MULTIREFERENCE STATE-SPECIFIC COUPLED-CLUSTER THEORY AND MULTICONFIGURATIONALITY INDEX. BH DISSOCIATION

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Received March 24, 2005
Accepted April 21, 2005

We dedicate this work to Professor Joe Paldus on the occasion of his 70th birthday.

Multiconfigurationality index calculated for the coupled-cluster wave function based on an algorithm developed using a computer-aided generation approach is applied to analyze the multireference state-specific coupled-cluster method with the CAS reference (i.e. the so called the CAS(n,m)CCSD approach). The numerical results concern dissociation of the BH molecule where at larger displacement from the equilibrium significant quasi-degeneracy arises. The analysis shows that the CAS(n,m)CCSD approach performs very well in such a situation.

Keywords: Multireference coupled-cluster method; CAS reference; CAS(n,m)CCSD; Acidity; Wave function; *Ab initio* calculations; Quantum chemistry.

Despite considerable efforts over the past several decades, quantitative treatment of electron correlation for states of arbitrary configurational complexity remains one of the most challenging problems in quantum chemistry. Apart from our work in this field concerning the development of the state-selective multireference coupled-cluster (SS-MRCC) approach[1–13], there have been other MR-based state-specific many-body formalisms providing access to just a single root. Among them one should mention the theories of Malrieu and co-workers[14], Mukherjee and co-workers[15–18] and Hubac and co-workers[19]. All of them exploited the wave operator inducing separate cluster expansions about each reference functions in the manner of Jeziorski and Monkhorst[20]. The approach in ref.[14] uses low-order quasi-linearized truncation schemes, and those in refs[15,16,19] suggest full-blown MRCC formulations which allow systematic improvements. The SS-MRCC theory that ought to be developed needs to be size-extensive,

doi:10.1135/cccc20051017

size-consistent, bypasses intruders naturally, and needs to use completely relaxed model space coefficients. The method in ref.[19] uses equations which are structurally simpler than in other methods, but they are not size-extensive. Suggestions have been made to alleviate this via a Rayleigh Schrödinger expansion[21], but care then has to be exercised to bypass intruders. An analysis demonstrating how a continuous transition from the state-universal theory of Jeziorski and Monkhorst[20] to the state-specific theories of Hubac and co-workers[19] and of Mukherjee and co-workers[15,16] can be accomplished has recently been presented by Pittner[22]. In all the above methods the state energy is obtained via diagonalization of an effective operator in the model space, which implies that the method uses relaxed coefficients for the functions of the model space.

The development of the MRCC methodology has been paralleled by the development of CC approaches that are capable of describing electronic excited states without relying on the generalized Bloch equation, on which the “genuine” MRCC methods are based. Examples of the most successful CC approaches to excited states that are not based on the genuine MRCC formalism are the linear-response CC method[23–33], and the closely related (often equivalent) equation-of-motion (EOM) CC method[34–40], and the symmetry-adapted cluster configuration interaction (CAS-CI) method[41–43]. There have also been some other important developments in this field coming from other groups. Paldus and coworkers have advanced their direct iterative solution of the generalized Bloch equation[45,46]. The method exploited the concepts of a multidimensional reference or model space, a (non-Hermitian) effective Hamiltonian, and the generalized Bloch equation. They have also advanced their reduced multireference coupled-cluster method which represents the MR-CISD-based version of the so-called externally corrected CCSD developed in the framework of the unitary group based coupled-cluster theory (UGA CCSD)[47–49]. The Bloch equation approach has been a subject of recent investigations in Piecuch’s group[50,51]. They also applied our SSMRCC approach in the context of the EOMCCSD method to excited state calculations and demonstrated an improved trend in vertical excitation energies when selected triple and quadruple excitations are included in the calculation as described in our scheme[52]. Our scheme has also been followed by Bartlett and his group. The method that they term CCSDt and CCSDtq [53] is essentially identical to our earlier-developed SSMRCCSD(T) and SSMRCCSD(TQ) approaches.

