Charge density difference

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Definition

Charge density difference of system AB:

$$\Delta\rho = \rho_{\mathrm{AB}} - \rho_{\mathrm{A}} - \rho_{\mathrm{B}}$$

NOTE: In calculation of the latter two quantities, the atomic positions are fixed as those they have in the AB system.

In VASP, three calculations should be perform to obtain the charge density of AB, A, and B systems. CHGCAR file contains the information about charge density.

Files

The geometry optimization is supposed to have been done.

For the three calculations of charge density of A, B, and AB systems, INCAR and KPOINTS files are same. POSCAR file should be prepared separately, as well as the corresponding POTCAR file.

Example:
CO adsorbed on Pt (111) surface

A B

❖INCAR file

```
PREC=accurate
ENCUT=500
NELMIN=10
EDIFF=1E-5
NSW=0
IBRION=-1
ALGO=Fast
ISMEAR=1
SIGMA=0.1
ADDGRID=T
LCHARG=T
LREAL=F
LASPH=T
LORBIT=10
IDIPOL=3
LDIPOL=T
```

Only electronic-SC loops are performed

CHGCAR is written

Example

Pt (2X2) supercell is used. When the geometry optimization is finished, CONTCAR is obtained.

❖KPOINTS

```
Automatic mesh
0
Gamma
   6     6     1
   0.00  0.00  0.00
```

➢CO/Pt (AB system)

mv CONTCAR POSCAR

```
CO adsorption on Pt111
   1.00000000000000
     5.6248002051999997    0.0000000000000000    0.0000000000000000
    -2.8124001025999998    4.8712198688999999    0.0000000000000000
     0.0000000000000000    0.0000000000000000   21.8889007567999982
   Pt   C    O
    16     1     1
Selective dynamics
Direct
  0.3078998535024776  0.1157908176504095  0.2092395708219017   T   T   T
  0.4722200040000004  0.4444400069999972  0.0000000000000000   F   F   F
  0.4722270478465680  0.4444435289232810  0.3223780958481174   T   T   T
  0.1388899980000033  0.2777799959999996  0.1049100010000004   F   F   F
  0.8055593647218970  0.1111096878609436  0.2078349845427296   T   T   T
  0.9722200040000004  0.4444400069999972  0.0000000000000000   F   F   F
  0.9725427394145848  0.4450750238233668  0.3118070194434971   T   T   T
  0.6388900279999987  0.2777799959999996  0.1049100010000004   F   F   F
  0.3078998535024776  0.6087690168520634  0.2092395708219017   T   T   T
  0.4722200040000004  0.9444400069999972  0.0000000000000000   F   F   F
  0.4715953867044669  0.9441276983522304  0.3118068634523949   T   T   T
  0.1388899980000033  0.7777799959999996  0.1049100010000004   F   F   F
  0.8008779549745275  0.6087689529872636  0.2092396681127095   T   T   T
  0.9722200040000004  0.9444400069999972  0.0000000000000000   F   F   F
  0.9725427394145848  0.9441277255912126  0.3118070194434971   T   T   T
  0.6388900279999987  0.7777799959999996  0.1049100010000004   F   F   F
  0.4722253163793889  0.4444426631896916  0.4068328727876835   T   T   T
  0.4722244901200938  0.4444422500600438  0.4597422040913705   T   T   T
```

POTCAR file is same with the geometry optimization.

➢CO (A system)

Delete the Pt part in POSCAR of AB system

```
CO adsorption on Pt111
   1.00000000000000
     5.6248002051999997    0.0000000000000000    0.0000000000000000
    -2.8124001025999998    4.8712198688999999    0.0000000000000000
     0.0000000000000000    0.0000000000000000   21.8889007567999982
  C    O
  1     1
Selective dynamics
Direct
  0.4722253163793889  0.4444426631896916  0.4068328727876835   T   T   T
  0.4722244901200938  0.4444422500600438  0.4597422040913705   T   T   T
```

POTCAR file should match the POSCAR.

➢Pt (B system)

Delete the CO part in POSCAR of AB system

```
CO adsorption on Pt111
   1.00000000000000
     5.6248002051999997    0.0000000000000000    0.0000000000000000
    -2.8124001025999998    4.8712198688999999    0.0000000000000000
     0.0000000000000000    0.0000000000000000   21.8889007567999982
   Pt
    16
Selective dynamics
Direct
  0.3078998535024776  0.1157908176504095  0.2092395708219017   T   T   T
  0.4722200040000004  0.4444400069999972  0.0000000000000000   F   F   F
  0.4722270478465680  0.4444435289232810  0.3223780958481174   T   T   T
  0.1388899980000033  0.2777799959999996  0.1049100010000004   F   F   F
  0.8055593647218970  0.1111096878609436  0.2078349845427296   T   T   T
  0.9722200040000004  0.4444400069999972  0.0000000000000000   F   F   F
  0.9725427394145848  0.4450750238233668  0.3118070194434971   T   T   T
  0.6388900279999987  0.2777799959999996  0.1049100010000004   F   F   F
  0.3078998535024776  0.6087690168520634  0.2092395708219017   T   T   T
  0.4722200040000004  0.9444400069999972  0.0000000000000000   F   F   F
  0.4715953867044669  0.9441276983522304  0.3118068634523949   T   T   T
  0.1388899980000033  0.7777799959999996  0.1049100010000004   F   F   F
  0.8008779549745275  0.6087689529872636  0.2092396681127095   T   T   T
  0.9722200040000004  0.9444400069999972  0.0000000000000000   F   F   F
  0.9725427394145848  0.9441277255912126  0.3118070194434971   T   T   T
  0.6388900279999987  0.7777799959999996  0.1049100010000004   F   F   F
```

POTCAR file should match the POSCAR.

