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Deriving accurate work functions from thin-slab calculations

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Abstract. Quantum-size effects have been shown to influence significantly the determination of work functions from thin-slab calculations. We show here that a technique based on macroscopic averages can be used to reduce such effects and determine more precisely the work functions of metals from *ab initio* thin-film calculations. The technique combines the mean electrostatic potential step across the slab surface with the Fermi energy of a bulk crystal. The method is applied to Al(100) slabs containing 1–14 atomic layers.

Ionization potentials of solids, and in particular work functions of metals, are nowadays best calculated by *ab initio* methods in the framework of density functional theory [1, 2]. These calculations present a theoretical challenge, since the work function depends sensitively on the surface ionic and electronic charge distributions, and may be influenced by any surface atomic relaxation or reconstruction. The most efficient first-principles methods generally make use of slab configurations to calculate surface properties. In view of the heavy numerical operations involved, one is usually restricted to studying slabs containing only a small number of atomic planes. If adsorbed atoms or molecules are included in the analysis, the substrate is often reduced to a few atomic layers [3, 4]. Quantum-size effects (QSE) are known to influence the physical properties, including the surface energies and the work functions, of thin metallic slabs [5–8]. In particular, persistent quantum-size oscillations of 0.1 eV have been exhibited recently in the work functions of Al(111) slabs up to twelve atoms thick [9]. These oscillations and the resulting slow convergence of the work functions with slab thickness hinder a precise determination of the work functions of semi-infinite crystals. In this paper, we apply an accurate post-processing method based on a macroscopic averaging technique to solve this problem. We show that this approach reduces QSE and allows one to extract precise work functions for semi-infinite metals from *ab initio* thin-slab calculations.

Before introducing this procedure, we will first briefly discuss the approach that is generally used to evaluate work functions from thin-film calculations. We will then describe our proposed technique and compare the results obtained using the two schemes. As a prototypical system, we focus on the aluminum (100) surface. The *ab initio* calculations are performed within the local density approximation (LDA) to density-functional theory, using the Ceperley–Alder exchange and correlation functional [10]. An aluminum pseudopotential generated with the method of Troullier and Martins [11] is used in the Kleinman–Bylander [12] non-local form. These methods have been used with success in a large number of previous bulk, surface and interface studies [13, 14]. We consider *unrelaxed* thin slabs of the metal separated by six equivalent vacuum layers in a supercell geometry. We use a plane-wave basis set with a kinetic energy cut-off of 16 Ry and 45 Monkhorst–Pack [15] *k*-points in the irreducible part

of the Brillouin zone. The Fermi level is positioned with a Gaussian broadening scheme of the electronic levels [16], with a standard deviation of 0.01 Ry. With these parameters, and for a given slab thickness, the numerical uncertainty on the slab Fermi energy is estimated to be ~ 0.03 eV.

By definition, the work function W is the minimum energy required to extract one electron to an infinite distance from the surface: $W = [V_{el}(+\infty) + E_{N-1}] - E_N$, where $V_{el}(+\infty)$ is the electrostatic potential energy of the electron far from the surface. E_N and E_{N-1} are the total energies of the system with N and $N - 1$ electrons respectively. Following Lang and Kohn [17], this expression is exactly equivalent to:

$$W = \Delta V_{el} - E_F \quad (1)$$

where $\Delta V_{el} = V_{el}(+\infty) - V_{el}(-\infty)$ is the rise in the mean electrostatic potential energy across the metal surface, and E_F is the Fermi energy relative to the mean electrostatic potential $V_{el}(-\infty)$ in the metal interior. Alternatively, if the energies are referred to the potential in the vacuum far from the surface, the work function is directly given by the negative of the Fermi energy (which we now write E_F^s) [5, 18]:

$$W = -E_F^s. \quad (2)$$

Work functions are commonly evaluated using this expression, by measuring the Fermi energy E_F^s of thin slabs with respect to the potential in the vacuum region [5–8, 19–22].