Most of the recent activities in the excited state CC studies have been centered around the EOMCC approach[37,54–56]. In particular, the most recent works of Bartlett, Kucharski and coworkers should be noted[57]. Although not strictly size-extensive, this methodology has been gaining popularity as a practical and accurate multistate method for calculating electronic excitation energies. It has been used to calculate excitation spectra of both smaller and larger molecular systems[58,59]. Recently an interesting development concerning a renormalized CC approach and its application to electronic excited states has come from the Piecuch's group[60]. Among the multistate methods one should also mention interesting works coming from Head-Gordon, Krylov, and Sherrill laboratories[44,61–63], and the spin-restricted CC theory based on a linear-response approach of Szalay and Gauss[64] and Szalay et al.[65]

In this context we should also mention the works carried on by our group[66] and by others on the computerized development of algorithms for amplitude equations in various advanced forms of the SR and MR CC wave functions. Very recently, special determinant-based CI versions of such algorithms have been developed in three different groups[67–69] permitting one to generate CC solutions for arbitrary levels of excitation. In related developments, Olsen coded a string-based algorithm which takes advantage of Bruckner orbitals[70] and Nooijen and Lotrich implemented a general procedure to generate formulas and program codes of many-body and CC methods[71,72]. Also recently, Kállay and Surján[68] demonstrated how the CC equations can be effectively solved up to an arbitrary excitation level by the combination of diagrammatics and the string-based formalism. In this approach, a general algorithm for generation and factorization of the CC diagrams that minimizes the operation count and the storage requirement of the CC calculation by optimal definition of intermediates was presented. The procedure scaled as $n_\mathrm{o}^n n_\mathrm{v}^{n+2}$ where n is the highest excitation in the cluster operator, n_o and n_v are the numbers of occupied and virtual orbitals, respectively, which is the same scaling as for the conventional CC procedure.

In brief, the following have been the major contributions of our group dealing with development and implementation the state-specific multireference coupled-cluster approach. The SSMRCCSD(T) and SSMRCCSD(TQ) levels of the state-selective, multireference coupled-cluster theory based on the doubly-exponential form of the wave function has been developed, implemented, and applied. In this approach, the reference wave function is represented by the exponentiated CC excitation operator $\hat{T}^{(\mathrm{int})}$ defined using the orbitals from the active space and acting on a formal reference determinant (Fermi vacuum). The excitations to the non-active orbital space, as well as mixed excitations (or as they are also called semi-internal excitations) are represented by the operator $\hat{T}^{(\mathrm{ext})}$:

$$|\Psi_{\mathrm{SSMRCC}}\rangle = \mathrm{e}^{\hat{T}^{(\mathrm{ext})}}|\Phi^{(\mathrm{int})}\rangle = \mathrm{e}^{\hat{T}^{(\mathrm{ext})}}\mathrm{e}^{\hat{T}^{(\mathrm{int})}}|0\rangle\,. \tag{1}$$

More recently our works have concerned an approach where the internal part of the SSMRCC wave function is represented in the CI-like form as a linear combination of the model reference-space determinants:

$$|\Psi_{\mathrm{SSMRCC}}\rangle = \mathrm{e}^{\hat{T}^{(\mathrm{ext})}}|\Phi^{(\mathrm{int})}\rangle = \mathrm{e}^{\hat{T}^{(\mathrm{ext})}}(1+\hat{\mathrm{C}}^{(\mathrm{int})})|0\rangle\,. \tag{2}$$

That approach will be discussed in more detail later in this work.

In conclusion, it is apparent that the development of the MRCC theory has attracted significant attention of the best theoretical groups and that a number of fundamental problems still remain unsolved in this area. Furthermore, it is clear that the current level of the theoretical development does not yet offer a simple, robust and flexible MRCC procedure which can be applied to chemically interesting systems in a routine “black box” fashion.

MULTICONFIGURATIONALITY INDEX APPLIED TO COUPLED-CLUSTER ELECTRON CORRELATION PROBLEM

In the single-reference CC method the wave function ($|\Psi_{\mathrm{CC}}\rangle$) is represented by the following general expression ($|\Psi_{\mathrm{CC}}\rangle$, the standard expansion is assumed):

$$|\Psi_{\mathrm{CC}}\rangle = \exp(\hat{T})\,|0\rangle = (1+\hat{T}+\tfrac{1}{2}\hat{T}^2+\ldots)\,|0\rangle \tag{3}$$

where the $|0\rangle$ is the reference determinant. The cluster operator $\hat{T}$ can be expressed as a sum of one-, two-, three-electron, etc., excitation operators:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots \tag{4}$$

which generate a superposition of the corresponding electron-excited configurations from the reference determinant $|0\rangle$:

$$\hat{T}_1|0\rangle = \sum_{\substack{i_1\\a_1}} t_{i_1}^{a_1}\,|_{i_1}^{a_1}\rangle \tag{5}$$

