

Article

Convergence of Surface States on Al(001) Slabs: Implications for Optoelectronic Modeling

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Abstract

Density functional theory (DFT) calculations of metallic surfaces routinely employ periodic slab models in which spurious coupling between top and bottom surfaces artificially splits surface states, yet the thickness required to eliminate this artifact remains poorly characterized. Here, we systematically investigate convergence of surface states at the $\bar{\Gamma}$ point of Al(001) slabs as a function of slab thickness (11–81 atomic layers) and relaxation depth (3–11 layers). The splitting and energy position of the surface states are largely insensitive to the relaxation depth, but depend strongly on the slab thickness. At $\bar{\Gamma}$, for symmetric relaxation, the splitting decays exponentially with slab thickness, requiring at least 55 layers to fall below 10 meV; for asymmetric relaxation, a persistent splitting of ~ 35 meV does not vanish even in the thick-slab limit. We interpret this behavior using a two-state coupling model. For practical comparison with experimental binding energies, the midpoint energy E_{mid} of a symmetric 31-layer slab offers a computationally efficient alternative to full decoupling for the $\bar{\Gamma}$ surface states. For asymmetric slabs, however, the lower-energy branch E_{low} , corresponding to the relaxed surface, should be used instead of midpoint averaging. These results establish validated convergence criteria for Al(001) and provide a methodological framework transferable to other metallic optoelectronic materials.

Keywords: density functional theory; surface states; aluminum; slab convergence

1. Introduction

Metallic thin films, such as aluminum films, are indispensable building blocks in modern optoelectronic devices. They serve as plasmonic resonators in nanolasers [1,2], hot-electron generators in photodetectors [3–6], electrodes in solar cells [7,8], and sensing layers in surface-plasmon-resonance biosensors [9–12]. The metallic surface states—localized electronic states at the crystal–vacuum interface—play an important role in these applications [13–16]. Their sensitivity to surface geometry and the atomic environment makes them valuable diagnostics for the convergence and fidelity of surface electronic structure calculations. In plasmon-mediated processes, for instance, surface plasmons decay nonradiatively via Landau damping, generating hot carriers whose energy distributions and injection efficiencies are strongly influenced by the electronic band structure near the surface [17–19]. A reliable description of surface-state energetics is therefore critical for predictive modeling of optoelectronic properties [20–22].



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Density functional theory (DFT) calculations have become the standard framework for investigating optoelectronic properties [23–26] such as surface plasmons [27–29] and photovoltaic response [30–32]. In practical DFT simulations, periodic slab models represent the dominant approach for modeling semi-infinite surfaces, favored for their simplicity and compatibility with mainstream DFT packages. However, periodic thin slab models suffer from spurious coupling between top and bottom surfaces due to finite slab thickness, which splits each surface state into an unphysical pair [33–35]. To mitigate these finite-size artifacts, the conventional practice for metal surfaces is to use a symmetric or asymmetric slab with a fixed bulk-like central region. Alternative formalisms, such as surface Green's function and embedding methods [36–38] (including methods based on Wannier functions [16,39]), can treat the substrate as genuinely semi-infinite, but are less widely implemented in standard plane-wave DFT codes. Within the practical slab geometry, surface passivation—effective for semiconductors—is incompatible with metals [40–42]. Consequently, slab thickness and the relaxation protocol (symmetric versus asymmetric) remain the primary practical control parameters for metals.

In the symmetric relaxation protocol, both surfaces are relaxed identically. Intuitively, this geometry represents a free-standing film with two equivalent surfaces. It is also used here to model the semi-infinite limit: when the slabs are sufficiently thick and the vacuum regions between periodic replicas are sufficiently large, the two surfaces effectively decouple, and each becomes an equivalent representation of a semi-infinite Al(001) surface. In the asymmetric protocol, only one surface is relaxed, while the opposite side is held in the bulk-truncated geometry. This configuration represents a slab with inequivalent surfaces or, equivalently, a single surface of a semi-infinite crystal [43–45]. It is widely used to model adsorbate-covered surfaces, supported films, and heterostructures [46–48]. Comparing the two protocols allows us to separate finite-size inter-surface coupling from the effects of surface structural inequivalence.

Although the thickness of metallic films in modern optoelectronic devices shrinks to the nanometer scale—exemplified by a 100 nm Al film in plasmonic nanolasers [2] and a 30 nm Al film in hot-electron generators [5]—these thicknesses remain well above the decay length of the surface-state wavefunction and therefore lie within the bulk-like regime [49,50]. Their surfaces are effectively modeled as semi-infinite for theoretical purposes, which brings us back to the question of slab convergence discussed above. For truly thin films, inter-surface coupling is a genuine physical effect and requires no correction. However, when an insufficiently thick slab models a thicker or semi-infinite system, this coupling becomes a spurious numerical artifact that must be eliminated to achieve converged surface-state properties [51]. This raises a practical question that is often overlooked in DFT studies of metal surfaces: how thick must a slab be for its surface state to converge to a physically meaningful representation of the semi-infinite limit?

Among metals and crystallographic facets, aluminum serves as an ideal prototypical system for studying this convergence problem. As a typical nearly free-electron metal, aluminum hosts a well-characterized Shockley surface state on its (001) surface at approximately 2.8 eV below the Fermi level at the $\bar{\Gamma}$ point; this state has been extensively studied both experimentally and theoretically [52–59]. This well-characterized surface state makes the Al(001) surface a particularly suitable benchmark for systematically investigating the thickness-dependent convergence of surface-state energies.

Despite this recognized importance, the critical thickness required for convergence of Al(001) surface states remains unsettled. While some prior DFT studies have used slabs of various thicknesses (e.g., up to 11 layers in reference [60]), neither the converged thickness nor the convergence behavior at high-symmetry points such as $\bar{\Gamma}$ has been systematically examined [60–66]. In some cases, even the well-documented surface states at $\bar{X}$ were

not resolved, further highlighting the need for systematic convergence analysis [60,66]. Additionally, the effects of atomic relaxation depth and slab structural consistency remain unquantified. The absence of standardized slab parameters thus introduces uncontrolled errors into Al(001) surface calculations, leading to inconsistent and incomparable results across studies.

To address these gaps, we systematically investigate the convergence of surface states at $\bar{\Gamma}$ in Al(001) slabs as a function of slab thickness and the number of relaxed atomic layers. We employ slabs ranging from 11 to 81 atomic layers with controlled relaxation depths. Our objectives are threefold: (1) to quantify how surface-state energy splitting evolves with slab thickness and relaxation depth; (2) to establish validated, optimized slab parameters for surface states at $\bar{\Gamma}$; and (3) to provide a methodology—combining thickness scans, relaxation-depth analysis, and probability-density characterization—that can be adapted to convergence studies of other metallic surfaces. Although Al(001) is the focus of this work, the underlying mechanism—the exponential decay of wavefunction overlap with slab thickness—is general to periodic slab models. We therefore expect the qualitative convergence behavior to extend to other simple metals. However, the quantitative thresholds obtained here (e.g., $N_{\text{slab}} \geq 55$) are specific to Al(001) and depend on material-specific properties such as surface-state decay length.