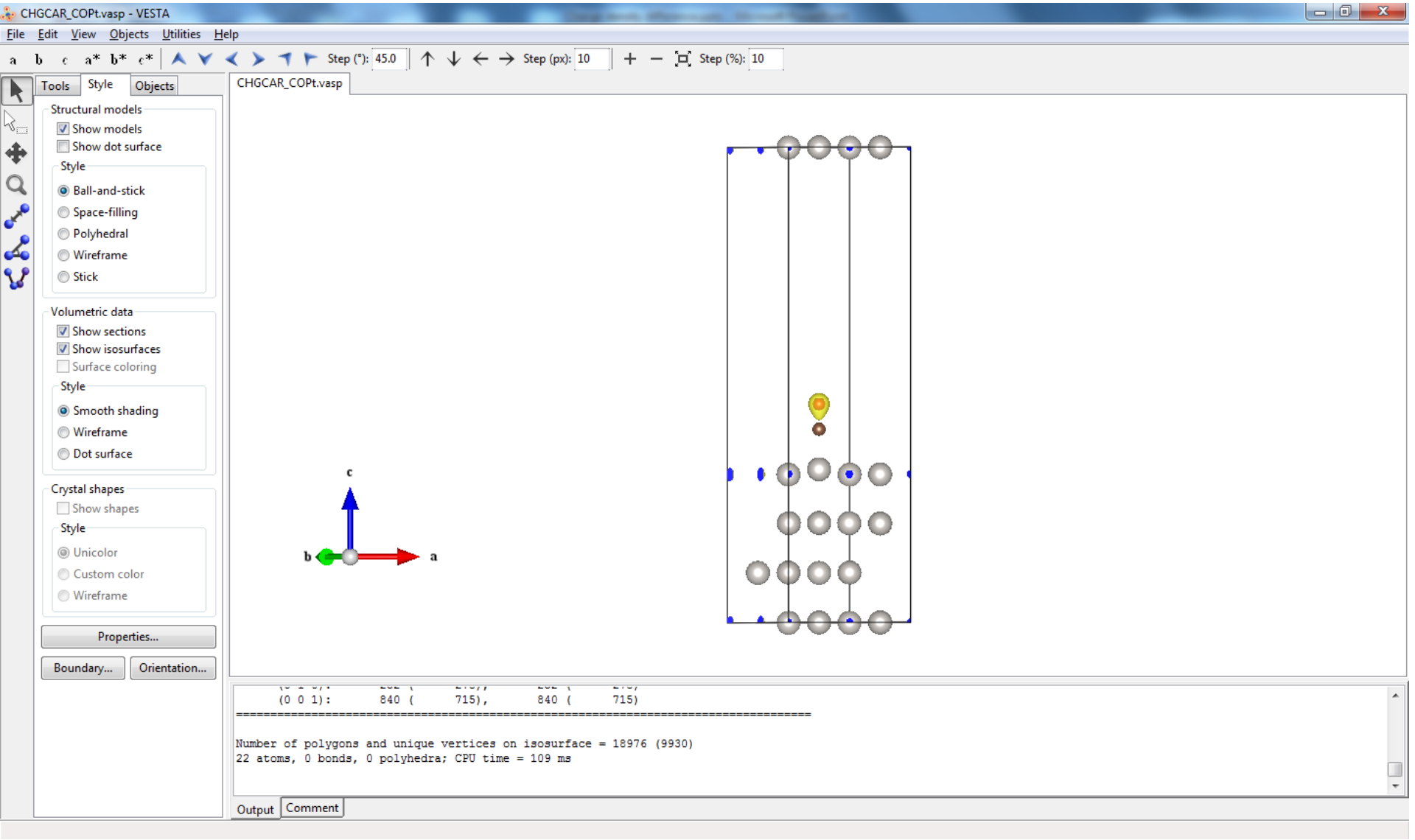
Example

When the above three calculations are finished, three CHAGCAR files are obtained.

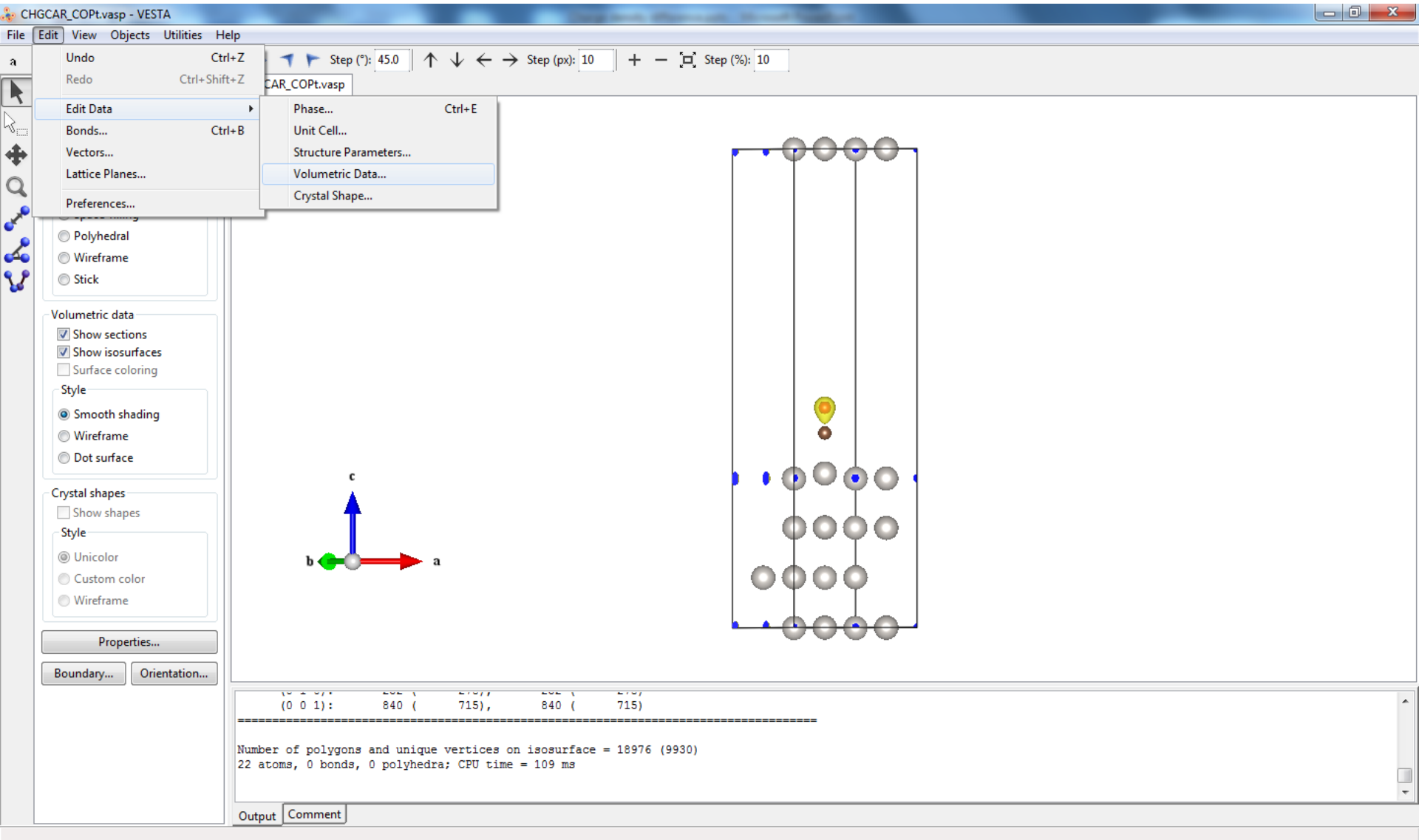
A: CO	CHGCAR_CO
B: Pt	CHGCAR_Pt
AB: CO/Pt	CHGCAR_COPt

Next step: Utilizing the software of VESTA to make subtract.

