LDRD
Laboratory Directed Research and Development

# Computing properties of Pt surfaces for understanding electron emission


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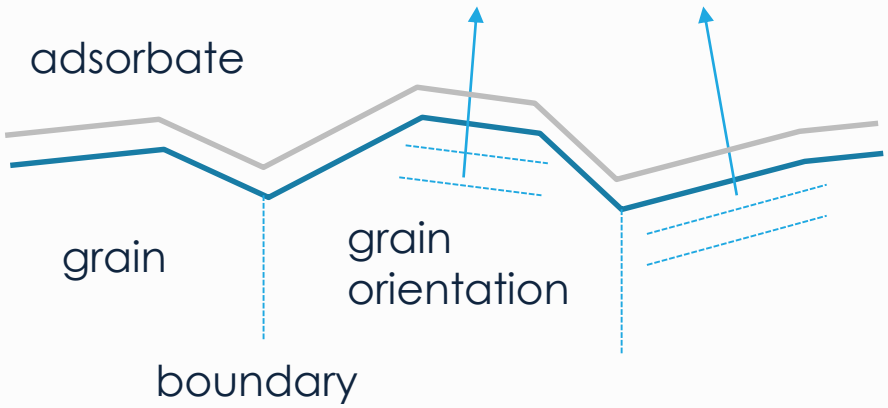
# Fowler-Nordheim picture

- **Fowler-Nordheim emission (empirical )**

$$J = \frac{A\beta^2 E^2}{\varphi} \exp\left(-\frac{B\varphi^{3/2}}{\beta E}\right)$$




- Current density $J$ ( $E$, $\phi$, $A$, $\beta$ )
- $E$ field
- $\phi$ work function
- Empirical fitting parameters: β
- $\beta$ varies from 10-1000 *inside exponential*

Work function has spatial variability
Structure folded into empirical β-factor

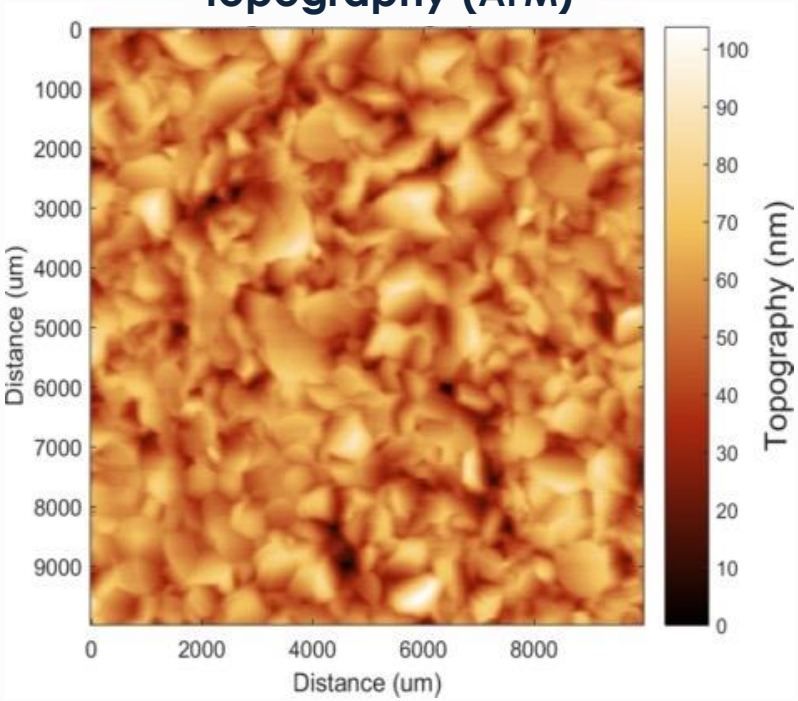
Our goals …

(1) understand local structure on Pt surfaces
(2) correlate local structure with local work function
(3) and augment empiricism with finer understanding
(4) add adsorbates and contaminants, and repeat

# Pt thin films – structure to emission

## Structure …

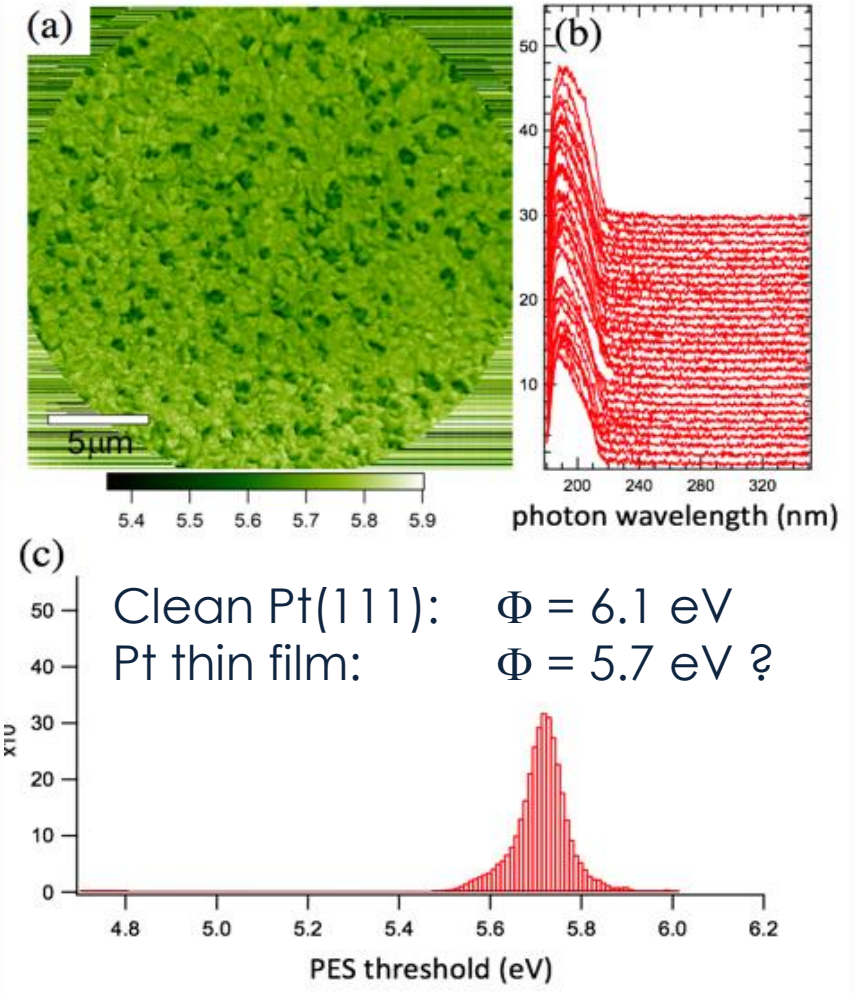
**topography (AFM)**




Sputtered thin films
Polycrystalline
(111)-oriented grains
Few-100's nm sized

## … to work function spatial variation

**photoemission electron microscopy (PEEM)**



# Simple Pt surfaces … are not simple

- All low-Miller-index Pt surfaces reconstruct
  - Pt(100) reconstructs to dense, close-packed hexagonal surface
  - Pt(110) reconstructs to (2x1) or (3x1) missing row
  - Pt(111) into 8% denser incommensurate hexagonal (high-T, or high-Pt)
  - "Simple surfaces" are complicated
- Our surfaces are polycrystalline! (though 111-oriented)
- Growth on real Pt(111) surfaces is not planar (111)!



