REGULAR ARTICLE

Theoretical investigation for spectroscopic constants of ground-state alkaline-earth dimers with high accuracy

Dong-Dong Yang · Fan Wang

Abstract In this work, we provide highly accurate theoretical estimates for spectroscopic constants of the ground-state alkaline-earth dimers (Ca_2, Sr_2, and Ba_2). Electron correlation energies are calculated with coupled-cluster method at the single, double, and noniterative triple excitations [CCSD(T)] level, and the effects of full triples as well as quadruple excitations are also taken into account at the CCSDT and the CCSDT(Q) level. Our results demonstrate that high-order electron correlation is important to achieve results with high accuracy. We also find that results for Ca_2 with counterpoise corrections, which are designed to eliminate the basis set superposition error, deviate further away from those at the complete basis set limit than the uncorrected ones. The calculated binding energies and equilibrium bond lengths for Ca_2 and Sr_2 are in excellent agreement with recent experimental data. On the other hand, our results for Ba_2 are quite different from previous theoretical data, and there is no available experimental equilibrium bond length and binding energy for calibration. Based on the performance of the adopted approach for Ca_2 and Sr_2, our results should be more reliable and could be helpful for future investigations.

Keywords Alkaline-earth dimers · High-level electron correlation · Basis set superposition error (BSSE)

1 Introduction

The alkaline-earth dimers have been the focus of many investigations due to different electronic structures between their weakly bonded ground state with a large equilibrium distance and more strongly bonded excited states at a significantly smaller internuclear distance. Recently, the developments of laser cooling and trapping techniques make it possible to investigate interactions and properties of cold and ultracold atoms. Nondegenerate ground state and zero nuclear spin make alkaline-earth atoms good candidates for the construction of ultracold molecules [1–8].
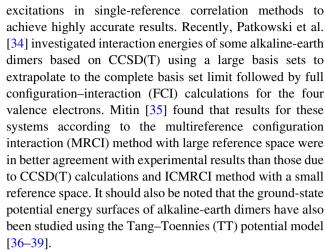
Many experimental investigations for the ground-state potentials of the alkaline-earth dimers have been reported based on vibrational and rotational electronic spectroscopy, from which a set of Dunham coefficients can be derived. The parameters in some analytical representation for the potential energy curve are subsequently determined using the Dunham coefficients. The electronic spectrum of calcium vapor was successfully measured first by Balfour and Whitlock [9], and a dissociation energy D_e of 1075 ± 150 cm^{-1} as well as other spectroscopic constants $\omega_e = 64.93$ cm^{-1}, $\omega_e x_e = 1.07$ cm^{-1} were determined based on the Rydberg–Klein–Rees (RKR) potential and the spectrum of A $^1\sum_u^+$ – X $^1\sum_g^+$ transition. In 1980, Vidal [10] reevaluated the spectroscopic data up to $v'' = 34$ by laser-induced fluorescence spectrum and yielded a binding energy of 1095 ± 0.5 cm^{-1} using the IPA (inverted perturbation approach) potential. In 1980 and 1984, through the measurement of the X $^1\sum_g^+$ – A $^1\sum_u^+$ transition, Bergeman et al. [11] and Gerber et al. [12] reported the ground potential parameters for Sr_2 dimer from the Morse potential and the RKR potential, respectively. Recently, the ground-state potentials of calcium and strontium dimers

D.-D. Yang · F. Wang (✉)
College of Chemistry, Sichuan University,
Chengdu 610064, People's Republic of China
e-mail: wangf44@yahoo.com.cn

were further derived with high-resolution Fourier-transform spectroscopy by Tiemann group [13–15] using some analytical form for the potential energy curve. Among the experimental investigations, the ground-state spectroscopic constants of calcium dimer are close to each other, while for strontium dimer [11, 12, 15], a difference of about 0.2 Å in equilibrium bond length exists, whose accurate determination requires further high-resolution spectroscopy investigations. Except for the vibrational frequency [16] and polarizability [17], no other experimental data have been reported on the ground-state potential and spectroscopic constants for barium dimer.

From the theoretical point of view, the first theoretical investigations of the diatomic alkaline-earth molecules [18, 19] have been performed based on the density functional theory (DFT) [20], and the results are often far away from each other. Recently, Mirick et al. [21] studied the electronic structure of calcium clusters using the general gradient approximation (GGA) for the exchange–correlation (XC) functional. However, there still exist discrepancies in binding energy by as much as 5–46% depending on the XC functionals used in the calculations. In fact, it is well known that DFT approaches with commonly used XC functionals without special corrections could not reproduce the correct r^{-6} behavior of the interaction potentials for weakly bonded van der Waals complexes [22, 23], which is the case for Ca_2, Sr_2, and Ba_2 dimers. The results of these previous calculations based on DFT are thus unreliable.

