

First-principles calculations for charged defects at surfaces, interfaces, and two-dimensional materials in the presence of electric fields

Christoph Freysoldt and Jörg Neugebauer

Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40227 Düsseldorf, Germany

(Received 7 March 2018; published 16 May 2018)

We present a methodology to calculate the formation energy of a charged defect at a surface, an interface, or a two-dimensional material in the presence of a macroscopic electric field. We demonstrate that the proposed formalism corrects for electrostatic artifacts in standard repeated-slab calculations and allows us to extract reliably the formation energy in the isolated defect limit independently of vacuum thickness, slab thickness, or lateral supercell size. The formalism does not enter the self-consistency loop of a density functional theory (DFT) calculation, but requires as input only the electrostatic potential of the converged calculation. Thus, employing the proposed scheme does not require any changes in the DFT code, but only a postprocessing module that we provide for various codes.

DOI: [10.1103/PhysRevB.97.205425](https://doi.org/10.1103/PhysRevB.97.205425)

I. INTRODUCTION

Charges at surfaces, interfaces, or two-dimensional (2D) materials play an important role in creating or tuning macroscopic electric fields in a variety of technical applications, for instance in electronic and optoelectronic devices, in chemical sensors, or in electrochemistry and corrosion. These charges are often trapped at special sites, such as surface defects, dopants, or impurity atoms. For understanding the trapping sites' role in technical applications and ultimately controlling their impact, it is necessary to determine their thermodynamic and electronic properties. Significant progress has been made in recent years in calculating formation energies of point defects within bulk materials from first-principles electronic-structure calculations, notably within the framework of density functional theory (DFT) [1]. Yet, charged defects at surfaces and interfaces pose additional challenges to theoretical modeling. In particular, the energy changes associated with forming and charging surface defects depend on location of the countercharge, i.e., on the specific experimental scenario [2–6].

Two prototypical cases are sketched in Fig. 1. The first scenario (a) is a band-bending situation near the surface of a doped semiconductor. The surface charges (blue minus signs in Fig. 1) are compensated by dopants in the bulk material (blue plus signs). The electric potential (shown in green) decays into the bulk material within 10–100 nm (or even more), depending on the available dopant concentration. Outside the surface, in the vacuum or gas phase region, the potential is constant. The reservoir for additional electrons in this case is the Fermi energy. Deep inside the bulk, the position of the Fermi energy with respect to the potential is determined by the charge neutrality condition. The accumulation of charge at the surface, on the other hand, depends on the energetic position of the electronic trap states with respect to the Fermi energy: states above the Fermi level will be empty, while states below it will be filled. Obviously, the potential drop between the surface and the bulk is an essential aspect for understanding the energetics of the charge transfer process,

as has been recently discussed for vacancies in oxides and molecules on surfaces [4,5]. Case (b), on the other hand, depicts a situation where surface charging is induced by an external electrode. Here, the origin of charge (and hence the natural point of reference) is the counterelectrode. In consequence, the potential drop is between the electrode and the surface. The formal thermodynamics of this situation, notably when comparing constant-charge and constant-voltage processes, has been laid out in detail by Lozovoi and Alavi [3].

These two scenarios are of course extreme cases out of a continuum of possible situations where the countercharge is located on both sides of the surface. These intermediate cases are common for *interfaces* between two bulk materials. For instance, an electrically active interface between two doped semiconductors may acquire charge from both sides,

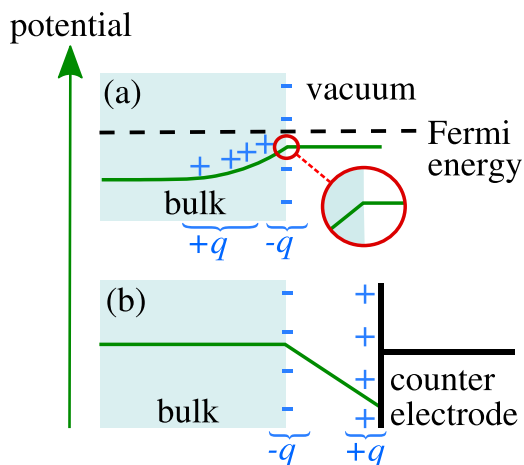


FIG. 1. Sketch of electron potential in prototypical scenarios across a charged surface: (a) Band bending due to an electron transfer from the (doped) bulk to the surface. The zoom-in (red circle) highlights the potential near the surface. (b) Charging due to an external electrode. The compensation charge sits on the counterelectrode.

depending on the doping levels, the intrinsic band alignment, and eventually the interface dipole for the interface at hand.

The electrostatics of such a situation will typically be described by continuum theory, in particular in device modeling [7–9]. Continuum modeling can easily bridge over length and time scales. Moreover, it may be augmented to also describe other device aspects (kinetic, optical, mechanical, etc.) in a common framework. When it comes to nanoscale devices, however, a proper mapping between the atomistic picture and its continuum model becomes important. For this purpose, we introduce a surrogate model of the defect at the interface that reproduces the macroscopic electrostatic potential of DFT as well as the dependence of the DFT energy on macroscopic boundary conditions. The boundaries enclose the region of interest within the atomistic model; in practice, planes parallel to the surface, interface, or 2D sheet are used.

The surrogate model’s purpose is to reduce the full complexity of electrostatic interactions to a few key parameters, notably dielectric constants as well as interface and defect positions that dominate the asymptotic behavior generally associated with macroscopic fields. The term “macroscopic” is to be understood here as exceeding the atomic length scale sufficiently such that continuum models can be applied. As continuum theory is scale free it is then no longer relevant for the constitutive equations whether the actual electric fields in experiment vary over a few nanometer or truly macroscopic distances. The surrogate model thereby accurately connects the true atomic-scale electrostatics with the macroscopic one in a controlled way. Likewise, the surrogate model completely (and purposefully) neglects artifacts due to other physical effects contained in the underlying DFT calculation, such as wave function overlap, strain, and quantum confinement [1]. Additional schemes may be needed to remove such artifacts from the calculated results.

As we name “surfaces,” “2D materials,” and “interfaces,” one should note that there is no conceptual difference between them as far as electrostatics is concerned. A surface is nothing but an interface between a bulk material on one side and vacuum or a gas phase on the other side. A “2D material” exhibits two dielectric interfaces, but in contrast to the artificial slab systems used for surfaces, the thickness is not an artificial modeling parameter but an intrinsic property of the material. The general theory can therefore be formulated in terms of interfaces. For readability, we will intermix the two terms. We shall typically use “interface” when we imply that the properties of the phases on *both* sides are relevant for the subsequent discussion, while we use “surface” when we focus mostly on one side.

As was mentioned earlier, surface and interface defects pose additional challenges to theoretical modeling. First, the broken 3D translational symmetry of the host material by the surface or the interface makes it necessary to use slab or superlattice models. Notably when using computer codes developed for 3D-periodic crystalline materials, the repeated-slab approach is commonly used for surfaces. The surface of interest and a small number of layers of the underlying host material form a thin slab, which is repeated periodically throughout space. A thin (~ 1 – 2 nm) vacuum region separates the slabs from each other in the direction normal to the surface plane. 2D materials are treated analogously. Interfaces can also be

modeled similarly (with a few layers of the bulk material on either side of the interface), or in the superlattice approach, where the vacuum layer separating the slabs is omitted in favor of a second interface. Unfortunately, the number of atoms that can be feasibly treated in electronic-structure calculations is limited to a few hundred. Therefore, the unavoidable second interface or surface at the bottom side of the slab may be rather close to the defect of interest, notably as the lateral size is increased to avoid interactions between the defect and its lateral periodic images at the same surface. This artificial proximity may lead to artifacts in the calculated energy, which must be carefully controlled or corrected for.

Second, introducing a formal charge to the system requires using a compensating countercharge, either put explicitly somewhere into the system [2–5] or implicitly by adjusting the boundary conditions [6,10]. The most common implicit condition is to set the average potential to zero and use periodic boundary conditions otherwise, which is equivalent to a homogeneous background [1,11–13]. This artificial placement of the countercharge must be corrected for or extrapolated to the limit of the isolated defect [4,5,12–14].

In this work, we present a formalism to calculate via DFT the formation energy of charged defects at surfaces and interfaces in the presence of an electric field. The formalism is based on a surrogate model for the electrostatics, detailed in Sec. II A, that can directly be used in subsequent continuum calculations. We demonstrate our approach for the dangling-bond defect at the H-saturated Si(111) surface. We describe in detail the steps necessary to remove the electrostatic artifacts due to the use of the repeated-slab approach (or supercell approach) in Secs. II C–II E. The electrostatic correction scheme developed for this purpose can be equally applied to defects at field-free surfaces, interfaces with and without field, and 2D materials, with various setups for the compensation charge. The implementation is interfaced to several DFT codes (VASP, Quantum Espresso, Socorro, SPHInX) and will be provided for download at our website [15]. We demonstrate convergence of the formation energy with respect to vacuum (Sec. II B), surface cell (Sec. II C), and slab thickness (Sec. II D). Last, in Sec. II E we report the inclusion of explicit electric fields in the DFT calculations and compare the results to the predictions from the surrogate model.

II. METHODOLOGY

A. Continuum electrostatics and the surrogate model

The main idea of our approach is to introduce a surrogate model within the framework of continuum electrostatics. This model shall reproduce the macroscopic behavior of the DFT electrostatic potential as well as the dependence of the DFT formation energies on the boundary conditions, notably the macroscopic electric field.

At the level of continuum theory, the electrostatic potential is defined by the effective Poisson equation (in hartree atomic units, notably with $\epsilon_0 = 1/4\pi$)

$$\nabla \cdot [\epsilon(\mathbf{r}) \nabla V(\mathbf{r})] = -4\pi \rho(\mathbf{r}). \quad (1)$$

Here, $\rho(\mathbf{r})$ is the charge density and $\epsilon(\mathbf{r})$ is the local dielectric constant that may vary throughout space. In contrast, dielectric screening is truly nonlocal in electronic structure theory. It may

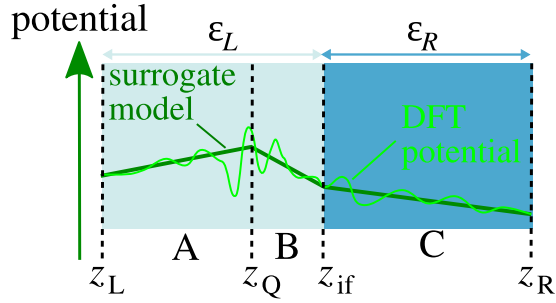


FIG. 2. Sketch of the electrostatic potential from DFT (light green) and the surrogate model (dark green). The special positions (z_L , etc.) and the regions A, B, and C are discussed in the text.

be formally expressed via

$$\delta V(\mathbf{r}) = \int d^3\mathbf{r}' \epsilon(\mathbf{r}, \mathbf{r}') \delta V^{\text{ext}}(\mathbf{r}'), \quad (2)$$

where δV^{ext} denotes a variation of the external potential (not due to electrons) that leads to a variation δV in the effective potential. The nonlocality of the microscopic dielectric function $\epsilon(\mathbf{r}, \mathbf{r}')$ is a consequence of the quantum nature of the electrons responsible for the screening. It is obvious that there is no unique way of mapping the nonlocal screening to a *local* dielectric constant. Only in bulklike regions, the average (macroscopic) dielectric constant is well defined. In transition regions, there is a variety of possibilities to define a local dielectric constant that reproduces asymptotically (i.e., far from the location of the charge) the same result. For the purpose of this work, we shall focus on the variation of the local dielectric constant across the interface, the *dielectric profile* $\epsilon(z)$, where z is the coordinate running perpendicular to the interface plane.

