Unraveling the electronic structure of LuH, LuN, and LuNH: Building blocks of potential new materials

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Table S1 - CI vectors from CASSCF calculations for the equilibrium bond lengths of LuH. 0, α, β, and 2, correspond to orbital occupations: zero, one (α-spin), one (β-spin), and two (doubly occupied). CI vectors with weights above 0.25 were considered.

States	Coeff	$1s$ (H)	$6s$ (Lu)	$6p_z$ (Lu)	$5d_{x2-y2}$ (Lu)	$5d_{z2}$ (Lu)+ $2s$ (H)	$6p_x$ (Lu)	$5d_{xz}$ (Lu)	$6p_y$ (Lu)	$5d_{yz}$ (Lu)	$5d_{xy}$ (Lu)
$X^1\Sigma^+$	0.94	2	2	0	0	0	0	0	0	0	0
$1^3\Delta$	0.98	2	α	0	α	0	0	0	0	0	0
$1^3\Pi$	0.96	2	α	0	0	0	α	0	0	0	0
$1^3\Sigma^+$	0.97	2	α	α	0	0	0	0	0	0	0
$1^1\Delta$	0.61	2	α	0	β	0	0	0	0	0	0
	0.61	2	β	0	α	0	0	0	0	0	0
$1^1\Pi$	-0.59	2	α	0	0	0	0	β	0	0	0
	0.59	2	β	0	0	0	0	α	0	0	0
$2^3\Pi$	0.94	2	α	0	0	0	0	α	0	0	0
$2^1\Sigma^+$	0.60	2	α	β	0	0	0	0	0	0	0
	-0.60	2	β	α	0	0	0	0	0	0	0
$2^1\Pi$	-0.47	2	α	0	0	0	β	0	0	0	0
	0.47	2	β	0	0	0	α	0	0	0	0

Table S2 - Bond lengths (R_e), harmonic vibrational frequencies (ω_e), anharmonicity constants ($\omega_e\chi_e$), $\Delta G_{1/2}$, and excitation energies (T_e) for the lowest electronic excited states of LuH. The state compositions were obtained at the ground state equilibrium bond length. MRCI spin-orbit calculations were performed using cc-pVTZ-DK3 for Lu and aug-cc-pVTZ-DK with DKH3.

States	R_e (Å)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	$\Delta G_{1/2}$ (cm^{-1})	T_e (cm^{-1})	Composition
$X^1\Sigma^+{}_{0+}$	1.927	1539.2	54.3	1430.6	0	99.71% $X^1\Sigma^+$, 0.30% $1^3\Pi$
	1.906[1]	1540.98	22.06	-	0	-
$1^3\Pi_{0-}$	1.952	1519.2	76.2	1366.8	11105.7	77.30% $^3\Pi$, 22.70 $1^3\Sigma^+$
	1.947[1]	1456.30	42.53		10797	-
$1^3\Delta_1$	1.973	1435.9	59.8	1316.4	11871.0	56.11% $1^3\Pi$, 41.89% $1^3\Delta$, 9.07% $1^3\Sigma^+$
	1.951[1]	1442.10	39.59	-	12873	-

