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REGULAR ARTICLE

Core-valence correlating basis sets for alkali and alkaline earth metal atoms

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Abstract For 12 alkali and alkaline earth metal atoms from Li to Ra, contracted Gaussian-type function sets are developed for the description of correlations among the $(n-1)s$, $(n-1)p$, and ns electrons, where n is the principal quantum number of the outermost shell. A segmented contraction scheme is employed for the compactness and efficiency. Contraction coefficients and exponents are determined so that the deviation from accurate natural orbitals of the ground states is minimized. For heavy atoms from Cs to Ra, the spin-free relativistic effects are considered through the third-order Douglas–Kroll approximation. To test the present correlating sets, all-electron calculations are performed for the ground state of 12 diatomic hydrides, 6 alkali metal dimers, 4 alkaline earth metal oxides, and 12 diatomic fluorides. The calculated spectroscopic constants are in excellent agreement with the experimental values.

Keywords Correlating basis set · Core-valence correlation · Segmented contraction

1 Introduction

In molecular calculations, the inclusion of electron correlations is inevitable to obtain a reliable description of the electronic structure. In many cases, the frozen-core approximation is used, in which the electrons in core orbitals are kept frozen and only the electrons in valence orbitals are correlated. The frozen-core approximation is based on the fact that the core correlation energy is almost constant against the change in molecular geometries and little affects the computational spectroscopic constants of molecules, whereas the valence correlation energy strongly depends on the geometry. In highly accurate calculations, however, the error in the treatment of valence electrons is so small that it is comparable to the error associated with the frozen-core treatment, and hence the correlation in the core electrons cannot be neglected. Correlation consistent (cc) type core-valence basis sets for B–Ne and Al–Ar were constructed for this purpose by Dunning et al. [1–3]. Pople et al. [4, 5] also developed core-valence basis sets for the main group atoms of the first three rows. For the alkali and alkaline earth metal atoms, the core-valence correlations are more important among the main group atoms. In fact, Partridge et al. [6] found in their study on alkali diatomics that the inclusion of core-valence correlations is necessary to obtain reliable results for ionization potentials, atomic level splittings, and bond lengths. For the Li, Be, Na, Mg, K, and Ca atoms, Iron et al. [7] proposed core-valence cc-type basis sets and showed their validity in the calculation of spectroscopic constants of a variety of diatomic molecules involving these atoms. They also constructed basis sets for the 'deep core' correlation, where the 2s and 2p electrons participate, in the K and Ca atoms.

In this paper, we report correlating basis sets for $(n-1)s$, $(n-1)p$, and ns orbitals for the 12 alkali and alkaline earth

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metal atoms from Li through Ra, where n is the principal quantum number of the outermost shell. The present work is a part of our continuing effort to develop basis sets for the description of the electron correlation [8–13], covering the entire periodic table of the elements. These basis functions are contracted (C) Gaussian-type functions (GTFs) in a segmented form for the compactness and efficiency. The contraction coefficients and exponents were determined by minimizing the deviation from accurate natural orbitals (NOs) generated from large-scale configuration interaction (CI) calculations of atoms. The present basis sets are named Natural Orbital based Segmented Contracted Gaussian (NOSeC) basis sets. We developed non-relativistic correlating sets for the atoms up to Xe and relativistic sets for the heavier atoms. The relativistic contribution was incorporated into the CI calculations through the third-order Douglas–Kroll (DK3) approximation [14], intending the use of basis sets in two-component quasi-relativistic calculations.

The next section outlines our computational procedures and presents new correlating basis sets. Molecular applications to 12 diatomic hydrides, 6 alkali metal dimers, 4 alkaline earth metal oxides, and 12 diatomic fluorides are given in Sect. 3. The following symbols are used throughout this paper: ( ) for primitive GTFs, [ ] for CGTFs, and { } for segmented contraction patterns of CGTFs.

