

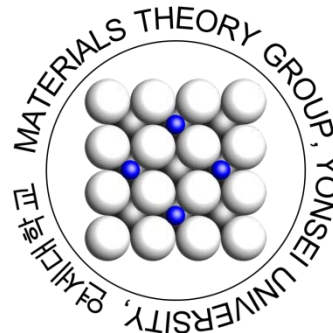
# Charge density difference

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# Definition

Charge density difference of system AB:

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

**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 performed 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

1.0000000000000000

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
1.0000000000000000
 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
1.0000000000000000
| 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 CHGCAR files are obtained.

A: CO

CHGCAR\_CO

B: Pt

CHGCAR\_Pt

AB: CO/Pt

CHGCAR\_CO Pt

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



# Open CHGCAR\_COPT

CHGCAR\_COPT.vasp - VESTA

File Edit View Objects Utilities Help

a b c a\* b\* c\* Step (°): 45.0 Step (px): 10 Step (%): 10

Tools Style Objects

Structural models

- Show models
- Show dot surface

Style

- Ball-and-stick
- Space-filling
- Polyhedral
- Wireframe
- Stick

Volumetric data

- Show sections
- Show isosurfaces
- Surface coloring

Style

- Smooth shading
- Wireframe
- Dot surface

Crystal shapes

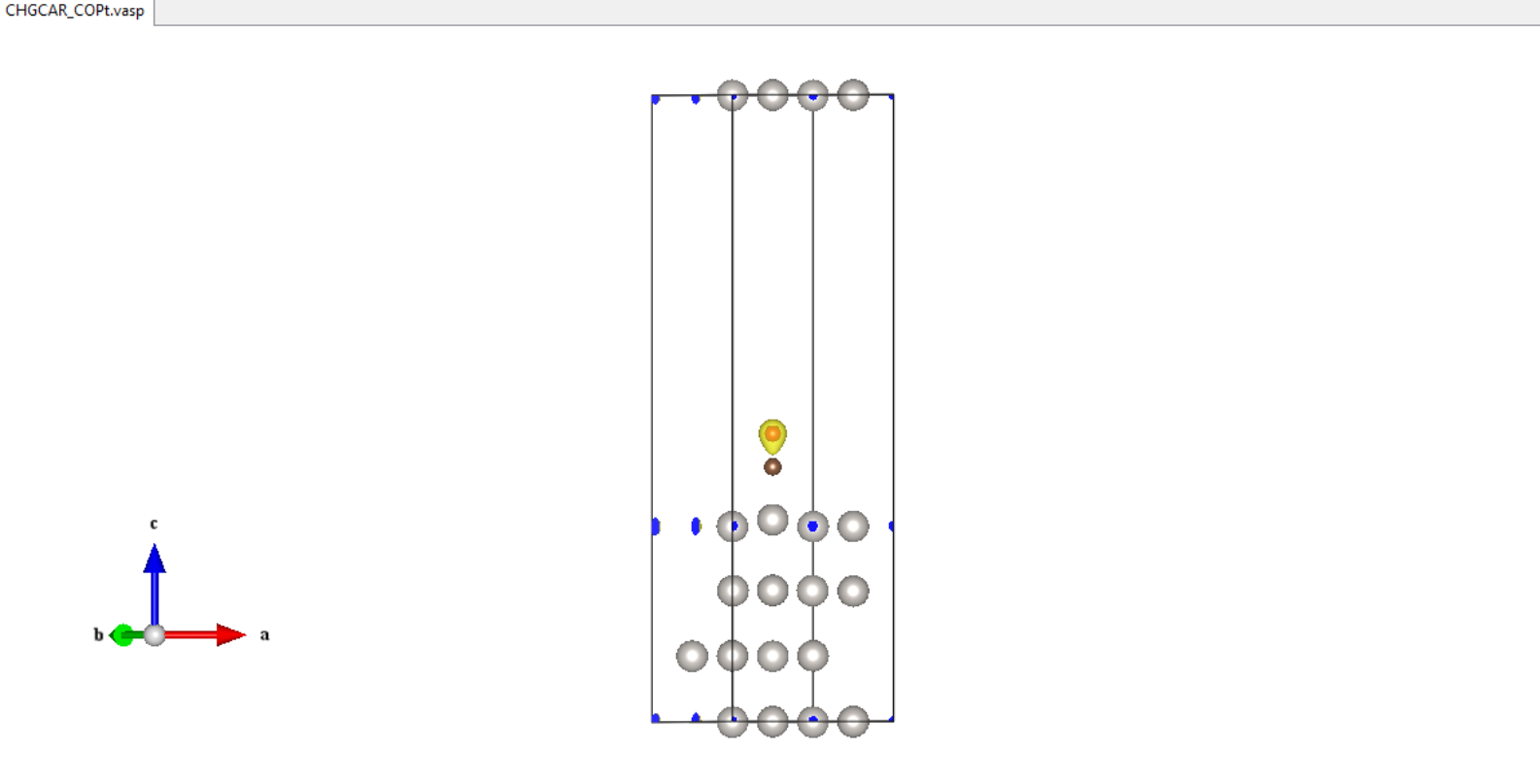
- Show shapes

Style

- Unicolor
- Custom color
- Wireframe

Properties...

Boundary... Orientation...



CHGCAR\_COPT.vasp

```
-----  
