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REGULAR ARTICLE

Relativistic segmented contraction basis sets with core-valence correlation effects for atoms $_{57}$La through $_{71}$Lu: Sapporo-DK-*n*ZP sets (n = D, T, Q)

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Abstract For the 15 lanthanide atoms $_{57}$La through $_{71}$Lu, we report Sapporo-DK-*n*ZP sets (n = D, T, Q), which are natural extensions of the Sapporo-(DK)-*n*ZP sets for lighter atoms and efficiently incorporate the correlation among electrons in the N through P shells as well as the relativistic effect. The present sets well describe the correlation among the 4s and 4p electrons, which are important in the excitation of 4f electrons. Atomic test calculations of $_{57}$La, $_{58}$Ce, $_{59}$Pr, and $_{60}$Nd at configuration interaction with the Davidson correction level of theory confirm high performance of the present basis sets. Molecular test calculations are carried out for $_{57}$LaF and $_{70}$YbF diatomics at the coupled-cluster level of theory. The calculated spectroscopic constants approach smoothly to the experimental values as the quality of the basis set increases.

Keywords Segmented basis sets · Core-valence correlations · Relativistic all electron calculations · Lanthanide atoms

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1 Introduction

In order to obtain reliable theoretical results for molecules containing lanthanide atoms, both the relativistic and electronic correlation contributions must be considered based on high-quality all-electron basis sets. In the present paper, we construct relativistic DZP, TZP, and QZP contracted (C) Gaussian-type function (GTF) basis sets for the 15 lanthanide atoms $_{57}$La through $_{71}$Lu as a member of the Sapporo-DK-*n*ZP sets [1] for atoms, where the relativistic effects are considered through the third order of Douglas-Kroll-Hess approximation (DK3) [2, 3] and the correlations are considered not only for valence electrons but also for core electrons of the second outermost s and p subshells in the s- and d-block elements, and of the second outermost s, p, and d subshells in the p-block elements. These basis sets show high performance and effectiveness, which stem from the adoption of the segmented contraction scheme. For the lanthanide atoms, we will consider the correlation effects among the 4s–4f, 5s–5d, and 6s subshells. The 4s–4f, 5s, and 5p electrons mutually correlate in a nontrivial manner. Actually, the influence of the 4s and 4p subshells is important in the excitations of the 4f electrons [4]. However, all-electron basis sets available in the literature, such as four-component basis sets by Gomes et al. [5] and ANO basis sets by Roos et al. [6], do not consider these effects. Previously, we constructed [7] relativistic correlating functions for the lanthanide elements as members of NOSeC-DK-*n*ZP (n = D, T, Q) [7–18], in which we considered the correlation effects among the 4f, 5s–5d, and 6s electrons, but not the 4s–4d electrons. In this work, we decided to generate new basis sets *combining* all the core, valence, and correlating functions, where the correlation effects from the 4s–4d subshells are also incorporated.

In Sect. 2, we describe our computational procedures in the generation of new basis sets. Atomic tests for $_{57}$La through $_{71}$Lu and molecular applications to $_{57}$LaF and $_{70}$YbF are given in Sects. 3 and 4, respectively. The following symbols are used throughout this paper: [ ] for CGTFs, ( ) for primitive Gaussians, { } for contraction patterns of CGTFs where powers imply repetition of the same size.

2 Construction of Sapporo-DK-*n*ZP sets

2.1 Minimal-type self-consistent field (SCF) basis sets

First, we construct minimal-type segmented CGTF sets for the ground states of the lanthanide atoms $_{57}$La through $_{71}$Lu, with scalar relativistic effects included through DK3 Hamiltonian [3] using a Gaussian nucleus model [19]. For the optimization of the contraction coefficients and exponents, we used the conjugate direction algorithms [20] following the previous works of Koga et al. [21–23]. In the determination of relativistic CGTF sets, we tested several patterns of contractions, checking the total energy error and the basis set size for practical applications. We finally adopted (943333/8433/74) for $_{57}$La with vacant 4f (943333/8433/743/7) for $_{58}$Ce, $_{64}$Gd, and $_{71}$Lu with occupied 5d, and (943333/8433/74/7) for the rest of lanthanide atoms. In Table 1, we list the DK3 SCF energies, and their errors from the B-spline DK3 Hartree–Fock energies [24]. The error ranges from 0.140 to 0.296 hartree, which is comparable to that of 0.257 hartree in the Xe atom [25].

