SINGLET–TRIPLET SPLITTING IN METHYLENE: AN ACCURATE DESCRIPTION OF DYNAMIC AND NONDYNAMIC CORRELATION BY REDUCED MULTIREFERENCE COUPLED CLUSTER METHOD

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Received June 16, 1998
Accepted June 18, 1998

This paper is affectionately dedicated to Professor Rudolf Zahradnik – an esteemed scientist and teacher, a cherished colleague and friend – on the occasion of his 70th birthday.

A classical multireference problem – the singlet–triplet separation in methylene – is examined by the recently introduced reduced multireference (RMR) singles and doubles coupled cluster (CCSD) method, using both double zeta plus polarization (DZP) and large atomic natural orbital (ANO) basis sets. In the former case, the performance of the RMR CCSD as well as of other approaches is assessed by a comparison with the full configuration interaction (FCI) result that represents the exact solution for this basis, while in the latter case a comparison is made with the experiment. It is shown that using a minimal two-configuration reference space, the RMR CCSD result compares well with either FCI or experiment; and is of the same quality as that provided by the two-reference state universal MR CCSD theory. Both MR CCSD approaches give a balanced description for the singlet and triplet states involved and correct the shortcomings of the single reference CCSD approach that is lacking in the presence of nondynamical correlation effects.

Key words: Multireference coupled clusters; Methylene; Electron correlation; Singlet-triplet separation; *Ab initio* calculations.

The single reference (SR) coupled cluster (CC) and multireference (MR) configuration interaction (CI) methods with singles and doubles (SD) are two highly correlated methods that are routinely used for an accurate account of electron correlation effects. Nonetheless, when dealing with states having a multireference character – which often arise when a molecule separates into fragments or is promoted to one of its excited states, as well as in certain other cases – neither SR CCSD nor MR CISD is completely

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satisfactory. Although the SR CCSD method handles very effectively the dynamic correlation effects, its performance deteriorates when nondynamic correlation plays a significant role. On the other hand, the MR CISD method is very effective in treating the nondynamic correlation, but less so when accounting for the dynamic correlation effects. In fact, MR CISD relying on a small reference space is incapable to properly describe dynamic correlation. One thus compensates this deficiency by employing a much larger reference space than is required for an appropriate zero-order description, which in turn leads to problems associated with large active spaces. It is thus important to develop a MR CC approach which can accurately describe both dynamic and nondynamic correlation effects, while relying on a minimal reference space, thus requiring a minimal computational effort. For this very reason we have developed the so-called reduced multi-reference (RMR) CCSD approach[1–3] described below.

In this paper we discuss the above points and apply the RMR CCSD method to a simple, yet important problem of the singlet–triplet ($^3B_1$–$^1A_1$) separation in methylene (CH_2). While the Hartree–Fock (HF) limit[4] gives a splitting of 25 kcal/mol, which is about 2.5 times larger than the experimental estimate[5] (≈9.4 kcal/mol), all correlated methods, including the multiconfigurational self consistent-field (MCSCF) method, generalized valence bond (GVB) method, many-body perturbation theory (MBPT), as well as limited CI or CC methods, give a qualitatively correct value for this separation[4,6–10]. Nonetheless, the nondynamical correlation plays here an important role. The inadequacy of the HF result stems from the fact that the $^3B_1$ and $^1A_1$ zero-order wave functions employ different active spaces. Since the highest occupied molecular orbital (HOMO) ($3a_1$) and the lowest unoccupied MO (LUMO) ($^1b_1$) are utilized in the $^3B_1$ zero-order HF wave function, the same two orbitals should be used as the active orbitals in the zero-order description of the $^1A_1$ state in order to achieve an unbiased treatment. Such a two-electron/two-orbital active space leads to a one-configuration wave function for the $^3B_1$ state and a two-configuration wave function for the $^1A_1$ state. In the basis set limit, such simplest correlated method predicts the separation of 11 kcal/mol (ref.[4]).