$$\hat{T}_2|0\rangle = \sum_{\substack{i_1>i_2\\a_1>a_2}} t_{i_1 i_2}^{a_1 a_2}\,|_{i_1 i_2}^{a_1 a_2}\rangle \tag{6}$$

$$\hat{T}_3|0\rangle = \sum_{\substack{i_1>i_2>i_3\\a_1>a_2>a_3}} t_{i_1 i_2 i_3}^{a_1 a_2 a_3}\,|_{i_1 i_2 i_3}^{a_1 a_2 a_3}\rangle \tag{7}$$

and

$$\hat{T}_4|0\rangle = \sum_{\substack{i_1>i_2>i_3>i_4\\a_1>a_2>a_3>a_4}} t_{i_1 i_2 i_3 i_4}^{a_1 a_2 a_3 a_4}\,|_{i_1 i_2 i_3 i_4}^{a_1 a_2 a_3 a_4}\rangle\text{ , etc.} \tag{8}$$

Here, the notation $|_{i_1}^{a_1}\rangle$, $|_{i_1 i_2}^{a_1 a_2}\rangle$, $|_{i_1 i_2 i_3}^{a_1 a_2 a_3}\rangle$ and $|_{i_1 i_2 i_3 i_4}^{a_1 a_2 a_3 a_4}\rangle$ denotes singly-, doubly-, triply, etc., excited determinants. The coefficients $t_{i_1}^{a_1}$, $t_{i_1 i_2}^{a_1 a_2}$, $t_{i_1 i_2 i_3}^{a_1 a_2 a_3}$ and $t_{i_1 i_2 i_3 i_4}^{a_1 a_2 a_3 a_4}$ are the cluster amplitudes. The spin-orbital indices i_1, i_2, i_3, etc., designate occupied orbitals in the reference determinant ($|0\rangle$) while the spin-orbital indices a_1, a_2, a_3, etc., denote vacant spin-orbitals in $|0\rangle$.

A distinctive feature of the CC theory is the fact that in contributions to the total wave function from high-order excitations consist in part of products of contributions from lower-order excitations. To determine the contribution from the excited determinant $\langle_{i_1 i_2 i_3 \dots}^{a_1 a_2 a_3 \dots}|$ to the CC wave function one needs to calculate the scalar product of that determinant and the CC wave function. In particular, the contribution from the one-particle excited configuration, $|_{i_1}^{a_1}\rangle$, which corresponds to promotion of an electron from i_1-spin-orbital to the spin-orbital a_1 is determined as:

$$C_{i_1}^{a_1} = \langle_{i_1}^{a_1}|\Psi_{\text{CC}}\rangle = \langle_{i_1}^{a_1}|\hat{T}_1|0\rangle\ . \tag{9}$$

Analogously, the contributions from the two-, three- and four-electron excited configurations are calculated as:

$$C_{i_1 i_2}^{a_1 a_2} = \langle_{i_1 i_2}^{a_1 a_2}|\Psi_{\text{CC}}\rangle = \langle_{i_1 i_2}^{a_1 a_2}|\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^{\,2}|0\rangle \tag{10}$$

$$C^{a_1a_2a_3}_{i_1\,i_2\,i_3} = \langle {}^{a_1a_2a_3}_{i_1\,i_2\,i_3} \,|\, \hat{T}_3 + \hat{T}_1\hat{T}_2 + \tfrac{1}{3!}\hat{T}_1^{\,3}|0\rangle \tag{11}$$

$$C^{a_1a_2a_3a_4}_{i_1\,i_2\,i_3\,i_4} = \langle {}^{a_1a_2a_3a_4}_{i_1\,i_2\,i_3\,i_4} \,|\, \hat{T}_4 + \hat{T}_1\hat{T}_3 + \tfrac{1}{2}\hat{T}_2^{\,2} + \tfrac{1}{2}\hat{T}_1^{\,2}\hat{T}_2 + \tfrac{1}{4!}\hat{T}_1^{\,4}|0\rangle\,. \tag{12}$$

Thus, in general, the contribution to the wave function (*3*) from an arbitrary electron-excited configuration can be determined by the following product:

$$C^{a_1a_2a_3\ldots}_{i_1\,i_2\,i_3\ldots} = \langle {}^{a_1a_2a_3\ldots}_{i_1\,i_2\,i_3\ldots} |\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3\ \ldots)\,|0\rangle\ . \tag{13}$$

