Theor Chem Acc (2010) 126:117–127
DOI 10.1007/s00214-009-0584-2

REGULAR ARTICLE

Quasirelativistic f-in-core pseudopotentials and core-polarization potentials for trivalent actinides and lanthanides: molecular test for trifluorides

**Anna Weigand · Xiaoyan Cao · Jun Yang ·
Michael Dolg**

Received: 10 February 2009 / Accepted: 7 May 2009 / Published online: 26 May 2009

Abstract Calibration studies of actinide and lanthanide trifluorides are reported for actinide and lanthanide scalar-relativistic energy-consistent f-in-core pseudopotentials, respectively, accompanying valence basis sets as well as core-polarization potentials. Results from Hartree–Fock and coupled-cluster singles, doubles, and perturbative triples f-in-core pseudopotential calculations are compared to corresponding data from f-in-valence pseudopotential and all-electron calculations as well as to experimental data. In general, good agreement is observed between the f-in-core and f-in-valence pseudopotential results, whereas due to the lack of experimental data for the actinides only a good agreement of the calculated and experimentally determined bond lengths of the lanthanide systems can be established. Nevertheless, the results indicate that the core-polarization potentials devised here for actinides improve the f-in-core results.

Keywords Actinides · Lanthanides · Pseudopotentials · Core-polarization potentials · Valence basis sets · Trifluorides

1 Introduction

The chemical investigation of actinide and lanthanide elements and their compounds is important, particularly with regard to the separation of trivalent actinides and lanthanides, which is one of the key problems faced in partitioning and transmutation nuclear waste management strategies. However, these studies involve several difficulties for both experimental and theoretical work. While the toxicity, radioactivity, and scarcity of the actinides are the main obstacles for the experimentalists [1], theoreticians face particular challenges in the significant contributions of relativity as well as electron correlation for both actinides and lanthanides [2–5]. Especially the complexities arising from partially occupied f shells make first-principle studies of actinide and lanthanide systems frequently cumbersome and motivates the development of approximate schemes based on chemical intuition [4, 5].

One of the most successful approximations to cope with some of these problems in quantum chemical calculations is the pseudopotential (PP) approach, in which the explicit calculations are restricted to the chemically relevant valence electron system and relativistic effects are only implicitly accounted for by a proper adjustment of free parameters in the valence model Hamiltonian. For the f elements at least two kinds of energy-consistent PPs with different core definitions, i.e. f-in-valence [6, 7] and f-in-core [8–12] PPs, are available. In the case of the f-in-core PPs, one PP for each oxidation state, or rather, for each corresponding 5f/4f subconfiguration is needed. For

---

Dedicated to the memory of Professor Jean-Pierre Daudey and published as part of the Daudey Memorial Issue.

Electronic supplementary material The online version of this article (doi:10.1007/s00214-009-0584-2) contains supplementary material, which is available to authorized users.

A. Weigand (✉) · X. Cao · M. Dolg (✉)
Institute for Theoretical Chemistry, University of Cologne,
Greinstr. 4, 50939 Cologne, Germany
e-mail: anna.weigand@uni-koeln.de

M. Dolg
e-mail: m.dolg@uni-koeln.de

J. Yang
Theoretische Chemie, Ruhr-Universität Bochum,
Universitätsstr. 150, 44780 Bochum, Germany

actinides di- [9], tri- [8], tetra- [9], penta- [10], and hexavalent [10] PPs were adjusted recently for Pu–No, Ac–Lr, Th–Cf, Pa–Am, and U–Am, respectively. For lanthanides di- [11], tri- [11], and tetravalent [12] PPs are available for La–Yb, La–Lu, and Ce, Pr, Nd, Tb, Dy, respectively. The f-in-core PPs avoid many difficulties due to the open f shell, and despite their approximate nature are an efficient computational tool for those actinide/lanthanide compounds, where the f shell does not significantly contribute to bonding. Hence, calculations even on large molecules as actinide(III) motexafins [13], actinide(III) polyhydrates [14], lanthanide(III) texaphyrins [15], or lanthanide borohydride complexes [16] become feasible.

While the open 4f shell has a core-like character for all lanthanides, the open 5f shell only becomes more core-like with increasing nuclear charge along the actinide series. This can be seen, e.g. from the preferred oxidation states [17], which are trivalent for all lanthanides but only for the later actinides (Am–Lr). For the early actinides the 5f shell can easily contribute to chemical bonding due to its diffuse character, and thus these actinides may reach formal oxidation states up to +7. Therefore, the range of possible applications of the recently published actinide 5f-in-core PPs is certainly somewhat smaller than for the lanthanide 4f-in-core PPs, which have already successfully been used during the last two decades by many researchers [5]. However, we found ample quantitative evidence that the 5f-in-core approximation can be made without too much loss of accuracy for many cases, e.g. actinide fluorides AnF_n ($n = 2$–5) and UF_6 [8–10], actinide(III) mono- [8] and polyhydrates [14], actinide(III) motexafin complexes [13], actinocenes [18], the uranyl ion [10], and crystalline uranium nitride [19].

Core-polarization potentials (CPPs) account for both static and dynamic polarization of the PP core and are particular important for large-core PPs as the f-in-core PPs. Since the CPPs accompanying the newly developed actinide 5f-in-core PPs have not been applied so far, they are tested in calculations for actinide trifluorides AnF_3 (An = Ac–Lr) using the Hartree–Fock (HF) and coupled-cluster method with single and double excitation operators and a perturbative estimate of triple excitations [CCSD(T)]. Furthermore, HF and CCSD(T) calculations for lanthanide trifluorides LnF_3 (Ln = La–Lu) using 4f-in-core PPs in connection with recently published improved molecular basis sets [20] are presented, in order to show the reliability of these basis sets, which up to now have only been used for DyCl_3 [21].

2 Method

All pseudopotentials and basis sets used in this contribution were previously published elsewhere [8, 11, 20] and will be described here only briefly. The 5f-in-core and 4f-in-core PPs corresponding to trivalent actinides ($5\mathrm{f}^n$, $n = 0$–14 for Ac–Lr) [8] and lanthanides ($4\mathrm{f}^n$, $n = 0$–14 for La–Lu) [11], respectively, treat only 11 valence electrons explicitly, while the 1s–5f and 1s–4f shells are included in the PP core. The PP parameters were adjusted to all-electron (AE) scalar-relativistic Wood–Boring (WB) [22] reference data, wherefore the major relativistic effects and averaged spin–orbit (SO) coupling are accounted for. To allow for some participation of the 5f/4f orbitals in chemical bonding the f-parts of the PPs are designed to describe partial occupations of the 5f/4f shell, i.e. the 5f/4f occupation numbers q modeled with the PPs might be $n \leq q < n + 1$ for trivalent actinide/lanthanide atoms in molecules. For the actinides, the f-PPs consist of two types of potentials V_1 and V_2 which are linearly combined as follows [8]

$$V = \left(1 - \frac{n}{14}\right)V_1 + \frac{n}{14}V_2. \tag{1}$$

Here n is the number of electrons in the 5f orbitals. V_1 and V_2 model 5f shells, which can and cannot accommodate an additional electron, respectively. Thus, $V = V_1$ is the exact potential for a $5\mathrm{f}^0$ occupation, whereas $V = V_2$ is exact for $5\mathrm{f}^{14}$. In the case of the lanthanides, for all elements with open 4f shell, i.e. La–Yb, V_1 potentials were adjusted, while for Lu, whose 4f shell is fully occupied, a V_2 potential was created [23].

