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Multireference state-specific coupled cluster approach with the CAS reference: inserting Be into H₂

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Abstract An algorithm for generation of the spin-orbital diagrammatic representation, the corresponding algebraical formulas, and the computer code of the coupled cluster (CC) method with an arbitrary level of the electronic excitations developed earlier in our laboratory have been employed to generate the CAS(2,2)CCSD code. CAS(2,2)CCSD is the state-specific, multireference coupled cluster (SSMRCC) approach with single and double excitations based on the CASSCF(2,2) reference wave function. The CAS(2,2)CCSD was used to describe the model process of inserting the Be atom into the H₂ molecule. We show that our method performs better than the “fully-blown” SSMRCC approach of Mukherjee and coworkers (J Chem Phys 110:6171, 1999).

1 Introduction

The coupled cluster (CC) [1–13] theory has become one of the most popular methods for non-empirical, high-quality quantum-mechanical calculations of small- and medium-size molecular systems. The size extensivity in accounting for the electron correlation effects and the high accuracy of the results are among the most important features of the CC method. Those features have led to implementation of the method in the most popular quantum chemistry packages (Gaussian, SAPT, GAMESS, DALTON). The implementation has concerned various levels of the electron excitations, starting with the simplest including double (CCD) and single and double excitations (CCSD), to more sophisticated versions including triple or even quadruple excitations (CCSDT and CCSDTQ).

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However, there is a major drawback to the current implementations of the CC approach. The standard CC approach based on the Hartree–Fock reference wave function (i.e. the wave function used as the zeroth-order approximation to describe the system) fails to describe cases where quasi degeneracy of two or more electronic states occurs (this usually happens in bond breaking, transition states, excited states etc.). This failure is usually reflected in a significant over/underestimation of the total energy of the system or even as a failure in converging the CC calculations to a physically meaningful solution. In general, it is possible to resolve this problem in one of the following two ways within the CC framework. The first involves including higher-order excitations in the single-reference CC wave function (higher than doubles; $|\Psi_{CCSDT\dots}\rangle = \exp(\hat{T})|0\rangle = (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots)|0\rangle$, with the expansion of the cluster operator \hat{T} in terms of one-, two-, three-, etc., electron operators:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots, \quad (1)$$

where, as usual, the operators $\hat{T}_1, \hat{T}_2, \hat{T}_3, \dots$, are linear combinations of generators of single, double, triple, etc., electron excitations from the reference Hartree–Fock determinant, $|0\rangle$. However, this way of resolving the problem is computationally demanding and impractical for most applications. An alternative way to deal with quasi degenerate electronic problems is to use a multireference (MR) approach.

The existing MRCC approaches can be divided into three major MRCC formalisms [14–20]: the so-called Fock-space or valence-universal (VU) methods, the Hilbert-space or state-universal (SU) methods, and the State-specific (SS) methods. The VU and SU theories are based on an effective Hamiltonian and on solving the Bloch equation for the wave operators that, when acting on a small model space of states, generate a set of the target eigenstates. A single UV or SU calculation can simultaneously generate *several electronic states* of the system. This is different in the SSMRCC theory (the term state-specific was first introduced by Jeziorski and Paldus in Ref. [12]) where only one state is generated in a single calculation.

The SS CC approach we have been developing in our laboratory is based on using the so-called “formal reference state” (a single Slater determinant) in the CC exponential expression for the target wave function. The exponential wave operator generates all determinants that provide the most important contributions to the wave function, as well as all singly and doubly excited determinants from those important determinants. Some key concepts of our approach were described in the previous works [20–27], including the works coauthored by Jean-Paul Malrieu. [28,29]

Several groups have been involved in the development of the SS CC methodology, including Paldus and coworkers with the so-called externally corrected CCSD (ecCCSD) method [30–32]. In that approach, the \hat{T}_3 and \hat{T}_4 contributions are included in a SS manner in order to describe a quasi-degenerate chemical situation. They are taken from either a configuration interaction (CI) or a many-body perturbation theory (MBPT) calculation [13,33]. Another SS CC approach has been derived based on the Brillouin–Wigner CC theory by Hubac, Pittner and coworkers [34–36]. Recent calculations have shown that this approach produces very promising results in some difficult quasi-degenerate situations.

