Symmetry constrained relaxation in FHI-aims

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PhD student at Northumbria University

Imperial College London, 10th June 2022

Personal background

Past

- Physics (Hons) degree with a undergraduate thesis on diagonalization of sparse matrices from $\mathcal{O}(N^3)$ to $\mathcal{O}(N)$
- Research assistant for 3 years at TIFR India working with small molecules, quasi-1D materials and 3D materials
- Became fluent in Python but stammered with Fortran90
- Machine learning project based on regression problems and generating databases with high-throughput computation techniques

Personal background

Present

- PhD student with Dr Lucy Whalley at Northumbria University
  - CDT for Renewable Energy for Northeast Universities (ReNU)
- Overall PhD is focused on chalcogenide materials for energy generation and storage
- First project is modelling the $BaZrS_3$ chalcogenide-based perovskite material
  - Thermodynamics of the perovskite and competing phases
  - Verifying synthesis techniques with computed IR and Raman spectra
- Disorder in Mg-based spinel battery materials $MgM_2(S,Se)_4$

Talk overview

- Symmetry constrained relaxation: what it is, how it’s done and why it’s needed
- FHI-aims routines with AFLOW
- How to save CPU time with geometries in correct symmetries: examples from systems of interest
- Where symmetry constrained relaxation is invalid

Introduction to FHI-aims

- FHI-aims is a numeric atom-centered orbital code in contrast with VASP which is a pseudopotential based code
- It is open-source and adopts more recent software sustainability practices
- It has fantastic documentation
- A very responsive community through their Slack channel and other forums

Geometry relaxation

- As a default, in a geometry.in (POSCAR) file, 3N+9 coordinates are relaxation parameters for the optimizer. This is unnecessary, unless the system prefers a monoclinic $P1$ space group
- When one knows the space group of the system, the input can be designed to only include lattice constants and internal parameters of the particular space group
- Internal parameters are defined through Wyckoff positions of the space group and can be predetermined through the International Tables of Crystallography

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AFLOW + FHI-aims

- This method is not very widely used yet, the goal of this presentation is to convince you to try this in your next project
- An interface with AFLOW defines the specific symmetries of the system through parametric equations in the geometry.in file

```
lattice_vector -2.5292500000000002 2.5292500000000002 3.6696000483250000
lattice_vector 2.5292500000000002 -2.5292500000000002 3.6696000483250000
lattice_vector 2.5292500000000002 2.5292500000000002 -3.6696000483250000
atom_frac 0.3750000000000001 0.7121884100000000 0.8371884100000001 O
atom_frac 0.8750000000000000 0.5378115899999999 0.1628115900000001 O
atom_frac 0.2878115900000000 0.1249999999999999 0.6628115899999999 O
atom_frac 0.4621884100000001 0.6249999999999999 0.3371884100000000 O
atom_frac 0.0000000000000000 -0.0000000000000000 0.0000000000000000 Si
atom_frac 0.7500000000000001 0.2499999999999999 0.5000000000000000 Si
```

```
lattice_vector -2.5292500000000002 2.5292500000000002 3.6696000483250000
lattice_vector 2.5292500000000002 -2.5292500000000002 3.6696000483250000
lattice_vector 2.5292500000000002 2.5292500000000002 -3.6696000483250000
atom_frac 0.3750000000000001 0.7121884100000000 0.8371884100000001 O
atom_frac 0.8750000000000000 0.5378115899999999 0.1628115900000001 O
atom_frac 0.2878115900000000 0.1249999999999999 0.6628115899999999 O
atom_frac 0.4621884100000001 0.6249999999999999 0.3371884100000000 O
atom_frac 0.0000000000000000 -0.0000000000000000 0.0000000000000000 Si
atom_frac 0.7500000000000001 0.2499999999999999 0.5000000000000000 Si
symmetry_n_params 3 2 1
symmetry_params a c x2
symmetry_lv -0.5*a, 0.5*a, 0.5*c
symmetry_lv 0.5*a, -0.5*a, 0.5*c
symmetry_lv 0.5*a, 0.5*a, -0.5*c
symmetry_frac 0.375, 0.125 + x2, 0.25 + x2
symmetry_frac 0.875, 1.125 - x2, 0.75 - x2
symmetry_frac 0.875 - x2, 0.125, 1.25 - x2
symmetry_frac -0.125 + x2, 0.625, -0.25 + x2
symmetry_frac 0, 0, 0
symmetry_frac 0.75, 0.25, 0.5
```

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AFLOW + FHI-aims

How to make an input geometry.in for SiO_2

Step 1

Results per page: 50 | Select page: 1 | *Found 471 entries*

ENTRY	space group	Pearson symbol	DATA
O_2Si [009b39705d1c3115]	$P3_221$ (#154)	hP9	[API, Out, JSON]
O_2Si [006068d16ebfef92]	*Fddd* (#70)	oF96	[API, Out, JSON]
O_2Si [012580c76137accc]	$C222_1$ (#20)	oS24	[API, Out, JSON]
O_2Si [01b0704ecadf9ec9]	$Pa\bar{3}$ (#205)	cP12	[API, Out, JSON]
O_2Si [02d8b57eeb87de27]	$P3_221$ (#154)	hP9	[API, Out, JSON]
O_2Si [02980204caec92e8]	$C222_1$ (#20)	oS24	[API, Out, JSON]
O_2Si [033712fec2d90a1c]	$P3_221$ (#154)	hP9	[API, Out, JSON]
O_2Si [031ff90831bddc49]	$I2_13$ (#199)	cI72	[API, Out, JSON]
O_2Si [03186361f1b877d2]	$P4_32_12$ (#96)	tP36	[API, Out, JSON]
O_2Si [04fb7862623235b0]	$P3_121$ (#152)	hP9	[API, Out, JSON]
O_2Si [068eeedb53be0875]	$Pa\bar{3}$ (#205)	cP12	[API, Out, JSON]
O_2Si [068e3294df46f7b4]	$R\bar{3}$ (#148)	hR72	[API, Out, JSON]
O_2Si [088983067b706310]	$P4_12_12$ (#92)	tP12	[API, Out, JSON]
O_2Si [0a18c1a34f68e2e2]	$P3_121$ (#152)	hP9	[API, Out, JSON]
O_2Si [0d07d3c41cb5da23]	**$I\bar{4}2d$ (#122)**	**tI12**	**[API, Out, JSON]**
O_2Si [0e7071de7a46c90a]	$P6_3/mmc$ (#194)	hP12	[API, Out, JSON]
O_2Si [0ef28cf72e724afe]	$P4_2/mnm$ (#136)	tP6	[API, Out, JSON]

http://aflowlib.org/search/

AFLOW + FHI-aims

How to make an input geometry.in for SiO_2

Step 1

Si , O

Search (60389 entries)