In order to account for both static (polarization of the core at the HF level) and dynamic (core-valence correlation) polarization of the PP core, CPPs of the form suggested by Müller et al. [24, 25] were added to the f-in-core PPs.

$$V_{\mathrm{CPP}} = -\frac{1}{2}\sum_{\lambda}^{N} \alpha_{\mathrm{D}}^{\lambda} \vec{f}_{\lambda}^{\,2} \tag{2}$$

with

$$\vec{f}_{\lambda} = -\sum_{i} \frac{\vec{r}_{i\lambda}}{r_{i\lambda}^{3}}\,\omega(r_{i\lambda}) + \sum_{\mu \neq \lambda} Q_{\mu} \frac{\vec{r}_{\mu\lambda}}{r_{\mu\lambda}^{3}}\,\omega(r_{\mu\lambda}). \tag{3}$$

Here $\alpha_{\mathrm{D}}^{\lambda}$ denotes the dipole polarizability of the PP core λ and $\vec{f}_{\lambda}$ is the electric field at this core generated by the valence electrons (at relative positions $\vec{r}_{i\lambda}$) and the other cores or nuclei (with charges Q_{μ}, at relative positions $\vec{r}_{\mu\lambda}$). Since the validity of the underlying multipole expansion breaks down for small distances from the core λ, the electric field $\vec{f}_{\lambda}$ has to be multiplied by a cutoff factor ω. In case of the trivalent 5f-in-core PPs, the following form also adapted for the di- and tetravalent cases [9] is used

$$\omega(r) = 1 - \exp\left(-\delta r^2\right). \tag{4}$$

The Dirac–Hartree–Fock (DHF) dipole polarizabilities α_{D} of Ac^{11+} (0.8982 a.u.) and Lr^{11+} (3.7501 a.u.) were used to interpolate those of the other An^{11+} cores, because the DHF program package [26] can only handle closed-shell systems. Since the dipole polarizabilities of the high-charged PP cores An^{11+} are strongly dependent on the presence of the valence electrons, the polarizabilities were calculated using the orbitals of the low-charged ions An^{1+} with the subconfiguration $6s^2 6p^6 7s^2$. The cutoff parameters δ were fitted at the CCSD(T) level to the first and second and to the second and third ionization potentials (IPs) of Ac and Lr, respectively. The reason why Ac and Lr were chosen is their unoccupied and fully occupied 5f orbitals, respectively, since in these cases more accurate reference data are available, i.e. 5f-in-valence PP CCSD(T) calculations without SO coupling using extrapolation to the basis set limit [27]. The 5f-in-core PP CCSD(T) calculations were carried out with the MOLPRO program package [28] using (10s10p10d8f6g) even-tempered basis sets, which were CCSD(T) energy-optimized for the $6d^1 7s^2$ and $7s^2 7p^1$ valence subconfigurations of Ac and Lr, respectively. The cutoff parameters δ of the other actinide elements were interpolated using the values of Ac (0.8727) and Lr (0.2696).

For the previously published CPPs of the 4f-in-core PPs, the cutoff factor is slightly different

$$\omega(r) = \left(1 - \exp\left(-\delta r^2\right)\right)^{0.5}. \tag{5}$$

Analogous to the actinides, the DHF dipole polarizabilities α_D of La^{11+} (0.4777 a.u.) and Lu^{11+} (1.9812 a.u.) were used to interpolate those of the other Ln^{11+} cores [29]. The cutoff parameter δ was fitted at the CCSD(T) level to the second and third experimental IPs of Lu (0.5592) and this parameter is also used for all other lanthanide elements [29].

The CPPs described so far use a common cutoff factor for all angular symmetries of the atom. In view of the different radial extent of the An/Ln 5f/4f shells, which still may be partially occupied in our approach, and the explicitly treated $6l/5l$ (l = s, p, d) shells, one might consider a l-dependent cutoff factor, e.g. in the form devised by Daudey and coworkers [30], in order to further improve the model.

Corresponding to the recently published HF calibration studies on AnF_3 (An = Ac–Lr) [8] using 5f-in-core large-core PPs (LPPs) in comparison to 5f-in-valence small-core PPs (SPPs), HF calculations using LPPs in connection with CPPs were carried out with MOLPRO [28]. For An (7s6p5d2f1g)/[5s4p3d2f1g] basis sets [8] were used and for F Dunning's aug-cc-pVQZ (augmented correlation-consistent polarized VQZ) basis set [31, 32] was applied. For all PPs the geometries were completely optimized imposing C_{3v} symmetry. Moreover, CCSD(T) calculations using LPPs with and without CPPs were performed. In these calculations the F 1s orbitals were kept frozen.

In the case of LnF_3 (Ln = La–Lu) HF and CCSD(T) calculations using 4f-in-core LPPs [11] with and without CPPs [29] were carried out with MOLPRO [28], in order to test the recently developed basis sets [20]. However, only the largest basis sets, i.e. (8s7p6d)/[6s5p5d], with newly optimized 3f2g polarization functions were used for Ln. These polarization functions were energy-optimized in multireference configuration interaction calculations. For F Dunning's aug-cc-pVQZ basis set [31, 32] was applied. As comparison SPP state-averaged multiconfiguration self-consistent field (MCSCF) calculations were performed using (14s13p10d8f6g)/[6s6p5d4f3g] basis sets [33]. For all PPs the geometries were completely optimized imposing C_{3v} symmetry, and the F 1s orbitals were kept frozen at the CCSD(T) level. Furthermore, SPP CCSD(T) calculations for LaF_3 as well as LuF_3 and an AE CCSD(T) calculation for LuF_3 applying the Douglas–Kroll–Hess Hamiltonian (DKH) were carried out [28] using C_{3v} symmetry and Dunning's aug-cc-pVQZ basis set for F [31, 32]. In the SPP calculations for Ln (14s13p10d8f6g)/[6s6p5d4f3g] basis sets [33] were used and the Ln 4s, 4p, and 4d as well as the F 1s orbitals were kept frozen. In the AE calculation for Lu a (26s22p18d14f6g)/[10s8p6d5f3g] generalized contracted basis set was applied and the Lu 1s–4s, 2p–4p, and 3d–4d as well as the F 1s orbitals were kept frozen.

The parameters of PPs, basis sets, and CPPs are compiled in the electronic supplementary material of this publication. They are also available from the authors and will be incorporated, e.g. into the MOLPRO [28] basis set library [34].

3 Results and discussion

In the following the results for bond lengths R_e, bond angles $\angle$, ionic binding energies ΔE_{ion}, and atomization energies ΔE_{at} of AnF_3 (An = Ac–Lr) and LnF_3 (Ln = La–Lu) from HF and CCSD(T) calculations using f-in-core LPPs with and without CPPs will be presented. Furthermore, the comparison of results for AnF_3 and LnF_3 is given in the electronic supplementary material (cf. "comparison_AnF3_LnF3.pdf").

The LPP HF and SPP state-averaged MCSCF atomization energies for LnF_3 $\Delta E_{at} = E(Ln) + 3 \times E(F) - E(LnF_3)$ calculated with respect to the lanthanide atom in the lowest state of the $4f^n 5d^1 6s^2$ configuration show rather large differences, i.e. the mean and maximum error amount to 0.38 (2.5%) and 0.85 eV (5.7%), respectively (cf. "binding_energies.pdf" of the electronic supplementary material). This is due to the different kinds of coupling between the 4f and 5d shell. In the case of the SPP calculations the 4f shell is treated explicitly and therefore the

5d shell is coupled in such a way that the lowest LS state according to Hund's rule arising from $4f^n5d^16s^2$ is obtained. In the case of the LPP calculations only ^2D valence substates are calculated, since the 4f shell is included in the PP core. Thus, 4f intrashell and 4f–5d intershell coupling is treated in an averaged manner and the results are obtained for averages over all states belonging to the molecular Ln^{3+} $4f^n$ $(F^-)_3$ and atomic Ln $4f^n5d^16s^2$ superconfigurations.