Within this context, the indispensable ingredients in our surrogate model are (1) the presence of a dielectric interface and (2) the presence of a finite charge; see Fig. 2. The dielectric interface implies that the macroscopic (bulklike) screening changes from one side of the interface to the other. The most simple realization is a sharp interface, characterized by the interface position z_{if} . The bulk dielectric constants ϵ_L and ϵ_R are dictated by the materials to the left (index L) and right (index R). Similarly, the most simple charge distribution for such a surrogate model is a point charge. Its position z_Q is a further

key parameter of the model. Its actual value is determined by the specific surface reconstruction (in most cases the position of the broken bond where the charge is localized) and thus is independent of z_{if} . The total amount of charge (Q) is not a free parameter; as the total charge determines the leading term in asymptotic behavior of the potential, it must agree with the underlying DFT calculation, i.e., with the defect charge. The left and right boundary planes for the surrogate model (at z_L and z_R , respectively) must enclose the entire interface and the charge, and therefore lie sufficiently deep in the bulklike region (or within vacuum for a surface) on each side.

Let us briefly discuss the model in one-dimensional form. The changes in the electric field $\mathcal{E} = dV/dz$ from the left ($\mathcal{E}_L$) to the right side ($\mathcal{E}_R$) are uniquely controlled by the dielectric interface contrast ϵ_L/ϵ_R and the surface charge Q/A , where A is the surface area:

$$\epsilon_L \mathcal{E}_L - \frac{4\pi Q}{A} = \epsilon_R \mathcal{E}_R. \quad (3)$$

The positions of interface and charge, z_{if} and z_Q , on the other hand, are essential to reproduce within the same surrogate model both the potential

$$V(z) = V_L + \int_{z_L}^z d\zeta \mathcal{E}(\zeta) \quad (4)$$

at and near the boundaries, *and* the energy

$$E = A \int_{z_L}^{z_R} dz [\rho(z) - \rho_{\text{ref}}(z)] \times \left\{ V_{\text{ref}}(z) + \frac{1}{2} [V(z) - V_{\text{ref}}(z)] \right\}. \quad (5)$$

The energy necessarily depends on the choice of the reference system (index ref), i.e., on the electrostatic situation when the point charge is removed. The reference case is characterized by a background charge, ρ_{ref} , and the associated potential V_{ref} . Different choices can be made [3]. For now, we will assume that the potential V_L and field $\mathcal{E}_L$ at z_L originate from the charge-free reference ($\rho_{\text{ref}} = 0$), which leads to

$$E = QV(z_Q). \quad (6)$$

Other references are possible, too [3]. In the sharp-interface plus point-charge surrogate model, the potential is explicitly given by

$$V(z) = \begin{cases} \text{region A: } z < z_Q, & V_L + \mathcal{E}_L(z - z_L), \\ \text{region B: } z_Q \leq z \leq z_{\text{if}}, & V_L + \mathcal{E}_L(z - z_L) - \frac{4\pi Q}{\epsilon_L A}(z - z_Q) \\ & = V_R + \mathcal{E}_R(z_{\text{if}} - z_R) + \frac{\epsilon_R}{\epsilon_L} \mathcal{E}_R(z - z_{\text{if}}), \\ \text{region C: } z > z_{\text{if}}, & V_L + \mathcal{E}_L(z_{\text{if}} - z_L) - \frac{4\pi Q}{\epsilon_L A}(z_{\text{if}} - z_Q) + \mathcal{E}_R(z - z_{\text{if}}) \\ & = V_R + \mathcal{E}_R(z - z_R). \end{cases} \quad (7)$$

Here, $\mathcal{E}_R$ is obtained from Eq. (3), and the potential on the right boundary is

$$V_R = V(z_R) = V_L + \mathcal{E}_L \left[z_{\text{if}} - z_L + \frac{\epsilon_L}{\epsilon_R} (z_R - z_{\text{if}}) \right] - \frac{4\pi Q}{\epsilon_L A} \left[z_{\text{if}} - z_Q + \frac{\epsilon_L}{\epsilon_R} (z_R - z_{\text{if}}) \right]. \quad (8)$$

The potential at the position of the charge reads

$$V(z_Q) = V_L + \mathcal{E}_L(z_Q - z_L) = V_R + \mathcal{E}_R \left[\frac{\epsilon_R}{\epsilon_L} (z_Q - z_{\text{if}}) + z_{\text{if}} - z_R \right]. \quad (9)$$

The expressions from the left side and the right side are obviously different; this is because we assumed the charge in Fig. 2 to be *left* of the interface, i.e., $z_Q < z_{if}$. If we had chosen it to be right of the interface, the corresponding expressions are obtained by exchanging the $_L$ and $_R$ indices. This distinction becomes a bit annoying when treating the field dependence in practical situations as discussed in Sec. II D below: we typically choose first a boundary plane, and then determine the surrogate model parameters, which show whether the charge position is before or behind the interface. To circumvent the need to give conditional expressions, we introduce an effective position z_{eff} of the charge with respect to the left boundary via

$$z_{eff} := z_L + \frac{\epsilon_L A}{Q} \int_{z_L}^{z_R} dz \rho(z) \int_{z_L}^z dz' \frac{1}{\epsilon(z')}. \quad (10)$$

The form of this equation is motivated by the analytic solution of the 1D Poisson equation provided in Appendix A. For the simple sharp-interface plus point-charge surrogate model, where $\rho(z) = \frac{Q}{A} \delta(z - z_Q)$, we obtain

$$z_{eff} = \begin{cases} z_Q, & \text{for } z_Q \leq z_{if}, \\ \frac{\epsilon_L}{\epsilon_R} (z_Q - z_{if}) + z_{if}, & \text{for } z_Q > z_{if}, \end{cases} \quad (11)$$

and the potential is given by

$$V(z_Q) = V_L + \mathcal{E}_L (z_{eff} - z_L). \quad (12)$$

We would like to emphasize that z_{eff} is not a new, independent parameter in the model. Instead, it is a slightly different way of expressing the position of the charge, a way which is ideally suited for discussing the dependence of energies with respect to the field at one specific boundary. Also, as the definition of the effective position is tied to one boundary, the effective positions for the left and right boundary do *not* agree. However, they can be easily converted; see Eq. (11).

This type of surrogate modeling is appealing because it is easy to extend. First, we may treat electrostatics in three dimensions to account for lateral interactions. We may add further dielectric interfaces to account for image effects in repeated-slab calculations. We may add a homogeneous background charge to allow for periodic boundary conditions. We may even allow for continuous changes in the dielectric profile (which is advantageous for numerical reasons) and similarly replace the point charge by an extended charge distribution. The connection of continuous profiles to the sharp-interface parameters is discussed Appendix A.

The key parameters of surrogate models (ϵ_L , ϵ_R , z_{if} , z_{eff}) that are fitted to reproduce the potential from repeated-slab DFT calculations not only provide a consistent picture of the formation energy of an isolated defect at a bulk surface (Secs. III B–III D), but also reproduce the field dependence (Sec. III E) required to simulate different experimental scenarios with a finite surface charging. Before we come to the details of how the parameters entering the surrogate model are obtained from the DFT calculation, we first summarize the algorithm used to solve the effective Poisson equation in three dimensions for continuous dielectric profiles and charge distributions.

B. Discretized image charge method

The method described here is an improved version of the image charge approach developed by some of us earlier [16]. It differs from the previous approach by employing a 2D Fourier transform parallel to the surface, which greatly enhances the convergence for lateral lattice summations, as well as a flexible use of open and periodic boundary conditions. For the purpose of completeness, we will describe again all steps of the algorithm in the following.

The image charge method is usually introduced for a single dielectric interface between region A and B with dielectric constants ϵ_A and ϵ_B , respectively [17]. The potential due to a point charge Q in region A can be obtained as follows. For region B, it can be described by a modified charge at the location of the original charge (i.e., in region A), screened by ϵ_B . However, the value of the effective charge for region B is [17]

$$\frac{2\epsilon_B}{\epsilon_A + \epsilon_B} Q = \frac{2\epsilon_A^{-1}}{\epsilon_A^{-1} + \epsilon_B^{-1}} Q. \quad (13)$$

The latter form is directly applicable to metals with $\epsilon^{-1} = 0$. For lack of a better name, and because the new effective charge propagates the effect of the charge from region A to region B, we call it *propagated* charge [16]. For region A, the potential arises from the original charge and an additional image charge, both screened by ϵ_A . The image charge is located in region B, at a position arising from mirroring the original location at the interface plane. The value of the image charge is

$$\frac{\epsilon_A - \epsilon_B}{\epsilon_A + \epsilon_B} Q = \frac{\epsilon_B^{-1} - \epsilon_A^{-1}}{\epsilon_A^{-1} + \epsilon_B^{-1}} Q. \quad (14)$$

Note that the propagated and the image charge are *not* located in the region for which they apply.

If region A is bounded by another dielectric interface (parallel to the one just considered) to region C, the effect of the image charge in region B requires an additional image charge in region C, which in turn requires a new image charge in region B, etc. Conversely, the interface to an additional region D adjacent to region B (the interfaces being again parallel) will require a new image charge in region D due to the propagated charge for region B (located in region A). The effect of this image charge must then be propagated through the B/A interface to region A, and will likewise produce an infinite series of further image charges. It may seem impractical to track all these image charges in the presence of a large number of interfaces, and probably is so in the general case. However, if the interfaces are all equidistant, the image charges can be computed and summed very efficiently.

