Efficient quantum chemical valence-only treatments of lanthanide and actinide systems

Michael Dolg

Institute for Theoretical Chemistry, University of Cologne, Greinstr. 4, D-50939 Cologne, Germany

Abstract. Recent progress in the development of lanthanide and actinide relativistic energy-consistent ab initio pseudopotentials is reported. Lanthanide 4f-in-core and actinide 5f-in-core pseudopotentials form an efficient tool for quantum chemical ab initio and first-principles calculations on larger systems, whenever the detailed electronic structure of the f shell is not of primary interest. The reliability of the 4f-in-core approximation is demonstrated for molecular lanthanide trihalides by comparison of calculated structural data with recommended experimental values. Due to the scarceness of experimental reference data the calibration of the 5f-in-core approximation is performed with respect to results from other more rigorous calculations. Lanthanide 4f-in-valence and actinide 5f-in-valence pseudopotentials allow the study of individual electronic states arising from a given f occupancy in a system. Recent progress to develop highly accurate small-core pseudopotentials which model all-electron calculations using the Dirac-Coulomb-Breit Hamiltonian is summarized and first applications are outlined.

Keywords: lanthanides, actinides, pseudopotentials
PACS: 31.10.+z, 31.15.A-, 31.15.aj, 31.15.am

INTRODUCTION

Relativistic ab initio effective core potentials (ECPs) [1, 2] are still a workhorse in quantum chemical calculations of heavy element compounds, despite the development of various practical relativistic all-electron (AE) schemes during the last two decades. ECPs restrict the explicit quantum mechanical treatment to the valence electron system and thus lead to computational savings with respect to AE approaches. Moreover and even more important, ECPs allow for an implicit inclusion of the most important relativistic contributions into formally non-relativistic calculations. ECPs essentially fall in two categories, i.e. model potentials (MPs) keeping the correct radial nodal structure of the valence orbitals [3] and pseudopotentials (PPs) working with pseudo-valence orbitals exhibiting a simplified radial nodal structure [1, 2]. Since the PPs require less extended basis sets than MPs, they have been more popular among computational chemists than MPs. Among the mostly used PPs are the so-called shape-consistent ab initio sets provided by Hay and Wadt for main group and transitions metals [4, 5, 6], of Stevens, Krauss, Cundari and coworkers for most elements except the actinides [7, 8, 9], as well as of Pitzer, Christiansen and collaborators for almost the entire periodic table [10, 11, 12, 13, 14, 15, 16, 17, 18]. Another quite frequently used variant are the energy-consistent ab initio PPs of Stoll, Schwerdtfeger, Dolg and coworkers [19, 20, 21, 22, 23, 24]. In contrast to the shape-consistent PPs which are derived from reference data defined in an effective one-particle picture for a single reference state, i.e. orbital energies and the radial shape of orbitals in the spatial valence region, the energy-consistent PPs are based on quantum mechanical observables, i.e. total valence energies of a multitude of electronic configurations and states for the atom/ion under consideration. Energy-consistent PPs in their most recent variant are adjusted to reference data taken from multi-configuration (MC) Dirac-Hartree-Fock (DHF) calculations using the Dirac-Coulomb (DC) Hamiltonian and including perturbative estimates of the Breit interaction (+B). Finite nucleus effects are usually also included, as well as sometimes higher order relativistic corrections [25, 26, 27, 28, 29, 30, 31, 32, 33, 34].

In this contribution we will focus on recent developments of relativistic energy-consistent PPs for elements with open f shells, i.e. lanthanides and actinides [35, 36, 37, 38]. These elements are probably the most difficult to deal with for quantum chemists, not only due to the large number of low-lying electronic states arising from open f shells, but also due to the large relativistic effects and correlation effects. The importance of the latter two contributions is obvious for example from studies of the third and fourth ionization potential of lanthanum and cerium, respectively. Fig. 1 reveals that both effects are larger when the compact 4f shells are involved in comparison to the more diffuse 5d shells (left side). The accurate ab initio evaluation of the correlation contributions is feasible, but suffers from the slow convergence of the results with basis set size (right side). We will briefly discuss two approaches for PP-based quantum chemical calculations of lanthanide and actinide compounds: a very simple strategy eliminating most of

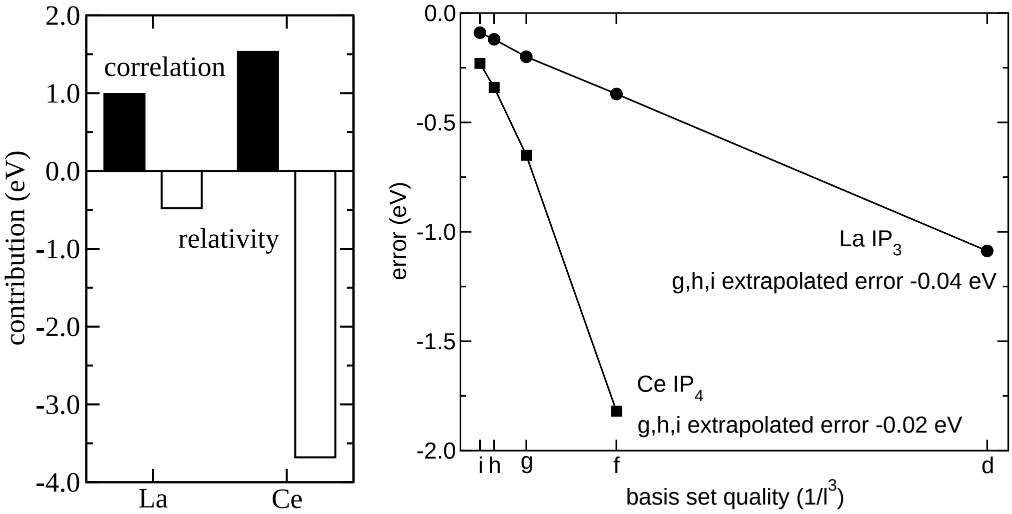

FIGURE 1. Left: relativistic (empty bars) and correlation (filled bars) contributions to IP_3 of La (removal of $5d^1$) and IP_4 of Ce (removal of $4f^1$) from finite difference AE HF and MCDHF/DC+B calculations as well as experimental data (La: 19.18 eV, Ce: 36.76 eV). Right: basis set dependence of IP_3 of La and IP_4 of Ce in spin-orbit corrected CCSD(T) calculations using energy-consistent relativistic small-core pseudopotentials and up to (16s15p12d10f10g10h10i) valence basis sets [74].

the mentionned difficulties arising from the open f shell by attributing it to the PP core (f-in-core PPs) and a more involved one treating the f shell explicitly in the valence (f-in-valence PPs). Whereas the former approach allows to get information for all electronic states belonging to the same superconfiguration [39], i.e. all states with the same valence substate and the same f occupation on the lanthanide/actinide, the latter approach is able to study individual electronic states, although with a much higher computational effort.

METHOD

The energy-consistent PP approach is outlined here only very briefly. More detailed descriptions may be found in several review articles as well as the references to original work therein [1, 2]. The molecular valence-only model Hamiltonian for n_v valence electrons used in the current work can be written as

$$\hat{H}_v = -\frac{1}{2}\sum_i^{n_v}\nabla_i^2 + \sum_{i<j}^{n_v}\frac{1}{r_{ij}} + \sum_i^{n_v}\hat{V}_{cv}(i) + \sum_{\lambda<\mu}\frac{Q_\lambda Q_\mu}{r_{\lambda\mu}} + \hat{V}_{cpp} \tag{1}$$

Here i and j are electron indices and λ and μ core/nucleus indices. Q_λ and Q_μ stand for the core/nucleus charges. The first term corresponds to the kinetic energy of the valence electrons, the second one to the interelectronic Coulomb interaction. The third term stands for the electron-core/nucleus interaction and the fourth term represents the point charge Coulomb repulsion between cores/nuclei. In case of very large overlapping cores correction terms may follow the leading Coulomb repulsion. The fifth and last term is the core-polarization potential (CPP) which accounts for static and dynamic core-valence correlation.