To correct for this discrepancy, we numerically calculated [35] the AE WB energy differences between the energies, where $4f^n$ is in its lowest LS state and the 5d electron is coupled in an averaged manner, and the energies of the lowest LS states according to Hund's rule. If this energy differences are subtracted from the LPP atomization energies, we obtain LPP HF atomization energies with respect to the lowest LS states according to Hund's rule $\Delta E_{\text{coupl.}}$. By this correction the mean and maximum deviations between LPP and SPP atomization energies are clearly reduced to 0.16 (1.0%) and 0.58 eV (3.6%), respectively (cf. "binding_energies.pdf" of the electronic supplementary material).

For Ce ($4f^15d^1$) and Yb ($4f^{13}5d^1$) this energy correction could also be determined more exactly by subtracting the SPP state-averaged MCSCF atomization energy calculated with respect to the lowest LS state according to Hund's rule (Ce: ^1G 15.18, Yb: ^3H 16.16 eV) from the atomization energy calculated with respect to the averaged energy of all possible LS states for $4f^n5d^1$ ($n = 1$, 13 for Ce, Yb), namely 35 triplet and 35 singlet microstates (^3P, ^3D, ^3F, ^3G, ^3H, ^1P, ^1D, ^1F, ^1G, ^1H; Ce: 15.88, Yb: 16.41 eV). In the first case the lowest SPP state-averaged MCSCF energy of CeF_3 and YbF_3 was used to calculate the atomization energy, while for the latter case the average of these energies was taken. Here, the seven molecular energies of CeF_3 and YbF_3 corresponding to the ^2F state of $4f^1$ and $4f^{13}$, respectively, are not degenerate due to the ligand field generated by the fluorine atoms. The energy corrections for Ce and Yb are 0.70 and 0.25 eV, respectively, which is in good agreement with the AE WB corrections of 0.68 and 0.31 eV. Therefore, the AE WB energy values should be a good approximation for these corrections.

Since both LPPs and SPPs are only adjusted to reference configurations of neutral atoms and singly charged cations [7, 11], the triply charged cations may not be described accurately. To estimate this shortcoming, we first numerically calculated [35] the AE WB, LPP HF, and SPP HF energy differences between the configurations $5s^25p^65d^16s^2$ and $5s^25p^6$ of the neutral lanthanides and the triply charged cations, respectively. Then we subtracted the AE WB from the LPP and SPP HF energies, respectively, to obtain the corresponding energy corrections. Although the obtained LPP and SPP atomization energies $\Delta E_{\text{coupl.+Ln}^{3+}}$ and $\Delta E_{\text{at+Ln}^{3+}}$ show a slightly larger mean absolute and relative error (m.a.e. and m.r.e.) of 0.24 eV and 1.6%, respectively, the maximum deviation is reduced to 0.36 eV (2.3%).

In order to directly compare LPP and SPP energies without these corrections, we calculated ionic binding energies, which were defined as $\Delta E_{\text{ion}} = E(M^{3+}) + 3\times E(F^-) - E(MF_3)$ (with M = An, Ln). However, in the case of the LPP CCSD(T) calculations for LnF_3 we calculated atomization energies, since for these compounds experimental atomization energies [36, 37] are available. In order to compare the LPP CCSD(T) atomization energies to the experimental values, the energies have to be calculated with respect to the experimentally observed ground states. Therefore, for those cases, where the $4f^n5d^16s^2$ subconfiguration corresponds to an excited state, the atomization energies were corrected to account for the experimentally observed ground state by subtracting the energy separation taken from experiment [38]. This energy difference could also be determined, e.g. at the AE DHF [39] or AE WB [35] level, whereby electron correlation contributions are neglected. Tables summarizing some possible corrections are included in the electronic supplementary material (cf. "energy_corrections.pdf").

3.1 Actinide trifluorides

The HF calculations for AnF_3 (An = Ac–Lr) using LPPs in connection with CPPs will be compared to those using pure LPPs respectively SPPs [8] (cf. Table 1). Furthermore, CCSD(T) calculations using LPPs with and without CPPs will be compared to density functional theory (DFT), second-order Møller–Plesset perturbation theory (MP2), and complete active space second-order perturbation theory (CASPT2) data from the literature [40–42] (cf. Table 2).

Since for Th and Pa the trivalent oxidation state is not preferred (Th) or even not stable (Pa) in aqueous solution [17], the trivalent subconfiguration $5f^n$ mixes strongly with the corresponding energetically low-lying tetravalent subconfiguration $5f^{n-1}6d^1$ yielding significantly smaller SPP 5f occupations than assumed for the LPP core [8]. Thus, for ThF_3 and PaF_3 the assumption of a near-integral 5f occupation is too crude [8], and all mean absolute and relative errors were calculated neglecting the results for these two systems.

3.1.1 Molecular structure

Using the recently published trivalent 5f-in-core LPPs [8] in connection with CPPs, the LPP HF An–F bond lengths and F–An–F bond angles decrease on average by 0.015 Å

Table 1 An–F bond lengths R_e (in Å), bond angles ∠F-An-F (in °), and ionic binding energies ΔE_{ion} (in eV) for AnF_3 (An = Ac–Lr) from HF calculations using LPPs with and without CPPs as well as from SPP state-averaged MCSCF calculations

An	R_e			∠F-An-F			ΔE_{ion}			f occupation	
	LPP[a]	CPP[b]	SPP[a]	LPP[a]	CPP[b]	SPP[a]	LPP	CPP[b]	SPP	LPP[a,c]	SPP[a]
Ac	2.207	2.200	2.213	115.7	115.4	115.9	42.99	43.18	42.92	0.13	0.23
Th	2.193	2.184	2.125	115.1	114.7	101.8	43.36	43.59	46.53	0.10	0.60
Pa	2.179	2.170	2.109	115.1	114.6	113.6	43.71	43.99	45.33	0.09	1.52
U	2.166	2.154	2.124	115.4	114.7	108.5	44.06	44.40	44.88	0.08	3.02
Np	2.152	2.139	2.118	115.8	114.9	110.6	44.41	44.81	45.04	0.07	4.05
Pu	2.139	2.125	2.109	116.2	115.1	112.4	44.75	45.20	45.56	0.07	5.07
Am	2.126	2.110	2.100	116.6	115.3	112.9	45.08	45.58	45.82	0.06	6.07
Cm	2.114	2.096	2.097	117.2	115.6	114.5	45.41	45.97	45.71	0.06	7.07
Bk	2.102	2.084	2.085	117.6	115.7	114.7	45.70	46.31	46.24	0.06	8.07
Cf	2.090	2.071	2.078	118.1	116.0	114.7	46.03	46.67	46.62	0.05	9.07
Es	2.080	2.060	2.059	118.5	116.2	114.8	46.31	46.98	46.82	0.05	10.07
Fm	2.069	2.050	2.045	118.9	116.4	113.9	46.58	47.27	47.10	0.05	11.06
Md	2.058	2.039	2.043	119.5	117.0	116.0	46.90	47.58	47.46	0.05	12.06
No	2.047	2.031	2.039	119.7	117.6	116.0	47.18	47.83	47.61	0.05	13.05
Lr	2.037	2.023	2.034	120.0	118.4	117.1	47.47	48.06	47.57	0.05	14.04

Additionally, LPP and SPP HF f orbital occupations obtained from a Mulliken population analysis are given. Basis sets: LPP (7s6p5d2f1g)/[5s4p3d2f1g]; SPP (14s13p10d8f6g)/[10s9p5d4f3g]; F aug-cc-pVQZ

[a] Results taken from Moritz et al. [8]

[b] LPP calculations using CPPs

[c] 0–14 electrons in the 5f shell are attributed to the LPP core for Ac–Lr, respectively

