PHYSICAL REVIEW B **103**, 195426 (2021)

First-principles calculations of metal surfaces. I. Slab-consistent bulk reference for convergent surface properties

Peter A. Schultz[*]
Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

(Received 9 January 2021; accepted 5 May 2021; published 20 May 2021)

The first-principles computation of the surfaces of metals is typically accomplished through slab calculations of finite thickness. The extraction of a convergent surface formation energy from slab calculations is dependent upon defining an appropriate bulk reference energy. I describe a method for an independently computed, slab-consistent bulk reference that leads to convergent surface formation energies from slab calculations that also provides realistic uncertainties for the magnitude of unavoidable nonlinear divergence in the surface formation energy with slab thickness. The accuracy is demonstrated on relaxed, unreconstructed low-index aluminum surfaces with slabs with up to 35 layers.

DOI: 10.1103/PhysRevB.103.195426

I. INTRODUCTION

Fundamental physical properties of metal surfaces such as the atomic relaxations and surface reconstructions, or electronic work functions, have long been targets of first-principles electronic structure studies using density functional theory (DFT). In state-of-the-art approaches, slab calculations of thin metal films of finite thickness within a supercell approximation are used to model semi-infinite solid surfaces. In the limit of infinitely thick slabs, the desired limit of an isolated surface is recovered. However, with the thin slab models of a metal surface dictated by computational considerations, the two surfaces of the slab will interact with one another and engender quantum size effects [1] from confining long-range electronic states into a slab of finite thickness. Friedel oscillations in metals can extend long distances [2] suggesting that computationally intractable thick slabs might be necessary to compute properties converged to a semi-infinite bulk surface. Defining the slab formation energy as the relative energy of a slab with respect to a bulk reference energy of the same number of atoms (and assuming the two opposite surfaces of a slab are equivalent) the surface energy of a slab $E_{\text{surface}}(n)$ with n atomic layers—the energy to cleave an infinite bulk crystal—can be written as

$$E_{\text{surface}}(n) = \tfrac{1}{2}(E_{\text{slab}} - nE_{\text{bulk}}), \tag{1}$$

where E_{slab} is the computed total energy of a slab. Use of this basic relationship shows the crucial role of the bulk reference energy E_{bulk}: the surface energy diverges linearly with n with any error in defining E_{bulk}, and specifically for E_{bulk} obtained through an independent bulk crystal calculation [3]. I describe a method that, in principle, rigorously and exactly defines the bulk crystal limit of a slab model. The results will prove that a bulk reference energy obtained directly through this slab-consistent bulk crystal calculation leads to convergent surface formation energies. Moreover, this definition provides a direct estimate of the uncertainty in surface energy calculation due to the computed bulk reference energy. This approach is demonstrated on relaxed, unreconstructed low-index surfaces calculations of aluminum.

Boettger [3] was the first to document the nonconvergence of surface energies obtained from thin-film calculations using independent bulk crystal calculations for a bulk reference energy. The insight that a thicker slab is created by inserting additional nominal "bulk" atoms into the slab led to the proposal that the bulk energy might be better approximated by the incremental energy of adding an extra layer—an extra bulk atom—in a slab. Fiorentini and Methfessel [4] showed that using E_{bulk} derived from a linear fit of Eq. (1) over a range of slab thicknesses led to better convergent surface energies. As Boettger *et al.* [5] pointed out, this intuitive notion had (implicitly) been applied much earlier by Gay *et al.* [6] to fit a surface energy. The linear fit acquires, by definition, a "convergent" surface energy. Such a fit, however, requires numerous slab calculations larger than a converged slab thickness to verify that a converged surface energy is actually obtained. The uncontrolled variability due to quantum size effects means that surface formation energies are unreliable until a minimum thickness is reached, which is not known *a priori*. That minimum thickness can only be empirically determined.

This slab-thickness extrapolation becomes less practical with larger surface cells, such as those needed to investigate larger surface reconstructions. Da Silva *et al.* [7] showed that independent slab and bulk reference calculations could lead to convergent surface energies, provided slab and bulk calculations were both performed at high accuracy. However, a high level of accuracy for the slab calculation can be impractical, particularly for slab calculations with large area surface cells. Singh-Miller and Marzari [8] analyzed these various approaches for extracting surface properties from slabs, and concluded that the extrapolation methods gave the most reliable convergence. Feibelman [9], in trying to compute step

---

[*] paschul@sandia.gov

formation energies on Pt(111) surface with slab models of vicinal surfaces, mentioned a different alternative: compute E_{bulk} directly from a three-dimensionally periodic bulk crystal, but design the bulk crystal unit cell to specifically align to the orientation of the slab surface calculation, and ensure that the bulk unit cell and slab unit cell sample the bulk and surface Brillouin zone equivalently. In this paper I describe how to extract a meticulously slab-consistent bulk reference energy for any slab calculation that within Eq. (1) is guaranteed to yield directly convergent surface energies to within a predictive uncertainty, without depending upon any fit of surface energy of slabs of incremental thicknesses.

II. SLAB-COMPATIBLE BULK CRYSTAL REFERENCE CELLS

Construction of a compatible bulk reference to a slab calculation requires that atoms in the two limits are treated equivalently, in real space grids and in sampling of the Brillouin zone (BZ) [10,11]. This mandates a different bulk crystal unit cell specific to each surface, which will generally mean different, surface-consistent, values for the bulk reference energy for different surfaces. A surface-consistent bulk unit cell has the identical two-dimensional lattice vectors that define the slab surface supercell, and then a third lattice vector normal to the surface that extends until the top surface layer repeats. This is illustrated in Fig. 1 for the low-index surfaces of an fcc lattice with lattice constant a.

The primitive cell (dashed) for the (100) surface is a square in the surface plane $a/\sqrt{2}$ on a side. The three-dimensional (100)-consistent bulk crystal cell is defined by using these and a third vector and along the (100) surface normal, a $(a/\sqrt{2})^2 \times a$ tetragonal unit cell containing two atoms. The (110)-consistent bulk cell is also a two-atom tetragonal cell, defined by the $a \times a/\sqrt{(2)}$ rectangle matching the slab surface primitive cell vectors, and a full lattice constant a along the (110) surface normal for the bulk repeat vector. The (111)-consistent cell is hexagonal, $\sqrt{3}a$ deep, and contains three atoms.

