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State-selective multi-reference coupled-cluster theory employing the single-reference formalism: Application to an excited state of H8

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The state-selective (SS) multi-reference (MR) coupled-cluster (CC) method exploiting the single-reference (SR) formalism [P. Piecuch, N. Oliphant, and L. Adamowicz, J. Chem. Phys. **99**, 1875 (1993)] is applied to the first excited totally symmetric singlet state of a prototype molecular system composed of eight hydrogen atoms. Minimum basis set is employed and various geometries are considered. The SS CC energies are compared with the results of the state-universal (SU) MR CC calculations involving single and double excitations (CCSD) as well as with the exact energies obtained using the full configuration interaction method. Comparison is also made with the results of the standard SR CCSD calculations. In both nondegenerate and quasidegenerate regions, our SS CC theory truncated at double excitations [SS CCSD(TQ) method] provides much better description of the first excited state than the genuine multi-determinantal SU CCSD formalism. © *1995 American Institute of Physics.*

I. INTRODUCTION

The single-reference (SR) coupled-cluster (CC) theory[1] is known as an extremely accurate tool for description of the closed-shell (CS) nondegenerate ground states.[2–4] In the last 10–15 years, several advances have been made towards generalization of the CC formalism to arbitrary open-shell (OS) or highly quasidegenerate CS systems, bond-breaking phenomena, and excited states (see, e.g., Refs. 4–8, and references therein).

Genuine multi-configurational OS CC approaches employ a general multi-reference (MR) formalism and use the concept of the effective Hamiltonian acting in a conveniently chosen low-dimensional model space (see, e.g., Refs. 4–8). These formalisms can be divided into the so-called *Fock-space* or *valence-universal* (VU) methods and *Hilbert-space* or *state-universal* (SU) methods. A separate category of the OS CC methods is formed by the so-called *one-state* or *state-selective* (SS) theories, in which the wave operator acts on a SR but multi-configurational state.

Recently, we have proposed a new SS MR CC method, which should be equally efficient in quasidegenerate and nondegenerate situations[9] (cf. also, Refs. 10 and 11). It results from a simple realization that any MR scheme can be regarded as a clever technique of accounting for the most important high-order excitations from all high-order clusters appearing in the SR cluster expansion, when the latter is applied to a quasidegenerate state. In particular, our SS CCSD(TQ) theory emerges through a suitable selection of the presumably most significant tri- and tetraexcited cluster components appearing in the full SR CCSDTQ formalism.[9] A similar SS CCSD(T) approximation emerges through selection of the most important triply excited clusters in the SR CCSDT formalism. The use of a SR CC-like ansatz in our theory guarantees that the most important properties of all CC methods, like the connectivity of the cluster coefficients

and size extensivity of the results or the energy-independent character of the wave function equations, are preserved.

In the present paper, we focus on the applicability of the SR-like SS CC theory of Ref. 9 to excited states. First attempts to directly apply the SR CC formalism to calculate excited states of simple diatomic molecules were made in Ref. 12. The results proved that if an excited state has a clearly defined principal determinant, then it is possible to perform a CC calculation in precisely the same way as for the ground state, i.e., using the principal determinant as the reference configuration. Both the convergence of the iterative procedure for solving CC equations and the reproduction of the full configuration interaction (FCI) energy turned out to be similar to those for the ground state.[12] More recently, the problem of applicability of the SR CC theory to excited states was addressed in Refs. 13 and 14.

Successful applications of our SR-like SS CC method for calculations of the highly degenerate ground states of molecules undergoing severe geometrical transformations were discussed in Refs. 15–17. In the present work we demonstrate that the SS CC method can be directly extended to excited states which exhibit multi-configurational character. We rely on the ability of the SS CC formalism to correctly handle severely degenerate problems without resorting to genuine MR function techniques.[15–17]

In this paper, we explore the performance of our SS CC approach by calculating the first excited totally symmetric singlet state of a simple, yet very demanding, eight-electron model system consisting of four interacting, slightly stretched, hydrogen molecules.[18] This model, referred to as H8,[18] enables us to continuously vary the degree of degeneracy between the two reference configurations spanning the model space by changing a single parameter describing its geometry. This should allow us to test an efficiency of various levels of the SS CC theory.