The difficulty in development of higher-level CC approaches has been the complexity of the algorithms resulting from complicated algebraic manipulations of non-linear terms in the CC wave operator. A considerable complexity is also involved in translating the algorithms (usually done by hand) into efficient computer codes. To make these tasks easier, we have recently developed a computer program for deriving energy and amplitude equations for any level of the CC method with the wave function expressed in terms of an exponential cluster operator acting on a single-determinantal or a multi-determinantal wave function [21]. This program has allowed generation of computer codes for various variants of the Complete-active-space CC (CASCC) method. In the present work it has been used to generate the code for the CAS(2,2)CCSD method (i.e. the State-specific multi-reference coupled cluster (SSMRCC) method based on the CASSCF reference wave function with two active electrons and two active orbitals).

The development of computer-aided approaches for generating the algebraic formulas for the CC equations has been carried out in several laboratories. Probably one of the first pioneering works in this area was presented by Paldus and Wong [37,38]. They described a computer algorithm specifically designed for generation of diagrams that appear in the perturbation theory approach to the electron correlation problem. The first attempt to use a computer-assisted approach for generating CC algebraic formulas was the work of Janssen and Schaefer [39]. They applied the approach to the CCSD model for the special case of a high-spin, open-shell system. Their computerized approach performed automated manipulation of the second quantization operators involved in the CC wave operator using the so-called SQSYM interpreter which was developed for automated evaluation of the quasi-vacuum expectation values of products of creation and annihilation operators. We also should mention the interesting

computerized approach proposed by Harris and based on the Maple V program [40] for generating diagrams for the single-reference CC theory. Very recently Hirata [41] developed yet another purely algebraic method named the tensor contraction engine (TCE) that is close in spirit to the Janssen and Schaefer approach, yet has a wider range of application not only for generating diagrammatic representations for different CC theories, but also for other types of the many-electron theories.

2 State-specific multi-reference coupled cluster theory with the CAS reference

Our method for the automated generation of the CC diagrams can be used for the development of any level of implementation of the CC or CI theory. In this work we show an example of using the approach for generating the diagrammatic representation and the corresponding computer code for the particular version of our SSMRCC method termed CAS(2,2)CCSD.

There are two steps involved in defining the *reference model space* for the SSMRCC calculation. In the first step, a suitable model space of determinants (or configurations $\{|\Phi_\mu\rangle\}$) that provide a reasonably good configurational basis set for describing the state of interest in the zeroth-order approximation is selected. A systematic way to define the reference model space is to choose a one-particle, spin-orbital space first and divide it into three classes: [14,42]: the *core* spin-orbitals, the *active (or valence)* spin-orbitals, and *virtual or excited* spin-orbitals. The core orbitals are those which are occupied in all determinants in the reference space; the active (valence) orbitals are those which are occupied at least in one of the reference determinants and unoccupied in at least another determinant; and, the virtual (excited) spin-orbitals are always empty in the reference determinants. All possible different distributions of the valence (active) electrons among the active (valence) spin-orbitals generate the so-called *complete* model reference space.

The partition of the spin-orbital space into the core, active and virtual orbital subspaces is at the origin of almost every contemporary MRCC theory (the Hilbert-space, Fock-space and SS frameworks). However, apart from selecting the orbitals subspaces, the SS theory is also based on the idea of selecting a *single formal reference state (determinant)*. This constitutes the second step. The formal reference determinant, $|0\rangle$, is usually the most important determinant in the wave function of the state of interest.¹ It is used for the generation of all necessary electronic excitations in the cluster model used in the CC calculation.

