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Towards a standardized set-up for surface energy calculations

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High-throughput design of new materials with desired electronic properties, based on screening of large collections of crystal structures organized in the from of libraries or databases require fast, widely applicable, consistent and unsupervised methods to calculate the property of interest. In this work we present a new approach for the calculation of surface energies of 2D periodic crystal lattices which meets all these requirements. For materials slabs which are terminated with two identical surfaces, the task of calculating the surface energy is trivial. More problematic are the cases where both terminating surfaces are different, as there is no single established method allowing for equal treatment of a wide range of surface morphologies and orientations. Our proposed new approach addresses this problem. It relies on appropriately chosen capping atoms, whose bonding energy contributions are used to approximate the total energy of the surface. The choice of the capping atoms is governed by a set of simple guidelines that are applicable for surfaces with different terminations. We present the results for different semiconductor materials and show that our approach leads to surfaces energies with errors that are below 10%, and that are as low as 2% in many cases . We show that hydrogen is not always the best choice for a capping atom if accurate surface energies are the target of the calculations.

I. INTRODUCTION

The constantly increasing availability of distributed computer resources and established modern techniques for data storage and data analysis[1] enables high-throughput approaches where large libraries of chemical structures are analyzed, combined, and screened in a search for groups of compounds with specified target properties. For instance, such targets can be catalysts for hydrogen evolution[2], materials for photovoltaic cells, or the discovery of new battery chemistries [3]. Irrespective of the application, high-throughput screening heavily relies on computational methods and algorithms that are fast and "black-box" approaches (i.e. don't require human input), and are universally applicable to a wide range of chemical compounds. In the case where the subject of high-throughput characterization and design relies on efficient computations of surface energies of crystal lattices no universal method that meets these requirements is available until now. It is the purpose of our work to bridge this gap.

In computational material science, surface energy calculations are performed routinely to characterize properties of different materials. For slabs with two dimensional periodicity (see Fig. 1a for example) the surface energy γ can be computed as:

$$\gamma = \frac{1}{2}\left(E - \sum_{i}^{N_{spec}} N_i \mu_i\right) \quad , \tag{1}$$

where μ_i is the chemical potential of atom i in the material obtained from separate calculations of the bulk periodic structure. The factor $\frac{1}{2}$ accounts for the fact that the material is terminated by two identical surfaces on the top and the bottom of the slab. The surface energy is simply half of the difference between the total energy of the slab and the sum of the chemical potentials.

In the present paper, the materials where the top and the bottom surfaces are identical are dubbed *symmetric* (Fig. 1a) and Eqn. 1 is universally applicable. In contrast, materials with different top and the bottom surfaces are labeled as *non-symmetric* (Fig. 1b). We note that in the literature symmetric and non-symmetric are sometimes referred to as non-polar and polar systems, respectively, but we believe that simply referring to the symmetry of the system is more correct. For such cases Eqn. 1 can no longer be used. Instead, γ can be formally calculated from the following equation:

$$\gamma = E - \sum_{i}^{N_{spec}} N_i \mu_i - \gamma_e \quad . \tag{2}$$

where γ_e is the energy of one of the surfaces that can be conveniently chosen subject to only a few constraints. One requirement is that the top and bottom surfaces are essentially decoupled. The key question that we will address in this paper is: how can we calculate this surface energy γ_e efficiently?

Several methods have been developed that enable the estimation of surface energies of non-symmetric systems. In the wedge method, a special atomic structure with triangular cross section is used that is infinite only in one direction. If the total energy as well as two surface energies are known, the surface energy of the third, unknown surface can be calculated. Compared to the slab method, the advantage lies in the fact that no bottom surface is needed. A possible disadvantage is the energetic contribution of edge energies that only become negligible in the limit of a very large cross section of the wedge, i.e. for a very large number of atoms[4,5]. Although this method gives results with small errors ($\sim 2\%$)[5], it requires individual investigation and modeling of each surface substitution for every material. This is particulary relevant when one wants to compare the surface energies of different surface orientations (which all require different pyramid constructions), which also have different areas. We therefore believe that such an approach is not applicable in high-throughput screening studies, where it is required that the calculations are performed in algorithmic fashion without human input. Another approach that has been suggested in the literature is the introduction of an energy density[6,7]. But this approach is non-trivial and not well suited for high-throughput calculations. The reason is that the energy density method requires one to divide the slab into an upper and a lower part and integrate over each part separately to obtain the surface energy. This requires one to define a dividing surface. For the method to be accurate, it is required that the gradient of the wave function, vanishes on this dividing surface. This can be achieved for some systems, but not all. Our goal is to develop a general method for the calculation of surface energies that has an accuracy of at least 10% (or better) and that can be applied to any material and any surface morphology, without preparation, pre-modeling, or manual inspection of any of the structures in any way.

In the present paper we address these requirements and propose a new procedure for the calculation of surface energies that is applicable across a wide range of materials with *non-symmetric* and *symmetric* surfaces. Based on the work by Sakong et al.[8], we directly approximate the energy of the unknown surface γ_e in Eq. 2 as a sum of the bond energies between the surface and carefully chosen capping atoms. A similar approach was also recently used by Zhang et al.[9,10] These capping atoms should saturate all bonds of the bottom surface in order to prevent any charge transfer between the top and bottom surfaces, such that they are decoupled. We show that hydrogen, which is the most commonly used capping atom in computational material science, is not always the optimal choice for a capping atom when the surface energy is the property of interest. We argue that it is not universally applicable for all the materials and leads to a deterioration of the results with increasing complexity of the surface morphology. Instead, we provide simple guidelines for the selection of capping atoms with the size and electronic structure tuned for given a material, and discuss how this choice is reflected in the accuracy of γ_e. We note that hydrogen might still be a better choice for a capping atom when other properties of the material are of interest. For example, in some cases hydrogen perturbs the electronic structure less than other, heavier atoms.We also present the relevance of the new approach in the fast and unsupervised high-throughput screening applications. We note that Zhang et al.[10] also found that capping atoms other than hydrogen lead to improved results. They show results that pertain to systems with one dangling bond, while our method is more general and we also show results below for systems with two and three dangling bonds.

II. METHODOLOGY

Application of Eqn. 2 to calculate the surface energy γ in a slab requires a separate set of computations to find the chemical potentials μ_i of species i that constitute the given material, as well as the energy of the second surface γ_e. For symmetric systems $\gamma_e = \gamma$ and Eqn. 2 is equivalent to Eqn. 1. For non-symmetric materials where the exact value of γ_e is not always accessible, it can be approximated by a sum of the bond energies as demonstrated by Sakong et al.[8]. A fundamental assumption is that all slab atoms up to the last layer are essentially bulk like. Figure 2a shows an example of a non-symmetric slab, where the top surface of Si(111) is capped with hydrogen atoms, and where we want to use Eqn. 2 to calculate the surface energy γ of the bottom surface.