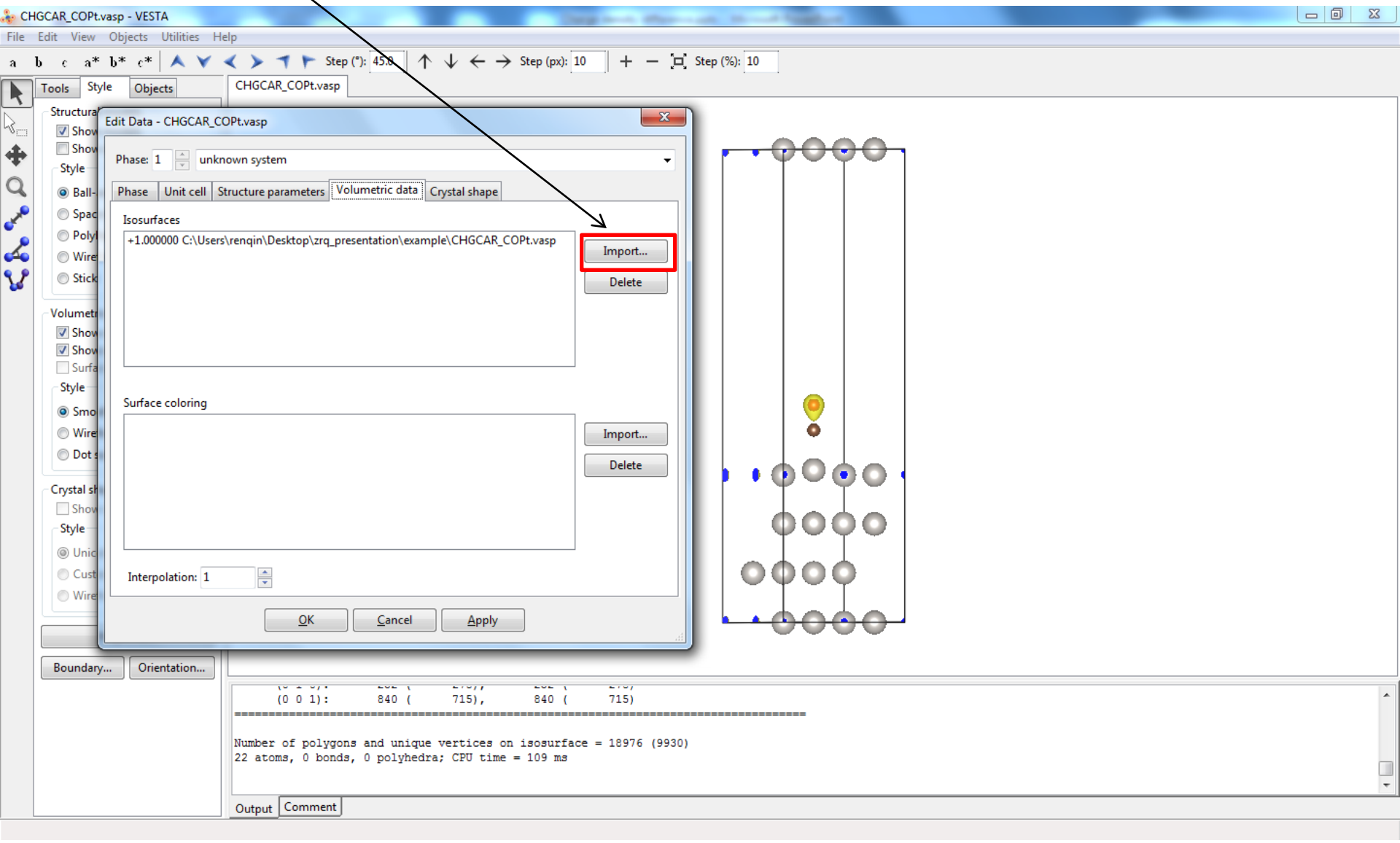
Open CHGCAR_COPt



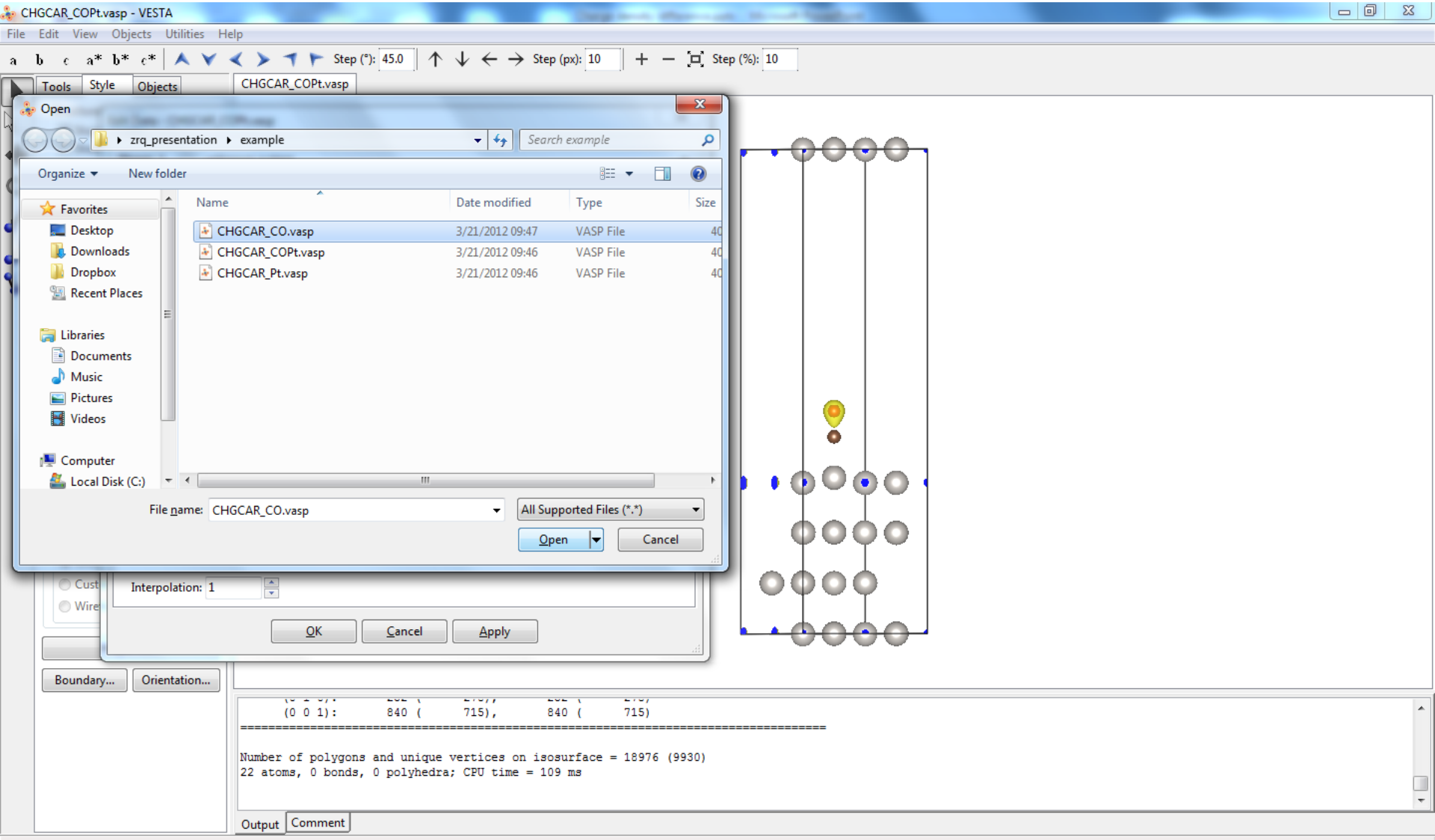
Edit → Edit Data → Volumetric Data…



Click Import…

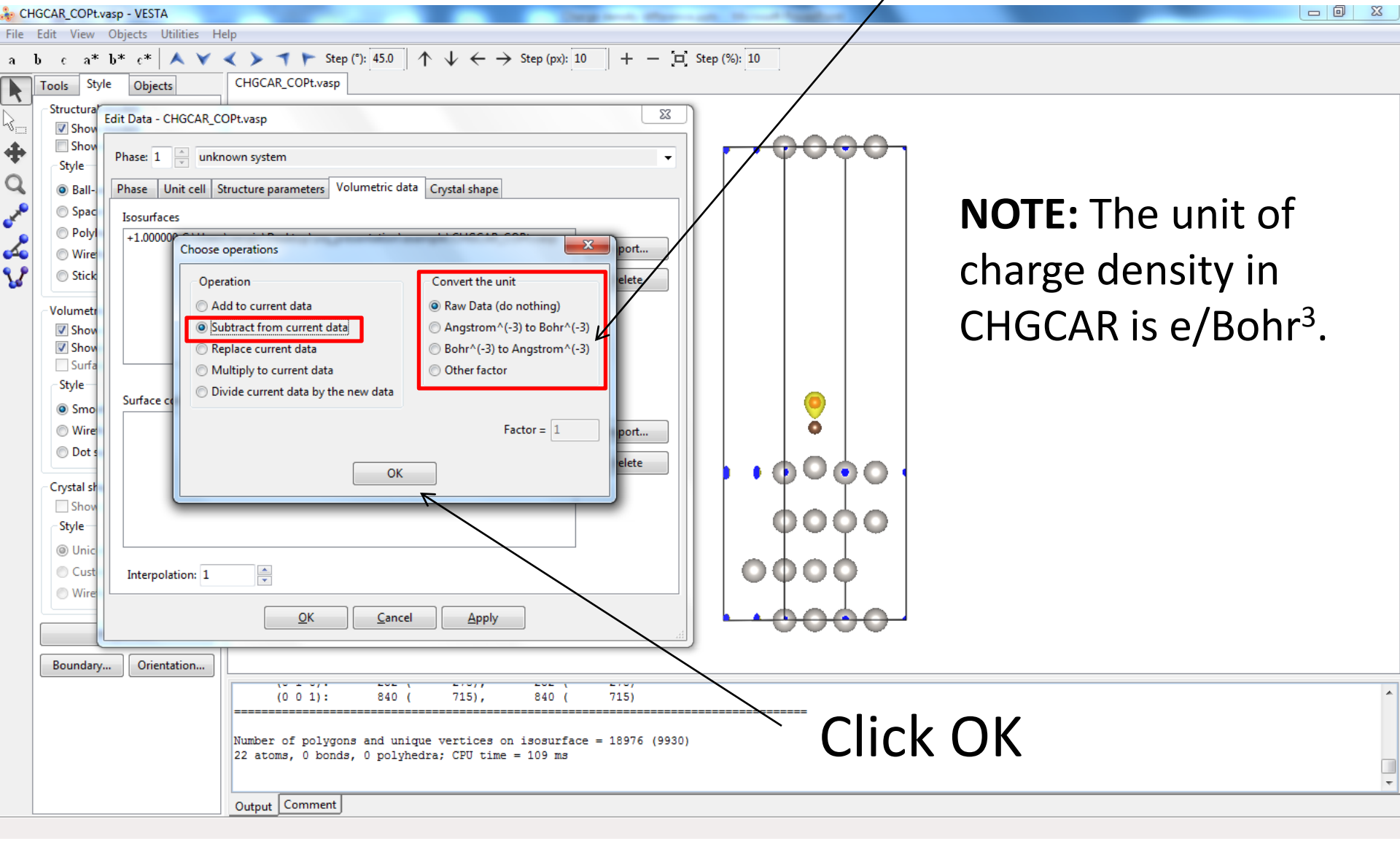


