with the M-dimensional reference space $\mathcal{M}_0$ (also called the P space) of M unperturbed states $|\Psi_i^{(0)}\rangle$, i.e.,

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle, \quad i = 1, \dots, M, \tag{4}$$

is transformed into a generalized Bloch equation

$$H\Omega P = \Omega H\Omega P = \Omega P H_{\text{eff}} P, \tag{5}$$

where $H_{\text{eff}} \equiv PH\Omega P$ is the effective Hamiltonian. Once Eq. (4) is solved for the wave operator Ω, the energies E_i, $i = 1, \dots, M$, are computed in the "perturb then diagonalize" approaches by diagonalizing the effective Hamiltonian H_{eff} in the M-dimensional reference space $\mathcal{M}_0$, while the "diag-onalize then perturb" schemes employ other ways of dealing with Eq. (4), as mentioned below.

Equation (5) is the basic equation for most multirefer-ence perturbation theory approaches. (It is also used to for-mulate all genuine MR-CC methods.[29–32]) As noted earlier, depending on the choice of the zeroth-order wave function and energy, we distinguish between the diagonalize then per-turb and perturb then diagonalize MR-MBPT methods. In the perturb then diagonalize varieties, the wave operator Ω is determined by projecting Eq. (5) onto the Q-space states be-longing to $\mathcal{M}_0^\perp$, whereas the eigenvalues E_i and the zeroth-order wave functions $|\Psi_i^{(0)}\rangle$ are obtained by diagonalizing the $M \times M$ effective Hamiltonian matrix H_{eff} in $\mathcal{M}_0$. On the other hand, in the diagonalize then perturb methods such as CASPT2, a multiconfigurational wave function $|0\rangle \equiv |\Phi_i\rangle$, which defines the zeroth-order state $|\Psi_i^{(0)}\rangle$, is generated from a CASSCF (or small CI) calculation. The first-order correc-tion to the wave function $|\Psi_i\rangle$ is then expanded in terms of the suitably defined configuration state functions (CSFs) $|j\rangle$,

$$|\Psi_i^{(1)}\rangle = \sum_{j=1}^{M} C_j |j\rangle, \tag{6}$$

where the coefficients C_j are determined by solving a system of linear equations of the form

$$\sum_{j=1}^{M} \langle k|H^{(0)} - E_i^{(0)}|j\rangle C_j = -\langle k|H|0\rangle, \quad k = 1, \ldots, M, \tag{7}$$

where $E_i^{(0)} = \langle 0|H^{(0)}|0\rangle \equiv \langle \Phi_i|H^{(0)}|\Phi_i\rangle$ is the zero-order energy corresponding to the multiconfigurational wave function $|\Phi_i\rangle$. The zeroth-order Hamiltonian $H^{(0)}$ in Eq. (7) is totally different than that used in the diagonalize then perturb methods. (For more details, see the work of Andersson *et al.*[1] and Hirao.[2])

The choice of reference space, orbitals, orbital energies, and the zeroth-order Hamiltonian, as well as the specific formulation of MR-MBPT can severely affect the convergence behavior, size extensivity, and accuracy of the results. For example, the diagonalize then perturb approaches of the CASPT2 type use projectors to define the zeroth-order Hamiltonian, and this may lead to departures from strict size extensivity.[55] A similar problem occurs when the MCPT method is employed, though a size consistent version of MCPT has recently been developed.[56]

III. OVERVIEW OF SELECTED MULTIREFERENCE PERTURBATION THEORY METHODS

Since the details of the CASPT2, MR-MP, and MDSPT methods (and their variants) are extensively discussed elsewhere, we only outline the effective valence Hamiltonian (H^v) approach and the recently developed SS-MRPT, NEVPT2, and MCPT schemes.

The effective Hamiltonian method (H^v) belongs to the less common perturb then diagonalize category. The H^v scheme determines the unoccupied valence orbitals and their energies from a V^{N-1} Fock operator and defines the zero-order Hamiltonian $H^{(0)}$ as

$$H^{(0)} = \sum_c |\phi_c\rangle \epsilon_c \langle \phi_c| + \sum_v |\phi_v\rangle \bar{\epsilon}_v \langle \phi_v| + \sum_e |\phi_e\rangle \epsilon_e \langle \phi_e| \tag{8}$$

to remove the most egregious intruder state problems and thereby improve the perturbative convergence.[57] The valence orbital energies $\bar{\epsilon}_v$ are evaluated from the original set of valence orbital energies ϵ_v by the democratic averaging,

$$\bar{\epsilon}_v = \frac{\sum_v \epsilon_v}{N_v}, \tag{9}$$

with N_v representing the number of valence orbitals spanning the CAS. Because of the averaging procedure, an additional diagonal perturbation $V_d = \bar{\epsilon}_v - \epsilon_v$ appears in the H^v procedure, beginning with the third order.

