Performance of Block Correlated Coupled Cluster Method with the CASSCF Reference Function for the Prediction of Activation Barriers, Spectroscopic Constants in Diatomic Molecules, and Singlet−Triplet Gaps in Diradicals

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The spatial orbital formulations of block correlated coupled cluster (BCCC) theory with a general CASSCF reference function (CAS-BCCC in short) is derived and an efficient implementation of this approach at the four-block correlation level (abbreviated CAS-BCCC4) is reported. We have applied the CAS-BCCC4 approach to investigate energy barriers for several reactions (the ring-opening isomerization of the cyclopropyl radical, cyclobutene, cyclobutadiene, and bicyclo[3.1.0]hex-2-ene), spectroscopic constants in several multibond diatomic molecules (C_2, O_2, CO, and N_2), and singlet−triplet gaps in two diradicals (trimethylenemethane and oxyallyl). A comparison of CAS-BCCC4 results with the experimental data or other theoretical estimates shows that the present approach can provide very satisfactory descriptions for all the studied systems.

1. Introduction

When molecules are stretched from their equilibrium geometries (such as in transition states), the zero-order wave functions usually require a combination of several or a number of determinants. In such circumstances, the multiconfiguration self-consistent-field (MCSCF) wave function, especially the complete active space self-consistent-field (CASSCF) wave function, is often employed to provide qualitative descriptions for the electronic structures. However, to achieve quantitative descriptions, the CASSCF wave function must be augmented by dynamic correlation. A number of approaches have been developed to treat dynamic correlation, which can be divided into three categories: (1) multireference configuration interaction with single and double excitations (MR-CISD);[1] (2) multireference perturbation theory (MR-PT), such as CASSCF-based second-order perturbation theory (CASPT2);[2,3] and (3) multireference coupled cluster (MR-CC) methods.[4–35] Among these methods, MR-CISD and CASPT2 methods have been well-established and widely used for studying various chemistry problems. For MR-CC methods, although they are all based on the effective Hamiltonian theory, they can be further subdivided into the Fock-space or valance-universal approach,[4–12] the Hilbert-space or state-universal approach,[13–22] and the state-selective state-specific approach.[23–35] Significant progress has been made in recent years to implement these MR-CC methods, but the applications of these methods are still limited to systems containing a few reference determinants. Besides these approaches, many alternative approaches within the single reference CC framework have also been proposed for treating the multireference problem, which include the method of moment CC,[36–41] the renormalized CC approach,[42–51] the CAS-CCSD method,[52–57] the reduced multireference method,[58–64] the spin flip method,[65–71] the orbital-optimized CC approach,[72–79] and others.[80–88] Compared to standard MR-CC methods, some of these alternative approaches have the advantage of being "black-box" and cost-effective, and they can also provide accurate descriptions for molecular electronic states with strong multireference characters in many cases. However, when there is an avoided crossing of potential energy surfaces, leading to the dramatic change of the leading configurations, some of these approaches are unsuitable.[36–51,65–71]

In our previous work,[89,90] we developed an alternative MR-CC approach, the block correlated coupled cluster (BCCC) approach. Within the BCCC framework, the orbitals in a system are divided into blocks (a subset of orbitals), and the reference function of the BCCC expansion is expressed as the tensor product of the most important many-electron state in each block, which is expected to recover nondynamic correlation. The cluster operator in BCCC is introduced to incorporate dynamic correlation among blocks. In general, BCCC methods may exist in many variants, depending on how blocks are defined. Very recently, we have implemented the CAS-BCCC4 approach, in which the CASSCF wave function is employed as the reference function.[91–93] With the CASSCF(2,2) wave function as the reference function, we have demonstrated that the CAS(2,2)-BCCC4 approach is capable of giving quantitative descriptions for the potential energy surfaces (PESs) of single bond-breaking processes and the singlet−triplet gaps in various diradicals.[92] For larger active spaces, our preliminary implementation (in spin orbital form) has allowed the applicability and accuracy of the CAS-BCCC4 method to be assessed.[93] The CAS-BCCC4 method was shown to be also quite successful in describing the double-bond-breaking PESs in C_2 and H_2O, and the triple-bond-breaking PESs in N_2.

In this paper, we will report an efficient implementation (in spatial orbital form) of the CAS-BCCC4 approach with a general CASSCF reference function. The present implementation allows CAS-BCCC4 calculations with the general reference function to be computationally feasible for medium-sized molecules with moderate basis sets (or small molecules with large basis sets). We will apply this approach to compute activation barriers for four isomerization reactions, spectroscopic constants in multibond diatomic molecules, and the singlet−triplet energy gaps

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in two typical diradicals. The results will be compared with the corresponding internally contracted CASPT2[94,95] and MR-CISD[96–99] results and experimental data (if available).

