Surface Energies of Simple Metals from Slabs: Comparison of Exchange-Correlation Density Functionals

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ABSTRACT: Surface energies of some simple metals (Be, Al, Mg, Li, and Na) were calculated within density functional theory. Various approximations for the exchange and correlation were tested: local density approximation (LDA), generalized gradient approximations (GGA), and meta–generalized gradient approximation (MGGA). We used the Crystal98 code to calculate slabs with one to 10 layers using both all-electron and pseudopotential approaches. The extraction of the surface energy from the series of slab energies was done by the linear-fitting method. Our LDA and GGA results agree reasonably well with those from other authors. The MGGA values are, in general, close to LDA and higher than GGA ones, a pattern also observed in the jellium model. They also agree reasonably well with the experimental data. © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 101: 645–650, 2005

Key words: density functional theory; Gaussian-type orbitals; meta generalized gradient approximation; simple metals; slabs; surface energies

Introduction

The importance of the surface energy is well known in surface science and technology. It plays an essential role in understanding physical processes such as adhesion and corrosion. It represents also the main contribution to the vacancy formation energy [1]. Surface energies are measured only indirectly. The difficulty in obtaining good experimental values reinforces the need for accurate calculations.

The extraction of the surface energy of a given material from a series of slabs with different thickness turns out to be easier than the calculation of the semi-infinite system. But then the extrapolation from thin slabs to the semi-infinite system is neces-

sary. The main drawback of thin-slab calculations is the occurrence of quantum-size effects, that is, energy fluctuations due to the finite size of the slab [2].

The energy of a slab with N layers may be written as the sum of a bulk term, which is proportional to the volume V, and a surface term, which is proportional to the area S:

$$E_{\mathrm{slab}} = \epsilon_{\mathrm{bulk}}V + 2\sigma S, \qquad (1.1)$$

where ϵ_{bulk} is the energy density of the bulk crystal and σ is the surface energy. From this equation, we may extract the surface energy

$$\sigma = \frac{1}{2S}(E_{\mathrm{slab}} - \epsilon_{\mathrm{bulk}}V). \qquad (1.2)$$

The surface energy is expected to be very sensitive to the two parcels from which it is calculated, because it is small compared with them.

Boettger [3] pointed out a technical problem associated with Eq. (1.2): its right side diverges linearly with the number of layers in the slab. Because of the separate calculation of ϵ_{bulk}, the bulk contribution to the slab energy is not canceled by the energy of a bulk piece with the same size. Various methods for evaluating the surface energy from slab energies that avoid an independent calculation of the bulk energy have been proposed [3–6].

Here we present one of these methods. Rearranging Eq. (1.2) we obtain

$$\frac{E_{\mathrm{slab}}(N)}{S} = dN\epsilon_{\mathrm{bulk}} + 2\sigma, \qquad (1.3)$$

where d is the slab thickness and N the number of layers. Using a series of slabs with different N, it is possible to fit the parameters ϵ_{bulk} and σ. This linear fitting method [4] is more reliable than the incremental method, which requires only two slabs with consecutive number of layers [7].

The slab energies E_{slab} may be obtained solving the Kohn–Sham equations of density functional theory [8]. The generalized gradient approximation (GGA), whose inputs are the density and its gradient, goes beyond the original local density approximation (LDA) for exchange and correlation. A widely used GGA is Perdew–Burke–Ernzerhof (PBE) [9]. Another GGA was proposed by Becke [10] for exchange, which, together with the Lee–Yang–Parr [11] correlation, results in a functional widely used by chemists, known as BLYP. The PBE is constructed in a nonempirical way, whereas BLYP is semiempirical, that is, it contains parameters adjusted to molecular data. A step beyond GGA in the hierarchy of functionals towards the "exact" one is the meta–generalized gradient approximation (meta-GGA, or MGGA), a scheme that includes the kinetic energy density in the exchange and correlation functional together with the density and its gradient. One of the most widely used MGGA functionals is PKZB [12], which was designed by Perdew and co-workers (Kurth, Zupan, and Blaha) to respect more exact constraints than PBE and which contains a single parameter adjusted to experimental data. An improvement of PKZB that is completely free from parameters adjusted to experimental data was proposed recently [13], but its results should not differ much from PKZB ones.