Display

ICSD only | All AFLOW

Results per page: 50

Select page: 1

Found 471 entries

ENTRY	space group	Pearson symbol	DATA
O_2Si [009b39705d1c3115]	$P3_221$ (#154)	hP9	[API, Out, JSON]
O_2Si [006068d16ebfef92]	$Fddd$ (#70)	oF96	[API, Out, JSON]
O_2Si [012580c76137accc]	$C222_1$ (#20)	oS24	[API, Out, JSON]
O_2Si [01b0704ecadf9ec9]	$Pa\bar{3}$ (#205)	cP12	[API, Out, JSON]
O_2Si [02d8b57eeb87de27]	$P3_221$ (#154)	hP9	[API, Out, JSON]
O_2Si [02980204caec92e8]	$C222_1$ (#20)	oS24	[API, Out, JSON]
O_2Si [033712fec2d90a1c]	$P3_221$ (#154)	hP9	[API, Out, JSON]
O_2Si [031ff90831bddc49]	$I2_13$ (#199)	cI72	[API, Out, JSON]
O_2Si [03186361f1b877d2]	$P4_32_12$ (#96)	tP36	[API, Out, JSON]
O_2Si [04fb7862623235b0]	$P3_121$ (#152)	hP9	[API, Out, JSON]
O_2Si [068eeedb53be0875]	$Pa\bar{3}$ (#205)	cP12	[API, Out, JSON]
O_2Si [068e3294df46f7b4]	$R\bar{3}$ (#148)	hR72	[API, Out, JSON]
O_2Si [088983067b706310]	$P4_12_12$ (#92)	tP12	[API, Out, JSON]
O_2Si [0a18c1a34f68e2e2]	$P3_121$ (#152)	hP9	[API, Out, JSON]
O_2Si [0d07d3c41cb5da23]	**$I\bar{4}2d$ (#122)**	**tI12**	**[API, Out, JSON]**
O_2Si [0e7071de7a46c90a]	$P6_3/mmc$ (#194)	hP12	[API, Out, JSON]
O_2Si [0ef28cf72e724afe]	$P4_2/mnm$ (#136)	tP6	[API, Out, JSON]

Step 2

- Structure Visualization
- Entry
- Relaxed Structure
  - Structure (as calculated)
  - AFLOW Prototype
  - Bravais Lattice of the Crystal
  - Bravais Lattice of the Lattice
  - Point Group of the Crystal
  - Reciprocal Space Lattice
  - Superlattice
- Thermodynamic Properties
- Chemistry
  - Bader charges
- Magnetic Properties
- Scintillation Properties
- Electronic Properties
  - Electronic structure
- Calculation Details
- Downloadable Files
  - Entry
  - Relaxed Structure
  - Bader charges
  - Computational parameters

DOWNLOADABLE FILES

ENTRY

aflowlib.out: [aflowlib.out]

aflowlib.json: [aflowlib.json]

RELAXED STRUCTURE

Relaxed positions (VASP): [VASP-CONTCAR]

Relaxed positions (QE): [QE-GEOMETRY]

Relaxed positions (ABINIT): [ABINIT-GEOMETRY]

Relaxed positions (AIMS): [AIMS-GEOMETRY]

Extended crystallographic data for the relaxed structure: [edata.relax.out]

Extended crystallographic data for the band structure: [edata.bands.out]

http://aflowlib.org/search/

AFLOW + FHI-aims

How to make an input geometry.in for SiO_2

Step 3

aflow_prototype_label_orig=A2B_tI12_122_d_a | aflow_prototype_params_list_orig=a,c/a,x2 | aflow_prototype_params_values_orig=5.0313,1.440582,0.9138 |
aflow_prototype_label_relax=A2B_tI12_122_d_b | aflow_prototype_params_list_relax=a,c/a,x2 | aflow_prototype_params_values_relax=5.0585,1.4508649,0.58718841 |

http://aflowlib.org/search/

AFLOW + FHI-aims

How to make an input geometry.in for SiO_2

Step 3

```
aflow_prototype_label_orig=A2B_tI12_122_d_a | aflow_prototype_params_list_orig=a,c/a,x2 | aflow_prototype_params_values_orig=5.0313,1.440582,0.9138 |
aflow_prototype_label_relax=A2B_tI12_122_d_b | aflow_prototype_params_list_relax=a,c/a,x2 | aflow_prototype_params_values_relax=5.0585,1.4508649,0.58718841 |
```

Step 4

```
Prakritis-MacBook-Air:~ prakritikayastha$ aflow --proto=A2B_tI12_122_d_a:O:Si --params=5.0585,1.4508649,0.58718841
 --aims --add_equations
# OSi/A2B_tI12_122_d_a.AB params=5.0585,1.4508649,0.58718841 SG=122 [ANRL doi: 10.1016/j.commatsci.2017.01.017 (pa
rt 1), doi: 10.1016/j.commatsci.2018.10.043 (part 2)]
# AFLOW::AIMS BEGIN
lattice_vector   -2.52925000000000   2.52925000000000   3.66960004832500
lattice_vector    2.52925000000000  -2.52925000000000   3.66960004832500
lattice_vector    2.52925000000000   2.52925000000000  -3.66960004832500
atom_frac    0.37500000000000    0.71218800000000    0.83718800000000  O
atom_frac    0.87500000000000    0.53781200000000    0.16281200000000  O
atom_frac    0.28781200000000    0.12500000000000    0.66281200000000  O
atom_frac    0.46218800000000    0.62500000000000    0.33718800000000  O
atom_frac    0.00000000000000    0.00000000000000    0.00000000000000  Si
atom_frac    0.75000000000000    0.25000000000000    0.50000000000000  Si
# format: symmetry_n_params [n n_lv n_fracpos]
symmetry_n_params 3 2 1
symmetry_params a c x2
symmetry_lv -0.5*a , 0.5*a , 0.5*c
symmetry_lv 0.5*a , -0.5*a , 0.5*c
symmetry_lv 0.5*a , 0.5*a , -0.5*c
symmetry_frac 0.375 , x2+0.125 , x2+0.25
symmetry_frac 0.875 , -x2+0.125 , -x2+0.75
symmetry_frac -x2+0.875 , 0.125 , -x2+0.25
symmetry_frac x2+0.875 , 0.625 , x2+0.75
symmetry_frac 0 , 0 , 0
symmetry_frac 0.75 , 0.25 , 0.5
# AFLOW::AIMS END
```

http://aflowlib.org/search/

AFLOW + FHI-aims (a gotcha!)

- In FHI-aims the Wyckoff positions outside the unit cell are not treated as equivalent sites which can cause geometry relaxations to fail
- For a system with translational symmetry with unit cell ‘size’ 1, [-x,0,0] and [1-x,0,0] are equivalent sites, but they are not to the FHI-aims solver

Atoms and constraints don’t match

```
atom_frac  0.24447000000000  0.24447000000000  0.00000000000000 Ba
atom_frac  0.75553000000000  0.75553000000000  0.00000000000000 Ba
atom_frac  0.25553000000000  0.74447000000000  0.50000000000000 Ba
atom_frac  0.74447000000000  0.25553000000000  0.50000000000000 Ba
symmetry_frac x3 , x3 , 0
symmetry_frac -x3 , -x3 , 0
symmetry_frac -x3+0.5 , x3+0.5 , 0.5
symmetry_frac x3+0.5 , -x3+0.5 , 0.5
```

