

Convergence of surface energy calculations for various methods: (001), (012), (100) hematite and the applicability of the standard approach

Thomas Stirner^{1,3} , David Scholz¹ and Jizhong Sun²

¹ Department of Applied Natural Sciences, University of Applied Sciences Deggendorf, Dieter-Görlitz-Platz-1, D-94469 Deggendorf, Germany

² Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Ministry of Education), School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, People's Republic of China

E-mail: thomas.stirner@th-deg.de

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Abstract

Three different methods for the calculation of the surface energy, namely the standard approach, the Boettger relation and the linear-fit method, are applied to the (001), (012) and (100) hematite surfaces. The standard approach was previously shown to suffer from a divergence problem, and the Boettger relation was shown to exhibit quantum size effects. While the linear-fit method, in general, leads to a good convergence behavior of the surface energy, the questions arise whether the relative order of the calculated surface energies depends on the chosen calculation method, and whether there is any merit at all in employing the standard approach. The present work investigates these questions with hematite as a benchmark material system. The simulations show that, for the surface facets and slab thicknesses studied here, the relative order of the surface energies is unaffected by the chosen calculation method. A regime is found where the three methods are in reasonably good agreement with respect to the obtained surface energies. Finally, a procedure is put forward to extract meaningful surface energy values from the standard approach.

Keywords: Hartree–Fock simulation, surface energy, convergence, hematite

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

The surface free energy (energy per unit surface area) or surface energy represents the energy required for the formation of a new surface, e.g. in the process of breaking chemical bonds, and is thus of fundamental importance in crystal growth. The surface energy of crystalline solids depends on the orientation of the crystal facets at the surface. Indirect

measurements of the surface energy exist using surface wettability and the Young equation [1]. The relative surface energies of different crystal facets can also be obtained from a Wulff construction [2–5]. However, direct measurements of the surface energy of crystals [6] are fraught with problems and are usually obtained from quantum-mechanical simulations [7–19]. The standard approach is to simulate a slab of the material of interest with corresponding orientation and to evaluate the surface energy from the expression $E_S = (E_{\text{slab}}(n) - n \cdot E_{\text{bulk}})/(2A)$, where A is the area of the primitive

³ Author to whom any correspondence should be addressed.

surface unit cell, $E_{\text{slab}}(n)$ is the energy of a n -unit layer slab, and E_{bulk} is the energy of a unit layer of the bulk. Since this approach was shown [20, 21] to have divergence problems arising from small discrepancies in the numerical conditions for the bulk and slab simulations, other methods were put forward that avoid the use of bulk simulation results. One of these methods, described by Boettger [20], approximates the bulk energy by the energy difference between two consecutive slab simulations, i.e. $E_{\text{bulk}} \approx E_{\text{slab}}(n) - E_{\text{slab}}(n-1)$. However, this method was shown to exhibit quantum size effects [22, 23], i.e. an oscillating behavior in the surface energy values with increasing n due to fluctuations in the numerical derivative. Another method, described by Gay *et al* [24], uses a linear fit of the E_{slab} versus n data set to obtain the bulk energy from the gradient of the straight-line fit via the expression $E_{\text{slab}}(n) \approx 2A \cdot E_{\text{S}} + n \cdot E_{\text{bulk}}$. This method was shown to give rise to a good convergence behavior of the surface energy for metal surfaces [21]. However, with regard to the computational cost, the linear-fit method is the least efficient of the three methods described due to the large number of data points required for the straight-line fit, while the standard method is the most efficient due to the few data points required.

Very recently [25] we investigated these three methods also for the convergence behavior of the surface energy in the metal oxide hematite ($\alpha\text{-Fe}_2\text{O}_3$) with an Fe-terminated (001) surface. Previous findings for metal surfaces were corroborated for the metal oxide (001) hematite surface, namely a divergence of the standard approach and the occurrence of quantum size effects in the Boettger relation. It was also found that under certain circumstances the Boettger relation leads to a good convergence of the surface energy. The linear-fit method, however, is ultimately the most accurate and reliable method to extract convergent surface energy values from slab simulations [21, 25].

