Scientific Computing

Stress and cell relaxation in ONETEP

Manuel dos Santos Dias
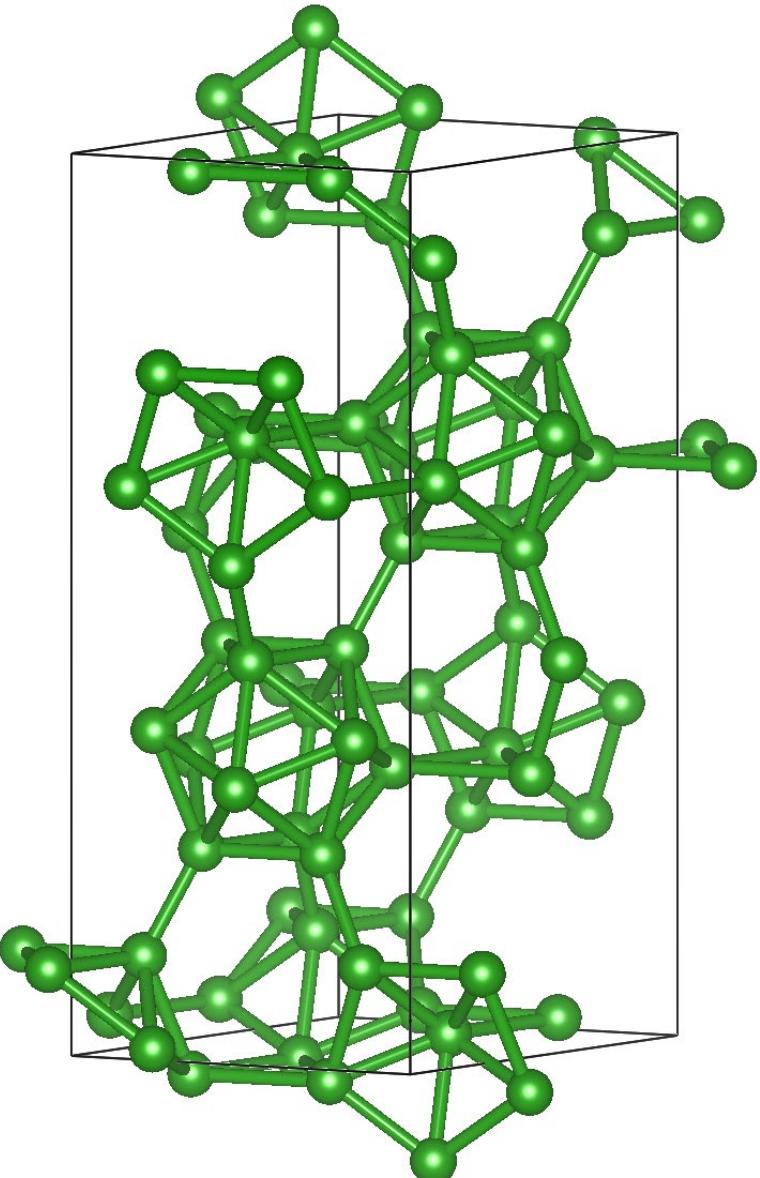
Contents

Stress and strain: definitions

- **Strain:** deformation of a material with respect to a reference state

- **Stress:** forces acting on the surfaces of a small portion of the material

tension

com-
pression

shear

bending   torsion
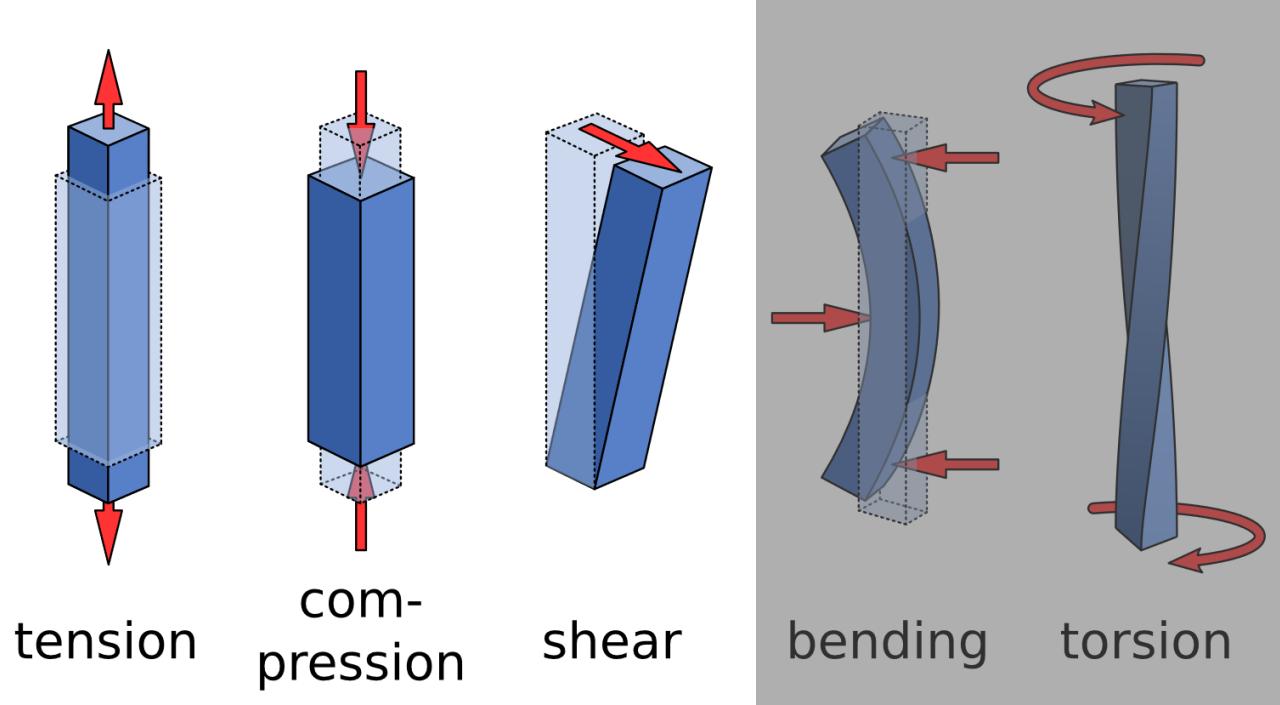
Mike Run,
Wikimedia Commons

