

# On the ground states of CaC and ZnC: A multireference Brillouin–Wigner coupled cluster study

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We test the recently developed state-specific multireference Brillouin–Wigner coupled cluster (MRBWCCSD) method against the single reference CCSD method by examining theoretically the competing  $X^3\Sigma^-$  and  $^5\Sigma^-$  states of the (experimentally unknown) isovalent calcium and zinc carbide diatomics (CaC, ZnC). At the CCSD level, CaC is “incorrectly” predicted to have a ground  $^5\Sigma^-$  state; however, the MRBWCCSD treatment restores the correct state ordering, and improves significantly the energetics for both molecules. Further comparison with various single- and multireference treatments shows that the latter are absolutely necessary for obtaining meaningful results for the ground states in both molecules. © 2002 American Institute of Physics. [DOI: 10.1063/1.1516809]

## I. INTRODUCTION

Since our recent development of a state-specific (single-root) multireference coupled cluster method based on the Brillouin–Wigner resolvent (MRBWCCSD),<sup>1–6</sup> we have been performing a series of tests by applying this method to a number of chemical problems of multireference nature, in order to assess its capability of providing quantitative results with less computational cost than other MRCC methods. So far, applications have included the geometrical and electronic structure of the ozone molecule,<sup>5</sup> the singlet O<sub>2</sub> system,<sup>6</sup> the automerization of cyclobutadiene,<sup>7</sup> the potential energy curves of the dihalogens F<sub>2</sub><sup>8</sup> and IBr,<sup>9</sup> and the singlet–triplet splittings of CH<sub>2</sub>,<sup>5</sup> SiH<sub>2</sub>,<sup>5</sup> twisted ethylene,<sup>5</sup> and the tetramethyleneethane biradical.<sup>10</sup> In the present paper, we continue applying the MRBWCCSD method to a different case of multireference nature caused by “near-degeneracy” effects.

Such effects are expected to be observed in the cases of the closed-shell ( $ns^2$ ) atoms of the 2nd (alkaline-earth metal) and 12th columns of the periodic table due to the near-degeneracy of their  $ns$  and  $np$  orbitals. For the alkaline-earth metal carbide diatomics, the lack of proper account of this effect, together with the complete nonavailability of experimental data has led to some controversy in the past regarding the identity of their ground states.<sup>11–14</sup> BeC and MgC<sup>11,12</sup> have now been established theoretically to have a  $^3\Sigma^-$  ground state with a  $^5\Sigma^-$  state lying closely above,<sup>12</sup> but for

CaC the situation had been less clear. Early theoretical calculations by Canuto *et al.*<sup>13</sup> using the fourth-order many-body perturbation theory [MBPT(4)] postulated a ground state of  $^3\Sigma^-$  symmetry, originating from the Ca( $^1S$ ) + C( $^3P; M_L=0$ ) atomic fragments. A few years later, Da Silva *et al.* pointed out the existence of a low-lying  $^5\Sigma^-$  state, which actually stems from the Ca( $^3P$ ) + C( $^3P$ ) channel (*vide infra*), but was incorrectly considered to originate from the Ca( $^1S$ ) + C( $^5S$ ) fragments.<sup>12</sup> Apparently, due to a poor GVB description and a moderate-sized basis set, this state was claimed to be the ground state of the CaC molecule at the configuration interaction generalized valence bond (SDCI-GVB+Q) level of theory, with the  $^3\Sigma^-$  state lying 2.6 kcal/mol above.<sup>12</sup> A year later, Serrano and Canuto<sup>14</sup> revisited the ground-state problem of CaC by calculating the triplet–quintet splitting with different size-extensive single-reference methods including second and fourth-order MBPT, as well as spin-unrestricted coupled cluster without (UCCSD) and with [UCCSD(T)] the inclusion of the triple excitations in a perturbative way. Although at the MBPT and UCCSD levels of theory, the  $^5\Sigma^-$  was found to be the ground state, the ordering of the two states was reversed after including the triple excitations, predicting finally a  $^3\Sigma^-$  ground state, with the  $^5\Sigma^-$  lying 2.4 kcal/mol above.<sup>14</sup> Very recently, Papakondylis and Mavridis<sup>15</sup> have performed quantitative multireference configuration interaction (MRCI) calculations for the ground and several low-lying states of CaC; the  $^3\Sigma^-$  symmetry of the ground state was indeed confirmed,

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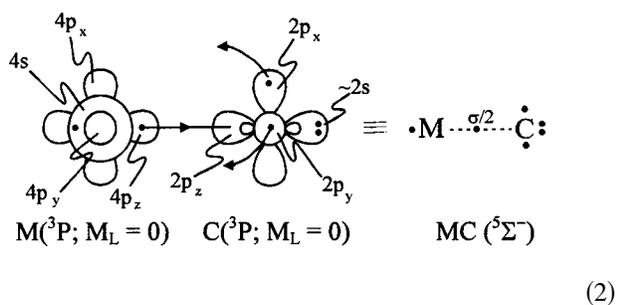
with the  $^5\Sigma^-$  state located at least 4.2 kcal/mol above the  $X^3\Sigma^-$  state.<sup>15</sup>

The situation is less dramatic for the isovalent ZnC molecule. Boldyrev and Simons<sup>16</sup> after investigating 4 states of ZnC at the quadratic configuration interaction, QCISD(T) level of theory reported a  $X^3\Sigma^-$  state, with the  $^5\Sigma^-$  state lying now much higher ( $T_e=23.9$  kcal/mol) than in CaC, apparently due to the much higher atomic  $^3P(4s^14p^1) \leftarrow ^1S(4s^2)$  energy separation in Zn (4.054 eV) than in Ca (1.892 eV).<sup>17</sup> Our very recent large calculations for the ground and several excited states of ZnC at the MRCI level<sup>18</sup> have confirmed these results. As will be shown later, the  $^5\Sigma^- \leftarrow X^3\Sigma^-$  gap is also underestimated (but not reversed in this case) in ZnC with various single reference methods. Similarly to CaC, we are also not aware of any published experimental data for ZnC.

