Supplementary Information: Greater Transferability and Accuracy of Norm-conserving Pseudopotentials using Nonlinear Core Corrections

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Table S1. Electronic configurations of core and valence regions for pseudopotentials of elements studied.

Element	Functional	NLCC	Core	Valence
H, Li, Be	PBE	N	None	All
	PBE0	N	None	All
	ωB97M-rV	N	None	All
	B97M-rV	N	None	All
B, C, N, O, F	PBE	Y	[He]	$2s^2 2p^x$
	PBE0	Y	[He]	$2s^2 2p^x$
	ωB97M-rV	Y	[He]	$2s^2 2p^x$
	B97M-rV	Y	[He]	$2s^2 2p^x$
Na, Mg	PBE	N	[Ne]	$3s^2 3p^x$
	PBE0	N	[Ne]	$3s^2 3p^x$
	ωB97M-rV	N	[Ne]	$3s^2 3p^x$
	B97M-rV[a]	N	[Ne]	$3s^2 3p^x$
Al, Si, P, S, Cl	PBE	Y	[Ne]	$3s^2 3p^x$
	PBE0	Y	[Ne]	$3s^2 3p^x$
	ωB97M-rV	Y	[Ne]	$3s^2 3p^x$
	B97M-rV[a]	N	[Ne]	$3s^2 3p^x$

[a] At the B97M-rV level, we initially tried to optimize the third-row elements. However, due to substantial errors, we were unable to obtain reliable results. Therefore, we resorted to using the GTH/MOLOPT method without B97M-rV to generate accurate results for these heavier elements.

Table S2. Comparison of mean absolute deviations (kcal/mol) for a specific atom type within the G2 dataset.[1–3] Predictions were made at the PBE and B97M-rV levels using the complete basis set def2-TZVPPD, with and without NLCC correction.

Functional	Pseudopotential/Basis	B	C	N	O	F
PBE	GTH/def2-TZVPPD	12.76	20.52	22.19	19.51	16.58
	GTH-NLCC-2013/def2-TZVPPD	2.44	2.19	1.56	1.28	9.13
B97M-rV	GTH/def2-TZVPPD	29.90	29.42	38.98	24.47	18.25
	GTH-NLCC-OPT-all[a]/def2-TZVPPD	27.55	11.28	10.79	11.14	9.00
	GTH-NLCC-OPT[b]/def2-TZVPPD	4.07	6.43	10.70	6.68	8.06
Functional	Pseudopotential/Basis	Al	Si	P	S	Cl
PBE	GTH/def2-TZVPPD	4.11	2.83	2.91	9.40	7.71
	GTH-NLCC-2013/def2-TZVPPD	8.34	2.23	1.30	1.21	6.62
B97M-rV	GTH/def2-TZVPPD	4.22	5.96	7.85	11.38	10.19
	GTH-NLCC-OPT-all[a]/def2-TZVPPD	25.61	10.26	9.03	30.51	18.92
	GTH-NLCC-OPT[b]/def2-TZVPPD	2.86	5.10	7.17	4.17	2.80

[a] GTH-NLCC-OPT-all means that NLCC parameters are optimized for all elements including the second and third rows.[b] GTH-NLCC-OPT means that NLCC parameters are optimized only for the second-row elements.

