Solutions for excercise sheet 2

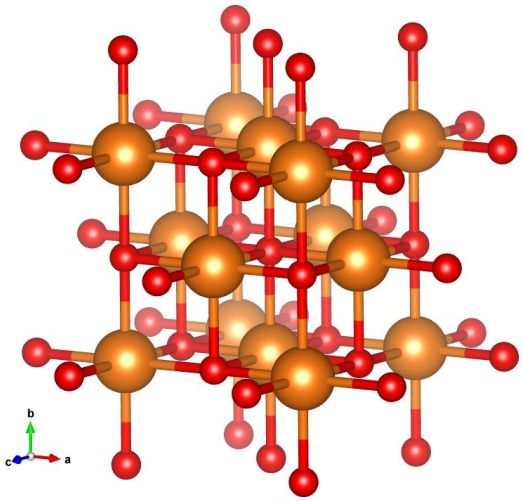
Exercise 1: Geometry optimization of MgO

(a) For the conventional cell:

```
          total   stress  (Ry/bohr**3)                   (kbar)     P=    0.03
   0.00000018   0.00000000   0.00000000          0.03      0.00      0.00
   0.00000000   0.00000018   0.00000000          0.00      0.03      0.00
   0.00000000   0.00000000   0.00000018          0.00      0.00      0.03


     bfgs converged in   5 scf cycles and   4 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  4.0E-04Ry/Bohr, cell <  5.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =    -606.0955898960 Ry
Begin final coordinates
     new unit-cell volume =    488.47164 a.u.^3 (    72.38403 Ang^3 )
     density =      3.69804 g/cm^3

CELL_PARAMETERS (angstrom)
   4.167550922   0.000000000   0.000000000
   0.000000000   4.167550922   0.000000000
   0.000000000   0.000000000   4.167550922

ATOMIC_POSITIONS (crystal)
Mg       0.000000000   0.000000000  -0.000000000
Mg       0.500000000   0.500000000   0.000000000
Mg       0.500000000   0.000000000   0.500000000
Mg       0.000000000   0.500000000   0.500000000
O        0.500000000   0.000000000   0.000000000
O        0.000000000   0.500000000   0.000000000
O        0.000000000   0.000000000   0.500000000
O        0.500000000   0.500000000   0.500000000
End final coordinates
```

(the cell pressure does not converge further, which is ok in this case, because 0.03 kbar already is very small)

Plot of the geometry with atomsk and VESTA:



In order to get to plot above, one needs to tweak the calculations a bit: Atomsk apparently takes the lattice vectors from the geometry optimization and then, for some reason, multiplies them with the value of alat that is defined at the beginning of the QE output file. With the form of the QE input files that were provided, this means that the lattice vectors extracted by atomsk are about a factor 4 too large in this case, because Quantum Espresso initially sets alat to the lattice constant in Bohr. A work around is to explicitly give alat=celldm(1) in the input file as the conversion factor between Angstrom and Bohr, like in the following input file:

```
&control
    calculation = 'vc-relax'
    prefix='MgO',
    tprnfor = .true.
    pseudo_dir = '../',
    outdir='TMP_DIR/',
    forc_conv_thr = 0.0004
 /
 &system
    ibrav=0, nat= 8, ntyp= 2, celldm(1)=1.88973,
    ecutwfc =80.0, input_dft = 'lda'
 /
 &electrons
    conv_thr =  1.0d-6
 /
&ions
 ion_dynamics = 'bfgs'
 /
&cell
 cell_dynamics = 'bfgs',
 press = 0.0,
 press_conv_thr = 0.01
/
ATOMIC_SPECIES
 Mg  24.3  Mg.nc.UPF
 O   16.0   O.nc.UPF
ATOMIC_POSITIONS (crystal)
Mg       0.000000000   0.000000000  -0.000000000
Mg       0.500000000   0.500000000   0.000000000
Mg       0.500000000   0.000000000   0.500000000
Mg       0.000000000   0.500000000   0.500000000
O        0.500000000   0.000000000   0.000000000
O        0.000000000   0.500000000   0.000000000
O        0.000000000   0.000000000   0.500000000
O        0.500000000   0.500000000   0.500000000
K_POINTS {automatic}
8 8 8 0 0 0
CELL_PARAMETERS
   4.167550922   0.000000000   0.000000000
   0.000000000   4.167550922   0.000000000
   0.000000000   0.000000000   4.167550922
```