In the absence of experimental data it is usually the relative magnitude of the surface energies, and hence the order of the different facets in terms of increasing surface energy, that is of interest in the simulations. The question that now arises is whether this order is affected by the employed method to determine the surface energy, e.g. standard approach, Boettger relation or linear-fit method. A further question is whether there is any merit at all in using the standard approach, considering its divergence problems. We will address these questions in the present work. For this purpose we will compare the various surface energy calculations for the scientifically and technologically important (001), (012) and (100) surfaces of hematite.

2. Computational details

All of the present calculations are performed with the computer code CRYSTAL14 [26, 27], which is an *ab initio* LCAO (linear combination of atomic orbitals) Hartree–Fock program for the treatment of periodic systems. The surfaces are described by a slab model with 2D periodicity and the unrestricted open-shell Hamiltonian is used for Fe_2O_3 [28, 29]. Since there are unpaired 3d electrons in isolated Fe^{3+} ions, the use of

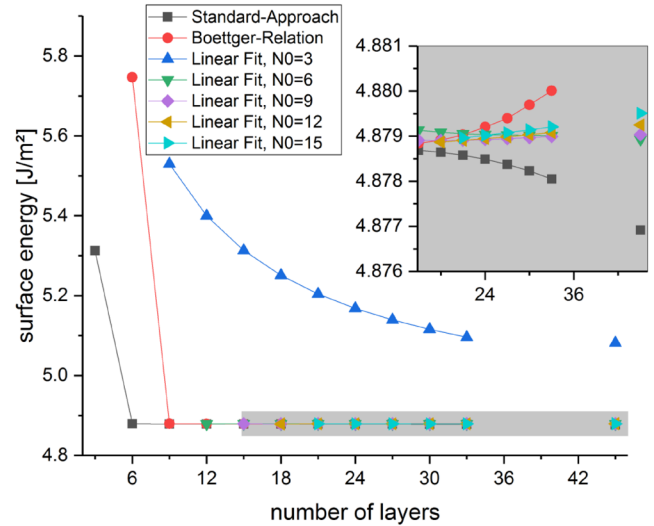


Figure 1. Calculated surface energies for the (001) hematite surface using the standard approach, the Boettger relation and the linear-fit method (for different values of the starting point n_0). The shaded area is shown magnified in the inset.

the unrestricted treatment of the spin-dependent part of the wavefunction in the open-shell systems is necessary to obtain spin-polarized eigenfunctions of the Fock Hamiltonian [30]. $\alpha\text{-Fe}_2\text{O}_3$ (hematite) has the corundum-type structure (space group $R\bar{3}c$). We study here the (001), (012) and (100) surfaces. The repeat units are selected as $\text{Fe}-3\text{O}-\text{Fe}\dots$ for (001), $2\text{O}-2\text{Fe}-2\text{O}-2\text{Fe}-2\text{O}\dots$ for (012) and $2\text{O}-4\text{Fe}2\text{O}-2\text{O}\dots$ for (100), with surface terminations giving rise to a minimal dipole moment [31] (see e.g. figure 1 of [3, 25] for a schematic illustration of the stoichiometric hematite surfaces). We found that the magnetic phase has no significant influence on the surface energy and its convergence behavior (we estimate its influence to be less than 0.2% for all cases). Consequently, we consider here the computationally less demanding ferromagnetic structure of hematite. We also found previously [15] that the order of the surface energies for the three surfaces (001), (012) and (100) is unaffected both by the relaxation of the slabs and *a posteriori* corrections of the exchange and correlation energy. Therefore, we consider here the unrelaxed slabs under the pure Hartree–Fock approach. The all-electron level basis sets, structural parameters, the tolerances for the level of numerical approximation and shrinking factors are the same as in our earlier investigations [15, 32].