In this work we present surface energies of a set of simple metals based on different density functionals. For LDA we adopted the Perdew–Wang 92 [14] parametrization of the correlation energy, which is based on the release-node diffusion Monte Carlo calculation of Ceperley and Alder [15] for the uniform electron gas. Beyond LDA the energies were calculated with PBE densities. It has been shown [16–18] that the energy corrections due to full self-consistency are typically small.

All surface energies are extracted from slab energies with unrelaxed ionic planes (faces (111), (110), and (100) for fcc and bcc structures and (0001) face for hcp structures). The relaxation of the outermost layers is experimentally known and confirmed by ab initio calculations [19]. However, the influence of this effect on the surface energy is quite small [19–21] (typically 2–5%). We do not aim with this work to obtain optimal energies but to compare different exchange-correlation functionals. We believe that the differences between surface energies given by the various functionals will remain close to the values found here after structure optimization.

After describing the computational method in the second section, our results are shown and discussed in the third section. Short conclusions appear at the end.

Computational Method

All calculations presented in this work were performed with the Crystal98 program package [22].

They are either all-electron (full potential) or pseudopotential (effective core potential), always using Gaussian basis sets. Pseudopotentials offer the advantage of dealing with few electrons and having a much reduced energy scale. The chosen pseudopotential was the Durand–Barthelat [23], because it is implemented in the code.

The PBE and BLYP functionals for exchange and correlation are options in Crystal98. However, the PKZB functional is not part of the standard code and had to be inserted by us [17].

To obtain surface energies we performed a series of slab calculations, going from one to 10 atomic layers. In all-electron calculations, the exponents of the uncontracted Gaussians of the most outer shells belonging to the basis sets referred to in Ref. [17] were reoptimized for slabs with three layers. For sodium a d shell was added to the basis sets in order to improve the surface energy. The basis sets used in pseudopotential calculations are shown in Table I. The exponents were optimized as in the all-electron case.

The convergence of the energy with respect to the number of special **k** points within the Monkhorst–Pack [24] scheme was checked. A shrinking factor of 16 in the Monkhorst–Pack net was found to be adequate for all our slabs. A temperature smearing of 0.001 hartree in the Fermi surface was also used, to improve the iteration procedure.

To extract the surface energy we have adopted the fitting procedure expressed by Eq. (1.3) and explained by Fiorentini and Methfessel [4]. The quantum-size effects exhibited by ultrathin slabs is the most severe problem in extracting the surface energy. The confirmed expectation is that they become smaller for larger N [7]. Figure 1 illustrates the influence of the number of slabs taken in the fit. Our final results, shown in the third section, were obtained, considering always the whole set of 10 slabs.

Results

Table II shows the surface energies we have found for the various density functionals. The LDA
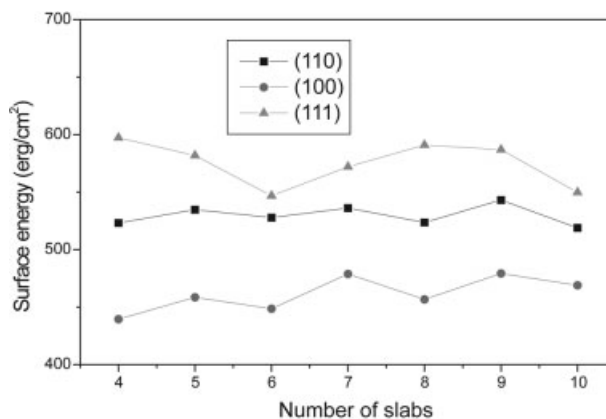

FIGURE 1. Dependence of the PBE surface energy of lithium on the number of fitted slabs (all-electron results). The slabs used in the fitting are always the thickest ones up to 10 layers.

and PBE values resulted from fully self-consistent calculations, whereas PKZB and BLYP used the PBE density. The lattice constants were chosen to take the PBE values used by Vitos et al. [25], who applied the full-charge density method, derived from the linear muffin-tin orbital method, for the semi-infinite system. Given the uncertainty associated with the fitting method, our all-electron PBE results are in good agreement with those of Vitos et al. [25].