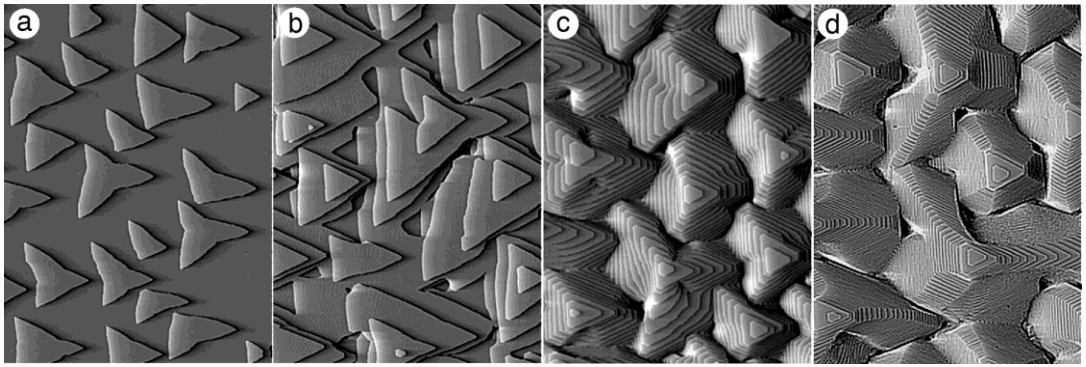



Fig. 1. STM topographs of Pt/Pt(111) after growth at 440 K with $R = 7\times 10^{-3}$ ML s$^{-1}$ (a) 0.3 ML, (b) 3 ML, (c) 12 ML, (d) 90 ML. The scan size in (a)–(d) is 2590× 3450 Å2.

Pyramids

Jung, etal, APL 83, 2160 (2003)

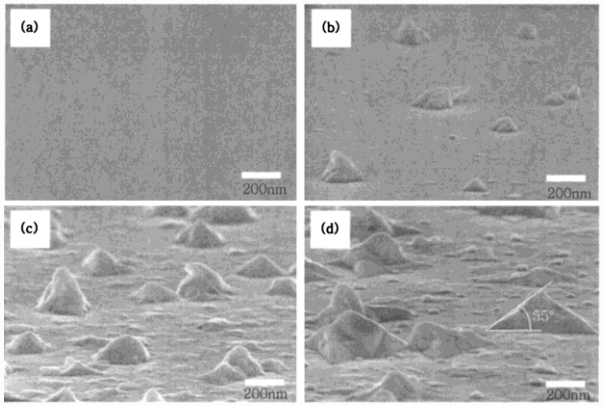



FIG. 1. Sideview SEM micrographs of hillocks in the Pt/Ti electrode stack after annealing. Annealing temperatures were (a) 450 °C, (b) 500 °C, (c) 600 °C, and (d) 650 °C. The angle between the basal plane and facet of the hillock is about 55°, as indicated in (d).

Hillocks

Heterogeneity in structure → variations in Φ

# Goals for DFT modeling

The goal of DFT are to augment empiricism with finer understanding

- Characterize surface structure of clean Pt
  - *what are the common surface structures on "real" Pt surfaces?*
- Correlate local structure with local work function
  - how does local structure affect local work function?
- Establish baseline understanding between theory and STM/PEEM
- How do features and structure affect emission and arc initiation?
  - band structure for device simulations, field enhancement at features?
- How do adsorbates/contaminants affect these?

# Basic process for surface DFT calculations

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1. Choose DFT code, functional, pseudopotential
   - *SEQQUEST – Sandia-developed pseudopotential DFT code*
   - *local orbital "LCAO" basis – need "floating orbitals" for surfaces*
   - *LDA, PBE, PW91, and AM05 functionals*

2. Optimize bulk *fcc* properties: $a_0$ and *B*
   - *verify convergence*

3. Create surface models – thin flim "slab"
   - thickness of *N layers – test convergence*
   - *define surface k-sampling, real space grids, etc – verify sufficiency*

4. Compute slab energy: $E_{surface} = ( E_{slab} – N*E_{bulk} ) / 2$

5. Extract surface properties, esp. work function $\Phi${surface}

# Some DFT surface calculation issues

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- JC Boettger, PRB **49**, 16798 (1994); JCB, etal, JPCM **10**, 893 (1998).
  - "non-convergence" of surface energy from bulk-referenced slabs.
- Fiorentini and Methfessel JPCM **8**, 6525 (1996).
  - use extrapolation/fits to increasing thick slab to get surface E
- Fall, Binggeli & Baldereschi, JPCM **11**, 2689 (1999).
  - work functions from extrapolations (Al to 14 layers)
- Da Silva, Stampfl, & Scheffler, SS **600**, 703 (2006).
  - "direct method" with bulk and slab with "Same high accuracy"
- Singh-Miller and Marzari, PRB **80**, 235407 (2009).
  - compare "Boettger", extrapolation, and "direct" methods
- Lazar and Oteypka, PRB **91**, 115402 (2015).
  - functionals for accurate surface E (EXX+RPA) – only up to 8 layers!

# Non-convergence issues

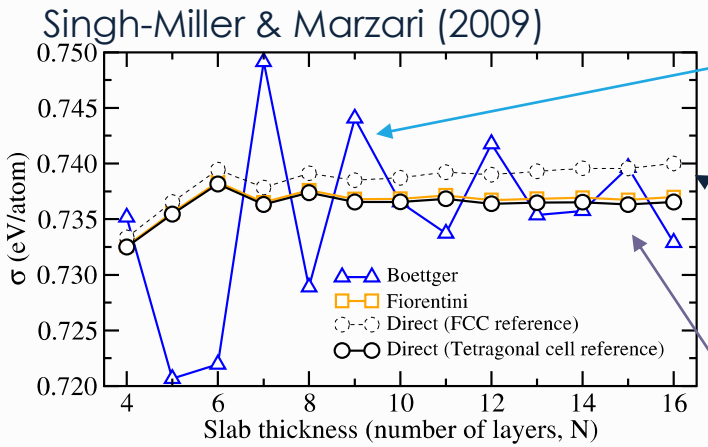



FIG. 2. (Color online) Surface energy versus slab thickness for the Pd(100) surface calculated with the methods of Boettger (Ref. 8), Fiorentini and Methfessel (Ref. 64), and directly from Eq. (1) with two different values for $E_{bulk}$.

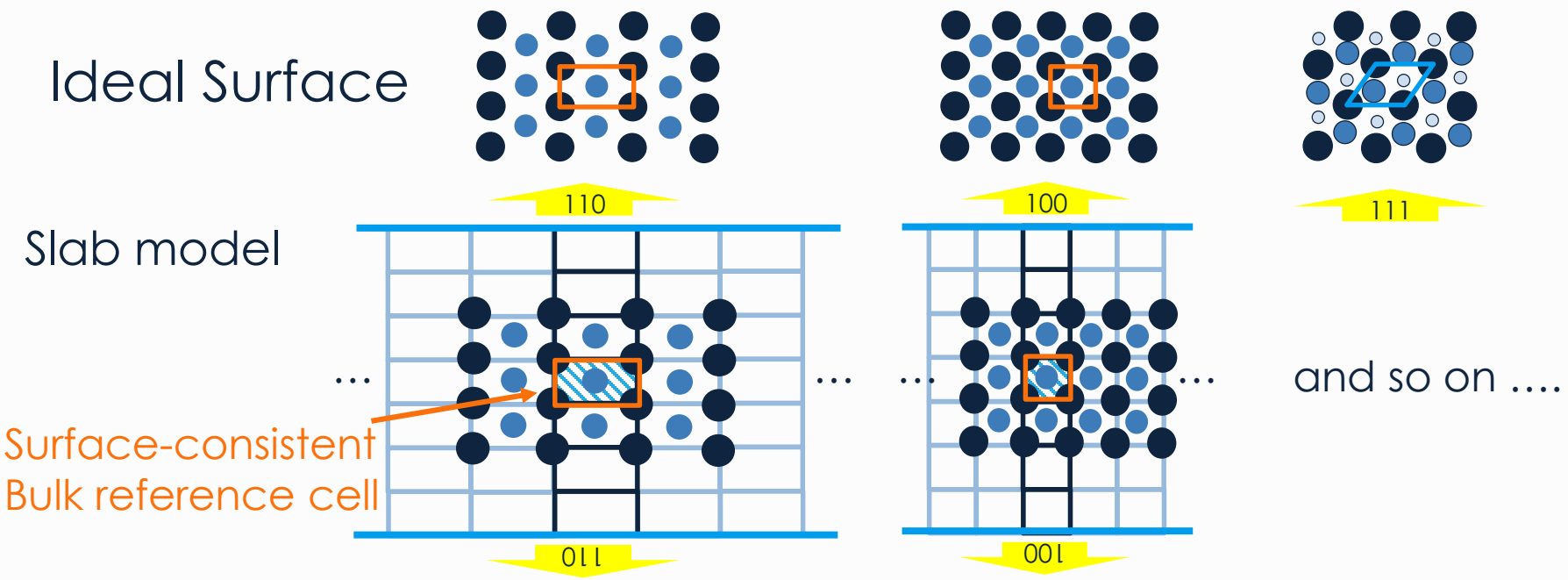
Layer by layer ("Boettger")
- simple additive
- *what is possible for large cells*

**"Direct" method → divergence**
- if use naïve $E_{bulk}$, get divergence of $E_{surf}$
- good iff both slab and bulk *very* converged
- *impractical for large surface cells*

Extrapolated fit of $E_{bulk}$
- thick slabs to establish convergence, fit $E_{bulk}$
- *impractical for large surface cells*

And then functional/methods accurate enough?
- LDA - (mostly) correct numbers, but wrong physics
- PBE - better physics, but wrong numbers
- AM05 – targeted for surface properties (Mattsson/SNL)
- EXX+RPA computationally impractical

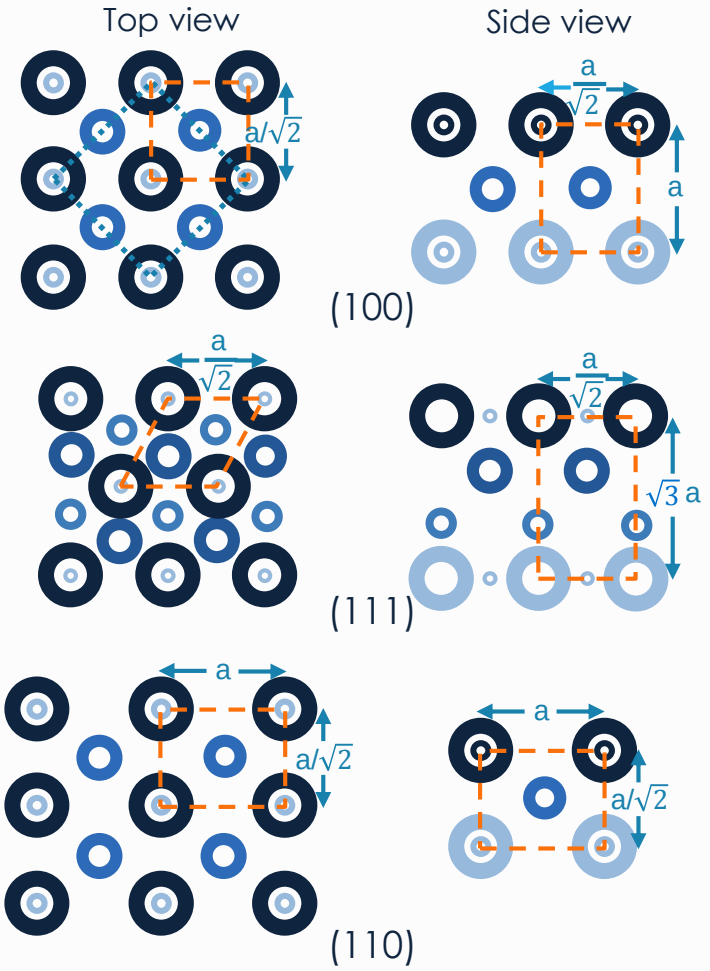
# Refined method for DFT surface calculations

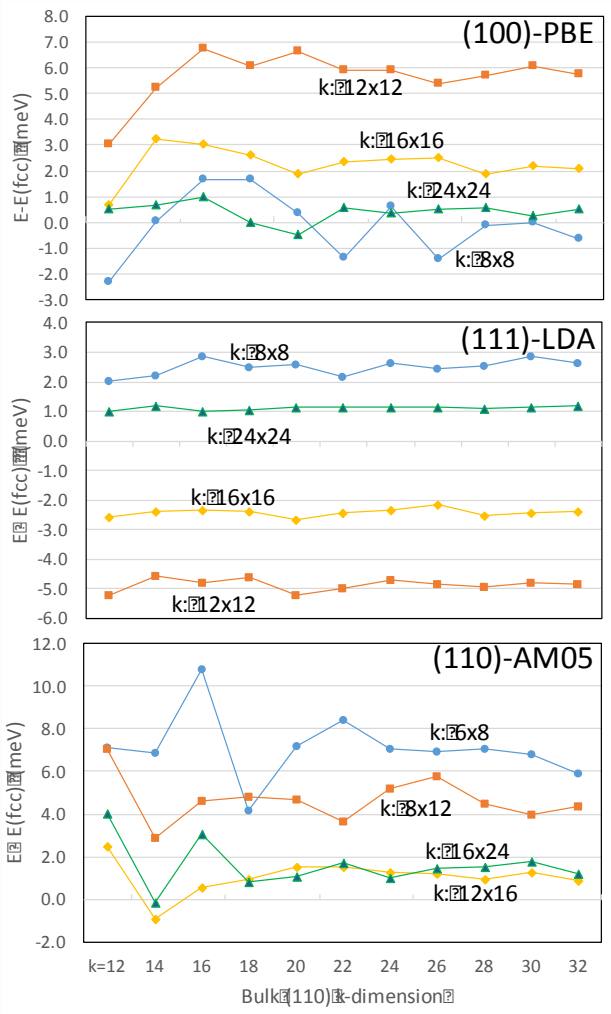



- AM05 functional – tailored to surfaces (but also PBE and LDA)
- Use converged *fcc* bulk $a_0$
- Developed "surface-consistent" bulk reference $E_{bulk}\{k;surf\}$

