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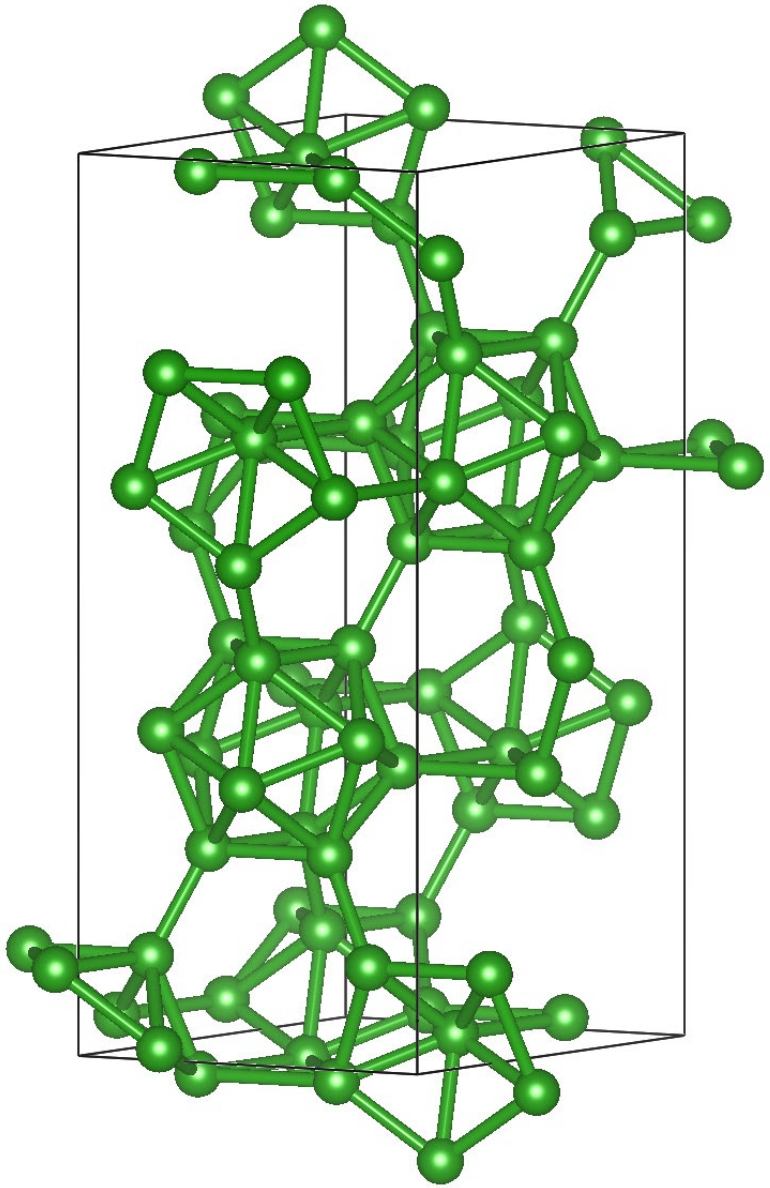

Stress and cell relaxation in ONETEP

Manuel dos Santos Dias

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Definition of stress & other quantities

