

Introduction

Gaussian (14s13p10d8f6g)/[66p5d4f3g] atomic natural orbital valence basis sets have been derived for relativistic energy-consistent small-core lanthanide and actinide pseudopotentials of the Stuttgart-Bonn variety. The existing set of lanthanide pseudopotentials has been supplemented by corresponding potentials for lanthanum and lutetium in order to arrive at a set analogous to the one available for the actinides. MCSCF and subsequent multi-reference ACPF calculations were carried out for the first to fourth ionization potentials of all elements, both for the derived standard basis sets as well as for large uncontracted basis sets containing up to f-functions. In the latter case extrapolation techniques are used to estimate the basis set limit. Molecular calibration studies using the CCSD(T) approach are reported for the monohydrides, monoxides and monofluorides of lanthanum and lutetium as well as thorium monoxide. The electronic ground state configurations for lanthanum and lutetium dimers are also investigated using the CCSD(T) and MRCI methods.

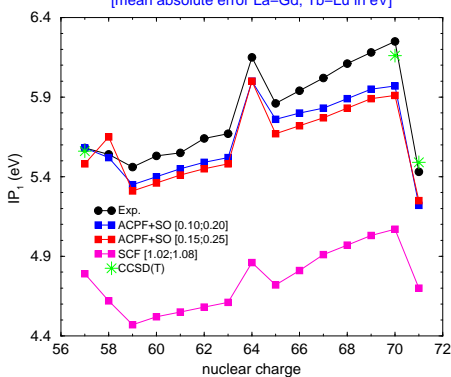
Method

- Small-core relativistic energy-consistent PP
- Generalized contracted ANO basis sets
 Ln(An): (14s13p10d8f6g)/[66p5d4f3g]
- Extrapolation (1/I³) to basis set limit using uncontracted basis sets
 Ln: (16s15p12d10f8g8h8i)
 An: (14s13p10d8f6g6h6i)

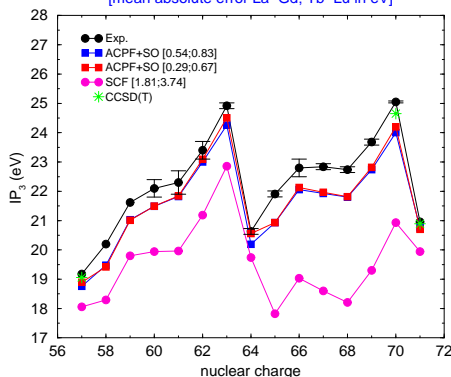
Results

- Mean absolute errors for standard basis sets (basis set limit): Ln IP₁ and IP₂ 0.2 eV, IP₃ and IP₄ 0.6 eV (0.3 eV); An IP₁ 0.2 eV.
- The experimental IP₃ for Gd appears to be too low by almost 1 eV and should be remeasured.
- The ground states for La₂ and Lu₂ are most likely ¹Σ_g⁺(σ_g²π_u⁴) and ³Σ_g⁻(4f¹⁴4f¹⁴σ_g²σ_u²π_u²), respectively.

first ionization potential La – Lu
 [mean absolute error La–Gd; Tb–Lu in eV]



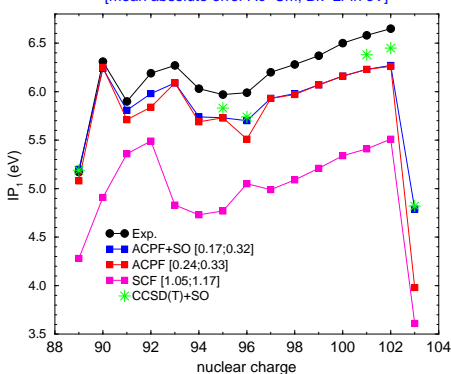
third ionization potential La – Lu
 [mean absolute error La–Gd; Tb–Lu in eV]