2. Methodology

Within the CAS-BCCC framework, the wave function is formulated as

$$\Psi_{\mathrm{BCCC}} = \mathrm{e}^{T}\Phi_0 \tag{1}$$

where

$$\Phi_0 = A_0^{+} i^{+} j^{+} \ldots |0\rangle \tag{2}$$

Here A_0^+ represents the creation operator for the reference state of block **A**, and i^+ stands for the creation operator in the *i*th occupied spin orbital. The multiorbital block **A** is defined to include all active orbitals. The reference state of block **A** and its "excited" states are unambiguously specified provided that the CASSCF(N_0, K) (N_0 electrons in K spatial orbitals) wave function is available for a given state. For the sake of consistency, one spin orbital is also called a block.

Within CAS-BCCC, if the total cluster operator is truncated up to the four-block correlation level, i.e.,

$$T \approx T_1 + T_2 + T_3 + T_4 \tag{3}$$

the approximate CAS-BCCC method is abbreviated as CAS-BCCC4. The explicit expressions of all cluster operators up to the four-block correlation level have been given elsewhere.[93] For example, the three-block cluster operator T_3 has the following form

$$T_3 = T_{3A} + T_{3B} + T_{3C} \tag{4}$$

$$T_{3A} = \frac{1}{2}\sum_{U}^{N_0-2}\sum_{a,b}^{\mathrm{vir}} A_U^{+} A_0^{-} a^{+} b^{+} t_{3A}(U,a,b) \tag{5}$$

$$T_{3B} = \frac{1}{2}\sum_{U}^{N_0+2}\sum_{i,j}^{\mathrm{occ}} A_U^{+} A_0^{-} i^{-} j^{-} t_{3B}(U,i,j) \tag{6}$$

$$T_{3C} = \sum_{U}^{N_0}\sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{vir}} A_U^{+} A_0^{-} a^{+} i^{-} t_{3C}(U,i,a) \tag{7}$$

In the equations above $t_{3A}(U,a,b)$ (and so on) are the excitation amplitudes to be determined. By projecting the Schrödinger equation onto Φ_0 and all excited configuration functions, one can obtain a set of coupled equations (as show below),[91] from which the excitation amplitudes and the correlation energy can be obtained.

$$\langle\Phi_0|H|\Psi_{\mathrm{BCCC}}\rangle = E_{\mathrm{BCCC}}\langle\Phi_0|\Psi_{\mathrm{BCCC}}\rangle = E_{\mathrm{BCCC}} \tag{8}$$

$$\langle\Phi^{V}|H|\Psi_{\mathrm{BCCC}}\rangle = E_{\mathrm{BCCC}}\langle\Phi^{V}|\Psi_{\mathrm{BCCC}}\rangle \tag{9}$$

$$\langle\Phi^{V,a}|H|\Psi_{\mathrm{BCCC}}\rangle = E_{\mathrm{BCCC}}\langle\Phi^{V,a}|\Psi_{\mathrm{BCCC}}\rangle \tag{10}$$

$$\cdots$$

The resulting nonlinear equations can be efficiently solved in the iterative manner, as done in the single reference CC methods.

To develop an efficient code of the CAS-BCCC4 approach, one has to transform the spin orbital formulations of the CAS-BCCC4 method into spatial orbital formulations by integrating out the spin coordinates. Take T_{3A} as an example. Assume that N_0 and M_0 represent the number of active electrons and the *z*-component of the total spin, respectively, for the reference state of block **A**. Then, T_{3A} can be decomposed into three parts associated with only spatial orbitals: T_{3A1}, T_{3A2}, and T_{3A3}, as shown below:

$$T_{3A} = T_{3A1} + T_{3A2} + T_{3A3} \tag{11}$$

$$T_{3A1} = \sum_{U}^{(N_0-2,M_0-1)}\sum_{a(\alpha),b(\alpha)}^{\mathrm{vir}} A_U^{+} A_0^{-} a^{+} b^{+} t_{3A1}(U,a,b) \tag{12}$$

$$T_{3A2} = \sum_{U}^{N_0-2,M_0}\sum_{a(\alpha),b(\beta)}^{\mathrm{vir}} A_U^{+} A_0^{-} a^{+} b^{+} t_{3A2}(U,a,b) \tag{13}$$

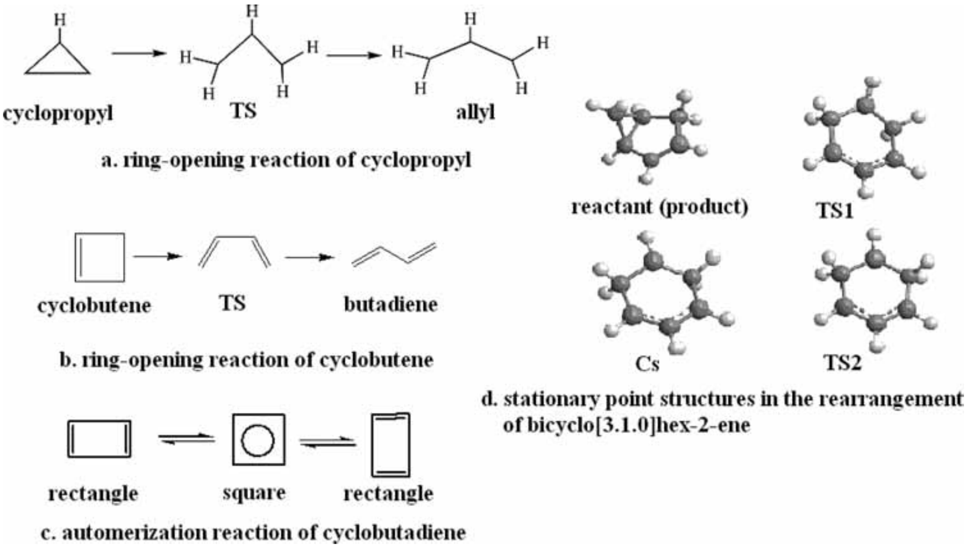
$$T_{3A3} = \sum_{U}^{N_0-2,M_0+1}\sum_{a(\beta),b(\beta)}^{\mathrm{vir}} A_U^{+} A_0^{-} a^{+} b^{+} t_{3A3}(U,a,b) \tag{14}$$