In order to solve the Poisson equation for arbitrary dielectric profiles, Eq. (1), using the image charge method, the dielectric profile and charge distribution are discretized in the z direction. The dielectric profile will consist of a series of dielectric slabs with thickness d and constant dielectric properties (ϵ_i) throughout the slab, and sudden jumps at the interfaces located at $z = (i + \frac{1}{2})d$, where i is an integer number. The charge distribution is confined to the center of each dielectric slab, with an arbitrary lateral distribution

$$\rho(x, y, z) = \sum_i \rho(x, y, z_i) \delta(z - z_i), \quad (15)$$

where $z_i = i \cdot d$. The advantage of this approach is that all image charges sit again in the center of the slabs. The potential in each slab is then given by the charges inside the slab (intralayer) and the real and image charges outside this layer (interlayer). While the intralayer potential is ill defined for charge delta sheets (it cancels when making differences, as explained below), the interlayer one is given by

$$V(x, y, z_i) = \frac{1}{\varepsilon(z_i)} \int dx' \int dy' \sum_{n=1}^{\infty} \sum_{\sigma=\pm 1} q(x', y', i, \sigma, n) \times \frac{q(x', y', i, \sigma, n)}{\sqrt{n^2 d^2 + (x - x')^2 + (y - y')^2}}. \quad (16)$$

Here, $q(x, y, i, \sigma, n)$ is the effective charge for the calculation of the potential in layer i , sitting at a position $z_i + \sigma n$. The effective charges combine the image and propagated charges arising from the various interfaces. They are recursively determined via

$$q(x, y, i, \sigma, n+1) = \frac{2\epsilon_i}{\epsilon_i + \epsilon_{i+\sigma}} q(x, y, i + \sigma, \sigma, n) + \frac{\epsilon_i - \epsilon_{i+\sigma}}{\epsilon_i + \epsilon_{i+\sigma}} q(x, y, i, -\sigma, n) \quad (17)$$

with the start value

$$q(x, z, z_i, \pm 1, 0) = \rho(x, y, z_i). \quad (18)$$

Last, Fourier transformation of the x and y coordinates to $\mathbf{k}_{||} = (k_x, k_y)$ does not change the structure of the vertical discretization [Eq. (15)], effective charge recursion [Eq. (17)], and initialization [Eq. (18)], but the potential [Eq. (16)] simplifies to

$$V(\mathbf{k}_{||}, z_i) = \frac{2\pi}{|\mathbf{k}_{||}| \varepsilon(z_i)} \sum_{n, \sigma} q(\mathbf{k}_{||}, z_i, \sigma, n) e^{-n|\mathbf{k}_{||}|d}. \quad (19)$$

Here we have used the 2D Fourier transform of the Coulomb potential

$$\begin{aligned} \int dx dy \frac{1}{\sqrt{x^2 + y^2 + z^2}} e^{-i(k_x x + k_y y)} \\ = \int dk_z \frac{4\pi}{k_x^2 + k_y^2 + k_z^2} e^{ik_z z} = \frac{2\pi}{\sqrt{k_x^2 + k_y^2}} e^{-\sqrt{k_x^2 + k_y^2}|z|}. \end{aligned} \quad (20)$$

For $|\mathbf{k}_{||}| > 0$, the exponential factor makes the sum over n unconditionally convergent, and can be straightforwardly generalized to include also the intralayer potential. Thus, the ill-definedness of the intralayer potential arises exclusively from the $\mathbf{k}_{||} = \mathbf{0}$ component.

For $\mathbf{k}_{||} = \mathbf{0}$, the image charge method is not applicable. Instead, we solve the original Poisson equation Eq. (1) directly, subject to the same discretization as used for $|\mathbf{k}_{||}| > 0$. For $\mathbf{k}_{||} = \mathbf{0}$, the Poisson equation reduces to the ordinary differential equation

$$\frac{d}{dz} \left[\epsilon(z) \frac{d}{dz} V(\mathbf{k}_{||} = \mathbf{0}, z) \right] = -4\pi \rho(\mathbf{k}_{||} = \mathbf{0}, z), \quad (21)$$

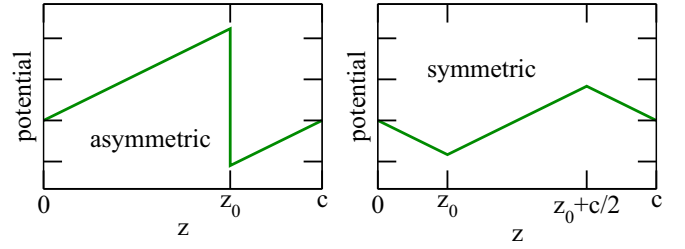


FIG. 3. Sketch of an asymmetric sawtooth potential [Eq. (25)] and a symmetric one [Eq. (26)].

which can be piecewise integrated to

$$V(\mathbf{k}_{||} = \mathbf{0}, z) = \begin{cases} V_i + (z - z_i) \epsilon_i^{-1} D_i, & \text{for } z_i - \frac{1}{2}d \leq z < z_i, \\ V_i + (z - z_i) \epsilon_i^{-1} D_{i+1}, & \text{for } z_i \leq z < z_i + \frac{1}{2}d, \end{cases} \quad (22)$$

$$V_{i+1} = V_i + \frac{d}{2} (\epsilon_i^{-1} + \epsilon_{i+1}^{-1}) D_{i+1}, \quad (23)$$

$$D_{i+1} = D_i - 4\pi \rho(\mathbf{0}, z_i). \quad (24)$$

Here, V_i is the potential at the center of slab i , and D_i is the electric displacement between z_{i-1} and z_i . For finite systems, some start values must be chosen to reflect the desired boundary conditions. For periodic boundary conditions, the total charge must be zero, and the initial D_0 must be chosen such that $V_i = V_{i+N}$. In practice, we compute first the two cases (a) $V_0 = 0$, $D_0 = 0$ with the given $\rho(\mathbf{0}, z)$ and (b) $V_0 = 0$, $D_0 = 1$ and $\rho(z) = 0$, and then set $D_0 = -V_N^{(a)} / V_N^{(b)}$.

The proposed discretization converges only slowly to the limit of a continuous distribution. However, for calculating energy differences between isolated and periodic systems which have identical localized charge distributions and dielectric profiles in the region of interest, the discretization errors cancel to a very large degree.

C. Determination of dielectric interface parameters

The bulk dielectric constants to the left and right of a dielectric interface are properties of the respective materials. They can be determined from density functional perturbation theory [18], or from the response to a finite sawtooth potential [19]. In the latter approach, the response in the plane-averaged electrostatic potentials is fitted to straight line segments, and the slope is compared to the applied field in that region. This approach is particularly convenient to determine the equivalent position of a sharp dielectric interface. For this, we apply a periodic asymmetric sawtooth potential

$$V_{\text{saw}}(z) = \mathcal{E}(z - z_0) - \frac{1}{2} \mathcal{E}c \text{ for } z_0 \leq z < z_0 + c \quad (25)$$

for slabs in vacuum (with the cut being in the middle of the vacuum), or a periodic symmetric sawtooth potential

$$V_{\text{sym-saw}}(z) = \mathcal{E} |z - z_0 - \frac{1}{2}c| \text{ for } z_0 \leq z < z_0 + c \quad (26)$$

in the case of superlattices for modeling interfaces between two bulk materials. The shape of the two variants is sketched in Fig. 3. If the supercell is large enough, there will be distinct regions within the supercell where a constant electric field

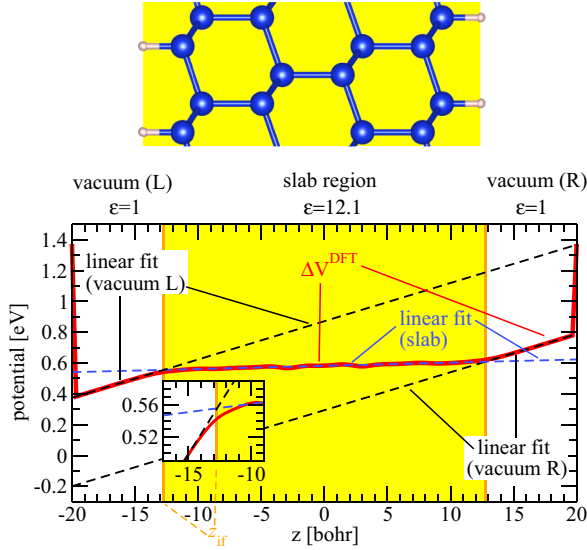


FIG. 4. Change in the DFT electrostatic potential ΔV^{DFT} (red solid line) of an 8-layer H-saturated Si(111) slab, averaged over the xy plane, upon applying an external sawtooth potential across the slab. The dipole correction [20] was used in addition. The dashed lines are linear fits in the two vacuum (L and R) and slab regions, respectively. The crossing points of the vacuum and slab linear fits define the dielectric interface position z_{if} (orange line) for a dielectric slab model (yellow region) with sharp interfaces. The jump at $z = \pm 20$ bohrs arises from the dipole correction.

is applied to a bulklike material and a bulklike response is observed. This is demonstrated in Fig. 4 for an 8-layer H-saturated silicon slab in vacuum. These bulklike regions are separated by transitional regions (see inset) that encompass the actual dielectric interfaces. In order to determine the interface position z_{if} , the plane-averaged change in the electrostatic potential is fitted to a macroscopic, straight-line behavior (see Fig. 4). Extrapolating these straight line segments to the material interface yields crossing points that define the equivalent position of a sharp dielectric interface. On the other hand, the reduction factor of the applied effective field compared to the fitted one (the slope) yields the effective dielectric constant of the material.

Figure 4 demonstrates the procedure for an 8-layer H-saturated Si(111) slab. The slab is located in the yellow-shaded region. The change in the DFT electrostatic potential clearly shows three distinct spatial regions: the vacuum below the slab ($z < -13$ bohrs), the vacuum above the slab ($z > 13$ bohrs), and the Si slab in between. Linear fits to the potential change within these regions (dashed lines) allow us to extract the effective dielectric constant of the slab (12.13), which is in reasonable agreement with the known value of 12.7 from density functional perturbation theory [18]. The small discrepancy (-4.5%) arises from the finite size of the slab, which may not yet have acquired the properties of the extended bulk. It turns out that the corrections derived below are not very sensitive to such small variations in the dielectric constant, and using the bulk value of 12.7 yields practically the same results. In addition to the dielectric constant, the linear fits define the dielectric interface positions z_{if} by their crossing

points. They turn out to be located approximately at the height of the saturating H atoms. Similarly to the case of the dielectric constant, variations in the interface position by a few 0.1 bohrs do not lead to significant changes in the corrections.

We note in passing that the well-known dipole correction [20] for neutral slabs implicitly employs an asymmetric sawtooth potential. Therefore, if the DFT code at hand does not have the option of adding arbitrary external potentials (as SPHInX [21] does), the implementation of the dipole correction may offer easy access to asymmetric sawtooth potentials. But even when the dielectric interface properties cannot be determined correctly and are estimated instead, the scheme sketched out below yields robust results as discussed at the end of Sec. II E.

D. Defect formation energy

We begin by recalling the formalism for defects in the absence of an external field in bulk materials. For a defect with charge Q , it can be written as [1]

$$E^f(E^F - V_0, \mu_i) = E_0^f - \sum_i \mu_i \Delta n_i + Q(E^F - V_0). \quad (27)$$

μ_i are the chemical potentials of all chemical species added ($\Delta n_i > 0$) or removed ($\Delta n_i < 0$) to create the defect from the defect-free case [1]. E_0^f denotes the reference energy of the defect at zero chemical potentials and when the electronic reservoir, the Fermi energy E^F , coincides with the zero of the potential energy scale V_0 . V_0 is typically taken to be the valence band maximum far from the defect. The value of E_0^f is extracted from DFT calculations for a defect-containing supercell, the defect-free bulk of the host material, and bulk or molecular reference systems that define the chemical potential for atoms added or removed in the defect [1]. For charged defects in finite supercells, additional corrections (or extrapolation) must be applied [1,11,22,23].

The main challenge introduced by an electric field is that there no longer is a unique energy zero “far from the defect.” This challenge is solved by referencing with respect to a specific boundary plane instead [3]. We therefore replace V_0 by a suitable expression that reflects how the formation energy changes as we change (a) the boundary potential V_L or (b) change the boundary electric field $\mathcal{E}_L$, namely,

$$V_0 \rightarrow V_L + \Delta U(\mathcal{E}_L) = V_L + \frac{d\Delta U}{d\mathcal{E}_L} \mathcal{E}_L + O(\mathcal{E}_L^2). \quad (28)$$

Here, ΔU denotes the change of the potential near the defect when the field at the boundary plane is varied.