For an atom in a slab calculation to have a numerically equivalent environment to the bulk reference calculation, the atoms must have the same registry to the real space integration grid. Hence, the (nonperiodic) slab repeat vector should be an integral number of the slab-consistent bulk layer repeat vector, and the atomic layers aligned to be an integer number of layers away from the vacuum boundary. Additionally, to take advantage of the equivalence of the individual layers in each of these bulk reference cells, the real space grid dimensions in the bulk should be even numbers for the (100) and (110) compatible bulk cells so as to make the two atoms in these cells in identical registry to the real space grid, and evenly divisible by three in the (111) cell to make the atoms in each of the three equivalent layers in the same registry with respect to the real space grid.

A slab calculation with a $k_A \times k_B$ BZ sampling in the limit of an infinitely thick slab is then formally equivalent to a (slab-consistent) bulk calculation with an identically aligned $k_A \times k_B \times k_\perp$ sampling of the BZ, in the limit of infinitely large $k_\perp$. Extrapolations to larger $k_\perp$ to achieve convergence of the slab-consistent bulk calculations is straightforward. In the following I show that this extrapolation can be used to directly calculate a bulk reference energy that ensures convergence of the computed surface energy in Eq. (1). This eliminates the need to extrapolate from fits to slab energies of varied thickness, and provides good accuracy even with coarser two-dimensional surface BZ sampling. The bulk calculations also provide a diagnostic to determine how coarse a surface sample can be made before significant errors emerge.

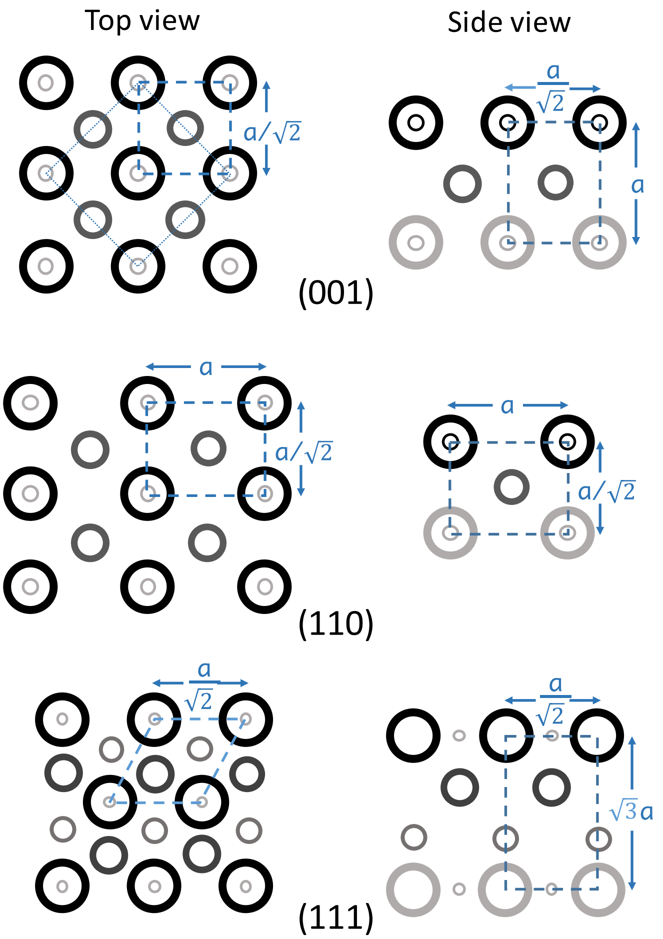

FIG. 1. Construction of slab-consistent bulk crystal unit cells for low index surfaces of a simple fcc crystal with lattice constant a. The dashed lines in the top view outline the two-dimensional primitive unit cells for the slab models of the (100), (110), and (111) surfaces of an fcc crystal, which define the primitive vectors, constrained to the surface plane, of the slab-consistent bulk crystal reference cell. The third primitive vector of the slab-consistent cell is normal to the surface plane. The (100) and (110) have two equally spaced (equivalent) layers in the slab-consistent bulk cell, while the (111) requires three equally spaced (equivalent) layers to form the slab-consistent bulk cell.

III. COMPUTATIONAL METHODS

The DFT calculations are executed with the SeqQuest code, which uses pseudopotentials to eliminate explicit treatment of core electrons and carefully optimized contracted Gaussian basis sets to represent the electronic wave functions.

I present calculations using both the local density approximation (LDA) [12] as formulated by Perdew and Zunger [13], and the generalized gradient approximations (GGA) created by Perdew, Burke, and Ernzerhof (PBE) [14], functionals standardly used in studies of metal surfaces, including aluminum [7,8]. I complement these with results using the PW91 functional [15] and using the AM05 functional developed by Armiento and Mattsson [16] specifically designed to improve upon the treatment of surface effects in DFT.

The LDA pseudopotentials were generated with Hamann's generalized norm-conserving pseudopotential (GNCPP) code [17] and the PBE and AM05 pseudopotentials, while also using the GNCPP form [17], were generated with the FHI98PP code [18]. The Ne-core three-electron Al pseudopotential used the default settings for *s* and *p* potentials, and added a *d* potential with a cutoff of $R = 1.2$ bohrs to give a more faithful description of the local potential, all these potentials left in the unmodified "semilocal" form. Where indicated, a nonlinear core correction (NLCC) [19] is included.

The aluminum atom basis set is a "double-zeta plus polarization" contracted Gaussian basis, providing two radial degrees of freedom for the strongly occupied *s* and *p* orbitals, plus a single *d* function to allow for angular polarization. To give accurate treatment of the evanescent electron density extending outside the surface, the atomic-centered basis is augmented with "floating orbitals": ghost atoms fixed to the positions of the first missing layer of atoms above the last aluminum atoms on the (100), (110), and (111) surfaces. A ghost atom has single-Gaussian *s*, *p*, and *d* orbitals, where the Gaussians are roughly the same as the outermost (polarization) Gaussian in each aluminum atom basis orbital: decay constants of 0.09, 0.08, and 0.20/bohr^2, respectively. This simple prescription is shown (below) to be quantitatively effective in removing basis set errors from localized orbitals for calculations of surface properties of Al.

A Fermi function filling factor with an electronic temperature of 0.003 Ryd ($\sim$41 meV) is used to smear the occupations near the Fermi level. This artificial temperature is large enough to achieve electronic self-consistency (up to slabs of $\sim$40 layers), but smaller than that which might significantly affect the energy and might otherwise unacceptably begin to corrupt results [20].