The electron-core/nucleus interaction is written as a sum of atomic contributions with a leading point charge Coulomb contribution and a correction term

$$\hat{V}_{cv}(i) = -\sum_\lambda [\frac{Q_\lambda}{r_{\lambda i}} + \Delta\hat{V}_{cv}^\lambda(i)] \quad . \tag{2}$$

In the semilocal approximation the latter is written as a sum over products of radial potentials and projectors onto the spherical harmonics associated with core λ

$$\Delta\hat{V}_{cv}^\lambda(\vec{r}_{\lambda i}) = \sum_l V_l^\lambda(r_{\lambda i}) \sum_{m=-l}^{m=l} |lm,\lambda><lm,\lambda| \quad . \tag{3}$$

The ansatz described so far is suitable for scalar-relativistic PPs. In case that spin-orbit (SO) interaction is considered, the correction term is written as a sum over products of radial potentials and projectors onto the spinor spherical harmonics associated with core λ

$$\Delta\hat{V}^{\lambda}_{cv}(\vec{r}_{\lambda i}) = \sum_{l,j} V^{\lambda}_{lj}(r_{\lambda i}) \sum_{m=-j}^{m=j} |ljm,\lambda><ljm,\lambda| \qquad . \tag{4}$$

The sums over l and lj are usually terminated at l values which are larger than the highest l value present in the core λ by one or two. The CPP is only at frist glance a simple sum of atomic contributions, i.e.

$$\hat{V}_{cpp} = -\frac{1}{2}\sum_{\lambda} \alpha_{\lambda} \hat{\vec{f}}^{\,2}_{\lambda} \qquad . \tag{5}$$

Since the electrostatic field at core/nucleus λ depends on all other core/nuclei and all valence electrons

$$\hat{\vec{f}}_{\lambda} = -\sum_{i} \frac{\vec{r}_{i\lambda}}{r^3_{i\lambda}} F(r_{i\lambda},\delta^{\lambda}_{e}) + \sum_{\mu\neq\lambda} Q_{\mu} \frac{\vec{r}_{\mu\lambda}}{r^3_{\mu\lambda}} F(r_{\mu\lambda},\delta^{\lambda}_{c}) \qquad , \tag{6}$$

the final expression for $\hat{V}_{cpp}$ also contains two-electron contributions. Since the underlying multipole expansion is not valid when the polarizing charges approach the site of the polarized core, cut-off functions have to be applied for the electron-core and core/nucleus-core distances, i.e.

$$F(r_{i\lambda},\delta^{\lambda}_{e}) = [1-exp(-\delta^{\lambda}_{e} r^2_{i\lambda})]^{n_e} \qquad \text{and} \qquad F(r_{\mu\lambda},\delta^{\lambda}_{c}) = [1-exp(-\delta^{\lambda}_{c} r^2_{\mu\lambda})]^{n_c} \ . \tag{7}$$

The radial potentials V^{λ}_{l} and V^{λ}_{lj} usually have the form of a linear combination of Gaussian functions times powers of $r_{\lambda i}$, with the expansion coefficients and the exponential parameters being free for adjustment to suitable reference data. In case of the energy-consistent PP approach the free parameters for a given atom λ are chosen in such a way, that the following expression becomes a minimum:

$$S = \sum_{I} w_I (E^{PP}_{I} - E^{AE}_{I} + \Delta E_{shift})^2 := min \qquad . \tag{8}$$

Here E^{PP}_{I} and E^{AE}_{I} denote the total valence energies for the electronic LS- or LSJ-state I of the atom under consideration from PP and AE reference calculations. The weights w_I are usually chosen to give the same overall weight to all configurations included in the fit, independent from the number of underlying LS or LSJ states. The older one-component PPs used reference data obtained from the scalar-relativistic Wood-Boring (WB) Hartree-Fock scheme [40] and were partly augmented by two sets of valence SO terms to be used in first-order perturbation theory or valence-only self-consistent SO treatments, respectively. The more recent two-component PPs make use of MCDHF reference data obtained with the finite nucleus DC Hamiltonian and a perturbative treatment of the Breit interaction [41]. Whereas the adjustment of the older WB-based PPs typically comprised 10 to 20 LS states, the newer MCDHF/DC+B-based PPs are adjusted to several hundred or even thousand LSJ levels. In the adjustment of newer PPs a small shift ΔE_{shift} of the core energies is considered, which does not change low-energy valence spectrum of the atom, but allows a higher overall accuracy as well as the inclusion of higher ionized states [30].

Choice of the Core

Fig. 2 depicts frozen-core errors for Ce and Th evaluated at the finite difference AE MCDHF/DC level [41] for cores taken from the ground state configuration of the neutral atoms, i.e. Ce $4f^1$ $5d^1$ $6s^2$ and Th $6d^2$ $7s^2$. From the left part of the figure it is clear that when modelling a trivalent Ce (with a $4f^1$ subconfiguration) or a tetravalent Th (with a $5f^0$ subconfiguration) only small errors of at most 0.01 eV arise when 11 and 12 electrons are treated explicitly in the valence shell, respectively. Thus, for a fixed f occupation number a large-core PP (LPP) or f-in-core PP approach may be adopted without significant loss of accuracy. In order to achieve the same accuracy also for a variable f occupation number, one has to use a significantly smaller core with 30 electrons treated explicitly, as implied by the right part of the figure. Despite the relatively large number of valence electrons these small-core PPs (SPP) or f-in-valence PPs still allow to use significantly smaller basis sets than in the most favourable AE case, e.g. for the lanthanides.

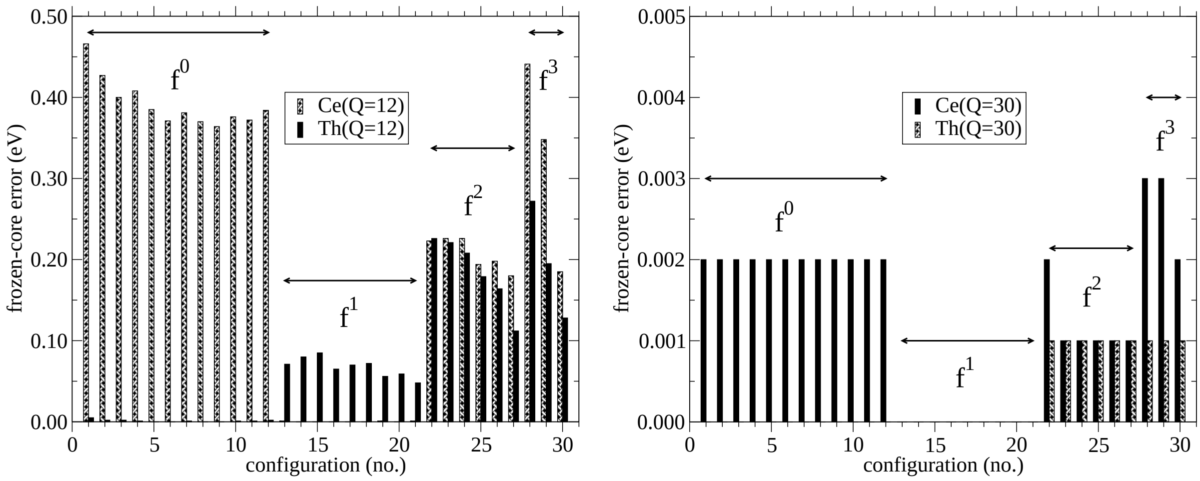

FIGURE 2. Frozen-core errors (eV) for Ce and Th from AE DKH/DC calculations [41]. The cores have a charge Q and were taken from the Ce $4f^1$ $5d^1$ $6s^2$ and Th $6d^2$ $7s^2$ ground state configurations. The configurations are ordered according to increasing f occupation number and for a given f occupation with increasing d occupation number.

