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

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

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

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

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

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

No

Yes

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

Kohn–Sham potential

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

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

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

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

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

Hartree potential (hartree_pot@rho_v.F90)

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

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

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

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

$$v_{\mathrm{H}}(\boldsymbol{r}) = \sum_{G} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}\, \tilde{v}_{\mathrm{H}}(\boldsymbol{G})$$

Periodic atomic potential (generate_vps@rho_v.F90)

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

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

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

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

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

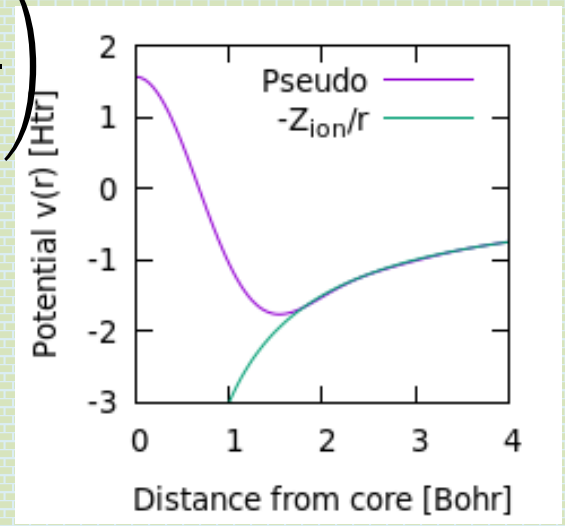
$$v(\boldsymbol{r}) = \sum_{G} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}\, \tilde{v}(\boldsymbol{G})$$

Pseudopotential (generate_vps@rho_v.F90)

$$\tilde{v}_s(\boldsymbol{G}) = 4\pi \int_0^\infty dr\, r^2 \frac{\sin(|\boldsymbol{G}|r)}{|\boldsymbol{G}|r} v_s(r) \qquad v_s(r) = \begin{cases} v_s(r) \text{ Pseudopotential } (r \le r_c) \\ -\dfrac{Z_S}{r} \ (r \ge r_c) \end{cases}$$

$$= 4\pi \left(\int_0^{r_c} dr\, r^2 \frac{\sin(|\boldsymbol{G}|r)}{|\boldsymbol{G}|r} v_s(r) - \int_{r_c}^\infty dr\, r^2 \frac{\sin(|\boldsymbol{G}|r)}{|\boldsymbol{G}|r} \frac{Z_S}{r} \right)$$

$$- \frac{Z_S \cos(|\boldsymbol{G}|r_c)}{|\boldsymbol{G}|^2}$$



Al (Z_{ion}=3)

Conpensation of $\tilde{v}(G=0)$ and $\tilde{v}_{\mathrm{H}}(G=0)$

$$\lim_{\boldsymbol{G}\to 0}\left(\tilde{v}_s(\boldsymbol{G}) + \tilde{v}_{\mathrm{H}}(\boldsymbol{G})\right) \qquad \frac{N_{s,a}}{V_{uc}} \qquad \frac{N}{V_{uc}}$$

$$= 4\pi \lim_{\boldsymbol{G}\to 0} \left[\sum_{s=1}^{N_S} F_s(\boldsymbol{0}) \left(\int_0^{r_c} dr\, r^2 v_s(r) - \frac{Z_S \cos(|\boldsymbol{G}|r_c)}{|\boldsymbol{G}|^2} \right) + \frac{\tilde{\rho}(0)}{|\boldsymbol{G}|^2} \right]$$

$$= 4\pi \sum_{s=1}^{N_S} F_s(\boldsymbol{0}) \left(\int_0^{r_c} dr\, r^2 v_s(r) + \frac{Z_S r_c^2}{2} \right)$$

Exchange-correlation potential in LDA (xc_pot@rho_v.F90)

$$v_{XC}^{LDA}\big(\rho(\boldsymbol{r})\big) = \varepsilon_{XC}\big(\rho(\boldsymbol{r})\big) + \rho(\boldsymbol{r})\frac{d\varepsilon_{XC}(\rho)}{d\rho}\Big|_{\rho=\rho(\boldsymbol{r})} = \varepsilon_{XC}\big(\rho(\boldsymbol{r})\big) - \frac{r_s}{3}\frac{d\varepsilon_{XC}(\rho)}{dr_s}$$

$$\varepsilon_{XC}(\rho) = \varepsilon_X(\rho) + \varepsilon_C(\rho)$$

$$\frac{4\pi}{3}r_s^3 = \frac{1}{\rho}$$

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

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

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

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

Update $v_{KS}(\boldsymbol{r})$

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

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

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

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

$v_{KS,in}(r)$ → $v_{KS,out}(r)$

Plane mixing

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

$$0<\beta\leq 1$$

Broyden's method

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

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

Solve $\boldsymbol{F}(\boldsymbol{v}) = \boldsymbol{0}$

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

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

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

Newton's method

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

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

Minimize $\left|\left(\hat{J}^{-1}_{approx}\right)^{(m)} - \left(\hat{J}^{-1}_{approx}\right)^{(m-1)}\right|^2$