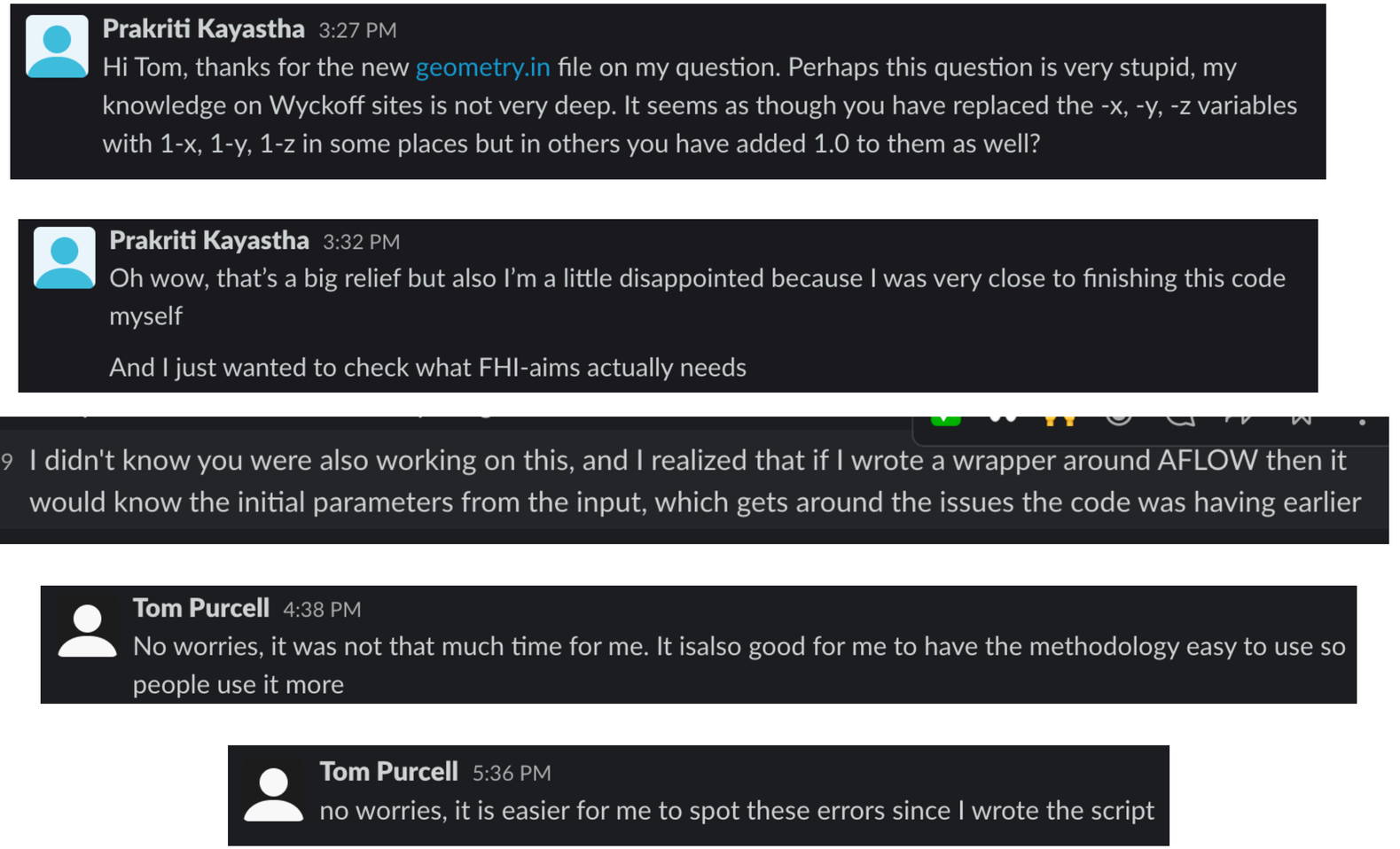
Atoms and constraints match

```
atom_frac  0.24447000000000  0.24447000000000  0.00000000000000 Ba
atom_frac  0.75553000000000  0.75553000000000  0.00000000000000 Ba
atom_frac  0.25553000000000  0.74447000000000  0.50000000000000 Ba
atom_frac  0.74447000000000  0.25553000000000  0.50000000000000 Ba
symmetry_frac x3 , x3 , 0
symmetry_frac 1-x3 , 1-x3 , 0
symmetry_frac -x3+0.5 , x3+0.5 , 0.5
symmetry_frac x3+0.5 , -x3+0.5 , 0.5
```

- FHI-aims needs the positions listed in the file and constraints to point to the same atom

Anecdote from a few months ago..

From the FHI-aims Slack channel



Prakriti Kayastha 3:27 PM
Hi Tom, thanks for the new geometry.in file on my question. Perhaps this question is very stupid, my knowledge on Wyckoff sites is not very deep. It seems as though you have replaced the -x, -y, -z variables with 1-x, 1-y, 1-z in some places but in others you have added 1.0 to them as well?

Prakriti Kayastha 3:32 PM
Oh wow, that's a big relief but also I'm a little disappointed because I was very close to finishing this code myself

And I just wanted to check what FHI-aims actually needs

3:39 I didn't know you were also working on this, and I realized that if I wrote a wrapper around AFLOW then it would know the initial parameters from the input, which gets around the issues the code was having earlier

Tom Purcell 4:38 PM
No worries, it was not that much time for me. It isalso good for me to have the methodology easy to use so people use it more

Tom Purcell 5:36 PM
no worries, it is easier for me to spot these errors since I wrote the script

AFLOW + FHI-aims (a gotcha!)

```
python3 aflow_structure_wrapper.py --proto=A2B_tI12_122_d_a:O:Si --params=5.0585,1.4508649,0.58718841
```

- The wrapper script (*now available* in the utilities directory of FHI-aims) calls the AFLOW within it's routine and ensures the atoms are inside the unit cell
- Note: The wrapper script is based on a symmetry module in ASE, so it should be extensible for every DFT code
- Side note: It is possible that the crystal prototype you are looking for is not present in the AFLOW database such as $Y_2Ti_2O_5S_2$. This is how the community moves forward — by asking for what you need

Brlec *et al*., 2022 10.26434/chemrxiv-2022-zk09d

How a single atom affects symmetry of the system

Manually adding noise to show it's affect on symmetry

Tetrahedral $I\bar{4}2d$ symmetry

```
lattice_vector     -2.49455040      2.49455040      3.66755776
lattice_vector      2.49455040     -2.49455040      3.66755776
lattice_vector      2.49455040      2.49455040     -3.66755776
atom_frac        0.37500000      1.02953838      1.15453838 O
atom_frac        0.87500000      0.22046162     -0.15453838 O
atom_frac       -0.02953838      0.12500000      0.34546162 O
atom_frac        0.77953838      0.62500000      0.65453838 O
atom_frac        0.00000000      0.00000000      0.00000000 Si
atom_frac        0.75000000      0.25000000      0.50000000 Si
```

Monoclinic $P1$ symmetry

```
lattice_vector     -2.51556912      2.51556912      3.68737330
lattice_vector      2.51556912     -2.51556912      3.68737330
lattice_vector      2.51556912      2.51556912     -3.68737330
atom_frac        0.37500000      1.03312012      1.15812012 O
atom_frac        0.87500000      0.21687988     -0.15812012 O
atom_frac       -0.03312012      0.12500000      0.34187988 O
atom_frac        0.78312012      0.62500000      0.65812012 O
atom_frac        0.00000000      0.00000000      0.00000000 Si
atom_frac        0.75000000      0.25000000      0.51000000 Si
```

