computing and visualizing charge density differences

This document describes how to compute the *charge density difference* (*) by Quantum Espresso, and how to visualize it in 3 (or is it 4?) dimensions.

(*) by *charge density difference*, we mean here "charge density minus superposition of atomic densities" (quote from the QE input reference document). The opposite quantity (superposition of free atom densities minus the charge density of the crystal) is used equally often in the literature. You always have to check which of both definitions is used before interpreting a picture in a book or paper.

In this document, we will use rocksalt (NaCl) as the example.

First make a regular DFT calculation for rocksalt, starting from the input file given underneath, with this pseudopotential for Na and this pseudopotential for Cl, with ecutwfc=60, ecutrho=360 and a 7x7x7 k-mesh. Pay particular attention to `prefix` and `outdir`: the names/choices you take for these, will need to be used later on in other files as well.

In the rocksalt (halite) calculation we did in a previous exercise, we started from a cif file that specified a primitive unit cell of rocksalt (more about primitive cells in the chapters on crystallography and supercells). A primitive cell has the minimal number of atoms (2). It is not always, though, easy to visualize because the shape of the cell can be nontrivial. Therefore, in this exercise, we will use a conventional unit cell for rocksalt. This one has 8 atoms, so it's four times as large as the primitive cell. The calculation will therefore take a little longer.

You can visually inspect this cell by xcrysden:

```
xcyrsden --pw_inp rocksalt.in
```

(compare that with a picture of the primitive unit cell you used earlier).

This is how your rocksalt input file for the conventional unit cell should look like. The lines marked in red are different from the primitive cell:

```
#*******************************************************************************
#*                  Generated by cif2cell 1.2.10 2018-09-22 15:20                *
#*  T. Bjorkman, Comp. Phys. Commun. 182, 1183-1186 (2011). Please cite generously. *
#*                                                                               *
#*                Data obtained from COD. Reference number : 9008678             *
#*                                    (Halite)                                   *
#*              Wyckoff, R. W. G., Crystal Structures 1, 85-237 (1963)           *
#*******************************************************************************

&CONTROL
  calculation='scf',
  outdir='.',
  prefix='rocksalt',
  pseudo_dir='.',
  verbosity='low',
  tprnfor=.true.,
  tstress=.true.,
/


&SYSTEM
  ibrav = 0
  A =    5.64056
  nat = 8
  ntyp = 2
  ecutwfc=60,
  ecutrho=360,
```

```
  input_dft='pbe',
  occupations='smearing',
  smearing='mv',
  degauss=0.005d0,
/

&ELECTRONS
  conv_thr=1d-08,
  mixing_beta=0.7d0,
/

CELL_PARAMETERS {alat}
  1.000000000000000   0.000000000000000   0.000000000000000
  0.000000000000000   1.000000000000000   0.000000000000000
  0.000000000000000   0.000000000000000   1.000000000000000

ATOMIC_SPECIES
  Na   22.98900  Na.pbe-spn-kjpaw_psl.0.2.UPF
  Cl   35.45150  Cl.pbe-n-kjpaw_psl.0.1.UPF

ATOMIC_POSITIONS {crystal}
Cl   0.500000000000000   0.500000000000000   0.500000000000000
Cl   0.000000000000000   0.000000000000000   0.500000000000000
Cl   0.000000000000000   0.500000000000000   0.000000000000000
Cl   0.500000000000000   0.000000000000000   0.000000000000000
Na   0.000000000000000   0.000000000000000   0.000000000000000
Na   0.500000000000000   0.500000000000000   0.000000000000000
Na   0.000000000000000   0.500000000000000   0.500000000000000
Na   0.500000000000000   0.000000000000000   0.500000000000000

K_POINTS {automatic}
  7 7 7 0 0 0
```