Stress and strain: symmetric tensors

Sanpaz, Wikimedia Commons
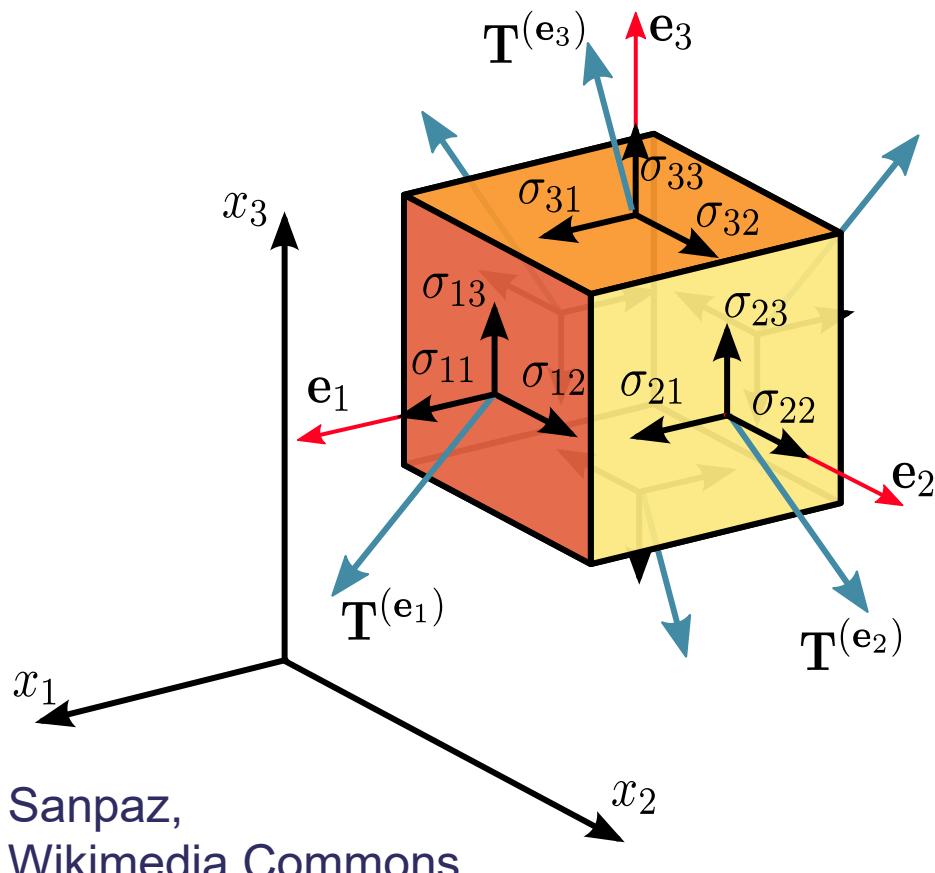
- **Stress is a tensor:** orientation of force with respect to a given surface of the material

- **Strain is also a tensor:** relation between the material points in the deformed and in the reference state

$$r'_\alpha = r_\alpha + \sum_\beta \epsilon_{\alpha\beta} r_\beta \,, \quad \alpha, \beta = x, y, z$$

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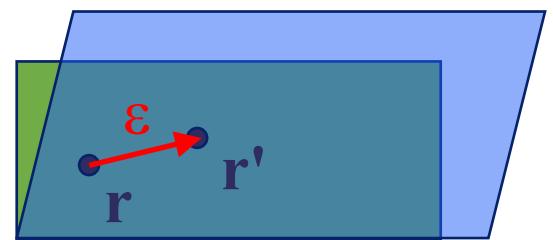
Stress and strain: energy

- **Stress is related to strain:** $\qquad \sigma_{\alpha\beta} = -\dfrac{1}{V_0}\dfrac{\partial E}{\partial \epsilon_{\alpha\beta}}\ ,\qquad \alpha,\beta = x,y,z$

- **Elastic energy:**

$$E(\epsilon) = E_0 + \sum_{\alpha,\beta}\frac{\partial E}{\partial \epsilon_{\alpha\beta}}\epsilon_{\alpha\beta} + \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\frac{\partial^2 E}{\partial \epsilon_{\alpha\beta}\partial \epsilon_{\gamma\delta}}\epsilon_{\alpha\beta}\epsilon_{\gamma\delta} + \dots$$

$$= E_0 - \sum_{\alpha,\beta}\sigma_{\alpha\beta}\epsilon_{\alpha\beta} + \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}C_{\alpha\beta\gamma\delta}\epsilon_{\alpha\beta}\epsilon_{\gamma\delta} + \dots$$

stress $\qquad\qquad$ elastic constants
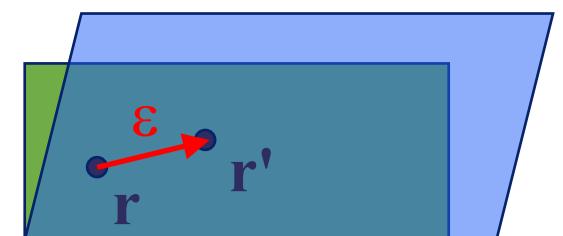
$$r'_\alpha = r_\alpha + \sum_\beta \epsilon_{\alpha\beta}r_\beta\ ,\qquad \alpha,\beta = x,y,z$$

Elementary strain matrices

- **Elongation or compression:**

$$\epsilon_{xx}^{\pm}(h) = \begin{pmatrix} \pm h & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad \frac{\Delta V}{V_0} = \det(1 + \epsilon) = 1 \pm h$$

- **Shear:** $\epsilon_{xy}^{\pm}(h) = \begin{pmatrix} 0 & \pm h & 0 \\ \pm h & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad \frac{\Delta V}{V_0} = \det(1 + \epsilon) = 1 - h^2$

- **Strain is a linear combination of elementary strains:**

$$r'_{\alpha} = r_{\alpha} + \sum_{\beta} \epsilon_{\alpha\beta} r_{\beta}, \qquad \alpha, \beta = x, y, z$$
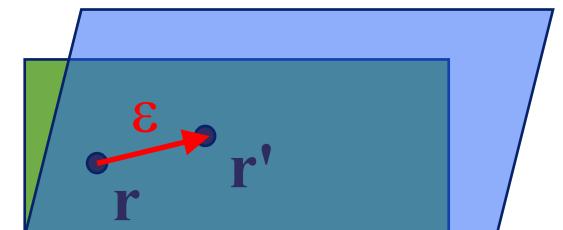
Crystals and unit cells