Many other theoretical investigations for the ground-state potentials of alkaline-earth dimers have also been carried out based on ab initio quantum chemistry approaches, such as configuration interaction with perturbation of multiconfiguration wave function selected iteratively (CIPSI) [24, 25], coupled-cluster (CC) methods [26–29], symmetry-adapted perturbation theory (SAPT) methods [30] and relativistic valence bond configuration interaction method (RVB-CI) [31]. Theoretical results depend significantly on the level of theory as well as basis sets employed. Czuchaj et al. [27–29] and Wang et al. [26] have yielded dissociation energies of the alkaline-earth species from coupled-cluster calculations with single, double and noniterative triple excitations [CCSD(T)] [32], which agree reasonably well with experiment results. This agreement, however, may owe to the core polarization potential associated with large-core pseudopotential employed in these calculations. In fact, excitation energies from the ns orbital to the np or the (n − 1)d orbitals for Ca, Sr, and Ba atoms are quite small [33], which means the occupied ns orbital is fairly close in energy to the virtual np and (n − 1)d orbitals. The single-reference-based CCSD(T) approach may thus be problematical in providing estimates on properties for these systems with high accuracy. Instead, one should resort to multireference approaches or including high-order excitations in single-reference correlation methods to achieve highly accurate results. Recently, Patkowski et al. [34] investigated interaction energies of some alkaline-earth dimers based on CCSD(T) using a large basis sets to extrapolate to the complete basis set limit followed by full configuration–interaction (FCI) calculations for the four valence electrons. Mitin [35] found that results for these systems according to the multireference configuration interaction (MRCI) method with large reference space were in better agreement with experimental results than those due to CCSD(T) calculations and ICMRCI method with a small reference space. It should also be noted that the ground-state potential energy surfaces of alkaline-earth dimers have also been studied using the Tang–Toennies (TT) potential model [36–39].

In present study, we calculated the ground-state spectroscopic constants of these alkaline-earth dimers using the CC approach. To achieve highly accurate results, the contributions due to high-level electron correlation from triple and quadruple excitations were included at the CCSDT [40, 41] and CCSDT(Q) [42, 43] level. Furthermore, we also investigated effects of relativity and basis set superposition error (BSSE) on the spectroscopic constants of these systems. This paper is organized in the following manner: the computational details are given in Sect. 2, the obtained results and comparisons with available experimental and theoretical results are presented in Sect. 3.

2 Computation details

Similar to those used in the investigation of group 12 elements [44, 45], the following total energy expressions for Ca_2 have been adopted:

$$E_{\text{total}} = E_{\text{HF}} + \Delta E_{\text{CCSD(T)}}^{\infty} + \Delta E_{\text{CCSDT}} + \Delta E_{\text{REL}}, \qquad (1)$$

$$\Delta E_{\text{CCSD(T)}}^{\infty} = \Delta E_{\text{CCSD(T)}}^{X} - \frac{a}{X^3}, \qquad (2)$$

$$\Delta E_{\text{CCSDT}} = E_{\text{CCSDT}}^{QZ} - E_{\text{CCSD(T)}}^{QZ}. \qquad (3)$$

To take into account the effects of core-valence correlations, the polarized core-valence basis set cc-pCVXZ [46] was chosen. In this work, the inner shell $(n − 1)s^2(n − 1)p^6$ electrons were included in all the correlation energy calculations for these molecules. Due to the weak interaction between Ca atoms in Ca_2, diffuse basis functions must be included, and the exponential of the most diffuse s and p functions are 0.01829 and 0.02142 in the cc-pCV5Z basis set, which should provide a reliable description for this weakly bonded molecule. The Hartree–Fock (HF) energy E_{HF} in Eq. 1 was calculated using the cc-pCV5Z basis set. $\Delta E_{\text{CCSD(T)}}^{X}$ in Eq. 2 [47] is the CCSD(T) correlation energy obtained with the cc-pCVXZ

(X = Q, 5) basis sets and the parameters in Eq. 2, i.e. a and the extrapolated complete basis set limit CCSD(T) correlation energy $\Delta E^\infty_{CCSD(T)}$, were determined from the cc-pCVQZ and cc-pCV5Z correlation energies. As for correlation energies based on high-level excitations, it is usually impossible to perform the full triple CCSDT and the quadruple CCSDT(Q) calculations using the cc-pCV5Z basis set due to expensive time and memory cost. Furthermore, the largest contribution to the correlation energy is already covered at the CCSD(T) level, and correlation energies beyond CCSD(T) level are expected to be small. Smaller basis sets may thus be sufficient to estimate these high-level correlation energies. In present work, the correlation energy differences between the CCSDT and the CCSD(T) approaches were calculated with the cc-pCVQZ basis set as indicated in Eq. 3. On the other hand, we did not try to calculate the contribution of the quadruple excitations to total energy in Eq. 1. Instead, the effects of the quadruples on spectroscopic constants of these molecules were estimated directly from the differences between the results derived from CCSDT(Q) and those due to CCSDT with the even smaller def2-QZVPP basis set [48]. In addition, the effects of relativistic correction to the total energy ΔE_{REL} for Ca_2 were also considered at the CCSD(T) level with the cc-pCVQZ basis set based on the second-order direct perturbation theory (DPT2) [49–51].

