Error-balanced basis sets for large-core ECPs for elements La–Lu

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- Supplementary Material -

All calculations were done with TURBOMOLE.[1] Basis sets were optimized in restricted open-shell Hartree–Fock (ROHF) calculations. Roothaan parameters for the different states are given in Table S1. Even-tempered reference basis sets for the valence shell are defined in Table S2, a 3f2g polarization set was taken from Reference 2 (Weigand, Yang, Cao, Dolg, WYCD). Table S3 lists ROHF energies of the different states (relative to the one that is most favourable for the late lanthanides) for the reference basis. Tables S4–S8 list the differences to these numbers for newly developed QZV, TZV and SV as well as for the bases from Reference 3 (Dolg, Stoll, Savin, Preuss, DSSP) and for WYCD bases. The remaining Tables contain results of molecular calculations at DFT (PBE0[4]) level. Structure data (distances, angles, lowest frequencies) for compounds with f^n occupation are shown in Table S9 for the large-core ECPs (lcecp-0) and the reference bases for Ln; for H, F and O decontracted cc-pV5Z[5] and for Cl cc-pV(5+d)Z bases[6] without the polarizing h function were employed. Further, in this Table the errors (differences to reference) for lcecp-0-QZVPP bases at Ln (other elements: def2-QZVPP bases) are shown as well as the differences of these to all-electron scalar relativistic X2C[7] with x2c-QZVPPall bases[8] used for all elements. Table S10 lists the errors for lcecp-0-QZVP, lcecp-0-TZVP and lcecp-0-SV(P) bases at Ln (corresponding def2-bases[9] for the other elements), as well as the errors of DSSP (def2-TZVP for the other elements). Tables S11–S14 are the analogues to Tables S9–S10 for large-core ECPs lcecp-1 and lcecp-2, and Table S15 samples related data for selected Hf compounds for comparison (for error assessing consistency with subsequent d elements). Table S16 contains energies for exchange reactions of type $Ln^A H_3 + Ln^B Cl_3 \rightarrow Ln^A Cl_3 + Ln^B H_3$, Ln^A, Ln^B=La–Lu obtained with lcecp-1 ECPs and reference bases, Tables S17–S21 contain the differences to these for lcecp-1-QZVPP, lcecp-1-QZVP, lcecp-1-TZVP, lcecp-1-SV(P) (with corresponding def2-bases for H, Cl) and DSSP with def2-TZVP bases for H, Cl. Table S22 lists the differences of lcecp-1-QZVPP and the all-electron scalar relativistic X2C treatment with x2c-QZVPPall bases. The lcecp-k-XVP/PP bases (k=0,1,2, X=S,TZ,QZ) are stored in the file ln-lcecp-bases.txt, together with the ECPs from DSSP for simplicity, renamed lcecp-k (k=0,1,2).

Table S1. Roothaan parameters for restricted open-shell Hartree–Fock treatments of the considered states for I_h symmetry.

	h_g-h_g		a_g-a_g		h_g-a_g	
	a	b	a	b	a	b
s^1			0	0		
d^1	0	0				
s^1d^1	0	0	0	0	1	2
d^2	5/8	5/4				
s^2d^1	0	0				
s^1d^2	5/8	5/4	0	0	1	2
d^3	5/6	5/3				
s^2d^2	5/8	5/4				
s^1d^3	5/6	5/3	0	0	1	2
d^4	15/16	15/8				

Table S2. Lowest s/p/d exponents of the 22s18p12d even-tempered reference basis set (ratio of subsequent exponents amounting to $10^{1/4}$=1.778). Optimized at the s^1d^1 state for f^n ECPs, at s^2d^1 for f^{n-1} ECPs, and at s^2d^2 for f^{n-2} ECPs.

	n	f^n			f^{n-1}			f^{n-2}		
		s	p	d	s	p	d	s	p	d
La	1	0.00421	0.02294	0.00559	0.00418	0.02300	0.00599			
Ce	2	0.00452	0.02453	0.00601	0.00443	0.02442	0.00643	0.00473	0.02529	0.00669
Pr	3	0.00485	0.02316	0.00639	0.00470	0.02586	0.00685	0.00494	0.02642	0.00710
Nd	4	0.00515	0.02792	0.00687	0.00498	0.02736	0.00729			
Pm	5	0.00549	0.02972	0.00736	0.00526	0.02894	0.00776			
Sm	6	0.00585	0.03169	0.00815	0.00557	0.03057	0.00823			
Eu	7	0.00623	0.03377	0.00875	0.00588	0.03233	0.00881			
Gd	8	0.00663	0.03596	0.00916	0.00622	0.03407	0.01441	0.00521	0.02773	0.00754
Tb	9	0.00705	0.03834	0.00981	0.00657	0.03598	0.01092	0.00642	0.03413	0.00973
Dy	10	0.00751	0.04095	0.01035	0.00695	0.03799	0.01638	0.00666	0.03538	0.01015
Ho	11	0.00801	0.04370	0.01101	0.00734	0.04008	0.01236			
Er	12	0.00856	0.04666	0.01160	0.00776	0.04226	0.01241			
Tm	13	0.00912	0.05004	0.01236	0.00821	0.04462	0.01985			
Yb	14	0.00976	0.05377	0.01304	0.00867	0.04698	0.01373			
Lu	15				0.00916	0.04944	0.01440			

Table S3. Restricted open-shell Hartree–Fock energies for neutral ($q=0$) and monocationic ($q=1$) atoms, in mE_h, of occupations occ with respect to reference occupation occ_{ref} for ECPs covering n, n-1 or n-2 f electrons, obtained with the reference basis sets specified in Table S2.

	n	f^n ECP			f^{n-1} ECP				f^{n-2} ECP			
occ_{ref}		$s^2(q=0)$		$s^1(q=1)$	$s^2d^1(q=0)$		$s^2(q=1)$		$s^1d^3(q=0)$		$s^1d^2(q=1)$	
occ		s^1d^1	d^2	d^1	s^1d^2	d^3	s^1d^1	d^2	s^2d^2	d^4	s^2d^1	d^3
La	1	33.73	99.21	31.18	-3.37	45.87	-40.42	-35.79				
Ce	2	37.49	106.95	35.10	0.07	53.41	-37.93	-29.64	43.22	28.60	89.55	-25.64
Pr	3	41.65	115.24	39.62	4.12	62.07	-34.37	-21.55	39.28	33.52	86.23	-21.07
Nd	4	46.26	124.15	44.89	8.50	71.31	-30.26	-12.46	34.96	38.70	82.31	-16.05
Pm	5	51.06	133.41	50.36	13.17	80.96	-25.61	-2.44				
Sm	6	56.01	142.84	56.21	18.14	91.16	-20.40	8.59				
Eu	7	61.06	152.47	62.23	23.35	101.74	-14.80	20.27				
Gd	8	66.17	162.17	68.51	29.06	113.35	-9.03	32.66				
Tb	9	71.29	171.95	74.87	34.44	124.14	-2.76	45.41	9.25	67.94	55.80	15.03
Dy	10	76.40	181.75	81.41	40.10	135.48	3.83	58.83	3.53	74.27	49.42	22.14
Ho	11	81.49	191.60	88.07	45.80	146.91	10.76	72.76				
Er	12	86.53	201.43	94.82	51.57	158.45	17.95	87.12				
Tm	13	91.49	211.26	101.65	57.62	170.52	25.25	101.86				
Yb	14	96.36	221.05	108.58	63.49	182.28	32.93	117.02				
Lu	15				69.55	194.43	40.73	132.51				
avg		64.07	158.25	66.96	30.37	115.47	-5.61	38.34	26.05	48.61	72.66	-5.12
std		20.57	39.71	25.38	23.75	48.19	26.61	54.98	18.29	20.97	18.62	22.05