Reducing relaxation steps (and time)

A SiO_2 example

- Convergence criteria of 5E-3 eV/A

Constrained relax (14 steps)

```
grep 'Maximum force component is ' outfile
  Maximum force component is  0.195626E+01 eV/A.
  Maximum force component is  0.359697E+01 eV/A.
  Maximum force component is  0.616373E+01 eV/A.
  Maximum force component is  0.199599E+01 eV/A.
  Maximum force component is  0.110042E+01 eV/A.
  Maximum force component is  0.188100E+00 eV/A.
  Maximum force component is  0.147833E+00 eV/A.
  Maximum force component is  0.170031E+00 eV/A.
  Maximum force component is  0.876995E-01 eV/A.
  Maximum force component is  0.974468E-01 eV/A.
  Maximum force component is  0.111949E+00 eV/A.
  Maximum force component is  0.943848E-01 eV/A.
  Maximum force component is  0.415194E-01 eV/A.
  Maximum force component is  0.928476E-02 eV/A.
  Maximum force component is  0.105587E-02 eV/A.
```

Full relax (40 steps)

```
grep 'Maximum force component is ' outfile
  Maximum force component is  0.293440E+01 eV/A.
  Maximum force component is  0.321741E+01 eV/A.
  Maximum force component is  0.541133E+01 eV/A.
  Maximum force component is  0.641221E+01 eV/A.
  Maximum force component is  0.113899E+02 eV/A.
  Maximum force component is  0.652963E+01 eV/A.
  Maximum force component is  0.669594E+01 eV/A.
  Maximum force component is  0.360859E+01 eV/A.
  Maximum force component is  0.163467E+01 eV/A.
  Maximum force component is  0.157145E+01 eV/A.
  Maximum force component is  0.123634E+01 eV/A.
  Maximum force component is  0.547127E+00 eV/A.
  Maximum force component is  0.181153E+01 eV/A.
  Maximum force component is  0.886020E+00 eV/A.
  Maximum force component is  0.109194E+01 eV/A.
  Maximum force component is  0.234305E+01 eV/A.
  Maximum force component is  0.497395E+00 eV/A.
  Maximum force component is  0.101806E+01 eV/A.
  Maximum force component is  0.371355E+00 eV/A.
  Maximum force component is  0.738073E+00 eV/A.
  Maximum force component is  0.274962E+00 eV/A.
  Maximum force component is  0.208805E+00 eV/A.
  Maximum force component is  0.125885E+00 eV/A.
  Maximum force component is  0.767748E+00 eV/A.
  Maximum force component is  0.266856E+00 eV/A.
  Maximum force component is  0.348235E+00 eV/A.
  Maximum force component is  0.133958E+00 eV/A.
  Maximum force component is  0.107640E+00 eV/A.
  Maximum force component is  0.176962E+00 eV/A.
  Maximum force component is  0.766319E+00 eV/A.
  Maximum force component is  0.136109E+00 eV/A.
  Maximum force component is  0.120321E+00 eV/A.
  Maximum force component is  0.126349E+00 eV/A.
  Maximum force component is  0.102609E+00 eV/A.
  Maximum force component is  0.652688E-01 eV/A.
  Maximum force component is  0.288235E-01 eV/A.
  Maximum force component is  0.195064E-01 eV/A.
  Maximum force component is  0.148230E-01 eV/A.
  Maximum force component is  0.836319E-02 eV/A.
  Maximum force component is  0.532721E-02 eV/A.
  Maximum force component is  0.119471E-02 eV/A.
```

Relaxed geometries

Constrained relax vs full relax for SiO_2

- Recall: default symmetry constraint in spglib is 1E-5 A

Constrained relax

```
lattice_vector     -2.49455040      2.49455040      3.66755776
lattice_vector      2.49455040     -2.49455040      3.66755776
lattice_vector      2.49455040      2.49455040     -3.66755776
atom_frac       0.37500000      1.02953838      1.15453838 O
atom_frac       0.87500000      0.22046162     -0.15453838 O
atom_frac      -0.02953838      0.12500000      0.34546162 O
atom_frac       0.77953838      0.62500000      0.65453838 O
atom_frac       0.00000000      0.00000000      0.00000000 Si
atom_frac       0.75000000      0.25000000      0.50000000 Si
```

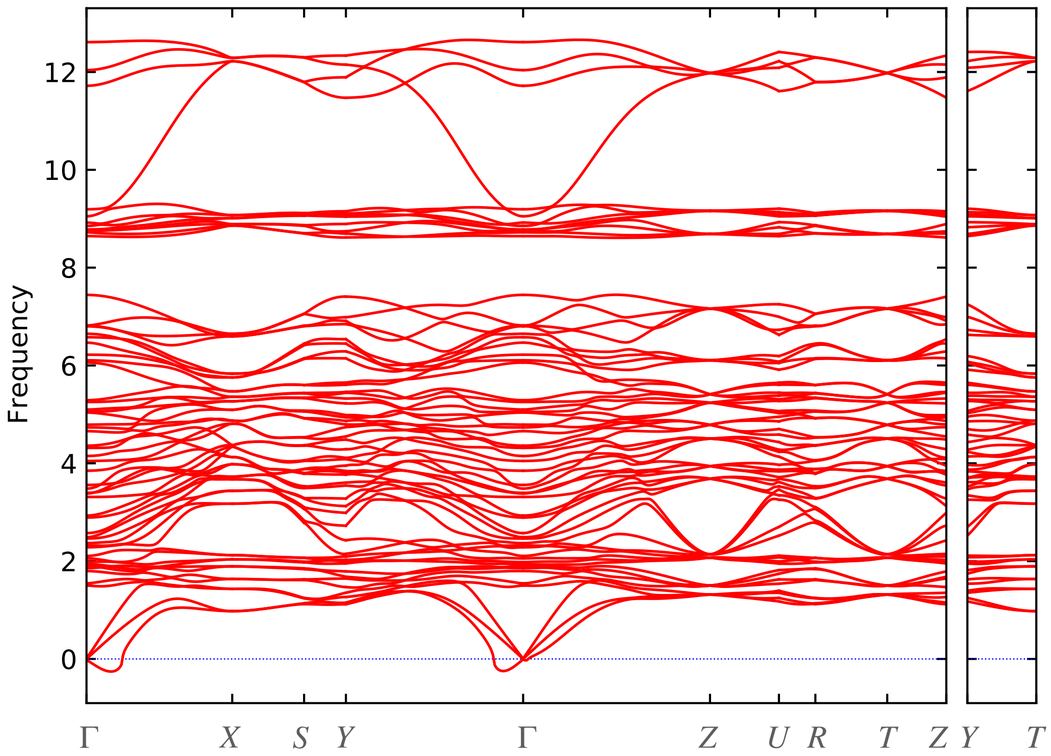
Full relax

```
lattice_vector     -2.49217989      2.49639512      3.66875702
lattice_vector      2.49648700     -2.49193006      3.66738771
lattice_vector      2.49226588      2.49225500     -3.67135077
atom_frac       0.37529619      1.02969598      1.15507918 O
atom_frac       0.87550820      0.22077655     -0.15407198 O
atom_frac      -0.02939474      0.12513916      0.34567591 O
atom_frac       0.77980559      0.62521446      0.65481740 O
atom_frac       0.00030066      0.00020939      0.00038296 Si
atom_frac       0.75028585      0.25019365      0.50035111 Si
```