Table 2 An–F bond lengths R_e (in Å), bond angles ∠F-An-F (in °), and ionic binding energies ΔE_{ion} (in eV) for AnF_3 (An = Ac–Lr) from CCSD(T) calculations using LPPs with and without CPPs

An	R_e		∠F-An-F		ΔE_{ion}	
	LPP	CPP[a]	LPP	CPP[a]	LPP	CPP[a]
Ac	2.189	2.185	112.5	112.5	43.82	43.91
Th	2.176	2.172	111.7	111.6	44.18	44.30
Pa	2.163	2.158	111.4	111.2	44.54	44.68
U	2.149	2.143	111.5	111.2	44.89	45.07
Np	2.135	2.128	111.7	111.3	45.24	45.45
Pu	2.122	2.114	112.0	111.4	45.57	45.82
Am	2.109	2.100	112.2	111.5	45.90	46.19
Cm	2.097	2.086	112.6	111.7	46.22	46.56
Bk	2.085	2.074	112.9	111.7	46.51	46.89
Cf	2.073	2.061	113.2	112.0	46.83	47.25
Es	2.062	2.050	113.5	112.1	47.11	47.56
Fm	2.052	2.040	113.7	112.3	47.39	47.86
Md	2.041	2.029	114.2	112.7	47.70	48.18
No	2.031	2.020	114.5	113.2	47.99	48.46
Lr[b]	2.020	2.012	114.9	113.6	48.28	48.72

Basis sets: An (7s6p5d2f1g)/[5s4p3d2f1g]; F aug-cc-pVQZ

[a] LPP calculations using CPPs

[b] SPP CCSD(T): $R_e = 2.002$ Å, ∠F-Lr-F = 111.5°, $\Delta E_{ion} = 48.83$ eV

(0.7%) and 1.5° (1.2%), respectively. Since the SPP state-averaged MCSCF bond lengths and angles are overestimated by about 0.020 Å (0.9%) and 3.7° (3.2%), respectively, using pure LPPs, the application of CPPs reduces the m.a.e. (m.r.e.) to 0.010 Å (0.5%) and 2.1° (1.9%). Thus, the use of CPPs clearly improves the results of the LPPs. In comparison to the Cm–F bond length ($R_e = 2.095$ Å) from an AE DHF calculation [43] the LPP + CPP HF result is also considerably better than the pure LPP HF result, i.e. the LPP and LPP + CPP bond lengths are by 0.019 and 0.001 Å too long, respectively.

If correlation effects are taken into account via CCSD(T), the LPP bond lengths and angles are reduced by about 0.017 Å (0.8%) and 4.5° (3.8%) with respect to the HF values, respectively. The decrease in CCSD(T) bond lengths and angles due to the application of CPPs is almost by 50% smaller than that for the HF calculations, i.e. it amounts to 0.009 Å (0.4%) and 0.8° (0.7%), respectively. The reason for this smaller decrease is most likely that the CCSD(T) bond lengths and angles are already reduced by valence correlation effects and that consequently the further reduction is complicated due to the increased F–F repulsion. The LPP/LPP + CPP CCSD(T) bond length and angle of UF_3 show reasonable agreement with those from a SPP DFT/PBE0 calculation ($R_e = 2.069$ Å; ∠ = 105°)

[40], i.e. the deviations amount to 0.080/0.074 Å (3.9/3.6%) and 7°/6° (6.7/5.7%), respectively. The same is true for the DFT and MP2 results for UF_3 published by Joubert and Maldivi [41], who included scalar-relativistic corrections either by a frozen core approximation with a quasi-relativistic treatment of the valence electron shells or by an energy-adjusted quasirelativistic pseudopotential, where the 5f, 6s, 6p, 6d, and 7s electrons are treated explicitly. Depending on the method the obtained bond lengths and angles are in-between 2.051–2.122 Å and 104.7–118.4°, respectively. Therefore, the LPP and LPP + CPP results deviate in a range of 0.027–0.098 and 0.021–0.092 Å as well as from −6.9 to +6.8 and from −7.2 to +6.5°, respectively. Compared to the Am–F bond length ($R_e = 2.078$ Å) from a AE DFT/BP calculation including the 5f, 6s, 6p, 6d, 7s, and 7p orbitals in the valence space and using the zero-order regular approximation (ZORA) [42], our LPP and LPP + CPP CCSD(T) bond lengths deviate just by 0.031 (1.5%) and 0.022 Å (1.1%), respectively. Furthermore, the differences between our LPP/LPP + CPP CCSD(T) Am–F bond lengths and those from CASPT2 calculations using either a scalar Douglas–Kroll–Hess Hamiltonian or the SPP [42] are 0.046/0.037 and 0.027/0.018 Å, respectively (DKH $R_e = 2.063$; SPP $R_e = 2.082$ Å). Thus, the LPP CCSD(T) results show good agreement with the available data from the literature and the CPPs improve the pure LPP results.

3.1.2 Ionic binding energy

In the case of the LPP HF ionic binding energies the use of CPPs causes a mean increase by 0.50 eV (1.1%). Therefore, the deviations from the SPP HF results become more than 50% smaller, if CPPs are applied, i.e. the m.a.e. (m.r.e.) amount to 0.51 (1.1%) and 0.24 eV (0.5%) for LPP and LPP + CPP HF calculations, respectively.

The LPP CCSD(T) ionic binding energies are higher than the LPP HF values by about 0.82 eV (1.8%). Compared to the HF results the application of CPPs results in a smaller mean increase of the ionic binding energies by 0.32 eV (0.7%). Because of this increase, a clear improvement due to CPPs is found in comparison to the SPP CCSD(T) optimization of LrF_3, in which only the F 1s orbitals were frozen and all valence orbitals of Lr, i.e. 5s, 5p, 5d, 5f, 6s, 6p, 6d, and 7s, were chosen to be active ($R_e = 2.002$ Å; $\angle = 111.5°$; $\Delta E_{ion} = 48.83$ eV). The deviations from the SPP CCSD(T) ionic binding energy amount to 0.55 (1.1%) and 0.11 eV (0.2%) for LPP and LPP + CPP calculations, respectively. Furthermore, the LPP + CPP bond lengths and angles are also in better agreement with the SPP data than the pure LPP results, i.e. the differences between SPP and LPP/LPP + CPP results are 0.018/0.010 Å and 3.4/2.1° for bond lengths and angles, respectively. Hence, the use of CPPs also leads to an improvement of the ionic binding energies.

3.2 Lanthanide trifluorides

The LnF_3 HF and CCSD(T) results calculated using LPPs with and without CPPs and the new (8s7p6d3f2g)/[6s5p5d3f2g] basis sets [20] will be compared to SPP state-averaged MCSCF and experimental [36, 37, 44] data from the literature, respectively (cf. Tables 3, 4 for HF and CCSD(T) results, respectively). However, the experimental atomization energies [36] were not measured directly, but calculated from a thermochemical cycle, where sometimes estimated values were used. The assumed uncertainty is ±0.22 eV if all quantities are measured (La, Pr, Nd, Gd, Er) and ±0.43 eV if one or more estimated values are used (Ce, Sm, Eu, Tb–Ho, Tm–Lu).

In the case of Gd the contraction coefficients of the s basis functions were modified, because new coefficients reduce the energy of Gd^{3+} by more than 1 Hartree (s coefficients: old −0.9361, 1.3080, −0.8824; new −0.0801, 0.5277, −0.9570). This modification has been included on the PP webpage [34].