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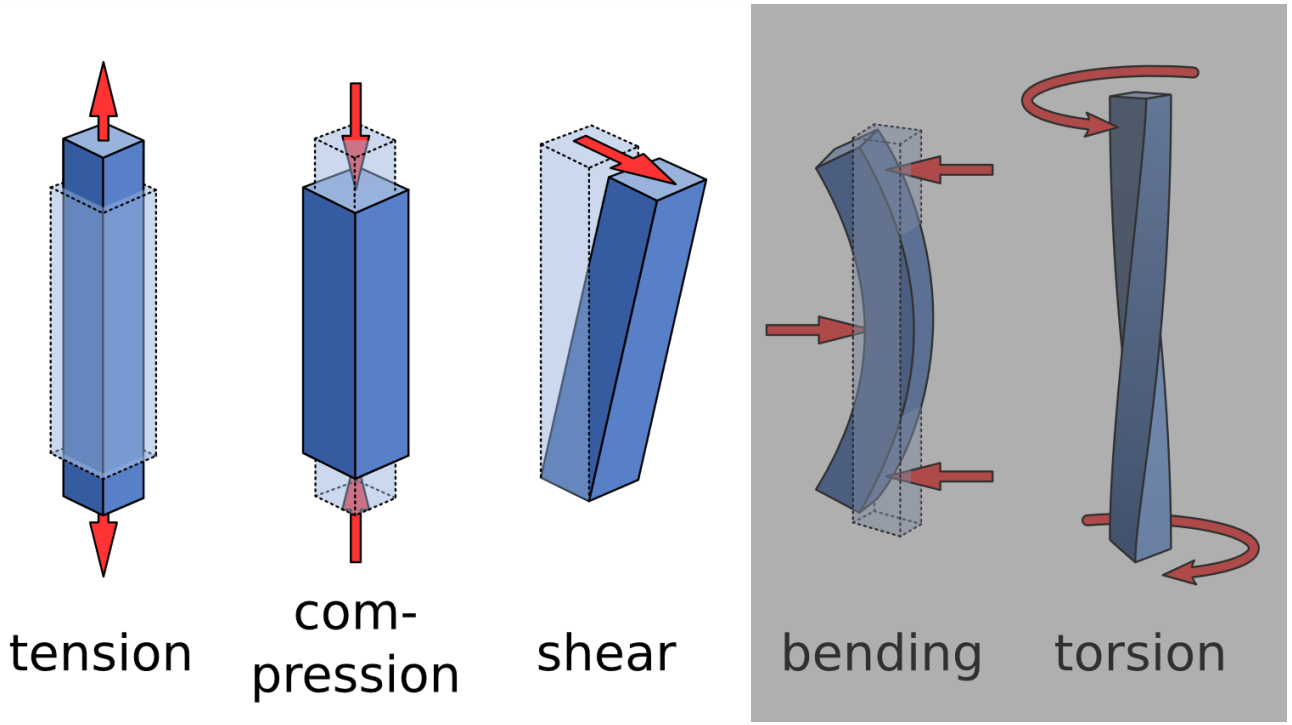
Stress and strain: definitions

- **Strain:** deformation of a material with respect to a reference state
- **Stress:** forces acting on the surfaces of a small portion of the material



Mike Run,
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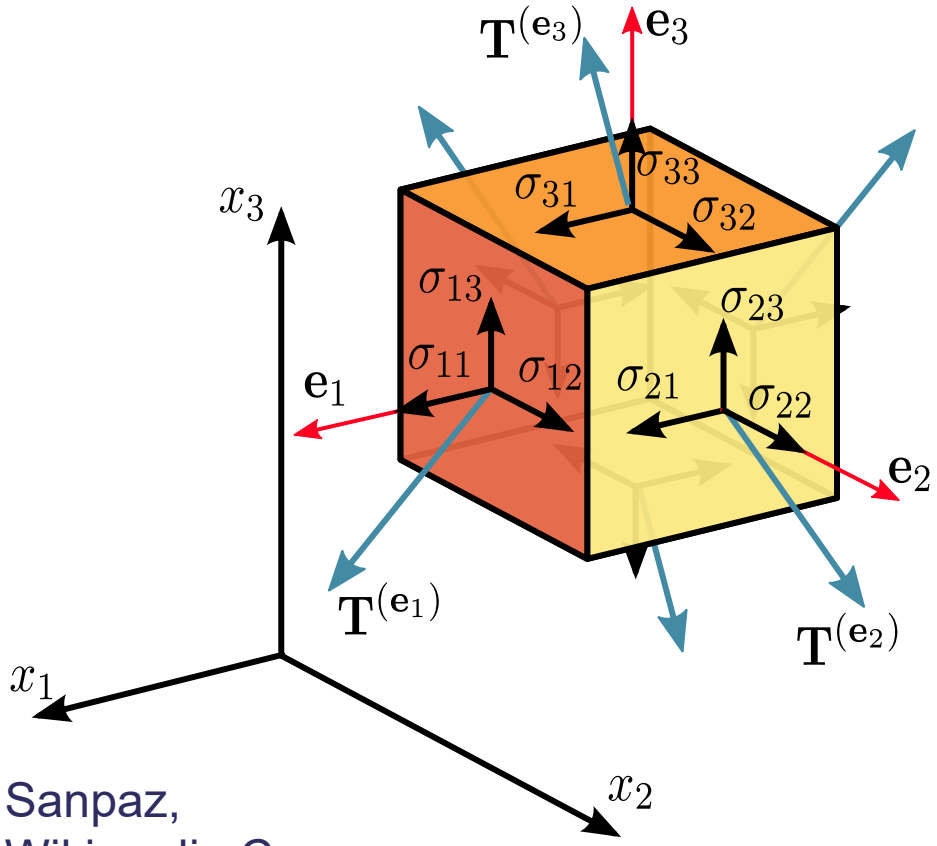
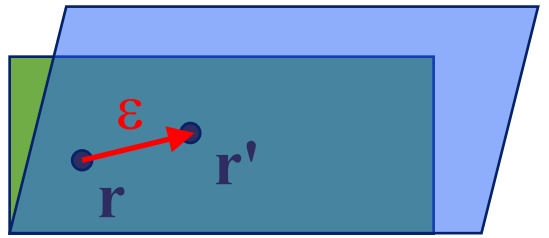
Stress and strain: symmetric tensors