(b)

```
          total   stress  (Ry/bohr**3)                   (kbar)     P=    0.00
   0.00000003   0.00000000   0.00000000          0.00      0.00      0.00
   0.00000000   0.00000003   0.00000000          0.00      0.00      0.00
   0.00000000   0.00000000   0.00000003          0.00      0.00      0.00


     BFGS Geometry Optimization

     bfgs converged in   1 scf cycles and   0 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  4.0E-04Ry/Bohr, cell <  5.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =    -606.0955647332 Ry
Begin final coordinates
     new unit-cell volume =    488.47164 a.u.^3 (    72.38403 Ang^3 )
     density =      3.69804 g/cm^3

CELL_PARAMETERS (angstrom)
   4.167550922   0.000000000   0.000000000
   0.000000000   4.167550922   0.000000000
   0.000000000   0.000000000   4.167550922

ATOMIC_POSITIONS (crystal)
Mg       0.000000000   0.000000000   0.000000000
Mg       0.500000000   0.500000000   0.000000000
Mg       0.500000000   0.000000000   0.500000000
Mg       0.000000000   0.500000000   0.500000000
O        0.500000000   0.000000000   0.000000000
O        0.000000000   0.500000000   0.000000000
O        0.000000000   0.000000000   0.500000000
O        0.500000000   0.500000000   0.500000000
End final coordinates
```

(c)

```
     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                   (kbar)     P=    0.02
   0.00000010   0.00000000   0.00000000          0.02      0.00      0.00
   0.00000000   0.00000010   0.00000000          0.00      0.02      0.00
   0.00000000   0.00000000   0.00000010          0.00      0.00      0.02


     bfgs converged in   3 scf cycles and   2 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  4.0E-04Ry/Bohr, cell <  5.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =    -606.0965514132 Ry
Begin final coordinates
     new unit-cell volume =    490.03141 a.u.^3 (    72.61516 Ang^3 )
     density =      3.68627 g/cm^3

CELL_PARAMETERS (angstrom)
   4.171982101   0.000000000   0.000000000
   0.000000000   4.171982101   0.000000000
   0.000000000   0.000000000   4.171982101

ATOMIC_POSITIONS (crystal)
Mg       0.000000000   0.000000000   0.000000000
Mg       0.500000000   0.500000000   0.000000000
Mg       0.500000000  -0.000000000   0.500000000
Mg       0.000000000   0.500000000   0.500000000
O        0.500000000   0.000000000  -0.000000000
O        0.000000000   0.500000000   0.000000000
O        0.000000000   0.000000000   0.500000000
O        0.500000000   0.500000000   0.500000000
End final coordinates
```

(d) ecutwfc=100 Ry

```
          total   stress  (Ry/bohr**3)                   (kbar)     P=    0.01
   0.00000009   0.00000000   0.00000000          0.01      0.00      0.00
   0.00000000   0.00000009   0.00000000          0.00      0.01      0.00
   0.00000000   0.00000000   0.00000009          0.00      0.00      0.01


     bfgs converged in   3 scf cycles and   2 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  4.0E-04Ry/Bohr, cell <  5.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =    -606.9173217108 Ry
Begin final coordinates
     new unit-cell volume =    506.37138 a.u.^3 (    75.03650 Ang^3 )
     density =      3.56732 g/cm^3

CELL_PARAMETERS (angstrom)
   4.217847255   0.000000000   0.000000000
   0.000000000   4.217847255   0.000000000
   0.000000000   0.000000000   4.217847255

ATOMIC_POSITIONS (crystal)
Mg       0.000000000  -0.000000000   0.000000000
Mg       0.500000000   0.500000000   0.000000000
Mg       0.500000000   0.000000000   0.500000000
Mg       0.000000000   0.500000000   0.500000000
O        0.500000000   0.000000000  -0.000000000
O        0.000000000   0.500000000   0.000000000
O        0.000000000   0.000000000   0.500000000
O        0.500000000   0.500000000   0.500000000
End final coordinates
```