2. Results and Discussion

2.1. Evolution of Surface-State Splitting with Slab Thickness

2.1.1. Thickness Dependence of Surface-State Splitting

We first examine the thickness dependence of the surface-state splitting at $\bar{\Gamma}$. Here and throughout, “splitting” refers to the energy difference between the two surface-states, denoted as $\Delta E = E_{\text{high}} - E_{\text{low}}$, where E_{high} and E_{low} are the energies of the higher-energy and lower-energy surface states, respectively. Figure 1 shows six representative band structures of Al(001) slabs along the $\bar{M}$ – $\bar{\Gamma}$ – $\bar{X}$ path in the surface Brillouin zone, for 11-, 31-, and 81-layer slabs with Top5 and Both5 relaxation. Here, Top n denotes single-side relaxation of the top n layers, and Both n denotes symmetric relaxation of both top and bottom n layers. The notation Top n /Both n is used throughout. The surface states in Figure 1 are identified following the method in Reference [50]. For the 11-layer slab, the band structures obtained with either Top5 or Both5 relaxation provide too few bands to represent the projected bulk continuum (Figure 1a,d), and the surface-state bands exhibit large splitting, making visual identification difficult without charge-density analysis. By contrast, the 31- and 81-layer slabs exhibit progressively denser bulk band structures with well-defined gaps, within which the surface states at $\bar{\Gamma}$ and $\bar{X}$ are clearly identifiable. As the slab thickness reaches 81 layers, the splitting for Both5 relaxation diminishes to 0.9 meV, rendering the two bands visually indistinguishable at the scale of Figure 1c. By contrast, the Top5 configuration exhibits a splitting of 34.6 meV, with the two bands still visually resolved in Figure 1f.

Figure 2 presents the surface-state splitting (ΔE) at $\bar{\Gamma}$ as a function of slab thickness N_{slab} (in atomic layers) for all relaxation configurations. For both symmetric and asymmetric relaxations, ΔE drops dramatically from ~ 700 meV at 11 layers to ~ 85 meV at 31 layers. Beyond 41 layers, however, their behaviors diverge. For symmetric configurations, ΔE continues to decrease monotonically with increasing N_{slab} and approaches 0 meV at 81 layers. In contrast, for asymmetric relaxations, ΔE approaches approximately 35 meV for $N_{\text{slab}} \geq 41$ and shows no significant further reduction within the thickness range studied. These trends are consistent with the visual inspection of the band structures in Figure 1, where Both5 splitting becomes barely discernible at 81 layers (Figure 1c), while Top5 splitting remains resolvable (Figure 1f).

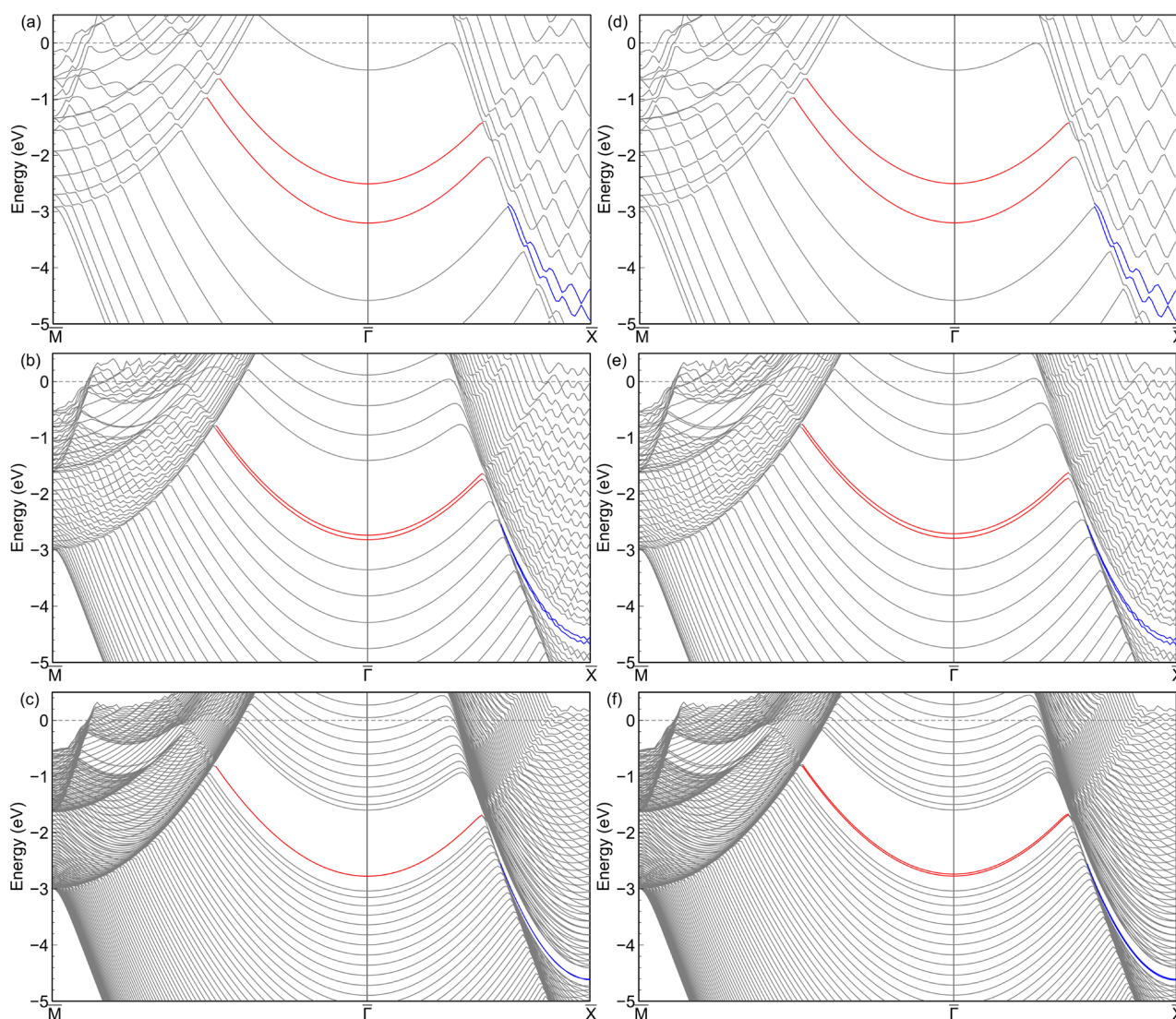


Figure 1. Band structures of Al(001) slabs along the $\bar{M}-\bar{\Gamma}-\bar{X}$ path in the surface Brillouin zone. Panels (a–c) show 11-, 31-, and 81-layer slabs with symmetric Both5 relaxation, respectively; panels (d–f) show the same thicknesses with asymmetric Top5 relaxation, respectively. Here, Top n and Both n denote asymmetric and symmetric relaxation, respectively (see text for details). The Fermi level (E_F) is set to 0 eV. The surface-state bands in the projected bulk band gaps, with their minima at $\bar{\Gamma}$ and $\bar{X}$, are highlighted in red and blue, respectively.

