Properties of real metallic surfaces: Effects of density functional semimolarity and van der Waals nonlocality

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We have computed the surface energies, work functions, and interlayer surface relaxations of clean (111), (100), and (110) surfaces of Al, Cu, Ru, Rh, Pd, Ag, Pt, and Au. We interpret the surface energy from liquid metal measurements as the mean of the solid-state surface energies over these three lowest-index crystal faces. We compare experimental (and random phase approximation) reference values to those of a family of nonempirical semimolarity functionals, from the basic local density approximation (LDA) to our most advanced general purpose meta-generalized gradient approximation, strongly constrained and appropriately normed (SCAN). The closest agreement is achieved by the simplest density functional LDA, and by the most sophisticated one, SCAN+rVV10 (Vydrov–Van Voorhis 2010). The long-range van der Waals interaction, incorporated through rVV10, increases the surface energies by about 10%, and increases the work functions by about 3%. LDA works for metal surfaces through two known error cancellations. The Perdew–Burke–Ernzerhof generalized gradient approximation tends to underestimate both surface energies (by about 24%) and work functions (by about 4%), yielding the least-accurate results. The amount by which a functional underestimates these surface properties correlates with the extent to which it neglects van der Waals attraction at intermediate and long range. Qualitative arguments are given for the signs of the van der Waals contributions to the surface energy and work function. A standard expression for the work function in Kohn–Sham (KS) theory is shown to be valid in generalized KS theory. Interlayer relaxations from different functionals are in reasonable agreement with one another, and usually with experiment.

metallic surfaces | density functional theory | van der Waals interaction

The rapid development of electronic structure theory has made it easier to analyze and describe the complexity of metallic surfaces (1), but understanding the underlying physics behind surface energies, work functions, and interlayer relaxations has remained a long-standing challenge (2). Metallic surfaces are of particular importance because of their wide range of applications, including catalysis (3–8). A detailed knowledge of the electronic structure is required for accurate theoretical investigations of metallic surfaces (9, 10).

Consequently, metal surfaces have played a key role in the development and application of Kohn–Sham density functional theory (KS DFT) (11). The work of Lang and Kohn (12–14) in the early 1970s demonstrated the ability of the simple local density approximation (LDA) (11, 15) for the exchange-correlation (xc) energy to capture the surface energies and work functions of real metals. Their work stimulated the effort to understand why simple approximate functionals work and how they can be improved (16, 17). Later, correlated wave function calculations (18, 19) gave much higher surface energies for jellium, but were not supported by further studies (20, 21) and were eventually corrected by a painstaking Quantum Monte Carlo calculation (22). The too-low surface energies from the Perdew–Burke–Ernzerhof (PBE) (23) generalized gradient approximation (GGA) led, in part, to the AM05 (24) and PBESol (25) (PBE for solids) GGAs, and to general purpose meta-GGAs (26–30) that remain computationally efficient, including the recent strongly constrained and appropriately normed (SCAN) meta-GGA (30, 31). There have also been surface studies based upon the random phase approximation (RPA) (32).

SCAN captures intermediate-range van der Waals (vdW) interaction [responsible for the equilibrium binding of two closed-shell atoms (30, 31, 33)], but capturing longer-ranged vdW interaction requires the addition of a nonlocal vdW correction as from the revised Vydrov–Van Voorhis 2010 (rVV10) functional (34, 35). The intermediate-range vdW interaction is crucial for SCAN’s correct description of liquid water (36).

Ref. 35 suggests that the vdW interaction is semilocal at short and intermediate range, but displays pairwise full nonlocality at longer ranges, and displays many-body full nonlocality (37, 38) at the longest and often least energetically important distances. Accounting for intermediate and long-ranged vdW interactions is especially important for layered materials (35, 39, 40) and ionic solids (41–43). The vdW interactions are also needed to correct the errors of GGAs for bulk metallic systems (42). Ref. 44 reports long-range vdW interaction between two jellium slabs. The importance of the vdW contribution for the surface energy and the work function will be demonstrated here. By naturally accounting for both intermediate- and long-range interactions, SCAN+rVV10 (35) represents a major improvement over previous functionals for many properties of diversely bonded systems (31). Its pairwise interactions at long range even match the RPA binding energy curve for graphene on a nickel surface (35).

Significance

It is primarily at their surfaces that solids interact with their environments. What is the physics behind the measurable properties of clean metallic surfaces? To answer this question, we calculate surface energies, work functions, and surface interlayer relaxations for aluminum and seven d-electron metals, using a sequence of exchange-correlation density functionals of increasing sophistication. While the simplest one, the local density approximation, works well through error cancellation, the usually more realistic Perdew–Burke–Ernzerhof functional underestimates both surface energies and work functions. The more advanced functionals, including the new strongly constrained and appropriately normed (SCAN) and SCAN+rVV10, demonstrate the unexpected importance of intermediate and long-range van der Waals attraction (seamlessly included in the random phase approximation).

