

# 物質科学のための計算数理 II

## Numerical Analysis for Material Science II

10th: Density Functional Theory (3)

Dec. 14 (Fri)

Lecturer: Mitsuaki Kawamura (河村光晶)

# Schedule (This semester W1, W2)

1. Sep. 28 (Fri) Guidance Y
2. Oct. 5 (Fri) Monte Carlo method O
3. Oct. 12 (Fri) Monte Carlo method O
4. Oct. 19 (Fri) Monte Carlo method O
5. Oct. 26 (Fri) Exact diagonalization Y
6. Nov. 2 (Fri) Exact diagonalization Y
7. Nov. 9 (Fri) Molecular dynamics O (1st report problem will be announced.)
8. Nov. 30 (Fri) Standard DFT code K
9. Dec. 7 (Fri) Density functional theory K
10. Dec. 14 (Fri) Density functional theory K
11. Dec. 21 (Fri) Density functional theory K
12. Dec. 25 (Tue) Density functional theory K (遠隔講義室)
13. Jan. 11 (Fri) (2nd)Report problem K

※ Lecturers: Y ... Yamaji, K ... Kawamura, O ... Ohgoe

# Schedule in this section (DFT)

1. Nov. 30 (Fri) Standard DFT code
  - First-principles calculation and Density functional theory (Lecture)
  - One-body Schrödinger eq. for periodic system and Bloch theorem (L)
  - Numerical solution of Kohn-Sham (one-body Schrödinger) eq. (L)
  - Hands-on DFT code (Tutorial)
  - Version control system : Git (T)
2. Dec. 7 (Fri) Kohn-Sham eq.
  - Plane-wave basis and Pseudopotentials (L)
  - Iterative eigenvalue solution method (L & T)
3. Dec. 14 (Fri) Self-Consistent loop
  - Hartree potential (Poisson eq.), Atomic potential, XC potential
  - Update (Broyden's method)
  - Visualization of grid data (T)
4. Dec. 21 (Fri) Total Energy
  - Total energy
  - Brillouin-zone integral (Tetrahedron method)
  - Coulomb potential for periodic point charge (Ewald sum)
5. Dec. 25 ([Tue](#)) Advanced subjects for productive calculation ([遠隔講義室](#))
  - Generalized gradient correction
  - Non-local pseudopotentials (Norm-conserving, ultrasoft, PAW)
  - Procedure
6. Jan. 11 (Fri) (2nd) Report problem, Question time

# Today's Schedule

Kohn-Sham potential

- Hartree term

- (Pseudo) atomic potential

- Exchange-correlation term

SCF loop (Solution of non-linear equation)

- (Quasi) newton method

- Broyden's method

Visualization of grid data

- Xcrysden structure format (XSF)

# DFT loop

Unit lattice vector  
atomic position  
pseudopotential file

$$\rho(r) = \frac{N}{V_{uc}}$$

Initial density is  
uniform

$$v_{KS}[\rho](\mathbf{r})$$

$$\left( -\frac{(\nabla + \mathbf{k})^2}{2} + v_{KS}(\mathbf{r}) \right) u_{nk}(\mathbf{r}) = \varepsilon u_{nk}(\mathbf{r})$$

$$N = \frac{1}{V_{BZ}} \int_{BZ} d^3k \sum_{n=1}^{\infty} \theta(\varepsilon_F - \varepsilon_{nk})$$

$$\rho(\mathbf{r}) = \frac{1}{V_{BZ}} \int_{BZ} d^3k \sum_{n=1}^{\infty} |u_{nk}(\mathbf{r})|^2 \theta(\varepsilon_F - \varepsilon_{nk})$$

$|v_{KS,out}(\mathbf{r}) - v_{KS,in}(\mathbf{r})|^2$  is small ?

No

Yes

End  
Output  $v_{KS}(\mathbf{r})$   
for post process

# Kohn–Sham potential

$$\left( -\frac{(\nabla + \mathbf{k})^2}{2} + v_{KS}(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon u_{n\mathbf{k}}(\mathbf{r})$$

$$v_{KS}[\rho](\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}[\rho](\mathbf{r})$$

Atomic (pseudo) potential : 
$$v(\mathbf{r}) = \sum_{L=1}^{N_C} \sum_{s=1}^{N_s} \sum_{a=1}^{N_{s,a}} v_s(|\mathbf{r} - \boldsymbol{\tau}_{s,a} - \mathbf{R}_L|)$$

Hartree potential : 
$$v_H(\mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Exchange–correlation potential : 
$$v_{XC}[\rho](\mathbf{r}) = \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})}$$