Since relaxation depth is held constant for each curve in Figure 2, increasing N_{slab} effectively adds more fixed bulk-like layers. The overall decreasing trend of ΔE with N_{slab} indicates that bulk thickness is the primary factor governing decay of surface-state coupling.

It is worth noting that the evolution of ΔE with N_{slab} for symmetric relaxations can be accurately fitted by an exponential decay function, $\Delta E = E_0 e^{-\alpha N_{\text{slab}}}$. The fitted results and associated goodness-of-fit (R^2) are listed in Table S1 in the Supplementary Materials. For all five symmetric configurations, the slab thicknesses required to achieve $\Delta E < 10$ meV are 52.1–53.3 layers. However, since all our symmetric slab models contain an odd number of layers to maintain a mirror plane on a central atom, we recommend a threshold of $N_{\text{slab}} \geq 55$ for $\Delta E < 10$ meV for the five relaxation schemes to maintain consistency. This level of convergence is sufficient for quantitative comparison with experimental measurements, where typical energy resolutions are in the order of tens of meV. However, most previous DFT studies on Al(001) surfaces employed slab models with fewer than 30

atomic layers [60,66]. Our results indicate that such thicknesses are insufficient to suppress inter-surface coupling, leading to splitting greater than 80 meV.

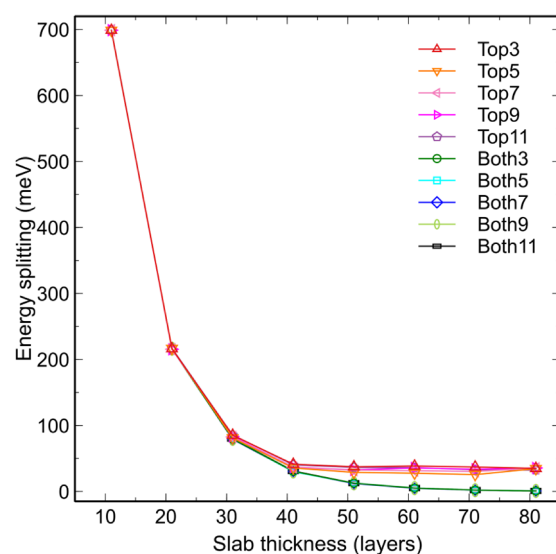


Figure 2. Surface-state splitting (ΔE) at $\bar{\Gamma}$ as a function of slab thickness (N_{slab}) for all relaxation configurations (see Figure 1 caption for notation). The dependence on relaxation depth is shown in Figure 5.

2.1.2. Physical Origin of the Contrasting Behavior

To understand the contrasting behavior in Figure 2, we examine the probability density distributions ($|\psi|^2$) of the surface states along the slab normal direction for selected representative slab thicknesses and relaxation schemes (Figure 3). We adopt a two-state coupling model [67,68]. In this model, each surface hosts its own surface-localized state—an uncoupled single-surface reference state whose energy, denoted E_{single} , is that of a semi-infinite surface free from inter-surface coupling. Although a rigorous numerical construction of these reference states is not pursued in this work, they serve as a useful conceptual tool for interpreting the inter-surface coupling. The spatial overlap between these reference states plays a significant role in how strongly the two surfaces couple. The surface-state splitting thus arises from two distinct physical effects: (1) inter-surface quantum coupling via the spatial overlap of the evanescent tails of the reference states, and (2) structural inequivalence between the two surfaces.

Within the two-state coupling model, the strength of the inter-surface coupling is governed by the spatial overlap of the evanescent tails of the two reference states. While these reference states are not directly accessible in the DFT calculation, their behavior can be inferred from the computed Kohn–Sham eigenstates shown in Figure 3. In the thin-slab case ($N_{\text{slab}} < 41$), for both symmetric and asymmetric relaxation schemes, the wavefunctions of the reference states penetrate deeply into the bulk and their evanescent tails overlap significantly in the central region. This overlap produces strong quantum coupling that hybridizes the two reference states into bonding and antibonding combinations—the two Kohn–Sham eigenstates observed in the band structure—resulting in a large energy splitting. The resulting Kohn–Sham eigenstates are delocalized across the entire slab, as shown in Figure 3a,d. As the slab thickens, the two reference states move progressively farther apart, and the overlap of their evanescent tails diminishes; consequently, the coupling weakens and the eigenstates become increasingly localized on their respective surfaces (Figure 3b,c,e,f). For the 81-layer slab with symmetric relaxation (Figure 3c), the probability density at the central layer is less than 0.05% of the surface maximum, indicating that the

two surfaces are effectively decoupled. This trend is reflected in the weakening of the surface-state splitting with increasing slab thickness, as shown in Figure 2.