Here the sum for orbitals runs over spatial MOs and the sum for electronic states U (block **A**) is only limited to a subset of electronic states (with the number of active electrons and the M_S value in parentheses). Since the working equations of the CAS-BCCC4 method are very complicated, we have developed a computer program to transform all amplitudes and all integrals (one-electron and two-electron) with spin orbital indices in the equations into corresponding quantities with only spatial orbital indices.

After introducing a number of intermediate arrays, we find that in the present CAS-BCCC4 method the most time-consuming step scales as $n_o^2 n_v^4$, with n_o (n_v) being the number of occupied (virtual) spatial orbitals. Thus, the CAS-BCCC4 method and the traditional CCSD method share the same computational scaling, but the former has a larger prefactor. However, for relative smaller active spaces (say, with no more than six active orbitals), our present implementation allows CAS-BCCC4 calculations to become routinely feasible for medium-sized molecules with moderate basis sets. On the other hand, since the CAS-BCCC4 wave function is invariant to separate unitary transformation among occupied, active, and virtual orbitals, any orbitals (canonical or localized orbitals) obtained from the CASSCF calculations can be employed for the subsequent CAS-BCCC4 calculations.

3. Results and Discussions

In this section, the CAS-BCCC4 approach is applied to study the reaction barriers for four isomerization reactions, spectroscopic constants in four multibond diatomic molecules (C_2, O_2, CO, and N_2), and the singlet−triplet gaps in two typical diradicals [trimethylenemethane (TMM) and oxyallyl (OXA)]. In all the CAS-BCCC4 calculation, a CASSCF calculation is first carried out with the GAMESS program.[100] Then, our program, linked to the GAMESS program, is used to obtain the CAS-BCCC4 energy. In this work, several different basis sets are employed, in which six Cartesian d-like and 10 Cartesian f-like functions are used, unless stated otherwise. As shown previously,[91–93] T_{2C} usually has a very minor effect on the relative energies and thus will be neglected to save computational time. Similarly, for active spaces used in this study, the inclusion of two four-block correlation operators, T_{4D} and T_{4E}, will lead to little gain in dynamic correlation energy at the expense of increasing significant computational times, so T_{4D} and T_{4E} will be neglected in all calculations. The effect of adding the operators T_{4D} and T_{4E} will be demonstrated later for several systems. One reason why T_{4D} and T_{4E} contribute little to the correlation energy is because the excited configurations generated by these two operators will not directly interact with the reference function, i.e., $\langle\Phi_0|H|T_{4D}\Phi_0\rangle = 0$ and $\langle\Phi_0|H|T_{4E}\Phi_0\rangle = 0$.[93] Another reason is that active spaces used in this study are



a. ring-opening reaction of cyclopropyl

b. ring-opening reaction of cyclobutene

c. automerization reaction of cyclobutadiene

d. stationary point structures in the rearrangement of bicyclo[3.1.0]hex-2-ene

Figure 1. Four isomerization reactions.

TABLE 1: Total Energies of the Reactant and Relative Energies[a] of the Transition State and the Product (Relative to the Reactant) in the Ring-Opening Reaction of Cyclopropyl Calculated Using Different Methods with the cc-pVTZ Basis Set

method	total energy of the reactant (au)	E_a[a] (kcal/mol) TS	E_a[a] (kcal/mol) product
CASSCF	−116.471 024	23.92 (21.08)	−35.19 (−36.68)
CAS-BCCC4	−116.959 147	24.63 (21.79)	−30.47 (−31.96)
CASPT2	−116.943 227	22.86 (20.02)	−29.68 (−31.17)
MR-CISD	−116.915 187	25.16 (22.31)	−31.27 (−32.76)
expt[b]		22 ± 2	

[a] Energy barriers with ZPE corrections (as described in the text) are included in parentheses. [b] Reference 102.

relatively small. The CAS-BCCC4 results will be compared with the experimental data (if available) and the results from the internally contracted MR-CISD and CASPT2. For comparison, MR-CISD and CASPT2 calculations with the same active space as in corresponding CAS-BCCC4 calculations are carried out with the MOLPRO package.[101] In all the post-CASSCF calculations, the core orbitals of the heavy atoms are kept frozen.

3.1. Barrier Heights for Four Isomerization Reactions.

3.1.1. The Ring-Opening Reaction of the Cyclopropyl Radical. This is the simplest example of an electrocyclic reaction of a free radical. The reaction passes through a triradical transition state (TS) to form the allyl radical (Figure 1a). Throughout the reaction path, a (3,3) active space is adopted. For the reactant and TS, the active space contains the radical orbital and the σ and σ^* orbitals of the breaking C−C bond. Then, these orbitals transform into three π orbitals of the allyl radical. The structures of the reactant, TS, and the product have been optimized previously[102] at the CASSCF(3,3)/cc-pVTZ level. Our CAS(3,3)-BCCC4 calculations will be performed at these optimized geometries (See the Supporting Information). As is shown in Table 1, the calculated CAS-BCCC4 barrier height with the zero-point energy (ZPE) corrections (calculated with the same method as used in the optimization) is 21.79 kcal/mol, very close to the experimental value of 22.2 kcal/mol[103,104] and the previous CCSD(T)/6-311G(2d) value (22.5 kcal/mol).[102] MR-CISD and CASPT2 also give comparable results.

3.1.2. The Ring-Opening Reaction of Cyclobutene. The isomerization of cyclobutene to butadiene is the simplest electrocyclic reaction of hydrocarbons. The structures of stationary points involved in the reaction have been determined at various theoretical levels,[105,106] and those obtained at the B3LYP/6-31G(d) level will be used for our CAS-BCCC4 calculations. As shown in Figure 1b, one C−C σ bond is breaking and two π bonds are forming in the transition state. So the active space will include four electrons in four orbitals (for the reactant, four orbitals consist of two π orbitals and two σ orbitals in the breaking C−C bond). The CAS(4,4)-BCCC4 calculations are carried out with 6-31G(d) and 6-311G++(d,p) basis sets, with the results listed in Table 2. With the ZPE corrections obtained from B3LYP/6-31G(d) calculations,[106] the barrier heights calculated from three approaches (with the 6-311++G(d,p) basis set) are reasonably close to the experimental value. Compared to the 6-31G(d) results, the energy barriers obtained at the 6-311G++(d,p) level are significantly improved (with respect to the experimental value).

With the basis set 6-31G(d), we also investigate how the inclusion of T_{4D} and T_{4E} will affect the calculated relative energies. One can see (from Table 2) that the relative energies of the transition state and the product (relative to the reactant) are changed by less than 0.01 kcal/mol after T_{4D} and T_{4E} are included.

3.1.3. Automerization Reaction of Cyclobutadiene (CBD). This reaction involves the interconversion of two equivalent D_{2h} structures via a square transition structure D_{4h} (Figure 1c). The rectangle equilibrium structure of CBD is a closed-shell singlet, but the square transition state is an open-shell diradical, which requires the treatment of multireference methods. Thus, the barrier height for this automerization reaction has received much attention from theoretical chemists for many years.[107−110] Experimentally, the energy barrier was estimated to be in the range of 1.6−10 kcal/mol.[111,112] Our study for this reaction is based on the optimized geometries (for both minimum and transition state) obtained with multireference average-quadratic coupled cluster (MR-AQCC) method.[110] In our CAS-BCCC4

TABLE 2: Total Energies of the Reactant and Relative Energies[a] of the Transition State, and the Product (Relative to the Reactant) in the Ring-Opening Reaction of Cyclobutene Calculated Using Different Methods

			E_a[a] (kcal/mol)	
basis set	method	total energy of the reactant (au)	TS	product
6-31G(d)	CASSCF	−154.944 578	37.53 (35.82)	−18.98 (−19.90)
	CAS-BCCC4[b]	−155.442 942	37.48 (35.77)	−11.90 (−12.85)
	CAS-BCCC4[c]	−155.442 909	37.49 (35.78)	−11.91 (−12.83)
	CASPT2	−155.413 145	35.54 (33.83)	−10.36 (−11.28)
	MR-CISD	−155.391 413	37.38 (35.67)	−13.34 (−14.26)
6-311G ++(d,p)	CASSCF	−154.982 313	36.12 (34.41)	−20.85 (−21.77)
	CAS-BCCC4	−155.547 738	35.83 (34.12)	−12.87 (−13.79)
	CASPT2	−155.520 442	32.69 (30.98)	−11.51 (−12.43)
	MR-CISD	−155.483 865	35.70 (33.99)	−14.60 (−15.52)
	expt[d]		31.9 ± 0.2	

[a] Energy barriers with ZPE corrections (as described in the text) are included in parentheses. [b] With the T_{4D} and T_{4E} operators. [c] Without the T_{4D} and T_{4E} operators. [d] Reference 106.