C. G. Broyden, Marh. Compur. **19**, 577 (1965).

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

Practical algorithm (scf_loop@scf.F90)

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

Compute $\boldsymbol{F}(\boldsymbol{v})$

if $|F|^2$ is small → exit

if $m > 1$

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

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

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

end if

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

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

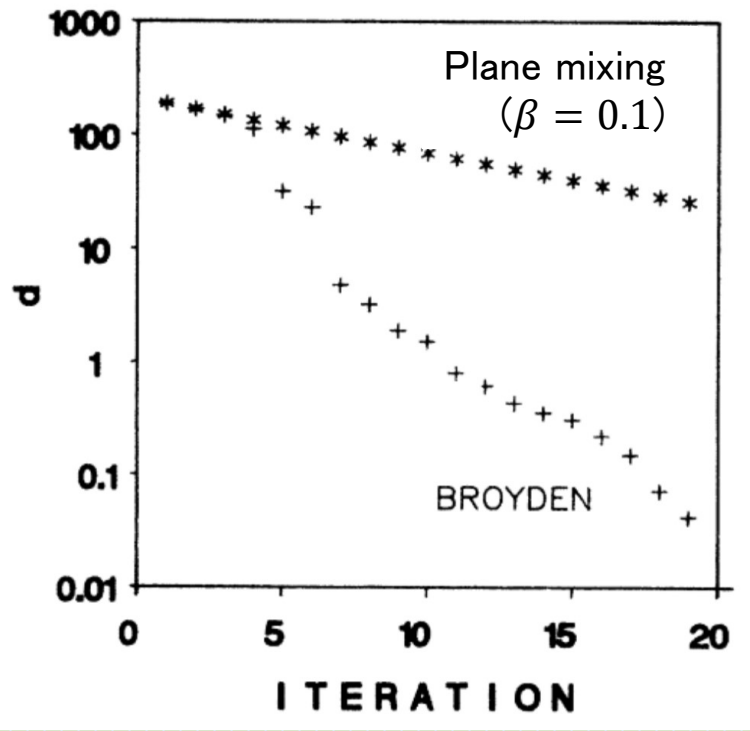
$$\boldsymbol{v} = \boldsymbol{v} + \Delta \boldsymbol{v}$$