2 Correlating functions

2.1 Computational method

As in our previous work [8–13], the contraction coefficients and exponents of the CGTFs were so determined as to minimizing the deviation Δ from accurate NOs,

$$\Delta = \sum_{k=1}^{N} \nu_k \int \mathrm{d}\mathbf{r}\, |\xi_k(\mathbf{r}) - \psi_k(\mathbf{r})|^2 w(\mathbf{r}), \tag{1}$$

where

$$\psi_k(\mathbf{r}) = \sum_{i=1}^{M} C_{ki}\chi_i(\mathbf{r}). \tag{2}$$

In Eq. 1, $\{\xi_k\}$ are N reference NOs with occupation numbers $\{\nu_k\}$ and $w(\mathbf{r})$ is a weight function, for which $1/r^2$ is employed since it was found [8] to give the most appropriate results. In Eq. 2, $\{\chi_i\}$ are M CGTFs to be determined and $\{C_{ki}\}$ are linear coefficients. In this work, we included the outermost occupied d and f orbitals in $\{\chi_i\}$ if they are. The conjugate direction algorithm [15] was used for the nonlinear optimization of contraction coefficients and exponents of the CGTFs, which minimize the functional Δ defined by Eq. 1. The determination of CGTFs can be performed independently for each azimuthal quantum number l.

In this paper, we construct correlating basis sets for $(n-1)s$ and $(n-1)p$ orbitals. Thus, we first performed single and double substitution configuration interaction (SDCI) calculations for the ground state to consider the electronic correlation among $(n-1)s$ and $(n-1)p$ subshell electrons in order to obtain reference NOs in Eq. 1. All SDCI calculations were carried out with full spherical symmetries using the program ATOMCI [16] that had been modified to include the relativistic effects through the DK3 method with a Gaussian nucleus model [17]. The spin-free part of the DK3 Hamiltonian was used in one-electron integrals for the Cs, Ba, Fr, and Ra atoms. We employed well-tempered primitive sets by Huzinaga et al. [18, 19] and uncontracted sets by Koga et al. [20] which were extended by adding higher l functions as follows: $(12s6p6d)$ for Li and Be, $(23s13p7d7f\,7g)$ for Na and Mg, $(26s16p8d8f8g)$ for K and Ca, $(28s20p\ 14f8f8g)$ for Rb and Sr, $(30s23p17f9f9g)$ for Cs and Ba, and $(29s23p16f8f8g)$ for Fr and Ra. We used the resultant NOs as reference NOs in Eq. 1.

2.2 Core correlating functions

We constructed correlating function sets of $[1p]$ and $[2p1d]$ for Li and Be, and $[1d]$, $[1d1f]$, and $[2d1f1g]$ for Na–Ra. The contraction forms shown in Table 1 were chosen based on our intention that correlating CGTFs would recover more than 99% of the core correlation energy produced by the accurate NOs of the same size.

To test the quality of the developed sets, we performed two types of all electron SDCI calculations on the ground state with correlating $(n-1)s$ and $(n-1)p$ electrons; one with the present correlating CGTF sets and the other with the accurate NO set truncated to the same size. In these calculations, we used the self-consistent field (SCF) orbitals of the ground state for the occupied orbitals. We added a few correlating NOs to the correlating sets; the first s NO for Li–Be and the first s and the first two p NOs for Na–Ra. The results are given in Table 2. For all the atoms except Ba, the present

Table 1 Generated correlating CGTF sets

Atom	CGTFs/contraction patterns
Li, Be	$[1p]/\{p2\}$, $[2p1d]/\{p21d2\}$
Na, Mg	$[1d]/\{d2\}$, $[1d1f]/\{d2f2\}$, $[2d1f1g]/\{d21f2g2\}$
K, Ca	$[1d]/\{d3\}$, $[1d1f]/\{d3f2\}$, $[2d1f1g]/\{d21f2g2\}$
Rb, Sr	$[1d]/\{d3\}$, $[1d1f]/\{d3f2\}$, $[2d1f1g]/\{d21f2g2\}$
Cs, Ba	$[1d]/\{d4\}$, $[1d1f]/\{d4f2\}$, $[2d1f1g]/\{d32f2g2\}$
Fr, Ra	$[1d]/\{d5\}$, $[1d1f]/\{d4f2\}$, $[2d1f1g]/\{d42f2g2\}$