3. Results and discussion

Figure 1 shows the convergence behavior of the surface energy calculated for the (001) hematite surface. At first sight, the standard approach and the Boettger relation seem to converge well overall. However, the inset shows a different picture. Here it can be seen that the standard approach diverges for an increasing number of layers n . The latter is due to the fact that the small numerical discrepancies between the bulk and the slab simulations are multiplied by n . Also the Boettger relation does not converge very well for this surface, because the bulk energy is calculated from two slabs of similar thickness

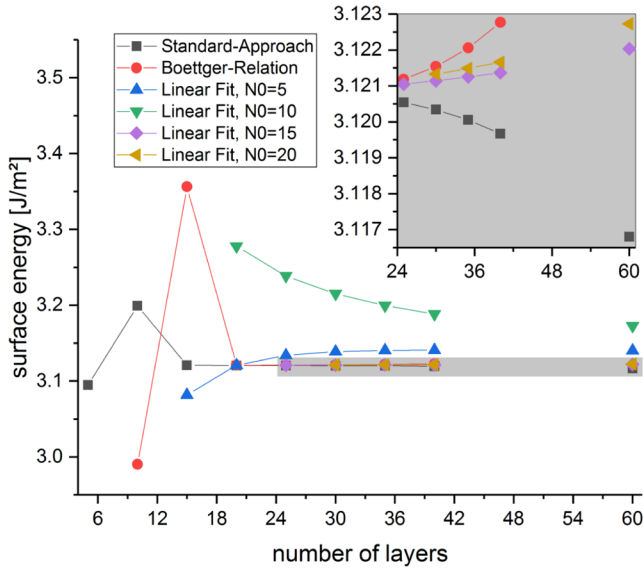


Figure 2. Calculated surface energies for the (012) hematite surface using the standard approach, the Boettger relation and the linear-fit method (for different values of the starting point n_o). The shaded area is shown magnified in the inset.

[21]. The linear-fit method is shown for different values of the starting point n_o , i.e. the straight-line fit is carried out for all data points between n_o and the maximum number of layers $n_{\max} = n$. Clearly, a starting point of $n_o = 3$ is too small for a good convergence of the linear-fit method since the influence of the inaccurate 3-layer-slab data point on the least-squares fit is too large. However, the linear-fit method converges reasonably well as long as the chosen starting point n_o is not too small. Interestingly, intermediate starting points (e.g. $n_o = 6$) lead to a slightly better convergence than large starting points (e.g. $n_o = 15$), since more data points overall give rise to an improved averaging out of numerical fluctuations. A striking feature of the inset to this graph is the fact that for intermediate values of n (i.e. approximately in the range 12–21) all three methods give rise to very similar results, i.e. a surface energy of $4.8789 \text{ J m}^{-2} \pm 0.0004 \text{ J m}^{-2}$, which also corresponds to the converged value of the linear-fit method of 4.879 J m^{-2} .

The convergence behavior of the surface energy for the (012) hematite surface is shown in figure 2. Again, the linear-fit method displays the best overall convergence behavior as long as the starting point n_o is not too small, i.e. $n_o > 10$ seems to give the best results. However, it has to be noted that here even for $n_o = 15$ and $n_o = 20$ the linear-fit method exhibits a small divergence, probably due to the small number of total data points. The standard approach is once more divergent for large n , while the Boettger relation exhibits a quantum size effect for small n and a divergent behavior for large n . Also, as before, for intermediate values of n (i.e. approximately in the range 25–35) all three methods lead to a surface energy of $3.1210 \text{ J m}^{-2} \pm 0.0011 \text{ J m}^{-2}$.

Figure 3 finally shows the convergence behavior of the surface energy calculated for the (100) hematite surface. Here, the Boettger relation displays a pronounced quantum size effect for small n and a reasonably good convergence for large

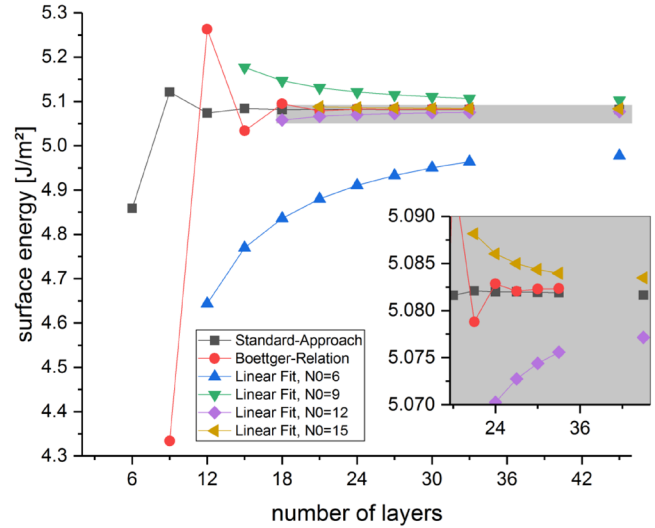


Figure 3. Calculated surface energies for the (100) hematite surface using the standard approach, the Boettger relation and the linear-fit method (for different values of the starting point n_o). The shaded area is shown magnified in the inset.

