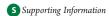# Segmented Contracted Douglas−Kroll−Hess Adapted Basis Sets for Lanthanides

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Ⓢ *Supporting Information*

ABSTRACT: Segmented contracted scalar-relativistic (23s16p12d6f)/[18s12p9d3f] all-electron basis sets for lanthanides La−Lu primarily for use in second-order Douglas−Kroll−Hess density functional calculations are presented. Atomic test calculations at the scalar-relativistic Hartree−Fock level reveal an accurate description of the first to fourth ionization potentials as well as low-energy d−f and d−p excitation energies; i.e., reference data obtained with optimized (34s28p22d16f) even-tempered basis sets are reproduced with mean absolute errors of 0.003 (IP_1), 0.013 (IP_2), 0.030 (IP_3), 0.098 (IP_4), 0.070 (d−f), and 0.018 (d−p) eV. Results of molecular test calculations are presented for the lanthanide trihalides LnX_3 (Ln = La−Lu, X = F, Cl, Br, I) at the PBE0 hybrid density functional theory level. Compared to recently published basis sets of identical size, the sets proposed here show substantially smaller errors in the atomic test calculations as well as lower total energies and produce results of similar accuracy in the molecular calibration study.

1. INTRODUCTION

Several Gaussian basis sets are nowadays available from literature for accurate wave-function-based relativistic all-electron (AE) quantum chemical calculations of lanthanide systems when using the Douglas−Kroll−Hess (DKH) Hamiltonian.[1−4] Hirao and co-workers optimized (27s23p15d10f) basis sets at the Hartree−Fock (HF) level for Ce to Lu for use with the third-order DKH (DKH3) Hamiltonian, both for a point nucleus as well as for a finite nucleus with a Gaussian charge distribution.[5,6] The corresponding La basis sets do not contain f functions, i.e., (27s23p15d). Koga and collaborators developed segmented contracted correlating basis sets for Ce to Lu also to be used with the DKH3 Hamiltonian.[7] The underlying primitive set sizes are (30s26p23d16f10g10h) for Ce to Tb, (29s25p22d15f9g9h) for Dy to Yb, as well as (28s24p21d14f9g9h) for Lu. A corresponding basis set for La is based on a (30s24p20d15f10g10h) primitive set.[8] Quite recently, Roos et al. published generalized contracted (25s22p15d11f4g2h)/[12s11p8d7f4g2h] atomic natural orbital[9] (ANO-RCC) basis sets for Ce to Lu for use with the second-order DKH (DKH2) Hamiltonian.[10] The corresponding La basis set is slightly smaller, i.e., (24s21p15d11f4g)/[11s10p8d5f3g]. Averaged density matrices for the ground state of the atom and the monocation as well as one excited state of the atom were diagonalized, and the coefficients for all orbitals with occupation numbers larger than 10^{-6} were kept for the contractions. Basis sets of pVXZ quality (X = D, T, Q) as well as minimal basis sets can be derived by omitting a suitable number of least populated ANO contractions in each angular symmetry. For an overview of DKH-adapted basis sets covering also elements other than the lanthanides, the reader is referred to recent review articles by Peterson[11] and Nakajima and Hirao.[4]

Recently, Pantazis and Neese proposed loosely segmented contracted (23s16p12d3f)/[18s12p9d3f] (La) and (23s16p12d6f3g)/[18s12p9d3f3g] (Ce−Lu) AE relativistic contracted (SARC) basis sets for the lanthanides to be used in the framework of density functional theory (DFT) in connection with either the DKH or the zeroth-order regular approximation (ZORA) Hamiltonian.[12] The basis sets were tested for 56 lanthanide trihalides LnX_3 (Ln = Ce−Lu; X = F, Cl, Br, I) at the DKH level using the PBE0 hybrid functional of Adamo and Barone,[13] which is obtained from the Perdew, Burke, and Ernzerhoff (PBE) gradient corrected density functional[14,15] by admixing 25% of the exact exchange. The lanthanum trihalides were not considered, but some results for La as well as Lu diatomics LnX (Ln = La, Lu; X = H, O, F) were provided. The authors emphasized that their basis sets, despite their compact size, provide a balanced treatment of different electronic configurations of the lanthanides. Thus, they can be used with confidence for the prediction of energetic properties and provide an unbiased description of processes involving changes in oxidation states and the concomitant changes of the 4f and 5d occupation numbers. Pantazis and Neese also proposed an AE DKH2 or ZORA treatment applying their basis sets as a very efficient alternative to effective core potentials (ECPs) in routine DFT studies of chemically relevant systems.

In the present contribution, we first compare the accuracy of the SARC DKH2 basis sets at the HF level for the first four ionization potentials as well as the low-energy f−d and f−p excitations to results obtained with scalar-relativistic Wood−Boring (WB) adjusted ab initio pseudopotentials (PP) and corresponding standard segmented contracted (14s13p10d8f6g)/[10s8p5d4f3g] valence basis sets[16,17] as well as with near-HF-limit AE DKH2 and DKH3 results obtained with optimized uncontracted even-tempered (34s28p22d16f) basis sets. Since the results obtained with the SARC basis sets are found to be in an overall lesser agreement with the reference data than the PP results, we present (23s16p12d6f)/[18s12p9d3f] DKH2 basis sets using the same contraction pattern as the SARC sets, but performing

significantly better and also leading to substantially lower total energies. Second, we present a calibration study for the lanthanide trihalides LnX_3 (Ln = La—Lu, X = F, Cl, Br, I) at the PBE0 density functional theory level and show that the new basis sets lead to equally good results for geometries and atomization energies as the SARC basis sets, despite the absence of very diffuse functions. A brief preliminary report on the performance of the new basis sets in atomic calculations was already given in a discussion of the accuracy and efficiency of density functional calculations applying 4f-in-core PPs on these systems.[18]

2. COMPUTATIONAL DETAILS

The HF and DFT calculations reported here were performed with the MOLPRO program system[20] using the general-order DKH (DKHn) routines of Hess and co-workers.[3] In the atomic HF calculations, symmetry breaking was avoided by calculating a state average including all components of the LS state under consideration by means of the multiconfiguration self-consistent field (MCSCF) code[21,22] and applying the suitable orbital occupation number restrictions. In order to obtain DKH2 HF reference data, an even-tempered (30s24p18d12f) basis set was optimized by minimizing the sum of the lowest LS state energies of the $4f^{n+1}6s^2$, $4f^n5d^16s^2$, and $4f^n6s^26p^1$ configurations.[23] Since an energy optimization will usually not produce diffuse enough functions, the basis sets were systematically increased by adding n times (1s1p1d1f), keeping the center of gravity as well as the ratio between the exponents fixed. For $n = 4$, the changes in the total energy dropped to below 1 mH (milli-Hartree), and the f—d and f—p excitation energies were typically converged to 0.001 eV. The largest (34s28p22d16f) basis sets thus result by an addition of two tight and two diffuse functions for each angular symmetry to the final (30s24p18d12f) uncontracted even-tempered set. Only this largest set was applied in the evaluation of the DKH2 first to fourth ionization potentials as well as the corresponding DKH3 calculations. The DKH2 ground state energies are found to be slightly lower than the values reported by Pantazis and Neese for their extended universal Gaussian basis sets (34s24p20d14f). Although our total energies are also not fully converged, we think that our ionization potentials and excitation energies are within 0.01 eV of the HF limit.

In order to derive segmented contracted (23s16p12d6f)/[18s12p9d3f] DKH2 basis sets similar to the SARC sets of Pantazis and Neese,[12] a (22s15p11d5f) set was first energy optimized for La—Lu as described above for the even-tempered sets. Thereafter, keeping the (22s15p11d5f) set fixed, one diffuse function for each angular momentum symmetry was optimized in the same manner yielding a (23s16p12d6f) uncontracted set. The derivation of the contraction coefficients from the eigenvectors of various averaged density matrices was explored; however, the adoption of the coefficients for the lowest state of $4f^{n+1}6s^2$ for La—Yb and $4f^n5d^16s^2$ for Lu led to the best overall results. It should be noted that, similar to Pantazis and Neese, the basis sets were derived entirely at the HF level of theory, although they are intended to be later used in DFT calculations. However, in contrast to Pantazis and Neese, La is treated identically to the other lanthanides Ce to Lu, since it is well-known that, although the 4f shell is not occupied in the La ground state, a flexible enough f function set is needed for accurate molecular results.[19]

The pseudopotential (PP) calculations reported here for comparison used the WB adjusted energy-consistent PPs of the Stuttgart type[16,24] and corresponding (14s13p10d8f6g)/[10s8p5d4f3g]

segmented contracted valence basis sets.[25] Although the associated (14s13p10d8f6g)/[6s6p5d4f3g] generalized contracted valence basis sets[24] are more compact and lead to much better total valence energies, we use the segmented contracted sets here in order to get an unbiased comparison with the AE DKH segmented contracted basis sets.