3.2.1 Molecular structure

The LPP HF bond lengths calculated using the new basis sets overestimate the SPP bond lengths on average by 0.005 Å (0.2%). If CPPs are applied, the LPP bond lengths decrease by about 0.012 Å. Since this decrease grows along the lanthanide series (La $\Delta R_e = -0.003$ Å; Lu $\Delta R_e = -0.021$ Å), the LPP + CPP values still overestimate the SPP bond lengths for the lighter (La–Nd) and underestimate them for the heavier lanthanides (Pm–Lu). Altogether the CPPs increase the deviations from the SPP data, i.e. the m.a.e. (m.r.e.) amounts to 0.011 Å (0.5%). It should be noted here that the CPP models static as well as dynamic core-polarization, whereas the SPP state-averaged MCSCF calculations only account for the former. The bond lengths from LPP HF calculations [45] using the original (7s6p5d)/[5s4p3d] basis sets [11] also differ by about 0.005 Å (0.3%) from the SPP data. The differences between these and our LPP HF bond lengths are negligible, i.e. they amount to ca. 0.003 Å (0.1%), which is in agreement with the finding of other authors for $DyCl_3$ [21], where the original basis set also gives by 0.001–0.003 Å longer bond lengths than the new one.

The planarity or nonplanarity of LnF_3 has been the subject of some controversy. However, both experimental and theoretical evidence point to C_{3v} structures for the majority of LnF_3 [44–46]. Geometry optimizations without any symmetry restrictions at the LPP DFT/B3PW91 level showed that LnF_3, which is significantly pyramidal at the beginning of the lanthanide series, becomes increasingly

Table 3 Ln–F bond lengths R_e (in Å), bond angles ∠F-Ln-F (in °), and ionic binding energies ΔE_{ion} (in eV) for LnF_3 (Ln = La–Lu) from HF calculations using LPPs with and without CPPs in comparison to SPP state-averaged MCSCF and LPP HF [45] calculations

Ln	R_e				∠F-Ln-F				ΔE_{ion}			f occupation	
	LPP	CPP[a]	SPP	Joubert et al. [45]	LPP	CPP[a]	SPP	Joubert et al. [45]	LPP	CPP[a]	SPP	LPP[b]	SPP
La	2.146	2.143	2.138	2.15	118.8	118.7	119.5	116.0	44.48	44.60	44.65	0.10	0.17
Ce	2.132	2.128	2.119	2.13	119.4	119.3	118.4	116.8	44.83	44.98	45.08	0.10	1.16
Pr	2.118	2.113	2.107	2.12	119.7	119.7	118.8	117.4	45.17	45.35	45.43	0.09	2.15
Nd	2.105	2.098	2.096	2.11	119.9	119.9	119.5	118.0	45.50	45.72	45.72	0.09	3.13
Pm	2.092	2.085	2.086	2.09	120.0	120.0	120.0	118.9	45.81	46.07	46.00	0.09	4.12
Sm	2.080	2.071	2.075	2.08	120.0	120.0	120.0	119.8	46.11	46.41	46.28	0.09	5.11
Eu	2.067	2.057	2.065	2.06	120.0	120.0	120.0	120.0	46.42	46.77	46.53	0.09	6.10
Gd	2.056	2.045	2.054	2.06	120.0	120.0	120.0	120.0	46.69	47.09	46.81	0.09	7.10
Tb	2.043	2.031	2.043	2.05	120.0	120.0	120.0	120.0	47.00	47.45	47.06	0.09	8.09
Dy	2.032	2.018	2.032	2.03	120.0	120.0	120.0	120.0	47.29	47.80	47.36	0.09	9.09
Ho	2.020	2.005	2.021	2.02	120.0	120.0	120.0	120.0	47.58	48.16	47.64	0.09	10.08
Er	2.009	1.992	2.010	2.01	120.0	120.0	120.0	120.0	47.87	48.51	47.92	0.09	11.07
Tm	1.999	1.980	2.000	2.00	120.0	120.0	120.0	120.0	48.14	48.85	48.19	0.09	12.07
Yb	1.988	1.968	1.989	1.99	120.0	120.0	120.0	120.0	48.43	49.21	48.46	0.09	13.06
Lu	1.984	1.963	1.978	1.98	120.0	120.0	120.0	120.0	48.58	49.44	48.80	0.08	14.04

Additionally, LPP and SPP HF f orbital occupations obtained from a Mulliken population analysis are given. Basis sets: LPP (8s7p6d3f2g)/[6s5p5d3f2g]; SPP (14s13p10d8f6g)/[6s6p5d4f3g]; F aug-cc-pVQZ; [45]: Ln (7s6p5d)/[5s4p3d], F (10s4p1d)/[3s2p1d]

[a] LPP calculations using CPPs

[b] 0–14 electrons in the 4f shell are attributed to the LPP core for La–Lu, respectively

planar towards the end of the lanthanide series (bond angles: LaF_3 113.1, LuF_3 119.3°) [47]. Furthermore, a MP2 study on the LaF_3 molecule embedded in argon matrix using an effective core potential pointed out that the argon packing structure around LaF_3 determines the molecular shape, i.e. two groups of clusters very close in energy ($\Delta E < 1$ kcal/mol) were obtained, where one contains a planar LaF_3 and is thermodynamically favored and the other one contains a pyramidal LaF_3 and is kinetically favored [48]. These results explain why the interpretation of experimental data is not univocal, because similar but not identical infrared spectra may arise due to differences in apparatus and conditions for matrix deposition [48].

Our LPP HF and SPP state-averaged MCSCF calculations yield C_{3v} symmetry only in the beginning of the lanthanide series, i.e. for LaF_3–NdF_3 (four elements) and PmF_3–LuF_3 (11 elements) C_{3v} and D_{3h} symmetry is obtained, respectively. The differences between the LPP and SPP bond angles are quite small, i.e. the m.a.e. and m.r.e. are 0.2° and 0.2%, respectively. The application of CPPs has nearly no effect [$\Delta\angle_{max} = 0.05°$ (0.04%)], wherefore the differences between LPP + CPP and SPP bond angles are the same as those of pure LPPs. The bond angles of the former LPP HF calculations [45] using the original basis sets deviate slightly more from the SPP results, i.e. the m.a.e. (m.r.e.) amounts to 0.6° (0.5%). Here, C_{3v} symmetry is found for LaF_3–SmF_3 (6 elements). Analogous to the bond lengths, the deviations between these former and our LPP HF bond angles are very small, i.e. the differences are on average 0.7° (0.6%).

If correlation effects are included via CCSD(T), the LPP HF bond lengths are shortened by 0.008 Å (0.4%). The differences from the experimental bond lengths [44] are quite small, i.e. the m.a.e. (m.r.e.) amounts to 0.007 Å (0.3%). The use of CPPs at the CCSD(T) level shows a smaller bond length contraction than for the LPP HF calculations, i.e. the reduction is 0.008 (0.4%) instead of 0.012 Å (0.6%). Analogous to the LPP CCSD(T) An–F bond lengths (cf. Sect. 3.1.1), the reason for this smaller contraction is most likely the increased F–F repulsion due to the bond length reduction by the consideration of correlation effects. Thus, the improvement of the LPP CCSD(T) results by using CPPs is only ca. 0.002 Å (0.1%), i.e. the m.a.e. (m.r.e.) of the LPP+CPP CCSD(T) bond lengths amounts to 0.005 Å (0.2%). The bond lengths from former LPP calculations using the original basis sets and MP2 [45] differ by ca. 0.013 Å (0.7%) from the experimental values. Thus, these deviations are slightly larger than those of our LPP CCSD(T) results. However, with regard to the different methods and basis sets the deviations between the LPP MP2 and CCSD(T) bond lengths are quite small, i.e. they amount at most to 0.017 Å (0.8%). For LaF_3 and LuF_3 the deviations of the LPP CCSD(T) bond lengths from AE DFT/PBE optimizations using ZORA [49]

Table 4 Ln–F bond lengths R_e (in Å), bond angles ∠F-Ln-F (in °), and atomization energies ΔE_{at} (in eV) for LnF_3 (Ln = La–Lu) from CCSD(T) calculations using LPPs with and without CPPs in comparison to experimental data [36, 44] as well as to LPP MP2 [45] and CISD + Q [54] calculations