For Sr_2 and Ba_2, we used the following total energy expression:

$$E_{total} = E_{CCSD(T)} + \Delta E_{CCSDT} + \Delta E_{CCSDT(Q)} + \Delta E_{SO}. \quad (4)$$

The latest small-core energy-consistent relativistic pseudopotential (PPs) of the Stuttgart/Cologne group [52] for Sr and Ba atoms [53] were adopted. Due to the lack of systematic correlation consistent basis sets associated with these PPs, the (14s11p5d4f1g)/[8s8p5d4f1g] basis set for Sr and the (13s12p6d4f2g)/[9s9p6d4f2g] basis set for Ba developed together with these PPs were used. However, to account for the contributions of correlation energy due to inner shell electrons (the $4s^2 4p^6$ electrons for Sr and the $5s^2 5p^6$ electrons for Ba), the fully uncontracted form of these basis sets was employed. Furthermore, basis functions with high angular momentum were found to have significant effects on spectroscopic constants of Sr_2 and Ba_2. In CCSD(T) calculations, the (14s11p5d4f1g) basis set augmented with two sets of g polarization functions (0.4713990, 0.1656890) and two sets of h functions (0.5590605, 0.2191600) was employed for Sr, and the (13s12p6d4f2g) basis set with additional 1 g (0.104792) and 2 h (0.642352, 0.273064) polarization functions was adopted for Ba. Similarly, smaller basis sets have to be used in CCSDT and CCSDT(Q) calculations, the (14s11p5d4f2g)/[8s8p5d4f2g] and (13s12p6d4f2g)/[9s9p6d4f2g] basis sets based on those developed together

with the PPs for Sr and Ba were adopted in CCSDT calculations, while the (8s8p5d3f1g)/[7s5p4d3f1g] basis set for Sr and the (13s12p5d3f1g)/[7s5p4d3f1g] basis set for Ba derived from the def2-QZVPP basis sets [48] were employed in CCSDT(Q) calculations. In addition, spin–orbit coupling effects on spectroscopic constants of Sr_2 and Ba_2 were also investigated at the CCSD(T) level using a recently developed CC approach with spin–orbit coupling for close-shell molecules [54]. Furthermore, the effects of BSSE [55] were also investigated for Ca_2, Sr_2, and Ba_2 with the counterpoise (CP) correction method proposed by Boys and Bernardi [56]. All calculations were performed with the CFOUR program package [57] except for the CCSDT(Q) calculations, which were carried out with the MRCC program developed by Kállay [58] through an interface to the CFOUR program package.

The potential energy surfaces $V(r)$ were obtained by fitting the total energies in Eqs. (1) and (4) of seven points with a space of 0.05 Å around the equilibrium bond length with polynomial functions up to sixth order. Preliminary geometry optimizations have been performed for all the calculations except for the CCSDT(Q) results, and the fourth point is chosen with the optimized bond length. The following equations are adopted to calculate the rotational and vibrational spectroscopic constants [59, 60],

$$f_n = \frac{d^n V(r)}{dr^n}\Big|_{r=r_e}, \quad (n = 2, 3, 4 \ldots) \quad (5)$$

$$\omega_e = \frac{1}{2\pi c}\left(\frac{f_2}{\mu}\right)^{\frac{1}{2}}, \quad (6)$$

$$\alpha_e = -\left(6B_e^2/\omega_e\right)\left(1 + \frac{f_3 r_e}{3f_2}\right), \quad (7)$$

$$\omega_e x_e = \frac{1}{8}B_e r_e^2\left(\frac{5f_3^2}{3f_2^2} - \frac{f_4}{f_2}\right), \quad (8)$$

where ω_e is the vibrational frequency, $\omega_e x_e$ is the anharmonicity constant, α_e is the vibrational–rotational coupling constant, and B_e is the rotational constant determined using $B_e = h/(8\pi^2 \mu c r_e^2)$, c is speed of light, μ is the reduced mass, and r_e is the equilibrium bond length. It should be noted that the spectroscopic constants, i.e. ω_e, $\omega_e x_e$, α_e, and B_e, are expressed in cm^{-1}.

3 Results and discussion

3.1 Calcium dimer

The results of the present work for calcium dimer are presented in Table 1, and previous experimental and theoretical results are also listed for comparison. It can be seen from this table that the dissociation energy D_e predicted by

Table 1 Bond distance r_e (in Å), dissociation energies D_e, harmonic frequency ω_e, and anharmonicity constant $\omega_e x_e$ (in cm^{-1}), rotational constant B_e (in 10^{-2} cm^{-1}), and the vibrational–rotational coupling constant α_e (in 10^{-4} cm^{-1}) for Ca_2 dimer

	r_e	D_e	ω_e	$\omega_e x_e$	B_e	α_e
Present work						
QZ/CCSD(T)	4.339	930	61.3	1.1482	4.48	7.56
5Z/CCSD(T)	4.329	963	61.1	1.1542	4.50	7.62
CBS/CCSD(T)	4.319	996	60.9	1.1588	4.52	7.67
CBS/CCSD(T) + ΔT	4.301	1052	62.6	1.1701	4.56	7.45
CBS/CCSD(T) + ΔT + Δ(Q)	4.275	1132	65.3	1.1816	4.61	7.07
CBS/CCSD(T) + ΔT + Δ(Q) + ΔE_{REL}	4.287	1095	63.8	1.1514	4.58	7.23
Experimental work						
Exp[9]	4.281	1075 ± 150	64.93	1.0651	4.61	7.03
Exp[10]	4.276	1095 ± 0.5	65.07			
Exp[13,14]	4.277	1102.08 ± 0.09	64.4			
Previous theoretical work						
PP(10) + CCSD(T)[28]	4.366	1015	62.4			
4e-QDPT[61]	4.292	943	61.7	0.8		
AE-CCSD(T)[34]	4.339	983				
AE-CCSD(T) + FCI[34]	4.339	1152 ± 51(1189 ± 51)[a]				
AE-SAPT[30]	4.339	1113(1134)[a]				