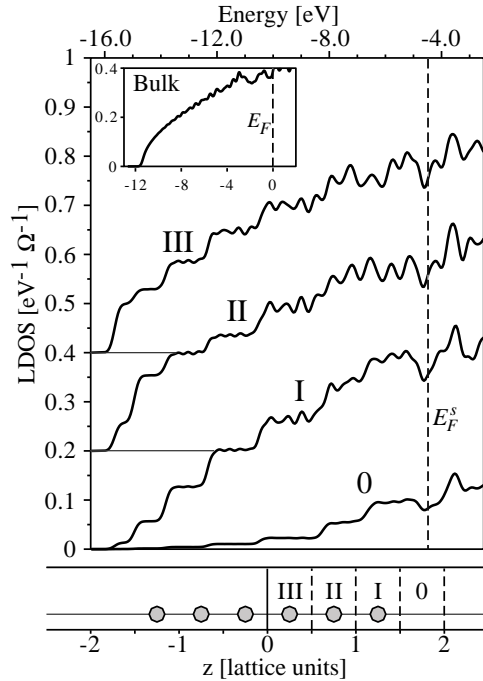


Figure 1. Local density of states in an Al(100) six-layer thin slab, per eV and per unit cell Ω . Curves 0 to III have been calculated in the corresponding regions indicated at the bottom of the figure and exhibit the LDOS of layers increasingly deep in the slab. Curves II and III have been shifted vertically to enhance the readability. The energy zero is set at the vacuum level and the Fermi energy of the slab E_F^s is indicated by the vertical dashed line at -4.41 eV. The inset shows the density of states in a bulk Al crystal, referenced to the bulk Fermi energy E_F .

In figure 1, we show the calculated local density of states (LDOS) of a six-layer-thick Al(100) slab. The calculated energies are referenced to the potential energy in the vacuum region, and the Fermi energy E_F^s therefore yields the work function of the thin film, according to equation (2). Given the smallness of the interslab tunnelling across the vacuum region, the electronic wave functions of the system are practically confined in the well formed by the thin metallic slab and are quantized in the transverse direction. This is clearly reflected in the LDOS of figure 1 which exhibits a series of steps that are reminiscent of two-dimensional systems. Even at the centre of the film, the LDOS does not recover the parabolic shape of the Al bulk density of states, emphasizing the importance of QSE. In this respect, the situation is quite different from that observed in supercell calculations of the Al/GaAs(100) heterostructure [23], where QSE are smaller.

The individual electronic wave functions and energies of the metal slab in a vacuum are thus influenced by QSE, and are different from those of the bulk metal. The slab Fermi energy, therefore, depends sensitively on the film thickness and induces large size effects on the work function. In figure 2, we present the work functions of a series of thin slabs of Al(100) with an increasing number of atomic planes. The work functions have been calculated using equation (2), and represent the position of the slab Fermi level with respect to the electrostatic potential in the middle of the vacuum region. These values are close to the work functions found by other authors for 9- and 15-layer slabs using similar computational approaches [20, 21]. Quantum-size effects in the slab Fermi level appear across the full range of slabs displayed in figure 2.

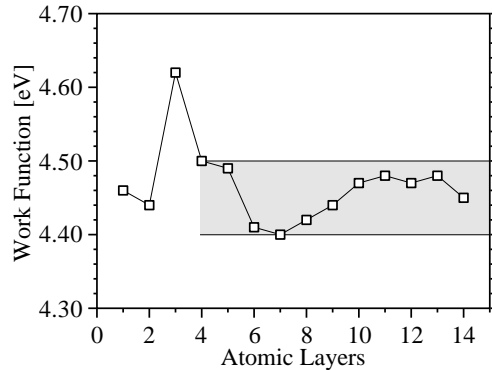


Figure 2. Work functions W of Al(100) thin films (in eV), as a function of the slab thickness, computed using the position of the slab Fermi level: $W = -E_F^s$. The shaded area indicates the uncertainty range for slabs thicker than three atomic layers.