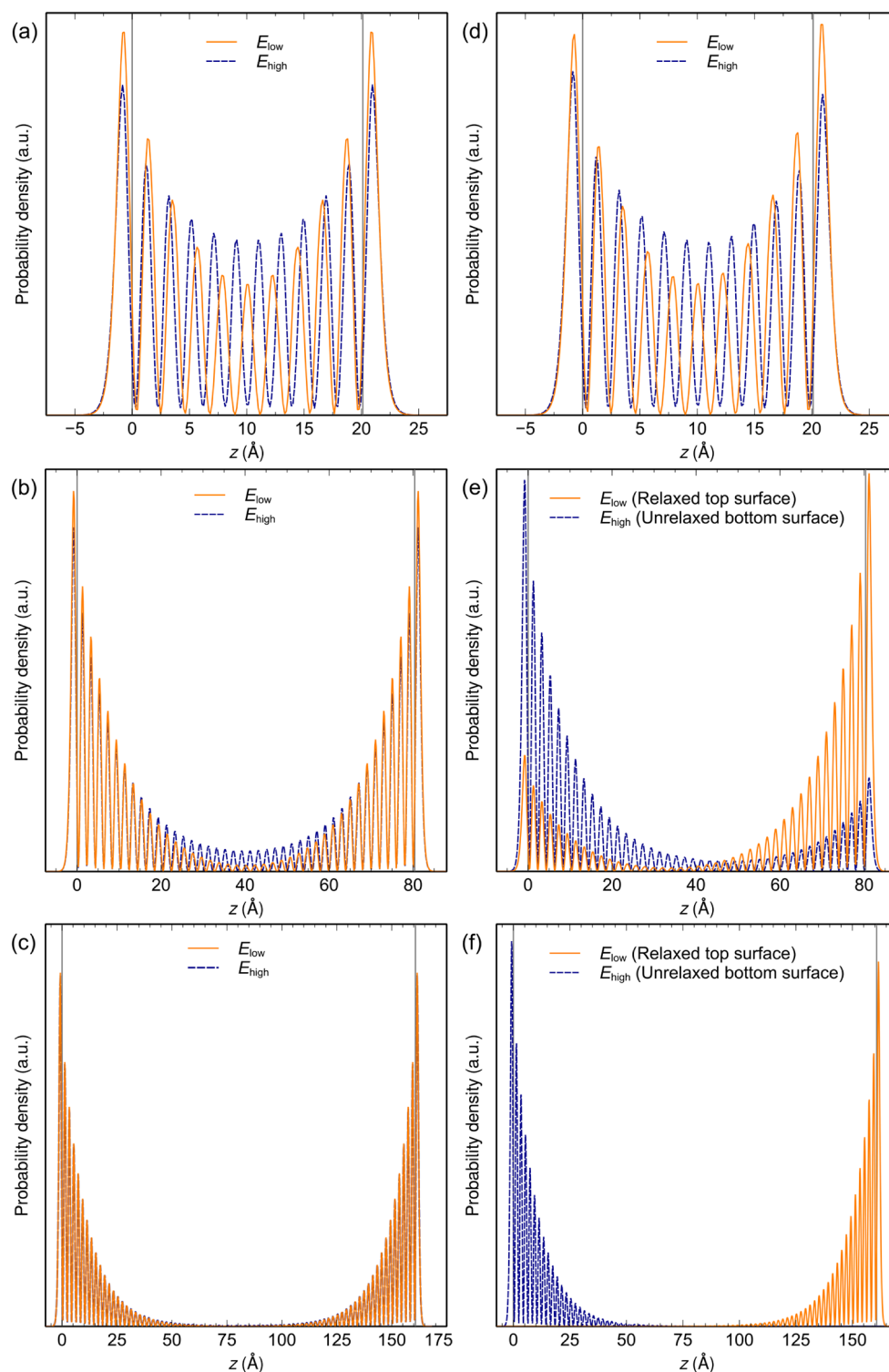


Figure 3. Probability density distribution of the two surface states at $\bar{\Gamma}$ along slab thickness direction (z axis) of Al(001) slabs for selected thicknesses and relaxation configurations: Panels (a–c) show 11-, 41-, and 81-layer slabs with symmetric Both5 relaxation, respectively; panels (d–f) show the same thicknesses with asymmetric Top5 relaxation, respectively. The two grey vertical lines mark the bottom surface ($z = 0$) and the top surface, respectively.

However, if the two surfaces are structurally inequivalent (e.g., one relaxed and one unrelaxed), their E_{single} values differ, introducing a finite energy detuning. This intrinsic detuning, combined with the overlap-induced coupling, yields the total splitting observed in asymmetric slabs. For symmetric relaxations, the two surfaces are structurally equivalent, so there is no detuning between the E_{single} values. The surface-state splitting therefore arises solely from inter-surface quantum coupling, whose strength is governed by the spatial overlap of the evanescent tails. In the thick-slab limit, the evanescent tails decay to negligible amplitude in the slab interior, so the inter-surface coupling is effectively quenched. Taking the 81-layer slab as a representative example, the two surface states become nearly degenerate with ΔE approaching zero (0.9 meV)—the semi-infinite limit.

The two surface states in Figure 3c appear almost identical yet remain distinct. These two surface states are DFT output Kohn–Sham eigenstates with opposite parity and strict orthogonality. This parity and the symmetric probability density distributions are the consequence of symmetric geometry [69]. The vanishing splitting, however, does not originate from orthogonality itself, but from the exponential decay of the underlying inter-surface coupling.

In contrast, under asymmetric relaxation, the inter-surface coupling decays with increasing slab thickness and vanishes in the thick-slab limit, similarly to the symmetric case. Unlike the symmetric case, however, the relaxed top surface and the unrelaxed bottom surface remain structurally inequivalent and therefore possess different E_{single} . This intrinsic detuning, which is independent of wavefunction overlap, causes ΔE to level off at ~ 35 meV for $N_{\text{slab}} \geq 41$ rather than vanishing. As shown in Figure 3f, the Kohn–Sham eigenstates localize onto the individual surfaces at $N_{\text{slab}} = 81$, effectively coinciding with the reference states. The vanishing spatial overlap thus directly reflects the decay of the inter-surface coupling with slab thickness.

To characterize the structural changes induced by surface relaxation, we examine the interlayer relaxation as a function of layer index for the relaxed top surface. As shown in Figure 4, the topmost layers of our 81-layer slab with Top5 relaxation undergo outward expansion, consistent with the known relaxation behavior of the Al(001) surface reported by Zheng et al. [70] and Sferco et al. [71]. The outward relaxation of the top-surface Al layers modifies the local electronic environment in a complex manner: it weakens interlayer orbital overlap, redistributes the surface charge density, and alters the effective surface potential experienced by the surface-state electrons [70–74]. A detailed quantitative decomposition of this energy shift into individual contributions—such as changes in screening, surface dipole moment, and potential well depth—would require sophisticated theoretical treatment beyond the scope of the present work. Nevertheless, to quantify the net effect of relaxation on the surface-state energy, we computed the midpoint energy $E_{\text{mid}} = (E_{\text{high}} + E_{\text{low}})/2$ at $\bar{\Gamma}$ for an 81-layer slab with both surfaces fully relaxed (Both5) and for an 81-layer slab with both surfaces held at the bulk-truncated geometry. The difference between the two is 35.6 meV, which is in good agreement with the ~ 35 meV splitting observed in the asymmetric Top5 slab. This quantitative agreement confirms that relaxation itself—through the combined action of the above mechanisms—is the primary origin of the downward shift in the surface-state energy on the relaxed side relative to the unrelaxed side.

To assess whether a spurious electric field arising from the asymmetric slab geometry might contribute to the observed splitting, we analyzed the planar-averaged electrostatic potential energy across the vacuum region of the 41- and 71-layer slabs with Top5 and Top11 relaxation. For the 41- and 71-layer slabs with Top5 (Top11) relaxation, the potential energy differences are 1 and 4 meV for Top5, and 3 and 6 meV for Top11, respectively (see Figure S1 for the 71-layer slab with asymmetric Top5 relaxation in the Supplementary

Materials). These values are an order of magnitude smaller than the ~ 35 meV surface-state splitting. This confirms that the structural asymmetry does not induce a significant net dipole moment, rendering periodic-boundary-condition artifacts negligible, which indicates that the persistent splitting stems from intrinsic surface structural inequivalence rather than from an artificial field.

