Simulasi Material dengan Quantum Espresso

QUASI One Day Workshop

02 Agustus 2021

EDI SUPRAYOGA

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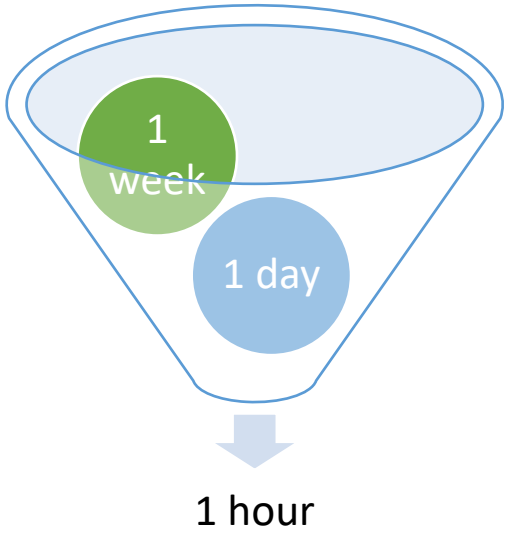
QUAntum design and Simulation Laboratory

Pusat Penelitian Fisika

Lembaga Ilmu Pengetahuan Indonesia



Introduction to QE

Materials Theory & Computation Research Group

Subgrup: High-Energy Physics

- HPC and Instrumentation
- Experimental Particle Physics

Suharyo

Agmal

Jauhar

Subgrup: Condensed Matter Physics