## Hartree potential (hartree\_pot@rho\_v.F90)

$$v_H(\mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \sum_{L=1}^{N_C} \int_{uc} d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}_L|}$$

$$\tilde{v}_H(\mathbf{G}) = \int_{uc} d^3r e^{\frac{-i\mathbf{G}\cdot\mathbf{r}}{V_{uc}}} v_H(\mathbf{r}) = \int_{uc} d^3r e^{\frac{-i\mathbf{G}\cdot\mathbf{r}}{V_{uc}}} \sum_{L=1}^{N_C} \int_{uc} d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}_L|}$$

$$= \int_{uc} d^3r e^{\frac{-i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}'-\mathbf{R}_L)}{V_{uc}}} \sum_{L=1}^{N_C} \int_{uc} d^3r' \frac{\rho(\mathbf{r}')e^{-i\mathbf{G}\cdot\mathbf{r}'}}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}_L|}$$

$$= \int_{uc} d^3r e^{\frac{-i\mathbf{G}\cdot\mathbf{r}'}{V_{uc}}} \rho(\mathbf{r}') \int d^3\mathbf{r} \frac{e^{-i\mathbf{G}\cdot\mathbf{r}}}{|\mathbf{r}|} = \tilde{\rho}(\mathbf{G}) \frac{4\pi}{|\mathbf{G}|^2}$$

$$v_H(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \tilde{v}_H(\mathbf{G})$$

8/23 Periodic atomic potential  
(generate\_vps@rho\_v.F90)

$$v(\mathbf{r}) = \sum_{L=1}^{N_C} \sum_{s=1}^{N_s} \sum_{a=1}^{N_{s,a}} v_s(|\mathbf{r} - \boldsymbol{\tau}_{s,a} - \mathbf{R}_L|)$$

$$\tilde{v}(\mathbf{G}) = \int_{uc} d^3r e^{\frac{e^{-i\mathbf{G}\cdot\mathbf{r}}}{V_{uc}}} v(\mathbf{r}) = \int_{uc} d^3r e^{\frac{e^{-i\mathbf{G}\cdot\mathbf{r}}}{V_{uc}}} \sum_{L=1}^{N_C} \sum_{s=1}^{N_s} \sum_{a=1}^{N_{s,a}} v_s(|\mathbf{r} - \boldsymbol{\tau}_{s,a} - \mathbf{R}_L|)$$

$$= \sum_{s=1}^{N_s} \sum_{a=1}^{N_{s,a}} \frac{e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{s,a}}}{V_{uc}} \sum_{L=1}^{N_C} \int_{uc} d^3r e^{-i\mathbf{G}\cdot(\mathbf{r}-\boldsymbol{\tau}_{s,a}-\mathbf{R}_L)} v_s(|\mathbf{r} - \boldsymbol{\tau}_{s,a} - \mathbf{R}_L|)$$

$$= \sum_{s=1}^{N_s} F_s(\mathbf{G}) \tilde{v}_s(\mathbf{G}) \quad F_s(\mathbf{G}) \equiv \sum_{a=1}^{N_{s,a}} \frac{e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{s,a}}}{V_{uc}}$$

$$\tilde{v}_s(\mathbf{G}) \equiv \int d^3r e^{-i\mathbf{G}\cdot\mathbf{r}} v_s(|\mathbf{r}|) = 4\pi \int_0^\infty dr r^2 \frac{\sin(|\mathbf{G}|r)}{|\mathbf{G}|r} v_s(r)$$

$$v(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \tilde{v}(\mathbf{G})$$





# Exchange-correlation potential in LDA (xc\_pot@rho\_v.F90)

$$v_{XC}^{LDA}(\rho(\mathbf{r})) = \varepsilon_{XC}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \left. \frac{d\varepsilon_{XC}(\rho)}{d\rho} \right|_{\rho=\rho(\mathbf{r})} = \varepsilon_{XC}(\rho(\mathbf{r})) - \frac{r_s}{3} \frac{d\varepsilon_{XC}(\rho)}{dr_s}$$

$$\varepsilon_{XC}(\rho) = \varepsilon_X(\rho) + \varepsilon_C(\rho) \qquad \frac{4\pi}{3} r_s^3 = \frac{1}{\rho}$$