Slab models are constructed starting from an atom in a central layer in the middle of the slab supercell and creating slabs of greater thickness by incrementally adding an atom layer on both sides, topping both surfaces of the slab with ghost atoms at the positions of the next layer of (missing) atoms. The vacuum boundary is set to be an integer number of bulk repeat layers from the center, with sufficient vacuum ($\sim$10 Å) to separate the repeating slabs (SeqQuest explicitly checks for overlap of electronic density at the vacuum boundary). All atom positions in the slab calculations are relaxed to minimum energy configurations, invoking all available symmetry, using a modified Broyden method due to Johnson [21] adapted for geometry updates. An atomic relaxation is deemed converged when the total force on every atom is less than 0.0002 Ryd/bohr (5 meV/Å). Relaxation of ghost atoms leads to negligible energy lowering. To avoid the noisy numerics that accompanies resolving their positions in the optimization, in the results reported here, ghost atom positions are always held fixed.

IV. RESULTS AND ANALYSIS

A. Bulk fcc properties

The slab calculations of aluminum surfaces all use the optimal (*k*-converged) bulk fcc lattice parameter obtained with each functional. Table I presents my calculated lattice parameter and bulk modulus for Al using the LDA, PBE, PW91, and AM05 functionals. These bulk Al calculations are done in a one-atom rhombohedral fcc cell with an 18^3 real space integration grid and Γ-centered regular (even-dimension) *k* meshes ranging from 16^3 to 32^3.

The lattice parameter and bulk modulus are obtained from a (cubic polynomial) fit using a Birch-Murnaghan equation of state [22–24] to 14–16 fixed a_0 calculations equally spaced within $\sim \pm 2\%$ around a_0. The optimized a_0 are converged to $\sim$0.001 Å after a *k* mesh of 16^3. The bulk modulus *B* fit for each *k* mesh exhibits intrinsic numerical uncertainties (to the number and locations of data points, and to the form of

TABLE I. Bulk properties of aluminum: lattice parameters a_0 (Å) and bulk modulus *B* (GPa).

	4.032[a]	79.38[b]						
	LDA		PBE		PW91		AM05	
Experiment	a_0	B	a_0	B	a_0	B	a_0	B
This work	3.970	82.5	4.053	76.2	4.048	74.1	4.024	82.8
w/NLCC	3.976	84.1	4.034	78.1	4.041	74.2	3.998	86.1
PAW[c]	3.99	84	4.04	78	4.05	74	–	–
RSPT[d]	3.986	82.5	4.043	77.1	–	–	4.008	86.2
Da Silva *et al.*[e]	3.98	84	4.04	78	–	–	–	–
Singh-Miller and Marzari[f]	–	–	4.06	74	–	–	–	–

[a] Extrapolated to 0 K from a_0 (293 K) = 4.0490 Å, following Ref. [27] and the thermal expansion data collated in Ref. [28].

[b] At 4 K, Ref. [27].

[c] Reference [26] using a projector augmented wave method.

[d] Reference [25] using the full potential RSPT code.

[e] Reference [7] using a full-potential linear augmented plane wave method FP-LAPW.

[f] Reference [8] using a norm-conserving pseudopotential plane wave method.

equation of state) of ∼1 GPa. The computed B quoted in Table I also varies $\sim \pm 0.8$ GPa for k meshes from 16^3 through 32^3. Even assuming a perfect representation of the form of the equation of state, the B can be trusted to no better than 1 GPa. Similarly, the equilibrium total energy (not shown) varies by 1 meV/Al over this same range of k samplings. Above 16^3 k samplings are generally considered very highly converged k meshes [7]. This magnitude of variability foreshadows the limits in defining a precise bulk reference for surface formation energy computations.

The DFT structural properties agree well with experiment, confirming the suitability of DFT for aluminum, and agree well with results from all-electron [7,25] and projector augment wave based [26] calculations, verifying the quality of the pseudopotentials and basis sets used in this work. The results also agree well with the previous DFT studies for aluminum surfaces of Da Silva *et al.* [7], and Singh-Miller and Marzari [8], making possible meaningful quantitative comparisons to their results. Nonlinear core corrections improve agreement with the all-electron bulk benchmarks, but have only minor effects on my pseudopotential surface results, and are ignored henceforward.

B. Slab-consistent bulk reference energies

While the one-atom bulk fcc calculations produce a bulk energy for aluminum, these are not directly usable as bulk reference energies in surface formation energy calculations, unless the two-dimensional slab k-point sampling is similarly highly converged [7].

The vertical tetragonal 100-consistent bulk reference cell has real space grid dimensions of 16×16 in the square $\frac{a_0}{\sqrt{2}} \times \frac{a_0}{\sqrt{2}}$ surface plane and 24 along $a_\perp = a_0$, while the flat tetragonal 110-consistent bulk reference cell has a 24×16 real space grid in the rectangular $a_0 \times \frac{a_0}{\sqrt{2}}$ surface place and 16 along its $a_\perp = \frac{a_0}{\sqrt{2}}$. With even-dimensioned grids, both atom positions in the cell are coincident with a grid point. The hexagonal (111)-consistent bulk reference cell has a 15^2 real space grid in-plane, and 42 grid points spanning the three Al layers in this cell. Each of the three atoms are in identical registry with the real space grid, the grid dimension purposefully made evenly divisible by three.

Variations in the $k_\perp$-dependent slab-consistent aluminum reference energy are depicted in Fig. 2 for the (100)-consistent bulk reference calculation with the PBE, the (111) with the LDA, and the (110) with the AM05 functional. Plotted as differences from the k-limit averages of Al energies in the fcc calculations, these results highlight the perils of using a single bulk reference energy for all surface formation energies, and the need to use appropriate surface- and planar-k-sample-specific averages for reference energy. The (111), with the longest $a_\perp$, converges (within variations of 0.5 meV/Al) with modest $k_\perp < 16$. The (100) varies within a range of 1 meV/Al at $k_\perp \geqslant 16$ and above. The (110), with the smallest layer thickness $a_\perp$, varies almost as much as 8 meV/Al for $k_\perp \geqslant 16$, and only dampens variations to 1–2 meV after $k_\perp \geqslant 24$.

Even for the (111) however, the different $k_\parallel$ samples converge values that differ by as much as 10 meV/Al. For a bulk-specific calculation, this precision might be acceptable. For plausibly converged slab calculations requiring 10–20 layers, this uncertainty would inject large errors, especially for the (110)-oriented cell. The variability in these $k_\perp$-limit values represent a practical limit on the accuracy with which the bulk reference energy can be determined. This irreducible uncertainty can be used to estimate uncertainties in derived quantities such as the surface energy.

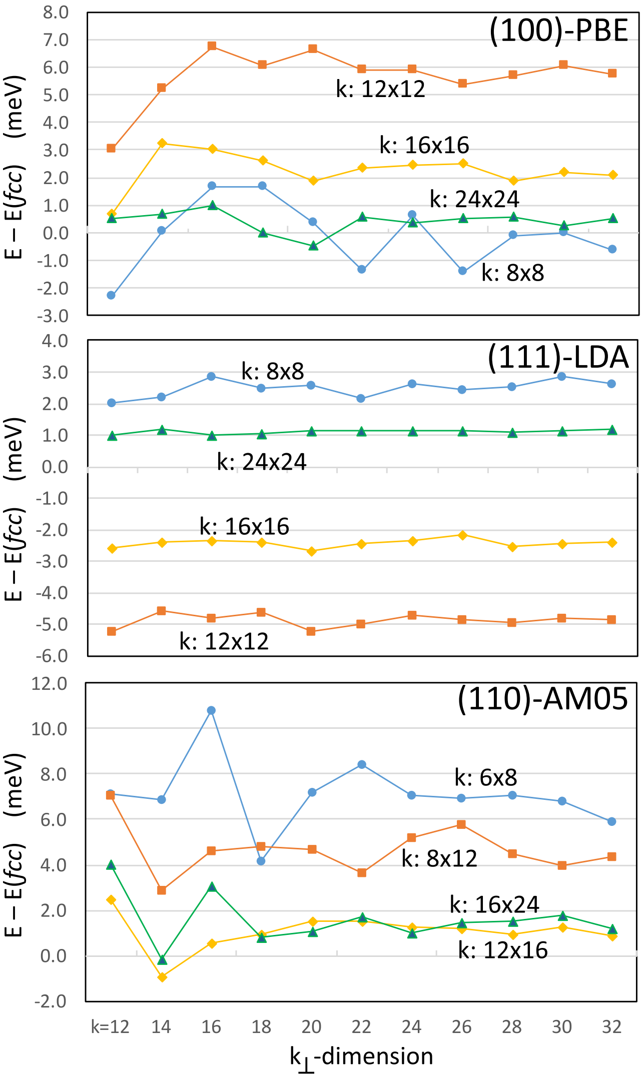

FIG. 2. Variations of surface-consistent aluminum bulk reference energies versus $k_\perp$ dimension, referenced to the k-limit average of the one-atom fcc bulk energy.

That it requires a 24×24 $k_\parallel$ sampling to obtain a bulk reference energy converged within 1–2 meV/Al of the bulk fcc energy, indicates that this would be the minimum $k_\parallel$-sampling necessary to converge a surface energy from an independent surface calculation. The construction of a slab-consistent bulk reference energy cancels this variability in the bulk reference energy in the computation of the surface energy, leading to the accelerated convergence with $k_\parallel$ described in the next section.

For constructing the slab-consistent bulk reference energies, I average energies over well-converged $k_\perp = 16$ through 32 to obtain a $k_\perp$-limit reference energy specific to the surface and the in-plane $k_\parallel$ sample, and an associated uncertainty from the variability over that range.

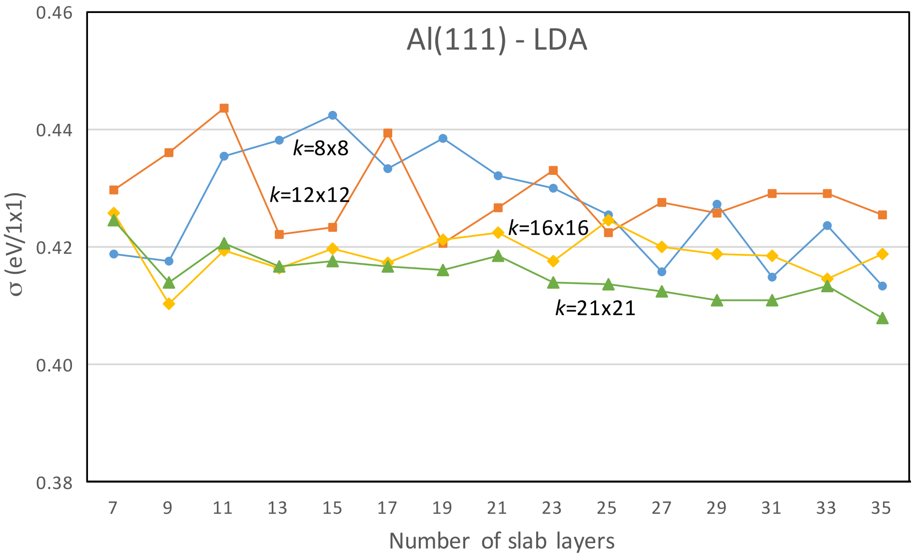

FIG. 3. Surface formation energy of the unrelaxed Al(111) surface using the LDA functional, as a function of the surface *k*-sample grid versus the slab thickness (number of layers). Lines are guides for the eye.

C. Analysis of surface energies

The low-index aluminum surfaces exhibit minimal relaxations. In these calculations, the relaxed (100) surfaces show a typical energy lowering of 3 meV from the unrelaxed (bulk-terminated) structure, the (111) a negligible 1 meV, and the (110) a larger, but still minor, relaxation of 10–15 meV, irrespective of functional (LDA, PBE, AM05, or PW91) or slab thickness. For simplicity, most of the analysis that follows will be focus on the unrelaxed slab results, the relaxed slab analysis being almost identical (except for one illuminating example discussed below).

Figure 3 shows the LDA surface formation energy of the unrelaxed Al(111) surface obtained with the slab-consistent (surface and *k* sample) bulk reference energy defined above, for slab thicknesses up to 35 layers. As anticipated by Da Silva *et al.* [7], and confirmed by Singh-Miller and Marzari [8], there is no divergence when a large and matching *k*-point sampling is used.

