Manual for sxdefectalign version 2.2

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Contents

1 Description

The general formalism is described in Ref. [1]. The present version contains a bug fix concerning the alignment constant Δ_q [2]: instead of calculating it from the short-range average, it is set to $-C$ to take into account alignments that do not arise from charging effects, e.g. from pseudopotentials.

1.1 Changes since version 2.1

- the `vAtoms.dat` column order has changed

- support for quantum espresso file format

1.2 Changes since version 1.3

- support for dielectric tensors

- atomic sphere averages

- support for soccorro file format

- planar averages are computed along all 3 cell vectors, into `vline-eV-a0.dat`, `vline-eV-a1.dat`, and `vline-eV-a2.dat`.

1.3 Implementation details

The charge model presently supported by `sxdefectalign` is

$$q_d(r) = qxN_\gamma e^{-r/\gamma} + q(1-x)N_\beta e^{-r^2/\beta^2} \ , \tag{1}$$

where N_γ and N_β are appropriate normalization constants, and q is the charge[1] In reciprocal space, it reads (excluding the Fourier normalization constant)

$$q_d(g) = \frac{q\,x}{(1+\gamma^2 g^2)^2} + q(1-x)e^{-\frac{1}{4}\beta^2 g^2} \tag{2}$$

The unscreened electrostatic self-energy is computed as

$$E^{\mathrm{iso}} = \frac{1}{2}\frac{1}{(2\pi)^3}\int d^3\mathbf{g}\,\frac{4\pi}{|\mathbf{g}|^2}[q_d(|\mathbf{g}|)]^2 = \frac{1}{\pi}\int_0^{g_{\mathrm{cut}}} dg\ [q_d(g)]^2 \ . \tag{3}$$

The periodic energy is computed as (Ω denotes the unit cell volume)

$$\frac{2\pi}{\Omega}\sum_{\mathbf{G}\neq 0,|\mathbf{G}|\leq g_{\mathrm{cut}}} \frac{[q_d(|\mathbf{G}|)]^2}{|\mathbf{G}|^2} + \frac{q}{\sqrt{\Omega}}V(0) \ , \tag{4}$$

where the second term is the alignment correction for the model charge array. In contrast to the original paper, the alignment correction of the model charge density is included in the periodic energy, because lattice energies of non-overlapping models then agree with the point-charge result (provided that the potentials are aligned) [2]. The average electrostatic potential along the sample direction a reads

$$V(G_a \neq 0) = \frac{4\pi}{\sqrt{\Omega}}\frac{q_d(G_a)}{|G_a|^2}e^{-iG_a\tau_a} \tag{5}$$

with τ being the position of the defect center, while

$$V(0) := \frac{2\pi}{\sqrt{\Omega}}\left.\frac{d^2 q_d(g)}{dg^2}\right|_{g=0} \ . \tag{6}$$

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[1] **Note:** most DFT codes define potentials for the electrons, not for classical test charges. For consistency, the charge q must be given in units of electrons (i.e. a +1 defect has -1 electrons).

This convention ensures a constant alignment of the potential as the model parameters x, β, and γ, are varied. The real-space average potential is obtained from a Fourier series

$$\overline{V}(r_a) = \frac{1}{\sqrt{\Omega}} \sum_{G_a} V(G_a) e^{iG_a r_a} \ . \tag{7}$$

The short-range potential V^{sr} is obtained from the above long-range model potential and the actual local electrostatic potentials from the defect and reference DFT calculations as

$$V^{\mathrm{sr}} = V^{\mathrm{DFT}}(\text{defect}) - V^{\mathrm{DFT}}(\text{reference}) - V(\text{long-range model}) \ . \tag{8}$$

Please note that we require that the supercell of the defect is an exact multiple of the reference supercell,i.e., no lattice relaxation is allowed.

The full source code is part of the S/PHI/nX package[2], which is freely available at `https://sxrepo.mpie.de`.

1.4 Anisotropic screening

Originally, the scheme was developed for isotropic screening. In this case, the unscreened energies and potentials are simply scaled by the inverse dielectric constant.