TABLE 3: Total Energies of the Reactant and Relative Energies of the Transition State (Relative to the Reactant) in the Automerization Reaction of Cyclobutadiene Calculated Using Different Methods

basis set	method	total energy of the rectangle structure (au)	E_a (kcal/mol)[a] of the TS
cc-pVDZ	CASSCF	−153.722 185	6.41 (3.91)
	CAS-BCCC4[b]	−154.220 154	7.56 (5.06)
	CAS-BCCC4[c]	−154.220 125	7.55 (5.05)
	CASPT2	−154.195 934	3.40 (0.90)
	MR-CISD	−154.168 090	7.30 (4.80)
	MR-AQCC[c]		7.70 (5.20)
cc-pVTZ	CASSCF	−153.761 908	7.38 (4.88)
	CAS-BCCC4	−154.353 314	8.71 (6.21)
	CASPT2	−154.341 082	3.75 (1.25)
	MR-CISD	−154.290 699	8.45 (5.95)
	MR-AQCC[d]		8.90 (6.40)
	expt[e]		1.6−10

[a] Energy barriers with ZPE corrections (as described in the text) are included in parentheses. [b] With the T_{4D} and T_{4E} operators. [c] Without the T_{4D} and T_{4E} operators. [d] Reference 110. [e] References 111 and 112.

calculations, we will employ the active space with four π electrons in four π orbitals (two π and two π^*) (as in corresponding MR-AQCC calculations) and two different basis sets (cc-pVDZ and cc-pVTZ). The calculated energy barriers without and with ZPE corrections (the ZPE corrections at the MR-AQCC/cc-pVDZ level is −2.5 kcal/mol[110]) are listed in Table 3. One can see that the barrier height from CAS-BCCC4/cc-pVTZ calculations is 6.21 kcal/mol, quite close to the corresponding MR-AQCC (6.4 kcal/mol) and MR-CISD (5.95 kcal/mol) values. Nevertheless, it seems like the CASPT2 method significantly underestimates the barrier height, compared to other theoretical methods used here. On the other hand, since the single reference CC method is expected to provide quantitative descriptions for the equilibrium D_{2h} structure, it is worthwhile to compare the electronic energies from the CAS-BCCC4 and CCD methods (single excitations are not considered in both methods). The results show that the CAS-BCCC4/cc-pVTZ energy (−154.353 31 au) is almost identical to the CCD/cc-pVTZ energy (−154.353 14 au), as expected.

With the basis set cc-pVDZ, we also find from Table 3 that the inclusion of T_{4D} and T_{4E} only changes the energy barrier by 0.01 kcal/mol, an indication that the two operators T_{4D} and T_{4E} have little effect on the relative energy.

3.1.4. The Automerization of Bicyclo[3.1.0]hex-2-ene. This automerization reaction has been studied by Suhrada and Houk at various theoretical levels.[113] The structures of the reactant (product), an intermediate of C_S symmetry, and two transition states (**TS1** and **TS2**) involved in the reaction pathways have been located at the CASSCF(4,4)/6-31G(d) level (Figure 1d).[113] The reactant is likely to first convert into a C_S intermediate via **TS1**, and then this intermediate will transform back to the product (reactant). **TS2** is the planar transition state connecting this C_S intermediate and its another isomer with identical energy. The C_S intermediate and two transition states were characterized to be diradical in nature, and have very close energies. Our aim here is to perform single point CAS-BCCC4 calculations at the optimized geometries obtained previously[113] to calculate the corresponding barriers. The present calculations employ the same basis set (6-31G(d)) and CASSCF(4,4) reference function, as used in previous work.[113] The results are listed in Table 4 (the ZPE corrections at the CASSCF(4,4) level are taken from the previous work[113]). It can be seen that all the three different approaches predict the C_S minimum and two transition states to be almost identical in energy, but the barrier (from the reactant to **TS1**) predicted from the CAS-BCCC4 approach is slightly closer to the experimental value.

To summarize the discussions above for the four isomerization reactions, one can find that the barrier heights predicted from the CAS-BCCC4 approach are quite consistent with those from CASPT2 and MR-CISD methods. Nevertheless, the total CAS-BCCC4 energies are always lower than the corresponding MR-CISD or CASPT2 energies. For example, the CAS-BCCC4 energy is 0.119 au lower than the MR-CISD energy for the bicyclo[3.1.0]hex-2-ene. When the size of the system increases, the difference between CAS-BCCC4 and MR-CISD energies always increases. This is due to the fact that the size-consistency error of the MR-CISD method increases with the size of the system, but that of the CAS-BCCC4 method only depends on the size of the active space (this issue is addressed later in the next subsection). Thus, for larger molecules, it is expected that

TABLE 4: Total Energies of the Reactant and Relative Energies of the Transition State (Relative to the Reactant) in the Rearrangement of Bicyclo[3.1.0]hex-2-ene Calculated Using Different Methods with the 6-31G(d) Basis Set

		E_a[a] (kcal/mol)		
method	total energy of the reactant (au)	**TS1**	C_S	**TS2**
CASSCF	−231.855 386	35.63 (32.27)	33.72 (30.98)	34.29 (31.02)
CAS-BCCC4	−232.619 072	43.68 (40.32)	42.72 (39.98)	42.97 (39.70)
CASPT2	−232.581 541	42.30 (38.94)	41.71 (38.97)	41.98 (38.71)
MR-CISD	−232.500 319	42.12 (38.76)	40.87 (38.13)	41.14 (37.87)
expt[b]		43.8−44.8		

[a] Energy barriers with ZPE corrections (as described in the text) are included in parentheses. [b] Reference 114.