Plotted in Fig. 3, the surface energy varies with slab thickness progressively more strongly as the $k_\parallel$ mesh gets coarser, from 16 × 16 to 12 × 12 and reduced even further to 8 × 8. The 8 × 8 might have a slant, amounting to a small shift of ~20 meV in surface energy from 15 to 35 layers. This is within the 0.02 eV scatter of computed surface formation energies across this entire series, and could be entirely attributable to the *k*-limit uncertainty, ±0.5 meV/atom, in the computation of the 8 × 8 (111) bulk reference energy (see Fig. 1). All of the series converge to within the uncertainties in the *k*-limit averages of the slab-consistent bulk reference energies.

The $k_\parallel$-resolved bulk reference energies differ by as much as 8 meV/atom from each other for the Al(111) surface (see Fig. 1), and are as distant as 5 meV from the highly converged *k*-limit fcc bulk energy. Errors in a reference energy of this magnitude would lead to an unacceptable drift of $\geqslant 0.1$ eV in the ensuing surface energy calculations out to 35 layers. The absence of this divergence in any of the current results demonstrates that a slab-consistent bulk energy is the correct reference energy to use in Eq. (1) to obtain convergent surface energies from DFT slab calculations.

Each *k*-resolved series converges, and converges to the same surface formation energy, $\gtrsim 0.41$ eV/surface atom (1 × 1 surface cell). Even the coarse 8 × 8 *k* mesh is sufficient to give a surface energy within 0.01 eV/surface atom of the largest highly converged *k*-mesh result.

The close-packed (111) surface is typically the most stable surface of an fcc metal, and surface calculations are usually numerically well behaved. This is convenient to show convergence of different methods for extracting surface energies from slabs with increasing thickness [7,8,11], but does not illustrate the challenge that slab-based calculations of surface can face. The other, more open surfaces are less well behaved and represent more stringent and discriminating tests of convergence with slab thickness.

The computed formation energies for the Al(100) surface, in this case using PBE (the overall convergence behavior is insensitive to the choice of functional), are depicted in Fig. 4. The *k* samples larger than 12 × 12 mostly overlap each other and converge well to a (100) surface formation energy of 0.46 eV/atom (1 × 1 surface cell). The unrelaxed 8 × 8 series (the solid blue line connecting solid circles), however, diverts from the others. Out to 15 layers, this formation energy decreases almost linearly with slab thickness, and then flattens only above 25 layers, converging to 0.42 eV/atom. Furthermore, in contrast to the denser *k* sampling, a full geometry optimization for the 8 × 8 series results in a significant lowering. Rather than the 1–3 meV total relaxation energy lowering characteristic for the other series on the 100 surface, the $k_\parallel = 8 \times 8$ surface energy relaxes ~0.02 eV for thin slabs, increasing to > 0.06 eV for thick slabs, and appears to be diverging.

The unrelaxed 8 × 8 series illustrates the hazard of using an empirical fit to extract an effective bulk reference energy and surface energy. Truncated at 15 layers, an empirical fitting

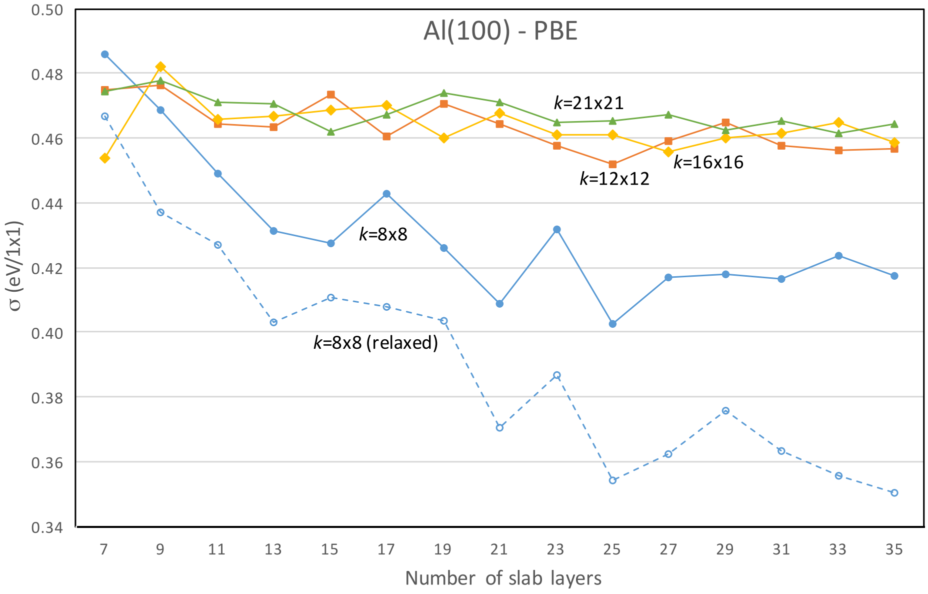

FIG. 4. Surface formation energy of the unrelaxed Al(100) surface (solid lines) using the PBE functional, as a function of the surface k-sample grid versus the slab thickness (number of layers). The dashed line traverses the surface formation energies for the relaxed surface with an 8×8 k sampling.

approach to a bulk reference energy might plausibly be mistaken to show good convergence, incorporating the apparent (roughly) linear decrease out to 15 layers into an erroneous bulk reference energy. The more rigorous surface-consistent bulk reference indicates a decreasing surface formation energy, and convergence to a fixed surface energy only above 25 layers.

Hints of similar behavior might be inferred in the plots for the denser $k_{\parallel}$-point series. This suggests that the extent of quantum size effects (QSE) in Al might be more significant than generally believed, as seen in previous work for Al surfaces [29,30]. The current calculations indicate that effects of QSE on the surface energy, albeit small, can be detected out to a slab thickness of 24 a_0.