The H8 model was employed in the past to investigate the performance of SR and MR CI methods,[18] various SR CC approaches,[15,18–20] and genuine MR CC theories.[19,21,22] In particular, it was shown that accuracy of the two-reference

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SU CCSD description of the first excited ^1A_g state (hereafter designated as the 2 ^1A_g state; in general, n ^1A_g, $n=1,2,...$, designates the n-th state of the ^1A_g symmetry) is strongly affected by an intruder state problem[19] (cf. also, Ref. 15). This indicates that some higher than doubly excited cluster components, such as the semi-internal[5,23] components present in our SS CC formalism, must be accounted for to improve rather poor description of the 2 ^1A_g state within the two-reference framework. Unlike the genuine MR CC theories, our SS CC scheme is not affected by the intruder state problem, so that the SS CC description of the first excited ^1A_g state should be essentially better in comparison with the SU CC results.[15,16] As in our previous papers,[15,16] we investigate the minimum basis set (MBS) H8 model,[18] for which the exact FCI results are available.

II. THEORY

In general OS or highly quasidegenerate CS cases, the choice of the Fermi vacuum is no longer unambiguous, since there are several single-determinantal functions, whose contribution to a given state is significant. In our theory,[9] we resolve this problem by selecting one of the reference configurations (usually, the one which dominates in the CI expansion), designated as $|0\rangle$, as the formal reference which serves as the Fermi vacuum, and partition the spin-orbitals occupied in $|0\rangle$ $(i,j,k,l,...)$ into two disjoint classes of inactive core (i,j,k,l,...) and active hole (I,J,K,L,...) states and, similarly, the spin-orbitals unoccupied in $|0\rangle$ $(a,b,c,d,...)$ into two classes of the vacant (particle) active (A,B,C,D,...) and inactive virtual (a,b,c,d,...) states. Although the concept of the multi-dimensional reference or model space, which is present in the genuine MR CC theories,[4–8] can be entirely avoided in our formalism, the above partitioning of the spin-orbitals corresponds to a choice of the space

$$\mathscr{M}_0 = \mathrm{span}\{|\mu\rangle\}_{\mu=0}^{M_0-1} \equiv \mathrm{span}\{|0\rangle, |0_I^A\rangle, |0_{IJ}^{AB}\rangle, ...\}_{I>J>...}^{A>B>...} \quad (1)$$

as the reference space ($|0_{i_1 i_2...i_\kappa}^{a_1 a_2...a_\kappa}\rangle$ is the κ-fold excited configuration). Thus, all model space configurations result as the excitations from $|0\rangle$ involving only active labels. Configurations belonging to the orthogonal complement $\mathscr{M}_0^\perp$, that are needed to describe the excitations *outside* the complete[5] reference space, carry at least one inactive label.

The SS CC approach of Ref. 9 is based on an observation that all excitations from the reference determinants $|\mu\rangle$ into $\mathscr{M}_0^\perp$, as well as all configurations $|\mu\rangle$, can be regarded as certain classes of excitations from the selected formal reference configuration $|0\rangle$. Thus, the multi-determinantal character of a given quantum state $|\Psi\rangle$ can be incorporated into the SR CC formalism by including only certain selected excitations from $|0\rangle$ in the standard CC ansatz for $|\Psi\rangle$,

$$|\Psi\rangle = e^T |0\rangle, \quad \langle 0|\Psi\rangle = \langle 0|0\rangle = 1. \quad (2)$$