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



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

Stress and strain: energy

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

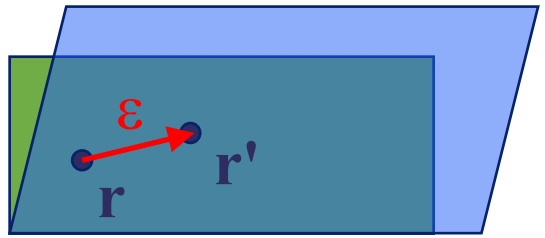
- **Elastic energy:**

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

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

stress

elastic constants



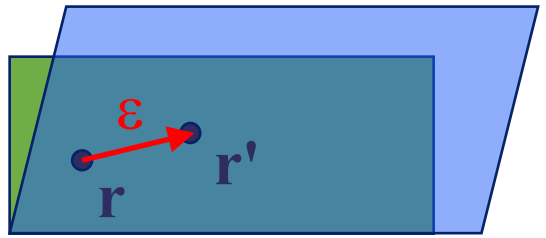
$$r'_\alpha = r_\alpha + \sum_\beta \epsilon_{\alpha\beta} r_\beta\ , \quad \alpha,\beta = x,y,z$$

Elementary strain matrices

- **Elongation or compression:**

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

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

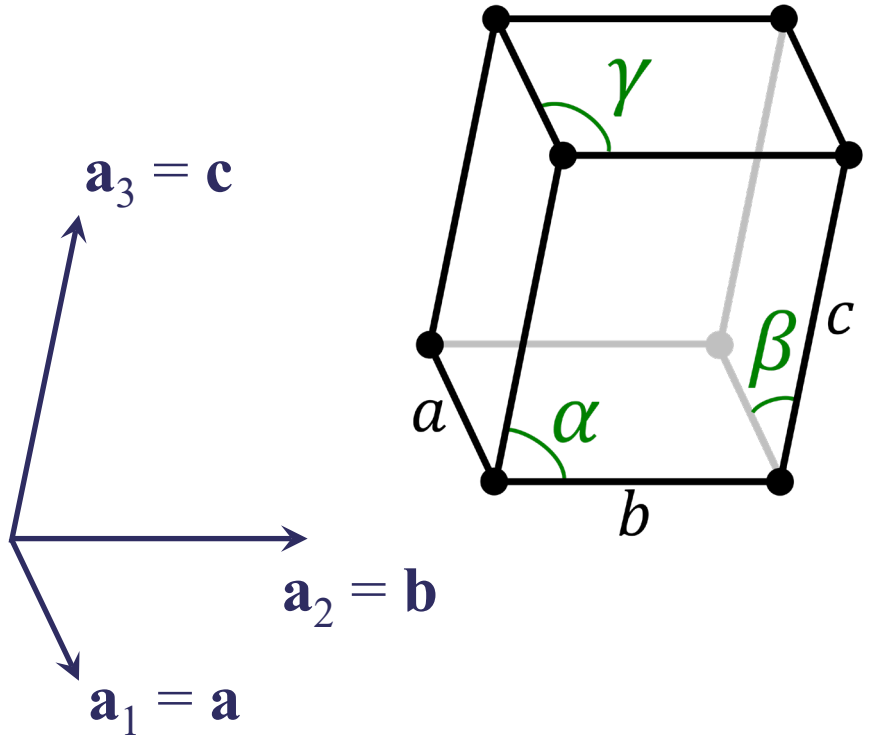


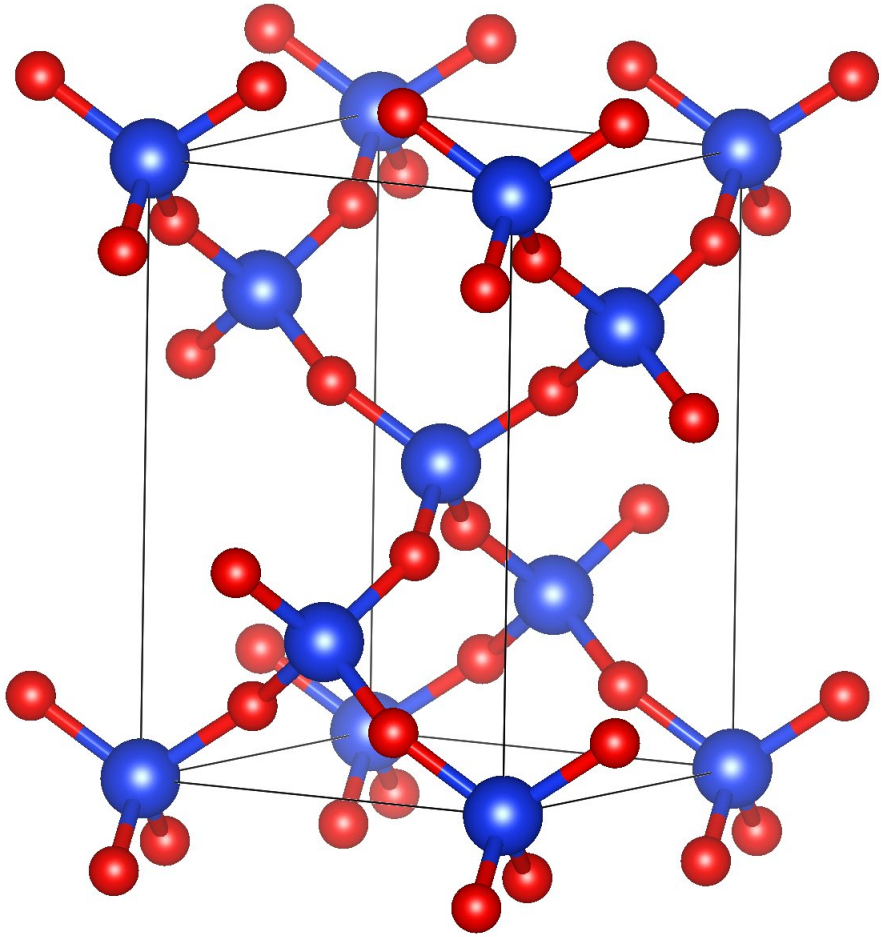
- **Strain is a linear combination of elementary strains:**

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

Crystals and unit cells

- **Unit cell parameters:**





Tetragonal SiO_2: space group I-42d

Stress and crystal symmetry

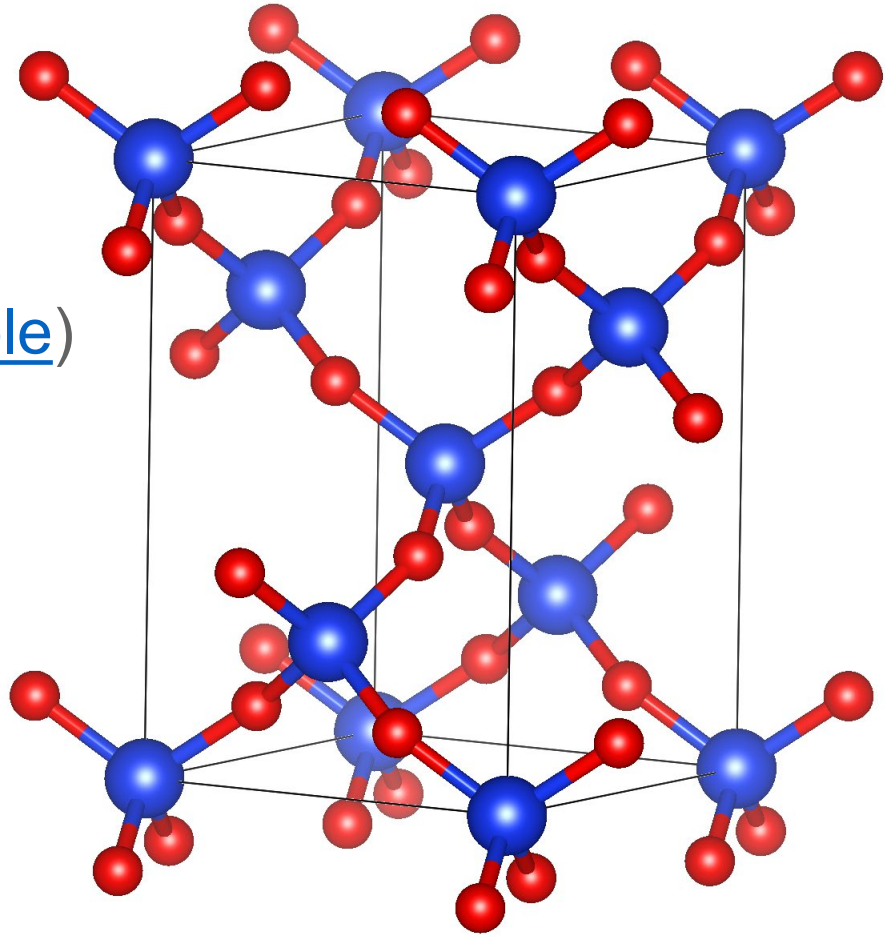
- **Neumann's principle:** physical properties must be invariant with respect to the crystal (point group) symmetry operations (https://dictionary.iucr.org/Neumann's_principle)