A variant of diagonalize then perturb MR-MBPT, called n-electron valence space perturbation theory (NEVPT2), has recently been proposed by Angeli *et al.*[6] This formalism also chooses zeroth-order CASSCF/CASCI wave functions. The NEVPT2 method differs from CASPT2 in the choice of wave functions external to CAS and in the definitions of

zeroth-order energies. The NEVPT2 method first divides the orbital space into three orbital subspaces of inactive orbitals with occupations of 2, active orbitals with variable occupations, and virtual orbitals with occupation number 0. Eight classes of spaces $S_l^{(k)}$ are generated by the action of excitation operators, and these classes differ in the number of electrons (k) promoted to and from the CAS space, where l denotes the occupation of inactive orbitals. Different numbers of perturbing functions are chosen for the $S_l^{(k)}$ spaces by further subdividing these spaces into various categories, viz., strongly contracted spaces, partially contracted spaces, etc. For further details, we refer to the work of Angeli *et al.*[6,7]

The SS-MRPT scheme is a diagonalize then perturb approach that is designed to facilitate relaxation of the reference function and that is, thus, very effective in treating states of mixed parentage. The emphasis in this approach is to develop a state-specific theory, targeting only a single state rather than several states simultaneously. This goal is achieved by invoking a wave operator which acts on just one reference space function.

The CAS-based SS-MRPT version of Mukherjee and co-workers[8,9] uses Rayleigh–Schrödinger and Brillouin–Wigner type perturbation expansions with robust denominators to avoid intruder state problems in a natural manner. The method is rigorously size extensive, and, hence, the energy obtained is also size consistent because the reference determinants span a CAS and because the CAS is invariant under separate transformations among the core orbitals and among the active orbitals. Since the SS-MRPT method of Mukherjee and co-workers[8,9] uses an approach based on relaxed coefficients, it might appear to involve extensive computations to remove redundancies in the excitation amplitudes. This drawback is largely minimized by an appropriate organization of the computational algorithm.[10]

This section is closed by describing the recently developed single-state multiconfigurational perturbation theory (MCPT).[11] The essence of MCPT is that perturbative corrections can be derived for an arbitrary reference (zeroth-order) function through the definition of virtual excited states. In this way, no special character of the reference function must be assumed at the outset; in particular, the reference state is not required to be a CAS wave function. At the same time, the formulation of the theory remains so simple that there is no need to apply numerical orthogonalization procedures nor to solve linear systems of equations, such as Eq. (7), in order to evaluate perturbative corrections, and the reduced resolvent in MCPT is always diagonal. Another noteworthy feature of this scheme is the presence of adjustable parameters—the zeroth-order excited state energies—which can be used to tune the zeroth-order Hamiltonian to the problem of interest. In other words, the partitioning of the Hamiltonian in MCPT is not fixed *a priori*. Thus, MCPT is a general framework rather than one single method. A specific variant of MCPT follows by fixing the zeroth-order excited state energies in a particular way. Here, we consider the following four variants of MCPT (for more details, see Refs. 12 and 13).

TABLE I. The ground state energies of Be, relative to the FCI (in hartree). The [1,0] Padé approximant is constructed from the H^v expansion. The FCI energies for the 6-31G, 6311G**, and DZ-ANO bases are $-14.613\,545$, $-14.633\,954$, and $-14.626\,388$ hartree, respectively.

	Basis		
Method	6-31G	6-311G**	DZ-ANO
SCF	0.046 781	0.062 062	0.053 402
MP2	0.022 470	0.019 900	0.018 507
MP3	0.010 598	0.008 641	0.008 459
CCSD	0.000 028	0.000 307	0.000 276
CCSDT	0.000 002	0.000 007	0.000 010
CCSD(T)	0.000 001	0.000 022	0.000 021
R-CCSD(T)	0.000 002	0.000 048	0.000 045
CR-CCSD(T)	0.000 003	0.000 047	0.000 042
CR-CCSD(T),ID	0.000 002	0.000 017	0.000 019
MR-CCSD	0.000 023	0.000 271	
MR-CCSDT	0.000 001	0.000 005	
CASSCF (APSG)	0.001 696	0.018 344	0.009 598
IVO-CASCI	0.003 653	0.021 523	0.013 007
DK-MCPT2	0.000 168	0.003 199	
DK-MCPT3	0.000 042	0.001 305	
DK-MCPT4	−0.000 005	0.000 719	
EN-MCPT2	0.000 010	0.001 432	
EN-MCPT3	0.000 025	0.001 029	
EN-MCPT4	−0.000 113	0.000 086	
OPT-MCPT2	0.000 008	0.000 638	
MDSPT2	−0.000 759	0.000 888	−0.000 262
MDSPT3	0.000 183	0.000 823	0.000 953
MDSPT4	−0.000 026	−0.000 058	−0.000 128
CASPT2	0.000 283	0.002 745	0.005 586
SS-MRPT[a]	0.012 129	0.001 343	0.001 216
SS-MRPT[b]	0.003 470	0.000 640	0.000 570
MR-MP	0.000 273	0.002 742	0.005 449
H^v (2nd)	0.000 281	0.001 892	0.000 788
H^v (3rd)	0.000 124	0.000 456	0.000 346
[1,0]Padé	0.000 116	0.000 342	0.000 329
OPT	0.000 005	0.000 018	