In any case, an accurate computation of this quantity proved to be a challenging problem in spite of the fact that we deal with a very simple molecular system. For this very reason this problem is often employed to test various sophisticated treatments of electron correlation. The key problem is the correct description of the $^1A_1$ state, which has a two-reference character. Even the very powerful CCSD method in its SR form is unable to provide a highly accurate result, not to mention other “lower level” theories. The SR CCSD basis set limit is likely to exceed the value of 10 kcal/mol (one gets 10.1 kcal/mol when h type functions are included[11]), so that one has to include triples in order to achieve a sufficient accuracy[10]. The MR CISD method relying on a two-configuration reference space (2R) also yields a very good, highly correlated wave function, yet a definite non-negligible discrepancy from the experiment remains. To eliminate this discrepancy, one has to use a large reference space, such as the all valence 6-electron/6-orbital complete active space (CAS).

The shortcomings of both the SR CCSD and 2R-CISD methods are easy to understand. In the first case, single and double excitations are accounted for explicitly, while higher excitations are handled *via* their disconnected components. Thus, only one- and two-body connected clusters, relative to the leading configuration that is used as a reference, appear explicitly in the theory. However, in view of the importance of the second leading configuration, as implied by the structure of the two-configuration MCSCF wave function, the connected singles and doubles relative to both leading configurations should appear explicitly in the theory. Otherwise, the important nondynamical correlation effects will not be properly accounted for. This is clearly the major source of the inadequacy of the SR CCSD description. On the other hand, in the 2R-CISD wave function, only singly and doubly excited configurations from two references are considered. Consequently, most higher than doubly excited configurations (relative to, *e.g.*, the first reference) will be absent from the resulting wave function. In order to account for these higher excited configurations, it is thus necessary to increase the size of the active or model space employed. Thus, while the 2R-CISD method can account for the most important nondynamical correlation effects, it will be lacking in the description of dynamical correlation, unless based on a much larger than 2R active space.

Since the CC Ansatz handles very effectively dynamic correlation, while the MR-type wave function is required to describe nondynamical correlation effects, the most satisfactory and cost effective approach should be achieved *via* a suitable version of MR CCSD: The exponential Ansatz would eliminate a large active space problem of the MR CISD method, while an appropriate zero-order reference space would ensure an unbiased account of both dynamic and nondynamic correlations. In the past, much attention has been devoted to the development of MR CC theories, in the hope of achieving the above stated objective (*cf.* ref.[12]). Our recently developed RMR CCSD method[1–3] represents a rather simple and straightforward approach directly combining the MR CISD and SR CCSD Ansätze. As the above discussion of methylene implies, these Ansätze are mutually complementary: The connected SD clusters that originate from the second configuration are absent in the SR CCSD Ansatz, but are contained in the 2R-CISD wave function, while an inadequate description of higher than SD excitations out of the two references is automatically taken care of by the disconnected clusters arising from the SR CCSD exponential cluster Ansatz. Thus, in the RMR CCSD method[1–3], one accounts for the SD connected clusters relative to the second configuration by exploiting a 2R-CISD wave function, thus enhancing the performance of the SR CCSD approach.

In this paper, we first briefly describe basic idea of the RMR CCSD method and subsequently apply it to the problem of the singlet–triplet separation in methylene. In contrast to our earlier study of this problem, which used a rather small basis set[1], we employ here a large basis set enabling a meaningful comparison with the experimental data. This study thus represents one of the first large scale RMR CCSD applications. We must also point out our earlier study of this problem that exploited the state universal (SU) MR CCSD method[5,9] for the singlet state. We will thus be able to compare the performance of SU CCSD and RMR CCSD employing both small and large basis sets.

RMR CCSD METHOD

The single reference coupled cluster method with singles and doubles (SR CCSD) that is based on the exponential cluster Ansatz for the exact wave function $|\Psi\rangle$,

$$|\Psi\rangle = e^T |\Phi_0\rangle, \qquad (T \approx T_1 + T_2), \tag{1}$$

is often used to efficiently account for the many-electron correlation effects, particularly the dynamic ones. When the nondynamical correlation is also important, the SR approach becomes inadequate and the zero-order wave function is required to involve more than one configuration. The starting point of any MR approach is thus a proper choice of the model space M_0, $M_0 = \mathrm{Span}\{\Phi_0, \Phi_1, \Phi_2, \ldots,\Phi_{M-1}\}$, that can accommodate a zero-order wave function. Once this choice is made, all singles and doubles relative to all the configurations $|\Phi_p\rangle \in M_0$ should be explicitly considered *via* the corresponding connected cluster amplitudes. However, since the generalization of the SR cluster Ansatz to the MR case is not unambiguous, this requirement is handled differently by various existing MR CC theories.

In the so-called state universal (SU) or Hilbert space MR CC approach, one associates a distinct cluster operator $T(p)$ with each reference configuration $|\Phi_p\rangle \in M_0$, and employs the Jeziorski–Monkhorst cluster Ansatz[13]

$$|\Psi_q\rangle = \sum_{p=0}^{M-1} c_{qp}\, e^{T(p)}\, |\Phi_p\rangle \ . \tag{2}$$

At the SU CCSD level of the theory, one thus has to determine M sets of T_1 and T_2 cluster amplitudes. Of course, singles and doubles arising from other references than $|\Phi_0\rangle$ can be regarded as a subset of higher than pair cluster amplitudes, so that we can formally rewrite the MR CCSD wave function (*2*) in the SR CC form, namely

$$|\Psi_0\rangle = e^{\mathrm{T}_1 + \mathrm{T}_2 + \{\mathrm{T}_3 + \mathrm{T}_4 + \ldots\}_{\mathrm{subset}}} |\Phi_0\rangle \ . \tag{3}$$

The symbol $\{\ldots\}_{\text{subset}}$ emphasizes that only a subset of relevant higher than pair cluster amplitudes is involved. A formally SR, yet *de facto* an MR CC approach, based on such an Ansatz, belongs to the so-called state selective or state specific (SS) category, which in general includes a number of distinct approaches (see, *e.g.*, ref.[12]). The Ansätze (*2*) and (*3*) are equivalent in a sense that both involve the same number of connected cluster amplitudes.

The general SU CC theory is an M-reference/M-state approach that employs an M dimensional model space to simultaneously generate M target wave functions. The major problems of such an approach, in addition to its complexity and computational demands, are the so-called intruder state problem and the multiplicity of possible solutions. The SS-type approaches can usually avoid these problems, since they handle one state at a time: However, a general implementation of the Ansatz (*3*) is not easy, since the subset of higher than pair clusters that are involved may contain even five- or six-body, or even higher order clusters, when a large model space is employed.

The RMR CCSD method that is used in this study represents an SS-type approach, thus avoiding the intruder state problem, yet is relatively easy to implement thanks to the way it handles higher than pair clusters. As in other externally corrected CCSD methods[14–17], these are obtained from an independent source, which in the RMR CCSD case is a suitable MR CISD wave function involving only a modest number of configurations. Moreover, since a subset of the required higher than pair cluster amplitudes is determined prior to the evaluation of the T_1 and T_2 clusters, only a subset of all possible T_3 and T_4 cluster amplitudes needs to be explicitly determined, all higher order ones being automatically accounter for implicitly. This is an essential feature of all externally corrected CCSD methods[14–17]. An earlier exploitation of this idea[14–17] led to the RMR CCSD approach, as described in our preceding papers[1–3] (see also ref.[12]). In the following we thus only give a brief description of this method.

