CMS II-3: crystal structure, reciprocal lattice, and Brillouin zone

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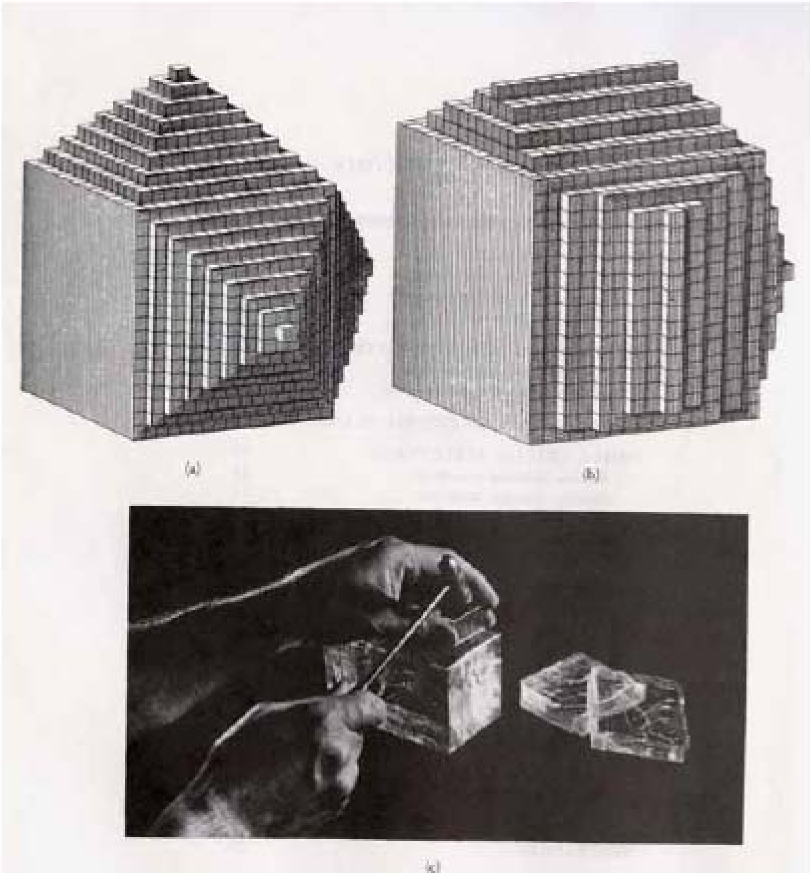
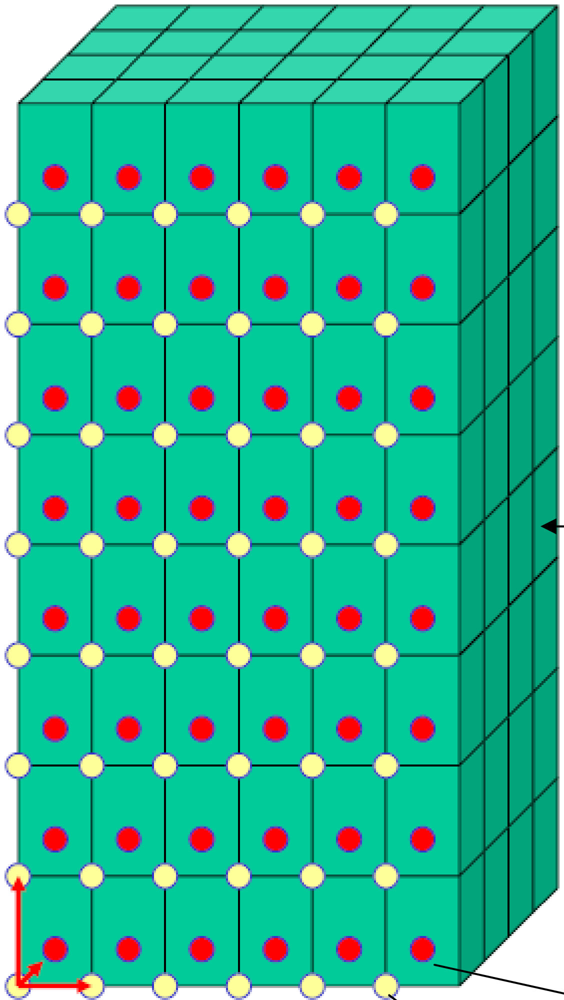
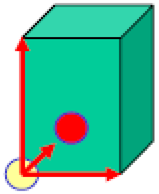
Crystal structure



An ideal crystal is constructed by the infinite repetition of identical structure units in space with long range order.

Crystal structure: lattice + basis





A Bravais lattice consists of all points with position vectors R

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$\vec{a}_1, \vec{a}_2, \vec{a}_3 : primitive \quad vectors$$

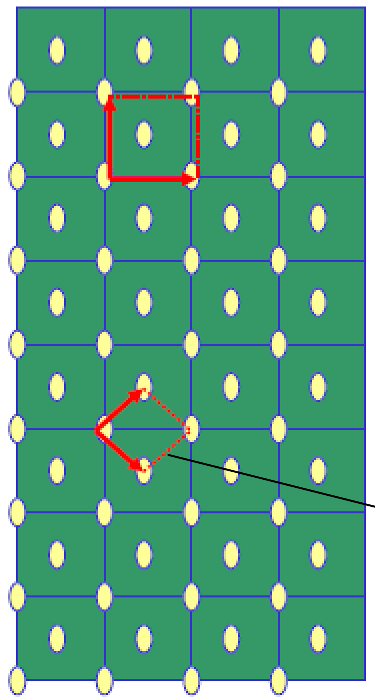
A basis of atoms is attached to every lattice point, with every basis identical in composition.

$$\vec{\tau}_i = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3$$

$$where \qquad 0 \le x_1, x_2, x_3 \le 1$$

Face center square lattice

Square lattice

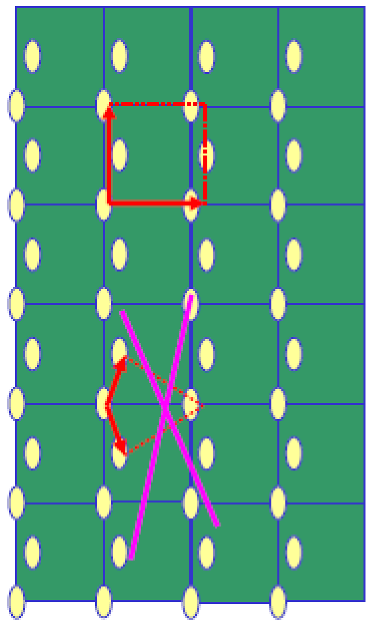


convention cell
Square lattice

Primitive cell

Face centered

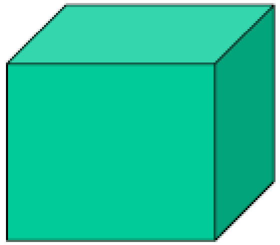
Square lattice



Not face centered

Primitive lattice

1. Simple cubic lattice



$$\vec{a}_1 = a\hat{i}$$

$$\vec{a}_2 = a\hat{j}$$

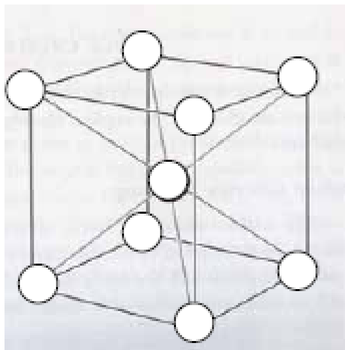
$$\vec{a}_3 = a\hat{k}$$

2. Body center cubic lattice

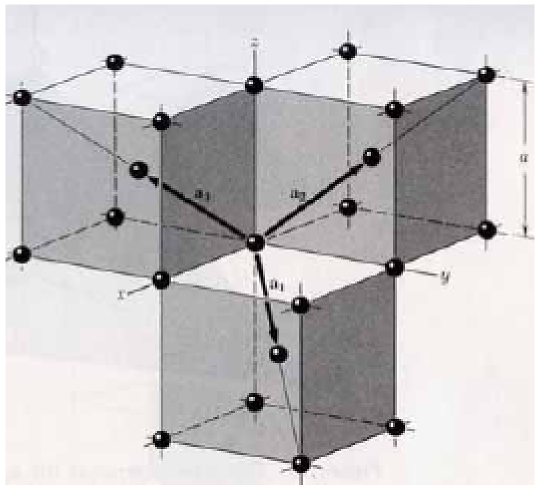
$$\vec{a}_1 = \frac{a}{2}\left(-\vec{i} + \vec{j} + \vec{k}\right)$$

$$\vec{a}_2 = \frac{a}{2}\left(\vec{i} - \vec{j} + \vec{k}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\vec{i} + \vec{j} - \vec{k}\right)$$



convention cell
simple cubic
(2 atoms)