Let it run as usual:

```
pw.x -input rocksalt.in > rocksalt.out
```

After having run this calculation, prepare an input file for PP (the Post-Processing tool of QE). The file can have any name, let's call it here `ppinput.in`. This is how it should look like (explanations are given underneath):

```
&INPUTPP
  prefix='rocksalt',
  outdir='.',
  filplot='ppoutputfile.txt',
  plot_num=9,
/

&PLOT
  nfile=1,
  iflag=3,
  output_format=3,
  fileout='rocksalt.xsf',
  e1(1)=1.0,e1(2)=0.0,e1(3)=0.0,
  e2(1)=0.0,e2(2)=1.0,e2(3)=0.0,
  e3(1)=0.0,e3(2)=0.0,e3(3)=1.0,
  x0(1)=0.0,x0(2)=0.0,x0(3)=0.0,
  nx=101, ny=101, nz=101,
/
```

These are the meanings of the lines in this file:

&INPUTPP block : this instructs pp.x to calculate the requested quantity (yet not to plot it)

- prefix : this should be exactly the same as 'prefix' in the preceding pw.x calculation.
- outdir : this should be exactly the same as 'outdir' in the preceding pw.x calculation.
- filplot : name of a file that will contain the requested object, albeit in a format that cannot yet be visualized. Possible error information will be in this file as well.
- plot_num = 9 : for this value, pp.x will calculate the 'charge difference density', defined as "charge density minus superposition of atomic densities". See the QE input reference manual for other values of plot_num, to calculate other quantities (charge density, potential, spin density, STM-image,…)

&PLOT block : this instructs pp.x to write (part of) the quantity calculated in the previous step into a format that can be read by plotting tools.

- nfile = 1 : for a charge difference density there will be only one file to plot
- iflag = 3 : this instructs to create a three-dimensional plot
- output_format = 3 : this instructs to write the three-dimensional plot into an xsf format that can be read by Xcrysden.
- fileout = 'rocksalt.xsf' : the name of the file in xsf format that contains your final image. You can use any file name here. The *.xsf extension is logical, yet not strictly necessary.
- Then comes a set of 4 coordinates. The first three define three vectors that together span the volume that will be plot. These three vectors must be orthogonal to each other. The 4th set of coordinates defines the origin from which these vectors start.
- The last line contains the number of grid points for which plottable data will be generated, along each of the three vectors specified above.

Once you prepared this file (named ppinput.in), run pp.x:

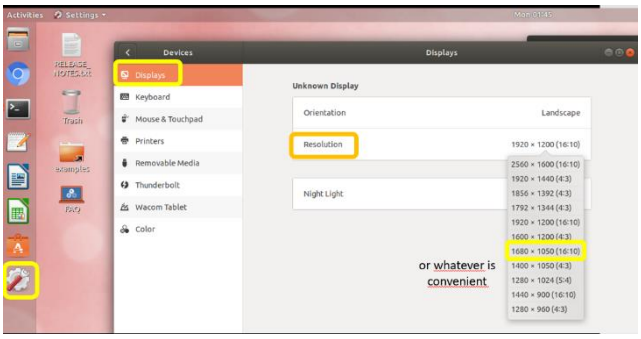
```
pp.x -input ppinput.in > ppoutput.out
```

The last step is visualizing this charge density difference with Xcrysden:

```
xcrysden --xsf rocksalt.xsf
```