[a]Using SCF orbitals.
[b]Using CASSCF orbitals.

(i) The Møller–Plesset-like partitioning (denoted as MP-MCPT) constructs the energy denominators as the differences of the eigenvalues of the multiconfigurational Fock matrix.

(ii) The diagonal elements of the multiconfigurational Fock matrix are defined in terms of the one-particle energies for the Davidson–Kapuy partitioning (DK-MCPT) proposed by Davidson.

(iii) The generalized Epstein–Nesbet partitioning (designated in Table I as EN-MCPT) defines the energy denominators of a given determinant $|k\rangle$ as $\langle k|H|k\rangle - \langle 0|H|0\rangle$.

(iv) The optimized partitioning (OPT-MCPT in Table I) determines the energy denominators from a suitably designed optimization equation.[11–13,58]

The IH method[15] is of the perturb then diagonalize variety in which the reference space is further partitioned into the main space whose energies are of interest and an intermediate space whose properties are adjusted to optimize the per-

formance in the main space. While it is beyond the scope of the present work to discuss all the pros and cons of each perturbative scheme, the benchmarks against FCI partially serve this purpose.

IV. RESULTS AND DISCUSSION

A. Be

The ground and excited state energies of the Be atom are computed with three different basis sets, viz., 6-31G,[59] 6311G**,[60] and DZ-ANO.[61] A 2×2 CAS reference space comprising the $1s^2 2s^2$ and $1s^2 2p^2$ CSFs is used for the multireference perturbative calculations that also yield the ^1S excited state energy. All single-reference treatments (MP2, CC) are based on the restricted Hartree–Fock $1s^2 2s^2$ CSF.

The Be atom provides a simple, yet nontrivial benchmark for assessing the relative performance of various multireference perturbation theory approaches. Several single-reference methods are considered for comparison purposes. The single-reference methods include the second-and third-order MBPT approaches (MP2 and MP3, respectively) and a few CC and equation-of-motion CC (EOM-CC) methods. The CC approaches are computationally more expensive than the low-order MR-MBPT methods (assuming that the multidimensional reference spaces used in MR-MBPT calculations are not too large and that the perturbation theory calculations are truncated at second or third orders), but the CC treatments have the advantage of including important classes of many-body diagrams through infinite order. Along with the standard CC methods, such as CCSD (CC singles and doubles)[62] and CCSD(T),[23] we include results of the renormalized (R) and completely renormalized (CR) CCSD(T) calculations,[24–28,63,64] as well as full CCSDT (CC singles, doubles, and triples)[65,66] computations. The R-CCSD(T) and CR-CCSD(T) methods are designed to improve the CC results in cases of configurational quasidegeneracy accompanying chemical bond breaking where the standard CCSD(T) approach fails,[24–28,63,64] but their performance in cases of orbital quasidegeneracy characterizing the ground and excited states of the Be atom has not received much attention. In addition to the original formulation of the CR-CCSD(T) theory,[27,28] we apply the newest variant, which is termed the CR-CCSD(T),ID model[63] and which uses the diagonal matrix elements of the triples-triples block of the similarity transformed Hamiltonian of the CCSD theory instead of the bare orbital energies that are used in standard CCSD(T) treatments to specify the perturbation theory denominators defining the noniterative triples correction. Calculations are also presented using the excited state extensions of the CCSD and CR-CCSD(T),ID methods via the EOM-CC formalism [the EOM-CCSD[67] and CR-EOMCCSD(T),ID[63] methods] and the MR-CCSD and MR-CCSDT schemes,[68] which represent two different SS-MRCC approximations based on the active-space CC theory originally proposed by Oliphant and Adamowicz,[40–42] and fully developed by Piecuch, Oliphant, and Adamowicz[43] (see Refs. 44–52 for important further developments and extensions to excited electronic states). The CCSD, CCSD(T), R-CCSD(T), CR-

TABLE II. The energies of the $^1S(2p^2)$ excited state of Be relative to the corresponding FCI data (in hartree). The FCI energies for the 6-31G, 6-311G**, and DZ-ANO bases are $-14.211\,088$, $-14.271\,117$, and $-14.273\,547$ hartree, respectively.