Table 1 The present SCF energies (hartree)

Atom	Configuration	SCF energy
$_{57}$La	[Xe] $5d^1 6s^2$ (^{2}D)	−8,489.258510 (0.140118)
$_{58}$Ce	[Xe] $4f^1 5d^1 6s^2$ (^{1}G^o)	−8,856.322492 (0.148260)
$_{59}$Pr	[Xe] $4f^3 6s^2$ (^{4}I^o)	−9,233.065740 (0.158088)
$_{60}$Nd	[Xe] $4f^4 6s^2$ (^{5}I)	−9,619.658363 (0.166943)
$_{61}$Pm	[Xe] $4f^5 6s^2$ (^{6}H^o)	−10,016.18225 (0.17650)
$_{62}$Sm	[Xe] $4f^6 6s^2$ (^{7}F)	−10,422.80405 (0.18573)
$_{63}$Eu	[Xe] $4f^7 6s^2$ (^{8}S^o)	−10,839.71275 (0.19608)
$_{64}$Gd	[Xe] $4f^7 5d^1 6s^2$ (^{9}D^o)	−11,266.89099 (0.20455)
$_{65}$Tb	[Xe] $4f^9 6s^2$ (^{6}H^o)	−11,704.28084 (0.21864)
$_{66}$Dy	[Xe] $4f^{10} 6s^2$ (^{5}I)	−12,152.51893 (0.23066)
$_{67}$Ho	[Xe] $4f^{11} 6s^2$ (^{4}I^o)	−12,611.54339 (0.24378)
$_{68}$Er	[Xe] $4f^{12} 6s^2$ (^{3}H)	−13,081.47168 (0.25658)
$_{69}$Tm	[Xe] $4f^{13} 6s^2$ (^{2}F^o)	−13,562.55377 (0.27081)
$_{70}$Yb	[Xe] $4f^{14} 6s^2$ (^{1}S)	−14,054.93591 (0.28489)
$_{71}$Lu	[Xe] $4f^{14} 5d^1 6s^2$ (^{2}D)	−14,558.73920 (0.29583)

The values in parentheses show errors relative to the B-spline SCF energies [24]

We note that the CGTF sets thus constructed can be safely used in molecular calculations with different relativistic models such as DK3 with a point charge nucleus, as are the Sapporo-DK-*n*ZP sets for lighter atoms [25]. All atomic calculations were carried out using the ATOMCI program package [26].

2.2 Determination of standard accurate sets

In the determination of segmented CGTF sets, we need accurate standard sets from which the deviation of our CGTF sets is minimized. We first explain the size of the accurate standard sets. We construct DZP, TZP, and QZP sets, following the definition of the correlation-consistent type of basis set for the basis set size of each subshell. For example, the sizes of DZP, TZP, and QZP sets of $_{58}$Ce, $_{64}$Gd, and $_{71}$Lu atoms with a 5d electron are determined as follows. A minimal set for the occupied atomic orbitals is [6s4p3d1f]. In the DZP set, [1s1p1d1f1 g], [1s1p1d1f], and [1s1p] correlating sets are considered for the N (4s4p4d4f), O (5s5p5d), and P (6s) shells, respectively. The addition of these correlation sets to the minimal set gives [9s7p5d3f1g]. For the TZP set, we increase the correlation function by one for each azimuthal quantum number *l* and add a higher *l* function for each shell. Namely, we increase [1s1p1d1f1g1h], [1s1p1d1f1g], and [1s1p1d] correlating sets for the N, O, and P shells. Thus, the size of the TZP set is [12s10p8d5f3g1h], and similarly the size of the QZP set becomes [15s13p11d8f5g3h1i]. For the DZP set, we additionally included extra one d and one f functions to improve the description of excited states.

In the construction of the standard sets, we used the minimal-type SCF basis set constructed in Sect. 2.1 augmented by (13s12p12d10f8g7h5i) primitives, which are the valence part of well-tempered primitive sets by Huzinaga et al. [27] extended for the g, h, and i azimuthal quantum numbers. We carried out two separate configuration interaction (CI) calculations for core and valence electrons, in which the N shell electrons were considered in a core CI calculation, and the O and P shell electrons were in a valence CI calculation. In these calculations, relativistic effects are considered through the DK3 Hamiltonian with a Gaussian nucleus model. Then we constructed accurate standard DZP, TZP, and QZP sets by selecting the important natural orbitals (NOs) from the resultant inner and valence NO sets.

2.3 Optimization of the segmented Sapporo-*n*ZP sets

The segmented Sapporo-*n*ZP (n = D, T, Q) sets are constructed so as to minimize the deviations from the accurate standard *n*ZP sets. The procedure is summarized as follows:

1. For the occupied core orbitals, 1s–3s, 2p, 3p, and 3d, we used the minimal-type SCF basis set described in Sect. 2.1. For the N, O, and P shell orbitals, we decontracted the 4s–4d, 5s–5d, and 6s minimal-type SCF orbitals and reoptimized the contraction coefficients and orbital exponents to best reproduce the accurate standard sets.
2. Also fully optimized were higher *l* CGTFs of g, h, and i types, which describe the inner correlation effect of the N and O shell electrons. When the numbers of decontracted s, p, d, and f type functions are deficient in the standard size of the *n*ZP set, we added extra optimal s, p, d, and f type primitive GTFs.
3. To determine the contraction patterns of CGTFs, we tested several different patterns and finally we found the best contractions $\{94321^{5}/841^{5}/72^{2}1^{3}/41^{3}/3\}$ for DZP, $\{94321^{7}/841^{7}/721^{5}/31^{4}/21^{2}/2\}$ for TZP, and $\{9431^{10}/841^{9}/71^{8}/31^{6}/1^{4}/1^{3}/2\}$ (from $_{57}$La through $_{59}$Pr) or $\{9431^{10}/841^{9}/71^{8}/31^{6}/1^{5}/1^{3}/2\}$ (from $_{60}$Nd through $_{71}$Lu) for QZP.

In the procedure 1, we added the 5d SCF orbital of the excited state to describe wave functions for the excited states if the 5d subshell is unoccupied in the ground state. Although we did not explicitly consider a 6p-like orbital, it is represented by p correlating functions for the 6s electrons. In the optimization of the contraction coefficients and orbital exponents, we used the conjugate directions algorithm [20] as before [1]. In Table 2, we show the sum of core and valence correlation energies together with its reproduction rate relative to the corresponding sum by the accurate standard sets. The present CGTF sets give high reproduction rates that are 92–97 % in DZP, 95–98 % in TZP, and 98–99 % in QZP.

3 Atomic tests

To test the quality of the present sets, we performed configuration interaction plus quadruple correction by Davidson (CI + Q) [28] calculations on the ground and low-lying excited states of the $_{57}$La, $_{58}$Ce, $_{59}$Pr, and $_{60}$Nd, where the electron correlations were considered in the N, O, and P shells and the relativistic effects were taken into account through the DK3 approximation with a Gaussian nucleus. In order to examine the correlation contribution of N shell electrons, we carried out three types of CI calculations, in which (1) only the 4f electrons are correlated, (2) the 4d and 4f electrons are correlated, and (3) all the electrons in the N shell are correlated. Hereafter, these three different core correlation schemes are referred to as C-1, C-2, and C-3.

The resultant excitation energies are summarized in Table 3 along with the corresponding experimental values [29], where the experimental values are averaged over the total angular momentum quantum number *J*. For the transitions of [Xe]5d^{1}6s^{2} (^{2}D) → [Xe]4f^{1}6s^{2} (^{2}F^{o}) in $_{57}$La and [Xe]4f^{1}5d^{1}6s^{2} (^{1}G^{o}) → [Xe]4f^{2}6s^{2} (^{3}H) in $_{58}$Ce, the number of electrons in the 4f subshell increases. The correlation energy of the 4f electron is larger in magnitude than the 5d electron so that the calculated excitation energy tends to be overestimated. Actually, the excitation energy of $_{57}$La at the SCF level is larger than the experimental value by about 0.8–0.9 eV. Inclusion of electronic correlation

Table 2 Sappro-DK-*n*ZP correlation energies (hartree)

Atom	Configuration (term)	Correlation energy		
		DZP	TZP	QZP
$_{57}$La	[Xe] 5d^{1}6s^{2} (^{2}D)	−0.77478 (92.5 %)	−0.90675 (95.6 %)	−0.98865 (98.8 %)
$_{58}$Ce	[Xe] 4f ^{1}5d^{1}6s^{2} (^{1}G^{o})	−0.78069 (93.7 %)	−0.92371 (97.0 %)	−0.99642 (98.4 %)
$_{59}$Pr	[Xe] 4f ^{3}6s^{2} (^{4}I^{o})	−0.79806 (93.8 %)	−0.96212 (96.8 %)	−1.04769 (98.2 %)
$_{60}$Nd	[Xe] 4f ^{4}6s^{2} (^{5}I)	−0.83267 (94.0 %)	−1.01067 (96.9 %)	−1.10676 (98.5 %)
$_{61}$Pm	[Xe] 4f ^{5}6s^{2} (^{6}H^{o})	−0.87570 (94.4 %)	−1.06770 (97.1 %)	−1.17175 (98.6 %)
$_{62}$Sm	[Xe] 4f ^{6}6s^{2} (^{7}F)	−0.91602 (94.5 %)	−1.12223 (97.2 %)	−1.23438 (98.6 %)
$_{63}$Eu	[Xe] 4f ^{7}6s^{2} (^{8}S^{o})	−0.94613 (94.5 %)	−1.16611 (97.3 %)	−1.28597 (98.7 %)
$_{64}$Gd	[Xe] 4f ^{7}5d^{1}6s^{2} (^{9}D^{o})	−0.93774 (94.7 %)	−1.16184 (97.6 %)	−1.28289 (98.7 %)
$_{65}$Tb	[Xe] 4f ^{9}6s^{2} (^{6}H^{o})	−1.00461 (97.3 %)	−1.31702 (97.6 %)	−1.45798 (98.8 %)
$_{66}$Dy	[Xe] 4f ^{10}6s^{2} (^{5}I)	−1.04858 (97.1 %)	−1.38286 (97.9 %)	−1.53391 (99.0 %)
$_{67}$Ho	[Xe] 4f ^{11}6s^{2} (^{4}I^{o})	−1.16164 (96.1 %)	−1.45795 (98.0 %)	−1.61885 (99.0 %)
$_{68}$Er	[Xe] 4f ^{12}6s^{2} (^{3}H)	−1.22612 (96.5 %)	−1.54184 (98.1 %)	−1.71244 (99.1 %)
$_{69}$Tm	[Xe] 4f ^{13}6s^{2} (^{2}F^{o})	−1.28752 (96.6 %)	−1.62150 (98.2 %)	−1.80343 (99.1 %)
$_{70}$Yb	[Xe] 4f ^{14}6s^{2} (^{1}S)	−1.33784 (96.3 %)	−1.69288 (97.0 %)	−1.87915 (98.7 %)
$_{71}$Lu	[Xe] 4f ^{14}5d^{1}6s^{2} (^{2}D)	−1.31700 (93.2 %)	−1.66781 (98.4 %)	−1.85828 (99.2 %)