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

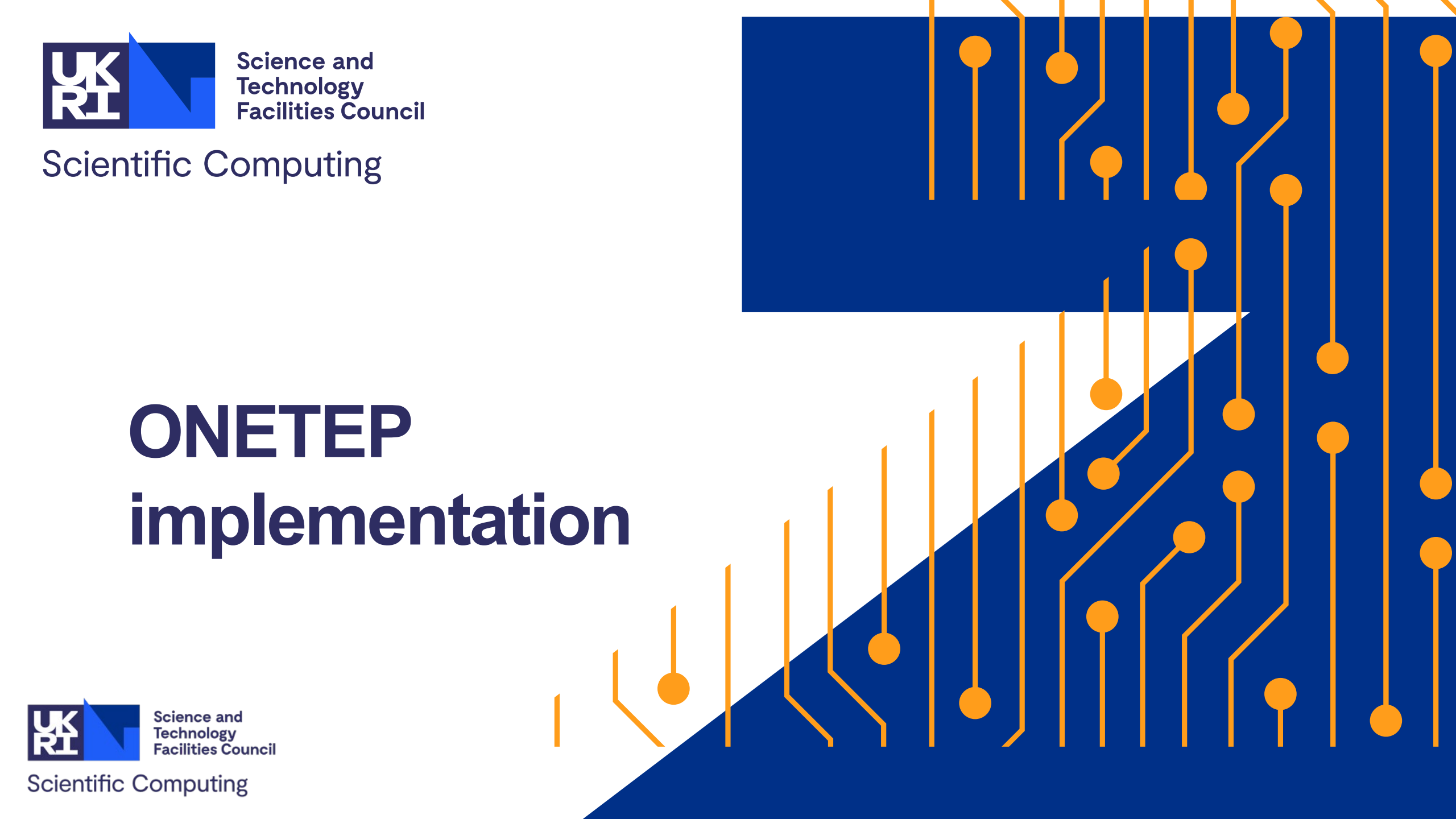
Table of space groups in 3 dimensions [edit]

