Supplemental Information: Random Structure Searching with Orbital-free Density Functional Theory

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Preliminary Benchmarking: Equilibrium Volumes and Bulk Moduli

Tables S1 and S2 show the equilibrium volumes and bulk moduli corresponding to the relative energies in Table 1 of the main paper.

Table S1: Equilibrium volumes (\mathring{A}^3 /atom) for several elements and crystal structures as predicted by OFDFT using LPPs and eight variations of the same KE functional (Wang-Teter, Perrot, Smargiassi-Madden, and Wang-Govind-Carter, along with their exponential-stabilized forms) and as predicted by KSDFT using both LPPs (KS-L) and NLPPs (KS-NL). The italicized rows hold the optimized c/a ratios corresponding to the hcp structures.

Li												
	WT	WT-e	Р	Р-е	SM	SM-e	WGC	WGC-e	KS-L	KS-NL		
$\overline{\text{fcc}}$	20.2	20.3	20.3	20.4	19.9	20.0	20.2	20.3	20.2	20.2		
hcp	20.3	20.3	20.4	20.4	19.9	20.0	20.2	20.3	20.2	20.3		
c/a	1.63	1.63	1.63	1.63	1.63	1.63	1.63	1.63	1.63	1.63		
bcc	20.2	20.2	20.3	20.3	19.9	19.9	20.2	20.2	20.2	20.3		
sc	21.9	22.0	22.0	22.1	21.6	21.6	21.9	21.9	21.9	20.4		
cd	30.3	29.8	30.2	29.8	30.8	30.1	30.4	29.8	30.5	25.6		
Na												
	WT	WT-e	Р	Р-е	SM	SM-e	WGC	WGC-e	KS-L	KS-NL		
fcc	37.1	37.1	37.2	37.3	36.7	36.8	37.1	37.1	37.1	37.1		
hcp	37.1	37.2	37.3	37.3	36.8	36.8	37.1	37.1	37.1	37.2		
c/a	1.63	1.63	1.63	1.63	1.63	1.63	1.63	1.63	1.63	1.63		
bcc	37.0	37.1	37.2	37.2	36.7	36.7	37.0	37.1	37.0	37.1		
sc	39.7	39.7	39.8	39.8	39.4	39.4	39.7	39.7	39.6	39.8		
$_{\rm cd}$	53.0	51.7	52.8	51.7	54.4	52.3	53.2	51.9	53.4	54.8		
Mg												
	WT	WT-e	Р	Р-е	SM	SM-e	WGC	WGC-e	KS-L	IZC MI		
	*** 1	** I C		1 0	5111	DIVIC	Wac	wacc	IZO-L	KS-NL		
-hcp	23.1	23.2	23.4	23.5	21.5	21.9	23.0	23.1	22.9	22.9		
$\frac{1}{c/a}$		23.2 1.63	23.4 1.63	23.5 1.63	21.5 1.63	21.9 1.63	23.0 1.63	23.1 1.63		22.9 1.62		
_	23.1 1.63 23.2	23.2 1.63 23.3	23.4 1.63 23.6	23.5 1.63 23.6	21.5 1.63 21.8	21.9 1.63 22.1	23.0 1.63 23.2	23.1 1.63 23.3	22.9 1.63 23.1	22.9 1.62 23.1		
c/a	23.1 1.63	23.2 1.63 23.3 23.1	23.4 1.63	23.5 1.63 23.6 23.4	21.5 1.63 21.8 21.4	21.9 1.63 22.1 21.8	23.0 1.63 23.2 22.9	23.1 1.63	22.9 1.63 23.1 22.8	22.9 1.62		
$c/a \ m fcc$	23.1 1.63 23.2 23.0 27.2	23.2 1.63 23.3 23.1 27.1	23.4 1.63 23.6 23.4 27.4	23.5 1.63 23.6 23.4 27.3	21.5 1.63 21.8 21.4 26.5	21.9 1.63 22.1 21.8 26.5	23.0 1.63 23.2 22.9 27.2	23.1 1.63 23.3 23.0 27.1	22.9 1.63 23.1 22.8 27.1	22.9 1.62 23.1 22.9 27.5		
c/a fcc bcc	23.1 1.63 23.2 23.0	23.2 1.63 23.3 23.1	23.4 1.63 23.6 23.4	23.5 1.63 23.6 23.4	21.5 1.63 21.8 21.4	21.9 1.63 22.1 21.8	23.0 1.63 23.2 22.9	23.1 1.63 23.3 23.0	22.9 1.63 23.1 22.8	22.9 1.62 23.1 22.9		