The parentheses show the reproduction percentage of the present set relative to accurate NO set of the same size

Table 3 Excitation energies of La, Ce, Pr, and Nd atoms

Atom	Excitation	Method	Scheme	Basis	DZP	TZP	QZP	
$_{57}$La		SCF	–	Present	2.821	2.820	2.753	
	[Xe] $5d^1 6s^2$ (^{2}D)	CI + Q	C-1	Large	2.917	2.737	2.675	
	↓	CI + Q	C-2		2.760	2.474	2.359	
	[Xe] $4f^1 6s^2$ (^{2}F^o)	CI + Q	C-3		2.628	2.272	2.131	
		Exptl. [29]						1.901
$_{58}$Ce		SCF	–	Present	1.558	1.613	1.587	
	[Xe] $4f^{1}5d^1 6s^2$ (^{1}G^o)	CI + Q	C-1		1.479	1.324	1.308	
	↓	CI + Q	C-2		1.411	1.165	1.077	
	[Xe] $4f^2 6s^2$ (^{3}H)	CI + Q	C-3		1.340	1.026	0.938	
		Exptl. [29]						0.799
$_{59}$Pr		SCF	–	Present	−0.078	−0.130	−0.121	
	[Xe] $4f^3 6s^2$ (^{4}I^o)	CI + Q	C-1		0.115	0.209	0.219	
	↓	CI + Q	C-2		0.155	0.319	0.379	
	[Xe] $4f^{2}5d^1 6s^2$ (^{4}I)	CI + Q	C-3		0.200	0.429	0.514	
		CI + Q	C-3	Gomes et al. [5]	0.002	0.378	0.478	
		Exptl. [29]						~0.495
$_{59}$Pr		SCF	–	Present	−0.062	−0.115	−0.106	
	[Xe] $4f^3 6s^2$ (^{4}I^o)	CI + Q	C-1		0.178	0.260	0.271	
	↓	CI + Q	C-2		0.200	0.349	0.409	
	[Xe] $4f^{2}5d^1 6s^2$ (^{4}K)	CI + Q	C-3		0.234	0.448	0.533	
		CI + Q	C-3	Gomes et al. [5]	0.033	0.399	0.495	
		Exptl. [29]						~0.539
$_{60}$Nd		SCF	–	Present	−0.225	−0.275	−0.262	
	[Xe] $4f^4 6s^2$ (^{5}I)	CI + Q	C-1		0.438	0.537	0.544	
	↓	CI + Q	C-2		0.413	0.573	0.621	
	[Xe] $4f^{3}5d^1 6s^2$ (^{5}L^o)	CI + Q	C-3		0.477	0.682	0.749	
		CI + Q	C-3	Gomes et al. [5]	0.271	0.632	0.723	
		Exptl. [29]						~0.845
$_{60}$Nd		SCF	–	Present	1.649	1.646	1.644	
	[Xe] $4f^4 6s^2$ (^{5}I)	CI + Q	C-1		1.279	1.247	1.236	
	↓	CI + Q	C-2		1.267	1.243	1.237	
	[Xe] $4f^{4}6s^2$ (^{5}F)	CI + Q	C-3		1.187	1.179	1.178	
		CI + Q	C-3	Gomes et al. [5]	1.179	1.179	1.178	
		Exptl. [29]						~0.976

effects decreases the excitation energy smoothly as the basis set quality is improved and the number of correlated N shell electron increases. At the C-3 level calculation with QZP, we reach a good agreement with the experiment, where the deviations from the experimental values are only 0.1–0.2 eV for these transitions. In the other transitions except for the last case in $_{60}$Nd, on the other hand, the number of the 4f electrons decreases through the excitation. In this case, the calculated excitation energy tends to be underestimated, and it approaches to the experimental value from below as the quality of the calculation is increased. We obtained excellent excitation energies at the C-3 level with the QZP set: The deviations from the experiments are less than 0.1 eV. We note that in these transitions, the correlation contributions of the N shell electrons including the 4s and 4p electrons are very important. Moreover, a high-quality basis set such as TZP or QZP is also needed to account for these transition energies. On the other hand, in the [Xe]$4f^{4}6s^2$ (^{5}I) → [Xe]$4f^4 6s^2$ (^{5}F) transition of $_{60}$Nd where the electronic configuration is unchanged, the correlation contribution of N shell electrons is rather small.