Ln	R_e				∠F-Ln-F[a]			ΔE_{at}[b]				$\Delta E_{coupl.+Ln^{3+}}$[b]	
	LPP	CPP[c]	Exp.[d]	Joubert et al. [45]	LPP	CPP[c]	Joubert et al. [45]	LPP	CPP[c]	Exp.[e]	Dolg et al. [54]	LPP	CPP[c]
La[f]	2.133	2.130	*2.139*	2.15	115.8	115.8	112.9	20.13	20.16	19.86	18.17	20.07	20.11
Ce	2.119	2.116	*2.127*	2.13	116.3	116.2	113.7	20.10	20.15	20.08	18.23	19.32	19.36
Pr	2.105	2.101	2.091	2.12	116.5	116.5	114.1	19.50	19.55	19.08	17.63	18.92	18.97
Nd	2.092	2.088	*2.090*	2.10	116.8	116.7	114.6	19.17	19.23	19.04	17.33	18.44	18.50
Pm	2.080	2.076	*2.077*	2.09	117.4	117.2	115.5	19.99	20.06			19.07	19.14
Sm	2.069	2.063	*2.065*	2.08	117.9	117.7	116.3	17.71	17.78	17.30	15.93	16.65	16.73
Eu	2.058	2.051	*2.054*	2.06	118.5	118.2	118.3	16.51	16.59	17.22	14.86	15.52	15.60
Gd	2.048	2.041	2.053	2.06	119.1	118.8	117.8	19.92	20.00	19.21	18.16	19.24	19.33
Tb	2.037	2.029	*2.030*	2.05	119.7	119.5	119.1	19.90	19.99	18.99	18.18	19.58	19.67
Dy	2.026	2.017	*2.019*	2.04	120.0	119.8	120.0	19.01	19.11	17.35	17.25	18.77	18.87
Ho	2.015	2.005	2.007	2.02	120.0	120.0	120.0	18.94	19.05	17.22	17.15	18.66	18.76
Er	2.004	1.993	*1.997*	2.01	120.0	120.0	120.0	19.14	19.25	17.17	17.31	18.76	18.87
Tm	1.994	1.982	*1.987*	2.00	120.0	120.0	120.0	18.43	18.53	17.04	16.55	18.00	18.11
Yb	1.984	1.970	*1.975*	1.99	120.0	120.0	120.0	17.26	17.36	16.05	15.29	16.91	17.02
Lu[f]	1.982	1.967	*1.968*	1.98	120.0	120.0	120.0	20.07	20.14	18.43	18.21	20.05	20.12

Additionally, LPP and LPP + CPP CCSD(T) atomization energies corrected to account for the coupling between $4f^n$ and $5d^1$ as well as for the proper description of triply charged ions Ln^{3+} $\Delta E_{coupl.+Ln^{3+}}$ (in eV) are given. Basis sets: LPP: Ln (8s7p6d3f2g)/[6s5p5d3f2g], F aug-cc-pVQZ; [45]: Ln (7s6p5d)/[5s4p3d], F (10s4p1d)/[3s2p1d]; [54]: Ln (7s6p5d1f)/[5s4p3d1f], F 1s-in-core PP and (6s6p1d)/[3s3p1d]

[a] Experimental ∠F-Ln-F (in °): Pr 105.0 ± 1.5, Gd 109.0 ± 2.3, Ho 110.8 ± 1.2 [44]

[b] Except for Pm, atomization energies are given with respect to the real ground states using experimental energy corrections

[c] LPP calculations using CPPs

[d] Numbers in italics represent estimated values

[e] The experimental data [36] were not measured directly, but calculated from a thermochemical cycle, where sometimes estimated values were used. The errors are assumed to be ±0.22 eV for La, Pr, Nd, Gd, and Er and ±0.43 eV for the other lanthanides. Further experimental values for ΔE_{at} (in eV): Sm 17.74(9), Eu 16.48(9), Tm 17.52(9) [37]

[f] SPP CCSD(T): La $R_e = 2.121$ Å, ∠F-Ln-F = 116.2°, $\Delta E_{at} = 20.38$ eV; Lu $R_e = 1.962$ Å, ∠F-Ln-F = 120.0°, $\Delta E_{at} = 20.19$ eV; AE/DKH CCSD(T): Lu $R_e = 1.967$ Å, ∠F-Ln-F = 120.0°, $\Delta E_{at} = 20.75$ eV

are also quite small, i.e. the La–F and Lu–F bond lengths are overestimated by 0.022 (1.0%) and 0.013 Å (0.7%), respectively (AE bond lengths: LaF_3 2.111, LuF_3 1.969 Å).

In the case of bond angles the inclusion of correlation effects via CCSD(T) results in a decrease of about 1.3° (1.1%). Due to this decrease, for LaF_3–TbF_3 (9 elements) C_{3v} symmetry is obtained. The mean deviation from experimental data [44] amounts to 10.3° (9.5%). The application of CPPs at the CCSD(T) level gives a larger bond angle decrease compared to the HF level, i.e. the bond angles are reduced by 0.12° (0.1%). Because of this decrease, at the LPP + CPP CCSD(T) level also for DyF_3 C_{3v} symmetry is obtained and the mean deviation from experimental data is slightly reduced to 10.2° (9.4%). The former LPP MP2 bond angles [45] differ even slightly less from the experimental data, i.e. the m.a.e. (m.r.e.) amounts to 9.0° (8.3%). However, both LPP MP2 and CCSD(T) calculations yield C_{3v} symmetry for the same compounds (LaF_3–TbF_3; 9 elements) and deviate only by about 1.1° (0.9%). One reason for the large deviations (ca. 10%) between computational and experimental bond angles is possibly that the experimental structures were determined according to electron diffraction data without anharmonicity corrections [44]. However, the anharmonicity in angle bending vibration may seriously affect the angle parameters, i.e. the conclusion on equilibrium molecular geometries cannot be considered fully unambiguous [50]. Furthermore, the LPP CCSD(T) bond angles of LaF_3 and LuF_3 are in good agreement with SPP CCSD(T) data (cf. Table 4), i.e. the differences amount to 0.4 and 0.0° for LaF_3 and LuF_3, respectively.

Compared to the AE DFT/PBE bond angle of LaF_3 (∠ = 113.6°) [49] the LPP CCSD(T) value deviates only by 2.2° (1.9%). However, in the case of LuF_3 the AE DFT bond angle (∠ = 101.4°) [49] is by more than 18° smaller than the LPP CCSD(T) result, i.e. at the AE DFT level a nonplanar LuF_3 structure is obtained, whose bond angle is even smaller than that of LaF_3. Clavaguera et al. [49] confirmed this small bond angle by a SPP MP2 calculation using (14s13p10d8f6g)/[10s8p5d4f3g] [51] and cc-pVDZ basis sets for Lu and F, respectively. This finding stands in contrast to all calculations, which we performed for LuF_3, i.e. LPP, SPP, and AE/DKH CCSD(T) optimizations [28] using C_{3v} symmetry yield planar structures (cf. Table 4). Furthermore, a planar AE/DKH CCSD structure ($R_e = 1.966$ Å) was confirmed as a true energy minimum by a numerical vibrational frequency analysis [28]. In order to exclude that this discrepancy is due to different methods or basis sets, we performed a SPP MP2 optimization in GAUSSIAN03 [52] using exactly the same basis sets as Clavaguera et al. [49]. We obtained a slightly nonplanar structure confirmed as a true energy minimum by a numerical vibrational frequency analysis, but our bond angle amounts to 119.0° and not to 101.4°. Therefore, we agree with the recently published results from Roos et al. [53], where the LuF_3 molecule is found to be planar (AE/DKH results: CASPT2 $R_e = 1.961$ Å; DFT/B3LYP: $R_e = 1.985$ Å) and the 4f shell is affirmed to be essentially inert.