The molecular calculations on the lanthanide trihalides LnX_3 (Ln = La—Lu; X = F, Cl, Br, I) were performed with the PBE0 hybrid functional of Adamo and Barone,[13] which is based on the Perdew, Burke, and Ernzerhof (PBE) gradient corrected functional.[14] This functional was also used in the study of Pantazis and Neese and turned out to give the overall best results in our recent PP study of the lanthanide trihalides.[18,26] Since the lanthanum trihalides have not been included in the study by Pantazis and Neese, the corresponding calculations were carried out also using their La basis set. However, since their basis set does not provide enough f functions, the corresponding results are not included when calculating the mean absolute deviations between theoretical and recommended or experimental reference data. The basis sets applied for the halides, i.e., relativistically recontracted polarized triple-ζ basis sets, were taken from the ORCA basis set library.[27] It should be noted that these basis sets only keep the innermost contraction for s and p symmetry and thus are in fact larger than their nonrelativistic polarized triple-ζ counterparts. The DKH2 sets denoted as TZVP in the ORCA basis set library, i.e., F (11s6p1d)/[6s3p1d], Cl (14s9p1d)/[8s4p1d], Br (17s13p7d)/[10s8p3d], and I (19s15p10d)/[12s10p6d], were applied in DFT calculations using the ORCA code,[27] whereas extended DKH2 sets denoted as TZVPP, i.e., F (11s6p2d1f)/[6s3p2d1f], Cl (14s9p2d1f)/[8s4p2d1f], Br (17s13p8d1f)/[10s8p4d1f], and I (19s15p11d2f)/[12s10p7d2f], were applied in calculations using MOLPRO.[20,28] For the lanthanides, the (23s16p12d6f)/[18s12p9d3f] sets presented here as well as the SARC sets of Pantazis and Neese were used. A g set was not added, since it was found to lead only to slight changes at the DFT level in test calculations; i.e., the bond lengths and the atomization energies of the lanthanide triiodides LnI_3 (Ln = La—Lu) changed on average by 0.003 Å and 0.04 eV, respectively. These values are far below the experimental errors bars and most likely smaller than errors introduced by the usage of DFT.

The results reported here refer to the unrestricted Kohn—Sham formalism and a single Slater determinant as a model wave function. The determinant leading to the lowest total energy was searched for by applying successively all possible rotations between the differently occupied 4f orbitals. The DFT calculations were performed in C_1 symmetry; i.e., all orbital rotations and mixings were allowed by symmetry. However, except as otherwise noted, C_{3v} symmetry was imposed on the molecular structure during the optimization.[23] The target accuracy for integration within the MOLPRO DFT module[20,28] was changed to 10^{-11} or better, compared to a default value of 10^{-6}. The calculations with the SARC basis sets were repeated here with the ORCA DFT module,[27] since from the publication of Pantazis and Neese[12] it is not entirely clear how the open f shells were treated and to which atomic and molecular states or averages the atomization energies refer.[29,30]

The destabilization of chemical bonds by spin—orbit (SO) splitting is a well-known effect for heavy element molecules,[31,32] since typically the atomic total energy SO lowerings are larger than the molecular ones. For halogen compounds, the SO induced reductions of the atomization energies might roughly amount to the values one may estimate from the experimental

Table 1. Ground State DKH2 Hartree−Fock Energies (Hartree) Obtained with the Proposed Basis Sets of This Work in Comparison to the SARC Basis Sets of Pantazis and Neese[12] and Near HF-Limit Values Obtained with Optimized Uncontracted Even-Tempered (34s28p22d16f) Sets

Ln		this work		SARC		near HF
		E	error	E	error	E
La	$5d^1 6s^2\ ^2D$	−8486.3096	0.1109	−8485.4449	0.9756	−8486.4205
Ce	$4f^1 5d^1 6s^2\ ^3F$	−8853.0578	0.2367	−8852.0936	1.2009	−8853.2945
Pr	$4f^3 6s^2\ ^4I$	−9229.4752	0.2729	−9228.3765	1.3716	−9229.7481
Nd	$4f^4 6s^2\ ^5I$	−9615.7139	0.2979	−9614.4993	1.5125	−9616.0118
Pm	$4f^5 6s^2\ ^6H$	−10011.8533	0.3276	−10010.5149	1.6660	−10012.1809
Sm	$4f^6 6s^2\ ^7F$	−10418.0751	0.3617	−10416.6038	1.8330	−10418.4368
Eu	$4f^7 6s^2\ ^8S$	−10834.5405	0.4029	−10832.9265	2.0169	−10834.9434
Gd	$4f^7 5d^1 6s^2\ ^9D$	−11261.2456	0.4485	−11259.5479	2.1462	−11261.6941
Tb	$4f^9 6s^2\ ^6H$	−11698.1351	0.4886	−11696.1825	2.4412	−11698.6237
Dy	$4f^{10} 6s^2\ ^5I$	−12145.8345	0.5376	−12143.6953	2.6768	−12146.3721
Ho	$4f^{11} 6s^2\ ^4I$	−12604.2724	0.5914	−12601.9349	2.9289	−12604.8638
Er	$4f^{12} 6s^2\ ^3H$	−13073.6050	0.6408	−13071.0476	3.1982	−13074.2458
Tm	$4f^{13} 6s^2\ ^2F$	−13554.0235	0.7054	−13551.2397	3.4892	−13554.7289
Yb	$4f^{14} 6s^2\ ^1S$	−14045.7231	0.7696	−14042.6902	3.8025	−14046.4927
Lu	$4f^{14} 5d^1 6s^2\ ^2D$	−14548.7669	0.8521	−14545.6043	4.0147	−14549.6190
m.a.e.			0.4696		2.3516	

atomic $^2P_{3/2}-^2P_{1/2}$ SO splittings,[33] i.e., LnF_3, −0.050; $LnCl_3$, −0.109; $LnBr_3$, −0.456; and LnI_3, −0.942 eV. The situation however is more complex due to the atomic-like character the open Ln 4f shell retains in the LnX_3 molecules. In those few cases where the 4f occupation number is the same in the free Ln atom and the LnX_3 molecule, the contributions from the 4f shell may approximately cancel, and a further SO induced reduction of the atomization energies only results from the atomic SO splitting of the 5d shells, e.g., for LaX_3, CeX_3, GdX_3, and LuX_3 (X = F, Cl, Br, I). However, the majority of cases involve different 4f occupations in the Ln atom and the LnX_3 molecule. The 4f SO contributions may not cancel and cannot be simply estimated on the basis of atomic data. Therefore, atomic and molecular SO contributions to the total energy were calculated using the MOLPRO code[20,34] at the DKH2 RHF level using the Breit−Pauli Hamiltonian in quasi-degenerate first-order perturbation theory. To the best of our knowledge, such corrections have not been included in previous studies of the lanthanide trihalides,[12,35−41] except for a relativistic AE DFT study by Adamo and Maldivi.[42] These corrections of the atomization energies were only derived for the basis sets proposed here; however, they were also applied to the scalar-relativistic DKH2 results obtained with the Ln basis sets of Pantazis and Neese[12] for comparison to experimental data.

3. RESULTS AND DISCUSSION

The following section summarizes results for atomic test calculations at the HF level and molecular test calculations on the lanthanide trihalides LnX_3 (Ln = La−Lu; X = F, Cl, Br, I) at the DFT level. For a few cases, results of HF and coupled cluster calculations with single, double, and perturbative triple excitations (CCSD(T)) performed with the MOLPRO code[20,43,44] are also reported for comparison.

3.1. Atomic Calculations. One criterion on which to judge the quality of a basis set is the total energy. The ground state HF energies derived with the proposed basis sets are between 0.87

(La) and 3.16 (Lu) Hartree lower than the energies obtained with the SARC basis sets,[12] cf. Table 1. The total ground state energies of the new sets are still at least between 0.11 (La) and 0.85 (Lu) Hartree above the HF limit (mean absolute error (m.a.e.) 0.47 hartree), which is most likely close to the values obtained with our optimized uncontracted even-tempered (34s28p22d16f) sets. The corresponding errors of the sets of Pantazis and Neese are between 0.98 (La) and 4.01 (Lu) Hartree (m.a.e. 2.35 hartree). Our estimates of the DKH2 HF limit are for all 15 lanthanide atoms lower than the values obtained by Pantazis and Neese with (34s24p20d14f) sets based on the universal Gaussian basis sets (UGBS) of de Castro et al.[45,46] Our HF results for the SARC basis sets in some cases deviate from the spin-averaged restricted open-shell HF (ROHF) values published by Pantazis and Neese.[12] We can only speculate about the reasons and want to point out that in our calculations symmetry breaking is avoided; i.e., all components of the LS state under consideration are calculated and are degenerate. Moreover, in corresponding nonrelativistic calculations, we approach finite difference HF results obtained with the atomic code MCHF77[47] for the LS state.