For comparison, we performed the C-3 calculations on $_{59}$Pr and $_{60}$Nd using the DZP, TZP, and QZP sets constructed from the spin-free relativistic SCF basis set and correlating functions of Gomes et al. [5] following their prescription. The resultant excitation energies show that their basis sets are clearly inferior to the present sets in

Table 4 Timing data in seconds for integral generations of $_{60}$Nd by MOLPRO 2010 on 2 × 2.66 GHz 6-Core Intel Xeon

Size	Basis set	
	Present Sapporo-DK	Gomez et al. [5]
DZP	4.97	5.69
TZP	10.25	26.62
QZP	31.33	110.80

DZP, and nearly equivalent with the present sets in TZP and QZP. In Table 4, we compare the integral generation time. Since the ATOMCI is not oriented to the integral generation of generally contracted basis sets, we used the Molpro program system [30], which performs the integral generation efficiently by calculating unique integrals over primitives once and then applying the contraction through matrix operation. The sizes of their basis sets are slightly larger than ours, but their CPU time in the integral generation is considerably longer than ours. This is because their basis sets use the general contraction scheme in the occupied orbitals like the correlation-consistent basis sets. The advantage of the present set over the Gomes et al.'s set on the compactness and flexibility are clear and stems from the contraction patterns. In the present basis set, the valence, correlating, and even core orbitals, except deep core such as 1s and 2s, are represented in terms of several primitives and a few very short CGTFs.

4 Molecular applications

In order to test the quality of the present basis sets in molecular calculations, we performed SCF and coupled-cluster singles and doubles with non-iterative triples correction (CCSD(T)) calculations with the Sapporo-DK-*n*ZP sets on the $_{57}$LaF and $_{70}$YbF molecules, in which the relativistic effects were considered in the DK3 approximation with the point charge nucleus model, and the electronic correlations were included for the N, O, and P shell electrons of $_{57}$La and $_{70}$Yb, and the L shell electrons of F. We used the Sapporo-*n*ZP sets augmented by diffuse s, p, and d functions for the F atom. All molecular calculations were performed using the MOLPRO 2010 program system [30].

4.1 LaF

The calculated spectroscopic data for the ground state and two excited states of $_{57}$LaF are shown in Table 5 and

Table 5 Spectroscopic constants of the LaF molecule

State	Method	r_e (Å)	ω_e (cm^{-1})	T_e (eV)	D_e (eV)
$^1\Sigma^+$	CCSD(T)/DZP	2.067	558.3	0	6.62[a]
	CCSD(T)/TZP	2.032	573.0	0	6.78[a]
	CCSD(T)/QZP	2.026	577.4	0	6.81[a]
	CCSD(T) [31]	2.027 (2.034)[b]	578 (574)[b]	0	6.92 (6.83)[b]
	CI + Q [32]	2.057	583.4	0	
	MC-QDPT[c] [4]	2.052	533.5	0	
	Exptl. [35, 36]	2.0234	575.20538	0	6.89 ± 0.14[d]
$^3\Delta$	CCSD(T)/DZP	2.103	524.1	0.403	
	CCSD(T)/TZP	2.068	534.6	0.347	
	CCSD(T)/QZP	2.060	538.6	0.277	
	CI + Q [32]	2.095	543.5	0.241	
	MC-QDPT[c][4]	2.085	543.0	0.275	
	Exptl. [37]	2.0550	541.92046	0.231	
$^3\Pi$	CCSD(T)/DZP	2.144	499.7	1.023	
	CCSD(T)/TZP	2.107	504.6	0.979	
	CCSD(T)/QZP	2.099	507.8	0.920	
	CI + Q [32]	2.117	517.8	0.895	
	MC-QDPT[c] [4]	2.115	536.8	1.018	
	Exptl. [38]	2.09183	511.5978	0.864	