f-in-core Pseudopotentials

The initial motivation to generate f-in-core PPs originated from the wide-spread chemical knowledge that the 4f shells of the lanthanide atoms are not actively participating in chemical bonding, which was supported by early quantum chemical studies [35]. A similar ansatz avoiding the explicit treatment of the 4f shell was previously used in semiempirical calculations [42]. Field advocated the so-called superconfiguration model to rationalize the complex spectra of lanthanide diatomics auch as LnO or LnF [39]. A superconfiguration is defined to consist of all electronic states with a common valence substate, arising from all partially occupied orbitals besides 4f, and a common 4f occupation on the lanthanide. Independent from the explicit electronic coupling within the 4f shell, i.e. independent of the 4f substate, and independent from the explicit electronic coupling between the 4f shell and the valence shells all states belonging to a superconfiguration usually have very similar spectroscopic constants.

A typical example is CeO, which might be looked at as a Ce^{2+} O^{2-} ionic system. Here the Ce 6s and 6p orbitals strongly hybridize and form a diffuse singly occupied σ valence orbital localized essentially on Ce, pointing away from the O^{2-} ion. Thus a $^2\Sigma$ valence substate arises. The other electron on Ce is in the atomic-like 4f shell and from the atomic ^{2}F substate molecular $^2\Sigma$, $^2\Pi$, $^2\Delta$ and $^2\Phi$ substates result. Coupling of the two substates leads to $^{1,3}\Sigma,\Pi,\Delta,\Phi$ states belonging to the $4f^1\sigma^1$ superconfiguration. These ΛS states, which correspond to 16 Ω states, are energetically separated by about 0.3 eV (0.5 eV with SO effects) and have bond lengths of 1.82–1.83 Å and vibrational constants of 830–840 cm^{-1} [43]. Table 1 summarizes results obtained with a Ce $4f^1$-in-core PP, which directly yields results for the superconfiguration, and compares them to those obtained with a 4f-in-valence PP. Since Ce keeps one of its four valence electrons in the PP core and leaves three in the valence space, the Ce $4f^1$-in-core PP models a trivalent

TABLE 1. Spectroscopic constants of electronic states belonging to the $4f^1\sigma^1$ superconfiguration of CeO from 4f-in-core (PPc) and 4f-in-valence (PPv) PP calculations. PPv avg. denotes the average over all 8 PPv results for the individual states [43].

	R_e (Å)	ω_e (cm^{-1})	D_e (eV)	T_e (eV)		R_e (Å)	ω_e (cm^{-1})	D_e (eV)	T_e (eV)
PPv avg.	1.821	836	7.16 (87%)		PPc	1.819	834	7.25 (88%)	
exp.	1.820	824	8.22 (100%)						
PPv $^3\Phi$	1.827	838	7.28 (89%)		PPv $^1\Phi$	1.827	837		0.04
PPv $^3\Delta$	1.819	840		0.10	PPv $^1\Delta$	1.818	836		0.15
PPv $^3\Pi$	1.819	833		0.17	PPv $^1\Pi$	1.826	829		0.21
PPv $^3\Sigma$	1.816	835		0.18	PPv $^1\Sigma$	1.821	834		0.31

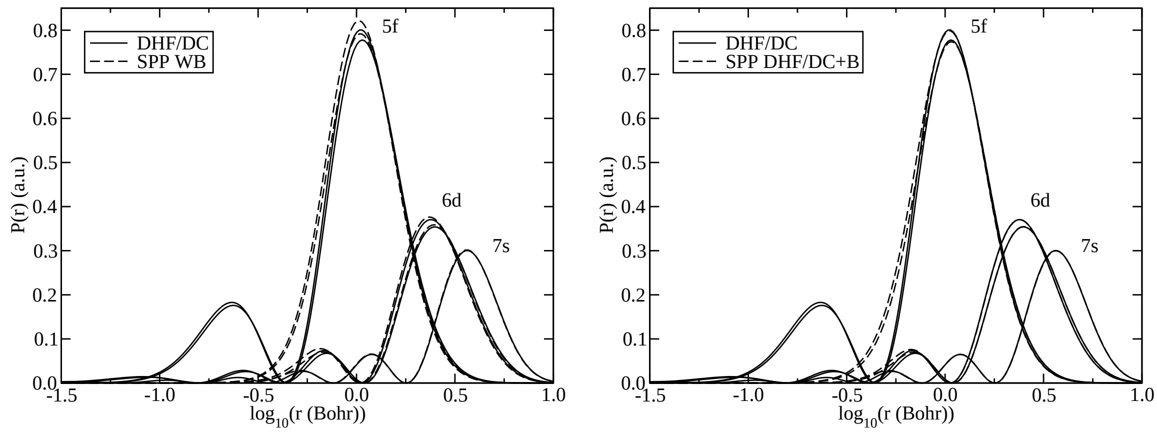

FIGURE 3. Radial densities of valence shells of uranium in the $5f^3\ 6d^1\ 7s^2$ ground state configuration from SPP WB (left) [24] and SPP MCDHF/DC+B (right) [58] calculations in comparison to AE MCDHF/DC results [41].

Ce atom. The 4f-in-core PP approach can be combined with simple ligand field theory in order to estimate individual levels of the superconfiguration under investigation [44].

For lanthanides 4f-in-core PPs for di-, tri- and tetravalent cases have been adjusted and valence basis sets of various sizes, including ones suitable for solid state calculations, were optimized [20, 45, 46, 47]. Only electrons with $n \geq 5$ are treated explicitly in the valence space, i.e. 10, 11 and 12 electrons for the di-, tri- and tetravalent cases. These PPs found numerous applications during the last two decades [35, 38], including ones to solids [48], and proved to be reliable, as long as the f occupancy of the state/configuration under study agrees with the one modelled by the PP.

Although the 5f shell of the actinides is radially more extended than the 4f shell of the lanthanides and for the lighter actinides also actively participates in chemical bonding, it proved to be possible to derive 5f-in-core PPs for actinides with valencies ranging from two to six [49, 50, 51]. Their applications saves a significant amount of computer ressources with respect to an explicit treatment of the 5f shell, especially with respect to AE calculations. However, the range of applicability is smaller than for the lanthanide 4f-in-core PPs and, as for these, it has to checked carefully if the state/configuration of interest corresponds to the f occupancy modelled by the PP. We note that f-in-core PPs also allow to calculate energy differences between states/configurations with different f occupation number, e.g. by using the experimental or calculated energy differences between the lowest atomic states/levels with the corresponding f occupations as a correction for the corresponding atomic energy-difference evaluated with f-in-core PPs. Although this procedure is quite rough, it turns out to be quite successful in practise as will be demonstrated below.

The f-in-core PPs rely on scalar-relativistic Wood-Boring reference data. Due to the severe approximation to include the f shell in the core it makes little sense to account explicitly for spin-orbit coupling in the valence space. However, static core-polarization and core-valence correlation turned out to be important [52] and thus the f-in-core PPs are usually supplemented by CPPs.

f-in-valence Pseudopotentials

If the f shell of a lanthanide or actinide atom is treated explicitly in the valence space and an accuracy of better than 0.1 eV is seeked also for energy differences between configurations with differing f occupation, one needs to use a small-core definition (SPP), i.e. include all orbitals with $n \geq 4$ and $n \geq 5$ in the valence space for lanthanides and actinides, respectively. The right part of Fig. 2 implies that PP errors for this choice of the core may be below 0.005 eV for energy differences between configurational averages. However, the existing sets of f-in-valence PPs are based on scalar-relativistic WB reference data [40] for typically 10–20 LS states with a target adjustment accuracy of 0.1 eV or better [21, 24] and thus do not come close in accuracy to the limits arising from the frozen-core approximation. They have been supplemented with SO terms to be used in first order perturbation theory for the valence orbitals as well as valence basis sets of polarized double- to quadruple-zeta quality [53, 54, 55, 56].

Higher accuracy than with WB PPs was achieved for main group and transition metals with PPs derived from fully-relativistic reference data [25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. However, except for U, such new MCDHF/DC+B-

TABLE 2. Mean absolute errors in Ln-X bond distances (Å) of the lanthanide trihalides LnX_3 with respect to the recommended values provided by Kovacs and Konings (KK) [63] and Hargittai (H) [62].

	LnF_3		**$LnCl_3$**		**$LnBr_3$**		**LnI_3**	
	KK	**H**	**KK**	**H**	**KK**	**H**	**KK**	**H**
AE DKH2, PBE0*	0.016	0.017	0.018	0.021	0.017	0.022	0.023	0.024
LPP, PBE0†	0.021	0.013	0.036	0.006	0.039	0.006	0.062	0.019
LPP+CPP, PBE0**	0.006	0.028	0.017	0.023	0.013	0.024	0.027	0.016
SPP, PBE0‡	0.011	0.023	0.012	0.029	0.017	0.019	0.041	0.017
MP, CASPT2§	0.035	0.007	0.042	0.007	0.055	0.019	0.079	0.036

* relativistic Douglas-Kroll-Hess all-electron study [61]; basis sets: Ln [18s12p9d3f], F, Cl, Br, I TZVP.

† pseudopotential study [60]; Ln 4f-in-core PP, 5s5p5d6s valence space; F, Cl, Br, I nsnp (n=2,3,4,5) valence space; basis sets: Ln [6s5p4d3f], F, Cl, Br, I [3s3p2d].

** as LPP, PBE0, but with effective core-polarization potentials on Ln and F, Cl, Br, I added.

‡ mixed pseudopotential and all-electron study [61]; Ln 4f-in-valence PP, 4s4p4d4f5s5p5d6s valence space; F, Cl, Br, I nonrelativistic all-electron treatment; basis sets: Ln [10s8p5d4f3g], F, Cl, Br, I TZVP.

§ model core potential study [65]; Ln 4f5s5p5d6s valence space; F, Cl, Br, I nsnp (n=2,3,4,5) valence space; basis sets: Ln [4s4p3d3f], F, Cl [2s2p1d], Br, I [3s3p2d].

based PPs have not been adjusted for f elements yet. The case studies for U prove that a significantly higher accuracy can be achieved with this type of PPs, and effects beyond the DC Hamiltonian such as the Breit interaction or even finite nucleus effects can be efficiently folded into the PP [2, 57, 58]. Thus results going beyond the accuracy of those from calculations applying e.g. the Douglas-Kroll-Hess Hamiltonian can be obtained in valence-only calculations [58]. The generation of such highly accurate PPs for all lanthanides and actinides is a task for the near future. In case of the U MCDHF/DC+B-based PP the reference data for the adjustment of the parameters up to f symmetry comprised 30190 J levels arising from 100 configurations of the neutral U atom to the U^{7+} ion. The valence energies of the configurations are described with a root mean square error (r.m.s.e.) of 16 cm^{-1}, the individual J levels with one of 306 cm^{-1}; the corresponding mean absolute errors (m.a.e.) are 12 cm^{-1} and 197 cm^{-1}, respectively [57, 58].

In addition to the better performance in terms of energy differences, one can also observe for the MCDHF/DC+B SPP (Fig. 3 right) a better agreement of the radial densities of the valence shells with corresponding results of AE MCDHF/DC calculations than for the WB SPP (Fig. 3 left). In the latter case the variational two-component treatment was restricted to the 5f, 6d and 7s shells, freezing the 5s, 5p, 5d, 6s and 6p shells in their scalar-relativistic shape, whereas in the former case all explicitly treated orbitals were variationally treated including the SO terms.

RESULTS

In the following selected results from recent calibration studies of f-in-core and f-in-valence lanthanide and actinide PPs will be briefly surveyed. For details the reader is referred to the original articles.

TABLE 3. Mean absolute errors in atomization energies (eV) of lanthanide trihalides LnX_3 with respect to the values provided by Myers (M) [64] without and with (+SO) spin-orbit corrections taken from experimental values for the free halogen atoms.

	LnF_3		**$LnCl_3$**		**$LnBr_3$**		**LnI_3**	
	M	**+SO**	**M**	**+SO**	**M**	**+SO**	**M**	**+SO**
AE DKH2, PBE0*	0.45	0.47	0.49	0.57	0.25	0.59	0.92	0.30
PP, PBE0†	0.66	0.62	0.40	0.31	0.74	0.36	1.05	0.28
PP+CPP, PBE0**	0.65	0.61	0.44	0.35	0.84	0.46	1.33	0.47

* relativistic Douglas-Kroll-Hess all-electron study [61]; basis sets: Ln [18s12p9d3f], F, Cl, Br, I TZVP.

† pseudopotential study [60]; Ln 4f-in-core PP, 5s5p5d6s valence space; F, Cl, Br, I nsnp (n=2,3,4,5) valence space; basis sets: Ln [6s5p4d3f], F, Cl, Br, I [3s3p2d].