Once we have chosen a suitable model or active space that can properly describe the studied dissociation or reaction channel, the RMR CCSD method involves the following three steps: First, we variationally optimize the linear version of the Ansatz (*2*) or (*3*), obtaining the MR CISD wave function corresponding to the chosen model space. Since the MR CISD method is based on the variation principle, the coefficients associated with individual configurations do not represent connected quantities in the sense of the MBPT, but also contain the size nonextensive unlinked contributions.

Thus, in the second step, we extract connected cluster components from the chosen MR CISD wave function. This is done *via* a standard cluster analysis. For the lowest state of a given symmetry, we choose a leading configuration $|\Phi_0\rangle$ and express the MR CISD wave function in the SR CI form,

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_I c_I^0 \, |\Phi_I\rangle \ , \tag{4}$$

where the configuration set $\{|\Phi_I\rangle\}$ contains singles and doubles relative to $|\Phi_0\rangle$, as well as the subset of higher than doubles as implied by Eq. (*3*). The cluster analysis is carried out by expressing $|\Psi_0\rangle$, Eq. (*4*), in the exponential form,

$$|\Psi_0\rangle = \mathrm{e}^{T_1^0 + T_2^0 + T_3^0 + T_4^0 + \cdots} |\Phi_0\rangle \ . \qquad (5)$$

The connected cluster components T_i^0 are obtained by comparing the right hand sides of Eqs (*4*) and (*5*), proceeding from the lower rank clusters to the higher ones. However, as already pointed out, at most T_4^0 component needs to be evaluated. Note that we use the superscript 0 to indicate that these cluster components are derived from the MR CISD wave function. We also use the one- and two-body components T_1^0 and T_2^0 in the next step as the initial guess when solving iteratively the externally corrected CCSD equations.

In the third step, we employ the RMR CCSD Ansatz

$$|\Psi_0\rangle = \mathrm{e}^{T_1 + T_2 + T_3^0 + T_4^0 + \cdots} |\Phi_0\rangle \ , \qquad (6)$$

with T_3^0 and T_4^0 representing the fixed subset of three- and four-body cluster amplitudes determined in the second step above. The unknown T_1 and T_2 amplitudes, Eq. (*6*), then satisfy a set of SR CCSD-like equations that arise through a simple modification of standard SR CCSD equations. This modification accounts for the coupling between the unknown T_1 and T_2 clusters and the known T_3^0 and T_4^0 clusters. The resulting SR CCSD-like equations are then referred to as the externally corrected CCSD equations (*i.e.*, SR CCSD corrected by known T_3 and T_4 from some external source). These equations are no more difficult to solve than standard CCSD equations. Here we can clearly see why only T_3^0 and T_4^0 are calculated in the cluster analysis (step 2 above): This is because higher than four-body clusters are not directly coupled with T_1 and T_2.

The actual implementation of the RMR CCSD method, using various types of model spaces, was described in our earlier papers[1–3], where we refer an interested reader for details.

COMPUTATIONAL DETAILS

The results presented below were obtained using two different basis sets: a double zeta plus polarization (DZP) basis of Bauschlicher and Taylor[7] and an atomic natural orbital (ANO) basis of Comeau *et al.*[18]. To facilitate a comparison with the exact FCI results that are available for a DZP basis[7], we also used the same geometries.

For the details concerning the basis set and the geometries employed we refer the reader to ref.[7].

The large ANO basis set of Comeau *et al.*[18] consists of a 5s4p3d2f1g set for the carbon atom and a 3s2p1d set for hydrogen. A smaller, truncated ANO set, which does not include g functions, was also employed. The equilibrium geometries used with this basis were large scale MR CISD optimized geometries[18]. The bond distance and the bond angle for the $^3B_1$ state were, respectively, 1.079441 Å and 133.576°, and 1.111223 Å and 101.954° for the $^1A_1$ state.