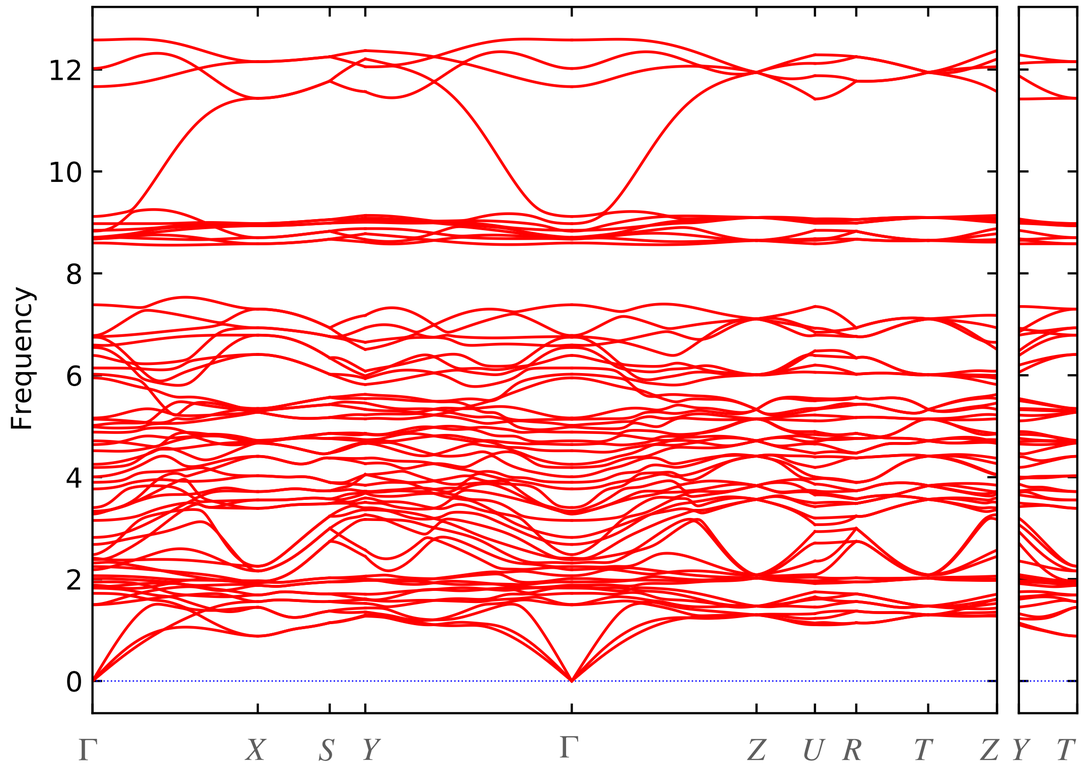
- Not every coordinate needs to be treated as a free parameter
- Often one has to loosen this constraint to obtain the correct space group (not recommended)

Loss of symmetry affecting the phonon BS

Full relax



Constrained relax



- Example from my research: 2x2x2 supercell calculation on $BaZrS_3$ perovskite
- Full relax creates unnecessary soft phonon modes which do not appear with constrained relaxation

Symmetry and no. of lattice displacements

- A system with N atoms has to be evaluated at 6N displacement during phonon calculations

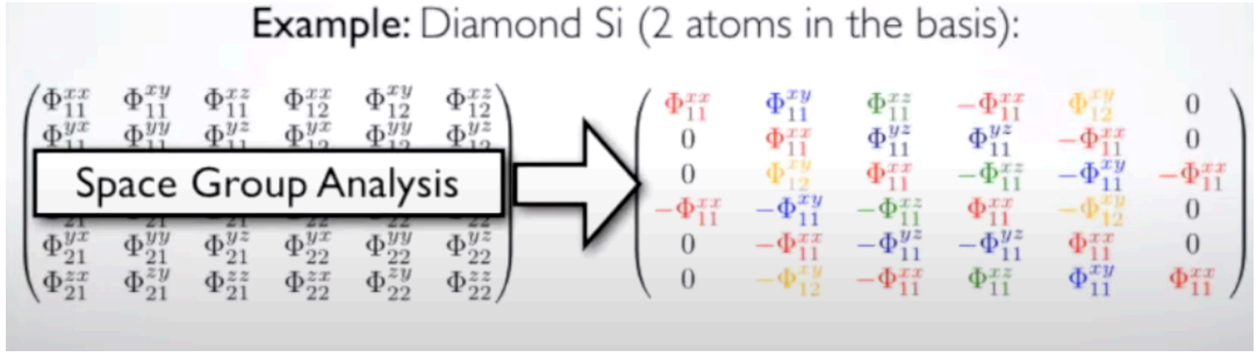
Example: Diamond Si (2 atoms in the basis):

$$\begin{pmatrix} \Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & \Phi_{12}^{xx} & \Phi_{12}^{xy} & \Phi_{12}^{xz} \\ \Phi_{11}^{yx} & \Phi_{11}^{yy} & \Phi_{11}^{yz} & \Phi_{12}^{yx} & \Phi_{12}^{yy} & \Phi_{12}^{yz} \\ \Phi_{11}^{zx} & \Phi_{11}^{zy} & \Phi_{11}^{zz} & \Phi_{12}^{zx} & \Phi_{12}^{zy} & \Phi_{12}^{zz} \\ \Phi_{21}^{xx} & \Phi_{21}^{xy} & \Phi_{21}^{xz} & \Phi_{22}^{xx} & \Phi_{22}^{xy} & \Phi_{22}^{xz} \\ \Phi_{21}^{yx} & \Phi_{21}^{yy} & \Phi_{21}^{yz} & \Phi_{22}^{yx} & \Phi_{22}^{yy} & \Phi_{22}^{yz} \\ \Phi_{21}^{zx} & \Phi_{21}^{zy} & \Phi_{21}^{zz} & \Phi_{22}^{zx} & \Phi_{22}^{zy} & \Phi_{22}^{zz} \end{pmatrix}$$

Hessian has **36** entries:
⇒ 6 displacements ***d*** required

Symmetry and no. of lattice displacements

- A system with N atoms has to be evaluated at 6N displacement during phonon calculations



- Matrix elements of the Hessian are equivalent due to symmetry and only 1 displacement is needed

- If incorrect symmetries are provided, unnecessary displacements are created

https://fhi-aims-club.gitlab.io/tutorials/phonons-with-fhi-vibes/ FHI-aims lecture delivered by Christian Carbogno