Table S4. Differences to the relative energies in Table S3, in mE_h, for the **QZV** bases. For details see Table S3.

	n	f^n ECP			f^{n-1} ECP				f^{n-2} ECP			
occ_{ref}		$s^2(q=0)$		$s^1(q=1)$	$s^2d^1(q=0)$		$s^2(q=1)$		$s^1d^3(q=0)$		$s^1d^2(q=1)$	
occ		s^1d^1	d^2	d^1	s^1d^2	d^3	s^1d^1	d^2	s^2d^2	d^4	s^2d^1	d^3
La	1	0.02	0.06	0.03	0.12	0.40	0.04	0.14				
Ce	2	0.02	0.08	0.02	0.09	0.23	0.03	0.11	-0.01	0.04	0.11	-0.01
Pr	3	0.02	0.09	0.03	0.06	0.19	0.04	0.08	-0.02	0.08	0.07	-0.01
Nd	4	0.03	0.09	0.04	0.06	0.21	0.04	0.09	-0.01	0.04	0.07	-0.01
Pm	5	0.03	0.09	0.03	0.06	0.27	0.03	0.08				
Sm	6	0.03	0.10	0.04	0.05	0.21	0.04	0.09				
Eu	7	0.03	0.10	0.04	0.05	0.19	0.04	0.09				
Gd	8	0.03	0.12	0.06	0.04	0.25	0.05	0.07				
Tb	9	0.03	0.13	0.07	0.07	0.47	0.02	0.06	-0.02	0.20	0.06	-0.02
Dy	10	0.04	0.14	0.08	0.06	0.46	0.04	0.07	-0.03	0.23	0.05	-0.02
Ho	11	0.05	0.13	0.10	0.05	0.27	0.03	0.07				
Er	12	0.05	0.14	0.11	0.09	0.57	0.04	0.09				
Tm	13	-0.01	-0.01	0.01	0.10	0.57	0.04	0.09				
Yb	14	0.11	0.22	0.21	0.09	0.53	0.05	0.11				
Lu	15				0.12	0.64	0.09	0.15				
avg		0.03	0.11	0.06	0.07	0.36	0.04	0.09	-0.02	0.12	0.07	-0.01
std		0.03	0.05	0.05	0.03	0.16	0.02	0.03	0.01	0.09	0.02	0.01

Table S5. Differences to the relative energies in Table S3, in mE_h, for the **TZV** bases. For details see Table S3.

	n	f^n ECP			f^{n-1} ECP				f^{n-2} ECP			
occ_{ref}		$s^2(q=0)$		$s^1(q=1)$	$s^2d^1(q=0)$		$s^2(q=1)$		$s^1d^3(q=0)$		$s^1d^2(q=1)$	
occ		s^1d^1	d^2	d^1	s^1d^2	d^3	s^1d^1	d^2	s^2d^2	d^4	s^2d^1	d^3
La	1	-0.04	0.19	-0.35	0.15	0.73	-0.36	-0.28				
Ce	2	-0.03	0.23	-0.32	0.16	0.83	-0.37	-0.30	-0.05	0.33	0.35	-0.03
Pr	3	0.00	0.30	-0.26	0.17	0.91	-0.39	-0.35	-0.06	0.35	0.35	-0.05
Nd	4	0.01	0.32	-0.22	0.19	1.05	-0.37	-0.32	-0.06	0.38	0.35	-0.03
Pm	5	0.03	0.35	-0.16	0.20	1.15	-0.35	-0.29				
Sm	6	0.04	0.38	-0.12	0.22	1.22	-0.34	-0.26				
Eu	7	0.05	0.39	-0.07	0.23	1.27	-0.35	-0.27				
Gd	8	0.08	0.43	0.02	0.23	1.29	-0.31	-0.24				
Tb	9	0.08	0.44	0.07	0.23	1.28	-0.32	-0.22	-0.10	0.62	0.31	-0.04
Dy	10	0.12	0.47	0.15	0.26	1.42	-0.30	-0.21	-0.12	0.68	0.31	-0.04
Ho	11	0.14	0.48	0.22	0.29	1.47	-0.28	-0.18				
Er	12	0.17	0.50	0.31	0.32	1.58	-0.25	-0.12				
Tm	13	0.18	0.40	0.34	0.34	1.64	-0.22	-0.09				
Yb	14	0.29	0.65	0.60	0.36	1.67	-0.18	-0.03				
Lu	15				0.39	1.72	-0.13	0.05				
avg		0.08	0.39	0.02	0.25	1.28	-0.30	-0.21	-0.08	0.47	0.33	-0.04
std		0.09	0.12	0.28	0.07	0.31	0.08	0.11	0.03	0.16	0.02	0.01

Table S6. Differences to the relative energies in Table S3, in mE_h, for the **SV** bases. For details see Table S3.

	n	f^n ECP			f^{n-1} ECP				f^{n-2} ECP			
occ_{ref}		$s^2(q=0)$		$s^1(q=1)$	$s^2d^1(q=0)$		$s^2(q=1)$		$s^1d^3(q=0)$		$s^1d^2(q=1)$	
occ		s^1d^1	d^2	d^1	s^1d^2	d^3	s^1d^1	d^2	s^2d^2	d^4	s^2d^1	d^3
La	1	-0.75	-0.41	-1.15	0.24	0.33	-0.75	-0.97				
Ce	2	-0.74	-0.39	-1.11	0.25	0.40	-0.72	-0.95	-1.71	2.88	2.00	1.51
Pr	3	-0.58	-0.23	-0.70	0.26	0.44	-0.73	-1.01	-1.34	2.20	3.19	0.93
Nd	4	-0.61	-0.26	-0.76	0.23	0.44	-0.69	-1.02	-1.58	2.61	3.55	1.07
Pm	5	-0.54	-0.20	-0.55	0.22	0.47	-0.65	-1.02				
Sm	6	-0.53	-0.18	-0.51	0.24	0.50	-0.63	-1.03				
Eu	7	-0.53	-0.19	-0.48	0.31	0.64	-0.61	-0.96				
Gd	8	-0.45	-0.12	-0.21	0.32	0.63	-0.57	-1.02				
Tb	9	-0.41	-0.10	-0.01	0.40	0.75	-0.54	-0.91	-1.52	2.24	3.17	1.14
Dy	10	-0.34	-0.07	0.22	0.46	0.92	-0.49	-0.82	-1.34	1.81	2.64	1.05
Ho	11	-0.28	-0.05	0.48	0.52	1.02	-0.44	-0.74				
Er	12	-0.24	-0.03	0.78	0.57	1.15	-0.38	-0.63				
Tm	13	-0.20	-0.06	1.06	0.63	1.27	-0.34	-0.57				
Yb	14	-0.16	-0.03	1.35	0.67	1.33	-0.26	-0.47				
Lu	15				0.73	1.42	-0.20	-0.37				
avg		-0.45	-0.17	-0.11	0.40	0.78	-0.53	-0.83	-1.50	2.35	2.91	1.14
std		0.19	0.12	0.79	0.18	0.37	0.18	0.22	0.16	0.41	0.60	0.22

Table S7. Differences to the relative energies in Table S3, in mE_h, for the **DSSP** bases. For details see Table S3.