Table 2 Correlation energies (in hartree) from all-electron SDCI calculations with the present correlating CGTF sets for the $(n-1)s$ and $(n-1)p$ subshell electron correlation

Atom	[1*p*]		[2*p*1*d*]
Li	−0.034482 (99.20)[a]		−0.038697 (99.49)
Be	−0.034246 (99.19)		−0.038806 (99.50)
	[1*d*]	[1*d*1*f*]	[2*d*1*f*1*g*]
Na	−0.204637 (99.26)	−0.232201 (99.26)	−0.272228 (99.56)
Mg	−0.203097 (99.29)	−0.231864 (99.28)	−0.272210 (99.59)
K	−0.173424 (99.58)	−0.213066 (99.64)	−0.241726 (99.32)
Ca	−0.181319 (99.65)	−0.223250 (99.64)	−0.252274 (99.28)
Rb	−0.135273 (99.98)	−0.175298 (99.98)	−0.203278 (99.79)
Sr	−0.139100 (100.00)	−0.181818 (100.07)	−0.210424 (99.97)
Cs	−0.108970 (99.90)	−0.147364 (99.20)	−0.174420 (99.27)
Ba	−0.110895 (99.90)	−0.151676 (98.93)	−0.178472 (98.57)
Fr	−0.091932 (99.16)	−0.126298 (99.32)	−0.151789 (99.76)
Ra	−0.092025 (99.80)	−0.128550 (99.16)	−0.154486 (99.02)

[a] The values in parentheses show the reproduction percentage of the present CGTF set relative to the reference NO set of the same size

three types of CGTF sets for the $(n-1)s$ and $(n-1)p$ electron correlation reproduce more than 99% of the correlation energies obtained by the reference NO sets. For the Ba atom, the [1*d*1*f*] and [2*d*1*f*1*g*] sets are very slightly smaller than 99%, but we do not wish to use larger CGTFs.

2.3 Recommended core-valence correlating functions

The above core correlating sets are combined with our valence correlating sets previously prepared, in order to describe the core-valence (CV) correlation among the $(n-1)s$, $(n-1)p$, and *ns* electrons. We make three types of correlating sets; double, triple, and quadruple zeta plus polarization (dzp, tzp, and qzp) sets. Here, we assume that the occupied SCF orbitals exist and the $(n-1)s$, $(n-1)p$, and *ns* orbitals are decontracted properly to give flexibility. The smallest [1*d*] CGTF is added to the [1*p*] CGTF of the *ns* valence correlating set. For Li and Be, we used [1*p*] as the core correlating set instead of [1*d*]. We refer these sets as NOSeC-CV-dzp sets. Next, the [2*p*1*d*] of Li–Be and the [1*d*1*f*] of Na–Ra are added to the [2*p*1*d*] valence correlating set. These sets are NOSeC-CV-tzp sets. As the largest sets, named NOSeC-CV-qzp sets, the [3*p*2*d*1*f*] valence correlating sets are combined with the [2*p*1*d*] and [2*d*1*f*1*g*] core correlating sets for Li–Be and Na–Ra, respectively. The names of these basis sets refer to the fact that their size and quality are comparable to other all-electron dzp, tzp, and qzp correlating sets, respectively.

In Table 3, we exemplify the NOSeC-CV-dzp $\{p3d3\}$, NOSeC-CV-tzp $\{p21d32f2\}$, and NOSeC-CV-qzp $\{p111d2111f21g2\}$ sets for the K atom. When these three sets are added to the occupied and the *s*- and *p*-type correlating orbitals described in the previous subsection, we obtain the core-valence correlation energies −0.180, −0.221, and −0.250 hartree, respectively, by SDCI calculations. By replacing the present correlating sets with the cc-type basis sets by Iron et al. [7], we obtained the correlation energies of −0.167 hartree for the dzp $\{p111d11\}$ set, −0.237 hartree for the tzp $\{p11111d1111f11\}$ and −0.257 hartree for the qzp $\{p1111111d111111f1111g11\}$ sets. Comparison of these results demonstrates that despite their compactness, the present sets are superior at the dzp level and similar in quality at the tzp and qzp levels to the corresponding cc-type sets.