In the SSMRCC method, the formal reference determinant, $|0\rangle$, defines yet another partition of the spin-orbital space into the occupied spin-orbitals or *holes*, which are

¹ The possibility of using a formal reference determinant which does not contribute to the total wave function was also considered in Ref [29] in connection with calculating electronic excited states.

occupied in $|0\rangle$, and unoccupied spin-orbitals or *particles*, which are unoccupied in $|0\rangle$. Among the holes there are active and inactive holes and among the particles there are active and inactive particles. All possible electron excitations from the active occupied to the active unoccupied spin-orbitals in $|0\rangle$ generate the model space of determinants ($|\Phi_\mu\rangle$). In the spin-orbital notation used in this work we follow the standard convention, i.e., the inactive occupied spin-orbitals are denoted with letters i, j, k, l, \dots ; active occupied spin-orbitals with letters: I, J, K, L, \dots ; the active unoccupied spin-orbitals with letters: A, B, C, D, \dots ; and inactive unoccupied spin-orbitals with letters: a, b, c, d, \dots . The italic-style lower-case letters i, j, k, l, \dots and a, b, c, d, \dots denote both active and inactive occupied spin-orbitals and both active and inactive unoccupied spin-orbitals, respectively.

Several variants of the SSMRCC method that provide very accurate description of the quasi-degenerate states have been proposed before by our group. Among them there is a method based on the so-called fully exponential (FE) *ansatz* of the CC wave function [23–26]:

$$|\Psi_{\text{SSFE}}\rangle = \exp(\hat{T}^{(\text{ext})}) |\Phi^{(\text{int})}\rangle \\ = \exp(\hat{T}^{(\text{ext})}) \exp(\hat{T}^{(\text{int})})|0\rangle, \quad (2)$$

where $\hat{T}^{(\text{int})}$, by acting on the formal reference determinant, $|0\rangle$, generates the model-space (internal) reference function, $|\Phi^{(\text{int})}\rangle$, being a superposition of the model-space determinants. The second exponentiated cluster operator, $\hat{T}^{(\text{ext})}$, generates semi-internal and external excitations from the model space. Both $\hat{T}^{(\text{int})}$ and $\hat{T}^{(\text{ext})}$ are defined in terms of creation and annihilation corresponding to holes and particles of the formal reference determinant, $|0\rangle$. It has been shown on a number of examples that fully exponential *ansatz* (2) handles very well the bond-dissociation process which, at larger internuclear distances, usually leads to a strong quasi-degeneracy of electronic states. As an alternative to the FE approach, we recently proposed a so-called semi-linearized (SL) SSMRCC *ansatz*, which is based on the following representation of the wave function:

$$|\Psi_{\text{SSSL}}\rangle = \exp(\hat{T}^{(\text{ext})}) (1 + \hat{C}^{(\text{int})})|0\rangle. \quad (3)$$

In this case, the model space is generated by a CI-like operator $(1 + \hat{C}^{(\text{int})})$. In order for the SL *ansatz* represented by Eq. (3) to provide size-extensive results, the internal part of the wave function, $\hat{C}^{(\text{int})}|0\rangle$, needs to include the complete set of configurations constructed by using the active orbitals (holes and particles). If the complete set of configurations is used, the internal part of the wave function, $(1 + \hat{C}^{(\text{int})})|0\rangle$, can alternatively be expressed using the equivalent exponential form, $e^{\hat{T}^{(\text{int})}}|0\rangle$. This leads to a fully exponential representation of the CASCC wave function and proves its size-extensivity.

The first numerical implementation of (3) was based on the CAS reference and included only double excitations in the external part, $\exp(\hat{T}^{(\text{ext})})$, and up to four-particle excitations in the internal part $\hat{C}^{(\text{int})}$ (we termed the approach CASCCD) [27]:

$$|\Psi_{\text{CASCCD}}\rangle = \exp(\hat{T}_2) (1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \hat{C}_4)|0\rangle. \quad (4)$$

In the CASCCD wave function there are 12 amplitude types. Among them eight are generated by the \hat{T}_2 operator and four are generated by the $\hat{C}^{(\text{int})}$ operator:

$$t_{ij}^{ab}, t_{Ij}^{ab}, t_{ij}^{Ab}, t_{IJ}^{ab}, t_{ij}^{AB}, t_{Ij}^{Ab}, t_{IJ}^{Ab}, t_{IJ}^{AB}, C_I^A, C_{IJ}^{AB}, C_{IJK}^{ABC}, \\ C_{IJKL}^{ABCD}.$$