Our pseudopotential values are, in general, close to all-electron ones. The current LDA pseudopotential calculations agree in general with reported ones [21, 28, 32–34]. We note that our LDA values are all higher than PBE ones, in agreement with the jellium model prediction [30] and with real metals results [25]. The fact that LDA values reported by various authors (see Table II) are lower than the PBE values of Ref. [25] is due to the use of different methods and approximations in those calculations.

For both all-electron and pseudopotentials, PKZB surface energies lie between the LDA and PBE ones, with the exception of aluminum.

Regarding the face anisotropy, we obtain for PBE the same trend as in Ref. [25], with the exception of aluminum. Using LDA and pseudopotentials the agreement with the anisotropy found by other authors is complete.

Our results agree with experimental data. However, the comparison between calculated and experimental surface energies has to be done with care. Experimental values, which are obtained for an undifferentiated face, are not very reliable. They are

TABLE I _____

Basis sets used for the Durand–Barthelat pseudopotential calculations.

Metal	Be	Al	Mg	Li	Na
Basis set	111G	11(d1)G	11(d1)G	11(d1)G	111(d1)G

TABLE II _____

Surface energies of simple metals obtained from fitting the Crystal98 energies of a series of slabs with 1 to 10 layers.[a]

Metal	Structure and lattice constant	Surface	Current work				Other works		
			LDA	PBE	PKZB	BLYP	LDA	PBE[b]	Experiment
Be	hcp	(0001)	2273	1677	1766	1110		1834	1628,[c] 2700[d]
	2.236		2180	1865	2082	1273	1924,[e] 2100[f]		
Al	fcc	(111)	1272	1103	1280	636		1199	1143,[b] 1160[c]
			1196	1002	1097	570	1016,[g] 939[h]		
	4.049	(100)	1499	1326	1527	820		1347	
			1411	1220	1309	772	1081[i]		
		(110)	1543	1358	1551	829		1271	
			1436	1229	1312	758	1090[j]		
Mg	hcp	(0001)	777	682	745	427		792	785,[c] 760[d]
	3.196		677	584	624	335	641[k]		
Li	bcc	(110)	608	519	553	367		556	522,[c] 525[d]
			569	516	543	362	545[l]		
	3.431	(100)	565	469	489	338		522	
			511	468	488	332	506[l]		
		(111)	634	550	564	431		590	
			618	578	592	453	623[l]		
Na	bcc	(110)	297	229	260	127		253	261,[c] 260[d]
			250	223	228	126			
	4.197	(100)	323	242	267	144		264	
			254	235	240	147			
		(111)	359	294	329	187		287	
			304	279	278	189			

[a] The first row for each face shows all-electron results, whereas the second row shows pseudopotential results. Lattice constants are in Å. The ideal ratio $c/a = 2/3\sqrt{6}$ was adopted for hcp structures. All energies are in erg/cm^2.
[b] Ref. [25].
[c] Ref. [26].
[d] Ref. [31].
[e] Ref. [21].
[f] Ref. [32].
[g] Ref. [2].
[h] Ref. [28].
[i] Ref. [29].
[j] Ref. [20].
[k] Ref. [33].
[l] Ref. [34].

obtained from measurements of the gas–solid surface tension, which has to be extrapolated to zero temperature [26]. Another way to obtain surface energies uses elastic constants and bulk modulus measurements [27]. Thus, we give more importance to the comparison of our values with good ab initio results than to comparison with experimental data.

The BLYP surface energies are always too low compared with those of the other functionals and with experimental data so that this functional does not seem to be adequate for metal surfaces.