The open 4f shell causes various difficulties in calculations on lanthanide systems, e.g., large differential relativistic effects usually destabilizing states with high 4f occupation and large counteracting correlation effects stabilizing states with high 4f occupation have to be dealt with.[48,49] Such problems become relevant, e.g., for the calculation of the LnX_3 atomization energies, since in these molecules according to the ionic charge distribution $Ln^{3+}(X^-)_3$ the Ln^{3+} centers have a $4f^n$ configuration (n = 0−14 for La−Lu), whereas in the ground states of the neutral Pr−Eu and Tb−Yb atoms one has a $4f^{n+1} 6s^2$ configuration.[50] Thus, only for La, Ce, Gd, and Lu, where the neutral atoms have a $4f^n 5d^1 6s^2$ configuration, may one expect a rough cancellation of differential relativistic and correlation effects in the calculation of the atomization energies.

Aside from questions of the accuracy of the relativistic Hamiltonian itself and the applied density functional for the evaluation of $4f^{n+1} 6s^2 - 4f^n 5d^1 6s^2$ energy differences, it is also

Table 2. First to Fourth AE DKH2 Ionization Potentials, $4f^n5d^16s^2 \to 4f^{n+1}6s^2$ and $4f^n5d^16s^2 \to 4f^n6s^26p^1$ Excitation Energies Obtained at the HF Level with the (34s28p22d16f) Basis Sets (DKH2 Limit), and the (23s16p12d6f)/[18s12p9d3f] Segmented Contracted Sets of This Work As Well As the SARC Basis Sets of Pantazis and Neese[a,b,12]

	IP$_1$			IP$_2$			IP$_3$		
Ln	DKH2 limit	this work	SARC	DKH2 limit	this work	SARC	DKH2 limit	this work	SARC
La	4.37	4.37	4.40	10.36	10.36	10.35	18.10	18.10	18.07
Ce	4.56	4.55	4.57	11.14	11.30	11.47	18.24	18.11	17.97
Pr	4.43	4.43	4.44	9.89	9.89	9.91	19.68	19.60	19.39
Nd	4.47	4.47	4.48	10.04	10.04	10.06	19.81	19.75	19.67
Pm	4.52	4.52	4.52	10.19	10.19	10.21	19.83	19.80	19.80
Sm	4.56	4.56	4.56	10.34	10.34	10.36	21.05	21.03	21.07
Eu	4.59	4.59	4.60	10.48	10.47	10.50	22.73	22.72	22.78
Gd	4.79	4.79	4.80	11.36	11.37	11.38	19.51	19.51	19.51
Tb	4.76	4.76	4.76	10.71	10.71	10.73	17.62	17.65	17.84
Dy	4.83	4.83	4.84	10.82	10.82	10.84	18.85	18.87	19.07
Ho	4.91	4.91	4.92	10.93	10.93	10.95	18.50	18.48	18.74
Er	4.99	4.98	5.00	11.04	11.04	11.07	18.10	18.08	18.35
Tm	5.07	5.06	5.07	11.16	11.15	11.18	19.21	19.20	19.47
Yb	5.14	5.13	5.15	11.26	11.26	11.28	20.92	20.90	21.16
Lu	4.35	4.35	4.34	12.59	12.59	12.61	19.94	19.94	19.97
MAD	0.000	0.003	0.009	0.000	0.013	0.041	0.000	0.030	0.153
	0.003	0.006	0.005	0.006	0.016	0.035	0.009	0.027	0.155

	IP$_4$			d−f			d−p		
Ln	DKH2 limit	this work	SARC	DKH2 limit	this work	SARC	DKH2 limit	this work	SARC
La	49.89	49.90	49.89	2.74	2.96	a)	1.86	1.84	1.81
Ce	34.90	34.67	34.30	1.34	1.48	1.63	2.12	2.13	2.13
Pr	37.23	37.11	36.76	0.11	0.21	0.48	2.10	2.12	2.15
Nd	38.93	38.88	38.82	0.26	0.33	0.48	2.21	2.24	2.27
Pm	39.17	39.18	39.40	0.52	0.57	0.64	2.27	2.30	2.31
Sm	39.31	39.37	39.79	−0.47	−0.43	−0.41	2.26	2.30	2.29
Eu	40.81	40.91	41.42	−2.09	−2.07	−2.09	2.09	2.14	2.12
Gd	42.83	42.94	42.93	4.68	4.67	5.14	1.72	1.74	1.72
Tb	35.25	35.42	36.45	3.24	3.23	3.06	1.87	1.89	1.88
Dy	37.46	37.63	38.62	2.11	2.09	1.93	1.79	1.81	1.79
Ho	38.95	39.06	40.10	2.11	2.08	1.89	1.32	1.33	1.31
Er	38.73	38.83	39.92	2.42	2.36	2.18	1.05	1.05	1.03
Tm	38.45	38.57	39.66	1.61	1.57	1.38	1.14	1.14	1.11
Yb	39.84	39.95	41.01	0.10	0.05	−0.13	1.12	1.12	1.10
Lu	41.85	41.85	42.18				0.30	0.30	0.30
MAD	0.000	0.098	0.667	0.000	0.070	0.215	0.000	0.018	0.024
	0.008	0.103	0.673	0.008	0.064	0.218	0.005	0.020	0.023

[a] The results are for the lowest LS states (cf. Supporting Information). The mean absolute deviations (MAD) listed in the first line at the bottom refer to the AE DKH2 near HF results from this table, those in the second line to corresponding DKH3 data from Table 3. [b] Value 10.66 eV not included in MAD

important to assess the quality of the applied basis set. Tables 2 and 3 present DKH2 and DKH3 AE HF results, respectively, obtained with the large optimized uncontracted even-tempered (34s28p22d16f) basis sets for ionization potentials and excitation energies, which are assumed to be quite close to the basis set limit. Reduced basis sets containing one or two primitives for each angular quantum number less virtually give the same values. The differences between the DKH2 and DKH3 results are quite small, and it thus may be hoped that the DKH2 Hamiltonian provides already a quite good scalar-relativistic description for lanthanide systems.

Table 2 also lists the DKH2 HF results obtained with the SARC basis sets of Pantazis and Neese.[12] The errors are quite small for the first and second ionization potentials, but they amount to several tenths of an electronvolt for the third and fourth ionization potentials (mean absolute deviations (MAD) of 0.01, 0.04, 0.15, and 0.67 eV for IP$_1$, IP$_2$, IP$_3$, and IP$_4$, respectively), especially in the cases where the 4f occupation is changing. These results can be compared to those obtained with the WB-adjusted small-core PPs[16,24] and their corresponding standard segmented contracted (14s13p10d8f)/[10s8p5d4f] basis sets[25] listed in Table 3 (MAD = 0.04, 0.13, 0.11, and 0.32 eV).

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Table 3. First to Fourth AE DKH3 Ionization Potentials, $4f^n5d^16s^2 \rightarrow 4f^{n+1}6s^2$ and $4f^n5d^16s^2 \rightarrow 4f^n6s^26p^1$ Excitation Energies Obtained at the HF Level Obtained with the (34s28p22d16f) Basis Sets (DKH3 Limit), and Corresponding Small-Core PP[16] Results Using the (14s13p10d8f)/[10s8p5d4f] Segmented[24] As Well As the (14s13p10d8f)/[6s6p5d4f] Generalized[25] Valence Basis Sets[a]