Anisotropic screening requires to use a dielectric tensor $\underline{\epsilon} = \epsilon_{\alpha\beta}$, where α and β are cartesian indices (x, y, z) [3]. Dielectric tensors are specified using the `--tensor` option instead of the `--eps` option. If your dielectric tensor is aligned to the coordinate system (all off-diagonal elements = 0), it is sufficient to provide the diagonal elements. If you provide 6 elements, these define the dielectric tensor in Voigt notation: $\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}, \epsilon_{yz}, \epsilon_{xz}, \epsilon_{xy}$. If you provide 9 elements, you give the dielectric tensor (which must be symmetric!) in its 3×3 representation row by row: $\epsilon_{xx}, \epsilon_{xy}, \epsilon_{xz}, \epsilon_{xy}, \epsilon_{yy}, \epsilon_{yz}, \epsilon_{xz}, \epsilon_{yz}, \epsilon_{zz}$.

However, we follow a different approach than Kumagai and Oba for evaluating the anisotropically screened energy. The screened periodic potential reads[3]

$$V(\mathbf{G} \neq \mathbf{0}) = \frac{4\pi}{\sqrt{\Omega}} \frac{q_d(\mathbf{G})}{\mathbf{G}^T \underline{\epsilon} \mathbf{G}} \tag{9}$$

and we use the alignment convention for $\mathbf{G} = \mathbf{0}$

$$V(0) := \frac{2\pi}{\overline{\epsilon}\sqrt{\Omega}} \left. \frac{d^2 q_d(g)}{dg^2} \right|_{g=0} \ . \tag{10}$$

Here, $\overline{\epsilon}$ is the appropriate spherical average from

$$\frac{1}{\overline{\epsilon}} = \int d\hat{\mathbf{g}} \frac{1}{\hat{\mathbf{g}}^T \underline{\epsilon} \hat{\mathbf{g}}} \tag{11}$$

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[2]The source is in `sphinx/src/tools/SxDefectAlign.cpp`, but makes heavy use of the S/PHI/nX libraries, so you cannot compile it without S/PHI/nX.

[3] In the denominator, $\mathbf{G}^T \underline{\epsilon} \mathbf{G} = \sum_{\alpha\beta} G_\alpha \epsilon_{\alpha\beta} G_\beta$

where the integration in $\hat{\mathbf{g}}$ is over the unit sphere. In practice, we determine it from a 110-point Lebedev spherical grid [4]. The screeened periodic energy reads

$$E = \frac{1}{2\sqrt{\Omega}} \sum_{\mathbf{G} \neq 0} V(\mathbf{G}) q_d(|\mathbf{G}|) + \frac{q}{\sqrt{\Omega}} V(0) \, , \tag{12}$$

The isolated energy is obtained from the spherically averaged screening, i.e., from Eq. (3) scaled by $1/\bar{\epsilon}$.

Please note that the presently implemented **dielectric anisotropy has not been thoroughly tested**; I would greatly appreciate feedback if you use it. Preliminary tests on weakly anisotropic systems ($\sim$10% difference in the main components of the dielectric tensor) showed a marginal change in the calculated correction, while slightly improving the agreement for the alignment in the different directions. For these cases, the effort of determining the dielectric tensor may not be worthwhile. For more strongly anisotropic systems (e.g. layered systems), treating the dielectric anisotropy is a must [3].

1.5 Atomic sphere averages

The original scheme for evaluating the shift in the potential from planar averages works nicely for systems dominated by electronic screening, but gets painful when ionic screening becomes important. The main reason is that as ions move between the defect and reference system, the strong contribution from the ionic core does not cancel, leading to wild oscillations in the potential difference. While this can be damped partly by averaging, the present version offers an alternative scheme: evaluation of the potential near the ionic cores (similar to [3]). In practice, we compute the potential average around each atom with a Gaussian weight function. As the center of the Gaussian moves with the atom, the ionic cores largely cancel out.

The spherical average for an atom located at τ' is obtained from

$$\overline{V}_{\tau'} = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G} \neq 0, |\mathbf{G}| \leq g_{\text{cut}}} V(\mathbf{G}) e^{i\mathbf{G}\tau'} e^{-\frac{1}{2}|\mathbf{G}|^2 \beta^2} \tag{13}$$

where the Gaussian broadening β defaults to 1.5 bohr; it can be changed via the `--atomAverage` option.

Atomic sphere averages are automatically computed if the atomic positions are available (VASP, socorro, quantum espresso, SPHInX structure files). In practice, we map defect atoms to the bulk atoms with a tolerance of 0.5 bohrs in the coordinates.