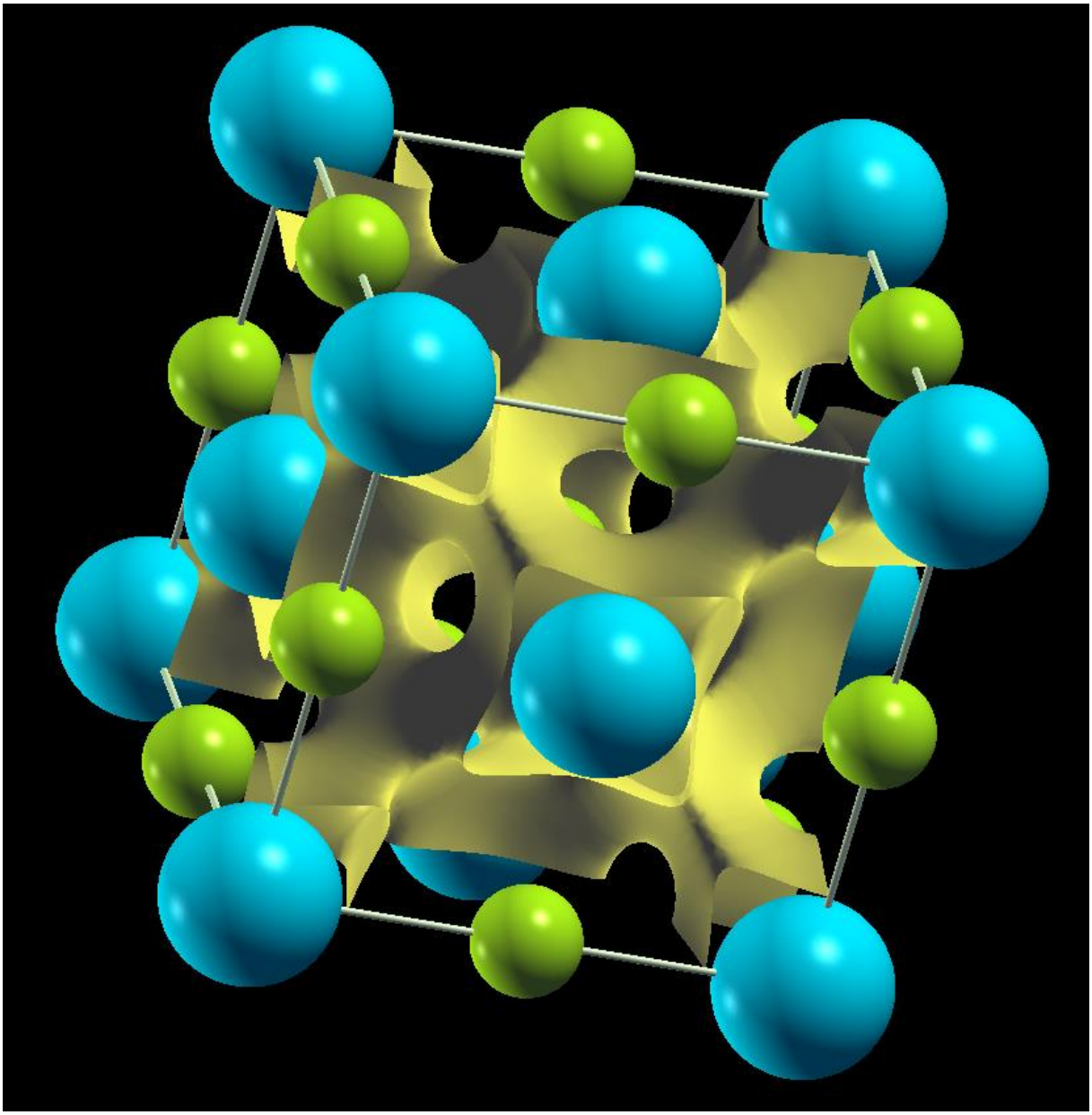
When xcrysden opens, choose Tools => Data Grid => OK.

In case you cannot see the entire menu because it is outside the scope of your screen, then adjust the resolution of your screen in the following way (settings/displays/resolution) :