$$E_{surface} = ( E_{slab} - N*E_{bulk} ) / 2$$

# Side excursion: Al(100) – Bulk reference energy

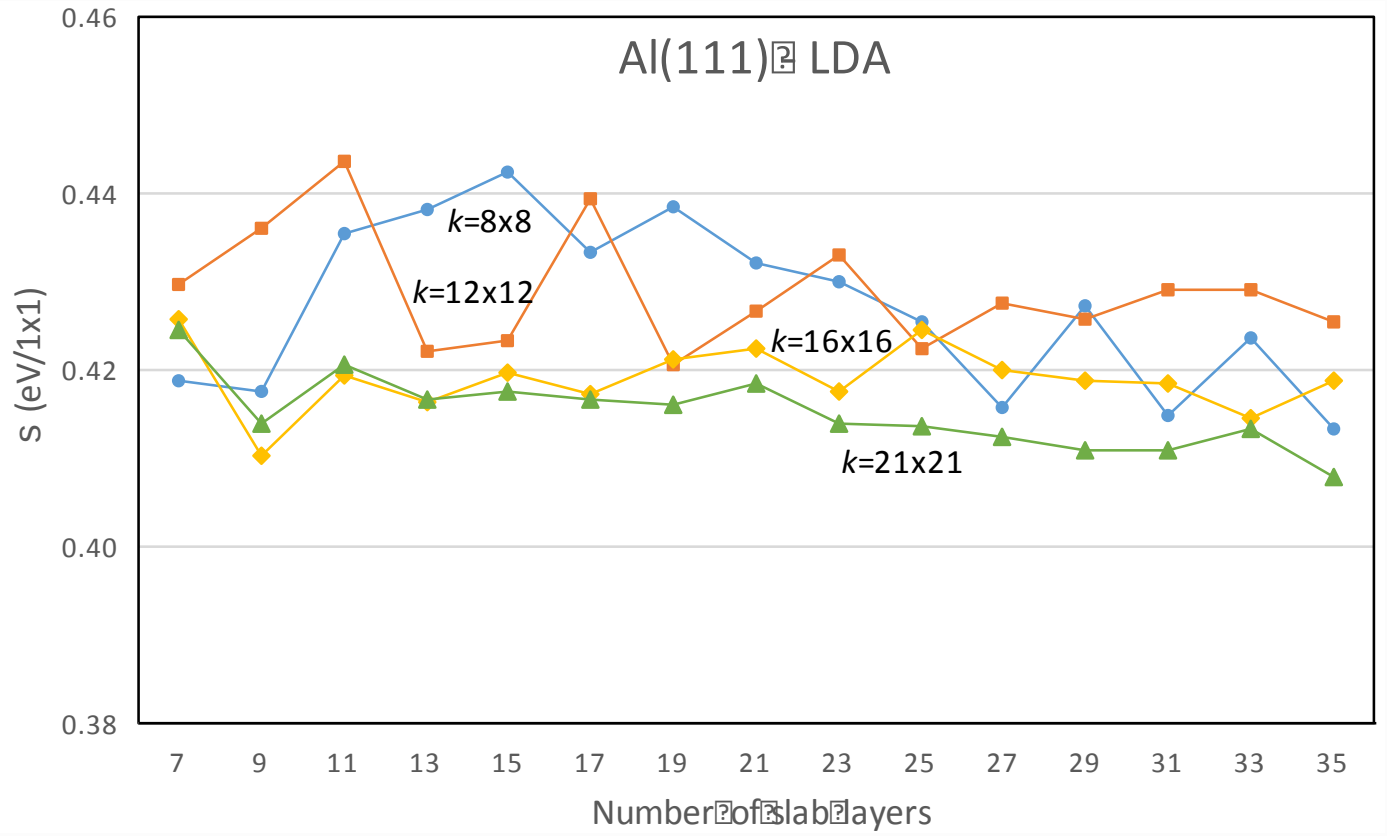



Use large $k_z$-limit average of slab-consistent bulk reference cell energy

# Al(111) surface energy

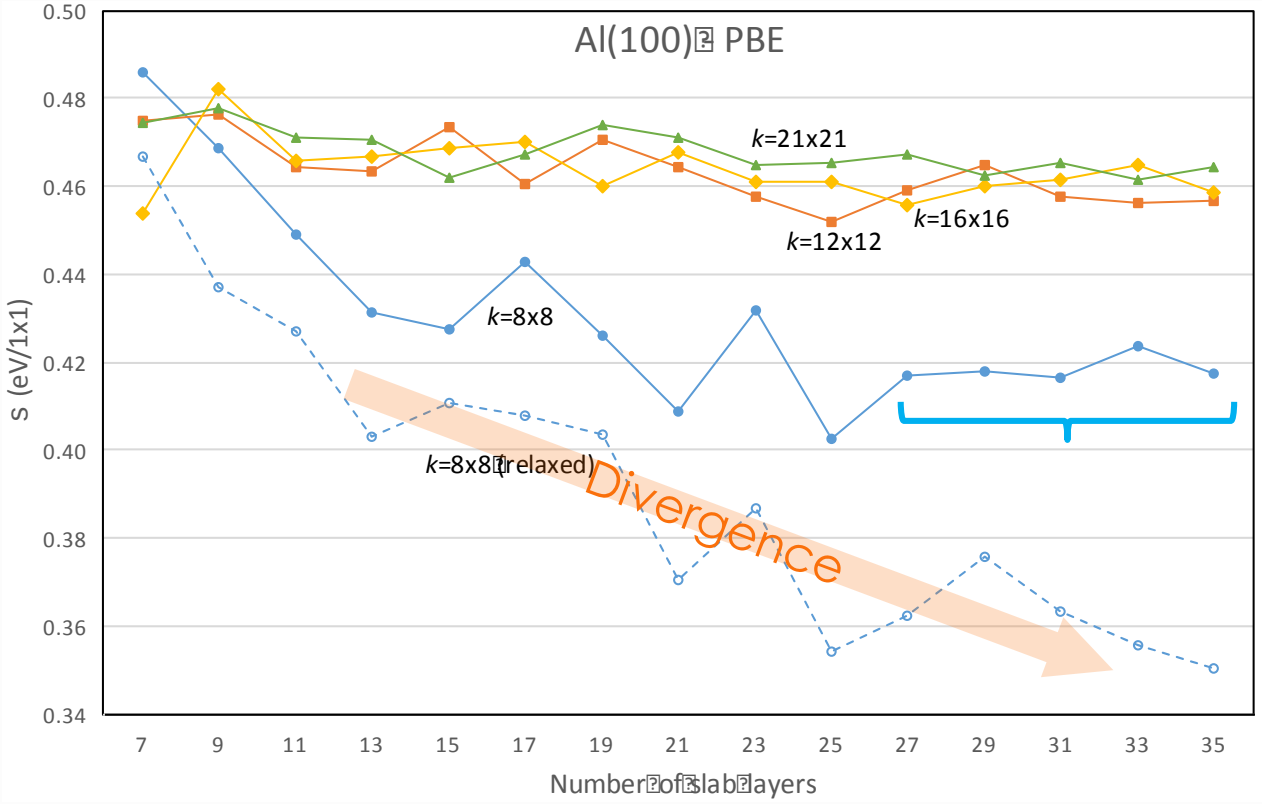
Coarse k=8x8 and dense high-accuracy k=21x21 all converge quickly




Converge to same energy

"Direct" slab-consistent bulk reference energy solves convergence

# Al(100) surface energy - cautions




} Good convergence for dense k-sample

Convergence > 25 for coarse k=8x8

Divergence if bulk reference faulty

Must monitor "bulk reference"! In k=8x8x$k_z$ bulk $a_0$ changes!

