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Spectroscopic Constants of Single-Bond Diatomic Molecules and Singlet−Triplet Gaps of Diradicals by the Block-Correlated Coupled Cluster Theory

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The spatial orbital formulations of block-correlated coupled cluster (BCCC) theory with a complete active-space self-consistent-field (CASSCF) reference function and its efficient implementation is presented. In the present implementation, the cluster operator is truncated to the four-block correlation level, and the CASSCF(2,2) reference function is assumed (thus, the method is abbreviated as CAS-BCCC4). We have applied this method to investigate the spectroscopic constants in seven single-bond diatomic molecules (LiH, HF, HCl, Li_2, F_2, ClF, and Cl_2) and the singlet−triplet gaps in a series of typical diradicals, including carbon, oxygen, and silicon atoms, methylene (CH_2) and its isovalent species (NH_2^+, SiH_2, and PH_2^+), and three benzyne isomers. A comparison of our results with the experimental data or other theoretical estimates shows that the present approach can provide quantitative descriptions for all of the studied systems.

1. Introduction

It is well-known that the Hartree−Fock (HF) determinant is not a good zero-order wave function for molecules in the presence of near degeneracy of some occupied with some virtual orbitals. This is because other determinants may be equally important as the HF determinant. For example, to describe the open-shell singlet states for molecules with stretched single bonds or diradicals, one should employ a complete active-space self-consistent-field (CASSCF) method to provide a qualitatively correct wave function, which can be expressed as follows:

$$|\Psi\rangle = c_1|(\text{core})^2(\text{valence})^2\phi_1\bar{\phi}_1\rangle + c_2|(\text{core})^2(\text{valence})^2\phi_2\bar{\phi}_2\rangle + c_3|(\text{core})^2(\text{valence})^2\phi_1\bar{\phi}_2\rangle + c_4|(\text{core})^2(\text{valence})^2\bar{\phi}_1\phi_2\rangle \quad (1)$$

Here, $(\text{core})^2$ and $(\text{valence})^2$ denote the doubly occupied core and valence orbitals, and (φ_1,φ_2) represents a pair of near-degenerate orbitals. Since the determinants in eq 1 are generated by distributing two electrons in two active orbitals, the resulting CASSCF(2,2) wave function is truly multiconfigurational. However, to achieve quantitative accuracy, the zeroth-order CASSCF(2,2) wave function must be augmented by dynamic correlation. A number of approaches that can incorporate dynamic correlation have been established, which include (1) multireference CI with single and double excitations (MR-CISD);[1] (2) multireference perturbation theory (MRPT), such as CASSCF with second-order perturbation corrections (CASPT2)[2,3] or multiconfigurational quasidegenerate perturbation theory;[4,5] and (3) multireference coupled cluster (MRCC) methods.[6–40] Among these approaches, the first two types are the most commonly used theoretical methods, while MRCC methods have not been established as practical tools for routine uses, although they are expected to provide more accurate results than those MRCI or MRPT methods with similar computational costs.

It should be mentioned that within the single reference coupled cluster (SRCC) framework, some effective approaches for treating the multireference character of the wave function have also been developed. These approaches include the reduced multireference CCSD,[41–47] the spin-flip method,[48–53] the valence active space optimized orbital CC approaches,[54–59] the method-of-moments CC and renormalized CC methods,[60–63] active-space CC approaches,[64–70] the tailored coupled cluster approach,[71] and so forth. The common feature of these CC approaches is to include higher excitations (in addition to single and double excitations) in the CC wave function through some approximate ways.

In our previous work, we developed the block-correlated coupled cluster (BCCC) approach,[72,73] which is an alternative MRCC approach. This BCCC approach is conceptually very similar to the traditional SRCC approach, except that the reference function and the corresponding cluster operator have different definitions in these two approaches. In BCCC, 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 give a satisfactory description for nondynamic correlation. The cluster operator is then introduced to evaluate dynamic correlation among blocks. Recently, we reported the formulation of CAS-BCCC4 (in spin orbital form),[74] in which a CASSCF(2,2) reference function is used and the cluster operator is truncated up to the four-block correlation level. This method was applied to study the ground-state dissociation potential energy surfaces (PESs) for single bond breaking in some small molecules (with small basis sets). Our test calculations have demonstrated that this approach can provide quite accurate results for all of the studied molecules, which are very close to the corresponding full CI results throughout the PESs.

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In this paper, we will derive the corresponding spatial orbital formulations of the CAS-BCCC4 theory and report an efficient implementation of this approach. The present implementation is able to allow CAS-BCCC4 calculations with the CASSCF(2,2) reference function to be computationally feasible for some medium-sized molecules with moderate basis sets or small molecules with quite large basis sets. We will apply this approach to compute spectroscopic constants in some single-bond diatomic molecules and the singlet−triplet gaps in a number of typical diradicals. By comparing the present results with the corresponding experimental data and other theoretical estimates (if available), the effectiveness and accuracy of this approach will be assessed.

2. Methodology

2.1. CAS-BCCC4 Approach. With the BCCC framework, the exact ground-state wave function is expressed as

$$\Psi_{\mathrm{BCCC}} = e^{T}\Phi_0 \tag{2}$$

where

$$e^T = 1 + T + \frac{T^2}{2!} + \frac{T^3}{3!} + \cdots = \sum_{k=0}^{\infty} \frac{T^k}{k!} \tag{3}$$

and the cluster operator T represents the sum of n-block correlation operators

$$T = T_1 + T_2 + T_3 + \cdots \tag{4}$$

For the ab initio Hamiltonian, each block is defined as a subset of spin orbitals, and all spin orbitals of the whole system are divided into disjoint blocks. In the CAS-BCCC4 approach, a multireference block **A** that contains M spatial orbitals is defined to describe nondynamic correlation, and each of the other blocks is defined to contain only one spin orbital. Correspondingly, the reference function of the whole system is formulated as

$$\Phi_0 = A_0^+ i^+ j^+ \cdots |0\rangle \tag{5}$$

Here, A_0^+ represents the creation operator for the reference state of block **A**, and i^+ stands for the creation operator in the ith-occupied spin orbital. Clearly, eq 5 is the second-quantized form of the CASSCF wave function.

As in SRCC methods, the cluster operator T must be truncated to a given n-block correlation level. Within BCCC, a reasonable approximation is $T \approx T_1 + T_2 + T_3 + T_4$, which defines the BCCC4 scheme. For the CASSCF(2,2) reference, the definition of up to four-block correlation operators has been given in previous work.[74] To make the following discussions more convenient, the expressions of one-block and two-block correlation operators are listed below

$$T_1 = \sum_{U}^{N_0} A_U^+ A_0^- t_1(U) \tag{6}$$

$$T_2 = T_{2\mathrm{A}} + T_{2\mathrm{B}} + T_{2\mathrm{C}} \tag{7}$$

$$T_{2\mathrm{A}} = \sum_{U}^{N_0-1} \sum_{a}^{\mathrm{vir}} A_U^+ A_0^- a^+ t_{2\mathrm{A}}(U,a) \tag{8}$$

$$T_{2\mathrm{B}} = \sum_{U}^{N_0+1} \sum_{i}^{\mathrm{occ}} A_U^+ A_0^- i^- t_{2\mathrm{B}}(U,i) \tag{9}$$

$$T_{2\mathrm{C}} = \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{vir}} a^+ i^- t_{2\mathrm{C}}(i,a) \tag{10}$$

Here, the capital letter U is used to represent the many-electron states of block **A** (the reference state is excluded), labels i, j, and k are used to denote occupied spin orbitals, and a, b, and c are for virtual spin orbitals. As discussed in previous work,[74] $T_{2\mathrm{C}}$ corresponds to the single excitation operators, describing the correlation among spin orbitals (called external exciations), while $T_{2\mathrm{A}}$ and $T_{2\mathrm{B}}$ describe the correlation between block **A** and all single-orbital blocks (called semi-internal excitations).

As in the traditional SRCC methods, we can project the Schrödinger equation onto Φ_0 and all excited configuration functions derived from n-block correlations ($n = 1-4$) to obtain a set of equations for determining the amplitudes occurring in eqs 6−10. Then, the resulting nonlinear equations can be solved iteratively to determine the amplitudes and the CAS-BCCC4 energy.

2.2. Implementation Details. Since the spin−orbital formulations of CAS-BCCC4 equations are very involved, we have developed a computer program to derive the corresponding spatial orbital expressions. In this formulation, all amplitudes and one-electron and two-electron integrals are defined with spatial MOs. Take $T_{2\mathrm{A}}$ as an example. Depending on the M_S value (the z-component of the total spin) of the electronic state U and the spin of the virtual spin orbital a, $T_{2\mathrm{A}}$ can be further decomposed into two parts, $\mathrm{T}_{2\mathrm{AR}}$ and $\mathrm{T}_{2\mathrm{AB}}$, as shown below

$$T_{2\mathrm{A}} = T_{2\mathrm{AR}} + T_{2\mathrm{AB}} \tag{11}$$

$$T_{2\mathrm{AR}} = \sum_{U}^{N_0-1,-1/2} \sum_{a(\alpha)} A_U^+ A_0^- a^+ t_{2\mathrm{AR}}(U,a) \tag{12}$$

$$T_{2\mathrm{AB}} = \sum_{U}^{N_0-1,1/2} \sum_{a(\beta)} A_U^+ A_0^- a^+ t_{2\mathrm{AB}}(U,a) \tag{13}$$

Assume that the reference state of block **A** has $M_\mathrm{S} = 0$, then $T_{2\mathrm{AR}}$ (or $T_{2\mathrm{AB}}$) corresponds to the case that a spin-up (or spin-down) electron transfers from block **A** to an unoccupied spin orbital (or single-orbital block). From the corresponding expression, say, eq 12, one can see that the electronic state U should have ($N_0 - 1$) electrons (N_0 is the number of electrons in the reference state of the block **A**), and $M_\mathrm{s} = -1/2$ so that the number of electrons and the M_S value in the excited configuration functions are the same as those in the CASSCF reference function. In similar ways, all other amplitudes can be redefined with spatial orbitals. With these definitions, the CAS-BCCC4 formulas can be readily transferred from the spin−orbital form to the spatial orbital form with our computer program. In the implementation, some intermediate arrays were introduced to reduce the computational scaling. For the present CAS-BCCC4, the most time-consuming step scales as N^6, with N being the total number of basis functions. In addition, two electron integrals are sorted, and the largest type involving four virtual orbitals is stored on the disk. Thus, with the present implementation, CAS-BCCC4 calculations are computationally feasible for medium-sized molecules with moderate basis sets.

3. Results and Discussions

In this section, the CAS-BCCC4 method is applied to compute the dissociation PESs of several single-bond diatomic molecules, and the singlet−triplet gaps in a series of diradicals. For each system, we first carry out a CASSCF(2,2) calculation with the Gaussian03 program[75] and then extract the orbitals from

TABLE 1: Exact Equilibrium Distances, Dissociation Energies, And Harmonic Vibrational Frequencies for the Ground State of Seven Diatomic Molecules and Deviations Using The CAS-BCCC4 Method with the 6-311G++(3df,3p) Basis Set

	R_e/Å		D_e/kcal/mol		ω_e/cm^{-1}	
molecule	exact[a]	CAS-BCCC4	exact[b]	CAS-BCCC4	exact[a]	CAS-BCCC4
LiH	1.596	−0.002	57.7	−0.8	1406	11
HF	0.917	−0.002	141.3	−4.8	4138	35
HCl	1.275	0.002	106.4	−2.4	2991	4
Li_2	2.673	−0.021	24.4	−0.2	351	4
F_2	1.412	0.006	38.2	−6.5	917	−52
ClF	1.628	0.007	60.2	−4.8	786	−23
Cl_2	1.988	0.013	58.0	−6.4	560	−24
MAE		0.008		3.7		22

[a] Refs 83 and 95a. [b] Refs 83 and 95b,c. Values are from the experimental atomization energies at 0 K, corrected by the zero-point energy calculated from the experimental spectroscopic constants.

TABLE 2: Total Energies (au) for the Ground State (^{3}P) and the ^{3}P−^{1}D Energy Gaps (Δ*E*) in Carbon, Oxygen, and Silicon Atoms

atom	basis set	^{3}P	Δ*E* (eV)	SF-OD[a]
C	cc-pVDZ	−37.761690	1.495	1.465
	cc-pVTZ	−37.789145	1.350	1.316
	cc-pVQZ	−37.816787	1.303	1.270
	aug-cc-pVQZ	−37.818108	1.290	
	expt.[b]		1.26	
O	cc-pVDZ	−74.912779	2.146	2.131
	cc-pVTZ	−74.984562	2.041	2.024
	cc-pVQZ	−75.024908	1.996	1.981
	aug-cc-pVQZ	−75.027380	1.989	
	expt.[b]		1.97	
Si	cc-pVDZ	−288.921358	1.014	
	cc-pVTZ	−289.001842	0.842	0.793
	cc-pVQZ	−289.050589	0.798	0.747
	aug-cc-pVQZ	−289.056832	0.788	
	expt.[b]		0.75	

[a] Ref 51. [b] Ref 96.

CASSCF calculations to generate all block states. Next, our program, linked to the GAMESS program,[76] is used to solve the CAS-BCCC4 equations. In this work, several different basis sets[77] are employed, in which 6 Cartesian d-like and 10 Cartesian f-like functions are always used. In addition, in CAS-BCCC4 calculations the inclusion of T_{2C} leads to significant computational costs but little gain in dynamic correlation energy; therefore, T_{2C} will be neglected in all calculations to save the computational time. The effect of this neglect will be mentioned later for some molecules with moderate basis sets. For one system, methylene, we also perform MR-CISD calculations based on the same CASSCF(2,2) reference function with the GAMESS program and compare MR-CISD energies with CAS-BCCC4 results.

3.1. Spectroscopic Constants in Single-Bond Diatomic Molecules. The dissociation PESs in diatomic molecules have been extensively studied with various theoretical methods.[27,30,35,46,47,50,83–94] Here, we will focus on the following single-bond diatomics, including LiH, HF, HCl, Li_2, F_2, ClF, and Cl_2. For these molecules, the CASSCF(2,2) reference function is sufficient for a qualitatively correct description for the whole dissociation curve. The basis set we use here is 6-311G++ (3df, 3p). For all of these molecules, the two orbitals in the active space are the bonding σ and antibonding σ^* orbitals. 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 around the equilibrium bond length 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 is shown in Table 1, the largest absolute errors with respect to the corresponding experimental values for R_e, ω_e, and D_e are, respectively, 0.021 Å, 52 cm^{-1}, and 6.5kcal/mol, and the mean absolute errors are only 0.008 Å, 22 cm^{-1}, and 3.7 kcal/mol.

It is worthwhile to investigate the effect of the size-consistency error inherent in the CAS-BCCC4 approach on the calculated dissociation energies. We take F_2 as an example to analyze the effect. In the dissociation limit (the F−F distance is 100 bohrs), the CAS-BCCC4 energy is −199.314390 au for F_2, while for a separated F atom, the corresponding CAS-BCCC4 energy is −99.656502 au (the computational details were discussed previously[74]). Thus, the size-consistency error for the CAS-BCCC4 method is only 1.38 millihartrees (or 0.87 kcal/mol). Therefore, the size-consistency error does not make major contributions to the deviation between the calculated dissociation energy and the experimental value. In addition, for F_2, we also investigate how the inclusion of T_{2C} affects the calculated dissociation energy. With the basis set 6-311G+(d), we find that the inclusion of T_{2C} only changes the calculated dissociation energy by 0.02 kcal/mol. This result indicates that the neglect of T_{2C} is a reasonable approximation for CAS-BCCC4 calculations.

3.2. Singlet−Triplet Gaps in Diradicals. ***3.2.1. Carbon, Oxygen, and Silicon Atoms.*** These three atoms represent the simplest diradicals, in which the calculated singlet−triplet (ST) gaps can be directly compared with the experimental ST gaps without ambiguity due to the absence of zero-point energies (ZPE). For these atoms, the ground state is a triplet ^{3}P state, and the lowest singlet state is a ^{1}D state. For both the triplet and singlet states, the CASSCF(2,2) reference function (M_S = 0) is used for the subsequent CAS-BCCC4 calculations in order to describe both states in a balanced way. To investigate the basis set dependence on the calculated ST gaps, we employ a series of correlation-consistent basis sets, cc-pVDZ, cc-pVTZ, cc-pVQZ, and aug-cc-pVQZ.[81,82] Our results, together with theoretical estimates from the SF-OD method[51] (the spin-flip variant of EOM optimized orbital coupled cluster doubles), are collected in Table 2 for comparison. One can see that, when the basis set increases, the calculated gaps decrease monotonously toward the experimental values for all three atoms. In the largest basis set used, aug-cc-pVQZ, the CAS-BCCC4 results are within 0.04 eV of the experimental values. The performance of the CAS-BCCC4 method is competitive with that of the SF-OD approach (both approaches have similar computational scaling).

3.2.2. Methylene and Other Isovalent Molecules. Methylene (CH_2) and its isovalent species, NH_2^+, SiH_2, and PH_2^+, have been studied by various experimental[97–102]and theoretical approaches.[51,103–112] Here, we will focus on the lowest singlet and triplet states (and their adiabatic energy gaps) of these four diradicals. For CH_2 and NH_2^+, two near-degenerate orbitals are $3a_1$ and $1b_1$. The ground state of these two species is the triplet $\tilde{X}^3B^1$, and the first excited state is a closed-shell singlet $\tilde{a}^1A_1$ state (only two doubly occupied configurations contribute in eq 1). However, for SiH_2 and PH_2^+, two near-degenerate orbitals are $5a_1$ and $2b_1$, and they have a closed-shell singlet $\tilde{X}^1A_1$ as the ground state, and the triplet $\tilde{a}^3B_1$ as the first excited state. For CH_2, its equilibrium structures in both states are taken as

TABLE 3: Total Energies (au) for the Ground State of CH_2 and Adiabatic Excitation Energies (eV) to the Lowest Excited State[a]

	CAS-BCCC4		MR-CISD		SF-OD[b]	
basis set	$\tilde{X}^3B_1$	$\tilde{a}^1A_1$	$\tilde{X}^3B_1$	$\tilde{a}^1A_1$	$\tilde{X}^3B_1$	$\tilde{a}^1A_1$
DZP	−39.058838	0.544	−39.057006	0.562		
TZ2P[c]	−39.080236	0.482	−39.078244	0.501	−39.08045	0.514
TZ2P(f,d)	−39.094220	0.441	−39.091959	0.462	−39.09229	0.480
TZ2P(f,d)+diff	−39.094350	0.437	−39.092086	0.459	−39.09253	0.474
TZ3P	−39.082202	0.460	−39.080189	0.480		
TZ3P(2f,2d)	−39.104304	0.414	−39.101776	0.436	−39.09613	0.454
TZ3P(2f,2d)+2diff	−39.104602	0.413	−39.102067	0.435		
cc-pVDZ	−39.042527	0.493	−39.041213	0.509	−39.04117	0.524
cc-pVTZ	−39.088945	0.441	−39.086895	0.462	−39.08793	0.483
cc-pVQZ	−39.119181	0.398	−39.116103	0.421	−39.11097	0.451
ept.[d]		0.390				

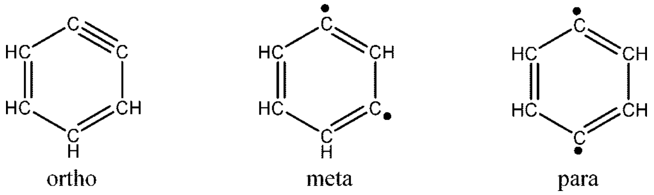
[a] The experimental value (T_0) corresponds to the energy difference between the lowest vibrational states of both electronic states. [b] From ref 51. [c] The $^3B_1-^1A_1$ gap from the frozen-core FCI calculation is 0.483 eV, from ref 111. [d] From ref 97.

TABLE 4: Total Engies (au) for the Ground State of NH_2^+, SiH_2, and PH_2^+ and Adiabatic Excitation Energies (eV) to the Lowest Excited State[a]

		CAS-BCCC4		SF-OD[b]	
molecules	basis set	$\tilde{X}^3B_1$	$\tilde{a}^1A_1$	$\tilde{X}^3B_1$	$\tilde{a}^1A_1$
NH_2^+	TZ2P	−55.388850	1.324		
	TZ2P(f,d)	−55.404331	1.277	−55.40259	1.305
	TZ3P(2f,2d)+2diff	−55.417194	1.259		
	expt.[c]		1.306 ± 0.010		
molecules	basis set	$\tilde{X}^1A_1$	$\tilde{a}^3B_1$	$\tilde{X}^1A_1$	$\tilde{a}^3B_1$
SiH_2	TZ2P	−290.288555	0.875		
	TZ2P(f,d)	−290.302002	0.904	−290.29961	0.866
	TZ3P(2f,2d)+2diff	−290.349927	0.920		
	expt.[d]		0.91 ± 0.03		
PH_2^+	TZ2P	−341.809221	0.768		
	TZ2P(f,d)	−341.828876	0.804	−341.74916	0.761
	TZ3P(2f,2d)+2diff	−341.878345	0.818		
	expt.[e]		0.75 ± 0.05		

[a] The experimental value (T_0) corresponds to the energy difference between the lowest vibrational states of both electronic states. [b] Ref 51. [c] Ref 98. [d] Ref 99. [e] Ref 100.

SCHEME 1: Three Isomers of Benzyne



the corresponding FCI/TZ2P-optimized geometries[111] in CAS-BCCC4 calculations. For the other three species, their equilibrium structures in both states are taken as the optimized geometries at the CISD/TZ2P(f,d) level.[104–106] With several basis sets, the calculated CAS-BCCC4 energies for the lowest singlet and triplet states are collected in Tables 3 and 4. It can be seen that the polarization functions are more important than the diffuse functions in determining the ST gaps. Let us take CH_2 as an example to illustrate this point. For this molecule, the ST gap differs by 0.042 eV from TZ3P to TZ3P(2f,2d), but by only 0.01 eV from TZ3P(2f,2d) to TZ3P(2f,2d)+2diff. With the TZ2P basis set, our calculations also show that the inclusion of T_{2C} changes the CAS-BCCC4 gap by 0.004 eV for CH_2. Thus, the neglect of T_{2C} has a minor impact on the calculated ST gaps.

In Table 3, we also list the corresponding MR-CISD results and SF-OD values for CH_2. With the same (2, 2) CAS reference function, one can see that CAS-BCCC4 energies are always lower than MR-CISD values, as expected. For each basis set, the calculated ST gaps are in the order of SF-OD > MR-CISD > CAS-BCCC4. It should be mentioned that the ST gap from the FCI calculation (one core orbital and one virtual orbital are frozen) at the TZ2P basis set, 0.483 eV, could be used for comparison. Clearly, the CAS-BCCC4 result is closer to this value than the corresponding MR-CISD or SF-OD result. The same trend is expected to hold true for other basis sets.

For other diradicals, the results in Table 4 show that the CAS-BCCC4 energies are quite close to the corresponding SF-OD energies (except for PH_2^+). The overall agreement between the ST gaps calculated by the CAS-BCCC4 and SF-OD methods is quite good. However, for PH_2^+, the CAS-BCCC4 energy (−341.828876 au) is very close to the corresponding CCSD energy but considerably different from the SF-OD value.

When comparing the calculated adiabatic ST gaps (T_e) with the experimental values, we should notice that the experimental value (T_o) corresponds to the energy difference between the lowest vibrational states of both electronic states. Thus, the experimental ST gaps are the sum of T_e and the ZPE difference (ΔZPE) from the ground state to the first excited state. Using frequencies estimated with the same method as that for the geometry optimizations,[104–106,111] ΔZPE was estimated to be −0.021, 0.021, 0.012, and −0.006 eV, respectively, for CH_2, NH_2^+, SiH_2, and PH_2^+. After including the ZPE corrections, the CAS-BCCC4 ST gaps calculated with the largest basis set (cc-pVQZ for CH_2 and TZ3P(2f,2d)+2diff for others) deviate

TABLE 5: Total Ground-State Energies (au) and Adiabatic Excitation Energies (kal/mol) to the Lowest Triplet State for *Ortho*-, *Meta*-, and *Para*-benzynes

species	method	$^1A_1$ (or ^1A_g)[a]	$^3B_2$ (or $^3B_{1u}$)[a]	MkCCSD[b]	expt.[c]
o-benzyne	CASSCF	−229.451324	27.8	35.1	37.5 ± 0.3
	CAS-BCCC4	−230.248055	33.8		
m-benzyne	CASSCF	−229.430066	11.3	18.7	21.0 ± 0.3
	CAS-BCCC4	−230.226738	17.3		
p-benzyne	CASSCF	−229.415618	0.7	4.5	3.8 ± 0.4
	CAS-BCCC4	−230.206265	3.0		

[a] ^1A_g and $^3B_{1u}$ for *p*-benzyne. [b] Ref 117. The 1s orbitals of the carbons are frozen in MkCCSD calculations. [c] Ref 118.

from the experimental data by only 0.013, 0.026, 0.022, and 0.062 eV, respectively. It should be mentioned that the available experimental data are not very accurate for PH_2^+.[51,100] Thus, the overall agreement between the CAS-BCCC4 gaps and the experimental data is very encouraging.