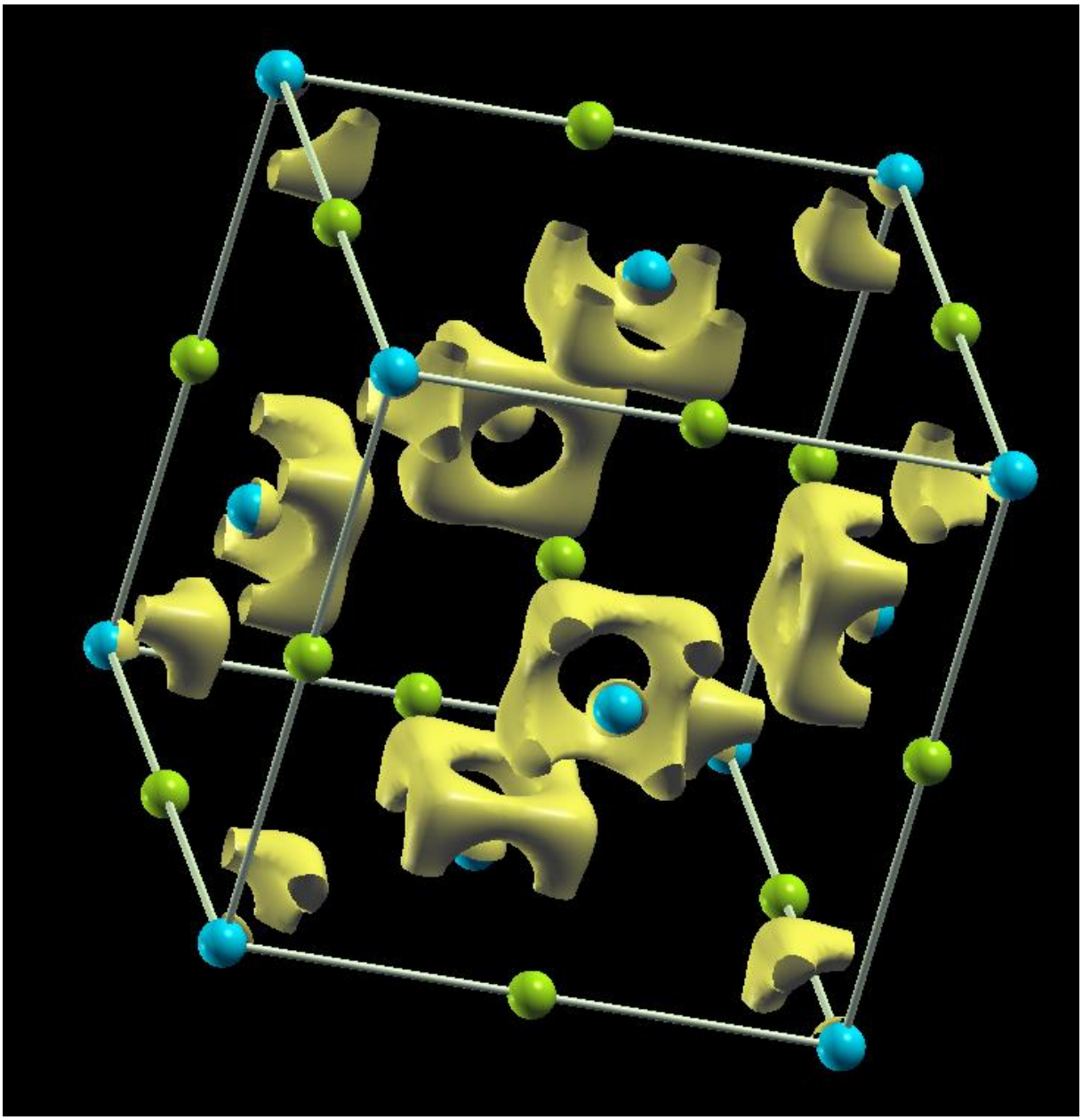
A new pop-up window opens. What matters there is the section with grid value/iso value. A minimal and maximal value are indicated. These are the smallest (largest) values of the charge density difference function over your unit cell. The smallest value is negative (this will be a region of space where there are less electrons in the crystal then there are at that place in a superposition of free

atoms. The largest value is positive (=more electrons in the crystal then in the superposition of free atoms). When you fill out an iso value, all points in space where the charge density difference function reaches that value, will be coloured. Let us fill out ‘0’, which means: colour all points in space where there is no difference between the charge density of the rocksalt crystal, and a superposition of free atoms. Click ‘submit’, and you’ll get this kind of picture:



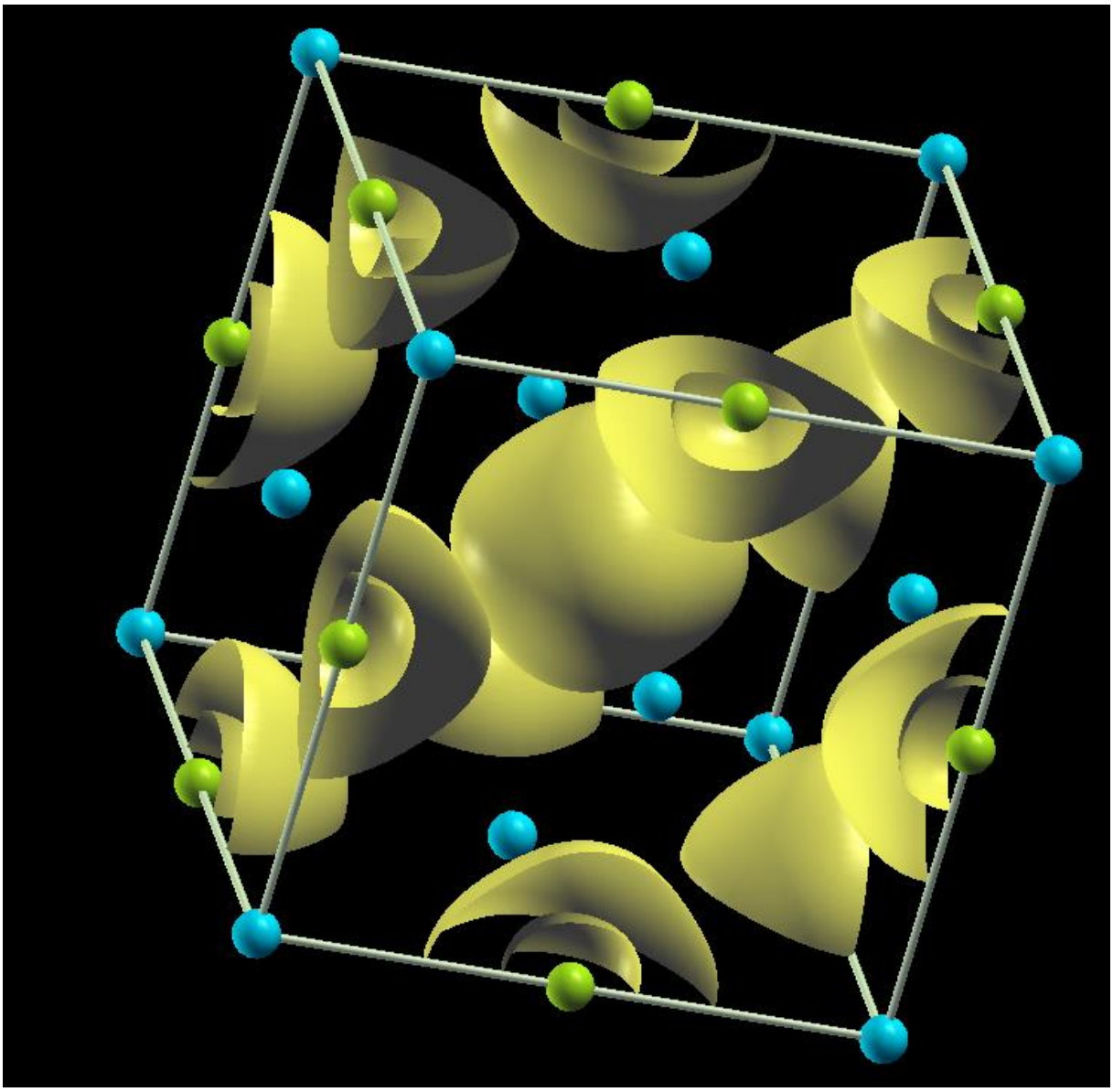
This is a rather complex surface, that tends to be in the regions far away from the atomic nuclei.