The bond energy between the top-most slab atoms and the capping atoms (including the internal energy of the capping atoms themself) can then be approximated with the help if an auxiliary molecule SiH_4 (Fig. 2b) by

$$\varepsilon_{Sa-Ca} = \frac{E_{SaCa_4} - \mu_{Sa}}{4} \tag{3}$$

where Sa denotes a surface atom, Ca is the capping atom, μ_{Sa} is the chemical potential of the surface atoms as obtained from periodic bulk structure computations, and E_{SaCa_4} is the total energy of the auxiliary molecule. The factor $\frac{1}{4}$ stems from the fact that the Si atom creates four bonds, but the energy of only one bond is the quantity of interest. For Si(111) and the SiH_4 molecule (Fig. 2) $Ca =$ Si and $Sa =$ H. Next, Eq. 2 can be rewritten in terms of ε_{Sa-Ca} as:

$$\gamma = E - \sum_{i}^{N_{spec}} N_i \mu_i - N_b \varepsilon_{Sa-Ca} \tag{4}$$

where N_b is number of $Ca - Sa$ bonds in the material slab ($N_b = 3$ for the example shown in Fig. 2a). For Si(111) this approximation leads to very good results and the calculated surface energy γ differs by only 1.9% from the exact reference value.

In Ref. 8 it was shown, however, that this method would fail for surfaces whose atoms are terminated with two- or more dangling bonds. Such a situation is presented in detail in Figure 3 for Si(100), where it can be seen that two capping atoms attached to two different surface atoms are close enough to each other to interact. This interaction is not reflected in the geometry of the auxiliary molecule shown on Fig. 2b. Therefore, it will not be included in the bond energy ε_{Si-H} that is obtained from Eq. 3. This in turn will lead to a poor estimation of the surface energy γ in Eq. 4.

We address this issue in the present work by proposing a new procedure that allows the accurate calculation of surface energies of non-symmetric surfaces terminated with multiple dangling bonds using equations 3 and 4. Our approach consists of two principal tasks: *i)* choosing an appropriate capping atom, and *ii)* constructing an auxiliary molecule.

First, we replace the mutually interacting capping atoms (as shown in the example in Figure 3) with a single capping atom that is bound to the N atoms in the surface, where N is the number of dangling bonds per unit cell sticking out from the surface atoms. This has the advantage that the capping atoms are interacting only with the surface atoms, whereas there is no direct interaction between any two (or more) capping atoms. As we will discuss below, this significantly facilitates the construction of the auxiliary molecules used to calculate the bond energies $\varepsilon_{S_aC_a}$.

The choice of the capping atom is an important issue. In this paper we will develop a set of general rules to choose an optimal capping atom for a given material that yields the smallest error in calculations of the surface energy. Several possibilities are considered. For surface atoms with N dangling bonds (each occupied with a single electron) it is intuitive to use a capping atom that is an acceptor of N electrons. For instance, the matching atom for silicon with $N = 2$ would be oxygen or sulfur. Similarly, for silicon with $N = 1$ bonds, elements from group VII of the periodic table of elements can be used. The position of the capping atom with respect to the surface needs to be decided as well. The most convenient choice, which does not require any additional calculations, is to place the capping atom in the positions determined from the symmetry of the crystal lattice of the given material, i.e. in the positions where the next atom in the material is expected if the bulk structure was continued above the surface. The alternative is to optimize the position of the capping atoms, and we will explore this route as well. We note that a similar idea for choosing different capping atoms was reported in a recent studiy on ZnO and GaN[10].

The new capping scheme is also reflected in the geometry of the auxiliary molecules. As proposed by Sakong et al., the structures of these molecules correspond to the structures of the capping atom on the surface and enable easy extraction of the bond energies used in Eq. 4. Note that the auxilliary molecules in our approach are fictitious objects and need not be stable in the geometry we are using. We will now describe in detail how this can be accomplished for surfaces with different numbers of dangling bonds N.

A. Auxiliary molecules for surfaces terminated with one dangling bond

For surfaces terminated with one dangling bond, the structure of the auxiliary molecule is not different from the molecules used in Ref. 8. But instead of using hydrogen atoms as in the case shown in Fig. 2b, capping atoms from group VII of the periodic table are chosen. The geometry of the molecule reflects the bonding pattern of the surface. If the capping atom is put in the crystal lattice positions, the same bond lengths and angles are found in the auxiliary molecule. Similarly, if the position of the capping atom is optimized, then the new (optimized) geometrical parameters are also incorporated in the geometry of the molecule.

B. Auxiliary molecules for surfaces terminated with two and more dangling bonds

We will start this discussion for surfaces with $N = 2$. In that case, it is most intuitive to use group VI elements as capping atoms. Each such atom is bonded to two different atoms on the surface (Fig. 4a). The structure of the auxiliary molecule reflecting this geometry is illustrated in Fig. 4b for the Si(100) surface that is capped with sulfur. It consist of one capping atom (sulfur) bonded to two surface atoms (silicon). In the case of Si, each atom creates four tetrahedral bonds in the material, therefore each Si atom in the auxiliary molecule is additionally capped with three hydrogen atoms in the tetrahedral configuration. In materials where atoms create different number of bonds, the number of H atoms needs to be adjusted accordingly.

The bond energy between the surface atoms (Sa) and the capping atom (Ca), ε_{Sa-Ca}, is calculated from the following formula

$$\varepsilon_{Sa-Ca} = \frac{E_{aux} - N_{Sa}\mu_{Sa} - N_H\varepsilon_{Sa-H}}{N_{aux}} \quad , \tag{5}$$

where N_{Sa} is the number of surface atoms in the molecule, N_{aux} is the number of bonds between surface atoms and capping atoms in the auxiliary molecule, μ_{Sa} is the chemical potential of the surface atom, N_H is the number of hydrogen atoms, and E_{aux} is the total energy of the auxiliary molecule. For example, for the auxiliary molecule used for Si(100) (Fig. 4b) $N_{Sa} = 2$ and $N_H = 6$.

The additional bond energy ε_{Sa-H} on the right hand side of Eq. 5 is obtained using an additional small molecule with a geometry reflecting Sa-H bonding geometry in the auxiliary molecule. In the discussed example of the Si(100) surface this molecule will be simply SiH_4 (cf. Fig. 4b) and ε_{Sa-H} is calculated from Eq. 3. The bond energy ε_{Ca-Sa} is then substituted into Eqn. 4 to calculate surface energy γ.

For the surfaces terminated with three dangling bonds (for example, Si(111) as illustrated in Fig. 5a), the auxiliary molecule is created in a similar fashion with $N_{Sa} = 3$ surface atoms, each connected to the capping atom with one bond, and then saturated with the appropriate number of hydrogen atoms ($N_H = 9$ in total for Si(111)). An auxiliary molecule for the Si(111) surface capped with phosphorus is shown in Fig. 5b.

This strategy can easily be generalized and we suggest the following general rules for constructing the appropriate auxiliary molecule to calculate ε_{Ca-Sa}: *i)* the molecule should be as small as possible; *ii)* the positions of the atoms in the molecules (bonds, angles) should be identical to the ones in the surface; *iii)* its atoms (other than hydrogen) should fulfill the octet rule. For example, in GaAs each of the four-fold coordinated Ga atoms contributes 3/4 electrons to each bond. If it is capped with a hydrogen atom, each H atoms needs to contribute 5/4 electrons, and hence it must have fractional charge $1.25e$[11]; and *iv)* equations for ε_{Sa-Ca} should be of the general form:

$$\varepsilon_{Sa-Ca} = f(E, \mu, \varepsilon) \quad , \tag{6}$$

i.e., it only depends on the energy of the auxiliary molecule, the chemical potential of the involved atoms, and the bond energies calculated with the use of an additional auxiliary molecule. We will show in the following sections that these general rules lead to good results in almost all cases, and will suggest in the conclusion a simple algorithm that can be used systematically for high-throughput calculations.

III. COMPUTATIONAL DETAILS

All KS-DFT[12,13] calculations in the present work have been performed with the FHI-AIMS package[14]. This is an all-electron full potential DFT code that uses numeric atom centered orbitals as its basis set. We have carefully tested convergence of our results for the calculated surface energies. The results are converged within less than two meV/$\AA^2$ with respect to the basis set, and the density of the (numerical) integration mesh. We have used *light* basis set settings with scalar ZORA[15,16] corrections and the non-spin-polarized local density-approximation (LDA)[17–19] approximation for the exchange-correlation functional. The crystal structures of the materials have been obtained from the ICSD database[20]. For all material slabs discussed in this paper, convergence studies with respect to the thickness of the structures were performed to assure that the two surfaces and capping atoms are not interacting with each.

IV. RESULTS AND DISCUSSION

In this section we discuss the results of surface energy calculations using Eqn. 4 with help of Eqns. 3 and 5 for surfaces terminated with one, two, and three dangling bonds. Different possibilities to construct the auxiliary molecules are considered. The systems we have chosen belong to group IV and III-V semiconductors. We note that for those materials it is always possible to create symmetric slabs by exposing their low-index faces, such as those that are given by Miller indices (100) and (111) for group IV semiconductors. The surface energy in such slabs can be calculated rigorously according to Eq. 1, which provides us with a reference result. To simulate non-symmetric slabs in these materials, we terminate only one of the exposed surfaces with capping atoms and thus create structures where the top and bottom surfaces are not equivalent (see Fig. 2a). We emphasize that it is the goal of this paper to illustrate the feasibility and accuracy of our method (by comparing it to the rigorous results), and not to report calculated unknown surface energies (which is of course what this method is designed for). We are not interested in surface reconstructions and study the unreconstructed surfaces for simplicity. Moreover, surface energies for unreconstructed surfaces are useful in providing a convenient reference for future studies of interface formation energies.

A. Surfaces terminated with one-dangling bond

The (111) plane of crystals with the diamond structure, such as Carbon, Silicon or Germanium, is terminated either by one- or three- dangling bonds. In this section we will examine the case of one dangling bond. As discussed in Section II, we anticipate that the optimal capping atoms have a similar size as the atoms on the surface, and are an acceptor of N-electrons, where N is the number of dangling bonds. Thus, for $N = 1$ the capping atoms should belong to group VII of the periodic table of elements. The corresponding auxiliary molecules were constructed as described in section II A. We tested two scenarios: in the first scenario, the capping atoms are placed in a position that corresponds to the crystal lattice, while in the second scenario, the positions of the capping atoms are optimized. The errors that we obtained are referred to as Δ_{bulk} and Δ_{opt}, respectively. In each case, all other atoms were fixed. The auxiliary molecule was constructed with a $Ca - Sa$ bond length that corresponds to the slab geometry.

The results are summarized in Table I. For Si(111) it can be seen that the lowest error $\Delta_{bulk} = 0.2\%$ for calculating the surface energies is obtained when the material is capped by Cl, the atom that lies in the same period in table of elements as Si. Using hydrogen as a capping atom leads to an error that is higher (reaching 4%). We note that as the capping atom is changed going down along the group VII from F to Br, the error is reduced, until it reaches a minimum for Cl, and than it rises again for Br.

Similar observation are made for Ge(111) with one dangling bond. Bromine (which is in the same period as Ge) leads to $\Delta_{bulk} = 1.2\%$, and it is much smaller than for H (3.0%). Similarly as for Si, the error changes with the progression down column VII of the periodic table from F to Br; however it is the smallest for fluorine (0.8%).

In the case of C(111) the smallest Δ_{bulk} is observed when hydrogen is used - 6.5%. However, this error is significantly larger than the smallest error for Si(111) (0.2%)and Ge(111) (0.8%). Additionally, as the size of the capping atom increases from F to Br, the error also significantly increases from 13.1% to 159%. This result suggests that due to the small C-C distance on the surface, the capping atoms (even the ones as small as hydrogens) are interacting with each other. The strength of this interaction increases with the size of the capping atom and is the strongest for Br. The auxiliary molecule, constructed as presented in Section II A and Fig. 2b, does not capture this interaction as ε_{Ca-Sa} is only the energy of a single capping atom with a surface bond. To increase the accuracy of the approximation, it would be required that ε_{Ca-Sa} includes the contribution of the interaction. However, this is not easy to incorporate by either constructing a different auxiliary molecule or by changing the capping scheme. This leads to the conclusion that for surfaces terminated with one dangling bond the applicability limit of our method is determined by the magnitude of the interaction between the capping atoms.

For the systems where the positions of the capping atoms were optimized, the errors Δ_{opt} in Table I indicate that in all but two cases this procedure does not lead to an improved accuracy of the surface energy calculations. The reduction of error is observed for C(111) capped with hydrogen to 1.9%, and for this material it is the best result. The error is also reduced for Ge(111) capped with H (from 3.0% to 1.1%), however, the best result for this system remains for Ge(111) capped with F in the bulk position.

The results for materials with one dangling bond indicate that using capping atoms that

	C(111)		Si(111)		Ge(111)	
capping atom	Δ_{bulk}	Δ_{opt}	Δ_{bulk}	Δ_{opt}	Δ_{bulk}	Δ_{opt}
H	-6.5	1.9	-4.0	6.0	3.0	1.1
F	**13.1**	**22.8**	-3.1	24.7	-0.8	12.8
Cl	97.5	79.2	**0.2**	**11.5**	-6.9	4.2
Br	159.0	nc	5.7	9.3	**-1.2**	**3.4**
γ_{ref}	459.1		103.3		69.8	

TABLE I. Surface energies (in meV/Å^2) and errors (in % with respect to the exact reference surface energy) for different (111) surfaces with different capping atoms. Surfaces are terminated with one dangling bond. Δ_{bulk} denotes the error when the capping atoms are kept on the crystal lattice positions of the material. Δ_{opt} denotes the error when the positions of the capping atoms are optimized while all other atoms in the material slab are kept fixed. Δ^H_{bulk} and Δ^H_{opt} denote that additionally the hydrogen atoms in the auxiliary molecule have been optimised in the gas phase, whereas all other atoms were kept on positions as in Δ_{bulk} and Δ_{opt} respectively. γ_{ref} denotes the reference surface energy obtained with Eq. 1. Boldface font highlights the capping atom from the same period in the table of elements as the surface atom.

lie in the same period of table of elements as the capped atom leads to more accurate surface energies than when capping surfaces with hydrogen. Moreover it is preferable to keep the capping atoms in the crystal lattice positions. Optimizing their coordinates does not improve the results.