This is exactly the question discussed above in Sec. II A for the surrogate model in one dimension, where we had shown that the potential near the localized charge can be written as [cf. Eq. (12)]

$$V(z_Q) = V_L + \mathcal{E}_L(z_{\text{eff}} - z_L) \quad (29)$$

with a suitably chosen effective position z_{eff} with respect to the boundary plane. It should be pointed out again that z_{eff} also accounts for the dielectric screening effects between the boundary plane and the actual defect. It may therefore be different from the actual center of charge z_Q . Rather, it is a convenient way of expressing the field dependence of the

potential drop

$$\Delta U(\mathcal{E}_L) = (z_{\text{eff}} - z_L)\mathcal{E}_L + O(\mathcal{E}_L^2). \quad (30)$$

By combining Eq. (28) with Eq. (27) and neglecting the nonlinear contributions, we arrive for the field-dependent formation energy at

$$\begin{aligned} E^f(E^F - V_L, \mathcal{E}_L, \mu_i) \\ = E_0^f - \sum_i \mu_i \Delta n_i + Q[E^F - V_L - (z_{\text{eff}} - z_L)\mathcal{E}_L]. \end{aligned} \quad (31)$$

E_0^f now denotes the reference energy of the defect at zero field, zero chemical potentials, and when the electronic reservoir, the Fermi energy E^F , coincides with the electron potential at the reference plane z_L . The effective position z_{eff} is not known *a priori*. Rather, we should at this point regard Eq. (31) as the implicit definition of z_{eff} , namely the one that reproduces the field-dependence of the formation energy. On the other hand, once it is known for a particular boundary plane, it is straightforward to use continuum theory to switch to a different reference in the continuum model. We remind the reader at this point that this change of reference is exactly the step where the experimental scenario can be adopted, based on the boundary-plane referenced data discussed in this section. What remains to be explained is how we arrive at the boundary-plane reference from standard electronic-structure calculations, that typically work with a very different implicit reference for charged calculations. The corrections needed for this are described in the next section.

E. Extrapolation of defect parameters from the repeated slab approach

Once the dielectric modeling parameters for the defect-free slab system have been determined, the dielectric modeling can be used to extrapolate calculated defect formation energies from the slab system to the limiting case of isolated defects on a bulk surface. We will start by focussing on the field-free case first, and discuss the field dependence later in Sec. III E. For this, we employ an adapted version of the correction formalism proposed by us earlier for bulk systems [11]. In brief, it consists of a “periodicity” correction and an alignment-like term. The periodicity correction accounts for the fact that the DFT energy corresponds to placing the charged defect in a periodic array with a compensating background. It is obtained by modeling the periodic and isolated defects in an electrostatic continuum model, which in the bulk case reduces to a screened Madelung energy of point charges (or Gaussians). The alignment-like correction is necessary because the alignment convention in DFT and in the model calculation is different [11,24]. The successful adaptation of this scheme to slab systems has been demonstrated first by Komsa *et al.* [12], who employed a FFT-based solver for the effective Poisson equation, Eq. (1).

In the present work, we estimate the electrostatic interaction energy in the slab system as compared to a defect at a bulk surface from our dielectric model as

$$\Delta E^{\text{model}} = E_{Q/\text{slabs}}^{\text{model}} - E_{Q/\text{surface}}^{\text{model}}. \quad (32)$$

Here $E_{Q/\text{slabs}}^{\text{model}}$ is the energy of a periodic array of slabs with a periodic arrangement of localized Gaussian charges near the slabs’ surfaces, calculated from the Poisson solver described in Sec. II B. Likewise $E_{Q/\text{surface}}^{\text{model}}$ is the energy of an isolated Gaussian charge at a bulk surface. The charge distributions of the localized model charge as well as the dielectric profiles agree locally between the periodic slab and isolated surface cases. Differently from the approach taken by Komsa *et al.* [12], we take advantage of being able to apply periodic boundary conditions for the periodic slab case, and open boundary conditions for the surface case in the *same* scheme, while they had to resort to finite-size extrapolation within the model calculation to obtain the isolated surface reference [12]. We note in passing that an alternative algorithm to compute potentials for open boundary conditions has been proposed based on a truncated Green’s function approach [25]. This algorithm—like ours—may also treat periodic boundary conditions, but has not been used for this purpose in practice.

For the alignment term, we then subtract from the change in the DFT electrostatic potential

$$\Delta V^{\text{DFT}} = V^{\text{DFT}}(\text{slab} + \text{defect}) - V^{\text{DFT}}(\text{slab}) \quad (33)$$

the corresponding model potential to determine the unknown alignment constant C between the two cases, such that the “short-range potential”

$$\Delta V^{\text{DFT}} - C - V_{Q/\text{slabs}}^{\text{model}} \quad (34)$$

approaches zero far from the defect [11], notably in the vacuum region [cf. Fig. 5(b)]. The correction energy for a defect with charge Q then reads [11,12,24]

$$\Delta E^{\text{corr}} = \Delta E^{\text{model}} + QC. \quad (35)$$

We would like to emphasize that these corrections do not rely on the use of our particular DFT code SPHInX. The `sxdefectalign2d` program, which implements the Poisson solver, is interfaced to the potential format of several common DFT programs, but it can also be used as a stand-alone program to produce only the model potential and energies.

Of course, the scheme is designed to remove the influence of the artificial electric fields within the DFT calculation. The key point with respect to the treatment of electric fields according to Eq. (31) is that the precise location of the center of the Gaussian charge z_Q along the z direction is a hitherto free parameter in the modeling. This freedom can now be used to reflect the actual charge distribution in the DFT calculation. Similarly to the bulk case, the criteria for this is that the corrected potential, Eq. (34), is free of an electric field. We achieve this by manually varying the position of the charge along z until the corrected potential [Eq. (34)] becomes flat in the vacuum region; see Fig. 5. The upper graph, Fig. 5(a), shows the case where the charge is incorrectly placed. Specifically z_Q was chosen such that z_{eff} coincides with the interface plane z_{if} . Figure 5(b) shows the correct placement. As this adaptation of position is an essential part of the alignment procedure, it is controlled via a command-line option and might be automatized in the future. The physical position of the charge within the model is not the effective position z_{eff} , but uniquely determines it via Eq. (10). Likewise, the model charge distribution by itself as well as the precise shape of the dielectric interface are not critical for the

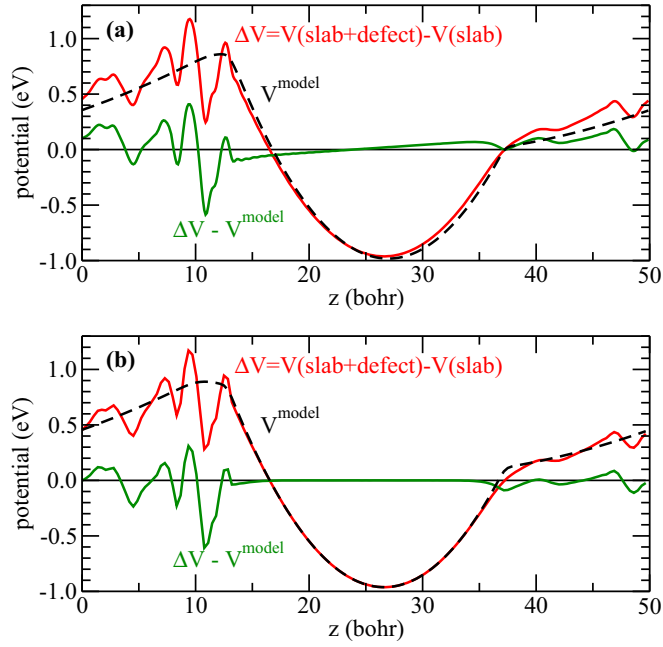


FIG. 5. Alignment of the model potential for a $Q = -1$ dangling-bond defect at a 2×2 Si(111) surface (cf. Fig. 6). (a) Incorrect placement of Gaussian charge at $z_Q = 11.61 \Leftrightarrow z_{\text{eff}} = 12.74$ bohrs $= z_{\text{if}}$. (b) Correct placement of Gaussian charge at $z_Q = 10.33 \Leftrightarrow z_{\text{eff}} = 10.38$ bohrs. All potentials are averaged over the xy plane. Red (light) solid line: defect-induced change in the DFT electrostatic potential without corrections. Dashed line: potential from the surrogate model (interface broadening: 0.5 bohrs). Green (dark) solid line: DFT potential with correction from model.

success of the scheme. What matters is that they reproduce the macroscopic effects, which are condensed in $\Delta E^{\text{model}}, z_{\text{eff}}$, and the alignment constant C . We will demonstrate below in Sec. III E that the effective position determined in this way is in excellent agreement with actual finite-field DFT calculations, while the convergence tests discussed in Secs. III B to III D demonstrate how the corrections largely remove the influence of artificial slab geometry.

An example of a successful alignment is shown in Fig. 5(b). Clearly, the dielectric model (black dashed line) excellently reproduces the defect-induced change in the DFT potential (red line) in the vacuum region. Inside the slab, the DFT potential fluctuates around the continuum model which reflects the details of microscopic screening neglected in continuum theory due to the use of a somewhat averaged local dielectric constant instead of the full nonlocal dielectric screening (see Sec. II A). An important aspect of the modeling is that the short-range potential (green line) shows no visible electric fields inside the slab, highlighting that the charge is indeed localized. If it was not, the charge separation between the model charge and the actual charge distribution would induce a slope in the short-range potential. Thus, the shape of the short-range potential within the slab serves as an indicator for the validity of the underlying assumption of a localized defect charge. In other words, similarly to the bulk case, the scheme allows us to verify that the expectation of a localized charge (and hence the reliability of the correction) is fulfilled.

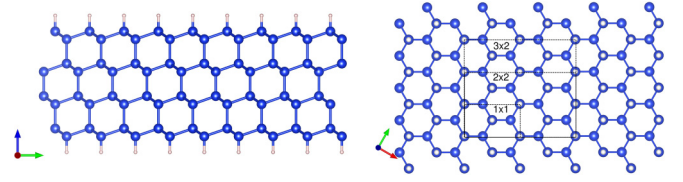


FIG. 6. Si(111) slabs used in this work. Left: side view of the 8-layer Si slab. Right: top view on the surface, showing the topmost H and the top two Si layers. Orthonormal surface unit cells are indicated. Blue large spheres depict Si atoms, white small spheres H atoms.