** as LPP, PBE0, but with effective core-polarization potentials on Ln and F, Cl, Br, I added.

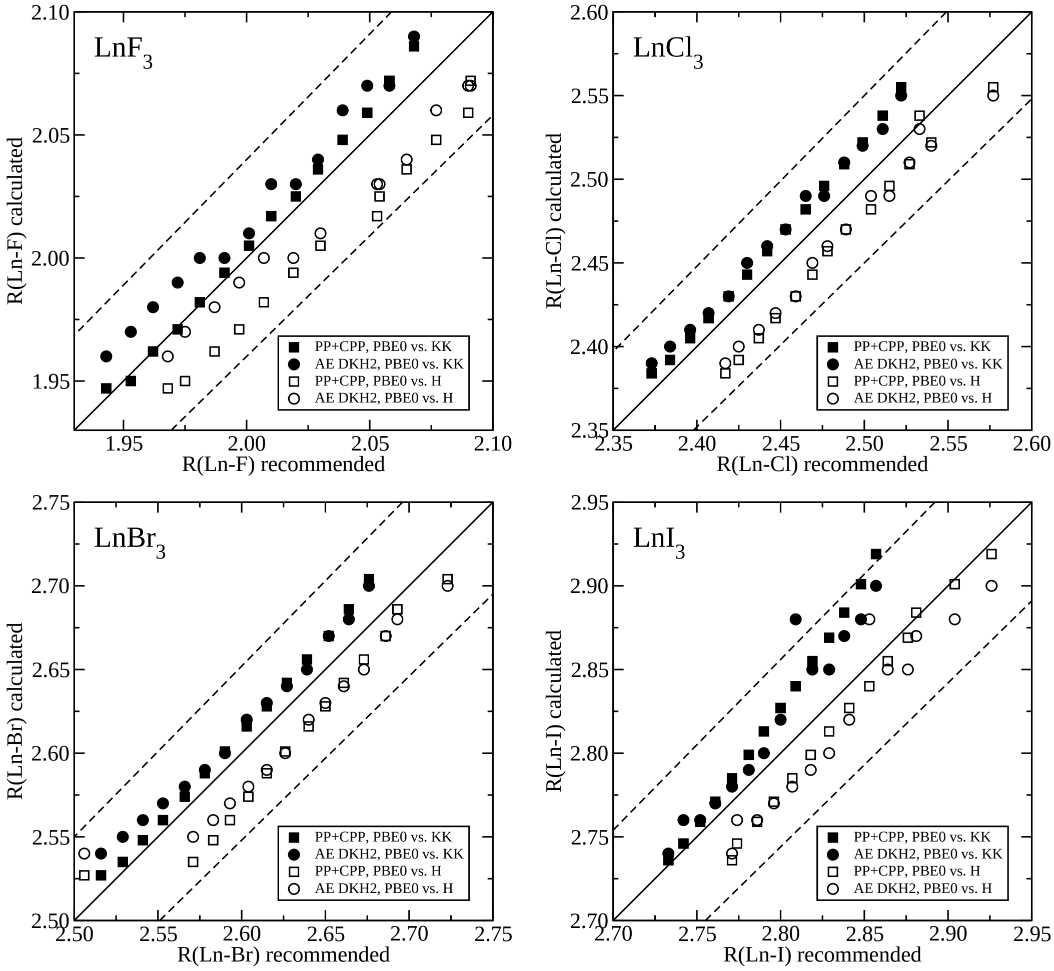

FIGURE 4. Ln-X bond distances (Å) of lanthanide halides LnX_3 (Ln = Ce–Lu, X = F, Cl, Br, I). Values from PBE0 density functional AE DKH2 [61] and PP+CPP [60] calculations are compared to values recommended by Kovacs and Konings (KK) [63] and Hargittai (H) [62]. The dashed lines denote deviations of ±2%

f-in-core Pseudopotentials

The 4f-in-core LPP (large-core PP) approach for lanthanides was tested for the lanthanide trihalides LnX_3 (Ln=La-Lu, X=F,Cl,Br,I) in the framework of density functional theory (hybrid functionals PBE0, B3LYP; gradient corrected functionals PBE, B-LYP, B-P) as well as wavefunction-based correlation treatments (CCSD(T), MP2, SCS-MP2) [59, 60]. Here we only report PBE0 results, since corresponding AE calculations applying the second-order Douglas-Kroll-Hess (DKH2) Hamiltonian have recently been published [61]. Figs. 4 and 5 show a comparison of the calculated Ln-X bond distances and atomization energies, respectively, with recommended experimental/estimated reference values [62, 63, 64]. The corresponding m.a.e. are listed in tables 2 and 3. The LPP results have been corrected by experimental atomic energy differences to the lanthanide atomic ground state, if the molecular and atomic 4f occupation differ [20]. In table 2 we also include values for results published recently for 4f-in-valence SPP (small-core PP) PBE0 [61] and MP CASPT2 calculations [65].

It is obvious that the 4f-in-core LPP+CPP PBE0 approach works as well as the more costly AE DKH2 or SPP PBE0 treatments, yielding very similar m.a.e. values for all series. Difficulties of the calibration become especially apparent from Fig. 4. Two sets of recommended/experimental Ln-X bond lengths exist [62, 63], which are typically quite consistently over- or underestimated by both the AE DKH and LPP+CPP PBE0 calculations. The deviations between these two recommended sets are larger than between the two theoretical approaches.

The computational effort of the LPP+CPP PBE0 approach is similar for all 60 molecules studied here, e.g. the

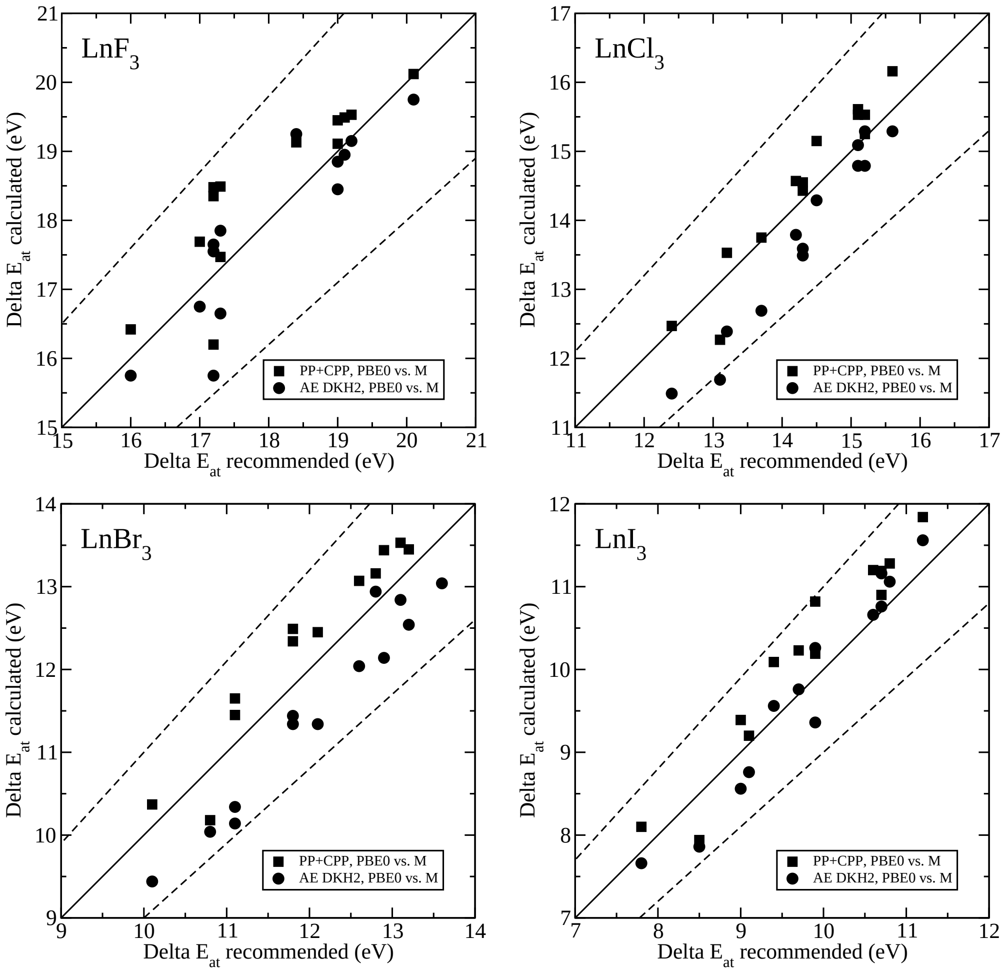

FIGURE 5. Atomization energies (eV) of lanthanide halides LnX_3 (Ln = Ce–Lu, X = F, Cl, Br, I). Values from PBE0 density functional AE DKH2 [61] and PP+CPP [60] calculations are compared to experimental and estimated values recommended by Myers (M) [64]. The dashed lines denote deviations of $\pm$10%.

integral evaluation in C_1 symmetry amounts to less than 30 CPU seconds a Pentium IV 2.4 GHz personal computer. We note that in the LPP treatment the lanthanide and halogen atoms were treated as 11- and 7-valence electron systems, respectively, and effective CPPs were used on all nuclei. Without these core-valence correlation and static core polarization is not accounted for and somewhat larger errors arise. The corresponding results are parallel those obtained recently at the CASPT2 level with the MP approach. The SPP PBE0 results [61] are most likely affected by the neglect of relativistic effects arising from the halogen atoms, since SPPs were used for the lanthanides, whereas apparently a nonrelativitic Hamiltonian contribution was spplied for the halides. This might explain the increasing differences between AE DKH and SPP PBE0 results when going from lighter to heavier halides.

