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Extracting convergent surface energies from slab calculations

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Abstract. 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.

1. 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 [1] of this quantity play a relevant role in surface science.

The standard method for calculating the surface energy σ 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

$$\sigma = \lim_{N \rightarrow \infty} \frac{1}{2} (E_{\text{slab}}^N - N E_{\text{bulk}}) \quad (1)$$

with E_{slab}^N the total energy of an N -layer slab and E_{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 that of what value should be chosen for the bulk energy. While at first sight this point might be dismissed as irrelevant, in a recent paper [2] Boettger pointed out that any difference between E_{bulk} and the change in E_{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 versus N .

In [2], 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 behaviour 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 calculational 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 the FP-LMTO and pseudopotentials-plane-waves methods. Further, we compare different approaches for remedying 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.

2. The relevance of the surface energy divergence problem to state-of-the art calculations

In this section we present *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 [2] 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.

2.1. Different ways to evaluate the surface energy

For the standard methods, we first of all use equation (1) whereby the bulk energy was obtained from a well-converged bulk calculation (see below). We also considered the slightly modified version [3]

$$\sigma = \lim_{N \rightarrow \infty} \frac{1}{2} \left(E_{\text{slab}}^N - \frac{N}{N_B} E_{\text{full}}^{N_B} \right) \quad (2)$$

whereby the total energies needed are that of a slab containing N layers (E_{slab}^N) and that of an N_B -atom supercell consisting of the slab plus the vacuum space between the slabs filled with atoms ($E_{\text{full}}^{N_B}$). In other words, the weighted energy of the filled slab is taken as the bulk energy. Using equation (2), many sources of difference between the slab and bulk energies can be eliminated since the same supercell is used for the bulk and slab systems, albeit at the cost of an increase in computational effort. For this approach, we used $N_B = N + 7$ with N up to 11.

Boettger [2] suggested the following method for avoiding the divergence problem. For each slab thickness N , pick as the bulk energy E_{bulk} the differential increase in the slab total energy upon addition of one layer of material:

$$\sigma = \lim_{N \rightarrow \infty} \frac{1}{2} (E_{\text{slab}}^N - N \Delta E_N) \quad (3)$$

where $\Delta E_N = E_{\text{slab}}^N - E_{\text{slab}}^{N-1}$. This formula has the obvious merit of using only slab-related quantities, making no reference to separately calculated bulk energies. Consequently, the calculated surface energy should not suffer from the divergence problem of equation (1). The

price to pay is that of repeatedly calculating total energies for slabs of increasing thickness. At slight variance with [2], we use $\Delta E_N = (E_{\text{slab}}^N - E_{\text{slab}}^{N-2})/2$ in order to maintain inversion symmetry in our slabs.

As a fourth alternative, we note that as N becomes large and convergence is approached, the definition of the surface energy in equation (1) implies that

$$E_{\text{slab}}^N \approx 2\sigma + NE_{\text{bulk}}. \quad (4)$$

This linear-in- N behaviour is already dominant for very thin slabs. This can be understood on the basis that the energy of a given atom is determined to a large extent by its nearest-neighbour environment [4]. The most straightforward way to extract the quantity E_{bulk} is to fit a straight line to all of the slab total-energy data versus N (except for in the case of the thinnest slabs) and to take its slope. This value is then used in equation (1). This procedure uses the same data as are 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 linear behaviour; indeed, apart from for the very thinnest slabs, the error bar in E_{bulk} when starting the fit at different N s in the range from 3 to 13 is ± 0.01 mRyd (see also table 1 below).

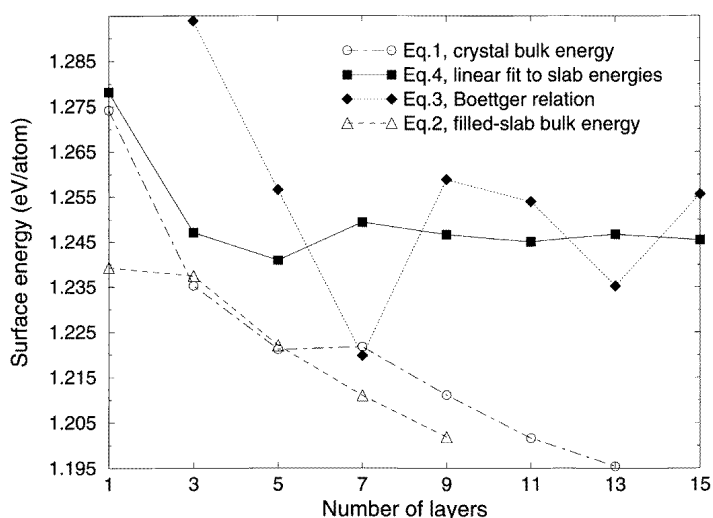


Figure 1. Calculated surface energies for Pt(001) as functions of the slab thickness (see the text for an explanation of the symbols).

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 the density functional theory [5], using the all-electron full-potential LMTO method [6]. 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 [1].

2.2. Results and discussion

Figure 1 shows the calculated surface energies as functions of slab thickness when the four above-described methods are used. The two approaches using a separately calculated bulk

energy (equations (1) and (2)) 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 the 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_{slab}^N -data to obtain E_{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 1 we list the raw data for the slab total energies, where a constant offset of $-36\,800$ Ryd/atom was subtracted for convenience, and the bulk energies obtained by linear fittings to E_{slab}^N versus N starting at different values of the slab thickness N .)

Table 1. In columns from left to right: total energies (Ryd) per atom in Pt(100) slabs of thickness N after subtraction of $N \times 368\,00$ Ryd (centre); bulk energies as the slopes extracted from linear fitting of slab total energies versus N , starting the fit at different values of N .

N	E_{slab}^N	E_{bulk}^N
1	-6.654 51	-6.8426
3	-20.343 88	-6.8424
5	-34.029 59	-6.8424
7	-47.713 15	-6.8425
9	-61.398 35	-6.8424
11	-75.083 39	-6.8424
13	-88.767 93	-6.8425
15	-102.452 92	—
Bulk	—	-6.8418

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_{slab}^N -data ($-368\,06.842\,40$ Ryd) with that from the well-converged bulk crystal calculation ($-368\,06.841\,82$ Ryd), finding a difference of only 0.6 mRyd $\simeq 0.01$ eV. Despite this very small discrepancy, the undesirable linear behaviour in the calculated surface energy is already prominent for thicknesses of eight or more layers. The accumulated bulk error for the (typically used) slab thickness of around seven layers is already uncomfortably large, namely 4.2 mRyd $\simeq 0.06$ eV. Optimistically going to thicker slabs would soon lead to unacceptable values of the surface energy. Although surface energies calculated previously 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 mRyd. Thus, the discrepancy in E_{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, independently of the exact *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 figure 1 show small but definite oscillations of the surface energy as a 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_{slab}^N -data, such as ours, eliminates this problem.

Finally, we point out that our tests up to now, while informative, used all of the E_{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) [7], and Rh and Ir low-index faces [8].

3. Summary

In summary, it has been previously pointed out [2] 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 versus 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_{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 a function of the thickness.

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