3.2.3. *Benzyne Isomers.* *Ortho*-, *meta*-, and *para*-benzynes (scheme 1) are classical compounds with various diradical characters.[113] Theoretical studies[114–117] have revealed that the ground state of three benzyne isomers is a closed-shell singlet state, and the lowest excited state is a triplet state. In both states, the optimized geometries were determined to be of C_{2v} symmetry for *o*- and *m*-benzyne but of D_{2h} symmetry for *p*-benzyne. Experimentally, the ST gaps for *o*-, *m*-, and *p*-benzyne were found to decrease in the order[118] ortho (37.5 kcal/mol) > meta (21.0 kcal/mol) > para (3.8 kcal/mol).

In our calculations, we have adopted the optimized geometries for all three isomers obtained previously,[117] whose geometrical parameters are provided in the Supporting Information. The same basis set cc-pVDZ (as that used in the corresponding geometry optimizations) is employed here. For *o*-, *m*-, and *p*-benzyne, the active orbitals in CAS-BCCC4 calculations are ($10a_1$ and $8b_2$), ($11a_1$ and $7b_2$), and ($5b_{1u}$ and $6a_g$), respectively. As shown in Table 5, the ST gaps calculated from the CAS-BCCC4 method are in good agreement with previous MkCCSD estimates for all three isomers.[117] Using the ZPE corrections obtained previously at the CCSD level,[117] which are −0.3, 0.7, and 0.3 kal/mol, respectively, the ZPE-corrected adiabatic ST gaps (T_o) are estimated from the present method to be 33.5, 18.0, and 3.3 kal/mol for *o*-, *m*-, and *p*-benzynes, which agree reasonably with the corresponding experimental data. Nevertheless, the use of larger basis sets (or the inclusion of triple excitations) is still required to provide more definitive ST gaps.

4. Conclusions

In this paper, we have developed the spatial orbital formulations of the CAS-BCCC4 method and presented an efficient implementation of this approach. The present implementation is able to extend the applications of the CAS-BCCC4 method to small molecules with quite large basis sets or medium-sized molecules with moderate basis sets. We have applied this method to study the ground-state dissociation curves of several single-bond diatomic molecules and the singlet−triplet gaps in a series of typical diradicals, including carbon, oxygen, and silicon atoms, methylene (CH_2) and its isovalent species, NH_2^+, SiH_2, and PH_2^+, and three benzyne isomers. For seven single-bond diatomic molecules, the mean average errors (with respect to the experimental data) of the calculated equilibrium bond distances, harmonic frequencies, and dissociation energies are about 0.008 Å, 22 cm^{-1}, and 3.7 kcal/mol, respectively. For various diradicals, their singlet−triplet gaps calculated by the present CAS-BCCC4 method are in excellent agreement with the available experimental data and other theoretical estimates.

It is worthwhile making some comparisons between the CAS-BCCC4 and MR-CISD methods. For CH_2, we have shown that the CAS-BCCC4 method could predict more accurate ground-state energies and the singlet−triplet gap than the MR-CISD method, provided that the same CASSCF reference function is used. As addressed earlier in this paper, the computational cost of the CAS-BCCC4 method scales as the sixth power of the total number of basis functions, being similar to the traditional MR-CISD method. However, when a small active space such as CASSCF(2,2) is used, the amplitudes in CAS-BCCC4 calculations are significantly less than those in the corresponding MR-CISD calculations; therefore, the CAS-BCCC4 method has a relatively smaller prefactor than that of the MR-CISD method. For example, the CAS-BCCC4 calculation for the ground state of CH_2 at the cc-pVQZ basis set costs about one hour, but the corresponding MR-CISD calculation (with the GAMESS program) requires about five hours, both on a single-node Xeon 2.66 GHz workstation. However, the amplitudes in the CAS-BCCC4 calculation increase quickly with enlarging of the active space; thus, for relatively large active spaces such as CASSCF(8,8), the computational cost of the CAS-BCCC4 method may be comparable to (or even longer than) that of the MR-CISD method. To conclude, the present study shows that the CAS-BCCC4 method is a promising theoretical tool for calculating the electronic structures of molecules with strong multireference characters. Our future work is to further optimize the code to develop a production-level CAS-BCCC program and to develop the algorithms for analytic energy gradients in the CAS-BCCC4 method. These developments will be essential for wide applications of the CAS-BCCC approach to real chemical problems with 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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