[a] Values in parentheses are nonrelativistic results

CCSD(T) with the polarized core-valence cc-pCV5Z basis set is 963 cm^{-1} with a bond length of 4.329 Å. At the complete basis set (CBS) limit, which is extrapolated from the cc-pCVQZ and cc-pCV5Z basis sets, the bond length is reduced by about 0.02 Å, and the dissociation energy is increased to 996 cm^{-1}. The binding energy agrees very well with the theoretical value 983 cm^{-1} (993 ± 10 cm^{-1} with CBS-extrapolation) by Patkowski et al. [34] with a different large basis set based on a CCSD(T) all-electron calculation. It also compares well with the CCSD(T) values of 1015 cm^{-1} by Czuchaj et al. [28] listed in Table 1. On the other hand, the present equilibrium bond length is 0.05Å smaller than the result of Czuchaj et al. [28], which may be attributed to the difference in basis set and the pesudopotential used in calculations.

In addition to CCSD(T) calculations, we also investigated the contributions of electron correlation due to the full triple and the quadruple excitations at the CCSDT and CCSDT(Q) levels using the cc-pCVQZ basis set and def2-QZVPP basis set, respectively. According to Table 1, electron correlation due to full triple excitations leads to an increase in binding energy by about 56 cm^{-1} and a decrease in the equilibrium bond distance by about 0.02 Å compared with the CCSD(T) results. On the other hand, including quadruple excitations in electron correlation energy have a more pronounced effect on the properties of Ca_2, i.e. an increase in D_e by about 80 cm^{-1} and a decrease in r_e by about 0.03 Å. From these results, one can see that electron correlation from high-order excitations has a significant effect on the properties of Ca_2. Similar conclusion will also be drawn for Sr_2 and Ba_2. This is consistent with previous findings that due to the small energy gap between

the virtual np, (n − 1)d orbitals, and the occupied ns orbital; multireference approaches or single-reference approaches with high-order excitations have to be adopted to reach a reliable estimate on properties of these molecules. With the CBS-extrapolation and high-order correlation energy corrections included, the dissociation energy obtained in this work is 1132 cm^{-1} at the equilibrium internuclear distance of 4.275 Å and with a harmonic frequency ω_e of 65 cm^{-1}. Recently Bussery–Honvault et al. [30] provided a nonrelativistic binding energy D_e of 1134 cm^{-1} based on the symmetry-adapted perturbation theory (SAPT), which agrees very well with our present result. Patkowski et al. [34] estimated the contribution of high-order correlation based on a FCI approach for the valence electrons only, and they found that high-order correlation increased interaction energy D_e by 196 cm^{-1} compared with the CCSD(T) result. Furthermore, they predicted the dissociation energy to be 1189 ± 51 cm^{-1}, which is 67 cm^{-1} larger than our result. Recently, Bouissou et al. [61] provided a new theoretical prediction of 943 cm^{-1} based on the quasi-degenerate perturbation theory (QDPT), and the underestimation of dissociation energy may stem from the absence of g functions in their basis set. Compared to previous works, large basis sets and high-level electron correlation ensure the accuracy of the present calculations.

Calcium is a relatively light element, and one might expect a small relativistic effect on the ground-state properties. To investigate relativistic effect on spectroscopic constants of Ca_2, the second-order direct perturbation theory approach (DPT2) was employed at the CCSD(T) level [51] with the cc-pCVQZ basis set. In the

DPT2 approach, relativistic corrections due to both one-electron and two-electron operators were taken into account. The one- and two-electron terms yield opposite contributions to the total energy, and the one-electron correction is found to be much larger than the two-electron correction. However, when it comes to the binding energy, the contributions of these two terms are similar and cancel with each other to a large extent. This means both the one- and two-electron relativistic corrections are important in determining the binding energy of Ca_2.

As can be seen from Table 1, relativistic effect decreases the well depth by about 37 cm^{-1} and increases the bond length by 0.01 Å. This shows that relativistic effect is already important for Ca_2 to achieve highly accurate results. By including relativistic effect, the ultimate binding energy D_e for Ca_2 obtained in this work is 1095 cm^{-1} with the equilibrium distance r_e of 4.287 Å, which is only about 7 cm^{-1} smaller than the experimental value of 1102.08 ± 0.09 cm^{-1} by Allard et al. [13, 14], and is in excellent agreement with the earlier experimentally estimated value of 1095 ± 0.5 cm^{-1} by Vidal [10]. The bond length is about 0.01 Å larger than experimental internuclear distance. Recently, relativistic effect was also estimated for this system by Bussery–Honvault et al. [30] and Patkowski et al. [34], respectively. The former provided a theoretical determination of the ground-state dissociation energy of 1113 cm^{-1} based on SAPT method, and relativistic effect was found to decrease D_e by about 21 cm^{-1}. On the other hand, in a latter work, Patkowski et al. [34] provided dissociation energy of 1152 ± 51 cm^{-1} with frozen-core full CI method, and relativistic effect was found to decrease D_e by about 37 cm^{-1}, which is exactly equal to the present estimation. It should be noted that both of their calculations were performed at the nonrelativistic equilibrium bond length. The final dissociation energy in our work is smaller than that of Patkowski et al. [34], which is probably due to the difference in the employed method and basis set.