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However, it had not been tested for real metallic surface energies and work functions. By studying metallic surfaces with this general purpose functional, we can better understand why LDA can be accidentally accurate, and demonstrate the systematic improvement of SCAN over other nonempirical functionals. Furthermore, we will also be able to untangle the effects of intermediate- and long-range dispersion.

The surface energy is the work required per unit area to cleave an infinite crystal and create a new surface (12). Accurate theoretical face-dependent surface energies are straightforward to obtain from accurate bulk and surface calculations, since we have absolute control over morphology and purity. Experimentally, however, surface energies have been determined by measuring the surface tension of the liquid metal and then extrapolating to 0 K using a phenomenological method (45–47). The surface tension of the liquid phase is generally different from the actual surface energy of the solid-state metals and can be considered as an “average” surface energy. Available experimental values are also rather old (1970–1980). They provide useful but uncertain estimates for the low-energy faces of bulk crystals.

The work function, on the other hand, is easier to measure (48–51) than is the surface energy. However, it still remains an open question which experimental work function one should compare with theoretical values. In practice, the work function can be calculated using DFT by accurately determining the Fermi energy and vacuum potential (13, 14).

Another fundamental property of surfaces is geometric relaxation of the surface layer spacings. This effect can be accurately measured experimentally using low-energy electron diffraction (46, 52) intensity analysis. The role played by the xc functional in surface relaxations was unclear and worth exploring in more detail.

Despite the theoretical challenges of modeling and explaining these metallic surface properties, DFT (11, 26, 30, 31, 53) has proven to be one of the leading electronic structure theory methods for understanding characteristics of metal surfaces. Lang and Kohn (12–14) pioneered the density functional calculation of surface energies and work functions using the jellium model without and with perturbative lattice corrections. Skriver and Rosengaard (54) reported the surface energies and work functions of close-packed metal surfaces from across the periodic table using Green’s function techniques based on linear muffin-tin orbitals within the tight-binding and atomic sphere approximations. In other work, Perdew et al. (55) used the stabilized jellium and liquid-drop models to understand the dependency of surface energies and work functions of simple metals on the bulk electron density as well as the atomic packing of the exposed crystal face. For related work, see refs. 56–59. Developing functionals that are accurate for surfaces has been an active area of research (24, 25, 60–62).

Previous works (16, 62, 63) gave very reasonable descriptions of metallic surfaces, despite their limitations (64). Wang and Wang (65) calculated surface energies and work functions of six close-packed fcc and bcc metal surfaces using LDA and PBE, confirming the face dependence of the surface energy and work function. Singh-Miller and Marzari (66) used PBE to study surface relaxations, surface energies, and work functions of the low-index metallic surfaces of Al, Pt, Pd, Au, and Ti. Ref. 66 found that LDA qualitatively agrees with the experimental surface energies, but neither LDA nor PBE can be considered as a default choice for quantitative comparison with experimental values for surface properties. Following what they have suggested, we will demonstrate that higher rungs of Jacob’s ladder in DFT (3), such as meta-GGAs or the RPA (60), must be used to accurately study surface properties.

In this work, we investigate the surface energies, work functions, and interlayer relaxations of the low-index clean metallic surfaces of Al, Cu, Ru, Rh, Pd, Ag, Pt, and Au. (We do not include the more difficult 3d elements Mn, Fe, Co, and Ni, for which semilocal functionals may make nonnegligible self-interaction errors.) The effects of interlayer relaxation are included in our calculated surface energies and work functions. Here we focus on three main crystallographic faces, (111), (100), and (110), to explore the face dependence of the surface properties (67). Furthermore, we have explored the xc functional dependence to demonstrate the improvements nonempirical meta-GGAs can achieve compared with GGAs. We used the following approximations: LDA (11, 15), the PBE GGA (23) and its modification for solids, PBEsol (25, 68), and the newly constructed meta-GGA SCAN (30), as well as SCAN+rVV10 (35).

Definitions

Surface Energy. To define the surface energy σ, we consider a solid with a finite number n of infinitely extended planar atomic layers, and a slab of finite area A embedded in this solid. The slab has n layers, each with Nl atoms. Then

\[ \sigma = \lim_{n \to \infty} \frac{E_{\text{slab}}(n) - nN_l \epsilon_{\text{bulk}}}{2A} \]  

[1]

where \( E_{\text{slab}}(n) \) is the total energy of the slab and \( \epsilon_{\text{bulk}} \) is the energy per atom of the infinite bulk. The factor of 1/2 in this equation comes from the fact that the slab is bounded by two symmetric surfaces. If the two terms in Eq. 1 are calculated similarly, numerical errors in each can cancel. If not, Eq. 1 can diverge (69), unless both energies are computationally well converged (2). Eq. 1 can also be written for large n as

\[ E_{\text{slab}}(n) \approx nN_l \epsilon_{\text{bulk}} + 2\sigma A. \]  

[2]

The linear fit method (70, 71) is one way to find converged values for the surface energies. We have applied this method (as illustrated in SI Appendix), using equivalent cutoff energies and k meshes for the bulk and slab calculations. For each surface, we used nine slabs with \( n = 4 \) to 12 layers.

Work Function. The work function of a metallic surface is the minimum energy needed to remove an electron to a distance that is large on the microscopic scale but small on the macroscopic scale of facet dimensions:

\[ \phi = V_{\text{vacuum}} - \epsilon_{\text{Fermi}}. \]  

[3]

The electrostatic potential \( V(r) \) and the Fermi energy \( \epsilon_{\text{Fermi}} \) each contain the same additive arbitrary constant, which cancels out of \( \phi \) in Eq. 3. \( V_{\text{vacuum}} \) is the maximum of \( V(r) \) at the center of the vacuum region. The work function defined in this way depends upon the chosen crystallographic face. However, the work to remove an electron from a finite crystal to a distance much greater than the dimension of any crystal facet is, of course, independent of the face through which it is removed.

Surface Lattice Relaxation. Surface relaxations arise due to the minimization of the energy at the surface, and can be computed using the simple formula

\[ d_{ij}\% = \frac{d_{ij} - d_0}{d_0} \times 100, \]  

[4]

where \( d_{ij} \) is the distance between neighboring layers \( i \) and \( j \), and \( d_0 \) is the distance between the layers of the unrelaxed slab.

Crystal Structure. All of the studied metals are fcc except Ru, which is really hcp. Both hcp and fcc are close-packed, and, for convenience, we have also treated Ru as fcc. For fcc, the lowest-index crystal faces, in decreasing order of packing density in the face layer, are (111), (100), and (110).
Results and Discussion

Surface Energy. Surface energies from measured liquid metal surface tensions (45–47, 72) are usually average surface energies over crystal faces. Hence, the experimentally measured surface energy can be compared with the mean of the surface energies for (111), (110), and (100) surfaces (73). As we will see later in this section, the calculated face dependencies are not strong, which helps to justify this choice. Here we also use the mean surface energies to compare with the experimentally measured values, but from a different perspective: LDA is known to yield accurate surface energies for jellyum, within the uncertainty of the latest quantum Monte Carlo (QMC) values (22), and an equally weighted average over the three lowest-index faces from LDA reproduces the experimental surface energies to within their uncertainties. LDA displays a remarkable error cancellation between its exchange and correlation contributions (16, 17). Usually, the LDA exchange contribution to the surface energy is an overestimate, while the correlation contribution is a significant underestimate, and their combination results in an accurate prediction. PBE improves both the exchange and the correlation contributions, but loses the remarkable error cancellation of LDA.

In Table 1, we report the mean surface energies calculated using different density functionals, including results from the RPA. Fig. 1 (Left) shows the error (in joules per square meter) of the computed values of the mean surface energies compared with the best available experimental results for each metal. The consistent performance of SCAN+rVV10 can be seen in all cases, whereas PBE and SCAN both perform less well. The RPA results are overall in good agreement with the experimental results; however, the computational cost is higher. One can argue that SCAN+rVV10 is the “best” candidate for predicting metallic surface energies, with its moderate computational cost and high accuracy.

The errors and mean absolute percentage errors (MAPEs) of the computed mean surface energies are shown in Fig. 1. The errors are computed with respect to the experimental values. Our results are in agreement, within an acceptable margin, with those previously reported in the literature (65, 66, 73, 74). For Al, Fig. 1 (Left) illustrates the accuracy of all methods for simple metals that are close to the jellium limit.

Table 1 demonstrates that there is an overall systematic improvement from PBE to PBEsol or SCAN and then to SCAN+rVV10 in the Al surface energy, due to the sequential incorporation of intermediate-range dispersion in PBEsol or SCAN and long-range dispersion in rVV10. We expect that PBEsol+rVV10 could be comparably accurate for solids and surfaces (but not for molecules, unlike the general purpose SCAN+rVV10). The long-range contribution from rVV10 in Al accounts for 12% of the total surface energy, and foreshadows the importance of including this contribution for the d metals. Transition and noble metal surfaces are more challenging due to their localized d orbitals, which cause strong inhomogeneities in the valence electron density. These inhomogeneities lead to a wider spread in the results from the different functionals. PBE yields the largest errors for the transition metal surface energies, because it neglects most of the vdW interaction, i.e., it radically underestimates the equilibrium binding energy of two closed-shell atoms or molecules. PBEsol and SCAN incorporate intermediate-range vDW, and so improve the surface energy. With the addition of the long-range vdW from rVV10, SCAN+rVV10 surpasses the accuracy of SCAN, indicating that the long-range vdW contribution to the surface energy is more important than previously recognized. The intermediate- and long-range vdW attraction between separating half spaces must increase the work needed to pull them apart, and thus the surface energy.

In LDA, the vdW attraction is overestimated at intermediate range but neglected at long range, leading to another remark-

| Metals | LDA | PBE | PBEsol | SCAN | SCAN+rVV10 | RPA * | Experimental (45, 46) |
|--------|-----|-----|--------|------|------------|------|----------------------|
| Al     | 1.08| 0.89| 1.06   | 1.03 | 1.16       | 1.07 | 1.14 ± 0.2           |
| Cu     | 1.98| 1.48| 1.74   | 1.68 | 1.89       | 2.03 | 1.79 ± 0.19          |
| Ru     | 3.19| 2.48| 2.89   | 2.77 | 2.99       | 3.45 | 3.04 ± 0.33          |
| Rh     | 2.86| 2.47| 2.71   | 2.6  | 2.81       | 3.17 | 2.66 ± 0.29          |
| Pd     | 2.19| 1.59| 1.90   | 1.8  | 2.04       | 2.25 | 2.00 ± 0.22          |
| Ag     | 1.2 | 0.84| 1.08   | 1.03 | 1.22       | 1.40 | 1.25 ± 0.13          |
| Pt     | 2.26| 1.79| 2.12   | 1.92 | 2.15       | 2.84 | 2.49 ± 0.26          |
| Au     | 1.41| 0.87| 1.16   | 1.06 | 1.29       | 1.55 | 1.51 ± 0.16          |
| MAE    | 0.18| 0.64| 0.35   | 0.46 | 0.24       | 0.23 |                      |

The mean absolute error (MAE) of each functional is also shown.

* GPAW.
Table 2. Surface energies $\sigma$ (in joules per square meter) of the (111), (100), and (110) surfaces for the selected metals

| Metals | Surface | LDA | PBE | PBEsol | SCAN +rVV10 | LDA (other works) | GGA (other works) |
|--------|---------|-----|-----|--------|-------------|-------------------|------------------|
| Al     | 111     | 0.99| 0.77| 0.99   | 0.91 1.11 0.91 (2), 1.27 (54) | 0.67 (66), 1.19 (74) |
|        | 100     | 1.15| 0.95| 1.08   | 1.08 1.18 | 0.86 (66), 1.35 (74) |
|        | 110     | 1.09| 0.96| 1.11   | 1.09 1.19 | 0.93 (66), 1.27 (74) |
| Cu     | 111     | 1.99| 1.48| 1.76   | 1.70 1.91 | 2.09 (54), 2.17 (74), 2.15 (65) |
|        | 100     | 2.16| 1.43| 1.83   | 1.84 2.02 | 2.31 (54), 2.24 (74), 2.19 (65) |
|        | 110     | 2.23| 1.44| 1.93   | 1.97 2.05 | 1.97 (77), 1.55 (66), 2.33 (74), 2.23 (65) |
| Ru     | 111     | 2.67| 2.09| 2.53   | 2.61 2.78 (54), 2.53 (77) | 2.47 (74), 2.61 (65) |
|        | 100     | 3.04| 2.77| 2.97   | 3.00 2.90 (54), 2.81 (77) | 2.79 (74), 3.01 (65) |
|        | 110     | 3.34| 2.58| 2.94   | 3.08 2.88 (77) | 2.89 (74), 3.08 (65) |
| Rh     | 111     | 1.89| 1.36| 1.54   | 1.77 1.88 (54), 1.64 (77) | 1.31 (66), 1.92 (74), 1.90 (65) |
|        | 100     | 2.43| 1.85| 2.12   | 2.29 1.90 (54), 1.86 (77) | 1.49 (66), 2.33 (74), 2.15 (65) |
|        | 110     | 2.45| 1.92| 2.13   | 2.45 1.97 (77) | 1.55 (66), 2.33 (74), 2.23 (65) |
| Ag     | 111     | 2.45| 1.78| 1.91   | 2.05 1.12 (54), 1.12 (77) | 1.17 (74), 1.15 (65) |
|        | 100     | 2.98| 2.04| 2.12   | 2.18 1.20 (54), 1.21 (77) | 1.20 (74), 1.27 (65) |
|        | 110     | 3.42| 2.27| 2.40   | 2.45 1.32 (54), 1.26 (77) | 1.24 (74), 1.35 (65) |
| Pd     | 111     | 1.88| 1.36| 1.54   | 1.77 1.88 (54), 1.64 (77) | 1.31 (66), 1.92 (74), 1.90 (65) |
|        | 100     | 2.43| 1.79| 2.15   | 2.29 1.90 (54), 1.86 (77) | 1.49 (66), 2.33 (74), 2.15 (65) |
|        | 110     | 2.25| 1.61| 1.83   | 2.05 1.97 (77) | 1.55 (66), 2.33 (74), 2.23 (65) |
| Au     | 111     | 2.46| 1.94| 2.31   | 2.00 2.18 (54), 2.00 (74), 2.00 (65) |
|        | 100     | 2.35| 1.88| 2.21   | 2.48 (54) | 1.81 (66), 2.73 (74), 2.47 (65) |
|        | 110     | 1.61| 0.99| 1.26   | 1.2 1.47 (54), 1.55 (80) | 0.96 (66), 1.74 (74), 1.41 (65) |

While we could not find corresponding experimental values for any of our metals, the numbers in Table 2 could be used to predict the equilibrium shapes of the elemental solids by the Wulff construction. SCAN+rVV10 frequently overlaps with LDA, while the systematic underestimation of the surface energies by PBE is easy to see. We find excellent agreement of our PBEsol results with those of Sun et al. (81), and that our LDA and PBE values and trends are in good agreement with others recently reported (65, 66, 73). The general trend of $\sigma_{111} < \sigma_{100} < \sigma_{110}$ can be seen from Fig. 2 for most metals. However, this trend seems to be broken for Ru, Rh, and Pd.

Work Function. The errors of the mean work functions (averaged over crystal faces) and the MAPE of the face-dependent work functions are plotted in Fig. 3. Ru is hcp, and the experimental work function we have for it is for polycrystalline Ru, so Ru is excluded from the MAPE and mean absolute error cancellation. Without using the vdW language, the same cancellation can be seen in the wave vector analysis of the RPA xc surface energy of jellium (32). RPA includes vdW attraction at all ranges, but overestimates the magnitude of short-range correlation that is properly described by our LDA, GGAs, and meta-GGA. RPA tends to overestimate the surface energy slightly. This is expected based upon the results for jellium slabs (75, 76).

Fig. 1 (Right) shows MAPE. SCAN+rVV10 is the best semilocal density functional, although LDA is a close second. Incorporation of vdW interactions is important for dealing with the interactions of clean metallic surfaces and their surroundings. Because it treats intermediate and long-range vdW interactions accurately, SCAN+rVV10 can be expected to perform more systematically than LDA for a broader set of properties.

Table 2 (with some inputs from refs. 77–80) and Fig. 2 display the calculated surface energy for each crystallographic face.

![Fig. 2. Surface energies $\sigma_{111}$ (Left), $\sigma_{100}$ (Middle), and $\sigma_{110}$ (Right) for the selected metals in this work. The chemical trends are similar for all functionals.](image)
error (MAE). Calculated values of the work function for each face can be found in Table 3 (with some inputs from refs. 82–101), and are plotted in Fig. 4. Our results for LDA and PBE are generally within ~0.15 eV of those reported in the literature (66, 102). For Al, LDA overestimates the work function for the (111) surface by 0.1 eV, but is dead on experiment for the other two faces. PBE and SCAN perform similarly for Al, but show larger deviations from one another for the d-block metals. PBEsol and SCAN+rV V10 yield the smallest errors for Al.

Fig. 3 also shows the errors in the calculated values of the work function for the transition and noble metals. These systems have entirely or partly filled d orbitals which are localized on the atoms. Hybridization between the d and s orbitals varies with the crystallographic orientation, resulting in changes in the surface dipole and, consequently, the work function. The redistribution of the d electrons in noble metals also impacts the work function, and these changes vary from one face to another (103).

From Fig. 3, it is clear that PBE systematically underestimates the work function, and its accuracy is erratic. In general, SCAN improves upon PBE through its incorporation of vdW contributions to the surface potentials. Although PBEsol and SCAN differ in many ways, both incorporate intermediate-range vdW interactions. Their overall performance for work functions is quite similar, and, typically, the errors from these functionals are within the experimental uncertainties. They also outperform LDA for the work functions, which was not the case for the surface energies above.

The inclusion of intermediate-range vdW interactions is not enough, however, as the long-range contributions can still raise the work function by an appreciable amount. The (110) surface of Rh is one such case, where the addition of rV V10 to SCAN increases the work function by nearly 0.2 eV, significantly reducing the error compared with experiment. Incorporating the long-range dispersion amounts to between 3% and 6% of the total work function, underscoring the importance of its inclusion. Although LDA and SCAN+rV V10 were of similar quality for the surface energies, SCAN+rV V10 clearly takes the top spot for computing accurate work functions. We note that the trend ϕ_{110} < ϕ_{100} < ϕ_{111} predicted by Smoluchowski (104) is

Table 3. Work functions ϕ (eV) for the (111), (100), and (100) surfaces of different metals

| Metals | Surface | LDA | PBE | PBEsol | SCAN | SCAN+rV V10 | LDA (other work) | GGA (other work) | Experiment |
|--------|---------|-----|-----|--------|------|------------|-----------------|-----------------|------------|
| Al     | 111     | 4.36| 4.2 | 4.24   | 4.19 | 4.23       | 4.25 (82)       | 4.02 (66)       | 4.26 ± 0.03 (85), 4.32 ± 0.06 (87) |
|        | 100     | 4.41| 4.27| 4.32 | 4.35 | 4.42       | 4.38 (82)       | 4.09 (66)       | 4.41 ± 0.03 (87), 4.32 ± 0.06 (87) |
|        | 110     | 4.08| 3.96| 3.98 | 3.99 | 4.00       | 4.3 (82)        | 4.3 (66)        | 4.06 ± 0.03 (89), 4.23 ± 0.13 (87) |
| Cu     | 111     | 5.20| 4.88| 4.98 | 4.98 | 5.09       | 4.94 (91), 4.9 ± 0.02 (87) |
|        | 100     | 4.79| 4.42| 4.43 | 4.47 | 4.54       | 4.59 ± 0.03 (94), 4.73 ± 0.1 (87) |
|        | 110     | 4.68| 4.38| 4.48 | 4.47 | 4.53       | 4.59 (93), 4.56 ± 0.1 (87) |
| Ru     | 111     | 4.78| 4.37| 4.51 | 4.38 | 4.65       | 5.33 (77)       | 4.71 (51)       | 5.44 ± 0.03 (83), 5.67 ± 0.12 (87) |
|        | 100     | 5.1 | 4.78| 4.86 | 4.9 | 4.97       | 5.03 (77)       | 5.11 (101), 5.3 ± 0.15 (87) |
|        | 110     | 4.68| 4.42| 4.55 | 4.52 | 4.72       | 4.65 (77)       | 5.1 (84), 5.07 ± 0.2 (87) |
| Rh     | 111     | 5.23| 5.00| 5.12 | 5.16 | 5.20       | 5.3 (100), 5.46 ± 0.09 (87) |
|        | 100     | 5.44| 5.12| 5.38 | 5.34 | 5.37       | 5.25 (77)       | 5.11 (101), 5.3 ± 0.15 (87) |
|        | 110     | 4.9 | 4.53| 4.66 | 4.65 | 4.83       | 4.98 (77)       | 4.8 ± 0.05 (99), 4.86 ± 0.21 (87) |
| Pd     | 111     | 5.66| 5.32| 5.52 | 5.39 | 5.47       | 5.64 (2)        | 5.25 (66)       | 5.44 ± 0.03 (83), 5.67 ± 0.12 (87) |
|        | 100     | 5.54| 5.12| 5.25 | 5.19 | 5.26       | 5.11 (66)       | 5.3 (86), 5.48 ± 0.23 (87) |
|        | 110     | 5.32| 4.95| 5.07 | 5.04 | 5.09       | 4.87 (66)       | 5.2 (84), 5.07 ± 0.2 (87) |
| Ag     | 111     | 4.97| 4.49| 4.66 | 4.57 | 4.63       | 4.75 ± 0.01 (88), 4.53 ± 0.07 (87) |
|        | 100     | 4.64| 4.26| 4.35 | 4.3 | 4.37       | 4.42 ± 0.02 (90), 4.36 ± 0.05 (87) |
|        | 110     | 4.61| 4.16| 4.28 | 4.21 | 4.26       | 4.25 ± 0.03 (92), 4.1 ± 0.15 (87) |
| Pt     | 111     | 6.08| 5.72| 5.85 | 5.90 | 5.97       | 6.06 (2)        | 5.69 (66)       | 6.08 ± 0.15 (95), 5.91 ± 0.08 (87) |
|        | 100     | 6.06| 5.69| 5.82 | 5.94 | 6.01       | 5.66 (66)       | 5.9 (99), 5.75 ± 0.13 (87) |
|        | 110     | 5.6 | 5.18| 5.31 | 5.27 | 5.36       | 5.52 (80)       | 5.26 (66)       | 5.4 (96), 5.53 ± 0.13 (87) |
| Au     | 111     | 5.49| 5.12| 5.19 | 5.32 | 5.41       | 5.63 (103)      | 5.15 (66)       | 5.3 to 5.6 (100), 5.33 ± 0.06 (87) |
|        | 100     | 5.49| 5.07| 5.17 | 5.26 | 5.28       | 5.53 (103)      | 5.1 (66)        | 5.22 ± 0.04 (104), 5.22 ± 0.31 (87) |
|        | 110     | 5.36| 4.94| 5.02 | 5.17 | 5.3       | 5.41 (103)      | 5.04 (66)       | 5.2 (105), 5.16 ± 0.22 (87) |
| MAE    |        | 0.16| 0.21| 0.11 | 0.11 | 0.08       |                 |                 |            |
not observed for Al, Ru, and Rh, but is observed for the other metals.