The approach described by Eq. (*13*) provides a procedure to represent a general CC wave function with an arbitrary level of the electron excitation as a CI-like wave function:

$$\begin{aligned}|\Psi_{\mathrm{CC}}\rangle = |0\rangle + \sum_{i,a} C^{a_1}_{i_1}\left|{}^{a_1}_{i_1}\right\rangle + \sum_{\substack{a_1>a_2\\ i_1>i_2}} C^{a_1a_2}_{i_1\,i_2}\left|{}^{a_1a_2}_{i_1\,i_2}\right\rangle + \sum_{\substack{a_1>a_2>a_3\\ i_1>i_2>i_3}} C^{a_1a_2a_3}_{i_1\,i_2\,i_3}\left|{}^{a_1a_2a_3}_{i_1\,i_2\,i_3}\right\rangle + \\ + \sum_{\substack{a_1>a_2>a_3>a_4\\ i_1>i_2>i_3>i_4}} C^{a_1a_2a_3a_4}_{i_1\,i_2\,i_3\,i_4}\left|{}^{a_1a_2a_3a_4}_{i_1\,i_2\,i_3\,i_4}\right\rangle + \ldots\end{aligned} \tag{14}$$

This representation can be used to analyze the importance of contributions corresponding to particular excitation levels to the electronic state of interest. Interpretation of the CC wave function using Eqs (*9*)–(*12*) or Eq. (*13*) also provides a useful tool to compare the CC wave function with the wave functions generated with other methods, for example, FCI (the full configuration interaction method) or MRCI (the multireference configuration interaction method). Such a comparison can be made using squares of individual CI coefficients or, what is more convenient, sums of squares of the CI coefficients corresponding to particular excitation levels. Such a cumulative quantity provides information on the total weight of all configurations corresponding to the certain *k*-fold excitation level to the CC wave function. Since, as it is customary, the intermediate normalization is used in the CC wave function the contribution from the reference determinant $|0\rangle$ is equal to one:

$$W_0 = \langle 0 | \Psi_{\mathrm{CC}} \rangle = 1 \,. \tag{15}$$

The total contribution from all excited determinants of the *k*-order (*k* = 1, 2, 3, 4, etc.) to the CC wave function can be calculated as:

$$W_1 = \sum_{i,a} (C_{i_1}^{a_1})^2 \tag{16}$$

$$W_2 = \sum_{\substack{a_1 > a_2 \\ i_1 > i_2}} (C_{i_1 i_2}^{a_1 a_2})^2 \tag{17}$$

$$W_3 = \sum_{\substack{a_1 > a_2 > a_3 \\ i_1 > i_2 > i_3}} (C_{i_1 i_2 i_3}^{a_1 a_2 a_3})^2 \tag{18}$$

$$W_4 = \sum_{\substack{a_1 > a_2 > a_3 > a_4 \\ i_1 > i_2 > i_3 > i_4}} (C_{i_1 i_2 i_3 i_4}^{a_1 a_2 a_3 a_4})^2 \tag{19}$$

etc.

The total sum of all weights W_k is the normalization factor:

$$N_0 = \sum_k W_k = \sum_k \sum_{\substack{a_1 < a_2 < \ldots < a_k \\ i_1 < i_2 < \ldots < i_k}} |\langle {}_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k} | \Psi_{\mathrm{CC}} \rangle|^2 \,. \tag{20}$$

This quantity can be used as a multiconfigurationality index since its deviation from unity indicates how significantly the total CC wave function differs from the reference determinant (i.e., large contributions from determinants other than $|0\rangle$).

STATE-SPECIFIC MULTIREFERENCE COUPLED-CLUSTER THEORY

In the present work we have used the above described multiconfigurationality indices for the analysis of the wave function obtained using the state-specific multireference (MR) CC method (SSMRCC) which has been developed in our laboratory.

In our SSMRCC method, the formal reference determinant, $|0\rangle$, defines the partition of the spin-orbital space into the occupied spin-orbitals or *holes*, which are occupied in $|0\rangle$, and the unoccupied spin-orbitals or *particles*, which are unoccupied in $|0\rangle$. The formal reference determinant is usually taken as the most important determinant in the wave function of the calculated state.