Select CHGCAR_CO ⟹ Click Open



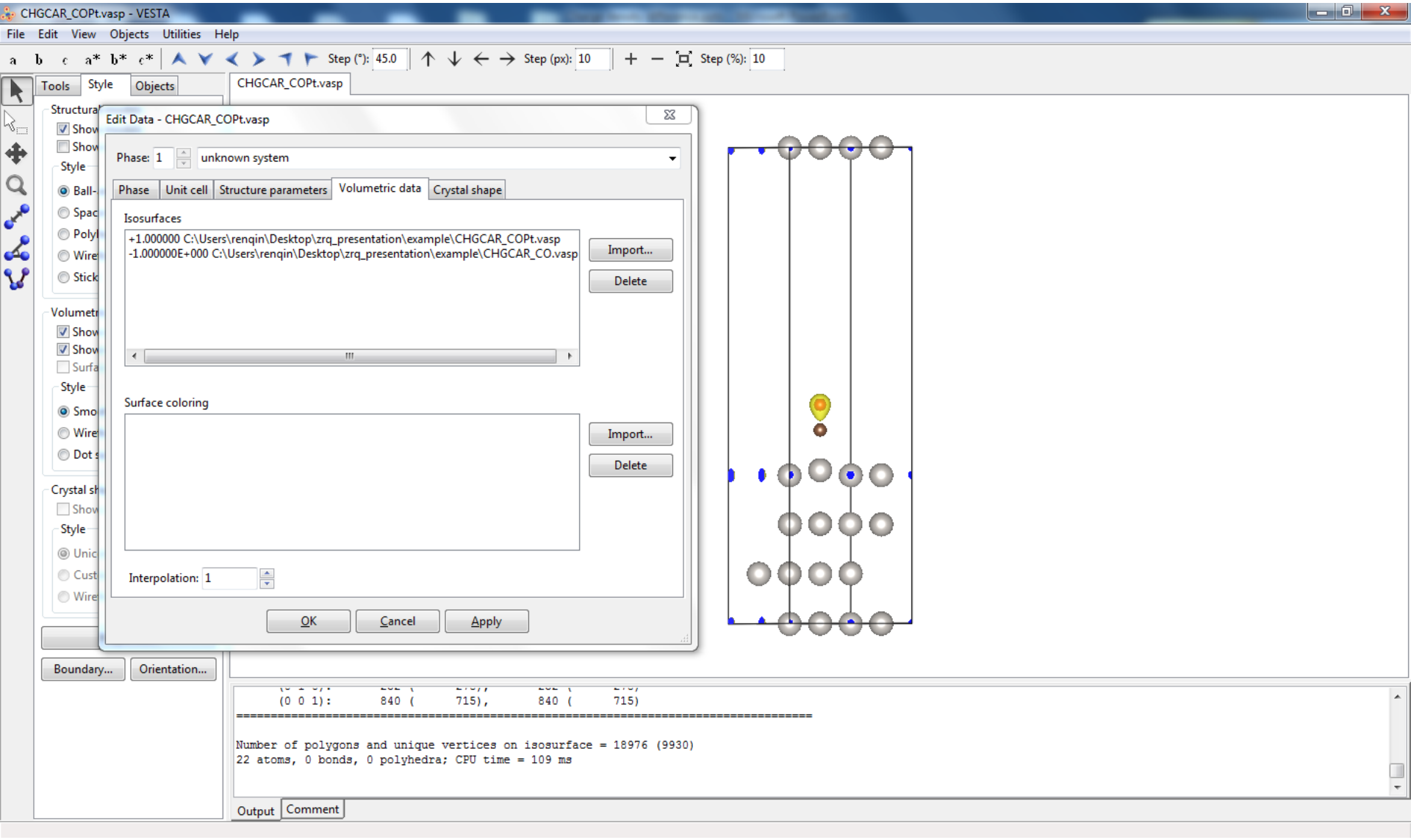
Select Substract from current data

If you want to change the unit, do it here.