c/a fcc bcc sc	23.1 1.63 23.2 23.0 27.2	23.2 1.63 23.3 23.1 27.1	23.4 1.63 23.6 23.4 27.4	23.5 1.63 23.6 23.4 27.3	21.5 1.63 21.8 21.4 26.5 41.8	21.9 1.63 22.1 21.8 26.5	23.0 1.63 23.2 22.9 27.2	23.1 1.63 23.3 23.0 27.1	22.9 1.63 23.1 22.8 27.1	22.9 1.62 23.1 22.9 27.5		
c/a fcc bcc sc	23.1 1.63 23.2 23.0 27.2	23.2 1.63 23.3 23.1 27.1	23.4 1.63 23.6 23.4 27.4	23.5 1.63 23.6 23.4 27.3	21.5 1.63 21.8 21.4 26.5 41.8	21.9 1.63 22.1 21.8 26.5 38.2	23.0 1.63 23.2 22.9 27.2	23.1 1.63 23.3 23.0 27.1	22.9 1.63 23.1 22.8 27.1	22.9 1.62 23.1 22.9 27.5		
c/a fcc bcc sc	23.1 1.63 23.2 23.0 27.2 39.5	23.2 1.63 23.3 23.1 27.1 37.8	23.4 1.63 23.6 23.4 27.4 40.1	23.5 1.63 23.6 23.4 27.3 38.0	21.5 1.63 21.8 21.4 26.5 41.8	21.9 1.63 22.1 21.8 26.5 38.2	23.0 1.63 23.2 22.9 27.2 40.0	23.1 1.63 23.3 23.0 27.1 38.0	22.9 1.63 23.1 22.8 27.1 39.9	22.9 1.62 23.1 22.9 27.5 40.3		
c/a fcc bcc sc cd	23.1 1.63 23.2 23.0 27.2 39.5	23.2 1.63 23.3 23.1 27.1 37.8 WT-e	23.4 1.63 23.6 23.4 27.4 40.1	23.5 1.63 23.6 23.4 27.3 38.0	21.5 1.63 21.8 21.4 26.5 41.8	21.9 1.63 22.1 21.8 26.5 38.2 Al SM-e	23.0 1.63 23.2 22.9 27.2 40.0	23.1 1.63 23.3 23.0 27.1 38.0 WGC-e	22.9 1.63 23.1 22.8 27.1 39.9 KS-L	22.9 1.62 23.1 22.9 27.5 40.3 KS-NL		
c/a fcc bcc sc cd fcc	23.1 1.63 23.2 23.0 27.2 39.5 WT 16.8	23.2 1.63 23.3 23.1 27.1 37.8 WT-e 16.8 16.9 1.66	23.4 1.63 23.6 23.4 27.4 40.1 P 17.0 17.1 1.66	23.5 1.63 23.6 23.4 27.3 38.0 P-e 17.0 17.1 1.66	21.5 1.63 21.8 21.4 26.5 41.8 SM 15.7 15.8 1.66	21.9 1.63 22.1 21.8 26.5 38.2 Al SM-e 15.8 15.9 1.66	23.0 1.63 23.2 22.9 27.2 40.0 WGC 16.7 16.8 1.66	23.1 1.63 23.3 23.0 27.1 38.0 WGC-e 16.8	22.9 1.63 23.1 22.8 27.1 39.9 KS-L 16.6 16.7 1.64	22.9 1.62 23.1 22.9 27.5 40.3 KS-NL 16.5 16.6 1.66		
c/a fcc bcc sc cd fcc	23.1 1.63 23.2 23.0 27.2 39.5 WT 16.8 16.9	23.2 1.63 23.3 23.1 27.1 37.8 WT-e 16.8 16.9	23.4 1.63 23.6 23.4 27.4 40.1 P 17.0 17.1	23.5 1.63 23.6 23.4 27.3 38.0 P-e 17.0 17.1 1.66 17.4	21.5 1.63 21.8 21.4 26.5 41.8 SM 15.7 15.8	21.9 1.63 22.1 21.8 26.5 38.2 Al SM-e 15.8 15.9	23.0 1.63 23.2 22.9 27.2 40.0 WGC 16.7 16.8	23.1 1.63 23.3 23.0 27.1 38.0 WGC-e 16.8 16.9	22.9 1.63 23.1 22.8 27.1 39.9 KS-L 16.6 16.7	22.9 1.62 23.1 22.9 27.5 40.3 KS-NL 16.5 16.6		
$ \begin{array}{c} c/a \\ fcc \\ bcc \\ sc \\ cd \end{array} $ $ \begin{array}{c} fcc \\ hcp \\ c/a \end{array} $	23.1 1.63 23.2 23.0 27.2 39.5 WT 16.8 16.9 1.66	23.2 1.63 23.3 23.1 27.1 37.8 WT-e 16.8 16.9 1.66	23.4 1.63 23.6 23.4 27.4 40.1 P 17.0 17.1 1.66	23.5 1.63 23.6 23.4 27.3 38.0 P-e 17.0 17.1 1.66	21.5 1.63 21.8 21.4 26.5 41.8 SM 15.7 15.8 1.66	21.9 1.63 22.1 21.8 26.5 38.2 Al SM-e 15.8 15.9 1.66	23.0 1.63 23.2 22.9 27.2 40.0 WGC 16.7 16.8 1.66	23.1 1.63 23.3 23.0 27.1 38.0 WGC-e 16.8 16.9 1.67	22.9 1.63 23.1 22.8 27.1 39.9 KS-L 16.6 16.7 1.64	22.9 1.62 23.1 22.9 27.5 40.3 KS-NL 16.5 16.6 1.66		