B. Surfaces terminated with two-dangling bonds

For group IV semiconductors the representative example of surfaces terminated with two dangling bonds are the (100) planes. We will start the discussion for $N = 2$ for Si(100). Capping Si(100) with hydrogen atoms as depicted in Figure 3 and using SiH$_4$ as the auxiliary molecule (cf. Fig. 2b) to obtain the bond energy ε_{Si-H} for Eq. 4 leads to an error of 18.9% (see Table II). As discussed earlier, this large error stems from the fact that two hydrogen atoms attached neighboring Si surface atoms are interacting with each other, which is not accounted for in the single bond energy ε_{Si-H}. To circumvent this problem we are using capping atoms that are chosen from group VI of the table of elements, that are acceptors of two electrons and create bonds to two different atom on the surface (cf. Fig. 4a). We have considered two possibilities for the placement of the capping atoms: *i)* we place the capping atoms in the crystal lattice positions of the material (Δ_{bulk} in Table II), or *ii)* the position of the capping atoms is allowed to relax while the positions of all other atoms in the slab are kept fixed (Δ_{opt} in Table II). In the latter case, the geometry of the auxiliary molecule also reflects the changes in the surface - capping atom bonding after the optimization.

The structure of the corresponding auxiliary molecule is shown in Fig. 4b. We note that the atoms representing the surface in the auxiliary molecule (i.e. C, Si, Ge) are capped with hydrogen atoms. In the calculations for Δ_{bulk} and Δ_{opt} their orientation is determined by the crystal lattice positions in order to mimic the length and orientation of the bonds in the material. We have also considered the scenario where the positions of all H atoms in the molecule are optimized while all other atoms are kept fixed. This is represented by Δ^{H}_{bulk} and Δ^{H}_{opt} in Table II.

All the results are presented in Table II. We will start the discussion with the first case, when the coordinates of all atoms in the auxiliary molecule correspond to the crystal lattice positions (Δ_{bulk}). For Si(100), sulfur leads to the smallest error in surface energy estimations (5.4%). Sulfur is also the atom that is in the same period as Si in the table of elements. For Ge(100) the lowest errors are obtained both for S and Se (12.4% and 12.9%, respectively). We find an error with a imilar magnitude for C(111) when oxygen is used as a capping atom.

In all the cases the results are further improved when the positions of the hydrogen atoms are optimized in the auxiliary molecule. The lowest overall error Δ^{H}_{bulk} for Si(100) is obtained when it is capped by O (0.9%). The error for sulfur is also reduced from 5.4% to 2.9% and it is the second best estimation. Significant error reduction is also observed for Si(100) when it is capped with Se, from 35.6% to 2.8%. In the case of Ge(100) Se leads to the smallest overall error (9.9%). Se is also the atom from the same period as Ge in the table of elements. Optimization of the hydrogen atoms also slightly reduces the error in the estimation of the surface energy for Ge(100) that is capped with S. For C(100) the smallest overall error is obtained when the C atoms are capped with oxygen (0.4%), which is a significant reduction from an error of 12%.

Similar to the case of $N = 1$ dangling bonds, optimization of the positions of the capping atoms does not lead to an improvement of the results. All Δ_{opt} errors in Table II are higher

	C(100)				Si(100)				Ge(100)			
capping atom	Δ_{bulk}	Δ^H_{bulk}	Δ_{opt}	Δ^H_{opt}	Δ_{bulk}	Δ^H_{bulk}	Δ_{opt}	Δ^H_{opt}	Δ_{bulk}	Δ^H_{bulk}	Δ_{opt}	Δ^H_{opt}
H	-	-	nc	-	-	-	18.9	-	-	-	22.5	-
O	**12.0**	**-0.4**	**16.8**	**3.7**	8.0	-0.9	-13.7	-21.8	18.8	-23.9	10.3	1.4
S	86.4	44.9	51.1	39.6	**5.4**	**2.9**	**9.6**	**13.3**	12.4	-10.7	16.9	4.7
Se	nc	nc	58.0	56.4	35.6	2.8	34.7	30.9	**12.9**	**-9.9**	**13.1**	**5.54**
γ_{ref}	551.0				133.4				87.5			

TABLE II. Surface energies (in meV/Å^2) and errors (in % with respect to the reference surface energy) for different (100) surfaces with different capping atoms. Surfaces are terminated with two dangling bonds. Δ_{bulk} denotes the error when the capping atoms are kept on the crystal lattice positions of the material. Δ_{opt} denotes the error when the positions of the capping atoms are optimized while all other atoms in the material slab are kept fixed. Δ^H_{bulk} and Δ^H_{opt} denote that additionally the hydrogen atoms in the auxiliary molecule have been optimised in the gas phase, whereas all other atoms were kept on positions as in Δ_{bulk} and Δ_{opt} respectively. γ_{ref} denotes the reference surface energy obtained with Eq. 1. Boldface font highlights the capping atom from the same period in the table of elements as the surface atom. nc denotes a lack of convergence due to steric interactions. For H, Δ_{bulk} can not be calculated due to steric interactions between hydrogen atoms.

than other estimates. In almost all cases there is an additional improvement when the hydrogen atoms in the auxiliary molecule are optimized as well. Overall, similar to the case with one dangling bond, the best (or very close to the best) results are obtained for capping atoms that lie in the same period in the table of elements as the capped atoms. Those are the atoms that have similar size as the atom in the surface and and are acceptors of N electrons.

C. Surfaces terminated with three-dangling bonds

The surfaces with three-dangling bonds were created by exposing the (111) planes of materials (Fig. 5a). The auxiliary molecule was prepared in a similar manner as in the for two-dangling bonds. However, now it consists of one capping atom and three surface atoms capped with hydrogen atoms (Fig. 5b). We are also considering two different cases, where the capping atoms are placed on crystal lattice positions (Δ_{bulk}) or optimized while all other atoms in the material are kept fixed (Δ_{opt}). For both of these cases we have also performed calculations where the hydrogen atoms in the auxiliary molecule are optimized as well (Δ^{H}_{bulk} and Δ^{H}_{opt} respectively).

The results are presented in Table III. In the non-optimized case the lowest Δ_{bulk} errors in surface energy calculations for Si(111) are obtained when the surface is capped with N (6.0%) and P (6.6%). Similarly, for Ge(111), the best Δ_{bulk} are obtained when the surface is capped with P (17.0%) and As (17.9%). In the case of C(111) nitrogen leads to much smaller error than phosphorus, 14.6% vs 61.7%.