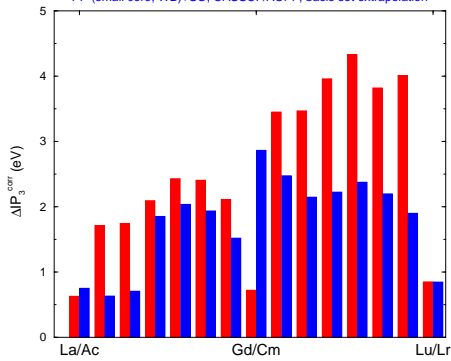
ACPF results for the third ionization potentials (IP₃ in eV)

Ln	r	h	f	extr.	Exp.
La	18.56	18.69	18.76	18.78	19.18
Ce	18.49	19.48	19.76	19.88	20.20
Pr	20.06	20.99	21.26	21.38	21.54
Nd	20.58	21.46	21.71	21.83	21.98
Pu	20.97	21.80	22.05	22.15	22.30
Sm	22.18	23.02	23.25	23.36	23.44
Eu	23.42	24.13	24.34	24.45	24.58
Gd	20.36	20.50	20.58	20.60	20.65
Tb	19.96	20.85	21.13	21.26	21.42
Dy	21.18	21.99	22.25	22.37	22.53
Er	21.17	21.91	22.15	22.27	22.41
Tm	21.09	21.77	22.01	22.13	22.28
Yb	22.12	22.72	22.94	23.05	23.18
Lu	23.43	23.99	24.16	24.27	24.37
m.a.e. La-Gd	1.22	0.54	0.33	0.24	0.14
m.a.e. Tb-Lu	1.47	0.85	0.65	0.55	0.42

first ionization potential Ac – Lr
 [mean absolute error Ac–Cm; Bk–Lr in eV]



Differential correlation contributions IP₃ Ln, An
 PP (small core, WB)+SO, CASSCF/ACPF, basis set extrapolation



Selected CCSD(T) results for IP₃ and IP₄ (in eV)

Ln	IP ₃	r	h	f	extr.	Exp.
La	IP ₃	18.81	18.98	19.06	19.09	19.14
La	IP ₄	49.68	49.91	49.99	50.02	50.07
Ce	IP ₃	34.93	36.11	36.42	36.53	36.74
Eu	IP ₃	23.79	24.55	24.78	24.89	25.02
Gd	IP ₃	43.55	44.34	44.59	44.71	44.86
Yb	IP ₃	23.95	24.58	24.76	24.88	25.00
Lu	IP ₃	20.78	20.87	20.90	20.92	20.96
Lu	IP ₄	44.26	44.37	45.07	45.21	45.33
m.a.e.*		0.84	0.31	0.17	0.10	0.06

* except for Gd IP₃

Spectroscopic constants for LaX (X=H, O, F)

molecule	method	R _e (Å)	D _e (eV)	ω _e (cm ⁻¹)
LaH ⁺ Σ ⁺	CCSD(T)	2.027/2.028	2.88/2.89	1447/1447
	B3LYP	2.006	2.91	1461
	Exp.	2.032		
LaO ⁺ Σ ⁺	CCSD(T)	1.841/1.843	8.13/8.12	807/806
	B3LYP	1.827	8.32	824
	Exp.	1.826	8.29	813
LaF ⁺ Σ ⁺	CCSD(T)	2.034/2.035	6.83/6.85	574/574
	B3LYP	2.024	6.86	576
	Exp.	2.027	6.90	570

The notation ... refers to results using a generalized/segmented contraction scheme. B3LYP results correspond to the segmented contraction scheme.

Spectroscopic constants for LuX (X=H, O, F)

molecule	method	R _e (Å)	D _e (eV)	ω _e (cm ⁻¹)
LuH ⁺ Σ ⁺	CCSD(T)	1.914/1.916	3.35/3.37	1507/1502
	B3LYP	1.901	3.16	1515
	Exp.	1.912	-3.47	ω = 1520
LuO ⁺ Σ ⁺	CCSD(T)	1.795/1.795	6.90/6.91	840/840
	B3LYP	1.793	6.79	846
	Exp.	1.790	7.04	842
LuF ⁺ Σ ⁺	CCSD(T)	1.923/1.923	7.51/7.54	604/605
	B3LYP	1.922	7.28	605
	Exp.	1.917	-5.94	612

The notation ... refers to results using a generalized/segmented contraction scheme. B3LYP results correspond to the segmented contraction scheme.