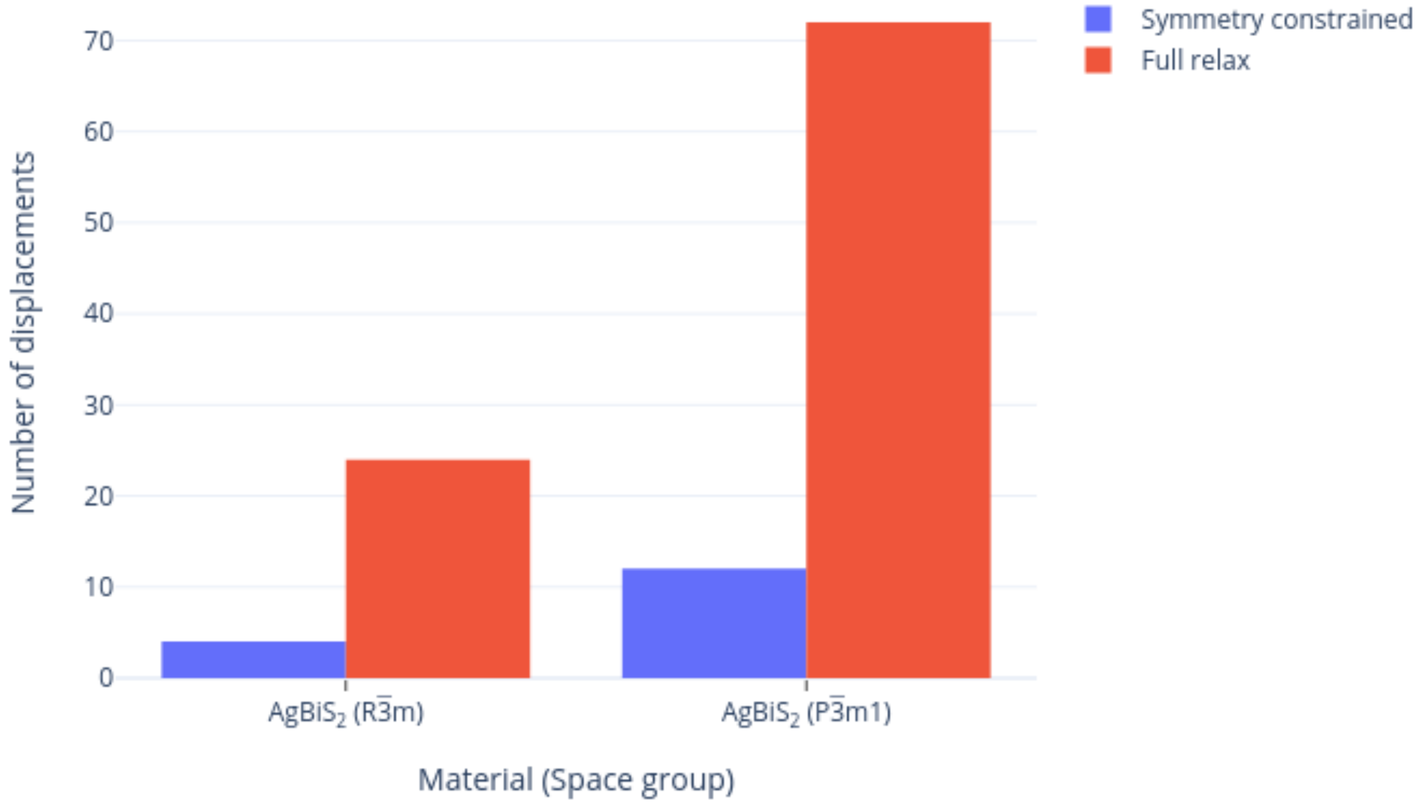
No. of displacements for finite difference calculations

This is determined by:

- Number of atoms in the unit cell
- Space group symmetry
- Number of inequivalent species of atoms

Comparing no. of displacements for materials

- Same atom types, but different number of atoms in the unit cell

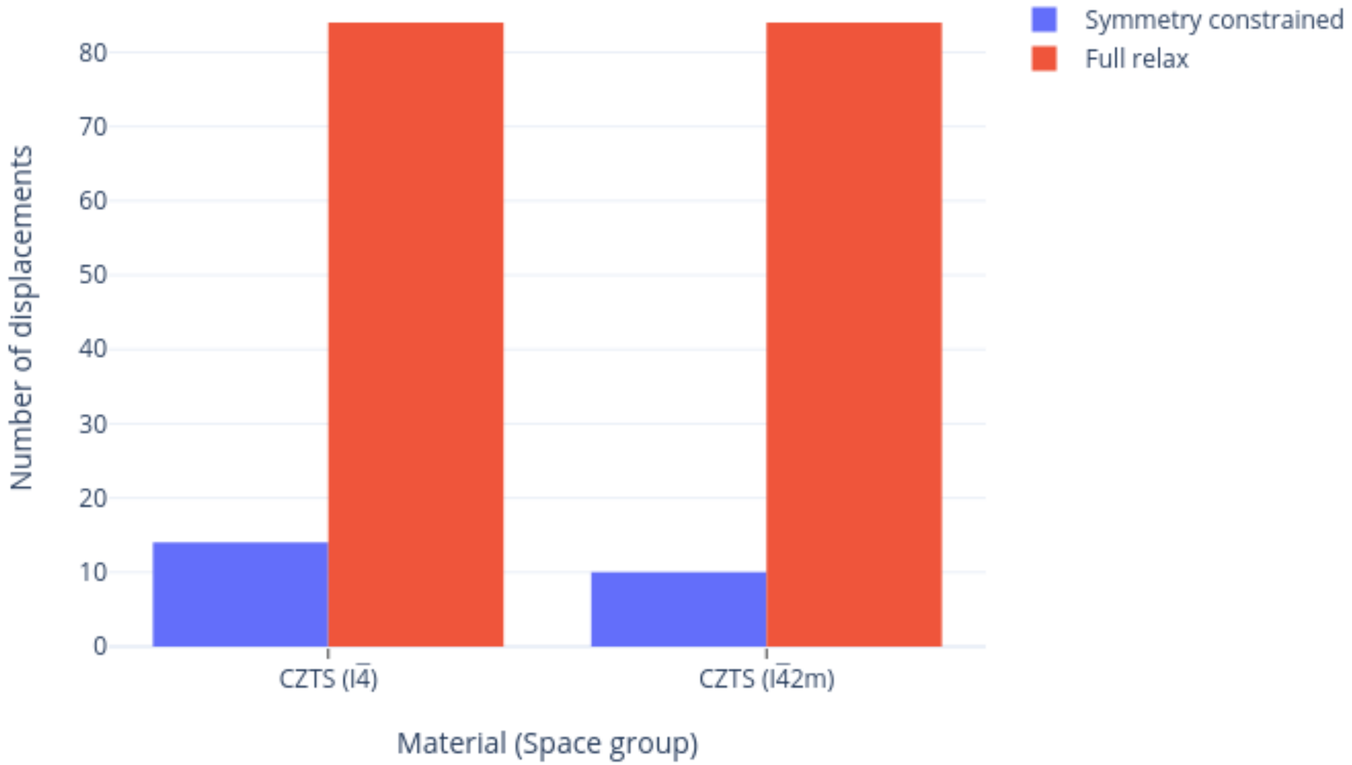


$AgBiS_2$ in $R\bar{3}m$ has 4 atoms

$AgBiS_2$ in $P\bar{3}m1$ has 12 atoms

Comparing no. of displacements for materials

- Same atom types, same number of atoms and Bravais lattices, but different space groups