The results are considerably improved when the auxiliary molecules are partially optimized. For Si(111) the overall lowest Δ^{H}_{bulk} is obtained with P as the capping atom (1.3%). The error is very close when As is chosen as the capping atom (1.6%). For Ge(111), As yields the best estimation (8.8%). A big reduction of the error is also observed for C(111) capped with N, from $\Delta_{bulk} = 14.6\%$ to $\Delta^{H}_{bulk} = 4.1\%$. The observed trend that Δ^{H}_{bulk} yields smaller errors than Δ_{bulk} is in agreement with the trend that we found for $N = 2$ surfaces.

We note that for $N = 3$ dangling bonds, the errors Δ_{opt} are slightly smaller than Δ_{bulk}. This is opposite to the trend that we found for $N = \{1, 2\}$. Further optimization of the hydrogen atom in the auxiliary molecules Δ^{H}_{opt} does not follow any trend and results vary case by case. In all cases, the best results are obtained when the capping atoms are placed in the crystal lattice positions and the positions of the H atoms are optimized (Δ^{H}_{bulk}).

Altogether, for $N = \{1, 2, 3\}$ the best results for all possible optimization scenarios are obtained when for each material the capping atom lies in the same period in the table of elements as the surface atoms and is an acceptor of N electrons. To obtain the lowest error in the surface energy estimations it is best to place the capping atoms in the crystal lattice positions of the material. An optimization of the geometry is not required (and in fact increases the error). For $N = \{2, 3\}$, additional relaxation of the hydrogen atoms in the auxiliary molecules leads to improved results (we note that for $N = 1$, the auxiliary molecule does not have hydrogen atoms; therefore nothing can be further optimized).

	C(111)				Si(111)				Ge(111)			
capping atom	Δ_{bulk}	Δ^H_{bulk}	Δ_{opt}	Δ^H_{opt}	Δ_{bulk}	Δ^H_{bulk}	Δ_{opt}	Δ^H_{opt}	Δ_{bulk}	Δ^H_{bulk}	Δ_{opt}	Δ^H_{opt}
H	-	-	nc	-	-	-	19.6	-	-	-	23.7	-
N	**14.6**	**4.1**	**14.9**	**-4.8**	6.0	-9.4	-58.3	76.4	20.3	37.8	-42.1	108.0
P	61.7	19.7	40.2	21.5	**6.6**	**1.3**	**4.4**	**-4.5**	17.0	-10.2	14.8	-16.8
As	79.7	36.7	56.2	58.9	8.7	1.6	4.6	-9.0	**17.9**	**-8.8**	**13.4**	**-21.0**
γ_{ref}	782.6				173.4				115.15			

TABLE III. Surface energies (in meV/Å^2) and errors (in % with respect to the reference surface energy) for different (111) surfaces with different capping atoms. Surfaces are terminated with three dangling bonds. Δ_{bulk} denotes the error when the capping atoms are kept on the crystal lattice positions of the material. Δ_{opt} denotes the error when the positions of the capping atoms are optimized while all other atoms in the material slab are kept fixed. Δ^H_{bulk} and Δ^H_{opt} denote that additionally the hydrogen atoms in the auxiliary molecule have been optimised in the gas phase, whereas all other atoms were kept on positions as in Δ_{bulk} and Δ_{opt} respectively. γ_{ref} denotes the reference surface energy obtained with Eq. 1. Boldface font highlights the capping atom from the same period in the table of elements as the surface atom. nc denotes a lack of convergence due to steric interactions. For H, Δ_{bulk} can not be calculated due to steric interactions between hydrogen atoms.

D. III-V semiconductors with two dangling bonds

As a representative material for III-V semiconductors we have chosen GaAs. Unfortunately, using planes characterized with Miller indices (111) it is not possible to create a symmetric slab terminated with one dangling bond that can be used for reference calculations. We therefore start our discussion with GaAs(100) which is terminated by two dangling bonds. In that case two variants are possible - the surfaces can be terminated either with Ga or As atoms (Fig. 6a and b). The reference molecule is presented in Fig. 6c. It is worth to point out that both Ga and As atoms contribute fractional number of electrons to the bonds, $\frac{3}{4}$ and $1\frac{1}{4}$, respectively. To ensure a total of two electrons per bond, we need a fractional number of electrons in the capping atom (both on the surface and in the auxiliary molecule), and we also need to augment the corresponding nuclear charge Z by a fraction of the unit charge. Since each capping atom is bonded with $N = 2$ different surface atoms (Fig. 6a and 6b), this increment/decrement will be +/-0.5e depending on whether the bonding is to two Ga or two As atoms, respectively. The value of γ is calculated using Eqn. 4 and Eqn. 5. One of the two chemical potentials μ_{Ga} and μ_{As} can be eliminated from Eqn. 4 if we assume thermodynamic equilibrium. We choose to eliminate μ_{Ga} when we report results for As-rich conditions, and eliminate μ_{As} when we report results for Ga-rich conditions.

The results for surface energy calculations are presented in Table IV. We present results for the case when hydrogen atoms in the auxiliary molecule are kept in the crystal lattice positions (Δ_{bulk}) and when their positions are optimized while all other atoms are kept fixed (Δ^{H}_{bulk}). The absolute values of the errors for Ga-rich and As-rich conditions are identical (by construction) and all results for the relative errors are qualitatively very similar for Ga-rich and As-rich conditions. Based on the trends established in Sections IV A- IV C, the anticipated ideal capping atom for GaAs(100) is Se. It can be seen immediately that a smaller error $\Delta_{bulk} = 5.3\%$ (Ga-rich) and $\Delta_{bulk} = 4.3\%$ (As-rich) is obtained when the slab is Ga-terminated vs. $\Delta_{bulk} = -16.3\%$ (Ga-rich) and $\Delta_{bulk} = -19.8\%$ (As-rich) when the slab is As terminated. Δ_{bulk} is the lowest, however, when the slab is capped with oxygen, and in that case $\Delta_{bulk} = 3.6\%$ (Ga-rich) and $\Delta_{bulk} = 2.9\%$ (As-rich) when the slab is Ga terminated and $\Delta_{bulk} = -10.4\%$ (Ga-rich) and $\Delta_{bulk} = 12.7\%$ (As-rich) when the slab is As terminated.

The error Δ^{H}_{bulk} (which denotes that the positions of the hydrogen atoms are relaxed) is larger than Δ_{bulk} in almost all cases, which does not follow the trend from Sections IV B and IV C for group IV semiconductors. This needs to be studied in more detail, and is the subject of future work.