The reason for the aforementioned difficulties in predicting correctly the  $^5\Sigma^- \leftarrow ^3\Sigma^-$  energy difference, lies apparently in the multireference nature of the  $X^3\Sigma^-$  state contrasted to the, in essence, purely single reference nature of the high-spin  $^5\Sigma^-$  state. As mentioned before, the latter traces its lineage to the  $M(^3P; M_L=0) + C(^3P; M_L=0)$  components ( $M=\text{Ca, Zn}$ ) and is adequately described by the configuration

$$|^5\Sigma^-\rangle \sim |1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^1\rangle, \quad (1)$$

where the numbers in front of the molecular orbitals (MOs) refer to the ordering within the valence space of each molecule. A qualitative view of the bonding can be captured by the following valence-bond-Lewis (vbL) icon

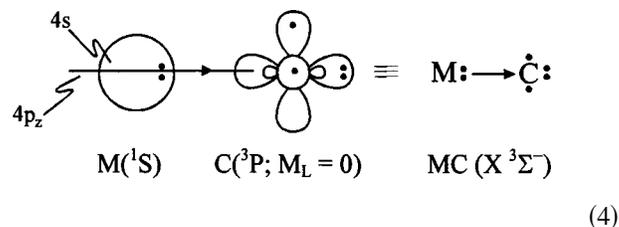


indicating that the M(Ca-Zn) and C atoms are “formally” kept together by three “half” (one-electron) bonds, although our Mulliken population analysis<sup>15,18</sup> has shown that charge transfer along the  $\pi$  frame is almost negligible. The configuration (1) is found to dominate the full-valence (fv) complete active space (CASSCF) wave function(s) of CaC and ZnC with a coefficient of 0.98 in both cases,<sup>15,18</sup> testifying to the single-reference nature of this state.

For the ground  $X^3\Sigma^-$  state however, emanating from the  $M(^1S) + C(^3P; M_L=0)$  channel, the full-valence CASSCF wave function is composed by six significantly contributing determinants

$$\begin{aligned}
 |X^3\Sigma^-\rangle \sim & C_0 |1\sigma^2 2\sigma^2 1\pi_x^1 1\pi_y^1\rangle + C_1 |1\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^1\rangle \\
 & + C_2 |1\sigma^2 \overline{1\sigma^2} 3\sigma^1 1\pi_x^1 1\pi_y^1 + 2\sigma^1 \overline{3\sigma^1} 1\pi_x^1 1\pi_y^1 \\
 & + 2\sigma^1 3\sigma^1 \overline{1\pi_x^1} 1\pi_y^1 + 2\sigma^1 3\sigma^1 1\pi_x^1 \overline{1\pi_y^1}\rangle. \quad (3)
 \end{aligned}$$

At the equilibrium M-C distance(s), the coefficients  $C_0, C_1, C_2$  are found to be 0.71, -0.48, 0.26 for CaC, and 0.87, -0.36, 0.17 for ZnC, while at infinity  $C_2=0$ , and the  $2\sigma$  and  $3\sigma$  MOs correspond to the  $4s$  and  $4p_z$  atomic orbitals of  $M(=\text{Ca-Zn})$ . The qualitative features of the bonding can be depicted through the vbL icon.



The  $X^3\Sigma^-$  state owes its multireference character mainly to the doubly excited ( $2\sigma^2 \rightarrow 3\sigma^2$ ) determinant  $|1\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^1\rangle$  with coefficient  $C_1$  [Eq. (3)], or in other words to the “near degeneracy” of the  $4s$  and  $4p(4p_z)$  orbitals of the M atom. Apparently, this can explain why almost all single reference theoretical treatments which do not account for nondynamical correlation (including CCSD) fail to describe the  $X^3\Sigma^-$  state quantitatively, thus underestimating (or even reversing) the  $^5\Sigma^- \leftarrow X^3\Sigma^-$  energy gap (see below).

Our primary aim in this work is not to predict the ground states of the two molecules, as we believe this to be an already resolved issue.<sup>15,18</sup> The motivation is rather to test the capability of the MRBWCCSD method to account for the nondynamical correlation effects and, hopefully, improve the single reference CCSD treatment which fails to predict the  $^3\Sigma^-, ^5\Sigma^-$  ordering for CaC and an accurate  $^5\Sigma^- \leftarrow X^3\Sigma^-$  energy separation for ZnC. To ensure their overall credibility, the MRBWCCSD results were monitored against comparable MRCI results.

## II. THEORY AND COMPUTATIONAL DETAILS

For both molecules, we have calculated the full potential energy curves of the  $X^3\Sigma^-$  and  $^5\Sigma^-$  states employing a variety of methods, including MRBWCCSD. We report dissociation energies ( $D_e$ ), spectroscopic constants ( $r_e, \omega_e, \omega_e x_e$ ), and the important  $^5\Sigma^- \leftarrow ^3\Sigma^-$  energy splitting.