end do

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

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

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



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
```

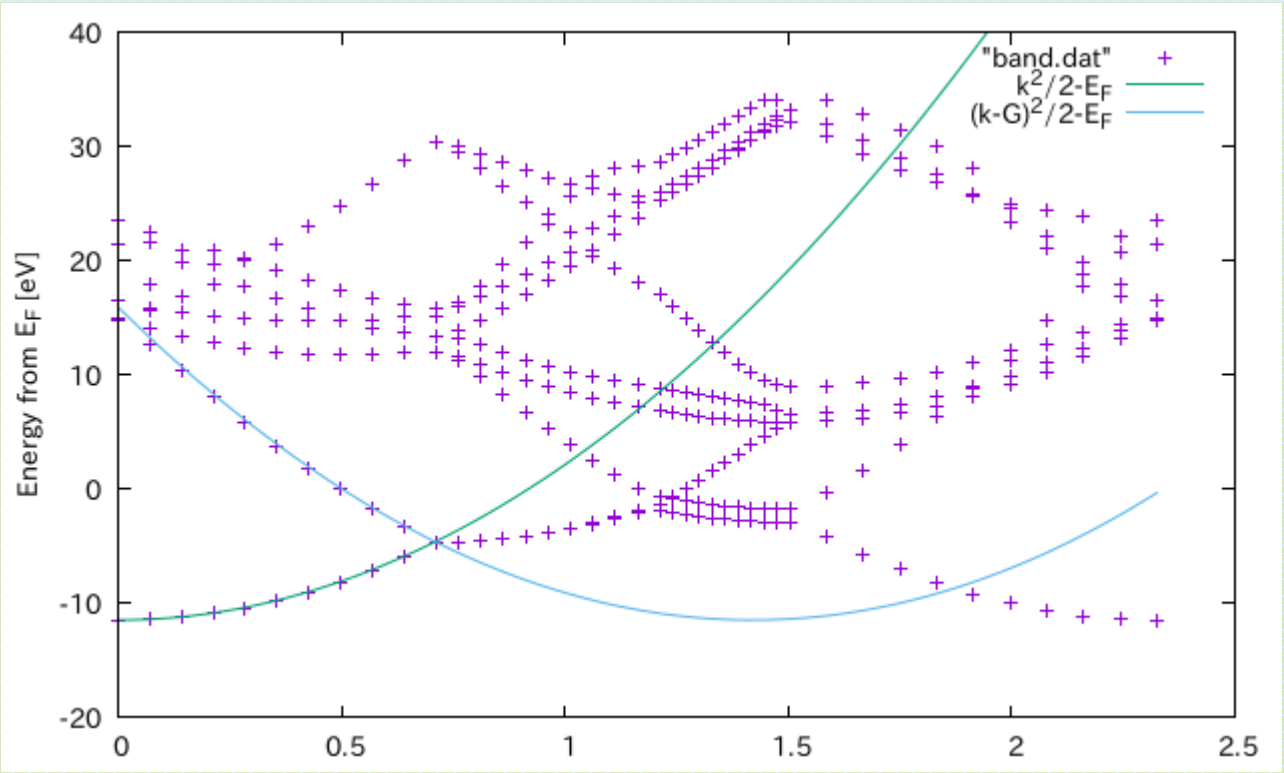
```
   Iteration             1
     Average LOBPCG steps :            20
     delta Vks [eV] :    2.7895180896787383E-003
   Iteration             2
     Average LOBPCG steps :             8
     delta Vks [eV] :    1.9722767387705393E-003
   Iteration             3
     Average LOBPCG steps :             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 $v_{KS}(\boldsymbol{r})$

```
$ ../../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

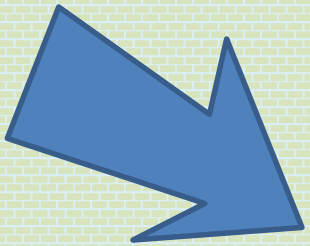
Visualization of grid data

Real-space grid data

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

Reciprocal-space grid data

- Kohn-Sham energy $\varepsilon_{n\boldsymbol{k}}$
- Fermi velocity $\boldsymbol{\nabla_k}\varepsilon_{n\boldsymbol{k}}$
- Berry connection $\langle u_{n\boldsymbol{k}}|i\boldsymbol{\nabla_k}|u_{n\boldsymbol{k}}\rangle$
- Berry curvature $\boldsymbol{\nabla_k} \times \langle u_{n\boldsymbol{k}}|i\boldsymbol{\nabla_k}|u_{n\boldsymbol{k}}\rangle$
- Etc.



- Isosurface
- Section

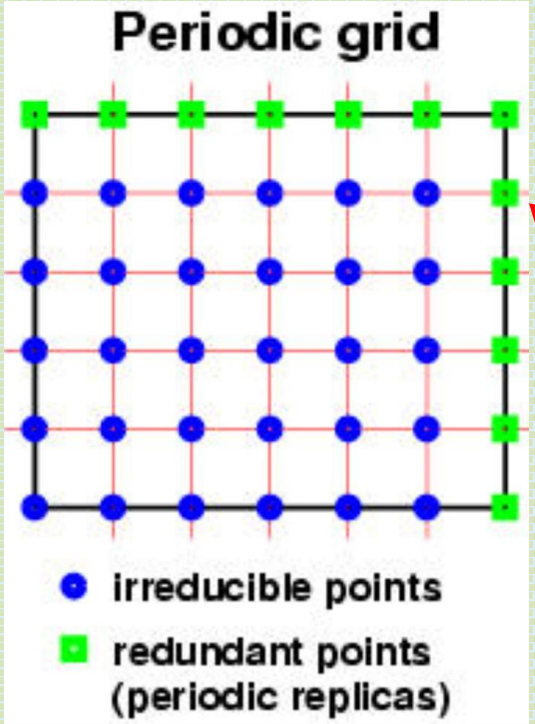
Real space : XSF

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

