Extracting convergent surface energies from slab calculations

Vincenzo Fiorentini and M. Methfessel

(1) Istituto Nazionale di Fisica della Materia and Dipartimento di Scienze Fisiche, Università di Cagliari, via Ospedale 72, I-09124 Cagliari, Italy
(2) Institut für Halbleiterphysik, P.O. Box 409, D-15204 Frankfurt(Oder), Germany
(8 March 1996)

The formation energy of a solid surface can be extracted from slab calculations if the bulk energy per atom is known. It has been pointed out previously that the resulting surface energy will diverge with slab thickness if the bulk energy is in error, in the context of calculations which used different methods to study the bulk and slab systems. We show here that this result is equally relevant for state-of-the-art computational methods which carefully treat bulk and slab systems in the same way. Here we compare different approaches, and present a solution to the problem that eliminates the divergence and leads to rapidly convergent and accurate surface energies.

PACS numbers: 68.35.-p, 68.35.Md

I. INTRODUCTION

The knowledge of the formation energy of solid surfaces is of obvious importance for surface physics and technology. Given the difficulties of a direct measurement of the surface energy, accurate calculations of this quantity play a relevant role in surface science.

The standard method for calculating the surface energy \( \sigma \) is to evaluate the total energy of a slab of the material of interest (generally with a thickness between 5 to 15 layers) and to subtract from that the bulk energy obtained from a separate calculation. This procedure singles out the total energy contribution due to the presence of the surface. It is based on the general and intuitively appealing expression

\[
\sigma = \lim_{N \to \infty} \frac{1}{2} (E_{\text{slab}}^N - N E_{\text{bulk}})
\]

with \( E_{\text{slab}}^N \) the total energy of a \( N \)-layer slab and \( E_{\text{bulk}} \) the bulk total energy; the limit is approximated in practice by the \( N \)th term. The factor of 1/2 accounts for the two surfaces of the slab.

A central but often underestimated problem with this approach is what value should be chosen for the bulk energy. While at first sight this point might be dismissed as irrelevant, in a recent paper Boettger pointed out that any difference between \( E_{\text{bulk}} \) and the change in \( E_{\text{slab}} \) with slab thickness will cause the calculated surface energy to diverge linearly with \( N \). Thus, increasing the slab thickness must sooner or later lead to unacceptable results, because the bulk energy from a separate calculation will never exactly equal the slope of the slab energy vs \( N \).

In Ref. Boettger, severe errors incurred by this standard approach were reported. Their unusual magnitude was presumably due to a technical matter, namely the use of two completely different methods for calculating the bulk and surface properties. Thus, the practical importance of the divergent behavior of the surface energy remains unassessed for state-of-the-art methods, which carefully treat bulk and slab systems in the same way. The aim of this paper is to supply such an assessment.

In particular, the natural objection to Boettger’s argument would be that, when using the same computational method in a technically consistent way to obtain both bulk and slab quantities, this problem would simply not show up. We show in this paper that this is not the case: the proper choice of the bulk energy according to Boettger’s principle is an important issue in surface energy calculations even when the bulk and slab systems are handled consistently within accurate methods such as FP-LMTO, pseudopotentials-plane waves, or such. Further, we compare different approaches to remedy the problem, presenting what seems to be the best solution. As modern calculations advance to study more subtle surface effects and employ thicker slabs, these results will become increasingly relevant.

II. RELEVANCE OF THE SURFACE ENERGY DIVERGENCE PROBLEM TO STATE-OF-THE-ART CALCULATIONS

In this section we present \textit{ab initio} surface calculations demonstrating that the surface energy is not only formally, but also practically divergent for accurate calculations. To this end, we compare results obtained by the standard approach with those calculated using an alternative procedure suggested by Boettger and with a modified approach to be described below. It will become clear that the latter method is the most reliable by a wide margin and should be preferred for high-accuracy applications.
A. Different ways to evaluate the surface energy

For the standard methods, we first of all use Eq. (1) whereby the bulk energy was obtained from a well-converted bulk calculation (see below). We also considered the slightly modified version

\[ \sigma = \lim_{N \to \infty} \frac{1}{2} (E_{\text{slab}}^N - N \Delta E_N), \]

where \( E_{\text{slab}}^N \) is the total energy of a given atom is determined to a large extent by its nearest-neighbor environment. The most straightforward way to extract the quantity \( E_{\text{slab}}^N \) is to fit a straight line to all the slab total-energy data vs. \( N \), except for the thinnest slabs, and to take its slope. This value is then used in Eq. (3). This procedure uses the same data needed in Boettger’s suggested approach. It is free of the divergence problem because no separately-calculated bulk energy enters. The only uncertainty in the procedure is the assumed onset of the straight-line behaviour; indeed, apart from the very thinnest slabs, the error bar in \( E_{\text{bulk}} \) when starting the fit at different \( N \)’s in the range from 3 to 13 is \( \pm 0.01 \) mRy (see also Table I below).

As a test case, we report results for the surface energy of Pt (001), evaluated by the four schemes just described. Total energies were calculated within the local density approximation to density functional theory, using the all-electron full-potential LMTO method. Slab thicknesses of up to 15 layers, and a vacuum spacing equivalent to seven bulk layers were used. The slabs were left unrelaxed in the ideal fcc geometry. The technical ingredients (basis set, k-point summation, etc.) are given in Ref. [1].