	IP$_1$			IP$_2$			IP$_3$		
Ln	DKH3 limit	PP seg.	PP gen.	DKH3 limit	PP seg.	PP gen.	DKH3 limit	PP seg.	PP gen.
La	4.38	4.40	4.39	10.35	10.35	10.36	18.10	18.06	18.06
Ce	4.56	4.62	4.62	11.15	11.18	11.20	18.23	18.29	18.29
Pr	4.43	4.47	4.47	9.89	9.97	9.97	19.67	19.80	19.80
Nd	4.47	4.51	4.52	10.04	10.13	10.13	19.80	19.94	19.94
Pm	4.52	4.55	4.55	10.19	10.26	10.26	19.82	19.97	19.96
Sm	4.56	4.58	4.58	10.34	10.38	10.38	21.04	21.19	21.19
Eu	4.60	4.61	4.61	10.48	10.50	10.50	22.72	22.86	22.86
Gd	4.80	4.86	4.86	11.37	11.48	11.49	19.50	19.74	19.74
Tb	4.76	4.71	4.72	10.72	10.62	10.61	17.61	17.83	17.82
Dy	4.84	4.81	4.81	10.83	10.78	10.77	18.84	19.05	19.03
Ho	4.91	4.90	4.91	10.94	10.92	10.92	18.49	18.60	18.60
Er	4.99	4.97	4.97	11.05	11.00	11.00	18.09	18.21	18.21
Tm	5.07	5.03	5.03	11.16	11.09	11.08	19.21	19.30	19.30
Yb	5.14	5.06	5.07	11.27	11.11	11.11	20.91	20.92	20.93
Lu	4.34	4.38	4.38	12.60	12.67	12.67	19.95	19.97	19.94
MAD	0.003	0.037	0.035	0.073	0.125	0.128	0.009	0.113	0.111
	0.000	0.036	0.035	0.000	0.065	0.069	0.000	0.121	0.119

	IP$_4$			d−f			d−p		
Ln	DKH3 limit	PP seg.	PP gen.	DKH3 limit	PP seg.	PP gen.	DKH3 limit	PP seg.	PP gen.
La	49.89	49.94	49.94	2.74	2.67	2.68	1.83	1.84	1.85
Ce	34.89	35.09	35.09	1.34	1.34	1.35	2.12	2.18	2.19
Pr	37.23	37.50	37.50	0.11	0.09	0.10	2.10	2.20	2.21
Nd	38.92	39.23	39.23	0.27	0.24	0.25	2.21	2.31	2.32
Pm	39.16	39.50	39.49	0.53	0.49	0.50	2.27	2.36	2.37
Sm	39.30	39.65	39.64	−0.46	−0.53	−0.52	2.25	2.31	2.32
Eu	40.80	41.14	41.12	−2.08	−2.17	−2.16	2.08	2.13	2.14
Gd	42.82	43.48	43.46	4.69	4.65	4.68	1.72	1.86	1.87
Tb	35.24	35.69	35.69	3.25	3.10	3.13	1.87	1.87	1.88
Dy	37.46	37.92	37.90	2.12	1.97	2.01	1.78	1.80	1.82
Ho	38.94	39.35	39.33	2.12	2.01	2.04	1.32	1.34	1.35
Er	38.72	39.15	39.12	2.43	2.28	2.30	1.05	1.04	1.05
Tm	38.45	38.80	38.77	1.62	1.46	1.49	1.13	1.10	1.12
Yb	39.83	40.04	40.03	0.11	−0.07	−0.05	1.12	1.00	1.03
Lu	41.83	41.91	41.91				0.30	0.30	0.35
MAD	0.008	0.319	0.308	0.008	0.082	0.064	0.005	0.053	0.059
	0.000	0.327	0.316	0.000	0.090	0.072	0.000	0.054	0.061

[a] A diffuse p function was added to the PP basis sets for the evaluation of d−p excitation energies. The results are for the lowest LS states (cf. supplementary material). The mean absolute deviations (MAD) listed in the first line at the bottom refer to the AE DKH2 near HF results from Table 2, those in the second line to corresponding DKH3 data from this table.

Essentially identical results are obtained for the small-core PPs when the more compact generalized contracted (14s13p10d8f)/[6s6p5d4f] basis sets are used (MAD = 0.04, 0.13, 0.11, and 0.32 eV). We note here in passing that the HF PP results for IP$_1$ of La, Ce, Gd, and Lu in Table 2 are by 0.2−0.4 eV lower than the CAS PP results reported previously,[24,25] where the 6s shell was included together with the 5d and 4f shells in the active space.

Although the SARC basis sets perform slightly better for the first and second ionization potentials, and slightly worse for the third one, they exhibit substantially larger errors for the fourth ionization potentials, which involve a change of the 4f occupation number for all elements except for La. These errors are most likely not due to the contraction, since the uncontracted SARC sets exhibit different but not really better results. We note that the SARC sets are characterized by the presence of unusually diffuse outermost exponents, and that their exponents have been simply adopted from universal Gaussian basis sets optimized by Jorge et al. in Dirac−Hartree−Fock (DHF) calculations for the Dirac−Coulomb Hamiltonian (DC)[45,46] instead of optimizing them for the DKH2 or ZORA target Hamiltonian. It is thus not surprising that the tighter exponents describing inner regions of the atom, where (upper component) DHF/DC and DKH2 or ZORA spinors certainly differ in shape, are not optimal. The seemingly favorable DKH2 SARC ionization energies presented by Pantazis and Neese[12] were obtained at the Becke exchange and Lee, Young, Parr correlation hybrid functional (B3LYP) level and compared to experimental values. In view of the quite large error bars for the higher ionization potentials, the omission of SO contributions, and the probably not too accurate description of 4f shell correlation effects by B3LYP and a single reference DFT ansatz, it is thus quite difficult to come to a conclusion on possible basis set errors on the basis of their results.

Similarly, for d−f and d−p excitation energies, the SARC HF DKH2 results (MAD = 0.22 and 0.02 eV) are not clearly better than the PP HF results (MAD = 0.08 and 0.05 eV). As for the ionization potentials, the performance of the segmented[25] and generalized[24] contracted basis sets is rather similar. It has to be noted, however, that a diffuse p function had to be added to the PP basis sets in order to get a reasonable description of the 6p shell, i.e., reliable d−p excitation energies, whereas the addition of this function changed the calculated ionization potentials and d−f excitation energies only negligibly.

In contrast to this, the optimized DKH2 basis sets proposed here exhibit clearly the best overall performance (MAD = 0.00, 0.01, 0.03, 0.10, 0.07, and 0.02 eV for IP$_1$, IP$_2$, IP$_3$, IP$_4$, d−f, and d−p, respectively). Although the diffuse outermost exponents in each angular symmetry are somewhat larger than in the SARC sets, they are able to describe quite well the configurations with relatively diffuse valence orbitals, e.g., $4f^{n+1}6s^2$, $4f^n5d^16s^2$, and $4f^n6s^26p^1$. Since in most molecules the lanthanides are charged Ln^{x+} (x = 3 and also 2 or 4) ions, we expect the present basis sets to be sufficiently accurate. An addition of diffuse functions might be considered for calculations of weakly interacting systems, e.g., dimers with van der Waals bonding contributions such as Yb$_2$, but in these cases, the application of DFT, for which the basis sets are designed, is questionable.

A brief comment on the performance of the small-core PPs[16] is in order. The reasons for the errors are most likely 2-fold. On one hand, only Ln and Ln$^+$ configurations, excluding those with an occupied 6p shell, have been considered in the adjustment; i.e., only IP$_1$ and the d−f excitation energy have been included in the reference data set. On the other hand, the reference energies were

Table 4. Mean Absolute Deviations (cm^{-1}) in Relative Energies of J Levels with Respect to the Parent Ln^{3+} $4f^n$ LS Ground State[a]

Ln		AE DKH2/BP		PP	
		this work	SARC	seg.	gen.
Ce	$4f^1$ ^2F	94.5	231.1	218.8	210.6
Pr	$4f^2$ ^3H	106.4	341.3	251.3	244.6
Nd	$4f^3$ ^4I	119.0	383.5	254.4	248.7
Pm	$4f^4$ ^5I	119.7	381.4	223.9	220.6
Sm	$4f^5$ ^6H	104.7	327.7	157.2	155.2
Eu	$4f^6$ ^7F	78.9	242.0	90.2	89.1
Tb	$4f^8$ ^7F	92.3	299.0	296.8	297.2
Dy	$4f^9$ ^6H	140.1	447.9	418.5	420.7
Ho	$4f^{10}$ ^5I	160.9	569.4	485.3	490.5
Er	$4f^{11}$ ^4I	172.4	620.2	266.5	272.8
Tm	$4f^{12}$ ^3H	162.8	560.5	15.9	29.6
Yb	$4f^{13}$ ^2F	119.7	393.3	250.2	250.6
avg. MAD		122.6	399.8	244.1	244.2

[a] The reference values were obtained by CASSCF DKH2 calculations using (34s28p22d16f) basis sets and applying the BP Hamiltonian in first-order quasidegenerate perturbation theory. The corresponding results obtained with the segmented contracted (23s16p12d6f)/[18s12p9d3f] basis sets of this work and the corresponding SARC basis sets[12] are compared to results obtained with small-core PPs[16] and (14s13p10d8f)/[10s8p5d4f] segmented[25] as well as (14s13p10d8f)/[6s6p5d4f] generalized[24] contracted basis sets.