Number of polygons and unique vertices on isosurface = 18976 (9930)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms
```

Output Comment

# Edit $\longrightarrow$ Edit Data $\longrightarrow$ Volumetric Data...

The screenshot shows the VESTA software interface for the file 'CHGCAR\_COPT.vasp'. The 'Edit' menu is open, and 'Volumetric Data...' is selected. The main window displays a 3D unit cell with a grid of atoms and a central yellow and brown feature. The left sidebar contains various settings for visualization, including 'Volumetric data' (Show sections, Show isosurfaces, Surface coloring) and 'Style' (Smooth shading, Wireframe, Dot surface). A 3D coordinate system with axes 'a', 'b', and 'c' is shown in the lower-left. The bottom status bar displays the following information:

```
(0 0 1): 840 ( 715), 840 ( 715)
```

---

Number of polygons and unique vertices on isosurface = 18976 (9930)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms

Output Comment

# Click Import...

CHGCAR\_COPT.vasp - VESTA

File Edit View Objects Utilities Help

a b c a\* b\* c\* Step (%): 45.8 Step (px): 10 Step (%): 10

Tools Style Objects CHGCAR\_COPT.vasp

Structure

- Show
- Show
- Show

Style

- Ball-and-stick
- Space-filling
- Polyhedra
- Wireframe
- Stick

Volumetric

- Show
- Show
- Show
- Surface

Style

- Smooth
- Wireframe
- Dot

Crystal shape

- Show
- Show

Style

- Unit cell
- Custom
- Wireframe

Boundary... Orientation...