$1^3\Pi_{0+}$	1.951	1420.2	32.7	1346.2	12133.2	99.70% 1³Π, 0.30% X¹Σ⁺
	1.936[1]	1474.71	40.47	-	11838	-
$1^3\Delta_2$	1.981	1419.0	50.6	1317.8	12700.1	81.65% 1³Δ, 13.20% 1³Π, 5.16% 1¹Δ
	1.939[1]	1471.51	42.98	-	14498	-
$1^3\Pi_1$	1.962	1420.2	32.7	1356.1	12730.9	56.11% 1³Π, 34.82% 1³Δ, 9.07% 1³Σ⁺
	1.951[1]	1448.38	43.02	-	11506	--
$1^1\Delta_3$	1.974	1573.2	32.7	-	14009.8	1³Δ 100%
	1.945[1]	1457.80	44.66	-	15342	
$1^3\Pi_2$	1.958	1434.4	17.9	1398.5	14503.3	84.90% 1³Π, 14.79% 1³Δ, 0.32% 1¹Δ
	1.953[1]	1436.15	23.61	-	1436.15	
$1^3\Sigma^+_1$	1.963	1403.2	30.9	1341.3	15248.8	70.04% 1³Σ⁺, 29.17% 1³Π, 0.79% 1³Δ
	1.945[1]	1467.16	42.04	-	14163	-
$1^3\Sigma^+_{0-}$	1.964	1532.2	41.17	-	15401.1	77.31% 1³Σ⁺, 22.70% 1³Π
	1.951[1]	1457.14	42.91	-	14057	-
$1^1\Delta_2$	1.998	1578.4	45.86	-	16944.2	94.56% 1¹Π, 3.54% 1³Δ, 1.90% 1³Π
	1.976[1]	1413.90	42.35	-	16798	-

Table S3 - CI vectors from CASSCF calculations for the equilibrium bond lengths of LuN. 0, α, β, and 2, correspond to orbital occupations: zero, one (α-spin), one (β-spin), and two (doubly occupied). CI vectors with weights above 0.25 were considered. The $3p_{x,y,z}$ of nitrogen were omitted, because their occupation is always zero.

States	R_{eq} (Å)	Coeff	$2p_z$ (N)	$6s$ (Lu)	$5d_{x^2-y^2}$ (Lu)	$6p_z$ (Lu)	$5d_{z^2}$ (Lu)	$2p_x$ (N)	$6p_x$ (Lu)	$5d_{xz}$ (Lu)	$2p_y$ (N)	$6p_y$ (Lu)	$5d_{yz}$ (Lu)	$5d_{xy}$ (Lu)
$X^1\Sigma^+$	1.85	0.54	2	0	0	0	0	2	0	0	2	0	0	0
		-0.46	β	α	0	0	0	2	0	0	2	0	0	0
		0.46	α	β	0	0	0	2	0	0	2	0	0	0
$1^3\Sigma^+$	1.85	0.89	α	α	0	0	0	2	0	0	2	0	0	0
$1^3\Pi$	1.95	-0.43	α	2	0	0	0	α	0	0	2	0	0	0
		0.79	2	α	0	0	0	α	0	0	2	0	0	0
$1^1\Pi$	1.95	0.61	2	β	0	0	0	α	0	0	2	0	0	0
		-0.61	2	α	0	0	0	β	0	0	2	0	0	0
$1^3\Sigma^-$	2.20	0.94	2	2	0	0	0	α	0	0	α	0	0	0
$1^3\Delta$	2.00	0.44	2	0	0	0	0	2	0	0	α	α	0	0
		-0.44	2	0	0	0	0	α	α	0	2	0	0	0
		-0.29	α	α	0	0	0	α	β	0	2	0	0	0
		0.29	α	α	0	0	0	2	0	0	α	β	0	0
		0.26	α	α	0	0	0	β	α	0	2	0	0	0
		-0.26	α	α	0	0	0	2	0	0	β	α	0	0
$2^3\Pi$	2.20	0.42	α	2	0	0	0	α	0	0	2	0	0	0
		0.66	2	α	0	0	0	α	0	0	2	0	0	0

Table S4 - Bond lengths (R_e), harmonic vibrational frequencies (ω_e), anharmonicity constants ($\omega_e\chi_e$), $\Delta G_{1/2}$, and excitation energies (T_e) for the lowest electronic excited states of LuN. The state compositions were obtained at the ground state equilibrium bond length. MRCI spin-orbit calculations were performed using ECPMWB28-Seg for Lu and aug-cc-pVTZ for N.