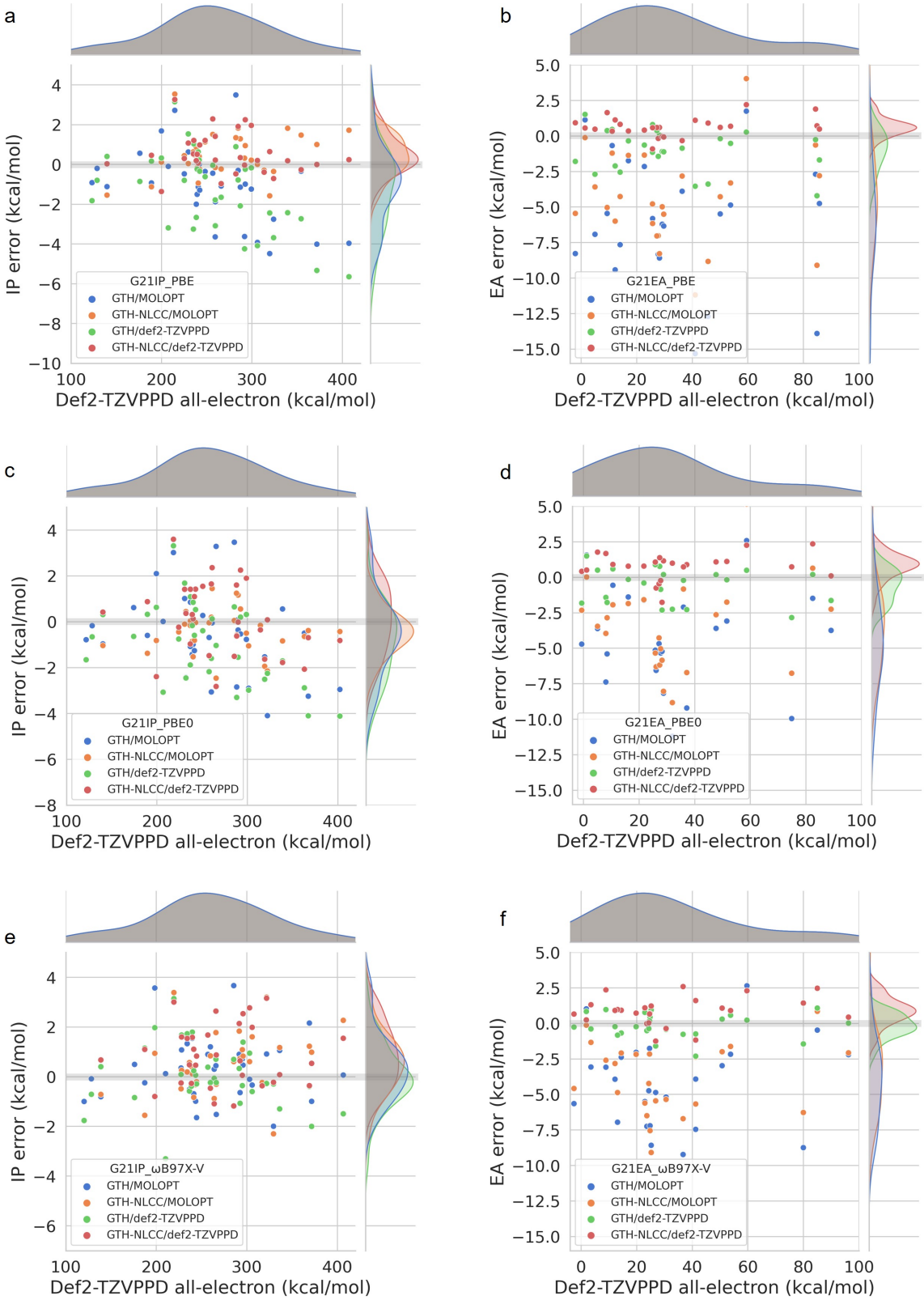

Figure S1: Distributions of MADs and all-electron calculations at the levels of PBE, PBE0 and ωB97X-V for IP and EA datasets.[4,5]