	Basis		
Method	6-31G	6-311G**	DZ-ANO
EOM-CCSD	0.000 221	0.002 350	0.002 253
CR-EOMCCSD(T),ID	0.000 023	0.000 066	0.000 153
H^v (2nd)	0.008 566	0.017 064	0.021 313
H^v (3rd)	0.003 569	0.003 462	0.005 849
[1,0]Padé	0.000 299	0.001 664	0.001 933

CCSD(T), CR-CCSD(T),ID, EOM-CCSD, and CR-EOMCCSD(T),ID calculations are performed with the CC computer codes[63,64] that are part of the GAMESS package[69] and the recently developed open-shell extensions of these codes[70] that are interfaced with GAMESS. The CCSDT treatment employs the computer program described in Ref. 51, which is interfaced with GAMESS, and with the codes described in Refs. 71 and 72. The aforementioned MR-CCSD and MR-CCSDT calculations are performed using the code written by Kállay,[68] which employs a string-based algorithm to represent and solve the CC equations.

Tables I–III summarize the deviations from the corresponding FCI results, i.e., $E_{\text{theory}} - E_{\text{FCI}}$, in the computed ground and excited state energies of Be as obtained with various perturbative and CC techniques. Tables I–III demonstrate that the standard CCSD(T) method and its renormalized and completely renormalized versions, which are based on the idea of adding relatively inexpensive noniterative corrections due to triples to CCSD/EOM-CCSD energies, provide very accurate estimates of the ground and excited state energies of Be, particularly when the CR-CCSD(T),ID/CR-EOMCCSD(T),ID approach is employed. The only methods that can compete with the CR-CCSD(T),ID approach in the ground-state calculations are the expensive full CCSDT and MR-CCSDT schemes. The superb accuracies obtained with the iterative or noniterative CC triples methods could be expected due to the infinite-order nature of the CC theory. There are minor (typically, microhartree-type) differences between the CCSD(T), R-CCSD(T), CR-CCSD(T), CCSDT,

TABLE III. The energies of the $^3P(2s2p)$ excited state of Be relative to the corresponding FCI data (in hartree). The FCI energies for the 6-31G, 6-311G**, and DZ-ANO bases are $-14.508\,386$, $-14.532\,798$, and $-14.526\,502$ hartree, respectively.

	Basis		
Method	6-31G	6-311G**	DZ-ANO
EOM-CCSD	0.000 080	0.000 176	0.000 172
CR-EOMCCSD(T),ID	0.000 000	0.000 008	0.000 007
MDSPT2	0.000 349	0.002 723	0.001 773
MDSPT3	0.000 062	0.000 318	0.000 209
MDSPT4	0.000 009	0.000 054	0.000 033
H^v (2nd)	0.000 289	0.001 582	0.001 937
H^v (3rd)	0.000 079	0.000 234	0.000 286
[1,0]Padé	0.000 007	0.000 105	0.000 090

and MR-CCSDT energies for the Be ground state energy and between the results of CC calculations with noniterative or iterative triples and the FCI, indicating that the $2s$-$2p$ orbital degeneracy in Be does not pose a problem for the infinite order CC theory, particularly when contributions from triply excited clusters are included. The CR-EOMCCSD(T),ID approach provides equally accurate energies for the $^1S(2p^2)$ (Table II) and $^3P(2s2p)$ (Table III) excited states. In fact, the CR-EOMCCSD(T),ID $^3P(2s2p)$ excited state energy is virtually exact. For both excited states, the CR-EOMCCSD(T),ID method provides considerable improvements over the standard EOM-CCSD treatment, but these improvements are particularly dramatic for the $^1S(2p^2)$ state, where the basic EOM-CCSD approximation produces relatively large errors. The latter behavior reflects the fact that all CR-EOM CCSD(T) methods[63] [including the CR-EOMCCSD(T),ID approach used here] have been designed to improve significantly the relatively poor description by the EOM-CCSD approach of quasidegenerate excited states that are dominated by two-electron transitions, such as the $2s^2 \rightarrow 2p^2$ excited state of Be. Because the $^3P(2s2p)$ state has a predominantly singly excited character, the basic EOM-CCSD method is already quite accurate, and the CR-EOM-CCSD(T),ID method improves the already very good EOM-CCSD energy, making it essentially exact.