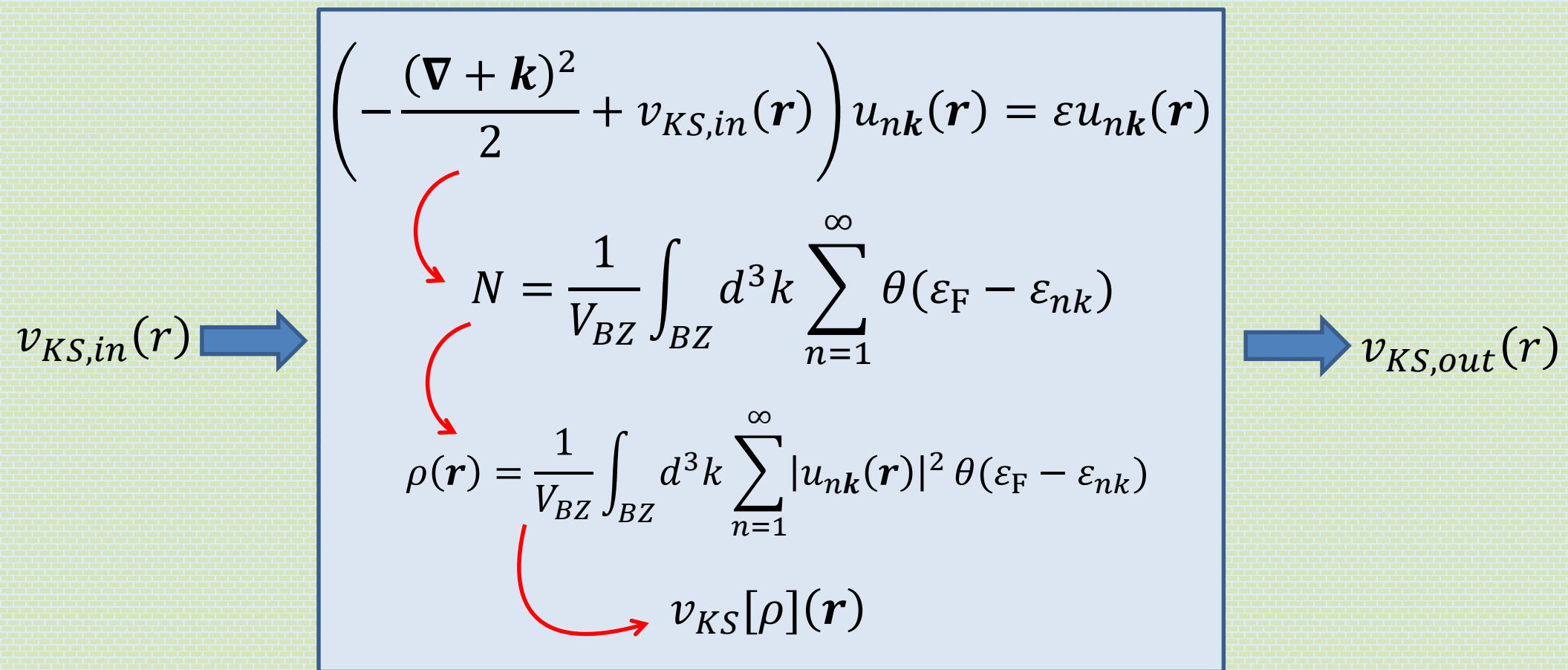
$$\varepsilon_X(\rho) = -\frac{3}{4\pi} \left( \frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s}$$

$$\varepsilon_C(\rho) = -0.0480 + 0.031 \ln r_s - 0.0116 r_s + 0.0020 r_s \ln r_s \quad (r_s \leq 1)$$

$$= -\frac{0.1423}{1 + 1.0529\sqrt{r_s} + 0.3334r_s} \quad (r_s \geq 1)$$

J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

# Update $v_{KS}(\mathbf{r})$



Plane mixing

$$v_{KS,new}(\mathbf{r}) = v_{KS,in}(\mathbf{r}) + \beta \left( v_{KS,out}(\mathbf{r}) - v_{KS,in}(\mathbf{r}) \right)$$

$$0 < \beta \leq 1$$

# Broyden's method

$$F[v_{in}](\mathbf{r}) = v_{out}[v_{in}](\mathbf{r}) - v_{in}(\mathbf{r})$$

$$\mathbf{F}(\mathbf{v}) = \mathbf{v}_{out}(\mathbf{v}) - \mathbf{v}$$

$$\text{Solve } \mathbf{F}(\mathbf{v}) = \mathbf{0}$$

$$\mathbf{F}(\mathbf{v}) + \hat{\mathbf{J}}\Delta\mathbf{v} = \mathbf{0} \quad J_{ij} \equiv \frac{\partial F_i}{\partial v_j}$$

$$\Delta\mathbf{v}^{(m)} = -(\hat{\mathbf{J}}^{-1})^{(m)} \mathbf{F}^{(m)}$$

$$\mathbf{v}^{(m+1)} = \mathbf{v}^{(m)} + \Delta\mathbf{v}^{(m)}$$

Newton's method

Approximate  $\hat{\mathbf{J}}^{-1}$ , and update it iteratively  $\rightarrow$  Quasi Newton's method

$$\mathbf{F}^{(m)} - \mathbf{F}^{(m-1)} = (\hat{\mathbf{J}}_{approx}^{-1})^{(i)} (\mathbf{v}^{(m)} - \mathbf{v}^{(m-1)})$$

$$\text{Minimize } \left| (\hat{\mathbf{J}}_{approx}^{-1})^{(m)} - (\hat{\mathbf{J}}_{approx}^{-1})^{(m-1)} \right|^2 \quad \text{C. G. Broyden, Math. Comput. } \mathbf{19}, 577 \text{ (1965).}$$

$$(\hat{\mathbf{J}}_{approx}^{-1})^{(m)} = (\hat{\mathbf{J}}_{approx}^{-1})^{(m-1)} + \frac{\left( \mathbf{v}^{(m+1)} - \mathbf{v}^{(m)} - (\hat{\mathbf{J}}_{approx}^{-1})^{(m-1)} (\mathbf{F}^{(m)} - \mathbf{F}^{(m-1)}) \right)}{(\mathbf{F}^{(m)} - \mathbf{F}^{(m-1)}) \cdot (\mathbf{F}^{(m)} - \mathbf{F}^{(m-1)})} (\mathbf{F}^{(m)} - \mathbf{F}^{(m-1)})^T$$