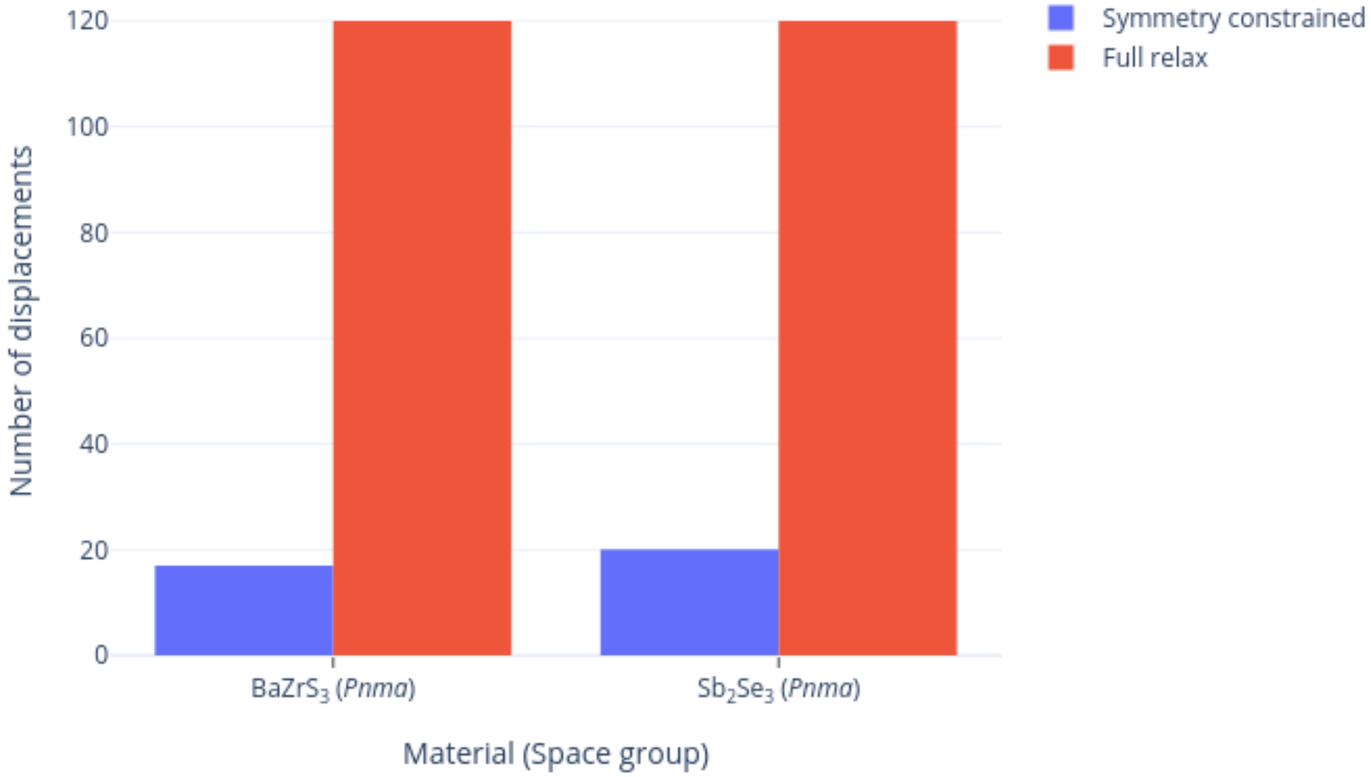


CZTS in $I\bar{4}$

CZTS in $I\bar{4}2m$

Comparing number of displacements for materials

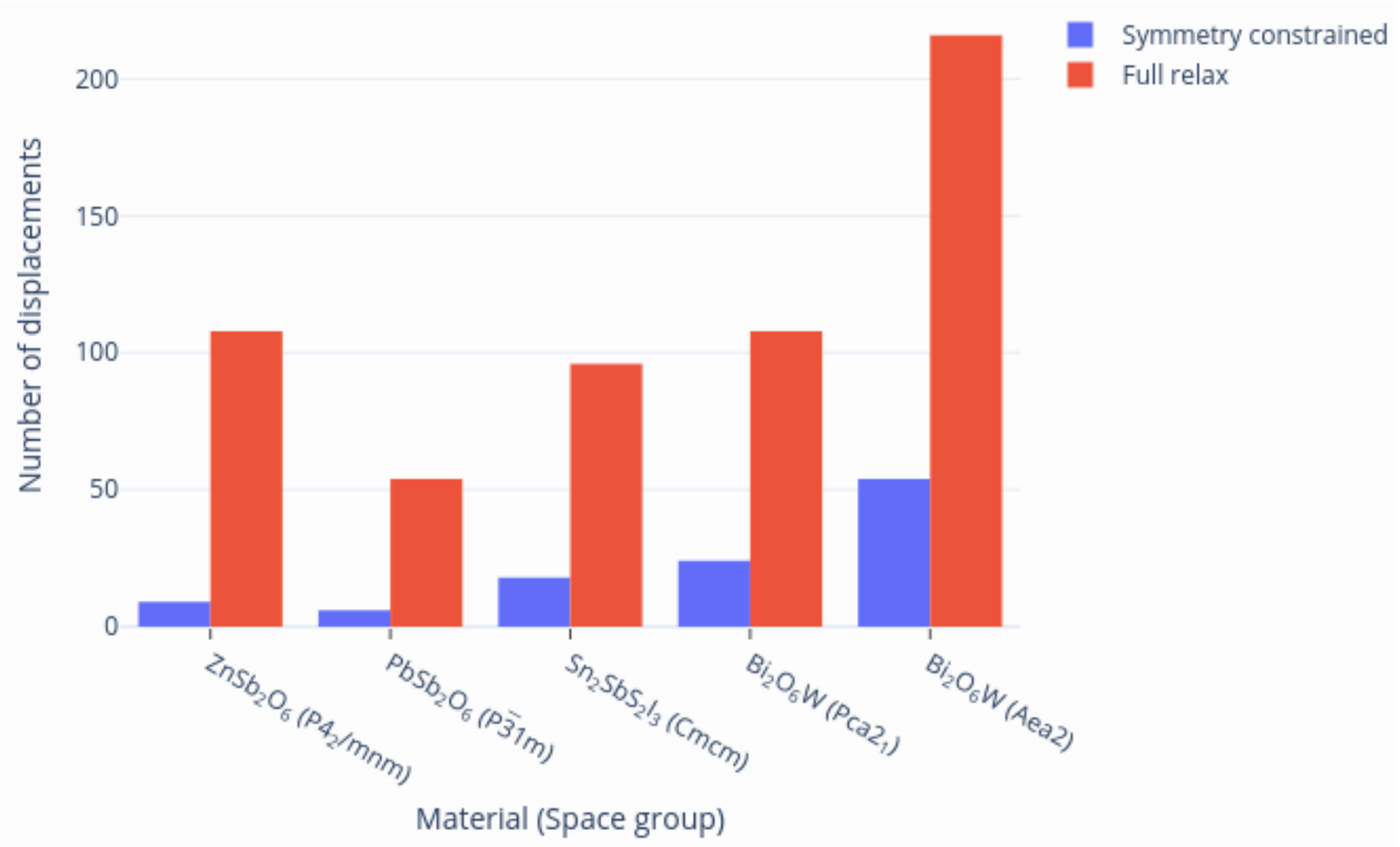
- Same space group and same number of atoms in unit cell, but inequivalent atom sites