- **Unit cell parameters:**

$\mathbf{a}_3 = \mathbf{c}$

$\mathbf{a}_2 = \mathbf{b}$

$\mathbf{a}_1 = \mathbf{a}$
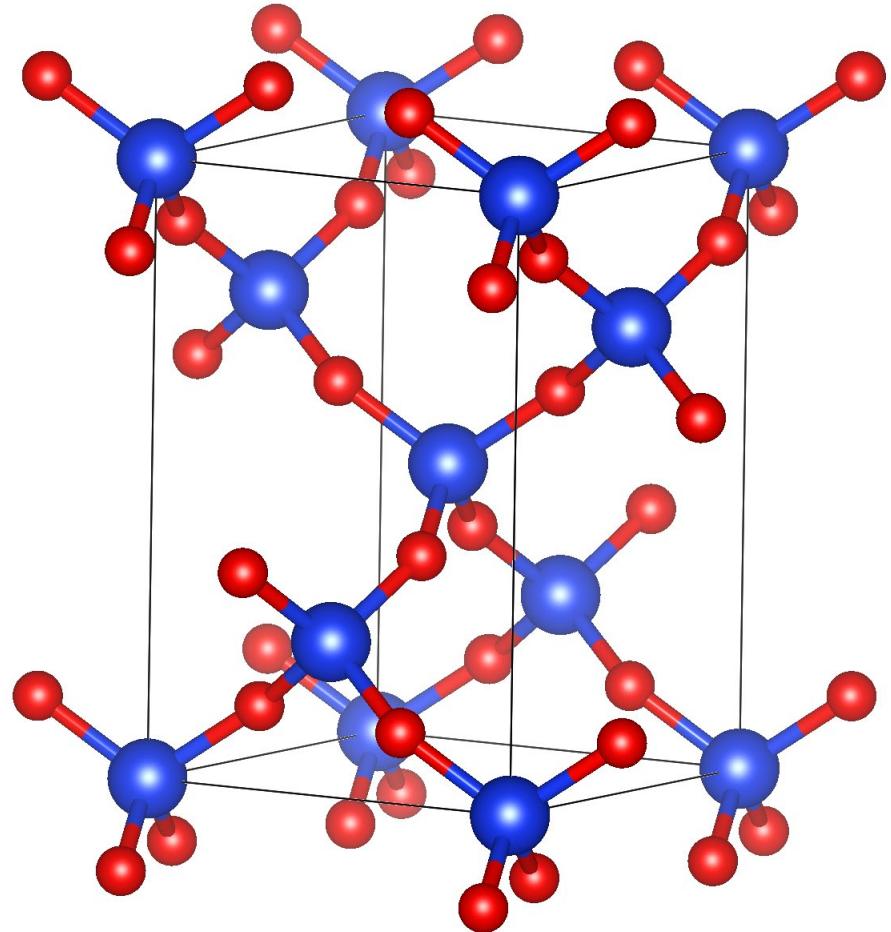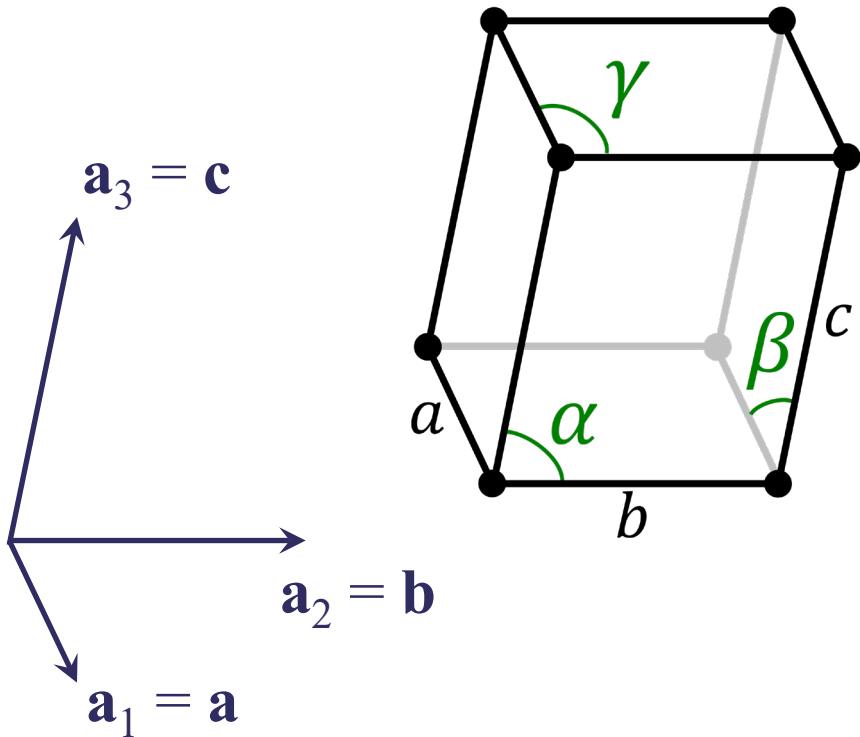
Tetragonal SiO_2: space group I-42d

Stress and crystal symmetry

- **Neumann's principle:** physical properties must be invariant with respect to the crystal (point group) symmetry operations (https://dictionary.iucr.org/Neumann's_principle)

$$\underline{\sigma} = U \underline{\sigma} U^{-1}$$

Table of space groups in 3 dimensions [edit]

$\bar{4}2m$	D_{2d}	2*2	$[2^+,4]$	8	$P\bar{4}2m, P\bar{4}2c, P\bar{4}2_1m, P\bar{4}2_1c, P\bar{4}m2, P\bar{4}c2, P\bar{4}b2, P\bar{4}n2$ $I\bar{4}m2, I\bar{4}c2, I\bar{4}2m, I\bar{4}2d$

$$\underline{\sigma} = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$$

Tetragonal SiO_2: space group I-42d

Computing the stress with small distortions

- There are six types of strains/distortions: $\{\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}, \epsilon_{yz}, \epsilon_{zx}, \epsilon_{xy}\}$

  elongations   shears
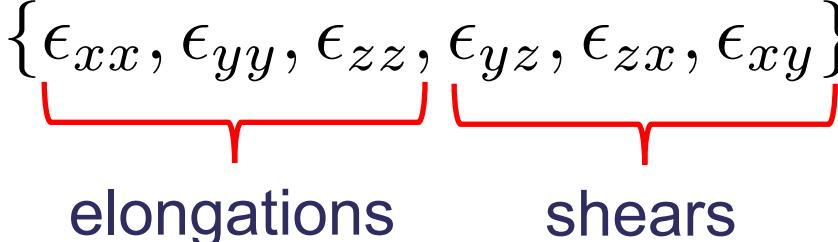
- An element of the stress tensor is computed by finite differences:

$$\sigma_{xx} = -\frac{1}{V_0}\frac{\partial E}{\partial \epsilon_{xx}} \approx -\frac{1}{V_0}\frac{E\big(\varepsilon_{xx}(+h)\big) - E\big(\varepsilon_{xx}(-h)\big)}{2h}$$

- Total number of scf calculations: 6 x (+*h*) + 6 x (-*h*) + 1 reference = 13

➢ Use symmetry to reduce the computational effort

Specifying the symmetry (for stress only)

- **3D:** *c*-axis for tetragonal, hexagonal and rhombohedral should be the *z*-axis

- **2D:** the non-periodic (vacuum) direction should be the *z*-axis

	cubic	ortho	tetra1	tetra2	hexa3d	rhomb1	rhomb2
3D	$m\bar{3}$, $m\bar{3}m$	mmm	$4/mmm$	$4/m$	$6/mmm$, $6/m$	$\bar{3}m$	$\bar{3}$
2D	recta	squar1	squar2	hexa2d			
	$2mm$	$4mm$	4	6, $6mm$			

- The point groups in the boxes are equivalent for the stress calculations

- **1D**: use   `stress_components`   Logical   T T T   Which rows/columns of the stress tensor to compute. The flags match X Y Z.

Cell and geometry optimisation

- Automatic optimisation of the cell parameters: `stress_relax T`

  ➢ Find ε that approximately minimises the elastic energy

$$E(\epsilon) = E_0 + \sum_{\alpha,\beta} \frac{\partial E}{\partial \epsilon_{\alpha\beta}} \epsilon_{\alpha\beta} + \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \frac{\partial^2 E}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\delta}} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta}$$

- If the unit cell parameters change, will the atoms inside it want to move?
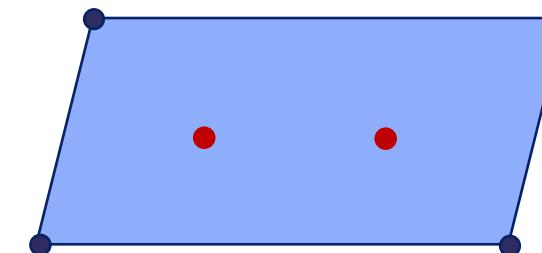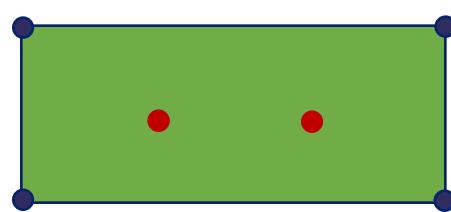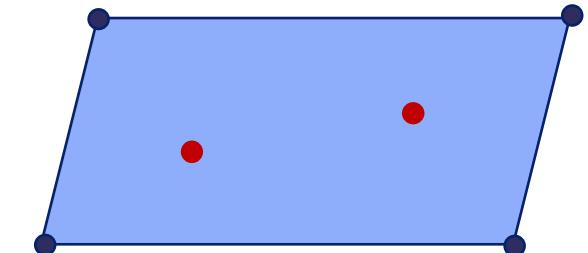
`stress_relax T`   `stress_relax_atoms T`

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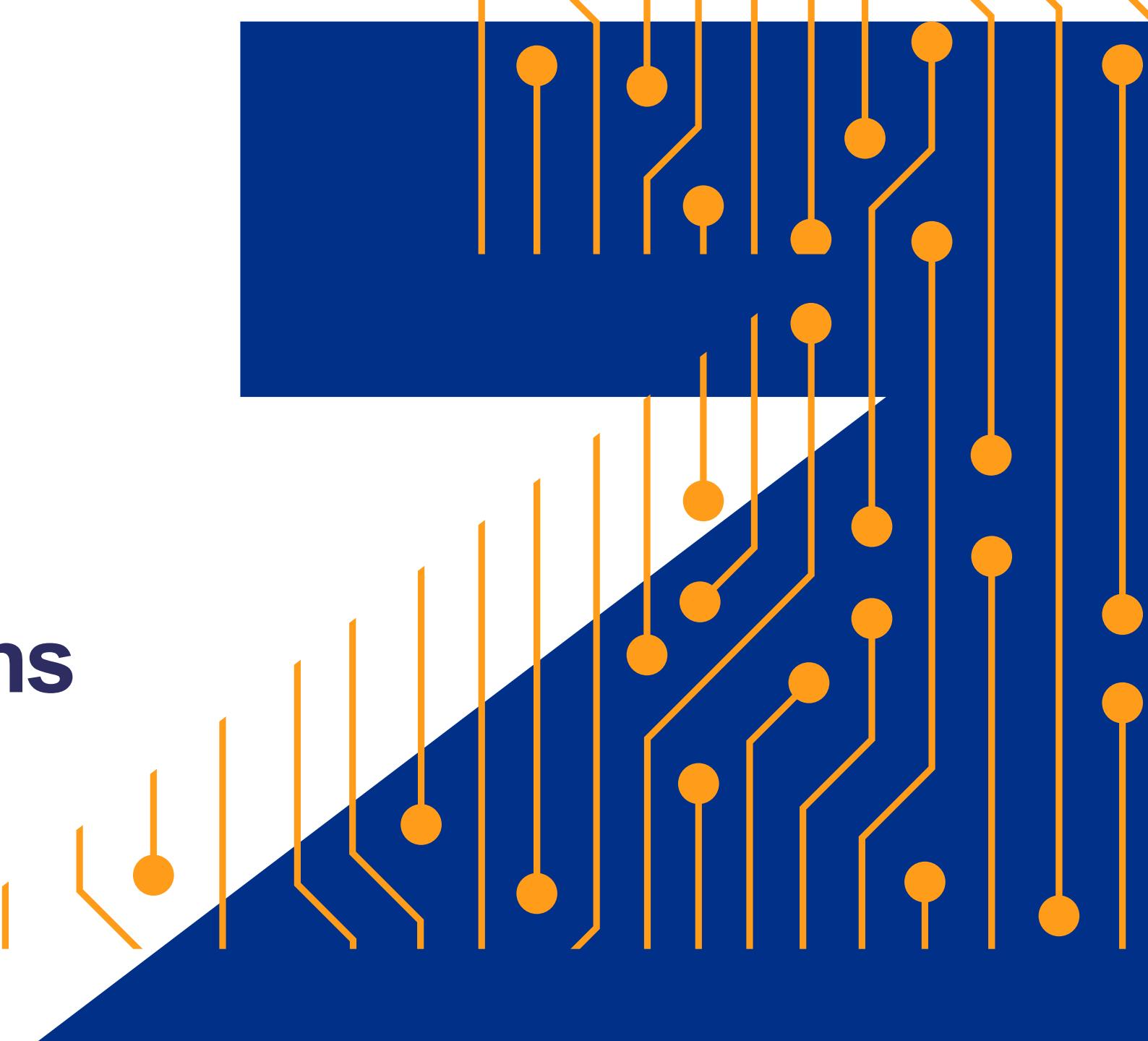
Full list of keywords for stress calculations