Now take an isovalue of -0.001. This leads to this picture (for better visualization, a ball-and-stick mode with smaller spheres has been selected from the menu bar at the right) :

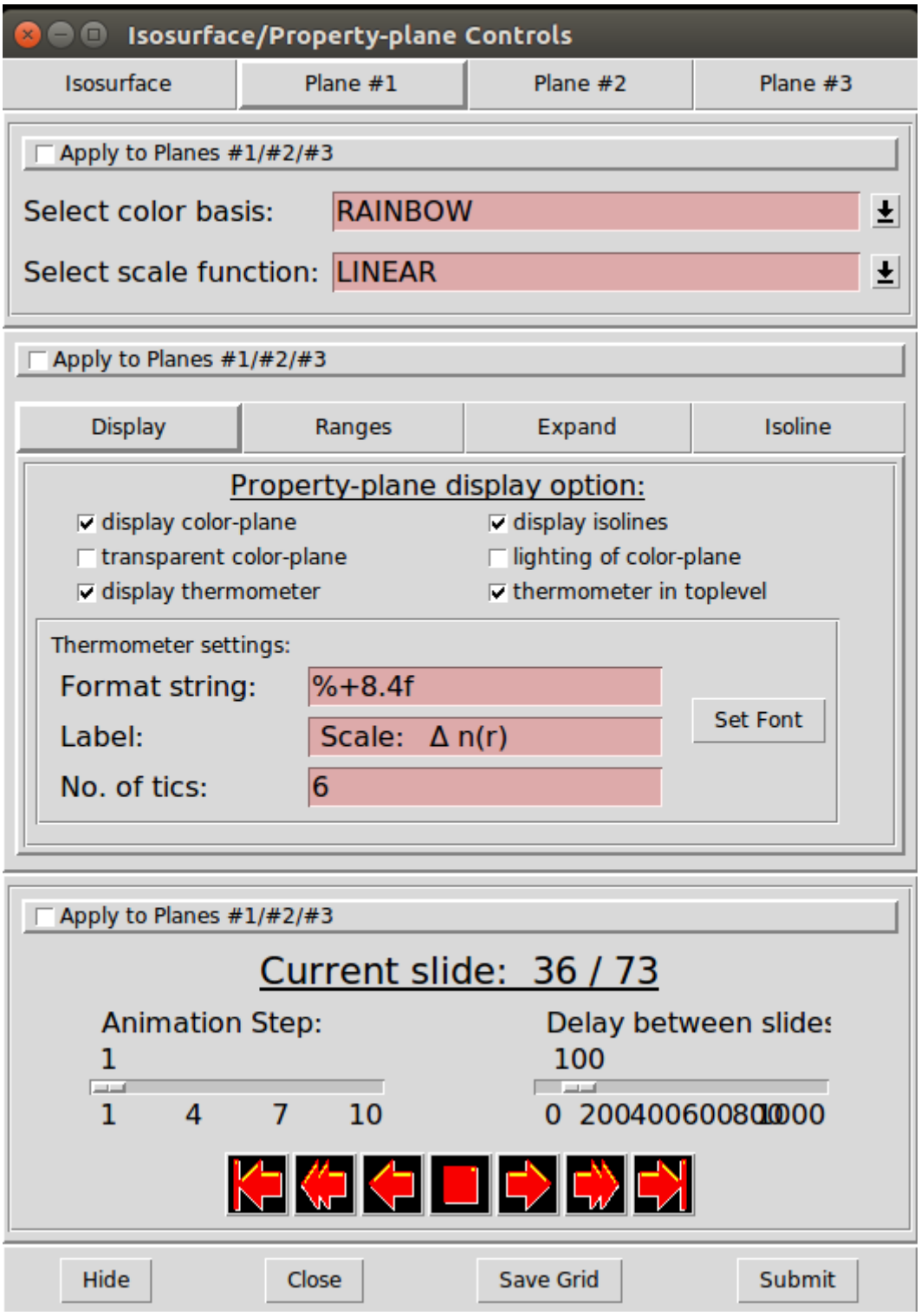


These isosurfaces are centered around the Na-atoms. Which makes sense, as Na is the electron-donating atom in rocksalt. It should have a region of electron depletion around its nucleus.