n , while the standard approach shows virtually no divergence. The linear-fit method converges again very well for $n_o > 12$, albeit relatively slowly. For this surface, for a large range of values of n (i.e. from about 30 to 45) all three methods lead to a surface energy of $5.0827 \text{ J m}^{-2} \pm 0.0016 \text{ J m}^{-2}$. The converged surface energy obtained from the linear-fit method ($n_o = 15$) is 5.083 J m^{-2} . From the inset to this figure it can also be seen how quickly the standard approach converges for this surface compared to the other two methods.

The obtained order of the surface energies for the three investigated surfaces is $(012) < (001) < (100)$. The corresponding surface energy values are 3.12 J m^{-2} for (012), 4.88 J m^{-2} for (001) and 5.08 J m^{-2} for (100). The present simulation results show that, in the range of n -values investigated here, this order is unaffected by the method of calculation, i.e. standard approach, Boettger relation or linear-fit method, as long as the initial fluctuations have subsided. Details of this behavior are provided as supplementary material (stacks.iop.org/JPhysCM/32/185002/mmedia). In fact, for these three surfaces this order is also retained after a full relaxation of the slabs [15]. In addition, for these three surfaces there is a range of values of n for which all three surface energy calculation methods give approximately the same value, and this value agrees very well with the converged linear-fit result. In general, the standard approach converges initially very rapidly after only a few data points, but exhibits a small divergence for an increasing number of layers in the slab. Since the initial convergence of the standard approach is so fast, there is usually a range of intermediate values for n where the small divergence for large n can be neglected, and the standard approach gives results in good agreement with the other methods. Without being identified as such, this behavior was also found for the (001) Pt surface (see figure 1 of [21]) and for the fully relaxed (001) hematite surface (see figure 7 of [25]).

Consequently, from the present data and the available data in the literature [21, 25] we can now put forward the

following procedure for obtaining meaningful surface energy values from the standard approach. First, the surface energy is calculated for an increasing number of layers until the surface energy has converged to approximately 1% between two consecutive simulations. This accuracy is sufficient for most determinations of the surface energy. Second, an additional increment in the number of layers should be avoided as this leads to a small divergence of the surface energy. The standard approach has the advantage that the initial convergence in the first few data points is very rapid, i.e. in general much faster than the convergence of the Boettger relation or the linear-fit method. Also, the standard approach requires overall significantly fewer data points to reach this initial convergence than the linear-fit method. The agreement in the obtained surface energy values between the three methods and using the above described procedure is better than 0.4% for the three hematite surfaces investigated here.

4. Conclusions

Three different methods for the calculation of the surface energy, namely the standard approach, the Boettger relation and the linear-fit method, were applied to the (001), (012) and (100) hematite surfaces. While the linear-fit method, in general, leads to the best overall convergence behavior of the surface energy, it requires a large number of data points for different slab sizes as its convergence is relatively slow. In contrast, the standard approach converges initially very quickly after only a few data points, but suffers from a small divergence for increasing slab thicknesses. The present simulation results show that there is an intermediate regime of slab sizes where the standard approach has already sufficiently converged for most purposes, whilst the divergence is still small enough to be neglected. Consequently, we would argue that the standard approach is viable for a first, and in many cases very good, estimate of the surface energy. For a more accurate calculation of surface energy values the linear-fit method should be employed. We note that we have found a similar behavior for alumina and chromia, and hence believe the present conclusions to be applicable to a wider family of metal-oxide surfaces. Finally, the results indicate that the relative stability of the investigated surfaces is unaffected by the calculation method.

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Supplementary material

Supplementary data associated with this article can be found in the online version.

ORCID iDs

Thomas Stirner  <https://orcid.org/0000-0001-7278-7867>

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