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REGULAR ARTICLE

Quasirelativistic energy-consistent 4f-in-core pseudopotentials for tetravalent lanthanide elements

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Abstract Quasirelativistic energy-consistent 4f-in-core pseudopotentials modeling tetravalent lanthanides ($4f^{n-1}$ occupation with $n = 1, 2, 3, 8, 9$ for Ce, Pr, Nd, Tb, Dy) have been adjusted. Energy-optimized (6s5p4d) and (7s6p5d) valence basis sets contracted to polarized double- to quadruple-zeta quality as well as 2f1g correlation functions have been derived. Corresponding smaller (4s4p3d) and (5s5p4d) basis sets suitable for calculations on lanthanide(IV) ions in crystalline solids form subsets of these basis sets designed for calculations on neutral molecules. Calculations for lanthanide tetrafluorides using the 4f-in-core pseudopotentials at the Hartree–Fock level show satisfactory agreement with calculations using 4f-in-valence pseudopotentials. For cerium tetrafluoride the experimental bond length is well reproduced using the 4f-in-core pseudopotential at the coupled-cluster level with single and double excitation operators and a perturbative estimate of triple excitations. For cerium dioxide 4f-in-core and 4f-in-valence pseudopotential calculations agree quite well, if a proper f basis set instead of f polarization functions is applied.

Keywords Lanthanides · Rare earth elements · Pseudopotentials · Valence basis sets · Lanthanide tetrafluorides · Cerium dioxide

1 Introduction

Quantum chemical calculations for lanthanide compounds face particular challenges in the significant contributions of relativity as well as electron correlation [1, 2]. A commonly used approximation to cope with some of these problems 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 lanthanides two kinds of energy-consistent PPs with different core definitions are available, i.e. 4f-in-valence [3, 4] and 4f-in-core [5, 6] PPs. In contrast to the 4f-in-valence PPs, the 4f-in-core PPs avoid all difficulties due to the open 4f shell and are therefore an efficient computational tool for many lanthanide compounds, because the 4f shell normally behaves quite core-like and does not directly participate in chemical bonding. Hence, calculations even on large molecules also containing several lanthanides become feasible within this approximation and have been successfully performed for almost 20 years.

Since the 4f orbitals are included in the core, one PP for each oxidation state, or rather for each corresponding 4f subconfiguration is needed. While for di- ($4f^{n+1}$, $n =$ 0–13 for La–Yb) and trivalent ($4f^{n}$, $n =$ 0–14 for La–Lu) lanthanides 4f-in-core PPs were already adjusted in 1989 [5], analogous tetravalent PPs are still missing. The 4f-in-core PPs ($4f^{n-1}$, $n =$ 1, 2, 3, 8, 9 for Ce, Pr, Nd, Tb, Dy) for tetravalent lanthanides and various valence basis sets for use in calculations of molecules as well as solids presented in this paper are intended to fill this gap. However, they have only been adjusted for those lanthanide elements, which are known to form tetravalent compounds [7], i.e. Ce, Pr, Nd, Tb, Dy. Thus, together with the recently

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published 5f-in-core actinide PPs [8–10] and the now completed 4f-in-core lanthanide PPs [5, 6] a simplified treatment of all commonly occurring valencies in lanthanides and actinides within the superconfiguration model [11] is now at hand. Results of Hartree–Fock (HF) test calculations using the newly developed tetravalent PPs for lanthanide tetrafluorides LnF_4 (Ln = Ce, Pr, Nd, Tb, Dy) are compared to corresponding calculations using 4f-in-valence PPs. In the case of CeF_4, where an experimental bond length [12] is available, also a coupled-cluster calculation with single and double excitation operators and a perturbative estimate of triple excitations [CCSD(T)] is discussed. Furthermore, for cerium dioxide CeO_2 HF and CCSD(T) calculations using the new tetravalent PP will be compared to 4f-in-valence reference data [13].

