

Manual for `sxdefectalign2d` – 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 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 $\Delta V^{\text{DFT}} - V^{\text{model}}$. The latter can be used for potential alignment.

4. It then prints the 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.

1.2 Implementation details

1.2.1 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.

1.2.2 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 typical be 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 $Q = -1$.

1.2.3 Isolated case

The electrostatic energy in the cylindrically symmetric isolated case reads

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

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 $\mathbf{k}_{\parallel} = \mathbf{0}$ has vanishing weight in the isolated case. The only possible contribution for $\mathbf{k}_{\parallel} = \mathbf{0}$ is from the boundary conditions. The isolated reference energy in `sxdefectalign2d` employs zero potential boundary conditions (i.e., no contribution from $\mathbf{k}_{\parallel} = \mathbf{0}$).

1.2.4 Periodic case

The periodic energy reads

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

Here, V_i denotes the potential values for z_i from the direct integration of the one-dimensional Poisson equation for $\mathbf{k}_{\parallel} = \mathbf{0}$ (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

$$E^{\text{pol}} = -\frac{A}{2\pi c} \left[\frac{1}{\overline{\epsilon^{-1}}} - 1 \right] U^2 \tag{7}$$

where c denotes the supercell height along the z direction and

$$\overline{\epsilon^{-1}} = \frac{1}{N} \sum_{i=0}^{N-1} \epsilon_i^{-1} \tag{8}$$

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

2 Options for the `sxdefectalign2d` executable

Option	argument	description
<code>--help</code>		show all the available options
<code>--log</code>		create a log file
<code>--quiet</code>		don't produce output on stdout
<code>--input</code>	filename	input file (default: <code>system.sx</code>)
<code>--ecut</code>	cutoff	plane-wave cutoff energy (in Rydberg)
<code>--shift</code>	Δz	shift all charges along z (in bohr)
<code>--onlyProfile</code>		do not compute energies, only the periodic $\mathbf{k} = 0$ profile for alignment purposes.
<code>-C</code>	potential shift C	shift model potential by C (in eV)
<code>--vref</code>	filename	potential file for reference system
<code>--vdef</code>	filename	potential file for defect system
<code>--vasp</code>		potentials are in VASP format
<code>--socorro</code>		potentials are in socorro format
<code>--qe</code>		potentials are in quantum espresso format
<code>--average</code>	d	average potentials in <code>vline-eV.dat</code> over a range of d (in bohr)
<code>-n</code>	N	Set the number of points in the periodic profile
<code>-p</code>	N	Set the number of points per FFT mesh point (default: 1)
<code>--dk</code>	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. 1.2.1), 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 isolated region of interest. 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
dropV	(optional) Request a sawtooth potential with the potential step <code>dropV</code> (in eV).
cut	(optional) z position of the sawtooth cut.

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

$$V^{\text{sr}}(z) = \Delta V^{\text{DFT}}(z) - V^{\text{model}}(z) \tag{9}$$

5 Usage

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 [1]. Alternatively, one can estimate the extent of the slab and its dielectric constant (not recommended). 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
```

The outcome is shown in Fig. 1. Overall, the shape is well reproduced in the vacuum region, but the zoom-in shows a small slope. 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
```

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

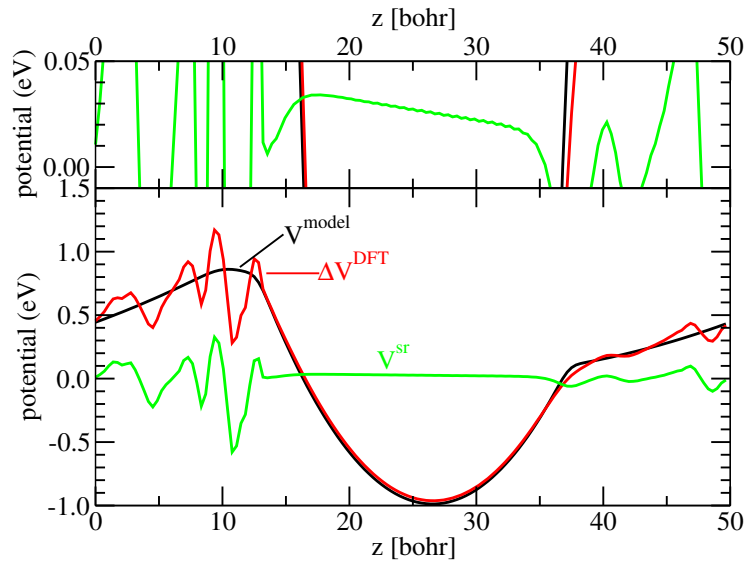


Figure 1: Potential profiles for the original estimated charge position $z_Q=10$ bohr. The upper graph shows a zoom in. The defect charge is too far left.