# Practical algorithm (scf\_loop@scf.F90)

do iteration :  $m = 1, 2, 3, \dots$

  Compute  $\mathbf{F}(\mathbf{v})$

  if  $|\mathbf{F}|^2$  is small  $\rightarrow$  exit

  if  $m > 1$

$$\Delta \mathbf{F} = \mathbf{F} - \mathbf{F}_{old}$$

$$\mathbf{J}_1^{(m)} = \beta \Delta \mathbf{F} + \Delta \mathbf{v} - \sum_{n=2}^{m-1} \left( \mathbf{J}_2^{(n)} \cdot \Delta \mathbf{F} \right) \mathbf{J}_1^{(n)}$$

$$\mathbf{J}_2^{(m)} = \frac{\Delta \mathbf{F}}{\Delta \mathbf{F} \cdot \Delta \mathbf{F}}$$

end if

$$\Delta \mathbf{v} = \beta \mathbf{F} - \sum_{n=2}^m \left( \mathbf{J}_2^{(n)} \cdot \mathbf{F} \right) \mathbf{J}_1^{(n)}$$

$$\mathbf{F}_{old} = \mathbf{F}$$

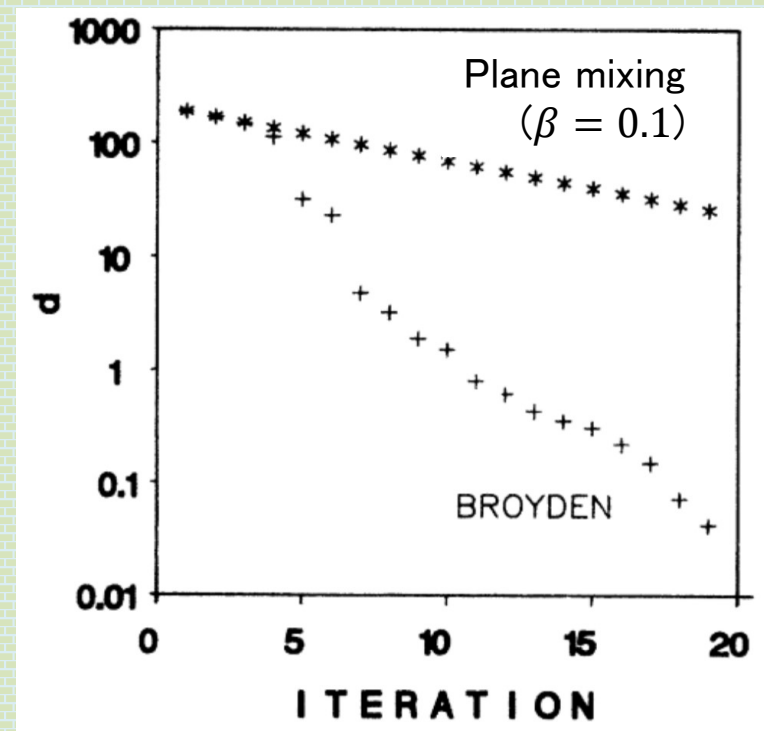
$$\mathbf{v} = \mathbf{v} + \Delta \mathbf{v}$$

end do

G. P. Srivastava, J. Phys. A: Math. Gen. 17, L317 (1984).

G. P. Srivastava J. Phys. A: Math. Gen. 17, 2737 (1984).

$$\left( \hat{J}_{approx}^{-1} \right)^{(m)} = -\beta + \sum_{n=2}^m \mathbf{J}_1^{(n)} \mathbf{J}_2^{(n)T}$$



W(001) surface

D. Singh, *et al*, Phys. Rev. B 34, 8391, (198).

# Tutorial

```
$ cd ~/pwdft/
$ git checkout master
$ git pull
$ make clean; make
$ cd sample/Al/
$ ../../src/pwdft.x < scf.in
```

```
Iteration           1
  Average LOBPCG steps :           20
  delta Vks [eV] :    2.7895180896787383E-003
Iteration           2
  Average LOBPCG steps :           8
  delta Vks [eV] :    1.9722767387705393E-003
Iteration           3
  Average LOBPCG steps :           9
  delta Vks [eV] :    3.3737045076316851E-005
Iteration           4
  Average LOBPCG steps :           1
  delta Vks [eV] :    2.3594012412709303E-005
Iteration           5
  Average LOBPCG steps :           2
  delta Vks [eV] :    1.0001898370361127E-006
```