- Electronic Structure Calculation,
- Catalysts, Battery, Thermoelectrics

Ferensa

Hesky

Yusrul

Ridwan

Edi

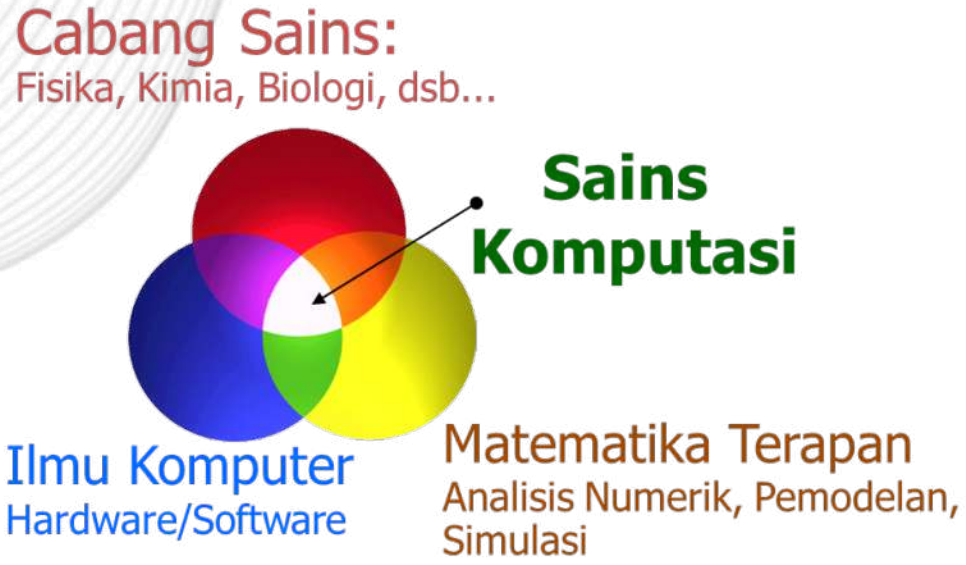
Gagus

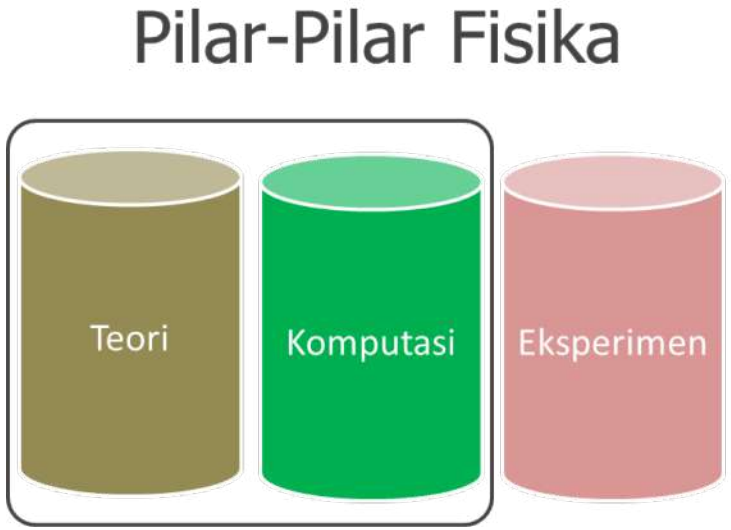
Arman

Shoufie

Dita

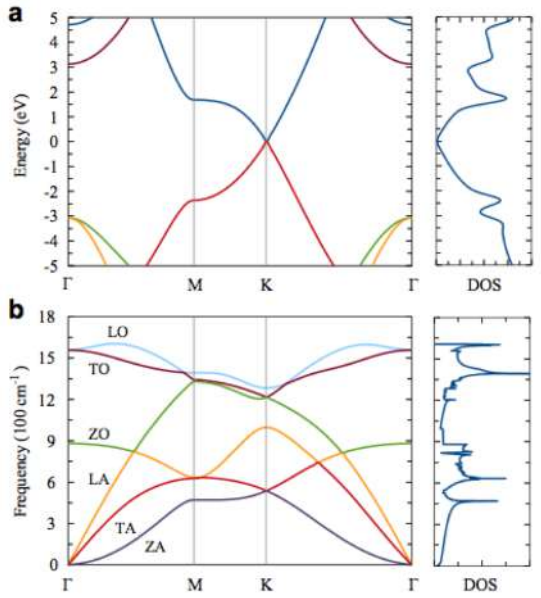
Mengapa “teori & komputasi”?



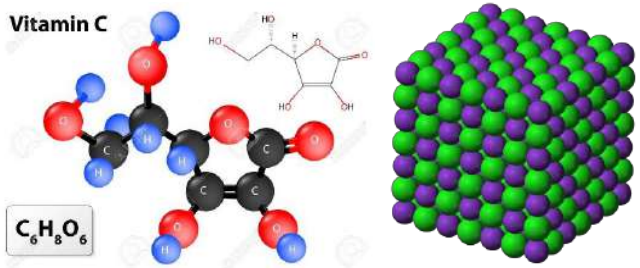


- Teori dan komputasi adalah 2 dari 3 pilar utama fisika
- Hanya membutuhkan pensil, kertas, komputer, dan ide
- Perangkat prediktif ketika eksperimen sulit dilakukan

