# Supporting material: Large-scale surface reconstruction energetics of Pt(100) and Au(100) by all-electron DFT

Paula Havu[1],* Volker Blum[1], Ville Havu[1,2], Patrick Rinke[1], and Matthias Scheffler[1]
*1) Fritz-Haber-Institut, Berlin, Germany and*
*2) Department of Applied Physics, Aalto University, Helsinki, Finland*
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We here add supporting material for the methodological aspects of our work on large-scale reconstructed Au(100) and Pt(100) surfaces: A brief account of convergence aspects, and comparison of the reconstruction geometries found by us to the available literature data.

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**Methodological aspects:**
As described in the main text, a (5×$N$) plane ($N$ >1) contains ($N$+5+1) additional atoms in the unit cell, compared to a (1×1) layer. In terms of total energies for individual surface slabs, $E^{\rm slab}$, and the total energy per atom in the bulk, $E^{\rm atom,bulk}$, the reconstruction energy $\Delta E_{5\times N}$ (here defined to be positive if a reconstruction is favored) is

$$-\Delta E_{5\times N} = E^{\rm slab}_{5\times N} - 5N E^{\rm slab}_{1\times 1} - (N+6)E^{\rm atom,bulk} \quad . \quad (1)$$

All DFT total energies are based on the LDA,[1] or the generalized gradient functional PBE.[2] We use fcc lattice parameters $a_{\rm Au}$=4.055 (4.169) Å and $a_{\rm Pt}$=3.899 (3.974) Å in LDA (PBE), respectively, computed for the highly converged *tier 1* basis level (*spdfg* for Pt, *spdfgh* for Au [3]), and essentially converged already for (10×10×10) $k$-point grids. The *tier 1* basis set level is also used to obtain converged geometry relaxation (residual forces <$10^{-2}$ eV/Å) and total energies for all surfaces considered here. The convergence of our surface calculations is verified by explicit tests for (5×1) approximants (a-c below): (a) Compared to (much larger) *tier 2* basis sets, reconstruction energies are converged to better than 0.003 eV/1×1. (b) Nine-layer slabs (four relaxed) yield an energy lowering of 0.01 eV/1×1 for Au and Pt. (c) 0.01 eV/1×1 accuracy is obtained by 10×10 $k$-point grids in units equivalent to the 1×1 cell. In our calculations with variable cell length $N$ (data points in Fig. 2 of the main paper), we further reduce the $k$-grid noise by using 2×2 and equivalent $k$-grids for $N$ <20, and 1×2 and equivalent $k$-meshes for $N$ ≥20. In terms of the 1×1 periodicity, this amounts to 20×10 or denser grids throughout this work. Our *overall* accuracy is verified by explicit FP-LAPW [4] (5×1) calculations, yielding agreement within 0.01 eV/1×1.

**Comparison of reconstruction geometry characteristics to the available literature:**
Table I compares some key surface geometry parameters from our study with the available diffraction experiments. The agreement is remarkable, especially since the most detailed study [5] used a surface-averaged (5×1) model for Au(100), yielding a "hex" layer buckling inbetween our maximum and mimimum corrugations (see Fig. 3 of the main paper and its description there).

| | Au(100) | | Pt(100) | |
|---|---|---|---|---|
| | This work | Experiment | This work | Experiment |
| $b_1/d_{\rm bulk}$ | 0.32(0.32) | 0.275[a] | 0.29(0.29) | ≈0.2[b] |
| | | | | 0.25-0.38[c] |
| $b_2/d_{\rm bulk}$ | 0.044(0.044) | 0.069[a] | 0.042(0.042) | |
| $d_{12}/d_{\rm bulk}$ | 1.21(1.22) | 1.20[a] | 1.20(1.20) | |
| $d_{23}/d_{\rm bulk}$ | 0.99(0.98) | | 0.99(1.00) | |

TABLE I: Averaged interlayer distances $d_{ij}$ and peak-to-peak buckling amplitudes $b_i$ for Au(100)-"(5×20)" and Pt(100)-"(5×25)" in LDA (PBE in brackets), compared to experiment: [a]SXRD, Refs. [5]; [b]LEED, Ref. [6]; [c]Helium atom scattering, Ref. [7].

* Present address: Helsinki University of Technology (TKK), Finland

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