B. Results and discussion

Figure 1 shows the calculated surface energies as function of slab thickness when the four described methods are used. The two approaches using a separately-calculated bulk energy [Eqs. (1) and (3)] are shown by open circles and triangles, respectively. Both evidently suffer from the divergence problem, shown by the linear decrease as the slabs are made thicker. Boettger’s approach (taking the bulk energy as differential increase of the slab energy, filled diamonds) does indeed give a surface energy which does not have this systematic linear behaviour. Unfortunately, it shows large oscillations which decrease only very slowly as the slab is made thicker. If only these three techniques were available, the best legitimate conclusion would be that the surface energy lies somewhere between 1.21 and 1.26 eV/atom. This is an uncertainty of 5% even though slabs as thick as 15 layers were considered.

The fourth technique (fitting a straight line to the \( E_{\text{slab}}^N \) data to obtain \( E_{\text{bulk}} \)) is shown by filled squares. In comparison to the other approaches, very fast convergence to a stable value is achieved. We can now accurately determine the calculated surface energy to be 1.246 eV, a value which is numerically stable to within 0.5 meV. This reduces the uncertainty to below 0.1%. In order to suppress the weak residual oscillation, we averaged over the last three points in the curve: however, the deviations from the average are below 0.5 meV. (For completeness, in Table I we list the raw data for the slab total energies, where a constant offset of \(-36800\) Ry/atom was subtracted for convenience, and the bulk energies obtained by linear fittings to \( E_{\text{slab}}^N \) vs. \( N \) starting at different values of the slab thickness \( N \).

Our main point here is that one should be wary of the standard technique (which uses a separately calculated bulk energy) even for calculations of high accuracy. We can compare the bulk energy as deduced from the slope of the \( E_{\text{slab}}^N \) with that from the well-converged bulk crystal calculation \((\approx 36806.84240\) Ry) with an uncertainty of only 0.6 mRy \( \approx 0.01 \) eV. Despite this very small discrepancy, the desired linear behaviour in the calculated surface energy is already prominent for thicknesses of eight or more layers. The accumulated bulk error for the (typi-
cally used) slab thickness of around seven is already uncomfortably large, namely 4.2 mRy \( \simeq 0.06 \) eV. Optimistically going to thicker slabs would soon lead to unacceptable values of the surface energy. Although previously calculated surface energies using the standard technique with slab thicknesses of below ten layers can be considered reasonably reliable, it is clearly important to keep the problem addressed here in mind when doing surface calculations.

To some extent, the severity of the problem will depend on the calculational method used. In terms of k-points and selfconsistency iterations, our bulk crystal energy was converged to within 0.01 mRy. Thus, the discrepancy in \( E_{\text{bulk}} \) presumably comes from the k-point mesh for the slab, which consisted of 15 irreducible special points in the \( xy \) plane. It is highly desirable to be able to use a mesh of this typical size, independent of the exact \textit{ab-initio} scheme used. In this context, our conclusions apply in exactly the same way to other methods.

Although our suggested scheme at first sight looks like a mere numerical procedure, there is a clear theoretical background to it. The squares in Fig. 1 show small but definite oscillations of the surface energy as function of the slab thickness with a period of about six to eight layers. These quantum size effects are due to the finite thickness of the slab. The problem of Boettger’s scheme is that it artificially magnifies these oscillations by a large factor because the bulk energy is calculated from two slabs of similar thickness. A technique which exploits the overall linear behaviour of the \( E_{\text{slab}}^N \) data, such as ours, eliminates this problem.

Finally, we point out that our tests up to now, while informative, used all the \( E_{\text{slab}}^N \) data up to \( N=15 \) to obtain the converged surface energy. In practice, the aim is to use the data from slabs up to a thickness of typically 7 to 9 layers. Using the same procedure as before, this gives surface energies of 1.2456 and 1.2457 eV/atom, respectively. These values are much closer to the converged value than those of the three competing approaches. For completeness, we mention that analogous results have been obtained for Al (001) \( ^{[8]} \), and Rh and Ir low-index faces \( ^{[8]} \), as will be presented elsewhere.

### III. SUMMARY

In summary, it has been previously pointed out \( ^{[8]} \) that the calculated surface energy will diverge with slab thickness if a bulk energy is used which is not exactly equal to the slope of the slab energy vs. slab thickness. Here, we have investigated this phenomenon in the context of accurate state-of-the-art computational methods which are careful to treat bulk and slab systems in the same way. The results show that the effect must be taken seriously for this type of calculation also. The problem can be easily solved by obtaining the bulk crystal energy directly as the slope of the \( E_{\text{slab}}^N \) data, but care should be taken to eliminate quantum size effects. This can be done by making an overall linear fit to the slab total energy as function of the thickness.

---

**FIG. 1.** Calculated surface energy for Pt (001) as a function of slab thickness (see text for symbol explanation).

| \( N \) | \( E_{\text{slab}}^N \) | \( E_{\text{bulk}}^N \) |
|---|---|---|
| 1 | -6.65451 | -6.8426 |
| 3 | -20.34388 | -6.8424 |
| 5 | -34.02959 | -6.8424 |
| 7 | -47.71315 | -6.8425 |
| 9 | -61.39835 | -6.8424 |
| 11 | -75.08339 | -6.8424 |
| 13 | -88.76793 | -6.8425 |
| 15 | -102.45292 | -6.8418 |

**TABLE I.** In columns from left to right: total energies per atom in Pt (100) slabs of thickness \( N \) after subtraction of \( N \times 36800 \) Ry (center); bulk energy as the slope extracted from linear fitting of slab total energies vs. \( N \), starting the fit at different values of \( N \).
Fiorentini-Methfessel -- "Extracting convergent surface energies..." -- Fig. 1

Number of layers

Surface energy (eV/atom)

- Eq.1, crystal bulk energy
- Eq.4, linear fit to slab energies
- Eq.3, Boettger relation
- Eq.2, filled-slab bulk energy