The relaxed $k_{\parallel} = 8 \times 8$ series for Al(100) aggravates this behavior, seeming to contradict the hypothesized convergence of this surface-consistent bulk reference approach. The surface relaxation energy steadily increases and the total surface energy continues to diverge even after 25 layers. The relaxations, rather than being small and limited to the top two or three layers, are seen to extend to the center of the slab, the interlayer spacing increasing by 2.2(2)% from the bulk value. This divergence of the surface energy is not directly due to an incorrect bulk reference *energy*, but stems from the coarse 8×8 surface k sample that leads to an incorrect bulk reference *structure*. The surface-compatible $8 \times 8 \times k_{\perp}$ k sampling is inadequate for bulk Al. A bulk cell optimization shows the in-plane lattice constant shrinking by 1.4(1)% and the normal

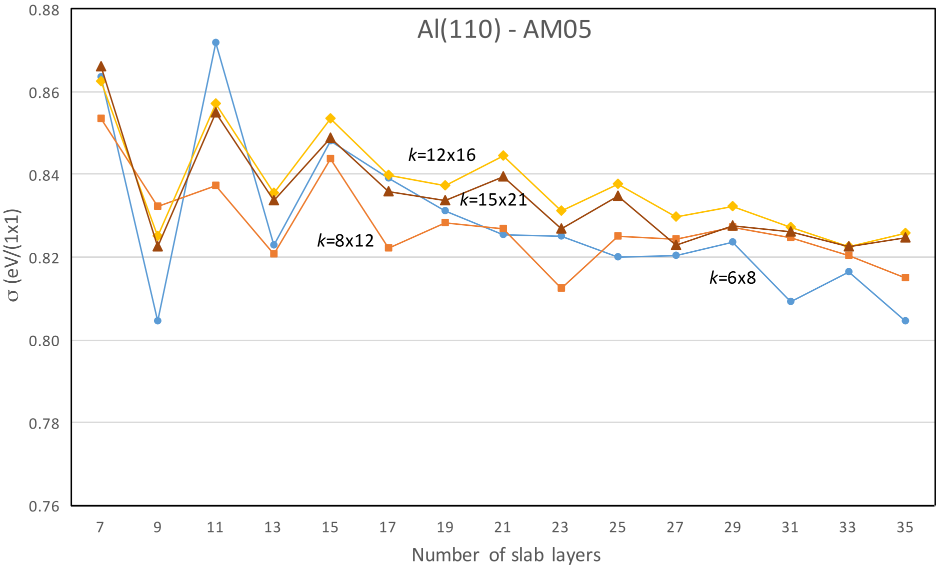

FIG. 5. Surface formation energy of the unrelaxed Al(110) surface using the AM05 functional as a function of the surface k-sample grid versus the slab thickness (number of layers).

TABLE II. Properties of low-index aluminum surfaces: surface energy σ (eV/surface atom) and work function Φ (eV). Computed uncertainties in σ (slab thickness, k-point variation) is 0.01 eV, and in Φ is 0.03 eV.

	Al(100)		Al(111)		Al(110)	
	σ	Φ	σ	Φ	σ	Φ
Experiment						
	–	4.41(±0.03)[a]	0.51[b]	4.24(±0.02)[a]	–	4.28(±0.03)[a]
LDA						
Unrelaxed[c]	0.54	4.53	0.41	4.27	0.82	4.22
Relaxed[c]	0.53	4.49	0.41	4.26	0.80	4.22
Fall (1998)[d]	–	4.38	–	4.25	–	4.30
Da Silva (2006)[e]	–	–	0.39	4.21	–	–
Nguyen (2019)[h]	–	–	–	–	0.82	4.22
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)[g]	0.45	4.30	0.30	4.02	0.70	4.09
Nguyen (2019)[h]	0.48	4.20	0.24	4.05	0.72	4.06
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
AM05						
Unrelaxed[c]	0.55	4.34	0.42	4.10	0.83	4.04
Relaxed[c]	0.54	4.33	0.42	4.10	0.82	4.04

[a] Reference [31].

[b] Reference [32], converted from quoted 1.14 J/m^2 to eV/atom using $a_0(293\ \mathrm{K}) = 4.05$ Å.

[c] Current work, quoting large $k_{\parallel}$ (21×21 for the 100 and 111 and 24×16 for the 110) and averaging over slab thickness of 17–35 layers.

[d] Reference [34], using a norm-conserving pseudopotential code with 9 (for 111) or 8 (100,110) layers.

[e] Reference [7], using a full-potential code with 7 layers [for the Al(111) surface].

[f] Reference [33], using a full potential code with between 15 (for 111) and 23 (for 110) layers.

[g] Reference [8], using a norm-conserving pseudopotential plane wave method code with 13 layers.

[h] Reference [30], using a plane-wave code with up to 30 layers.

lattice constant increasing by 3.7(2)% from the fcc bulk value (the uncertainty in parentheses due to variations in cell parameters with $k_{\perp}$). The optimal slab-compatible (tetragonally distorted) bulk crystal lattice parameters differ significantly from the optimized bulk fcc lattice parameter used to construct the slab model, leading to artificial interlayer relaxations in the slab calculations [10].

Using the $k_{\parallel}$ sampling—and orientation-specific lattice constants—modifying the bulk reference structure in the construction of the slab model would remove this divergence and lead to a convergent surface energy. Simply fixing the inner layers to their bulk positions would also mitigate this pathology. Depending upon the quantity of interest, these fixes might be sufficient. However, the significant restructuring of the crystal indicates that this surface $k_{\parallel}$ sample leads to a poor description of the bulk metal. This serves as a warning and defines an assessable criterion for accepting a computational model. This failure could be anticipated by bulk cell optimization of k samplings suspected to be too coarse, testing adequacy of the $k_{\parallel}$ sampling in the bulk reference calculations before attempting the more expensive surface calculations.

Figure 5 presents the convergence behavior for the Al(110) surface, this time using AM05 as the representative functional. Unlike the (111) or (100) surface, where the surface energy was well converged at 15 layers, the (110) surface energy is still varying significantly, and does not appear to fully stabilize until more than 25 layers. Without a rigorous slab-compatible bulk reference, it would be very difficult to infer convergence to a surface energy for the more open (110) surface.

D. Converged surface properties

The surface-consistent bulk reference approach enables computing surface properties that are converged, with a realistic measure of quantitative confidence. In Table II I summarize the fully converged (layer thickness and k-point) results for low-index Al surfaces, using slab-consistent references, and incorporating realistic estimates of uncertainties. In addition to the surface energies discussed above, the results for computed work functions are also presented. Work functions are a very sensitive numerical quantity in DFT surface calculations—and highly discriminating tests of localized orbital methods. Experimental work function data is available for each of the low index Al surfaces [31], whereas the surface formation energy has only been measured for the Al(111) surface [32].