As shown in our previous work, the CASCCD method performs very well in describing the dissociation curves of some simple model systems. However, the CASCCD wave function (4) has a noticeable drawback. A correct MR theory should equivalently include all important excitations from *all* reference determinants. Thus the first-order interacting space should include double excitations not only from the formal reference, but also from *all* determinants in the chosen model space. If the active orbital space includes two orbitals and two electrons [CAS(2,2); this is sufficient to describe a single-bond dissociation], the model space in addition to $|0\rangle$ should also include two additional singlet configurations, which are single and double excitations from $|0\rangle$,

$$|0\rangle, |I^A\rangle, |IJ^{AB}\rangle.$$

Hence, in addition to the double excitations from $|0\rangle$, the CASCCD wave function should also explicitly include in the external operator, $\hat{T}^{(\text{ext})}$, all two-electron excitations from the other two model-space configurations. Some of those excitations are three- and four-electron excitations from $|0\rangle$.

By including these missing excitations, the SL SSMRCC wave function with all single and double excitations from all the CAS(2,2) references can be written as:

$$|\Psi_{\text{CAS(2,2)CCSD}}\rangle = \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3^{(Abc)} \\ + \hat{T}_4^{(ABcd)}) (1 + \hat{C}_1 + \hat{C}_2)|0\rangle. \quad (5)$$

In the above expression, the cluster operator, which corresponds to the three-electron excitations from $|0\rangle$ ($\hat{T}_3^{(Abc)}$), generates all two-electron excitations from the singly excited reference determinant $|I^A\rangle$ while all the one-electron excitations from this reference are generated by a subset of the \hat{T}_2 operator that contains the amplitudes t_{Ij}^{Ab} , i.e., only those involving the I and A spin-orbital indices. The $\hat{T}_4^{(ABcd)}$ operator generates two electron excitations from the $|IJ^{AB}\rangle$ reference determinant while the \hat{T}_3 generates one electron excitations from that determinant. One should notice that in the indices shown in the \hat{T}_3 and \hat{T}_4 operators in Eq. (5), the italic lower-case letters, j, k, l and b, c, d , denote both active and inactive orbitals, but at least one of these indices must be inactive since all active excitations are already included in the $\hat{C}^{(\text{int})}$ operator. The same applies to the \hat{T}_1 and \hat{T}_2 operators.

The set of coupled equations for the energy and for the amplitudes involved in the \hat{C} and \hat{T} operators for the general CAS(n, m)CCSD method (where “ n ” denotes the number of active electrons and “ m ” denotes the number of active orbitals) corresponding to the following wave function:

$$|\Psi_{\text{CAS}(n,m)\text{CCSD}}\rangle = \exp(\hat{T}_1 + \dots + \hat{T}_{n+2}) \\ \times (1 + \hat{C}_1 + \dots + \hat{C}_n)|0\rangle, \quad (6)$$

is obtained by using the ordinary projection scheme of the CC theory (i.e. the method of momenta). The expression for the energy can be derived by projecting the Schrödinger equation for the CC wave function against the formal reference determinant $|0\rangle$:

$$\langle 0 | \hat{H} - E_{\text{CAS}(n,m)\text{CCSD}} | \Psi_{\text{CAS}(n,m)\text{CCSD}} \rangle = 0. \quad (7)$$

Simple manipulation leads to the equation for the CAS(n, m) CCSD energy in the form of a sum of one- and two-electron parts:

$$\begin{aligned} \Delta E_{\text{CAS}(n,m)\text{CCSD}} = & \langle 0 | \hat{H} | \hat{T}_1 + \hat{C}_1 | 0 \rangle \\ & + \langle 0 | \hat{H} | \hat{T}_2 + \hat{C}_2 + \frac{1}{2} \hat{T}_1^2 + \hat{T}_1 \hat{C}_1 | 0 \rangle, \end{aligned} \quad (8)$$

where

$$\Delta E_{\text{CAS}(n,m)\text{CCSD}} = E_{\text{CAS}(n,m)\text{CCSD}} - E_0. \quad (9)$$

The E_0 is the expectation value of the Hamiltonian for the formal reference $|0\rangle$.