```
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
Al       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
```

Unit lattice vectors [Å]

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

Atomic position in [Å]
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

Input/Output grid data (griddata.F90)

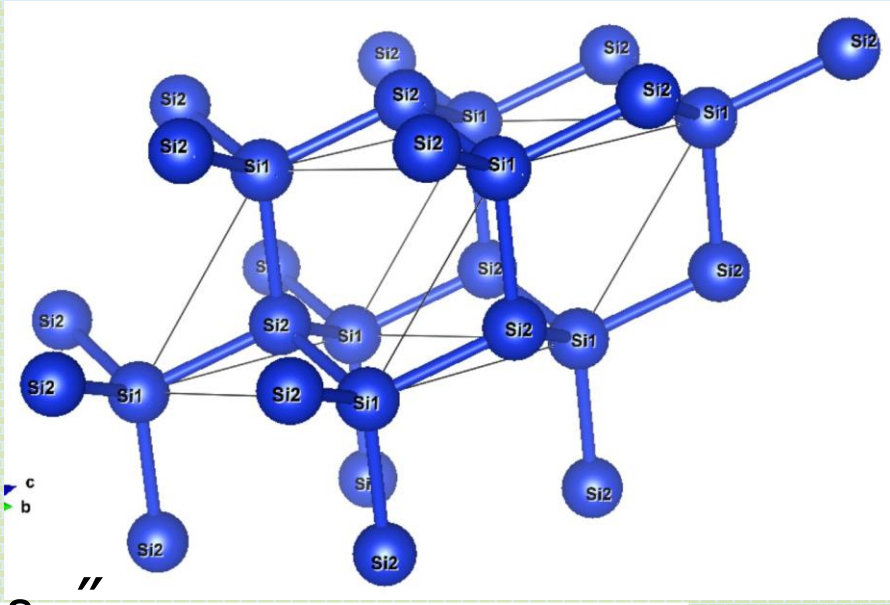
```
module griddata
contains
  subroutine read_griddata(filename, gdata)
    use gvec, only : g_rh
    character(*),intent(in) :: filename
    real(8),intent(out) :: gdata(g_rh%nft(1),g_rh%nft(2),g_rh%nft(3))
  end subroutine read_griddata
  subroutine write_griddata(filename, gdata)
    use gvec, only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

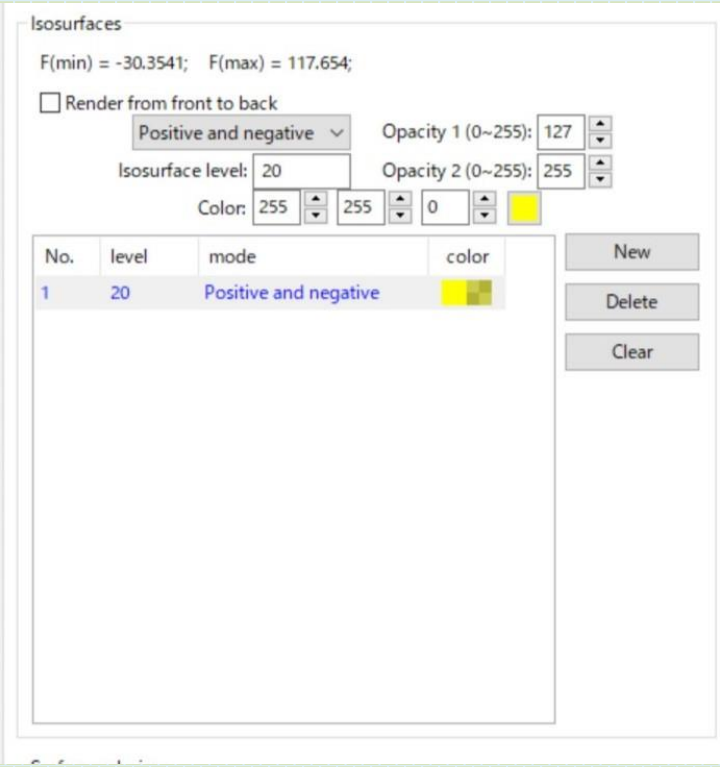
Display $v_{KS}(\boldsymbol{r})$ with VESTA