With the use of a rigorous surface-consistent bulk reference energy, with its $k_\perp$-limit uncertainty and from extrapolation with slab thickness, I determine a numerical uncertainty of 0.01 eV/surface atom in the surface energy for each surface. This is ten times smaller than the physical error (difference from experiment) due to the DFT approximations. The computed surface energies closest to experiment, using the LDA and AM05 approximations, are 0.1 eV smaller than experiment. This numerical uncertainty is also comparable to the differences between the current converged extrapolations and the surface formation energies computed in previous works [7,8,33]. And also comparable to differences between these previous works—as should be expected as these all are typically quoted as single-point results of different thicknesses and different k-point samplings.

There is good agreement between the current local orbital results for the surface energy and the previous plane-wave basis works [7,8,33,34] for each of the low-index Al surfaces. This is testimony that the simple prescription of adding ghost atoms with floating orbitals at the first set of vacated sites at the surface of a metal slab is an effective means to fix basis set insufficiencies in surface calculations using local orbitals.

Surface energies are exceedingly challenging to determine experimentally. Only the (111) surface energy has been obtained for aluminum: a surface energy of 0.51 eV/surface atom quoted by Gay *et al.* [32]. The predictions using the LDA and AM05 are within 0.1 eV, a very good accuracy—the best physical accuracy one can reasonably expect of the DFT approximation for structural energies.

The GGA is commonly preferred to the LDA for bulk metal calculations, but the GGA has been shown to lead to generally inferior predictions of surface properties [16]. The PBE results and PW91 results (often taken to be synonymous with GGA) presented in Table II deviate slightly (but not greatly) more from experiment than the LDA and AM05 results. While these two GGA functionals are less equivalent than typically assumed [26], in the case of aluminum, the PBE and PW91 surface results are very similar to each other, and also not that dissimilar from the LDA and AM05 results. The aluminum system is, fortuitously, very forgiving with respect to the choice of DFT functional.

The work function can be more readily measured experimentally, and the work function for aluminum have been reported to be 4.41, 4.24, and 4.28 eV for the (100), (111), and (110) faces, respectively [31]. These can be measured with good accuracy (within 0.03 eV experimental uncertainty), and are straightforwardly extracted from DFT calculations for metals (as the position of the computed Fermi level below the vacuum level).

The computed LDA work function is within 0.1 eV of the experimental work function for each surface, higher for the (100), lower for the (110), and within experimental and theoretical uncertainties for the (111) faces. The GGA functionals systematically underestimate the work function, by about 0.2 eV. The AM05 functional mimics the GGA results, rather than the rather good LDA results. This is unexpected, given that AM05 incorporates specific modifications to better treat surface effects [16], and that AM05 gave improved results comparable to the LDA for the Al surface energies. The deviation is small, however, and might benefit from more systematic study in other materials.

The work function is an exceedingly sensitive computational quantity, and, in particular, the work function is strongly dependent upon accurately describing the long-range evanescent density above the surface that is short changed in an atom-centered local orbital method. The work function results presented in Table II show good agreement between the current local orbital basis calculations and previous, plane-wave basis results, The differences are within the computational uncertainties, comparable to differences between the different plane-wave results, and less than the physical uncertainties, i.e., the difference of any of the DFT results and experiment.

V. SUMMARY AND CONCLUSIONS

A slab-consistent bulk reference approach has been described and shown to produce convergent surface formation energies in slab-based calculations. This bulk reference energy, designed to be meticulously consistent with the target slab surface model, leads to assured determination of convergence, in contrast to an *a posteriori* reference energy obtained from empirical fits to varied slab thicknesses. Moreover, this definition describes an (irreducible) uncertainty in the bulk reference energy, leading to predictable, *a priori* estimates of numerical uncertainties in surface energy calculations. Rather coarse surface $k_\parallel$ meshes were shown to give good results for the surface energy (and work function), demonstrating that one does not need extremely high quality meshes for both slab and for bulk calculations to obtain accurate, converged surface properties. This can be particularly valuable in reducing computational costs for larger-area surface slab models, such as might be needed for investigating extended surface reconstructions or multicomponent alloys with large unit cells. An *a priori* criterion can be applied on the bulk reference structure to detect and assess the minimum k-point sampling necessary to obtain good results to a predictable accuracy.

It was further shown that local orbital methods, despite their lack of long-range tails, can give results as converged as plane-wave calculations. The simple expedient of adding ghost atoms is seen to eliminate any meaningful deficiencies in the atom-centered basis sets. The explicit consideration of numerical uncertainties is pivotal in making this assessment: any basis set errors are less than or comparable to other numerical uncertainties in the DFT slab calculations, which, in turn, are much less than the physical uncertainties (errors) in the DFT approximation itself. It is possible to benefit from the computational efficiencies of local orbital methods, without compromising the accuracy in the calculation.

These methods were tested and verified with comprehensive assessment for three different low-index aluminum surfaces, (100), (111), and (110), with thickness extending out to 35 layers. The customary use of closed-packed (111) surfaces for assessing methods to compute surface properties is shown to be not very discriminating because of the conveniently good numerical behavior of close-packed surfaces. The properties of more open (100) and (110) surfaces show greater variability with slab thickness, these exhibiting detectable quantum size effects in slab calculations as thick as 25 layers (or beyond). These more open surfaces are better (more discriminating) tests for slab-based surface calculations. The slab-consistent bulk reference enables definitive determination of convergence, modulo the uncertainty in the $k_\perp$ limit, which would not be possible with empirical *a posteriori* fits to a reference bulk energy. This was specifically illustrated in the coarsest ($k_\parallel = 8 \times 8$) Al(100) surface model, where the insufficiency in the model was easily detected, where an empirical fit to thin slabs could be deceiving.

The notion of a slab-consistent bulk reference makes for more rapidly convergent surface calculations, but additional import stems from the systematic treatment of uncertainties that this definition makes possible. For the aluminum example considered here, the uncertainties could be used to assess convergence, in making quantitative assessments numerical aspects of the calculations and of basis set sufficiencies, about the comparative assessment of functionals and methods with respect to each other, and with respect to experiment, all with quantitative confidence. This framework will be crucial for probing subtle energetics of more complex systems, such as assessing subtle energetics of different reconstructed surfaces such as in Pt [35].

ACKNOWLEDGMENTS

I am grateful to Dwight Jennison for many informative discussions surrounding the physics of aluminum surfaces, and to Peter Feibelman for useful discussions regarding the modeling of metal surfaces. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the US Department of Energy's National Nuclear Security Administration under Contract No. DE-NA0003525. This work was supported by a Laboratory Directed Research and Development (LDRD) project. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the US Departments of Energy or the United States Government.