Here, T designates the cluster operator which, when acting on $|0\rangle$, creates all possible fully connected cluster components of $|\Psi\rangle$. We decompose the operator T into a sum of its various many-particle contributions,

$$T = \sum_{\kappa=1}^N T_\kappa, \quad (3)$$

where, using the Einstein summation convention,

$$T_\kappa = \sum_{\substack{i_1>i_2>...>i_\kappa \\ a_1>a_2>...>a_\kappa}} t_{a_1 a_2...a_\kappa}^{i_1 i_2...i_\kappa} E_{i_1 i_2...i_\kappa}^{a_1 a_2...a_\kappa}$$
$$= (\kappa!)^{-2} t_{a_1 a_2...a_\kappa}^{i_1 i_2...i_\kappa} E_{i_1 i_2...i_\kappa}^{a_1 a_2...a_\kappa}, \quad (4)$$

and N designates the number of electrons in the system. The excitation operators $E_{i_1 i_2...i_\kappa}^{a_1 a_2...a_\kappa}$ are defined in a usual way, i.e., acting on $|0\rangle$, they generate the κ-fold excited configurations $|0_{i_1 i_2...i_\kappa}^{a_1 a_2...a_\kappa}\rangle \equiv E_{i_1 i_2...i_\kappa}^{a_1 a_2...a_\kappa}|0\rangle$. The scalar factors $t_{a_1 a_2...a_\kappa}^{i_1 i_2...i_\kappa}$ represent the corresponding cluster amplitudes.

Formally, our SS CC method results from the SR CC theory by decomposing the SR cluster operator T, Eq. (3), into two commuting parts, T^{int} and T^{ext}, defined as[9]

$$T^{\mathrm{int}} = \sum_{\kappa=1}^{N_{ao}} T_\kappa^{\mathrm{int}}, \quad T_\kappa^{\mathrm{int}} = (\kappa!)^{-2} \, ^{\mathrm{int}} t_{A_1 A_2...A_\kappa}^{I_1 I_2...I_\kappa} E_{I_1 I_2...I_\kappa}^{A_1 A_2...A_\kappa}, \quad (5)$$

$$T^{\mathrm{ext}} = \sum_{\lambda=1}^N T_\lambda^{\mathrm{ext}}, \quad T_\lambda^{\mathrm{ext}} = (\lambda!)^{-2} \, ^{\mathrm{ext}} t_{a_1 a_2...a_\lambda}^{i_1 i_2...i_\lambda} E_{i_1 i_2...i_\lambda}^{a_1 a_2...a_\lambda}, \quad (6)$$

where the amplitudes $^{\mathrm{ext}} t_{a_1 a_2...a_\lambda}^{i_1 i_2...i_\lambda}$ carry at least one inactive label, i.e., $^{\mathrm{ext}} t_{A_1 A_2...A_\lambda}^{I_1 I_2...I_\lambda} \equiv 0$, and N_{ao} designates the number of active electrons or active spin-orbitals occupied in $|0\rangle$. Various truncation schemes in T^{int} and T^{ext} lead to several approximate SR CC-like schemes, such as the SS CCSD(TQ) method, which is effectively equivalent to the standard SR CC theory with T approximated as[9,15]

$$T \cong T^{\mathrm{SS \, CCSD(TQ)}} = T_1 + T_2 + T_3\binom{abC}{Ijk} + T_4\binom{abCD}{IJkl}. \quad (7)$$

Here, the cluster components $T_3\binom{abC}{Ijk}$ and $T_4\binom{abCD}{IJkl}$ contain only the semi-internal and internal[5,23] terms $t_{abC}^{Ijk} E_{Ijk}^{abC}$ and $t_{abCD}^{IJkl} E_{IJkl}^{abCD}$, respectively. The SS CCSD(TQ) theory accounts for all single and double excitations from the model space spanned by at most double excitations from $|0\rangle$, i.e.,

$$\mathscr{M}_0 = \mathrm{span}\{|0\rangle, |0_I^A\rangle, |0_{IJ}^{AB}\rangle\}_{I>J,A>B}, \quad (8)$$

and, through the use of the SR CC-like ansatz, it describes some higher-order effects. The $\mathscr{M}_0$ component of $|\Psi\rangle$ is described by the T_1^{int} and T_2^{int} clusters. Along with the SS CCSD(TQ) method, it is worthwhile to consider the simpler SS CCSD(T) scheme, which results from the SR CCSDT formalism by restricting the general triexcited cluster amplitudes t_{abc}^{ijk} to t_{abC}^{Ijk} and neglecting all the others[9] (cf. also, Ref. 11). The corresponding cluster operator is given by the formula[9,15]

$$T \cong T^{\mathrm{SS \, CCSD(T)}} = T_1 + T_2 + T_3\binom{abC}{Ijk}. \quad (9)$$

As long as $|0\rangle$ is an important (not necessarily dominant) configuration in the FCI expansion of a given electronic state $|\Psi\rangle$, the SS CCSD(T) and SS CCSD(TQ) meth-
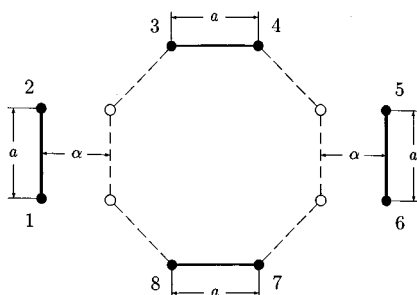
FIG. 1. Nuclear configuration and definitions of the parameters a and α for the H8 model.

FIG. 2. FCI energies of the first three singlet states of the MBS H8 model. The examined excited state is represented by a dashed line. The n-th state of symmetry X $(X = {}^1A_g, {}^1B_{1g})$ is designated by nX.

ods should be directly applicable. This includes both the ground and excited states $|\Psi\rangle$. In the case of the ground state, the formal reference determinant $|0\rangle$ is usually the ground-state Hartree–Fock (HF) configuration $|{}^{HF}0\rangle$.[15–17] In the case of excited state, we may have to choose one of the excited configurations $|{}^{HF}0^{ab...}_{ij...}\rangle$ as $|0\rangle$. A clear example of such a situation is provided by the $2\,{}^1A_g$ state of the H8 model system.

III. COMPUTATIONAL DETAILS

A. Model description

We study the H8 model of Jankowski $et\ al.$,[18] for which the range of the configurational and orbital quasi-degeneracies[24] can be continuously varied by changing a single parameter α defining its geometry (see Fig. 1). By proceeding from $\alpha = 0$ (D_{8h} structure) to $\alpha \to \infty$, we can investigate a continuous transition from highly quasidegenerate to nondegenerate situations (cf. later parts of this section). We study a wide spectrum of geometries ranging from an almost exactly degenerate $\alpha = 0.0001$ a.u. case to a practically nondegenerate $\alpha = 1.0$ a.u. configuration. The fixed interatomic H–H distance a for each hydrogen molecule (see Fig. 1) is chosen to be 2.0 a.u., so that the individual hydrogen molecules forming the H8 model system are slightly stretched. This enhances the quasidegeneracy effects.[25]

We restrict ourselves to the MBS H8 model described in Ref. 18. Computations with larger basis sets (cf., e.g., Ref. 19) prove the relevance of the chosen MBS model.

The FCI expansions of the two lowest totally symmetric singlet states (whose energies as functions of α are depicted in Fig. 2) obtained using the ground-state restricted HF (RHF) molecular orbitals (MOs) indicate a dominant role of two CS configurations, namely, the doubly excited (relative to the ground-state RHF determinant) CS configuration
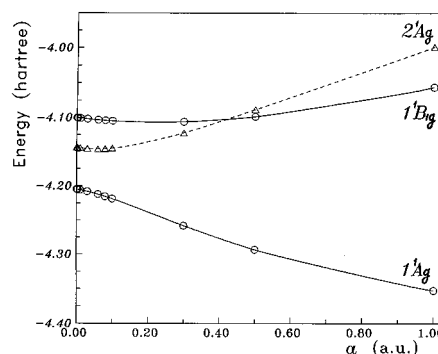
$$|0\rangle = |(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_5)^2|$$
$$\equiv |\phi_1^\alpha \phi_1^\beta \phi_2^\alpha \phi_2^\beta \phi_3^\alpha \phi_3^\beta \phi_5^\alpha \phi_5^\beta|$$
$$\equiv |12345678|, \tag{10}$$

which in the following is assumed to be the formal reference determinant, and the ground-state RHF determinant

$$|1\rangle = |(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_4)^2|$$
$$\equiv |\phi_1^\alpha \phi_1^\beta \phi_2^\alpha \phi_2^\beta \phi_3^\alpha \phi_3^\beta \phi_4^\alpha \phi_4^\beta|$$
$$\equiv |0^{21}_{87}\rangle, \tag{11}$$

which represents a double excitation from $|0\rangle$, Eq. (10). Here, the spin-orbitals occupied and unoccupied in $|0\rangle$ are numbered $i = 1 - 8$ and $a = 1 - 8$, respectively (odd numbers designate α spin-orbitals and even numbers label β spin-orbitals).