For these weakly bonded complexes, the BSSE may have significant effect on the interaction energy with incomplete basis set. BSSE is usually evaluated using the CP method [56]. For Ca_2, results at the CBS limit can be achieved from basis set extrapolation, and CP correction is in fact not necessary. However, for Sr_2 and Ba_2, due to lack of systematic basis sets, we could not obtain results at the CBS limit. Comparing the results at the CBS limit and the CP-corrected results for Ca_2 could thus provide valuable information on effects of BSSE for Sr_2 and Ba_2. The CP correction for Ca_2 was calculated at the CCSD (T) level with the cc-pCVXZ ($X = Q$, 5) basis sets as well as at the CBS limit, and results are listed in Table 2 together with the uncorrected ones for comparison. It can be seen from this table that CP correction will always increase the equilibrium bond length and decrease the dissociation energy, and it almost has no effects on these properties at the CBS limit as one would expect. On the other hand, the equilibrium bond length is always overestimated, and the binding energy is always underestimated with either the cc-pCVQZ basis set or the cc-pCV5Z basis set, compared with the results at the CBS limit. This is probably because the incompleteness in basis set for this molecule is more severe than that for the atom. This means CP-corrected results will deviate even further from the results at the CBS limit than uncorrected ones. In fact, similar conclusion has also been drawn previously. Dunning [62] and Alvarez-Idaboy and Galano [63] found that CP-corrected interaction energies were not systematically better than uncorrected ones compared with CBS extrapolated results and that the best way of dealing with BSSE was not based on CP corrections, but to increase the basis set. Based on these results, we expect uncorrected results should be more close to the results at the CBS limit for Sr_2 and Ba_2. In the following calculations for Sr_2 and Ba_2, CP-corrected results at the CCSD(T) level are provided, but spectroscopic constants with high-order electron correlation and spin–orbit coupling are estimated only based on uncorrected results.

Table 2 CP-corrected and uncorrected spectroscopic constants for Ca_2. Units are Å for r_e, cm^{-1} for D_e, ω_e, $\omega_e x_e$, B_e, and α_e

	r_e	D_e	ω_e	$\omega_e x_e$	$B_e(10^{-2})$	$\alpha_e(10^{-4})$
QZ[a]						
CCSD(T)	4.339	930	61.28	1.1482	4.48	7.56
BSSE	4.346	916	60.69	1.1321	4.46	7.61
5Z[b]						
CCSD(T)	4.329	963	61.12	1.1542	4.50	7.62
BSSE	4.332	956	60.93	1.1527	4.49	7.64
(QZ, 5Z)[a,b]						
CBS	4.319	997	60.91	1.1588	4.52	7.67
CBS + BSSE	4.317	997	61.15	1.1704	4.52	7.68

[a] cc-pCVQZ basis set are used

[b] cc-pCV5Z basis set are used

3.2 Strontium dimer

The spectroscopic constants of the ground-state Sr_2 dimer are collected in Table 3. In present calculations, we give the binding energy of 945 cm^{-1} and equilibrium bond length of 4.70 Å at CCSD(T) level with the fully uncontracted (14s11p5d4f3g2 h) basis set and the ECP28MDF pesudopotential [53]. This dissociation energy D_e agrees reasonably well with the theoretical value of 972 cm^{-1} by Mitin [35] at the CCSD(T) level with a different pseudopotential ECP28MWB [64] and the (7s7p6d4f2g1h) basis set. However, it is smaller than those obtained by Wang et al. [26] and Czuchaj et al. [29] at the CCSD(T) level. On the other hand, the obtained equilibrium bond length agrees well with the results of Wang et al. [26] and Czuchaj et al. [29] at the CCSD(T) level, but is much smaller than Mitin's result [35] with CCSD(T).

To improve the accuracy of our results, the full triple correction and the quadruple contribution were considered with the basis sets (14s11p5d4f2g)/[8s8p5d4f2g] and (8s8p5d3f1g)/[7s5p4d3f1g] at the CCSDT and CCSD T(Q) levels, respectively. As can be seen in Table 3, the full triple correction decreases the bond length by 0.01 Å and increases the dissociation energy by 30 cm^{-1}. On the other hand, quadruple excitations have more pronounced effects, i.e. 80 cm^{-1} on dissociation energy and 0.03 Å on bond length compared with the CCSDT results. Similar to the case for Ca_2, high-order electron correction again has

an important effect on the spectroscopic constants for Sr_2. We also investigated spin–orbit coupling (SOC) effects using a recently developed closed-shell CC approach with SOC at the CCSD(T) level. As shown in Table 3, SOC effects are minor for the ground-state properties of Sr_2 dimer. Our final binding energy D_e of 1055 cm^{-1} is only 2.5% (namely about 27 cm^{-1}) smaller than the recent experimental value of 1081.82 cm^{-1} by Stein et al. [15], and compares well with the experimental result of 1060 ± 30 cm^{-1} by Gerber [12]. Furthermore, our result also agrees with the recent theoretical value of 1066 cm^{-1} by Kotochigova [31] with an all-electron RVB-CI. In addition, the equilibrium bond length r_e of 4.66 Å is in excellent agreement with a recent experimental internuclear distance by Stein et al. [15], but much smaller than the MRCI result of Mitin [35]. In present calculations, the harmonic and anharmonicity constants also compare reasonably well with other theoretical and experimental results. Considering the good performance of the adopted approach for Ca_2, the error of the present estimates should mainly stem from the incompleteness of the basis set and the PP employed in the calculations.