The equations for the amplitudes involved in the \hat{T} and \hat{C} operators are obtained from appropriate projections involving excitations from the formal reference determinant $|0\rangle$. Namely, the equations for \hat{T}_1 amplitudes arise from the projections against $|i^a\rangle$:

$$\begin{aligned} & \left\langle i^a | \hat{H} - E_{\text{CAS}(n,m)\text{CCSD}} | \exp(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3) \right. \\ & \left. \times \left(1 + \sum_{\lambda=1, \min(3,n)} \hat{C}_\lambda \right) | 0 \right\rangle = 0. \end{aligned} \quad (10)$$

By expanding the exponent in Eq. (10) we get:

$$\begin{aligned} & \left\langle i^a | \hat{H} - E_{\text{CAS}(n,m)\text{CCSD}} | \left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \hat{T}_3 \right. \right. \\ & \quad + \hat{T}_1 \hat{C}_1 + \hat{T}_1 \hat{C}_2 + \frac{1}{2} \hat{T}_1^2 \hat{C}_1 + \hat{T}_2 \hat{C}_1 \\ & \quad \left. \left. + \dots + \sum_{\lambda=1, \min(3,n)} \hat{C}_\lambda \right) | 0 \right\rangle = 0. \end{aligned} \quad (11)$$

In general, the equations for the amplitudes involved in the \hat{T} operator corresponding to the k th excitation level have the following form:

$$\begin{aligned} & \left\langle i_1^{a_1} i_2^{a_2} \dots i_k^{a_k} | \hat{H} - E_{\text{CAS}(n,m)\text{CCSD}} | \exp(\hat{T}_1 + \hat{T}_2 + \dots) \right. \\ & \left. \times \left(1 + \sum_{\lambda=1, \min(k+2,n)} \hat{C}_\lambda \right) | 0 \right\rangle = 0. \end{aligned} \quad (12)$$

The corresponding equations for the amplitudes involved in the $\hat{C}^{(\text{int})}$ operator that generates the model-space wave function are obtained in an analogical way by the following

projection:

$$\begin{aligned} & \left\langle \begin{matrix} A_1, A_2, \dots, A_n \\ I_1, I_2, \dots, I_n \end{matrix} | \hat{H} - E_{\text{CAS}(n,m)\text{CCSD}} | \exp(\hat{T}_1 + \hat{T}_2 + \dots) \right. \\ & \left. \left(1 + \sum_{\lambda=1, n} \hat{C}_\lambda \right) | 0 \right\rangle = 0. \end{aligned} \quad (13)$$

In Eqs. (11), (12), and (13) the energy cannot be eliminated due the presence of the linear $\hat{C}^{(\text{int})}$ operator in the wave function (6). It results in the appearance of some disconnected diagrams that involve nonlinear components that contain contributions from the \hat{C} and \hat{T} operators. However, the disconnected diagrams that originate from the exponential part $\exp(\hat{T}_1 + \hat{T}_2 + \dots)$ can be removed as usual. It is important to stress that in the process of solving the CC equations, both $\hat{C}^{(\text{int})}$ and $\hat{T}^{(\text{int})}$ amplitudes are determined simultaneously. Hence, though in the first CC iteration, the $\hat{C}^{(\text{int})}$ amplitudes are usually set equal to the CASSCF amplitudes (renormalized), they change in the following iterations to account for the interaction of the dynamic and non-dynamic electron correlation effects.

From the complexity of the above amplitude equations, it is clear that derivation of all the different diagrams involved in the equations for the general CAS(n, m)CCSD method is rather difficult. It can be handled better with the assistance of a computer. The SS MRCC approach, in the form we have presented it, offers a simple logical structure that closely resembles the structure of the single reference CC scheme. Thus, the automated generation of the diagrammatic representation of the CAS(n, m)CCSD method is similar to that for the SRCC theory. The only difference between the SRCC and the CAS-CC method is the need to include the disconnected contributions mentioned before [27] in the computational scheme. Also, appropriate restrictions on the spin-orbital indices in the cluster amplitudes need to be implemented in order to include only selected types of higher-excitation contributions (i.e. those beyond two-electron) as shown in Eq. (5).