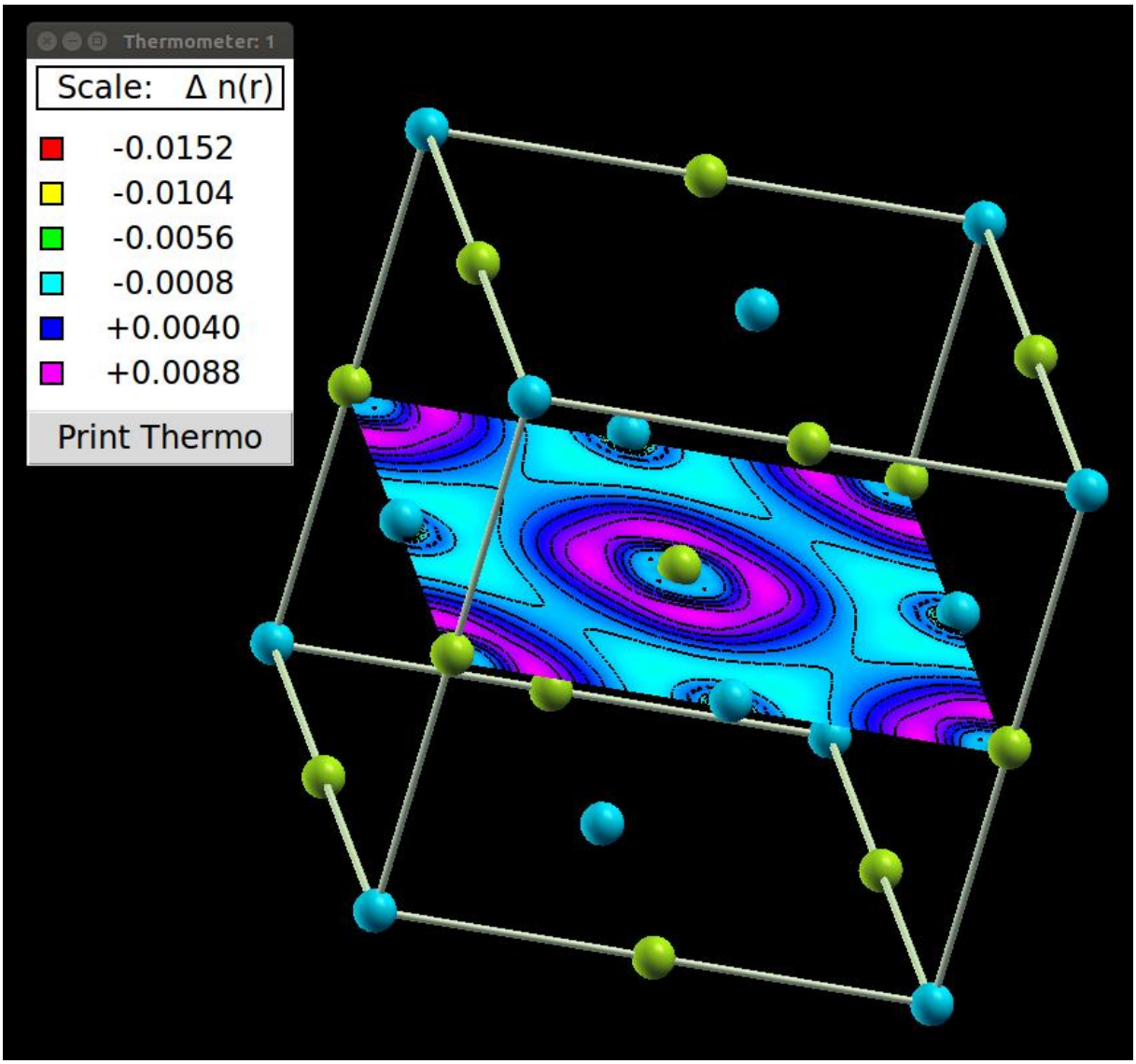
If you take a positive isovalue (say 0.005), then the isosurfaces are centered around the electron-receiving Cl-atoms:



If you take the tab ‘plane #1’ etc., and make the following ticks and selections:



you will display the charge density difference on a plane in the unit cell. By the red arrows at the bottom you can slide the plane through the cell. By taking the tabs ‘plane #2’ etc. you can select a different orientation of the plane.


Thermometer: 1
Scale: Δ n(r)
-0.0152
-0.0104
-0.0056
-0.0008
+0.0040
+0.0088
Print Thermo