3.3 Barium dimer

Up to now, little experimental information about the ground-state potential of Ba_2 dimer has been reported. Among the several theoretical investigations for barium

Table 3 Bond distance r_e (in Å), dissociation energies D_e, harmonic frequency ω_e, and anharmonicity constant $\omega_e x_e$ (in cm^{-1}), rotational constant B_e (in 10^{-2} cm^{-1}), and the vibrational–rotational coupling constant α_e (in 10^{-4} cm^{-1}) for Sr_2 dimer

	r_e	D_e	ω_e	$\omega_e x_e$	B_e	α_e
Present results						
BSSE/CCSD(T)	4.725	898	37.97	0.4358	1.71	1.79
CCSD(T)	4.702	945	38.54	0.4318	1.73	1.77
CCSD(T) + ΔT	4.692	975	39.10	0.4349	1.74	1.75
CCSD(T) + ΔT + Δ(Q)	4.664	1055	40.37	0.4353	1.76	1.72
CCSD(T) + ΔT + Δ(Q) + SO	4.663	1055	40.37	0.4353	1.76	1.71
Experimental work						
Exp[11]	4.50 ± 0.2[a]	1100 ± 100	39.6 ± 1.0	0.45 ± 0.02	1.89	
Exp[12]	4.446	1060 ± 30	40.32 ± 0.02	0.405	1.94	2.0
Exp[15]	4.672	1081.82	40.33	0.3994	1.76	1.68
Previous theoretical work						
PP(2) + CIPSI[25]	4.53	1088	43.0		1.87	
PP(10) + CCSD(T)[26]	4.72	1049	39.1			
PP(10) + CCSD(T)[29]	4.68	1024	40.68			
RVB-CI[31]	4.42	1066	39.2			
PP(10) + CCSD(T)[35]	4.823	972	38.51	0.408		
PP(10) + MRCI[35]	4.781	1115	40.93	0.386		

[a] This value was estimated from the values $r_e(Mg_2)$ = 3.89 Å and $r_e(Ca_2)$ = 4.28 Å

Table 4 Bond distance r_e (in Å), dissociation energies D_e, harmonic frequency ω_e, and anharmonicity constant $\omega_e x_e$ (in cm^{-1}), rotational constant B_e (in 10^{-3} cm^{-1}), and the vibrational–rotational coupling constant α_e (in 10^{-5} cm^{-1}) for Ba$_2$ dimer

	r_e	D_e	ω_e	$\omega_e x_e$	B_e	α_e
Present results						
BSSE/CCSD(T)	5.033	1168	32.75	0.2266	9.65	6.38
CCSD(T)	5.018	1216	33.25	0.2316	9.71	6.28
CCSD(T) + ΔT	5.009	1241	33.55	0.2342	9.74	6.23
CCSD(T) + ΔT + Δ(Q)	4.976	1349	34.93	0.2348	9.86	5.94
CCSD(T) + ΔT + Δ(Q) + SO	4.972	1353	34.99	0.2366	9.88	5.93
Experimental work						
Exp[16]			33.2	0.5 ± 0.2		
Previous theoretical work						
PP(10) + CIPSI[24]	4.881	1629	35	0.204	10.3	
PP(10) + CCSD(T)[35]	5.294	906	28.74	0.230		
PP(10) + MRCI[35]	5.220	1122	31.41	0.221		

dimer, large discrepancies still exist in spectroscopic constants. The spectroscopic constants for Ba$_2$ of the present work and available experimental results as well as some previous theoretical results are listed in Table 4. In present work, the CCSD(T) calculations were carried out with the fully uncontracted (13s12p6d4f3g2h) basis set and the ECP46MDF pseudopotential [53]. We obtained the binding energy $D_e = 1216$ cm^{-1} at the minimum bond length $r_e = 5.018$ Å. Our results differ significantly from the recent CCSD(T) values by Mitin [35] based on fully uncontracted (9s9p6d4f2g1h) basis set and a different pseudopotential ECP46MWB [64]. Besides difference in basis set and PP, different reference determinant in CCSD(T) calculations also contributes to this disagreement, where the HF determinant was adopted in the present work while the pseudo-nature orbitals were used to construct the reference determinant in Mitin's work [35].