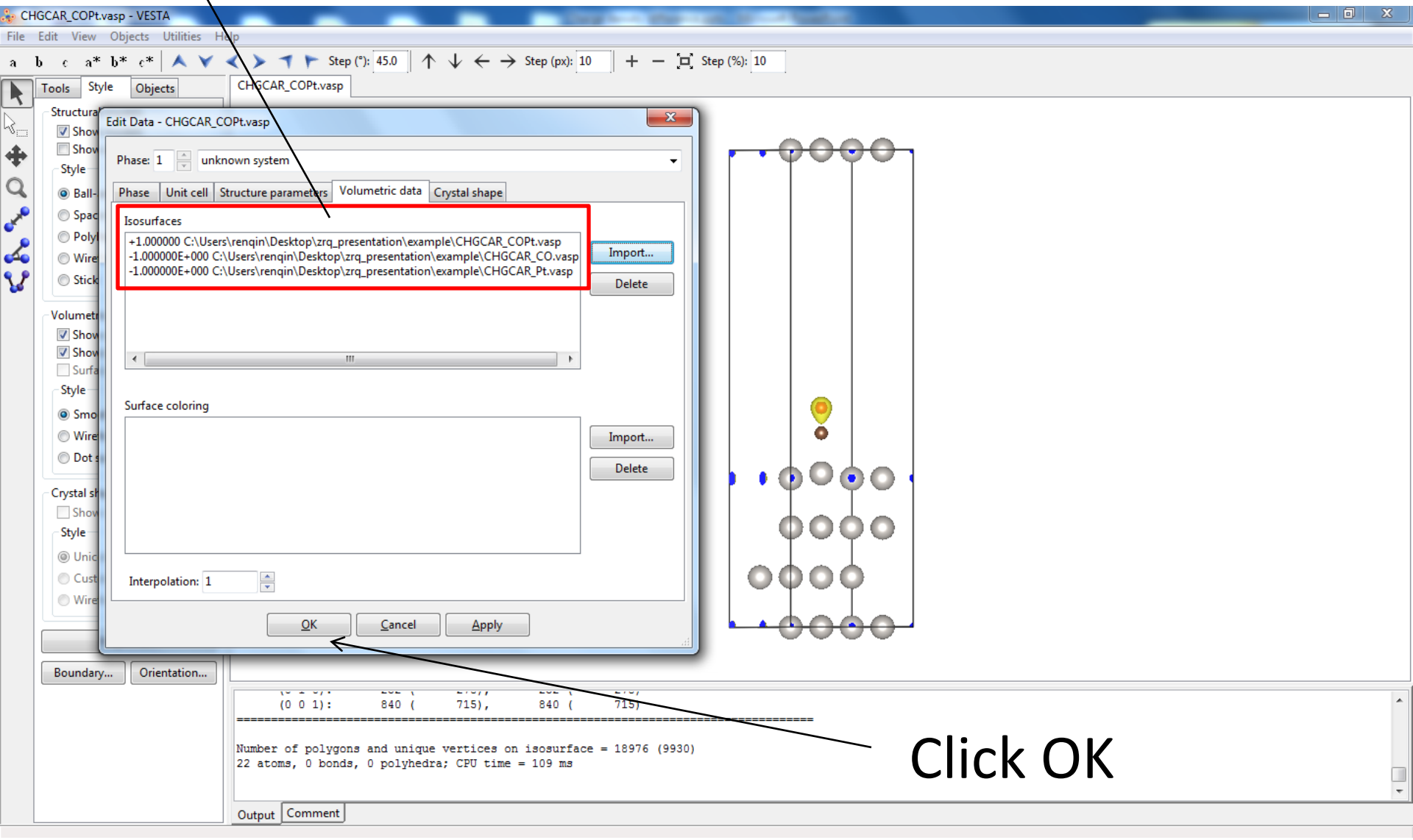
NOTE: The unit of charge density in CHGCAR is e/Bohr^3.

Click OK



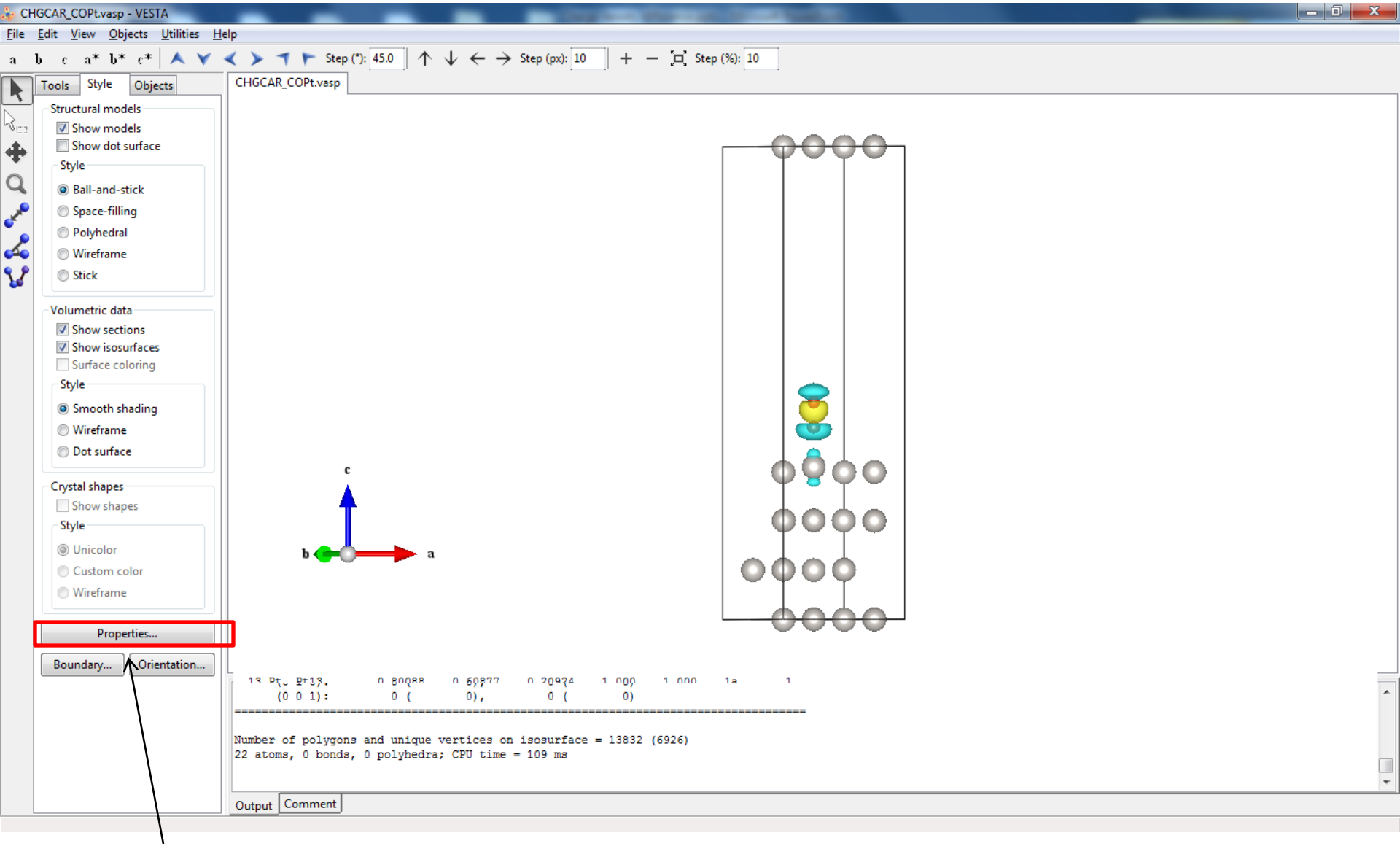
Repeat the steps and select CHGCAR_Pt

$$\Delta\rho = \rho_{AB} - \rho_A - \rho_B$$

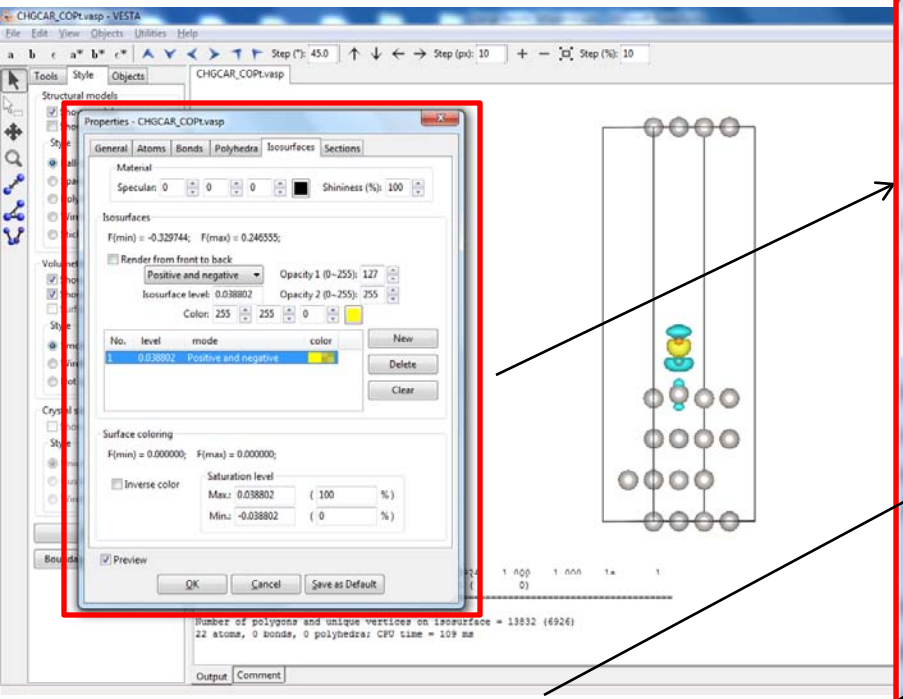


Click OK

The isosurface of charge density difference is obtained.