The reference space was optimized by distributing 4 electrons (the 2 valence  $e^-$  of M and the  $2 p_\pi e^-$  of C) in 4 orbitals ( $2\sigma, 3\sigma, 1\pi_x, 1\pi_y$ ) using the CASSCF methodology. This calculation will subsequently be denoted as CASSCF(4,4). A full-valence CASSCF calculation, where all 6 valence electrons are distributed in the 8 valence orbitals corresponding asymptotically to the  $4s+4p$  and  $2s+2p$  valence orbital spaces of  $M(=\text{Ca,Zn})$  and C, respectively, was also performed and will be denoted either as CASSCF(6,8) or as fvCASSCF.

For technical reasons, instead of Eq. (3), we have used a slightly modified reference wave function for the subsequent BWCCSD calculations keeping the two  $\pi$  electrons triplet coupled while always utilizing the CASSCF(4,4) optimized active space. Thus, our model (projected) reference wave

TABLE I. Atomic energies  $E$  (hartree) for the ground states of Zn ( $^1S$ ), Ca ( $^1S$ ), and C ( $^3P$ ) and singlet–triplet ( $^3P \leftarrow ^1S$ ) separations (eV) for Zn and Ca at different levels of theory.

Method	$E$			$^3P \leftarrow ^1S$	
	Ca ( $^1S$ )	Zn ( $^1S$ )	C ( $^3P$ )	Ca	Zn
NHF <sup>a</sup>	−676.758 186	−1777.848 12	−37.688 619		
saSCF <sup>b</sup>	−676.758 159	−1777.847 31	−37.688 330	1.076	2.644
CISD	−676.787 051	−1777.881 35	−37.784 099	1.685	3.420
CISD+Q <sup>c</sup>			−37.7893		
ACPF <sup>d</sup>			−37.785 795		
RCCSD <sup>e</sup>	−676.787 051	−1777.881 35	−37.784 586	1.685	3.420
RCCSD(T) <sup>f</sup>			−37.787 154		
BWCCSD <sup>g</sup>			−37.784 770		
CASSCF(2,2) <sup>h</sup>	−676.769 741	−1777.860 49		1.320	2.949
MRCI <sup>i</sup>	−676.787 043	−1777.879 48		1.681	3.359
MRBWCCSD <sup>j</sup>	−676.785 861	−1777.878 34		1.649	3.327
fvCASSCF <sup>k</sup>	−676.785 025	−1777.878 77	−37.705 690	1.807	3.500
fvMRCI	−676.787 053	−1777.881 35	−37.785 706	1.685	3.420
fvMRCI+Q			−37.7887		
fvMRACPF			−37.787 234		
C-RCCSD <sup>l</sup>	−676.988 525	−1778.349 80		1.794	3.734
C-RCCSD(T) <sup>l</sup>	−676.993 222	−1778.369 18		1.842	3.849
C-MRCI <sup>l</sup>	−676.981 767	−1778.322 00		1.864	3.556
C-MRCI+Q <sup>l</sup>	−676.993 3490	−1778.349 4		1.857	3.717
C-MRBWCCSD <sup>l</sup>	−676.988 055	−1778.349 58		1.779	3.727
Expt. <sup>m</sup>				1.892	4.054

<sup>a</sup>Numerical Hartree–Fock (Ref. 28).<sup>b</sup>Spherically averaged SCF.<sup>c</sup>CISD+Davidson correction.<sup>d</sup>Averaged coupled-pair functional.<sup>e</sup>Restricted coupled cluster singles and doubles.<sup>f</sup>RCCSD+perturbative triples.<sup>g</sup>Brillouin–Wigner CCSD.<sup>h</sup>Complete active space SCF; active space:  $4s+4p_z$ .<sup>i</sup>CASSCF+1+2.<sup>j</sup>Four-reference BWCCSD.<sup>k</sup>Full-valence CASSCF; active space:  $4s+4p_{x,y,z}$  for Ca and Zn, and  $2s+2p_{x,y,z}$  for C.<sup>l</sup>The  $3s^23p^6$  and  $3d^{10}$  electrons of Ca and Zn, respectively, were included in the correlation treatment.<sup>m</sup>Experimental data (Ref. 17).

function for the  $X^3\Sigma^-$  state(s) of CaC and ZnC,  $\Psi_0^P$ , is a linear combination of the first four determinants of Eq. (3)

$$\Psi_0^P = \sum_{i=0}^3 C_i \Phi_i. \quad (5)$$

This wave function is related to the “exact” ground-state wave function  $\Psi_0$  by means of the wave operator  $\hat{\Omega}_0$

$$\Psi_0 = \hat{\Omega}_0 \Psi_0^P, \quad (6)$$

and to the exact ground-state energy  $\mathcal{E}_0$  by means of the effective Hamiltonian,  $\hat{H}^{\text{eff}}$

$$\hat{H}^{\text{eff}} \Psi_0^P = \mathcal{E}_0 \Psi_0^P. \quad (7)$$

The wave operator  $\hat{\Omega}_0$  is subject to the state-specific (single-root) Brillouin–Wigner analogue of the Bloch equation

$$\hat{\Omega}_0 = 1 + \hat{B}_0 \hat{V} \hat{\Omega}_0, \quad (8)$$

where  $\hat{V}$  is the perturbation operator within the Møller–Plesset *ansatz*, and  $\hat{B}_0$  the Brillouin–Wigner resolvent

$$\hat{B}_0 = \sum_{q>3} \frac{|\Phi_q\rangle\langle\Phi_q|}{\mathcal{E}_0 - E_q}. \quad (9)$$