Table 5. Mean Absolute Errors in PBE0 Calculated Ln–X bond Lengths (Å) of LnX_3 with Respect to Recommended Values by Kovacs and Konings (KK)[63] and Hargittai (H)[64]

method	LnF_3		$LnCl_3$		$LnBr_3$		LnI_3	
	KK	H	KK	H	KK	H	KK	H
AE DKH[a]	0.016	0.017	0.018	0.021	0.017	0.022	0.023	0.024
PP+CPP[b]	0.006	0.028	0.017	0.023	0.013	0.024	0.027	0.016
AE DKH[c]	0.015	0.020	0.019	0.022	0.022	0.017	0.044	0.014
AE DKH[d]	0.018	0.017	0.021	0.020	0.021	0.018	0.021	0.010
AE DKH[e]	0.015	0.020	0.019	0.022	0.019	0.020	0.046	0.012

[a] Ref 12, including one-center approximation. [b] 4f-in-core PP+CPP results.[18] [c] This work using the proposed Ln basis sets and X TZVPP basis sets, MOLPRO.[20] [d] This work using the SARC basis sets of ref 12 and X TZVP basis sets, ORCA.[27] [e] This work using the proposed Ln basis sets and X TZVP basis sets, ORCA.[27]

derived with the scalar-relativistic WB HF formalism, which leads to slightly different results from those obtained with the DKH2 Hamiltonian. We note that the PPs were generated more than two decades ago and by now do not correspond to the state of the art. Modern energy-consistent PPs are adjusted to reference data going beyond the WB, DKH2, or ZORA Hamiltonians in accuracy,[51−56] i.e., they are based on multireference Dirac–Hartree–Fock data obtained with the Dirac–Coulomb–Breit finite nucleus Hamiltonian and possibly also include higher-order corrections from quantum electrodynamics. Such potentials, e.g., the one recently published for the U atom,[57,58] are certainly in terms of accuracy more competitive with AE calculations than the WB-adjusted PPs.

Spin–orbit (SO) effects cannot be neglected for lanthanide systems (*vide infra*), especially for energy differences between states with different 4f and/or 5d occupations.[30,59] Table 4 lists mean absolute deviations (MAD) in the relative energy of the J-levels of the Ln^{3+} ions with respect to the parent LS ground state configuration. The Breit–Pauli (BP) Hamiltonian was used in first-order quasidegenerate perturbation theory.[20] The average MAD for the 12 elements listed in Table 4 amounts to 400 cm^{-1} for the SARC basis sets, compared to 244 cm^{-1} for both the segmented and generalized contracted PP results. Again, the present AE basis sets perform best, i.e., the average MAD amounts to only 123 cm^{-1}. We assume that by optimizing the even-tempered basis sets underlying the segmented contracted sets proposed here, a better description of the compact 4f shell was obtained than is the case for the SARC basis sets. Detailed results for the individual J levels are available in the Supporting Information.

The number of s, p, d, and f primitives in the extended PP basis sets is 162, compared to 173 in the AE SARC basis sets and the

sets proposed here. The number of s, p, d, and f contractions is 90 and 80 for the segmented and generalized ANO contracted PP basis sets, respectively, compared to 120 for the AE basis sets. The PP basis sets appear to be relatively large; however, they have the advantage that they can also be used in wave-function-based correlation calculations without suffering from too large basis set superposition errors, which is not the case for the small AE basis sets discussed here. In addition, the PP ANO contracted PP sets of VQZ quality can be easily reduced and yield sets with fewer s, p, d, and f contractions, i.e., VTZ (64) and VDZ (48). Note that these numbers always include the diffuse p function, which might also be omitted for most purposes. The construction of more compact segmented contracted PP basis sets for usage in DFT calculations is currently underway in the group of Weigend and will also cover the lanthanides.[60−62] The segmented contracted AE DKH sets presented here and by Pantazis and Neese[12] have nearly as many s, p, d, and f contractions as the most extended ANO contracted DKH2 sets published by Roos and co-workers,[10] which consist of 134 s, p, d, and f contractions. Again, the advantage of the ANO sets is that smaller basis sets can easily be constructed by omitting the least populated ANO contractions.

3.2. Molecular Results. Molecular test calculations were performed for the lanthanide trihalides LnX_3 (Ln = La–Lu; X = F, Cl, Br, I). An overview over the various previous theoretical studies of these systems[12,35−42] up to 2004 was given by Kovacs and Konings.[63] In the present study, we compare mainly to the recent DKH AE PBE0 results of Pantazis and Neese.[12] A report on the performance of 4f-in-core PPs combined with effective core-polarization potentials (CPPs) in various DFT and CCSD(T) calculations will be given elsewhere.[26]

3.2.1. LnX_3 Bond Lengths and Angles. A summary of the overall performance of various approaches for LnX_3 bond lengths is listed in Table 5. Detailed geometry parameters of all calculations of this work are available from the Supporting Information. We make comparison to two reference data sets, i.e. the one published by Hargittai[64] and the one of Kovacs and Konings.[63] The latter set usually has shorter bond distances than the former, with the calculated results falling usually in between. In principle, a careful analysis of the recommended values and the calculated results should be carried out for each molecule, especially for those cases where irregularities or surprising results are present, e.g., for $YbBr_3$ and $LuBr_3$. Hargittai lists quite different values of 2.571 and 2.506 Å, respectively, whereas Kovacs and Konings

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Table 6. Ln−X Bond Lengths (Å) from Spin-Free AE DKH2 PBE0 Calculations Using the Ln (23s16p12d6f)/[18s12p9d3f] Basis Sets Proposed in This Work As Well As the Corresponding SARC Basis Sets[12] Together with F (11s6p1d)/[6s3p1d], Cl (14s9p1d)/[8s4p1d], Br (17s13p7d)/[10s8p3d], and I (19s15p10d)/[12s10p6d] Basis Sets (Denoted by TZVP in the ORCA Basis Set Library) for the Halides

Ln	LnF_3 this work	SARC	$LnCl_3$ this work	SARC	$LnBr_3$ this work	SARC	LnI_3 this work	SARC
La	2.107	2.114	2.576	2.581	2.729	2.735	2.952	2.957
Ce	2.085	2.090	2.554	2.555	2.704	2.704	2.926	2.926
Pr	2.070	2.074	2.535	2.535	2.683	2.685	2.906	2.905
Nd	2.068	2.071	2.519	2.520	2.669	2.669	2.890	2.890
Pm	2.052	2.055	2.506	2.506	2.655	2.654	2.875	2.876
Sm	2.037	2.040	2.493	2.494	2.643	2.645	2.872	2.873
Eu	2.028	2.030	2.487	2.489	2.649	2.651	2.921	2.915
Gd	2.029	2.029	2.470	2.472	2.617	2.619	2.835	2.838
Tb	2.012	2.013	2.456	2.458	2.602	2.604	2.821	2.824
Dy	2.003	2.004	2.442	2.444	2.589	2.592	2.808	2.812
Ho	1.999	2.000	2.431	2.434	2.578	2.580	2.796	2.800
Er	1.986	1.988	2.420	2.424	2.566	2.569	2.785	2.788
Tm	1.980	1.981	2.408	2.413	2.556	2.559	2.775	2.780
Yb	1.966	1.967	2.399	2.403	2.547	2.552	2.770	2.780
Lu	1.963	1.965	2.389	2.391	2.535	2.538	2.754	2.756
MAD	0.002		0.002		0.002		0.003	

give 2.529 and 2.516 Å, respectively. Such a discussion of individual molecules is beyond the scope of the present work.

One notes that large-core pseudopotentials (PPs), when augmented by core-polarization potentials (CPPs) on the lanthanides and halides, lead to results of similar overall quality as AE DKH2 calculations applying the same density functional.[18] As discussed in more detail elsewhere, the lanthanide PPs include the open 4f shell in the core and require significantly smaller computational ressources than the AE DKH2 calculations reported here.[19] They also avoid several difficulties which arise when applying density functional theory to open f shell systems, which actually would require a multireference treatment. It is also obvious that the differences between the results obtained with the basis sets proposed here and those of ref 12 are quite small, and even larger deviations arise from the usage of different program systems. This point will be discussed below in more detail.