A strong interaction of configurations $|0\rangle$ and $|1\rangle$, Eqs. (10) and (11), can be seen by examining the FCI expansions of the two lowest ${}^1A_g$ states for different values of the parameter α (cf. Refs. 15 and 16). The corresponding coefficients at $|0\rangle$ and $|1\rangle$ for the first excited ${}^1A_g$ state are given in Table I and Fig. 3. The configurational quasidegeneracy involving CS determinants $|0\rangle$ and $|1\rangle$ becomes more pronounced with decreasing value of the parameter α. For $\alpha = 0$ we reach the situation, where the two configurations $|0\rangle$ and $|1\rangle$ become exactly degenerate (their weights $|c_0|$ and $|c_1|$ in the FCI expansions of the $1\,{}^1A_g$ and $2\,{}^1A_g$ states become identical; cf. Table I and Fig. 3, and Ref. 15). With increasing α, participation of the configuration $|1\rangle$ in the FCI expansion of the $2\,{}^1A_g$ state decreases, so that for $\alpha > 0.1$ a.u. the first excited ${}^1A_g$ state exhibits practically nondegenerate character, with configuration $|0\rangle$, Eq. (10),

TABLE I. A comparison of the FCI expansion coefficients at the reference configurations $|0\rangle$ and $|1\rangle$ (designated by the orbital occupancies), Eqs. (10) and (11), respectively, for the first excited ${}^1A_g$ state of the MBS H8 model with $a = 2.0$ a.u. and several values of α (in a.u.).

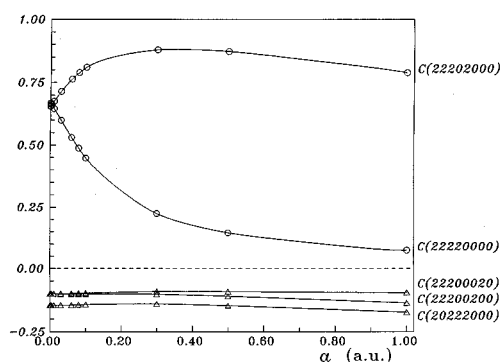| α	1.0	0.5	0.1	0.06	0.03	0.01	0.003	0.001	0.0001
$c_1 = C(22220000)$	0.074 712	0.146 314	0.448 118	0.530 787	0.599 519	0.645 837	0.661 713	0.666 195	0.668 203
$c_0 = C(22202000)$	0.788 778	0.872 548	0.810 218	0.763 391	0.714 488	0.675 483	0.660 821	0.656 551	0.654 618

FIG. 3. FCI coefficients of the dominant configurations (designated by the orbital occupancies) in the FCI expansion of the first excited ^1A_g state for the MBS H8 model.

playing the dominant role (see Table I and Fig. 3). The dominant role of the configuration $|0\rangle$ over the broad range of geometries is an argument for its choice as a formal reference in our SS CC study of the first excited ^1A_g state. For the same reason, we shall use $|0\rangle$ in the standard SR CCSD calculations for the $2\,^1A_g$ state. In the following, we distinguish between the highly degenerate $0 < \alpha \leqslant 0.1$ a.u. region and the nondegenerate region of 0.1 a.u. $< \alpha \leqslant 1.0$ a.u.