2 Method

The method of relativistic energy-consistent ab initio pseudopotentials is described in detail elsewhere [3, 5, 14] and will be outlined here only briefly. The valence-only model Hamiltonian for a system with n valence electrons and N cores with effective core charges Q is given as

$$H_v = -\frac{1}{2}\sum_i^n \Delta_i + \sum_{i<j}^n \frac{1}{r_{ij}} + \sum_i^n \sum_I^N V_I(r_i) + \sum_{I<J}^N \frac{Q_I Q_J}{R_{IJ}}. \quad (1)$$

Here i and j are electron indices, I and J are core indices. $V_I(r_i)$ denotes a semilocal effective core potential (ECP) for core I

$$V_I(r_i) = -\frac{Q_I}{r_{Ii}} + \sum_l \sum_k A^I_{lk} \exp\left(-a^I_{lk} r^2_{Ii}\right) P^I_l. \quad (2)$$

P^I_l is the projection operator onto the Hilbert subspace of core I with angular momentum l

$$P^I_l = \sum_{m_l} |lm_l\rangle\langle lm_l|. \quad (3)$$

The 4f-in-core PPs corresponding to tetravalent lanthanide atoms ($4f^{n-1}$, $n = 1, 2, 3, 8, 9$ for Ce, Pr, Nd, Tb, Dy) were generated analogous to the quasirelativistic di- ($4f^{n+1}$, n = 0–13 for La–Yb) and trivalent ($4f^n$, n = 0–14 for La–Lu) 4f-in-core PPs [5, 6]. The 1s–4f (spherically averaged) shells are included in the PP core, while all orbitals with main quantum number larger than 4 are treated explicitly, i.e. 12 valence electrons. The s-, p-, and d-PPs which are composed of two Gaussians each ($k_{max} = 2$ in (2), i.e. 12 parameters) were adjusted by a least-squares fit to the total valence energies of 18 reference states (Ln $5s^25p^65d^26s^2$, $5s^25p^65d^36s^1$, $5s^25p^65d^26s^16p^1$, $5s^25p^65d^16s^26p^1$, Ln^+ $5s^25p^65d^26s^1$, $5s^25p^65d^16s^2$, $5s^25p^66s^26p^1$, $5s^25p^66s^16p^2$, $5s^25p^65d^16s^16p^1$, Ln^{2+} $5s^25p^65d^2$, $5s^25p^65d^16s^1$, $5s^25p^65d^16p^1$, $5s^25p^66s^16p^1$, $5s^25p^66s^2$, Ln^{3+} $5s^25p^65d^1$, $5s^25p^66s^1$, $5s^25p^66p^1$, Ln^{4+} $5s^25p^6$). The reference data were taken from relativistic all-electron (AE) calculations using the so-called Wood–Boring (WB) scalar-relativistic HF approach. A brief description of the computational details was given in previous publications [5, 15]. Both AE WB as well as PP calculations were performed with an atomic finite-difference HF scheme [16]. In order to allow for some participation of the 4f orbitals in chemical bonding the f-parts of the PPs are designed to describe partial occupations of the 4f shell, which are larger than the integral occupation number implied by the valency, i.e. $4f^{n-1+q}$ (n = 1, 2, 3, 8, 9 for Ce, Pr, Nd, Tb, Dy) with $0 \leq q < 1$ for tetravalent lanthanide atoms [6]. In slight variation to the former PPs [6], the f-PPs consist of two types of potentials V_1 and V_2 which are linearly combined as follows [8]

$$V = \left(1 - \frac{m}{14}\right)V_1 + \frac{m}{14}V_2. \quad (4)$$

Here m is the integral number of electrons in the 4f orbitals kept in the core, i.e. $m = n-1$ for the tetravalent PPs. V_1 and V_2 model 4f shells, which can and cannot accommodate an additional electron, respectively. In particular, V_1 would be the exact potential for a $4f^0$ occupation in Ce, whereas V_2 would be exact for $4f^{14}$ in Hf. The errors in the total valence energies of finite-difference HF calculations are smaller than 0.07 and 0.20 eV (0.4%) for s-, p-, d- and f-parts, respectively.