Does the short-range potential also show problems in modeling the dielectric interface itself? Does it show problems, for instance, if the interface parameters (dielectric constants on either side as well as the interface position; see Sec. II C) have been estimated rather than determined via the procedure of Sec. II C? Test calculations with a purposefully incorrect dielectric model showed that variations of the slab dielectric constant of 12.13 by $\pm 10\%$ are difficult to detect, but changed the correction by ± 0.001 eV only. Variations in the interface position may yield much larger errors (up to 0.06 eV in the correction when shifting interfaces by $\Delta z_{\text{if}} = 1$ bohrs), but produce a pronounced potential drop at the interface:

$$\Delta V_{\text{if}} = (\mathcal{E}_1 - \mathcal{E}_2) \Delta z_{\text{if}} = \left(1 - \frac{\epsilon_1}{\epsilon_2}\right) \mathcal{E}_1 \Delta z_{\text{if}}. \quad (36)$$

Here $\mathcal{E}_1$ and $\mathcal{E}_2$ denote the electric field on either side of the interface, and ϵ_1, ϵ_2 the corresponding dielectric constants. By comparing the alignment of the short-range potential inside and outside the slab (which should be identical if the dielectric interface is correctly modeled), such mistakes are easily detected and might even be corrected pragmatically by adjusting the dielectric interface position from the alignment procedure. However, if the model charge itself overlaps with the uncertain part of the dielectric interface, such pragmatic procedures may lead to uncontrolled errors and cannot be recommended in general.

III. RESULTS

A. Dangling bond at the Si(111) surface

The methodology will be demonstrated for a dangling-bond defect at the H-saturated Si(111) surface. The Si(111) surface is a prototypical semiconductors surface. When truncated from the bulk, there is one broken bond per surface atom. The Si(111) undergoes a 7×7 reconstruction in vacuum [26], but maintains a 1×1 periodicity if each broken bond is saturated with hydrogen [27]. Removing a single hydrogen atom from an otherwise saturated surface leaves an isolated dangling-bond defect. The defect state associated with it can take 0, 1, or 2 electrons, corresponding to the +1, 0, and -1 charge states. The possibility to switch from positive to negative charge within the same defect was a major motivation for using this particular defect. Wherever the +1 and -1 charged states show the same energy dependence, it is likely that electrostatic effects are at play. The atomic structure of the slabs is depicted in Fig. 6. For the surface unit cell, we employed multiples of the orthonormal cell of this hexagonal surface.

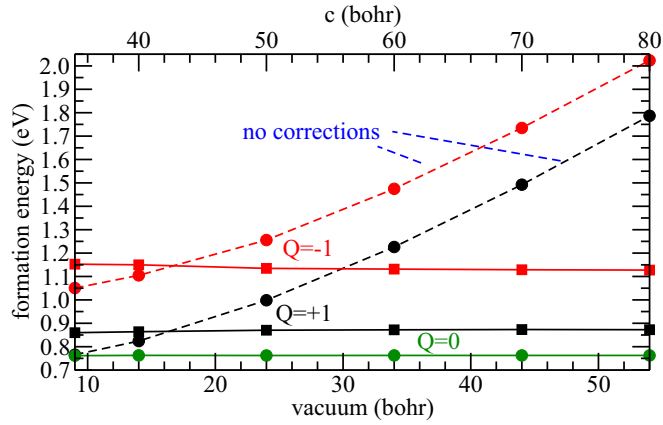


FIG. 7. Convergence of formation energy of a dangling-bond defect Si(111) with respect to vacuum separation in the repeated slab approach. The slab has 8 Si layers and a 2×2 orthorhombic surface unit cell (8 surface atoms). The c lattice constant (top scale) defines the vacuum separation between adjacent slabs. Different charge states are shown: -1 [red (light)], 0 [green (dark)], $+1$ (black). Circles show raw data. Squares show corrected values for the charged defects (see text).

The DFT calculations were performed with the SPHInX code [21] using norm-conserving pseudopotentials [28] and a plane-wave basis set with a cutoff of 20 Ry. For exchange and correlation, the local density approximation (LDA) was used. The lattice constant of bulk silicon in this approach is 10.2 bohrs. The $\mathbf{k}$ -point sampling for the slab system corresponded to at least a $4 \times 4 \times 1$ sampling in the orthorhombic cells. Test calculations with larger $\mathbf{k}$ -point sets indicate that the uncertainty in formation energies due to the $\mathbf{k}$ -point sampling is below 0.005 eV. From a pragmatic point of view, uncertainties on the order of 0.05–0.1 eV are expected to be sufficient for many practical applications when considering the many other sources of uncertainties, not least the underlying approximation for the exchange-correlation functional [1].

B. Convergence with respect to vacuum

We start our discussion by looking at the most dramatic artifact in charged slab supercell calculations, the formation energy as a function of the vacuum thickness. The Si(111) slab for this section consists of 8 layers of silicon, saturated by H on both sides (cf. Fig. 6). Starting from the orthorhombic surface cell (two surface atoms on each side), a 2×2 supercell (8 surface atoms/side) was constructed. From this, a single H atom was removed to create the dangling-bond defect. The total slab is ~ 26 bohrs thick (bottom H to top H).

Figure 7 shows the formation energy of charged and neutral dangling-bond defects as a function of the total cell height c (upper scale), or equivalently the vacuum thickness (computed as $c - 26$ bohrs, as 26 bohrs is the thickness of the slab region in the surrogate model; cf. Fig. 4). For charged defects, the Fermi energy was set to 4.78 eV below the vacuum level of the defect-free slab, which corresponds to the position of the bulk valence band maximum. The dashed line shows the results in the absence of any further corrections. Clearly, the charged defects suffer from a severe variation of the computed

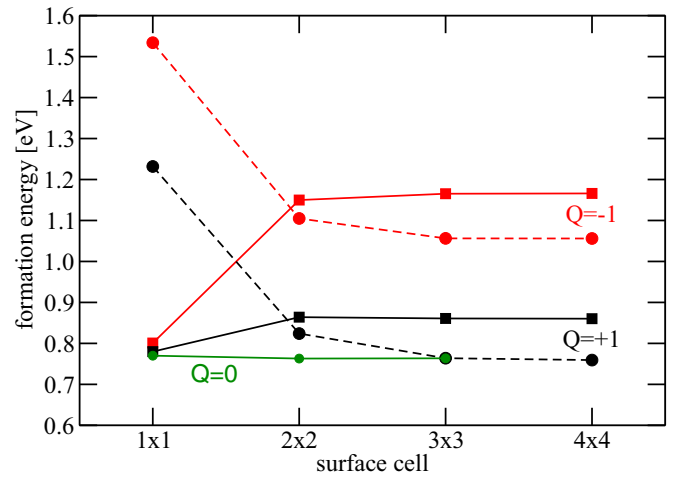


FIG. 8. Convergence of formation energy of a dangling-bond defect at Si(111) with respect to surface unit cell size in the repeated slab approach. The slab has 8 Si layers and a $N \times N$ orthorhombic surface unit cell as indicated (1×1 with two surface atoms). The cell height was $c = 40$ bohrs. Different charge states are shown: -1 [red (light)], 0 [green (dark)], $+1$ (black). Circles show raw data. Squares show corrected values for the charged defects (see text).

result on the cell height. Both charge states show a linear divergence in the computed energy (plus some higher-order term for small vacuum thicknesses), which is independent of the sign of the charge. In contrast, the neutral defect shows a formation energy practically independent from the vacuum thickness. The divergence for charged states can be qualitatively understood from the capacitor model [2]. In brief, the vacuum spacing determines the charge separation between the defect and the compensating background, such that the potential difference between the center of the slab and the center of vacuum increases linearly with vacuum size. Our dielectric modeling perfectly reproduces this effect. After correcting our energies with Eqs. (32)–(35), the result very rapidly converges with the vacuum thickness. For $c \geq 60$ bohrs (i.e., a vacuum separation of 34 bohrs), the results agree to within 5 meV. For a more realistic target accuracy of 0.05 eV, even the smallest vacuum thickness of 10 bohrs is sufficient.

C. Convergence with respect to surface unit cell

A further relevant parameter is the lateral supercell size used for the simulations. We investigated this by calculating $N \times N$ supercells of the orthonormal unit cell (cf. Fig. 6) for $N = 1, 2, 3$, and 4. We note in passing that the computational cost rapidly increases along this series, because the system size (number of atoms) increases like N^2 , and the computational cost of DFT increases like $N_{\text{atom}}^2 \dots N_{\text{atom}}^3$. In practice, the 4×4 calculation takes $1000\times$ more computer time than the 1×1 . For the vacuum thickness, we chose a cell height of 40 bohrs, where the absolute corrections due to the vacuum are small (below 0.1 eV; see Fig. 7).

Figure 8 shows the comparison between the corrected results and the raw results. Obviously, even the uncorrected results converge to some value as the lateral size is increased, but that value still depends on the vacuum size (not shown) and

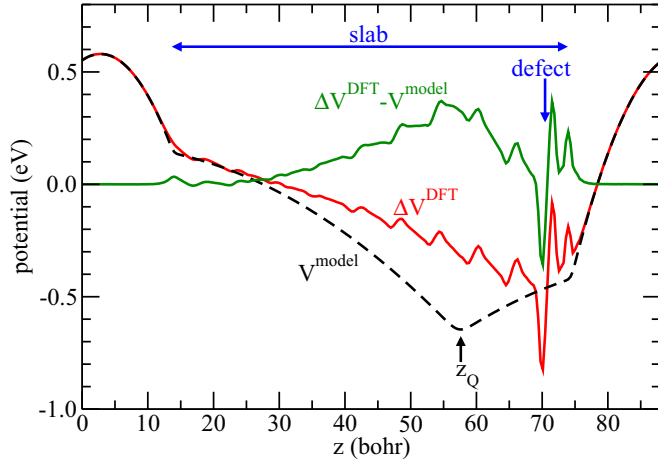


FIG. 9. Detection of dielectric breakthrough for a $Q = +1$ dangling-bond defect at a 3×2 Si(111) 20-layer slab in the potential alignment. All potentials are averaged over the xy plane. Red (light) solid line: defect-induced change in the DFT electrostatic potential without corrections. Dashed line: potential from the dielectric model with a Gaussian charge sitting at $z_Q = 57.3$ bohrs. Green (dark) solid line: DFT potential with correction from model.

therefore does not agree with the fully corrected one. Applying the corrections yields the laterally converged result already for a 2×2 cell to within 0.06 eV, at less than a tenth of the cost of the 4×4 calculation. The 1×1 case is clearly insufficient. A major problem in this case is that the lateral separation of the defects is comparable to the width of the dielectric transition region, rendering the simplifications to the dielectric interface profile inaccurate. In addition, also other direct interactions between the defects, such as wave function overlap, may contribute to the deviations from the converged result. On the other hand, the improvement in lateral convergence due to the corrections for the 2×2 cell is apparent.

D. Convergence with respect to slab thickness

The convergence with respect to slab thickness turned out to be more complex than for the vacuum thickness and surface unit cell. First, by modifying the thickness of the slab we vary quantum confinement effects in the slab for the bulklike states in the slab, the surface resonances due to the Si-H bond, and even the defect states, notably in the $+1$ charge state where the dangling-bond state lies close to the valence band maximum. Second, we face the possibility of dielectric breakthrough: The internal potential inside the slab set up by the charge separation between the defect and the compensating background may exceed the band gap. In this case, the slab charge is not localized at the defect only, but distributed in part to the other side of the slab. In consequence, the Fermi level is pinned from both sides of the slab. We observed this behavior for our slabs with a 3×2 surface unit cell if the slab thickness exceeded 12 layers for the $+1$ charge state and 16 layers for -1 , respectively.

