

Cite this: DOI: 10.1039/xxxxxxxxxx

# Supporting Information: Exploring the chemical nature of super-heavy main-group elements by means of efficient plane-wave density-functional theory.<sup>†</sup>

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Received Date  
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

## 1 Contents

Here we provide tables with the numerical values used for the figures in the main article, a more detailed description of the computational details for the adsorption study, as well as how we calculated the bulk cohesive energies.

In addition to this document, we provide several archives containing additional data. The file `structures.zip` contains the optimised geometries for the bare surface slabs, the adsorbed species, as well as the respective lowest energy structure for the bulk SHEs in VASP (POSCAR) format. The file `POTCARs.zip` contains the PAW potentials presented in this work. Note that for the atomic masses in the POTCAR files are set to the most stable isotopes, which are 285 u for Cn and Fl, 286 u for Nh, 289 u for Mc, 293 u for Lv and 294 u for Ts and Og. The file `D3Parameters.zip` contains spreadsheets in open-document format which collect the results of the polarizability-scans,  $r_{42}$  expectation values, and hydride structures and energetics used for the D3 model.

### 1.1 Adsorption on Gold

All optimisations were carried out with a locally modified version of VASP 5.4.4 that contains the new D3 parameters.<sup>1–5</sup> The core region of the gold atoms was modelled using the 11 VE PAW from the VASP library with a  $5d6s$  valence space in combination with a plane-wave basis set and a kinetic energy cutoff of 350 eV. The Brillouin zone was sampled on a Monkhorst-Pack grid with a spacing of  $0.2 \text{ \AA}^{-1}$ , which resulted in an  $8^3$  grid for gold *fcc* bulk. Both kinetic cutoff and  $k$ -spacing values were chosen such that the to-

tal energy of the system was converged to 10 meV per atom. The results for the bulk optimisations at the various scalar-relativistic (SR) and spin-orbit coupled (SO) levels are collected in table 1 (for a comparison to nonrelativistic results see Takeuchi et al.<sup>6</sup>).

**Table 1** Lattice constants  $a$  (in  $\text{\AA}$ ) and cohesive energy per atom  $E_{\text{coh}}$  (in eV) for *fcc* gold with at various DFT levels. Differences to the reference are given in parenthesis. All methods that include dispersion effects essentially provide quantitative agreement with the reference at the SO level.

		$a$ ( $\Delta a$ )	$E_{\text{coh}}$ ( $\Delta E$ )
ref. <sup>7</sup>		4.078	-3.81
PBE	SR	4.151 (+0.07)	-3.04 (+0.77)
	SO	4.142 (+0.06)	-3.17 (+0.64)
PBE-D3	SR	4.096 (+0.02)	-3.68 (+0.13)
	SO	4.087 (+0.01)	-3.82 (-0.01)
SCAN	SR	4.086 (+0.01)	-3.56 (+0.25)
	SO	4.077 (-0.00)	-3.70 (+0.11)
PBEsol	SR	4.078 (+0.00)	-3.72 (+0.09)
	SO	4.069 (+0.01)	-3.86 (-0.05)

Inspection of tab. 1 shows that while the lattice constants are in reasonable agreement with the reference value at all levels, the inclusion of dispersion interactions (PBE vs PBE-D3, PBEsol and SCAN) is required to obtain similar agreement for the cohesive energy. Moreover, also the explicit consideration of spin-orbit coupling (SO vs SR) improves the results, in particular the cohesive energy, which eventually leads to excellent quantitative agreement with PBE-D3, SCAN and PBEsol at the SO-DFT level.

**Creation of Slabs** – To study the adsorption of the SHEs on the (111) surface of gold, a slab cell had to be created from the optimised bulk structures. For this, the command line tool AFLOW was employed,<sup>8</sup> which is capable of creating slab cells given the Miller indices  $h, k, l$ , the number of layers in the slab  $n$  and the size of the vacuum layer  $v$  as input. For the slab cells investigated in this work the parameters were  $\{h, k, l\} = \{1, 1, 1\}$ ,  $n = 4$  and  $v = 6$ .

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**Table 3** Adsorption energies  $E_{\text{ads}}$  (in eV) of the lighter congeners of the investigated SHEs in the adsorption mode “hollow2”

M	PBE-D3	
	SR	SO
Hg	-0.69	-0.75
Tl	-2.90	-2.40
Pb	-3.72	-2.81
Bi	-3.37	-3.01
Po	-3.51	-2.77
At	-2.46	-1.96
Rn	-0.32	-0.36