The Gaussian type orbital (GTO) valence basis sets were constructed analogous to those for tetravalent 5f-in-core PPs for actinides [9]. First, basis sets for use in crystal calculations were created, i.e. (4s4p3d) and (5s5p4d) basis sets were HF energy-optimized [17] for the valence subconfiguration $5s^25p^65d^1$ of threefold-charged lanthanide cations. All exponents, which became smaller than 0.15, were fixed to this value and the remaining exponents were reoptimized. Furthermore, all optimizations were carried out with the requirement that the ratio of exponents in the same angular symmetry must be at least 1.5. The basis set errors in the valence energies with respect to numerical finite-difference 4f-in-core PP HF calculations are below 0.15 and 0.03 eV for (4s4p3d) and (5s5p4d), respectively.

Secondly, the valence basis sets were augmented by adding a set of 2s1p1d low-exponent Gaussians yielding (6s5p4d) and (7s6p5d) primitive sets for use in molecular calculations. The added exponents were HF energy-optimized [17] for the $5s^25p^65d^26s^2$ valence subconfiguration. The differences in the valence energies with respect to numerical finite-difference 4f-in-core PP HF calculations are below 0.15 and 0.03 eV for (6s5p4d) and (7s6p5d), respectively.

Thirdly, the basis sets were contracted using different segmented contraction schemes to yield basis sets of approximately valence double-, triple-, and quadruple-zeta quality (VDZ, VTZ, and VQZ) for the s and p symmetries. In the case of d symmetry at least a triple-zeta contraction was necessary and additional sets with a less tight d contraction are also offered (VDZ: [4s3p3d], VTZ: [5s4p3d], [5s4p4d], and VQZ: [6s5p4d]). The errors in total valence energies of the $5d^26s^2$ valence substates with respect to numerical finite-difference 4f-in-core PP HF calculations for the VDZ and VTZ contractions of the (6s5p4d) basis sets are below 0.21 and 0.17 eV, respectively. For the VDZ, VTZ, and VQZ contractions of the (7s6p5d) basis sets these errors are below 0.07, 0.05, and 0.03 eV, respectively.

Fourthly, sets of 2f1g polarization functions were energy-optimized in configuration interaction (CI) calculations [18] for the $5d^26s^2$ valence subconfiguration. The parameters of PPs and basis sets 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 [18] basis set library [19].

The test calculations for LnF_4 (Ln = Ce, Pr, Nd, Tb, Dy) were carried out with the MOLPRO program package [18] implying T_d symmetry and using tetravalent 4f-in-core LPPs (large-core PP with 12 valence electrons and 46, 47, 48, 53, 54 core electrons for Ce, Pr, Nd, Tb, Dy) as well as 4f-in-valence SPPs [3] (small-core PP with 28 core electrons and 30, 31, 32, 37, 38 valence electrons for Ce, Pr, Nd, Tb, Dy). For F Dunning's aug-cc-pVQZ (augmented correlation-consistent polarized VQZ) basis set [20, 21] was applied and for Ln (7s6p5d2f1g)/[6s5p4d2f1g] and (14s13p10d8f6g)/[6s6p5d4f3g] [4] valence basis sets were used for LPP HF and SPP state-averaged multiconfiguration self-consistent field (MCSCF) calculations, respectively. The state-averaging was necessary to avoid symmetry-breaking at the orbital level, since the program MOLPRO is limited to the D_{2h} point group and subgroups. For CeF_4 a LPP CCSD(T) calculation was performed, since an experimental bond length [12] is available for this compound. In the CCSD(T) calculation for F Dunning's aug-cc-pVTZ basis set [20, 21] was applied and the F 1s orbitals were kept frozen.

The LPP HF, LPP CCSD(T), and SPP [3] HF optimizations for CeO_2 were performed with MOLPRO [18] using C_{2v} symmetry. For Ce (7s6p5d2f1g)/[6s5p4d2f1g] and (14s13p10d8f6g)/[6s6p5d4f3g] [4] valence basis sets were used for LPP and SPP calculations, respectively, and for O Dunning's aug-cc-pVQZ basis set [20, 21] was applied. In the case of the CCSD(T) calculation the O 1s orbitals were kept frozen and for O Dunning's aug-cc-pVTZ basis set [20, 21] was used.