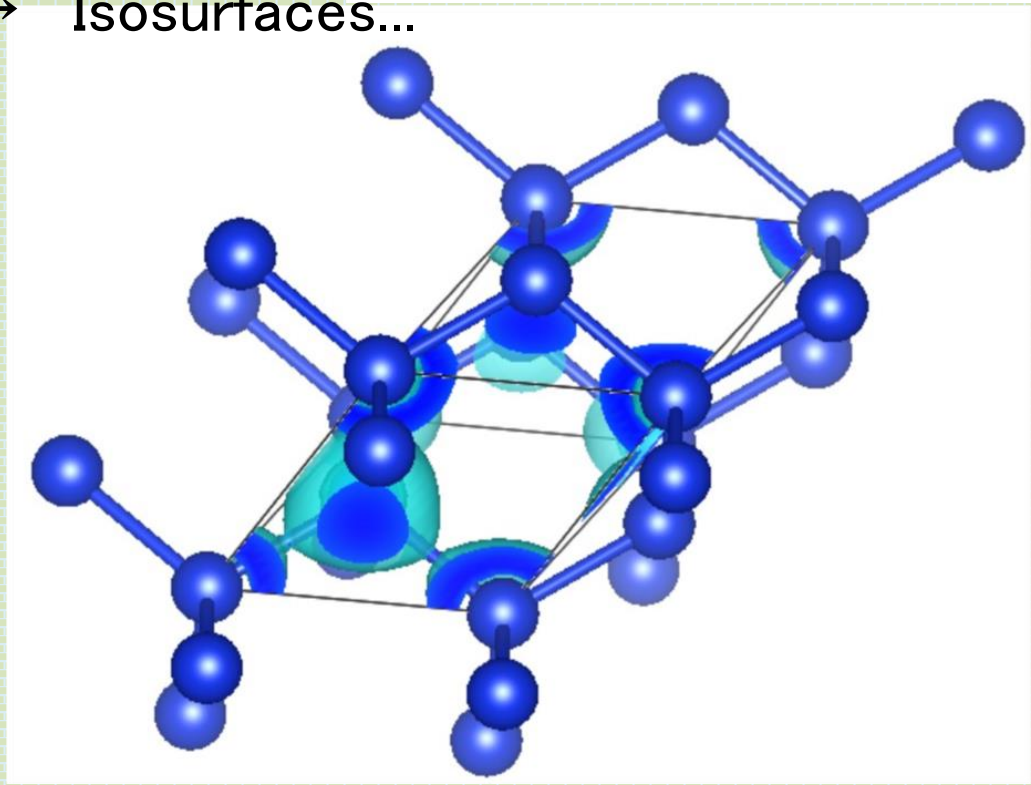
```
$ cd ~/pwdft/sample/Si/
$ ../../src/pwdft.x < scf.in
$ vesta vks.xsf
```



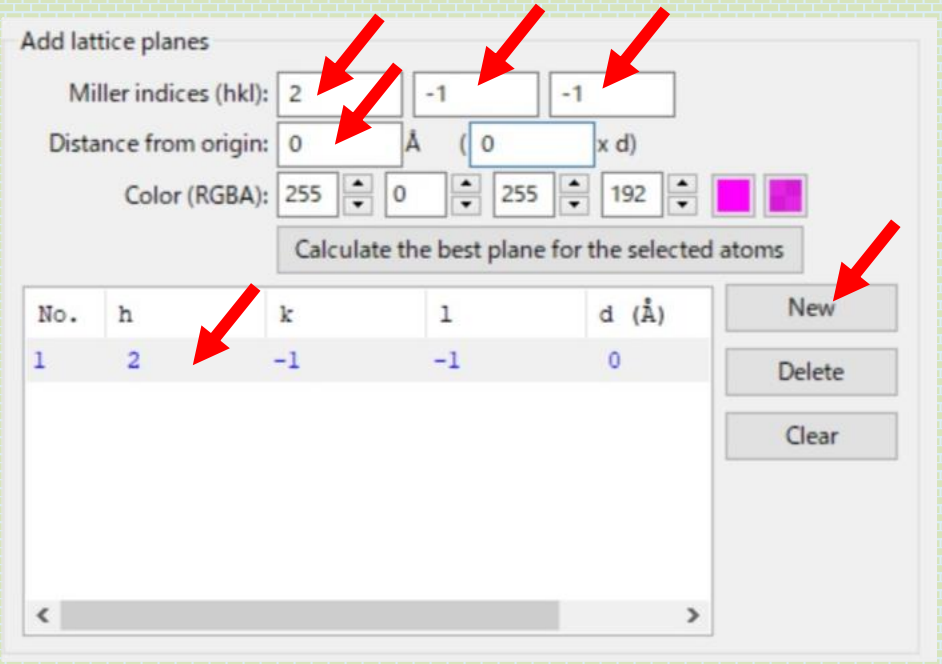
- Semiconductor
- Diamond structure (lattice is FCC)
- Each Si atom has 4 bonds.