States	R_e (Å)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	$\Delta G_{1/2}$ (cm^{-1})	T_e (cm^{-1})	Composition
$X^1\Sigma^+_{0+}$	1.876	790.3	6.2	777.8	0	97.26% $X^1\Sigma^+$, 2.72% $^3\Pi$
$1^3\Sigma^+_{0-}$	1.848	802.7	13.6	775.6	3215.3	99.64% $1^3\Pi$, 0.35% $^3\Pi$
$1^3\Sigma^+_1$	1.848	814.1	33.8	746.4	3219.9	97.89% $1^3\Sigma^+$, 0.98% $1^1\Pi$, 0.93% $1^3\Pi$, 0.20% $1^3\Pi$
$1^3\Pi_2$	2.001	-	-	-	3895.4	100% $1^3\Pi$
$1^3\Pi_1$	2.002	-	-	-	4392.9	96.35% $1^3\Pi$, 3.16% $1^1\Pi$, 0.49% $2^3\Pi_1$, $1^3\Sigma^+$ 0.01%
$1^1\Pi_1$	1.922	883.2	42.6	798.0	6574.8	98.58% $1^3\Pi$, 1.06% $2^3\Pi$, 0.36% $1^3\Sigma^+$
$1^3\Pi_{0-}$	1.942	-	-	-	4629.6	99.64% $1^3\Pi$, 0.35%
$1^3\Pi_{0+}$	1.982	-	-	-	4621.8	96.09% $1^1\Pi$, 2.98% $1^3\Pi$, 0.58% $2^3\Pi$, 0.35% $1^3\Sigma^+$
$1^1\Pi_1$	1.922	883.2	42.6	798.0	6574.8	97.26% $X^1\Sigma^+$, 2.72% $1^3\Pi$

Table S5 - CI vectors from CASSCF calculations for the equilibrium bond lengths of LuNH. 0, α, and 2, correspond to orbital occupations: zero, one (α-spin), and two (doubly occupied). CI vectors with weights above 0.25 were considered.

States	R_{eq} (Å)	Coeff	$2p_z$ (N) +1s (H)	$6s$ (Lu)	$5d_{x^2-y^2}$ (Lu)	$6p_z$ (Lu)	$5d_{z^2}$ (Lu)	$2p_x$ (N)	$6p_x$ (Lu)	$5d_{xz}$ (Lu)	$2p_y$ (N)	$6p_y$ (Lu)	$5d_{yz}$ (Lu)	$5d_{xy}$ (Lu)
$X^2\Sigma^+$	1.85	0.92	2	α	0	0	0	2	0	0	2	0	0	0
$1^2\Pi$	2.00	0.93	2	2	0	0	0	α	0	0	2	0	0	0
$1^4\Sigma^+$	2.10	0.69	2	α	0	0	0	α	α	0	2	0	0	0
		0.69	2	α	0	0	0	2	0	0	α	α	0	0

Table S6: Symmetries, bond lengths (R_e), angles, harmonic vibrational frequencies (ω_e), and excitation energies (T_e) of the LuNH isomers.

Structure	R_e (Å)	Angle - N-Lu-H (º)	ω_e (cm^{-1})	T_e (cm^{-1})
^{2}A' – N-Lu-H	1.866 (Lu-N)	123.9	278.80, 743.47	21373.5
	1.968 (N-H)		1448.91	
^{4}A' – N-Lu-H	2.076 (Lu-N)	132.2	187.62, 465.08	22915.9
	1.946 (N-H)		1469.15	
^{2}B$_2$ – N-Lu-H	1.869 (Lu-N)	180.0	243.89	29365.4
	2.047 (N-H)		758.26, 1356.92	
^{4}B$_2$ – N-Lu-H	2.112 (Lu-N)	180.0	194.00	29977.5
	1.983 (N-H)		545.15, 1452.16	

Table S7 - Bond lengths (R_e), harmonic vibrational frequencies (ω_e), anharmonicity constants ($\omega_e\chi_e$), $\Delta G_{1/2}$, excitation energies (T_e) for the lowest electronic excited states of LuNH. The state compositions were obtained at the ground state equilibrium bond length. MRCI spin-orbit calculations were performed using ECPMWB28-Seg for Lu and aug-cc-pVTZ for N and H.