E. III-V semiconductors with two different atoms in the surface

Exposing the (110) plane in GaAs leads to a surface where both Ga and As atoms are present (Fig. 7a). Each of the surface atoms creates one dangling bond. But as can be seen in Fig. 7a, terminating those bonds with capping atoms leads to the situation where two capping atoms are interacting with each other. This complicates the construction of the auxiliary molecule for surface energy calculations. We found that the structure proposed in Fig. 7b leads to most accurate results. This structure features a double bridge between

	Ga terminated (Ga-rich)		Ga terminated (As-rich)		As terminated (Ga-rich)		As terminated (As-rich)	
capping atom	Δ_{bulk}	Δ^{H}_{bulk}	Δ_{bulk}	Δ^{H}_{bulk}	Δ_{bulk}	Δ^{H}_{bulk}	Δ_{bulk}	Δ^{H}_{bulk}
H								
O	3.6	13.6	2.9	11.0	-10.4	21.7	-12.7	26.4
S	10.8	8.7	8.8	7.1	-16.5	16.7	-20.1	20.3
Se	**5.3**	**8.8**	**4.3**	**7.2**	**-16.3**	**18.7**	**-19.8**	**22.8**
γ_{ref}	83.5		102.7		107.3		88.1	

TABLE IV. Surface energies (in meV/Å^2) and errors (in % with respect to the exact reference surface energy) for GaAs(100) with different capping atoms. Two different surfaces are created depending on the cut - one with exposed Ga atoms and one with exposed As atoms. In both cases the surfaces are terminated with two dangling bonds. Δ_{bulk} denotes the error when the capping atoms are kept on the crystal lattice positions of the material. Δ^{H}_{bulk} denotes that additionally hydrogen atoms in auxiliary molecule has been optimised in the gas phase, whereas all other atoms were kept on positions as in Δ_{bulk}. γ_{ref} denotes the reference surface energy obtained with Eq. 1. Boldface font highlights the capping atom from the same period in table of elements as surface atom.

the capping atoms Cap+ and Cap-, which have positive and negative fractional charges, respectively. Each capping atom is an acceptor of two electrons. Therefore we use elements that are found in row VI of the periodic table. One bridge mimics capping atom positions on the surface, whereas the other simply substitutes Ga and As atoms found in the bulk. Similar to GaAs(100), the Ga and As surface atoms that have 3 or 5 electrons contribute a partial charge to the bond with the capping atom, and all other atoms in the auxiliary molecule are partially charged accordingly in order to meet the octet rule. For each of these atoms, its nuclear charge is changed by either +0.25e or -0.25e according the the scheme on Fig. 7b.

The energy of the Cap+ - Cap- bridge is calculated according to the equation:

$$\begin{aligned}\varepsilon_{Cap+-Cap-} &= \frac{1}{2}\left(E_{aux.mol.} - \mu_{Ga} - \mu_{As} - 2\varepsilon_{Ga-Hp} - 2\varepsilon_{As-Hm}\right) \\ &= \frac{1}{2}\left(E_{aux.mol.} - \frac{\mu_{Ga}}{2} - \frac{\mu_{As}}{2} - \frac{E_{Ga-Hp_4}}{2} - \frac{E_{As-Hm_4}}{2}\right)\end{aligned} \tag{7}$$

$$= \frac{1}{2}\left(E_{aux.mol.} - \frac{\mu_{GaAs}}{2} - \frac{E_{Ga-Hp_4}}{2} - \frac{E_{As-Hm_4}}{2}\right)$$

where ε_{Ga-Hp} and ε_{As-Hm} are calculated as in Eqn. 3 from the molecule $\{$Ga,As$\}$H$_4$, where hydrogen atoms with a nuclear charge of 1.25e and 0.75e, respectively, have been used. E_{Ga-Hp_4} and E_{As-Hm_4} are the total energies of the molecules that consist of a Ga (As) atom with 4 Hp (Hm) atoms. We want to point out that there is no dependence of $\varepsilon_{Cap+-Cap-}$ on μ_{Ga} and μ_{As} (which would change the results for the surface energy).

The results are summarized in Table V. We have considered two cases: in the first case the hydrogen atoms in the reference molecule (Fig. 7b) are placed in the positions of the Ga/As atoms (Δ_{bulk}), and in the second case we optimized their positions, keeping all other atoms fixed (Δ^{H}_{bulk}). In the latter case we have also optimized for consistency the positions of the hydrogen atoms in the $\{$Ga,As$\}$H$_4$ molecule that is used to calculate ε_{Ga-Hp} and ε_{As-Hm} in Eqn. 8. All errors Δ_{bulk} that we calculated are not satisfactory, with the smallest error being 33% when the surface is capped with oxygen, and it becomes as large as 81.2% when Se is used. The error is significantly reduced when the H atoms are optimized, and $\Delta^{H}_{bulk} = 11.2\%$ for sulfur. Based on the trends from Sections IV A- IV C, the optimal capping atom for GaAs should be Se. However it leads to a relatively large error of 58.9%. It is not clear why the trends established in Sections IV A- IV C do not work here, and more work for III-V semiconductor systems is needed.

F. Summary of the proposed procedure

Based on our results a set of simple guidelines that can be used for high-throughput calculations can be established as follows: Each atom in the surface is terminated by N dangling bonds. In the case of $N = 1$, the best capping atoms are from group VII of the periodic table. For surfaces with $N = 2$, group VI atoms are be used, and for $N = 3$ group V atoms are used. The capping atoms are placed in the positions expected from the crystal lattice symmetry of the given material. They are bound to N surface atoms and each atom in such a bonding pair meets the octet rule. The lengths and spatial orientations of these bonds are the same as in the bulk structure of the material, and no further geometry optimization is required. An example of such a geometry for the Si(100) slab with N=2 is presented in Fig. 4a. Additionally the error for γ (as calculated with with Eq. 2) can be minimized when the capping atom is chosen from the same period in the table of elements as the surface

	GaAs(110)	
capping atom	Δ_{bulk}	Δ_{bulk}^{H}
H	53.8	71.9
O	33.0	63.2
S	-35.5	11.2
Se	**-81.2**	**-58.9**
γ_{ref}	59.05	

TABLE V. Surface energies (in meV/Å^2) and errors (in % with respect to the reference surface energy) for GaAs(110) with different capping atoms. The surface is terminated with one dangling bond, but the capping atoms are interacting with each other. The fractional charge (+/- 0.25e) is enforced on each capping atom according to the scheme illustrated in Fig. 7b. Δ_{bulk} denotes the error when the capping atoms are kept on the crystal lattice positions of the material. Δ_{bulk}^{H} denotes that additionally hydrogen atoms in auxiliary molecule has been optimised in the gas phase, whereas all other atoms were kept on positions as in Δ_{bulk}. γ_{ref} denotes the reference surface energy obtained with Eq. 1. Boldface font highlights the capping atom from the same period in table of elements as surface atom.

atom, which means that it has a similar size as the surface atoms. As an example, the above selection rules suggest that chlorine is the best capping atom for Si(111) ($N = 1$), sulfur for Si(100) (N=2), and phosphorus for Si(111) (N=3). The optimal capping atoms selected according to these guidelines are marked with a bold font in the tables in Section IV. A summary of the results for all systems that can be obtained with our procedure according to these guidelines is shown in Fig. 8.