From the comparison of the LPP CCSD(T) structures to the experimental data [44] one can conclude that the new basis sets yield reasonable results especially for bond lengths, where the deviations are at most 0.014 Å (0.7%). Moreover, our LPP HF and CCSD(T) results are as good as those from former LPP HF and MP2 calculations [45], respectively, where the original (7s6p5d)/[5s4p3d] basis sets [11] were applied. In contrast to AnF_3 results, the CPPs show only at the CCSD(T) level a slight improvement of the structures.

3.2.2 *Ionic binding and atomization energy*

The LPP HF ionic binding energies calculated using the new basis sets underestimate the SPP values only by about 0.14 eV (0.3%). The effect of the CPPs grows with increasing nuclear charge, i.e. the ionic binding energies are increased by 0.12 and 0.86 eV for LaF_3 and LuF_3, respectively. Therefore, the CPPs reduce the deviations from the SPP data for LaF_3–SmF_3 and increase them for EuF_3–LuF_3. Altogether, the mean deviation from the SPP results is by ca. 0.2 eV larger than that using pure LPPs, i.e. the m.a.e. (m.r.e.) amounts to 0.33 (0.7%).

At the correlated level, our LPP CCSD(T) atomization energies ΔE_{at} deviate on an average by 0.94 (5.4%) and 0.33 eV (1.9%) from the experimental atomization energies determined in 1975 [36] and 1981 [37], respectively. The application of CPPs has a very small effect on the atomization energies, i.e. they are increased by at most 0.11 eV (0.5%). Since in the case of the LPP CCSD(T) calculations the atomization energies are overestimated, the use of CPPs results in slightly increased deviations, i.e. the m.a.e. (m.r.e.) amount to 1.01 (5.7%) and 0.39 eV (2.2%) for the experimental atomization energies from 1975 and 1981, respectively. Former LPP calculations using (7s6p5d1f)/[5s4p3d1f] basis sets for Ln and the configuration interaction method including all single and double excitations and the size-extensivity correction proposed by Langhoff and Davidson (CISD + Q) [54] show larger differences to the experimental data than our LPP CCSD(T) calculations, i.e. the mean deviations are 1.00 (5.4%) and 1.47 eV (8.5%) for the experimental atomization energies from 1975 and 1981, respectively. Our LPP CCSD(T) atomization energies are on average by 1.83 eV (10.7%) higher than those of the LPP CISD + Q calculations. However, this deviation is not necessarily due to the different basis sets for Ln, but probably results from the fact that in the older work [54] the original f-projector [11] not allowing any 4f participation in bonding was applied. Additional smaller deviations may result from the different core definitions and basis sets for F or the different molecular symmetries. Moreover, the size-extensivity of the CCSD(T) approach explains these results.

Since the experimental data are overestimated by up to 1.97 eV (11.5%), additional SPP CCSD(T) calculations for LaF_3 as well as LuF_3 and an AE/DKH CCSD(T) calculation for LuF_3 were carried out [28] (cf. Table 4). The obtained SPP and AE atomization energies are larger than the corresponding LPP and CPP results and thus overestimate the experimental values even more. The deviations between LPP and SPP atomization energies are very small, i.e. they amount to 0.25 (1.2%) and 0.12 eV (0.6%) for LaF_3 and LuF_3, respectively. Compared to the SPP data CPPs show an improvement of the pure LPP results, i.e. if CPPs are used, the differences to the SPP data are reduced to 0.22 (1.1%) and 0.05 eV (0.2%) for LaF_3 and LuF_3, respectively. Compared to the AE/DKH CCSD(T) atomization energy of LuF_3 the LPP and LPP+CPP CCSD(T) results are clearly too small, i.e. the differences amount to 0.68 (3.3%) and 0.61 eV (2.9%), respectively. These large deviations are most likely due to the basis set superposition error (BSSE), which tends to become larger with increasing number of explicitly treated electrons on the metal (LPP < SPP < AE).

Taking the BSSE into account via the counterpoise (CP) correction the LaF_3 atomization energies are reduced from 20.38 to 20.20 and from 20.13 to 19.98 eV for SPP and LPP calculations, respectively. In the case of LuF_3 these energies are reduced from 20.75 to 19.79, from 20.19 to 19.82, and from 20.07 to 19.81 eV for AE, SPP, and LPP calculations, respectively. As expected the BSSE using LPPs or SPPs are clearly smaller than that of the AE calculations, which constitutes an advantage compared to this more rigorous method. For the CP corrected atomization energies of LaF_3/LuF_3 the deviations between LPP and SPP values are reduced to 0.22/0.01 eV (1.1/0.05%), and the deviation between the LPP and AE value for LuF_3 is reduced to 0.02 eV (0.1%). Compared to the experimental data of LaF_3/LuF_3 from 1975 [36] the differences of the CP corrected energies amount to –/+1.36, +0.34/+1.39, and +0.12/+1.38 eV for AE, SPP, and LPP calculations, respectively.

Two possible reasons, why the experimental values are overestimated, are the neglect of SO effects and of the zero-point energy (ZPE). The SO splittings for La and Lu can be taken from experiment [38] and amount to ca. 0.08 and 0.15 eV, respectively. The ZPE is estimated to be 0.13 eV, which corresponds to the value determined by LPP MP2 calculations for ErF_3 and TmF_3 [55]. If these corrections are added to the experimental data [36], the atomization energies for LaF_3 and LuF_3 are 20.07 ± 0.22 and 18.71±0.43 eV, respectively. Compared to these energies for LaF_3/LuF_3 the deviations of the CP corrected values amount to –/+1.08, +0.13/+1.11, and −0.09/+1.10 eV for AE, SPP, and LPP calculations, respectively. While the computational atomization energies for LaF_3 are within the experimental error bars, those for LuF_3 are still by up to 1.11 eV (5.9%) too large. Since the more rigorous SPP and AE methods are known to be reliable, we suppose that the uncertainty of the experimental values, for which estimated values had to be used within the thermochemical cycle, might be larger than the assumed 0.43 eV.

In the case of the other lanthanide trifluorides CeF_3–YbF_3 aside these reasons for the large discrepancies, the LPP atomization energies are also somewhat too large due to the wrong coupling between $4f^n$ and $5d^1$ as well as to the bad description of triply charged ions (cf. Sect. 3). If this is taken into account using the energy corrections determined at the HF level ($\Delta E_{\mathrm{coupl.+Ln^{3+}}}$ in Table 4), the mean deviations compared to the experimental values from 1975 [36] are slightly reduced from 0.94 (5.4%) to 0.90 eV (5.1%). However, compared to the experiment from 1981 [37] the mean differences are increased by more than 50% from 0.33 (1.9%) to 0.84 eV (4.9%). Two possible reasons for the remaining deviations are the calculation of the energy corrections at the HF instead of the CCSD(T) level and the correction with respect to the lowest LS states according to Hund's rule, which do not always correspond to the lowest experimentally observed LS states. The AE WB corrections were calculated for LS states according to Hund's rule, since some LS states, e.g. ^4I of Pr $4f^25d^1$, cannot be calculated using the program MCHF95 [35], because there is more than one possibility to couple, e.g. $4f^2$ and $5d^1$ to obtain ^4I.

4 Conclusion

The AnF_3 results from LPP HF calculations are clearly improved by using CPPs, i.e. the LPP/LPP+CPP results deviate on average by 0.020/0.010 Å (0.9/0.5%), 3.7/2.1° (3.2/1.9%), and 0.51/0.24 eV (1.1/0.5%) from SPP state-averaged MCSCF bond lengths, bond angles, and ionic binding energies, respectively. The same conclusion can be drawn from the comparison of LPP CCSD(T) results calculated with and without using CPPs to the available DFT, MP2, and CASPT2 structures for UF_3 and AmF_3 from the literature and to the SPP CCSD(T) results for LrF_3.