The contributions of high-level electron correlation based on the full triple CCSDT and the quadruple CCSDT(Q) approaches were also estimated with the (13s12p6d4f2g)/[9s9p6d4f2g] and (13s12p5d3f1g)/[7s5p4d3f1g] basis sets, respectively. As shown in Table 4, compared to the CCSD(T) results, the full triple excitations increase the potential well depth by about 25 cm^{-1} and slightly decrease the equilibrium bond length by 0.01 Å, while the quadruple correction makes D_e deepen by as much as 108 cm^{-1} and decreases r_e by about 0.03 Å. Quadruple excitations again have a more pronounced effect on the spectroscopic constants than the full triple excitations. As for SOC, it is found to have only minor effects again. The results at the CCSD(T) + ΔT + Δ(Q) level with SOC are our final estimates, namely $D_e = 1353$ cm^{-1}, $r_e = 4.972$ Å, $\omega_e = 35$ cm^{-1}, and $\omega_e x_e = 0.237$ cm^{-1}. The present binding energy is much smaller than the theoretical value 1629 cm^{-1} by Allouche et al. [24] with (7s7p4d2f)/[6s6p4d2f] basis set based on CIPSI method, while the equilibrium bond length is larger.

On the other hand, the present dissociation energy is significantly larger, and the equilibrium bond length is much smaller than the recent theoretical values by Mitin based on MRCI calculations [35]. The harmonic and anharmonicity constants are in reasonable agreement with the experimental results of $\omega_e = 33.2$ cm^{-1} and $\omega_e x_e = 0.5 \pm 0.2$ cm^{-1} by Lebeault et al. [16] and also compare well with theoretical values by Allouche et al. [24] as presented in Table 4. Based on the performance of the adopted approach for Ca$_2$ and Sr$_2$, our results should be more reliable, where the main source of error comes from basis set incompleteness and the PPs. The present calculation provides a new ab initio estimation for spectroscopic constants of Ba$_2$ dimer, which should be useful for subsequent investigations.

4 Conclusions

In present work, we provided highly accurate theoretical estimates for the spectroscopic constants of the ground-state alkaline-earth dimers based on CC approach. It has been recognized previously that multireference approach or single-reference method with high excitation levels must be adopted to achieve high accuracy due to the small energy gap between the ns and np, (n − 1)d orbitals of alkaline-earth atoms. The effects of full triple excitations and quadruple excitations on the spectroscopic constants were investigated at the CCSDT and the CCSDT(Q) levels, respectively. Our results indicate that high-level electron correlation is imperative to give rise to accurate results.

For Ca$_2$, the cc-pCVXZ ($X = Q$, 5) basis set was employed in CCSD(T) calculations, which enable extrapolate to results at the CBS limit. We also investigated the BSSE with the CP correction method. It is found that the

CP-corrected results are actually even further away from the results at the CBS limit than the uncorrected results. In addition, relativistic effects were also included for Ca_2 at the CCSD(T) level based on the DPT2 method. The present results for Ca_2 agree very well with recent experimental data, with an error in binding energy of less than 10 cm^{-1} and an error in bond length of about 0.01Å. Relativistic effects for Sr_2 and Ba_2 were taken into account through relativistic PPs. For Sr_2, our calculated bond length is only about 0.01 Å smaller than a recent experimental result, and the binding energy is about 27 cm^{-1} smaller. Generally, the agreements between experimental data and our calculated values are better than previous calculations. As for Ba_2, our results differ significantly from previous theoretical results, and due to the lack of experimental data, it is difficult to estimate the error of the theoretical estimates. However, based on the performance of the adopted approach for Ca_2 and Sr_2, our results should be more reliable. The present calculations on barium dimer provide a new ab initio estimation of spectroscopic constants for Ba_2, which could be helpful for future experimental and theoretical investigations.