Table 6 provides a comparison of AE DKH PBE0 bond lengths obtained using the MOLPRO code[20] and the basis sets proposed here as well as the SARC basis sets.[12] It is seen that the agreement is excellent with mean average deviations of 0.003 Å or less for all four halides. Quite good agreement is also obtained when comparing to the results published by Pantazis and Neese[12] for the trifluorides and trichlorides, whereas the bond lengths of the tribromides and triiodides obtained here are slightly longer. The main reason for these deviations appears to be the usage of a one-center approximation in the ORCA code[27] applied by Pantazis and Neese for the evaluation of the DKH2 contributions in geometry optimizations. This computational detail, which is not mentioned in the original work, was later pointed out by the authors.[65] Corresponding results of calculations using the ORCA software,[27] i.e., applying the one-center approximation,

are summarized in the Supporting Information. Here again, excellent agreement is obtained between the results for both basis sets; i.e., the MAD in bond lengths is 0.003, 0.002, 0.002, 0.011, and 0.004 Å for LnF_3, $LnCl_3$, $LnBr_3$, LnI_3, and all LnX_3, respectively. When avoiding the one-center approximation by using ORCA for single-point calculations and an external geometry optimizer, the agreement is even better; i.e., the MAD is 0.002, 0.002, 0.002, 0.003, and 0.003 Å for LnF_3, $LnCl_3$, $LnBr_3$, LnI_3, and all LnX_3, respectively.

It has to be noted that both the bond angles and bond lengths published by Pantazis and Neese[12] are in fact averaged values, as it was later revealed by the authors.[65] Giving just average values is valid for bond lengths, which show variations of less than 0.01 Å; however, for some molecules, especially the europium trihalides, the mere stating of an average bond angle leads to the wrong impression that the molecules in the calculations have either C_{3v} or D_{3h} symmetry. In fact, quite noticeable distortions from these ideal symmetries may occur when imposing no symmetry restrictions in the calculation, and the X−Ln−X bond angles for some systems show mean absolute deviations of up to 8°. For example, for EuI_3, bond angles of 116.2, 116.2, and 127.6° and 116.4, 116.4, and 127.1° were obtained when using the SARC basis sets and the basis sets proposed here, respectively, cf. Supporting Information. The corresponding bond distances are 2.909, 2.914, and 2.914 Å and 2.885, 2.891, and 2.891 Å, respectively. At the multiconfiguration Hartree−Fock level, such distortions do not occur.

Table 7 summarizes the AE DKH PBE0 results obtained with the proposed basis sets and extended sets for the halogen atoms. The comparison is made to an average of the values recommended by Hargittai[64] and Kovacs and Konings,[63] i.e. $R_{avg} = (R_H + R_{KK})/2$. The values in parentheses denote the deviations of these recommended values from the average value in the last two printed digits, i.e., $n = 500|R_H − R_{KK}|$. It should be noted that $R_H > R_{KK}$, except for $LuBr_3$. The mean absolute deviations of the AE DKH PBE0 results from the averaged reference values is 0.006 Å for LnF_3, $LnCl_3$, and $LnBr_3$ but 0.022 Å for LnI_3. The major part of the deviations arises for the lighter lanthanide iodides; i.e., mean absolute deviations of 0.040 and 0.007 Å are observed for LaI_3 to EuI_3 and GdI_3 to LuI_3, respectively. In all cases, except for $LuBr_3$, the differences between the values of the two recommended sets are larger than between the calculated results and the values of any of the two sets. This indicates a need for relativistic higher-level correlated ab initio AE calculations to generate suitable reference data for calibration purposes.

The limited accuracy of a density functional description for lanthanide open f shell systems becomes especially apparent for the europium trihalides. The f population increases considerably above the value of 6 electrons at the density functional level, i.e., 6.24, 6.23, 6.30, and 6.56 for EuF_3, $EuCl_3$, $EuBr_3$ and EuI_3, respectively, whereas one obtains 6.16, 6.12, 6.09, and 6.08 at the HF level. Complete active space or multireference configuration interaction calculations lead to f populations of less than 6.1 electrons. The unphysical overfilling of the 4f shell leads for EuI_3 to a larger europium ion and thus also to a too long bond distance. The CCSD(T) bond distances of 2.027, 2.492, 2.650, and 2.836 Å for EuF_3, $EuCl_3$, $EuBr_3$, and EuI_3, respectively, compare favorably to the PBE0 results 2.027, 2.487, 2.650, and 2.919 Å only for the three lighter halogens. The same F−Eu−F bond angle of 113.8° was found for the pyramidal EuF_3 at the CCSD(T) and PBE0 levels, whereas for the three heavier halogens, a planar equilibrium geometry was found. Finally, the

Table 7. Ln−X Bond Distances (Å) of LnX$_3$ from AE DKH PBE0 Calculations Using the Extended Ln (23s16p12d6f)/[18s12p9d3f] Basis Sets Proposed in This Work, Relativistically Contracted F (11s6p2d1f)/[6s3p2d1f], Cl (14s9p2d1f)/[8s4p2d1f], Br (17s13p8d1f)/[10s8p4d1f], and I (19s15p11d2f)/[12s10p7d2f] Basis Sets for the Halides (Denoted TZVPP in the ORCA Basis Set Library), in Comparison to Averaged Recommended Values (rec.)[64,63a]

| Ln | LnF$_3$ | | LnCl$_3$ | | LnBr$_3$ | | LnI$_3$ | |
	this work	rec.	this work	rec.	this work	rec.	this work	rec.
La	2.106	2.108(31)	2.577	2.562(28)	2.731	2.715(26)	2.952	2.902(36)
Ce	2.084	2.098(29)	2.553	2.550(28)	2.705	2.700(23)	2.925	2.892(34)
Pr	2.068	2.075(17)	2.531	2.522(11)	2.684	2.679(14)	2.905	2.876(28)
Nd	2.065	2.069(20)	2.520	2.519(20)	2.670	2.669(17)	2.888	2.859(21)
Pm	2.051	2.058(19)	2.504	2.508(20)	2.656	2.656(17)	2.874	2.853(23)
Sm	2.036	2.047(18)	2.487	2.495(20)	2.646	2.644(17)	2.870	2.841(22)
Eu	2.027	2.037(17)	2.487	2.484(20)	2.650	2.633(17)	2.919	2.831(22)
Gd	2.027	2.031(22)	2.471	2.471(18)	2.619	2.622(18)	2.835	2.821(21)
Tb	2.018	2.015(14)	2.456	2.460(18)	2.609	2.608(18)	2.800	2.809(20)
Dy	2.003	2.005(14)	2.442	2.450(19)	2.591	2.596(19)	2.807	2.800(18)
Ho	1.999	1.994(13)	2.432	2.439(20)	2.583	2.585(19)	2.795	2.789(18)
Er	1.986	1.985(13)	2.421	2.427(20)	2.571	2.573(20)	2.783	2.779(17)
Tm	1.980	1.974(13)	2.410	2.417(20)	2.557	2.562(21)	2.773	2.769(17)
Yb	1.971	1.964(11)	2.399	2.404(20)	2.550	2.550(21)	2.768	2.758(16)
Lu	1.963	1.956(12)	2.390	2.395(22)	2.537	2.511(05)	2.752	2.752(19)
MAD	0.006		0.006		0.006		0.022	

[a] The numbers in parentheses denote the uncertainties for the last two digits as defined by the longer values of Hargittai and the shorter ones of Kovacs and Konings.

errors of the AE DKH PBE0 atomization energies with respect to the experimental values are always the highest for each series of lanthanide trihalides (*vide infra*), also confirming that Eu is a quite difficult case for DFT.

Finally, some brief comment concerning the structures applies. In our optimizations, we find the trifluorides to be slightly pyramidal (C_{3v}) and the other heavier trihalides to be essentially planar (D_{3h}), when the molecular point group is restricted to C_{3v}. Note that no symmetry constraints were imposed on the orbitals; i.e., for a single determinant description, symmetry breaking may occur. In particular, we do not find planar PmF$_3$ and SmF$_3$ molecules in variance with the results of Pantazis and Neese.[12] These authors comment that their observed structures are in remarkable agreement with the so-called asphericity model.[66] According to this model, originating from early work in solid state physics,[67] one has for LnX$_3$ pyramidal (Ln = Ce, Pr, Nd, Eu, Tb, Dy, Ho) and planar (Ln = La, Pm, Sm, Gd, Er, Tm, Yb, Lu) structures depending on the shape of the 4f shell charge distribution. It is noteworthy that already LaF$_3$, which was left out by Pantazis and Neese, does not obey this model. In addition, GdF$_3$ was found by these authors to be pyramidal and HoF$_3$ to be planar in disagreement with the model. Moreover, in view of the small energy differences between the pyramidal and planar structures, e. g., 0.036 eV for PmF$_3$ according to our PBE0 results, one may doubt if a single reference DFT model without consideration of SO coupling is able to describe accurately enough the LnX$_3$ electronic structure. In particular, it has to be noted that like most density functionals the PBE0 functional applied in this work as well as by Pantazis and Neese is not able to describe the degeneracy of different components of open shell states correctly, when these produce differing density distributions. This problem was already discussed, e.g., by Baerends and co-workers for main group and transition metals.[29] Already for the simplest case, the

