Ab Initio Study of the Lanthanide and Actinide Contraction

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Results for the spectroscopic constants of the monohydrides, monoxides, and monofluorides of the lanthanide elements lanthanum and lutetium as well as the actinide elements actinium and lawrencium from all-electron and valence-only ab initio electronic structure calculations are presented. The valence-only investigations were carried out using energy-consistent pseudopotentials for the heavy atoms. Electron correlation was accounted for by means of the coupled-cluster method. Multireference averaged coupled-pair functional calculations were carried out to describe effects due to the mixing of the energetic close-lying ns^{2-m} $(n-1)d^m$ $(0 \leq m \leq 2)$ configurations of the lanthanide ($n = 6$) and actinide ($n = 7$) cations. The counterpoise correction was applied to estimate the size of the basis set superposition errors. Nonrelativistic as well as quasirelativistic calculations were performed. The latter included also corrections for spin−orbit effects for the actinide compounds derived from limited configuration interaction calculations. The reliability of the pseudopotential approach is demonstrated by a comparison to the results of corresponding nonrelativistic and scalar-relativistic Douglas−Kroll−Hess all-electron self-consistent-field calculations performed with large basis sets. The influence of shell-structure effects, i.e. the filling of the 4f and 5f shell, and relativistic effects on the molecular properties is discussed. The values for the lanthanide and actinide contractions are found to depend strongly on the ligand and to vary from 6 to 11 pm for lanthanides and from 11 to 17 pm for actinides. Relativistic effects play a significant role; for example, their neglect even leads to a slight lanthanide/actinide expansion in the case of the monoxides.

1. Introduction

The filling of the 4f shell across the lanthanide series is accompanied by a considerable decrease in the ionic radii (cf. ref 1). This effect, known as the lanthanide contraction, is mainly due to an incomplete shielding of the nuclear charge by the 4f electrons,[2] although the 4f orbitals are rather compact in shape. A similar shrinkage can be observed when the 5f orbitals are filled across the actinide series. However, in addition to the increase of the effective nuclear charge, relativistic effects contribute considerably to the actinide contraction.[3] Across the lanthanide (actinide) series the 4f (5f) orbitals become more and more core-like, causing an improved shielding of the nuclear charge. As a consequence, the decrease in the ionic radii is larger at the beginning of the series than at the end.

The overall lanthanide (actinide) contraction Δ_{ln} (Δ_{an}) may be defined as the difference of the ionic radii of the first and last element of the lanthanide (actinide) series, lanthanum (actinium) and lutetium (lawrencium), respectively:

$$\Delta_{\mathrm{ln}} = r_{\mathrm{La}^{n+}} - r_{\mathrm{Lu}^{n+}} \tag{1}$$

$$\Delta_{\mathrm{an}} = r_{\mathrm{Ac}^{n+}} - r_{\mathrm{Lr}^{n+}} \tag{2}$$

The values depend on the coordination number and the charge of the ions. Using the radii for triply positive charged ions[1] with coordination number 6, a lanthanide contraction of 17 pm occurs. Due to the lack of experimental values for lawrencium, the actinide contraction is not known. A contraction of 18 pm is obtained by comparison of the ionic radii of Ac^{3+} (112 pm) and Es^{3+} (94 pm). The radii of the corresponding lanthanide ions La^{3+} (103.2 pm) and Ho^{3+} (90.1 pm) differ by only 13.1 pm. A simple linear extrapolation leads to a total actinide contraction of 25 pm. This value is definitely an upper bound since the decrease in ionic radii is larger for the first elements of the actinide series (12 pm from Ac^{3+} to Pu^{3+} compared to 6 pm from Pu^{3+} to Es^{3+}), so a value of 22 pm (obtained by extrapolation over the elements americium to einsteinium) may be a better guess.

Other quantities than the ionic radii may be used instead, e.g. the theoretical radial expectation values $\langle r \rangle$ or radii of maximum charge density r_{max} of valence orbitals taken from atomic calculations. In this work we refer to a definition of Pyykkö,[4] where the bond length r_e of compounds of the first and last element of the lanthanide (actinide) series is used:

$$\Delta_{\mathrm{ln}} = r_{\mathrm{e,LaX}} - r_{\mathrm{e,LuX}} \tag{3}$$

$$\Delta_{\mathrm{an}} = r_{\mathrm{e,AcX}} - r_{\mathrm{e,LrX}} \tag{4}$$

Since bond lengths are quantum mechanical observables (in contrast to ionic radii, radial expectation values, or radii of maximum orbital densities), both experimental and theoretical values can be used here. Pyykkö applied this definition to the bond lengths of the lanthanide and actinide monohydrides obtained by means of the Dirac−Hartree−Fock one-center expansion technique. The calculations resulted in far too long bond lengths especially for LaH and AcH. Therefore the results of $\Delta_{\mathrm{ln}} = 20.9$ pm and $\Delta_{\mathrm{an}} = 33.0$ pm appear a bit too large (cf. the estimate of 22−25 pm for the actinide contraction given above). In a recent study Wang and Schwarz[5] found values of

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$\Delta_{\rm ln}$ = 19, 6, and 12 pm for the diatomic lanthanide hydrides, oxides, and fluorides respectively. They conclude that compounds with "rigid" bonds (large force constant, large bond energy) like the oxides show only small contractions, while those with "soft" bonds (small force constant, small bond energy) show large contractions.