**Table 4** Distance of the ad-atom M to the plane going through the top 111 gold layer (in Å)

M	PBE		PBE-D3		SCAN		PBEsol	
	SR	SO	SR	SO	SR	SO	SR	SO
Cn <sup>a</sup>	2.95	2.84	2.77	2.70	2.64	2.54	2.64	2.60
Cn <sup>b</sup>	2.95	2.50	2.77	2.46	2.64	2.25	2.64	2.36
Nh	2.73	2.58	2.67	2.53	2.61	2.44	2.65	2.48
Fl	2.38	2.75	2.37	2.68	2.31	2.47	2.35	2.59
Mc	2.21	2.78	2.22	2.72	2.11	2.50	2.20	2.70
Lv	2.20	2.54	2.21	2.51	2.08	2.37	2.18	2.51
Ts	2.44	2.58	2.45	2.55	2.24	2.44	2.41	2.53
Og	3.42	3.04	3.13	2.92	3.17	2.93	3.11	2.90

<sup>a</sup>20VE <sup>b</sup>12VE

This resulted in slabs of size  $2 \times 2$ , which were used to create  $4 \times 4$  and larger cells by creating super-cells.

## 1.2 Calculation of SHE Bulk Cohesive Energies

**Table 2** Calculated cohesive energies and most stable phases of the SHEs Cn–Og with various DFT methods. In all cases, the energetically lowest phase is identical irrespective of the employed functional.

	lowest phase	PBE	PBE-D3	SCAN	PBEsol
Cn <sup>a</sup>	<i>hcp</i>	-0.11	-0.47	-0.35	-0.53
Cn <sup>b</sup>	<i>bcc</i>	-0.24	-0.67	-0.60	-0.77
Nh	<i>hcp</i>	-0.69	-1.10	-1.02	-1.25
Fl	<i>hcp</i>	-0.30	-0.58	-0.49	-0.71
Mc	<i>fcc</i>	-1.05	-1.39	-1.32	-1.51
Lv	<i>bcc</i>	-1.57	-2.00	-1.84	-1.84
Ts	<i>hcp</i>	-1.36	-1.89	-1.67	-1.50
Og	<i>fcc</i>	-0.18	-0.58	-0.35	-0.41

<sup>a</sup>20VE <sup>b</sup>12VE

Bulk cohesive energies are conducted with a locally modified version of VASP 5.4.4 that contains the new D3 parameters. Structures for Cn–Og are optimised at the spin-orbit DFT level with symmetry for the *hcp*, *fcc*, *bcc*, and *sc* phases using a plane-wave cutoff of 600 eV, a *k*-spacing of  $0.15 \text{ \AA}^{-1}$ , a convergence criterion for the SCF of  $\text{EDIFF} = 10^{-6}$ , and for the geometry of  $\text{EDIFFG} = 10^{-4}$ . To eliminate Pulay stress, the optimisations are repeated until convergence is achieved in the first step.

The results collected in table 2 show trends very similar to those observed for the adsorption energies on gold. The most significant difference concerns Mc, for which PBE-D3 predicts cohesive energies very similar to PBEsol and SCAN, whereas the adsorption energy calculated with PBE-D3 is distinctly larger than with PBEsol and SCAN. For Lv–Og, we observe the same trend as for the adsorption energies, *i.e.* PBE-D3 provides distinctly lower cohesive energies than PBEsol and SCAN.

The energetic ordering of the phases is identical with all employed functionals (PBE, PBE-D3, PBEsol and SCAN). Differences between the dense phases, *i.e.* *fcc*, *bcc* and *hcp* (not shown) are small and typically amount to less than 2% of the cohesive energy with few exceptions. The *sc* phase is distinctly higher in energy in most cases, coming close to the dense phases (to within 10%) only in case of Lv and Cn(12VE) and only with the SCAN functional. From the small differences between the dense structures, we conclude that even if there were other structures with an even lower energy, the difference would presumably be similarly small, and hence negligible for our purposes, *i.e.* the comparison with adsorption energies.

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Adsorption energies  $E_{\text{ads}}$  (in eV) of the investigated SHEs in the adsorption mode “hollow2” shown in figs. 3, 4, and 5

M	PBE		PBE-D3		SCAN		PBEsol	
	SR	SO	SR	SO	SR	SO	SR	SO
Cn <sup>a</sup>	-0.11	-0.15	-0.49	-0.54	-0.41	-0.47	-0.31	-0.38
Cn <sup>b</sup>	-0.11	-0.35	-0.49	-0.77	-0.42	-0.80	-0.31	-0.68
Nh	-2.51	-1.04	-2.92	-1.47	-2.82	-1.52	-2.83	-1.36
Fl	-3.13	-0.40	-3.54	-0.78	-3.49	-0.86	-3.56	-0.67
Mc	-2.77	-1.89	-3.21	-2.34	-3.45	-2.10	-3.20	-2.24
Lv	-2.90	-1.98	-3.41	-2.51	-3.55	-2.33	-3.35	-2.37
Ts	-2.02	-1.61	-2.60	-2.19	-2.48	-1.99	-2.40	-1.98
Og	-0.10	-0.39	-0.58	-0.93	-0.28	-0.62	-0.26	-0.66

<sup>a</sup>20VE <sup>b</sup>12VE