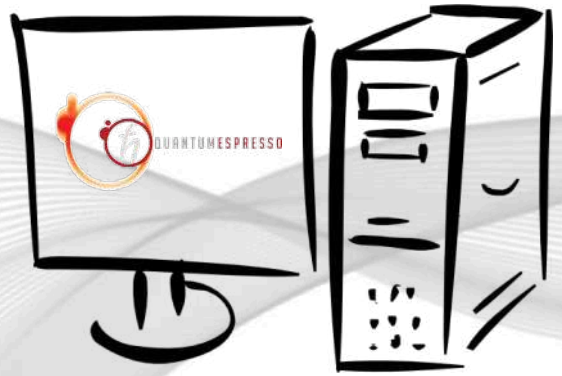
Design Material



New structure prediction

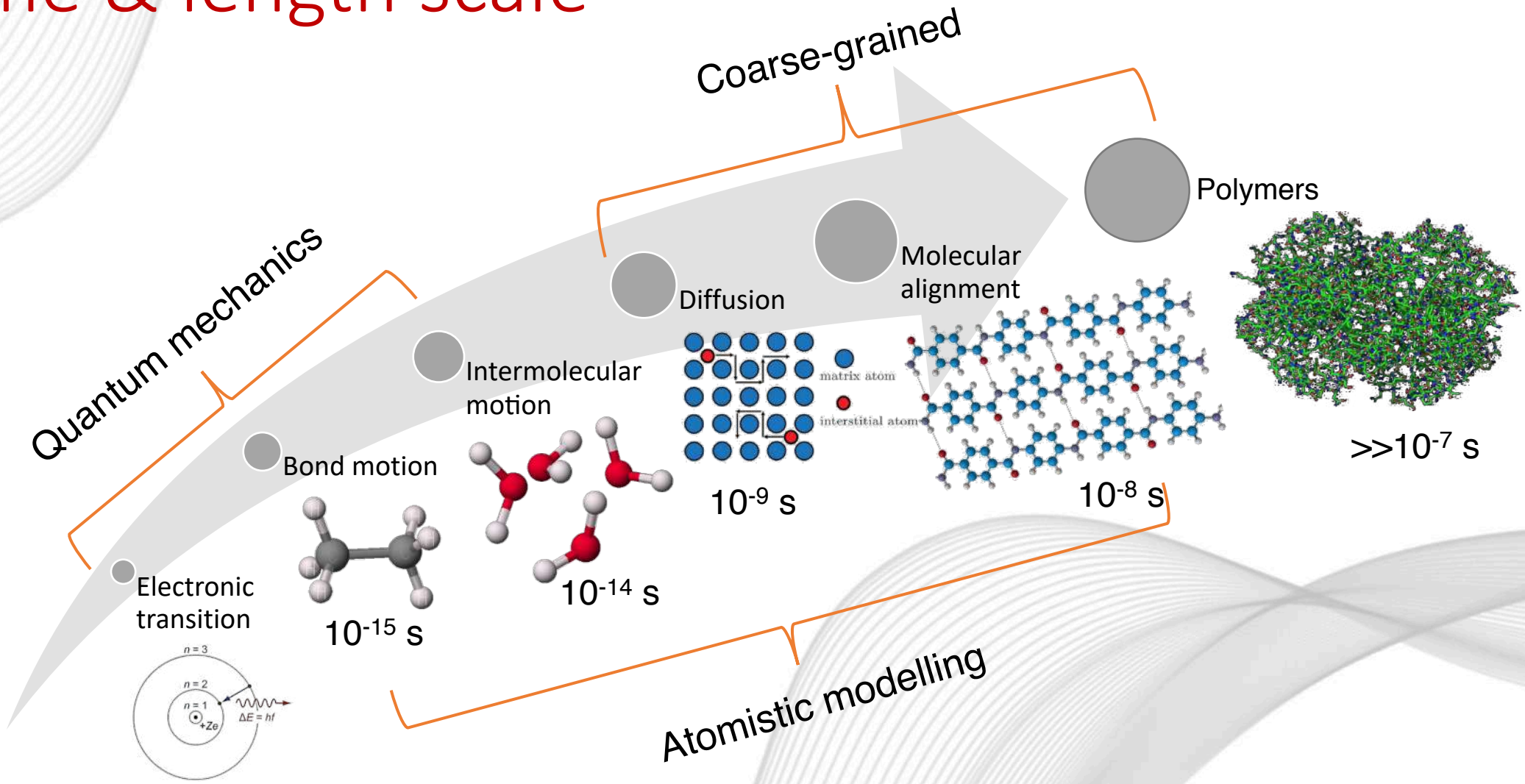


Quantum simulation



Properties analysis

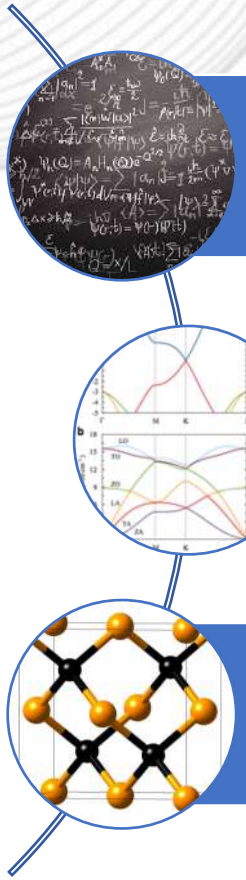
Time & length scale



Timeline of DFT methods

1964	Hohenberg–Kohn theorem and Kohn–Sham formulation
1972	Relativistic extension of density functional theory
1980	Local density approximation (**LDA**) for exchange and correlation
1984	Time-dependent density functional theory (**TD-DFT**)
1985	First-principles molecular dynamics (**MD**)
1986	Quasiparticle corrections for insulators
1987	Density functional perturbation theory (**DFPT**)
1988	Towards quantum chemistry accuracy
1991	Hubbard-corrected density functional theory (**DFT+U**)
1996	The generalized gradient approximation (**GGA**)