Phase: 1 unknown system

Phase Unit cell Structure parameters Volumetric data Crystal shape

Isosurfaces

+1.000000 C:\Users\renqin\Desktop\zrq\_presentation\example\CHGCAR\_COPT.vasp

Import... Delete

Surface coloring

Import... Delete

Interpolation: 1

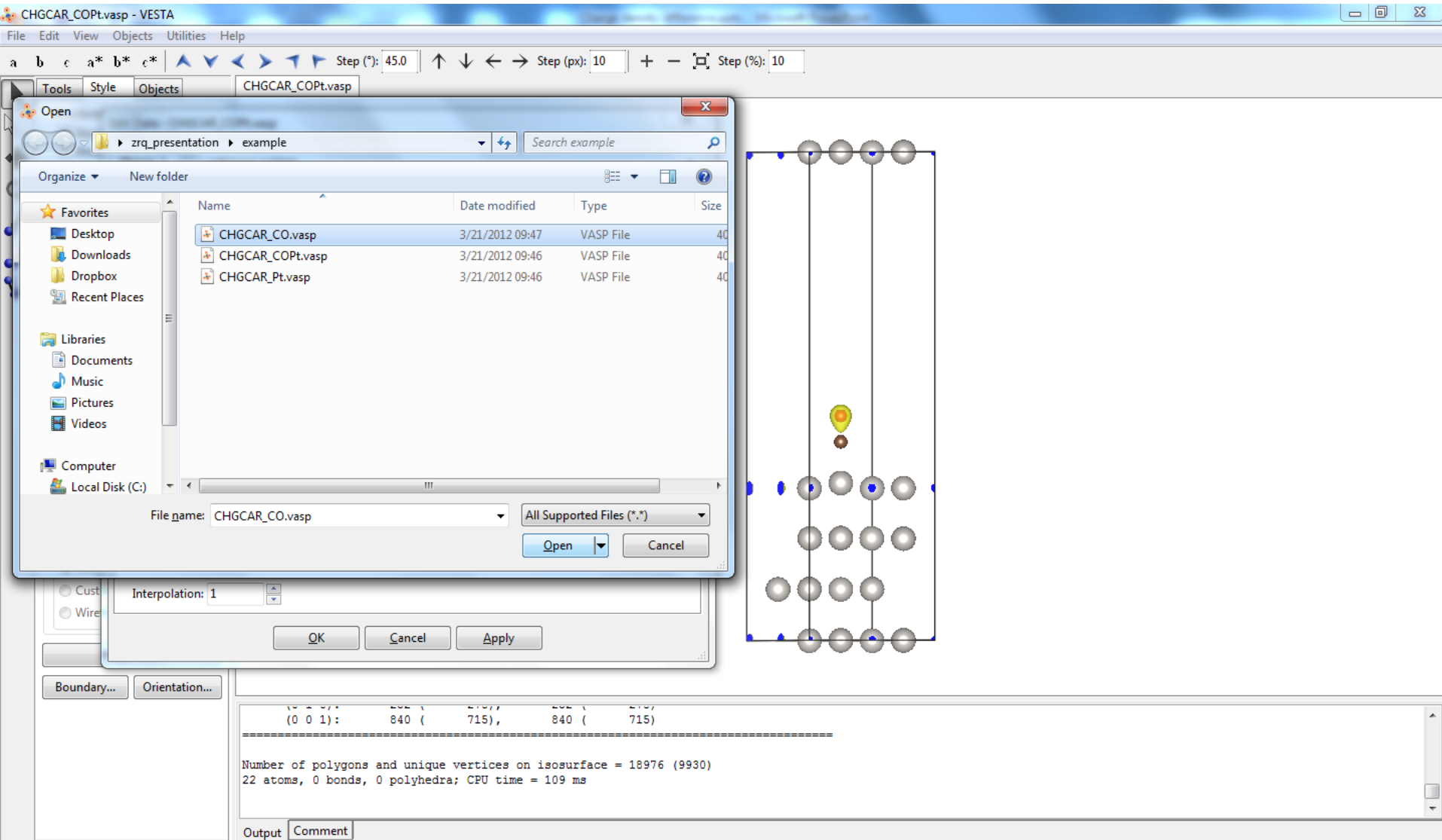
OK Cancel Apply

(0 0 1): 840 ( 715), 840 ( 715)

Number of polygons and unique vertices on isosurface = 18976 (9930)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms

Output Comment

# Select CHGCAR\_CO Click Open



The screenshot shows the VESTA software interface. An 'Open' dialog box is open, displaying a file explorer view of the directory 'zrq\_presentation > example'. The file 'CHGCAR\_CO.vasp' is selected. The 'File name' field contains 'CHGCAR\_CO.vasp' and the file type is set to 'All Supported Files (\*.\*)'. The 'Open' button is highlighted. In the background, the VESTA main window shows a 3D molecular model with a yellow sphere and a brown sphere. The 'Interpolation' is set to 1. The 'Output' tab is active, showing the following text:

```
(0 0 1): 840 ( 715), 840 ( 715)
```

---

Number of polygons and unique vertices on isosurface = 18976 (9930)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms

# Select Subtract from current data

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

The screenshot shows the VESTA software interface. The main window is titled 'CHGCAR\_COPT.vasp - VESTA'. The 'Edit Data' dialog box is open, showing the 'Phase' as 'unknown system'. The 'Choose operations' sub-dialog box is also open, with the 'Subtract from current data' option selected. The 'Convert the unit' sub-dialog box is also open, with the 'Raw Data (do nothing)' option selected. The 'Factor' is set to 1. The 'OK' button is highlighted. The background shows a 3D model of a crystal structure with a yellow isosurface.