110 Ry

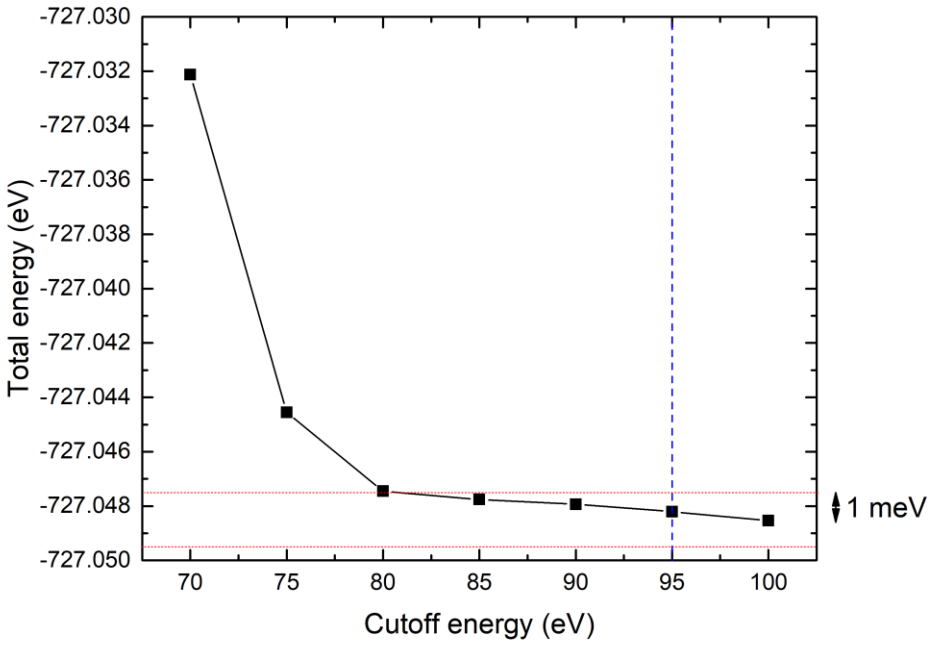
```
     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                   (kbar)     P=    0.01
   0.00000008   0.00000000   0.00000000          0.01      0.00      0.00
   0.00000000   0.00000008   0.00000000          0.00      0.01      0.00
   0.00000000   0.00000000   0.00000008          0.00      0.00      0.01


     bfgs converged in   3 scf cycles and   2 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  4.0E-04Ry/Bohr, cell <  5.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =    -606.9173743000 Ry
Begin final coordinates
     new unit-cell volume =    506.35193 a.u.^3 (    75.03361 Ang^3 )
     density =      3.56745 g/cm^3

CELL_PARAMETERS (angstrom)
   4.217793258   0.000000000   0.000000000
   0.000000000   4.217793258   0.000000000
   0.000000000   0.000000000   4.217793258

ATOMIC_POSITIONS (crystal)
Mg       0.000000000  -0.000000000   0.000000000
Mg       0.500000000   0.500000000  -0.000000000
Mg       0.500000000   0.000000000   0.500000000
Mg       0.000000000   0.500000000   0.500000000
O        0.500000000   0.000000000   0.000000000
O        0.000000000   0.500000000   0.000000000
O        0.000000000   0.000000000   0.500000000
O        0.500000000   0.500000000   0.500000000
End final coordinates
```