TABLE 5: Exact Equilibrium Distances (R_e), Dissociation Energies (D_e), and Harmonic Vibrational Frequencies (ω_e) for the Ground State of C_2, O_2, CO and N_2, and the Corresponding Deviations Calculated by Different Theoretical Methods with the 6-311G++(3df,3p) Basis Set

method	C_2	O_2	CO	N_2	MAE
			R_e (Å)		
expt[a]	1.243	1.208	1.128	1.098	
CASSCF	0.005	0.006	0.003	0.005	0.005
CAS-BCCC4	0.007	0.003	0.004	0.006	0.005
CASPT2	0.007	0.004	0.003	0.006	0.005
MR-CISD	0.006	0.002	0.004	0.005	0.004
			ω_e (cm^{-1})		
expt[a]	1855	1580	2170	2359	
CASSCF	−184	−25	−7	−15	58
CAS-BCCC4	−24	2	−31	−31	22
CASPT2	−24	−8	−30	−44	27
MR-CISD	−18	4	−29	−28	20
			D_e (kcal/mol)		
expt[a]	146.0	120.3	255.7	228.5	
CASSCF	2.0	31.5	3.6	−23.6	15.2
CAS-BCCC4	−1.7	−5.8	1.2	−10.3	4.8
CASPT2	5.3	−1.1	−3.7	−18.8	7.2
MR-CISD	−2.6	−8.3	0.8	−10.4	5.5

[a] Reference 120 for C_2, O_2 and N_2, and ref 121 for CO.

the CAS-BCCC4 and CASPT2 methods would give more reliable predictions for the barrier heights than the MR-CISD method.

3.2. Spectroscopic Constants in Diatomic Molecules C_2, O_2, CO, and N_2. The dissociation potential energy surfaces (PESs) in diatomic molecules have been extensively studied with various theoretical methods.[44,49,115−120] Here we will focus on the following multibond diatomic molecules: C_2, O_2, CO, and N_2. For these four molecules, the CASSCF wave function with the active space (4,6), (6,6), (6,6), and (8,6), respectively, can be used to provide qualitative descriptions. The basis set we use here is 6-311G++(3df,3p). The values of the equilibrium bond distance (R_e) and the harmonic vibrational frequency (ω_e) are obtained by fitting 16 points on the PESs to a cubic polynomial potential. The calculated dissociation energies (D_e) are obtained by subtracting the energy at a large interatomic distance (20 Å) from that at R_e. As shown in Table 5, the mean absolute errors for R_e, ω_e, and D_e predicted from CAS-BCCC4 calculations (with respect to the corresponding experimental values) are, respectively, 0.005 Å, 22 cm^{-1}, and 4.8 kcal/mol, which are comparable to those of the MR-CISD results (0.004 Å, 20 cm^{-1}, and 5.5 kcal/ mol) and the CASPT2 results (0.005 Å, 27 cm^{-1}, and 7.2 kcal/mol).

It is worthwhile to investigate the size-consistency errors inherent in three different approaches. For the bond-dissociation problem, the size-consistency error is defined to be the energy difference between the computed energy of the combined system in infinite separation and the sum of the energies calculated for two isolated open-shell subsystems. For the four diatomic molecules mentioned above and two additional molecules (F_2 and C_2H_4), the size-consistency errors of three theoretical approaches with the basis set 6-311G++(3df,3p) are listed in Table 6 (the computational details were discussed previously[91]). From this table, one can see that CASPT2 is nearly size-consistent, and CAS-BCCC4 has slightly smaller size-consistency errors than MR-CISD. As expected from our previous analysis,[91] the size-consistency error of the CAS-BCCC4 method increases with the size of the active space. For example, the size-consistency error is 0.87 kcal/mol for the single-bond F_2 with an active space (2,2), 3.01 kcal/mol for the double-bond C_2H_4 with an active space (4,4), and 4.17 kcal/mol for the triple-bond N_2 with an active space (6,6). However, the size-consistency error of MR-CISD is dependent on both the size of the active space and the number of electrons in the whole system, so its dependence on the size of the active space alone

TABLE 6: Size-Consistency Errors (kcal/mol) of Different Theoretical Methods for Several Molecules in the Dissociation Limit (20 Å) in the 6-311G++(3df,3p) Basis Set

species	active space	CAS-BCCC4	CASPT2	MR-CISD
F_2	(2,2)	0.84	0.01	8.93
C_2H_4[a]	(4,4)	3.01	0.03	8.02
C_2	(4,6)	4.52	0.08	5.36
N_2	(6,6)	4.17	0.06	5.02
CO	(6,6)	5.84	0.07	6.67
O_2	(8,6)	6.61	0.01	7.26

[a] For isolated CH_2, its structure is taken as the corresponding FCI/TZ2P optimized geometry in ref 122 (R_{C-H} = 1.0775 Å, $\ddot{H}$−C−H = 133.29°).