The purpose of this work is 3-fold: we want to calibrate energy-consistent pseudopotentials with respect to all-electron results obtained with large basis sets and, more important from a chemical point of view, we want to provide estimates for the actinide contraction of the monohydrides, monoxides, and monofluorides obtained with state-of-the-art methods and to compare them with the corresponding results for the lanthanide contraction.

2. Computational Details

Energy-consistent pseudopotentials from the Stuttgart group were applied for the lanthanide[6,7] and actinide elements.[8] These effective-core potentials replace a Kr[$4d^{10}4f^n$] core ($n = 0, ..., 14$) for the lanthanides and a Kr[$4d^{10}4f^{14}$] core for the actinides, respectively. Accordingly, the number of electrons to be treated explicitly is reduced to 11 for La and Lu, 29 for Ac, and 43 for Lr. To enable the discussion of relativistic effects, both nonrelativistic and quasirelativistic pseudopotentials were employed. The nonrelativistic calculations were carried out for the same states of the atoms ($s^2d^1\ ^2D$) and molecules ($^2\Sigma^+$ for the oxides, $^1\Sigma^+$ for fluorides and hydrides) as for their relativistic counterparts. We note that the actual nonrelativistic ground states differ for actinium, lanthanum, and their compounds. In our pseudopotential calculations for the diatomic hydrides, fluorides, and oxides (8s7p6d4f2g)/[6s5p4d4f2g] Gaussian type valence basis sets on the lanthanide atoms[9] and (12s11p10d8f2g)/[8s7p6d5f2g] basis sets on the actinide atoms[9] were used. The ligands were treated with augmented valence quadruple zeta basis sets[10,11]: (7s4p3d2f)/[5s4p3d2f] for H, (13s7p4d3f2g)/[6s5p4d3f2g] for O and F, respectively. A segmented contraction scheme was applied for the basis sets of H, La, and Lu, while a generalized contraction scheme was used for the other basis sets.

The self-consistent-field (SCF) treatment of the electronic ground state was followed by coupled-cluster calculations with inclusion of single and double excitations (CCSD) where all orbitals except 1s on oxygen and fluorine and 5s, 5p, and 5d on actinium and lawrencium were correlated. In our relativistic calculations a perturbative treatment of triple contributions (CCSD(T)) was also applied. To account for effects due to the mixing of the energetically close-lying $ns^{2-m}(n-1)d^m$ ($0 \leq m \leq 2$) configurations of the lanthanide ($n = 6$) and actinide ($n = 7$) cations, multireference averaged coupled-pair functional (MRACPF) calculations were carried out where all these configurations were included in the reference space.

Spin-orbit configuration-interaction (SO-CI)[13] calculations were performed for the actinide atoms and compounds, allowing single excitations from the scalar relativistic SCF ground state wave function. Spin-orbit effects and electron correlation were treated additively in this work. This is certainly a critical approximation for actinide systems; however SO-CI calculations on the spin-orbit splitting of Ac $7s^2\ 6d^1\ ^2D$ yielded values of 0.289 and 0.319 eV for a singles and singles + doubles CI, respectively, indicating a nonadditivity effect of only 0.03 eV, or 10%. The deviation from the experimental value of 0.277 eV may partly be due to the basis set. Use of a more flexible basis resulted in spin-orbit splittings of 0.244 and 0.270 eV for singles and singles + doubles CI calculations, respectively. On the basis of this data, we assume that nonadditivity effects are small for the closed-shell hydrides and fluorides and also for the oxides due to the absence of an open 5f shell. In addition, even with the use of the more heavily contracted basis set the computational demands for the singles + doubles CI calculation were quite high with approximately 7 h of CPU time on a Silicon Graphics PowerChallenge. It is not feasible currently to carry out similar calculations on the molecules under consideration without imposing strong restrictions on the number of virtual orbitals used to construct the excited determinants. Such restrictions could seriously affect the accuracy of the results and make the advantages of a singles + doubles treatment doubtful.