B. Active space choice

The dominant role of the CS configurations $|0\rangle$, Eq. (10), and $|1\rangle$, Eq. (11), in the FCI expansion of the $2\,^1A_g$ state justifies their choice as model configurations for our SS CC formalism. This is equivalent to selecting HOMO and LUMO orbitals, ϕ_4 and ϕ_5, respectively, as active orbitals, while regarding ϕ_p, $p=1-3$ as core and ϕ_p, $p=6-8$ as virtual orbitals. We thus have the occupied spin-orbitals I=7,8 (ϕ_5^α, ϕ_5^β) and the unoccupied spin-orbitals A=1,2 (ϕ_4^α, ϕ_4^β) in the active space, and consider the remaining spin-orbitals, i=1$-$6 and a=3$-$8, respectively, as core and virtual spin-orbitals. The same choice of the active space applies to the ground state. As explained in Ref. 15, the corresponding four-dimensional model space

$$\mathscr{M}_0' = \text{span}\{|0\rangle, |1\rangle, |0_7^1\rangle, |0_8^2\rangle\}, \tag{12}$$

spanned by two CS and two OS configurations separates into a two-dimensional subspace

$$\mathscr{M}_0 = \text{span}\{|0\rangle, |1\rangle\} \subset \mathscr{M}_0' \tag{13}$$

relevant to the ^1A_g problem investigated in this paper, and two one-dimensional subspaces describing singlet and triplet B_{1g} states. Thanks to different spatial symmetries of ϕ_4 and ϕ_5, the monoexcited contribution to the internal cluster operator T^{int} vanishes ($T_1^{\text{int}}=0$), so that the formula for the zeroth-approximation reference state $|\Phi\rangle$ of the SS CC formalism (cf. Ref. 9) reduces to[15,16]

$$|\Phi\rangle \equiv e^{T^{\text{int}}}|0\rangle = (1+T_2^{\text{int}})|0\rangle = |0\rangle + t_{21}^{87}|0_{87}^{21}\rangle = |0\rangle + t_{21}^{87}|1\rangle. \tag{14}$$

This means that the value of the leading pair-cluster coefficient t_{21}^{87} can provide a measure of the configurational quasidegeneracy involved. In particular, we can apply Eq. (14) to assess the quality of the first excited ^1A_g state obtained with the SS CC methods. The CI or SU CC equivalent of the coefficient t_{21}^{87} can be obtained by computing the ratio of the linear expansion coefficients c_1 and c_0 appearing at the configurations $|1\rangle$ and $|0\rangle$ in the corresponding CI or SU CC wave function expansions for the $2\,^1A_g$ state.

IV. RESULTS AND DISCUSSION

All SR and SS CC calculations were performed using the spin-orbital program written in our laboratory.[15,26] The two-reference SU CCSD calculations were carried out using the orthogonally spin-adapted program described in Ref. 27. The initial RHF calculations and the subsequent transformation to the MO basis, as well as the FCI calculations, were carried out with the electronic structure package GAMESS.[28]

In the entire degenerate region, the SS CCSD(TQ) approach represents an extremely accurate formalism to describe the first excited A_g singlet [see Tables II and III and Fig. 4 (dashed line)]. This applies to both the energy and the corresponding wave function. The differences between the SS CCSD(TQ) and FCI energies are uniform throughout the entire region considered and hardly exceed 2 mhartree, which favorably compares to the 8.4–25.9 mhartree error obtained with the SU CCSD approach. A similar trend can be seen in the excitation energy calculated as the difference between the energy of the first excited ^1A_g state and the ground-state energy, which was determined in our previous study[15] (see Table IV). Here again the SS CC results are significantly better than the SU CC values. The difference between the FCI and SS CCSD(TQ) excitation energies never exceeds 2.7 mhartree in the entire range of the α parameter considered, which should be compared to the 11.2–26.5 mhartree difference obtained with the SU CCSD approach.

TABLE II. A comparison of the FCI and various CC energies (in hartree, all signs reversed) for the first excited ^1A_g state of the MBS H8 model with $a=2.0$ a.u. and various values of α (in a.u.). RHF designates the Hamiltonian expectation value obtained with the reference configuration $|0\rangle$ defined by Eq. (10).