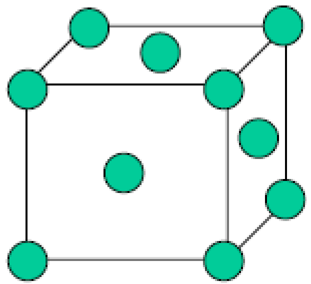
3. Face centered cubic lattice (fcc)

$$\vec{a}_1 = \frac{a}{2}\left(\vec{j} + \vec{k}\right)$$

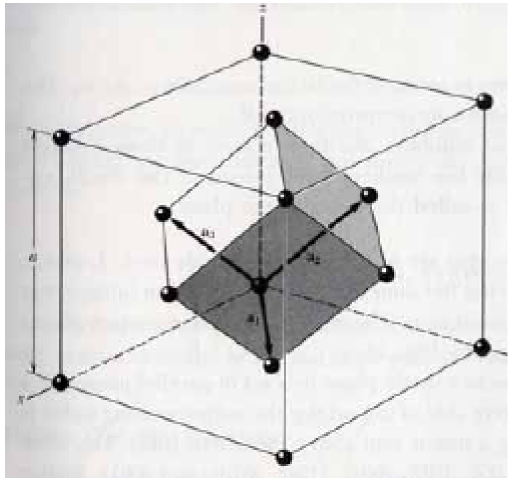
$$\vec{a}_2 = \frac{a}{2}\left(\vec{i} + \vec{k}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\vec{i} + \vec{j}\right)$$

(4 atoms)



convention cell
simple cubic

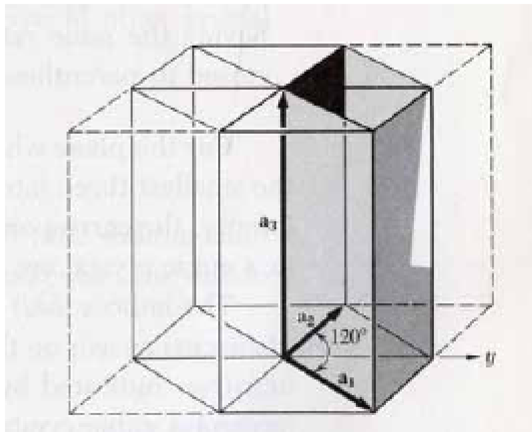


4. Hexagonal lattice

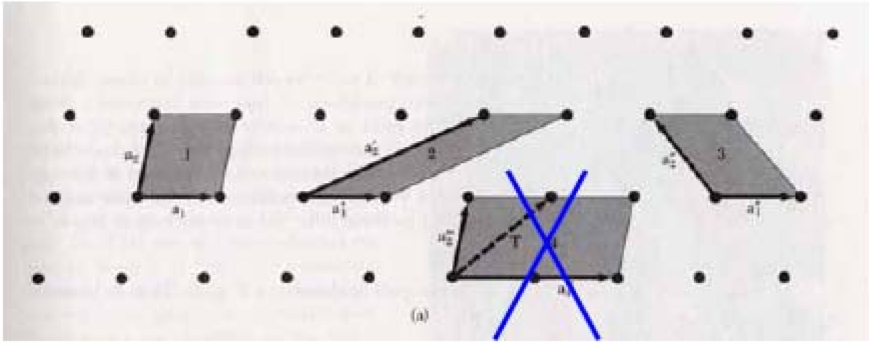
$$\vec{a}_1 = a\left(\frac{1}{2}\vec{i} + \frac{\sqrt{3}}{2}\vec{j}\right)$$

$$\vec{a}_2 = a\left(\frac{1}{2}\vec{i} - \frac{\sqrt{3}}{2}\vec{j}\right)$$

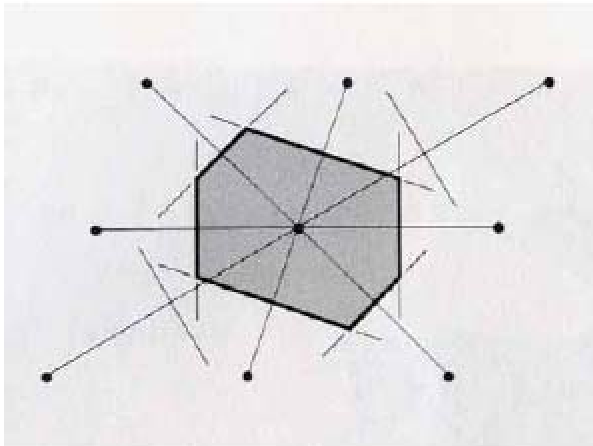
$$\vec{a}_3 = c\vec{k}$$



Primitive cell



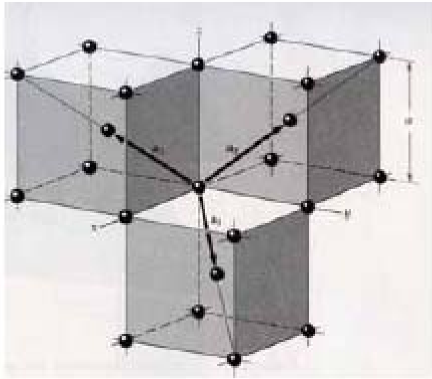
Wigner-Seitz primitive cell

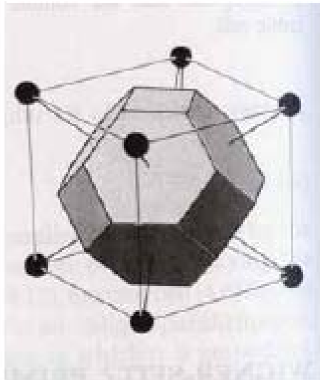


Drawing lines connecting the point to all others in the lattice, bisecting each line with a plane, and taking the smallest polyhedron containing the point bounded by these planes

Examples of Wigner-Seitz primitive cell

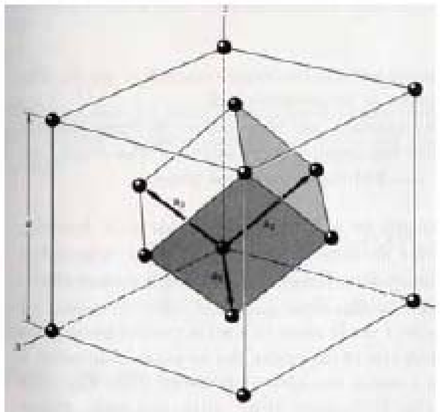
bcc

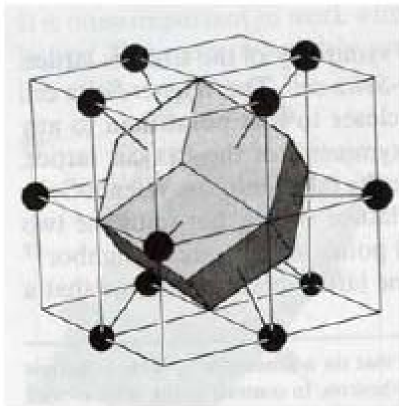




Wigner-Seitz primitive cell of bcc lattice

fcc





Wigner-Seitz primitive cell of fcc lattice

Periodic table

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

H^1 4K hcp 3.75 6.12																	He^4 2K hcp 3.57 5.83
Li 78K bcc 3.491	Be hcp 2.27 3.59											B rhomb.	C diamond 3.567	N 20K cubic 5.66 (N_2)	O complex (O_2)	F	Ne 4K fcc 4.46
Na 5K bcc 4.225	Mg hcp 3.21 5.21	Crystal structure a lattice parameter, in Å c lattice parameter, in Å										Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl_2)	Ar 4K fcc 5.31
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br_2)	Kr 4K fcc 5.64
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I_2)	Xe 4K fcc 6.13
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 ABAC	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —
Fr —	Ra —	Ac fcc 5.31															

Ce fcc 5.16	Pr hex. 3.67 ABAC	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55
Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 ABAC	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —

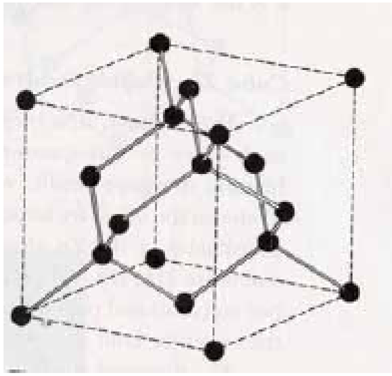
Examples of lattices with basis

1. Diamond structure

fcc lattice

$$\vec{\tau}_1 = 0$$

$$\vec{\tau}_2 = \frac{1}{4}(\vec{i} + \vec{j} + \vec{k})$$



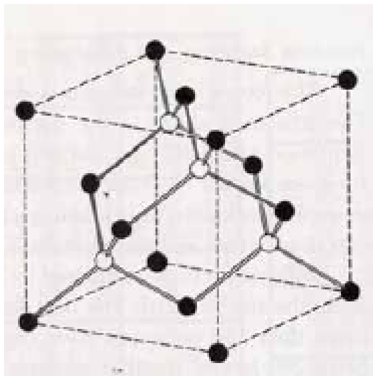
Diamond,Si,Ge

2. Zincblende structure

fcc lattice

$$\vec{\tau}_1 = 0$$

$$\vec{\tau}_2 = \frac{1}{4}(\vec{i} + \vec{j} + \vec{k})$$



ZnS, GaAs
SiC, ZnS

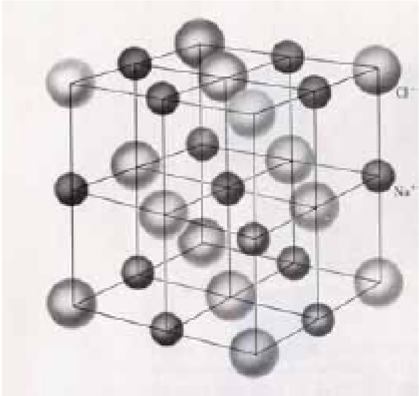
(Rocksalt)

3. Sodium chloride structure

fcc lattice

$\vec{\tau}_1 = 0$

$\vec{\tau}_2 = \frac{a}{2}\vec{i}$



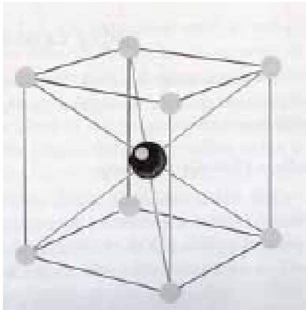
NaCl, LiH, MnO, KCl, KBr

4. Cesium chloride structure

sc lattice

$\vec{\tau}_1 = 0$

$\vec{\tau}_2 = \frac{a}{2}(\vec{i} + \vec{j} + \vec{k})$



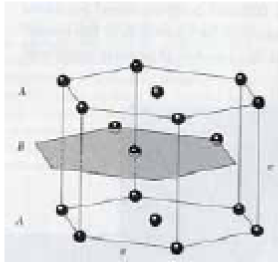
CsCl, AgMg, AlNi, CuPd

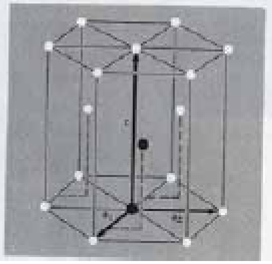
5. Hexagonal closed-packed structure (hcp)

hex lattice

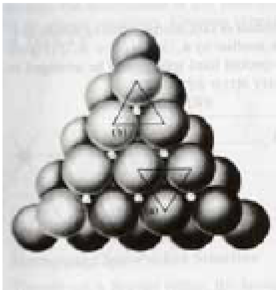
$$\vec{\tau}_1 = 0$$

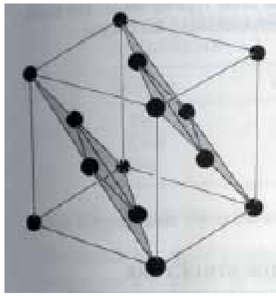
$$\vec{\tau}_2 = \frac{2}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3$$



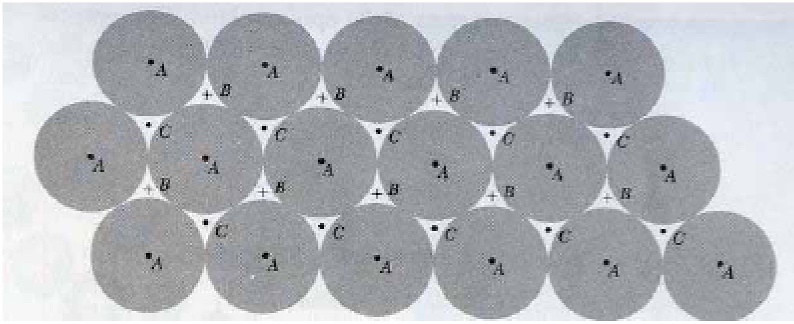


$c \cong 1.633a$





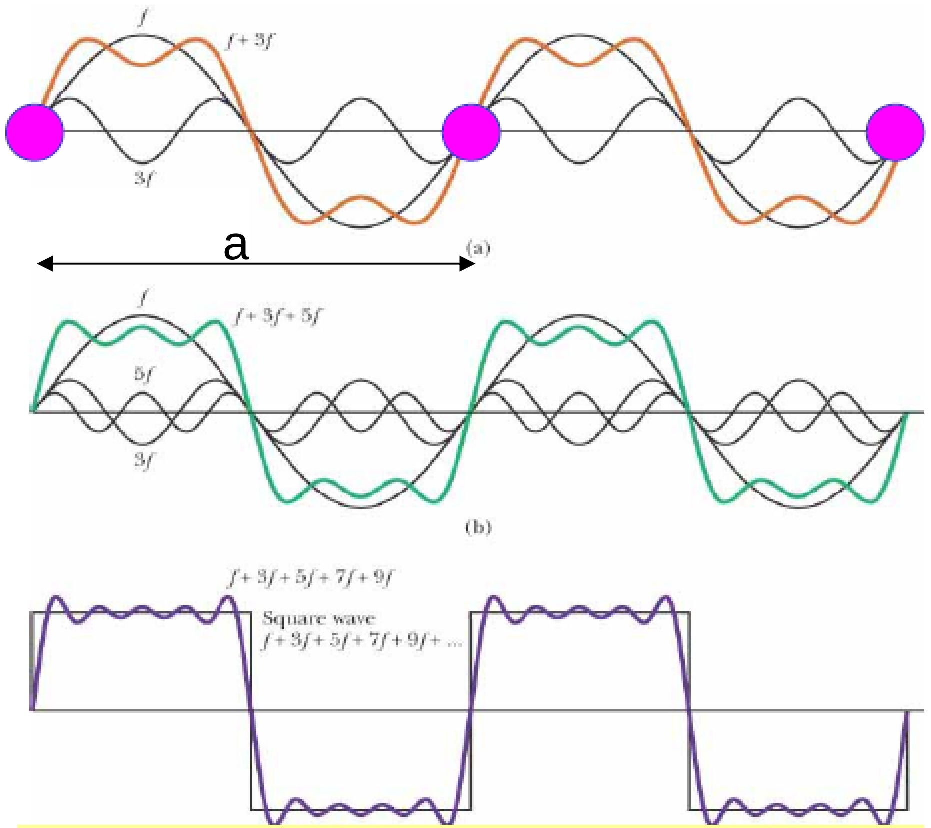
fcc along (111) direction



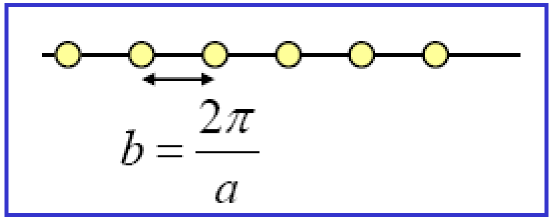
hcp: ABABABAB……

fcc: ABCABCABC….

One dimensional lattice



Reciprocal Lattice



$$\vec{a} \cdot \vec{b} = 2\pi$$

$$b = \frac{2\pi}{a}$$

$$k_n = n\frac{2\pi}{a}$$

$$y(x) = \sum_n C_n e^{ik_n x}$$

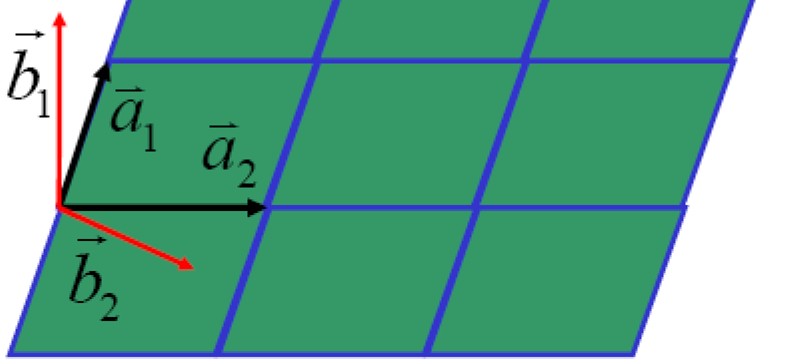
$$y(x) = A_0 + \sum_{n=1} (A_n \sin k_n x + B_n \cos k_n x)$$