By incorporating a long-range contribution to the potential from rVV10, SCAN+rVV10 systematically and accurately predicts work functions within experimental uncertainties. Addition of rVV10 to the GGAs would likely reduce their errors as well, since the bare functional underestimates the experimental reference, but it would worsen the LDA results. The systematic behavior of SCAN for diversely bonded systems lends itself to correction by rVV10, achieving a well-balanced performance for both surface and bulk (30, 31) properties.

Surface Lattice Relaxation and Other Studies. At the surface, the presence of fewer neighboring ions can change the equilibrium position of a given ion due to changes in the interionic forces. The distances between surface layers always relax as a result. Moreover, surface reconstructions have been observed for Pt and Au (105, 106, 107), in which the ions within the top layers rearrange to reach a new equilibrium. Our calculations here include the former effect but not the latter one.

SI Appendix, Tables S1–S3 show the tabulated values of the percentage relaxation for the top four layers of the three surfaces. Different xc functionals may predict different interlayer relaxations compared with the experimental data (52, 108–113). It is important to note that, for d34% and d34%, we have found only a few experimental results to compare with.

In most cases, SCAN+rVV10 and SCAN predict reasonably accurate interlayer relaxations in comparison with the experimental results. However, for the Au (100) surface, the experimental d12% is much stronger than any of our functionals predict, due to a corrugated surface reconstruction (112) not included in our calculation. SI Appendix, Tables S1–S3 also show that the LDA and PBE results calculated in this work are in agreement with ref. 66.

SI Appendix, Table S4 shows that SCAN and SCAN+rVV10 are highly accurate for the bulk lattice constants of all of the metals. Tables S5–S10 in the SI Appendix show surface properties of jellium and stabilized jellium, calculated using the code of ref. 114.

Why the vdW Attraction Raises Surface Energies and Work Functions, and Why Eq. 3 Is Valid even in Generalized KS Theory

Adding an attractive vdW correction to a semilocal functional increases the surface energies and work functions of metals, as we have seen numerically. It can also change the bulk energy.

By the work–energy theorem, the surface energy is the external work per unit area needed to cleave a bulk crystal along a plane and carry the two macroscopic fragments to a separation much greater than the bulk Fermi wavelength or screening length. Since the vdW forces between these fragments are attractive, they necessitate a positive contribution to this work and thus to the surface energy. Note that the bulk energy does not change in the separation process.

This conclusion can also be reached by comparing the total energies of the bulk crystal before and after the separation. Before the separation, there are negative vdW interactions between the two fragments, which disappear when the fragments are fully separated. Thus, the energy stored in the surface is raised by the addition of an attractive vdW correction.

The work function of a metal surface is the least work needed to remove an electron from the metal to a distance that is large compared with the bulk Fermi wavelength and screening length, and thus the least total energy increase that occurs when the electron is so removed. The total energy theory of the work function (114) uses Janak’s theorem to equate this total energy change to the one-electron-like Eq. 3 within KS DFT. Our meta-GGA calculations (like most meta-GGA and hybrid functional calculations) are carried out in a generalized KS theory, in which the xc potential is not constrained to be a multiplication operator. (It becomes a differential operator for a meta-GGA, and an integral operator for a hybrid of GGA with exact exchange.) The generalized Janak theorem (115) shows that Eq. 3 still provides the needed total energy difference that defines the work function.

The neutral system will have a lower vdW total energy than the singly positive system, since it has one more electron but the same bulk density. Thus, the addition of an attractive vdW correction raises the work function.

Summary

We studied three important surface properties of metals (Al, Cu, Ru, Rh, Pd, Ag, Pt, and Au) using the LDA, two GGAs (PBE and PBEsol), and a recent meta-GGA (SCAN) with and without a long-range vdW correction. The surface energy, work function,

| Metal | Ref. 117 | This work |
|-------|----------|-----------|
| Cu    | 0.06     | 0.21      |
| Ru    | 0.29     | 0.20      |
| Ag    | 0.30     | 0.14      |
| Pt    | -0.03    | 0.25      |
| Au    | -0.04    | 0.29      |

Shown for this work is the difference between SCAN+rVV10 and PBE.
and interlayer relaxation were calculated and compared with the best available experimental values. The choice of xc functional has a noticeable effect on the surface properties of metals, especially on the surface energy (116). For surfaces, the performance of SCAN is comparable to that of PBEsol, but PBEsol is a special purpose functional for solids, while SCAN is a general purpose functional.