The spin-orbit computations were carried out using the program package COLUMBUS,[14] while the program system MOLPRO[15-17] was employed for the one-component pseudopotential calculations. Due to the quite small spin-orbit splittings of the energy levels of lanthanide atoms, we didn't perform spin-orbit calculations for the lanthanide compounds.

Since no experimental data are available for the actinide compounds, nonrelativistic and relativistic SCF all-electron computations using the direct SCF program TURBOMOLE[18,19] were performed to provide some evidence for the accuracy of our pseudopotentials. In our relativistic calculations the one-component Douglas-Kroll-Hess[20,22] approach was employed. Very large uncontracted (22s19p16d10f) and (25s22p19d16f) Gaussian type basis sets[21] were applied for the lanthanides and actinides, respectively. For the ligands the basis sets used in the pseudopotential calculations were also applied in the all-electron treatment, but the two *g*-functions were left out and the basis sets were not contracted. The neglect of *g*-functions in our all-electron calculations was primarily due to program limitations and is justified by the very small influence of those functions at the SCF level of theory.

In our pseudopotential calculations the counterpoise correction (CPC) was applied to estimate the size of the basis set superposition error (BSSE) caused by the application of limited basis sets. Due to the high computational demands and based on the experience that BSSE effects are small at the SCF level of theory for reasonably large basis sets, no CPC calculations were carried out in our all-electron calculations.

3. Results

The results of our calculations on the lanthanide compounds are given in Tables 1-4. The comparison of the bond lengths obtained from all-electron SCF calculations with results from pseudopotential calculations listed in Table 1 shows good agreement except for LaO, where a difference of 2.9 pm is found in the nonrelativistic case. Improvement of the basis sets by adding diffuse functions did not affect this result, and the observed deviation has to be attributed to the pseudopotential. Effective core potentials with the given core are known to underestimate the considerable 4f participation,[23] causing a bond length that is too large. For the force constants listed in Table 2 the overall agreement between all-electron calculations and pseudopotential computations is very good, with the largest discrepancy being 23 N/m. Very good accordance is also found throughout for the computed dissociation energies (Table 4), with a maximum error of only 0.09 eV.

Tables 5-7 show the corresponding computed data for the actinide compounds. The bond lengths (Table 5) obtained by pseudopotential SCF calculations are very close to the corresponding all-electron values for the actinium compounds and the nonrelativistic results of the lawrencium compounds. However, the disagreement in the relativistic results of the lawrencium compounds is quite large, with deviations of 2.5,

TABLE 1: Bond Lengths of Lanthanide Compounds (in pm) Obtained by Relativistic (rel) and Nonrelativistic (nrel) Self-Consistent-Field (SCF) All-Electron (ae) and Pseudopotential Calculations and Correlated Pseudopotential Calculations Applying the Coupled-Cluster Method with Single and Double Excitations (CCSD) and Perturbative Treatment of Triple Excitations (CCSD(T)) as Well as the Multireference Averaged Coupled-Pair Functional Method (MRACPF), in Comparison with Experimental Results (expt) Taken from Ref 26 (LaH) and Ref 27; The Counterpoise Correction (+CPC) Was Applied To Account for Basis Set Superposition Errors

		SCF (ae)	SCF	CCSD	CCSD(T)	MRACPF	exptl
LaH	rel	205.3	206.3	200.1	200.1	199.8	203.2
	+CPC		206.4	204.0	203.9	203.7	
	nrel	204.2	205.1	199.9			
	+CPC		205.2	204.0			
LuH	rel	195.6	196.3	191.2	191.0	191.3	191.2
	+CPC		196.4	194.7	194.5	194.6	
	nrel	193.3	194.5	188.7			
	+CPC		194.5	192.5			
$\Delta_{\rm ln}$	rel	9.7	10.0	8.8	8.9	8.5	12.0
	+CPC		10.0	9.3	8.8	9.1	
	nrel	10.9	10.6	11.2			
	+CPC		10.7	11.5			
LaF	rel	205.0	205.6	203.2	203.3	203.2	202.7
	+CPC		205.6	204.4	204.4	204.4	
	nrel	204.0	205.0	203.0			
	+CPC		205.0	204.1			
LuF	rel	194.2	194.0	192.0	191.9	192.1	191.7
	+CPC		194.0	194.1	194.1	194.0	
	nrel	194.8	194.9	192.5			
	+CPC		194.9	194.4			
$\Delta_{\rm ln}$	rel	10.8	11.6	11.7	11.4	11.1	11.0
	+CPC		11.6	10.3	10.3	10.4	
	nrel	9.2	10.1	10.5			
	+CPC		10.1	9.7			
LaO	rel	181.2	182.9	184.2	185.7	185.2	182.6
	+CPC		182.9	185.2	186.9	186.1	
	nrel	176.7	179.6	181.5			
	+CPC		179.6	182.4			
LuO	rel	178.6	178.4	178.3	179.3	178.7	179.0
	+CPC		178.4	179.2	180.4	179.8	
	nrel	177.7	177.8	178.0			
	+CPC		177.8	178.9			
$\Delta_{\rm ln}$	rel	2.6	4.5	6.2	6.4	6.5	3.6
	+CPC		4.5	6.0	6.5	6.3	
	nrel	−1.0	1.8	3.5			
	+CPC		1.8	2.5			