The considerably poorer accuracy of the single reference MP2 and MP3 energies compared to the single and multireference CC and low-order MR-MBPT calculations clearly demonstrates the importance of higher-order MPn contributions for the ground state of Be. Tables I–III further indicate that the bulk of the correlation energies for the ground and excited states of the Be atom can be incorporated either through some of the low-order multireference approaches or through the infinite-order CC and EOM-CC methods.

Table I demonstrates that the performance of the MCPT method strongly depends on the applied partitioning scheme. For the Be calculations employing the small 6-31G basis set, the DK type partitioning seems to work better than the EN partitioning. Although the EN-MCPT2 result is quite accurate, the EN-MCPTn series diverges for the Be ground state. In contrast, the DK-MCPTn series seems to converge. The DK-MCPT4 energy drops slightly below the exact FCI energy, so that the convergence of the DK-MCPTn series is not necessarily monotonic for Be. Nevertheless, the results of the DK-MCPTn calculations are very encouraging. Second-order calculations using the optimized partitioning (the OPT-MCPT2) are also very accurate for the 6-31G basis set. The behavior of the EN-MCPTn versus the DK-MCPTn series for the 6-31G basis should be contrasted with that observed for the larger 6-311G** basis set, where both series appear to be convergent and the errors obtained with the EN partitioning are halved compared to the MP partitioning case. Considering the number of contracted Gaussian functions present in the DZ-ANO and 6-311G** basis sets, the accuracies of MCPT and OPT calculations with the DZ-ANO basis (not displayed in Table I) are expected to be quite similar to those obtained from the 6-311G** basis.

Apart from some technical differences, such as the choice of zeroth-order energy, the MDSPT method[14] is quite

TABLE IV. The ground state energy of H_2 obtained with various perturbative methods. All entries represent the absolute deviations from the corresponding FCI energies in hartree. The FCI energies at $R(H-H)=1.0$, 1.6, and 2.0 bohr are $-1.114\,534$, $-1.158\,707$, and $-1.127\,127$ hartree, respectively.

Method	$R(H-H)/bohr$		
	1.0	1.6	2.0
SCF	0.032 436	0.034 962	0.038 859
CASSCF	0.019 271	0.013 514	0.009 447
MP2	0.006 522	0.008 874	0.011 208
SS-MRPT	0.000 878	0.000 614	0.000 649
CASPT2	0.003 801	0.002 442	0.001 511
MRMP	0.003 825	0.002 464	0.001 526
MP-MCPT2	0.003 889	0.002 570	0.001 652
MP-MCPT3	0.000 848	0.000 603	0.000 411
MP-MCPT4	0.000 197	0.000 164	0.000 125
DK-MCPT2	0.007 573	0.004 999	0.003 075
DK-MCPT3	0.003 645	0.002 452	0.001 426
DK-MCPT4	0.001 792	0.001 204	0.000 632
MDSPT2	0.002 331	0.001 197	0.001 978
MDSPT3	0.000 572	0.000 360	0.000 138
MDSPT4	0.000 123	0.000 082	0.000 085
IH(2nd)	0.005 902	0.005 425	0.004 904
IH(3rd)	0.001 168	0.001 218	0.001 204
IH(4th)	0.000 207	0.000 198	0.000 124
H^v (2nd)	0.000 684	0.000 283	0.000 254
H^v (3rd)	0.000 221	0.000 531	0.000 607
H^v (4th)	0.000 029	0.000 019	0.000 062

TABLE V. The $X^1\Sigma_g^+ \equiv 1^1\Sigma_g^+ \to 2^1\Sigma_g^+$ transition energy of H_2 obtained with the H^v method. All entries represent the absolute deviations from the corresponding FCI energies in hartree. The FCI values at $R=1.0$, 1.6, and 2.0 bohr are 1.420 687, 0.979 485, and 0.765 371 hartree, respectively.

Method	$R(H-H)/bohr$		
	1.0	1.6	2.0
H^v (2nd)	0.033 3460	0.027 5880	0.021 7030
H^v (3rd)	0.013 8570	0.011 8820	0.009 2990
H^v (4th)	0.001 9920	0.005 1210	0.000 0450

pear to be most accurate. The SS-MRPT approach fares much better than the IH method for H_2. Since both the SS-MRPT and IH methods specify the same $1\sigma_u^2$ CSF as the "intermediate" space, the eigenvalue corresponding to the $1\sigma_u^2$ CSF is not an approximate eigenfunction of the physical Hamiltonian. This explains why only the ground state energy is displayed for the SS-MRPT and IH methods in Table IV. The H^v method provides a precise estimate (at each order) of the ground state and the $X^1\Sigma_g^+ \equiv 1^1\Sigma_g^+ \to 2^1\Sigma_g^+$ transition energy of H_2.