States	R_e (Å)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	$\Delta G_{1/2}$ (cm^{-1})	T_e (cm^{-1})	Composition

$X^2\Sigma^+_{1/2}$	1.892	801.4	-2.8	802.7	0	99.78 $X^2\Sigma^+$, 0.22% $1^2\Pi$
$1^2\Pi_{3/2}$	2.081	541.6	-2.7	541.6	5748.9	100% $1^2\Pi$
$1^2\Pi_{1/2}$	2.094	595.7	3.9	590.1	5331.0	99.78% $1^2\Pi$, 0.22% $X^2\Sigma^+$

Table S8: Bond dissociation energy contributions from f-ccCA. All results are in kcal mol^{-1}.

	LuH	LuN	NH	1) LuNH→LuN+H	2) LuNH→Lu+NH	3) LuNH→Lu+N+H
HF/triple-ζ	63.15	-24.75	48.35	140.71	67.61	115.96
HF/quadruple-ζ	63.25	-24.54	48.46	140.86	67.87	116.33
HF/CBS	63.27	-24.48	48.49	140.91	67.93	116.43
MP2/double-ζ	9.17	80.71	25.34	-0.34	55.03	80.37
MP2/triple-ζ	8.97	82.81	29.75	4.93	58.00	87.74
MP2/quadruple-ζ	8.64	84.03	30.62	6.82	60.21	90.84
MP2/CBS	8.43	84.78	31.07	7.90	61.61	92.68
ZPE	-2.13	-1.08	-4.66	-6.78	-3.20	-7.86
ΔCCSD(T)	5.98	26.82	2.46	-35.84	-11.49	-9.02
Core-valence double-ζ	0.73	0.79	0.15	0.72	1.36	1.51
Spin-orbit	-3.32	-2.88	0.00	0.06	-3.36	-3.36
f-ccCA D_0	72.96	83.95	77.50	106.96	112.86	190.36

Table S9: Bond dissociation energy contributions from HEAT. All results in kcal mol^{-1}. For LuNH CCSDT/cc-pVQZ was intractable so it was not calculated.

	LuH	LuN	NH	1) LuNH→LuN+H	2) LuNH→Lu+NH	3) LuNH→Lu+N+H
HF/double-ζ	62.53	-28.59	46.91	140.68	65.18	112.09
HF/triple-ζ	63.00	-25.38	48.27	141.26	67.61	115.88
HF/quadruple-ζ	63.15	-24.65	48.46	140.98	67.87	116.33
CBS	63.16	-25.15	48.38	140.89	67.37	115.74
CCSD/triple-ζ	15.19	84.05	31.11	-12.53	40.41	71.52
CCSD/quadruple-ζ	14.85	87.74	32.37	-12.40	42.97	75.33
CBS (CCSD)	14.60	90.43	33.29	-12.32	44.83	78.12
CCSD(T)/triple-ζ	-0.17	22.06	0.88	-15.08	6.10	6.99
CCSD(T)/quadruple-ζ	-0.21	23.42	1.37	-15.67	6.39	7.76
CBS (CCSD(T))	-0.23	24.42	1.72	-16.10	6.60	8.32
Core valence/triple-ζ	-0.29	3.67	0.47	-3.69	-0.49	-0.02
Core valence/quadruple-ζ	-0.20	1.21	-0.02	-1.55	-0.33	-0.34
CBS (core-valence)	-0.14	-0.59	-0.37	0.01	-0.21	-0.58
ZPE	-2.13	-1.08	-4.66	-6.78	-3.20	-7.86
Spin-orbit	-3.32	-2.88	0.00	-0.48	-3.36	-3.36
CCSDT/triple-ζ	-0.16	-9.35	0.07	8.74	-0.68	-0.61
CCSDT/quadruple-ζ	-0.11	-9.74	0.00	-	-	-
CBS (CCSDT)	-0.07	-10.03	-	-	-	-