Table 3 Recommended correlating CGTF sets for the K atom

Core				Valence			
NOSeC-CV-dzp set							
$\{d3\}$	8.222646	1.553291	0.538934	$\{p3\}$	0.253382	0.056121	0.025170
	0.046694	0.490972	0.604655		−0.072994	0.692577	0.382332
NOSeC-CV-tzp set							
$\{d3\}$	8.222646	1.553291	0.538934	$\{p21\}$	0.253382	0.056121/	0.025170
	0.046694	0.490972	0.604655		−0.072994	0.692577/	1.000000
$\{f2\}$	1.528579	0.638237		$\{d2\}$	0.273975	0.057199	
	0.567445	0.530194			0.080144	0.967129	
NOSeC-CV-qzp set							
$\{d21\}$	6.758703	1.343685/	0.444331	$\{p111\}$	0.253382/	0.056121/	0.025170
	0.091199	0.963982/	1.000000		1.000000/	1.000000/	1.000000
$\{f2\}$	1.528579	0.638237		$\{d11\}$	0.273975/	0.057199	
	0.567445	0.530194			1.000000/	1.000000	
$\{g2\}$	1.654834	0.701570		$\{f1\}$	0.089607		
	0.585631	0.527966			1.000000		

All the present basis sets NOSeC-CV-*n*zp (n = d,t,q), including all-electron and model core potential SCF occupied orbitals, are available at the web site http://setani.sci.hokudai.ac.jp/.

3 Molecular applications

3.1 Calculational details

To examine the quality of the present core-valence correlating sets, we performed SCF and coupled-cluster singles and doubles with noniterative triples correction [CCSD(T)] calculations to obtain spectroscopic constants of hydrides, dimers, oxides, and fluorides. The relativistic effects were considered through the DK3 approximation with a Gaussian nucleus model.

For the occupied orbitals of the alkali and alkaline earth metal atoms, we carried out atomic SCF calculations by using Koga et al. [20] primitives and considering the relativistic effect through the DK3 method with a Gaussian nucleus model. The $(n-1)s$, $(n-1)p$, and ns orbitals were decontracted and augmented by the recommended core-valence correlating sets, NOSeC-CV-dzp, NO-SeC-CV-tzp, and NOSeC-CV-qzp. For the hydrogen atom, Yamamoto and Matsuoka's [21] ($4s$), ($6s$), and ($8s$) sets were decontracted to $\{s31\}$, $\{s411\}$, $\{s5111\}$ and our valence correlating sets [11] $\{p3d3\}$, $\{p21d2\}$, and $\{p111d11f1\}$ were added, respectively. For the oxygen and fluorin atoms, we employed $[3s2p1d]$, $[4s3p2d1f]$, and $[5s4p3d1f1g]$, where the sp sets were taken from Tatewaki and Koga [22] and the $2s$ and $2p$ CGTFs were split into double, triple, and quadruple zeta functions and our correlating $[1d]$, $[2d1f]$, and $[3d2f1g]$ functions [8] were added. Then, these three sets of hydrogen, oxygen, and fluorine were combined with the above mentioned three types of the metal basis sets and are referred to as dzp, tzp, and qzp sets.