The matrix elements of  $\hat{H}^{\text{eff}}$  in a basis of 4 references  $\{\Phi_{ij}\}_{i=0}^3$ , have been given previously.<sup>3,6</sup> The MRBWCCSD energy  $\mathcal{E}_0$  is obtained by diagonalization of the  $4 \times 4$   $\mathbf{H}^{\text{eff}}$  matrix. The resulting size-extensivity error is practically eliminated by applying the recently developed *a posteriori* size-extensivity correction.<sup>4,5</sup>

For both CASSCF(4,4) and (6,8) reference spaces, we have also performed calculations at the MRCI, MRCI+Q (MRCI+multipreference Davidson correction), and MRACPF (multipreference averaged coupled-pair functional) levels of theory. Furthermore, our MRBWCCSD results are also compared against single reference methods like ROHF (restricted open-shell Hartree–Fock), CISD, CISD+Q, ROHF-RCCSD<sup>19</sup> and ROHF-RCCSD(T).<sup>19</sup> In most of our correlated calculations, we have kept “frozen” the  $1s^22s^22p^63s^23p^6$ ,  $1s^22s^22p^63s^23p^63d^{10}$ , and  $1s^2$  electrons of Ca, Zn, and C, respectively. To assess the effect of core/valence correlation, calculations were also performed

TABLE II. Total energies  $E$  (hartree), binding energies  $D_e$  (kcal/mol), bond lengths  $r_e$  (Å) and frequencies  $\omega_e$ ,  $\omega_e x_e$  ( $\text{cm}^{-1}$ ) of the CaC  $X^3\Sigma^-$  and  $5\Sigma^-$  states at different levels of theory. Unless otherwise noted, all results are from the present work.

Method <sup>a</sup>	$X^3\Sigma^-$					$5\Sigma^-$					
	$E$	$D_e$	$r_e$	$\omega_e$	$\omega_e x_e$	$E$	$D_e$	$r_e$	$\omega_e$	$\omega_e x_e$	$T_e$
ROHF	-714.448 459	1.2	2.838			-714.524 469	72.1	2.332	490.2	2.5	-47.6
CISD	-714.611 729	30.0	2.361	451.1	4.3	-714.640 049	82.9	2.339	480.2	2.5	-17.8
CISD+Q	-714.654 2	49.0	2.357	533.4	3.1	-714.647 2	83.6	2.343	476.4	2.5	4.4
RCCSD	-714.628 183	35.5	2.368	464.0	3.7	-714.642 142	83.0	2.340	479.2	2.5	-8.8
RCCSD(T)	-714.647 670	46.1	2.383	464.2	2.4	-714.647 113	84.5	2.343	475.6	2.5	0.3
CASSCF(4,4)	-714.526 978	43.2	2.351	480.0	2.6						3.3
MRCI	-714.644 174	49.0	2.362	468.9	2.6						2.6
MRCI+Q	-714.651 7	48.0	2.366	464.2	2.7						2.8
MRACPF	-714.649 391	48.0	2.365	465.1	2.6	-714.644 982	83.3	2.342	476.9	2.5	2.8
MRBWCCSD	-714.643 528	45.8	2.357	468.3	2.1	-714.642 595	83.2	2.339	479.3	2.9	0.6
fvCASSCF	-714.562 811	44.0	2.380	458.7	2.4	-714.559 266	81.8	2.360	469.9	2.3	2.2
fvmRCI	-714.649 964	48.6	2.364	462.4	2.4	-714.645 3	85.0	2.341	473.7	2.5	2.9
fvmRCI+Q	-714.6541	49.3	2.364	461.3	2.5	-714.649 340	85.2	2.340	473.0	2.5	3.0
fvmRACPF	-714.652 876	49.1	2.364	461.5	2.5	-714.648 130	85.1	2.340	473.2	2.4	3.0
SDCI-GVB <sup>b</sup>	-714.5899		2.384			-714.5950		2.357			-3.2
SDCI-GVB+Q <sup>b</sup>	-714.5949		2.389	424.87		-714.5990		2.359	474.06		-2.6
MRCI <sup>c</sup>	-714.652 46	51.1	2.363	458.5		-714.645 71	86.2	2.346	472.2		4.2
RCCSD( $14e^-$ )	-714.828 69	34.9	2.330			-714.844 64	86.2	2.291			-10.0
RCCSD(T)( $14e^-$ )	-714.852 75	45.4	2.330			-714.853 31	88.2	2.287			-0.4
MRBWCCSD( $14e^-$ )	-714.846 55	46.3	2.305			-714.845 06	86.3	2.291			0.9
MBPT(4)( $14e^-$ ) <sup>d</sup>	-714.798 152		2.306			-714.812 452		2.325			-9.0
UCCSD( $14e^-$ ) <sup>d</sup>	-714.805 325		2.335			-714.807 152		2.326			-1.1
UCCSD(T)( $14e^-$ ) <sup>d</sup>	-714.818 225		2.348			-714.814 471		2.325			2.4
MRCI( $14e^-$ ) <sup>e</sup>	-714.823 35	45.9	2.346	468.6		-714.818 54		2.320	477.2		3.0
MRCI+Q( $14e^-$ ) <sup>e</sup>	-714.846 4	47.3				-714.841 2					3.3

<sup>a</sup>See Table I for explanation of the acronyms. All correlated calculations correlate the 6 valence electrons, unless otherwise noted.

