

Converged properties of clean metal surfaces by all-electron first-principles calculations

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Abstract

All-electron full-potential linearized augmented plane-wave calculations of the surface energy, work function, and interlayer spacings of close-packed metal surfaces are presented, in particular, for the free-electron-like metal surfaces, Mg(0001) and Al(111), and for the transition metal surfaces, Ti(0001), Cu(111), Pd(111), and Pt(111). We investigate the convergence of the surface energy as a function of the number of layers in the slab, using the Cu(111) surface as an example. The results show that the surface energy, as obtained using total energies of the slab and bulk from separate calculations, converges well with respect to the number of layers in the slab. Obviously, it is necessary that bulk and surface calculations are performed with the same high accuracy. Furthermore, we discuss the performance of the local-density and generalized gradient approximations for the exchange–correlation functional in describing the various surface properties.

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1. Introduction

The surface energy, work function, and interlayer spacings of metal surfaces are important physical properties which play a role in determining the behavior of solid metal surfaces when used in various applications, for example, heterogeneous catalysis, electrochemistry, corrosion, lubrication, etc. [1,2]. The surface energy of the various crystallographic facets determine the equilibrium shape of crystals, however, the direct experimental measurements of the surface energy are difficult to perform and subject to various uncertainties, e.g., presence of impurities. In

addition, most of the available experimental surface-energy data of metals are obtained from surface tension measurements in the liquid phase and extrapolated to zero temperature [3,4], which does not provide the orientation dependence of the surface energy. Due to the difficulties in obtaining experimental surface energies, as well as their orientation dependence [5,6], accurate calculations based on modern first-principles methods play an important role [7–11].

There are two approaches by which to obtain surface energies from first-principles calculations: (i) one may evaluate the total energy of a slab of the particular solid and subtract the corresponding bulk total energy obtained from a separate calculation. Alternatively, (ii), one may use slabs of different thicknesses and extract from them the energy of a bulk atom. Boettger et al. [12,13] and Fiorentini and Methfessel [14] argued that approach (i) is problematic, yielding surface energies that diverge linearly as a function of the slab thickness. The origin of this problem is that

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often slab and bulk total energies are calculated with different levels of accuracy. Thus, Fiorentini and Methfessel suggested that approach (ii) is superior: extracting the bulk total energy from the slope of the slab total energy versus the number of layers in the slab ensures that surface and bulk are extracted with the same accuracy. We will show below, however, that well converged surface energies can be obtained from separate bulk and slab calculations, provided that slab and bulk systems are calculated with the same high accuracy.

The work function is the minimum energy required for an electron to escape from a solid through a certain surface and it is orientation dependent. In particular, the work function changes are an important source of information in the study of adparticles on surfaces [2]. Adsorbates that have higher electronegativities than the substrate atoms typically increase the work function, while those with lower electronegativities have the opposite effect. For example, Na atoms adsorbed on Al(111) decrease the substrate work function by a large amount, i.e., ≈ 1.40 eV at coverage 1/3 of a monolayer (ML) [2]. The electronegativity of Na is 0.93 and that of Al is 1.61, thus there is displacement of electron density from Na toward the substrate, which gives rise to an adsorbate-induced surface dipole. An opposite effect is observed for Cl adsorbed on Al(111) where there is charge transfer from the substrate to Cl, so that Cl is partially negatively charged and sits on an adsorption site which is positively charged [2]. The adsorption of rare-gas atoms on metal surfaces also induce a decrease in the substrate work function, e.g., Xe on Pt(111) for coverage 1/3 ML, reduces the work function by 1.36 eV. For these systems, the mechanism is due to an adsorbate-induced polarization of adparticle and substrate surface [15–17]. In many cases, experimental values of the work function are only available for *polycrystalline* materials [18,19]. Thus, first-principles calculations are valuable in order to predict work functions, or even better, work function *differences* for different surface crystallographic orientations.

Experimentally, the best accessible surface property is the atomic structure, i.e., the interlayer relaxations. The atomic structure can be obtained with high accuracy using quantitative low-energy electron diffraction (LEED) intensity analysis [20–33]. And theoretically, first-principles calculations also give an accurate description, see for example, Refs. [7,34–53], where it has been found that the majority of transition metal surfaces show a contraction of the first interlayer spacing, i.e., the spacing between the two outermost layers is smaller than in the bulk terminated (unrelaxed) surface. An expansion of the outermost interlayer spacing has been reported, e.g., for Mg(0001) [29, 33,37,44,45], Al(111) [11,22,24,28,31,46], and Pt(111) [21, 22,47,50].

In the present paper we employ the all-electron full-potential linearized augmented plane-wave (FP-LAPW) method for the study of the following problems: (i) Convergence of the surface energy with slab thickness using the close-packed Cu(111) surface as an example. The inter-

layer spacings and work function as a function of the thickness of the slab will be also discussed. (ii) Performance of the local-density approximation and the generalized gradient approximation in the study of the surface properties using, as an example, two free-electron-like metal surfaces, i.e., Mg(0001) and Al(111), and four transition metal surfaces, i.e., Ti(0001), Cu(111), Pd(111), and Pt(111). (iii) In the literature, one occasionally finds that calculated surface properties are still obtained at the experimental lattice constant, instead of the equilibrium theoretical value. Thus, it is interesting to see how the surface properties of metal surfaces differ when obtained at experimental and theoretical lattice constants. (iv) Due to the high accuracy of the FP-LAPW method, our well converged results may serve as a benchmark with which to compare the results of other computational approaches, e.g., semi-empirical calculations.

This paper is organized as follows: In Section 2, the theoretical approach and computational details are described. In Section 3, we present and discuss the bulk and surface properties, as well as comparison with other theoretical and experimental results. Section 4 summarizes the main conclusions, while Appendix A lists the total energies used to calculate the surface energies of Cu(111) for different slab thickness, and discusses the affect of the broadening parameter of the Fermi–Dirac distribution function on the surface properties.

2. Theoretical approach and computational details

All calculations are performed using density functional theory (DFT) [54,55] with the local-density approximation (LDA) [56,57] and the generalized gradient approximation (GGA) to describe the exchange–correlation energy functional. For the GGA functional, we use the formulation proposed by Perdew et al. [58], which is commonly called PBE. The Kohn–Sham equations are solved using the all-electron FP-LAPW method [59], as implemented in the WIEN code [60–62]. This implementation includes total energy and atomic force calculations, which allows a structural optimization via a damped molecular-dynamics approach [63].

The core states are treated fully relativistically, while the semi-core and valence states are treated by the scalar relativistic approximation, i.e., spin–orbit coupling is included (neglected) for the core (semi-core and valence) states. The FP-LAPW wave functions in the interstitial region are represented using a plane-wave expansion truncated to include only plane waves that have kinetic energies less than some particular cutoff energy, E^{wf} , and for the potential representation in the interstitial region, plane waves with kinetic energies up to E^{pot} are considered. Inside the muffin-tin spheres with radius R_{mt} , the wave functions are expanded in radial functions (solution of the radial Schrödinger equation) times spherical harmonics up to $l_{\text{max}}^{\text{wf}}$, and for the representation of the potential inside the muffin-tin spheres, a maximum of $l_{\text{max}}^{\text{pot}}$ is used. In the present work:

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