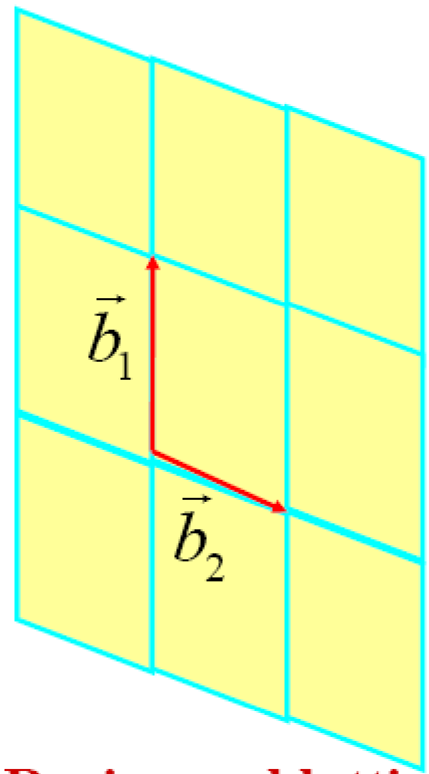
y(x)=y(x+a) $\rightarrow$ $k_n a=2\pi$ m $\rightarrow$ $k_n = 2\pi$ m/a=0,b,2b,3b, …, b=2 π /a, b: reciprocal lattice

Bloch theorem confines to the first Brillouin zone: 0~b (2 π /a)

Two dimensional lattice

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$





Reciprocal lattice

$$e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r}}$$

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2\,; \quad \vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2$$

Reciprocal lattice

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$\vec{a}_1, \vec{a}_2, \vec{a}_3$: *primitive vectors*

$$\Leftrightarrow$$

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

$\vec{b}_1, \vec{b}_2, \vec{b}_3$: *reciprocal lattice vectors*

3d Fourier Transform

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij} \qquad \text{where} \quad \delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases}$$

The reciprocal lattice vectors is given by:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad ; \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad ; \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$\boxed{\text{Plane waves}}$ $$e^{i\vec{k}\cdot\vec{r}} = \cos(\vec{k}\cdot\vec{r}) + i\sin(\vec{k}\cdot\vec{r})$$

Plane waves with the periodicity of a given Bravais lattice

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \quad ; \vec{a}_1, \vec{a}_2, \vec{a}_3 : \textit{primitive} \quad \textit{vectors}$$

$$e^{i\vec{k}\cdot(\vec{r}+\vec{R})} = e^{i\vec{k}\cdot\vec{r}} \quad \Rightarrow \quad \vec{k} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3 \equiv \vec{G}$$

Proof:

$$\vec{G}\cdot\vec{R} = 2\pi(n_1 h + n_2 k + n_3 l)$$

$$\Rightarrow \quad e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r}} e^{i\vec{G}\cdot\vec{R}} = e^{i\vec{G}\cdot\vec{r}}$$

The set of all wave vector G that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice.

Examples of reciprocal lattice and first Brillouin zone (The Wigner-Seitz primitive cell of the reciprocal lattice)

1. Simple cubic lattice (sc)

$$\vec{a}_1 = a\hat{i} \qquad \vec{b}_1 = \frac{2\pi}{a}\hat{i}$$

$$\vec{a}_2 = a\hat{j} \qquad \vec{b}_2 = \frac{2\pi}{a}\hat{j}$$

$$\vec{a}_3 = a\hat{k} \qquad \vec{b}_3 = \frac{2\pi}{a}\hat{k}$$

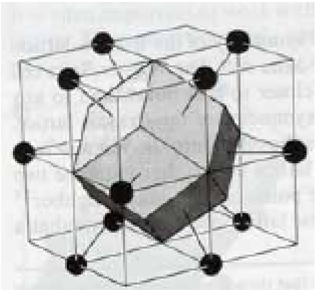
The reciprocal lattice of a sc lattice is a sc lattice of side $\frac{2\pi}{a}$

2. Body center cubic lattice (bcc)

$$\vec{a}_1 = \frac{a}{2}\left(-\vec{i} + \vec{j} + \vec{k}\right) \qquad \vec{b}_1 = \frac{4\pi}{a}\frac{1}{2}\left(\vec{j} + \vec{k}\right)$$

$$\vec{a}_2 = \frac{a}{2}\left(\vec{i} - \vec{j} + \vec{k}\right) \qquad \vec{b}_2 = \frac{4\pi}{a}\frac{1}{2}\left(\vec{i} + \vec{k}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\vec{i} + \vec{j} - \vec{k}\right) \qquad \vec{b}_3 = \frac{4\pi}{a}\frac{1}{2}\left(\vec{i} + \vec{j}\right)$$



1 BZ of a bcc lattice

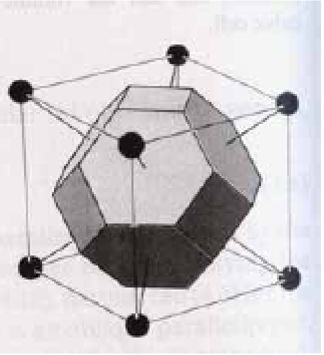
The reciprocal lattice of a bcc lattice is a fcc lattice of side $\frac{4\pi}{a}$

3. Face centered cubic lattice (fcc)

$$\vec{a}_1 = \frac{a}{2}\left(\vec{j} + \vec{k}\right) \qquad \vec{b}_1 = \frac{4\pi}{a}\frac{1}{2}\left(-\vec{i} + \vec{j} + \vec{k}\right)$$

$$\vec{a}_2 = \frac{a}{2}\left(\vec{i} + \vec{k}\right) \qquad \vec{b}_2 = \frac{4\pi}{a}\frac{1}{2}\left(\vec{i} - \vec{j} + \vec{k}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\vec{i} + \vec{j}\right) \qquad \vec{b}_3 = \frac{4\pi}{a}\frac{1}{2}\left(\vec{i} + \vec{j} - \vec{k}\right)$$



1 BZ of a fcc lattice

The reciprocal lattice of a fcc lattice is a bcc lattice of side $\dfrac{4\pi}{a}$

4. Hexagonal lattice (hex)

$$\vec{a}_1 = a\left(\frac{1}{2}\vec{i} + \frac{\sqrt{3}}{2}\vec{j}\right)$$

$$\vec{a}_2 = a\left(\frac{1}{2}\vec{i} - \frac{\sqrt{3}}{2}\vec{j}\right)$$

$$\vec{a}_3 = c\vec{k}$$

Homework: $\vec{b}_1, \vec{b}_2, \vec{b}_3 = ?$

CMS II-3 Hands-on: vaspview, density of state (DOS), and partial density of state (PDOS)

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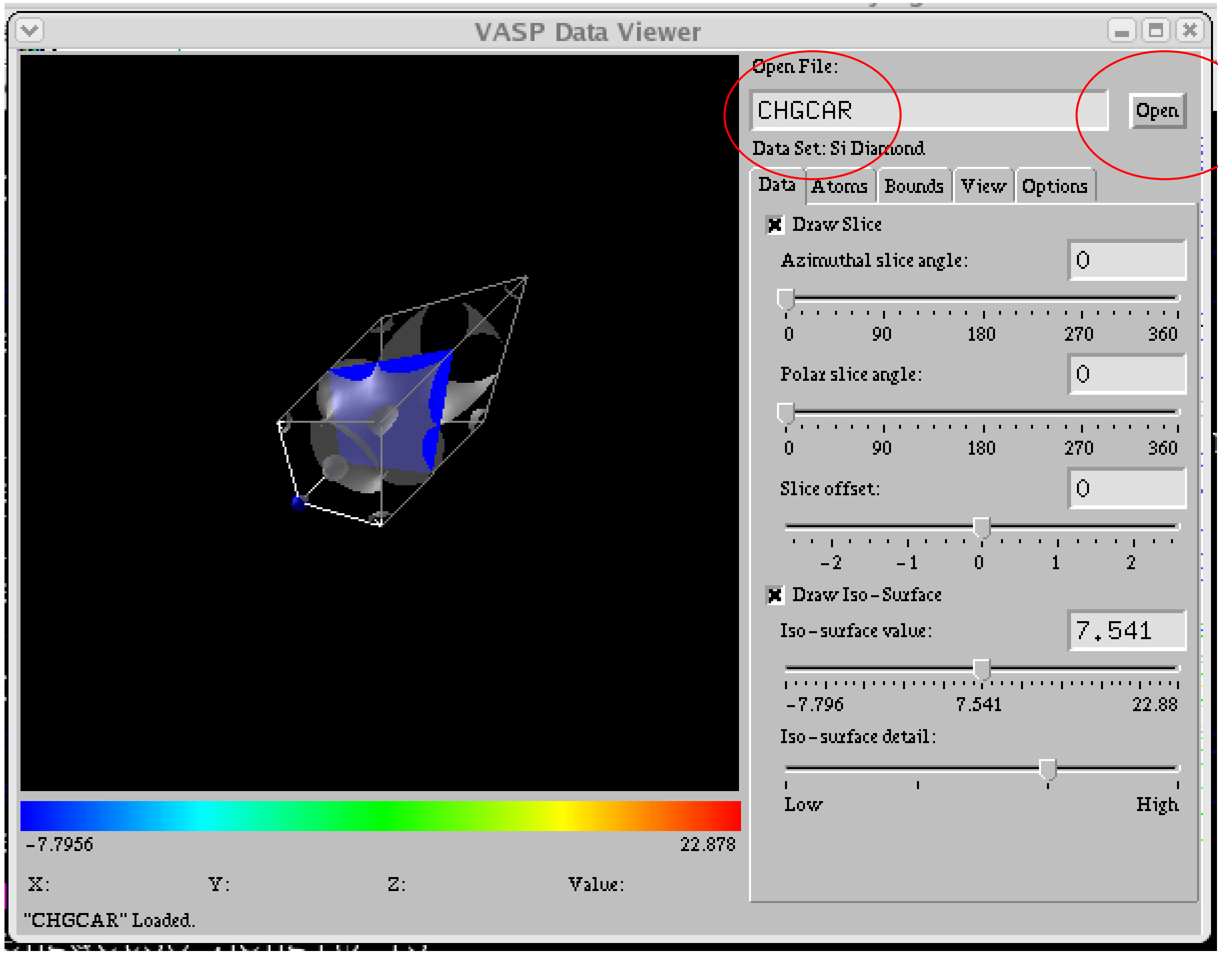
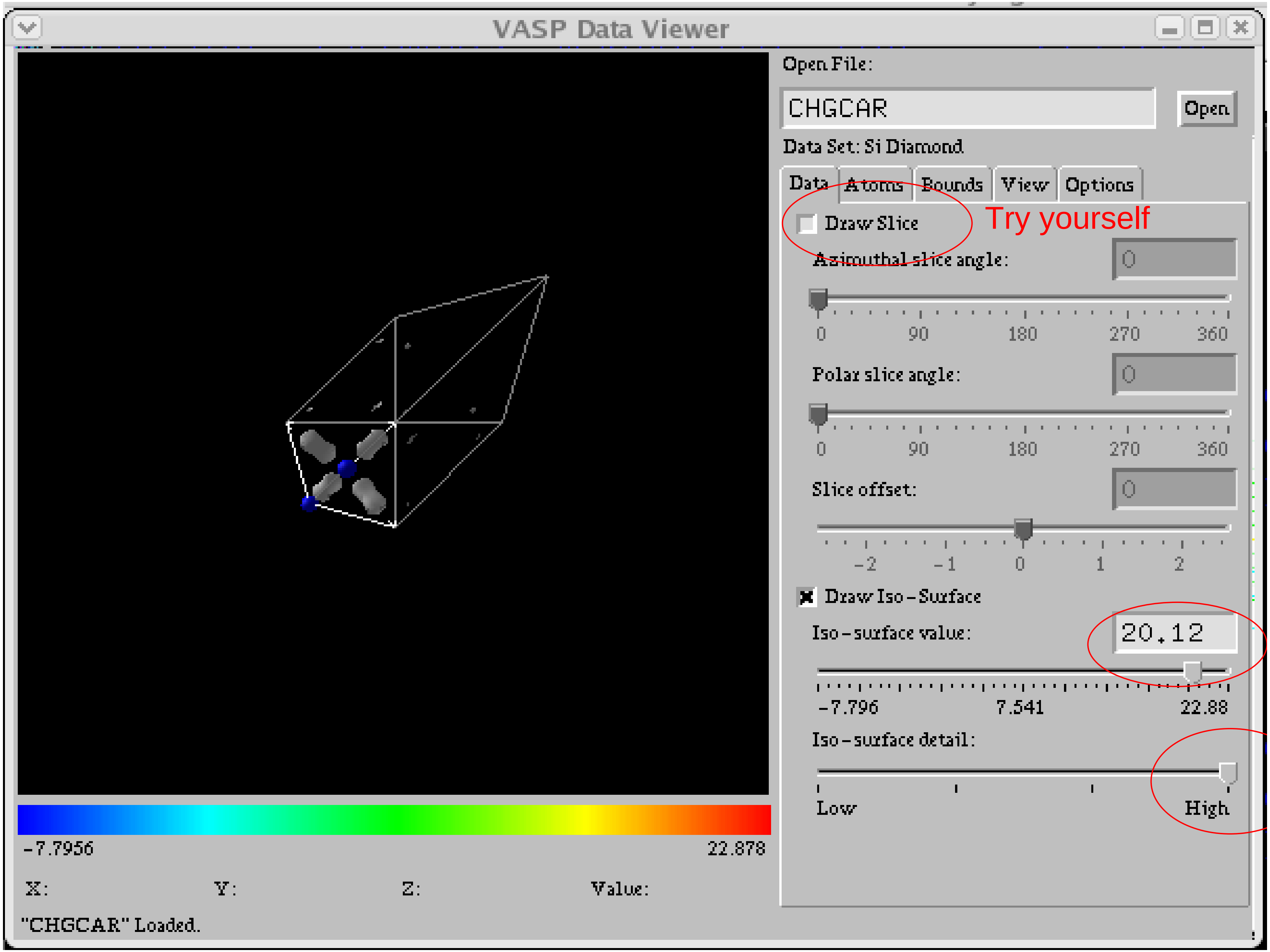
Vaspview