C. BeH$_2$

Treating the BeH$_2$ system presents well-known difficulties in describing the ground state potential energy surface for the C_{2v} insertion of the Be atom into H_2 with single-reference methods. Therefore, the BeH$_2$ insertion reaction has served as an important benchmark for testing new approaches.[74–77] As in earlier calculations, the insertion path of Be into H_2 is modeled as a straight line $r=2.54 -0.46R$ bohr, where r is the H–H separation and R is the distance between the Be atom and the midpoint of the H_2 internuclear bond. Our calculations for the BeH$_2$ system follow the earlier works[74–77] by being performed with a basis set constructed from a contracted $[12s3p]/(3s1p)$ Gaussian set for Be and a $[4s]/(2s)$ Gaussian set (with scaling factor of 1.2) for the H atom.

The FCI calculations show that the $1a_1^2 2a_1^2 1b_2^2$ and $1a_1^2 2a_1^2 3a_1^2$ CSFs dominate the ground state (1^1A_1) wave function along the C_{2v} insertion path. Specifically, the $1a_1^2 2a_1^2 1b_2^2$ determinant dominates the 1^1A_1 state at $R=2.5$ bohr (geometry A), whereas the $1a_1^2 2a_1^2 3a_1^2$ determinant dominates the FCI expansion of the 1^1A_1 state at $R=3$ bohr (geometry C). Thus, the 1^1A_1 state is nondegenerate at geometries A and C, and standard single reference methods, such as the CCSD(T) approach, work very well in this case, producing errors in the microhartree range (see Table VI). The situation dramatically changes, when the Be atom is placed 2.74 bohr from the center of the H_2 molecule (geometry B). In this case, the $1a_1^2 2a_1^2 1b_2^2$ and $1a_1^2 2a_1^2 3a_1^2$ configurations become equally important, largely because of the quasidegeneracy of the $2s$ and $2p$ orbitals of Be. This multiconfigurational nature of the wave function at geometry B leads to severe convergence problems for single-reference perturbative treatments. In particular, the error in the CCSD(T) energy relative to the FCI increases from 30–40 μhartree at geometries A and C to over 3 mhartree at geometry B (see Table VI). The R-CCSD(T) and CR-CCSD(T)

similar to CASPT2, so only the former is provided for the Be excited $^3P(2s2p)$ valence state. The MDSPT approach estimates the ground state energy of Be more accurately than other perturbative approaches in the diagonalize then perturb category.

Finally, Table I demonstrates that among the MR-MBPT theories, the H^v method provides better results in low orders than other low-order methods for the ground state of Be. The second- and third-order H^v results for the excited states in Tables II and III are also very good, particularly for the $^3P(2s2p)$ state and especially when combined with the [1,0] Padé approximant. (The $[N, N-1]$ Padè is constructed from the expressions given in Ref. 73.)

B. H$_2$

The low-order perturbative convergence for the ground state of the H_2 molecule is studied at three different geometries. We employ the same basis (6-31G**) and the same (2,2) CAS ($1\sigma_g^2$ and $1\sigma_u^2$ CSFs) as used by Rolik *et al.*[11] in their MCPT calculations. Tables IV and V, respectively, present the absolute deviations from the FCI values, i.e., $|E_{theory}^{gr} - E_{FCI}^{gr}|$, for the ground state and the $X^1\Sigma_g^+ \equiv 1^1\Sigma_g^+ \to 2^1\Sigma_g^+$ transition energies computed using various low-order perturbative schemes. (The CCSD and EOM-CCSD methods are exact in this case.)

Here we find that the MCPT results again strongly depend upon the choice of partitioning scheme as expected. Though the MCPT energies are satisfactory, they are not as accurate as other second-order approaches. Among the diagonalize then perturb category, the SS-MRPT calculations appear to be most accurate.

TABLE VI. The ground state energy of BeH_2 obtained with various methods. All entries represent the absolute deviations from the corresponding FCI energies in hartree. The FCI energies at the geometries A, B, and C are $-15.622\,88$, $-15.602\,92$, and $-15.624\,48$ hartree, respectively.