References

1. Dammalapati U, Norris I, Burrows C, Arnold AS, Riis E (2010) Phys Rev A 81:023424
2. Zelevinsky T, Kotochigova S, Ye J (2008) Phys Rev Lett 100:043201
3. De S, Dammalapati U, Jungmann K, Willmann L (2009) Phys Rev A 79:041402(R)
4. Kotochigova S, Zelevinsky T, Ye J (2009) Phys Rev A 79:012504
5. Zelevinsky T, Boyd MM, Ludlow AD, Ido T, Ye J, Ciuryło R, Naidon P, Julienne PS (2006) Phys Rev Lett 96:203201
6. Machholm M, Julienne PS, Suominen K-A (2001) Phys Rev A 64:033425
7. Kraft S, Vogt F, Appel O, Riehle F, Sterr U (2009) Phys Rev Lett 103:130401
8. Stellmer S, Tey MK, Huang B, Grimm R, Schreck F (2009) Phys Rev Lett 103:200401
9. Balfour WJ, Whitlock RF (1975) Can J Phys 53:472
10. Vidal CR (1980) J Chem Phys 72:1864
11. Bergeman T, Liao PF (1980) J Chem Phys 72:886
12. Gerber G, Möller R, Schneider H (1984) J Chem Phys 8:1538
13. Allard O, Pashov A, Knöckel H, Tiemann E (2002) Phys Rev A 66:042503
14. Allard O, Samuelis C, Pashov A, Knöckel H, Tiemann E (2003) Eur Phys J D 26:155
15. Stein A, Knöckel H, Tiemann E (2008) Phys Rev A 78:042508
16. Lebeault MA, Viallon J, Boutou V, Chevaleyre J (1998) J Mol Spectr 192:179
17. Schäfer S, Mehring M, Schäfer R (2007) Phys Rev A 76:052515
18. Jones RO (1979) J Chem Phys 71:1300
19. Ortiz G, Ballone P (1991) Phys Rev B 43:6376
20. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, Oxford
21. Mirick JW, Chien C-H, Blaisten-Barojas E (2001) Phys Rev A 63:023202
22. Pérez-Jordá JM, Becke AD (1995) Chem Phys Lett 233:134
23. Milet A, Korona T, Moszynski R, Kochanski E (1999) J Chem Phys 111:7727
24. Allouche AR, Aubert-Frecon M, Nicolas G, Spiegelmann F (1995) Chem Phys 200:63
25. Boutassetta N, Allouche AR, Aubert-Frecon M (1996) Phys Rev A 53:3845
26. Wang Y, Flad H-J, Dolg M (2000) J Phys Chem A 104:5558
27. Czuchaj E, Krośnicki M, Stoll H (2001) Theor Chem Acc 107:27
28. Czuchaj E, Krośnicki M, Stoll H (2003) Theor Chem Acc 110:28
29. Czuchaj E, Krośnicki M, Stoll H (2003) Chem Phys Lett 371:401
30. Bussery-Honvault B, Launay JM, Moszynski R (2003) Phys Rev A 68:032718
31. Kotochigova S (2008) J Chem Phys 128:024303
32. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) Chem Phys Lett 157:479
33. http://www.nist.gov/pml/data/asd.cfm
34. Patkowski K, Podeszwa R, Szalewicz K (2007) J Phys Chem A 111:12822
35. Mitin AV (2009) Russ J Phys Chem A 83:1160
36. Li P, Xie W, Tang KT (2010) J Chem Phys 133:084308
37. Yang DD, Li P, Tang KT (2009) J Chem Phys 131:154301
38. Yin GP, Li P, Tang KT (2010) J Chem Phys 132:074303
39. Li P, Ren J, Niu N, Tang KT (2011) J Phys Chem A 115:6927
40. Noga J, Bartlett RJ (1987) J Chem Phys 86:7041
41. Kállay M, Surján PR (2001) J Chem Phys 115:2945
42. Bomble YJ, Stanton JF, Kállay M, Gauss J (2005) J Chem Phys 123:054101
43. Kállay M, Gauss J (2005) J Chem Phys 123:214105
44. Pahl E, Figgen D, Thierfelder C, Peterson KA, Calvo F, Schwerdtfeger P (2010) J Chem Phys 132:114301
45. Pahl E, Figgen D, Borschevsky A, Peterson KA, Schwerdtfeger P (2011) Theor Chem Acc 129:651
46. Koput J, Peterson KA (2002) J Phys Chem A 106:9595
47. Helgaker T, Klopper W, Koch H, Noga J (1997) J Chem Phys 106:9639
48. Weigend F, Ahlrichs R (2005) Phys Chem Chem Phys 7:3297
49. Kutzelnigg W (1989) Z Phys D 11:15
50. Kutzelnigg W (1990) Z Phys D 15:27
51. Stopkowicz S, Gauss J (2008) J Chem Phys 129:164119
52. http://www.theochem.uni-stuttgart.de/pseudopotentials/
53. Lim IS, Stoll H, Schwerdtfeger P (2006) J Chem Phys 124:034107
54. Wang F, Gauss J, van Wüllen C (2008) J Chem Phys 129:064113
55. Liu B, McLean AD (1973) J Chem Phys 59:4557
56. Boys F, Bernardi F (1970) Mol Phys 19:553
57. CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum chemical program package by Stanton JF, Gauss J, Harding ME, Szalay PG with contributions from Auer AA, Bartlett RJ, Benedikt U, Berger C, Bernholdt DE, Bomble YJ, Cheng L, Christiansen O, Heckert M, Heun O, Huber C, Jagau T-C, Jonsson D, Jusélius J, Klein K, Lauderdale WJ, Matthews DA, Metzroth T, Mück LA, O'Neill DP, Price DR, Prochnow E, Puzzarini C, Ruud K, Schiffmann F, Schwalbach W, Stopkowicz S, Tajti A, Vázquez J, Wang F, Watts JD and the integral packages MOLECULE (Almlöf J and Taylor PR), PROPS (Taylor PR), ABACUS (Helgaker T, Jensen HJ Aa, Jørgensen P, and Olsen J) and ECP routines by Mitin AV and Wüllen C van. (For the current version, see http://www.cfour.de)
58. MRCC, a string-based quantum chemical program suite written by Kállay M. See also Kállay M, Surján PR (2001) J Chem Phys 115:2945 as well as http://www.mrcc.hu

59. Dunham JL (1932) Phys Rev 41:721
60. Herschbach DR, Laurie VW (1961) J Chem Phys 35:458
61. Bouissou T, Durand G, Heitz M-C, Spiegelman F (2010) J Chem Phys 133:164317
62. Dunning TH Jr (2000) J Phys Chem A 104:9062
63. Alvarez-Idaboy JR, Galano A (2010) Theor Chem Acc 126:75
64. Kaupp M, Schleyer PvR, Stoll H, Preuss H (1991). J Chem Phys 94:1360