occ_ref	n	$s^2(q=0)$		$s^1(q=1)$	$s^2d^1(q=0)$		$s^2(q=1)$		$s^1d^3(q=0)$		$s^1d^2(q=1)$	
		f^n ECP			f^{n-1} ECP				f^{n-2} ECP			
occ		s^1d^1	d^2	d^1	s^1d^2	d^3	s^1d^1	d^2	s^2d^2	d^4	s^2d^1	d^3
La	1	0.07	0.94	-0.03	0.22	1.01	-1.69	-1.63				
Ce	2	0.10	1.12	-0.01	0.23	0.96	-1.60	-1.49	0.03	0.27	0.85	-0.28
Pr	3	0.14	1.35	-0.03	0.24	1.02	-1.60	-1.50	0.04	0.22	0.78	-0.31
Nd	4	0.15	1.46	-0.08	0.25	1.08	-1.63	-1.57	0.02	0.24	0.71	-0.28
Pm	5	0.17	1.53	-0.07	0.25	1.21	-1.44	-1.28				
Sm	6	0.23	1.68	-0.03	0.26	1.36	-1.61	-1.52				
Eu	7	0.35	1.84	0.26	0.25	1.21	-1.37	-1.20				
Gd	8	0.11	1.53	-0.26	0.20	1.07	-1.49	-1.45				
Tb	9	0.05	1.32	-0.47	0.21	1.39	-1.39	-1.37	0.01	0.24	0.41	-0.38
Dy	10	0.02	1.15	-0.51	0.24	1.45	-1.30	-1.27	0.01	0.23	0.37	-0.42
Ho	11	-0.09	0.85	-0.77	0.30	1.65	-1.28	-1.25				
Er	12	-0.10	0.72	-0.86	0.33	1.73	-1.16	-1.09				
Tm	13	-0.38	-0.10	-1.36	0.40	2.07	-0.78	-0.70				
Yb	14	-0.48	-0.55	-1.33	0.56	2.52	-0.85	-0.70				
Lu	15				-2.03	-2.92	-4.78	-7.97				
avg[1]		0.02	1.06	-0.40	0.28	1.41	-1.37	-1.29	0.02	0.24	0.62	-0.33
std[1]		0.23	0.67	0.51	0.10	0.45	0.28	0.29	0.01	0.02	0.22	0.06

[1]Statistics calculated without Lu, see text.

Table S8. Differences to the relative energies in Table S3, in mE_h, for the **WCYD** bases. For details see Table S3.

occ_ref	n	$s^2d^1(q=0)$		$s^2(q=1)$	
		f^{n-1} ECP			
occ		s^1d^2	d^3	s^1d^1	d^2
La	1	-0.57	-0.38	-3.23	-5.88
Ce	2	-0.55	-0.32	-3.09	-5.68
Pr	3	-0.52	-0.26	-2.91	-5.40
Nd	4	-0.50	-0.24	-2.82	-5.27
Pm	5	-0.47	-0.17	-2.69	-5.07
Sm	6	-0.44	-0.11	-2.56	-4.88
Eu	7	-0.40	-0.03	-2.44	-4.70
Gd	8	-0.38	0.04	-2.34	-4.55
Tb	9	-0.34	0.12	-2.21	-4.35
Dy	10	-0.29	0.20	-2.06	-4.13
Ho	11	-0.24	0.25	-1.95	-3.94
Er	12	-0.20	0.30	-1.82	-3.74
Tm	13	-0.16	0.37	-1.69	-3.51
Yb	14	-0.11	0.42	-1.55	-3.28
Lu	15	-0.06	0.46	-1.41	-3.06
avg		-0.35	0.04	-2.32	-4.50
std		0.17	0.28	0.57	0.88

Table S9. Data for compounds with f^n occupation. Columns 2–4 ("lcecp/reference"): distances(pm), angles(°), and lowest vibrational frequencies (cm^{-1}) obtained at DFT(PBE0) level with lcecp-0 and the corresponding reference bases (for valence space see Table S2, polarization functions from WCYD[S2], decontracted cc-pV5Z/cc-pV(5+d)Z without h function for the other elements). Columns 5–7 ("lcecp/QZVPP"): Differences to the reference bases for lcecp-0-QZVPP bases at Ln and def2-QZVPP for the other elements. Columns 8-10 ("X2C/QZVPP"): Differences between the settings used for columns 5–7 and all-electron scalar relativistic X2C with x2c-QZVPPall bases used for all elements.

	lcecp/reference			lcecp/QZVPP			X2C/QZVPP		
	d	α	f	Δd	$\Delta\alpha$	Δf	Δd	$\Delta\alpha$	Δf
PrCl$_2$	266.71	128.2	49.21	0.02	0.14	-0.1	-8.515	-8.86	8.1
PrF$_2$	216.66	119.02	101.26	0	0.08	0	-12.45	-10.52	-17.7
PrH$_2$	220.57	114.02	397.67	0	0.05	0.9	-12.175	-4.19	50.2
NdCl$_2$	265.48	129.5	47.9	0.01	0.15	-0.1	-5.2	-8.31	6.8
NdF$_2$	215.67	119.85	100.52	-0.01	0.08	-0.1	-7.995	-8.41	12.6
NdH$_2$	219.58	114.71	396.47	0	0.05	0.8	-6.215	-3.7	31.9
PmCl$_2$	264.29	130.78	46.54	0.02	0.17	-0.1	-4.2	-4.86	5
PmF$_2$	214.72	120.62	99.41	-0.01	0.08	-0.1	-7.33	-6.5	14.4
PmH$_2$	218.54	115.4	394.65	0	0.06	0.8	-4.4	-1.52	22
SmCl$_2$	263.02	131.99	45.34	0.02	0.18	-0.1	-4.12	-2.21	1.1
SmF$_2$	213.64	121.29	98.45	-0.01	0.08	-0.1	-3.15	-6.68	12.8
SmH$_2$	217.43	116.12	392.65	0.01	0.06	0.7	-4.89	-3.77	24.9
SmO	189.96	-	691.49	0.06	-	0.8	-3.63	-	-47.5
EuCl$_2$	261.94	133.46	43.98	0.02	0.2	-0.1	-4.27	-6.32	6.8
EuF$_2$	212.75	122.14	96.85	-0.02	0.08	-0.2	-2.71	-6.94	11.7
EuH$_2$	216.52	116.99	389.05	0.01	0.06	0.6	-4.3	-2.71	23.9
EuO	189.75	-	688.17	0.04	-	0.8	-4.14	-	17.1
HoCl$_2$	257.9	140.11	38.31	0.03	0.27	-0.3	-6.88	-11.66	14
HoH$_2$	213.13	121.22	366.67	0.04	0.14	-0.5	-7.7	-4.88	67.8
ErCl$_2$	256.97	142.02	36.27	0.04	0.29	-0.4	-6.16	-9.4	9.6
TmCl$_2$	256.07	144.08	34.2	0.05	0.39	-0.5	-6.365	-9.72	10.1
TmF$_2$	207.77	127.87	87.03	0.04	0.26	-0.8	-7.955	-11.37	33.6
TmH$_2$	211.6	123.84	350.58	0.06	0.2	-1.6	-7.19	-5.82	69.3
YbCl$_2$	255.57	145.96	32.59	-0.01	0.27	-0.3	-7.14	-13.46	15
YbF$_2$	207.97	129.14	85.9	-0.16	0.08	-0.5	-5.43	-11.15	31.6
YbH$_2$	211.01	125.13	342.83	0.05	0.23	-2.2	-7.04	-5.24	68.5
YbO	190.65	-	660.84	-0.27	-	-2.2	-6.6	-	67.2

Table S10. Differences ("basis set errors") for compounds with f^n occupation in distances (pm), angles(°), and lowest vibrational frequencies(cm^{-1}) to the reference basis, at level DFT(PBE0), for the Ln bases specified in the first line. For the other elements the corresponding def2-bases were used, and def2-TZVP in case of DSSP.