visualizing the charge (spin, partial charge) density

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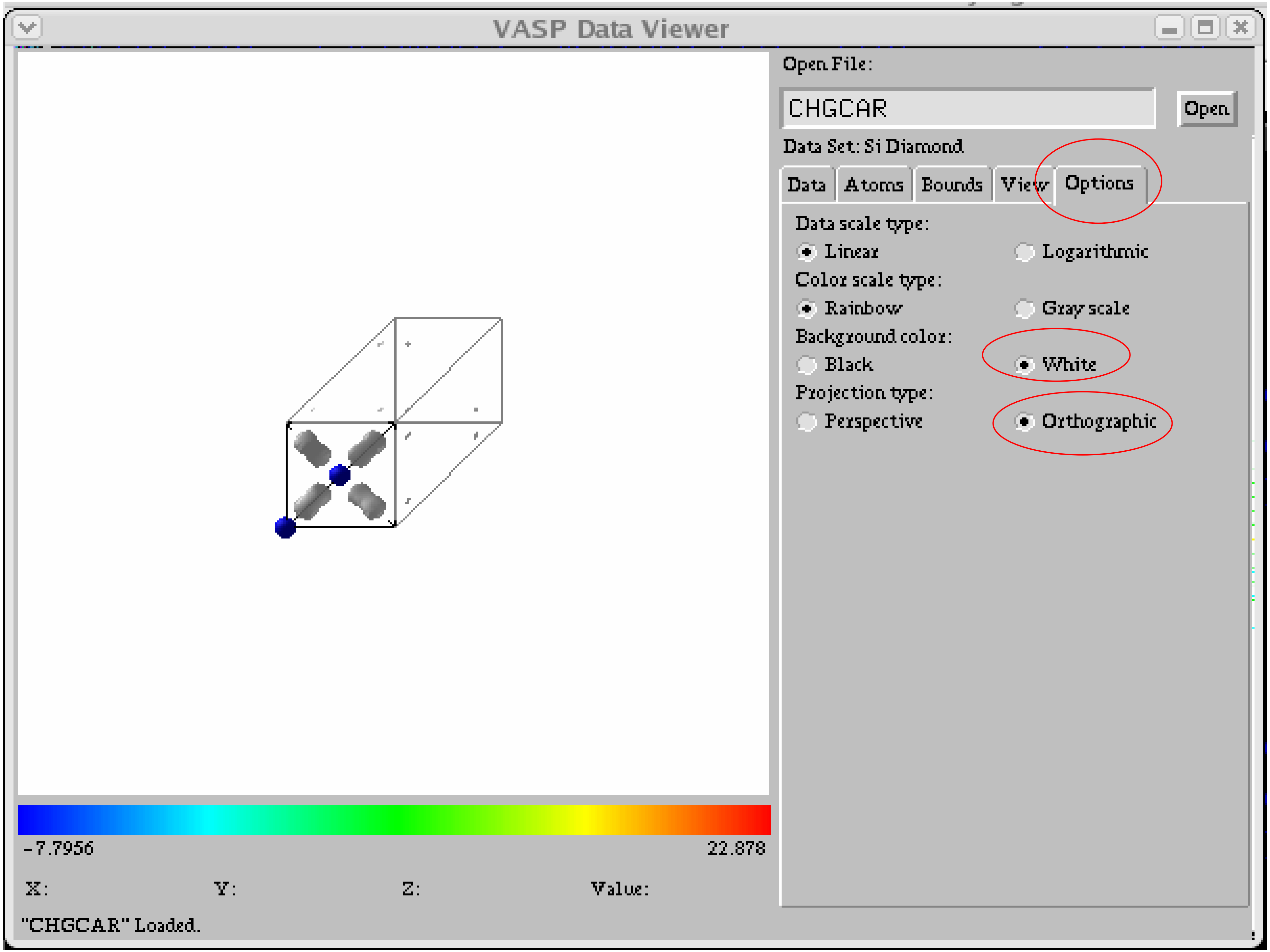
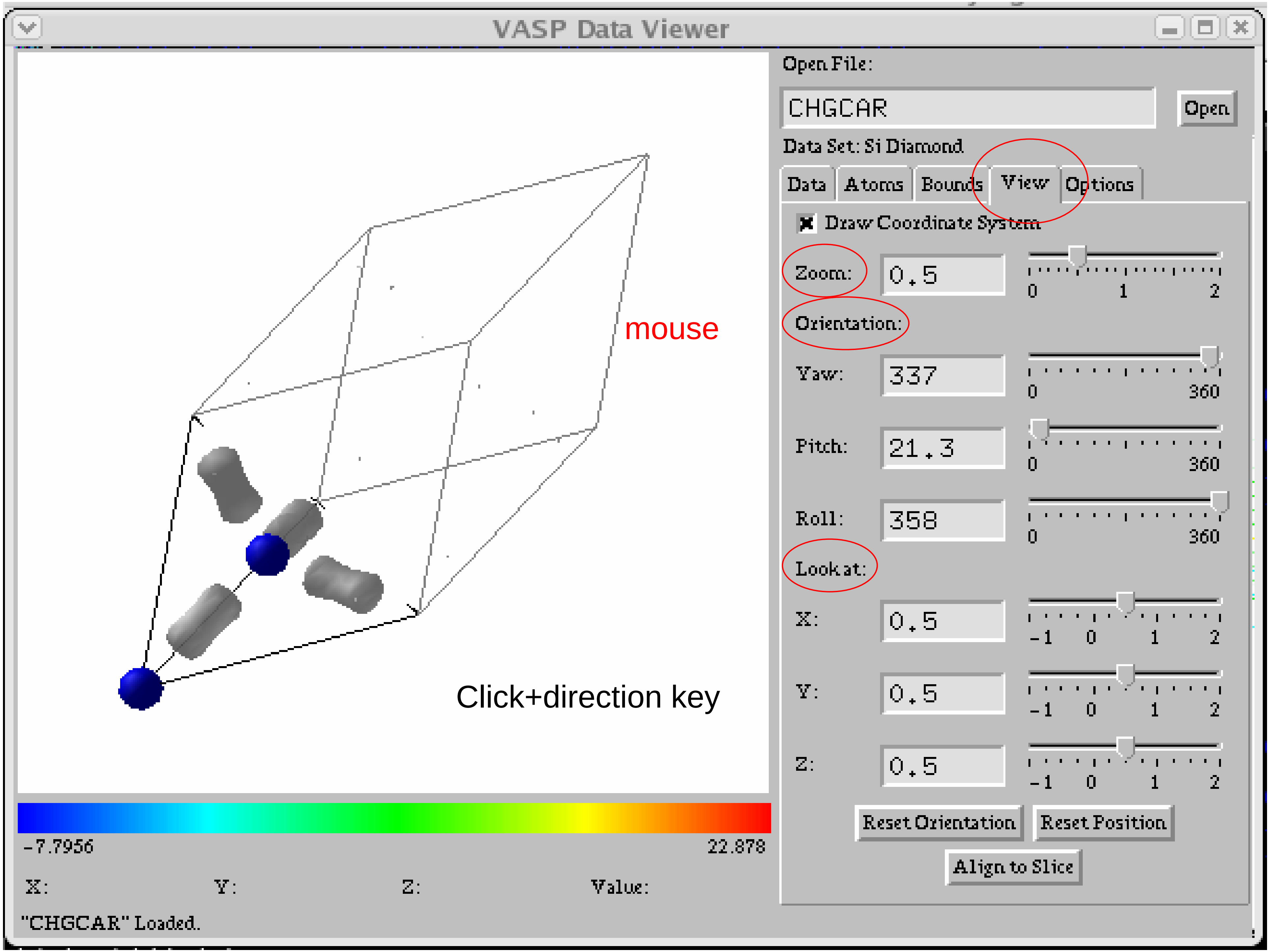
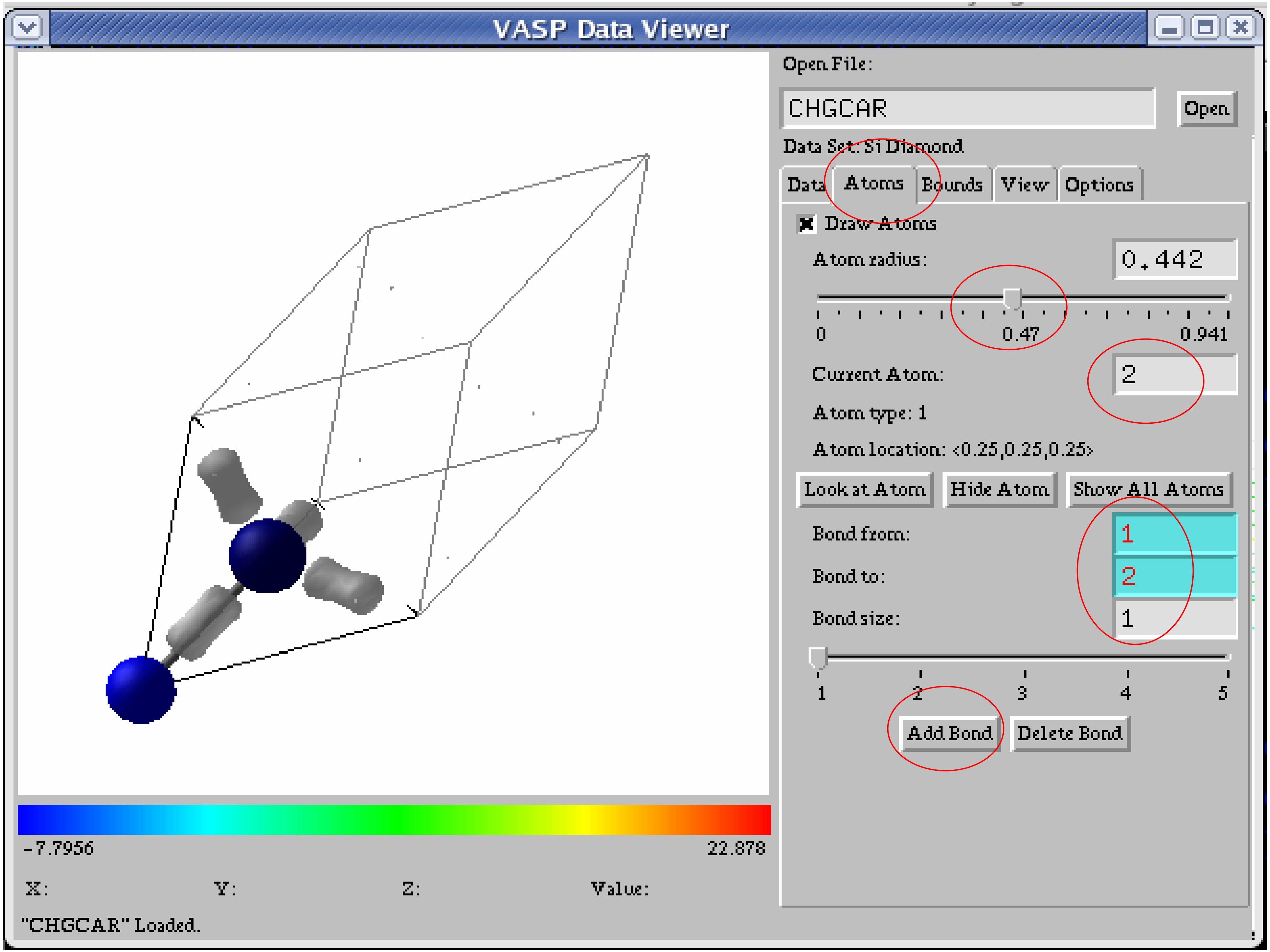
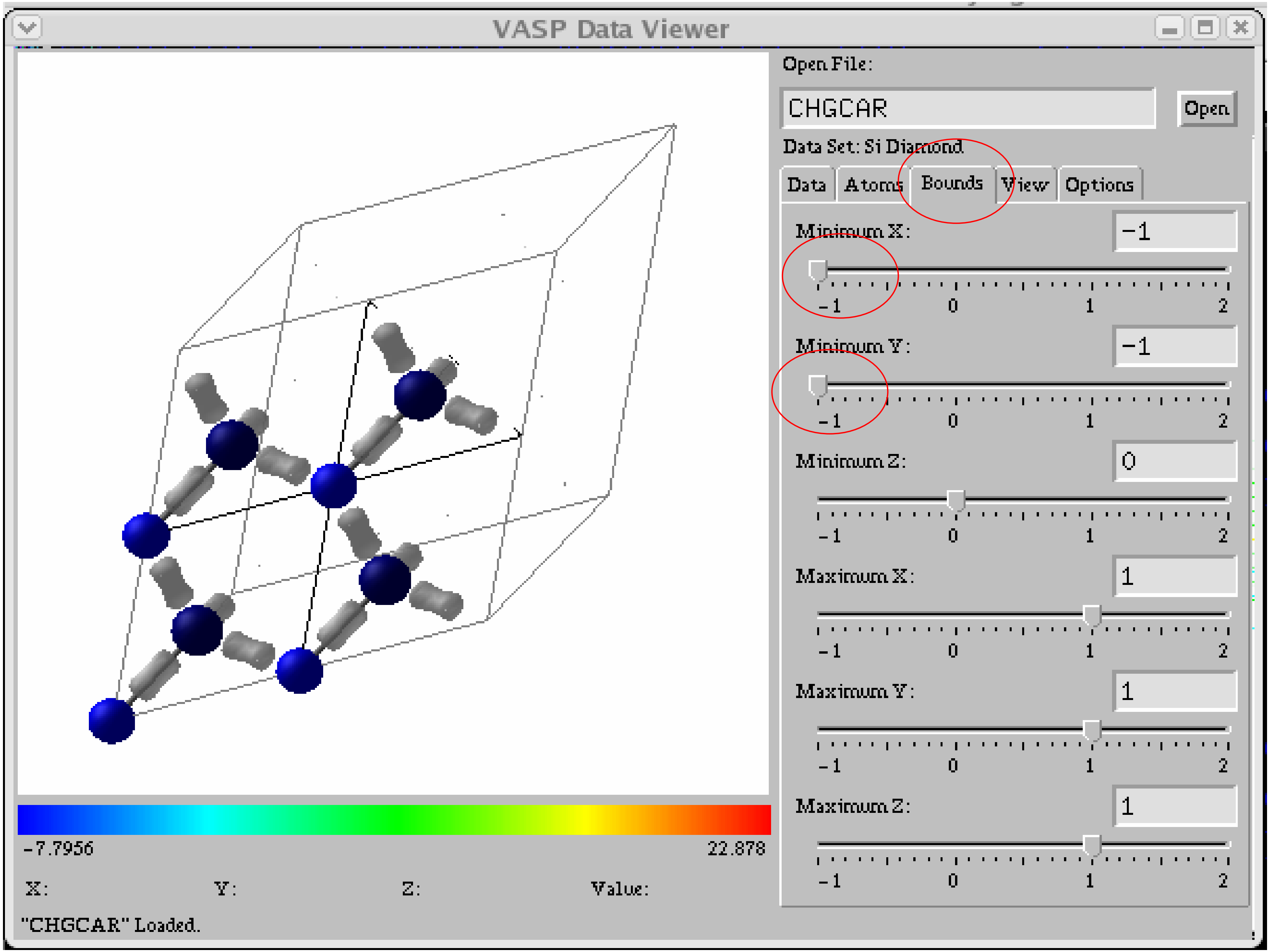
Open File:
CHGCAR
Open
Data Set: Si Diamond
Data
Atoms
Bounds
View
Options
Draw Slice
Try yourself
Azimuthal slice angle:
0
0 90 180 270 360
Polar slice angle:
0
0 90 180 270 360
Slice offset:
0
-2 -1 0 1 2
Draw Iso-Surface
Iso-surface value:
20.12
-7.796 7.541 22.88
Iso-surface detail:
Low High
-7.7956
22.878
X:
Y:
Z:
Value:
"CHGCAR" Loaded.