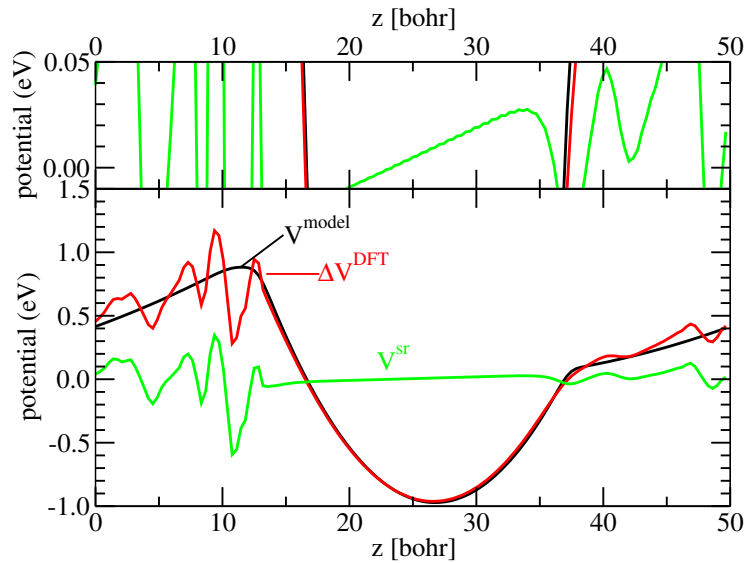


Figure 2: Potential profiles for a charge shifted by +1 bohr from the original estimated charge position $z_Q=10$ bohr. The upper graph shows a zoom in. The defect charge is too far right.

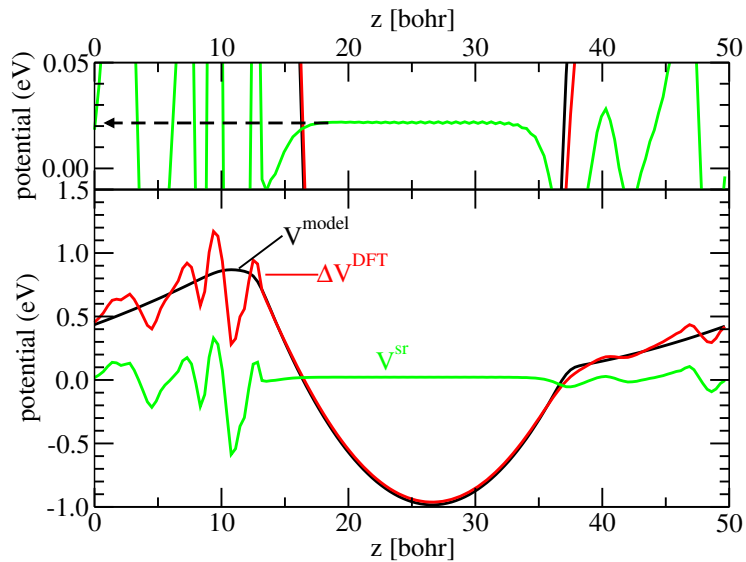


Figure 3: Potential profiles for a charge shifted by +0.3 bohr from the original estimated charge position $z_Q=10$ bohr. The upper graph shows a zoom in. The defect charge is positioned correctly now. The dashed arrow highlights how the potential alignment constant C is determined.

```

sxddefectalign2d --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. We add this to the command line with the `-C` option, and run the final calculation (without `-onlyProfile`) to get the correction:

```

sxddefectalign2d --ecut 20 --vdef vDef.sxb --vref vRef.sxb --shift 0.3 -C 0.02

```

which gives us the following output:

Final output from `sxdefectalign2d`:

```
cell defect = [a1={14.425,0,0},a2={-2e-06,24.9848,0},a3={0,0,50}]
cell bulk = [a1={14.425,0,0},a2={-2e-06,24.9848,0},a3={0,0,50}]
Cutoff = 20 Ry
N = 144
Shifting charge by 0.3
Shifting potential by 0.02 eV
--- Periodic
Q=1
--- Isolated
Isolated from -5.20833333333 to 20.1388888889 (73 points)
Q=1
Interface: 12.735
zL = -5.20833333333 eps = 12.13
E-field dependence left: zeff = 10.367490322
zR = 20.1388888889 eps = 1
E-field dependence right: zeff = 12.5398219556
---
isolated energy = 0.894920886119 eV
periodic energy = 1.01028612305 eV
iso - periodic energy = -0.115365236931 eV
```

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.

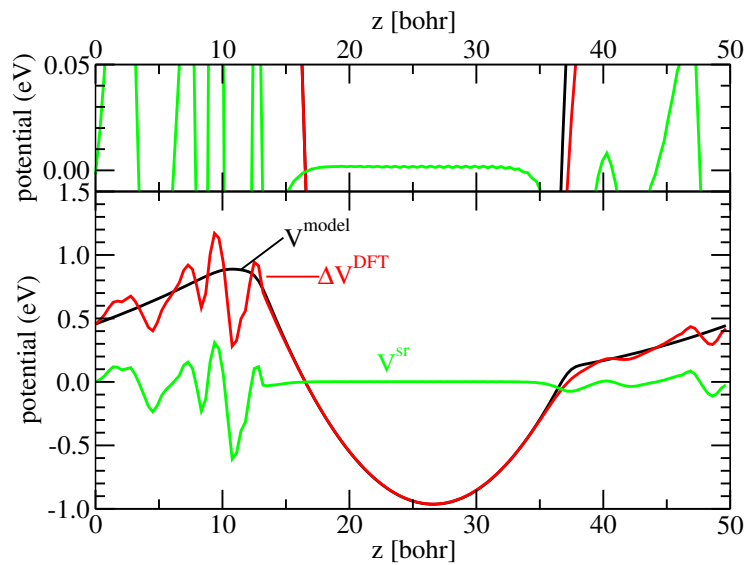


Figure 4: Potential profiles for a charge shifted by $+0.3$ bohr from the original estimated charge position $z_Q=10$ bohr, and with an alignment constant of $C = +0.02$ eV. The upper graph shows a zoom in.

6 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 format is being tested right now. Please report any trouble!

References

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