**NOTE:** The unit of charge density in CHGCAR is  $e/\text{Bohr}^3$ .

Click OK

CHGCAR\_COPT.vasp - VESTA

File Edit View Objects Utilities Help

a b c a\* b\* c\* Step (°): 45.0 Step (px): 10 Step (%): 10

Tools Style Objects CHGCAR\_COPT.vasp

Structure

Style

Phase: 1 unknown system

Phase Unit cell Structure parameters Volumetric data Crystal shape

Isosurfaces

+1.000000 C:\Users\renqin\Desktop\zrq\_presentation\example\CHGCAR\_COPT.vasp  
-1.000000E+000 C:\Users\renqin\Desktop\zrq\_presentation\example\CHGCAR\_CO.vasp

Import...  
Delete

Surface coloring

Import...  
Delete

Interpolation: 1

OK Cancel Apply

Boundary... Orientation...

(0 0 1): 840 ( 715), 840 ( 715)

Number of polygons and unique vertices on isosurface = 18976 (9930)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms

Output Comment

Repeat the steps and select CHGCAR\_Pt

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

The screenshot shows the VESTA software interface. The main window displays a 3D model of a crystal structure with atoms represented by spheres. A dialog box titled "Edit Data - CHGCAR\_COPT.vasp" is open, showing the "Isosurfaces" tab. The dialog box contains the following text:

Phase: 1 unknown system

Phase Unit cell Structure parameters Volumetric data Crystal shape

Isosurfaces

- +1.000000 C:\Users\renqin\Desktop\zrq\_presentation\example\CHGCAR\_COPT.vasp
- 1.000000E+000 C:\Users\renqin\Desktop\zrq\_presentation\example\CHGCAR\_CO.vasp
- 1.000000E+000 C:\Users\renqin\Desktop\zrq\_presentation\example\CHGCAR\_Pt.vasp

Buttons: Import... Delete

Surface coloring

Buttons: Import... Delete

Interpolation: 1

Buttons: OK Cancel Apply

Output window text:

```
( 0 0 1):      840 (      715),      840 (      715)
```

---

Number of polygons and unique vertices on isosurface = 18976 (9930)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms

Buttons: Output Comment

Click OK

# The isosurface of charge density difference is obtained.

The screenshot shows the VESTA software interface for the file CHGCAR\_COPT.vasp. The main window displays a ball-and-stick model of a crystal structure with a charge density difference isosurface. The isosurface is shown as a yellow and cyan shape centered on the crystal. The crystal axes are labeled a, b, and c. The 'Properties...' button is highlighted with a red box, and an arrow points to it from the text below. The 'Output' window at the bottom shows the following text:

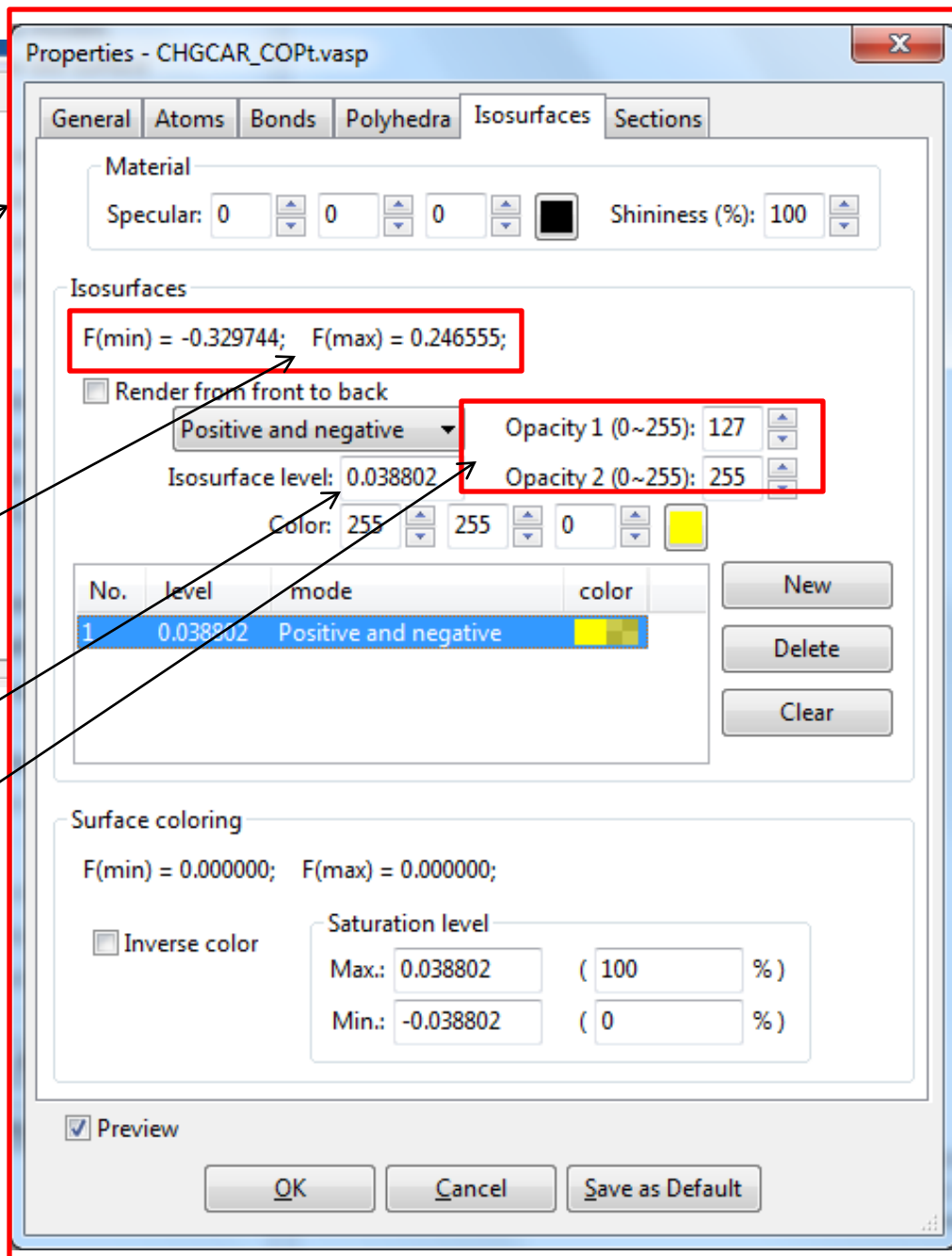
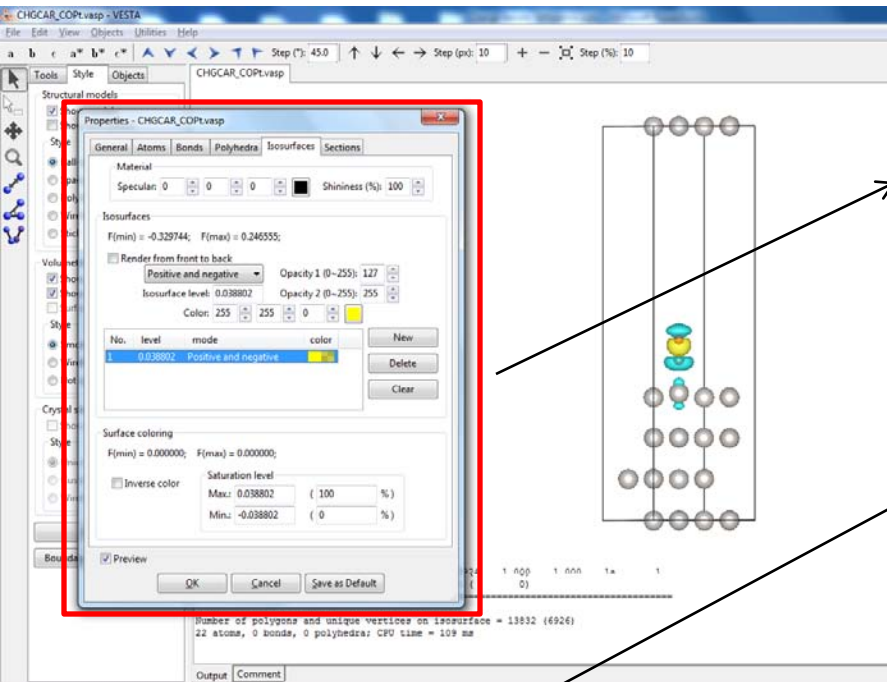
```
13 Pt Er13. 0 80088 0 60877 0 20924 1 000 1 000 1# 1  
(0 0 1): 0 ( 0), 0 ( 0)
```

---

Number of polygons and unique vertices on isosurface = 13832 (6926)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms

Click Properties... to modify the isosurface.