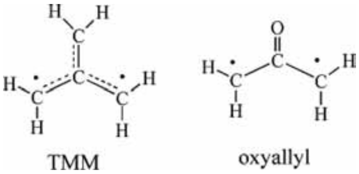


Figure 2. Structures of trimethylenemethane (TMM) and oxyallyl (OXA).

TABLE 7: Ground-State Energies (au) and Adiabatic Singlet-Triplet Gaps (eV) of TMM Calculated Using Different Methods with Two Different Active Spaces[a]

method	$^{3}A_2'$	$^{1}B_1$[b]	$^{1}A_1$[b]
	Active Space (2,2)		
CASSCF	−154.898 649	0.651 (0.609)	0.460 (0.372)
CAS-BCCC4	−155.447 627	0.658 (0.616)	0.718 (0.630)
CASPT2	−155.424 306	0.706 (0.664)	0.972 (0.884)
MR-CISD	−155.378 414	0.673 (0.631)	0.670 (0.582)
	Active Space (4,4)		
CASSCF	−154.936 880	0.642 (0.600)	0.843 (0.755)
CAS-BCCC4[c]	−155.449 651	0.676 (0.634)	0.826 (0.738)
CAS-BCCC4[d]	−155.449 617	0.676 (0.634)	0.826 (0.738)
CASPT2	−155.420 386	0.667 (0.625)	0.856 (0.768)
MR-CISD	−155.394 006	0.659 (0.617)	0.844 (0.756)
MCQDPT2[e]	−155.423 414	0.676 (0.634)	0.863 (0.775)
expt[f]			0.699 ± 0.006

[a] The DZP basis set is used. [b] Energy gaps with zero-point corrections (as described in the text) are included in parentheses. [c] With the T_{4D} and T_{4E} operators. [d] Without theT_{4D} and T_{4E} operators. [e] Reference 125. [f] Reference 126.

is not clear from the data in Table 6. For CAS-BCCC4, the existence of the size-consistency error may have minor impact on the calculated dissociation energies, energy barriers, and other properties.

3.3. Singlet−triplet Energy Gaps in Diradicals TMM and OXA. ***3.3.1. TMM.*** This is the simplest non-Kekulé hydrocarbon (Figure 2). The ground-state of this molecule has been well-established to be a triplet state ($^{3}A_2'$) with D_{3h} equilibrium geometry.[123–125] Since at the D_{3h} geometry, two electrons are required to occupy a pair of degenerate π orbitals (e′) ($1a_2$ and $2b_1$ orbitals, if C_{2v} symmetry labels are used), this molecule is a typical diradical, which obeys the Hund's rule. Due to the Jahn−Teller effect, the lowest two singlet excited states ($^{1}A_1$ and $^{1}B_1$) were predicted to have lower symmetry (C_{2v}) and their degeneracy (at the D_{3h} geometry) is lifted accordingly. In our CAS-BCCC4 calculations, the geometries of the ground-state and two lowest excited states are taken as those optimized at the SF-DFT/6-31G(d) level.[125] Two different active spaces are employed: the minimal active space (2,2) (two electrons in $2b_1$ and $1a_2$) and a larger active space (4,4) (four electrons in four π orbitals $1b_1$, $2b_1$, $1a_2$, and $3b_1$). The DZP basis set (with five Cartesian d-like functions) will be used in all calculations. The calculated adiabatic singlet−triplet separations for the two lowest singlet excited states are displayed in Table 7 (the ZPE corrections at the SF-DFT/6-31G(d) level[125] are −0.042 and −0.088 eV). When the larger (4,4) active space is used, for both singlet states, the calculated energy gaps from the three methods are quite close and also comparable to the corresponding MCQDPT2 value.[125] Since for this system, the increase of the basis set from DZP to cc-pVTZ was shown to have little effect on the calculated energy gaps,[125] one can see that the experimental value of the $^{3}A_2'-^{1}A_1$ gap[126] is well-reproduced by CAS-BCCC4 and other methods. For the $^{3}A_2' \rightarrow ^{1}B_1$ transition, it seems that CAS-BCCC4, CASPT2, and MR-CISD are all insensitive to the size of the active space. However, increasing the active space from (2,2) to (4,4) changes the $^{3}A_2'-^{1}A_1$ gap significantly for all methods used. This result suggests that the use of the active space (4,4) is necessary for very accurate predictions of the singlet−triplet gaps in TMM.

TABLE 8: Ground-State Energies (au) and Adiabatic Singlet-Triplet Gaps (eV) of Oxyallyl Calculated Using Different Methods with the 6-31G(d) Basis Set

method	$^{3}B_2$	$^{1}A_1$[a]
	Active Space (2,2)	
CASSCF	−190.700 945	−0.195 (−0.191)
CAS-BCCC4	−191.249 210	−0.004(0.000)
CASPT2	−191.237 024	0.149(0.154)
MR-CISD	−191.186 201	−0.065 (−0.061)
	Active Space (4,4)	
CASSCF	−190.742 729	0.215 (0.219)
CAS-BCCC4	−191.251 202	0.122 (0.126)
CASPT2	−191.233 006	0.133 (0.137)
MR-CISD	−191.202 171	0.138 (0.142)

[a] Energy gaps with zero-point corrections (as described in the text) are included in parentheses.