Table S2: Bulk moduli (GPa) for several elements and crystal structures as predicted by OFDFT using LPPs and eight variations of the same KE functional (Wang-Teter, Perrot, Smargiassi-Madden, and Wang-Govind-Carter, along with their exponential-stabilized forms) and as predicted by KSDFT using both LPPs (KS-L) and NLPPs (KS-NL)

						${f Li}$						
	WT	WT-e	Р	Р-е	SM	SM-e	WGC	WGC-e	KS-L	KS-NL		
fcc	16	16	16	16	16	16	16	16	16	14		
hcp	16	16	16	16	16	16	16	16	16	17		
bcc	16	16	16	16	16	16	16	16	16	14		
sc	12	12	12	12	13	13	12	12	12	12		
cd	6	7	6	7	5	6	6	7	6	5		
Na												
	WT	WT-e	Р	Р-е	SM	SM-e	WGC	WGC-e	KS-L	KS-NL		
fcc	7.2	7.2	7.2	7.2	7.2	7.3	7.2	7.2	7.2	7.7		
hcp	7.2	7.2	7.2	7.2	7.3	7.3	7.2	7.2	7.2	7.7		
bcc	7.2	7.2	7.2	7.2	7.3	7.3	7.2	7.2	7.3	7.8		
sc	5.9	5.9	5.9	5.9	5.8	5.8	5.8	5.9	5.8	6.2		
cd	2.9	3.3	2.9	3.3	2.5	3.1	2.8	3.2	2.9	3.0		
	Mg											
	WT	WT-e	Р	Р-е	SM	SM-e	WGC	WGC-e	KS-L	KS-NL		
hcp	37	37	37	37	39	40	37	38	39	36		
fcc	37	37										
bcc		31	36	37	38	39	37	37	38	35		
DCC	37	37 37	36 36	37 36	38 39	39 40	37 37	37 37	$\frac{38}{38}$	$\frac{35}{35}$		
sc	37 24											
		37	36	36	39	40	37	37	38	35		
sc	24	37 24	36 24	36 25	39 22	40 23	37 24	37 24	38 24	35 23		
sc	24	37 24	36 24	36 25	39 22	40 23 13	37 24	37 24	38 24	35 23		
sc	24 11	37 24 14	36 24 11	36 25 14	39 22 9	40 23 13 Al	37 24 11	37 24 14	38 24 10	35 23 11		
$\frac{\mathrm{sc}}{\mathrm{cd}}$	24 11 WT	37 24 14 WT-e	36 24 11 P	36 25 14 P-e	39 22 9 SM	40 23 13 Al SM-e	37 24 11 WGC	37 24 14 WGC-e	38 24 10 KS-L	35 23 11 KS-NL		
sc cd fcc	24 11 WT 79	37 24 14 WT-e 80	36 24 11 P 77	36 25 14 P-e 78	39 22 9 SM 82	40 23 13 Al SM-e 85	37 24 11 WGC 79	37 24 14 WGC-e 80	38 24 10 KS-L 77	35 23 11 KS-NL 79		
sc cd fcc hcp	24 11 WT 79 77	37 24 14 WT-e 80 78	36 24 11 P 77 75	36 25 14 P-e 78 76	39 22 9 SM 82 80	40 23 13 Al SM-e 85 83	37 24 11 WGC 79 77	37 24 14 WGC-e 80 78	38 24 10 KS-L 77 75	35 23 11 KS-NL 79 75		

The SHEAP Maps: Additional Information

As described in the main paper, the SHEAP maps are based on SOAP descriptors for the structures. We employed SOAP parameters of $r_{\rm cut} = 5$, $n_{\rm max} = 15$, $l_{\rm max} = 9$, and $\sigma = 0.5$. We classified two structures as identical if the norm of their SOAP difference vector fell below a threshold of 0.7/0.25/0.2/0.07 for Li/Na/Mg/Al, respectively. For the SHEAP algorithm itself, we used a perplexity of 30 and a minimum hard sphere radius of 0.01 when creating the images. (For the three-dimensional SHEAP visualizations discussed next, we used the same parameters aside from a minimum hard sphere radius of 0.015.)

Dimensionality reduction for data visualization is not restricted to two map dimensions. To complement the two-dimensional SHEAP maps (Figs. 2-5 in the main paper), we generated corresponding three-dimensional SHEAP maps, which are summarized in Fig. S1. These results show that two map dimensions are sufficient for capturing the salient features in the data. In fact, the three-dimensional SHEAP maps are nearly flat, with little along the third dimension aside from the depth of the spheres. Our general experience with SHEAP suggests that, often, a third dimension becomes beneficial only with larger data sets.

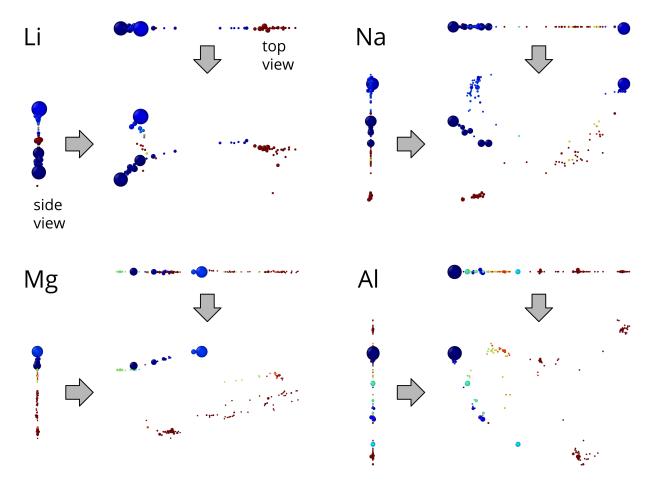


Figure S1: Three-dimensional SHEAP maps corresponding to the two-dimensional SHEAP maps found in Figs. 2-5 of the main paper. The maps are mostly flat, as seen from the side and top views, indicating that two dimensions are sufficient for representing the main features.

Assessing the Exchange-Correlation Functional

To build confidence that the PBE exchange-correlation functional is suitable for the nearly-free-electron metals considered, we repeated some geometry optimizations with the LDA and PBEsol functionals. Beginning with the OFDFT-derived structures from the top portions of Figs. 2-5 in the main paper, we re-relaxed them using KSDFT and both LDA and PBEsol. Exactly as with PBE, these relaxations were performed with CASTEP using C19 nonlocal pseudopotentials generated on-the-fly for the particular exchange-correlation functional.

The results are summarized in Figs. S2-S5. They show that the relative energies, even after geometry optimization, are insensitive to the choice of exchange-correlation functional. Frequently, the three lines representing the nonlocal pseudopotential calculations (for LDA, PBE, and PBEsol) are indistinguishable on the scale of the plots.