The vdW forces are present at metallic surfaces. They nonnegligibly increase the surface energies and work functions, as we have seen from numerical calculations and from qualitative arguments. Ferri et al. (117) found that vdW corrections to PBE can increase work functions significantly for some metals, while slightly reducing them for others, whereas we find consistent increases for all of the metals we have studied. Our results are compared with theirs in Table 4.

We have also justified the one-electron-like Eq. 3 for the work function, even when the vacuum potential and Fermi energy are calculated in a generalized KS scheme such as the one we used for SCAN and SCAN+rVV10.

All tested functionals predict comparable interlayer relaxations. Unlike the surface energies and work functions, these relaxations show no interesting trend as vdW attraction is added from PBE to SCAN to SCAN+rVV10.

LDA overestimates the intermediate-range vdW attraction but has no long-range component. These two errors of LDA may cancel almost perfectly for surface energies. PBE underestimates the intermediate-range vdW and has no long-range vdW, so it underestimates surface energies (by about 25%) and work functions (by about 5%). PBEsol and SCAN have realistic intermediate-range vdW and no long-range vdW, so they are more accurate than PBE but not as good as LDA for predicting surface energies. The asymptotic long-range vdW interactions missing in semilocal functionals can make up to a 10% difference in the surface energy or a 3% difference in the work function. SCAN+rVV10 stands out in this regard, as it is a balanced combination of the most advanced nonempirical semilocal functional to date and the flexible nonlocal vdW correction from rVV10. In addition to delivering superior performance for layered materials (35), SCAN delivers high-quality surface energies, work functions, and surface relaxations for metallic surfaces. SCAN+rVV10 includes realistic intermediate- and long-range vdW interactions, so it tends to yield more systematic and accurate results than LDA, PBEsol, or SCAN (however, all functionals other than RPA underestimate the surface energies of Pt and Au). More-accurate measurements for these properties are needed to validate the performance of new and existing density functionals. Overall, we find that SCAN is a systematic step up in accuracy from PBE, and that adding rVV10 to SCAN yields a highly accurate method for diversely bonded systems.

Computational Details. We performed first-principles DFT calculations using the Vienna Ab Initio Simulation Package (VASP) (118) in combination with projector augmented wave (PAW) method (119, 120). We used the PAW pseudopotentials recommended in the VASP 5.3.5 manual for LDA and PBE. For example, the electrons treated as valence are 5d10 6s1 for Au. Relativistic effects are included in the construction of the pseudopotential, but not otherwise. Because the PBE pseudopotential is transferable, we also used it for PBEsol and SCAN. For both bulk and surface computations, a maximum kinetic energy cutoff of 700 eV was used for the plane wave expansion. The Brillouin zone was sampled using Gamma-centered k-mesh grids of size 16 × 16 × 16 for the bulk and 16 × 16 × 1 for the surfaces. The top few layers (up to four) of the slab were translated without reconstruction until the total energy changes converged to less than 1.0 × 10−6 eV and the residual atomic forces converged to less than 0.01 eVÅ. Dipole corrections were used to cancel the errors of the electrostatic potential, atomic forces, and total energy, caused by periodic boundary condition.

For the slab geometry, 20 Å of vacuum was used to reduce the Coulombic interaction between the actual surface and its periodic image. These fcc surfaces are built using a cell containing one atom per layer. Theoretical lattice constants, obtained by fitting the Birch–Murnaghan equation of state for the bulk with each functional (see SI Appendix, Table S4), are used to build these cells. We used Pt (111) to test the convergence of the surface properties with respect to different computational variables such as k mesh, cutoff energy, layer, and vacuum thickness of the slab geometry. Four- to twelve-layer slabs were used in the linear fit for the surface energy, and eight-layer slabs were used for the work function. All of the computed surface properties presented in this work are well converged with respect to these computational variables.

The RPA calculations were made with the GPAW software. The PAWs included the scalar relativistic effect on the core, and the electrons treated as valence were 5d10 6s1 for Au. Because the RPA calculations are expensive, we have used only four-layer slabs. Our calculations with SCAN+rVV10 suggest that using only a four-layer slab overestimates the face-averaged surface energy by less than 0.05 J/m2, except in Pd, where the overestimation is by 0.1 J/m2.

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