α	1.0	0.5	0.1	0.06	0.03	0.01	0.003	0.001	0.0001
SR CCSD	3.970 168	4.075 182	4.129 853	4.128 224	4.124 653	4.123 250	4.119 117	4.118 594	4.118 353
SS CCSD(T)	3.990 188	4.085 327	4.143 428	4.143 823	4.141 967	4.138 924	4.137 921	4.137 502	4.137 306
SS CCSD(TQ)	3.996 054	4.086 530	4.143 895	4.144 964	4.144 366	4.143 192	4.142 626	4.142 449	4.142 368
SU CCSD	3.973 051	4.077 453	4.136 717	4.137 793	4.137 331	4.136 340	4.135 858	4.135 707	4.135 637
RHF	3.770 180	3.918 285	4.019 089	4.027 213	4.032 991	4.036 687	4.037 950	4.038 307	4.038 468
FCI	3.998 978	4.088 220	4.145 171	4.146 335	4.145 859	4.144 791	4.144 267	4.144 103	4.144 027

TABLE III. CC and FCI values of the t_{21}^{87} amplitude characterizing the first excited ^1A_g state of the MBS H8 model with $a = 2.0$ a.u. and various values of α (in a.u.). FCI and SU CCSD values of t_{21}^{87} are calculated as ratios of the linear expansion coefficients c_1 and c_0 at the reference configurations $|1\rangle$ and $|0\rangle$.

α	1.0	0.5	0.1	0.06	0.03	0.01	0.003	0.001	0.0001
SR CCSD	0.158 967	0.231 311	0.801 635	1.055 258	1.343 637	1.603 171	1.732 064	1.755 113	1.794 042
SS CCSD(T)	0.096 686	0.165 740	0.610 468	0.821 311	1.078 136	1.350 172	1.449 835	1.490 361	1.502 999
SS CCSD(TQ)	0.108 553	0.174 195	0.572 278	0.722 540	0.875 457	1.000 468	1.048 900	1.060 241	1.069 694
SU CCSD	0.152 270	0.212 514	0.591 153	0.717 828	0.840 434	0.937 314	0.974 237	0.985 077	0.989 998
FCI	0.094 719	0.167 686	0.553 083	0.695 302	0.839 090	0.956 111	1.001 350	1.014 689	1.020 753

In both the total and excitation energies one can see a consistent improvement in going from the SR CCSD to SS CCSD(T) and SS CCSD(TQ) methods (see Fig. 4 and Table IV), which indicates an important role of the semi-internal tri- and tetraexcited components $T_3\binom{abC}{Ijk}$ and $T_4\binom{abCD}{IJkl}$ in describing the $2\,^1A_g$ state. The SS CCSD(TQ) expansion is flexible enough to give a very good description of the $2\,^1A_g$ wave function. This is indicated by very good values of the pair-cluster coefficient t_{21}^{87} (see Table III). In the nondegenerate region they are essentially better than those provided by the SU CCSD approach, while being very close to the corresponding FCI values in the quasidegenerate region.

In the nondegenerate region of the H8 model, the two lowest singlets of the A_g symmetry have entirely different quasidegeneracy characteristics.[19,22] The two-dimensional model space (13) remains adequate only for the ground state, which is dominated by the ground-state RHF configuration $|1\rangle$. This results in a poor description of the first excited ^1A_g state by the SU CCSD method in this region [19] (cf., also, Table II and Fig. 4). Except for the quasidegenerate $\alpha \lesssim 0.1$ a.u. region, the errors characterizing the SR CCSD and SU CCSD methods are large and comparable in magnitude (similarity of the SR and SU CCSD approaches in the nondegenerate region shows up in both the energy values and values of the coefficient t_{21}^{87}; see Tables II and III and Fig. 4). Clearly, in the quasidegenerate region the two-reference SU CCSD method using the model space $\mathcal{M}_0$, Eq. (13), outperforms the SR CCSD theory. However, neither the SR CCSD method nor its MR SU CCSD counterpart are capable of