Among the holes, we distinguish active and inactive holes, and among the particles we distinguish 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 (the approximate wave function expanded in terms of model-space determinants will be denoted as $|\Phi_\mu^{(\mathrm{int})}\rangle$). In the spin-orbital notation in this work we use the following convention: the inactive occupied spin-orbitals are denoted with letters i_i, i_2, i_3, ...; the active occupied spin-orbitals with letters: I_1, I_2, I_3, ...; the active unoccupied spin-orbitals with letters: A_1, A_2, A_3, ...; and the inactive unoccupied spin-orbitals with letters: a_1, a_2, a_3, ... The italic-style lower-case letters i_1, i_2, i_3, ... and a_1, a_2, a_3, ... denote both active and inactive occupied spin-orbitals and both active and inactive unoccupied spin-orbitals, respectively.

Several variants of the SSMRCC approach that, as shown, provide very accurate descriptions of states with significant configuration quasi-degeneracy have been developed in our laboratory. Among them is a method termed CAS(n,m)CCSD which is based on the following ansatz for the CC wave function:

$$|\Psi_{\mathrm{CAS}(n,m)\mathrm{CCSD}}\rangle = \exp(\hat{T}^{(\mathrm{ext})})(1+\hat{C}^{(\mathrm{int})})|0\rangle \tag{21}$$

or more explicitly:

$$|\Psi_{\mathrm{CAS}(n,m)\mathrm{CCSD}}\rangle = \exp(\hat{T}_1 + \cdots + \hat{T}_{n+2})(1+\hat{C}_1 + \cdots + \hat{C}_n)|0\rangle \tag{22}$$

where “n” denotes the number of active electrons and “m” denotes the number of active orbitals. In (*22*) the model-space reference wave function is generated by a CI-like operator $(1+\hat{C}^{(\mathrm{int})})|0\rangle$ which represents the so-called internal part of the wave function. In order for the ansatz (*22*) to provide size-extensive results, the internal part needs to include all possible configurations constructed by using the active orbitals (holes and particles). The additional exponentiated cluster operator $\hat{T}^{(\text{ext})}$ in (*22*) generates semi-internal and external excitations from the model-space determinants. Both $\hat{C}^{(\text{int})}$ and $\hat{T}^{(\text{ext})}$ are defined in terms of creation and annihilation of spin-orbital operators corresponding to holes and particles of the formal reference determinant, $|0\rangle$.

In the first implementation of the CAS(n,m)CCSD method[13] based on Eq. (*22*) we used the complete-active-space (CAS) reference wave function and we included all single and double excitations from the model-space determinants in the external part, exp $(\hat{T}^{(\text{ext})})$. Those single and double excitations are represented in the $T^{(\text{ext})}$ operator in the form of excitations from the formal reference determinant $|0\rangle$. Thus they include all single and double, semi-internal and external excitations from $|0\rangle$, as well as some selected high-order excitations from $|0\rangle$ (i.e. higher than double) that need to be included because they are single and double excitations from other model-space determinants.

For example, including in $T^{(\text{ext})}$ all single and double excitations from all CAS(2,2) reference determinants leads to the approach termed CAS(2,2)CCSD where the CASCC wave function has the following form:

$$|\Psi_{\text{CAS(2,2)CCSD}}\rangle = \exp\left(\hat{T}_1 + \hat{T}_2 + \hat{T}_3\binom{A_1 a_1 a_2}{I_1 i_1 i_2} + \hat{T}_4\binom{A_1 A_2 a_1 a_2}{I_1 I_2 i_1 i_2}\right)(1 + \hat{C}_1 + \hat{C}_2)|0\rangle\,. \quad (23)$$

This level of theory should be sufficient to describe the dissociation of a single chemical bond. In the above expression for the CAS(2,2)CCSD wave function the cluster operator $\hat{T}_3\binom{A_1 a_1 a_2}{I_1 i_1 i_2}$ generates all two-electron excitations from the singly excited reference determinant $|{}^{A_1}_{I_1}\rangle$ while all one-electron excitations from that reference are generated by a subset of the $\hat{T}_2$ operator (among the indices $\binom{A_1 \ldots a_1 a_2 \ldots}{I_1 \ldots i_1 i_2 \ldots}$ at least one must correspond to an inactive label). The $\hat{T}_4\binom{A_1 A_2 a_1 a_2}{I_1 I_2 i_1 i_2}$ operator generates two-electron excitations from the $|{}^{A_1 A_2}_{I_1 I_2}\rangle$ reference determinant while the one-electron excitations from that determinant are generated by a subset of the $\hat{T}_3\binom{A_1 a_1 a_2}{I_1 i_1 i_2}$ operator.