Keyword	Type	Default	Description
STRESS	Task	—	Enable stress functionality.
stress_tensor	Logical	F	Enable the calculation of the stress tensor.
stress_elasticity	Logical	F	Enable the calculation of elastic constants.
stress_relax	Logical	F	Use the stress tensor to optimise the cell parameters.
stress_assumed_symmetry	String	nosymm	Use assumed symmetry to minimise calculations. Values are nosymm; 3D: cubic, ortho, tetra1, tetra2, hexa3d, rhomb1, rhomb2; 2D: recta, squar1, squar2, hexa2d. NOTE: Symmetry is assumed, the code will not check if it's correct!
stress_rescale_volume	Real	1.0	Rescaling for cell volume. Might be useful for 1D or 2D systems.
stress_components	Logical	T T T	Which rows/columns of the stress tensor to compute. The flags match X Y Z.

Keyword	Type	Default	Description
stress_deformation_step	Real	2.0e-3	Unitless strain parameter in finite differences. It controls how different the deformation matrix is from the identity.
stress_maxit_ngwf_cg	Integer	10	Maximum number of NGWF CG iterations for total energy calculations of distorted cells needed for the stress tensor.
stress_relax_energy_tol	Physical	1.0e-6 Ha	Convergence criterion for absolute change of total energy per atom in cell relaxation.
stress_relax_pressure	Physical	0.0 Ha/Bohr**3	External pressure applied during cell relaxation.
stress_relax_pressure_tol	Physical	2.0e-6 Ha/Bohr**3	Convergence criterion for absolute change of pressure in cell relaxation.
stress_relax_cell_rtol	Real	1.0e-3	Convergence criterion for relative change of cell parameters in cell relaxation.
stress_relax_max_iter	Integer	10	Maximum number of iterations in cell relaxation.
stress_relax_max_step	Real	0.01	Maximum step size for distortion in cell relaxation.
stress_relax_atoms	Logical	F	Atomic positions are relaxed together with cell parameters.

Flow of the stress/cell relaxation steps
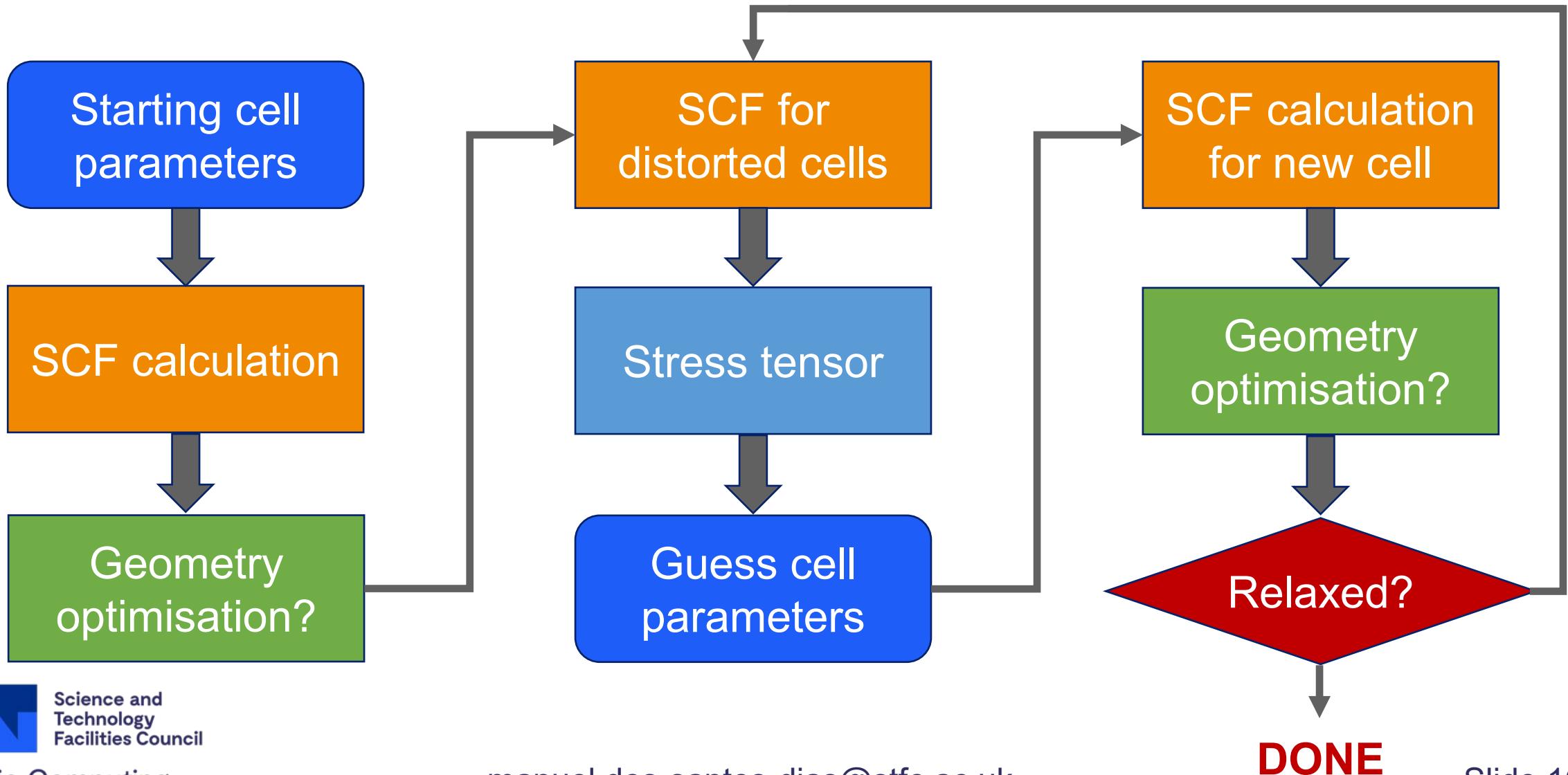
Cell optimisation for 2D *h*-BN — 1

```
task STRESS
stress_relax T
stress_assumed_symmetry hexa2d
stress_relax_max_iter 10
stress_relax_energy_tol 1.d-4 Ha
#stress_relax_pressure_tol 1.d-5
stress_relax_cell_rtol 1.d-3
```