(e)

```
          total   stress  (Ry/bohr**3)                   (kbar)     P=    0.00
  0.00000001   0.00000000   0.00000000          0.00      0.00      0.00
  0.00000000   0.00000001   0.00000000          0.00      0.00      0.00
  0.00000000   0.00000000   0.00000001          0.00      0.00      0.00


     bfgs converged in   5 scf cycles and   4 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  4.0E-04Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =    -151.6213860864 Ry
Begin final coordinates
     new unit-cell volume =    123.50439 a.u.^3 (    18.30146 Ang^3 )
     density =      2.54051 g/cm^3

CELL_PARAMETERS (angstrom)
   2.635291090   0.000000000   0.000000000
   0.000000000   2.635291090   0.000000000
   0.000000000   0.000000000   2.635291090

ATOMIC_POSITIONS (crystal)
Mg       0.000000000   0.000000000  -0.000000000
O        0.500000000   0.500000000   0.500000000
End final coordinates
```

Exercise 2: van-der-Waals interaction in hexagonal boron nitride

(a)



(b)

```
          total   stress  (Ry/bohr**3)                   (kbar)     P=   -0.04
  -0.00000048  -0.00000000  -0.00000000         -0.07     -0.00     -0.00
  -0.00000000  -0.00000048   0.00000000         -0.00     -0.07      0.00
  -0.00000000   0.00000000   0.00000013         -0.00      0.00      0.02

     Message from routine bfgs:
     history already reset at previous step: stopping

     bfgs converged in   4 scf cycles and   1 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  2.0E-04Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =     -53.4596328489 Ry
Begin final coordinates
     new unit-cell volume =    237.46448 a.u.^3 (    35.18860 Ang^3 )
     density =      2.26510 g/cm^3

CELL_PARAMETERS (angstrom)
   2.506702498  -0.000000000   0.000000000
   1.253351249   2.170868043  -0.000000000
  -0.000000000  -0.000000000   6.466448560

ATOMIC_POSITIONS (crystal)
B        0.000000000  -0.000000000   0.250000000
N        0.333333333   0.333333333   0.250000000
B        0.333333333   0.333333333   0.750000000
N        0.000000000  -0.000000000   0.750000000
End final coordinates
```

The pressure acting on the cell does not converge further.

(c)

```
          total   stress  (Ry/bohr**3)                   (kbar)     P=   -0.01
  -0.00000006   0.00000000   0.00000000         -0.01      0.00      0.00
   0.00000000  -0.00000006  -0.00000000          0.00     -0.01     -0.00
  -0.00000000   0.00000000   0.00000000         -0.00      0.00      0.00


     bfgs converged in  16 scf cycles and  15 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  2.0E-04Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =     -53.6340439194 Ry
Begin final coordinates
     new unit-cell volume =    309.22488 a.u.^3 (    45.82240 Ang^3 )
     density =      1.73945 g/cm^3

CELL_PARAMETERS (angstrom)
   2.511029759   0.000000000  -0.000000000
   1.255514880   2.174615560   0.000000000
   0.000000000  -0.000000000   8.391574893

ATOMIC_POSITIONS (crystal)
B        0.000000000  -0.000000000   0.250000000
N        0.333333333   0.333333333   0.250000000
B        0.333333333   0.333333333   0.750000000
N        0.000000000  -0.000000000   0.750000000
End final coordinates
```

(d)

```
          total   stress  (Ry/bohr**3)                   (kbar)     P=   -0.00
  -0.00000008   0.00000000   0.00000000         -0.01      0.00      0.00
   0.00000000  -0.00000008  -0.00000000          0.00     -0.01     -0.00
   0.00000000  -0.00000000   0.00000014          0.00     -0.00      0.02

     Message from routine bfgs:
     history already reset at previous step: stopping

     bfgs converged in   4 scf cycles and   3 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  2.0E-04Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =     -53.9243142017 Ry
Begin final coordinates
     new unit-cell volume =    243.11827 a.u.^3 (    36.02641 Ang^3 )
     density =      2.21243 g/cm^3

CELL_PARAMETERS (angstrom)
   2.515667489  -0.000000000   0.000000000
   1.257833745   2.178631954   0.000000000
  -0.000000000   0.000000000   6.573306470

ATOMIC_POSITIONS (crystal)
B        0.000000000  -0.000000000   0.250000000
N        0.333333333   0.333333333   0.250000000
B        0.333333333   0.333333333   0.750000000
N        0.000000000  -0.000000000   0.750000000
End final coordinates
```

(e)