The bond energy ε_{Sa-Ca} is obtained in a small, inexpensive separate calculation of a gas-phase auxiliary molecule. For $N = 1$, the auxiliary molecule consists of one surface atom Sa where each dangling bond is capped by one capping atom in a position that resembles the crystal structure. For $N = 2$ and $N = 3$, the auxiliary molecule contains N surface atoms Sa that are connected to one capping atom Ca in a bulk like geometry (without relaxation). The remaining dangling bonds of the surface atoms Sa are capped by H atoms. The distances $Sa - H$ are optimized, and the bond energy ε_{Sa-H} is obtained by one more calculation of an auxiliary molecule that is similar to the case with $N = 1$ (but with optimized hydrogen atoms as the capping atom). We note that the aforementioned hydrogen atoms in the auxiliary molecule for $N = 2$ and $N = 3$ can be also substituted with other atoms. For instance, in the molecule created for the $\gamma_{Si(100)}$ estimations (Fig. 4b), chlorine can be used. We have performed such calculations for all considered materials and did not find significant improvement in the results or any clear trends; therefore, for clarity they have not been included in this publication.

G. The method in the context of high-throughput screening

In high-throughput discovery of new materials, large libraries of crystal structures are scanned to build a ranking of the best candidates for a desired application.[2,3] It is crucial that such calculations are done fast and efficiently with black box methodology, i.e. without human supervision. If materials are ranked based on their surface energy, there is no single surface energy calculation method available up to date that allows a consistent and automatic treatment of different systems. This is particularly relevant for *non-symmetric* surfaces that either require detailed modeling of each surface, and where the chosen approach cannot be universally applied to different surface morphologies.

Our method addresses this issue allowing for equal treatment of both *non-symmetric* and *symmetric* materials. The only required input parameters are the type and number of valence electrons (or dangling bonds) of the surface atoms, and the materials's crystal lattice symmetry operations. The first input identifies an optimal capping atom, while the latter uniquely determines the position of the capping atom with respect to the surface. If the crystal lattice symmetry operations are not available, one can simply replace the atoms in the surface with the capping atoms. The input parameters also clearly determine the geometry of the auxiliary molecule, as it simply retrieves the structure of the capped surface.

Such well-defined rules can easily be turned into algorithms that can be implemented in the materials modeling software, requiring minimal computer resources. Moreover, the repetitiveness and consistency of the algorithm for any surface morphology and orientation, defined by the set of Miller indices, makes this approach ideal for unsupervised high-throughput screening applications. We have performed test implementation of this approach in our InterfaceBuilder software[21] for high-throughput screening of semiconductor interfaces.

V. CONCLUSIONS

In the present paper we have developed a new procedure for surface energy calculations that is applicable both for material surfaces that are *non-symmetric* and *symmetric*. Our approach is based on work by Sakong et al.[8], where under the fundamental assumption that all atoms in the slab (up to the last layer) are essentially bulk like, the energy of the surface can be obtained with the help of the bond energies ε_{Sa-Ca} between the surface atoms (Sa) and the capping atoms (Ca). Our results show that hydrogen is not always the best and universal candidate for a capping atom for material surfaces with different morphologies. We have given step-by-step guidelines how to implement our proposed procedure.

There are several limitations of the applicability of the described approach. It works well for materials such as semiconductors in which atoms are connected with well defined, directional covalent bonds that are able to bind to capping atoms. We have presented detailed results for several group IV semiconductors, and some results for GaAs (as a representative III/V semiconductor). More detailed studies for other III/V systems, as well as II/VI and I/VII systems are needed, and are subject to future work. In metals, on the other hand, bonding is characterized by an interaction between atoms and delocalized electrons, lacking strong angular dependence. Moreover, geometry optimization studies reveal that metallic surfaces do not create stable configurations with the capping atom. Therefore, our method cannot be used for this class of systems. We also note that our method was designed for the smallest error in calculating surface energies, and not for other properties such as band structures.

In conclusion we found that in most cases that were presented here the method introduced in this paper estimates the surface energies of any morphology and termination very well. For group IV atoms all the errors are less than 10% (with the exception of C(111)), and in many cases they are as small as $\sim 2\%$. Such small errors together with the clear rules for choosing and positioning the capping atoms and constructing the auxiliary molecules make this method particularly appealing in high-throughput screening applications, as it can easily be turned into an algorithm.

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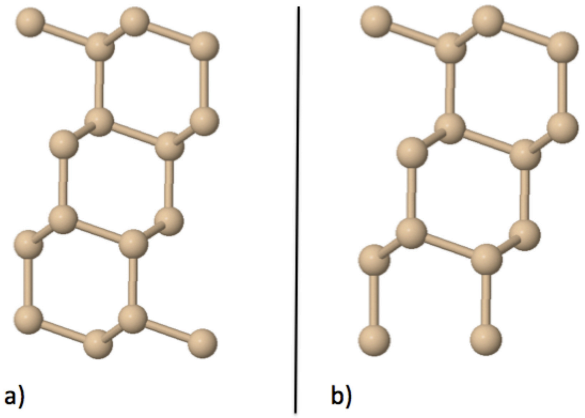

FIG. 1. Examples of 2D periodic material slabs with a) symmetric surfaces where the top and bottom surfaces have the same structure; and b) non-symmertic surfaces where the top and bottom surfaces have different structures.

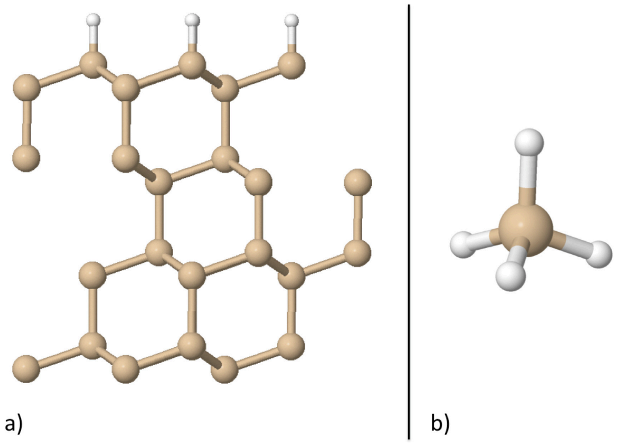

FIG. 2. An example of a 2D-dimensional periodic material slab in the diamond structure. Panel a) shows a (111) surface with one dangling bond per Si atom capped with hydrogen atoms. Panel b) shows the corresponding auxiliary molecule as discussed in the text.

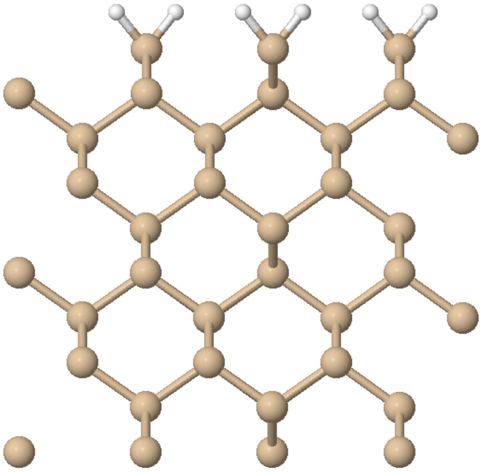

FIG. 3. An example of a 2D-dimensional periodic material slab in the diamond structure with the (100) surface that has two dangling bonds that are capped with two hydrogen atoms. Note the short distance between the hydrogen atoms attached to the two different surface atoms.