TABLE 2: Force Constants of Lanthanide Compounds (in N/m)

		SCF (ae)	SCF	CCSD	CCSD(T)	MRACPF
LaH	rel	123	123	135	134	136
	+CPC		123	124	126	130
	nrel	116	117	126		
	+CPC		117	119		
LaF	rel	311	316	340	339	340
	+CPC		316	323	323	324
	nrel	300	304	322		
	+CPC		304	311		
LaO	rel	640	631	609	562	555
	+CPC		631	583	533	531
	nrel	680	657	626		
	+CPC		657	611		
LuH	rel	130	129	131	131	131
	+CPC		129	128	128	128
	nrel	141	139	147		
	+CPC		139	142		
LuF	rel	370	362	382	364	368
	+CPC		362	350	341	342
	nrel	380	373	395		
	+CPC		373	368		
LuO	rel	702	681	655	631	638
	+CPC		681	632	620	623
	nrel	702	684	677		
	+CPC		684	653		

TABLE 3: Vibrational Frequencies of Lanthanide Compounds (in cm^{-1}), Experimental Values Taken from Ref 27

		CCSD	CCSD(T)	MRACPF	exptl
LaH	rel	1516	1510	1521	
+CPC		1453	1465	1488	
LaF	rel	588	587	587	570
+CPC		573	573	574	
LaO	rel	849	815	810	813
+CPC		831	794	793	
LuH	rel	1532	1530	1531	1500
+CPC		1514	1513	1515	
LuF	rel	615	600	604	612
+CPC		589	581	582	
LuO	rel	878	862	867	842
+CPC		862	854	856	

1.4, and 2.2 pm for LrH, LrF, and LrO, respectively. In pseudopotential calculations relativistic effects are taken into account only implicitly via parametrization and the valence electrons are subject to a formally nonrelativistic treatment. This is a considerable approximation for heavy elements like lawrencium, especially when a rather small pseudopotential core is used. The difficulty in modeling the relativistic effects clearly gets larger with a reduced core size, and as a consequence, the small-core potential for lawrencium seems to underestimate the relativistic effects, causing the errors mentioned above. We note that, on the other hand, a small core is often desirable to avoid frozen-core errors, cf. the discussion for La. Nevertheless, only small deviations from all-electron results occur for the other properties. The force constants (Table 6) from pseudopotential computations agree within 16 N/m, and a maximum discrepancy of only 0.1 eV is found for the dissociation energies (Table 7).

The calibration calculations discussed above demonstrate the reliability of our energy-consistent ab initio pseudopotentials at the SCF level. The lanthanide and actinide contractions are obtained with accuracies better than 2.8 and 1.9 pm, respectively.

In our correlated calculations on the lanthanide compounds considerable BSSE effects are found. The largest increase in the bond length caused by the counterpoise correction occurs for the hydrides (3.3−4.1 pm), probably due to the flat potential energy curve. However the more strongly bound fluorides (1.1−2.2 pm) and oxides (≤1.2 pm) still show a marked bond elongation . The dissociation energies are decreased by 0.13−0.25 eV for the lutetium compounds and for LaH. For LaF (0.38−0.61 eV) and LaO (0.31−0.43 eV) a somewhat larger decrease occurs. CPC also causes a decrease of the force constants by 11−32 N/m for the fluorides and oxides, while the effect is somewhat smaller for LaH (6−11 N/m) and LuH (3−5 N/m). In the following discussion of electron correlation effects we refer to the counterpoise-corrected values.

In our relativistic CCSD calculations, electron correlation effects on the bond lengths turn out to be more pronounced for the lanthanum compounds under consideration compared to the corresponding lutetium compounds. The hydrides undergo a bond diminution of 2.4 pm (LaH) and 1.7 pm (LuH), respectively. A reduction of the bond length is also found for LaF (1.2 pm), while the bond length of LuF remains nearly unaffected (increase of 0.1 pm). For the oxides, a bond elongation of 2.3 pm (LaO) and 0.8 pm (LuO) occurs. This increase in the bond lengths is accompanied by a decrease in the force constants by 48 N/m (8%) for LaO and 49 N/m (7%) for LuO, respectively. Only small electron correlation effects are found for the fluorides and hydrides. The force constants of the lanthanum compounds undergo a slight increase (7 N/m (2%) for LaF and 1 N/m (1%) for LaH, respectively), while a