In Table III we present pseudopotential exchange-correlation surface energies. A straightforward comparison can now be made with the jellium model and, to facilitate that comparison, all surface energies are now based on LDA densities. In the jellium model, which has proved very useful to describe some properties of simple metals, the ionic structure of solids is replaced by a uniform positive-charge density. For each metal, jellium values are indicated in Table III. We see that PKZB values are close but above LDA ones. On the other hand, for real metals, PKZB results are also close to LDA, although not necessarily above them. This result is a bit surprising. A formula that reproduces the jellium exchange-correlation surface energy as a

function of the valence-electron density parameter r_s can be found in Ref. [18]. Figure 2 compares the LDA exchange-correlation surface energies of the jellium model given by that formula with real-metal results. The conclusion is that the trend given by jellium model is indeed followed by real systems. The same holds for the other functionals.

We note that, in the jellium model, PBE underestimates what is known to be the most accurate exchange-correlation surface energy for that model [30], whereas LDA and PKZB are close to that "exact" value. It is astonishing that LDA works so well in such a strongly inhomogeneous situation, but this is certainly due to a cancellation of exchange and correlation errors.

Conclusions

We used Crystal98 to calculate slabs of simple metals with up to 10 layers to extract surface energies. The results found for Be, Al, Mg, Li, and Na agree well with the results of other authors and with experimental data, so that the use of localized Gaussian functions as basis sets seems appropriate even for that class of metals, in which the valence

FIGURE 2. Comparison of realistic LDA exchange-correlation surface energies with the prediction of the jellium model. The squares represent the exchange-correlation surface energies of real metals (different points for the same density refer to different exposed faces), whereas the solid line represents the same component of the surface energy using Eq. (15) of Ref. [18].

electrons are nearly free. Our LDA surface energies of real metals are higher than PBE ones, as in the jellium model. The PKZB surface energies are between the LDA and PBE energies, except for some aluminum cases. The available experimental data cannot decide which one of the three functionals is best for metal surfaces but can exclude BLYP, which is popular for molecules.

TABLE III

Exchange-correlation surface energies of simple metals in the jellium model and with pseudopotentials.[a]

	r_s (bohr)	Surface	LDA	PBE	PKZB	BLYP
Be	1.85	jellium	4448	4334	4511	3730
		(0001)	3622	3467	3681	2879
Al	2.07	jellium	2961	2880	3003	2424
		(111)	2558	2467	2560	2039
		(100)	2884	2795	2883	2353
		(110)	2973	2875	2958	2410
Mg	2.65	jellium	1204	1167	1221	916
		(0001)	976	930	970	681
Li	3.19	jellium	609	589	618	427
		(110)	521	495	522	340
		(100)	629	607	628	471
		(111)	643	623	638	498
Na	3.91	jellium	280	270	284	171
		(110)	239	226	232	129
		(100)	315	305	310	217
		(111)	307	295	294	205

[a] The LDA densities are used overall. The second column shows the bulk valence-electron densities for which the jellium values were calculated. Energies are in erg/cm^2.
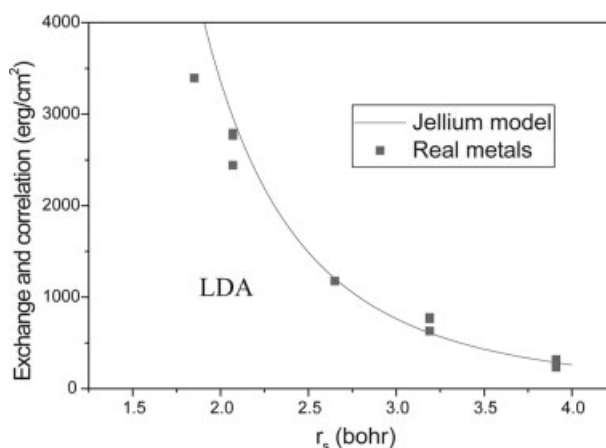
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