To estimate more precisely the work function of a semi-infinite crystal from thin-film calculations, one should avoid the use of equation (2) and instead calculate the work function using slab quantities which are less sensitive to size effects than the Fermi energy. The total (electronic and ionic) charge density of the slab and the corresponding electrostatic potential are such quantities, especially if one also introduces the macroscopic average technique. This technique has previously been employed successfully in the study of semiconductor heterojunction band-offsets [24] and Schottky barriers [23]. The electronic density $n(\vec{r})$ is the basic variable calculated by all standard *ab initio* codes within density-functional theory. When self-consistency is attained, we calculate the planar average $\bar{n}(z) = S^{-1} \int_S n(\vec{r}) dx dy$, where the z axis is chosen perpendicular to the slab surface S . The macroscopic average electronic density $\bar{\bar{n}}(z)$ is defined from the planar average by an integration over the interplanar distance

d of the slab:

$$\bar{\bar{n}}(z) = \frac{1}{d} \int_{-d/2}^{d/2} \bar{n}(z+z') dz'. \quad (3)$$

From the total charge density, including the ionic charge contribution, the electrostatic potential $V_{el}(\vec{r})$ is easily recovered via the Poisson equation. Since these operations are linear, the plane-averaged potential $\bar{V}_{el}(z)$ is related to its macroscopic average $\bar{\bar{V}}_{el}(z)$ by a relation analogous to equation (3): $\bar{\bar{V}}_{el}(z) = d^{-1} \int_{-d/2}^{d/2} \bar{V}_{el}(z+z') dz'$. By averaging over the interplanar distance, we evacuate all atomic-scale oscillations and expect stable values to be recovered not too far from the surface. This procedure is best applied to unrelaxed surfaces, where the interplanar distance d is constant. However, it can also be used for relaxed slabs, as long as a minimum number of planes in the centre of the film are kept fixed at their unrelaxed locations, so defining the bulk interplane spacing d to be used for the macroscopic averaging.

In figure 3 we display the planar and macroscopic averages of the electronic charge density and the total electrostatic potential V_{el} for the Al(100) slab with the six atomic layers previously studied in figure 1. The potential V_{el} includes the electron Hartree potential and the point-charge potential of the Al^{3+} ions. While the planar averages show oscillations in the metal with the periodicity of the atomic planes, the macroscopic averages exhibit very stable values both in the vacuum and in the metal not far from the slab surfaces. In this way, the potential difference ΔV_{el} between the metal and the vacuum can be precisely measured even in very thin films.

To determine more accurately the work function W of a semi-infinite crystal, we return

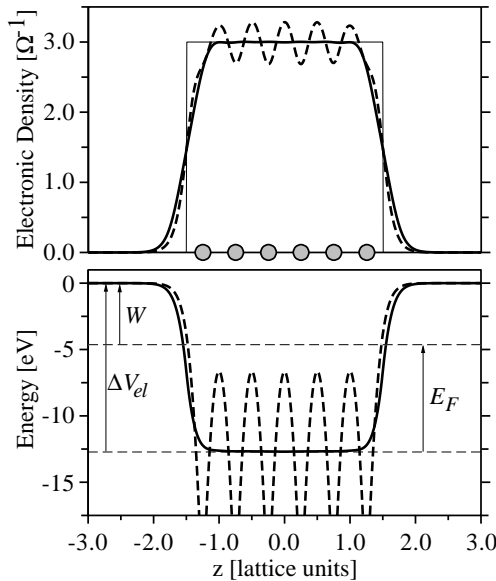


Figure 3. Upper panel: plane-averaged electronic charge density $\bar{n}(z)$ (dashed line) and corresponding macroscopic average $\bar{\bar{n}}(z)$ (solid line), in electrons per unit cell Ω , for an unrelaxed Al(100) six-layer thin film. The double-step function indicates the macroscopic average of the Al^{3+} point-ion charge density and the grey circles denote the atomic planes. Lower panel: plane-averaged total electrostatic potential $\bar{V}_{el}(z)$ (dashed line) and corresponding macroscopic average $\bar{\bar{V}}_{el}(z)$ (solid line) for the same film. The bulk Fermi level E_F , the surface electrostatic potential step ΔV_{el} , and the work function W are indicated.