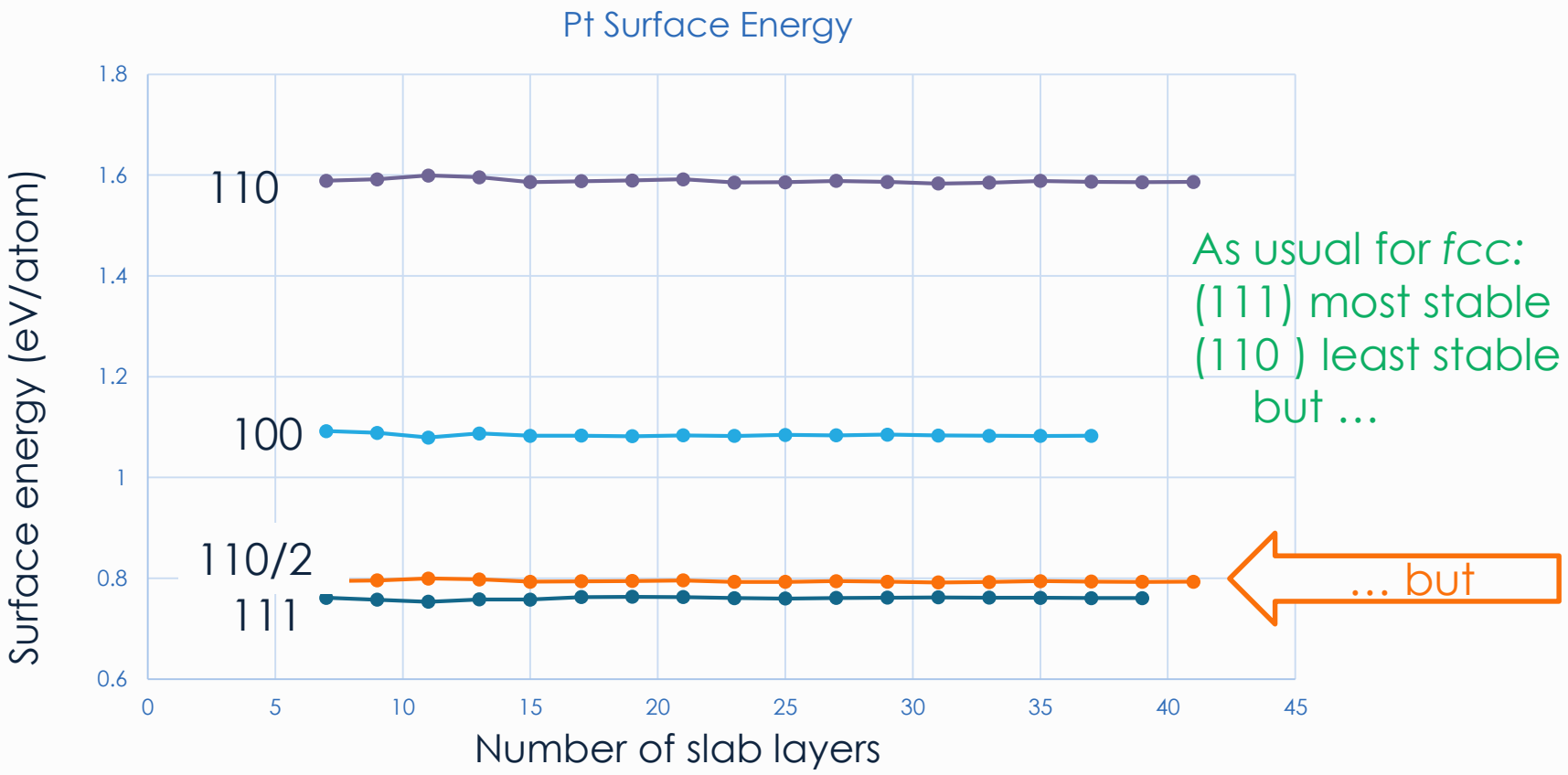
# Al surfaces properties: verification/validation

| | Al(100) | | Al(111) | | Al(110) | |
|---|---|---|---|---|---|---|
| | $\sigma$ | $\Phi$ | $\sigma$ | $\Phi$ | $\sigma$ | $\Phi$ |
| | Experiment | | | | | |
| | – | 4.42(±.03)[a] | 0.51[b] | 4.42(±.03)[a] | – | 4.12(±.03)[a] |
| | LDA | | | | | |
| Unrelaxed[c] | 0.54 | 4.53 | 0.41 | 4.27 | 0.82 | 4.22 |
| Relaxed[c] | 0.54 | 4.49 | 0.41 | 4.26 | 0.81 | 4.22 |
| Fall (1998)[d] | – | 4.38 | – | 4.25 | – | 4.30 |
| Da Silva (2006)[e] | – | – | 0.39 | 4.21 | – | – |
| | PBE | | | | | |
| Unrelaxed[c] | 0.47 | 4.34 | 0.35 | 4.12 | 0.71 | 4.07 |
| Relaxed[c] | 0.46 | 4.34 | 0.35 | 4.11 | 0.70 | 4.07 |
| Da Silva (2005)[f] | 0.48 | 4.24 | 0.36 | 4.06 | 0.72 | 4.07 |
| Da Silva (2006)[c] | – | – | 0.33 | 4.04 | – | 4.04 |
| Singh-Miller (2009)[c] | 0.45 | 4.30 | 0.30 | 4.02 | 0.70 | 4.09 |
| | AM05 | | | | | |
| Unrelaxed[c] | 0.54 | 4.34 | 0.42 | 4.10 | 0.83 | 4.04 |
| Relaxed[c] | 0.54 | 4.33 | 0.41 | 4.10 | 0.82 | 4.04 |
| | PW91 | | | | | |
| Unrelaxed[c] | 0.44 | 4.38 | 0.34 | 4.14 | 0.67 | 4.10 |
| Relaxed[c] | 0.44 | 4.35 | 0.33 | 4.12 | 0.66 | 4.10 |

(a). Ref. 9, converted from quoted 1.14 J/m$^2$ to eV/atom using $a_0(293K)$=4.05 Å.
(b) Ref. 10.
(c) This work, quoting large $k_\parallel$ and slab thickness (17-35 layers) average.
(d) Ref. 11 using a norm-conserving pseudopotential code with 9 (for 111) or 8 (100,110) layers.
(e) Ref. 7, using a full-potential code with 7 layers (for the Al(111) surface).
(f) Ref. ? , using a full potential code with from 15 (for 111), to 23 (110) layers.
(g) Ref. 8. using a norm-conserving pseudopotential plane wave method code with 13 layers.