<sup>b</sup> $[8s6p2d]_{\text{Ca}}/[6s4p2d]_{\text{C}}$  basis (Ref. 12).

<sup>c</sup>Based on CASSCF(6,13) results,  $[7s5p4d3f]_{\text{Ca}}/[6s5p4d3f2g]_{\text{C}}$  basis (Ref. 15).

<sup>d</sup> $[8s6p2d1f]_{\text{Ca}}/[6s4p2d1f]_{\text{C}}$  basis (Ref. 11).

<sup>e</sup>Based on CASSCF(6,8) results,  $[7s5p4d3f]_{\text{Ca}}/[6s5p4d3f2g]_{\text{C}}$  basis (Ref. 15).

around equilibrium for both  $3\Sigma^-$  and  $5\Sigma^-$  states including the  $3s^23p^6$  (Ca) and  $3d^{10}$  (Zn) electrons in the correlation process.

We have used the same basis sets as in our recent work on CaC<sup>15</sup> and ZnC,<sup>18</sup> but now employing Cartesian Gaussian functions. Thus, for the Ca atom the primitive set consists of the (23s15p) Gaussian set of Partridge<sup>20</sup> augmented by an extra  $p$  function ( $a=0.05$ ) to assist the proper description of the very important  $3P \leftarrow 1S$  gap. To this set we have added a  $8d6f$  polarization set taken from Bauschlicher's ANO (Atomic Natural Orbital) basis set of Sc<sup>21</sup> which was subsequently optimized. For Zn, the augmented ANO-triple- $\zeta$  (21s15p10d6f4g) basis set of Roos and co-workers was used.<sup>22</sup> Finally, for the C atom we have chosen the augmented quadruple- $\zeta$  correlation-consistent basis set of Dunning and coworkers, aug-cc-pVQZ (13s7p4d3f2g).<sup>23</sup> The use of the diffuse functions is necessary because carbon was observed to acquire significant negative charge in both molecules.<sup>15,18</sup> Our final generalized contracted basis sets are  $[7s5p4d3f]$  for Ca,  $[8s7p5d3f2g]$  for Zn, and  $[6s5p4d3f2g]$  for C, comprising 181 (CaC) and 224 (ZnC) Cartesian Gaussians (6d, 10f, and 15g). For our purposes, we consider these basis sets adequate, thus no attempt was made to consider basis set superposition errors.

Bond lengths for each state were determined by fitting the three lowest energy points of each potential energy curve. Related spectroscopic constants ( $\omega_e$ ,  $\omega_e x_e$ ) were calculated by solving the one-dimensional nuclear Schrödinger equation employing a Numerov technique.<sup>24</sup>

For the MRBWCCSD calculations we have used our own modified implementation<sup>3</sup> of the ACES II program<sup>25</sup> which, at present, supports the use of reference configurations which are no more than doubly excited among each other. All other calculations have been performed with the GAUSSIAN 98<sup>26</sup> and MOLPRO 2000<sup>27</sup> suite of codes.

### III. RESULTS AND DISCUSSION

#### A. The Ca, Zn, and C atoms

Table I lists ground state total energies of Ca, Zn, and C at various levels of theory needed for proper dissociation description, as well as the calculated  $3P \leftarrow 1S$  energy gap for Ca and Zn. In the case of Ca, and for both CCSD (1.685 eV) and MRBWCCSD (1.649 eV), there is acceptable agreement with the experimental  $T_e$  value of 1.892 eV.<sup>17</sup> For Zn however, when the Zn  $3d^{10}$  "semicore" correlation is not taken into account the same gap is underestimated compared to experiment by 0.5–0.7 eV, even at the full-valence MRCI