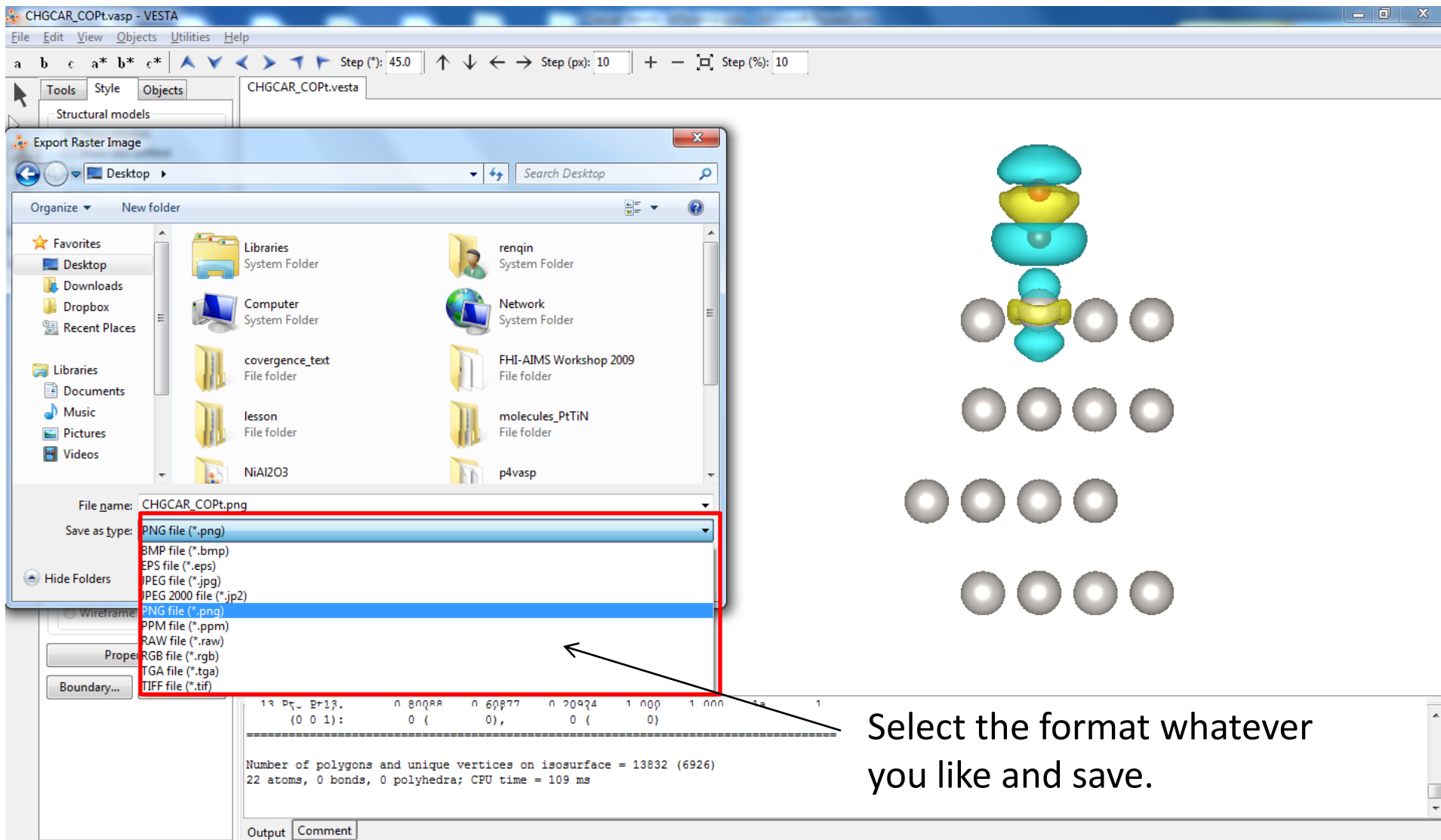
The min and max values of the isosurface.

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...