[a] The values are corrected by the experimental *J* splitting [29] at the dissociation limit

[b] The basis set superposition error corrected values are in parentheses

[c] The energies calculated by the multiconfigurational quasidegenerate perturbation theory (MC-QDPT) are averaged over the total electronic angular momentum along the molecular axis

[d] D_e is calculated from the experimental D_0

compared with other theoretical and available experimental data. The ground state has the electronic configuration of ($_{57}La^{+3}$ + F^-) $6s^2$, where two electrons in the 6s subshell move around the core that consists of $_{57}La^{+3}$ (=[Xe]) and F^- (=[Ne]). The two triplet excited states, Δ and Π, arise from the same one electron excitation from the 6s to 5d orbital. The calculated spectroscopic data are improved smoothly as the quality of the basis increases, and we reach satisfactory agreements with the experimental data at the QZP set, where the deviations from the experimental data are less than 0.01 Å and 4 cm^{-1} for the bond length r_e and the vibrational frequency ω_e, respectively. For the ground $^1\Sigma^+$ state, we also calculated the dissociation energy D_e, which shows the similar tendency with r_e and ω_e, and agrees with the experimental data within 0.1 eV. These agreements are almost the same as those of Cao et al. [31] and much better than those of the other works [4, 32]. Although the excitation energies T_e approach to the experimental values, we still have small deviations of 0.05–0.06 eV at the QZP set which are slightly larger than Fahs's deviations [32]. For both states, the correlation effects of the 4s–4d electrons are not so large, because both states arise from the 6s → 5d excitation, and the 4f electron does not participate in the excitation process.

4.2 YbF

In Table 6, we show the calculated spectroscopic data for the ground state of $_{70}$YbF together with other theoretical results and experimental data for comparison. For the bond

Table 6 Spectroscopic constants of the YbF ($^2\Sigma$) molecule

Property	Authors	Method	Scheme	DZP	TZP	QZP	Others
r_e (Å)	Present	SCF	–	2.068	2.063	2.061	
		CCSD(T)	C-1	2.051	2.037	2.027	
			C-2	2.067	2.040	2.028	
			C-3	2.064	2.041	2.029	
	Gomes et al. [5]	SCF	–	2.0627	2.0592	2.0585	(2.0579)[a]
		CCSD(T)	C-1	2.0756	2.0399	2.0338	(2.0289)[a]
	Heiberg et al. [33]	CCSD(T)	C-1				2.03
	Cao et al. [31]	CI + Q	C-2				2.022 (2.034)[b]
	Su et al. [34]	UCCSD(T)	C-1				2.0127 (2.185)[c]
	Exptl. [39]						2.0165
ω_e (cm^{-1})	Present	SCF	–	490.9	491.2	491.8	
		CCSD(T)	C-1	500.8	497.1	503.7	
			C-2	531.1	501.6	505.0	
			C-3	521.3	501.8	504.7	
	Gomes et al. [5]	SCF	–	489.5	491.8	491.9	(492.0)[a]
		CCSD(T)	C-1	610.9	539.8	534.1	(528.2)[a]
	Cao et al. [31]	CI + Q	C-2				514 (502)[b]
	Su et al. [34]	UCCSD(T)	C-1				566.8 (447.98)[c]
	Exptl. [40]						506.6674
D_e (eV)	Present	SCF	–	3.93[d]	3.92[d]	3.90[d]	
		CCSD(T)	C-1	4.93[d]	5.03[d]	5.06[d]	
			C-2	4.90[d]	5.01[d]	5.04[d]	
			C-3	4.90[d]	5.01[d]	5.04[d]	
	Gomes et al. [5]	SCF	–	3.77	3.96	3.95	(3.95)[a]
		CCSD(T)	C-1	4.85	4.98	5.05	(5.10)[a]
	Heiberg et al. [33]	CCSD(T)	C-1				4.82
	Cao et al. [31]	CI + Q	C-2				5.36 (5.22)[b]
	Su et al. [34]	UCCSD(T)					6.90 (6.03)[c]
	Exptl. [36]						5.44 ± 0.10