Click Properties… to modify the isosurface.



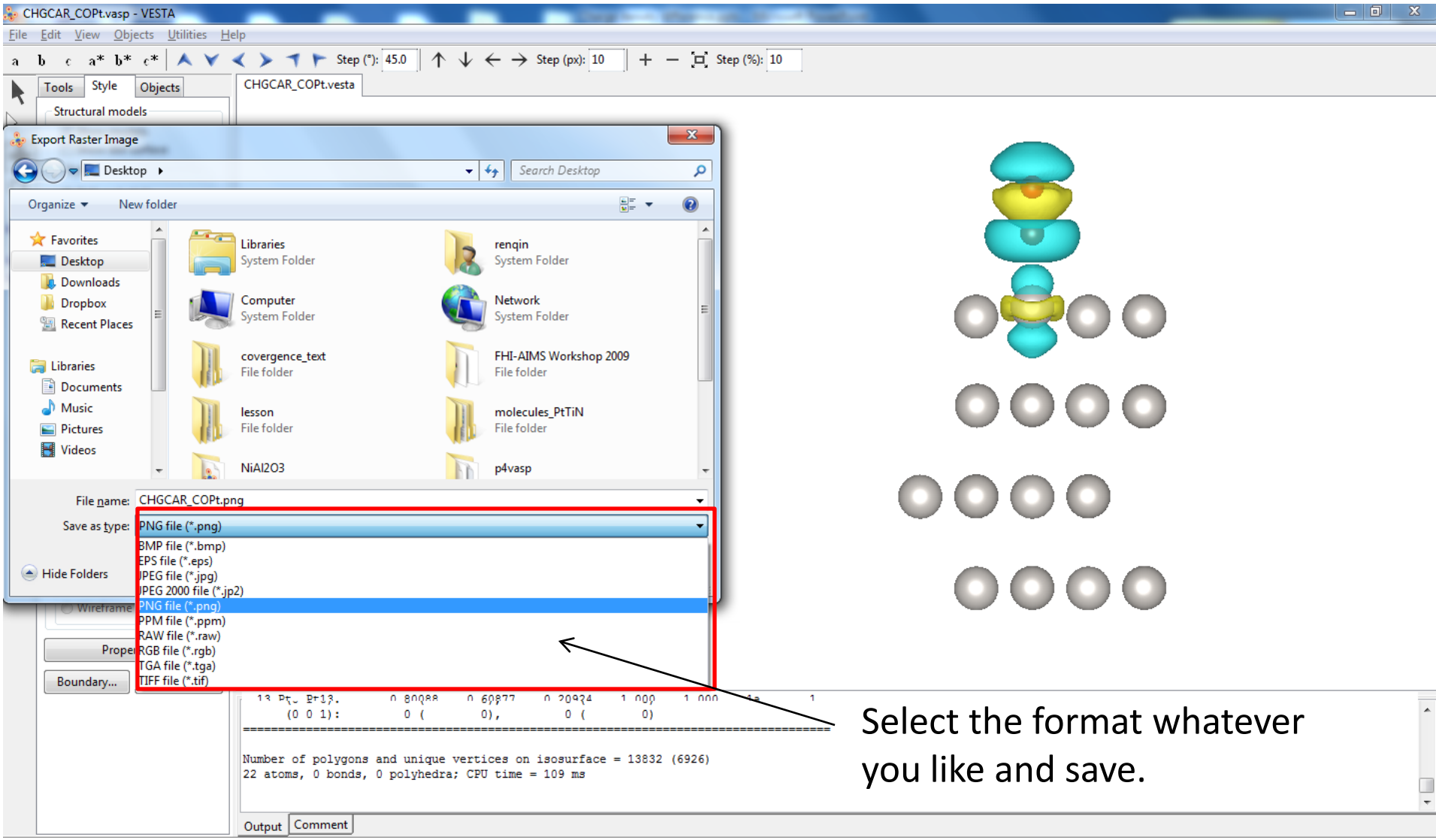
The min and max values of the isosurface.

Bigger (smaller)value, smaller (bigger) isosurface

Tune the Opacity

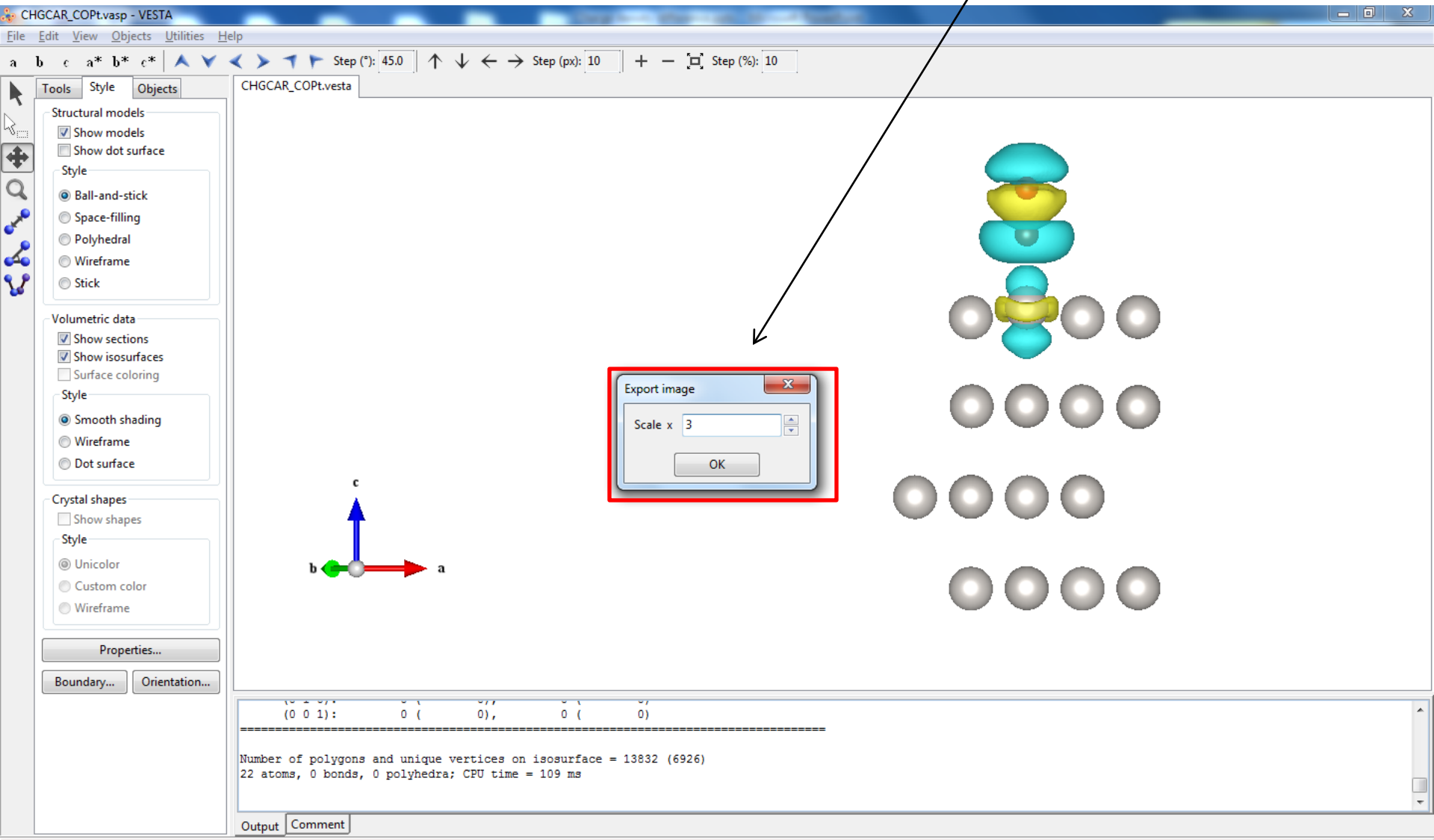
In a word, you can modify the properties of isosurface whatever you like.