Table 4 Comparison of equilibrium internuclear distances (r_e), harmonic vibrational frequencies (ω_e), and dissociation energies (D_0) of the KH and RbH molecules in the ground state

Basis	KH			RbH		
	r_e/Å	ω_e/cm^{-1}	D_0/eV	r_e/Å	ω_e/cm^{-1}	D_0/eV
Valence						
dzp	2.327	919	1.400	2.474	861	1.312
tzp	2.325	936	1.709	2.471	877	1.648
qzp	2.323	949	1.777	2.466	896	1.726
Core-valence						
dzp	2.284	932	1.351	2.420	866	1.249
tzp	2.256	960	1.668	2.380	902	1.601
qzp	2.246	983	1.726	2.370	928	1.668
Core-valence + CPC						
dzp	2.288	931	1.344	2.425	865	1.242
tzp	2.266	958	1.656	2.392	901	1.587
qzp	2.254	980	1.717	2.378	927	1.657
Exptl.	2.240164[a]	986.6484[a]	1.8[b]	2.367[b]	936.9[b]	

[a] See Ref. [25]

[b] See Ref. [26]

Table 5 Calculated equilibrium internuclear distances (r_e), harmonic vibrational frequencies (ω_e), and dissociation energies (D_0) of ten hydrides in the ground state. The experimental values are also given whenever available

Hydride	r_e/Å				ω_e/cm^{-1}				D_0/eV			
	dzp	tzp	qzp	Exptl.	dzp	tzp	qzp	Exptl.	dzp	tzp	qzp	Exptl.
LiH	1.622	1.607	1.594	1.595599[a]	1,347	1,369	1,417	1,405.49805[a]	2.029	2.297	2.388	2.42871[b]
BeH	1.361	1.348	1.342	1.3411[c]	2,007	2,032	2,071	2,061.66[c]	1.567	1.928	2.016	2.03[b]
NaH	1.894	1.891	1.878	1.88703[d]	1,167	1,173	1,189	1,171.968[d]	1.582	1.828	1.727	1.88[b]
MgH	1.736	1.732	1.729	1.729828[e]	1,478	1,515	1,513	1,495.2632[e]	0.918	1.066	1.279	1.34[b]
CaH	2.077	2.036	2.012	2.002366[f]	1,192	1,235	1,284	1,298.3999[f]	1.086	1.501	1.627	≤1.70[b]
SrH	2.237	2.170	2.151	2.1456[b]	1,087	1,141	1,184	1,206.2[b]	1.091	1.503	1.631	≤1.66[b]
CsH	2.580	2.516	2.414	2.4938[b]	814	866	862	891.0[b]	1.167	1.593	1.684	1.81[b]
BaH	2.351	2.258	2.245	2.23175[b]	1,005	1,151	1,169	1,168.31[b]	1.138	1.774	1.925	≤1.95[b]
FrH	2.602	2.557	2.553		833	902	901		1.072	1.476	1.542	
RaH	2.432	2.356	2.350		982	1,109	1,112		0.889	1.450	1.553	

[a] See Ref. [27]

[b] See Ref. [26]

[c] See Ref. [28]

[d] See Ref. [29]

[e] See Ref. [30]

[f] See Ref. [31]

In the CCSD(T) calculations, the $(n-1)s$, $(n-1)p$, and ns electrons of metal atoms, the $1s$ electron of hydrogen, and the $2s$, $2p$ electrons of oxygen and fluorine were correlated, while the $1s$ electrons of oxygen and fluorine were uncorrelated. The dissociation energy was calculated by subtracting the total energies of separated atoms from the molecular total energy at the CCSD(T) level. All molecular calculations were carried out using the MOLCAS64 [23] program system.

3.2 Hydrides

We first performed the calculation for 12 diatomic hydrides AH in their ground states, where A varies from Li to Ra. For the KH and RbH molecules, we also performed valence calculations, which include only the valence correlation, to see the effect of the core correlation. In Table 4, we give the calculated results of the equilibrium internuclear distances (r_e), harmonic vibrational frequencies (ω_e), and dissociation energies (D_0) along with their experimental results.

In Table 4, we find the effects of the core correlation are significant for r_e and ω_e. In the valence calculations of KH, we find that r_e changes only by 0.004 Å as we go from the dzp to qzp set and the error is still 0.083 Å at the qzp set. The ω_e value approaches smoothly to the experimental value, but still differs by 37 cm^{-1} at the qzp set. Inclusion of the core correlation, on the other hand, improves the r_e and ω_e values gradually with an increasing size of basis sets, and we reach a reasonable agreement at the qzp set. For D_0, improvements due to the increasing size of basis sets are observed both in the valence and core-valence calculations, but the convergence of D_0 is slower than r_e and ω_e. At the qzp set, the valence calculation gives almost satisfactory agreement, while the core-valence calculation still differs from the experimental value by 0.074 eV. Iron et al. [7] found analogous errors in core-valence SDCI calculations with quadruple zeta basis sets, but when the basis set size was enlarged to quintuple zetas, the errors were much reduced and the experimental values were essentially reproduced. For RbH, we observe a similar tendency, i.e., significant effects of the core correlation on r_e and ω_e and a slow basis set convergence of D_0. We also examined the basis set superposition error (BSSE) in the core-valence calculations by the use of the counterpoise correction (CPC) method [24]. The effects of BSSE are found to be small for all the sets: 0.01 Å in r_e, 1–3 cm^{-1} in ω_e, and 0.01 eV in D_0.

In Table 5, we summarize the calculated spectroscopic constants for the rest of diatomic hydrides obtained by the core-valence calculations without CPC. For all the cases, the present sets gave a smooth convergence for the spectroscopic constants, and a satisfactory agreement with the experiment is achieved at the qzp sets.

Table 6 Calculated equilibrium internuclear distances (r_e), harmonic vibrational frequencies (ω_e), and dissociation energies (D_0) of alkali dimers and alkaline earth metal oxides in the ground state

Basis	r_e/Å	ω_e/cm^{-1}	D_0/eV	r_e/Å	ω_e/cm^{-1}	D_0/eV
Alkali dimers						
	Li$_2$			Na$_2$		
dzp	2.717	351	0.897	3.132	150	0.621
tzp	2.702	361	1.029	3.109	158	0.741
qzp	2.677	368	1.067	3.036	163	0.797
Exptl.[a]	2.6729	351.43	1.04	3.0788	159.124	0.720
	K$_2$			Rb$_2$		
dzp	4.061	80	0.392	4.393	49	0.326
tzp	4.008	89	0.524	4.318	56	0.462
qzp	3.938	94	0.559	4.244	58	0.492
Exptl.	3.92435[b]	92.39766[b]	0.513717[b]	4.2099[c]	57.781[c]	0.49[a]
	Cs$_2$			Fr$_2$		
dzp	4.903	33	0.264	4.872	26	0.242
tzp	4.779	26	0.394	4.727	49	0.363
qzp	4.739	43	0.428	4.698	33	0.403
Exptl.	4.47[a]	42.022[a]	0.394[a]			
Alkaline earth metal oxides						
	BeO			MgO		
dzp	1.392	1,291	3.055	1.759	733	1.451
tzp	1.347	1,441	4.197	1.746	794	2.286
qzp	1.333	1,480	4.634	1.740	806	2.593
Exptl.[a]	1.3309	1,487.32	4.6	1.749	785.0	3.5
	CaO			SrO		
dzp	1.899	1,002	1.973	1.964	1,159	2.098
tzp	1.988	668	3.095	1.991	335	3.094
qzp	1.852	634	3.990	1.925	644	3.837
Exptl.[a]	1.8221	732.1	$\geq$4.7	1.91983	653.4	4.8

The experimental values are also given whenever available

[a] See Ref. [26]

[b] See Ref. [32]

[c] See Ref. [33]

3.3 Dimers, oxides, and fluorides

We performed the calculation of six alkali metal dimers and four alkaline earth metal oxides. The calculated spectroscopic constants were collected in Table 6. For alkali dimers, we obtain an increasing improvement of the spectroscopic constants, and reach a reasonable agreement with the experimental values at the qzp set. For alkaline earth metal oxides, on the other hand, we observe different tendency. For BeO, we obtained satisfactory agreement