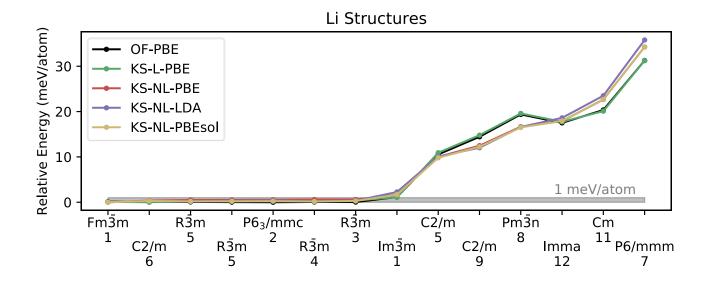


Figure S2: Relative energies of a subset of Li structures computed with OFDFT (OF) and KSDFT with local or nonlocal pseudopotentials (KS-L and KS-NL, respectively). The labels also include the exchange-correlation functional used for the final geometry optimization (LDA, PBE, or PBEsol). Compare with Fig. 2 (top) in the main paper.

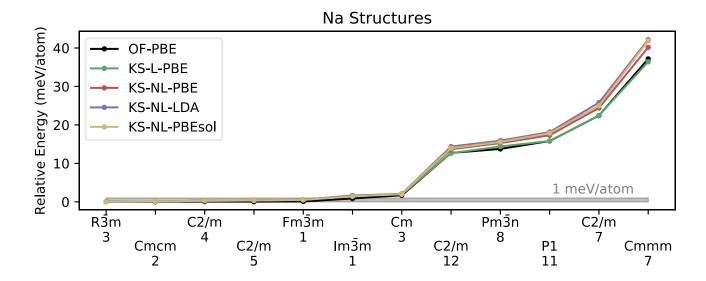


Figure S3: Relative energies of a subset of Na structures computed with OFDFT (OF) and KSDFT with local or nonlocal pseudopotentials (KS-L and KS-NL, respectively). The labels also include the exchange-correlation functional used for the final geometry optimization (LDA, PBE, or PBEsol). Compare with Fig. 3 (top) in the main paper.

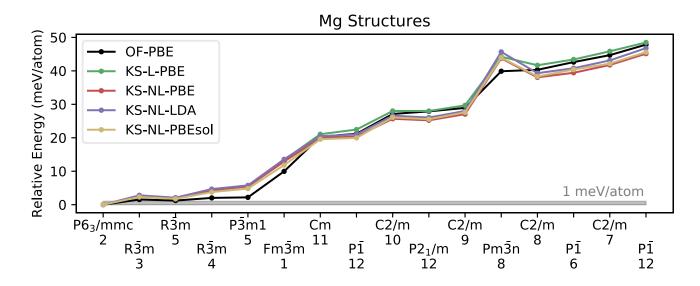


Figure S4: Relative energies of a subset of Mg structures computed with OFDFT (OF) and KSDFT with local or nonlocal pseudopotentials (KS-L and KS-NL, respectively). The labels also include the exchange-correlation functional used for the final geometry optimization (LDA, PBE, or PBEsol). Compare with Fig. 4 (top) in the main paper.

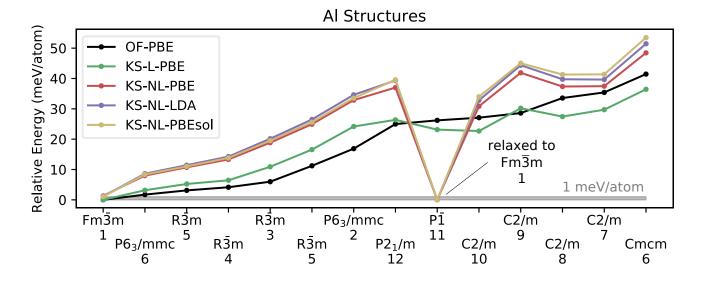


Figure S5: Relative energies of a subset of Al structures computed with OFDFT (OF) and KSDFT with local or nonlocal pseudopotentials (KS-L and KS-NL, respectively). The labels also include the exchange-correlation functional used for the final geometry optimization (LDA, PBE, or PBEsol). Compare with Fig. 5 (top) in the main paper.