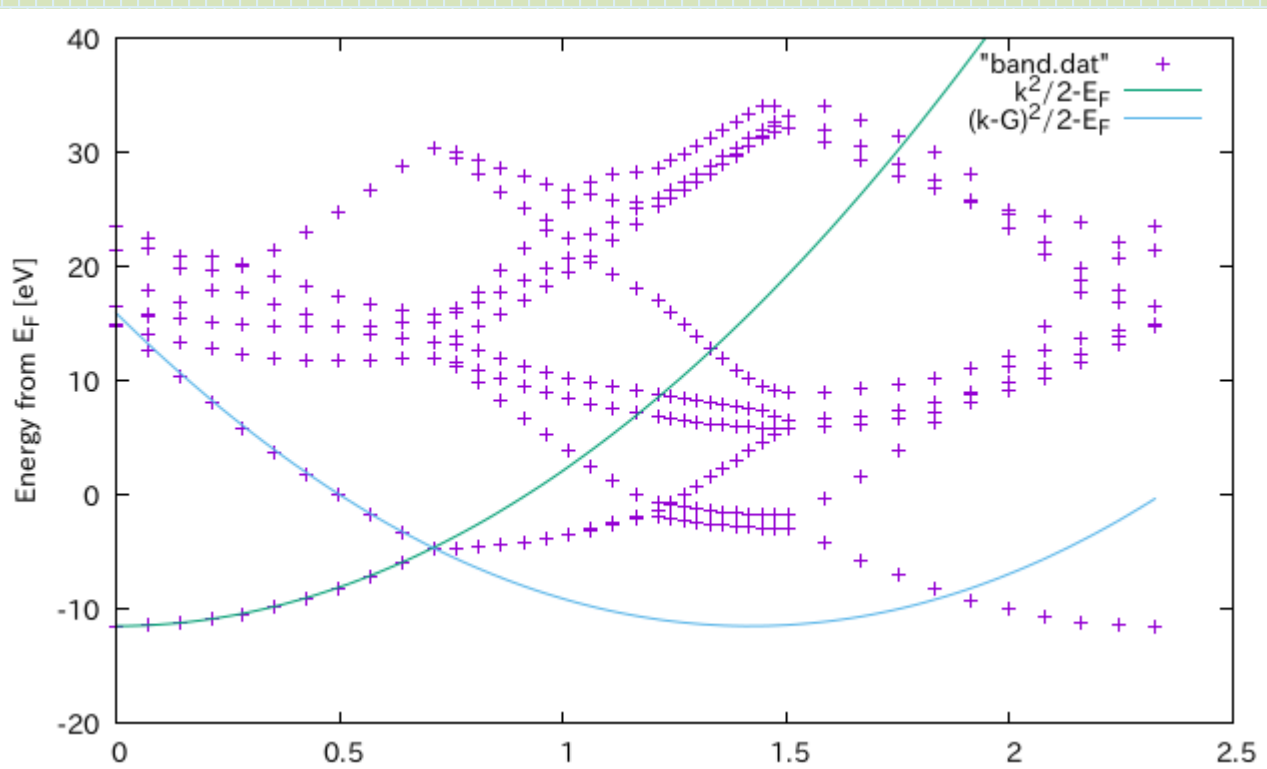
Converged ! iter = 5

```
&CONTROL
  calculation = 'scf'
/
&SYSTEM
nbnd = 5
      nat = 1
      ntyp = 1
      ecutwfc =30.000000
      ecutrho = 120.000000
/
&ELECTRONS
  mixing_beta = 0.3
  conv_thr = 1.000000e-5
  electron_maxstep = 100
/
CELL_PARAMETERS
  0.000000 2.024700 2.024700
  2.024700 0.000000 2.024700
  2.024700 2.024700 0.000000
ATOMIC_SPECIES
  Al al.lda.lps
ATOMIC_POSITIONS
  Al 0.000000 0.000000 0.000000
K_POINTS
  8 8 8
```

# Band structure plot

One-shot calculation with previously computed  $v_{KS}(\mathbf{r})$

```
$ ../../src/pwdft.x < band.in
$ gnuplot
gnuplot> set ylabel "Energy from E_F [eV]"
gnuplot> unset xlabel
gnuplot> plot [][:40] "band.dat", ¥
x**2*0.5*27.21138456-11.514956871425214 tit "k^2/2-E_F", ¥
(x-1.42)**2*0.5*27.2-11.5 tit "(k-G)^2/2-E_F"
```



Band structure of Aluminum  
 → Free electron  
 + Brillouin-zone periodicity (folding)  
 + small potential effect

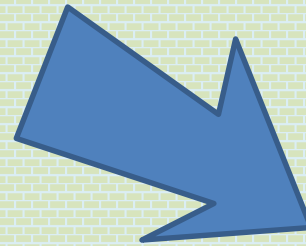
# Visualization of grid data

## Real-space grid data

- Potential  $v_{KS}(\mathbf{r}), v(\mathbf{r}), v_H(\mathbf{r}), v_{XC}(\mathbf{r})$
- Charge density  $\rho(\mathbf{r})$
- Kohn-Sham orbital  $u_{nk}(\mathbf{r})$
- Etc.