Spectroscopic constants for ThO

method	R _e (Å)	ω _e (cm ⁻¹)	D _e (D _e ⁺) (eV)
PP(WB,30), SCF	1.817/1.817	956/955	6.26/6.24
AIMP(CG,12), SCF	1.819	956	5.99
AE_DFR	1.874	957	7.61
RPCA/MRCI	1.891	892	8.48
EC-PP(WB,30), CCSD(T)	1.839/1.845	898/891	9.58/9.38
			(9.16/8.96)
Exp.	1.840	896	9.00(±0.09)
			8.87(±0.15)
			8.79(±0.13)

PP: pseudopotential; AE: all electron; AIMP: ab initio model potential; RPCA: reduced frozen-core approximation

Spectroscopic constants for La₂

state ^a	R _e (Å)	D _e (eV)	ω _e (cm ⁻¹)	Ref.
a ¹ Σ _g ⁺	2.635/2.659	0.81/1.26	245/228	CCSD/CCSD(T)
b ³ Σ _g ⁻	2.896/2.936	0.88/1.39	159/143	CCSD/CCSD(T)
c ¹ Σ _g ⁺	2.691/2.718	0.93/1.41	240/225	CCSD/CCSD(T)
d ³ Σ _g ⁻	3.078/3.108	1.34/1.62	111/111	CCSD/CCSD(T)
e ¹ Π _g	2.756/2.780	1.56/2.01	195/183	CCSD/CCSD(T)
f ³ Σ _g ⁻	2.673/2.694	1.89/2.34	202/188	CCSD/CCSD(T)
f ³ Σ _g ⁻	2.711/2.685	2.57/2.61	196/201	MRCI/MRCI-Q*
f ³ Σ _g ⁻	2.70±0.03	2.31(±0.13)	188(±13)	Est.
f ³ Σ _g ⁻	-2.80	2.52(±0.22)	236(±0.8)	Exp.

^a a₁, σ_g²σ_u²σ_g²σ_u²; b₁, σ_g²σ_u²σ_g²σ_u²σ_g²σ_u²; c₁, σ_g²σ_u²σ_g²σ_u²π_u²; d₁, σ_g²σ_u²σ_g²σ_u²π_u²π_u²; e₁, σ_g²σ_u²σ_g²σ_u²π_u²π_u²π_u²; f₁, σ_g²π_u²π_u²π_u²

* the number of reference CSFs: 174, the size of MRCI matrix after (before) contraction: 3.6·10⁷ (9.1·10⁷)

Estimated/calculated matrix effect: La₂ → Ar-La₂: Δω_e = 22 cm⁻¹

Spectroscopic constants for Lu₂

state ^a	R _e (Å)	D _e (eV)	ω _e (cm ⁻¹)	Ref.
a ¹ Σ _g ⁺	3.194/3.171	0.83/0.78	107/107	MRCI/MRCI-Q
a ³ Σ _g ⁻	3.168/3.150	0.90/0.82	111/110	MRCI/MRCI-Q
a ³ Σ _g ⁻	3.108/3.072	1.78/1.73	121/124	MRCI/MRCI-Q*
a ³ Σ _g ⁻	3.064/3.058	1.48/1.67	122/122	CCSD/CCSD(T)
a ³ Σ _g ⁻	3.07±0.03	1.40(±0.12)	123(±1)	Est.
a ³ Σ _g ⁻	1.43±0.24	121.6(±0.8)		Exp.

^a a₁, (4f¹⁴)σ_g²σ_u²π_u²

* the number of reference CSFs: 74, the size of MRCI matrix after (before) contraction: 1.2·10⁷ (3.3·10⁷)

Estimated/calculated matrix effect: Lu₂ → Ar-Lu₂: Δω_e = 3 cm⁻¹

References

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