	lcecp-0-QZVP			lcecp-0-TZVP			lcecp-0-SV(P)			DSSP		
	Δd	$\Delta\alpha$	Δf	Δd	$\Delta\alpha$	Δf	Δd	$\Delta\alpha$	Δf	Δd	$\Delta\alpha$	Δf
PrCl$_2$	0.04	0.18	-0.1	-0.38	-0.2	0.3	0.09	2.1	-3.3	1.29	-1.54	1.3
PrF$_2$	0.16	0.21	0.3	0.16	0.28	-0.6	-0.84	-2.55	-7.2	2.69	-0.86	-3.2
PrH$_2$	0.01	0	0.9	-0.33	-0.4	6.1	0.98	-0.83	12.1	0.91	-1.19	6.6
NdCl$_2$	0.02	0.2	-0.2	-0.41	-0.22	0.3	-0.07	2.6	-2.9	1.15	-1.49	1.7
NdF$_2$	0.13	0.17	0.3	0.09	0.26	-0.7	-0.89	-2.29	-6.5	2.45	-0.7	-3
NdH$_2$	0	0	0.8	-0.33	-0.29	5	1	-0.81	7.1	0.76	-1.05	6.7
PmCl$_2$	0.02	0.23	-0.2	-0.43	-0.21	0.3	0.02	3.01	-1.8	1	-1.49	1.7
PmF$_2$	0.11	0.17	0.3	0.03	0.23	-0.8	-0.87	-2.07	-5.8	2.24	-0.63	-3
PmH$_2$	-0.01	0.02	0.8	-0.34	-0.38	5.5	0.92	-0.77	9	0.69	-0.99	6.7
SmCl$_2$	0.02	0.24	-0.2	-0.43	-0.22	0.3	-0.04	3.54	-1.4	0.89	-1.51	1.6
SmF$_2$	0.08	0.15	0.2	-0.02	0.24	-0.9	-0.85	-1.82	-5.4	2.07	-0.6	-3
SmH$_2$	0	0.02	0.6	-0.32	-0.3	4.4	1.01	-0.78	4.5	0.67	-0.95	6.5
SmO	0.29	-	1.7	0.34	-	5.5	3.45	-	13.4	2.72	-	-10.7

EuCl₂	0.01	0.26	-0.1	-0.44	-0.2	0.3	-0.21	3.99	-1	0.95	-0.94	1
EuF₂	0.06	0.14	0.2	-0.05	0.3	-1.2	-0.87	-1.59	-4.6	2	-0.13	-3.9
EuH₂	-0.01	0.04	0.4	-0.31	-0.19	2.7	1.05	-0.94	-2.1	0.75	-0.69	4.4
EuO	0.24	-	1.5	0.3	-	4.9	3.51	-	11.7	2.29	-	-13.5
HoCl₂	-0.01	0.41	-0.4	-0.45	-0.18	0.1	0.37	8.56	-3.2	0.12	-1.18	2.1
HoH₂	0.02	0.14	-0.9	-0.29	-0.36	2.3	1.385	-0.6	-8.6	-0.45	-1.27	9.8
ErCl₂	0	0.43	-0.4	-0.43	-0.11	-0.3	0.55	9.63	-3.2	0.05	-1.17	2.2
TmCl₂	0.01	0.49	-0.4	-0.42	-0.18	-0.4	0.72	10.45	-4.5	-0.01	-1.21	2.1
TmF₂	0.03	0.19	-0.1	-0.19	0.13	0.1	0.2	2.57	-3	1.11	0.51	-0.5
TmH₂	0.05	0.21	-1.9	-0.31	-0.67	3.6	1.28	-0.42	-14.5	-0.41	-1.03	5.9
YbCl₂	-0.06	0.46	-0.2	-0.48	-0.2	-0.3	0.71	14.09	-8.7	0.09	-0.02	0.4
YbF₂	-0.19	0.01	0.2	-0.44	-0.07	1	0.08	2.95	-0.6	0.49	0.71	-1.4
YbH₂	0.04	0.25	-2.7	-0.29	-0.49	1.1	1.72	-0.11	-26.2	0.29	0.19	-6.1
YbO	-0.24	-	-1.8	-0.16	-	1.7	4.26	-	1	0.12	-	-5.1

Table S11. Data for compounds with f^{n-1} occupation. For details see Table S9.

	lcecp/reference			lcecp/QZVPP			X2C/QZVPP		
	d	α	f	Δd	Δα	Δf	Δd	Δα	Δf
LaCl₂	256.52	115.66	64.31	0.05	0.08	0	-2.07	0.78	-3.6
LaCl₃	259.17	118.21	24.26	0.05	0.14	-0.9	-1.65	0.98	-12
LaF₂	208.38	110.21	120.24	0.05	0.03	-0.2	-2.65	0.95	-6.9
LaF₃	212.08	114.5	76.06	0.03	0.08	-1.1	-2.02	0.47	-6.3
LaH₂	208.98	110.77	452.01	0.05	-0.02	0.6	-2.67	0.69	0.8
LaH₃	210.88	111.11	315.79	0.05	0.03	-0.6	-2.15	0.76	-4.1
LaO	186.61	-	830.2	0.16	-	-0.3	-6.15	-	24.9
CeCl₂	254.83	116.2	64.35	0.04	0.11	0	-2.9	0.9	-6.2
CeCl₃	257.49	118.67	21.1	0.05	0.14	-1.4	-2.76	-1.94	14.9
CeF₂	207	110.53	121.57	0.04	0.03	-0.1	-3.36	0.08	-9.2
CeF₃	210.68	114.85	73.18	0.03	0.09	-1.1	-2.89	-2.25	16.4
CeH₂	207.37	110.95	456.19	0.04	-0.01	0.9	-3.5	0.78	-3.7
CeH₃	209.26	111.16	314.19	0.04	0.03	-0.6	-3.03	0.13	2.5
CeO	185.6	-	833.12	0.14	-	-0.2	-7.06	-	31.9
PrCl₃	255.86	118.95	17.88	0.05	0.17	-1.9	-2.8	-0.94	15.8
PrF₃	209.3	114.97	72.22	0.01	0.09	-1	-2.73	-0.6	9.9
PrH₃	207.66	110.99	315.36	0.04	0.04	-0.6	-3.04	1.75	-14.5
PrO	184.66	-	836.72	0.12	-	0.1	-7.02	-	33
NdCl₃	254.36	119.31	13.45	0.05	0.19	-2.4	-2.9	-2.18	26.1
NdF₃	207.99	115.14	71.06	0.01	0.09	-1	-2.4	-1.68	23.5
NdH₃	206.2	110.92	315.66	0.03	0.05	-0.6	-3.35	-0.75	52.1
NdO	183.78	-	839.14	0.1	-	0.2	-5.98	-	23.7
PmCl₃	253.04	120	3.75	0.02	0	2.1	-2.63	-1.38	22.9
PmF₃	206.85	115.67	66.28	0	0.06	-0.6	-1.91	-0.27	10.5
PmH₃	204.97	111.12	312.29	0.03	0.05	-0.7	-3.01	2.16	32.2
PmO	183.04	-	841.25	0.09	-	0.4	-4.99	-	13.7
SmCl₃	251.66	120	11.89	0.02	0	0.9	-2.35	0	16.2
SmF₃	205.7	115.92	62.83	-0.01	0.1	-0.8	-2.13	-2.61	22.6
SmH₃	203.79	111.33	308.88	0.03	0.05	-0.8	-2.58	-0.17	8.4
EuCl₃	250.26	119.99	16.97	0.03	0	0.8	-2.28	-2.31	22
EuF₃	204.56	116.46	60.79	0	0.1	-1.2	-1.9	-2.66	30.4
EuH₃	202.62	111.68	303.37	0.04	0.06	-1.1	-1.06	-0.39	33.2
GdCl₂	247.02	122.08	60.49	0.03	0.02	0	-1.84	0.03	-1.5
GdCl₃	249.06	120	20.03	0.02	0	0.6	-1.93	0	-3.1
GdF₂	200.21	113.04	122.64	0.01	0.07	-0.1	-0.77	-0.53	-2.1
GdF₃	203.6	116.86	51.27	0.02	0.12	-0.8	-0.98	-0.53	1.8
GdH₂	199.94	112.99	475.1	0.03	-0.01	0.8	-1.9	0.18	-6.6
GdH₃	201.62	112.02	297.18	0.03	0.05	-1.1	-2.06	-0.14	0.4
GdO	181.12	-	846.19	0.04	-	0.3	-2.08	-	12.9
TbCl₂	245.83	122.96	59.7	0.04	0.12	0	-1.57	5.41	-8.9
TbCl₃	247.73	120	23.05	0.02	0	0.5	-2.24	-0.92	7.3
TbF₂	199.13	113.57	121.62	0	0.06	-0.3	-1.06	-0.78	0.1