One may wonder if a 5f-in-core approach leads to reasonable results, since the actinide 5f shells are radially more extended than the lanthanide 4f shells. In fact it does as long as the f occupation number of the state of interest is equal or slightly larger than the integral f occupation modeled by the LPP core. An example are complexes of actinide An^{3+} ions with water [66] or macrocyclic ligands such as texaphyrin [67], which are found to be as stable as their lanthanide counterparts [68]. As illustration we show An-O bond distances and An^{3+}-H_2O binding energies for actinide monohydrate ions in Fig. 6 [49]. It is obvious that the 5f-in-core LPP approach is able to reproduce trends obtained with the more rigorous 5f-in-valence SPP approach as well as with AE DHF/DC calculations [69]. One should note however, that the latter suffer from basis set superposition errors due to the small double-zeta basis sets used for the water molecule. It is noteworthy that the 5f-in-core approach is also able to describe the d/f-π metal-ring bonding in actinocenes reasonably [70].

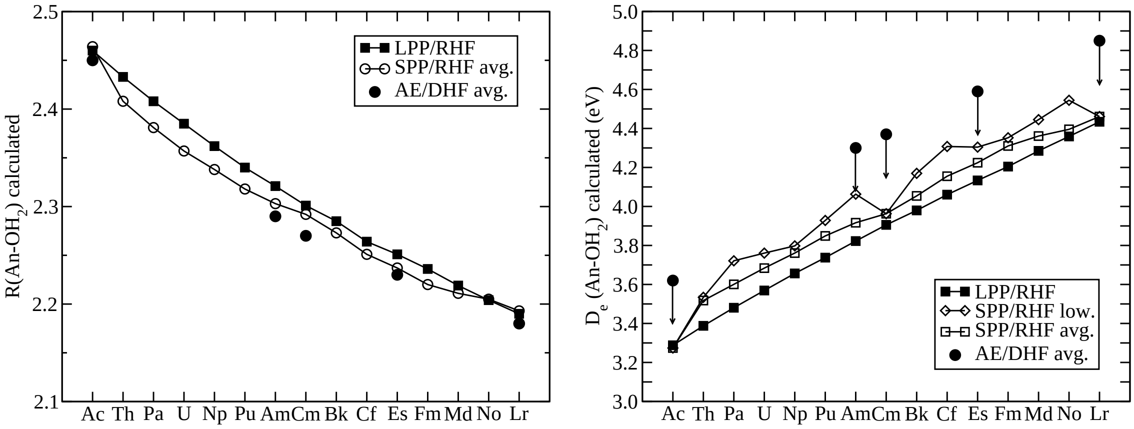

FIGURE 6. Actinide-oxygen distances (Å) and An^{3+}-H_2O binding energies (eV) from 4f-in-core (large-core, LPP) and 4f-in-valence (small-core, SPP) pseudopotential restricted Hartree-Fock (RHF) calculations [49] in comparison to all-electron Dirac-Hartree-Fock (AE DHF) results [69]. The arrows denote estimates of a correction of the basis set superposition error in the AE results taken from the corresponding lanthanide systems. Calculations for the lowest electronic state are denoted by *low.*, whereas those for an average of states by *avg.*.

f-in-valence Pseudopotentials

Energy-consistent f-in-valence WB SPPs supplemented by valence spin-orbit terms for usage in perturbation theory and corresponding optimized valence basis sets are available for lanthanides [21, 53, 54] and actinides [24, 55, 56]. In many studies atomic and molecular studies excellent results were obtained [36, 37], cf. e.g. applications on molecules such as UF_6 [71, 72], or solids such as UO_2 [73].

However, the situation is not completely satisfactory and the limitations arising from the scalar-relativistic WB reference data as well as the limited accuracy of adjustment of ≈0.1 eV sometimes become obvious. A case were a calibration for the whole lanthanide series is feasible are the atomic ionization potentials, cf. table 4. At the Hartree-Fock level the m.a.e. for IP_1 and IP_2 are well below 0.1 eV, however those of IP_3 and IP_4 are ≈0.1 eV and ≈0.3 eV, respectively. One should note that e.g. IP_2, IP_3, IP_4 and the f to p excitation listed in table 4 were not in the reference data set for the PP adjustment. The overall accuracy at the PP level still is slightly better than the one of AE

TABLE 4. Mean absolute errors (eV) in Hartree-Fock ionization potentials (IP) and excitation energies (EX) for DKH2 AE and PP calculations. The reference values were DKH2 AE results obtained with large basis sets (limit). The deviations of corresponding DKH3 results are also listed [60].

	AE DKH2 SARC*	**AE DKH2 SARG**†	**PP VQZ****	**AE DKH3 limit**‡
IP_1	0.008	0.003	0.036	0.004
IP_2	0.039	0.014	0.065	0.005
IP_3	0.153	0.030	0.115	0.008
IP_4	0.667	0.096	0.318	0.010
EX f→d	0.199	0.037	0.100	0.008
EX f→p	0.121	0.024	0.102	0.010

* relativistic all-electron study with segmented contracted Ln [18s12p9d3f] basis sets from Pantazis and Neese [61].
† relativistic all-electron study with segmented contracted Ln [18s12p9d3f] basis sets [60].
** small-core pseudopotential study with segmented contracted Ln [10s8p5d4f] basis sets; for EX2 one diffuse p function was added [60].
‡ differences between 2nd and 3rd order DKH results obtained with Ln (34s28p22d16f) uncontracted basis sets[60].

TABLE 5. Term energies (cm^{-1}) of J levels of U^{4+} $5f^2$ from intermediate Hamiltonian Fock-space coupled cluster (IHFSCC) pseudopotential (DC+B PP)[57] and all-electron (AE DCB) [76] calculations in comparison to experimental data (exp.). The mean absolute error (m.a.e.) refers to experimental data, the mean absolute deviation (m.a.d.) to the all-electron results.

J	DC+B PP IHFSCC*	DC+B PP IHFSCC†	AE DCB XIHFSCC**	exp.
4	0	0	0	0
2	3959	4233	4202	4161
5	5902	5890	6070	6137
3	8612	8825	8974	8984
4	9196	9264	9404	9434
6	11178	11144	11420	11514
2	15998	*16601*	16554	16465
4	16181	*16221*	16630	16656
0	17025	17960	17837	17128
1	19529	20420	20441	19819
6	22594	22441	22534	22276
2	24042	24799	24991	24653
0	43783	45329	45611	43614
m.a.e.	318	420	357	0
m.a.d.	567	162	0	357

* SPP, basis set: (14s13p10d8f6g)/[6s6p5d4f3g], no frozen orbitals.
† SPP, basis set: (16s15p12d10f8g7h7i), no frozen orbitals.
** basis set: (37s32p24d21f12g10h9i).

DKH calculations using recently published small basis sets [61]. However, compared to results obtained with properly optimized basis sets of identical size, leading also to lower total energies [60], the PPs clearly performs worse.