## Reciprocal-space grid data

- Kohn-Sham energy  $\varepsilon_{nk}$
- Fermi velocity  $\nabla_{\mathbf{k}}\varepsilon_{nk}$
- Berry connection  $\langle u_{nk} | i\nabla_{\mathbf{k}} | u_{nk} \rangle$
- Berry curvature  $\nabla_{\mathbf{k}} \times \langle u_{nk} | i\nabla_{\mathbf{k}} | u_{nk} \rangle$
- Etc.



- Isosurface
- Section



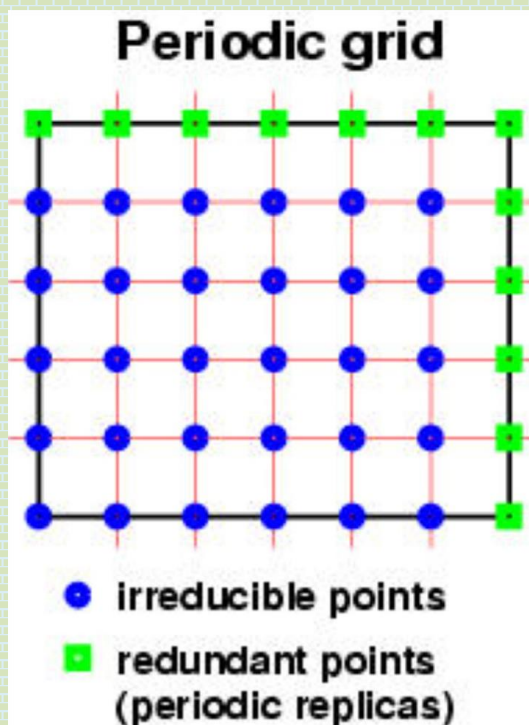
# Real space : XSF

XCrysDen : Crystalline structure viewer (like VESTA) <http://www.xcrysden.org/>

XCrysden Structure File (XSF) format <http://www.xcrysden.org/doc/XSF.html>

Unit cell + Atomic position (structure) + Volume (grid) data

Unit : Angstrom



The grid data should include data at **all** edge of the unit cell.

We need additional data at these points : copy from original points

# XSF format

Unit lattice vectors [ $\text{\AA}$ ]

Number of atoms in unit cell  
The second number is always "1"

Atomic position in [ $\text{\AA}$ ]  
Not fractional coordinate

Data grid number. FFT grid + 1  
(Including all edge of unit cell)

Grid shift from atomic position (usually 0)

Cell of grid data (usually the same as u.c.)

Volume data

```

CRYSTAL
PRIMVEC
    0.00000E+00    0.20247E+01    0.20247E+01
    0.20247E+01    0.00000E+00    0.20247E+01
    0.20247E+01    0.20247E+01    0.00000E+00
PRIMCOORD
    1 1
A1 0.00000E+00    0.00000E+00    0.00000E+00
BEGIN_BLOCK_DATAGRID_3D
3D_PWSCF
DATAGRID_3D_UNKNOWN
    21 21 21
    0.00000E+00    0.00000E+00    0.00000E+00
    0.00000E+00    0.20247E+01    0.20247E+01
    0.20247E+01    0.00000E+00    0.20247E+01
    0.20247E+01    0.20247E+01    0.00000E+00
    0.76311E+02    0.67851E+02    0.45909E+02    0.18866E+02    -0.39980E+01    -0.16986E+02
   -0.20120E+02   -0.17490E+02   -0.13890E+02   -0.11749E+02   -0.11130E+02   -0.11749E+02
   -0.13890E+02   -0.17490E+02   -0.20120E+02   -0.16986E+02   -0.39980E+01    0.18866E+02
    0.45909E+02    0.67851E+02    0.76311E+02    0.67851E+02    0.52697E+02    0.28399E+02
    0.40345E+01   -0.12896E+02   -0.19773E+02   -0.19031E+02   -0.15398E+02   -0.12470E+02
    :
END_DATAGRID_3D
END_BLOCK_DATAGRID_3D

```

# Input/Output grid data (griddata.F90)

```
module griddata
contains
  subroutine read_griddata(filename, gdata)
    use gvec, only : g_rh
    character(*),intent(in) :: filename
    real(8),intent(out) :: gdata(g_rh%nft(1),g_rh%nft(2),g_rh%nft(3))
  end subroutine read_griddata
  subroutine write_griddata(filename, gdata)
    use gvec, only : g_rh
    character(*),intent(in) :: filename
    real(8),intent(in) :: gdata(g_rh%nft(1),g_rh%nft(2),g_rh%nft(3))
  end subroutine write_griddata
end module griddata
```