[a] Extrapolated values are in parentheses

[b] The basis set superposition error corrected values are in parentheses

[c] All-electron results are in parentheses

[d] The values are corrected by the experimental J splitting [29] at the dissociation limit

length r_e and the dissociation energy D_e, the dependence on the quality of the basis sets and on the size of the correlated core is rather small, where the deviations from the experimental values are less than 0.03 Å for r_e and 0.5 eV for D_e. We have a reasonable agreement with the experimental value at the QZP set with the C-3 core correlation, in which the deviation is 0.013 Å and 0.4 eV for r_e and D_e, respectively. For the vibrational frequency ω_e, we observe a convergence to the experimental value when the quality of the basis set increases. At the QZP set with the C-3 core correlation, we reach a satisfactory agreement with the deviation of 2 cm^{-1}. This agreement seems to be better than those of the other works [5, 31, 33, 34]. The size of correlated core does not show apparent influence on ω_e when the TZP and QZP basis sets are used. We see the similar basis set dependence in the results by Gomes et al. [5], who did SCF-CCSD(T) with four-component relativistic calculations using all-electron basis sets. They pointed out the existence of a perturbing state near the minimum, which may cause the change of spectroscopic data. Actually, we also found a large T1 diagnostic value, which is defined as the norm of the singles amplitude vector divided by the square root of the number of electrons, in the vicinity of CCSD(T) potential curves. Thus, if the perturbing state is explicitly considered, the present spectroscopic data may be changed slightly.

5 Summary

We developed all-electron relativistic segmented-type basis sets for the 15 lanthanide atoms $_{57}$La through $_{71}$Lu as a member of Sapporo-DK-*n*ZP sets (n = D, T, Q), which efficiently incorporate the correlation among electrons in the valence and core shells as well as the relativistic effect. For the lanthanide atoms, we considered the correlation among the N, O, and P shell electrons. The new basis sets give more than 90 % of the N, O, and P shell correlation energies produced by the accurate NOs of the standard size.

In the test calculations on the $_{57}$La, $_{58}$Ce, $_{59}$Pr, and $_{60}$Nd atoms, we showed the correlation effects from N shell including the 4s and 4p electrons are important to obtain reliable excitation energies when the 4f subshell participates the excitation. The calculated excitation energies approach smoothly to the experimental value as the number of correlated N shell electrons increases and the quality of the basis sets is improved. When all electrons in the N shell are correlated with the QZP set, the deviations from the experiment are less than 0.2 eV.

Molecular test calculations were performed for $_{57}$LaF and $_{70}$YbF diatomics at the CCSD(T) level. For two excited states of $_{57}$LaF, the correlation effects of the N shell electrons are not so large, because these states arise from the 6s → 5d excitation and the 4f electron does not participate in the excitation process. The calculated spectroscopic constants for the two molecules are improved smoothly as the quality of the basis increases, and we reach satisfactory agreements with the experimental data at the QZP set, where the deviations from the experimental values are less than 0.013 Å and 4 cm^{-1} for r_e and ω_e, respectively. All the basis sets developed in this work are available at the web site http://setani.sci.hokudai.ac.jp/sapporo/, where these basis sets are provided in appropriately formatted forms for popular electronic program packages such as Gaussian, Gamess, Molpro, Molcas, Turbomole, Dirac, Nwchem, and Alchemy2. The Sapporo-(DK)-*n*ZP sets have been implemented in the Gamess program packages and can be used by a simple key word in input data.

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