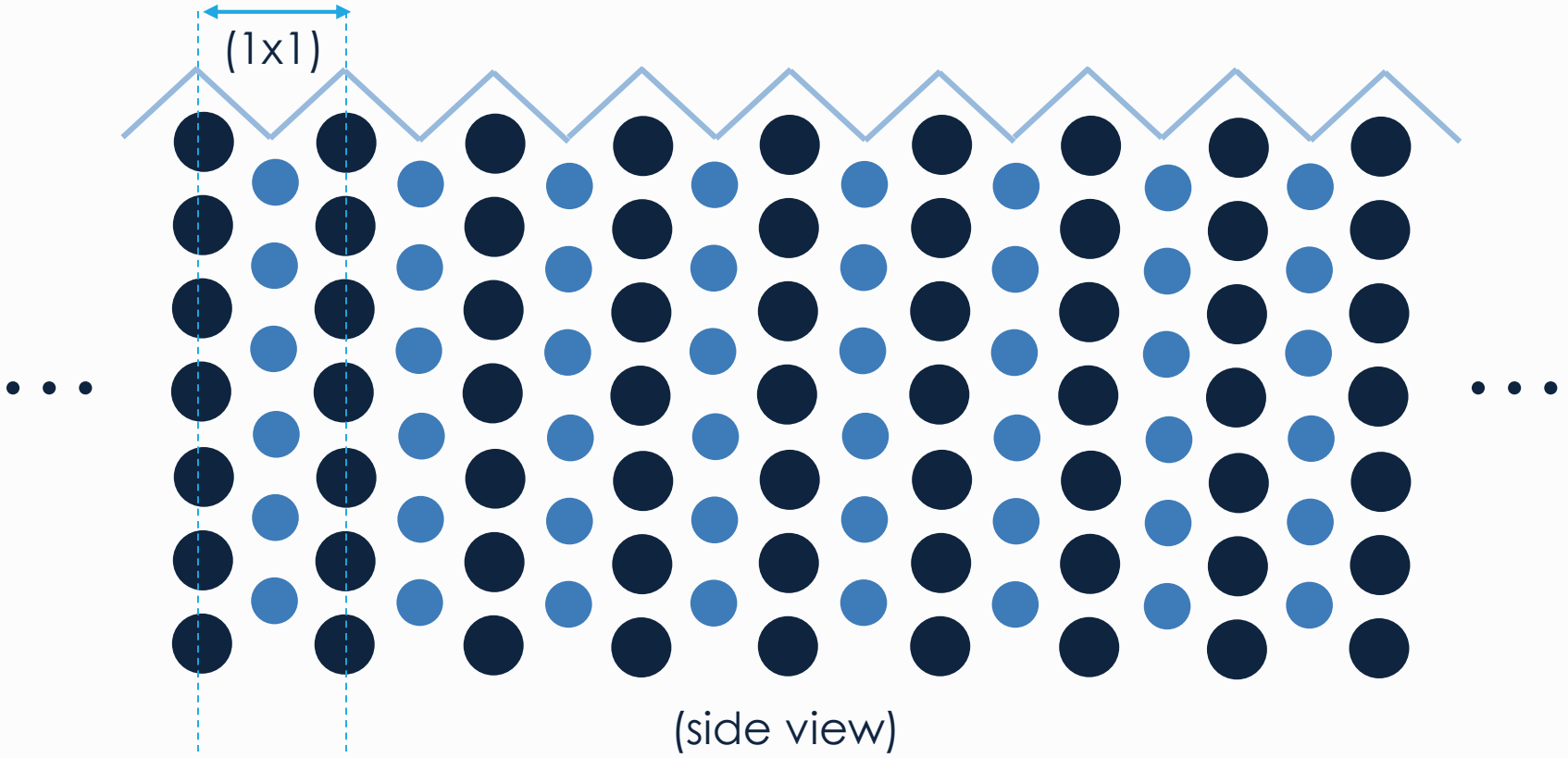
Local orbital methods with "floating orbitals" verified (cf. plane wave)
Sense of expected accuracy (validation) of DFT on known surfaces

# Pt ideal surface convergence

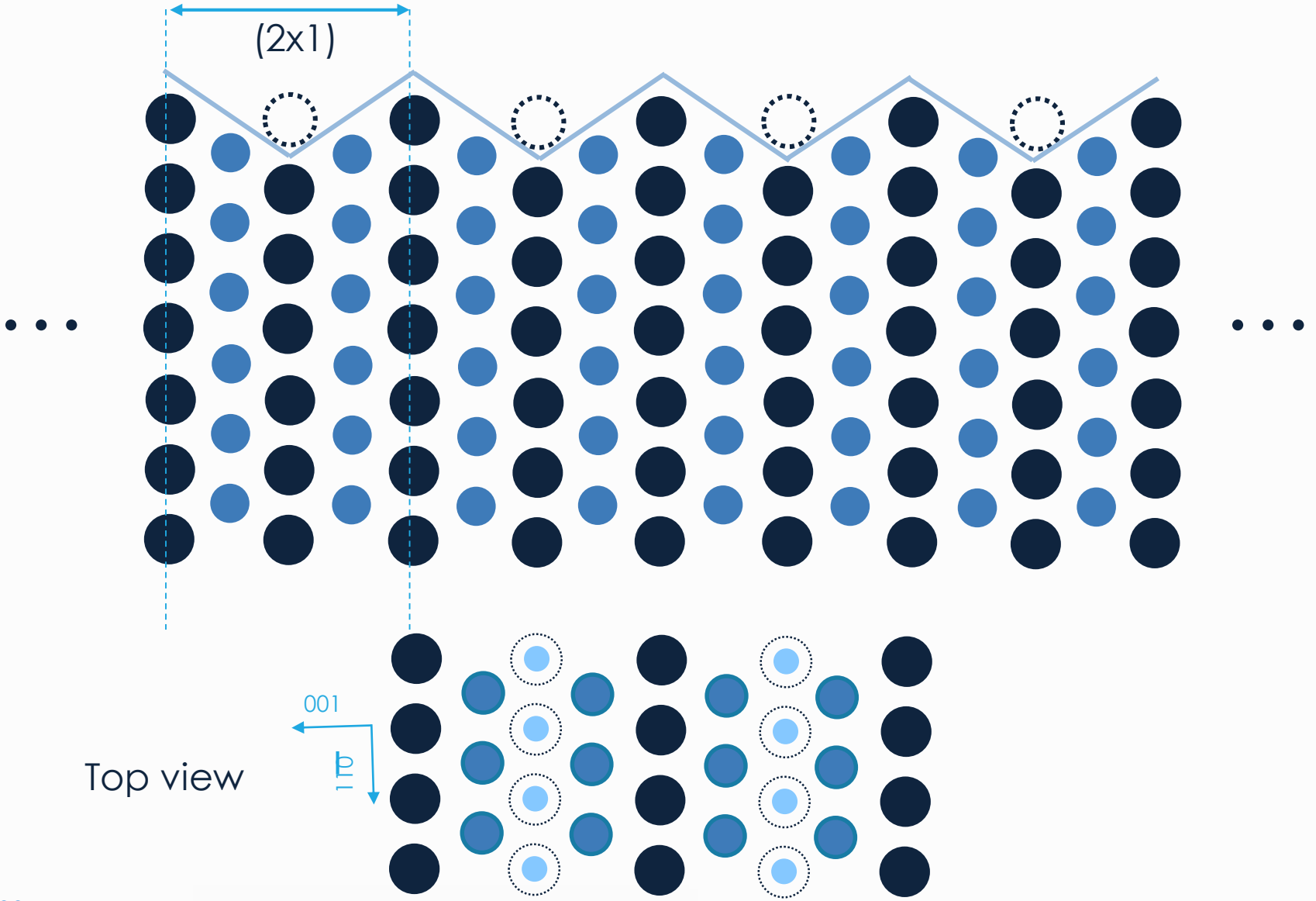



Surface energy for ideal surface converges quickly
So does the work function $\Phi$
*Passes verification checks – better behaved than Al*