TABLE 4: Dissociation Energies of Lanthanide Compounds (in eV), Experimental Values Taken from Ref 28 (LaO, LuO) and Ref 27

		SCF (ae)	SCF	CCSD	CCSD(T)	MRACPF	expt
LaH	rel	2.19	2.16	3.06	3.05	3.04	
	+CPC		2.16	2.87	2.84	2.82	
	nrel	2.07	2.01	3.68			
	+CPC		2.01	3.48			
LaF	rel	5.27	5.23	6.82	7.17	7.12	6.23
	+CPC		5.23	6.44	6.56	6.53	
	nrel	4.94	4.87	7.22			
	+CPC		4.87	6.80			
LaO	rel	5.34	5.26	7.93	8.35	8.24	8.29
	+CPC		5.26	7.61	7.92	7.87	
	nrel	5.90	5.81	9.16			
	+CPC		5.81	8.85			
LuH	rel	2.75	2.72	3.47	3.45	3.43	3.47[a]
	+CPC		2.72	3.29	3.26	3.25	
	nrel	2.21	2.17	3.06			
	+CPC		2.17	2.93			
LuF	rel	6.08	6.04	7.54	7.87	7.83	5.93[b]
	+CPC		6.04	7.29	7.63	7.59	
	nrel	5.38	5.34	6.97			
	+CPC		5.34	6.74			
LuO	rel	4.25	4.21	6.81	7.11	7.08	7.04
	+CPC		4.21	6.63	6.89	6.85	
	nrel	4.53	4.48	7.21			
	+CPC		4.48	7.02			

[a] Experimental value for LuD. [b] Estimated.

slight decrease (12 N/m (3%) for LuF and 1 N/m (1%) for LuH) occurs for the lutetium compounds.

For all systems a considerable increase in the dissociation energy due to electron correlation is observed. The smallest absolute effect is found for the hydrides (0.71 eV (33%) for LaH and 0.57 eV (21%) for LuH, respectively). This change approximately doubles for the fluorides (1.21 eV (23%) for LaF and 1.25 eV (21%) for LuF, respectively), and a further doubling occurs when proceeding to the oxides (2.35 eV (45%) for LaO and 2.42 eV (57%) for LuO, respectively).

Accounting for higher excitations (CCSD(T)) hardly affects the calculated properties of the hydrides. This holds also for LaF, while for LuF a further decrease in the force constant by 9 N/m (3%) and a further increase in the dissociation energy of 0.34 eV (5%) take place. A similar increase in the dissociation energy of the oxides of 0.31 eV (4%, LaO) and 0.26 eV (4%, LuO), respectively, also occurs. However, in contrast to the hydrides and fluorides, significant changes in the bond length occur for the oxides. The bond is further elongated by 1.7 pm (LaO) and 1.2 pm (LuO), respectively, accompanied with a further decrease of the force constant by 50 N/m (9%, LaO) and 12 N/m (2%, LuO). The results of the multireference treatment (MRACPF) are in very close accordance with the ones obtained from CCSD(T) calculations. Only the bond elongation of the oxides is found to be smaller, with values of 0.9 pm (LaO) and 0.6 pm (LuO).

The results of the MRACPF calculations show reasonable agreement with experimental data. However our counterpoise-corrected bond lengths turn out to be too long. Particularly large errors occur for LaO (3.5 pm), LuH (3.4 pm), and LuF (2.3 pm). For LaO the bond length error may be explained by too small a 4f contribution to the bond. Due to frozen-core errors forced by the large core of our lanthanide pseudopotentials, the 4f orbitals are slightly too high in energy, and therefore 4f participation in bonding is underestimated. The 4f orbitals contribute to π-bonding in the oxides, which mainly has 5d-2p character, and lead to a shortening of the bond. In the case of the lutetium compound it is a reasonable assumption to attribute the too long bond lengths partly to the neglect of core−valence correlation. The filled 4f shell is included into the core and therefore is not correlated. A bond elongation of 7 pm for the monohydride, 5 pm for the monofluoride, and 3 pm for the monoxide occurs for the lawrencium compounds if the 5f shell is not correlated. Since the 4f shell of lutetium is significantly less polarizable than the 5f shell of lawrencium, core−valence correlation effects should be distinctly smaller for the lutetium compounds. The bond shortening due to core−valence correlation also affects our earlier statement that correlation effects on the bond length are found to be larger for the lanthanum compounds than the lutetium compounds. A further reduction in the bond length of the lutetium compounds may reverse this trend in accordance with our findings for the actinide compounds where the correlation effect on the bond length tends to be more pronounced for the last element of the series.