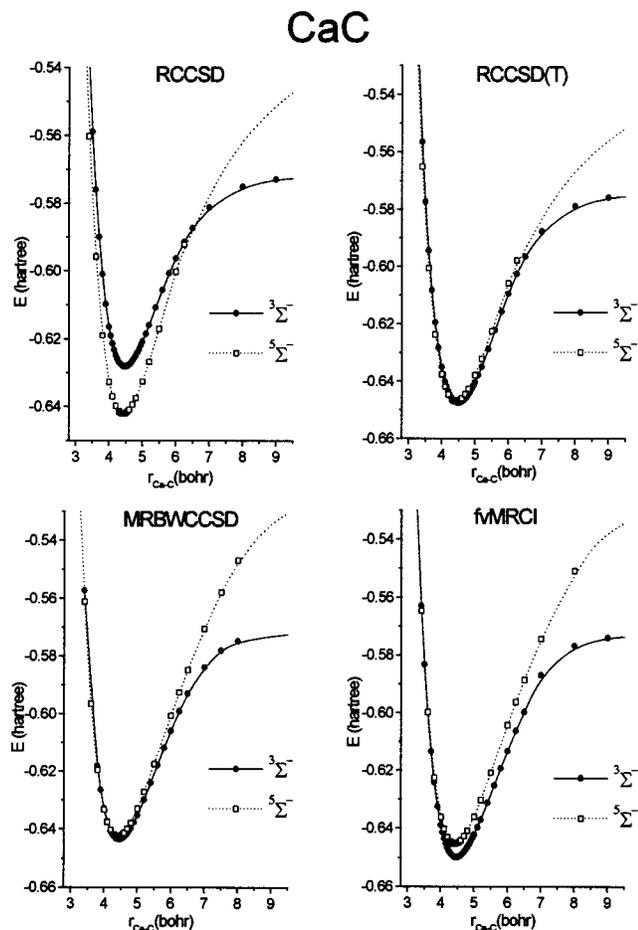


FIG. 1. Potential energy curves of the  $X^3\Sigma^-$  and  $^5\Sigma^-$  states of the CaC molecule at selected levels of theory. Energies have been shifted by +714 hartree.

level of theory. Including core correlation effects, the above Ca and Zn  $^3P \leftarrow ^1S$  splittings at the RCCSD and MRBWCCSD level, improve significantly.

## B. The CaC molecule

Table II summarizes our results for the  $X^3\Sigma^-$  and  $^5\Sigma^-$  states of CaC at different levels of theory, including the  $^5\Sigma^- \leftarrow X^3\Sigma^-$  energy gaps. Previous calculations for the two states are also listed in Table II. Potential energy curves for both states at selected levels of theory are depicted in Fig. 1. Notice that due to the electron donating bond character in the two states [Schemes (2) and (4)], one configuration is adequate for proper dissociation, thus it was indeed possible to construct full potential energy curves at all levels of theory included in Table II.

In accordance with previous calculations,<sup>12,14</sup> the ground state is predicted to be of  $^5\Sigma^-$  symmetry at the ROHF, CISD, and RCCSD levels of theory. The failure of these single reference treatments in describing quantitatively the  $X^3\Sigma^-$  state is indicated by both CISD+Q and RCCSD(T) results which recover part of the missing nondynamical correlation with a concomitant reversing of the  $^3\Sigma^- - ^5\Sigma^-$  ordering, caused by the dramatic increase in the  $D_e$  of the  $^3\Sigma^-$  state, 49.0 and 46.1 kcal/mol, respectively, as contrasted to

the CISD and RCCSD  $D_e$  values of 30.0 and 36.5 kcal/mol, respectively (Table II). When nondynamical valence correlation is included via the CASSCF(4,4) or the full-valence CASSCF(6,8) reference space, the subsequent dynamical correlation treatment (including MRBWCCSD) predicts undoubtedly the  $^3\Sigma^-$  as the ground state, the  $^5\Sigma^-$  located about 3 kcal/mol higher (Table II). The MRBWCCSD treatment improves significantly the RCCSD  $D_e$  value of the  $X^3\Sigma^-$  state (45.8 vs 35.5 kcal/mol respectively, Table II) bringing it in close agreement with the RCCSD(T) and MRCI  $D_e$  results, even though the MRBWCCSD method neglects the effect of triple excitations. At the same time, the ordering of the  $^3\Sigma^-$  and  $^5\Sigma^-$  states predicted with MRBWCCSD and RCCSD(T),  $T_e = 0.6$  and 0.3 kcal/mol, respectively, is at variance with the RCCSD ordering,  $T_e = -8.8$  kcal/mol, but in agreement with all multireference treatments (Table II, Fig. 1). This situation holds even after shifting the  $^5\Sigma^-$  curve to match the experimental Ca ( $^3P \leftarrow ^1S$ ) gap;<sup>17</sup> the respective RCCSD, RCCSD(T), MRBWCCSD and full-valence MRCI shifted  $T_e$  values then become -4.0, 5.1, 6.2, and 7.7 kcal/mol respectively, in other words, the  $^3\Sigma^-$ ,  $^5\Sigma^-$  ordering remains unchanged. In all four methods. However, it is interesting to observe that including the  $3s^2 3p^6$  core electrons of Ca, the  $^5\Sigma^- \leftarrow X^3\Sigma^- T_e$  values obtained at the CCSD, CCSD(T), MRBWCCSD, and MRCI(+Q)<sup>15</sup> level are -10.0, -0.4, 0.9, and 3.0(3.3) kcal/mol, respectively.

On the other hand, the single reference  $^5\Sigma^-$  state is well-described at almost all levels of theory as revealed from Table II, with a dissociation energy in the range of 83–86 (88, including the core  $e^-$ ) kcal/mol and a bond length of  $\sim 2.34$  (2.29, including the core  $e^-$ ) Å. We believe that inclusion of connected triple excitations in the MRBWCCSD treatment would certainly improve the 0.6 (0.9) kcal/mol  $^5\Sigma^- \leftarrow X^3\Sigma^-$  gap (Table II) towards the splitting of about 3 kcal/mol predicted by other multireference methods.