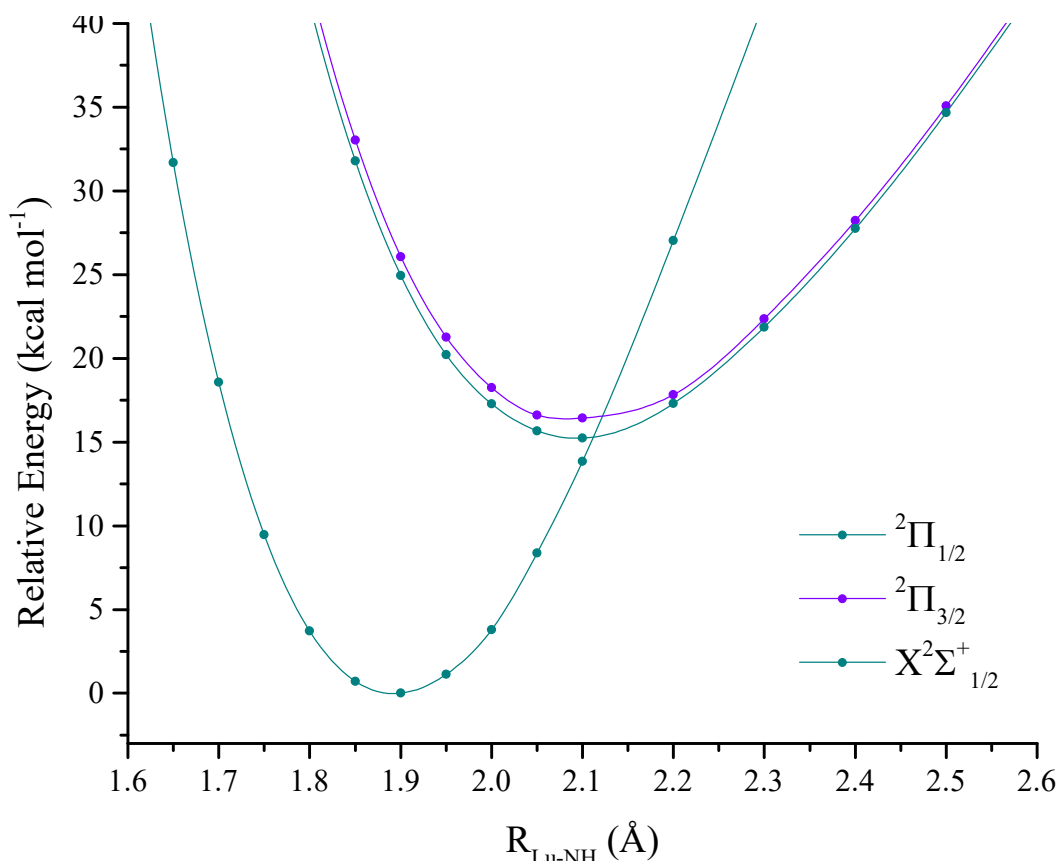| CCSDT-λ(Q)/double-ζ	-0.20	3.38	0.05	-2.91	0.41	0.46
HEAT D$_0$	71.67	78.50	78.47	111.05	111.76	190.23

Figure S1 - LuNH core MRCI+Q spin-orbit potential energy curves (kcal mol^{-1}) as a function of the Lu-NH distance

Extended Computational Details

The f-block ab initio correlation consistent composite approach (f-ccCA) and the high accuracy extrapolated *ab initio* thermochemistry (HEAT) scheme were used to determine the bond dissociation energies (BDEs) of LuH, LuN, as well as the different dissociation channels for LuNH. f-ccCA attempts to approximate coupled cluster singles, doubles and perturbative triples, extrapolated to the complete basis set limit with the core-valence electrons correlated, and relativistic effects addressed with third-order Douglas-Kroll-Hess core-valence (CCSD(T)-CV-DK3/CBS). HEAT in this study is used to approximate a full configuration interaction extrapolated to the complete basis set limit with core-valence electrons correlated and relativistic effects handled with a third-order Douglas-Kroll-Hess Hamiltonian (FCI-CV-DK3/CBS). Ref [2,3] provide the full details of these composites, with an overview of the scheme shown here.