Atom (Wyckoff position)		
	$BaZrS_3$	Sb_2Se_3
	Ba (4c)	Sb (4c)
	Zr (4a)	Sb (4c)
	S (4c)	Se (4c)
	S (8d)	Se (4c)
	S (8d)	Se (4c)

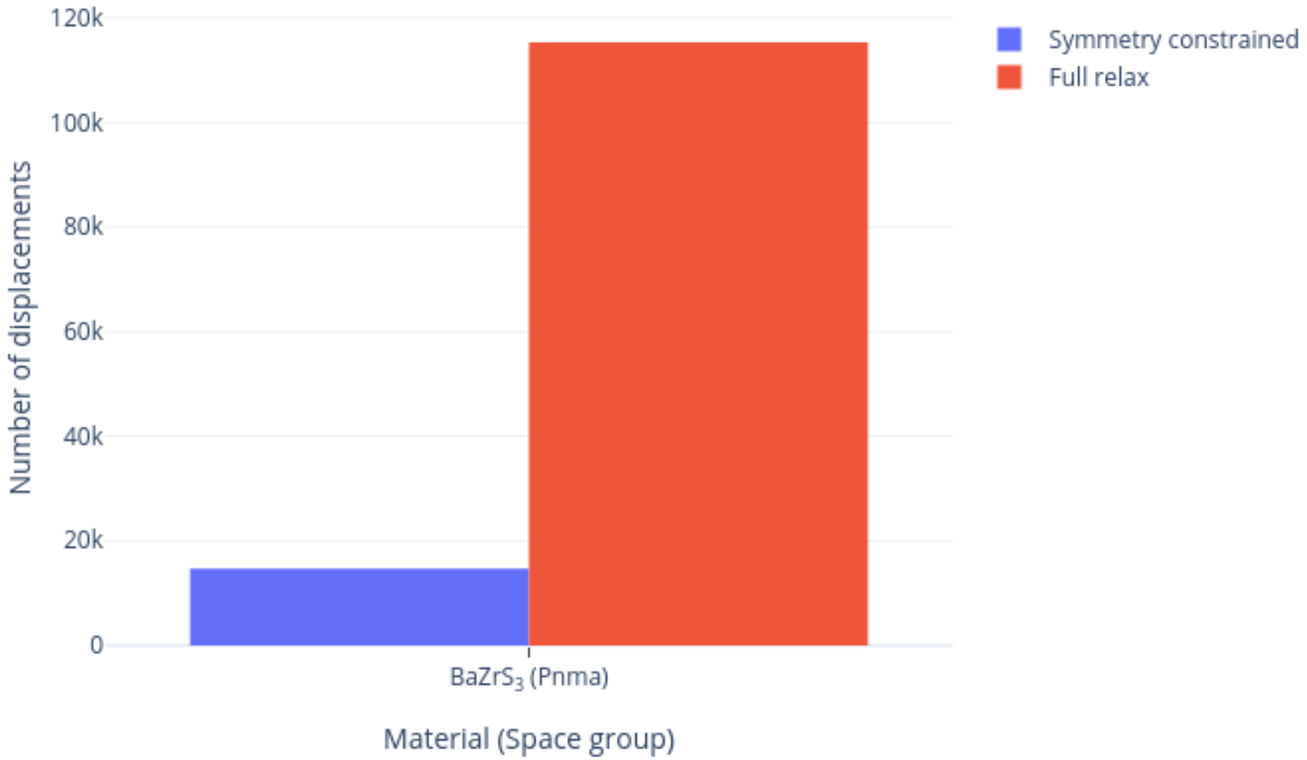
Comparing number of displacements for materials

More examples from popular materials



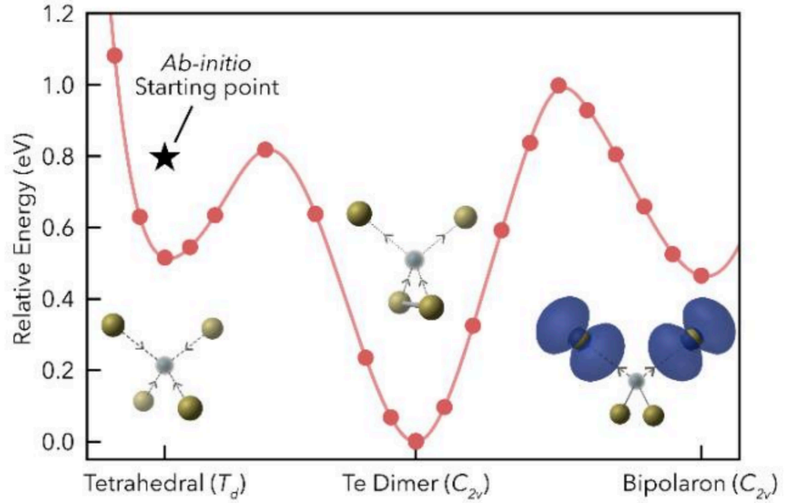
How it affects displacements with Phono3py

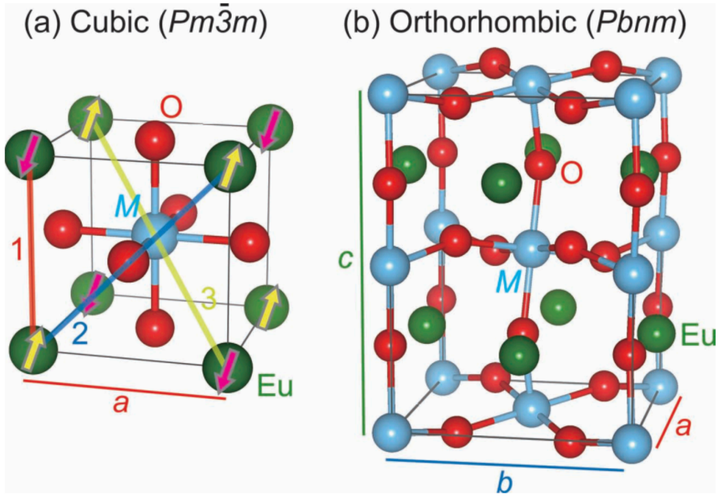
- Example from my research from the $BaZrS_3$ perovskite: 14k vs 115k displacements! Massive save on CPU time



Where symmetry constrained relaxation is incompatible

- For some systems, the symmetry *should* be lowered during relaxation
  - Defect systems with charge localisation
  - Magnetic systems with spin-lattice coupling





Mosquera-Lois *et al*., (2021) Matter **4** 2602; Akamatsu *et al*., (2013) Adv. Funct. Mater. **23** 1864

Where symmetry constrained relaxation is incompatible

- Surfaces - reconstruction mechanisms and catalysis (this *should* be easy to implement externally)
- Clusters - only particular modes are important in understanding the underlying chemistry
- Molecules - In Gaussian, the code identifies the point group of the system (within a threshold) and one can choose only to relax relevant coordinates

Take home messages

- Proper symmetry assignment during geometry relaxation can ensure the material remains in the correct space group
- The right symmetry ensures no undesirable imaginary appear in the phonon BS
- Save CPU time:
  - Reduce the number of displacement steps compared to 6N steps in harmonic Phonopy calculations
  - The difference in number of steps is even more pronounced for steps created for Phono3py calculations
- Symmetry constrained relaxation does not apply for all material science problems!

Thank you for listening!

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