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

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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.

PACS numbers:

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

$$-\Delta E_{5\times N} = E_{\text{slab}}^{5\times N} - 5NE_{\text{slab}}^{1\times 1} - (N+6)E_{\text{atom,bulk}}.$$  \hspace{1cm} (1)

All DFT total energies are based on the LDA[,] or the generalized gradient functional PBE.[2] We use fcc lattice parameters $$a_{\text{Au}}=4.055$$ (4.169) Å and $$a_{\text{Pt}}=3.899$$ (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 $$(10\times 10\times 10)$$ 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 $$(5\times 1)$$ 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 $$N \geq 20$$. 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] $$(5\times 1)$$ 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 $$(5\times 1)$$ model for Au(100), yielding a “hex” layer buckling inbetween.

<table>
<thead>
<tr>
<th></th>
<th>Au(100)</th>
<th>Experiment</th>
<th>Pt(100)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$$b_1/d_{\text{bulk}}$$</td>
<td>0.32(0.32)</td>
<td>0.275(^{a})</td>
<td>0.29(0.29)</td>
<td>0.25-0.38(^{c})</td>
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<tr>
<td>$$b_2/d_{\text{bulk}}$$</td>
<td>0.044(0.044)</td>
<td>0.069(^{a})</td>
<td>0.042(0.042)</td>
<td></td>
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<tr>
<td>$$d_{12}/d_{\text{bulk}}$$</td>
<td>1.21(1.22)</td>
<td>1.20(^{a})</td>
<td>1.20(1.20)</td>
<td></td>
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<tr>
<td>$$d_{23}/d_{\text{bulk}}$$</td>
<td>0.99(0.98)</td>
<td>0.99(1.00)</td>
<td></td>
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</table>

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

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References: