

Manual for `sxdefectalign2d` – Version 1.1:
Finite supercell size corrections for charged
defects at surfaces, interfaces, and 2D materials

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1 Description

The `sxdefectalign2d` tool calculates corrections to the formation energy of localized charged defects at surfaces, interfaces, and 2D materials calculated in the repeated slab/superlattice approach, but where the formation energy of interest is the limiting case of infinite separation. The general formalism is described in Ref. [1], based on ideas from Ref. [2]. Please read these papers first before trying to read the manual or using `sxdefectalign2d`.

1.1 Changes since version 1.0

- support for the generalized dipole correction [3]
- print estimated slope of the potential at the boundaries of the isolated region, and the corresponding potential value

1.2 Main features

The `sxdefectalign2d` tool does the following:

1. Given a dielectric profile $\epsilon(z)$ and a charge distribution (cylindrical or spherical symmetry), it solves the Poisson equation and computes the electrostatic energy for 3D boundary conditions (periodic case).
2. Taking a segment of the dielectric profile and the same charge distribution, it solves the Poisson equation and computes the electrostatic energy for open boundary conditions, which corresponds to a vanishing potential at infinity (isolated charge in zero field).
3. It optionally reads in two periodic potentials (from DFT code) corresponding to the defect-containing and defect-free cases, determines the difference

$$\Delta V^{\text{DFT}} = V^{\text{defect}} - V^{\text{ref}} \quad (1)$$

as well as the short-range potential $V^{\text{sr}} = \Delta V^{\text{DFT}} - V^{\text{model}}$. The latter can be used for potential alignment.

4. It then prints the energy difference between the isolated and the periodic case, which can be added to the energy difference from DFT to extrapolate from the periodic to the isolated case.

Additionally, the code provides some auxiliary information for the dependence of the defect formation energy on electric fields

- If the isolated case contains a dielectric interface, its position is printed.
- For the isolated case, the field-dependence z_{eff} with respect to the lower (left) and upper (right) boundary plane is printed (in bohr).

- If a sawtooth potential is applied, the electrode charges and potentials are printed.

The present implementation works only for supercells in standard orientation: the 3rd unit cell vector (\mathbf{a}_3) must be parallel to the Cartesian z axis (with positive z). The other two unit cell vectors must be perpendicular to the z -axis.

1.3 Implementation details

1.3.1 Profile broadening

In order to improve the numerical stability, dielectric profiles are broadened as follows: for a dielectric slab from z_{\min} to z_{\max} with dielectric constant ϵ_s , the dielectric profile is given by

$$[\epsilon(z)]^{-1} = \frac{1}{\epsilon_{\text{bg}}(z)} + \frac{1}{4}(\epsilon_s^{-1} - \epsilon_{\text{bg}}^{-1}(z))(1 + \operatorname{erf} \frac{z - z_{\min}}{\beta})(1 + \operatorname{erf} \frac{z_{\max} - z}{\beta}) \quad (2)$$

Here, $\epsilon_{\text{bg}}(z)$ is the dielectric profile before the dielectric slab is added. This allows to build complex dielectric profiles from a sequence of dielectric slabs. β is the broadening parameter (default: 0.7 bohr), that can be set via the **broadening** parameter in the **slab** group. The broadening via the inverse ensures that the effective (sharp) dielectric interface position is maintained.

1.3.2 Charges

At present, only Gaussian shapes for point charges are implemented. They have independent broadening widths β_{\parallel} parallel to the surface plane and β_z along the out-of-plane z -axis. The shapes read

$$q(x, y, z) = \frac{Q}{\sqrt{2\pi}\beta_z 2\pi\beta_{\parallel}} e^{-\frac{1}{2}[z^2/\beta_z^2 + (x^2+y^2)/\beta_{\parallel}^2]} \quad (3)$$

or in 2D transform

$$q(\mathbf{k}_{\parallel}, z) = \frac{Q}{\sqrt{2\pi}\beta_z} e^{-\frac{1}{2}[z^2/\beta_z^2 + |\mathbf{k}_{\parallel}|^2\beta_{\parallel}^2]} . \quad (4)$$

Note that due to the potential convention in most DFT codes – namely to produce the electron potential (negative test charge) rather than electrostatic potential (positive test charge) – the charge values Q used in the input file must be typically given in units of the (negative) electron charge, i.e., the negative of the classic charge.

Example: For a +1 ionized donor defect, one should use $Q = -1$.

1.3.3 Isolated case

The electrostatic energy in the cylindrically symmetric isolated case reads

$$\begin{aligned}
E^{\text{iso}} &= \frac{d}{2} \sum_i \frac{1}{(2\pi)^2} \underbrace{\int_0^{|\mathbf{k}_{||}| \leq k_{\text{max}}} d^2 \mathbf{k}_{||}}_{2\pi \int_0^{k_{\text{max}}} k_{||} dk_{||}} q(\mathbf{k}_{||}, z_i) V(\mathbf{k}_{||}, z_i) \\
&= \frac{d}{2} \sum_i \frac{1}{\varepsilon(z_i)} \int_0^{k_{\text{max}}} dk_{||} q(\mathbf{k}_{||}, z_i) \sum_{n, \sigma} q(\mathbf{k}_{||}, z_i, \sigma, n) e^{-n|\mathbf{k}_{||}|d}. \quad (5)
\end{aligned}$$

The d in the prefactor is the discretization in the z direction. The integral is in practice replaced by a finite sum using Simpson rule with a finite interval Δk . Note that the $\mathbf{k}_{||} = \mathbf{0}$ has vanishing weight in the isolated case. The only possible contribution for $\mathbf{k}_{||} = \mathbf{0}$ is from the boundary conditions. The isolated reference energy in `sxdefectalign2d` employs zero potential boundary conditions (i.e., no contribution from $\mathbf{k}_{||} = \mathbf{0}$).

1.3.4 Periodic case

The periodic energy reads

$$\begin{aligned}
E^{\text{periodic}} &= \frac{d}{2} \sum_{i=0}^{N-1} \frac{1}{A} \sum_{\substack{|\mathbf{k}_{||}| \leq k_{\text{max}} \\ \mathbf{k}_{||} \neq \mathbf{0}}} \frac{2\pi}{|\mathbf{k}_{||}|} \sum_{n, \sigma} q(\mathbf{k}_{||}, z_i, \sigma, n) e^{-n|\mathbf{k}_{||}|d} \\
&+ E^{\text{1D}} + Q \cdot C + E^{\text{pol}}. \quad (6)
\end{aligned}$$

Here, the average 1D energy (i.e, for $\mathbf{k}_{||} = \mathbf{0}$) is

$$E^{\text{1D}} = \frac{d}{A} \sum_{i=0}^{N-1} \left[\frac{1}{2} q(\mathbf{k}_{||} = \mathbf{0}, z_i) - \frac{Q}{N} \right] V_i + q(\mathbf{0}, z_i) V^{\text{bg}}(z_i) \quad (7)$$

Here, V_i denotes the potential values for z_i from the direct integration of the one-dimensional Poisson equation for $\mathbf{k}_{||} = \mathbf{0}$ (including boundary conditions, alignment, and possibly a sawtooth-related potential drop). C is the alignment constant from the command line (see Sec. 2). V_{bg} are possible additional background potentials (see `background` group in input file). The polarization energy E^{pol} occurs in case a asymmetric sawtooth potential with voltage drop U is applied (see `dropV` parameter in `background` group in the input file), and reads

$$E^{\text{pol}} = -\frac{A}{2\pi c} \left[\frac{1}{\overline{\epsilon^{-1}}} - 1 \right] U^2 \quad (8)$$

where $c = Nd$ denotes the supercell height along the z direction and

$$\overline{\epsilon^{-1}} = \frac{1}{N} \sum_{i=0}^{N-1} \epsilon_i^{-1} \quad (9)$$

the average inverse dielectric constant (serial capacitance average) across the cell.

In case the generalized dipole correction [3] (GDC) is used, V_i^{GDC} is computed with finite field boundary conditions and appropriate alignment convention [3], but the energy is computed without compensating background as

$$E^{\text{1D(GDC)}}(\mathbf{k}_{\parallel} = \mathbf{0}) = \frac{d}{A} \sum_{i=0}^{N-1} \left[\frac{1}{2} q(\mathbf{0}, z_i) V_i^{\text{GDC}} + q(\mathbf{0}, z_i) V^{\text{bg}}(z_i) \right]. \quad (10)$$

1.3.5 Estimating slopes

For convenience in fine-tuning the position of the defect charge (see Sec. 5.1), the code estimates the slope of the corrected potential V^{sr} near the boundaries of the isolated region. For this, the profile is first smoothed by taking the running average (default: 2 bohr, see `--slopeAvg` option), and then a simple symmetric 2-point approximation is taken:

$$s_j = \frac{V_{j+1}^{\text{sr,smooth}} - V_{j-1}^{\text{sr,smooth}}}{2d} \quad (11)$$

Since the short-range potential is defined within periodic boundary conditions, the boundaries of the isolated region are mapped into the periodic region between $0 \leq z < c$, and then rounded to the nearest mesh point. One should not rely on the textual output for the slopes only, always double-check the visual impression.

For the generalized dipole correction, the slopes are not relevant (but still printed). The key parameter for positioning becomes the step of the corrected potential at the cut position. If the defect is properly placed, the total dipole of the cell agrees between the DFT calculation and the model, and the step becomes zero.

1.4 Dielectric profile for 2D materials

For 2D materials or very thin slabs, the dielectric profile cannot be determined uniquely by fitting straight-line potentials to the potential in presence of an electric field, as suggested in Sec. 2C in Ref. [1]. The reason is that the potential inside the slab may show too many variations. In this case, an alternative approach is recommended based on the dielectric tensor for the total system [4]. The total dielectric tensor is available in many DFT codes from perturbation theory, from finite field calculations within the modern theory of polarization (Berry phase), or can be extracted from sawtooth potentials in two different orientations.

For `sxdefectalign2d`, we model the 2D material with a dielectric slab of thickness s and dielectric constant ε , while the rest of the cell is filled with vacuum (of thickness v). The dielectric tensor components of the total system

along the z -axis, ϵ_z , and parallel to the slab, ϵ_{\parallel} , respectively, can then be written as (cf. Eq. (8) and (9) in Ref. [4])

$$\epsilon_{\parallel} = \frac{\epsilon s + v}{s + v} = 1 + (\epsilon - 1) \frac{s}{c}, \quad (12)$$

$$\epsilon_z^{-1} = \frac{\epsilon^{-1} s + v}{s + v} = 1 - (\epsilon - 1) \frac{s}{\epsilon c}, \quad (13)$$

where $c = s + v$ denotes the total height of the simulation cell. These equations can be inverted to yield the model parameters from the dielectric tensor components. From Eqs. (12) and (13), we find

$$\epsilon = \frac{\epsilon_{\parallel} - 1}{1 - \epsilon_z^{-1}}, \quad (14)$$

$$s = c \left[\frac{1}{1 - \epsilon_{\parallel}} + \frac{1}{1 - \epsilon_z^{-1}} \right]^{-1}. \quad (15)$$

The center of the slab should then be placed in accordance with the nuclear coordinates of the DFT calculation (for asymmetric slabs, some empirical tuning may be needed).

2 Options for the sxdefectalign2d executable

Option	argument	description
--help		show all the available options
--log		create a log file
--quiet		don't produce output on stdout
--input	filename	input file (default: system.sx)
--ecut	cutoff	plane-wave cutoff energy (in Rydberg)
--shift	Δz	shift all charges along z (in bohr)
--onlyProfile		do not compute energies, only the periodic $\mathbf{k} = 0$ profile for alignment purposes.
-C	potential shift C	shift model potential by C (in eV)
--vref	filename	potential file for reference system
--vdef	filename	potential file for defect system
--vasp		potentials are in VASP format
--socorro		potentials are in socorro format
--qe		potentials are in quantum espresso/Gaussian cube format (output_format=6)
--average	d^{avg}	average potentials in <code>vline-eV.dat</code> over a range of d^{avg} (in bohr)
--slopeAvg	d^{avg}	average short-range potential over a range of d^{avg} (in bohr) before calculating the slope/value at the isolated region's boundaries (default: 2 bohr).
-n	N	Set the number of points in the periodic profile
-p	N	Set the number of points per FFT mesh point (default: 1)
--dk	Δk	dk for lateral integration in isolated case

3 Input file (system.sx)

The input format is best explained starting from an **example**:

```

structure {
  cell = [2*[7.212489, 0.0, 0.0],
           2*[0.0, 12.492398, 0.0],
           [0.0, 0.0, 35.0]];
}

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

```


The SPHInX input format is a structured, hierarchical format with a C-like syntax. It consists of named groups and parameters. The content of a **group** (such as **slab**) is enclosed in curly brackets `{}`. Groups may contain parameters, and other groups. **Parameters** (such as **fromZ**) are assigned values with the equal sign. Parameter assignments must be followed by a semicolon (`;`). Flags are special parameters, that normally do not carry a value. A flag is set by specifying its name, followed by a semicolon. Flags are unset by assigning the value 0. Some parameters/variables may be a vector (or a matrix). The values are comma-separated and enclosed by square brackets `[]`.

Comments can be added by the `//` and `/* */` syntax. A `//` comment extends until the rest of the line. A `/* */` comment omits everything between the `/*` and `*/` markers.

The SPHInX parser supports basic algebraic expressions, such as adding, subtracting, multiplying etc. At the top level, additional variables may be set and used in algebraic expressions.

At the top level, there must be the following groups: the **structure** group (supercell dimensions), one or more **slab** groups (dielectric profile), at least one **charge** group, and the **isolated** group that defines the open boundary region. If the **structure** group is omitted, the supercell is taken from the defect potential file.

3.1 The structure group

The structure group specifies the periodic supercell in SPHInX format.

Example:

```

structure {
  cell = [[10, 0, 0],
           [-5, sqrt(0.75) * 10, 0],
           [0, 0, 80]];
}

```

The only parameters that may be set in this group is **cell**. This is a list of the three basis vectors in Cartesian coordinates in bohr.

3.2 The slab group

The **slab** group defines the dielectric profile. It may appear multiple times.

The following parameters may be set:

parameter	description
fromZ	(required) lower end of the slab (in bohr).
toZ	(required) upper end of the slab (in bohr).
epsilon	(required) dielectric of the slab.
broadening	(optional) β parameter of interface broadening (Sec. 1.3.1), in bohr.

3.3 The charge group

The `charge` group defines a Gaussian charge. It may appear multiple times.

The following parameters may be set:

parameter	description
<code>posZ</code>	(required) z position of the charge.
<code>Q</code>	(required) charge.
<code>beta</code>	(optional) Gaussian width (both $\beta_{ }$ and β_z), see Eq. (3).
<code>betaPara</code>	(optional) Gaussian width $\beta_{ }$, see Eq. (3).
<code>betaZ</code>	(optional) Gaussian width β_z , see Eq. (3).

For the periodic case, the charges may be placed at any periodic z position.

For the isolated case, only charges falling in the isolated range (see `isolated` group) are considered.

3.4 The Qslab group

The `Qslab` group defines a layer charge of finite thickness. It may appear multiple times.

The following parameters may be set:

parameter	description
<code>fromZ</code>	(required) lower end of the slab (in bohr).
<code>toZ</code>	(required) upper end of the slab (in bohr).
<code>Q</code>	(required) charge.

For the periodic case, the charges may be placed at any periodic z position.

For the isolated case, only charges falling in the isolated range (see `isolated` group) are considered.

3.5 The isolated group

The optional `isolated` group 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. 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. If omitted, no isolated energy is calculated.

The following parameters may be set:

parameter	description
<code>fromZ</code>	(required) lower end of the isolated region (in bohr).
<code>toZ</code>	(required) upper end of the isolated region (in bohr). If smaller than <code>fromZ</code> , the next periodic image larger than <code>fromZ</code> is taken instead.

For the periodic case, the charges may be placed at any periodic z position.

For the isolated case, only charges (see `charge` and `Qslab` groups) falling in the isolated range are considered.

3.6 The background group

The `background` group defines the background potential.

The `background` group may contain one or more `Qslab` groups. In addition, the following parameters may be set to define a sawtooth potential:

parameter	description
<code>dropV</code>	(optional) Request a sawtooth potential with the potential step <code>dropV</code> (in eV).
<code>cut</code>	(optional) z position of the sawtooth cut.

3.7 The periodic group

The `periodic` group is needed when the generalized dipole correction[3] is used instead of the homogeneous background method. The following parameters may be set:

parameter	description
<code>cut</code>	(required) position of the dipole cut (in bohr).
<code>zField</code>	(optional) extra field on the left/bottom side (in eV/bohr).

Using the generalized dipole correction produces an energy for the periodic case consistent with the DFT implementation described in [3].

4 Output

4.1 System `system-profile.dat`

`system-profile.dat` contains z -dependent profiles for the dielectric constant ϵ , the charge density ρ , and the potential V^{model} . It contains 4 columns of data:

$$z \quad \epsilon(z) \quad \rho(z) \quad V^{\text{model}}(z)$$

where z (in bohr) is the coordinate along the z -axis. Each quantity is the planar average over the xy -plane at height z .

4.2 Potential profile: `vline-eV.dat`

`vline-eV.dat` contains 4 columns of data:

$$z \quad V^{\text{model}}(z) \quad \Delta V^{\text{DFT}}(z) \quad V^{\text{sr}}$$

where z (in bohr) is the coordinate along the z -axis, and $V^{\dots}(z)$ is the planar average over the xy -plane at height z . ΔV^{DFT} is the difference between the DFT potential from the defect-containing supercell and the reference potential, see Eq. (1) above. The last column is the short-range potential

$$V^{\text{sr}}(z) = \Delta V^{\text{DFT}}(z) - V^{\text{model}}(z) \tag{16}$$

5 Usage

5.1 Standard cases (homogeneous background)

We will demonstrate the usage by discussing the correction for a negatively charged Si dangling-bond defect at the surface of hydrogenated Si(111), calculated with a slab of 8 layers of silicon. These calculations were done with our DFT code, but this is relevant only for the file format of the potentials (`sxb` format).

The first step is to determine the dielectric parameters, e.g. from a sawtooth potential calculation as shown in detail in Ref. [1]. Alternatively, one can estimate the extent of the slab and its dielectric constant (not recommended). For 2D materials, please see Sec. 1.4.

For the system at hand, the interfaces (symmetric case) lie at $z = \pm 12.735$ bohr, and the dielectric constant is $\epsilon = 12.13$. For the position of the defect, we will start with an estimated position of $z = 10$ bohr (z -coordinate of the 3-fold coordinated atom rounded to full bohr). The position will be refined in the following. For the isolated case, we estimate that the lower plane should lie somewhere in the bottom part of the slab, and choose $z_L = -5$ bohr. The upper plane should be in the vacuum above, so we choose 10 bohr above the estimated defect position, i.e. $z_R = 20$ bohr.

The input file `system.sx` looks as follows:

```
slab { // from sawtooth calculation
  fromZ = -12.735;
  toZ   = 12.735;
  epsilon = 12.13;
}

charge {
  posZ = 10; // estimated position
  Q = +1.; // Classical charge state: -1
}

isolated {
  fromZ = -5;
  toZ = 20;
}
```

Note that we set `Q` to `+1` because SPHInX produces electron potentials (negative test charge) rather than classical potentials (positive test charge). I skipped the `structure` group because we will import the supercell dimensions from the potential files.

I also copy the DFT potential file (from SPHInX) for the defect-containing case to `vDef.sxb` and for the defect-free case to `vRef.sxb`. These calculations

were run with a plane-wave cutoff of 20 Ry, and we will use the same for the correction calculation.

The first step is to verify the defect position, so we run

```
sxdefectalign2d --ecut 20 --vdef vDef.sxb --vref vRef.sxb
```

and check the potential profiles. I like `xmgrace`, so I type

```
xmgrace -nxy vline-eV.dat
```

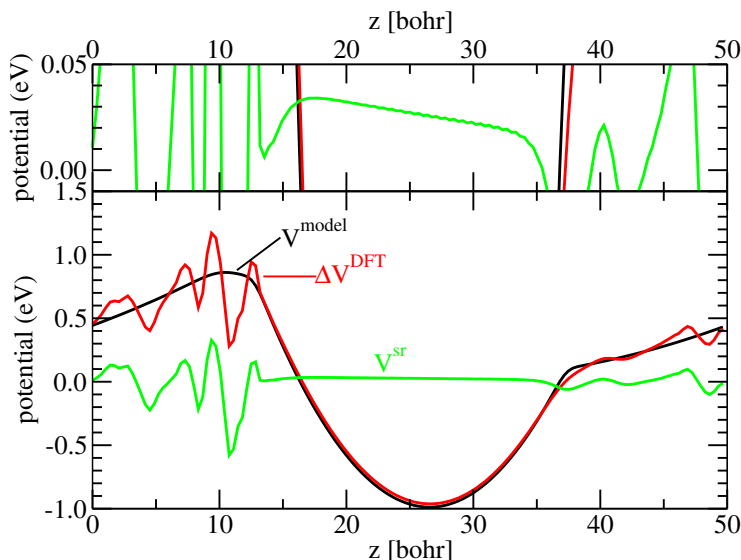


Figure 1: Potential profiles for the original estimated charge position $z_Q=10$ bohr. The upper graph shows a zoom in. The defect charge is too far left.

The outcome (with a bit of polishing the layout) is shown in Fig. 1. Overall, the shape is well reproduced in the vacuum region, but the zoom-in shows a small slope. Note that the approximate slope at the boundaries of the isolated region – as mapped into the periodic cell – is also printed in the output (since version 1.1):

```
Slope bottom (@z=44.7917)= 0.0261933 eV/bohr, value = 0.0286641 eV
Slope top (@z=20.1389) = -0.00102253 eV/bohr, value = 0.0321382 eV
```

This must be brought to a constant, so we try shifting our charge to the right. As we are going to compute potentials multiple times, we use the `--onlyProfile` option to suppress energy calculations until we have the defect position right. Our first attempt is $\Delta z = 1$ bohr:

```
sxdefectalign2d --ecut 20 --vdef vDef.sxb --vref vRef.sxb --onlyProfile --shift 1
```

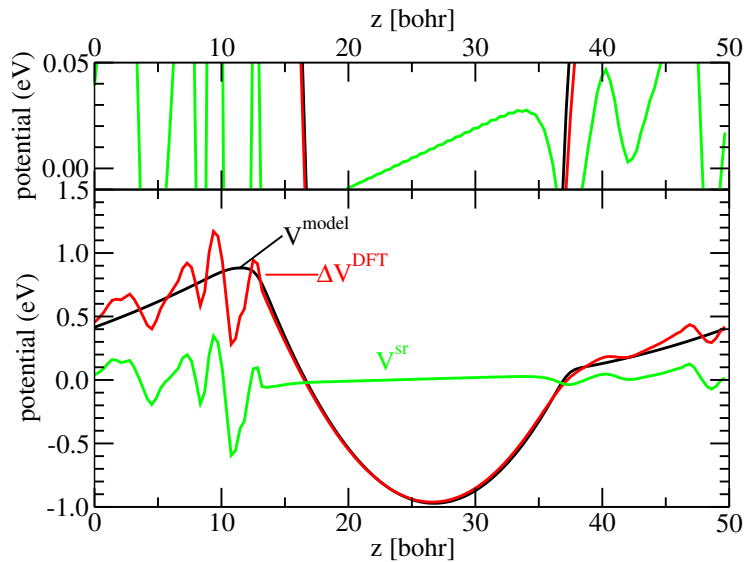


Figure 2: Potential profiles for a charge shifted by +1 bohr from the original estimated charge position $z_Q=10$ bohr. The upper graph shows a zoom in. The defect charge is too far right.

The outcome is in Fig. 2. Ooops, this was clearly too much! The slope is now in the opposite direction. A little trial and error gives us ultimately

```

sxdefectalign2d --ecut 20 --vdef vDef.sxb --vref vRef.sxb --onlyProfile --shift 0.3

```

with a nice flat shape in the vacuum, see Fig. 3.

The correct defect position in this particular example is thus $z_Q=10.3$ bohr. The next step is to read off the alignment constant from the value in the vacuum region, which is +0.02 eV (see dashed arrow in Fig. 3. Note that this can also be read off the terminal output (since version 1.1):

```

Slope bottom (@z=44.7917)= 0.0262748 eV/bohr, value = 0.0359256 eV
Slope top (@z=20.1389) = -3.38511e-05 eV/bohr, value = 0.0218541 eV

```

We add this to the command line with the -C option, and run the final calculation (without --onlyProfile) to get the correction:

```

sxdefectalign2d --ecut 20 --vdef vDef.sxb --vref vRef.sxb --shift 0.3 -C 0.02

```

which gives us the following output:

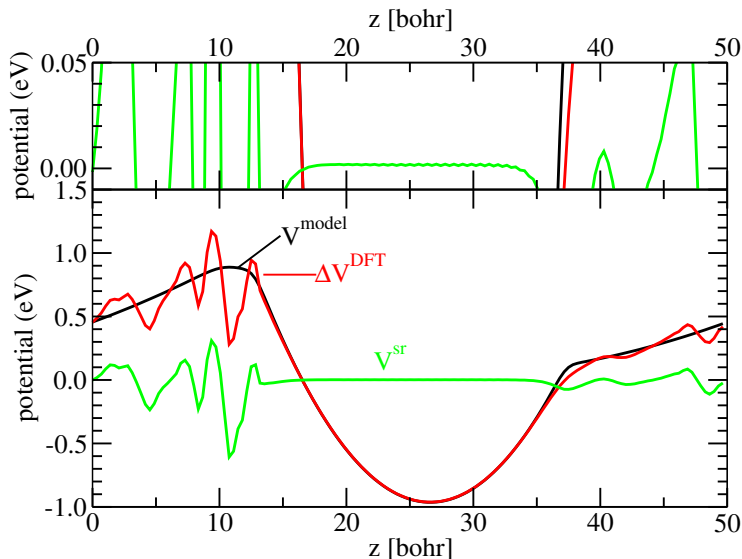


Figure 4: Potential profiles for a charge shifted by $+0.3$ bohr from the original estimated charge position $z_Q=10$ bohr, and with an alignment constant of $C = +0.02$ eV. The upper graph shows a zoom in.

The very last line tells us the defect correction (-0.12 eV) that must be added to the uncorrected DFT formation energy. We can also check the aligned potential a last time, see Fig. 4 and see that the agreement of the potentials is perfect in the vacuum region, while we see some oscillations from microscopic screening inside the slab.

5.2 Generalized dipole correction

If the generalized dipole correction[3] is used, the input file has to contain a `periodic group` (see Sec. 3.7).

As an example, we take a 6-layer MgO slab with a $+2$ oxygen vacancy at the top surface. The bottom two layers are frozen. In consequence, the dielectric profile for the slab has two regions: the relaxed region with a dielectric constant of 9.8 in the region $z=9.75-26.6$ bohr, and the frozen region with $\epsilon = 3.36$ in the region $z=0.8-9.75$ bohr. All numbers were obtained by fitting a line profile to the defect-free slab exposed to an electric field. The DFT calculation with the generalized dipole correction was run with a cutoff of 28 Rydberg and zero-field conditions at the bottom (low- z) side.

The input file `system.sx` looks as follows:


```

slab { // relaxed part
  fromZ = 5;
  toZ   = 26.6;
  epsilon = 9.8;
  broadening = 0.5;
}
slab { // frozen part
  fromZ = 0.8;
  toZ   = 9.75;
  epsilon = 3.36;
  broadening = 0.5;
}

charge {
  posZ = 23; // estimated position
  Q = -2.; // Classical charge state: +2
}

isolated {
  fromZ = 12;
  toZ = 40;
}

periodic {
  cut = 37.4;
}

```

Note how we set up the dielectric transition from the frozen to the relaxed region: we first define a relaxed region that extends beyond the intended transition at $z = 9.75$ (here we use `fromZ=5`). When we then introduce the frozen region, the relevant background dielectric profile [cf. Eq. (2)] near $z=9.75$ is constant, and the transition acquires the desired simple error-function shape. Since we want to extrapolate to the relaxed bulk case, our isolated region ends within the relaxed region (we choose $z = 12$). The cut position in the DFT calculation for the charged slab is at 37.4. Introducing the `periodic` group in the input file and setting the cut position requests the generalized dipole correction for the periodic part.

Our first attempt is to estimate the charge position at $z=23$ (see input file). Running

```

sxdefectalign2d --ecut 28 --vdef vDef.sxb --vref vRef.sxb

```

yields the following output for the periodic part:

```

--- Periodic
Q=-2

```

```

short-range potential with averaging width = 2 bohr
Slope bottom (@z=11.7707)= -0.184596 eV/bohr, value = -3.07385 eV
Slope top (@z=40.0204) = -1.64575e-07 eV/bohr, value = -3.08001 eV
step at z=37.372 bohr: -0.156563
---
```

and visual output as follows

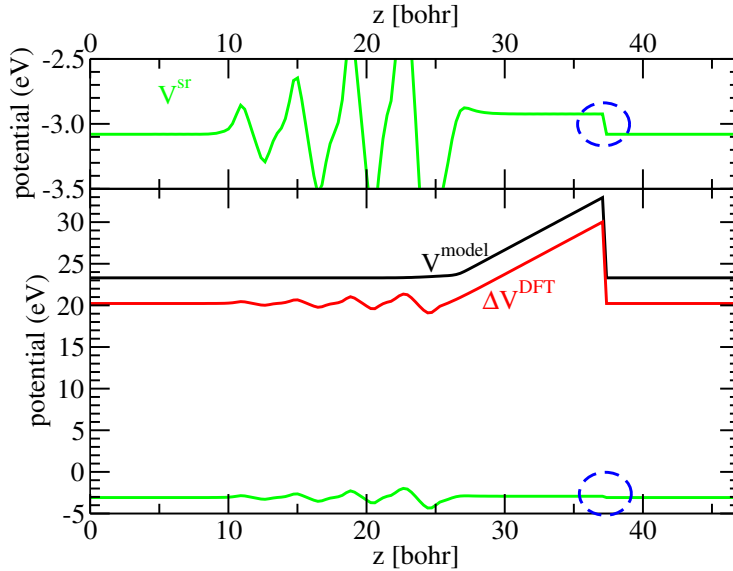


Figure 5: Potential profiles (with generalized dipole correction) for the original estimated charge position $z_Q=23$ bohr. The upper graph shows a zoom in. The short-range potential shows a step at the cut position. The defect charge is too far right.

Note that due to the use of the generalized dipole correction, the short-range potential in the vacuum should always be flat (zero slope) because the expected fields near the cut position are set by the boundary conditions of the generalized-dipole correction by construction. However, a step appears at the cut position (see blue circle) when the defect is not properly placed.

Adjusting the shift position by trial and error (using either the graphical overview or the step value printed on the screen) to $\Delta z = -1.73$, we arrive with

```

sxdefectalign2d --ecut 28 --vdef vDef.sxb --vref vRef.sxb --shift -1.73
```

at the following output for the periodic part:

```

--- Periodic
Q=-2
short-range potential with averaging width = 2 bohr
Slope bottom (@z=11.7707)= -0.184596 eV/bohr, value = -2.91692 eV
```

Slope top (@z=40.0204) = -1.64575e-07 eV/bohr, value = -2.92308 eV
 step at z=37.372 bohr: 0.000366682

Also the potential shape looks very good now:

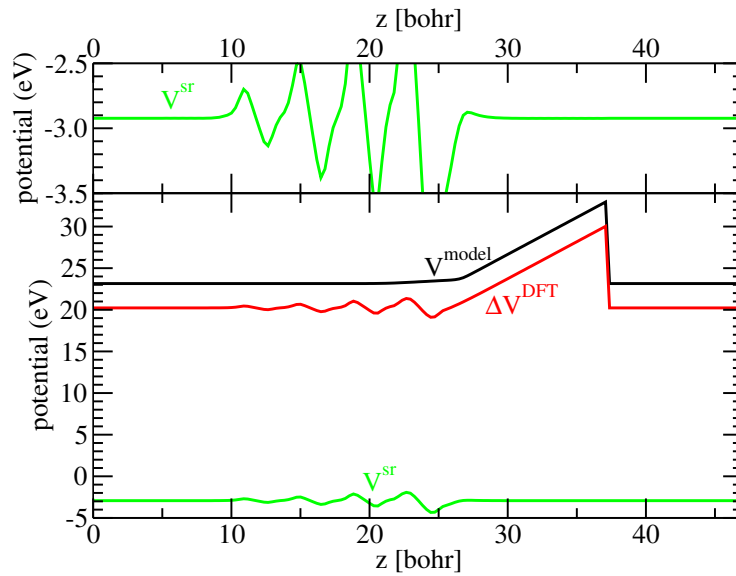


Figure 6: Potential profiles (with generalized dipole correction) for the adjusted charge position. The upper graph shows a zoom in. The short-range potential no longer shows a step at the cut position.

The alignment constant is easily read off as $C = -2.92$ eV. It is not uncommon to have large alignment constants when using the generalized dipole correction. The final energy correction is then obtained from

```
sxdefectalign2d --ecut 28 --vdef vDef.sxb --vref vRef.sxb --shift -1.73 -C -2.92
```

6 Troubleshooting

6.1 Negatively charged defects

For negatively charged slabs, the uncorrected vacuum potential can fall below the Fermi level. In consequence, part of the electron density may escape to the vacuum, which prevents a meaningful calculation of the defect properties. Such cases are easily detected by looking at the potential profiles. Fig. 7 shows an illustrative example (courtesy of Suhyun Yoo, MPI Eisenforschung).

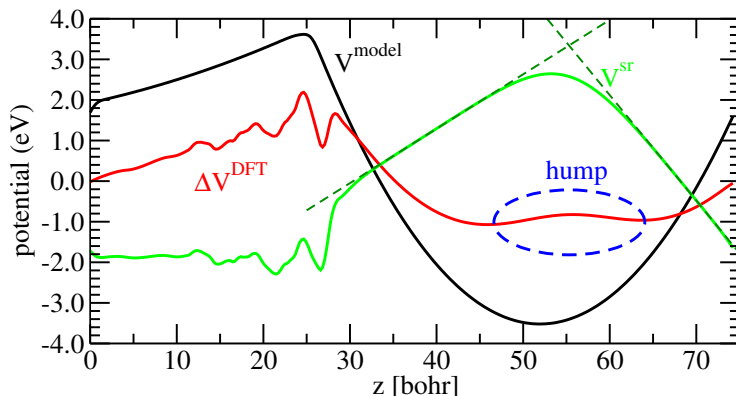


Figure 7: Potential profiles for a -1 hydrogen vacancy defect at a H-saturated GaN (10 $\bar{1}$ 0) (m-plane) surface, where some electron density escaped to the vacuum region. The uncorrected potential ΔV^{DFT} (red) shows a hump in the center of the vacuum. The corrected potential V^{sr} (green) shows finite electric fields, highlighted by linear fits (dashed lines in dark green).

The two most striking features are the hump in the center of the vacuum for the uncorrected potential (red line), and the appearance of finite electric fields in the corrected potential (green line). The origin of the hump is a Gaussian distribution of charge density sitting at the center of the (parabolic) vacuum potential (see model potential, black line in Fig. 7). Note that the parabolic potential in the vacuum corresponds to that of the 1D harmonic oscillator; the lowest eigenstate therefore is a Gaussian. Compared to the model, the true DFT charge distribution has shifted part of the negative charge from the defect to the center of the vacuum. In consequence, the corrected potential shows regions of finite electric field, because the charge shift creates a capacitor-like shape of the potential (cf. the linear fits/dashed lines in dark green in Fig. 7).

The problem can also be detected in the electron density profiles on a logarithmic scale. Good cases show an exponential decay of density down to the level of numerical noise or the density minimum. Let's compare the charge-neutral reference with the problematic -1 defect shown in Fig. 8.

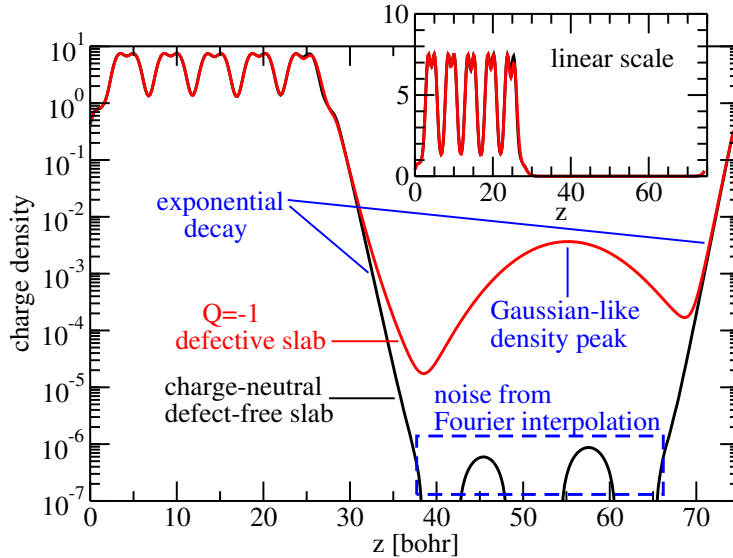


Figure 8: Electron density profiles for a H-saturated GaN (10 $\bar{1}$ 0) (m-plane) surface (black line) and the same slab with a hydrogen vacancy defect in charge state $Q=-1$ (red line), where some electron density escaped to the vacuum region. For the defect case, the accumulation of charge density in the vacuum in a Gaussian-like peak is clearly visible on a logarithmic scale, in contrast to a linear scale (inset).

Clearly, the density of the negatively charge H vacancy calculation (red line) rises in the center of the vacuum in a Gaussian-like peak (parabola on a logarithmic scale), even though the absolute value does not seem very large and is easily missed by looking at the data on a linear scale (see inset). Nonetheless, even this low-density feature is sufficient to disturb the electrostatic profile significantly. A reliable extrapolation to the isolated defect limit is not possible with this calculation.

To prevent such problems, the best strategies are to reduce(!) the size of the vacuum thickness as much as possible (cheap solution), or to increase the lateral size of the supercell such that the surface charge density (and hence the curvature of the potential in the vacuum) gets lower (which is the computationally expensive solution, but sometimes the only option). In the particular case of Fig. 8, the reference slab shows a region of numerical noise inside the vacuum about 20-25 bohr wide. This amount of vacuum can probably be removed without affecting the accuracy too much for the neutral slab, while it will improve

the situation for the defect case.

7 Potential file formats

At present, `sxdefectalign` supports SPHInX, VASP, socorro, and quantum espresso¹ potential files. For other programs, you have to generate the defect and reference profiles yourself. Please note that the alignment correction of the model potential is included in the periodic energy. The defect alignment constant can then be provided with the `-C` option to obtain the total correction. Alternatively, you can help me to implement support for your files into the program. For this, send a package to `freysoldt@mpie.de` with

1. Name of the code (or potential file type)
2. proposed flag name (e.g. `--vasp`)
3. Instructions how to read the potential file into a 3D mesh
4. Instructions how to read the cell from the potential file
5. units used for lattice vectors (Å vs. bohr) and potentials (eV vs. Hartree vs. Rydberg)
6. Example potential files (1 defect, 1 reference)
7. Optional: instructions for reading atomic positions

Instructions how to interpret the file can be given in written, or in form of an example code, preferentially C, C++. (FORTRAN90 or higher is OK, FORTRAN77 is not – I am too young to know this). Point 7 is needed if you want support for the atomic sphere averages. I like to emphasize that the tone of a request is important, see the excellent notes by Clint Whaley from the ATLAS package: <http://math-atlas.sourceforge.net/faq.html#utone>.

For testing purposes, a non-cubic cell with different mesh dimensions along the first and last direction will help to detect problems with mesh order. A non-symmetric orientation of the cell ($a_y^1 \neq a_x^2$), e.g. a hexagonal cell with a_1 parallel to the x-axis, will help to detect transpose mistakes in reading the lattice vectors. Telling me the charge and the dielectric constant (approximately) will help to detect problems with the units.

Acknowledgement

I appreciate help with implementing new potential file formats:

- Joel Varley and Björn Lange for VASP
- Alan Wright for socorro
- Julian Gebhardt for quantum espresso

¹Quantum espresso in Gaussian cube format, `output_format=6` for `pp.x`

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