TbF₃	202.48	117.32	54.5	0.01	0.1	-1.4	-1.39	-2.62	21.3
TbH₂	198.92	113.54	476.88	0.03	-0.01	0.5	-2.23	0.19	-6.4
TbH₃	200.58	112.63	286.81	0.03	0.05	-1.1	-2.42	-0.79	23.4
TbO	180.37	-	848.77	0.05	-	0.2	-1.89	-	20.5
DyCl₂	244.8	124.15	58.63	0.04	0.15	0	-1.21	12.41	-14
DyCl₃	246.5	120	24.51	0.02	0	0.6	-2.19	-0.35	5.5
DyF₂	198.17	114.18	122.11	0	0.09	-0.1	-1.15	-2.18	3.3
DyF₃	201.51	118.15	39.83	0	0.08	-0.4	-1.25	-1.36	25
DyH₂	198	114.06	477.11	0.03	0.01	0.7	-2.04	4.46	-7
DyH₃	199.65	113.27	274.5	0.03	0.06	-1.3	-2.21	1.13	-1.2
DyO	179.75	-	850.09	0.04	-	0.3	-2.44	-	23.9
HoCl₃	245.28	120	27.85	0.02	0	0.5	-2.05	-0.01	0.4
HoF₂	197.19	114.74	121.81	0	0.09	0	-0.54	1.01	4.4
HoF₃	200.49	118.68	39.18	0	0.11	-1	-1.15	-2.81	33
HoH₃	198.74	114	259.67	0.03	0.08	-1.8	-1.93	1.99	-47.5
HoO	179.1	-	851.72	0.04	-	0.4	-1.35	-	18.2
ErCl₃	244.08	120	30.01	0.02	0	0.4	-1.88	-0.12	2.3
ErF₂	196.23	115.28	121.55	0	0.08	0	-0.31	-0.1	4.4
ErF₃	199.43	118.9	29.3	0.01	0.14	-3.9	-0.75	-1.52	36.2
ErH₂	196.24	115.02	475.9	0.02	-0.01	0.6	-2.41	0.84	27.9
ErH₃	197.86	114.8	241.87	0.03	0.06	-1.6	-2.42	0.14	56.6
ErO	178.45	-	853.14	0.03	-	0.3	-0.87	-	26.2
TmCl₃	243.04	120	32.59	0.02	0	0.4	-1.98	0	1.7
TmF₃	198.65	120	23.23	-0.01	0	1.1	-0.59	0	8.5
TmH₃	197.19	115.81	216.58	0.03	0.07	-1.9	-2.22	0.66	25.9
TmO	178.05	-	853.14	0.02	-	0.3	-0.92	-	15.9
YbCl₃	241.9	120	34.71	0.01	0	0.3	-1.85	0	0.5
YbF₃	197.59	120	25.45	-0.01	0	1.3	-0.88	-3.02	44.5
YbH₃	196.39	116.79	189.11	0.04	0.08	-2.5	-2.31	-1.13	73.6
LuCl₂	240.6	129.11	52.94	0.03	0.12	0	-2.18	-1.22	3
LuCl₃	241.23	120	36.81	0.01	0	0.3	-2.13	0.01	-1.2
LuF₂	194.58	117.09	119.58	-0.01	0.08	0.1	-0.68	-1.05	4.8
LuF₃	197.32	119.89	18.02	0	0.05	-5.4	-0.93	-0.67	26.6
LuH₂	194.3	116.15	467.1	0.02	-0.08	0.5	-1.95	-0.39	9
LuH₃	195.92	117.81	154.99	0.04	0.08	-2.9	-2.19	-0.76	28.5
LuO	178.2	-	855.44	0.02	-	0.1	-0.34	-	16.4

Table S12. Basis set errors for compounds with f^{n-1} occupation. For details see Table S10.

	lcecp-1-QZVP			lcecp-1-TZVP			lcecp-1-SV(P)			DSSP		
	Δd	Δα	Δf	Δd	Δα	Δf	Δd	Δα	Δf	Δd	Δα	Δf
LaCl₂	0.22	0.26	0.0	0.03	0.22	0	1.29	0.97	-5.3	2.17	-1.53	1
LaCl₃	0.15	-0.01	0.4	-0.07	-0.09	0.6	0.89	1.41	-11.7	1.52	-1.95	8.8
LaF₂	0.48	0.4	0.0	0.53	0.48	-2.6	0.66	-1.01	-3.8	4.37	-1.42	-0.1
LaF₃	0.36	0.22	-0.6	0.45	0.37	-3.3	0.02	-0.23	3.6	3.47	-0.96	2
LaH₂	0.16	0.18	0.6	-0.02	0.33	3.5	0.73	0.21	-0.6	1.21	-1.65	-9.1
LaH₃	0.16	0.05	4.9	-0.02	0.21	-2	0.48	0.2	-7.1	0.91	-1.57	9.1
LaO	0.95	-	1.2	0.86	-	2.9	1.94	-	3.4	5.3	-	-33.1
CeCl₂	0.16	0.3	0.0	-0.06	0.24	0	1.1	1.05	-5.2	1.92	-1.41	0.9
CeCl₃	0.08	-0.02	0.9	-0.17	-0.14	1.5	0.71	1.33	-16.5	1.31	-1.84	9.8
CeF₂	0.37	0.35	-0.2	0.4	0.41	-2.3	0.5	-0.9	-4.3	3.95	-1.31	-0.9
CeF₃	0.27	0.19	-0.4	0.32	0.34	-3.4	-0.12	-0.24	2.3	3.12	-0.91	2.7
CeH₂	0.11	0.18	0.8	-0.1	0.28	3.4	0.61	0.2	-0.8	1.05	-1.54	-7.4
CeH₃	0.12	0.06	3.3	-0.1	0.15	-1.4	0.37	0.17	-6.8	0.77	-1.51	9.9
CeO	0.78	-	1.4	0.7	-	3.2	1.71	-	5.9	4.75	-	-29.6
PrCl₃	0.07	-0.02	1.1	-0.24	-0.26	3.2	0.39	1.02	-11.6	1.12	-1.78	11.3
PrF₃	0.21	0.19	-0.4	0.26	0.29	-3.4	-0.29	-0.22	2.9	2.81	-0.86	3.3
PrH₃	0.1	0.09	0.8	-0.14	0.11	-1	0.24	0.17	-6	0.63	-1.44	10.4
PrO	0.65	-	1.5	0.62	-	3.1	1.42	-	10	4.25	-	-26.7
NdCl₃	0.04	-0.07	3.4	-0.28	-0.32	4.7	0.3	0.68	-7.4	0.96	-1.78	14.5
NdF₃	0.17	0.17	-0.4	0.17	0.23	-3.2	-0.36	-0.32	4.3	2.56	-0.83	3.8

NdH$_3$	0.07	0.09	-1.3	-0.15	0.08	-0.8	0.22	0.13	-5.8	0.51	-1.4	11.4
NdO	0.55	-	1.4	0.51	-	3.2	1.24	-	11.2	3.85	-	-24
PmCl$_3$	0.03	-0.04	4.7	-0.3	-0.32	4.5	0.1	0	9.2	0.85	-1.66	19.6
PmF$_3$	0.13	0.11	0.0	0.15	0.34	-2.4	-0.32	0.3	-1.5	2.24	-0.8	-1.3
PmH$_3$	0.07	0.1	-2.0	-0.18	0.08	-0.3	0.18	0.15	-5.3	0.49	-1.18	10.4
PmO	0.47	-	1.2	0.43	-	3.5	1.1	-	12.8	3.43	-	-32
SmCl$_3$	0.02	0	-2.7	-0.28	-0.01	-3.9	0.06	0	6.1	0.79	-1.11	7
SmF$_3$	0.1	0.14	-0.3	0.08	0.26	-6.1	-0.38	-0.09	-6	2.02	-0.89	5.3
SmH$_3$	0.06	0.11	-0.2	-0.28	-0.01	2.3	0.11	0.07	-2.6	0.39	-1.19	11.7
EuCl$_3$	0.03	0	-1.0	-0.31	0	-2.8	0.01	0	4.7	0.83	-0.33	-8.4
EuF$_3$	0.08	0.13	0.2	0.04	0.26	-2.3	-0.39	0.13	0.4	1.88	-0.77	1.3
EuH$_3$	0.06	0.13	0.1	-0.31	-0.06	3.6	0.07	0.03	-1.9	0.33	-1.16	12.7
GdCl$_2$	0.04	0.05	0.1	-0.32	0	-0.4	0.47	2.1	-3.7	0.97	-1.03	-0.1
GdCl$_3$	0.01	0	-0.3	-0.33	0	-2.1	0.04	0	4.4	0.77	-0.01	-9.3
GdF$_2$	0.12	0.29	0.3	0.01	0.45	-2.4	0.05	-0.02	-7.1	2.33	-0.82	-3.2
GdF$_3$	0.07	0.12	0.6	0.03	0.47	-9.7	-0.31	0.68	-24.3	1.74	-1.01	6.3
GdH$_2$	0.05	0.23	0.8	-0.32	0.07	1.6	0.26	0.12	-2.6	0.51	-0.97	0.5
GdH$_3$	0.05	0.13	-0.5	-0.38	-0.13	5.8	0.02	-0.06	-0.2	0.26	-1.13	13.6
GdO	0.26	-	0.6	0.23	-	4	0.8	-	13.4	2.73	-	-15.5
TbCl$_2$	0.06	0.31	-0.1	-0.3	0.37	-0.7	0.52	2.78	-3.7	0.93	-0.47	-0.1
TbCl$_3$	-0.01	0	-0.8	-0.35	-0.01	-2	0.06	0	4.2	0.73	-0.01	-5.9
TbF$_2$	0.1	0.26	0.0	-0.03	0.5	-3.2	0.07	0.29	-8.1	2.05	-0.69	-4.3
TbF$_3$	0.04	0.07	0.8	-0.06	0.18	-1	-0.41	-0.04	3.1	1.58	-0.6	3.9
TbH$_2$	0.04	0.22	1.5	-0.34	0.06	1	0.26	0.14	-3.4	0.47	-0.83	1.5
TbH$_3$	0.04	0.12	-0.3	-0.4	-0.17	6.9	0.03	-0.05	-0.2	0.28	-0.94	12.9
TbO	0.24	-	0.6	0.19	-	4.1	0.77	-	13.6	2.38	-	-12.7
DyCl$_2$	0.06	0.31	0.2	-0.28	0.29	-0.6	0.49	2.7	-3.8	0.86	-0.33	-0.2
DyCl$_3$	-0.01	0	-0.9	-0.36	0	-1.5	0.02	-0.01	4.6	0.65	0	-4.9
DyF$_2$	0.09	0.27	0.3	-0.04	0.32	-2.2	0.01	-0.05	-7.5	1.9	-0.6	-5
DyF$_3$	0.01	0	0.9	-0.05	0.44	-1.9	-0.37	0.68	1.8	1.44	-0.68	-4.1
DyH$_2$	0.05	0.22	1.3	-0.25	0.1	1.6	0.3	0.2	-1.4	0.43	-0.77	2.3
DyH$_3$	0.04	0.13	-0.3	-0.33	-0.11	4	0.07	0.06	-3.6	0.23	-0.89	13.7
DyO	0.21	-	0.4	0.18	-	3.8	0.68	-	14.3	2.2	-	-11.5
HoCl$_3$	-0.01	-0.01	-1.0	-0.38	0	-1.8	0.02	0	3.3	0.56	0	-4.4
HoF$_2$	0.08	0.25	0.2	-0.07	0.31	-2.3	0.01	0.01	-7.9	1.77	-0.5	-5.4
HoF$_3$	0	0.02	0.7	-0.11	0.27	3	-0.43	0.35	10	1.39	-0.26	-2.8
HoH$_3$	0.04	0.15	-1.2	-0.35	-0.15	4.8	0.07	0.06	-3.8	0.19	-0.86	14.9
HoO	0.18	-	0.4	0.15	-	3.9	0.64	-	14.6	2.03	-	-10.4
ErCl$_3$	-0.02	0	-1.0	-0.39	0	-1.7	0.02	0	3.3	0.5	0	-4
ErF$_2$	0.07	0.22	0.1	-0.11	0.36	-2.5	0	0.26	-8.5	1.64	-0.41	-5.6
ErF$_3$	-0.02	-0.04	5.7	-0.15	0.16	-10.3	-0.48	-0.05	-7	1.21	-0.65	12
ErH$_2$	0.04	0.18	0.9	-0.33	0.02	0.3	0.26	0.22	-3.2	0.34	-0.72	3.1
ErH$_3$	0.04	0.13	-1.1	-0.42	-0.28	8.9	0.04	0	-1.2	0.16	-0.82	15.8
ErO	0.16	-	0.3	0.11	-	4.1	0.6	-	14.8	1.89	-	-9.3
TmCl$_3$	-0.04	0	-1.0	-0.41	0	-1.4	0.02	0	3.1	0.46	0	-3.5
TmF$_3$	-0.02	0	-2.1	-0.21	0	8.6	-0.51	0	16.8	1.24	0	4.9
TmH$_3$	0.03	0.13	-4.5	-0.34	-0.16	4.1	0.11	0.15	-5.9	0.17	-0.75	15.8
TmO	0.14	-	0.3	0.1	-	3.8	0.55	-	14.9	1.74	-	-9.8
YbCl$_3$	-0.05	0	-0.8	-0.43	0	-1.2	0.03	0	3.1	0.36	0	-3.2
YbF$_3$	-0.04	0	-2.4	-0.23	-0.01	5.7	-0.48	0	11.1	1.13	0	1.7
YbH$_3$	0.04	0.14	-2.7	-0.47	-0.39	12.1	0.05	0.02	-1.2	0.12	-0.79	19.1
LuCl$_2$	0.02	0.27	0.1	-0.34	0.92	-2.4	0.23	4.76	-3.5	0.11	0.19	-0.5
LuCl$_3$	-0.02	0	-0.8	-0.4	0	-1.4	-0.14	0	3.3	0	0	-2.8
LuF$_2$	0.04	0.24	0.1	-0.19	0.49	-3.6	-0.12	1.05	-9.2	0.67	-0.28	-5.1
LuF$_3$	-0.01	0.02	-4.7	-0.24	-0.14	13.9	-0.52	-0.23	25.6	0.46	-0.23	17.3
LuH$_2$	0.02	0.11	0.7	-0.42	-0.03	-1.4	0.21	0.28	-5.3	-0.01	-0.59	5.3
LuH$_3$	0.03	0.13	0.5	-0.59	-0.73	27.9	-0.06	-0.33	14.5	-0.07	-0.59	17.7
LuO	0.07	-	-0.1	-0.02	-	4.4	0.32	-	16.8	0.7	-	-3.1

Table S13. Data for compounds with f^{n-2} occupation. For details see Table S9. Compounds with unpaired f occupations (according to Mulliken analysis) that deviate in the X2C/QZVPP treatment by more than ~0.5 from the expected value for f^{n-2} are written in italics.

	lcecp/reference		lcecp/QZVPP		X2C/QZVPP	
	d	f	Δd	Δf	Δd	Δf
CeCl4	247.98	80.38	0.06	0	-0.67	-20.3
CeF4	203.82	141.15	0.01	-0.4	-1.6	-24.3
CeH4	198.99	517.68	0.04	0.3	-1.15	-25.6
PrCl4	246.81	82.13	-0.11	-0.1	-0.49	-29.4
PrF4	203.11	144.09	-0.29	-0.5	-1.87	-47.7
PrH4	*197.83*	*516.45*	*-0.11*	*1.3*	*7.16*	*-167.6*
NdCl4	*245.37*	*83.53*	*-0.08*	*0*	*15.43*	*-39.4*
NdF4	201.93	146.56	-0.25	-0.3	-1.66	-47.8
NdH4	*196.47*	*517.48*	*-0.07*	*1*	*10.41*	*-207.1*
TbCl4	238.87	90.4	-0.02	0.1	0.24	-16.9
TbF4	196.21	157.4	-0.19	-0.1	-0.57	-16.4
TbH4	*190.58*	*527.2*	*-0.01*	*0.9*	*1.79*	*-130.7*
DyCl4	*237.7*	*91.9*	*-0.02*	*0.1*	*10.08*	*-72*
DyF4	195.12	154.53	-0.19	-0.1	-0.36	-42.8
DyH4	*189.55*	*529.86*	*-0.01*	*0.9*	*12.50*	*-266.3*

Table S14. Basis set errors for compounds with f^{n-2} occupation. For details see Table S10.

	lcecp-2-QZVP		lcecp-2-TZVP		lcecp-2-SV(P)		DSSP	
	Δd	Δf	Δd	Δf	Δd	Δf	Δd	Δf
CeCl4	0.24	0.5	0.05	0.7	-0.01	-0.9	1.65	1.3
CeF4	0.3	0	0.38	0.5	-0.57	-1.8	2.93	1.9
CeH4	0.2	1.5	-0.01	-0.2	-1.21	-0.5	0.87	-8.8
PrCl4	0.0	0.3	-0.21	0.6	-0.05	-1.4	1.10	0.9
PrF4	-0.11	0	-0.04	0.2	-0.66	-3.1	2.07	1.5
PrH4	-0.02	2.9	-0.21	1.9	-0.66	-6.5	0.43	-4.9
NdCl4	-0.01	0.3	-0.22	0.6	-0.29	-2	0.88	0.7
NdF4	-0.13	0	-0.09	0.5	-0.85	-2.8	1.72	1.4
NdH4	-0.02	2.8	-0.25	2.3	-1.12	-1.6	0.29	-3.6
TbCl4	-0.02	0.2	-0.31	1	-0.28	-1.3	0.35	-0.3
TbF4	-0.17	0.5	-0.24	1.7	-0.86	-3.9	0.76	-1.7
TbH4	-0.01	2.6	-0.33	2.8	-0.98	-6.6	0.02	-0.6
DyCl4	-0.02	0.2	-0.325	0.9	0.06	-0.4	0.30	-0.3
DyF4	-0.16	0.5	-0.265	-0.8	-0.62	-8.7	0.63	-4.1
DyH4	-0.01	2.5	-0.24	1.8	-0.17	-15.2	0	-0.8

Table S15. Bond lengths (*d*, in pm), angles (*α*, in °) and in the lowest vibration frequency (*f*, in cm^{-1}) for selected Hf compounds with PBE0/def2-QZVPP and differences to these for the settings specified in the first line.

	def2-QZVPP			def2-QZVP			def2-TZVP			def2-SVP			def2-SV(P)		
	d	α	f	Δd	Δα	Δf	Δd	Δα	Δf	Δd	Δα	Δf	Δd	Δα	Δf
HfH2	186.30	120.67	570.62	0.01	-0.02	-0.18	0.01	0.11	5.19	-0.37	-0.13	23.70	0.23	0.26	18.24
HfF2	187.08	123.48	106.97	0.09	0.27	-0.8	0.36	1.01	-5.63	1.65	6.76	4.30	3.15	10.64	-7.05
HfCl2	231.54	156.40	34.34	0.06	0.70	-0.93	0.04	0.92	-0.75	1.01	-5.07	17.13	2.56	0.78	15.08
HfO	171.71	-	998.74	0.02	-	-0.74	0.4	-	1.29	0.86	-	1.69	2.56	-	-17.7
avg				0.04	0.32	-0.66	0.20	0.68	0.03	0.79	0.52	11.71	2.13	3.89	2.14
std				0.04	0.36	0.33	0.21	0.50	4.50	0.84	5.94	10.46	1.29	5.85	17.36

Table S16. Energies, in kJ/mol, of exchange reactions of type $Ln^AH_3+Ln^BCl_3\rightarrow Ln^ACl_3+Ln^BH_3$ obtained with lcecp-1 ECPs and reference bases for Ln (for valence space see Table S2, polarization functions from WCYD[S2], decontracted cc-pV5Z/cc-pV(5+d)Z bases without h function for the other elements) at DFT(PBE0) level.

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	-1.76													
Pr	-4.35	-2.59												
Nd	-6.51	-4.75	-2.16											
Pm	-7.53	-5.78	-3.19	-1.03										
Sm	-8.85	-7.09	-4.5	-2.34	-1.31									
Eu	-10.27	-8.52	-5.93	-3.77	-2.74	-1.43								
Gd	-12.97	-11.21	-8.63	-6.47	-5.44	-4.13	-2.7							
Tb	-13.98	-12.23	-9.64	-7.48	-6.45	-5.14	-3.71	-1.01						
Dy	-15.67	-13.91	-11.32	-9.17	-8.14	-6.83	-5.4	-2.7	-1.69					
Ho	-17.41	-15.65	-13.06	-10.9	-9.88	-8.57	-7.14	-4.44	-3.42	-1.74				
Er	-19.34	-17.58	-14.99	-12.83	-11.8	-10.49	-9.06	-6.36	-5.35	-3.66	-1.93			
Tm	-21.94	-20.18	-17.59	-15.43	-14.4	-13.09	-11.66	-8.97	-7.95	-6.27	-4.53	-2.6		
Yb	-24.33	-22.57	-19.98	-17.82	-16.79	-15.48	-14.05	-11.35	-10.34	-8.66	-6.92	-4.99	-2.39	
Lu	-30.17	-28.41	-25.82	-23.66	-22.63	-21.32	-19.89	-17.19	-16.18	-14.49	-12.75	-10.83	-8.23	-5.84

Table S17. Differences, in kJ/mol, to the data in Table S16 for lcecp-1-QZVPP bases at Ln (def2-QZVPP for the other elements).

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	0.02													
Pr	-0.04	-0.06												
Nd	-0.04	-0.06	0											
Pm	-0.07	-0.09	-0.03	-0.03										
Sm	-0.08	-0.1	-0.03	-0.04	-0.01									
Eu	-0.11	-0.13	-0.07	-0.07	-0.04	-0.03								
Gd	-0.07	-0.08	-0.02	-0.02	0.01	0.01	0.04							
Tb	-0.12	-0.14	-0.08	-0.08	-0.05	-0.04	-0.01	-0.06						
Dy	-0.13	-0.14	-0.08	-0.09	-0.06	-0.05	-0.02	-0.06	-0.01					
Ho	-0.16	-0.17	-0.11	-0.12	-0.09	-0.08	-0.05	-0.09	-0.04	-0.03				
Er	-0.16	-0.18	-0.12	-0.12	-0.09	-0.08	-0.05	-0.09	-0.04	-0.03	0			
Tm	-0.18	-0.2	-0.13	-0.14	-0.11	-0.1	-0.07	-0.11	-0.06	-0.05	-0.02	-0.02		
Yb	-0.2	-0.22	-0.16	-0.16	-0.13	-0.12	-0.09	-0.14	-0.08	-0.08	-0.05	-0.04	-0.02	
Lu	-0.23	-0.25	-0.19	-0.19	-0.16	-0.15	-0.12	-0.17	-0.11	-0.1	-0.07	-0.07	-0.05	-0.03

Table S18. Differences, in kJ/mol, to the data in Table S16 for lcecp-1-QZVP bases at Ln (def2-QZVP for the other elements).

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	0.04													
Pr	0.48	0.45												
Nd	0.54	0.5	0.06											
Pm	0.73	0.7	0.25	0.19										
Sm	0.85	0.81	0.36	0.3	0.11									
Eu	1.00	0.96	0.52	0.46	0.26	0.15								
Gd	1.03	0.99	0.54	0.48	0.29	0.18	0.03							
Tb	1.03	1.00	0.55	0.49	0.3	0.19	0.04	0.01						
Dy	1.15	1.12	0.67	0.61	0.42	0.31	0.16	0.13	0.12					
Ho	1.16	1.12	0.68	0.62	0.43	0.31	0.16	0.14	0.13	0.01				
Er	1.2	1.16	0.72	0.66	0.47	0.35	0.2	0.17	0.17	0.05	0.04			
Tm	1.18	1.14	0.69	0.63	0.44	0.33	0.18	0.15	0.14	0.02	0.01	-0.02		
Yb	1.12	1.08	0.64	0.58	0.38	0.27	0.12	0.09	0.08	-0.04	-0.04	-0.08	-0.06	
Lu	1.57	1.54	1.09	1.03	0.84	0.73	0.57	0.55	0.54	0.42	0.41	0.37	0.4	0.46

Table S19. Differences, in kJ/mol, to the data in Table S16 for lcecp-1-TZVP bases at Ln (def2-TZVP for the other elements).

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	0.06													
Pr	1.07	1.01												
Nd	1.07	1.01	0											
Pm	1.45	1.39	0.38	0.37										
Sm	1.75	1.69	0.68	0.68	0.3									
Eu	2.12	2.07	1.05	1.05	0.68	0.37								
Gd	1.99	1.93	0.92	0.92	0.54	0.24	-0.13							
Tb	2.18	2.12	1.11	1.11	0.73	0.43	0.05	0.19						
Dy	2.17	2.11	1.1	1.1	0.72	0.42	0.05	0.18	-0.01					
Ho	2.22	2.17	1.15	1.15	0.78	0.47	0.1	0.23	0.05	0.05				
Er	2.48	2.42	1.41	1.41	1.03	0.73	0.35	0.49	0.3	0.31	0.25			
Tm	2.07	2.01	1	1	0.62	0.32	-0.05	0.08	-0.11	-0.1	-0.16	-0.41		
Yb	2.44	2.38	1.37	1.37	0.99	0.69	0.32	0.45	0.26	0.27	0.22	-0.04	0.37	
Lu	4.39	4.33	3.32	3.32	2.94	2.64	2.27	2.4	2.21	2.22	2.17	1.91	2.32	1.95

Table S20. Differences, in kJ/mol, to the data in Table S16 for lcecp-1-SV(P) bases at Ln (def2-SV(P) for the other elements).

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	1.02													
Pr	3.35	2.33												
Nd	3.68	2.66	0.33											
Pm	5.23	4.21	1.88	1.55										
Sm	6.24	5.22	2.89	2.56	1.01									
Eu	7.08	6.06	3.73	3.39	1.85	0.84								
Gd	6.91	5.88	3.56	3.22	1.67	0.67	-0.17							
Tb	7.33	6.31	3.98	3.65	2.1	1.09	0.25	0.43						
Dy	7.27	6.25	3.92	3.59	2.04	1.03	0.19	0.36	-0.06					
Ho	7.28	6.26	3.93	3.59	2.04	1.04	0.2	0.37	-0.05	0.01				
Er	7.7	6.68	4.35	4.02	2.47	1.46	0.62	0.8	0.37	0.43	0.43			
Tm	6.79	5.77	3.44	3.11	1.56	0.55	-0.28	-0.11	-0.54	-0.48	-0.48	-0.91		
Yb	7.19	6.17	3.84	3.51	1.96	0.95	0.11	0.28	-0.14	-0.08	-0.09	-0.51	0.4	
Lu	11.32	10.29	7.97	7.63	6.08	5.08	4.24	4.41	3.98	4.05	4.04	3.61	4.52	4.13

Table S21. Differences, in kJ/mol, to the data in Table S16 for DSSP[3] bases at Ln (def2-TZVP for the other elements).

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	1.45													
Pr	2.92	1.48												
Nd	4.17	2.72	1.25											
Pm	4.68	3.23	1.76	0.51										
Sm	5.6	4.15	2.68	1.43	0.92									
Eu	6.56	5.12	3.64	2.39	1.88	0.96								
Gd	7.86	6.41	4.93	3.68	3.18	2.26	1.29							
Tb	8.26	6.82	5.34	4.09	3.58	2.66	1.7	0.41						
Dy	9.1	7.65	6.17	4.92	4.42	3.5	2.53	1.24	0.83					
Ho	9.89	8.45	6.97	5.72	5.21	4.29	3.33	2.04	1.63	0.8				
Er	10.61	9.16	7.68	6.43	5.93	5.01	4.04	2.75	2.34	1.51	0.71			
Tm	11.3	9.85	8.37	7.13	6.62	5.7	4.73	3.44	3.03	2.2	1.4	0.69		
Yb	11.92	10.47	8.99	7.75	7.24	6.32	5.35	4.06	3.65	2.82	2.03	1.31	0.62	
Lu	16.97	15.53	14.05	12.8	12.29	11.37	10.41	9.12	8.71	7.88	7.08	6.37	5.68	5.05

Table S22. Differences, in kJ/mol, for the PBE0 energies of exchange reactions of type $Ln^AH_3+Ln^BCl_3\rightarrow$ $Ln^ACl_3+Ln^BH_3$ between a) scalar relativistic all-electron X2C treatments with x2c-QZVPPall bases used throughout and b) lcecp-1 ECPs and lcecp-1-QZVPP bases at Ln and def2-QZVPP bases for Cl and H.

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	-4.53													
Pr	-4.64	-0.11												
Nd	-8.33	-3.8	-3.69											
Pm	-16.95	-12.42	-12.31	-8.62										
Sm	-21.08	-16.54	-16.43	-12.75	-4.13									
Eu	-23.84	-19.31	-19.2	-15.51	-6.89	-2.76								
Gd	-5.15	-0.62	-0.51	3.18	11.8	15.92	18.69							
Tb	-9.17	-4.63	-4.52	-0.84	7.78	11.91	14.67	-4.01						
Dy	-8.84	-4.31	-4.2	-0.51	8.11	12.24	15	-3.69	0.33					
Ho	-8.16	-3.63	-3.52	0.17	8.79	12.92	15.68	-3.01	1.01	0.68				
Er	-13.78	-9.25	-9.14	-5.45	3.17	7.3	10.06	-8.63	-4.61	-4.94	-5.62			
Tm	-14.13	-9.6	-9.49	-5.8	2.82	6.94	9.71	-8.98	-4.97	-5.29	-5.97	-0.35		
Yb	-12.68	-8.15	-8.04	-4.35	4.27	8.39	11.16	-7.53	-3.52	-3.84	-4.52	1.1	1.45	
Lu	-6.48	-1.95	-1.84	1.85	10.47	14.6	17.36	-1.33	2.69	2.36	1.68	7.3	7.65	6.2

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