	Bulk	Monolayer	Binding energy
PBE	-53.63404667 Ry	-26.81674171 Ry	0.56 mRy
optB88-vdW	-53.92431420 Ry	-26.95150179 Ry	21.3 mRy

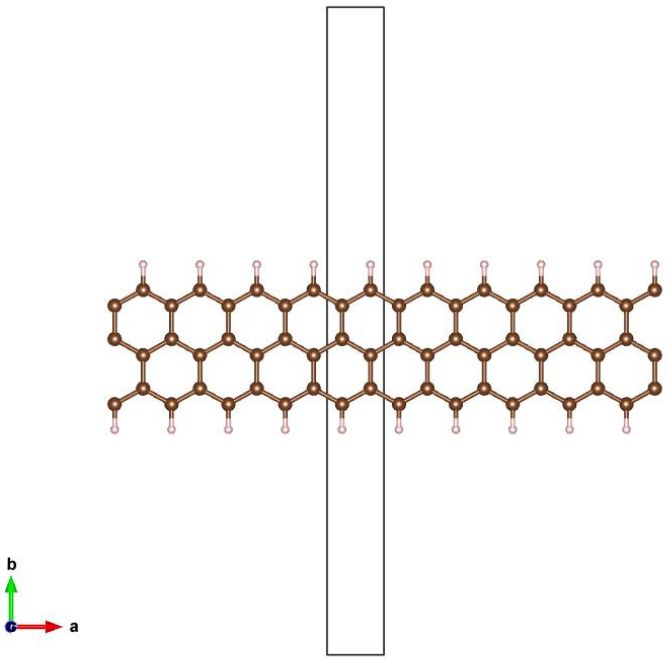
Exercise 3: Distorted graphene nanoribbon

(a) With smearing:

```
     Forces acting on atoms (cartesian axes, Ry/au):

     atom    1 type  2   force =     0.00014476   -0.00072021    0.00000000
     atom    2 type  2   force =     0.00007006   -0.00018920    0.00000000
     atom    3 type  1   force =    -0.00035964    0.00038438    0.00000000
     atom    4 type  1   force =    -0.00013679    0.00069139    0.00000000
     atom    5 type  1   force =    -0.00017135   -0.00067773    0.00000000
     atom    6 type  1   force =     0.00064332    0.00063610    0.00000000
     atom    7 type  1   force =     0.00000901   -0.00011989    0.00000000
     atom    8 type  1   force =    -0.00019937   -0.00000484    0.00000000

     Total force =     0.001648     Total SCF correction =     0.000026

     bfgs converged in  22 scf cycles and  20 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  1.0E-03 Ry/Bohr)

     End of BFGS Geometry Optimization

     Final energy   =     -74.3101287406 Ry
Begin final coordinates

ATOMIC_POSITIONS (crystal)
H        0.764353920   0.602091597   0.000000000
H        0.264693739   0.348211759  -0.000000000
C        0.764656072   0.462764983   0.000000000
C        0.764680519   0.562944772   0.000000000
C        0.264708173   0.539016979   0.000000000
C        0.264494259   0.487486088  -0.000000000
C        0.764806201   0.411260310  -0.000000000
C        0.264862764   0.387332611  -0.000000000
End final coordinates
```