Although all RMR CCSD results will be labelled by the acronym 2R-RMR CCSD, we should point out that a slightly different version of this method was used with the DZP and ANO basis sets. In the former case, the symmetry nonadapted 2-electron/2-orbital (2,2) model space was used as the reference space, so that the MR CISD wave function contained all single and double excitations from all configurations in the (2,2) space, regardless whether symmetry adapted or not. Thus, although some of the reference configurations are not symmetry adapted, and thus are absent from the wave function, the single and double excitations from them may be symmetry adapted and will be present in the wave function (and contribute to the energy). Nonetheless, these symmetry adapted singles and doubles that arise by excitations from symmetry nonadapted references are usually negligible, so that it is more economical to keep only symmetry adapted references. This option was implemented in the latter version of our RMR CCSD programs, which were employed in calculations using a large ANO basis set. Thus, in the latter case, the reference space for the $^1A_1$ state has only two spin and point-group symmetry adapted configurations.

We must also mention that the symmetry adapted (2,2) model space for the $^3B_1$ state involves only one configuration. Although, for the sake of brevity, we use the acronyms 2R or 2CSF also for the $^3B_1$ state, we must keep in mind that in this case we deal in fact with SR approaches, *i.e.*, SR CISD or SR CCSD. The actual program that was used in CC calculations employs the spin adapted CCSD method based on the unitary group approach[19,20] (UGA). Thus, for the $^3B_1$ state, we have that UGA CCSD ≡ 2R-SU CCSD ≡ 2R-RMR CCSD.

Throughout, only valence electrons are correlated, while the 1s core orbital of C is kept frozen. The SCF orbitals are generated by GAMESS (ref.[21]). The same package is also used for limited SR CI calculations, such as SR CISDT or SR CISDTQ. These results are labelled with an additional superscript +, since the SR CI wave functions for the open-shell triplet generated by GAMESS contain in fact more configurations than the designated excitation level.

The implementation of SU CCSD is described elsewhere[22].

RESULTS AND DISCUSSIONS

Prior to investigating any computationally demanding model that is characterized by a good quality basis set, it is expedient to assess the performance of the methods employed on a less demanding, yet realistic model, for which one can generate the exact FCI results. In this way, a definite comparison, that is not encumbered by any uncertainties, can be made. A DZP quality model of CH_2 serves well this purpose.

It is well-known that the prediction of the energy differences is very sensitive to a balanced description of the electron correlation in both states involved. To better appreciate this problem, consider the energy difference between the states labelled by 1 and 2, *i.e.*, $\Delta E = E_1 - E_2$. Assuming the computed energies are $E_i^{(\mathrm{calc})} = \rho_i E_i^{(\mathrm{exact})}$ for states $i = 1$ and 2, the computed energy difference $\Delta E^{(\mathrm{calc})}$ will be given by

$$\Delta E^{(\mathrm{calc})} = \left[\rho + \frac{\rho_1 - \rho_2}{\eta}\right] \Delta E^{(\mathrm{exact})} \ , \qquad (7)$$

where $\rho = (\rho_1 + \rho_2)/2$ and $\eta = 2\Delta E^{(\mathrm{exact})}/[E_1^{(\mathrm{exact})} + E_2^{(\mathrm{exact})}]$. Since even the HF method yields more than 99% of the total energy, implying that $\rho \approx 1$, the error in the computed ΔE is fully determined by the imbalance $\rho_1 - \rho_2$. Since η is a very small number, even a very small imbalance may lead to a sizeable error. For example, for the singlet–triplet separation in CH_2, η is only ≈0.05%. This means that even if we compute the energy of state 1 with a 99.99% accuracy and with a 99.94% accuracy for state 2, the computed singlet–triplet separation will be in error by 100%! This is precisely what happens when we use the HF method: With a DZP basis set (see Table I), the SCF method gives, respectively, 99.697% and 99.639% of the total exact energy (as given by the FCI) for the $^3B_1$ and $^1A_1$ states. The 0.058% imbalance causes then almost 120% error in the singlet–triplet separation. The same magnitude of the error is found even in the HF limit. Since the correlation in the $^1A_1$ state is slightly larger than in the $^3B_1$ state (0.36% of the total energy *vs* 0.3%), a well balanced correlated method should recover a slightly larger fraction of the correlation energy for the $^1A_1$ state than for the $^3B_1$ state. Thus, from the theoretical viewpoint, the primary challenge is to achieve an accurate and balanced treatment of the correlation effects in the two states having a different spin multiplicity.

For a DZP model, the performance of various SR, 2R, as well as large scale approaches employing all valence 6-electron/6-orbital active space, can be assessed by a comparison with the exact FCI energies. In Table I we present total energies, percentages of the recovered correlation energy, as well as the resulting singlet–triplet separations together with their deviation from the FCI value. The SR approaches are clearly unsatisfactory. The error of both SR CISD and SR $CISDT^+$ singlet–triplet separations is about 22%. The SR CCSD provides already a much improved result. In particular, the UGA CCSD error in the computed separation amounts to 0.85 kcal/mol, or 7%. Very similar results are obtained with UHF CCSD and spin-non-adapted ROHF CCSD (ref.[10]). The source of the remaining error is the imbalance in the recovered correlation energies, as already pointed out above. Thus, SR CISD recovers 2.38% more correlation energy for the $^3B_1$ state than for the $^1A_1$ state, leading to a large error in the singlet–triplet separation. This imbalance persists even for SR CISDT$^+$, since both states gain almost equally in correlation due to the inclusion of triples (2.1% *vs* 2.4%). The imbalance in the recovered correlation energies for UGA CCSD is still 0.7%. For this reason it is necessary to include quadruples in the SR CI methods or triples in the SR CC methods in order to overcome an inequitable treatment of correlation effects in both states involved. In either way, one then recovers almost 100% of the correlation energy before the desired balance is achieved.

The ability of the MR CCSD type methods, including both RMR and SU CCSD, to provide an equitable treatment of both states, and thus to properly describe highly sen-

TABLE I
Comparison of total energies (in a.u.), percentage correlation energies E_c (in %), and singlet–triplet separations $\Delta = E(^3B_1) - E(^1A_1)$ (in kcal/mol) for CH_2, as obtained with a DZP basis and various single- and multi-reference methods

Method	$E(^3B_1)^a$	$E(^1A_1)$	$E_c(^3B_1)$	$E_c(^1A_1)$	Δ	Error
FCI[b]	–39.046260	–39.027183	100.00	100.00	11.97	0.00
Single-reference approaches						
SCF	–38.927947	–38.886297	0.00	0.00	26.14	14.17
SR CISD	–39.041602	–39.018284	96.06	93.68	14.63	2.66
UGA CCSD	–39.044064	–39.023639	98.14	97.48	12.82	0.85
SR CISDT$^+$	–39.044420	–39.021176	98.44	95.74	14.58	2.61
UHF CCSDT[c]	–39.046243	–39.026976	99.99	99.85	12.09	0.12
SR CISDTQ$^+$	–39.046251	–39.027001	99.99	99.87	12.07	0.10
(2,2)-Active-space reference approaches[a]						
2CSF[b]	–38.927947	–38.907660	0.00	15.16	12.73	0.76
2CSF-CISD[b]	–39.041602	–39.022156	96.06	96.43	12.20	0.23
2R-SU CCSD[d]	–39.044064	–39.024914	98.14	98.39	12.02	0.05
2R-RMR CCSD	–39.044064	–39.024826	98.14	98.33	12.05	0.08
Large-active-space reference approaches						
CASSCF[d]	–38.965954	–38.945529	32.12	42.04	12.82	0.85
CASSCF-CISD[d]	–39.044872	–39.025804	98.83	99.02	11.97	0.00

[a] For the $^3B_1$ state, a (2,2) active space reduces to a single reference. The actual results were obtained with the interacting space UGA CCSD; [b] ref.[7]; [c] ref.[10]; [d] ref.[9].

sitive energetic quantities, such as the singlet–triplet separation in methylene, should be apparent from Table I. As alluded to above, the origin of an unbalanced description of both states by the SR, correlated methods stems from the presence of a rather strong nondynamic correlation in the $^1A_1$ state. Measured by the difference between the SCF and 2CSF based treatments, the nondynamic correlation amounts to about 15% of the total correlation energy. With 2R approaches, both nondynamic and dynamic correlations can be well described. The 2CSF-CISD method recovers about 96% of correlation for both triplet and singlet, with a small imbalance of 0.4%. The resulting singlet–triplet separation is thus in error by 0.23 kcal/mol, *i.e.*, by about 2%. Both MR CCSD methods, 2R-RMR CCSD and 2R-SU CCSD, give even better results: Both recover about 98% of the correlation energy in either state considered. Consequently, both approaches provide a very satisfactory result for the desired separation: The 2R-RMR CCSD and 2R-SU CCSD errors are only 0.08 and 0.05 kcal/mol, respectively (*cf.* Table I).

When we compare the 2CSF-CISD result for the multireference state $^1A_1$ with the 2R-RMR CCSD or 2R-SU CCSD one, we find that the latter CC approaches recover a significantly larger portion of the dynamic correlation energy (by about 2.7 millihartree or 2% more). This is easy to understand when we realize that the 2CSF-CISD wave function contains only SD excitations from the two references, so that a large number of higher excitations is not accounted for at all. On the other hand, the MR CC methods employing the same 2R reference space are able to recover a large portion of the dynamic correlation effects thanks to the product terms involving lower excitations. Thus, although the minimal 2-reference space is sufficiently large to handle nondynamic correlation, one has to employ a much larger active space when using MR CISD in order to recover more dynamic correlation. Indeed, when we use a 6-electron/6-orbital (6,6) active space, the CASSCF SOCI recovers slightly more correlation energy than the 2R-RMR CCSD or 2R-SU CCSD, and yields an excellent result for the singlet–triplet splitting (*cf.* Table I). Nonetheless, the MR CC approaches clearly represent the most efficient as well as economical way to adequately describe both dynamic and nondynamic correlation, while providing a balanced treatment for the triplet and singlet states involved.

An excellent performance of the 2R-RMR and 2R-SU CCSD methods for a DZP model provides a strong indication that with a sufficiently large basis set these methods will yield reliable results that withstand a comparison with experiment. We hasten to add, however, that such a comparison requires that we take into account zero-point energies (ZPEs) of both states, relativistic effects, and Born–Oppenheimer corrections. Correcting, thus, the experimentally determined separation T_0 for the ZPEs, we obtain a purely electronic value T_e, and taking into account the relativistic and Born–Oppenheimer corrections, we get the desired "experimental" value $T_e^{\mathrm{nr,BO}}$, which can be meaningfully compared with computed separations. In our previous paper[5], we used the value $T_e^{\mathrm{nr,BO}}$ = 9.37 kcal/mol, resulting from the T_e value of Jensen and Bunker[23], the relativistic correction of Davidson *et al.*[24] and the diagonal Born–Oppenheimer correction of Handy *et al.*[25] . We should mention, however, that the relativistic and Born–Oppenheimer corrections are often ignored: Even some very recent studies (cf., *e.g.*, ref.[26]) do not include them when comparing *ab initio* results with experiment.

The 2R-RMR CCSD results, obtained with a large ANO basis set, are compared with the 2R-SU CCSD and large reference space MR CISD ones in Table II. In fact, in this table we present only those results that give the energy gap below 10 kcal/mol. This excludes a number of approaches. As already mentioned, even the standard SR CCSD does not satisfy this criterion. For example, with UGA CCSD, the gap obtained with the [5s4p3d2f1g;3s2p1d] ANO basis set is 10.48 kcal/mol. Similarly, with a basis set of the [9s7p2d1f;5s2p] quality, the SR CCSDT-1 method gives the gap of 10.1 kcal/mol (ref.[8]), as does CASSCF SOCI with a TZ2P(f,d) + diff basis (ref.[26]).