to equation (1), exploiting the separation of the work function into a surface-dependent and a bulk contribution. The surface-dependent component ΔV_{el} is evaluated from the thin slab by means of the macroscopic average of the total electrostatic potential (see figure 3). The position of the Fermi level E_F with respect to the average electrostatic potential in the metal is evaluated by a *separate* calculation for bulk Al. This involves a small unit cell, can be performed very precisely with a high cut-off and a large density of k -points (we use 36 Ry and 570 reduced k -points), and eliminates QSE altogether for this contribution. The precision of the work function W is thus limited essentially by the surface-dependent term ΔV_{el} , whose numerical accuracy we estimate to be comparable to that of the Fermi energy (~ 0.03 eV). Although this technique is equivalent to the use of equation (2) for sufficiently thick slabs, we expect equation (1) to be less sensitive to QSE and to converge faster to the work function of the semi-infinite crystal as a function of the slab thickness. Equation (1) is less affected by QSE since it relies on the total electron charge density in the slab and not on the individual electronic states. This procedure is thus less sensitive to the details of the thin-film band structure, such as the position of the slab Fermi level, which is employed in equation (2).

In figure 4, we present the values of the work functions for the same series of thin slabs as in figure 2, but here computed using the macroscopic-average technique for the surface electrostatic potential step and the Fermi energy derived from a bulk calculation. Compared with the results of the standard technique shown previously in figure 2, QSE have been noticeably reduced, the oscillations of the work function above four atomic layers having been roughly halved, and convergence within 0.03 eV is achieved with a smaller number of atomic planes.

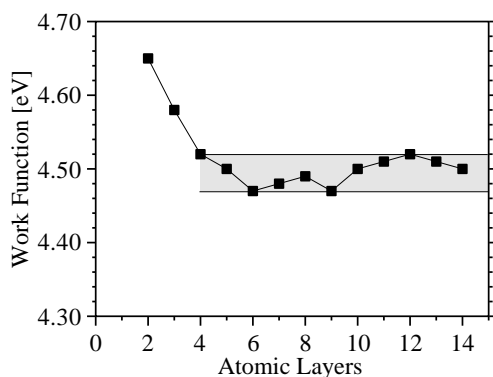


Figure 4. Work functions W of Al(100) thin films (in eV), as a function of the slab thickness, calculated by combining the surface potential step of the slab and the bulk Fermi level. The shaded area indicates the uncertainty region above three atomic layers.

The procedure we propose here exploits a separation of the work function into a bulk contribution and a surface-dependent term. Such a separation is not uniquely defined since the values of the two individual terms depend on the possibility of including a number of short-range local components of the crystal potential in either one or the other of the two contributions. If pseudopotentials are used, an additional arbitrariness on both the bulk and the surface-dependent contributions to the work function results from the choice of pseudopotential. Concerning the separation, we stress that it is only the sum of the two terms, i.e. the difference between the Fermi level and the vacuum potential, that is physically meaningful. We have found that the fastest convergence of work function values with slab thickness and plane-wave cut-off is obtained when the exchange-correlation and the so-called alpha terms [25] of the

average local crystal potential are included in the bulk contribution. Within LDA, the exchange-correlation term of the crystal potential is a local short-range potential, and its average value in the crystal can therefore be included in the bulk Fermi-energy contribution. Similarly, for the surface potential step it is convenient to use an ionic Coulomb potential generated by point ions, rather than the local part of the ionic pseudopotential. The alpha term, resulting from this difference, can then be included with the bulk contribution.

In figure 5 we compare the electrostatic potential V_{el} , consisting of the electronic Hartree and Coulombic point-ion potentials, with the total local potential V_{loc} , given by the sum of the electronic Hartree potential, the local part of the ionic pseudopotential and the LDA exchange-correlation potential. We also show the exchange-correlation potential V_{xc} only. The macroscopic average potentials are also represented and have been calculated directly from the corresponding plane-averaged potentials. The electrostatic potential decay in the vacuum is controlled by the extent of the electronic density $\bar{n}(z)$. Far from macroscopic metal surfaces, $\bar{n}(z)$ is known to decrease exactly as $z^{-1}e^{-2kz}$, where k is related to the work function W by $k = \sqrt{2mW}/\hbar$ [26]. The dominant term in the electrostatic potential far from the surface can be extracted by double integration of this charge density, and falls off as $\bar{n}(z)/W$. The convergence of the electrostatic potential V_{el} in the vacuum is thus extremely fast, and six equivalent vacuum layers are enough to separate the repeated slabs in figure 5. We note that if metals with smaller work functions than Al are considered, the number of equivalent vacuum planes in the supercell will have to be increased further to account for the increased spreading of the electronic charge into the vacuum.