File ⟹ Export Raster Image…



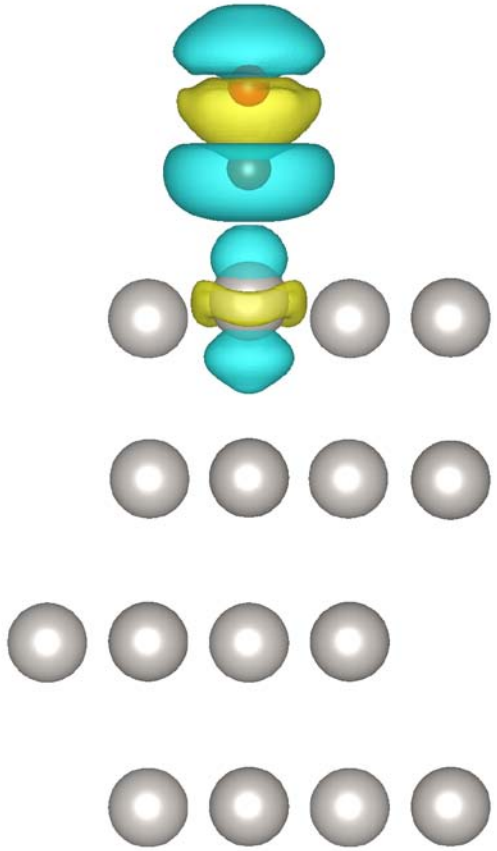
Select the format whatever you like and save.

The format of png is good. Select it and put the value in the rang of 3 to 5. And click OK.

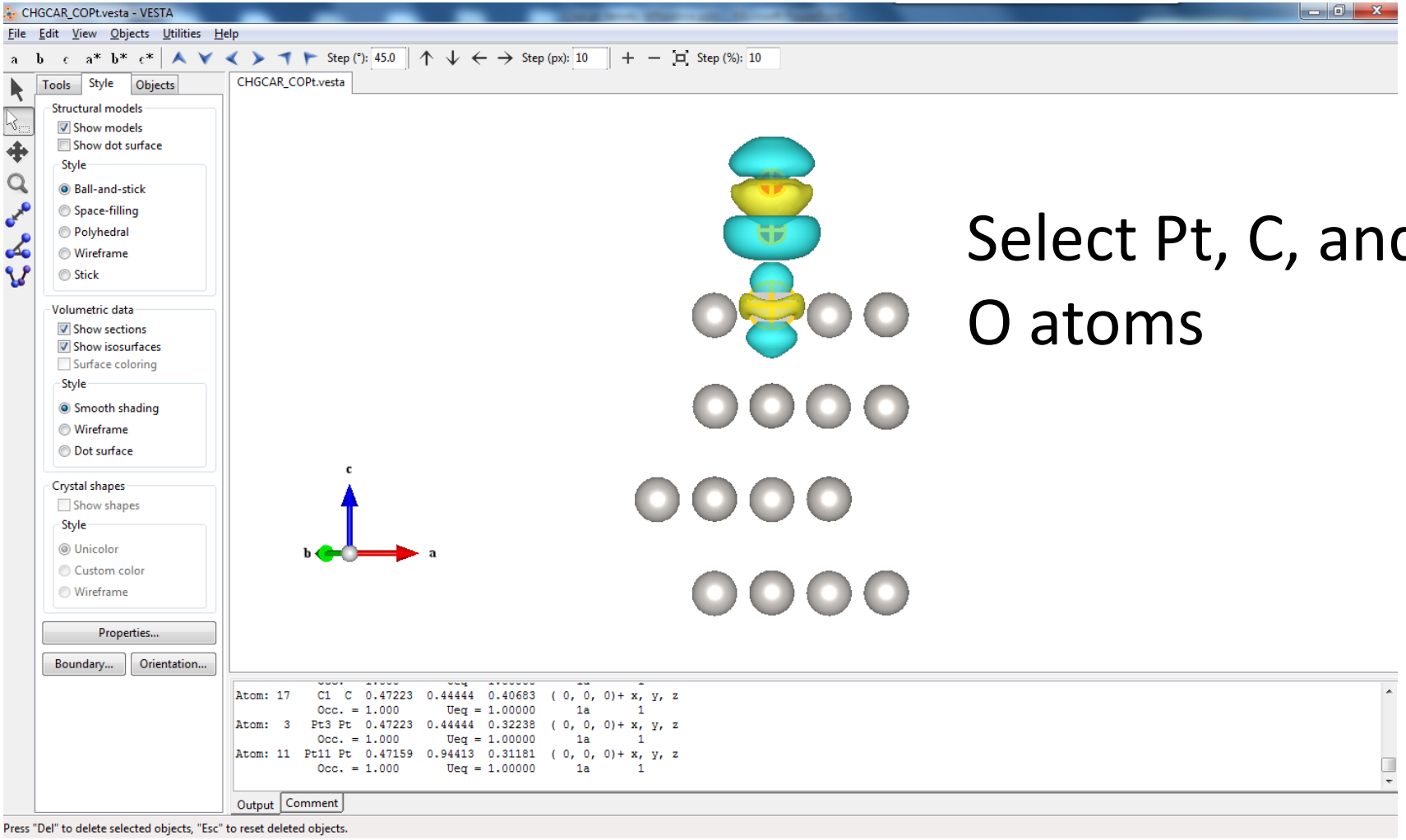


The final figure

This is the side view of the isosurface. You can also export other views of the isosurface.