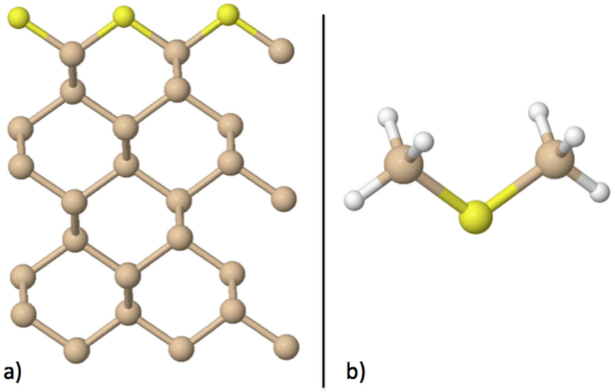

FIG. 4. A two-dimensional Si slab with an exposed (100) surface. Panel a) shows a surface capped with sulfur atoms. Panel b) shows the corresponding auxiliary molecule as discussed in the text.

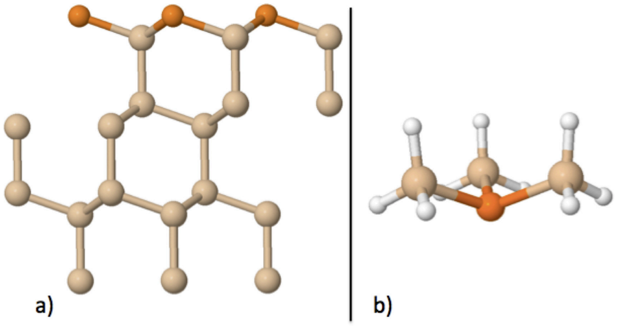

FIG. 5. A two-dimensional Si slab with an exposed (111) surface. Panel a) shows a surface capped with phosphorus atoms. Panel b) shows the corresponding auxiliary molecule as discussed in the text.

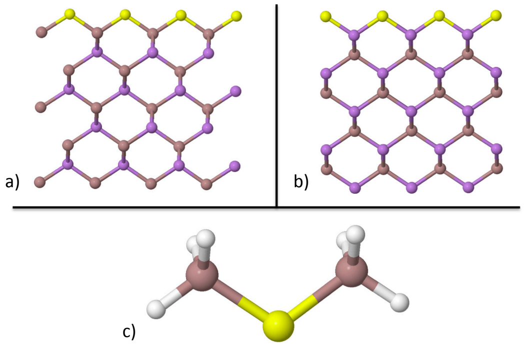

FIG. 6. A two-dimensional GaAs slab with an exposed (100) surface. Panel a) shows a GaAs(100) surface with Ga atoms exposed. Panel b) shows a GaAs(100) surface with As atoms exposed. Panel c) shows the corresponding auxiliary molecule used to calculate the GaAs(100) surface energy when the surface is Ga-terminated. Ga atoms are shown in grey and As atoms are shown in violet.

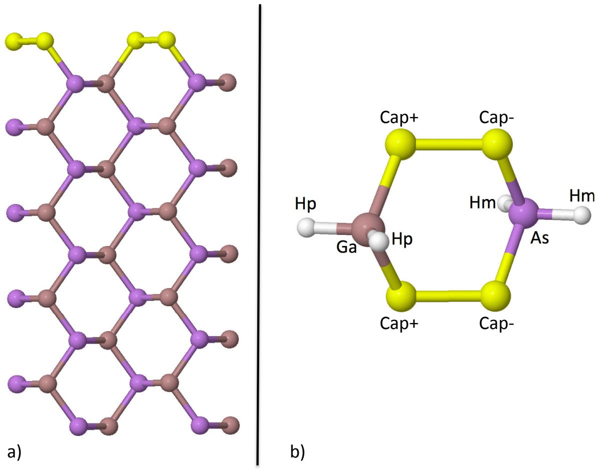

FIG. 7. A two-dimensional GaAs slab with an exposed (110) surface. Panel a) shows the GaAs(110) surface terminated with capping atoms. Panel b) shows the corresponding auxiliary molecule used in the calculations of the GaAs(110) surface energy. Hp and Hm denote partially charged hydrogen atoms, that have an extra charge of +0.25e/-0.25e respectively. Cap+ and Cap- denote the partially charged capping atoms (+0.25e/-0.25e respectively). The capping atoms in the bottom of the molecule are replacing Ga and As atoms in the bulk. Ga atoms are shown in grey and As atoms are shown in violet.

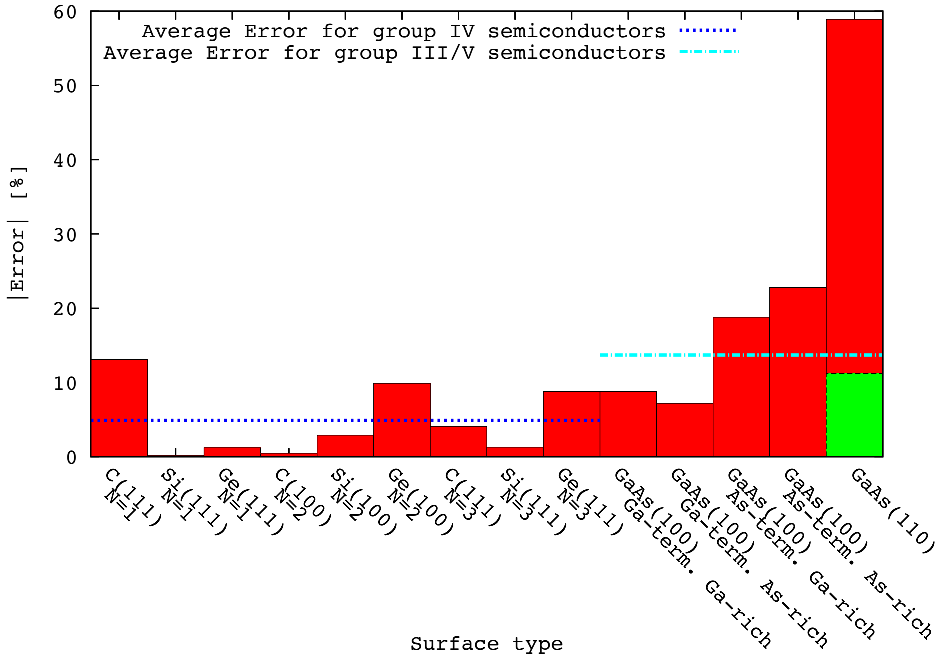

FIG. 8. A summary of the relative errors that are achieved with our method. Shown are the errors for Δ_{bulk}^{H} for each of the systems discussed in this paper that were obtained with the optimal capping atoms, as discussed in the text. The only exception is that Δ_{bulk} is shown for $N = 1$ (since Δ_{bulk}^{H} does not exist for N=1). For GaAs(110) we also show the error when S is used as a capping atom (green bar), since this gives significantly better results, as discussed in the text. The horizontal lines represent the average error for group IV semiconductors (blue, dotted line) and group III/V semiconductors (cyan, dashed-dotted line).

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