3 Numerical illustrations

In order to illustrate the performance of the CAS(n, m)CCSD method in comparison with some other MR methods and in comparison with the exact solution of the finite basis set solution provided by the full configuration interaction (FCI) method, we have performed calculations on the model reaction of inserting a Be atom into H_2 . In this process the C_{2v} symmetry is maintained in the system. The Be + H_2 model system had been used before as a test problem for various variants of the CC and MBPT [43–49]. There are two features that make the model a suitable test of the performance of a high-level calculation. The first is that at some distances of the Be atom from the middle of the H_2 bond the wave function becomes essentially multi-configurational. Secondly, intruder states appear for this problem if calculations are done with a non-SS CC MR approach.

In the present calculations we have used the same basis set ($3s1p/2s$) as used in the work where the Be + H₂ model was first introduced [43]. The geometry of the Be + H₂ complex described in the calculations is shown in Fig. 1 and the coordinates of the specific points along the reaction pathway, for which the calculations have been performed, are shown in Table 1. These are the same points as those used by Mahapatra et al. [47] in their MRCC calculations. The CASSCF calculations in the present work were performed using the GAMESS [49] package.

As the CASSCF calculations show, the dominant wavefunction configuration of the Be + H₂ system changes along the reaction pathway. At long distances from Be to H₂ (points *F* through *I*) the dominant configuration in the wave function is the $|0\rangle = |1a_1^2 2a_1^2 3a_1^2|$ determinant, but the configuration $|1\rangle = |1a_1^2 2a_1^2 1b_2^2|$ becomes more dominant at shorter Be–H₂ distances (points *A* through *E*). As the Be atom approaches the hydrogen molecule, the H–H bond elongates (see the geometry of points *A–E*). At the geometries corresponding to points *D*, *E*, *F*, there is strong configurational degeneracy and the two determinants ($|0\rangle$ and $|1\rangle$) are approximately equally important.

Thus to correctly describe the H–H bond breaking and the formation of two new Be–H bonds, two active orbitals (a_1 and b_2) have to be included in the active (CAS) space. All possible distribution of two electrons among the two active orbitals generates the reference configurational space. In addition to the active space, our approach requires the selection of the formal reference determinant (the Fermi vacuum). This deter-

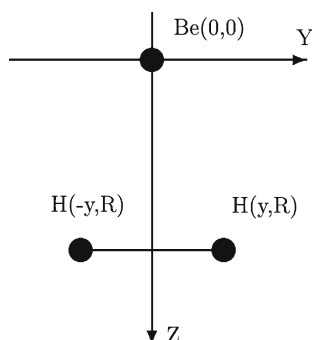


Fig. 1 The geometry and the coordinates of the BeH₂ complex

Table 1 The full configuration interaction (FCI) energy (in Hartrees) calculated at different points along the Be + H₂ reaction pathway

Geometrical point	Coordinates (y, R)	FCI
<i>A</i>	(2.54, 0.0)	−15.779172
<i>B</i>	(2.08, 1.0)	−15.737224
<i>C</i>	(1.62, 2.00)	−15.674818
<i>D</i>	(1.39, 2.50)	−15.622883
<i>E</i>	(1.275, 2.75)	−15.602919
<i>F</i>	(1.16, 3.00)	−15.624981
<i>G</i>	(0.93, 3.50)	−15.693194
<i>H</i>	(0.70, 4.00)	−15.736688
<i>I</i>	(0.70, 6.00)	−15.760878

minant was chosen to be the $|1\rangle$ determinant for points *A–E*, and for points *F–I* it was the $|0\rangle$ determinant.