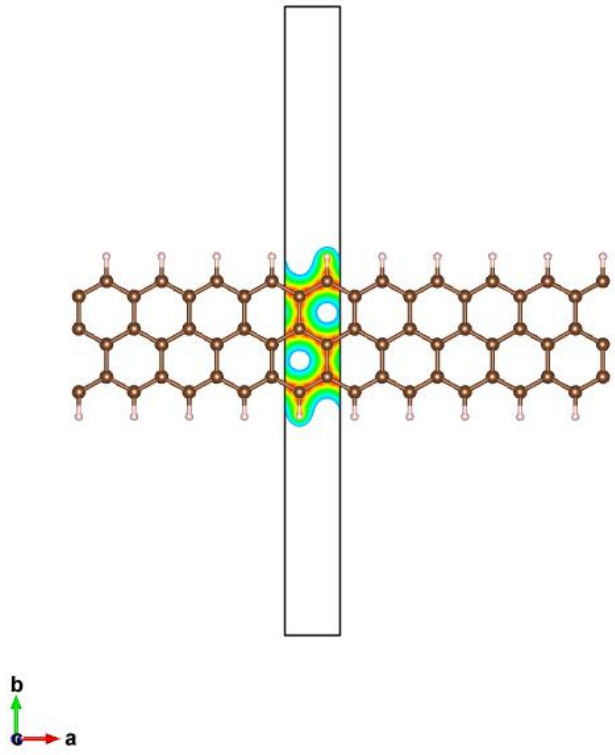
(b)

```
     atom    8 type  1   force =    -0.00007928    0.00008784    0.00000000

     Total force =     0.000339     Total SCF correction =     0.000002


     Computing stress (Cartesian axis) and pressure

          total   stress  (Ry/bohr**3)                   (kbar)     P=   -0.00
  -0.00000000   0.00000004   0.00000000         -0.00      0.01      0.00
   0.00000004  -0.00000004  -0.00000000          0.01     -0.01     -0.00
   0.00000000  -0.00000000   0.00000000          0.00     -0.00      0.00


     bfgs converged in  12 scf cycles and  11 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  4.0E-04Ry/Bohr, cell <  1.0E-02kbar)

     End of BFGS Geometry Optimization

     Final enthalpy =     -74.3137182003 Ry
Begin final coordinates
     new unit-cell volume =   6969.16759 a.u.^3 (  1032.72407 Ang^3 )
     density =      0.11899 g/cm^3

CELL_PARAMETERS (alat=  1.88972599)
   2.458867405   0.000000000   0.000000000
   0.000000000  28.000000000   0.000000000
   0.000000000   0.000000000  15.000000000

ATOMIC_POSITIONS (crystal)
H        0.764621999   0.602434046  -0.000000000
H        0.264688933   0.347844672   0.000000000
C        0.764623433   0.462644871   0.000000000
C        0.764633257   0.563333029  -0.000000000
C        0.264666963   0.539089792  -0.000000000
C        0.264647105   0.487631010  -0.000000000
C        0.764677540   0.411187116   0.000000000
C        0.264696418   0.386944564   0.000000000
End final coordinates
```

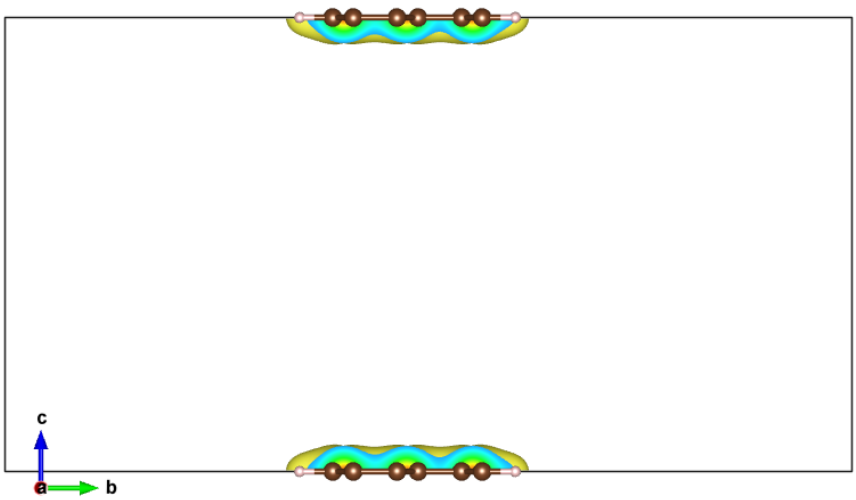


(Here, the plot worked as expected, due to the atomsk compatible definition of celldm in the input file)

(c) Electron density from the top



From the side:



Note that here, the density is “cut” into two halfs, because the nanoribbon is located at the edge of the unit cell. We can plot the density in one piece, if we move the nanoribbon towards the middle of the cell. This is, of course, a purely aesthetic choice.

Kohn-Sham-Potential: