物質科学のための計算数理 II
Numerical Analysis for Material Science II

9th: Density Functional Theory (2)
Dec. 7 (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) (2nd)Report problem K (遠隔講義室)
13. Jan. 11 (Fri) Density functional theory 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.)
   - Brillouin-zone integral (Tetrahedron method)
   - Visualization (T)
4. Dec. 21 (Fri) Total Energy
   - Coulomb potential for periodic point charge (Ewald sum)
5. Dec. 25 (Tue) (2nd)Report problem K (遠隔講義室)
6. Jan. 11 (Fri) Density functional theory K

Today's Schedule

Kohn-Sham eq. in periodic system
Plane-wave representation
Iterative diagonalization
Matrix-vector product
Kinetic energy term
Potential term
~~Visualize~~

last week

Kohn–Sham method

$$E[\rho] = \int d^3r \rho(\boldsymbol{r})\, v(\boldsymbol{r}) + E_{univ}[\rho] \qquad v(\boldsymbol{r}) \equiv \sum_{I=1}^{N_{\mathrm{atom}}} \frac{Z_I}{|\boldsymbol{r} - \boldsymbol{R}_I|}$$

$$E_{univ}[\rho] = T_{KS}[\rho] + \frac{1}{2}\iint d^3r d^3r' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + E_{XC}[\rho]$$

Kinetic energy of non-interacting system whose charge density is $\rho(\boldsymbol{r})$

$$\left(-\frac{\boldsymbol{\nabla}^2}{2} + v_{KS}[\rho](\boldsymbol{r})\right)\varphi_n(\boldsymbol{r}) = \varepsilon_n \varphi_n(\boldsymbol{r})$$

$$\rho(\boldsymbol{r}) = 2\sum_{n=1}^{N/2} |\varphi_n(\boldsymbol{r})|^2$$

$$v_{KS}[\rho](\boldsymbol{r}) = v(\boldsymbol{r}) + \int d^3r' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + v_{XC}[\rho](\boldsymbol{r}) \qquad v_{XC}[\rho](\boldsymbol{r}) \equiv \frac{\delta E_{XC}[\rho]}{\delta \rho(\boldsymbol{r})}$$

Self-consistent field (SCF)

last week

Kohn–Sham eq. for periodic system (1)

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

$v_{KS}(\boldsymbol{r})$ is periodic,

i.e., $v_{KS}(\boldsymbol{r}+n_1\boldsymbol{a}_1+n_2\boldsymbol{a}_2+n_3\boldsymbol{a}_3)=v_{KS}(\boldsymbol{r})$

Unit lattice vectors

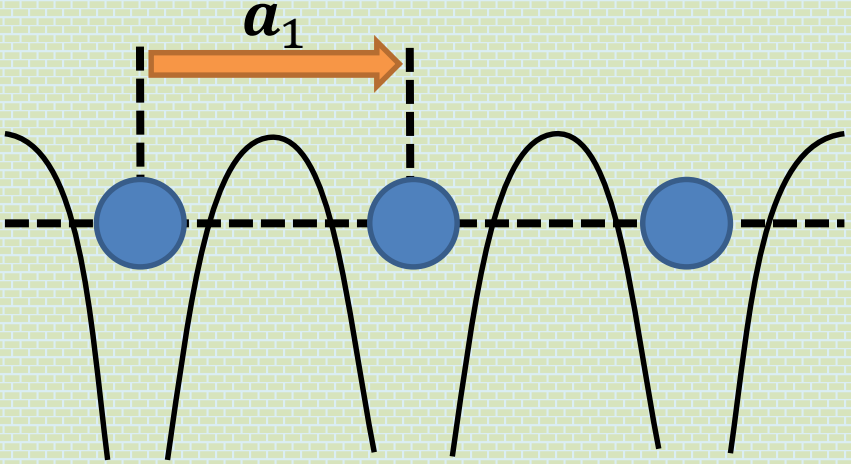
(Not unique)

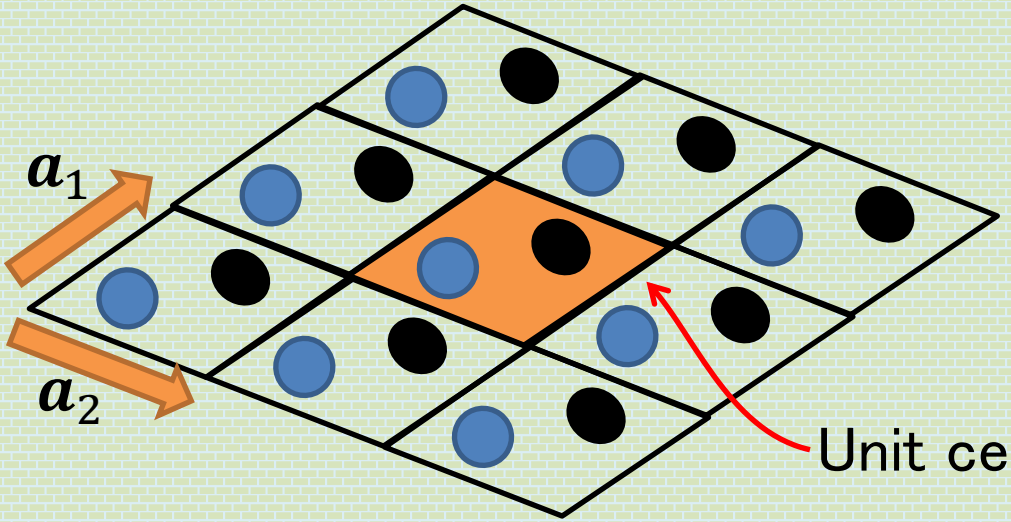
$$\rho(\boldsymbol{r})=\sum_{n=1}^{N\times N_c}|\varphi_n(\boldsymbol{r})|^2$$

N electrons per unit cell

N_c cells $\rightarrow \infty$

Equation to solve in the whole region of bulk crystal





last week

Kohn–Sham eq. for periodic system (2)

$\varphi(\boldsymbol{r})$ can be written as $\varphi(\boldsymbol{r}) = \frac{1}{N_C} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$ Bloch's theorem

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

$$\int_{U.C.} d^3r\rho(r) = N$$

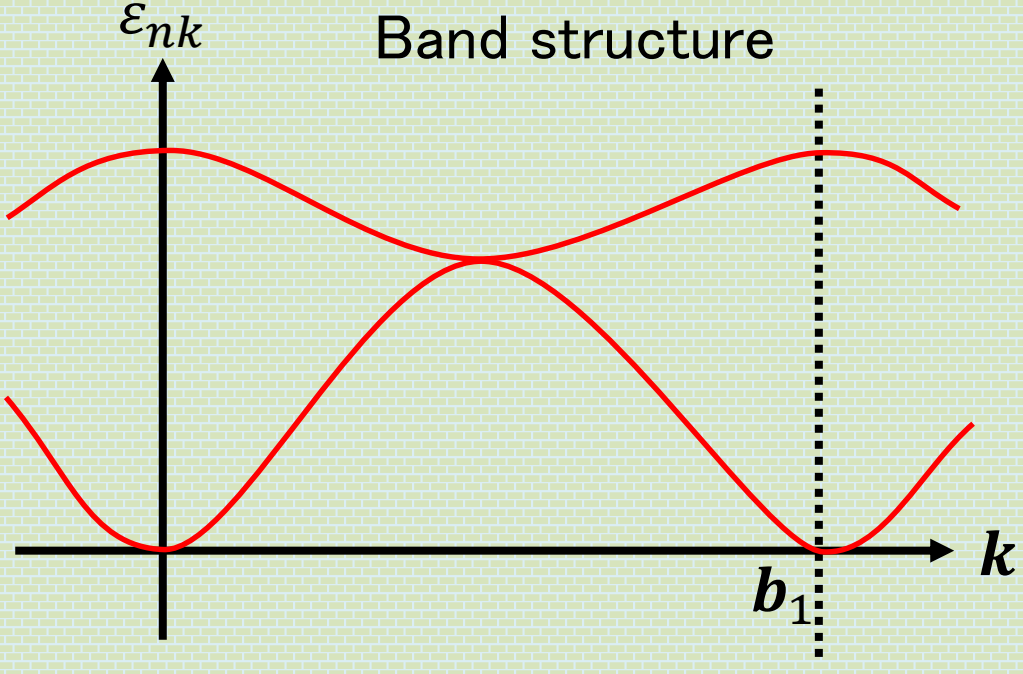
$$\rho(\boldsymbol{r}) = 2\frac{1}{V_{BZ}}\int_{BZ} d^3k \sum_{n=1}^{\infty} |u_{n\boldsymbol{k}}(\boldsymbol{r})|^2\, \theta(\varepsilon_F - \varepsilon_{nk})$$

Equation to solve only in the unit cell

$$\begin{pmatrix}\boldsymbol{a}_1\\ \boldsymbol{a}_2\\ \boldsymbol{a}_3\end{pmatrix}(\boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = 2\pi\hat{I}$$

Unit reciprocal lattice vectors

ε_{nk} and $u_{n\boldsymbol{k}}(\boldsymbol{r})$ is periodic with $\boldsymbol{b}_\alpha$ in the k space.



last week

How to solve Kohn–Sham eq. : Basis

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

$$u_{n\boldsymbol{k}}(\boldsymbol{r})=\sum_{G}\tilde{u}_{n\boldsymbol{k}}(\boldsymbol{G})\frac{e^{i\boldsymbol{G}\cdot\boldsymbol{r}}}{\sqrt{V_{uc}}}$$

$$\sum_{\boldsymbol{G}'}\left(\frac{(\boldsymbol{G}+\boldsymbol{k})^2}{2}\delta_{\boldsymbol{G}\boldsymbol{G}'}+\tilde{v}_{KS}(\boldsymbol{G}-\boldsymbol{G}')\right)\tilde{u}_{n\boldsymbol{k}}(\boldsymbol{G}')=\varepsilon_{nk}\tilde{u}_{n\boldsymbol{k}}(\boldsymbol{G})$$

$$\hat{v}_{KS}(\boldsymbol{G})=\int_{uc}d^3r\frac{e^{-i\boldsymbol{G}\cdot\boldsymbol{r}}}{V_{uc}}v_{KS}(\boldsymbol{r})$$

Unit in this lecture

Input and output :
Length : Angstrom
Energy : Electron volt

Useful to read by VESTA

Inside program code:
Length : Atomic unit (Bohr radius). 1 [Bohr] = 0.529177249 [Å]
Energy : Atomic unit (Hartree). 1 [E_h] = 27.21138456 [eV]

[Bohr^{-1}]

$$\sum_{\boldsymbol{G}'}\left(\frac{(\boldsymbol{G}+\boldsymbol{k})^2}{2}\delta_{\boldsymbol{G}\boldsymbol{G}'}+\tilde{v}_{KS}(\boldsymbol{G}-\boldsymbol{G}')\right)\tilde{u}_{n\boldsymbol{k}}(\boldsymbol{G})=\varepsilon_{n\boldsymbol{k}}\tilde{u}_{n\boldsymbol{k}}(\boldsymbol{G})$$

[E_h]

[E_h]

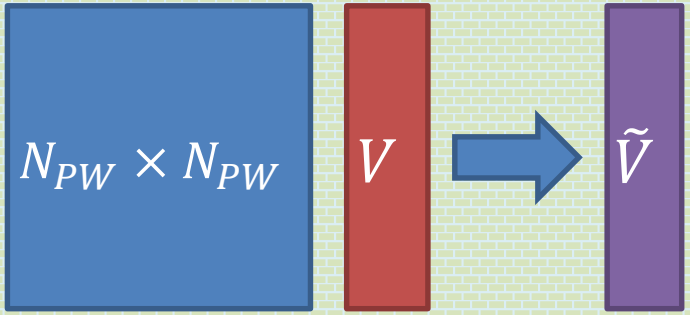
Fourier Transformation

$$\tilde{v}_{KS}(\boldsymbol{G}) = \int_{uc} d^3r \frac{e^{-i\boldsymbol{G}\cdot\boldsymbol{r}}}{V_{uc}} v_{KS}(\boldsymbol{r})$$

Discretize (considering one dimension)

$$\tilde{v}\left(\frac{2\pi}{L}m\right) = \sum_{n=1}^{N_{PW}} \frac{1}{N_{PW}} e^{-i\frac{2\pi}{L}m\times L\frac{n}{N_{PW}}} v\left(L\frac{n}{N_{PW}}\right) \quad N_{PW} \to \infty : \text{Exact}$$

$$m = -\frac{N_{PW}}{2}, \cdots, -1, 0, 1, \cdots, \frac{N_{PW}}{2}$$



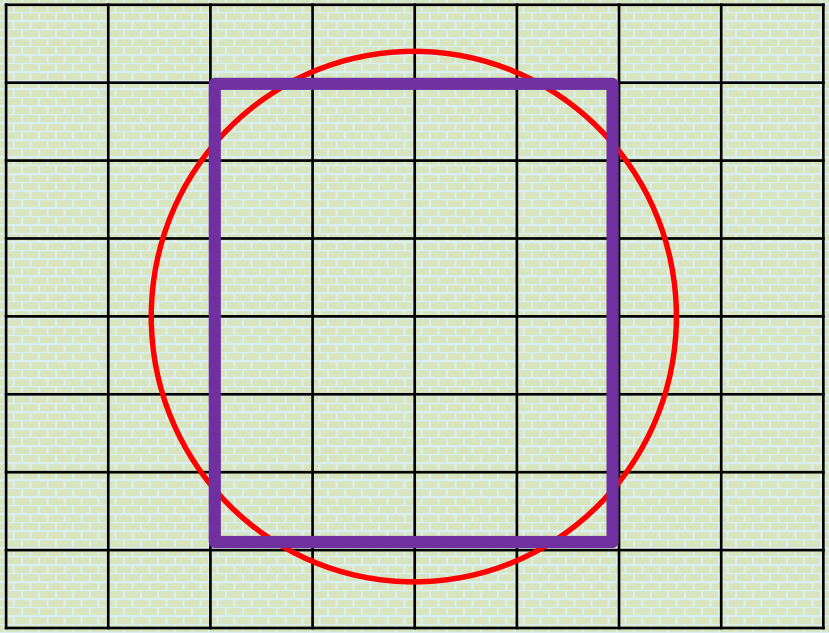
$O(N_{PW}^2)$ numerical cost

Fast Fourier Transformation (FFT) : $O(N_{PW} \ln N_{PW})$ numerical cost

We do not detail in this lecture. We just use FFT numerical library.

Cutoff frequency

$$u_{nk}(\boldsymbol{r}) = \sum_{\boldsymbol{G}}^{\frac{|\boldsymbol{G}|^2}{2}<E_{cut}} \tilde{u}_{nk}(\boldsymbol{G}) \frac{e^{i\boldsymbol{G}\cdot\boldsymbol{r}}}{\sqrt{V_{uc}}}$$



$$\tilde{u}\left(\frac{2\pi}{L}(N_{PW}-m)\right) = \sum_{n=1}^{N_{PW}} \frac{1}{N_{PW}} e^{-i2\pi\frac{n(N_{PW}-m)}{N_{PW}}} V\left(L\frac{n}{N_{PW}}\right) = \tilde{V}\left(-\frac{2\pi}{L}m\right)$$

Very simple plane-wave DFT program

```
$ cd ~
$ git clone git://git.osdn.net/gitroot/educational-pwdft/pwdft.git
$ cd pwdft
$ cp make.inc.mac make.inc
$ make
$ cd sample/Al/
$ ../../src/pwdft.x < direct.in
```

```
&CONTROL
 calculation = 'direct'
/
&SYSTEM
nbnd = 10
         nat = 1
        ntyp = 1
     ecutwfc = 60.000000
     ecutrho = 240.000000
/
&ELECTRONS
/
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
1
0.0 0.0 0.0
```

Aluminum

- Face centered cubic (fcc)
- Metal
- Almost free electron
- keep
  "ecutrho" ≧ 4*ecutwfc

Only perform first SCF step

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

Initial density is uniform

direct@diag_direct.F90

http://mitsuaki1987.github.io/pwdft/index.html

```
lwork = -1
allocate(work(1))
call zheev('V', 'U', npw, ham, npw, eval_full, work, lwork, rwork, info)
lwork = nint(dble(work(1)))
deallocate(work)
allocate(work(lwork))
call zheev('V', 'U', npw, ham, npw, eval_full, work, lwork, rwork, info)
deallocate(work)
```

Workspace (memory size) query : Do not need to care.

Diagonalize Hamiltonian matrix "ham"

Computational cost : $O(N_{PW}^3)$

Memory size : $O(N_{PW}^3)$

Changing "ecutrho" and "ecutwfc"
and see "Kohn-Sham Time" in Standard output

keep ecutrho $\geqq$ 4*ecutwfc

Large numerical cost for large N_{PW}

We only need lower energy (occupied) band.

Locally Optimal Block Preconditioned Conjugate Gradient (LOBPCG) method

One of the iterative eigen solution methods

A. V. Knyazev, SIAM J. Sci. Compute. 23, 517 (2001).

山田進 他, 日本計算工学会論文集, 20060027 (2006).

For computing N_b eigenvector, at each step

Approx. eigenvector $\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots \boldsymbol{x}_{N_b}$

Residual vector $\{\boldsymbol{w}_i = \hat{H}|\boldsymbol{x}_i\rangle - \varepsilon_i|\boldsymbol{x}_i\rangle\}$

CG vector $\boldsymbol{p}_1, \boldsymbol{p}_2, \cdots \boldsymbol{p}_{N_b}$

Construct subspace Hamiltonian ($3N_b$ dim.)

$$\begin{pmatrix} \{\boldsymbol{x}_i^\dagger\} \\ \{\boldsymbol{w}_i^\dagger\} \\ \{\boldsymbol{p}_i^\dagger\} \end{pmatrix} \hat{H}(\{\boldsymbol{x}_i\}, \{\boldsymbol{w}_i\}, \{\boldsymbol{p}_i\})$$

Diagonalize with direct method

Take lowest N_b vectors as approximate eigenvectors at next step

Loop until all $\{|r_i\rangle\}$ become smaller than the threshold

Computational cost : $O\left(\alpha N_b^3 + \beta N_b N_{PW} \ln N_{PW} + \gamma N_b^2 N_{PW}\right)$

Memory : $O(N_b N_{PW})$

Algorithm of LOBPCG method
lobpcg_main@lobpcg.F90

Initial guess $\{\boldsymbol{x}_i\}$ (Random or atomic) $\{\boldsymbol{p}_i\}=\boldsymbol{0}$ $\{\boldsymbol{P}_i\}=\boldsymbol{0}$

$\{\boldsymbol{X}_i=\hat{H}\boldsymbol{x}_i\}$ $\{\varepsilon_i=\boldsymbol{X}_i^{\dagger}\boldsymbol{x}_i\}$

do iteration

$\{\boldsymbol{w}_i=\boldsymbol{X}_i-\varepsilon_i\boldsymbol{x}_i\}$ All $|\boldsymbol{w}_i|$ are small enough ? → Exit

$\{\boldsymbol{w}_i=\hat{P}\boldsymbol{w}_i\}$

$\{\boldsymbol{w}_i=\boldsymbol{w}_i/|\boldsymbol{w}_i|\}$

$\{\boldsymbol{W}_i=\hat{H}\boldsymbol{w}_i\}$

$\hat{H}_{sub}=(\{\boldsymbol{W}_i\},\{\boldsymbol{X}_i\},\{\boldsymbol{P}_i\})^{\dagger}(\{\boldsymbol{w}_i\},\{\boldsymbol{x}_i\},\{\boldsymbol{p}_i\})$

$\hat{O}_{sub}=(\{\boldsymbol{w}_i\},\{\boldsymbol{x}_i\},\{\boldsymbol{p}_i\})^{\dagger}(\{\boldsymbol{w}_i\},\{\boldsymbol{x}_i\},\{\boldsymbol{p}_i\})$

Solve $\hat{H}_{sub}x_{i,sub}=\varepsilon_{i,sub}x_{i,sub}$ Take lowest N_b : $\{x_{i,sub}\}_{low}$

$(\{\boldsymbol{x}_i\})=(\{\boldsymbol{w}_i\},\{\boldsymbol{x}_i\},\{\boldsymbol{p}_i\})\left(\{x_{i,sub}\}_{low}\right)$ $(\{\boldsymbol{p}_i\})=(\{\boldsymbol{w}_i\},\{\boldsymbol{0}\},\{\boldsymbol{p}_i\})\left(\{x_{i,sub}\}_{low}\right)$

$(\{\boldsymbol{X}_i\})=(\{\boldsymbol{W}_i\},\{\boldsymbol{X}_i\},\{\boldsymbol{P}_i\})\left(\{x_{i,sub}\}_{low}\right)$ $(\{\boldsymbol{P}_i\})=(\{\boldsymbol{W}_i\},\{\boldsymbol{0}\},\{\boldsymbol{P}_i\})\left(\{x_{i,sub}\}_{low}\right)$

$\{\boldsymbol{x}_i=\boldsymbol{x}_i/|\boldsymbol{x}_i|\}$ $\{\boldsymbol{X}_i=\boldsymbol{X}_i/|\boldsymbol{X}_i|\}$ $\{\boldsymbol{p}_i=\boldsymbol{p}_i/|\boldsymbol{p}_i|\}$ $\{\boldsymbol{P}_i=\boldsymbol{P}_i/|\boldsymbol{P}_i|\}$

end do iteration

Hamiltonian vector product
h_psi@hamiltonian.F90

$$\{\boldsymbol{W}_i = \hat{H}\boldsymbol{w}_i\}$$

$$\hat{\mathrm{H}}\tilde{u}(\boldsymbol{G}) = \left(-\frac{(\boldsymbol{G}+\boldsymbol{k})^2}{2} + \hat{v}_{KS}\right)\tilde{u}(\boldsymbol{G})$$

$$\hat{v}_{KS}\tilde{u}(\boldsymbol{G}) = \int_{uc} d^3r \frac{e^{-i\boldsymbol{G}\cdot\boldsymbol{r}}}{\sqrt{V_{uc}}} v_{KS}(\boldsymbol{r})u(\boldsymbol{r})$$

$$\approx \sum_{\boldsymbol{r}} \frac{\sqrt{V_{uc}}}{N_{\boldsymbol{r}}} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} v_{KS}(\boldsymbol{r})u(\boldsymbol{r})$$

$$u_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \tilde{u}_{n\boldsymbol{k}}(\boldsymbol{G}) \frac{e^{i\boldsymbol{G}\cdot\boldsymbol{r}}}{\sqrt{V_{uc}}}$$

Done in subroutine hpsi in hamiltonian.F90

Running iterative method

```
$ cd ~/pwdft/sample/Al/
$ ../../src/pwdft.x < iterative.in
```

See "Kohn-Sham Time" in Standard output

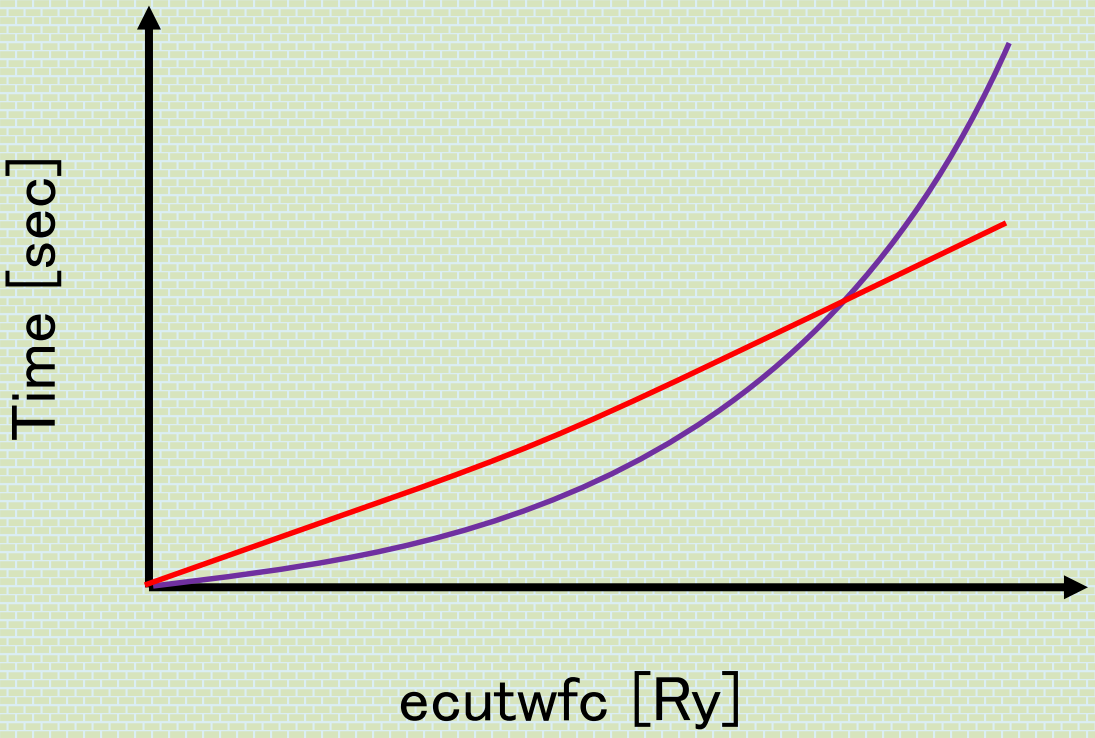
keep ecutrho ≧ 4*ecutwfc

```
&CONTROL
 calculation = 'iterative'
/
&SYSTEM
nbnd = 10
         nat = 1
        ntyp = 1
     ecutwfc = 60.000000
     ecutrho = 240.000000
/
&ELECTRONS
/
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
1
0.0 0.0 0.0
```

Report problem 1

(1) Compare the computational time of direct method and LOBPCG method by changing ecutrho and ecutwfc.

keep ecutrho $\geqq$ 4*ecutwfc



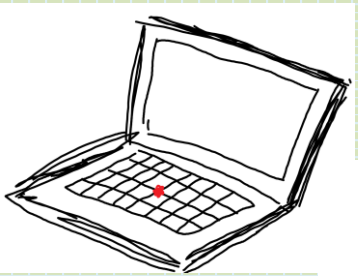
(2) Plot the cutoff-energy dependence of Kohn-Sham energy ε_{nk} for $k = (0,0,0)$ and $n = 1,2$ (they are outputted to a file band.dat).

What is the command "git"

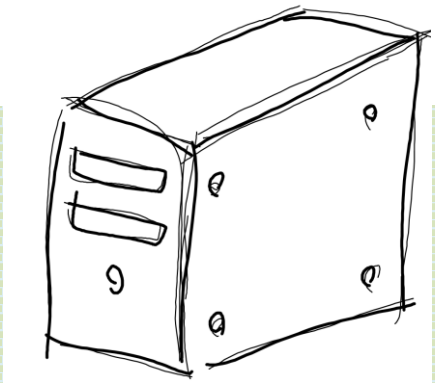
```
$ git clone ssh://user-name@133.11.72.58:/home/Student/Public/pwdft
```

- Backup code
- Port program in any system
- Merge modifications
- Compare diff
- Log each modification with comment
- Etc.

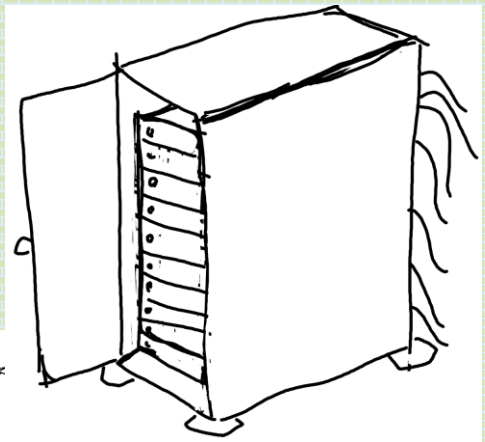
Considered case 1



Laptop PC

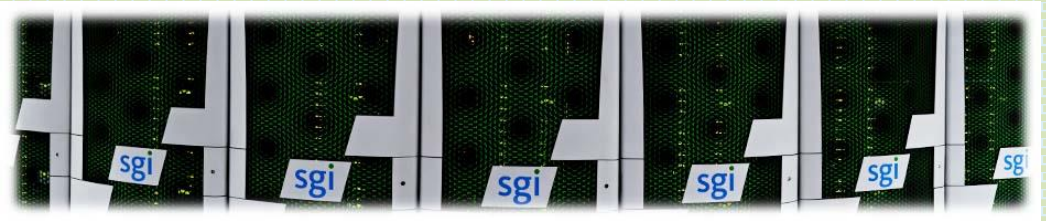


Labo PC



PC cluster

System C

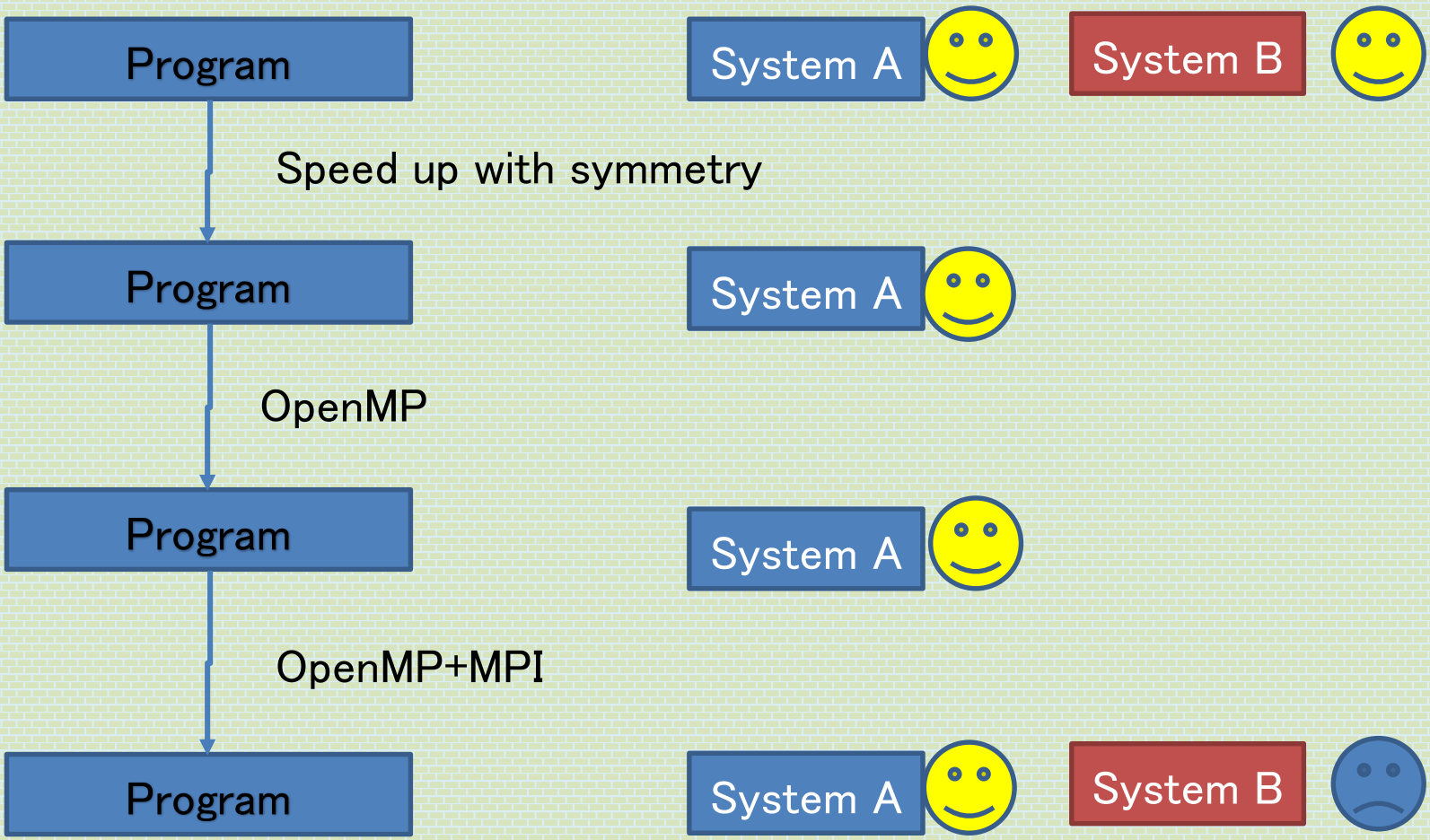


System B

Home PC

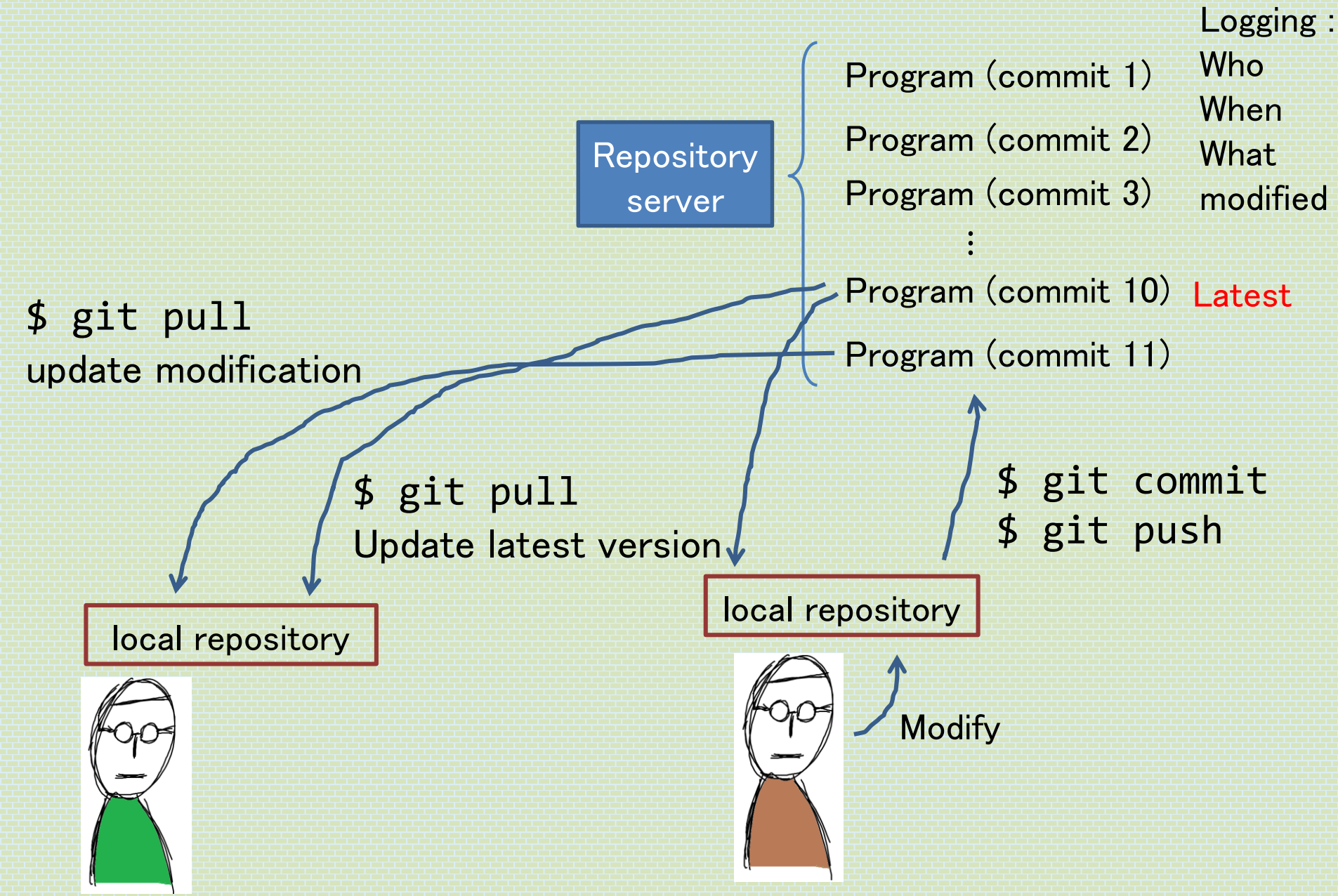
- Where is the latest source code ?
- We need to update source code easily.

Considered case 2

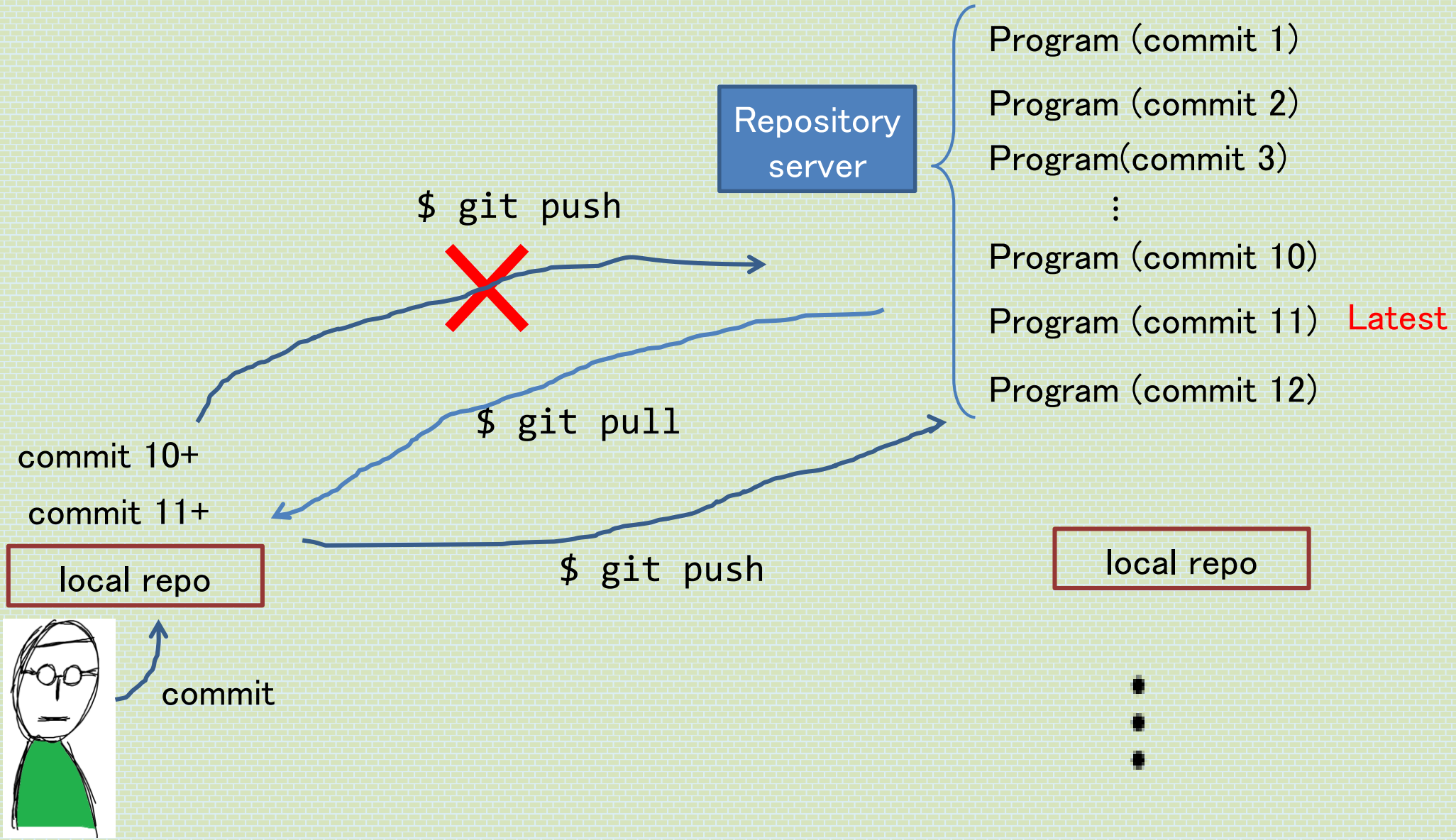


- We need to trace when was it broken.
- We need to be available to return the stable (no error) code.

Version control



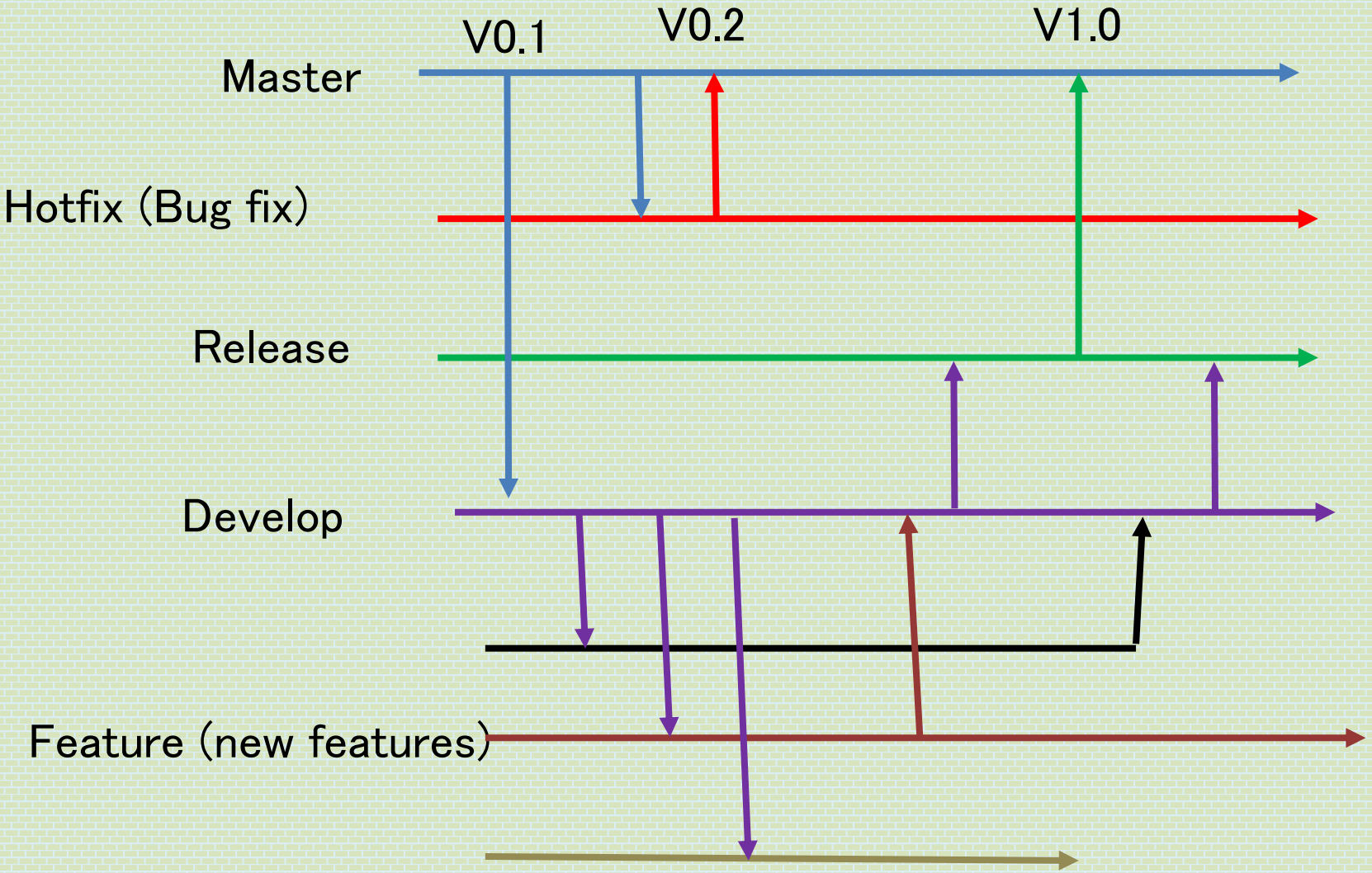
When modified simultaneously



Tutorial

```
$ cd ~/pwdft/
$ git branch -a
$ git config --global user.name "user-name"
$ git config --global user.email "user-name@bkks"
$ git checkout -b user-name
$ echo "Hello, I am user-name." > user-name.txt
$ git add user-name.txt
$ git commit  (vi is used)
$ git push --set-upstream origin user-name
$ git branch -a
```

Example of branches



"A successful branch in git"

Today's summary

- Plane-wave representation of Kohn-Sham eq.
- Direct method and LOBPCG method
- Hamiltonian-vector product with FFT
- Git