Method	Geometry		
	A	B	C
CCSD	0.001 08	0.003 48	0.000 29
CCSD(T)	0.000 89	0.003 31	0.000 27
R-CCSD(T)	0.000 47	0.000 29	0.000 17
CR-CCSD(T)	0.000 48	0.000 39	0.000 17
MP-MCPT2	0.015 78	0.020 06	0.000 88
MP-MCPT3	0.006 49	0.009 29	0.012 18
SS-MRPT	0.003 40	0.004 78	0.000 40
MR-MP	0.018 46	0.014 04	0.017 44
H^v (2nd)	0.017 04	0.020 06	0.022 96
H^v (3rd)	0.006 93	0.005 69	0.009 81
[1,0]Padé	0.003 47	0.002 23	0.005 76

methods are capable of restoring high accuracy at geometry B, which is a consequence of the well-known ability of these approaches to describe large nondynamic correlation or configurational quasidegeneracy effects in spite of the apparently single reference nature and relatively low cost of the R-CCSD(T) and CR-CCSD(T) calculations.[24–28]

None of the low-order MR-MBPT schemes, using the two $1a_1^2 2a_1^2 1b_2^2$ and $1a_1^2 2a_1^2 3a_1^2$ CSFs as reference determinants, is capable of matching the high accuracy of the R-CCSD(T) and CR-CCSD(T) calculations. In fact, some methods, such as the MP-MCPT scheme perform rather poorly, exhibiting slow (geometries A and B) or, perhaps, even no (geometry C) convergence. Unlike in the CR-CCSD(T) case, the errors in the MP-MCPT, SS-MRPT, and

MR-MP results vary considerably with the geometry, producing large nonparallelity errors relative to the FCI. The H^v method seems somewhat better in this regard, particularly when the [1,0] Padé approximants are employed. On the other hand, unlike the Be and H_2 cases, the SS-MRPT approach fares slightly better than the H^v method, producing errors that at geometry C begin to compete with the CC calculations.

D. Singlet-triplet splittings in CH_2 and SiH_2

The calculation of the singlet-triplet splittings in CH_2 and SiH_2 provides another well-known test case for calibrating quantum chemical methods because the poor quality of the SCF approximation for these splittings indicates that electron correlation effects contribute strongly to these splittings. Fortunately, FCI benchmarks by Bauschlicher and Taylor[78,79] are available for these two systems for testing the accuracy of various perturbative and nonperturbative many-body methods.

The H atom basis used in the CH_2 and SiH_2 calculations is Dunning's[80] $(4s)/[2s]$ scaled basis for the H atoms with one $2p$ polarization function ($\zeta_p = 1.0$). The C atom basis set is constructed from Dunning's $(9s5p)/[4s2p]$ contracted basis set, augmented with one optimized[81] $3d$ polarization function ($\zeta_d = 0.51$ for $^1A_1$, $\zeta_d = 0.74$ for $^3B_1$). For the Si atom, we employ Dunning's $[5s3p]$ contracted basis set with one $3d$ polarization function ($\zeta_d = 0.3$). All six components of the $3d$ functions are retained in the basis set. The structural parameters used for CH_2 (Ref. 81) are: $^1A_1$, $r_e(CH) = 2.11\ a_0$ and $\angle HCH = 102.4$ deg; $^3B_1$, $r_e(CH) = 2.045\ a_0$ and $\angle HCH = 132.4$ deg, while calculations for SiH_2 are performed at the

TABLE VII. The $^1A_1$–$^3B_1$ splitting in CH_2 obtained from various perturbative and nonperturbative approaches. The CCSD CCSD(T), R-CCSD(T) and CR-CCSD(T) results are obtained using ROHF (for the $^3B_1$ state) and RHF (for the $^1A_1$ state) references. The EOM-CCSD and CR-EOMCCSD(T),ID energies are computed using the RHF reference and treating the $^1A_1$ CCSD state as the reference for the EOM-CCSD calculations.

Method	$E(^3B_1)$ (hartree)	$E(^1A_1)$ (hartree)	$E(^1A_1)-E(^3B_1)$ (kcal/mol)
FCI	−39.046 260	−39.027 183	11.97
SCF	−38.927 947	−38.886 297	26.14
CASSCF	−38.965 954	−38.945 529	12.82
IVO-CASCI	−38.939 204	−38.918 750	12.84
CCSD	−39.044 057	−39.023 639	12.81
CCSD(T)	−39.045 742	−39.026 310	12.19
R-CCSD(T)	−39.045 654	−39.026 100	12.27
CR-CCSD(T)	−39.045 596	−39.025 970	12.32
EOM-CCSD	−39.043 851	−39.023 639	12.68
CR-EOMCCSD(T),ID	−39.045 166	−39.026 572	11.67
NEVPT2[a]			13.67
CASPT2[a]			15.43
MDSPT2	−39.030 721	−39.015 663	9.45
MDSPT3	−39.040 848	−39.021 453	12.17
MDSPT4	−39.042 013	−39.022 295	12.37
H^v (2nd)	−39.083 409	−39.064 795	11.68
H^v (3rd)	−39.041 328	−39.020 436	13.18
[1,0]Padé	−39.050 834	−39.030 770	12.59

[a]Taken from Ref. 84.