A calculation describing the dissociation process of a double bond (or simultaneous dissociation of two single bonds) has to involve four orbitals and four electrons in the active CAS space (CAS(4,4)). Hence the configuration model space in this case needs to include five types of configurations distinct by their levels of excitations from the formal reference determinant $|0\rangle$:

$$|0\rangle,\ \ \left|{}^{A_1}_{I_1}\right\rangle,\ \ \left|{}^{A_1A_2}_{I_1\,I_2}\right\rangle,\ \ \left|{}^{A_1A_2A_3}_{I_1\,I_2\,I_3}\right\rangle,\ \ \left|{}^{A_1A_2A_3A_4}_{I_1\,I_2\,I_3\,I_4}\right\rangle .$$

Including all two-electron excitations from the model space determinant $\left|{}^{A_1A_2A_3A_4}_{I_1\,I_2I_3I_4}\right\rangle$ requires including cluster operators in $T^{(\mathrm{ext})}$ involving as many as six-electron excitations from $|0\rangle$. Thus, the complete CAS(4,4)CCSD wave function has the following form:

$$\begin{aligned}|\Psi_{\mathrm{CAS(4,4)CCSD}}\rangle = \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3({}^{A_1a_1a_2}_{I_1\,i_1\,i_2}) + \hat{T}_4({}^{A_1A_2a_1a_2}_{I_1\,I_2\,i_1\,i_2}) + \\ + \hat{T}_5({}^{A_1A_2A_3a_1a_2}_{I_1\,I_2\,I_3\,i_1\,i_2}) + \hat{T}_6({}^{A_1A_2A_3A_4\,a_1a_2}_{I_1\,I_2\,I_3\,I_4\,i_1\,i_2}))(1+\hat{C}_1+\hat{C}_2+\hat{C}_3+\hat{C}_4)|0\rangle .\end{aligned} \qquad (24)$$

In the recent work[13] we discussed the numerical implementations of the CAS(2,2)CCSD and CAS(4,4)CCSD methods and we provided examples showing that the methods perform very well in situation where strong configurational quasidegeneracy arises due to stretching of covalent chemical bonds.

NUMERICAL RESULTS

In this section we will discuss an example of the application of the CASCC method to describe a strongly multiconfigurational character of the CC wave function of a model system. That model in the present calculations is boron hydride described using the standard DZV basis set. The Hartree–Fock calculation of B–H at the equilibrium geometry leads to the following orbital ordering:

$$1\sigma^2\,2\sigma^2\,3\sigma^2\,1\pi_x^0\,1\pi_y^0\,4\sigma_0\,2\pi_x^0\,2\pi_y^0\,5\sigma^0\,6\sigma^0\,7\sigma^0 \qquad (25)$$

where the superscripts indicate the occupation numbers of the orbitals in the lowest-energy (Hartree–Fock) determinant. This order does not change during the B–H dissociation.

In the first step of the analysis of the B–H dissociation we have calculated the total weights of different configurations which provide most dominant contributions to the wave function along the dissociation path. In the calculations we used the CCSD level of theory and the results are shown in Table I. As one can see by examining the results, the most important configurations are the two-electron excitations ($W_2 \approx 0.082$ at the equilibrium internuclear distance). There are also noticeable contributions from three- and four-electron excitations (of the order of $\approx 10^{-3}$). Stretching the B–H bond leads to increasing of the weights at all excitation levels. The normalization factor (N_0) clearly indicates the growth of the multiconfigurationality character of the wave function during the bond breaking. The conclusion that can be drawn from the results shown in Table I is that in order to increase the accuracy of the calculation one needs to more exactly account for the three- and four-electron excitations than is done by the CCSD approach. Such an account can be achieved by using the CAS(n,m)CCSD approach.