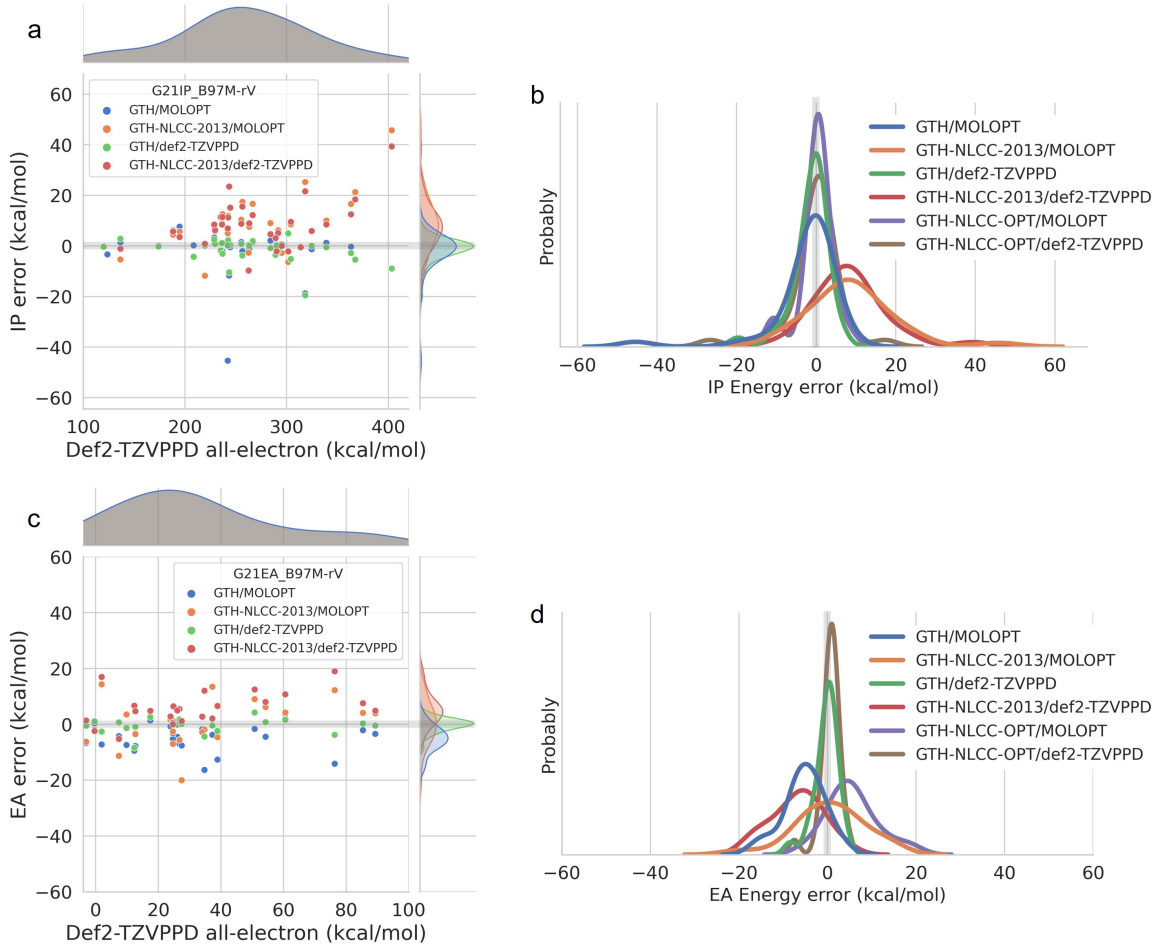

Figure S2: Distributions of MADs and all-electron calculations at the level of B97M-rV for IP and EA datasets.

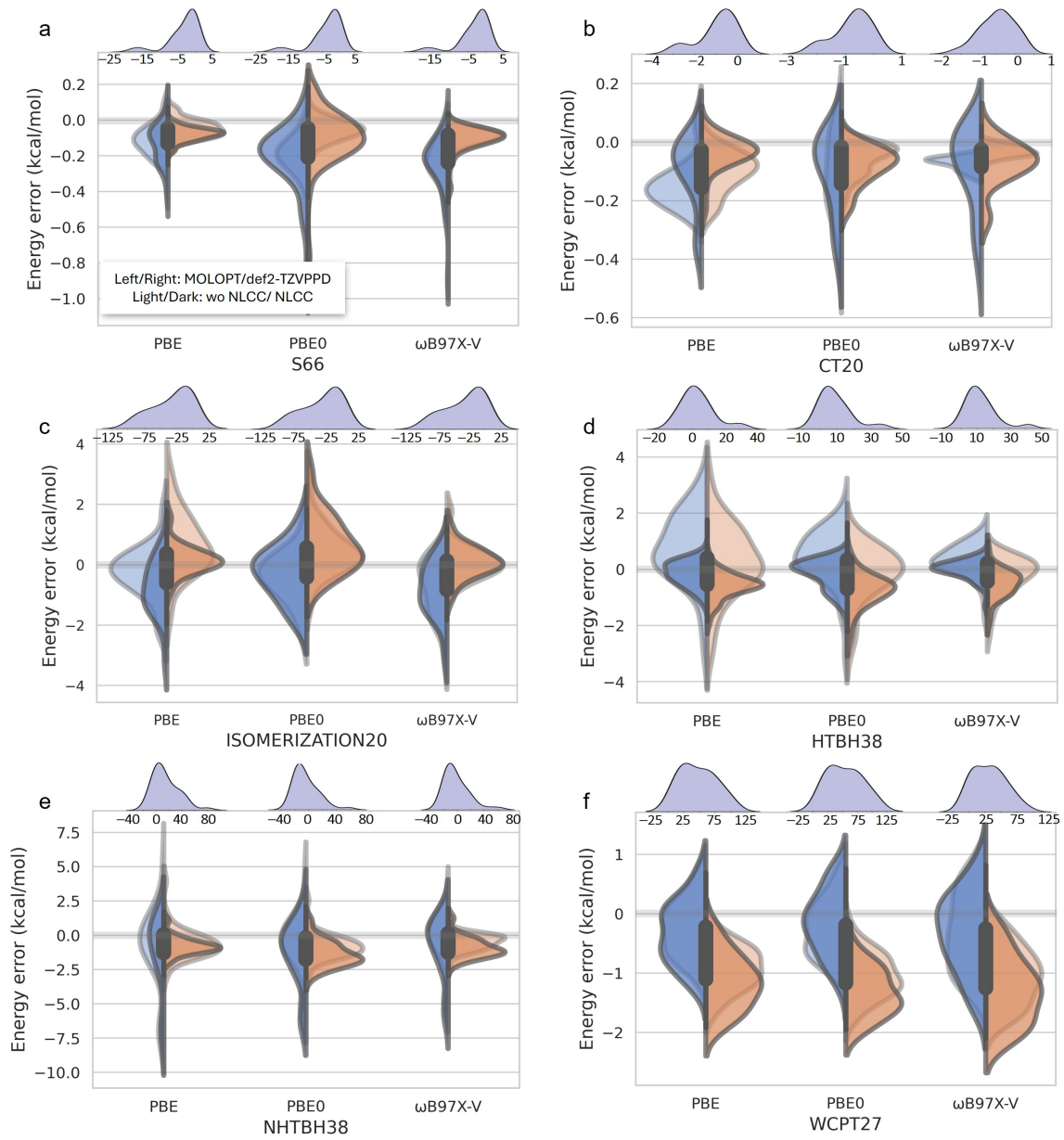

Figure S3: NLCC performance on non-thermochemical properties. The energy errors are compared with def2-TZVPPD all-electron calculations, of which the distribution and range are shown by the density plot on the top of each subplot.

References

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