Table 7 Calculated equilibrium internuclear distances (r_e), harmonic vibrational frequencies (ω_e), and dissociation energies (D_0) of fluorides in the ground state

Basis Fluorides	r_e/Å	ω_e/cm^{-1}	D_0/eV	r_e/Å	ω_e/cm^{-1}	D_0/eV
	LiF			BeF		
dzp	1.562	964	4.996	1.411	1,190	4.784
tzp	1.580	896	5.686	1.374	1,238	5.672
qzp	1.566	916	5.997	1.364	1,263	6.003
Exptl.[a]	1.563864	910.34	5.91	1.3610	1,247.36	5.85, 6.26
	NaF			MgF		
dzp	1.908	576	3.820	1.756	741	3.594
tzp	1.924	547	4.642	1.759	713	4.308
qzp	1.924	537	4.895	1.753	713	4.593
Exptl.	1.92594[a]	536[a]	5.3[a], 4.96[b]	1.7500[a]	711.69[a]	4.75[a]
	KF			CaF		
dzp	2.171	442	3.571	1.983	577	3.972
tzp	2.178	431	4.655	1.975	569	4.965
qzp	2.181	426	5.002	1.962	584	5.401
Exptl.[a]	2.17145	428	5.07	1.967	581.1	5.4
	RbF			SrF		
dzp	2.265	388	3.405	1.983	577	3.972
tzp	2.271	378	4.492	1.975	569	4.965
qzp	2.277	373	4.807	1.962	584	5.401
Exptl.[a]	2.270333	376	5.0	2.07537	502.4	5.58
	CsF			BaF		
dzp	2.346	371	3.573	2.195	477	4.172
tzp	2.350	359	4.780	2.180	470	5.415
qzp	2.361	350	5.188	2.181	466	5.808
Exptl.[a]	2.345351	352.56	5.1	2.162	468.9	6.05
	FrF			BaF		
dzp	2.407	361	3.418	1.983	577	3.972
tzp	2.404	354	4.609	1.975	569	4.965
qzp	2.417	339	4.995	1.962	584	5.401

The experimental values are also given whenever available

[a] See Ref. [26]

[b] See Ref. [34]

with the experimental values. For MgO, CaO, and SrO, however, we obtained reasonable agreement for r_e and ω_e, but still have significant discrepancy of D_0 by about 1 eV at the qzp set. This is caused by the multi-configuration character due to the $[\sigma^*(ns_A - 2p\sigma_O)]^2$ configuration, where A is an alkaline earth metal. The single reference theory such as CCSD(T) is not very suitable to these systems.

We also performed the calculation of 12 diatomic fluorides and summarized the resultant spectroscopic constants in Table 7. In all the cases, the present sets gave a smooth convergence for the spectroscopic constants, and a satisfactory agreement with the experiment is achieved at the qzp sets.

Iron et al. [7] performed the calculation of spectroscopic constants of a variety of diatomic molecules involving the molecules treated in this section to show the validity of their basis sets and obtained a similar agreement with the observed values as we did. When the sizes of their basis sets are compared with the present sets, we note their basis sets are about 1.6 times larger than ours: for example, their qzp set for K_2 yields 226 orbitals in D_{2h} symmetry, while ours 140 orbitals. Thus, we conclude that the present basis sets are compact and efficient.

4 Summary

We have constructed correlating CGTF sets describing the core ($(n-1)s$ and $(n-1)p$) and valence (ns) correlation for the 12 alkali and alkaline earth metal atoms, incorporating the relativistic effect through the DK3 approximation for heavy atoms from Cs to Ra. A segmented contraction scheme was used for their compactness and flexibility. The present core correlating sets give about 99 % or more of the core correlation energies calculated by the accurate NO sets of the same size. When the present correlating sets have been applied to the 12 diatomic hydrides, 6 alkali metal dimers, 4 alkaline earth metal oxides, and 12 diatomic fluorides, the spectroscopic constants obtained from the all-electron calculations are in excellent agreement with the experimental values.

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