TABLE VIII. The $^1A_1-^3B_1$ splitting in SiH_2 obtained from various perturbative and nonperturbative approaches. The CCSD, CCSD(T), R-CCSD(T), and CR-CCSD(T) results are computed using ROHF (for the $^3B_1$ state) and RHF (for the $^1A_1$ state) references.

Method	$E(^3B_1)$ (hartree)	$E(^1A_1)$ (hartree)	$E(^1A_1)-E(^3B_1)$ (kcal/mol)
Full CI	−290.082 313	−290.110 207	−17.50
SCF	−289.986 955	−289.994 434	−4.69
CASSCF	−290.016 813	−290.042 911	−16.38
IVO-CASCI	−289.998 715	−290.021 725	−14.44
CCSD	−290.079 700	−290.107 433	−17.40
CCSD(T)	−290.081 439	−290.109 534	−17.63
R-CCSD(T)	−290.081 336	−290.109 356	−17.58
CR-CCSD(T)	−290.081 287	−290.109 292	−17.57
NEVPT2[a]			−16.69
CASPT2[a]			−15.12
MDSPT 2	−290.073 605	−290.101 380	−17.42
MDSPT3	−290.082 374	−290.110 117	−17.41
MDSPT4	−290.082 968	−290.110 526	−17.29
H^v (2nd)	−290.110 362	−290.140 409	−18.85
H^v (3rd)	−290.097 108	−290.124 312	−17.07
[1,0]Padé	−290.098 514	−290.126 234	−17.40

[a]Taken from Ref. 84.

geometries reported by Colvin *et al.*:[82] $^1A_1$, r_e(SiH) $=2.84\ a_0$ and $\angle$HSiH$=95$ deg; $^3B_1$, r_e(SiH)$=2.77\ a_0$ and $\angle$HSiH$=118$ deg.

The CAS spaces for the multireference calculations for both systems are constructed by allocating six electrons to six orbitals (three of a_1, one of b_1, and two of b_2 symmetry). Tables VII and VIII summarize the calculations for the $\Delta = E(^1A_1)-E(^3B_1)$ splittings of CH_2 and SiH_2, respectively, as obtained from various perturbative and CC/EOM-CC methods. The IVO-CASCI method is the first-order approximation within the H^v scheme that has been shown to yield comparable excitation energies to CASSCF treatments without the need for time consuming iterations beyond those in an initial SCF calculation,[83] and both yield splittings of comparable quality.

The SCF splitting for CH_2 deviates from the FCI by 14.17 kcal/mol. Inclusion of electron correlation through CASSCF (IVO-CASCI) calculations provides a dramatic improvement, reducing the $\Delta_{theory}-\Delta_{FCI}$ to 0.85(0.87) kcal/mol. As shown in Table VII, all the approximate methods except H^v_{2nd}, MDSPT2, and CR-EOMCCSD(T),ID overestimate the singlet-triplet energy gap in CH_2. Quite the opposite trend is exhibited by perturbative and nonperturbative theories in the calculations of Δ for SiH_2. All the perturbative schemes except the H^v_{2nd} method underestimate the singlet-triplet splittings for SiH_2.

Tables VII and VIII shows that the singlet-triplet splittings of CH_2 and SiH_2 estimated from n-electron valence state perturbation theory (NEVPT2)[84] are better than the CASPT2 splittings but not as accurate as those obtained from the MDSPT and H^v methods. In fact, the splittings computed with the MDSPT scheme, the H^v method, and the [1,0] Padé approximant constructed from the H^v data are all comparable to the best CC and EOM-CC estimates. The only other relatively inexpensive approach that might improve these results even further is the genuine MRCCSD theory which, as

shown in Ref. 85, is capable of giving a 0.04 kcal/mol difference with FCI for the single-triplet splitting in CH_2.

V. CONCLUSION

Test calculations have been performed to benchmark and assess the relative accuracies of various different low-order multireference perturbation theory methods by comparing their predictions with one another and with the corresponding FCI and CC calculations. Test systems include cases with quasidegeneracy at the transition state or during bond breakage for which single-reference perturbation expansions are often uselessly divergent. The CC and EOM-CC methods with triples are the most accurate, and the accuracy of effective valence shell Hamiltonian (H^v) method is often better than that obtained with other multireference perturbation theories, although the performance of other multireference perturbation theory schemes is usually satisfactory from the practical standpoint. We have demonstrated that the MDSPT approach fares better than other diagonalize then perturb methods. The examples considered involve the use of complete reference spaces of minimal sizes. Another degree of freedom to be considered lies in the size of the reference space and, for some approaches, in the use of incomplete reference spaces.

ACKNOWLEDGMENTS

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