Table 8. Mean Absolute Errors in LnX$_3$ PBE0 Atomization Energies (eV) of Scalar-Relativistic (SR) and Spin-Orbit Corrected (SO) Calculated Values with Respect to Experimental Data[68]

| method | LnF$_3$ | | LnCl$_3$ | | LnBr$_3$ | | LnI$_3$ | |
	SR	SO	SR	SO	SR	SO	SR	SO
AE DKH[a]	0.45	0.47	0.49	0.57	0.25	0.59	0.92	0.30
PP+CPP[b]	0.65	0.61	0.44	0.35	0.84	0.46	1.33	0.47
AE DKH[c]	0.47	0.47	0.32	0.28	0.45	0.27	0.81	0.24
AE DKH[d]	0.44	0.44	0.41	0.41	0.43	0.20	0.80	0.19
AE DKH[e]	0.49	0.52	0.44	0.45	0.42	0.27	0.75	0.24

[a] Ref 12; SO corrections of this work were added. [b] 4f-in-core PP+CPP results.[18] [c] This work using the proposed Ln basis sets and X TZVPP basis sets, MOLPRO. [d] This work using the Ln basis sets of ref 12 and X TZVP basis sets, ORCA. [e] This work using the proposed Ln basis sets and X TZVP basis sets, ORCA.

boron atom, degeneracy errors of up to 0.2 eV were found for the 2p^1 ^{2}P ground state at the GGA level. In relativistic AE DKS calculations, a degeneracy error of up to 0.6 eV was found for the Yb^{3+} 4f^{13} ^{2}F$_{7/2}$ state at the LDA and GGA levels.[30] This defect resulted in a wrong ordering of molecular states for YbO. It is likely that such artifacts are also present for the LnX$_3$ open shell molecules and influence, besides the atomization energies, also the ground state equilibrium structures. We therefore do not discuss the bond angles here in detail and refer the reader interested in these results to the Supporting Information.

3.2.2. Atomization Energies. Table 8 summarizes the errors for the calculated LnX$_3$ atomization energies with respect to the data provided by Myers.[68] This author evaluated LnX$_3$ atomization

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energies rounded to 1 kcal/mol ($\sim$0.04 eV) by using a thermodynamic cycle. He estimated the data to be accurate within $\pm$5 kcal/mol ($\pm$0.22 eV) if only experimental values enter and $\pm$10 kcal/mol ($\pm$0.44 eV) if one value had to be estimated. In view of these uncertainties, we neglected zero-point vibration corrections, which only amount to about 0.10, 0.06, 0.04, and 0.03 eV for LnF_3, $LnCl_3$, $LnBr_3$, and LnI_3, respectively.[26] Note that in the present calculations, no symmetry restrictions were imposed, and the lowest-energy KS determinant was searched for by applying rotations between occupied and empty 4f orbitals. In order to have a unbiased comparison, we performed analogous calculations with the basis sets of Pantazis and Neese and the ones proposed here. From the data for the heavier trihalides, i.e., $LnBr_3$ and LnI_3, it is obvious that SO corrections improve the results significantly. It further can be seen that the overall quality of the results obtained with the proposed basis sets is similar to the one for the SARC basis sets.

It has to be noted, however, that since the applied DFT does not yield exact results, good performance may also partly be due to error compensations. Assuming a completely ionic electronic structure $Ln^{3+}(F^-)_3$ with a $4f^n$ ($n = 0-14$ for La—Lu) subconfiguration on the lanthanide, one may expect that errors in the first three lanthanide ionization potentials as well as the halogen electron affinity directly affect the results. Aside from the performance of the PBE0 functional, the basis set errors occurring, e.g., at the HF level, have to be considered. Whereas the errors in the halogen electron affinities affect equally the results for the present and the SARC basis sets, those in the sum of the first three lanthanide ionization potentials might lead to deviations. We note that the SARC basis sets yield somewhat larger errors (MAD 0.15 eV, maximum deviation 0.28 eV) than the present basis sets (MAD 0.03 eV, maximum deviation 0.08 eV).

Table 9 compares the DKH2 PBE0 LnX_3 atomization energies obtained with the proposed basis sets to the values obtained with the SARC basis of Pantazis and Neese.[12] Both sets produce very similar trends along the lanthanide series with a MAD of about 0.1 eV.

SO contributions to the atomization energies have been neglected in most of the previous work. The atomic and molecular SO total energy lowerings, however, can be substantial and usually do not cancel, as is obvious from the data compiled in Table 10. The molecular SO total energy contributions are very similar to the Ln^{3+} atomic energy lowerings, thus supporting models based on an ionic $Ln^{3+}(X^-)_3$ charge distribution. The results compiled in Table 10 are in disagreement with corresponding data derived by Adamo and Maldivi[42] for LnX_3 (Ln = La, Lu) from AE DFT calculations using the ADF package. These authors report strong stabilizations of LaF_3 and LuF_3 by 1.23 and 1.17 eV, respectively, due to SO contributions. It is not clear how the closed-shell molecules can be stabilized with respect to the open-shell separated atoms. On the other hand, for LaI_3 and LuI_3, a destabilization by 0.35 and 0.90 eV, respectively, due to SO effects was reported, which is at least in qualitative agreement with the present results. Still, it is unclear why the magnitude of the destabilization is so different for the two molecules, where the major contribution should arise from the three I atoms, whereas the much smaller contributions of the Ln atoms agree within 0.1 eV.

Finally, the basis set superposition error (BSSE) has to be considered. Corresponding corrections can be estimated according to the Boys and Bernardi counterpoise scheme[69] by calculating the atomic energies used for the evaluation of the atomization

Table 9. LnX_3 Atomization Energies (eV) from Spin-Free AE DKH2 PBE0 Calculations Using the Ln (23s16p12d6f)/-[18s12p9d3f] Basis Sets Proposed in This Work As Well As the Corresponding SARC Basis Sets[12] Together with F (11s6p1d)/[6s3p1d], Cl (14s9p1d)/[8s4p1d], Br (17s13p7d)/[10s8p3d], and I (19s15p10d)/[12s10p6d] Basis Sets (Denoted by TZVP in the ORCA Basis Set Library) for the Halides

	LnF_3		$LnCl_3$		$LnBr_3$		LnI_3	
Ln	this work	SARC	this work	SARC	this work	SARC	this work	SARC
La	19.86	19.71	15.78	15.66	14.30	14.17	12.43	12.32
Ce	19.77	19.80	15.67	15.70	14.20	14.22	12.31	12.34
Pr	18.76	19.05	14.66	14.96	13.18	13.45	11.28	11.57
Nd	18.09	18.32	14.08	14.30	12.58	12.80	10.70	10.92
Pm	17.75	17.93	13.71	13.89	12.22	12.40	10.35	10.53
Sm	16.64	16.80	12.62	12.78	11.14	11.31	9.32	9.48
Eu	15.66	15.79	11.63	11.77	10.19	10.33	8.53	8.65
Gd	19.16	19.16	15.20	15.22	13.69	13.71	11.81	11.83
Tb	18.89	18.91	14.89	14.92	13.38	13.41	11.49	11.52
Dy	18.04	17.99	14.02	14.00	12.51	12.47	10.60	10.58
Ho	17.74	17.67	13.75	13.72	12.23	12.18	10.33	10.30
Er	17.79	17.70	13.78	13.74	12.27	12.21	10.37	10.33
Tm	16.83	16.73	12.84	12.77	11.33	11.25	9.40	9.37
Yb	15.95	15.83	11.94	11.87	10.42	10.34	8.53	8.48
Lu	19.30	19.28	15.28	15.37	13.77	13.81	11.85	11.92
MAD	0.11		0.10		0.10		0.09	

Table 10. Atomic and Molecular Total Energy Lowerings (eV) Due to Spin-Orbit Interaction As Calculated from AE DKH2 Calculations Applying the Breit—Pauli—Hamiltonian in First-Order Perturbation Theory Based on Hartree—Fock Results