Figure 9 shows an example of the alignment procedure in the case of dielectric breakthrough, namely the $+1$ charge state on a 20-layer slab. In order to remove the total dipole moment, it was necessary to shift the effective position of the charge in the dielectric model to $z_Q = 57.3$ bohrs, 13 bohrs

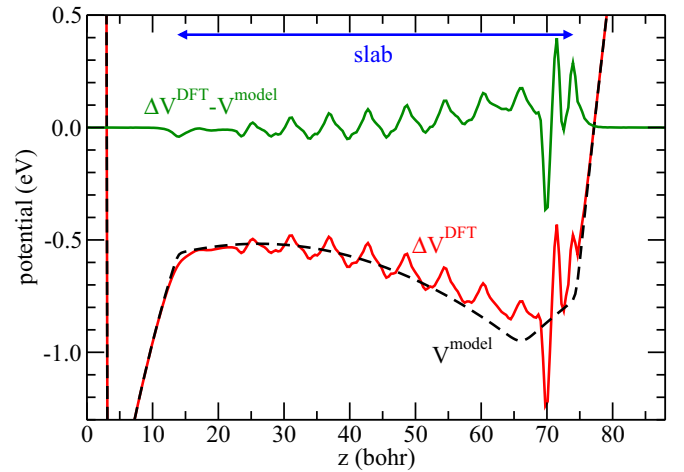


FIG. 10. Potential alignment for a $Q = +1$ dangling-bond defect at a 3×2 Si(111) 20-layer slab in the presence of an external sawtooth potential ($U = 5$ eV, cut at $z = 3$ bohrs). All potentials are averaged over the xy plane. Red (light) solid line: defect-induced change in the DFT electrostatic potential without corrections. Dashed line: potential from the dielectric model. Green (dark) solid line: DFT potential with correction from model.

away from the position of the Si atom with the dangling bond. Moreover, the short-range potential in the slab region shows a clear deviation from the ideal flat behavior. Instead, the potential drops almost linearly from the assumed center of charge at z_Q to a region around $z = 20$ bohrs at the bottom side of the slab. This is in line with a charge transfer from the defect to the lower side of the slab. Hence, the alignment process immediately indicates that the assumptions of a fully localized charge are *not* valid. The implicit verification of the model assumptions is a great advantage of the present scheme. A further analysis of the electronic structure confirmed that the valence states at the bottom end of the slab are almost degenerate with the defect state and partially depleted, while the defect states became partially occupied in conflict with their nominal zero occupation.

The origin of this artifact is the very high surface density of charged states in our calculations. Realistic scenarios in experiment yield surface charge densities of $1e$ per 100–1000 surface atoms, compared to $1e$ per 12 atoms in our case. Increasing the lateral size solves the problem in principle, but—as pointed out above—is impractical due to the computational effort. In order to extend the applicability of DFT calculations for thick slabs, we impose an external electric field to compensate in part for the internal field. This is done by applying an additional asymmetric sawtooth potential according to Eq. (25); cf. Fig. 3. Incorporating such a potential in the Poisson solver for dielectric modeling (Sec. II B) is achieved by imposing the characteristic discontinuous jump $\Delta V_{\text{saw}} = \mathcal{E}_{\text{saw}} c$ within the vacuum when solving the $\mathbf{k}_{\parallel} = 0$ equation for the potential [Eq. (23)]. The magnitude of the discontinuity is adjusted such that the potential buildup within the slab stays below the gap between the defect level and the band edge.

Figure 10 demonstrates the potentials for a $+1$ defect at a 20-layer slab in the presence of the external sawtooth potential. The reference potential was from the defect-free slab in

absence of the external field. The smaller intraslab potential drop in the model (0.4 eV, compared to 0.75 eV in Fig. 9) is clearly visible, and prevents dielectric breakthrough in practice. Correspondingly, the short-range potential after subtracting the model potential becomes flat inside the slab as well as in the vacuum region. Thus, the potential shape in the presence of both the sawtooth potential and the defect is well captured by the dielectric model. The associated changes in the electrostatic energy, however, require some additional considerations.

The energy change associated with the external potential consists of three major contributions: (1) the energy of the intrinsic dipole (i.e., the one already present in absence of an electric field) of the defect-free slab μ_{slab}^0 in the applied external field $\mathcal{E}_{\text{ext}}$, (2) the energy of the defect charge (including background) in the effective potential arising from the sawtooth potential, and (3) the polarization energy of the defect-free slab. The polarization energy of the defect is implicitly accounted for by adapting the center of charge for the defect as described in Sec. III E. Contribution (2) is straightforward to compute in the dielectric model, while contribution (1), which reads

$$E^{(1)} = \mu_{\text{slab}}^0 \mathcal{E}_{\text{ext}}, \quad (37)$$

is extrinsic to our present modeling because the slab's intrinsic dipole is unknown. However, μ_{slab}^0 can be easily extracted from the DFT calculation for the defect-free slab, e.g., by using the standard dipole correction scheme [20]. In our case (symmetric slab), this contribution vanishes. Last, the polarization energy

$$E^{(3)} = -\frac{1}{2} \alpha_{\text{slab}} \mathcal{E}_{\text{ext}}^2, \quad (38)$$

where α_{slab} denotes the slab's polarizability, which can be obtained indirectly as follows. Our setup is equivalent to a plate capacitor with a voltage U , where U corresponds to the potential jump of the sawtooth potential. In the absence of the slab, the capacitance is given by $C = \frac{A}{4\pi c}$ (note that in atomic units, $\epsilon_0 = 1/4\pi$), where A denotes the surface area and c the total cell height. The energy stored in the capacitor is $\frac{1}{2} C U^2$. Upon introducing the slab, the capacitance is enhanced by the "serial" average of the dielectric constant, i.e., a factor $(\overline{\epsilon^{-1}})^{-1}$. The average of the inverse dielectric constant across the cell, $\overline{\epsilon^{-1}}$, is straightforward to compute from the model dielectric profile. Comparing the two energies, the polarization energy of the slab is

$$E^{(3)} = -\frac{A}{2\pi c} \left[\frac{1}{\overline{\epsilon^{-1}}} - 1 \right] U^2. \quad (39)$$

We verified for defect-free slabs (and small $\mathcal{E}_{\text{ext}}$) that the polarization energy calculated via Eq. (39) is in excellent agreement with the results from DFT.

Figure 11 shows the results from calculations for various thicknesses. For thick slabs, we employed the additional external field as just described (squares). For thinner slabs, where dielectric breakthrough was not a problem, we used the standard setup (circles). Uncorrected values are not shown, because the external potential incurs very large alignment shifts. For the standard setup, the corrections vary only slowly with slab thickness (within 0.05 eV over 6–20 layers) due to the high screening inside the slab. It becomes obvious that the calculated formation energies for the neutral and negative charge states are practically independent from the slab thickness for more than

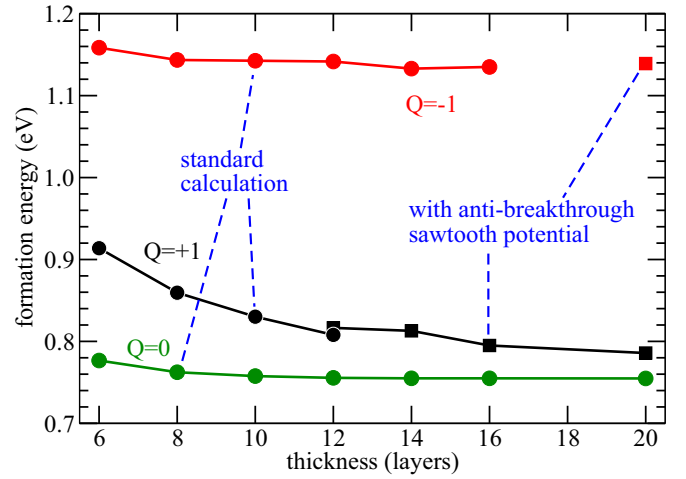


FIG. 11. Convergence of formation energy of a dangling-bond defect at Si(111) with respect to slab thickness. The surface unit cell was 3×2 (cf. Fig. 6). Different charge states are shown: -1 [red (light)], 0 [green (dark)], $+1$ (black). Circles show data (including corrections for charged states) from standard calculations. Squares show data (including corrections) from calculations with an additional sawtooth.

8 layers. In contrast, the $+1$ formation energy shows a slow convergence. We attribute this to confinement effects. Indeed, an analysis of the electronic state associated with the dangling-bond defect reveals a decaying tail into the slab. For the $+1$ charge state, the decay is particularly slow. Model calculations within a 1-dimensional tight-binding model [29] reproduce the confinement effect qualitatively. This finding highlights that finite-size corrections based on electrostatic considerations, that obviously succeed in removing electrostatic artifacts for the well-behaved -1 charge state, may not be sufficient when other mechanisms become important. From a pragmatic point of view, the remaining uncertainties observed here (< 0.05 eV) are within a typical target accuracy of 0.05–0.1 eV.

E. Field dependence

As laid out in the introduction, a major motivation for continuum modeling is the description of macroscopic fields. Up to now we have demonstrated that the surrogate model can be used to compensate for *artificial* electric fields in the repeated-slab approach to extrapolate to the isolated, field-free case. For this, we had adjusted the position of the charge in the surrogate model such that the macroscopic DFT potential under periodic boundary conditions is reproduced. We will now turn the logic around and demonstrate that the same surrogate model (i.e., without readjusting the position of charge) also describes the response to other boundary conditions, notably the dependence of the formation energy on the field across a reference plane according to Eq. (31). In order to do so, we calculated the formation energy of a -1 dangling bond defect in the presence of an electric field. The -1 charge state was chosen because it is less prone to dielectric breakthrough problems. To apply the field, an asymmetric sawtooth potential [Eq. (26)] was applied to a 3×2 8-layer silicon slab with and without the defect. The screening in the Si slab modifies

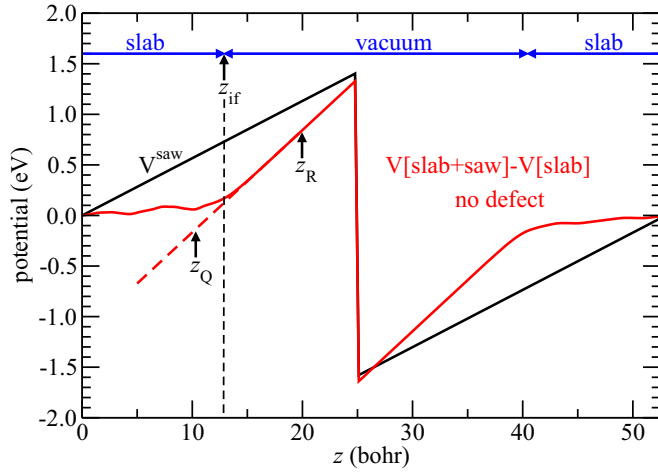


FIG. 12. Change in potential (red line) of a defect-free slab in the presence of an electric field due to an external sawtooth potential (black line). The effective field (slope) in the vacuum is modified by the screening within the slab. When the defect is placed near the position z_Q , its energy is referenced against some point in the vacuum region, z_R . z_{if} is the position of the effective slab-vacuum interface (see Fig. 4).

the effective potential in the vacuum region; see Fig. 12 (red dashed line). Therefore, the applied field was determined *a posteriori* from the effective potential profile of the defect-free slab. In order to give a reference point for the defect formation energy, the electron chemical potential was referenced to the average potential at $z_R = 20$ bohrs, which is ~ 10 bohrs above the outermost Si plane and where the potential in the vacuum is in close agreement with the continuum model (cf. Fig. 5). The Fermi level was then set to 4.78 eV below that level, which corresponds to the DFT valence band maximum of the bulk below the H-saturated (111) surface in the absence of an external field. As an external field $\mathcal{E}$ is applied, the position of the chosen reference point has a strong influence on the calculated formation energy due to the potential difference between the reference point and the position of the defect (cf. Fig. 12), but with a trivial dependence on the field. For a different choice z'_R , the formation energy (defect charge Q) in the new reference is given as

$$E^f(z'_R) = E^f(z_R) - Q\mathcal{E}(z_R) \int_{z_R}^{z'_{ref}} dz \frac{\epsilon(z_R)}{\epsilon(z)}, \quad (40)$$

which simplifies in the case of shifting the boundary in a homogeneous medium (no change of ϵ) to

$$E^f(z'_R) = E^f(z_R) - Q\mathcal{E}(z'_R - z_R). \quad (41)$$

Hence, it is sufficient to demonstrate agreement between DFT and continuum modeling for an arbitrarily chosen reference point. For each applied field, the defect potential was aligned within the correction scheme with respect to the potential of the defect-free slab *with the same field*. In consequence, all artifacts not arising from the field but from the homogenous background and the artificial periodicity are corrected for in the same way as for the field-free case.