For LnF_3 the 4f-in-core LPP HF calculations using the new (8s7p6d3f2g)/[6s5p5d3f2g] basis sets show good agreement with corresponding SPP reference data, i.e. the mean deviations amount to 0.005 Å (0.2%), 0.2° (0.2%), and 0.14 eV (0.3%) for bond lengths, bond angles, and ionic binding energies, respectively. Compared to experimental data only LPP CCSD(T) bond lengths show small deviations, i.e. the m.a.e. for bond lengths, bond angles, and atomization energies are 0.007 Å (0.3%), 10.3° (9.5%), and 0.94 eV (5.4%), respectively. If corrections for the neglected SO coupling and ZPE as well as the BSSE are taken into account, the deviation for LaF_3 lies within the experimental error bars, while that for LuF_3 still amounts to 1.10 eV (5.9%), which is more than 50% larger than the experimental error bar of 0.43 eV. However, the LPP and SPP/AE CCSD(T) bond angles and atomization energies for LaF_3 and LuF_3 are consistent with each other, i.e. the maximum deviations (using the counterpoise correction) are 0.4° (0.3%) and 0.22 eV (1.1%), both occurring for LaF_3. The reason for the large discrepancies from experimental atomization energies is most likely that the assumed uncertainties for atomization energies including estimated values in the thermochemical cycle are too small. In the case of bond angles the anharmonicity in angle bending vibration was neglected, which can seriously affect the angle parameters. In contrast to AnF_3 the CPPs do not improve the pure LPP results.

Acknowledgments This contribution is dedicated to the memory of Jean-Pierre Daudey. The financial support from the Deutsche Forschungsgemeinschaft (DFG) to A.W. is gratefully acknowledged. Furthermore, we thank D. Pape for the SPP MP2 calculation on LuF_3.

References

1. Katz JJ, Seaborg GT, Morss LR (1986) The chemistry of the actinide elements, vol 2. Chapman and Hall, London
2. Pepper M, Bursten B (1991) Chem Rev 91:719
3. Schreckenbach G, Hay PJ, Martin RL (1999) J Comp Chem 20:70

4. Dolg M, Cao X (2003) The relativistic energy-consistent ab initio pseudopotential approach. In: Hirao K, Ishikawa Y (eds) Recent advances in relativistic molecular theory. World Scientific, New Jersey
5. Cao X, Dolg M (2006) Coord Chem Rev 250:900
6. Küchle W, Dolg M, Stoll H, Preuss H (1994) J Chem Phys 100:7535
7. Dolg M, Stoll H, Preuss H (1989) J Chem Phys 90:1730
8. Moritz A, Cao X, Dolg M (2007) Theor Chem Acc 117:473
9. Moritz A, Cao X, Dolg M (2007) Theor Chem Acc 118:845
10. Moritz A, Dolg M (2008) Theor Chem Acc 121:297
11. Dolg M, Stoll H, Savin A, Preuss H (1989) Theor Chim Acta 75:173
12. Hülsen M, Weigand A, Dolg M (2009) Theor Chem Acc 122:23
13. Cao X, Li Q, Moritz A, Xie Z, Dolg M, Chen X, Fang W (2006) Inorg Chem 45:3444
14. Wiebke J, Moritz A, Cao X, Dolg M (2007) Phys Chem Chem Phys 9:459
15. Cao X, Dolg M (2003) Mol Phys 101:2427
16. Barros N, Schappacher M, Dessuge P, Maron L, Guillaume SM (2008) Chem Eur J 14:1881
17. Kaltsoyannis N, Scott P (1999) The f elements. Oxford University Press, Oxford
18. Moritz A, Dolg M (2007) Chem Phys 337:48
19. Evarestov RA, Losev MV, Panin AI, Mosyagin NS, Titov AV (2008) Phys Stat Sol (b) 245:114
20. Yang J, Dolg M (2005) Theor Chem Acc 113:212
21. Lanza G, Varga Z, Kolonits M, Hargittai M (2008) J Chem Phys 128:074301
22. Wood JH, Boring AM (1978) Phys Rev B 18:2701
23. Dolg M, Stoll H, Preuss H (1993) Theor Chim Acta 85:441
24. Müller W, Flesch J, Meyer W (1984) J Chem Phys 80:3297
25. Müller W, Meyer W (1984) J Chem Phys 80:3311
26. Kolb D, Johnson WR, Shorer P (1982) Phys Rev A 26:19
27. Cao X, Dolg M, Stoll H (2003) J Chem Phys 118:487
28. Amos RD, Bernhardsson A, Berning A, Celani P, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer G, Knowles PJ, Korona T, Lindh R, Lloyd AW, McNicholas SJ, Manby FR, Meyer W, Mura ME, Nicklass A, Palmieri P, Pitzer R, Rauhut G, Schütz M, Schuhmann U, Stoll H, Tarroni AJSR, Thorsteinsson T, Werner HJ (2002) MOLPRO is a package of ab initio programs. University of Birmingham, Birmingham
29. Wang Y, Dolg M (1998) Theor Chem Acc 100:124
30. Foucrault M, Millie Ph, Daudey JP (1992) J Chem Phys 96:1257
31. Dunning TH Jr (1989) J Chem Phys 90:1007
32. Kendall RA, Dunning TH Jr, Harrison RJ (1992) J Chem Phys 96:6769
33. Cao X, Dolg M (2001) J Chem Phys 115:7348
34. http://www.theochem.uni-stuttgart.de/pseudopotentials
35. Froese Fischer C (1977) The Hartree–Fock method for atoms. Wiley, New York; program MCHF77, modified for pseudopotentials and quasirelativistic calculations by Dolg M (1995)
36. Myers CE (1975) Inorg Chem 14:199
37. Kleinschmidt PD, Lau KH, Hildenbrand DL (1981) J Chem Phys 74:653
38. http://www.physics.nist.gov/PhysRefData/Handbook/element_name.htm
39. Dyall KG, Grant IP, Johnson CT, Parpia FA, Plummer EP (1989) GRASP: atomic structure code. Comput Phys Commun 55:425
40. Batista ER, Martin RL, Hay PJ (2004) J Chem Phys 121:11104
41. Joubert L, Maldivi P (2001) J Phys Chem A 105:9068
42. Vetere V, Roos BO, Maldivi P, Adamo C (2004) Chem Phys Lett 396:452
43. Mochizuki Y, Tatewaki H (2003) J Chem Phys 118:9201
44. Hargittai M (1988) Coord Chem Rev 91:35
45. Joubert L, Picard G, Legendre JJ (1998) Inorg Chem 37:1984
46. Cundari TR, Sommerer SO, Strohecker LA, Tippett L (1995) J Chem Phys 103:7058
47. Perrin L, Maron L, Eisenstein O (2003) Faraday Discuss 124:25
48. Lanza G (2009) Int J Quantum Chem submitted
49. Clavaguera C, Dognon JP, Pyykkö P (2006) Chem Phys Lett 429:8
50. Popenko NI, Zasorin EZ, Spiridonov VP, Ivanov AA (1978) Inorg Chim Acta 31:L371
51. Cao X, Dolg M (2002) J Molec Struct (Theochem) 581:139
52. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain AC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision D.02. Gaussian, Inc., Wallingford CT
53. Roos BO, Lindh R, Malmqvist P-Å, Veryazov V, Widmark P-O, Borin AC (2008) J Phys Chem A 112:11431
54. Dolg M, Stoll H, Preuss H (1991) J Mol Struct 235:67
55. Lesar A, Muri G, Hodoscek M (1998) J Chem Phys 102:1170