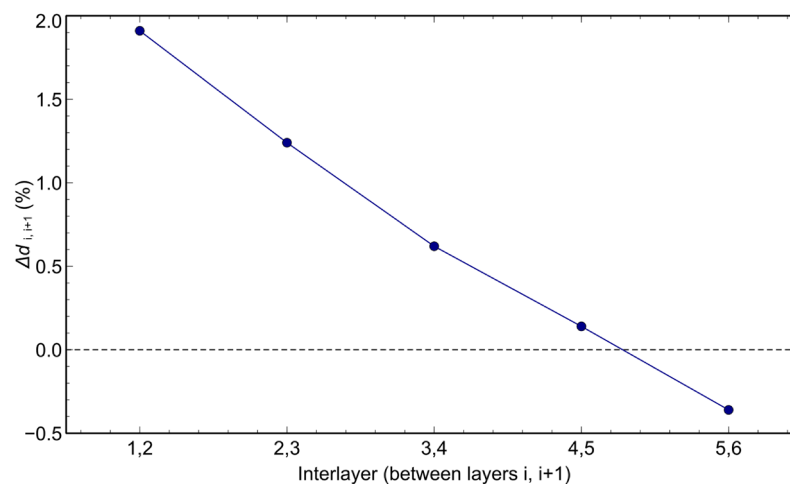


Figure 4. Calculated interlayer relaxation $\Delta d_{i,i+1}$ as a function of layer index i for the 81-layer Al(001) slab with Top5 relaxation. Here, $i = 1$ denotes the topmost (surface) layer, and i increases inward toward the slab interior. The $\Delta d_{i,i+1}$ is the percentage change in the interlayer spacing between layer i and layer $i + 1$ as compared to the bulk interlayer spacing. Positive (negative) values correspond to outward expansion (inward contraction). The horizontal dashed line marks zero interlayer relaxation, i.e., the bulk interlayer spacing. Filled circles denote the calculated data, and the solid line is included only to guide the eye.

2.2. Dependence of Surface-State Splitting on Relaxation Depth

While slab thickness exerts a pronounced effect on surface-state splitting, the relaxation of surface atomic layers also plays a critical role. Surface relaxation modifies interlayer distances, induces charge redistribution, alters the near-surface effective potential, and regulates the localization of surface states. To clarify its influence on convergence, we investigate the variation in splitting (ΔE) with the relaxation depth (N_{rlx}).

Figure 5 shows the evolution of ΔE with the relaxation depth $N_{\text{rlx}} = 3, 5, 7, 9, 11$ representative slab thicknesses (31, 51, and 81 layers) under asymmetric and symmetric relaxation schemes; the corresponding data for all slab thicknesses are presented in Figure S2. As shown in Figure 5, ΔE shows negligible variation (< 1 meV) with N_{rlx} at each slab thickness for symmetric relaxations. In contrast, ΔE for asymmetric relaxations exhibits fluctuations of up to 8.5 meV across N_{rlx} at a given slab thickness, though these variations are small and do not alter the overall trend. This behavior is expected from symmetry: for symmetric slabs, the detuning is identically zero regardless of relaxation depth, whereas for asymmetric slabs, the detuning itself depends on how deeply the relaxation is allowed to propagate. The observed fluctuations are therefore a natural consequence of the structural inequivalence, rather than numerical noise. These results demonstrate that symmetric relaxation provides a more robust and predictable convergence behavior with respect to both slab thickness and relaxation depth.

2.3. Evolution of Surface State Position with Slab Thickness and Relaxation Depth

Beyond the splitting energy, the absolute energy position of surface states is another critical quantity for electronic structure of metallic thin films. In this section, we investigate the thickness dependence of the surface-state energy positions at $\bar{\Gamma}$. Figures 6a and 6b

present the slab thickness dependence of E_{high} and E_{low} at $\bar{\Gamma}$ for symmetric and asymmetric relaxations, respectively.

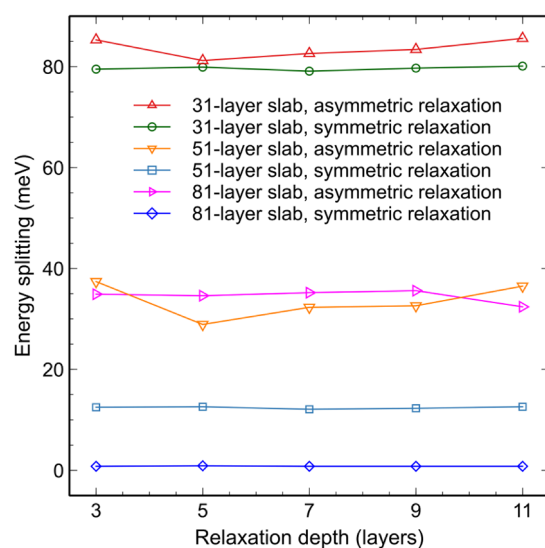


Figure 5. Dependence of ΔE at $\bar{\Gamma}$ on relaxation depth (N_{rlx}) for representative slab thicknesses (31, 51, and 81 layers). For symmetric relaxations, ΔE shows little variation with N_{rlx} at each thickness, while ΔE shows considerably larger fluctuations across N_{rlx} for asymmetric relaxations. Data for all slab thicknesses (11–81 layers) are provided in Figure S2.

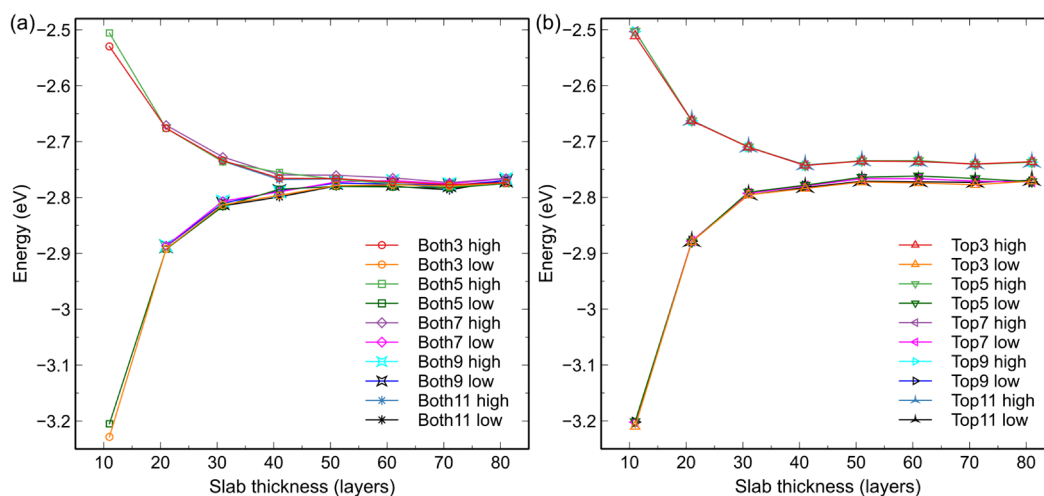


Figure 6. Energies of the upper (E_{high}) and lower (E_{low}) surface states at $\bar{\Gamma}$ as a function of slab thickness (N_{slab}) for (a) symmetric and (b) asymmetric relaxations. For symmetric relaxations, E_{high} and E_{low} converge to the same value as N_{slab} increases. For asymmetric relaxations, a gap between E_{high} and E_{low} persists for $N_{\text{slab}} \geq 41$.

For symmetric relaxations (Figure 6a), E_{high} decreases from ~ -2.51 eV (11 layers) to ~ -2.73 eV (31 layers), and then stabilizes at ~ -2.78 eV for $N_{\text{slab}} \geq 51$; E_{low} rises from ~ -3.20 eV (11 layers) to ~ -2.81 eV (31 layers), and then levels off at ~ -2.78 eV for $N_{\text{slab}} \geq 51$. This indicates that, for symmetric relaxations, the absolute energy positions are converged for $N_{\text{slab}} \geq 51$. Note that convergence of individual surface-state energies does not necessarily imply a vanishing splitting ΔE . As mentioned above, the conservative practical threshold for $\Delta E < 10$ meV is $N_{\text{slab}} \geq 55$.