VASP Data Viewer
Open File:
CHGCAR
Open
Data Set: Si Diamond
Data
Atoms
Bounds
View
Options
Data scale type:
Linear
Logarithmic
Color scale type:
Rainbow
Gray scale
Background color:
Black
White
Projection type:
Perspective
Orthographic
-7.7956
22.878
X:
Y:
Z:
Value:
"CHGCAR" Loaded.


VASP Data Viewer
Open File:
CHGCAR
Open
Data Set: Si Diamond
Data
Atoms
Bounds
View
Options
Draw Coordinate System
Zoom:
0.5
Orientation:
Yaw:
337
Pitch:
21.3
Roll:
358
Look at:
X:
0.5
Y:
0.5
Z:
0.5
Reset Orientation
Reset Position
Align to Slice
mouse
Click+direction key
-7.7956
22.878
X:
Y:
Z:
Value:
"CHGCAR" Loaded.



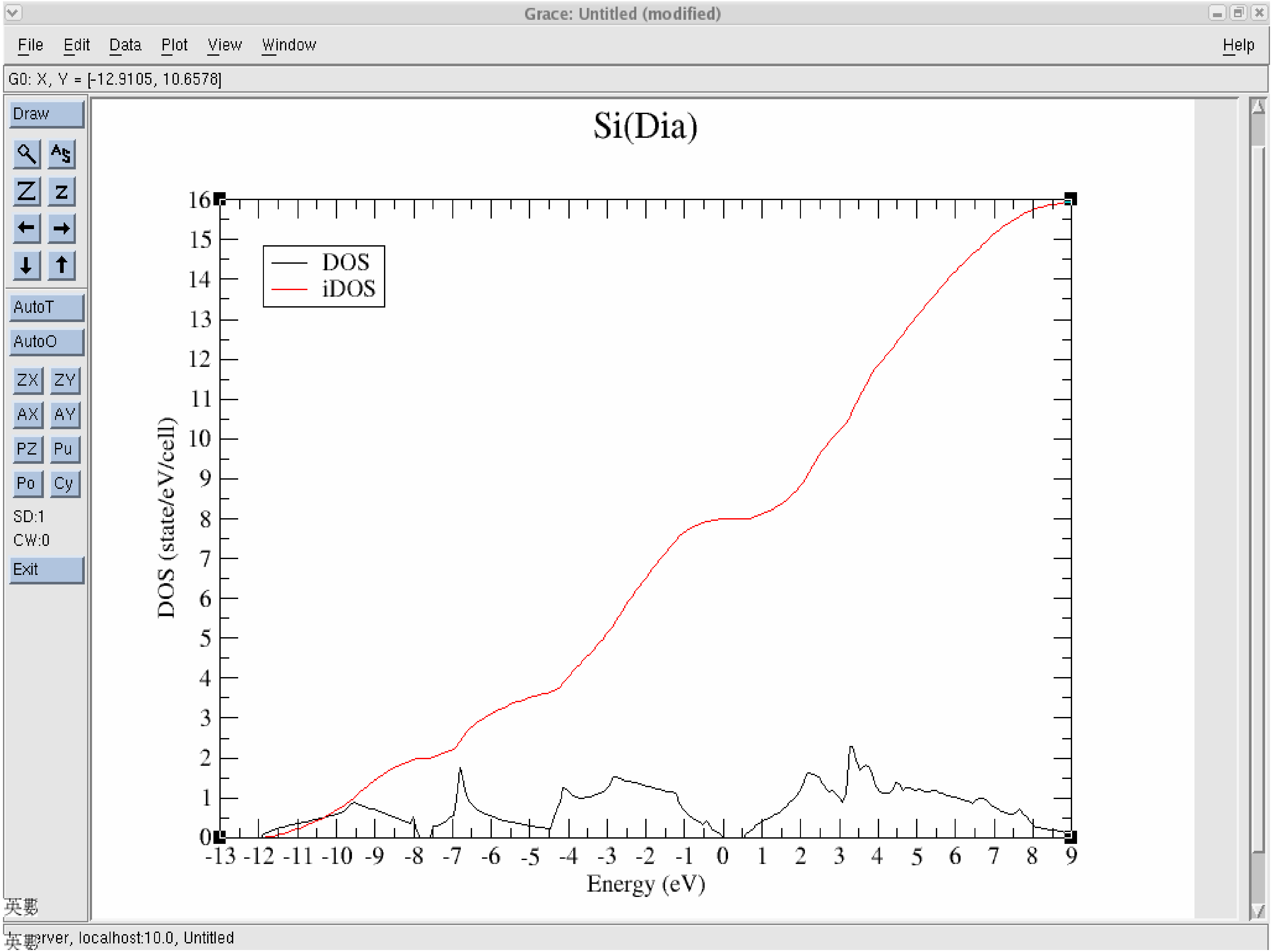
VASP Data Viewer
Open File:
CHGCAR
Open
Data Set: Si Diamond
Data
Atoms
Bounds
View
Options
Draw Atoms
Atom radius:
0.442
0
0.47
0.941
Current Atom:
2
Atom type: 1
Atom location: <0.25,0.25,0.25>
Look at Atom
Hide Atom
Show All Atoms
Bond from:
1
Bond to:
2
Bond size:
1
1
2
3
4
5
Add Bond
Delete Bond
-7.7956
22.878
X:
Y:
Z:
Value:
"CHGCAR" Loaded.