3 Results and discussion

The results for structures and energies of LnF_4 (Ln = Ce, Pr, Nd, Tb, Dy) and CeO_2 will be presented to demonstrate the transferability of the 4f-in-core PPs and the corresponding basis sets to a molecular environment.

The Ln–F bond energy was calculated by $E_{\mathrm{bond}} = [E(\mathrm{Ln}) + 4 \times E(\mathrm{F}) - E(\mathrm{LnF_4})]/4$, where the lanthanide atom was assumed to be in the lowest valence substate, i.e. $4f^{n-1}5d^26s^2$. The binding energy of CeO_2 was calculated by $E_{\mathrm{bond}} = E(\mathrm{Ce}) + 2 \times E(\mathrm{O}) - E(\mathrm{CeO_2})$, where the cerium atom was assumed to have the $4f^05d^26s^2$ valence subconfiguration. At this point one might ask how to calculate a bond energy with respect to the experimentally observed ground states of the lanthanides. We suggest to follow the strategy proposed for the di- and trivalent 4f-in-core PPs almost two decades ago [22]. First, one should calculate the bond energy with respect to the lanthanide atom in its lowest valence substate corresponding to the $4f^{n-1}$ subconfiguration for tetravalent LPPs. Then the energy difference to the experimentally observed ground state can be determined, e.g. at the AE WB [16] or Dirac–Hartree–Fock [23] level, and this difference has to be subtracted from the atomic energy $E(\mathrm{Ln})$ calculated with respect to the lowest valence substate corresponding to $4f^{n-1}$. In contrast to di- and trivalent PPs for tetravalent PPs an energy correction using experimental energy differences is not possible, since for the $5d^26s^2$ valence subconfiguration no experimental data are available [24]. If desired, correlation contributions can be obtained by 4f-in-valence PP or AE atomic calculations. Tables summarizing some possible corrections are included in the electronic supplementary material.

Furthermore, correlation effects can implicitly be included by calculating the bond energy via the ionic binding energy. For example in the case of CeF_4, the ionic binding energy is $D_e = E(\mathrm{Ce}^{4+}) + 4 \times E(\mathrm{F}^-) - E(\mathrm{CeF_4})$ and can be calculated directly at the correlated level using the 4f-in-core PP for Ce. The Ce–F bond energy E_{bond} is given by

$$E_{\mathrm{bond}} = \frac{1}{4}\left[D_e - \sum_{i=1}^{4} \mathrm{IP}_i(\mathrm{Ce}) + 4 \times \mathrm{EA(F)}\right]. \qquad (5)$$

The first to fourth ionization potential of Ce $\mathrm{IP}_i(\mathrm{Ce})$ (i = 1–4) as well as the electron affinity of fluorine EA(F) are taken from experimental data, i.e. they account for correlation contributions (Ce: $\mathrm{IP}_1 = 5.539$, $\mathrm{IP}_2 = 10.850$, $\mathrm{IP}_3 = 20.200$, $\mathrm{IP}_4 = 36.762$ eV [25]; F: EA = 3.401 eV [26]). The CCSD(T) Ce–F bond energy calculated in this manner amounts to 5.68 eV. This value has to be compared to the value of 6.72 eV calculated with respect to the neutral atoms with Ce in the $5d^26s^2$ ^3F excited state (cf. Table 1). SPP MRCI+Q (multi-reference configuration

Table 1 Ln–F bond lengths R_e (in Å) and energies E_{bond} (in eV) for LnF_4 (Ln = Ce, Pr, Nd, Tb, Dy) from LPP HF and SPP state-averaged MCSCF calculations

Ln	R_e		E^a_{bond}	
	LPP	SPP[b]	LPP	SPP
Ce	2.045	2.031	5.269	5.386
	2.048	*2.036(5)*	*6.715*	
Pr	2.033	2.017	5.236	5.291
Nd	2.021	2.005	5.219	5.222
Tb	1.963	1.957	5.245	4.989
Dy	1.952	1.946	5.265	5.043