To apply CAS(n,m)CCSD to the B–H molecule one needs to first select the appropriate active spin-orbital space. For this purpose we have used a simple energy decomposition scheme which can be applied to the CC approach. In the scheme, one attributes the following correlation energy contribution (ε_i) to the occupied orbital (i). The sum of ε_i gives the total correlation energy (ΔE):

TABLE I

Total weights of k-electron excited configurations (W_k) in the CCSD wave function in comparison with FCI for boron hydride at different internuclear distances. N_0 is the normalization factor of the wave function (the intermediate normalization of the wave function is assumed). The equilibrium B–H distance is $R_e = 2.34a_0$

W_k		R_e	2 R_e	3 R_e	4 R_e
W_1	CCSD	0.9912×10^{-3}	0.2406×10^{-1}	0.1608	0.2050
	FCI	0.1192×10^{-2}	0.2264×10^{-1}	0.1555	0.1997
W_2	CCSD	0.8245×10^{-1}	0.2313	0.6988	0.9749
	FCI	0.8435×10^{-1}	0.2409	0.7304	1.0091
W_3	CCSD	0.2208×10^{-3}	0.1395×10^{-2}	0.9513×10^{-2}	0.1248×10^{-1}
	FCI	0.5726×10^{-3}	0.2794×10^{-2}	0.1395×10^{-1}	0.1818×10^{-1}
W_4	CCSD	0.8571×10^{-3}	0.9176×10^{-2}	0.3608×10^{-1}	0.5153×10^{-1}
	FCI	0.9222×10^{-3}	0.9523×10^{-2}	0.3735×10^{-1}	0.5350×10^{-1}
W_5	CCSD	0.1636×10^{-7}	0.1380×10^{-7}	0.1185×10^{-6}	0.1891×10^{-6}
	FCI	0.7054×10^{-7}	0.5488×10^{-6}	0.1925×10^{-5}	0.2530×10^{-5}
W_6	CCSD	0.6907×10^{-8}	0.5910×10^{-7}	0.2385×10^{-6}	0.3454×10^{-6}
	FCI	0.1041×10^{-7}	0.8787×10^{-6}	0.3429×10^{-5}	0.4889×10^{-6}
N_0	CCSD	1.0845	1.2660	1.9052	2.2439
	FCI	1.0870	1.2758	1.9372	2.2805

$$\Delta E = \sum_i \varepsilon_i \tag{26}$$

where

$$\varepsilon_i = \sum_a f_i^{\,a} t_i^a + \sum_{\substack{a<b\\ j}} \langle ab||ij\rangle \, (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \; . \tag{27}$$

A similar decomposition can be done for vacant orbitals:

$$\Delta E = \sum_a \varepsilon_a \tag{28}$$

where

$$\varepsilon_a = \sum_i f_i^{\,a} t_i^a + \sum_{\substack{i<j\\ b}} \langle ab||ij\rangle \, (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \; . \tag{29}$$

TABLE II

Orbital contributions to the CCSD correlation energy at different internuclear separations of the BH molecule. ΔE, total correlation energy. All signs are reversed. The values in the parentheses are the percentages of the total correlation energy

Energy	R_e	$2R_e$	$3R_e$	$4R_e$
ΔE	0.05996	0.10474	0.16952	0.21281
		Occupied orbitals		
1σ	0.00039 (0.7)	0.00039 (0.4)	0.00038 (0.2)	0.00037 (0.2)
2σ	0.02705 (45.1)	0.04226 (40.3)	0.04284 (25.3)	0.04148 (19.5)
3σ	0.03251 (54.2)	0.06210 (59.3)	0.12630 (74.5)	0.17096 (80.3)
		Vacant orbitals		
$1\pi_x$	0.01098 (18.3)	0.01285 (12.3)	0.01338 (7.9)	0.01323 (6.2)
$1\pi_y$	0.01098 (18.3)	0.01285 (12.3)	0.01338 (7.9)	0.01323 (6.2)
4σ	0.00228 (3.8)	0.05603 (53.5)	0.12174 (71.8)	0.16461 (77.4)
$2\pi_x$	0.00473 (7.9)	0.00448 (4.3)	0.00395 (2.3)	0.00395 (1.9)
$2\pi_y$	0.00473 (7.9)	0.00448 (4.3)	0.00395 (2.3)	0.00395 (1.9)
5σ	0.01234 (20.6)	0.00473 (4.5)	0.00326 (1.9)	0.00399 (1.9)
6σ	0.00644 (10.7)	0.00464 (4.4)	0.00527 (3.1)	0.00491 (2.3)
7σ	0.00749 (12.5)	0.00468 (4.5)	0.00458 (2.7)	0.00495 (2.3)

In Table II we present orbital contributions to the correlation energy determined at the CCSD level of theory. As one notices, as the B–H bond stretches (to $2R_e$, $3R_e$ and $4R_e$), the most dominant contributions are due to the occupied 3σ orbital and the vacant 4σ orbital (underlined in the table). Contributions from those orbitals provide 80.3 and 77.4% of the total correlation energy, respectively, at the internuclear distance $R = 4R_e$. Thus it is clear that the 3σ and 4σ orbitals have to be included in the active space. All possible distributions of the two active electrons among the active orbitals generate the reference space. The determinant which gives the dominant contribution to the CASSCF wave function is selected as the "formal reference". In this way the form of the CAS(2,2)CCSD wave function is defined.