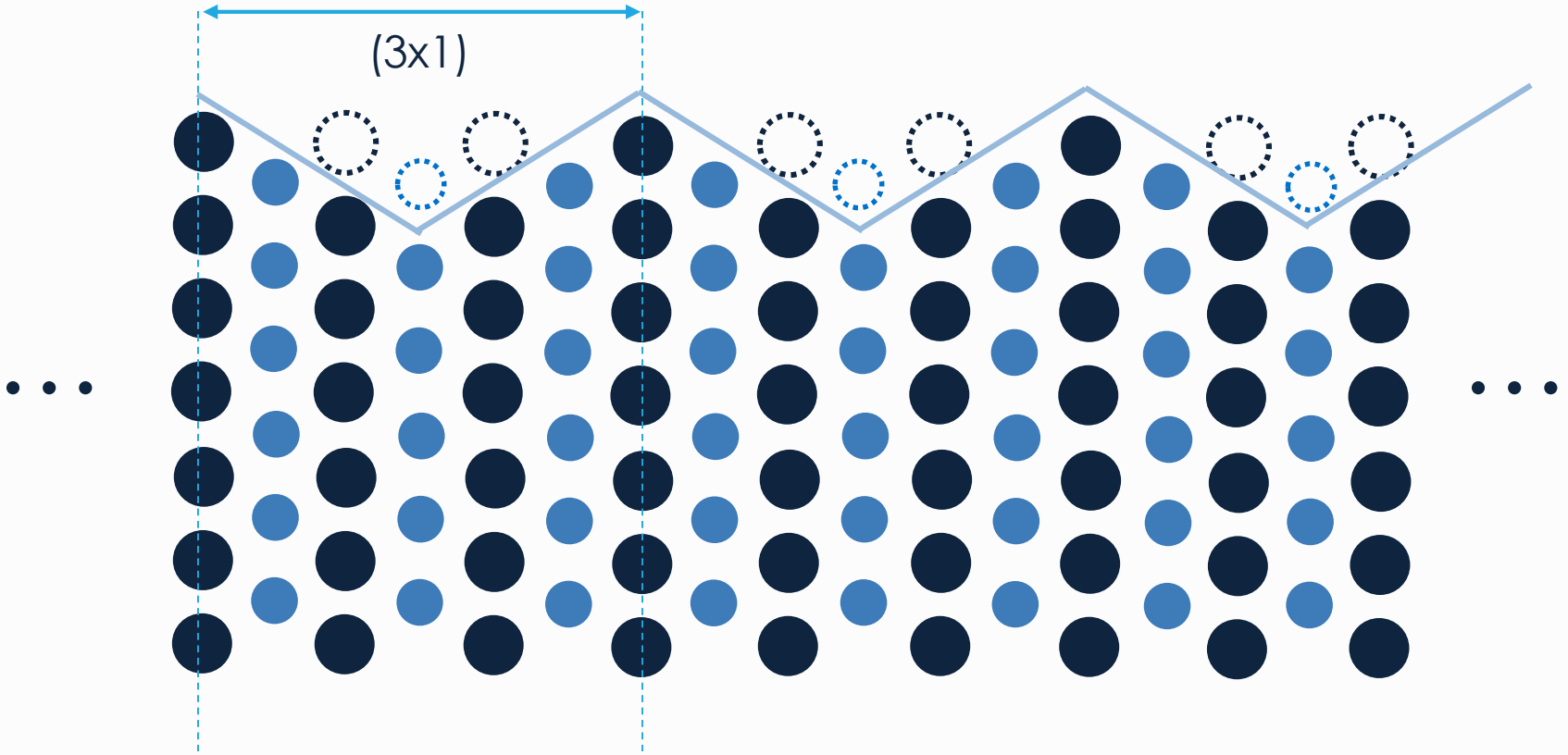
# (110) missing row reconstruction



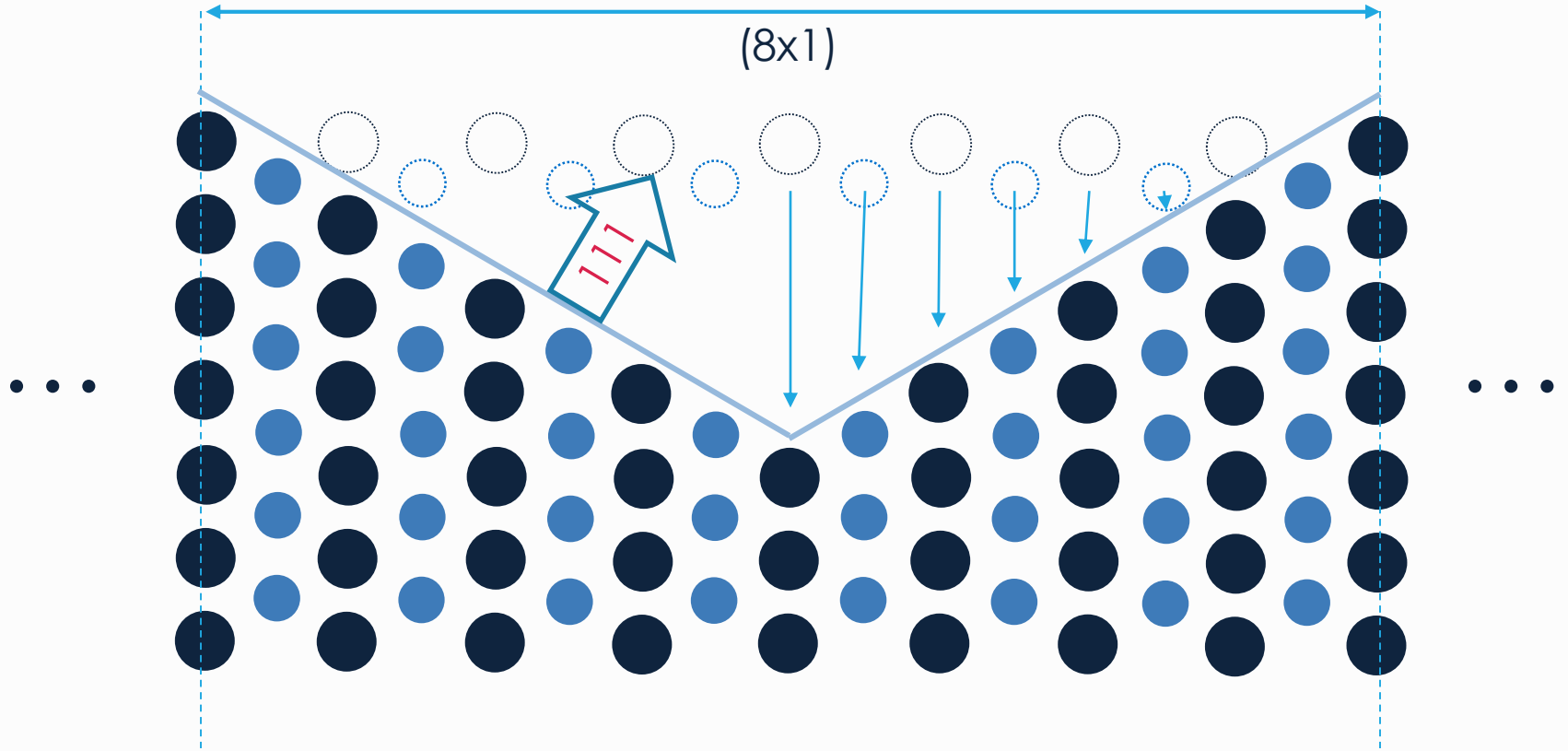
# (110) – (2x1) missing row



# (110) – (3x1) missing row

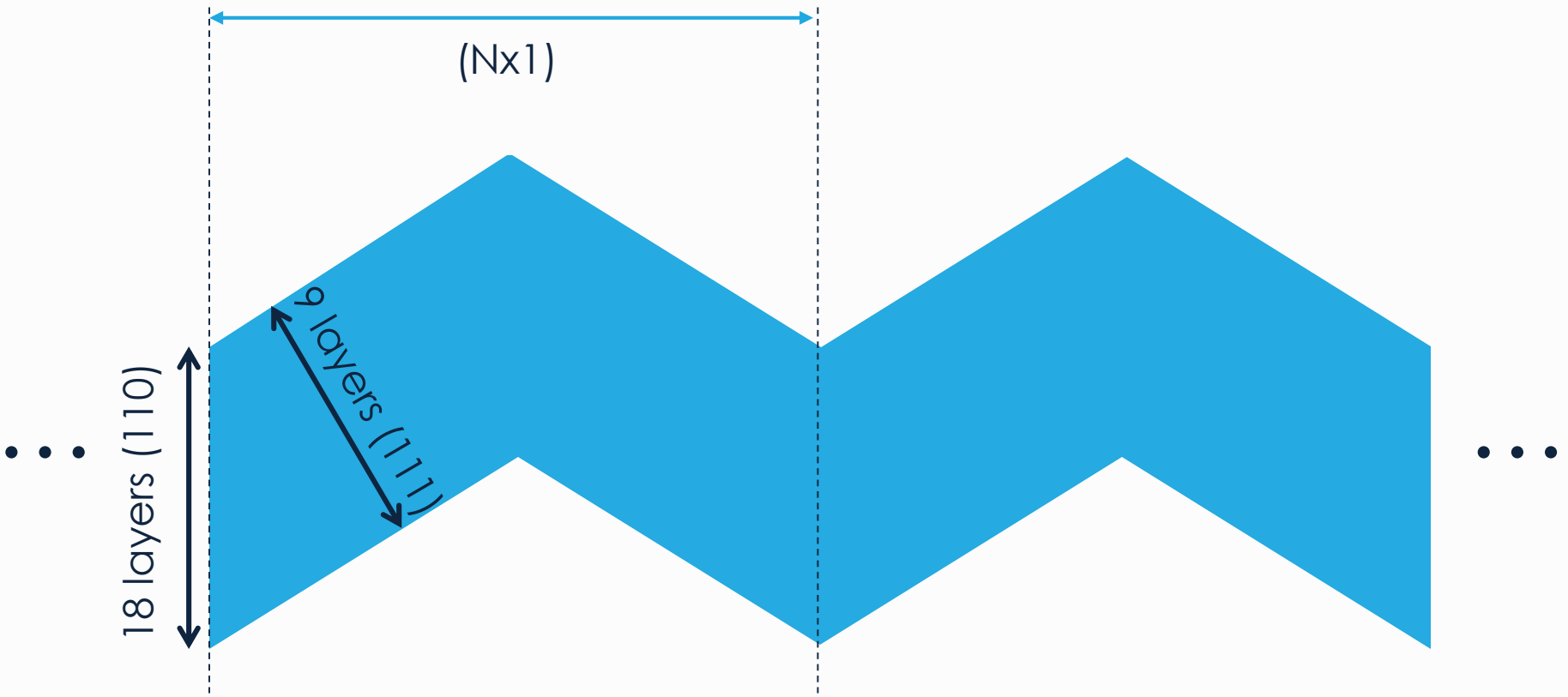


# (110)-(8x1) missing row - (111) nano-terraces



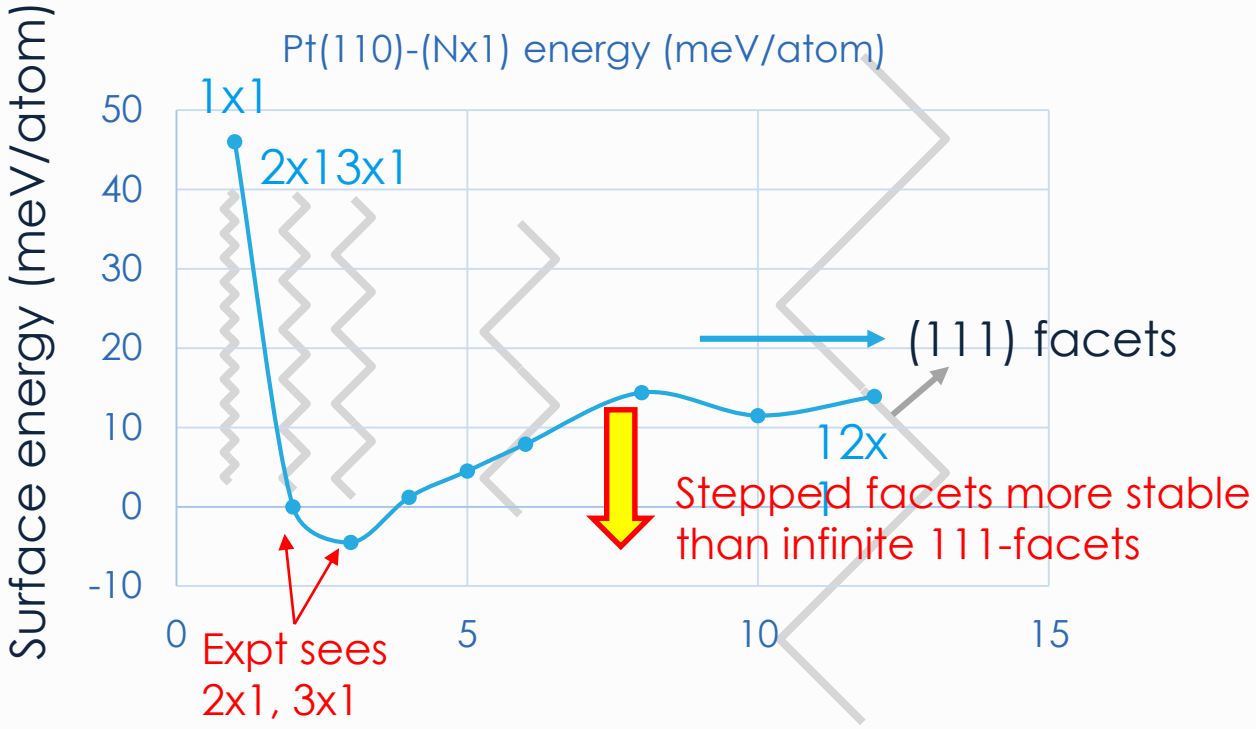

- (110) - (N x 1) missing row reconstruction …
  - directly maps to (111) terraces separated by ridges
  - if including counting the first ***two*** (110) layers in atom count

# (110) – (N x 1) computational model




To guarantee 9 layers (111), need 2 x 9 =18 layers of (110)

# (N x 1)-Pt(110) missing row reconstructions




Thermodynamics/kinetics vs. internal energy
There is a step-creation cost on the flat (111)

Thermodynamic tendency to form (111) stepped regions - pyramids

# Work functions of Pt surfaces

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| | | σ (eV/atom) / Φ (eV) (110) | (111) | (100) |
|---|---|---|---|---|
| Experiment | | — /5.35 | 1.03/6.08 | — /5.82 |