For CeF_4 LPP CCSD(T) as well as experimental [12] data are given in italics. Basis sets: LPP (7s6p5d2f1g)/[6s5p4d2f1g]; SPP (14s13p10d8f6g)/[6s6p5d4f3g]; F aug-cc-pVQZ (HF); F aug-cc-pVTZ (CCSD(T))

[a] Bond energies are not corrected to account for the experimentally observed ground states

[b] Given in italics: Experimental bond length for CeF_4

interaction with Davidson correction) calculations using standard pVQZ basis sets [4] and not allowing excitations from the 4s, 4p, and 4d shells yield a value of 3.21 eV for the $4f^1 5d^1 6s^2\ ^1G \rightarrow 5d^2 6s^2\ ^3F$ excitation energy, i.e. a corrected value of 5.92 eV would result for the dissociation to the neutral atoms in their ground states in reasonable agreement with the result of 5.68 eV derived above.

3.1 Lanthanide tetrafluorides

The LPP HF and CCSD(T) calculations for LnF_4 (Ln = Ce, Pr, Nd, Tb, Dy) and CeF_4 will be compared to corresponding SPP state-averaged MCSCF calculations and experimental [12] as well as computational [27] data from the literature, respectively. The results for bond lengths as well as bond energies and those of a Mulliken population analysis are listed in Tables 1 and 2, respectively.

3.1.1 Bond lengths

Due to the lanthanide contraction the Ln–F bond lengths calculated by using LPP HF and SPP state-averaged MCSCF decrease continuously with increasing nuclear charge by 0.093 and 0.085 Å, respectively. The LPP HF bond lengths are in good agreement with the SPP reference data, i.e. the mean absolute error (m.a.e.) and the mean relative error (m.r.e.) amount to 0.012 Å and 0.6%, respectively. The maximum error is 0.016 Å (0.8%). Compared to the Ce–F bond length of 2.036 Å [27] calculated by using an ECP (core: 1s–4d) at the HF level, our LPP HF value also deviates only by 0.009 Å corresponding to 0.4%.

If correlation is included via CCSD(T), the bond length of CeF_4 becomes slightly longer by 0.003 Å. The difference between the LPP CCSD(T) and experimental [12] Ce–F bond length amounts to 0.012 Å (0.6%). The deviation to the Ce–F bond length of 2.041 Å from an ECP second-order Møller–Plesset perturbation theory (MP2) calculation [27] is 0.007 Å (0.3%). Thus, the LPP CCSD(T) bond length of CeF_4 is also in good agreement with corresponding reference data and confirms the reliability of the newly developed LPPs.

3.1.2 Bond energy

While the LPP HF Ln–F bond energies (for the lowest valence substates of the superconfigurations) stay almost constant ($\Delta E_{max} = 0.05$ eV), the SPP state-averaged MCSCF bond energies (for the lowest states of the configuration) decrease with increasing nuclear charge and show a minimum for Tb ($\Delta E_{max} = 0.40$ eV), i.e. for the half-filled 4f shell. The LPP and SPP bond energies show a satisfactory agreement, i.e. the m.a.e. (m.r.e.) amounts to 0.13 eV (2.6%) and the maximum error, which occurs for terbium, is 0.26 eV (5.1%). For CeF_4 the LPP HF bond energy is by 0.34 eV (6.9%) larger than the value obtained by Lanza and Fragala in an ECP HF calculation (4.93 eV) [27]. However, this is most likely due to the different basis sets rather than to the different core definitions (basis sets: LPP: Ce (7s6p5d2f1g)/[6s5p4d2f1g], F (13s7p4d3f2g)/[6s5p4d3f2g]; ECP: Ce [4s4p2d2f], F (11s6p2d)/[5s3p2d]; core: LPP: 1s–4f; ECP: 1s–4d).

As expected the inclusion of electron correlation via CCSD(T) clearly increases the Ce–F bond energy by 1.45 eV. The LPP CCSD(T) bond energy agrees quite well with the ECP MP2 bond energy of 6.73 eV obtained by Lanza and Fragala [27], i.e. the difference amounts to 0.015 eV (0.2%).

3.1.3 Mulliken orbital populations

The Mulliken orbital populations show that the bonding in LnF_4 is basically ionic with significant back-bonding into the Ln 5d and 4f (less 6s) orbitals. For LPP and SPP calculations this results in charge separations up to 0.84 and 0.72 electrons per bond and in total atomic charges of up to 3.35 and 2.87 units on the lanthanide, respectively. The SPP 4f occupations deviate on average by 0.27 electrons and at most by 0.35 electrons from the assumed LPP $4f^{n-1}$ occupations. This demonstrates that the 4f orbitals participate to some extent in the Ln–F bonding. However, the 4f-in-core approach yields reasonable results, since the differences between LPP and SPP 4f occupations amount on average only to 0.13 electrons and at most to 0.19

Table 2 Mulliken 5s/6s, 5p, 5d, and 4f orbital populations and atomic charges (Q) on Ln in LnF_4 (Ln = Ce, Pr, Nd, Tb, Dy) from LPP HF and SPP state-averaged MCSCF calculations

Ln	s		p		d		f		Q	
	LPP	SPP	LPP	SPP	LPP	SPP	LPP[a]	SPP	LPP	SPP
Ce	1.98	2.13	5.86	5.91	0.69	0.79	0.16	0.35	3.30	2.78
Pr	1.97	2.14	5.86	5.90	0.70	0.81	0.15	1.33	3.31	2.77
Nd	1.97	2.15	5.85	5.90	0.71	0.80	0.14	2.30	3.32	2.80
Tb	1.97	2.23	5.84	5.88	0.73	0.82	0.12	7.18	3.34	2.87
Dy	1.97	2.25	5.83	5.87	0.73	0.90	0.11	8.17	3.35	2.79

A $5s^2 5p^6 5d^2 6s^2$ ground state valence subconfiguration is considered for Ln. Basis sets: LPP (7s6p5d2f1g)/[6s5p4d2f1g];

SPP (14s13p10d8f6g)/[6s6p5d4f3g]; F aug-cc-pVQZ

[a] 0, 1, 2, 7, and 8 electrons in the 4f shell are attributed to the LPP core for Ce, Pr, Nd, Tb, and Dy, respectively

electrons, because the f-part of the LPPs allows for some 4f occupation in addition to the integral $4f^{n-1}$ assumption.

3.2 Cerium dioxide

Table 3 shows the results of the LPP HF, LPP CCSD(T), and SPP HF calculations for CeO_2 in comparison to SPP data from the literature [13]. The LPP HF molecular structure for CeO_2 deviates significantly from the SPP HF reference data, i.e. the differences between the Ce–O bond lengths and the O–Ce–O bond angles amount to 0.049 Å (2.7%) and 9.1° (7.8%), respectively. Compared to the SPP HF data from the literature [13] these deviations are 0.047 Å (2.6%) and 10.5° (8.9%). In the case of the binding energies the deviation between LPP and SPP data is even clearly larger and amounts to 1.84 eV (16.6%). The reason for these significant discrepancies is the large deviation between the LPP and SPP f occupation, which amounts to 0.49 electrons.

The HF results using the old tetravalent LPP, which was adjusted in 1991 to calculate cerocene [28], deviate even more from the SPP data, i.e. the differences are 0.102 Å (5.7%), 9.6° (8.2%), 3.09 eV (27.9%), and 0.59 electrons for bond lengths, bond angles, binding energies, and f occupations, respectively. The reason for the larger deviations is that the f-projector of the old LPP does not allow for any 4f participation ($V = V_2$ in (4)). Therefore, the f occupation is very small (0.08 electrons) and corresponds only to the occupation of the 5f, 6f, ... shell. If we use a V_2 instead of a V_1 potential as f-projector for our LPP, the results become very similar to those using the old LPP and the remaining deviations can be explained by the different basis sets, i.e. the deviations amount to 0.006 Å, 0.3°, 0.11 eV, and 0.02 electrons. Thus, the use of a f-projector, which admits some 4f occupation, is important especially for Ce, where the 4f shell is unoccupied. However, with increasing 4f occupation along the lanthanide series this additional occupation should get less probable, wherefore the ratio of V_2 is increased continuously by 1/14 with increasing 4f occupation (cf. (4)). The differences between results for $V = V_1$ and $V = V_2$ are 0.047 Å, 0.8°, 1.14 eV, and 0.08 electrons. The influence of the mixing ratio of V_1 and V_2 within (4) should be smaller than these deviations.

Table 3 Ce–O bond lengths R_e (in Å), bond angles ∠ O–Ce–O (in degree), binding energies E_{bond} (in eV), and Mulliken f orbital populations for CeO_2 from LPP HF, LPP CCSD(T), and SPP HF calculations

Method	R_e	$\angle^a$	E^b_{bond}	f occupation
LPP HF	1.839	107.6	9.23	0.18
LPP HF[c]	1.782	118.4	11.61	0.50
LPP HF[d]	1.886	106.8	8.09	0.10
old LPP HF	1.892	107.1	7.98	0.08
SPP HF	1.790	116.7	11.07	0.67
SPP HF [13]	1.792	118.1		0.69
LPP CCSD(T)	1.877	104.2	15.36	0.19
LPP CCSD(T)[c]	1.818	124.4	18.65	0.51
SPP CISD + Q [13]	1.804	118.8		
SPP ACPF [13]	1.838	117.6		

Furthermore, results of a HF calculation using the old tetravalent LPP [28] as well as SPP data [13] from the literature are given. Basis sets: LPP (7s6p5d2f1g)/[6s5p4d2f1g]; SPP (14s13p10d8f6g)/[6s6p5d4f3g]; O aug-cc-pVQZ (HF); O aug-cc-pVTZ (CCSD(T)); old LPP (7s6p5d2f)/[5s4p3d2f] [28]; [13]: SPP (12s11p10d9f2g)/[8s7p6d5f2g], O (11s6p3d2f)/[5s4p3d2f]

[a] Experimental bond angle: ∠ O–Ce–O = 146 ± 2 [29]

[b] Bond energies are not corrected to account for the experimentally observed ground states

[c] LPP HF calculation using a (7s6p5d3f1g)/[6s5p4d3f1g] basis set for Ce, where the 3f basis functions were HF optimized for $4f^2 5s^2 5p^6 6s^2$

[d] LPP HF calculation using a V_2 potential as f-projector

In order to improve the LPP results, we tried to use 3f basis functions HF optimized [18] for the valence configuration $4f^2 5s^2 5p^6 6s^2$ instead of 2f polarization functions CI optimized [18] for $5s^2 5p^6 5d^2 6s^2$ (exponents: 3f: 8.4453, 2.7912, 0.7481; 2f: 0.9916, 0.3239). The new results are in good agreement with the SPP HF data, i.e. the deviations amount to 0.008 Å (0.4%), 1.7° (1.5%), 0.54 eV (4.9%), and 0.17 electrons. Moreover, the molecular energy $E(CeO_2)$ is reduced by 2.39 eV (−187.975 vs. −187.887 Hartree), which shows that the modified basis set performs clearly better. The reason for this better performance is probably that the 3f basis is not as diffuse as the 2f polarization functions and therefore allows for more additional 4f occupation. If the 3f basis is applied for CeF_4, the deviations from the SPP bond length, bond energy, and f occupation are slightly reduced to 0.004 Å, 0.09 eV, and 0.17 electrons, respectively (2f: 0.014 Å, 0.12 eV, 0.19

electrons). Furthermore, the molecular energy E(CeF_4) is reduced by 0.82 eV (−436.365 vs. −436.335 Hartree).

In the case of the other lanthanides Pr, Nd, Tb, and Dy f exponents HF optimized [18] for $4f^25s^25p^66s^2$ amount at most to 0.3140 and are thus more diffuse than the f polarization functions, where the smallest exponent is 0.3270. This is most likely due to the admixture of the V_2 potential in the f-PP (cf. (4)), which does not allow for an additional 4f occupation. For these elements LPP HF calculations for LnF_4 using the 3f basis sets give by 0.17–0.26 eV higher molecular energies E(LnF_4), which indicates that these basis sets are not as good as the original ones. Furthermore, the deviations between LPP and SPP bond lengths are increased, if the 3f basis sets are used (Pr 0.024 vs. 0.016, Nd 0.022 vs. 0.015, Tb 0.010 vs. 0.006, Dy 0.010 vs. 0.007 Å). Thus, in the case of these elements the 2f polarization functions should be used. However, if the 3f basis set is used for CeF_4 and the 2f polarization functions are used for Pr, Nd, Tb, and Dy, the bond lengths show no regular variation with increasing nuclear charge, but a skip of 0.007 Å between CeF_4 and PrF_4 (Ce 2.026, Pr 2.033, Nd 2.021, Tb 1.963, Dy 1.952 Å).

If CCSD(T) instead of HF calculations are carried out using the 2f polarization functions, the Ce–O bond length is increased by 0.038 Å, the O–Ce–O bond angle is decreased by 3.4°, the binding energy is increased by 6.13 eV, and the f occupation stays almost the same (Δf occupation = 0.01 electrons). The deviations from SPP structures determined by the CI method including all single and double excitations and the correction formula proposed by Langhoff and Davidson (CISD + Q) and by the averaged coupled pair-functional (ACPF) method [13] are quite large and amount to 0.073 (4.0%) and 0.039 Å (2.1%) and 14.6 (12.3%) and 13.4° (11.4%) for bond lengths and angles, respectively. The deviation from the experimental bond angle of 146 ± 2° [29] is even larger and amounts to 42° (29%). However, this deviation can partly be explained by the fact that the experimental value determined based on the infrared spectrum of CeO_2 in an Ar matrix does not include corrections for anharmonicity effects (estimated to reduce the bond angle by 5–10°) and the influence of the matrix on the bond angle.

Using the 3f basis instead of the 2f polarization functions yields clearly smaller differences from SPP CISD + Q and SPP ACPF data [13], respectively, i.e. the deviations are reduced to 0.014 (0.8%) and 0.020 Å (1.1%) and 5.6 (4.7%) and 6.8° (5.8%) for bond lengths and angles, respectively. Compared to the experimental bond angle the deviation amounts to 22°, which is by about 50% smaller than that using the 2f polarization functions. Thus, also at the correlated level the use of the f basis set adjusted to $4f^25s^25p^66s^2$ shows a considerable improvement.

4 Conclusion

Quasirelativistic 4f-in-core PPs and corresponding (6s5p4d) and (7s6p5d) valence basis sets for use in molecular calculations have been generated for tetravalent lanthanide atoms. Atomic HF calculations using these PPs and uncontracted basis sets deviate at most by 0.15 eV from corresponding numerical PP HF results. The differences using the contracted (7s6p5d) basis sets stay below 0.07 eV.

Results of HF test calculations on LnF_4 (Ln = Ce, Pr, Nd, Tb, Dy) using 4f-in-core LPPs show reasonable agreement with corresponding SPP state-averaged MCSCF data, i.e. the m.a.e. (m.r.e.) in bond lengths and energies amount to 0.012 Å (0.6%) and 0.13 eV (2.6%), respectively. For CeF_4 the LPP CCSD(T) bond length deviates only by 0.012 Å (0.6%) from the experimental value. Furthermore, LPP HF and CCSD(T) calculations for CeO_2 show a satisfactory agreement with SPP reference data, if f basis functions HF optimized for $4f^25s^25p^66s^2$ instead of f polarization functions CI optimized for $5s^25p^65d^26s^2$ are applied. Thus, the 4f-in-core PPs should be reliable tools to investigate compounds including tetravalent lanthanides within a reasonable amount of computer time, if the 4f shell does not participate significantly in bonding. The PP set presented here completes earlier published 4f- and 5f-in-core PP sets for lanthanides and actinides, respectively.

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