4

2 Options

Option	argument	description
`--help`		show all the available options
`--ecut`	energy	reciprocal space cutoff energy (Ry). This implicitly defines the Fourier mesh size.
`--charge`	q	defect charge in charge units used by the DFT program (note: most programs use q(electron) = +1, so q must be minus classical charge)
`--eps`	ε	dielectric constant
`--tensor`	$\varepsilon_{\alpha\beta}$	dielectric tensor.
`--pos`	x,y,z	center of defect (default: bohr)
`--relative`		center of defect is in relative coordinates
`--vref`	file	reference potential (bulk)
`--vdef`	file	defect potential
`--vasp`		all potentials are VASP LOCPOT files
`--socorro`		all potentials are socorro files
`--qe`		all potentials are quantum espresso files. **The potential reader is being tested right now. Report any trouble with it!**
`--average`	width	average in order to smoothen wiggly potentials (bohr)
`-C`	alignment	shift long-range potential (eV)
`--beta`	β	changes the width of the Gaussian $e^{-\beta^2/r^2}$ (bohr)
`--gamma`	γ	exponential decay constant
`--expnorm`	x	relative amount of exponential decay (0..1)
`--structDef`	file	structure file (SPHInX format) for defect
`--structRef`	file	structure file (SPHInX format) for reference
`--atomAverage`	width	Gaussian broadening for atomic-sphere averages (bohr)

3 Output

3.1 Planar averages: `vline-eV-a{0,1,2}.dat`

`vline-eV-a{0,1,2}.dat`, an xmgrace-style file, containg

```
z  V(long-range)
...
&
z V(defect)-V(ref)   V(defect)-V(ref)-V(long-range)
...
```

where z (in bohr) is the coordinate along the profiling axis, and V(..) is the planar average over the other two axes. In other words, there is a two-column

set and a three column set. The third column of the second set is the short-range potential.

3.2 Atomic sphere averages: `vAtoms.dat`

When structures and potentials are provided, there is a file `vAtoms.dat`. The format is[4]

```
r V(long-range) V(defect)-V(ref) V(defect)-V(ref)-V(long-range) x y z
...
```

with one line per atom in the defect cell that could be successfully mapped to the reference structure (tolerance: 0.5 bohr). Here, r is the distance from the defect center (in bohr), V(...) are spherical-Gaussian averaged potentials, and x,y,z are the coordinates of the atom in the defect cell. They are sorted by species, with an empty line separating the different chemical species.

4 Usage

> **Note**: After downloading the executable, make sure that the executable bit is set via
>
> ```
>     chmod u+x sxdefectalign
> ```
> and that the current directory (.) is in your `PATH`. Otherwise, mark the path with `./sxdefectalign` .

The procedure is to run the program once without -C parameter, check that the short-range potential reaches a plateau, and read off the plateau value C. Then run the program a second time, with -C C and take the correction from the output. The correction printed out must be added to the uncorrected formation energy.

4.1 Example: SPHInX

Assume you have two directories: one `vacancy/` that contains the calculation of a vacancy , and `bulk/` that contains an equivalent bulk calculation. Both calculations were run with a 40 Ry cutoff. The vacancy is in the +2 charge state (i.e. -2 electrons). The vacancy sits in the center of the cell. The dielectric constant of the host material is 8.9. Then use the following single line

```
sxdefectalign --ecut 40 --charge -2 --eps 8.9 --center 0.5,0.5,0.5 --relative
--vdef vacancy/vElStat-eV.sxb --vref bulk/vElStat-eV.sxb
```

to create `vline-eV-a0.dat`, `vline-eV-a1.dat`, and `vline-eV-a2.dat`. I use xmgrace for plotting the data (you may use any other program, of course).

```
xmgrace -nxy vline-eV-a0.dat
```

---

[4]The order of columns has changed from version 2.1 to 2.2: the long-range and V(defect) – V(ref) columns have been swapped.

Looking at the plot, you read off a plateau value of C=-0.12 eV for the green line. Thus you run

```
sxdefectalign --ecut 40 --charge -2 --eps 8.9 --center 0.5,0.5,0.5 --relative
--vdef vacancy/vElStat-eV.sxb --vref bulk/vElStat-eV.sxb -C -0.12
```

to get the final output. The correction is added to the formation energy.