For asymmetric relaxations (Figure 6b), a similar convergence behavior is observed: E_{high} decreases rapidly from approximately -2.50 eV (11 layers) to ~ -2.71 eV (31 layers), stabilizing at approximately -2.74 eV for $N_{\text{slab}} \geq 41$. Conversely, E_{low} increases sharply

from ~ -3.20 eV (11 layers) to ~ -2.79 eV (31 layers), thereafter leveling off at approximately -2.78 eV for $N_{\text{slab}} \geq 41$. In contrast to the symmetric case, asymmetric relaxations exhibit a persistent gap between E_{high} and E_{low} that remains essentially constant for $N_{\text{slab}} \geq 41$, consistent with the stable splitting of approximately 35 meV observed in Figure 2. The state localized on the relaxed surface consistently lies below that on the unrelaxed surface across all slab thicknesses, reflecting the structural inequivalence of the two surfaces discussed above.

Figure 7 shows the slab thickness dependence of the midpoint energy E_{mid} . For the thinnest slabs (e.g., 11 layers), E_{mid} deviates significantly from the thick-slab values. As the slab thickness increases, E_{mid} quickly enters a regime of small-amplitude oscillations as a function of slab thickness. These oscillations are consistent with the quantum size effect [75,76]. For the symmetric case, E_{mid} exhibits oscillations about -2.78 eV with a peak-to-peak amplitude of approximately 18 meV. Specifically, when both calculations are performed using the same k -point mesh and otherwise identical computational settings, the 31-layer result for E_{mid} lies within 2 meV of the thick-slab reference value, here taken as the 81-layer result. This 2 meV difference characterizes slab-thickness convergence under fixed computational setting; it does not represent the absolute accuracy of the calculated binding energy. The absolute value of E_{mid} carries an additional uncertainty associated with the k -mesh, as discussed in Section 3. This observation underpins a practical strategy for extracting converged surface-state energies at reduced computational cost, as discussed in detail in Section 2.4.

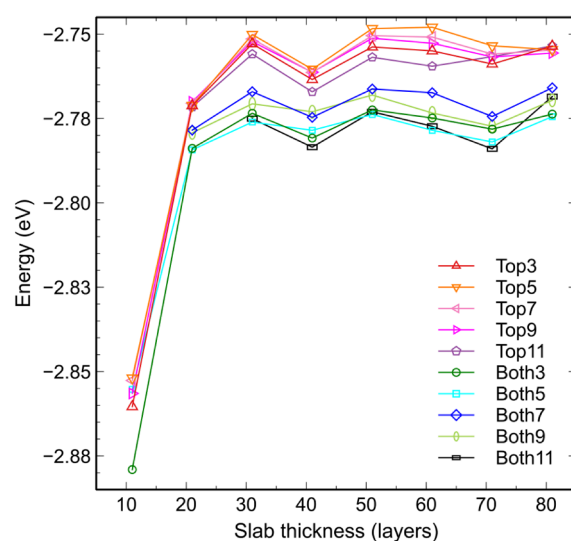


Figure 7. Midpoint energy E_{mid} as a function of slab thickness.

In contrast, the asymmetric case shows similar oscillatory behavior, but about a different mean value of approximately -2.76 eV, with a comparable peak-to-peak amplitude of about 19 meV. The ~ 20 meV higher mean value of E_{mid} in the asymmetric case is attributed to the structural inequivalence of the two surfaces.

Figure 8 displays E_{low} as a function of N_{rlx} for representative 31-, 51-, and 81-layer slabs under asymmetric and symmetric relaxations (data for all slab thicknesses are provided in Figure S3). As N_{rlx} increases, E_{low} exhibits no systematic trend for either relaxation scheme. For both relaxation schemes, once the slab thickness exceeds 51 layers, E_{low} varies only within a narrow range between approximately -2.78 eV and -2.76 eV across all N_{rlx} , indicating that the lower band energy is essentially independent of relaxation depth. This is consistent with the finding that slab thickness, rather than relaxation depth, is the dominant

factor governing convergence. These ~ 20 meV variations may reflect quantum size effects, but their amplitude is small compared with the thickness-induced energy shifts.

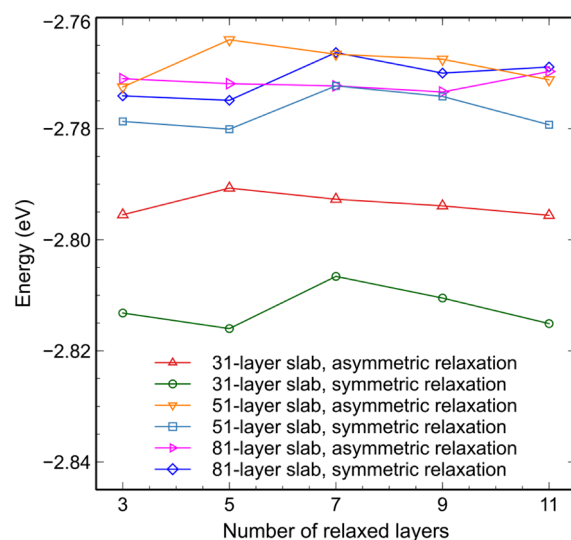


Figure 8. Energies of the lower surface states (E_{low}) at $\bar{\Gamma}$ as a function of relaxation depth (N_{rlx}) for representative 31-, 51-, and 81-layer slabs under asymmetric and symmetric relaxations. E_{low} varies mildly with N_{rlx} . Data for all slab thicknesses (11–81 layers) are provided in Figure S3.

Notably, the values of E_{low} for $N_{slab} \geq 51$ are reasonably consistent with the binding energy range of 2.75–2.80 eV reported from angle-resolved photoemission spectroscopy (ARPES) measurements [59,77,78]. This level of quantitative agreement is highly satisfactory for GGA-based DFT calculations [65,79].

2.4. Practical Implications for Slab Modeling

The contrasting behavior of symmetric and asymmetric relaxations can be summarized as follows. In symmetric relaxations, the two surfaces are structurally equivalent; the energy splitting ΔE arises solely from the finite-size coupling, which decays exponentially with slab thickness, yielding $\Delta E \rightarrow 0$ in the thick-slab limit. In asymmetric relaxations, the two surfaces are structurally inequivalent, resulting in a persistent splitting of the $\bar{\Gamma}$ surface states, $\Delta E \approx 35$ meV, even for thick slabs.

A practical consideration arising from our comparison is the choice between symmetric and asymmetric relaxation schemes. Symmetric relaxations converge to $\Delta E = 0$ with sufficiently thick slabs, making them the preferred choice for high-accuracy calculations where absolute surface-state energies and a small splitting are critical.