VASP Data Viewer
Open File:
CHGCAR
Open
Data Set: Si Diamond
Data
Atoms
Bounds
View
Options
Minimum X:
-1
-1 0 1 2
Minimum Y:
-1
-1 0 1 2
Minimum Z:
0
-1 0 1 2
Maximum X:
1
-1 0 1 2
Maximum Y:
1
-1 0 1 2
Maximum Z:
1
-1 0 1 2
-7.7956
22.878
X:
Y:
Z:
Value:
"CHGCAR" Loaded.

Density of state

```
DOSCAR:
2   2   1   0
 0.2001288E+02  0.3839590E-09  0.3839590E-09  0.3839590E-09  0.5000000E-15
  1.0000000000000000E-004
 CAR
Si Diamond
    17.62901345     -8.17412253  301      5.77032221      1.00000000
    -8.174  0.0000E+00  0.0000E+00
    -8.088  0.0000E+00  0.0000E+00
    -8.002  0.0000E+00  0.0000E+00
……………………………………………………
    17.457  0.0000E+00  0.1600E+02
    17.543  0.0000E+00  0.1600E+02
    17.629  0.0000E+00  0.1600E+02
    17.62901345     -8.17412253  301      5.77032221      1.00000000
    -8.174  0.0000E+00  0.0000E+00  0.0000E+00
    -8.088  0.0000E+00  0.0000E+00  0.0000E+00
    -8.002  0.0000E+00  0.0000E+00  0.0000E+00
………………………………………………………….
```

Save to dos.dat
Plot DOS using xmgrace
Shift Ef to zero


Grace: Untitled (modified)
File Edit Data Plot View Window Help
G0: X, Y = [-12.9105, 10.6578]
Draw
AutoT
AutoO
ZX ZY
AX AY
PZ Pu
Po Cy
SD:1
CW:0
Exit
Si(Dia)
DOS
iDOS
DOS (state/eV/cell)
Energy (eV)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
-13 -12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8 9
erver, localhost:10.0, Untitled

Partial density of state

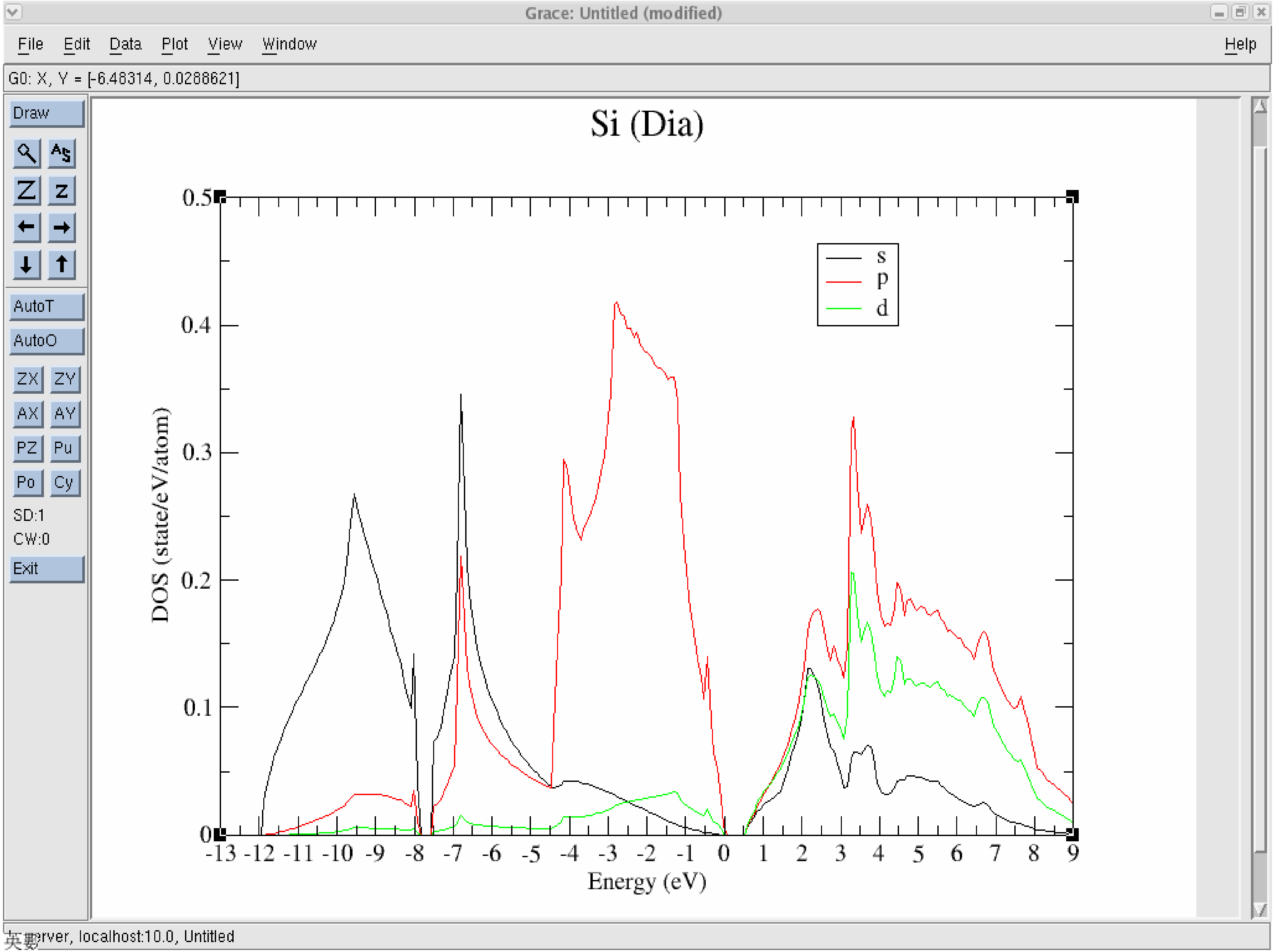
DOSCAR:

```
2   2   1   0
 0.2001288E+02  0.3839590E-09  0.3839590E-09  0.3839590E-09  0.5000000E-15
  1.0000000000000000E-004
 CAR
Si Diamond
   17.62901345    -8.17412253  301      5.77032221      1.00000000
   -8.174  0.0000E+00  0.0000E+00
   -8.088  0.0000E+00  0.0000E+00
   -8.002  0.0000E+00  0.0000E+00
……………………………………………………
   17.457  0.0000E+00  0.1600E+02
   17.543  0.0000E+00  0.1600E+02
   17.629  0.0000E+00  0.1600E+02
   17.62901345    -8.17412253  301      5.77032221      1.00000000
   -8.174  0.0000E+00  0.0000E+00  0.0000E+00
   -8.088  0.0000E+00  0.0000E+00  0.0000E+00
   -8.002  0.0000E+00  0.0000E+00  0.0000E+00
………………………………………………………….
   17.457  0.0000E+00  0.0000E+00  0.0000E+00
   17.543  0.0000E+00  0.0000E+00  0.0000E+00
   17.629  0.0000E+00  0.0000E+00  0.0000E+00
   17.62901345    -8.17412253  301      5.77032221      1.00000000
   -8.174  0.0000E+00  0.0000E+00  0.0000E+00
   -8.088  0.0000E+00  0.0000E+00  0.0000E+00
   -8.002  0.0000E+00  0.0000E+00  0.0000E+00
…………………………………………………………..
```

total DOS

Partial DOS of Si1
Save to pdos.dat
Plot PDOS

Partial DOS of Si2



Grace: Untitled (modified)
File Edit Data Plot View Window Help
G0: X, Y = [-6.48314, 0.0288621]
Draw
AutoT
AutoO
ZX ZY
AX AY
PZ Pu
Po Cy
SD:1
CW:0
Exit
Si (Dia)
s
p
d
DOS (state/eV/atom)
Energy (eV)
0 0.1 0.2 0.3 0.4 0.5
-13 -12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8 9
erver, localhost:10.0, Untitled

Homework

please Email to jeng@phys.sinica.edu.tw

- Plot charge density, DOS, and PDOS of Si(Dia) and C(Dia) using LDA with experimental lattice constant
- Plot charge density, DOS, and PDOS of Cu(FCC), V(BCC), and Ti(HCP) using GGA with experimental lattice constant (Hint: for HCP lattice, use Gamma Monkhorst-Pack k-mesh by adding ‘G’ in front of ‘Monkhorst-Pack’ in KPOINTS)