Using the [5s4p3d2f;3s2p1d] ANO basis set, the $^3B_1$–$^1A_1$ separation obtained with the 2R-RMR CCSD method is 9.83 kcal/mol. When the g functions are added on the C atom, the gap becomes 9.73 kcal/mol. This should be compared with the experimental estimate of 9.37 kcal/mol. Compared with the corresponding 2R-SU CCSD result, the 2R-RMR CCSD gap is about 0.25 kcal/mol larger, so that the 2R-SU CCSD result is closer to the experiment. Of course, these calculations have not yet reached the complete basis set limit. Moreover, the experimental value may have an uncertainty of about 0.05 kcal/mol. Even theoretical estimates of the ZPE differ by 0.15 kcal/mol (see Table 3 of ref.[5]). Although we used the value $T_e^{\mathrm{nr,BO}}$ = 9.37 kcal/mol, as obtained by Jensen and Bunker[23], the combination of all possible experimental bounds and two available ZPEs from Table 3 of ref.[5] imply a possible range for $T_e^{\mathrm{nr,BO}}$ to be 9.35–9.62 kcal/mol. It is

TABLE II
Selected results for the singlet–triplet separation $T_e^{\mathrm{nr,BO}}$ in CH_2

Method	Basis	$E(^3B_1)$ a.u.	$E(^1A_1)$ a.u.	$T_e^{\mathrm{nr,BO}}$ kcal/mol
2R-RMR CCSD	5s4p3d2f;3s2p1d	–39.081028	–39.065361	9.83
	5s4p3d2f1g;3s2p1d	–39.082499	–39.066998	9.73
2R-SU CCSD[a]	5s4p3d2f;3s2p1d	–39.081028	–39.065742	9.59
	5s4p3d2f1g;3s2p1d	–39.082499	–39.067393	9.48
(6,6)-CASSCF SOCI[b]	5s4p3d2f1g;4s3p2d	–39.084972	–39.070250	9.23
CASSCF MRCI[c]	5s4p3d2f1g;3s2p1d	–39.083083	–39.068308	9.27
CMRCI[d]	9s7p2d1f;5s2p	–39.1160	–39.1003	9.80
Experiment[a]				9.37

[a] Ref.[9]; [b] ref.[27]; [c] ref.[18]; [d] ref.[28].

unlikely that *ab initio* calculations can achieve a reliability of less than 0.2 kcal/mol. The MR CISD calculations[18,26–28] using a large active space predict separations ranging from 9.23 to 10.1 kcal/mol.

Let us finally mention that the performance of the 2R-SU CCSD method with a large ANO basis set was already examined in an earlier study[5], where we refer the reader for details. A good performance of the 2R-SU CCSD method was later reconfirmed by Balková and Bartlett[28], who used their two-determinant (TD) version of SU MR CCSD.

CONCLUSIONS

The RMR CCSD method was exploited to compute the singlet–triplet separation in methylene, using both a DZP and a large ANO basis sets. This problem requires a balanced treatment of both states involved. In turn, this requires that the method employed be capable to properly handle both dynamic and nondynamic correlation effects. Although the standard SR CCSD method is very effective in handling dynamic correlation, it is lacking when nondynamic correlation is present. On the other hand, the 2R-CISD wave function describes well nondynamic correlation in the present case, but leaves out a significant portion of the dynamic correlation effects. The above presented results show that the 2R-RMR CCSD description, which essentially combines the 2R-CISD and SR CCSD approaches, can overcome the weaknesses of both and provide an excellent, yet affordable description of the studied problem.

The continued support by the National Science and Engineering Research Council of Canada (J. P.) is gratefully acknowledged. The second author also gratefully acknowledges an Alexander von Humboldt Research Award as well as the hospitality of Prof. G. H. F. Diercksen and the Max Planck Institute for Astrophysics in Garching during his visit.

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