Despite these limitation the first to fourth atomic ionization potentials have been studied with large-scale correlation methods such as SO-corrected MRCI or CCSD(T) for single reference cases using standard contracted as well as large uncontracted basis sets [74, 75]. The main difficulty aside from the accuracy of the PPs is illustrated by Fig. 1. In order to converge with respect to the basis set to a deviation from the experimental values of less than ≈ 0.1 eV, i.e. about the accuracy of the applied La and Ce PPs, one has to include beyond i functions in the basis set when energy differences between states with different d or f occupation number are calculated. Thus, in standard molecular calculations the accurate treatment of electron correlation seems to be a more severe problem than the description of relativistic contributions or the accuracy of the applied PPs.

The new MCDHF/DC+B-adjusted small-core PP for uranium was tested atomic calculations for U^{5+} and U^{4+} [57]. At the Fock-space intermediate Hamiltonian coupled cluster (IHFSCC) level applying large basis sets the U^{5+} $5f^1$ SO splitting at the PP level agrees within a few wavenumbers with both the best AE DHF IHFSCC/DCB result of Infante

TABLE 6. Bond lengths R_e (Å), vibrational constants ω_e (cm^{-1}) and adiabatic term energies T_e (eV) for the five lowest states of UH from MCDHF/DC+B PP and AE DKH calculations with spin-orbit coupling (state interaction approach) [58].

		R_e		ω_e		T_e		LS(%)*
No.	Ω	PP	AE	PP	AE	PP	AE	PP;AE
1	4.5	2.025	2.021	1505	1511	0.000	0.000	$^4I(78;76)+^4H(19;19)+^4\Gamma(3;3)$
2	3.5	2.026	2.021	1499	1504	0.025	0.020	$^4H(58;57)+^4\Gamma(31;30)+^4\Phi(9;9)$
3	2.5	2.024	2.020	1496	1502	0.042	0.039	$^4\Gamma(42;41)+^4\Phi(37;37)+^4\Delta(17;16)+^4\Pi(3;3)$
4	1.5	2.025	2.020	1494	1502	0.054	0.053	$^4\Delta(40;39)+^4\Phi(30;30)+^4\Pi(24;24)+^4\Sigma(6;6)$
5	0.5	2.027	2.021	1494	1500	0.067	0.066	$^4\Pi(49;49)+^4\Sigma(30;30)+^4\Delta(21;21)$

* only contributions $\geq$ 3% are listed

et al. [76] as well as with experimental data. The corresponding results for U^{4+} $5f^2$ listed in table 5 reveal that the PP calculations are competitive in accuracy with the AE studies when compared to experiment, i.e. m.a.e. of 420 and 357 cm^{-1} are found at the PP and AE level, respectively. The m.a.d. between PP and AE values is only 162 cm^{-1}.

The low-lying electronic states of uranium monohydride were studied both with the WB [77] and the MCDHF/DC+B [58] SPP. The lowest 5 Ω levels from the latter work are compared to AE DKH results from the same work in table 6. It is seen that there is an excellent agreement between PP and AE results. For the next higher states not listed here deviations in the term energies of a few 0.01 eV occur which are mainly due to the neglect of the Breit interaction in the DKH approach and to a lesser extent due to remaining adjustment errors of the PP.

CONCLUSION

The present status of the energy-consistent ab initio pseudopotential approach for lanthanides and actinides was reviewed. Two sets of parametrizations, one treating the f shell explicitly in the valence space, one attributing it to the pseudopotential core, are presently available with corresponding valence basis sets, cf. `http://www.theochem.uni-stuttgart.de`. Whereas the work on f-in-core pseudopotentials is essentially completed, more accurate parametrizations should be derived for the f-in-valence pseudopotential approach. First results for uranium look very promising and let us expect that via an systematic adjustment to AE MCDHF/DC+B finite nucleus reference data pseudopotentials can be generated, which include effects beyond those usually accounted for in standard approximate relativistic all-electron calculations.

ACKNOWLEDGMENTS

The development of energy-consistent pseudopotentials was financially supported by the German Research Foundation (DFG). The author is grateful to Xiaoyan Cao, Michael Hülsen, Anna Moritz/Weigand, Jonas Wiebke, and Jun Yang for their collaboration.

REFERENCES

1. M. Dolg, “Relativistic effective core potentials”, in *Relativistic Electronic Structure Theory, Part 1: Fundamentals*, series *Theoretical and Computational Chemistry*, vol. 11, ch. 14, edited by P. Schwerdtfeger, Elsevier, Amsterdam (2002), pp. 793–862.
2. X. Cao, and M. Dolg, “Relativistic pseudopotentials,” in *Relativistic methods for chemists*, series *Challenges and Advances in Computational Chemistry and Physics*, vol. 10, edited by M. Barysz, and Y. Ishikawa, Springer, New York, 2009, in press.
3. L. Seijo, and Z. Barandiarán, “The ab initio model potential method: a common strategy for effective core potential and embedded cluster calculations”, in *Computional chemistry: Reviews of current trends*, vol. 4, edited by J. Leszczynski, J., World Scientific, Singapore, 1999, pp. 55–152.
4. P. J. Hay, and W. R. Wadt, *J. Chem. Phys.* **8**2, 270–282 (1985).
5. W. R. Wadt, and P. J. Hay, *J. Chem. Phys.* **8**2, 284–298 (1985).
6. P. J. Hay, and W. R. Wadt, *J. Chem. Phys.* **8**2, 299–310 (1985).
7. W. J. Stevens, H. Basch, and M. Krauss, *J. Chem. Phys.* **8**1, 6026–6033 (1984).
8. W. J. Stevens, M. Krauss, H. Basch, and P. J. Jasien, *Can. J. Chem.* **7**0, 612–630 (1992).
9. T. R. Cundari, and W. J. Stevens, *J. Chem. Phys.* **9**8, 5555–5565 (1993).
10. W. C. Ermler, R. B. Ross, and P. A. Christiansen, *Adv. Quantum. Chem.* **1**9, 139–182 (1988).
11. Y. S. Lee, W. C. Ermler, and K. S. Pitzer, *J. Chem. Phys.* **6**7, 5861–5876 (1977).
12. P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, *J. Chem. Phys.* **7**1, 4445–4450 (1979).
13. L. F. Pacios, and P. A. Christiansen, *J. Chem. Phys.* **8**2, 2664–2671 (1985).
14. M. M. Hurley, L. F. Pacios, P. A. Christiansen, R. B. Ross, and W. C. Ermler, *J. Chem. Phys.* **8**4, 6840–6853 (1986).
15. L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, *J. Chem. Phys.* **8**7, 2812–2824 (1987).
16. R. B. Ross, J. M. Powers, T. Atashroo, W. C. Ermler, L. A. LaJohn, and P. A. Christiansen, *J. Chem. Phys.* **9**3, 6654–6670 (1990).
17. R. B. Ross, S. Gayen, and W. C. Ermler, *J. Chem. Phys.* **1**00, 8145–8155 (1994).
18. W. C. Ermler, R. B. Ross, and P. A. Christiansen, *Int. J. Quant. Chem.* **4**0, 829–846 (1991).
19. M. Dolg, U. Wedig, H. Stoll, and H. Preuß, *J. Chem. Phys.* **86**, 866–872 (1987).
20. M. Dolg, H. Stoll, A. Savin, and H. Preuß, *Theor. Chim. Acta* **75**, 173–194, (1989).
21. M. Dolg, H. Stoll, and H. Preuß, *J. Chem. Phys.* **90**, 1730–1734, (1989).