TABLE 5: Bond Lengths of Actinide Compounds (in pm) Obtained by Relativistic (rel) and Nonrelativistic (nrel) Self-Consistent-Field (SCF) All-Electron (ae) and Pseudopotential Calculations and Correlated Pseudopotential Calculations Applying the Coupled-Cluster Method with Single and Double Excitations (CCSD) and Perturbative Treatment of Triple Excitations (CCSD(T)) as Well as the Multireference Averaged Coupled-Pair Functional Method (MRACPF) with Additional Treatment of Spin−Orbit Effects (+SO); The Counterpoise Correction (+CPC) Was Applied to Account for Basis Set Superposition Errors

		SCF (ae)	SCF	CCSD	CCSD(T)	MRACPF	+SO
AcH	rel	218.7	218.1	213.2	212.5	213.0	209.1
	+CPC		218.1	214.3	213.1	213.6	209.7
	nrel	210.4	210.1	205.7			
	+CPC		210.1	206.9			
LrH	rel	203.0	200.5	192.8	193.6	194.2	191.7
	+CPC		200.5	193.6	194.3	194.9	192.5
	nrel	198.6	198.0	192.3			
	+CPC		198.0	193.2			
Δ_{an}	rel	15.7	17.6	21.3	18.9	18.8	17.4
	+CPC		17.6	20.7	18.8	18.7	17.2
	nrel	11.8	12.1	13.4			
	+CPC		12.1	13.7			
AcF	rel	213.9	213.5	211.9	211.8	211.9	210.3
	+CPC		213.5	212.4	212.7	212.6	210.9
	nrel	209.5	208.9	207.5			
	+CPC		208.9	208.1			
LrF	rel	201.5	200.1	196.5	197.2	196.9	196.2
	+CPC		200.1	197.2	198.3	197.2	196.6
	nrel	202.9	202.2	199.2			
	+CPC		202.2	199.7			
Δ_{an}	rel	12.4	13.4	15.4	14.6	15.0	14.1
	+CPC		13.4	15.2	14.4	15.4	14.3
	nrel	6.6	6.7	8.3			
	+CPC		6.7	8.4			
AcO	rel	191.9	191.6	192.5	193.0	193.2	192.3
	+CPC		191.6	192.9	193.6	193.7	192.7
	nrel	180.3	179.9	181.3			
	+CPC		179.9	181.8			
LrO	rel	184.8	182.6	181.5	182.1	182.0	181.2
	+CPC		182.6	182.0	183.4	183.2	182.2
	nrel	183.0	182.4	182.4			
	+CPC		182.4	183.0			
Δ_{an}	rel	7.1	9.0	11.0	10.9	11.2	11.1
	+CPC		9.0	10.6	10.2	10.5	10.5
	nrel	−2.7	−2.5	−1.1			
	+CPC		−2.5	−1.2			

For all molecules under consideration the computed vibrational frequencies (Table 3) are in good agreement with experimental values, with a maximum deviation of 31 wavenumbers for LuH. The computed experimental dissociation energies are also quite close to their experimental counterparts. Only for LuF does a sizable discrepancy of 1.66 eV occur, but the experimental value of 5.93 eV is an estimate.[24] On the basis of the maximum energy difference of 0.42 eV for all other compounds we conclude that this value is considerably too low.

TABLE 6: Calculated Force Constants of Actinide Compounds (in N/m)

		SCF (ae)	SCF	CCSD	CCSD(T)	MRACPF	+SO
AcH	rel	107	108	115	116	115	115
	+CPC		108	110	110	110	109
	nrel	104	104	112			
	+CPC		104	109			
AcF	rel	290	290	296	299	298	347
	+CPC		290	287	288	288	334
	nrel	272	272	284			
	+CPC		272	277			
AcO	rel	580	589	558	555	553	573
	+CPC		589	554	549	547	565
	nrel	733	736	694			
	+CPC		736	688			
LrH	rel	113	113	125	125	125	134
	+CPC		113	119	119	117	126
	nrel	134	136	142			
	+CPC		136	135			
LrF	rel	324	322	343	346	344	354
	+CPC		322	336	338	339	344
	nrel	349	351	372			
	+CPC		351	365			
LrO	rel	674	690	653	657	659	665
	+CPC		690	647	652	653	657
	nrel	686	691	670			
	+CPC		691	664			

TABLE 7: Calculated Dissociation Energies of Actinide Compounds (in eV)