← input

3x3 supercell
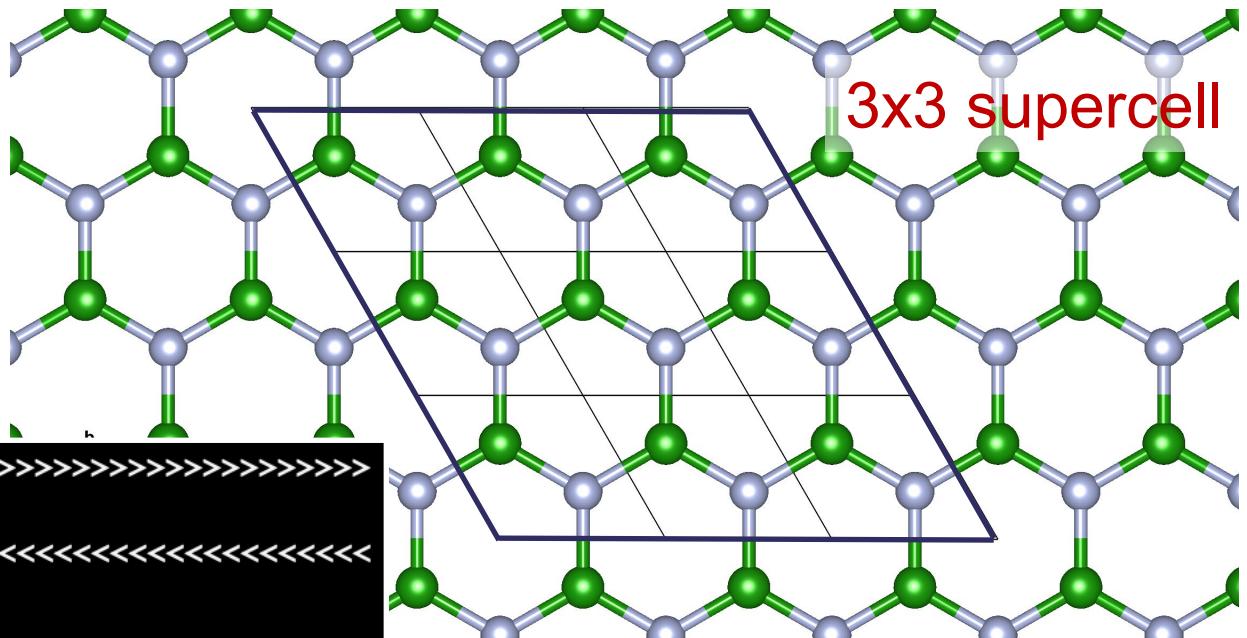
```
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
                    STRESS: undistorted starting cell
<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Hexagonal symmetry assumed!
2D Laue classes: 6, 6mm
Stress tensor:
          x    y    z
        / S1   0    0 \  x
sigma = |      S1   0 |  y
        \           0 /  z
```

```
Undistorted cell geometry
       a [a0]             b [a0]             c [a0]
     14.45640493       14.45640493       18.89726135
     alpha [deg]        beta [deg]        gamma [deg]
     90.00000000       90.00000000      120.00000000
Cell volume=    3420.18903237 [a0**3]

Atomic positions fixed relative to the unit cell
```

← output

Cell optimisation for 2D *h*-BN — 2

scf for starting cell

```
                      <<<<< CALCULATION SUMMARY >>>>>
|ITER|    RMS GRADIENT    |     TOTAL ENERGY     |   step   |      Epredicted
  0     0.00084608025392     -115.79381496345189    2.007037    -116.46433775519029
  1     0.00047391131769     -116.46756159848141    2.389115    -116.71885089117420
  2     0.00025376038431     -116.71636832776572    1.786279    -116.76911215348468
  3     0.00014336127369     -116.76882357761428    1.704069    -116.78507914165344
  4     0.00008083699497     -116.78507430675506    1.840265    -116.79068654118345
  5     0.00004432198565     -116.79069100192424    1.904609    -116.79243928923664
  6     0.00002126499451     -116.79241584882010    1.114055    -116.79264776378136
  7     0.0000009289304      -116.79263508080878    0.006789    -116.79263508386967
  8     0.00000051007890      -116.79263508236245    0.000811    -116.79263508246096
  9     0.00000042060488      -116.79263508226875    <-- CG

stress_calculation: saving starting cell

stress_calculation: copy_info sets maxit_ngwf_cg=  10
stress_calculation: copy_info sets write_tightbox_ngwfs= F
stress_calculation: copy_info sets read_tightbox_ngwfs= T
```