$\bar{4}2m$	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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Computing the stress with small distortions

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

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

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

- 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

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

- The point groups in the boxes are equivalent for the stress calculations
- **1D**: use

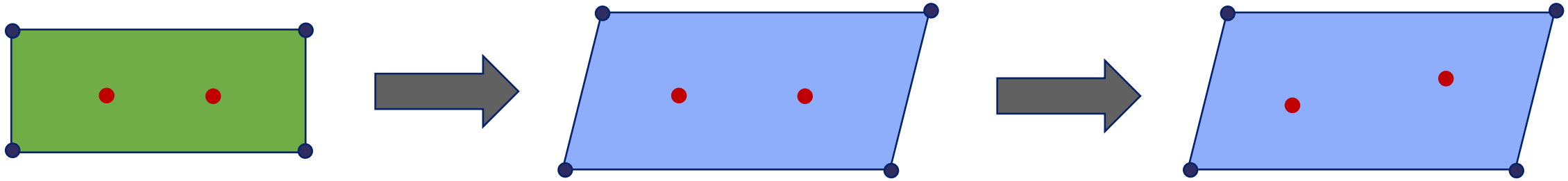
`stress_components`	Logical	`T T T`	Which rows/columns of the stress tensor to compute. The flags match X Y Z.

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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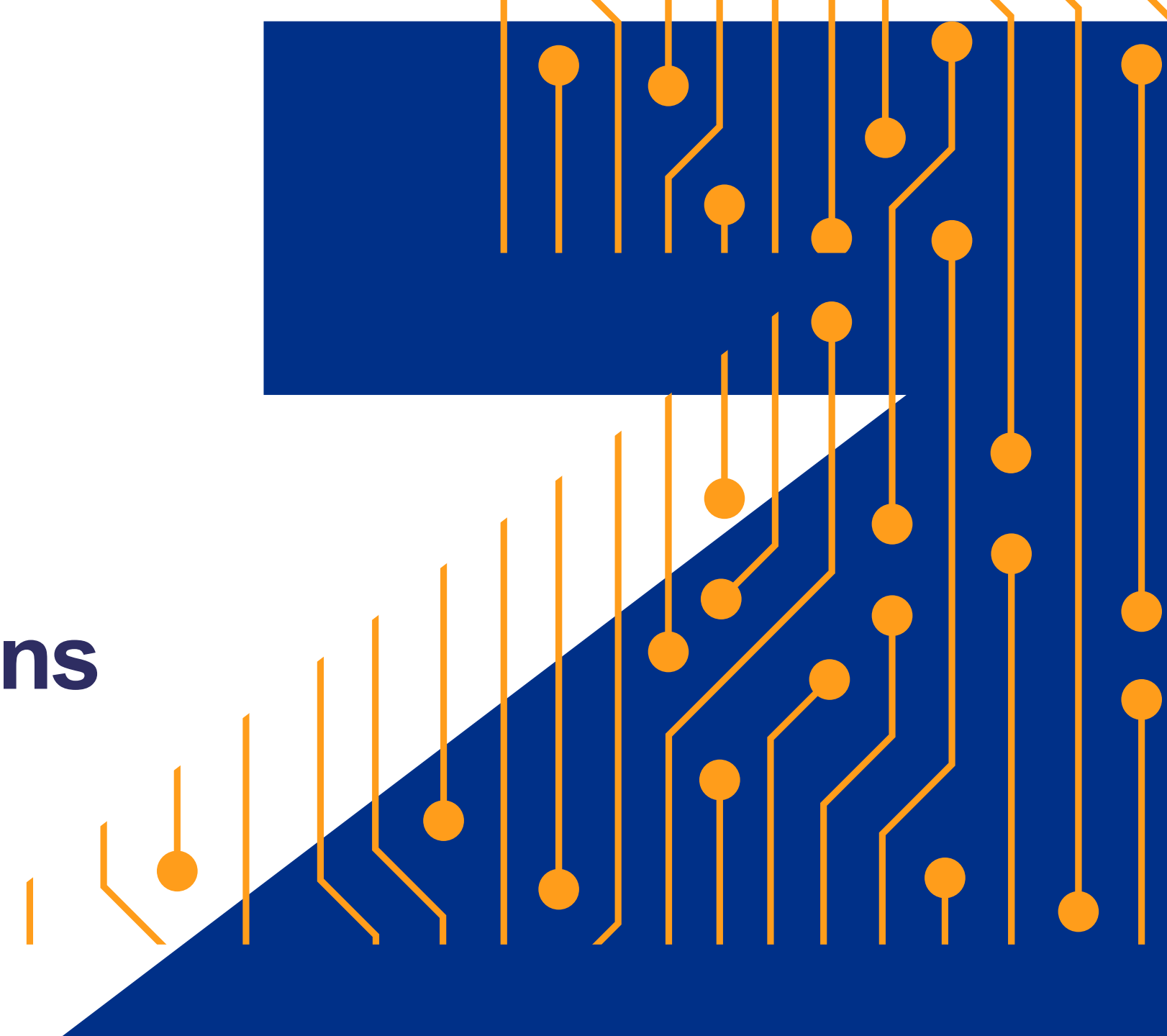
Practical considerations



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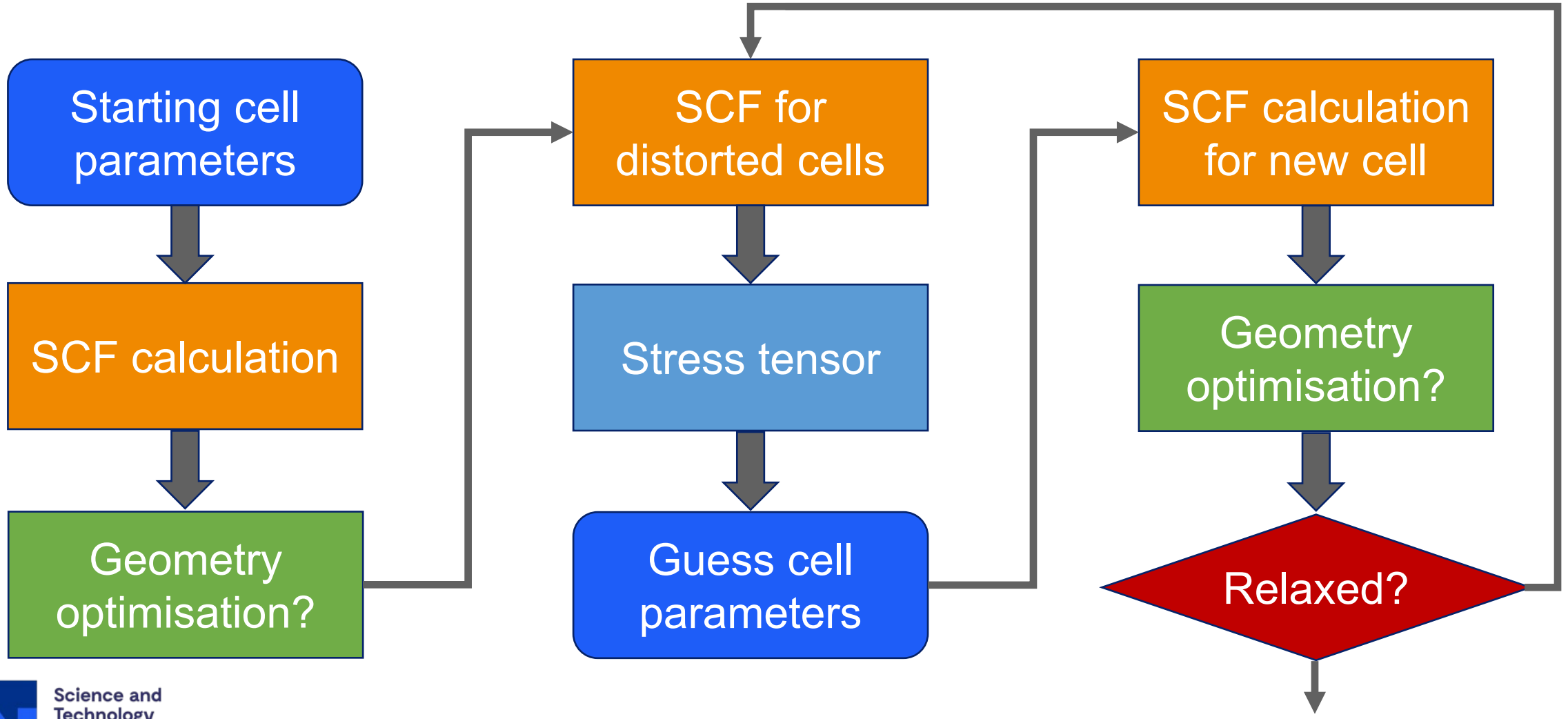
Full list of keywords for stress calculations

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.
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.