22. D. Andrae, U. Häußermann, M. Dolg, H. Stoll, and H. Preuß, *Theor. Chim. Acta* **77**, 123–141 (1990).
23. A. Bergner, M. Dolg, W. Küchle, H. Stoll, and H. Preuß, *Mol. Phys.* **80**, 1431–1441 (1993).
24. W. Küchle, M. Dolg, H. Stoll, and H. Preuß, *J. Chem. Phys.* **100**, 7535–7542, (1994).
25. M. Dolg, H. Stoll, H. Preuß, and R. M. Pitzer, *J. Phys. Chem.* **9**7, 5852–5859 (1993).
26. B. Metz, M. Schweizer, H. Stoll, M. Dolg, and W. Liu, *Theor. Chem. Acc.* **1**04, 22–28 (2000).
27. B. Metz, H. Stoll, and M. Dolg, *J. Chem. Phys.* **1**13, 2563–2569 (2000).
28. H. Stoll, B. Metz, and M. Dolg, *J. Comput. Chem.* **2**3, 767–778 (2002).
29. K. A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, *J. Chem. Phys.* **1**19, 11113–11123 (2003).
30. M. Dolg, *Theor. Chem. Acc.* **1**14, 297–304 (2005).
31. D. Figgen, G. Rauhut, M. Dolg, and H. Stoll, *Chem. Phys.* **3**11, 227–244 (2005).
32. I. S. Lim, P. Schwerdtfeger, B. Metz, and H. Stoll, *J. Chem. Phys.* **1**22, 104103-1–12 (2005).
33. I. S. Lim, P. Schwerdtfeger, and H. Stoll, *J. Chem. Phys.* **1**24, 034107-1–9 (2006).
34. D. Figgen, K. A. Peterson, M. Dolg, and H. Stoll, *J. Chem. Phys.* **1**30, 164108-1–12 (2009).
35. M. Dolg, and H. Stoll, “Electronic structure calculations for molecules containing lanthanide atoms”, in *Handbook of Chemistry and Physics of Rare Earths*, vol. 22, ch. 152, edited by K. A. Gschneidner, Jr., L. Eyring, Elsevier, Amsterdam (1996), pp. 607–729.
36. M. Dolg, and X. Cao, “The relativistic energy-consistent ab initio pseudopotential approach and its application to lanthanide and actinide compounds”, in *Recent Advances in Computational Chemistry*, vol. 6, edited by K. Hirao, and Y. Ishikawa, World Scientific, New Jersey (2004), pp. 1–35.
37. X. Cao, and M. Dolg, *Coord. Chem. Rev.* **250**, 900–912 (2006).
38. M. Dolg, and X. Cao, “Lanthanides and actinides: computational methods,” in *Computational Inorganic and Bioinorganic Chemistry*, edited by E. I. Solomon, R. B. King, and R. A. Scott, Wiley, Hoboken (2009) in press.
39. R. W. Field, *Ber. Bunsenges. Phys. Chem.* **8**6, 771–779 (1982).
40. C. Froese-Fischer, *The Hartree-Fock Method for Atoms*, Wiley, New York (1977). Dolg, M.: modifications for PP calculations/optimizations and WB calculations.
41. K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia, E. P. Plummer, *Comput. Phys. Commun.* **5**5, 425–456 (1989). Dolg, M., Metz, B.: modifications for PP calculations/optimizations.
42. C. E. Myers, L. J. Norman and L. M. Loew, *Inorg. Chem.* **1**7 1581–1584 (1978).
43. M. Dolg, H. Stoll, and H. Preuß, *J. Molec. Struct.* **2**31, 243–255 (1991).
44. M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **8**5, 441-450 (1993).
45. J. Yang, and M. Dolg, *Theor. Chem. Acc.* **113**, 212–224 (2005).
46. M. Hülsen, A. Weigand, and M. Dolg, *Theor. Chem. Acc.* **1**22 (2009) 23–29.
47. M. Hülsen, to be published (2009).
48. J. Yang, and M. Dolg, *J. Sol. State Chem.* **180**, 2763–2774 (2007).
49. A. Moritz, X. Cao, and M. Dolg, *Theor. Chem. Acc.* **117**, 473–481 (2007).
50. A. Moritz, X. Cao, and M. Dolg, *Theor. Chem. Acc.* **118**, 2763–2774 (2007).
51. A. Moritz, and M. Dolg, *Theor. Chem. Acc.* **121**, 297–306 (2008).
52. Y. Wang, and M. Dolg, *Theor. Chem. Acc.* **1**00, 124-133 (1998).
53. X. Cao, and M. Dolg, *J. Chem. Phys.* **115**, 7348–7355 (2001).
54. X. Cao, and M. Dolg, *J. Mol. Struct.* **581**, 139–147 (2002).
55. X. Cao, and M. Dolg, *J. Chem. Phys.* **118**, 487–496 (2003).
56. X. Cao, and M. Dolg, *J. Mol. Struct.* **673**, 203–209 (2004).
57. A. Weigand, X. Cao, V. Vallet, J.-P. Flament, M. Dolg, *J. Phys. Chem. A* (2009) in press; DOI 10.1021/jp9026933.
58. X. Cao, and M. Dolg, *J. Phys. Chem. A* (2009) in press; DOI 10.1021/jp9044594.
59. A. Weigand, X. Cao, J. Yang, and M. Dolg, *Theor. Chem. Acc.* (2009) in press; DOI 10.1007/s00214-009-0584-2.
60. M. Dolg, to be published.
61. D. A. Pantazis, and F. Neese, *J. Chem. Theor. Comput.* (2009) in press; DOI 10.1021/ct900090f.
62. M. Hargittai, *Coord. Chem. Rev.* **91**, 35–88 (1988).
63. A. Kovacs, and R. J. M. Konings, *J. Phys. Chem. Ref. Data* **33**, 377–404 (2004).
64. C. E. Myers, *Inorg. Chem.* **1**4 199–201 (1977).
65. S. Tsukamoto, H. Mori, H. Tatewaki, and E. Miyoshi, *Chem. Phys. Lett.* **474**, 28–32 (2009).
66. J. Wiebke, A. Moritz, X. Cao, M. Dolg, *Phys. Chem. Chem. Phys.* **9**, 459–465 (2007).
67. X. Cao, Q. Li, A. Moritz, Z. Xie, M. Dolg, X. Chen, and W. Fang, *Inorg. Chem.* **45**, 3444–3451 (2006).
68. X. Cao, and M. Dolg, *Mol. Phys.* **101**, 2427–2435 (2004).
69. Y. Mochizuki, and H. Tatewaki, *Chem. Phys.* **2**73, 135–148 (2001).
70. A. Moritz, and M. Dolg, *Chem. Phys.* **327**, 48–54 (2007).
71. E. R. Batista, R. L. Martin, P. J. Hay, J. E. Peralta, G. E. Scuseria, *J. Chem. Phys.* **1**21, 2144-2150 (2004).
72. E. R. Batista, R. L. Martin, P. J. Hay, *J. Chem. Phys.* **1**21, 11104-11111 (2004).
73. K. N. Kudin, G. E. Scuseria, R. L. Martin, *Phys. Rev. Lett.* **2**6, 266402-1–4 (2002).
74. X. Cao, M. Dolg, *Chem. Phys. Lett.* **3**49, 489–495 (2001).
75. X. Cao, M. Dolg, *Mol. Phys.* **1**01, 961–969 (2003).
76. I. Infante, E. Eliav, M. J. Vilkas, Y. Ishikawa, U. Kaldor, L. Visscher, *J. Chem. Phys.* **127**, 124308-1–12 (2007).
77. X. Cao, A. Moritz, and M. Dolg, *Chem. Phys.* **343**, 250–257 (2008).