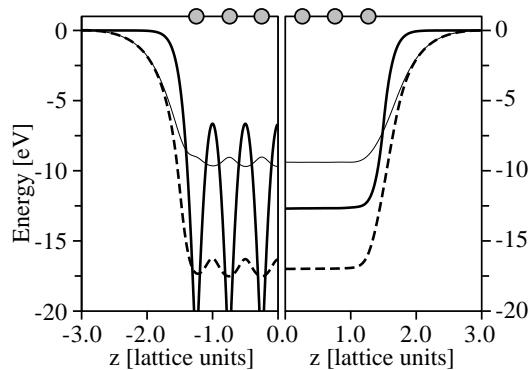


Figure 5. Plane average (left panel) and macroscopic average (right panel) of the electrostatic potential V_{el} (thick solid lines), total local potential V_{loc} (dashed lines), and LDA exchange-correlation potential V_{xc} (thin solid lines) for unrelaxed Al(100) six-layer thin slabs separated by six equivalent vacuum layers. The grey circles correspond to the atomic planes.

In figure 5, we observe that V_{xc} accounts for a large proportion of the total potential V_{loc} , and is seen to decrease more slowly in the vacuum than the electrostatic term. The number of equivalent vacuum layers used here proves insufficient for V_{loc} to converge adequately in the vacuum region of the supercell. Therefore, if the total local potential V_{loc} is used to evaluate the surface potential step ΔV_{loc} , a larger number of equivalent vacuum planes (at least eight) are needed in the supercell for the Al work function to converge within 0.03 eV, as observed in figure 6. Furthermore, we find that the cut-off for the slab calculation must be increased (up to 36 Ry for full convergence) when the exchange-correlation and alpha terms are included in the surface-dependent contribution ΔV_{loc} . Both these observations result mainly from the very slow convergence to zero of the LDA potential $V_{xc}(\vec{r})$ in the vacuum region of

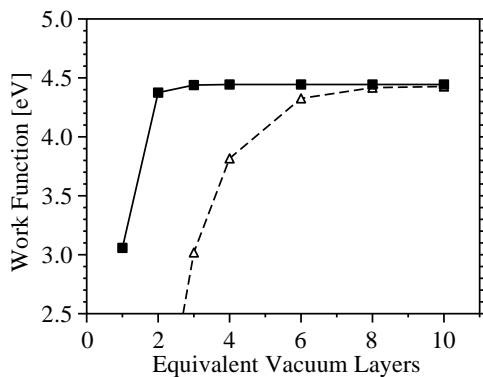


Figure 6. Work function of a six-layer Al(100) slab, as a function of the number of equivalent vacuum layers in the supercell, calculated by combining the bulk Fermi level with the electrostatic potential step ΔV_{el} (solid line) and with the total local potential step ΔV_{loc} (dashed line). The local potential step ΔV_{loc} was calculated with a cut-off of 36 Ry.

the supercell where the charge density $n(\vec{r})$ tends to zero and the LDA exchange-correlation potential behaves as $n(\vec{r})^{1/3}$. For example, charge densities below 10^{-10} a.u. (respectively 10^{-4} a.u.) are needed in the vacuum for the rise in the exchange-correlation (respectively electrostatic) potential across the surface to be converged within 0.01 eV.

In conclusion, we have studied the use of the macroscopic-average method to the calculation of work functions. This technique allows accurate work functions to be determined from thin-slab calculations. We recover very stable charge densities and potentials inside the slab by filtering the atomic oscillations in the electronic density. By relying only on the film charge density to determine the work function, and not on the position of the slab Fermi level, we have shown how quantum-size effects can be reduced. The work functions of semi-infinite crystals can then be obtained by studying slabs with a small number of atomic layers.

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