CHGCR\_COPT.vasp - VESTA

File Edit View Objects Utilities Help

Step (\*): 45.0 Step (px): 10 Step (%): 10

Tools Style Objects CHGCR\_COPT.vesta

Structural models

Export Raster Image

Desktop

Organize New folder

File name: CHGCR\_COPT.png

Save as type: PNG file (\*.png)

- BMP file (\*.bmp)
- EPS file (\*.eps)
- JPEG file (\*.jpg)
- JPEG 2000 file (\*.jp2)
- PNG file (\*.png)**
- PPM file (\*.ppm)
- RAW file (\*.raw)
- RGB file (\*.rgb)
- TGA file (\*.tga)
- TIFF file (\*.tif)

Number of polygons and unique vertices on isosurface = 13832 (6926)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms

Output Comment

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 screenshot displays the VESTA software interface for the file 'CHGCAR\_COPT.vasp'. The main window shows a 3D visualization of a crystal structure with a central yellow and cyan isosurface and surrounding grey spheres. A coordinate system with axes 'a', 'b', and 'c' is visible in the bottom-left corner. The left sidebar contains various tool and style options. A red box highlights the 'Export image' dialog box, which has 'Scale x' set to 3. An arrow points from the text above to this dialog box. The bottom status bar shows the following information:

```
(0 0 1): 0 ( 0), 0 ( 0)
```

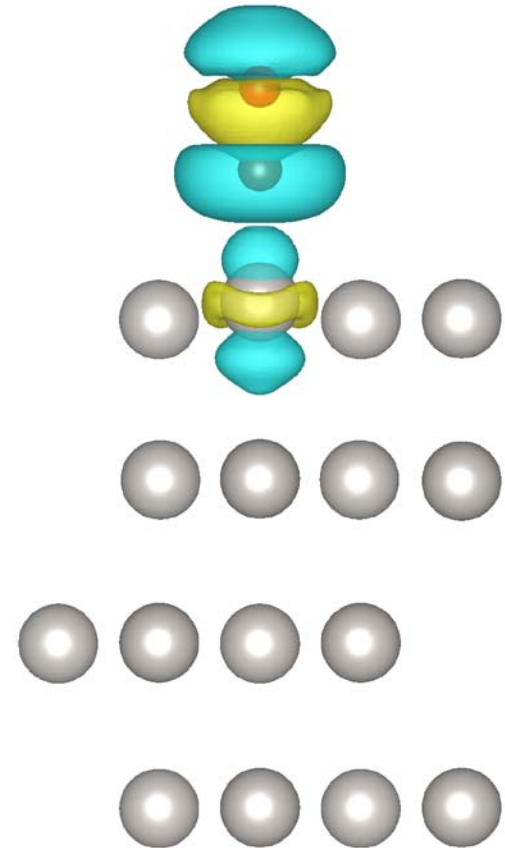
---

Number of polygons and unique vertices on isosurface = 13832 (6926)  
22 atoms, 0 bonds, 0 polyhedra; CPU time = 109 ms

Output Comment

## The final figure

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



# 2D slice

CHGCR\_COPT.VESTA - VESTA

File Edit View Objects Utilities Help

a b c a\* b\* c\* Step (°): 45.0 Step (px): 10 Step (%): 10

Tools Style Objects

Structural models

- Show models
- Show dot surface

Style

- Ball-and-stick
- Space-filling
- Polyhedral
- Wireframe
- Stick

Volumetric data

- Show sections
- Show isosurfaces
- Surface coloring

Style

- Smooth shading
- Wireframe
- Dot surface

Crystal shapes

- Show shapes

Style

- Unicolor
- Custom color
- Wireframe

Properties...

Boundary... Orientation...

Atom: 17 C1 C 0.47223 0.44444 0.40683 ( 0, 0, 0)+ x, y, z  
Occ. = 1.000 Ueq = 1.00000 1a 1

Atom: 3 Pt3 Pt 0.47223 0.44444 0.32238 ( 0, 0, 0)+ x, y, z  
Occ. = 1.000 Ueq = 1.00000 1a 1

Atom: 11 Pt11 Pt 0.47159 0.94413 0.31181 ( 0, 0, 0)+ x, y, z  
Occ. = 1.000 Ueq = 1.00000 1a 1

Output Comment

Press "Del" to delete selected objects, "Esc" to reset deleted objects.