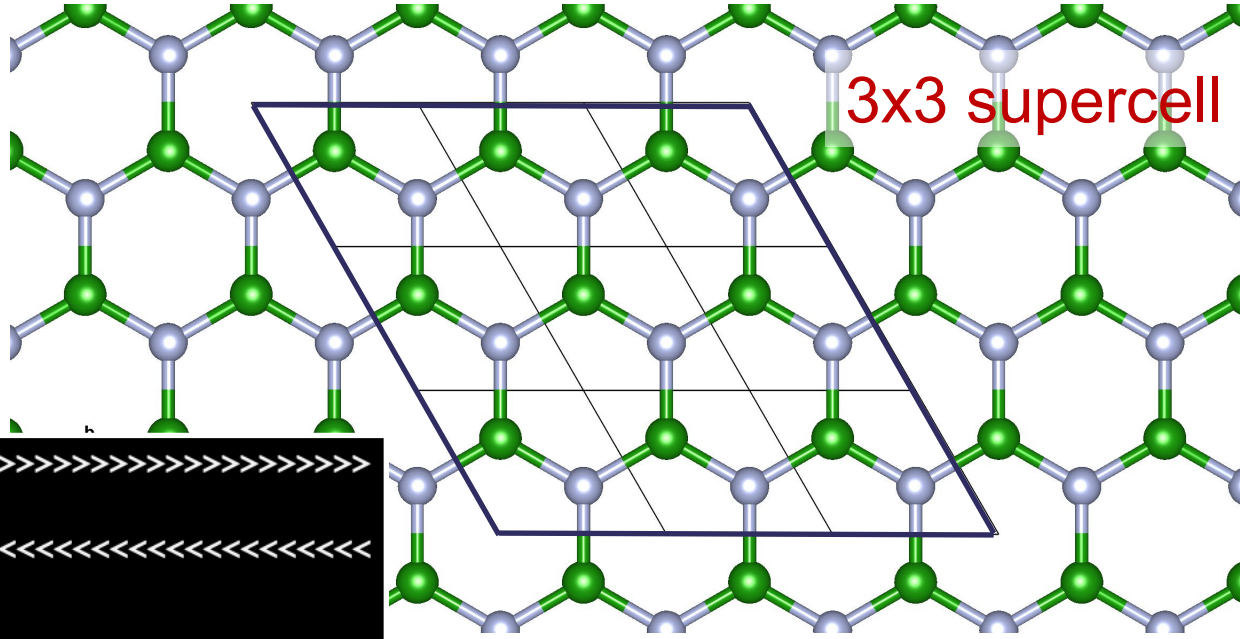
Flow of the stress/cell relaxation steps



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




```
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
                        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     0.00000098289304   -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
```

← If not enough can be adjusted in input

← This speeds up follow-up calculations

`elec_energy_tol 2.d-6 Ha`

(overkill…)

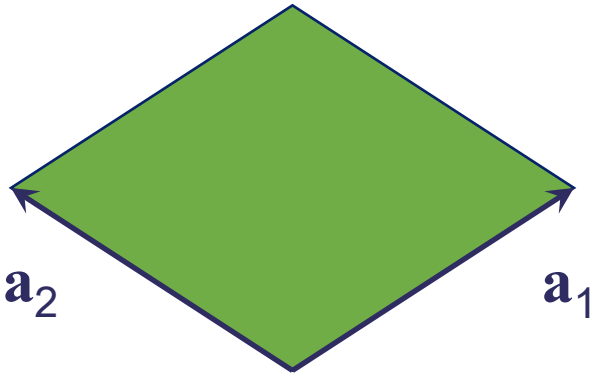
Cell optimisation for 2D *h*-BN — 3

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

Cell looks like this:



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
```

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

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

```
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

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

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
```

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Things to be done

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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