In pwdft.F90,

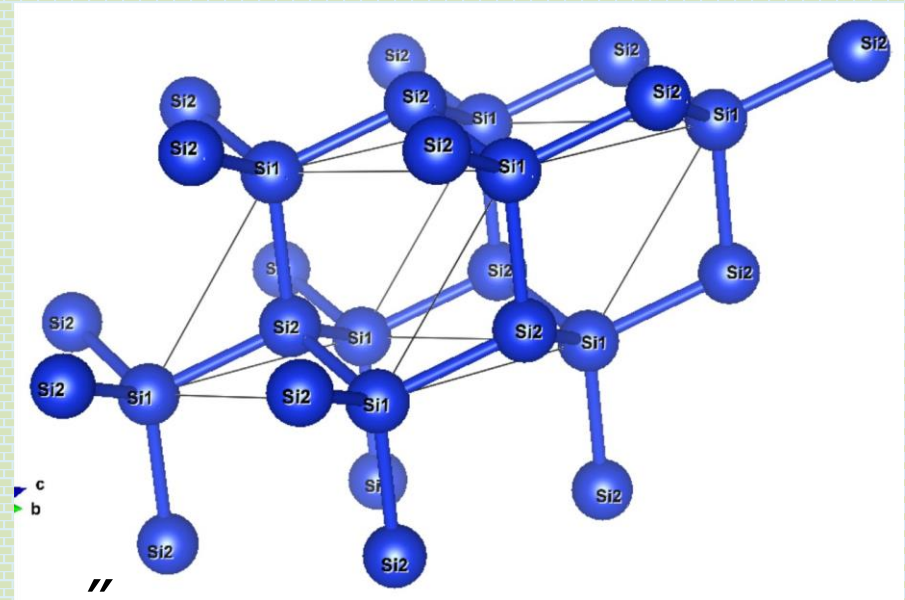
```
program pwdft
  use griddata, only : read_griddata, write_griddata
  if(calculation == "scf") then
    call write_griddata("vks.xsf", Vks)
  else
    call read_griddata("vks.xsf", Vks)
  end if
end program pwdft
```

# Display $v_{KS}(\mathbf{r})$ with VESTA

```
$ cd ~/pwdft/sample/Si/
$ ../../src/pwdft.x < scf.in
$ vesta vks.xsf
```

- Semiconductor
- Diamond structure (lattice is FCC)
- Each Si atom has 4 bonds.

“Objects” → “Properties” → “Isosurfaces...”



Isosurfaces

F(min) = -30.3541; F(max) = 117.654;

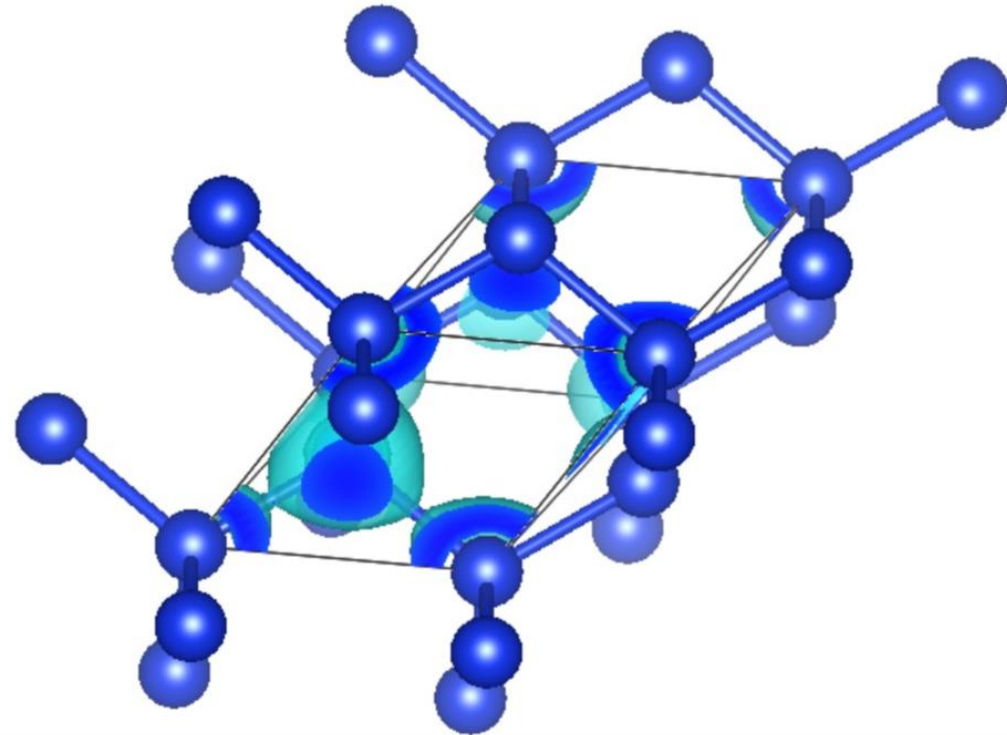
Render from front to back

Positive and negative  Opacity 1 (0~255): 127

Isosurface level: 20  Opacity 2 (0~255): 255

Color: 255  255  0

No.	level	mode	color
1	20	Positive and negative	<input type="button" value="v"/>



# Cross section

Add lattice planes

Miller indices (hkl):

Distance from origin:  Å ( x d)

Color (RGBA):

Calculate the best plane for the selected atoms

No.	h	k	l	d (Å)
1	2	-1	-1	0

New  
Delete  
Clear

"Objects" → "Properties" → "Sections..."