`elec_energy_tol 2.d-6 Ha`
(overkill…)

← If not enough can be adjusted in input
← This speeds up follow-up calculations

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Cell optimisation for 2D *h*-BN — 3


```
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
                    STRESS: distortions for starting cell
<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<


stress_calculation: distortion e11+ (i= 1)


Distorted cell [a0] = undistorted cell [a0] . distortion matrix:
/   12.5447     7.2282     0.0000 \ = /   12.5196     7.2282     0.0000 \   / 1.0020 0.0000 0.0000 \
|  -12.5447     7.2282     0.0000 | = |  -12.5196     7.2282     0.0000 | . | 0.0000 1.0000 0.0000 |
\    0.0000     0.0000    18.8973 / = \    0.0000     0.0000    18.8973 /   \ 0.0000 0.0000 1.0000 /
```

x' y' z' x y z $1 + \varepsilon_{xx}$

```
Geometry of distorted cell:
      a [a0]             b [a0]             c [a0]
   14.47809495      14.47809495       18.89726135
   alpha [deg]       beta [deg]      gamma [deg]
   90.00000000      90.000000000     120.09909054
Cell volume=     3427.02941043 [a0**3]
```

Cell looks like this:

a₂   **a₁**

This was probably enough →
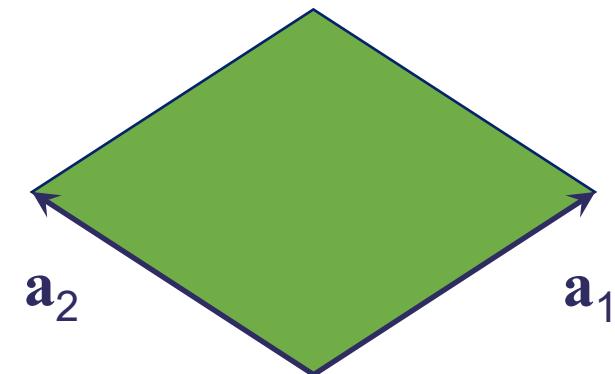
```
                                    <<<<< CALCULATION SUMMARY >>>>>
|ITER|     RMS GRADIENT     |      TOTAL ENERGY      |    step    |      Epredicted
   0     0.00002460485471      -116.78968299991004     1.619453    -116.79013964350077
   1     0.00001001381386      -116.79012376566590     1.092432    -116.79017315616854
   2     0.00000585970441      -116.79016176016987     0.945840    -116.79017688660599
   3     0.00000554096611      -116.79017108643492     0.262122    -116.79017625492283
   4     0.00000353933026      -116.79017460223119     0.292779    -116.79017631047392
   5     0.00000319036555      -116.79017571356499     0.091955    -116.79017628602254
   6     0.00000213207624      -116.79017610378513     0.095995    -116.79017630703056
   7     0.00000201392430      -116.79017621557031     0.035516    -116.79017630527409
   8     0.00000144749541      -116.79017627973985     <-- CG
```

Scientific Computing

Cell optimisation for 2D *h*-BN — 4

Total energy for the distorted cells must be precise enough →

```
stress_tensor:  iteration   1

stress_calculation: summary of distorted calculations
vratio = vol(distorted cell) / vol(undistorted cell)
dE/dh = (Etot(eij+) - Etot(eij-)) / h
d2E/dh2 = (Etot(eij+) + Etot(eij-) - 2Etot(0)) / (2h**2)
Distortion     vratio        dEtot (Ha)      dE/dh (GPa) d2E/dh2 (GPa)
e11+          1.00200000     0.00245880         8.1337     2441.8365
e11-          0.99800000    -0.00132335


stress_calculation: stress tensor in Eh/a0**3 ; in GPa
          x              y              z                  x         y         z
x /    -0.00027646     0.00000000     0.00000000\    /    -8.1337    0.0000    0.0000 \
y |     0.00000000    -0.00027646     0.00000000| ; |     0.0000    -8.1337    0.0000 |
z \     0.00000000     0.00000000     0.00000000/    \     0.0000     0.0000    0.0000 /
```

```
stress_calculation: next undistorted cell

Elements of transformation matrix computed from second order expansion of energy
in strain parameters, with derivatives approximated by dE/dh and d2E/dh2:
h1= -0.00333096
h2= -0.00333096
h3=  0.00000000
h4=  0.00000000
h5=  0.00000000
h6=  0.00000000
```

```
Transformation matrix for next cell:
/  0.99666904    0.00000000    0.00000000 \  =  / 1+h1    h6      h5 \
|  0.00000000    0.99666904    0.00000000 |  =  |  h6    1+h2     h4 |
\  0.00000000    0.00000000    1.00000000 /  =  \  h5     h4    1+h3 /

Cell vectors for next undistorted cell:
  bohr
    12.47791153      7.20412558      0.00000000
   -12.47791153      7.20412558      0.00000000
     0.00000000      0.00000000     18.89726135
```

← Guess at the cell parameters that minimize the elastic energy

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Cell optimisation for 2D *h*-BN — 5

```
|ITER|   RMS GRADIENT   |     TOTAL ENERGY     |   step   |     Epredicted
   0    0.00084169624909   -115.80216218541419   2.005799   -116.46978561363700
   1    0.00046880860308   -116.47287025680801   2.416930   -116.72327759055852
   2    0.00025157119877   -116.72074800581258   1.795234   -116.77317967127436
   3    0.00014204390201   -116.77289586344128   1.723713   -116.78914674209628
   4    0.00008019645856   -116.78914042564637   1.836123   -116.79468853980137
   5    0.00004339774611   -116.79469334476153   1.889875   -116.79636775772822
   6    0.00002091207440   -116.79634673311190   1.118563   -116.79657361551952
   7    0.00000216413782   -116.79656149608209   0.061071   -116.79656162324972
   8    0.00000078168929   -116.79656161281628   0.003755   -116.79656161389430
   9    0.00000049708337   -116.79656161321944   <-- CG

Writing current cell to file hBN18.cell ...
 done
```