Select Pt, C, and O atoms

Utilities



2D Data Display

# Click Slice

2D Data Display - (CHGCAR\_COPT.VESTA)

File View

Step (deg.): 45.0 Step (px): 10 Step (%): 10

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 ( -0.0443851 %)

Value: -0.00120938 Fractional coordinate: (-0.16279 1.36098 0.63825)

### Slice Properties

Phase: unknown system

Style: (hkl) plane in the bounding box

h 31169 k 21595 l 1

Distance from origin: 2.57815 Å ( 24316.9 x d)

Ranges of fractional coordinates

x(min) = 0 x(max) = 1

y(min) = 0 y(max) = 1

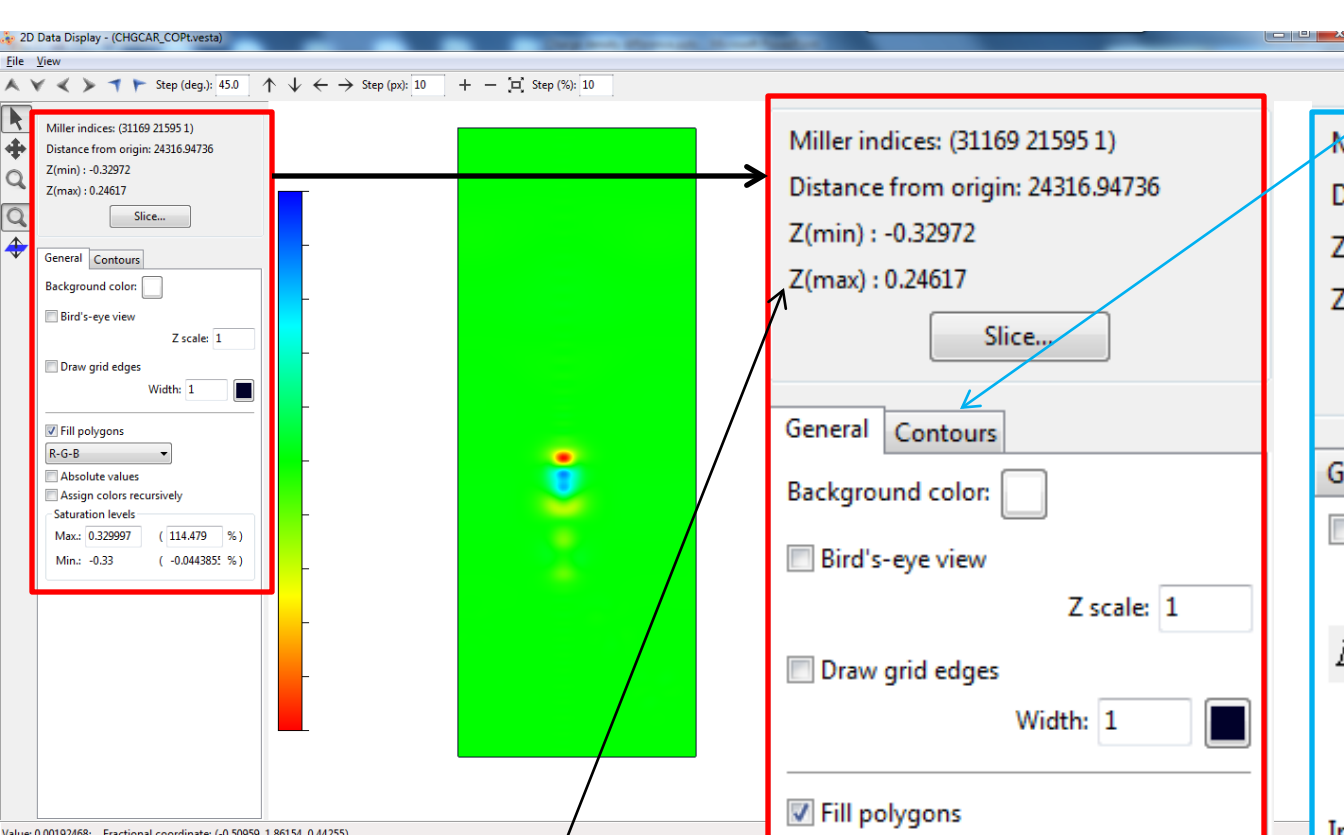
z(min) = 0 z(max) = 1

Calculate the best plane for the selected atoms

Set current orientation matrix in the 3D Graphics Area

OK Cancel Apply

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



Click Contours

The min and max values of the isosurface.

Tune the display of the figure whatever you like by using these two boxes.