To describe the configurational structure of the wave function obtained with different approaches, we use the cumulative weight index which for the manifold of the k -fold excitations, is defined as follows:

$$W_k = \sum_{\mu} \langle (k)_{\mu} | \Psi_{\text{cas}(2,2)\text{ccsd}} \rangle^2, \quad (14)$$

where $\langle (k)_{\mu} |$ is a k -electron excited configuration and the sum over μ runs over all configurations in the k -fold excitation manifold. If the intermediate normalization of the wave function is assumed (with respect to the formal reference determinant), the index W_k shows how well a particular method describes the MR character of the wave function in comparison with the wave function obtained in the FCI calculation. In this work we used the W_k index to test the CAS(2,2)CCSD approach in describing the Be + H₂ reaction. The results of the W_k calculations are shown in Table 2. For most points along the Be + H₂ reaction path, the single and double, as well as triple and quadruple, excitations play important roles in the wave function. The importance of the double excitations is particularly significant for points *D*, *E*, *F*. The importance of the four-electron excitations (W_4) increases from *A* to *E* and then stays almost constant. The single and triple excitations are also larger for points *D*, *E*, *F* than for the other points.

The CAS(2,2)CCSD W_k values are compared with the values obtained for the FCI wave function in Table 2. At the points with low configurational degeneracy (*A*, *B*, *C*, *D*, and *G*, *H*, *I*), the W_1 and W_2 values are almost identical for CAS(2,2)CCSD and FCI. For points with larger degeneracy, the difference between CAS(2,2)CCSD and FCI values of W_1 and W_2 increases, but the values are still very close.

Except for point *E*, the W_3 and W_4 FCI values are small. For point *E* those values are of the same order of magnitude as W_1 's. The closer look at the W_3 's and W_4 's reveals that there are some differences in those indices for CAS(2,2)CCSD and FCI. For W_3 the differences appear for all the geometries of the complex, and for W_4 they are more significant for points *A*, *B*, *F*, *G*, *H* and *I*. The appearance of the differences in the W_3 and W_4 values can probably be attributed to the constraints that the CAS(2,2)CCSD approach imposes on the higher-excitation configurational coefficients. The coefficients in CAS(2,2)CCSD are determined as products of lower level excitations and only amplitude corrections are explicitly included in the wave function for those which are single and double excitations from the model space determinants.

The Be + H₂ insertion reaction was studied by Mukherjee and coworkers [47] using their SSMRCC approach based on the following cluster expansion of the wave function:

$$\Psi = \sum_{\mu} \exp(T^{\mu}) \phi_{\mu} c_{\mu}, \quad (15)$$

originally introduced by Jeziorski and Monkhorst [42]. In a later work [48] Mukherjee and coworker refer to their approach as a “fully blown” SSMRCC approach. They have

Table 2 The weight index for different levels of the electron excitations determined for the CAS(2,2) and FCI wave functions at the different geometries of the BeH₂ complex

Point	Method	W_1	W_2	W_3	W_4
A	CAS(2,2)CCSD	0.937×10^{-4}	0.280×10^{-1}	0.173×10^{-3}	0.120×10^{-3}
	FCI	0.953×10^{-4}	0.283×10^{-1}	0.283×10^{-3}	0.163×10^{-3}
B	CAS(2,2)CCSD	0.729×10^{-3}	0.267×10^{-1}	0.130×10^{-3}	0.989×10^{-4}
	FCI	0.691×10^{-3}	0.270×10^{-1}	0.243×10^{-3}	0.142×10^{-3}
C	CAS(2,2)CCSD	0.303×10^{-2}	0.477×10^{-1}	0.165×10^{-3}	0.357×10^{-3}
	FCI	0.295×10^{-2}	0.483×10^{-1}	0.377×10^{-3}	0.390×10^{-3}
D	CAS(2,2)CCSD	0.583×10^{-2}	0.122	0.973×10^{-3}	0.126×10^{-2}
	FCI	0.589×10^{-2}	0.126	0.158×10^{-2}	0.148×10^{-2}
E	CAS(2,2)CCSD	0.108×10^{-1}	0.795	0.143×10^{-1}	0.701×10^{-2}
	FCI	0.114×10^{-1}	0.857	0.197×10^{-1}	0.810×10^{-2}
F	CAS(2,2)CCSD	0.285×10^{-2}	0.235	0.380×10^{-3}	0.300×10^{-2}
	FCI	0.294×10^{-2}	0.238	0.771×10^{-3}	0.595×10^{-2}
G	CAS(2,2)CCSD	0.114×10^{-2}	0.125	0.817×10^{-4}	0.104×10^{-2}
	FCI	0.113×10^{-2}	0.126	0.237×10^{-3}	0.248×10^{-2}
H	CAS(2,2)CCSD	0.565×10^{-3}	0.104	0.471×10^{-4}	0.490×10^{-3}
	FCI	0.565×10^{-3}	0.104	0.113×10^{-3}	0.126×10^{-2}
I	CAS(2,2)CCSD	0.349×10^{-3}	0.100	0.900×10^{-5}	0.414×10^{-3}
	FCI	0.349×10^{-3}	0.100	0.267×10^{-4}	0.124×10^{-2}

The formal reference is the determinant |1⟩ (see text) for points A–E and the determinant |0⟩ for points F–I

Table 3 Comparison of the CAS(2, 2)CCSD Be + H₂ calculations with the SSMRCC results of Mukherjee and Coworkers [47]. All energies are differences with respect to the FCI results. All values in mHartees

Geometry	SS MRCEPA(I)	SSMRCEPA(I)/Ur	SSMRCC (Ur)	SS MRCC (R)	CAS(2,2)CCSD
A			0.608	0.392	0.116
B			0.373	0.370	0.142
C			0.516	0.382	0.220
D	0.744	0.346	1.283	0.079	0.464
E	2.837	-0.330	7.241	-0.849	0.708
F	3.006	-0.155	3.892	-0.365	0.399
G			-0.161	0.103	0.191
H			0.156	0.164	0.108
I			0.048	0.030	0.023

also recently developed approximate schemes of their “fully blown” approach which they termed MRCEPA [48]. Since our approach provides an alternative to the SSMRCC methods developed by Mukherjee and coworker, we found it useful to show how well their results and our results compare with the FCI energies. The comparison is presented in Table 3. The values shown are differences between the FCI energies and the corresponding energies obtained in the calculations of Mukherjee et al. and generated in our CAS(2,2)CCSD calculations. In the Mukherjee et al. results, values obtained by two different implementations of the SS MRCEPA method, and the unrelaxed (Ur) and relaxed orbital approaches for the SSMRCC method are shown. Comparison of these results show that while our CAS(2,2)CCSD method consistently slightly overestimates the FCI energies (i.e., all differences with respect to FCI are positive), the Mukherjee et al. results vary between over and underestimation. Furthermore, the maximum spread of the CAS(2,2)CCSD results for the points along the reaction pathway ($0.708 - 0.023 = 0.685$ mHartree) is much smaller than for the SSMRCC(Ur) results ($7.241 + 0.161 = 7.402$ mHartree) and even for the SSMRCC(R) results ($0.392 + 0.849 = 1.241$ mHartree). The improved repre-

sentation of the Be + H₂ reaction path by the CAS(2,2)CCSD approach in comparison with the “fully blown” approach of Mukherjee et al. is notable considering that both methods aim to include all single and double excitations from the same two most important model-space determinants.

4 Conclusions

The purpose of this report is to show that our CAS(2, 2)CCSD method provides a correct description of the energy profile associated with a symmetric insertion of the Be atom into the H₂ molecule. The comparison of the CAS(2, 2)CCSD results and the results obtained for the Be + H₂ reaction by Mukherjee et al. using their SSMRCC approach shows that our energy curve determined for the symmetric insertion pathway is significantly more parallel to the FCI reference curve than their curve. The capability of the CAS(2, 2)CCSD method to describe the MR problem that appears in the Be + H₂ reaction indicates that the method may also be capable of describing more complicated MR situations, particularly those occurring in electronic excited states. Our current

effort is directed towards extending the CASCCSD approach to excited state calculations.

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