With the active space (4,4), we also investigate the effect of including the T_{4D} and T_{4E} operators in CAS-BCCC4 calculations on the calculated singlet−triplet gaps. The results (Table 7) show that the inclusion of these two operators lowers the triplet energy by less than 0.1 millihartrees but gives the same singlet−triplet gap as the calculation without these two operators.

3.3.2. OXA. As shown in Figure 2, oxyallyl may be looked at as a derivate of TMM by replacing a methylene group with oxygen. It was predicted to have a triplet ($^{3}B_2$) ground state, just like TMM, but the lowest singlet state ($^{1}A_1$) is only 1−2 kcal/mol above the $^{3}B_2$ ground state.[127–129] In this study, the geometries of the ground-state and the lowest singlet state are optimized at the CASSCF(4,4)/6-31G(d) level. The ZPE correction from $^{3}B_2$ to $^{1}A_1$ calculated at the same level is 0.004 eV. Again, we are interested in the active space dependence of the calculated energy gaps, so two active spaces, (2,2) and (4,4) (four electrons in four π orbitals), are employed in our CAS-BCCC4 calculations. The 6-31G(d) basis set is used. As shown in Table 8, when the minimum active space is used, the gaps from CAS-BCCC4 and MR-CISD are almost identical to zero, implying the near-degeneracy of the $^{3}B_2$ and $^{1}A_1$ states. Nevertheless, with the active space (4,4), the adiabatic $^{3}B_2-^{1}A_1$ separation calculated with CAS-BCCC4 is 0.126 eV (2.90 kcal/mol), which is very consistent with the values from CASPT2 and MR-CISD methods. Thus, the previous assignment of the $^{3}B_2$ ground-state is confirmed.[127–129] The results obtained here for OXA and TMM indicate that the use of the minimum active space may be not sufficient for very accurate predictions of the singlet−triplet gaps in some diradicals.

4. Conclusions

In this paper, we have derived the spatial orbital formulations of the CAS-BCCC4 method for the CASSCF wave function with general active spaces and developed an efficient code for performing CAS-BCCC4 calculations. The CAS-BCCC4 approach has been applied to investigate the activation barriers for several isomerization reactions, spectroscopic constants in several multibond diatomic molecules, and the singlet−triplet energy gaps in two diradicals. Our calculations demonstrated that the CAS-BCCC4 method provides predictions very consistent with CASPT2 and MR-CISD methods for some systems, especially when the systems are relatively small. However, there are also significant discrepancies between the predictions from CAS-BCCC4 and those from CASPT2 or MR-CISD. For instance, the energy barriers for the automerization of cyclobutadiene predicted from CAS-BCCC4 and CASPT2 calculations differ by about 5.0 kcal/mol, and the barrier height from the reactant to **TS1** in the automerization of bicyclo[3.1.0]hex-2-ene from CAS-BCCC4 calculations is 1.56 kcal/mol higher than that from MR-CISD calculations.

It would be worthwhile mentioning some advantages and disadvantages of the CAS-BCCC4 method compared to the well-established CASPT2 and MR-CISD methods. The major advantage of the CAS-BCCC4 method over MR-CISD and CASPT2 methods is that more dynamic correlation could be recovered by the former approach, as indicated by the CAS-BCCC4 energies, which are usually lower than the corresponding CASPT2 or MR-CISD energies. As a result, the relative energies predicted from CAS-BCCC4 are expected to be somewhat more reliable than those from CASPT2 or MR-CISD. Our previous calculations[93] for small molecules have demonstrated this viewpoint. In comparison with CASPT2 and MR-CISD, the main disadvantage of CAS-BCCC4 is that the computational cost of the CAS-BCCC4 method is significantly higher than that of CASPT2 and the internally contracted MR-CISD, as the CAS-BCCC4 method shares the same scaling as the traditional CCSD (but with a prefactor increasing rapidly with the size of the active space). In addition, the CAS-BCCC4 method is not size-consistent (or not size-extensive), but its size-consistency (or size-extensivity) error only depends on the number of active orbitals. In some sense, this method shares the core-extensivity feature of similarity transformed equation-of-motion coupled cluster methods.[130–132] In this regard, CAS-BCCC4 is inferior to CASPT2, which is nearly size-consistent, but superior to MR-CISD, because the size-consistency error of the latter increases with the system size. Thus, for relatively large molecules, the CAS-BCCC4 and CASPT2 methods tend to give more reliable predictions than the MR-CISD method. In summary, the applications presented here show that the CAS-BCCC4 method could be a promising tool for electronic structure calculations of molecules with strong multireference characters.

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Supporting Information Available: Geometrical parameters for some molecules under study. This material is available free of charge via the Internet at http://pubs.acs.org.

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