By contrast, asymmetric relaxation introduces a persistent splitting of approximately 35 meV for the $\bar{\Gamma}$ surface states of the Al(001) surface studied here, which does not vanish with increasing slab thickness. In asymmetric relaxations, E_{low} corresponds to the surface state localized on the relaxed top surface, while E_{high} originates from the unrelaxed bottom surface. This distinction is important when using such models to interpret experimental measurements (e.g., ARPES), which probe only the top surface. For the present Al(001) case, the relevant surface-state energy is E_{low} , not E_{high} , and this difference should therefore be taken into account when referencing calculated surface-state energies to experimental binding energies. Therefore, the use of asymmetric relaxations requires a clear distinction between E_{low} and E_{high} , particularly when quantitative agreement with experiment or accurate comparison between different surfaces is required.

The behavior observed in Figure 7 has a practical consequence. Within the two-state coupling model, the bonding and antibonding combinations for a symmetrically

relaxed slab are split approximately symmetrically about the E_{single} . Consequently, their midpoint energy E_{mid} effectively cancels the coupling-induced splitting and provides a useful estimate of the E_{single} . This means that a practitioner whose primary goal is to obtain the surface-state binding energy—for example, for comparison with ARPES measurements—does not need to converge the splitting itself to better than 10 meV. For the surface states at $\bar{\Gamma}$, a symmetric slab of 31 layers, combined with simple midpoint averaging, already yields E_{mid} within 2 meV of the thick-slab reference value obtained with the same k -mesh. This represents a substantial reduction in computational cost compared with the 55-layer threshold for ΔE . For applications that require a genuinely decoupled single surface at $\bar{\Gamma}$ (e.g., studying the splitting itself, or modeling surface-state dynamics with sub-10 meV accuracy), the stricter 55-layer criterion remains the appropriate choice. Because this averaging procedure relies on the symmetric nature of the slab, the midpoint energy does not represent E_{single} for asymmetrically relaxed slabs, where the surfaces are inequivalent.

Although the present work focuses primarily on the surface states at $\bar{\Gamma}$, we have also examined the thickness-dependent behavior of the surface states at $\bar{X}$ for comparison. We found that the splitting at $\bar{X}$ decreases monotonically from approximately 590 meV at 11 layers to about 19 meV (asymmetric relaxation) and 12 meV (symmetric relaxation) at 81 layers. The corresponding data for all relaxation configurations at $\bar{X}$ are compiled in Figure S4. Notably, the spatial decay length extracted from the exponential fit to the probability density distribution ($|\psi|^2$) along the slab normal is approximately 23.5 Å at $\bar{X}$, considerably larger than the 10.4 Å obtained at $\bar{\Gamma}$ [50]. This substantial difference reflects the deeper penetration of $\bar{X}$ surface states into the bulk, leading to a slower decay of the inter-surface coupling with increasing slab thickness. A systematic investigation of the $\bar{X}$ surface states is beyond the scope of this work, but would be a valuable direction for future studies.

2.5. Limitations and Outlook

While the present work establishes quantitative convergence criteria for Al(001), several limitations should be noted. The thresholds are specific to Al(001) and PBEsol-GGA; transition metals with d -band surface states, other facets, or different exchange–correlation functionals may exhibit different convergence behavior. The $\bar{\Gamma}$ versus $\bar{X}$ comparison within the same surface already demonstrates that convergence is sensitive to the specific surface state.

Our ideal zero-temperature slab models omit steps, grain boundaries, and oxide layers, and they neglect finite-temperature effects; all of these may modify surface-state energetics in real devices. Future work should extend this analysis to other metals, facets, and employ more advanced functionals, and incorporate realistic surface defects and interfaces.

Nevertheless, the methodology—systematic thickness and relaxation-depth scans combined with probability-density analysis—is transferable and provides a framework for convergence studies of other systems, with independent convergence tests for each case.

3. Materials and Methods

All DFT computations were performed using the Quantum ESPRESSO package (version 7.5) [80,81]. The PBEsol functional—a revised version of the Perdew–Burke–Ernzerhof form within the generalized gradient approximation (GGA)—was adopted for exchange and correlation [82]. PBEsol was chosen as it provides improved lattice constants and surface energies compared to standard PBE for metals [83]. Ion–electron interactions were handled with projector augmented-wave (PAW) pseudopotentials, treating Al 3s and 3p electrons as valence. The pseudopotentials were taken from the Standard Solid-State Pseu-

dopotential (SSSP) library (version 1.3.0), which is designed for high-precision solid-state simulations [84,85]. In the self-consistent field (SCF) procedure, the convergence threshold for total energy was fixed at 1×10^{-8} eV. The plane-wave basis was truncated at 450 eV, and the charge-density cutoff was set to 2250 eV; the Brillouin zone was sampled with a $23 \times 23 \times 1$ Monkhorst–Pack grid [86]. To promote stable convergence, a cold smearing scheme of 0.001 eV (Marzari–Vanderbilt) was employed, in combination with the local Thomas–Fermi mixing method [87]. Structural relaxations were performed with a residual force convergence threshold of 0.01 eV/Å on every atom.

Computational parameters—including SCF convergence threshold, vacuum-layer thickness, cutoff energies, k -mesh density, smearing width, and force threshold—were first systematically tested to ensure a total energy accuracy of 1 meV per atom. A subsequent convergence test was performed directly on the target quantities, ΔE and the midpoint energy E_{mid} . The 41- and 81-layer slabs with Both5 relaxation were used as the test systems for the full parameter scan. For ΔE , the variation across the tested parameter ranges is within ± 0.3 meV for the 81-layer slab and within ± 0.8 meV for the 41-layer slab, confirming that the reported splitting values are well converged. The convergence test results with respect to the vacuum-layer thickness and the number of k -points along z are shown in Tables S3 and S4, respectively. For E_{mid} , with the exception of the k -mesh density, all other tested parameters vary within ± 0.2 meV. The variation of E_{mid} is up to ~ 20 – 25 meV between $23 \times 23 \times 1$ and $27 \times 27 \times 1$ at both 41 and 81 layers. This reflects the sensitivity of the absolute surface-state energy to the precise sampling of the Fermi surface, which is not surprising for a metal [87,88]. This is well-known behavior in metallic systems: denser k -meshes slightly shift the Fermi level E_F , thereby rigidly translating the absolute eigenvalues relative to E_F . Since this shift affects both the upper and lower surface states equally, the splitting ΔE remains completely unaffected—which is the primary focus of our analysis. The E_{mid} values reported here should therefore be interpreted with an uncertainty of ~ 20 – 25 meV when comparing absolute binding energies. The relative trends (e.g., thickness dependence, differences between relaxation schemes) are robust and unaffected by this uncertainty, as they are derived from consistent k -mesh settings across all calculations.

The Al(001) slab structure was established on the basis of fully relaxed bulk aluminum, whose optimized lattice constant of 4.02 Å is consistent with experimental results [83]. The corresponding interlayer spacing along the [001] direction is approximately 2.01 Å. Slabs of varying thicknesses (11, 21, 31, 41, 51, 61, 71, and 81 atomic layers) were employed to examine the convergence behavior of surface states. Each slab was separated from its periodic replicas by a vacuum layer of 18 Å, ensuring that inter-slab interactions along the periodic direction were suppressed.

For each slab thickness, we employed a series of constrained relaxation schemes in which fixed layers were held at bulk lattice positions. In all cases, the relaxed layers were the outermost layers adjacent to the relaxed vacuum interface(s), counted inward from the surface. We defined relaxation depth as the number of atomic layers allowed to relax at a surface. We investigated both asymmetric (single-side) and symmetric (dual-side) relaxations with five relaxation depths (3, 5, 7, 9, 11), which were categorized as follows:

- Symmetric scheme: Both3, Both5, Both7, Both9, Both11;
- Asymmetric scheme: Top3, Top5, Top7, Top9, Top11.

Configurations that would leave no fixed central layer between the two relaxed regions were excluded. Specifically, Top11, Both7, and Both9 configurations were excluded for the 11-layer slab, and Both11 configuration was excluded for the 11- and 21-layer slabs.

All slab calculations were performed without dipole corrections. To justify this choice, we evaluated the drop in the planar-averaged electrostatic potential energy across the

vacuum region for selected asymmetric slabs without dipole correction. As shown in Section 2.1.2, the potential energy differences are an order of magnitude smaller than the ~ 35 meV surface-state splitting and are also below typical experimental energy resolutions (~ 10 – 30 meV). We therefore consider the artificial electric field arising from the asymmetric slab geometry under periodic boundary conditions to be negligible for the slab thicknesses considered in this work.

To further verify this assessment, we performed dipole-corrected calculations for representative asymmetric slabs (41 and 81 layers) with Top5 relaxation. We enabled the sawtooth potential by setting *tefield* = .true. and *dipfield* = .true., set *edir* = 3 for the surface-normal direction, and chose *emaxpos* and *eopreg* so that the potential step was located within the vacuum region. We set *eampr* = 0 to apply the dipole correction without an additional external field. The optimized atomic positions were identical with and without the dipole correction, within the relaxation convergence criterion. The surface-state energies differed by no more than ~ 2 meV, and ΔE by no more than ~ 3 meV—an order of magnitude smaller than the persistent ~ 35 meV splitting and at or below typical experimental energy resolutions (~ 10 – 30 meV). These results quantitatively confirm that the slab's structural asymmetry does not produce a significant artificial electric field under periodic boundary conditions, and that our conclusions are unaffected by the omission of dipole corrections.

The z -dependent probability density $|\psi(z)|^2$ (where z is perpendicular to the slab surface) was obtained using the *pp.x* post-processing module in Quantum ESPRESSO and further analyzed using in-house scripts written in Python (version 3.12.3). The module exports 3D charge densities in cube format; in-house scripts then read these files, reconstruct the volumetric data, and average over the lateral dimensions to extract one-dimensional profiles along the surface normal.

Atomic structure manipulations were performed with the Atomic Simulation Environment (version 3.25.0) [89], and all figures were generated using Veuze (version 4.1) [90].

4. Conclusions

In this work, we have established explicit convergence criteria for eliminating artificial surface-state splitting in Al(001) slab models through a systematic investigation of slab thickness and surface-relaxation effects. The splitting and energy position of the surface states are largely insensitive to the relaxation depth, but depend strongly on the slab thickness. For the surface state at $\bar{\Gamma}$, at least 55 atomic layers are required (a conservative practical threshold) to achieve a splitting below 10 meV under symmetric relaxation. For practical comparison of the $\bar{\Gamma}$ surface states with experimental binding energies (e.g., ARPES), the midpoint energy E_{mid} of a symmetric 31-layer slab is already within 2 meV of the thick-slab reference value obtained with the same k -mesh. Although the absolute value of E_{mid} carries an additional k -mesh-related uncertainty of approximately 20–25 meV, this approach still offers a computationally efficient alternative to full decoupling. For asymmetric slabs, however, the midpoint average converges to a different value because the two surfaces are structurally inequivalent. In this case, the lower branch E_{low} , which corresponds to the relaxed surface, should be used for comparison with experimental binding energies. For asymmetric relaxation, a residual splitting of approximately 35 meV at $\bar{\Gamma}$ persists beyond 41 layers, with the lower-energy state corresponding to the relaxed surface.

The optimized modeling schemes effectively suppress finite-size numerical artifacts and ensure physically reliable surface-state energy positions. While the specific convergence thresholds obtained here (e.g., $N_{\text{slab}} \geq 55$ for $\Delta E < 10$ meV at $\bar{\Gamma}$) are particular to Al(001) within the PBEsol-GGA framework, the methodology—systematic thickness and relaxation-depth scans combined with probability-density analysis—and the underlying

physical mechanism—the interplay between finite-size wavefunction overlap and structural inequivalence of the two surfaces—can serve as a methodological reference for similar convergence studies on other surfaces. Extension to transition metals with *d*-derived surface states and to other crystallographic facets remains an important direction for future work.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics14100254/s1>. Figure S1: Planar-averaged electrostatic potential energy along the slab normal for the 71-layer slab with asymmetric Top5 relaxation; Figure S2: Dependence of the surface-state splitting energy ΔE at $\bar{\Gamma}$ on relaxation depth for all slab thicknesses (11–81 layers); Figure S3: Energies of the lower surface states at $\bar{\Gamma}$ as a function of relaxation depth for all slab thicknesses (11–81 layers); Figure S4: Surface-state energy splitting (ΔE) at $\bar{X}$ as a function of slab thickness (N_{slab}) for all relaxation configurations; Table S1: Exponential fit parameters for $\Delta E(N_{\text{slab}}) = E_0 e^{-\alpha N_{\text{slab}}}$ and convergence thresholds at $\bar{\Gamma}$ for all five symmetric relaxation schemes, based on data for $N_{\text{slab}} \geq 31$; Table S2: Splitting energy (ΔE), midpoint energy (E_{mid}), energies of the lower and upper surface states (E_{low} , and E_{high}) at $\bar{\Gamma}$ for 41- and 81-layer slabs with Top5 relaxation, calculated with and without dipole correction; Table S3: Splitting energy (ΔE), midpoint energy (E_{mid}), energies of the lower and upper surface states (E_{low} , and E_{high}) at $\bar{\Gamma}$ for 41- and 81-layer slabs with Both5 relaxation, as a function of vacuum-layer thickness; Table S4: Splitting energy (ΔE), midpoint energy (E_{mid}), energies of the lower and upper surface states (E_{low} , and E_{high}) at $\bar{\Gamma}$ for 41- and 81-layer slabs with Both5 relaxation, calculated with $23 \times 23 \times 1$ and $23 \times 23 \times 2$ *k*-meshes.

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Abbreviations

The following abbreviations are used in this manuscript:

DFT	Density functional theory
ARPES	Angle-resolved photoemission spectroscopy
PBE	Perdew–Burke–Ernzerhof
GGA	Generalized gradient approximation

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