"Objects" → "Properties" → "Isosurfaces..."



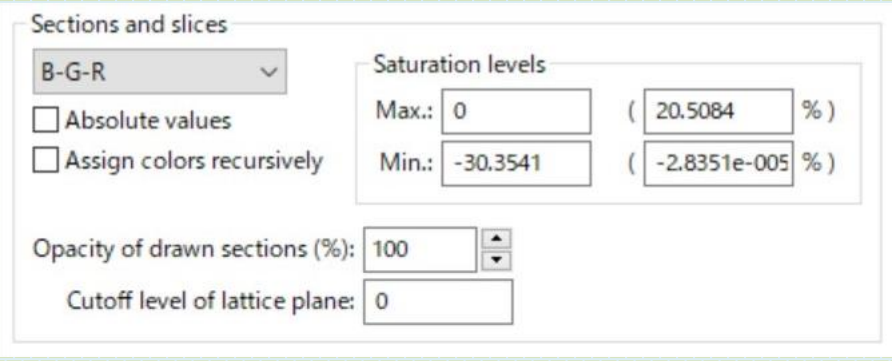


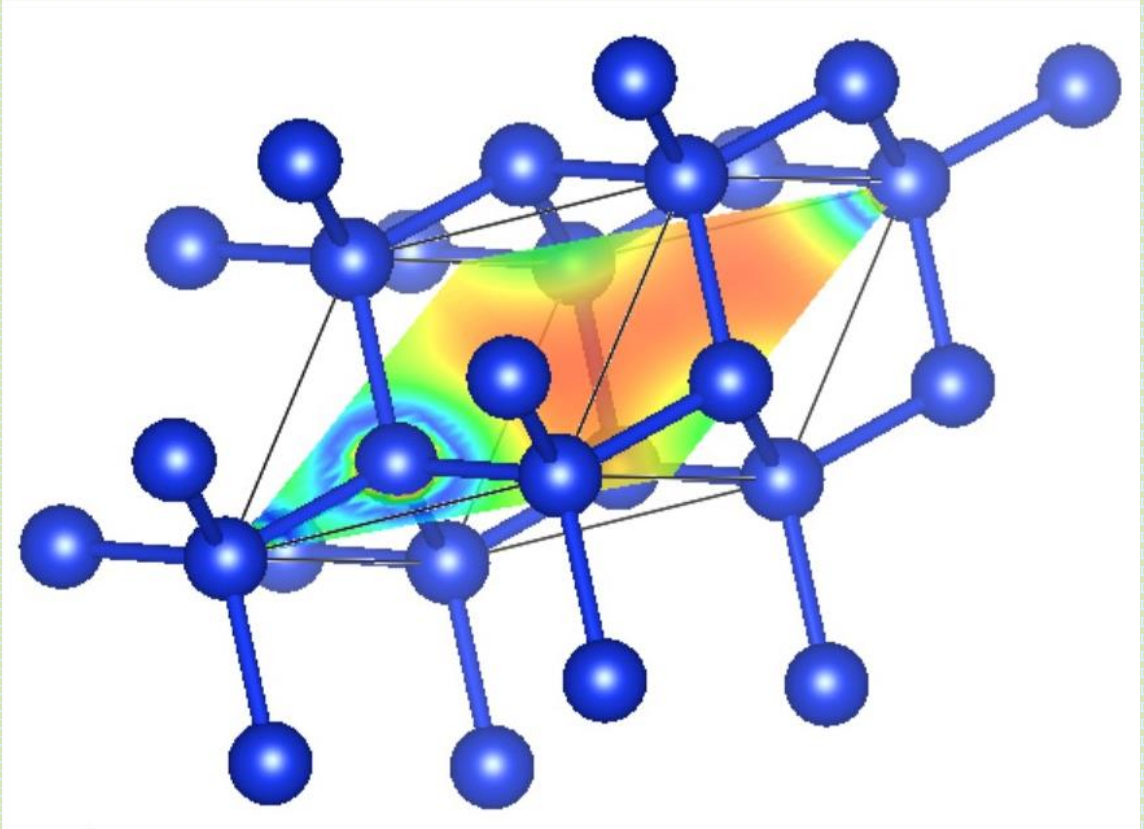
Cross section



"Edit" → "Lattice Planes..."

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





Report problem 2

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

Then plot the charge density of Si.

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

Hint : $\rho(\boldsymbol{r})$ 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.