Sections and slices

B-G-R   %

Absolute values

Assign colors recursively

Saturation levels

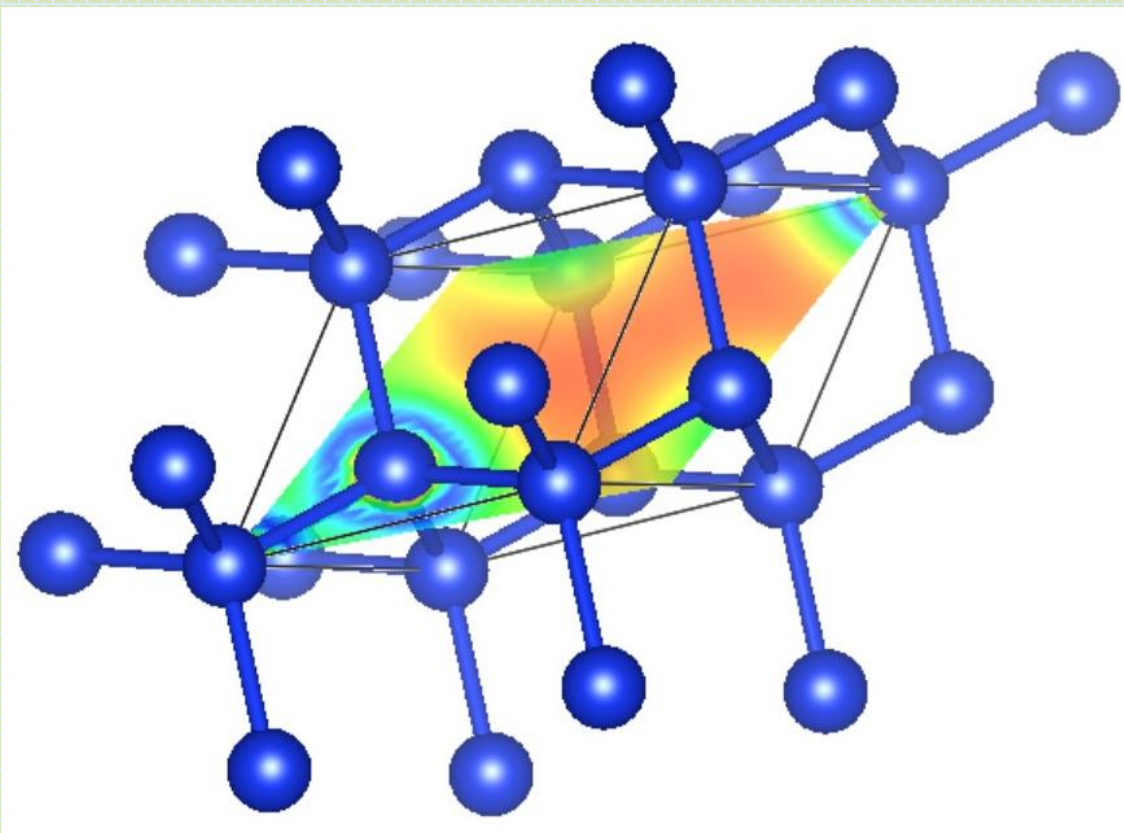
Max.:  ( %)

Min.:  ( %)

Opacity of drawn sections (%):

Cutoff level of lattice plane:

"Edit" → "Lattice Planes..."



# Report problem 2

Modify `pwdft.F90` to output the grid data of charge density  $\rho(\mathbf{r})$  as a file "rho.xsf".

Then plot the charge density of Si.

Explain the shape of  $\rho(\mathbf{r})$  (where do the electrons locate ?).

Hint :  $\rho(\mathbf{r})$  is stored in the following variable

```
module rho_v
!
implicit none
!
real(8),allocatable :: &
& Vks(:), & !< (g_rh%nr) Kohn-Sham potential [Htr]
& Vps(:), & !< (g_rh%nr) Pseudopotential [Htr]
& rho(:) !< (g_rh%nr) Charge density
```

Modified code should be submitted as a diff file generated by

```
$ cd ~/pwdft/
$ git add src
$ git commit
$ git show > 12142018.diff
```



# Today's summary

- Kohn–Sham potential
  - Hartree potential is computed with FFT
  - Charge compensation of Hartree and ionic potential
  - Exchange correlation potential
- SCF loop = Solving non-linear equation
  - Broyden's method
- Visualize grid data (Potential, charge density Kohn–Sham orbital) as a XSF data.