		SCF (ae)	SCF	CCSD	CCSD(T)	MRACPF	+SO
AcH	rel	2.53	2.50	3.52	3.63	3.60	3.52
	+CPC		2.50	3.44	3.54	3.53	3.40
	nrel	2.23	2.21	3.45			
	+CPC		2.21	3.37			
AcF	rel	5.79	5.76	7.49	7.65	7.68	7.58
	+CPC		5.76	7.28	7.38	7.41	7.26
	nrel	5.17	5.15	7.16			
	+CPC		5.15	6.98			
AcO	rel	4.83	4.81	7.60	7.71	7.73	7.52
	+CPC		4.81	7.46	7.57	7.60	7.36
	nrel	7.02	7.01	9.86			
	+CPC		7.01	9.69			
LrH	rel	2.95	2.85	4.21	4.31	4.28	4.03
	+CPC		2.85	4.12	4.19	4.18	3.93
	nrel	1.96	1.95	3.21			
	+CPC		1.95	3.10			
LrF	rel	6.06	6.01	10.52	10.73	10.68	10.39
	+CPC		6.01	10.31	10.36	10.33	10.04
	nrel	4.75	4.73	6.66			
	+CPC		4.73	6.48			
LrO	rel	3.72	3.63	9.42	9.54	9.52	9.16
	+CPC		3.63	9.28	9.31	9.34	8.99
	nrel	4.83	4.81	7.83			
	+CPC		4.81	7.72			

For LaH neither an experimental vibrational frequency nor an experimental dissociation energy is available. Our computed dissociation energy of 2.82 eV lies between the values reported by Wang et al.[5] ($D_e = 2.99$ eV) and Das et al.[25] ($D_e = 2.60$ eV), while our computed vibrational frequency of 1488 cm^{-1} is somewhat larger than the values suggested by Wang et al.[5] (1378 cm^{-1}) and Das et al.[25] (1433 cm^{-1}).

The comparison of the results of our relativistic and nonrelativistic CCSD calculations shows significant relativistic bond length expansions for LuH (2.2 pm) and LaO (2.8 pm). For the other compounds the relativistic change of bond length is at most 0.3 pm. Force constants of LaH and LaF are relativistically increased by 5 N/m (4%) and 12 N/m (4%), respectively, while a relativistic decrease by 28 N/m (5%) occurs for LaO. The force constants of the lutetium compounds also undergo a relativistic decrease by 14 N/m (10%, LuH), 18 N/m (5%, LuF), and 21 N/m (3%, LuO). For LaO and LuO the relativistic decrease of the force constant is accompanied by a drop of the dissociation energy by 1.24 and 0.39 eV, respectively. The dissociation energies of LaH and LaF are also relativistically decreased by 0.61 and 0.36 eV, respectively, while a relativistic increase occurs for LuH (0.36 eV) and LuF (0.55 eV).

Once again we want to point out that the values given in Table 4 are the energy differences between the atomic $6s^2\,6d^1$ ^2D state and the lowest $^1\Sigma^+$ (for hydrides and fluorides) and $^2\Sigma^+$ state (for the oxides), respectively. This energy difference corresponds to the dissociation energy in the relativistic case but not in the nonrelativistic case, where a couple of states with occupied 4f orbitals are lower in energy for lanthanum and its compounds. Therefore the proper nonrelativistic dissociation energy is significantly lower than the values given.

From our calculated bond lengths we derive lanthanide contractions of 9.1, 10.4, and 6.3 pm for the hydrides, fluorides, and oxides, respectively. For the hydrides the lanthanide contraction is only slightly affected by electron correlation (about 0.9 pm decrease), while relativistic effects lead to a decrease of 2.2 pm. The lanthanide contraction of the fluorides behaves in a similar way with a small correlation effect of 1.2 pm. Relativity increases the lanthanide contraction of the fluorides by 0.6 pm. A larger effect is found for the oxides with a relativistic increase of 3.5 pm. For the nonrelativistic all-electron SCF result this leads in fact to a lanthanide expansion. Electron correlation leads to an increase of 1.8 pm. The relativistic increase of the lanthanide contraction may be understood by the relativistic expansion of the 4f shell, resulting in a decreased shielding of the nuclear charge and therefore an enhanced contraction. This effect is especially important for LaO, where the 4f shell contributes to the double bond.

In our correlated calculations for the actinide compounds the BSSE effect remains moderate for all molecules and all properties under consideration. Applying the counterpoise correction increases the bond length by less than 1.2 pm, decreases the force constants by not more than 11 N/m, and decreases the dissociation energy by at most 0.37 eV. In our subsequent discussion of correlation effects we refer to the counterpoise-corrected values.

A comparison between our CCSD and SCF results indicates a considerable reduction of the bond length of the hydrides (3.8 and 6.9 pm for AcH and LrH, respectively) and fluorides (1.1 and 2.9 pm for AcF and LrF, respectively) due to electron correlation. A smaller bond shortening is found for LrO (0.6 pm), and a bond length expansion by 1.3 pm occurs for AcO. Only moderate changes of the force constants due to electron correlation are found for the actinide hydrides and fluorides with a slight increase for AcH (2 N/m), LrH (6 N/m), and LrF (14 N/m) and a decrease for AcF (3 N/m). The effect is more pronounced for the oxides, with decreases of 35 N/m (AcO) and 43 N/m (LrO), respectively.

As for the lanthanides, a large correlation effect is found for the dissociation energies with an increase of up to 5.65 eV for LrO. Inclusion of triple excitations or multireference treatments results in comparatively small changes with an increase of the dissociation energies by up to 0.21 eV, changes of force constants by not more than 10 N/m, and changes of the bond lengths by less than 1 pm except for LrH, with a bond elongation of 1.4 pm.

Although small in magnitude, the spin−orbit effects cause a considerable shortening of the bond lengths, 3.9 pm for AcH and 2.4 pm for LrH due to the flat potential energy curve. A bond length decrease is also found for the fluorides (1.7 pm for AcF and 0.6 pm for LrF, respectively) and the oxides (1 pm).

The force constants are slightly increased by 4−18 N/m except for AcH. The dissociation energy is lowered by 0.08−0.24 eV for the actinium compounds and 0.25−0.36 eV for the lawrencium compounds, respectively. On the basis of the good agreement of our pseudopotential SCF calculations with all-electron SCF results and the reasonable results for the lanthanides, we suggest that our values are reliable estimates for the experimental properties of the actinide compounds.

For the relativistic effects on the properties of the actinide compounds under consideration, qualitative agreement with the corresponding lanthanide systems is again found. Of course the magnitude of relativistic changes is significantly larger for the actinides. A relativistic bond length increase occurs for all actinium compounds as well as for LrH and for the SCF results of LrO, while a shrinkage of the bond length is observed for LrF and the correlated results of LrO. The largest effect occurs for AcO with a dramatic relativistic bond elongation of 11.1−11.7 pm. Like the large relativistic bond lengthening found for LaO, this is easily explained by the relativistic effect on the f orbitals which leads to a significantly reduced participation of the f shell in the double bond in both compounds. Obviously the 5f shell of the actinides undergoes a considerably enhanced relativistic destabilization compared to the 4f shell of the lanthanides. The force constants for the lawrencium compounds show a relativistic decrease, which is also found for AcO. In contrast, like their lanthanide counterparts, AcH and AcF show a slight increase. Qualitative agreement with the data of the lanthanides can also be seen for the dissociation energies obtained from SCF calculations, where a relativistic increase takes place for the hydrides and fluorides, while a decrease is observed for the oxides. Disagreement with the lanthanides is found for the correlated results of AcH, AcF, and LrO. The correlated calculations for AcH and AcF still predict a small increase of the dissociation energy by 0.07 and 0.33 eV, respectively, while for LrO the relativistic decrease at the SCF level is turned into an increase of 1.59 eV. As for the bond lengths and force constants, the relativistic effect on the dissociation energies is much larger for the actinides (up to 3.83 eV) than for the lanthanides (up to 1.24 eV).

We obtain actinide contractions of 17.2, 14.3, and 10.5 pm for the hydrides, fluorides, and oxides, respectively. This sequence is in qualitative agreement with the findings of Wang and Schwarz[5] for the lanthanides, i.e. bonds with large (small) force constants undergo small (large) contractions. Relativistic effects—both scalar-relativistic effects and spin−orbit effects—have a significantly larger impact on the actinide contraction compared to the lanthanide contraction. The scalar effects lead to a large increase in the actinide contraction by 3.9−7.9 pm for the hydrides, 5.8−7.1 pm for the fluorides, and 9.8−12.1 pm for the oxides, respectively. The spin−orbit interaction reduces the actinide contraction by 1.5 pm for the hydrides and 1.1 pm for the fluorides, but the contraction of the oxides remains unchanged. Inclusion of electron correlation leads to an increase of 1.1 pm for the hydrides, 2.0 pm for the fluorides, and 1.5 pm for the oxides.

For the oxides a nonrelativistic actinide expansion occurs even at the correlated level. This is a consequence of the unusally short bond length of nonrelativistic AcO caused by a strong 5f contribution to the 6d-2p-π bond.

4. Conclusion

In this work we have demonstrated the ability of energy-consistent pseudopotentials to give a reliable description of the properties of lanthanide and actinide compounds. Our results are in good agreement with data taken from experiment as well as results of all-electron SCF calculations. The actinide contractions caused by incomplete shielding of the nuclear charge by the diffuse 5f orbitals are found to be significantly larger than the corresponding lanthanide contraction. Relativistic effects are very important for the actinide contraction. The calculated contraction for the actinide oxides is a pure relativistic effect. The lanthanide and actinide contractions derived from bond lengths are significantly smaller than the values obtained from ionic radii. This is partly due to the change in the bonding when proceeding from the first to the last element in the lanthanide/actinide series.

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