Throughout the f-ccCA composite scheme third-order Douglas Kroll Hess (DKH3) is used to account for relativistic effects.

Eqn. 1 shows the components of f-ccCA

(1) E(f-ccCA) = E_0(f-ccCA) + ΔE(CC) + ΔE(CV) + ΔZPE + ΔE(SO)

E(f-ccCA) is the reference energy, ΔE(CC) is the correlation contribution to the total energy, ΔE(CV) is a term that accounts for core-valence correlation energy, ΔZPE is the zero-point energy, and ΔE(SO) the spin-orbit contribution, particularly important for the heavy elements.

E_0(f-ccCA) the reference energy of E(f-ccCA) is the sum of Hartree-Fock and Møller-Plesset second order (MP2) at complete basis set level with extrapolated energies. The Hartree Fock complete basis set energy is determined with the cc-pVTZ-DK3 and cc-pVQZ-DK3 basis sets for Lu[4] and aug-cc-pVTZ-DK, and aug-cc-pVQZ-DK for the lighter elements.[5–7] The energies are extrapolated to the CBS limit with the following formula[8,9]:

(2) $E(n)=E_{CBS}+A*exp(-1.63n)$

The MP2 contribution to E_0(f-ccCA) is determined with the inverse gaussian formula of Peterson and workers[10]:

(3) $E(n)=E_{CBS}+Aexp[-(n-1)]+Bexp[-(n-1)^2]$

using energies determined with the cc-pVnZ-DK3 (n=D,T,Q) basis sets for Lu, and the aug-cc-pVnZ-DK sets for the light elements. In equation 3 A and B are determined during the fitting of the energies. To account for electron correlation beyond MP2, coupled cluster singles, doubles, and perturbative triple excitations (CCSD(T)) with cc-pVTZ-DK3 for Lu and cc-pVTZ-DK for the light elements was used.

(4) E(CC) = E[CCSD(T)/cc-pVTZ-DK]-E[MP2/cc-pVTZ-DK]

To correct for missing core-valence and core-core correlation E(CV), CCSD(T) was paired with the cc-pwCVDZ[4] basis set with, and without core-electrons

(5) E(CV)=E[CCSD(T,FC1)/cc-pwCVDZ-DK3]-E[CCSD(T)/cc-pwCVDZ-DK3]

FC1 (Frozen Core 1) corresponds to the sub-valence computation. For Lu this corresponds to correlating the 4s, 4p, and 4d electrons beyond the 5s, 5p, 6s, 4f, and 5d electrons of lutetium. For nitrogen, it corresponds to correlating the 1s orbital. ZPE was obtained from a CCSD(T)/cc-pVTZ-DK3 optimization and frequency computation. The spin-orbit coupling E(SO) is computed with the following equation:

(6) E(SO)=SO(LuH, LuH, LuNH) – SO(Xi)

Where SO (LuH, LuN, LuNH) is the spin-orbit correction for the molecular species, and SO(Xi) is the atomic spin-orbit. For the atomic spin-orbit this is derived from j-averaging the energy levels obtained from NIST. The j-averaging is performed with the following equation:

(7) $SO(X_i) = \frac{\sum_J (2J+1)\Delta E_J}{\sum_J (2J+1)}$

J is the total angular momentum of the state and ΔE_J is the energy difference between the ground state and state J energies. For the molecular spin-orbit correction term, a multireference wavefunction was constructed with a mixture of ground and close lying excited states to obtain the spin-orbit correction.[11,12]

HEAT was adapted from Ref. [2] with a few modifications for a lutetium-containing molecular system; third-order Douglas-Kroll-Hess was used throughout to account for one-electron scalar relativistic effects. The

extrapolations for Hartree-Fock and the CCSD and (T) contributions were taken from Ref. [13] . Throughout this portion of the work ROHF references are used throughout.

HEAT consists of a series of computations to approximate a relativistic full configuration interaction (FCI) energy at a comparatively reduced cost. Equation 8 shows the implementation of HEAT.

(8) $E_{HEAT} = E_{HF} + E_{CCSD} + E_{(T)} + \Delta E_{CV} + \Delta E_{CCSDT} + \Delta E_{\Lambda\text{-CCSDT(Q)}} + E_{ZPE} + \Delta E_{SO}$

The Diagonal Born Oppenheimer Correction, which is usually included in the HEAT composite scheme, was not included due to convergence issues.

E_{HF} was extrapolated with the formula of Feller[14] with the cc-pVDZ-DK3, cc-pVTZ-DK3, and cc-pVQZ-DK3 sets on lutetium, and the aug-cc-pVDZ-DK, aug-cc-pVTZ-DK, and aug-cc-pVQZ-DK basis sets on H and N.

(9) $E_{HF} = E_{HF} + a\exp(-bX)$

E_{CCSD} and $E_{(T)}$ are extrapolated with the cc-pVTZ-DK3 and cc-pVQZ-DK3 sets on luteium, and aug-cc-pVTZ-DK and aug-cc-pVQZ-DK. The simple X^3 equation of Helgaker is used for both energies.[15]

(10) $E_{CCSD} = E_{CCSD} + ax^3$

(11) $E_{(T)} = E_{(T)} + ax^3$

The E_{CV} term is the difference between the CBS extrapolated core-valence definition used in *f*-ccCA and the frozen core CBS limit

(12) ECCSD(T,FC1)/CBS – ECCSD(T,VAL)

where for FC1 the cc-pWCVTZ-DK3 and cc-pWCVQZ-DK3 sets were used for the E(CCSDT,FC1)/CBS computations, and cc-pVTZ-DK3 and cc-pVQZ-DK3 for the frozen-core ECCSD(T,VAL) computation. For the light atoms (H, N) aug-cc-pCVTZ-DK and aug-cc-pCVQZ-DK were used.[16] Both energies were extrapolated with the Helgaker formula as in eqn. (10).

The E_{CCSDT} energy[17] was extrapolated to the CBS limit using eqn. (10). CCSD(T) is extrapolated with this equation as well with the cc-pVTZ-DK3 and cc-pVQZ-DK3 basis sets for Lu, and cc-pVTZ-DK and cc-pVQZ-DK on N and H.

(13) E_{CCSDT} = CCSDT(CBS) – CCSD(T)(CBS)

Eqn. (13) could only be performed with cc-pVTZ-DK3/cc-pVTZ-DK for LuNH due to the extreme costs.

Full iterative quadruples were intractable for even LuH, which lead to the need to for a treatment of quadruples. Perturbative quadruples approaches exist but are known to have issues with pathological systems (see LuN's CI vectors). Λ-CCSDT(Q) has been shown to obtain accurate results for the well-known multireference O_3[18], and was used to account for excitations beyond full triples.[19] This was done with the cc-pVDZ-DK3 set on lutetium, and cc-pVDZ-DK on N and H. Eqn. (12) shows the implementation.

(14) $E_{\Lambda\text{-CCSDT(Q)}} = E_{\Lambda\text{-CCSDT(Q)}} - E_{CCSDT}$

The geometry and ZPE used throughout this were obtained as per *f*-ccCA; the spin-orbit was obtained with the same strategy as in *f*-ccCA and will not be expanded upon further. All computations for *f*-ccCA were performed with MOLPRO 2020. All CCSD(T)[20] computations for HEAT were performed with MOLPRO 2020.[21] The higher order coupled cluster computations in HEAT were performed with MRCC.[22]

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