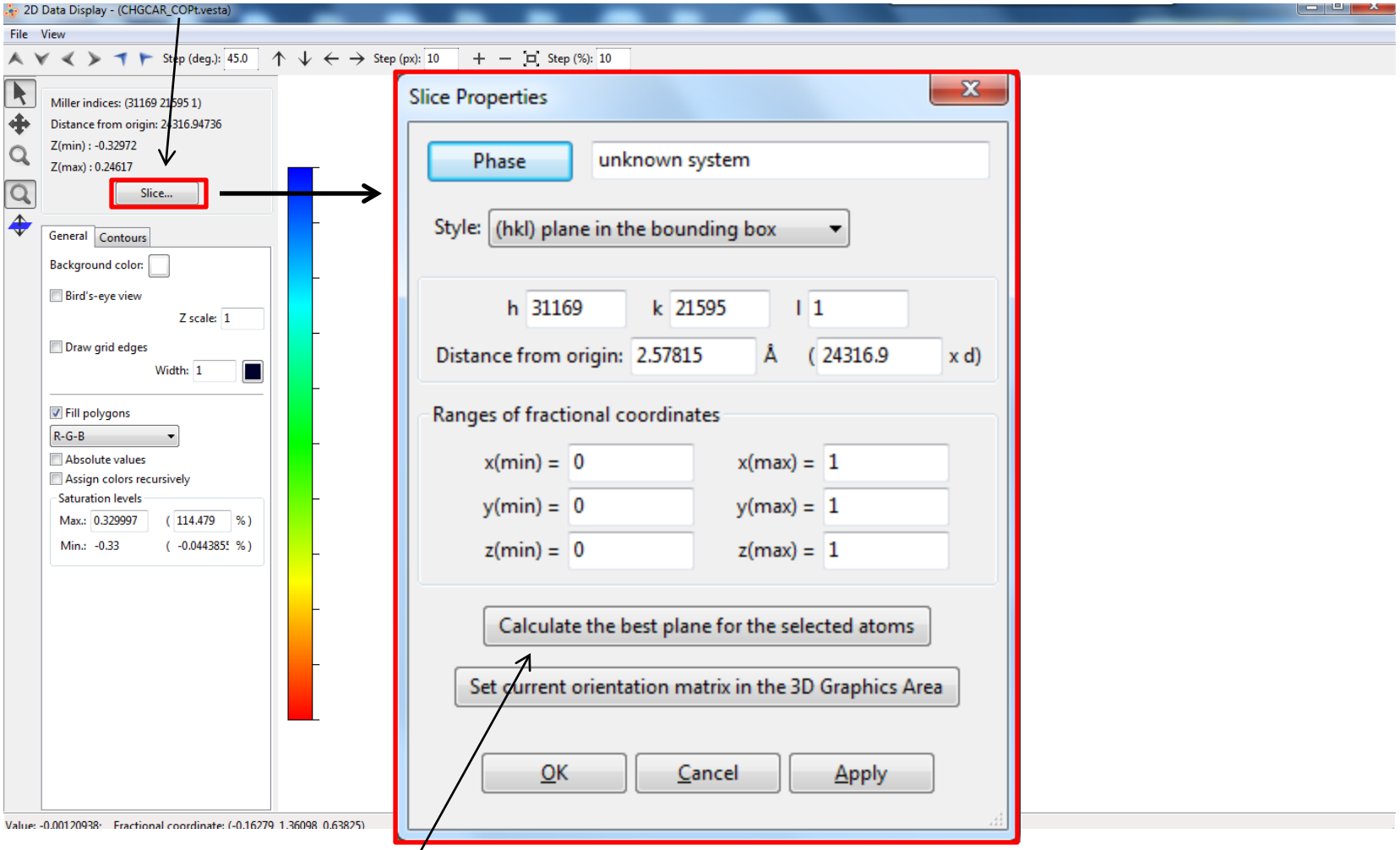
2D slice



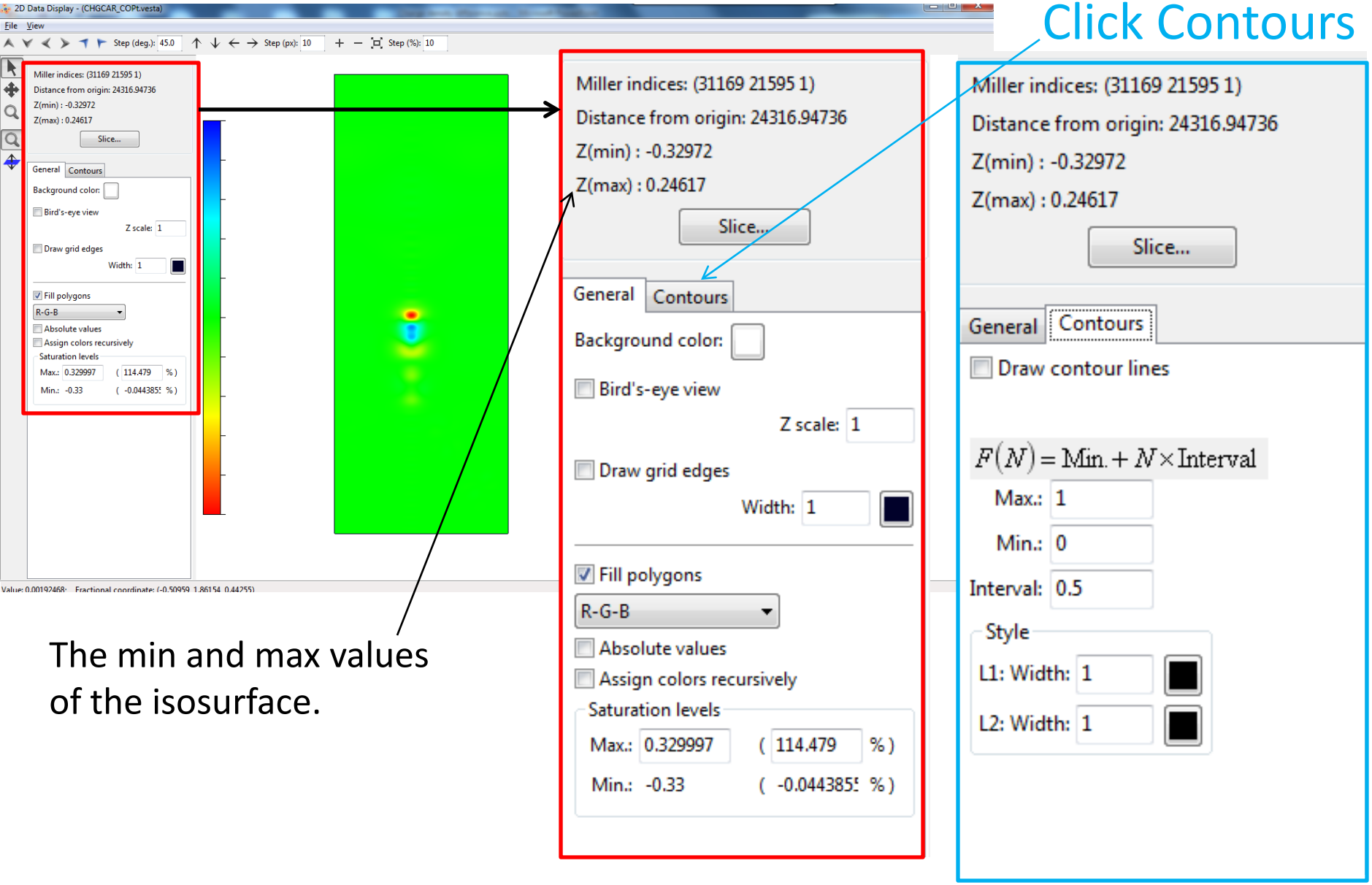
Select Pt, C, and O atoms

Utilities → 2D Data Display

Click Slice



Click Calculate the best plane for the selected atoms, and then OK.


Click Contours
2D Data Display - (CHGCAR_COPt.vesta)
File View
Miller indices: (31169 21595 1)
Distance from origin: 24316.94736
Z(min) : -0.32972
Z(max) : 0.24617
Slice...
General
Contours
Background color:
Bird's-eye view
Z scale: 1
Draw grid edges
Width: 1
Fill polygons
R-G-B
Absolute values
Assign colors recursively
Saturation levels
Max.: 0.329997 (114.479 %)
Min.: -0.33 (-0.044385 %)
Draw contour lines
F(N) = Min. + N × Interval
Max.: 1
Min.: 0
Interval: 0.5
Style
L1: Width: 1
L2: Width: 1
The min and max values of the isosurface.
Tune the display of the figure whatever you like by using these two boxes.