## C. The ZnC molecule

Similar arguments hold for the  $X^3\Sigma^-$  and  $^5\Sigma^-$  states of the ZnC molecule, the results of which are presented in Table III and Fig. 2. As mentioned earlier, the  $^3P \leftarrow ^1S$  gap of Zn (4.054 eV) is much larger as compared to the corresponding gap in Ca (1.892 eV, Table I).<sup>17</sup> As a result, the  $^5\Sigma^- \leftarrow X^3\Sigma^-$  energy splitting is much larger (Table III) and leaves no doubt as to the  $^3\Sigma^-$  symmetry of the ground state; indeed only the ROHF  $T_e$  value is so much underestimated that a wrong ground state is predicted at that particular level of theory (Table III). As in the case of CaC (*vide supra*), the single reference treatments underestimate the well depth of the  $X^3\Sigma^-$  state, leading subsequently to an underestimated  $^5\Sigma^- \leftarrow X^3\Sigma^-$  gap. For instance, the full-valence MRCI  $T_e$  value is more than twice as large as the respective CISD value (20.6 vs 9.1 kcal/mol, respectively). Here, the large Davidson correction (CISD+Q) and the RCCSD(T) results indicate, as in CaC, the inadequacy of the single reference treatments.

The multireference approaches increase the  $D_e$  value for the  $X^3\Sigma^-$  state, and also the  $^5\Sigma^- \leftarrow X^3\Sigma^-$  energy gap. In particular, the MRBWCCSD treatment improves the quanti-

TABLE III. Total energies  $E$  (hartree), binding energies  $D_e$  (kcal/mol), bond lengths  $r_e$  (Å) and frequencies  $\omega_e$ ,  $\omega_e x_e$  ( $\text{cm}^{-1}$ ) of the ZnC  $X^3\Sigma^-$  and  $5\Sigma^-$  states at different levels of theory. Unless otherwise noted, all results are from the present work.

Method <sup>a</sup>	$X^3\Sigma^-$					$5\Sigma^-$					
	$E$	$D_e$	$r_e$	$\omega_e$	$\omega_e x_e$	$E$	$D_e$	$r_e$	$\omega_e$	$\omega_e x_e$	$T_e$
ROHF	b	b	b			-1815.556 03	72.5	1.976	590.0	3.3	-19.8 <sup>c</sup>
CISD	-1815.679 05	12.4	2.158	359.5	6.6	-1815.664 51	78.6	2.061	560.2	3.3	9.1
CISD+Q	-1815.701 1	19.0	2.118	435.9	6.1	-1815.671 5	79.3	2.073	554.7	4.2	18.6
RCCSD	-1815.687 53	13.6	2.153	377.8	6.0	-1815.666 66	79.1	2.064	559.2	3.5	13.1
RCCSD(T)	-1815.697 69	18.3	2.131	418.2	5.1	-1815.671 50	80.5	2.072	553.3	3.8	16.4
CASSCF(4,4)	-1815.577 31	17.8	2.024	507.2	4.9						13.4
MRCI	-1815.694 92	21.9	2.120	470.0	5.7						19.1
MRCI+Q	-1815.703 7	22.1	2.135	458.5	5.7						20.2
MRACPF	-1815.700 98	22.0	2.130	462.0	5.9	-1815.669 23	79.0	2.070	554.8	4.0	19.9
MRBWCCSD	-1815.696 23	20.8	2.096	460.5	6.7	-1815.668 83	80.3	2.045	568.4	7.4	17.2
fvCASSCF	-1815.619 62	20.8	2.043	493.7	5.2	-1815.593 73	84.1	2.005	559.2	3.0	16.2
fvMRCI	-1815.708 57	26.2	2.039	487.6	4.1	-1815.675 73	84.4	2.006	553.1	3.2	20.6
fvMRCI+Q	-1815.712 7	26.8	2.041	484.6	4.6	-1815.679 14	84.4	2.008	550.6	3.0	21.1
fvMRACPF	-1815.711 45	26.7	2.040	485.4	4.4	-1815.678 08	84.4	2.007	551.4	3.2	20.9
QCISD(T)( $16e^-$ ) <sup>d</sup>	-1815.948 395	21.3	1.992 <sup>e</sup>			-1815.910 256	85.3	1.942 <sup>e</sup>			23.9
RCCSD( $16e^-$ )	-1816.164 42	18.8	2.000			-1816.136 15	87.2	1.939			17.7
RCCSD(T)( $16e^-$ )	-1816.195 61	24.6	1.973			-1816.157 97	89.8	1.935			23.6
MRCI( $16e^-$ )	-1816.122 40	24.1	1.986			-1816.091 24	85.2	1.936			19.6
MRCI+Q( $16e^-$ )	-1816.169 0	24.2	1.988			-1816.134 43	87.4	1.935			21.7
MRACPF( $16e^-$ )	-1816.171 85	22.9	1.992			-1816.136 59	87.4	1.940			22.1
MRBWCCSD( $16e^-$ )	-1816.172 24	23.9	1.988			-1816.136 78	87.3	1.935			22.3
fvMRCI( $16e^-$ ) <sup>f</sup>	-1816.138 12	24.5	1.983	512.9	4.7	-1816.102 64	88.7	1.948			22.3
fvMRCI+Q( $16e^-$ ) <sup>f</sup>	-1816.176 5	24.9	1.975	510.5	4.8	-1816.138 5	89.3	1.918			23.8

<sup>a</sup>See Table I for explanation of the acronyms. All correlated calculations correlate the 6 valence electrons, unless otherwise noted.

<sup>b</sup>Repulsive at the ROHF level.

<sup>c</sup>Vertical separation.

<sup>d</sup>6-311++G(2d,2f) basis (Ref. 16).

<sup>e</sup>QCISD/6-311++G(d,f) level of theory (Ref. 16).