[1] P. J. Feibelman, Static quantum-size effects in thin crystalline, simple metal films, Phys. Rev. B **27**, 1991 (1983).

[2] P. T. Sprunger, L. Petersen, E. E. Plummer, E. Laegsgaard, and F. Besenbacher, Giant Friedel oscilations on the Be(0001) surface, Science **275**, 1764 (1997).

[3] J. C. Boettger, Nonconvergence of surface energies obtained from thin-film calculations, Phys. Rev. B **49**, 16798 (1994).

[4] V. Fiorentini and M. Methfessel, Extracting convergent surface energies from slab calculations, J. Phys.: Condens. Matter **8**, 6525 (1996).

[5] J. C. Boettger, J. R. Smith, U. Birkenheuer, N. Rösch, S. B. Trickey, J. R. Sabin, and S. P. Apell, Extracting convergent surface energies from slab calculations, J. Phys. Condens. Matter **10**, 893 (1998).

[6] J. G. Gay, J. R. Smith, R. Richterm, F. J. Arlinghaus, and R. H. Wagoner, Summary abstract: Surface energies in *d*-band metals, J. Vac. Sci. Technol. **2**, 931 (1984).

[7] J. L. F. Da Silva, C. Stampfl, and M. Scheffler, Converged properties of clean metal surface by all-electron first-principles calculations, Surf. Sci. **600**, 703 (2006).

[8] N. E. Singh-Miller and N. Marzari, Surface energies, work functions, and surface relaxations of low index metallic surfaces, Phys. Rev. B **80**, 235407 (2009).

[9] P. J. Feibelman, Energetics of steps on Pt(111), Phys. Rev. B **52**, 16845 (1995).

[10] R. J. Magyar, A. E. Mattsson, and P. A. Schultz, Some practical considerations for density functional theory studies of chemistry at metal surfaces, in *Metallic Systems: A Quantum Chemist's Perspective*, edited by T. Allison, O. Coskuner, and C. A. Gonzalez (CRC, Taylor and Francis, Boca Raton, FL, 2011), p. 163.

[11] W. Sun and G. Ceder, Efficient creation and convergence of surface slabs, Surf. Sci. **617**, 53 (2013).

[12] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. **140**, A1133 (1965).

[13] J. P. Perdew and A. Zunger, Self-interaction correction to density-functional approximations for many-electron systems, Phys. Rev. B **23**, 5048 (1981).

[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. **77**, 3865 (1996).

[15] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, Phys. Rev. B **46**, 6671 (1992).

[16] R. Armiento and A. E. Mattsson, Functional designed to include surface effects in self-consistent density functional theory, Phys. Rev. B **72**, 085108 (2005).

[17] D. R. Hamann, Generalized norm-conserving pseudopotentials, Phys. Rev. B **40**, 2980 (1989).

[18] M. Fuchs and M. Scheffler, Ab initio pseudopotentials for electron structure calculations of polyatomic systems using density functional theory, Comput. Phys. Commun. **119**, 67 (1999).

[19] S. G. Louie, S. Froyen, and M. L. Cohen, Nonlinear ionic pseudopotentials in spin-density-functional calculations, Phys. Rev. B **26**, 1738 (1982).

[20] A. E. Mattsson, P. A. Schultz, M. P. Desjarlais, T. R. Mattsson, and K. Leung, Designing meaningful density functional theory calculations in materials science—A primer, Model. Simul. Mater. Sci. Eng. **13**, R1 (2005).

[21] D. D. Johnson, Modified Broyden's method for accelerating convergence in self-consistent calculations, Phys. Rev. B **38**, 12807 (1988).

[22] M. J. Mehl, Pressure dependence of the elastic moduli in aluminum-rich Al-Li compounds, Phys. Rev. B **47**, 2493 (1993).

[23] F. Birch, Finite strain isotherm and velocities for single-crystal and polycrystalline NaCl at high pressures and 300°K, J. Geophys. Res. **83**, 1257 (1978).

[24] F. D. Murnaghan, Finite deformations of an elastic solid, Am. J. Math. **59**, 235 (1937).

[25] A. E. Mattsson, R. Armiento, J. Paier, G. Kresse, J. M. Wills, and T. R. Mattsson, The AM05 density functional applied to solids, J. Chem. Phys. **128**, 084714 (2008).

[26] A. E. Mattsson, R. Armiento, P. A. Schultz, and T. R. Mattsson, Nonequivalence of the generalized gradient approximations PBE and PW91, Phys. Rev. B **73**, 195123 (2006).

[27] G. N. Kamm and G. A. Alers, Low-temperature elastic moduli of aluminum, J. Appl. Phys. **35**, 327 (1964).

[28] R. J. Corrucini and J. J. Gniewek, Thermal expansion of technical solids at low temperatures, NBS Monograph 29, National Bureau of Standards, U.S. Dept. of Commerce, Washington, DC, 1961.

[29] J. C. Boettger, Persistent quantum-size effect in aluminum films up to twelve layers thick, Phys. Rev. B **53**, 13133 (1996).

[30] D.-L. Nguyen, C.-M. Wei, and M.-Y. Chou, Theoretical study of quantum size effects in thin Al(100), Al(110), and Al(111) films, Phys. Rev. B **99**, 205401 (2019).

[31] J. K. Grepstad, P. O. Gartland, and B. J. Glagsvold, Anisotropic work function of clean and smooth low-index faces of aluminum, Surf. Sci. **57**, 348 (1976).

[32] W. R. Tyson and W. A. Miller, Surface free energies of solid metals: Estimation from liquid surface tension measurement, Surf. Sci. **62**, 267 (1977).

[33] J. L. F. Da Silva, All-electron first-principles calculations of clean surface properties of low-Miller-index Al surfaces, Phys. Rev. B **71**, 195416 (2005).

[34] C. J. Fall, N. Binggeli, and A. Baldereschi, Anomaly in the anisotropy of the aluminum work function, Phys. Rev. B **58**, R7544 (1998).

[35] P. A. Schultz, H. P. Hjalmarson, M. Berg, E. Bussmann, D. A. Scrymgeour, T. Ohta, and C. H. Moore, First-principles calculations of metal surfaces. II. Properties of low-index platinum surfaces toward understanding electron emission, Phys. Rev. B **103**, 195427 (2021).