← SCF for the guess
at the cell parameters

The .cell file contains the
current cell parameters
(and atomic positions)

```
cell_relax: iteration   1

cell_dE: change in total energy between current and previous cell, per atom
P: pressure, average of diagonal elements of the stress tensor
cell_da: relative change in cell parameters between current and previous cell
cell_dE=  -2.2E-04 Ha/nat, P=  -1.8E-04 Ha/bohr^3, cell_da=   2.2E-03


+----------+----------+----------+----------+
| Criterion |  Value   |  Target  | Passed?  |
+----------+----------+----------+----------+
| |cell_dE| |  2.2E-04 |  1.0E-04 |    NO    |
|    |P|    |  1.8E-04 |  1.0E-05 |    NO    |
|  cell_da  |  2.2E-03 |  1.0E-03 |    NO    |
+----------+----------+----------+----------+
```

These criteria decide
if the cell is relaxed

Cell optimisation for 2D *h*-BN — 6

```
cell_relax: iteration    4

cell_dE: change in total energy between current and previous cell, per atom
P: pressure, average of diagonal elements of the stress tensor
cell_da: relative change in cell parameters between current and previous cell
cell_dE=   7.0E-07 Ha/nat, P=  -1.7E-06 Ha/bohr^3, cell_da=    2.3E-05


+----------+----------+----------+----------+
| Criterion |  Value   |  Target  | Passed?  |
+----------+----------+----------+----------+
| |cell_dE| |  7.0E-07 |  1.0E-04 |    YES   |
|    |P|    |  1.7E-06 |  1.0E-05 |    YES   |
|  cell_da  |  2.3E-05 |  1.0E-03 |    YES   |
+----------+----------+----------+----------+


<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

stress_calculation: unit cell relaxed!

Total energy of starting cell:       -116.79263508226875
Total energy of relaxed cell:        -116.80338533101130
```

All is well that ends well?

```
Starting cell:
  bohr
     12.51961392      7.22820246      0.00000000
    -12.51961392      7.22820246      0.00000000
      0.00000000      0.00000000     18.89726135

Relaxed cell:
  bohr
     12.27664987      7.08792711      0.00000000
    -12.27664987      7.08792711      0.00000000
      0.00000000      0.00000000     18.89726135
```

Things to be done
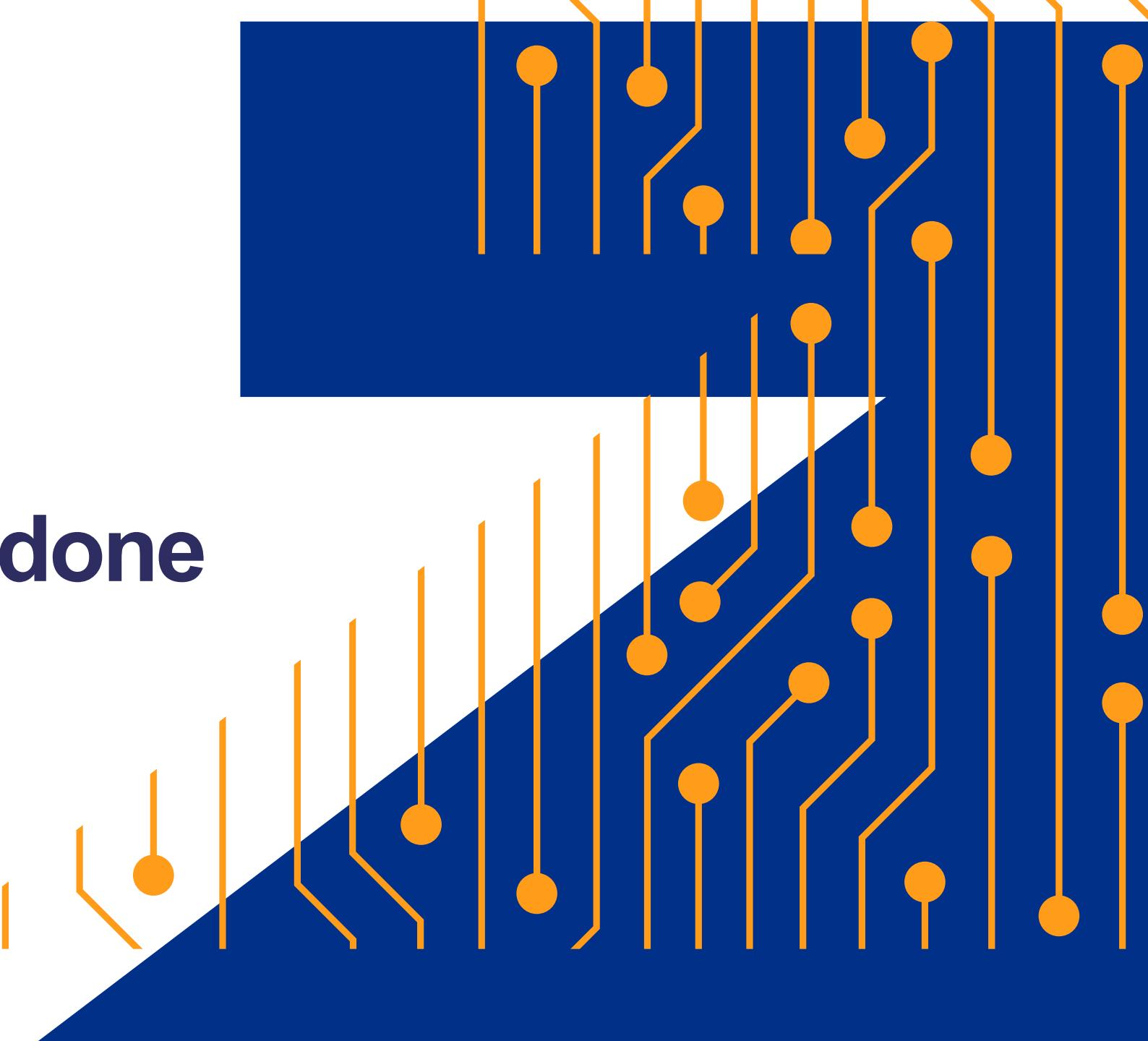
Wish list

- Analytic instead of numerical derivatives for stress

- Automatic calculation of elastic constants

- Full compatibility with all the scf calculation modes of ONETEP

Further reading

- Kittel, *Introduction to Solid State Physics*, chapter on Elastic Constants

- Martin, *Electronic Structure*, appendix G: Stress from Electronic Structure