giving the results of the same quality as those provided by our SS CCSD(T) or SS CCSD(TQ) approaches. This is an advantage of employing the one-state theory, which uses a single set of amplitudes optimized for a given (in our case, the first excited) quantum state. The SU CCSD method uses a single set of amplitudes for both $1\,^1A_g$ and $2\,^1A_g$ states and this certainly affects its performance and worsens the SU CCSD results in the nondegenerate region, where the $2\,^1A_g$ state interacts with higher excitations. Our results and the results for the ground state obtained in Refs. 15 and 16 show that the use of different amplitudes for different eigenstates of the Hamiltonian offered by our SS CC methods represents a preferred solution (not only in the nondegenerate region). Our SS CC approach allows for easy adoption of different active spaces for different states, which can be essential to assure a good description of the first excited A_g singlet in the nondegenerate region. An alternative solution would most likely be to include the connected triple and quadruple excitations of semi-internal type in the SU CC theory[23] [notice their inherent presence in the SS CCSD(TQ) method].

The above analysis shows that the cluster expansion used in the SS CCSD(TQ) formalism is potentially much richer than the one employed in the SU CCSD theory in its standard formulation and this is the reason for the observed large discrepancies between the SS CCSD(TQ) and SU CCSD energies of the $2\,^1A_g$ state. As explained in Ref. 15, the latter theory uses approximately the same number of amplitudes for two states as our SS CCSD(TQ) formalism for a single state.

In spite of this substantial difference between the SS CC and SU CC approaches, both methods exhibit some common features in the quasidegenerate region. In particular, differences between the SS CCSD(TQ) and SU CCSD energies and their FCI counterparts remain fairly constant as functions of the parameter α. The most remarkable feature of our SS CCSD(TQ) theory is the fact that the errors in the SS CCSD(TQ) energies relative to FCI energies are almost independent of the quasidegeneracy level (see Fig. 4). The fact that of all CC methods investigated in this study the SS CCSD(TQ) theory provides the most accurate description of the first excited ^1A_g state is very promising for future applications of the SS CC formalism to study excited states of genuine *ab initio* systems. In particular, it will be interesting to examine the behavior of the SS CCSD(TQ) approach in describing the low-lying excited states of the OS nature (such as OS singlets), which require a very accurate accounting for high-order excitations. Due to inclusion of semi-
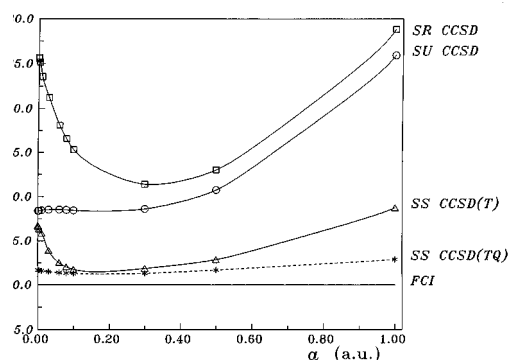

FIG. 4. Differences between CC and FCI energies, $E(\text{CC}) - E(\text{FCI})$ (in mhartree) as functions of the parameter α, for the first excited ^1A_g state of the MBS H8 model. The SR CCSD, SU CCSD, SS CCSD(T) and SS CCSD(TQ) results are designated by $\square$, $\bigcirc$, $\triangle$ and $*$, respectively.

TABLE IV. CC and FCI excitation energies for the $1\,^1A_g \rightarrow 2\,^1A_g$ transition (in mhartree) in the MBS H8 model with $a = 2.0$ a.u. and various values of α (in a.u.).

α	1.0	0.5	0.1	0.06	0.03	0.01	0.003	0.001	0.0001
SR CCSD	382.277	217.353	86.796	80.924	79.429	77.849	81.030	81.291	81.416
SS CCSD(T)	362.504	207.580	76.678	70.962	70.230	72.380	73.234	73.626	73.813
SS CCSD(TQ)	356.676	206.394	74.201	66.386	62.718	61.536	61.379	61.360	61.354
SU CCSD	380.503	216.311	84.433	77.073	73.540	72.282	72.061	72.019	72.003
FCI	354.012	205.001	73.593	65.834	62.178	60.977	60.807	60.783	60.776

internal and internal tri- and tetraexcitations, the SS CCSD(TQ) theory employing an OS determinant (such as $|0_7^1\rangle$) as a vacuum should preserve the spin-symmetry of the Hamiltonian and thus be applicable in the studies of the OS singlet states.[29]

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