<sup>f</sup>[8s7p5d3f2g]<sub>Zn</sub>/[6s5p4d3f2g]<sub>C</sub> basis (Ref. 18).

tative description of the ground state with respect to the CCSD results, while it compares favorably with the MRCI, MRCI+Q, and MRACPF results (Table III). When using a larger CASSCF(6,8) reference space, the energetics and bond lengths become now substantially improved, compared to CaC. Inclusion of the Zn  $3d^{10}$  electron correlation is followed by an even larger decrease in bond lengths, while its effect on the binding energy is not very clear. For most single reference and the multireference treatments out of the smaller CASSCF(4,4) reference space (including MRBWCCSD),  $3d^{10}$  correlation increases the dissociation energies by about 2 to 3 kcal/mol. On the other hand, the respective full-valence MRCI and MRCI+Q  $D_e$  values from our recent work<sup>18</sup> decrease by approximately 2 kcal/mol. In any case, MRBWCCSD performs much better than the single reference RCCSD, being in fair agreement with all other multireference methods [and RCCSD(T)]. An interesting remark that can be made though from the data on Table III is, that, in almost all cases where the  $3d^{10}$  correlation is included,  $D_e$  is predicted to lie in the range of 24–25 kcal/mol, while the  $5\Sigma^- \leftarrow X^3\Sigma^-$  gap is predicted to lie around 22–24 kcal/mol.

Observing the practically method-independent nature of the  $5\Sigma^-$  state, and after shifting our calculated minima and respective  $T_e$  values (Table III,  $3d^{10}$  correlation included) to

match the experimental Zn  $3P \leftarrow 1S$  gap (Table I), we reach our final (shifted) CCSD, MRBWCCSD, and full-valence MRCI+Q  $T_e$  values of 26.4, 31.2, and 33.0 kcal/mol, respectively.

#### IV. CONCLUDING REMARKS

The low-lying  $X^3\Sigma^-$  and  $5\Sigma^-$  states of the (experimentally unknown) calcium and zinc carbide diatomics (CaC, ZnC) were studied employing a variety of methods including the recently developed state-specific multireference Brillouin–Wigner coupled cluster (MRBWCCSD) method. Our purpose was to test and compare this method with more conventional single and multireference treatments, particularly with the single reference coupled cluster (CCSD) method which, for both systems, fails to properly describe the energetics of their  $X^3\Sigma^-$  states. This becomes more pronounced in the case of CaC, resulting to a reversed order of the two states, thus leading to an erroneous ground-state prediction. The MRBWCCSD description improves the energetics of the  $X^3\Sigma^-$  states for both molecules, restoring at the same time the correct state ordering for CaC. Comparison with other levels of theory reveals the inadequacy of routine single reference methods in describing quantitatively the  $3\Sigma^-$  states. The problem is cured by employing multirefer-

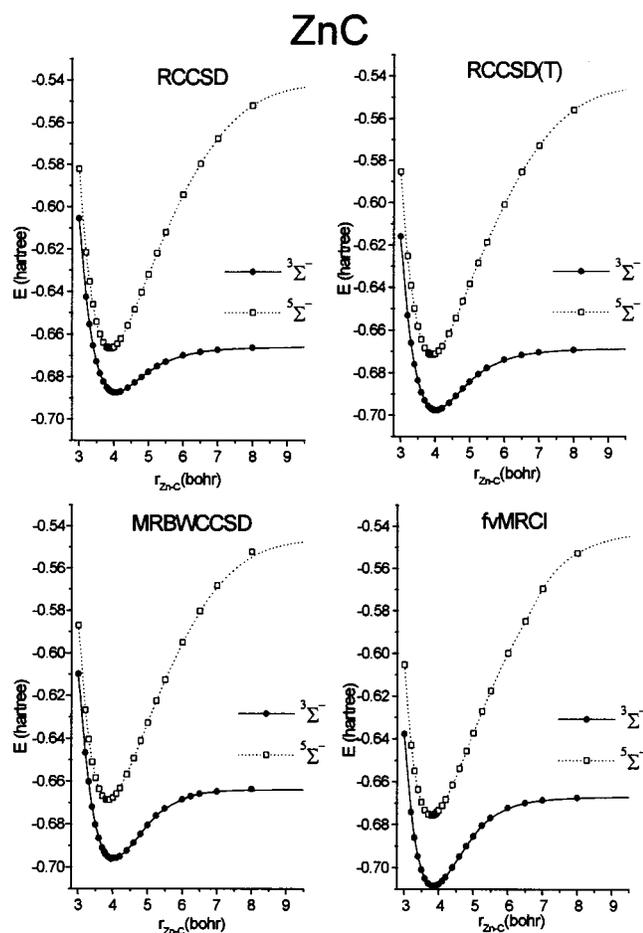


FIG. 2. Potential energy curves of the  $X^3\Sigma^-$  and  $^5\Sigma^-$  states of the ZnC molecule at selected levels of theory. Energies have been shifted by +1815 hartree.

ence approaches based on either a small (4,4) or a full-valence (6,8) CASSCF reference space to account for the multireference nature of the  $X^3\Sigma^-$  state, which in turn stems from the “near-degeneracy” of the  $4s$  and  $4p$  atomic orbitals of Ca and Zn. The MRBWCCSD results are in satisfactory agreement with rigorous multireference variational (MRCI) results. Inclusion of triple excitations in the MRBWCCSD treatment in a noniterative manner should further improve the description of these systems and the overall performance of the method.

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