| Singh-Miller'09 | (PBE) | 1.30/5.26 | 0.65/5.69 | 0.90/5.66 |
| Da Silva'06 | (PBE) | — / — | 0.71/5.69 | |
| | (LDA) | — / — | 0.91/6.06 | |
| Our work | (LDA) | 0.88/5.71 | 0.86/6.14 | 1.20/5.74 |
| | (PBE) | 0.69/5.35 | 0.67/5.79 | 0.95/5.74 |
| | (AM05) | 0.79/5.36 | 0.77/5.79 | 1.09/5.75 |

| Pt(110): | (2x1) | (3x1) | (4x1) | (5x1) | (6x1) | (8x1) | (10x1) | (12x1) | … | Pt(111) |
|---|---|---|---|---|---|---|---|---|---|---|
| Φ (eV) | 5.49 | 5.55 | 5.59 | 5.63 | 5.65 | 5.66 | 5.69 | 5.69 | … | 5.79 |

Distances between steps/ridges tunes work function

# Summary

- New "slab-consistent" bulk reference approach is robust
- Pt(110) (2x1) and (3x1) correctly predict reconstructions
  - per atom energy lower than Pt(111)
- Pt(110)-like ridges/Pt(111) terraces are likely common features
  - explaining non-uniform growth, pyramids
- Work function tuned by step/ridge density, terrace widths
- Even AM05 surface functional strangely has trouble with Pt(111)


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