The application of the CAS(2,2)CCSD approach to B–H has resulted in the energies for different points along the potential energy curve which are shown in Table III. In the table, a comparison is made between the CAS(2,2)CCSD results with the results obtained by CASSCF, CCSD, CR-CCSD(T) (the so-called completely renormalized (CR) CCSD(T) method[84] recently implemented in the GAMESS package), and FCI levels of theory. It is clear that the CAS(2,2)CCSD method is the most accurate in accounting for the electron correlation effects. The agreement of the CAS(2,2)CCSD energies with the FCI energies is the most constant among the four methods at all points on the B–H dissociation path.

The structure of the CAS(2,2)CCSD wave function, as analyzed in Table IV, also illustrates the high accuracy of the method. The agreement between the configurational coefficients obtained in the CAS(2,2)CCSD calculations

TABLE III

A comparison of the CASSCF(2,2), CCSD, CR-CCSD(T) and CAS(2,2)CCSD ground-state energies with the FCI results for different internuclear separations of the BH molecule. The standard valence double-zeta (DZV) basis set was used in the calculation. The FCI energies are given in hartrees and for the other methods in millihartrees relative to the corresponding FCI values

Geometry	CASSCF(2,2)	CCSD	CR-CCSD(T)	CAS(2,2)CCSD	FCI
R_e	45.30	0.81	0.35	0.46	–25.174185
$2R_e$	45.54	2.07	0.72	0.29	–25.094143
$3R_e$	42.98	3.90	0.85	0.38	–25.068909
$4R_e$	42.61	4.04	0.74	0.40	–25.067285

and the FCI coefficients is very good. This shows that the CAS(2,2)CCSD wave function represents very well the physical nature of the B–H dissociation process.

TABLE IV
CASSCF(2,2), CAS(2,2)CCSD and FCI configuration coefficients of the dominant configurations of BH at the internuclear separation of $4R_e$. Intermediate normalization is assumed in the wave function. All configurations with the coefficients larger than 0.1 (or smaller that –0.1) are shown

Determinant	CASSCF(2,2)	CAS(2,2)CCSD	FCI
Reference			
$\|0\rangle$	1	1	1
$\|1\rangle = \|0_{3\sigma 3\sigma}^{4\sigma 4\sigma}\rangle$	–0.9641	–0.9581	–0.9578
$\|2\rangle = \|0_{3\sigma}^{4\sigma}\rangle$	0.1267	0.1234	0.1231
External and semi–internal excitations from references			
$\|0_{2\sigma\,2\sigma}^{\pi_x \pi_x}\rangle$	–	–0.1233	–0.1246
$\|0_{2\sigma\,2\sigma}^{\pi_y \pi_y}\rangle$	–	–0.1233	–0.1246
$\|1_{2\sigma\,2\sigma}^{\pi_x \pi_x}\rangle$	–	0.1184	0.1196
$\|1_{2\sigma\,2\sigma}^{\pi_y \pi_y}\rangle$	–	0.1184	0.1196

CONCLUSIONS

We have shown that the dissociation of the BH molecule can be very accurately described using the CAS(2,2)CCSD method. In this approach, one first selects an orbital active space. As it was shown, this can be done by calculating correlation contributions corresponding to individual occupied and vacant molecular orbitals based on the CCSD wave function. The degree of the multiconfigurationality of the wave function of the considered problem can be examined by calculating cumulative weight factors that describe the importance of configurations at specific excitation levels to the wave function. The analysis can be done at the CCSD level of theory. For the BH molecule at larger internuclear distances the weight factor corresponding to double excitations clearly showed a much increased multiconfigurationality level. Such increased level cannot be correctly handled by the single-reference CCSD approach, but, as shown, can be very well described using the CAS(2,2)CCSD approach with two orbitals and two electrons in the active space. Both the energy and the configurational coefficients obtained in the CAS(2,2)CCSD calculations are very close to the respective FCI values at all the points along the dissociation path considered in the present calculations.

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