	Ln	Ln^{3+}	LnF_3	$LnCl_3$	$LnBr_3$	LnI_3
La	−0.11	0.00	0.00	0.00	0.00	0.00
Ce	−0.08	−0.16	−0.14	−0.15	−0.15	−0.15
Pr	−0.29	−0.28	−0.27	−0.28	−0.28	−0.28
Nd	−0.34	−0.38	−0.36	−0.37	−0.37	−0.37
Pm	−0.34	−0.44	−0.41	−0.43	−0.43	−0.43
Sm	−0.26	−0.41	−0.39	−0.40	−0.40	−0.40
Eu	0.00	−0.32	−0.23	−0.26	−0.26	−0.27
Gd	−0.15	0.00	0.00	0.00	0.00	0.00
Tb	−0.52	−0.34	−0.31	−0.32	−0.32	−0.29
Dy	−0.69	−0.62	−0.61	−0.61	−0.61	−0.61
Ho	−0.76	−0.82	−0.81	−0.81	−0.81	−0.81
Er	−0.70	−0.89	−0.89	−0.89	−0.89	−0.89
Tm	−0.46	−0.81	−0.81	−0.81	−0.81	−0.81
Yb	0.00	−0.51	−0.52	−0.53	−0.53	−0.53
Lu	−0.20	0.00	0.00	0.00	0.00	0.00
			F	Cl	Br	I
			−0.02	−0.04	−0.15	−0.32

energies in the atomic and molecular basis sets. Taking the ytterbium trihalides as examples, one obtains with the MOLPRO code at the PBE0 level for the Yb basis set proposed here reductions of the atomization energies of 0.10, 0.09, 0.10, and

0.11 eV for YbF_3, $YbCl_3$, $YbBr_3$, and YbI_3, respectively, when TZVP basis sets are applied for the halogen atoms and all calculations are performed without symmetry restrictions using the molecular grid. The corresponding corrections are slightly smaller for the Yb SARC basis set of Pantazis and Neese; i.e., they amount to 0.07, 0.05, 0.05, and 0.07 eV, respectively. The corrections for the basis sets proposed here decrease upon the addition of a diffuse f function; e.g., for YbF_3, a value of 0.05 eV is obtained, whereas the addition of diffuse s, p, or d functions does not lead to significant changes.

An alternative to the evaluation of the atomization energies with respect to the neutral atoms is a corresponding evaluation with respect to the ions Ln^{3+} and X^-. Taking $YbBr_3$ as an example, one obtains counterpoise corrections of 0.26 and 0.47 eV for the basis sets proposed here and the SARC sets of Pantazis and Neese, respectively. These large values almost exclusively arise from the contributions of the Br^- ions, whereas the Yb^{3+} ion contributes at most 0.01 eV for both lanthanide basis sets. The larger BSSE found for the SARC basis sets is due to the presence of the more diffuse functions than in the basis sets presented here.

In comparison to other errors of the calculations associated with the use of DFT, as well as the uncertainties of the experimental data, the relatively small BSSE found in the atomization energies calculated with respect to the neutral atoms is tolerable. For example, the atomic reference energies of the neutral halogen atoms in the atomic basis set were obtained by restricting the basis sets to the angular symmetries of the occupied shells, i.e., sp for F and Cl and spd for Br and I. By including the higher angular momentum functions used in the molecular calculations, i.e., d for F and Cl as well as f for Br and I, and allowing for symmetry breaking, lower total atomic energies are obtained. The energy lowerings by 0.07, 0.09, 0.04, and 0.05 eV for F, Cl, Br, and I, respectively, due to symmetry breaking are also automatically included in the atomic calculations performed in the molecular basis. Such contributions to the atomization energies arising from all three halogen atoms in a lanthanide trihalide are clearly larger than the BSSE corrections discussed above, which were therefore not evaluated for the final results compiled in Table 11. Note that corresponding energy lowerings would also arise for Ln atoms with open 4f and/or 5d shells.

The mean absolute deviations of the AE DKH PBE0 results from the experimental values of the atomization energies are largest for LnF_3 (0.47 eV) and very similar and about only half as large for the other trihalides $LnCl_3$ (0.28 eV), $LnBr_3$ (0.27 eV), and LnI_3 (0.24 eV), cf. Table 11. The mean unsigned relative errors are almost identical, i.e., 2.7, 2.0, 2.3, and 2.5% for LnF_3, $LnCl_3$, $LnBr_3$, and LnI_3, respectively. It is interesting to see that the mean absolute deviation of the four LnX_3 (X = F, Cl, Br, I) systems is for Eu (0.85 eV) more than twice as large as for any other lanthanide element Ln. The lowest mean absolute deviations occur for Gd (0.06 eV) and La (0.09 eV), whereas the values for the other elements range between 0.19 and 0.38 eV. This again might indicate that the description of Eu compounds at the DFT level is relatively poor, which was already obvious from the Eu–I bond distance (*vide supra*). In LaX_3, CeX_3, GdX_3, and LuX_3, the 4f occupation in the neutral atom is identical to the one in the trihalide molecule, i.e., the differential correlation contributions in the atomization energies should be small. In the case of Ce (0.27 eV), some problems may arise from the fact that the actual $4f^1 5d^1 6s^2$ $^1G_4$ ground state cannot be described at the DFT level and the higher ^3F state had to be chosen as a reference,

Table 11. LnX_3 Atomization Energies (eV) from AE DKH PBE0 Calculations Using the Extended Ln (23s16p12d6f)/[18s12p9d3f] Basis Sets Proposed in This Work, Relativistically Contracted F (11s6p2d1f)/[6s3p2d1f], Cl (14s9p2d1f)/[8s4p2d1f], Br (17s13p8d1f)/[10s8p4d1f], and I (19s15p11d2f)/[12s10p7d2f] Basis Sets for the Halides (Denoted TZVPP in the ORCA Basis Set Library), in Comparison to Experimental Values (exptl.)[68]a

Ln	LnF_3		$LnCl_3$		$LnBr_3$		LnI_3	
	this work	exptl.	this work	exptl.	this work	exptl.	this work	exptl.
La	19.94	19.86	15.83	15.87	13.80	13.70	11.41	11.28
Ce	20.09	20.08	15.98	15.57	13.93	13.57	11.54	11.19
Pr	19.00	19.08	14.87	15.22	12.82	13.18	10.42	10.58
Nd	18.30	19.04	14.26	14.48	12.22	12.62	9.80	9.93
Pm	18.12		14.08		12.03		9.64	
Sm	16.97	17.30	12.91	13.23	10.92	11.10	8.57	9.06
Eu	16.09	17.22	12.06	13.05	10.08	10.80	7.89	8.46
Gd	19.19	19.21	15.22	15.13	13.16	13.05	10.76	10.80
Tb	18.86	18.99	14.87	15.13	12.80	12.88	10.37	10.67
Dy	18.01	17.35	13.92	14.18	11.85	11.84	9.44	9.67
Ho	17.98	17.22	14.06	14.31	11.98	11.75	9.57	9.37
Er	18.19	17.22	14.19	14.31	11.96	12.14	9.70	9.93
Tm	17.39	17.04	13.39	13.66	11.30	11.10	8.91	8.98
Yb	16.56	16.05	12.67	12.40	10.46	10.06	8.19	7.85
Lu	19.28	18.43	15.29	15.18	13.21	12.79	10.78	10.67
MAD	0.47		0.28		0.27		0.24	

^{a} Spin-orbit corrections have been applied to the theoretical results.

whereas for Lu the larger deviations (0.37 eV) cannot be explained. We note however that large-scale AE DKH CCSD(T) calculations yielded without and with the counterpoise correction of the BSSE an atomization energy of 20.75 and 19.79 eV, respectively.[41] After adding SO corrections, the latter value reduces to 18.63 eV, which is much closer to the experimental value of 18.43 eV, i.e., about 18.53 eV after subtracting the zero-point vibration energy, compared to the SO-corrected AE DKH PBE0 result of 19.28 eV. These results for the relatively simple case of LuF_3 may point to some deficiencies of the PBE0 functional, which are not only present for open-4f-shell cases.

3.3. Conclusions. Segmented contracted lanthanide basis sets of modest size to be used in connection with the Douglas–Kroll–Hess second-order relativistic Hamiltonian and preferably density functional theory have been presented. The basis sets provide lower total energies than the previously proposed SARC basis sets of the same size and contraction pattern, and they give a more faithful description of electronic states with different valence occupations. Despite their slightly less diffuse outermost functions, they yield satisfactory results in molecular test calculations on the lanthanide trihalides. It was found that the one-center approximation for the evaluation of Douglas–Kroll–Hess second-order relativistic contributions leads on the average to 0.02 Å too short bond distances for the lanthanide triiodides. In addition, the single reference density functional theory description leads for some molecules to noticeable distortions from the ideal C_{3v} and D_{3h} geometries. Due to the uncertainties in the experimental reference data, a more rigorous calibration of the results of the present study has to wait for higher level ab

initio calculations using larger basis sets and also including spin−orbit effects.

ASSOCIATED CONTENT

ⓈSupporting Information. Listings of segmented contracted basis sets as well as even-tempered basis sets used to generate the Hartree−Fock-limit reference data. Structural and energetic information on all 60 lanthanide trihalides obtained with various basis sets at the density functional theory level. This material is available free of charge via the Internet at http://pubs.acs.org.

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