The actual comparison is made in Fig. 13, which shows the calculated formation energy in dependence on different fields.

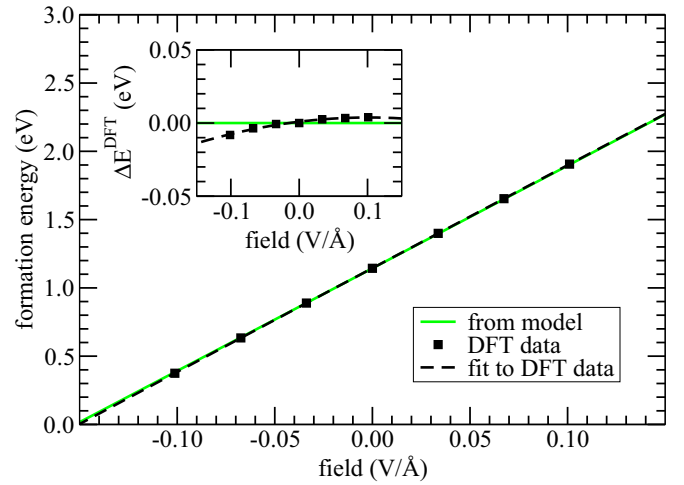


FIG. 13. Formation energy of a -1 dangling-bond defect at Si(111) with respect to a reference plane (see text) for different applied fields. The slab has 8 Si layers and a 3×2 orthorhombic surface unit cell (12 surface atoms). Black squares: DFT with finite-size corrections. Green solid line: field dependence from dielectric model and zero-field DFT data. Dashed line: parabolic fit to DFT data. The inset shows the deviation of the DFT data from the field dependence obtained by the dielectric model.

The formation energy shows the expected linear behavior [cf. Eq. (31)], where the slope is given by the distance of the effective center of charge of the defect from the reference plane. Clearly, the model predictions taken from the field-free case, i.e., the effective defect position in the continuum model that arises from the alignment procedure, is in excellent agreement with the DFT results. The inset in Fig. 13 shows the deviation from the model prediction. We find an absolute deviation of at most 0.01 eV within the observed field range ($\pm 2 \times 10^9$ V/m), in which the formation energy varies over a range of 2 eV. The deviation arises in part from a parabolic behavior of the calculated formation energy. Such a behavior is expected from the defect-induced change in the polarizability α of the slab, which implies a change in the total energy of

$$\Delta E^{\text{pol}} = -\frac{1}{2} \Delta \alpha \mathcal{E}^2. \quad (42)$$

As is obvious from Fig. 13, the dangling-bond defect enhances the polarizability ($\Delta \alpha > 0$). We also observe a slight misprediction of the slope at zero field, equivalent to misplacement of the center of charge by 0.06 bohrs. Such a deviation is at the limit of accuracy of our alignment procedure, and unlikely to be relevant for realistic fields.

IV. CONCLUSIONS

In summary, we have proposed an approach to incorporate charged point defects into the continuum modeling of space charges near material interfaces and surfaces. Using a local dielectric constant approximation $\epsilon(\mathbf{r})$ for the dielectric screening function, specifically a 1-dimensional dielectric profile $\epsilon(z)$ for flat surfaces, we showed that the asymptotic potential dependence to the left and right of a charged surface or interface can be accurately captured by a macroscopic surrogate model. This model requires as input only the effective position z_{eff} of

the charged defect with respect to a reference plane in addition to the formation energy E_0^f with respect to the potential at that point in the absence of macroscopic fields. Moreover, by using the dielectric modeling in connection with an image-charge method for solving the Poisson equation, we show how the key parameters E_0^f and z_{eff} can be reliably extracted from standard DFT calculations in the repeated slab approach. Test calculations for the dangling-bond defect at the H-saturated Si(111) surface demonstrate that the uncertainty of the defect formation energy can be brought down to ≈ 0.05 eV as estimated from a wide set of different supercell sizes, slab thicknesses, and external fields. In the absence of corrections, the most critical parameter in the commonly employed homogeneous background correction is the vacuum thickness, an effect that can be efficiently removed by the proposed corrections. To foster the applicability of the proposed correction scheme, we provide a GNU/Linux binary executable, `sxdefectalign2d`, at our web page [15]. Its usage is briefly summarized in Appendix B. We are confident that our work will help to reduce the uncertainties in charged defect calculations at surfaces due to electrostatic interactions in the supercell approach. Moreover, the proposed scheme can be directly applied to defects in 2D materials and is easily adapted to defects at interfaces.

APPENDIX A: INTEGRATION OF THE 1D POISSON EQUATION

Starting from the one-dimensional effective Poisson equation [cf. Eq. (21)]

$$\frac{d}{dz} \left[\epsilon(z) \frac{d}{dz} V(z) \right] = -4\pi\rho(z) \quad (\text{A1})$$

and introducing the running total charge (A being the interface area)

$$\tilde{Q}(z) = A \int_{z_L}^z dz' \rho(z'), \quad (\text{A2})$$

one obtains

$$V(z) = V_L + \int_{z_L}^z dz' \frac{1}{\epsilon(z')} \left[\epsilon_L \mathcal{E}_L - \frac{4\pi}{A} \tilde{Q}(z') \right]. \quad (\text{A3})$$

Next, we introduce

$$F(z) = \int_{z_L}^z dz' \frac{1}{\epsilon(z')} \quad (\text{A4})$$

and integrate Eq. (A3) by parts to arrive at

$$V(z) = V_L + F(z) \left[\epsilon_L \mathcal{E}_L - \frac{4\pi}{A} \tilde{Q}(z) \right] + 4\pi \int_{z_L}^z dz' F(z') \rho(z'). \quad (\text{A5})$$

In the absence of boundary charges, $\tilde{Q}(z_L)$ is zero and $\tilde{Q}(z_R)$ is the total charge Q . Moreover, $F(z_L)$ is zero. Equation (A5) evaluated at z_R then simplifies to

$$V_R = V(z_R) = V_L + F(z_R) \left(\epsilon_L \mathcal{E}_L - \frac{4\pi}{A} Q \right) + 4\pi \int_{z_L}^{z_R} dz F(z) \rho(z). \quad (\text{A6})$$

To link this expression with the sharp interface model, we first consider the complete absence of charge, i.e., $\rho(z) = 0$ and $Q = 0$. The difference in potential between the right and left boundary in the sharp interface model is given by

$$V_R - V_L = (z_{\text{if}} - z_L) \mathcal{E}_L + (z_R - z_{\text{if}}) \frac{\epsilon_L}{\epsilon_R} \mathcal{E}_L, \quad (\text{A7})$$

which by comparison to Eq. (A6) yields

$$F(z_R) = \frac{z_{\text{if}} - z_L}{\epsilon_L} + \frac{z_R - z_{\text{if}}}{\epsilon_R}. \quad (\text{A8})$$

We may see this as the defining equation for z_{if} as a key feature of an arbitrary dielectric profile, which can be resolved as

$$z_{\text{if}} = \frac{1}{\epsilon_L^{-1} - \epsilon_R^{-1}} \left(\frac{z_L}{\epsilon_L} - \frac{z_R}{\epsilon_R} + \int_{z_L}^{z_R} dz \frac{1}{\epsilon(z)} \right). \quad (\text{A9})$$

We now turn to the energy. For this, we will reference to a zero-charge, finite-field reference aligned at z_L . Then, all the V_L - and $\mathcal{E}_L$ -related terms in the potential Eq. (A5) are part of the reference potential, and all Q and ρ terms belong to the charge-induced potential ($V - V_{\text{ref}}$). From Eq. (5)

$$E = A \int_{z_L}^{z_R} dz \rho(z) \{ V_L + F(z) \epsilon_L \mathcal{E}_L - \frac{2\pi}{A} [F(z) \tilde{Q}(z) - A \int_{z_L}^z dz' F(z') \rho(z')] \}. \quad (\text{A10})$$

The second line can be interpreted as the Coulomb self-energy of the charge distribution, which is independent of the boundary conditions. The double integral from the last term in the self-energy can be integrated by parts to

$$A \int_{z_L}^{z_R} dz \rho(z) \int_{z_L}^z dz' F(z') \rho(z') = Q \int_{z_L}^{z_R} dz F(z) \rho(z) - \int_{z_L}^{z_R} dz \tilde{Q}(z) F(z) \rho(z). \quad (\text{A11})$$

The second term of this expression is the same as the first term in the second line of Eq. (A10). Noting that $2\tilde{Q}(z)\rho(z) = \frac{1}{A} \frac{d}{dz} \tilde{Q}^2(z)$ and integrating by parts yields for the self-energy

$$E_{\text{self}} = -\frac{2\pi}{A} \int_{z_L}^{z_R} dz \left\{ \frac{d}{dz} [\tilde{Q}(z)^2 - Q \tilde{Q}(z)] \right\} F(z) = -\frac{2\pi}{A} \int_{z_L}^{z_R} dz \frac{\tilde{Q}(z)[Q - \tilde{Q}(z)]}{\epsilon(z)}. \quad (\text{A12})$$

For a localized charge distribution fully contained within a certain region, the integrand vanishes outside that region. The self-energy then becomes independent of the integration limits.

With this, we rewrite Eq. (A10) as

$$E = QV_L + A\epsilon_L\mathcal{E}_L \int_{z_L}^{z_R} dz\rho(z)F(z) + E_{\text{self}}. \quad (\text{A13})$$

Last, we will turn our attention to the integral

$$\int_{z_L}^{z_R} dz\rho(z)F(z), \quad (\text{A14})$$

which appears in several places. A simple interpretation is suggested by Eq. (A13), where it appears in the field-dependency term: If we had to reflect all dependence on the potential and the field at z_L by a single representative point charge at an effective position z_{eff} and otherwise forget about all variations in the dielectric profile the field dependence would be given by

$$\frac{dE}{d\mathcal{E}_L} = Q(z_{\text{eff}} - z_L). \quad (\text{A15})$$

Comparison to Eq. (A13) gives us

$$z_{\text{eff}} = z_L + \frac{\epsilon_L A}{Q} \int_{z_L}^{z_R} dz\rho(z)F(z). \quad (\text{A16})$$

Using this effective position z_{eff} , which depends on the specific combination of charge profile and dielectric profile, and using also the above definition of the interface position z_{if} [cf. Eqs. (A8) and (A9)], we can eliminate all occurrences of $F(z)$ for the key quantities of the surrogate model

$$\begin{aligned} V_R &= V_L + \left(\frac{z_{\text{if}} - z_L}{\epsilon_L} + \frac{z_R - z_{\text{if}}}{\epsilon_R} \right) \left(\epsilon_L \mathcal{E}_L - \frac{4\pi}{A} Q \right) \\ &\quad + \frac{4\pi}{A} \frac{Q}{\epsilon_L} (z_{\text{eff}} - z_L) \\ &= V_L + \mathcal{E}_L \left[z_{\text{if}} - z_L + \frac{\epsilon_L}{\epsilon_R} (z_R - z_{\text{if}}) \right] \\ &\quad - \frac{4\pi}{A} Q \left(\frac{z_{\text{if}} - z_{\text{eff}}}{\epsilon_L} + \frac{z_R - z_{\text{if}}}{\epsilon_R} \right), \end{aligned} \quad (\text{A17})$$

$$E = Q[V_L + \mathcal{E}_L(z_{\text{eff}} - z_L)] + E_{\text{self}}. \quad (\text{A18})$$

Note that only the self-energy depends on the detailed shape of the dielectric profile and the charge distribution. All dependence on boundary conditions on the left (L) side is captured by the two key parameters, namely the effective interface position z_{if} and the effective charge position z_{eff} with respect to the left boundary.

APPENDIX B: `sxdefectalign2d` USAGE

In the following, we will illustrate the steps to take to obtain an extrapolation correction for isolated defects on bulk surfaces. A complete manual will be available on the download page [15]. The input to the `sxdefectalign2d` tool consists of the potential files for the defect-containing charged slab system (here: `vdef.sxb`) as well as for the defect-free reference slab (`vref.sxb`) and a SPHInX-format input file (`system.sx`) describing the dielectric model. A sample setup file is shown in Fig. 14.

```

system.sx
format imagecharge;

structure {
  cell = [2*[ 7.212489,    0.000000,   0.000000],
          2*[ 0.000000,   12.492398,   0.000000],
          [ 0.000000,    0.000000,   35.000000]];
}

slab {
  fromZ = -12.735;
  toZ   = 12.735;
  epsilon = 12.13;
}

charge {
  posZ = 8.70;
  Q = -1.;
}

isolated {
  fromZ = 0;
  toZ = 20;
}

```

FIG. 14. Input file for `sxdefectalign2d` (see text).

The setup file uses the SPHInX input syntax [21] and must contain four groups:

(1) The “structure” group, describing the periodic supercell (in units of bohrs). The third lattice parameter must be orthogonal to the first two and point along the z direction.

(2) The “slab” group, describing the dielectric slab. The slab is defined by its boundaries (`fromZ`, `toZ`) and the dielectric constant (`epsilon`). Interfaces are broadened by default (0.7 bohrs; can be changed with “broadening”) to improve the numerical integration in coarse grids.

(3) The “charge” group, describing the defect charge (Q) and position (`posZ`). Due to the sign convention for potentials in most DFT programs, charge is usually measured in “electronic charges”; i.e., Q must be the negative of the classical charge. Note that `posZ` is the unscreened charge’s center and may therefore differ from the effective position z_{eff} if the charge distribution lies within the dielectric interface’s transitional region.

(4) The “isolated” group, which defines the open boundary region (`fromZ`, `toZ`) used for isolated defect calculations. It is this region that is conceptually transferred by the charge correction from the repeated-slab calculation to the situation of interest (see Fig. 15). For bulk surfaces, the isolated region should encompass the slab’s surface with the defect, but not the artificial bottom boundary of the slab. For 2D materials, the isolated region should encompass the complete slab.

Note that the slab and charge groups may appear multiple times to set up more complex dielectric profiles and charge distributions. Additionally, the input may contain a “periodic” group to specify an asymmetric sawtooth potential via the cut position (“cut”) and the voltage drop (“dropV”).

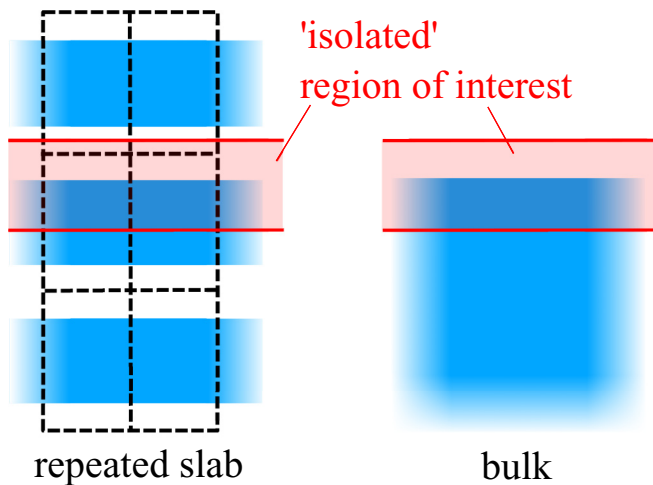


FIG. 15. Schematic: the “isolated” region is that part of the repeated slab system that is representative for the system of interest (here: surface of an extended bulk).

The `sxdefectalign2d` program is then run with several command line options:

<code>-i</code>	setup file name
<code>--ecut</code>	plane-wave cutoff (rydbergs)
<code>--vdef</code>	defect potential file
<code>--vref</code>	reference potential file
<code>--shift</code>	shift charges along z (bohrs)
<code>-C</code>	set alignment constant (eV)

The plane-wave cutoff not only truncates summations and integrations over reciprocal space (parallel to the surface), but also defines the default discretization along z to be compatible with standard Fourier meshes. The discretization can be fine-tuned with further parameters documented in the `sxdefectalign2d` manual. Additional flags are available to specify the potential file format (`--vasp` for VASP, `--qe` for Quantum Espresso, `--socorro` for Socorro).

A complete command line could look like this:

```
sxdefectalign2d -i system.sx --ecut 20 --vdef vdef.sxb --vref vref.sxb
```

The tool produces a text file “`vline-eV.dat`”, which contains in four columns the z coordinate, the difference between the DFT defect and reference potential ΔV^{DFT} [Eq. (33)], the model potential, and the difference between the two, i.e., the short-range potential according to Eq. (34). This file can now be inspected with a plotting program to check that there is no remaining field in the vacuum region (flat potential). Otherwise, the program is rerun with the `--shift` option to adjust the charge position. Once the appropriate position has been found—say, -2.2 (bohrs) as an example—one can read off the alignment constant C (value of the flat potential) and pass it to `sxdefectalign2d` via the `-C` option:

```
sxdefectalign2d -i system.sx --ecut 20 --vdef vdef.sxb --vref vref.sxb --shift -2.2 -C -0.021
```

The output on the screen then lists the defect correction (“iso – periodic”) according to Eq. (35), which must be added to the total energy difference from the DFT code. Further, the calculated interface position as well as the effective charge position [z_{eff} from Eq. (31)] with regard to the upper boundary plane is listed.

- [1] C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, *Rev. Mod. Phys.* **86**, 253 (2014).
- [2] G. Schwarz, Untersuchungen zu Defekten auf und nahe der (110) Oberfläche von GaAs und weiteren III-V-Halbleitern, Ph.D. thesis, Technical University Berlin, 2001.
- [3] A. Y. Lozovoi and A. Alavi, *Phys. Rev. B* **68**, 245416 (2003).
- [4] Y. Xu, O. T. Hofmann, R. Schlesinger, S. Winkler, J. Frisch, J. Niederhausen, A. Vollmer, S. Blumstengel, F. Henneberger, N. Koch, P. Rinke, and M. Scheffler, *Phys. Rev. Lett.* **111**, 226802 (2013).
- [5] N. A. Richter, S. Siculo, S. V. Levchenko, J. Sauer, and M. Scheffler, *Phys. Rev. Lett.* **111**, 045502 (2013).
- [6] M. Otani and O. Sugino, *Phys. Rev. B* **73**, 115407 (2006).
- [7] C. M. Snowden, *Rep. Prog. Phys.* **48**, 223 (1985).
- [8] D. Vasileska, D. Mamaluy, H. R. Khan, K. Raleva, and S. M. Goodnick, *J. Comput. Theor. Nanosci.* **5**, 999 (2008).
- [9] J. Piprek, editor, *Handbook of Optoelectronic Device Modeling and Simulation* (CRC Press, Boca Raton, 2017).
- [10] S. Ismail-Beigi, *Phys. Rev. B* **73**, 233103 (2006).
- [11] C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, *Phys. Rev. Lett.* **102**, 016402 (2009).
- [12] H.-P. Komsa and A. Pasquarello, *Phys. Rev. Lett.* **110**, 095505 (2013).
- [13] D. Wang, D. Han, X.-B. Li, S.-Y. Xie, N.-K. Chen, W. Q. Tian, D. West, H.-B. Sun, and S. B. Zhang, *Phys. Rev. Lett.* **114**, 196801 (2015).
- [14] D. Wang, D. Han, X.-B. Li, N.-K. Chen, D. West, V. Meunier, S. Zhang, and H.-B. Sun, *Phys. Rev. B* **96**, 155424 (2017).
- [15] See <https://sxrepo.mpie.de>.
- [16] C. Freysoldt, P. Eggert, P. Rinke, A. Schindlmayr, and M. Scheffler, *Phys. Rev. B* **77**, 235428 (2008).
- [17] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).
- [18] S. Baroni and R. Resta, *Phys. Rev. B* **33**, 7017 (1986).
- [19] K. Kunc and R. Resta, *Phys. Rev. Lett.* **51**, 686 (1983).
- [20] J. Neugebauer and M. Scheffler, *Phys. Rev. B* **46**, 16067 (1992).
- [21] S. Boeck, C. Freysoldt, A. Dick, L. Ismer, and J. Neugebauer, *Comput. Phys. Commun.* **182**, 543 (2011).
- [22] A. F. Wright and N. A. Modine, *Phys. Rev. B* **74**, 235209 (2006).
- [23] C. W. M. Castleton, A. Höglund, and S. Mirbt, *Phys. Rev. B* **73**, 035215 (2006).
- [24] C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, *Phys. Status Solidi B* **248**, 1067 (2011).

- [25] R. Sundararaman and Y. Ping, *J. Chem. Phys.* **146**, 104109 (2017).
- [26] K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, *Surf. Sci.* **164**, 367 (1985).
- [27] H. Ibach and J. Rowe, *Surf. Sci.* **43**, 481 (1974).
- [28] M. Fuchs and M. Scheffler, *Comput. Phys. Commun.* **119**, 67 (1999).
- [29] For an N -site chain, we set hopping elements $H_{i,i+1} = T$, the defect end $H_{1,1} = D$, the bottom end $H_{NN} = B > 0$, and all other elements to zero.