4.2   Example: VASP

Assume you have two directories: one `vacancy/` that contains the calculation of a vacancy , and `bulk/` that contains an equivalent bulk calculation. Both calculations were run with a 400 eV cutoff ($\approx$30 Ry). The vacancy is in the +2 charge state (i.e. -2 electrons). The vacancy sits in the center of the cell. The dielectric constant of the host material is 8.9. Then use the following single line

```
sxdefectalign --ecut 30 --charge -2 --eps 8.9 --center 0.5,0.5,0.5 --relative
--vdef vacancy/LOCPOT --vref bulk/LOCPOT --vasp
```

to create `vline-eV-a0.dat`, `vline-eV-a1.dat`, and `vline-eV-a2.dat`. I use xmgrace for plotting the data (you may use any other program, of course).

```
xmgrace -nxy vline-eV-a0.dat
```

Looking at the plot, you read off a plateau value of C=-0.12 eV for the green line. Thus you run

```
sxdefectalign --ecut 30 --charge -2 --eps 8.9 --center 0.5,0.5,0.5 --relative
--vdef vacancy/LOCPOT --vref bulk/LOCPOT --vasp -C -0.12
```

to get the final output. The correction is added to the formation energy.

4.3   Example: socorro

This example is a Ga vacancy in GaAs is in the -3 charge state (i.e. +3 electrons), including ionic relaxation. Assume you have two files for the electro-static potential: `els_potential_defect` and `els_potential_bulk`. We will use a plane-wave cutoff of 20 Ry. The vacancy sits in the origin of the cell. The dielectric constant of the host material is 12.9. As the ions move, the raw potential difference is very wiggly. We will therefore use a 5.2 bohr averaging. Then use the following single line

```
sxdefectalign -q 3 --eps 12.9 --vdef els_potential_defect
--vref els_potential_bulk --ecut 20 --socorro --average 5.2
```

to create `vline-eV-a0.dat`, `vline-eV-a1.dat`, and `vline-eV-a2.dat`. I use xmgrace for plotting the data (you may use any other program, of course).

```
xmgrace -nxy vline-eV-a0.dat
xmgrace -nxy vline-eV-a1.dat
xmgrace -nxy vline-eV-a2.dat
```

Looking at the plots, you estimate a plateau value of C=-0.01 eV for the green line. Thus you run

```
sxdefectalign -q 3 --eps 12.9 --vdef els_potential_defect
--vref els_potential_bulk --ecut 20 --socorro --average 5.2 -C -0.01
```

to get the final output. The correction is added to the formation energy.

4.4   Example: quantum espresso

This example is a Ga vacancy in GaAs is in the -3 charge state (i.e. +3 electrons), including ionic relaxation. We will use a plane-wave cutoff of 30 Ry. In quantum espresso, one first uses the pw.x executable to do the DFT calculation for the pristine and defected structures and then use the `pp.x` executable to get the potential as a cube file[5].

Example input for the generation of the cube file:

```
&INPUTPP
  prefix='GaAs'
  outdir='relax_pris'
  filplot='relax_pris.pp'
  plot_num = 11
/
&PLOT
  nfile=1
  filepp(1)='relax_pris.pp'
  iflag=3
  output_format=6
  fileout='v_elec_pristine.cube'
/
```

Assume you have two files for the electrostatic potential: `v_elec_defect.cube` and `v_elec_pristine.cube`.

The vacancy sits in the origin of the cell. The dielectric constant of the host material is 12.9. As the ions move, the raw potential difference is very wiggly. We will therefore use a 5.2 bohr averaging. Then use the following single line

```
sxdefectalign -q 3 --eps 12.9 --vdef v_elec_defect.cube
--vref v_elec_pristine.cube --ecut 30 --qe --average 5.2
```

to create `vline-eV-a0.dat`, `vline-eV-a1.dat`, and `vline-eV-a2.dat`. I use xmgrace for plotting the data (you may use any other program, of course).

```
xmgrace -nxy vline-eV-a0.dat
xmgrace -nxy vline-eV-a1.dat
xmgrace -nxy vline-eV-a2.dat
```

Looking at the plots, you estimate a plateau value of C=-0.01 eV for the green line. Thus you run

```
sxdefectalign -q 3 --eps 12.9 --vdef v_elec_defect.cube
--vref v_elec_pristine.cube --ecut 30 --qe --average 5.2 -C -0.01
```

to get the final output. The correction is added to the formation energy.

5   Potential file formats

At present, `sxdefectalign` supports SPHInX, VASP, socorro, and quantum espressopotential 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, and Zeeshan Ahmad for `pp.x` input example.

References

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[5] https://www.quantum-espresso.org/Doc/INPUT_PP.html