First-principles calculation



Based on quantum mechanics

Initially to calculate electronic structure

Now can predict the properties of materials

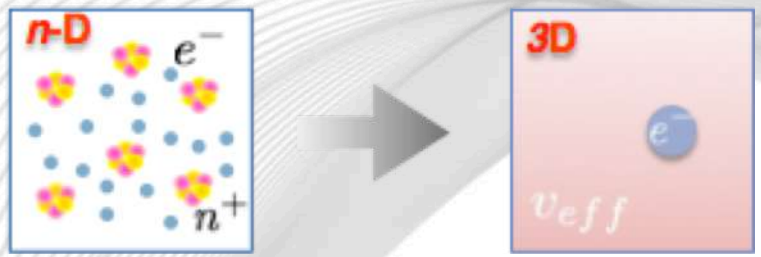
Solve Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H[n(r)] + V_{XC}[n(r)]\right]\psi_i(r) = \varepsilon_i\psi_i(r)$$

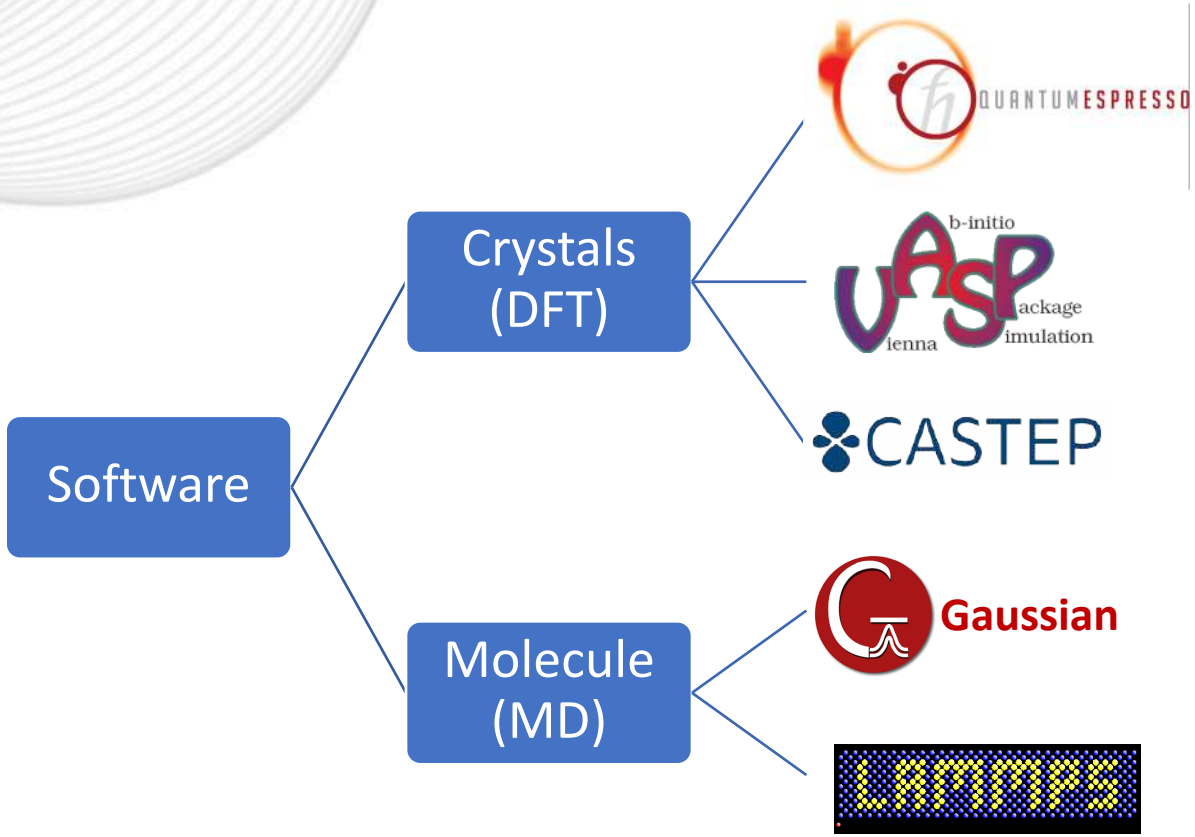
External nuclear potential

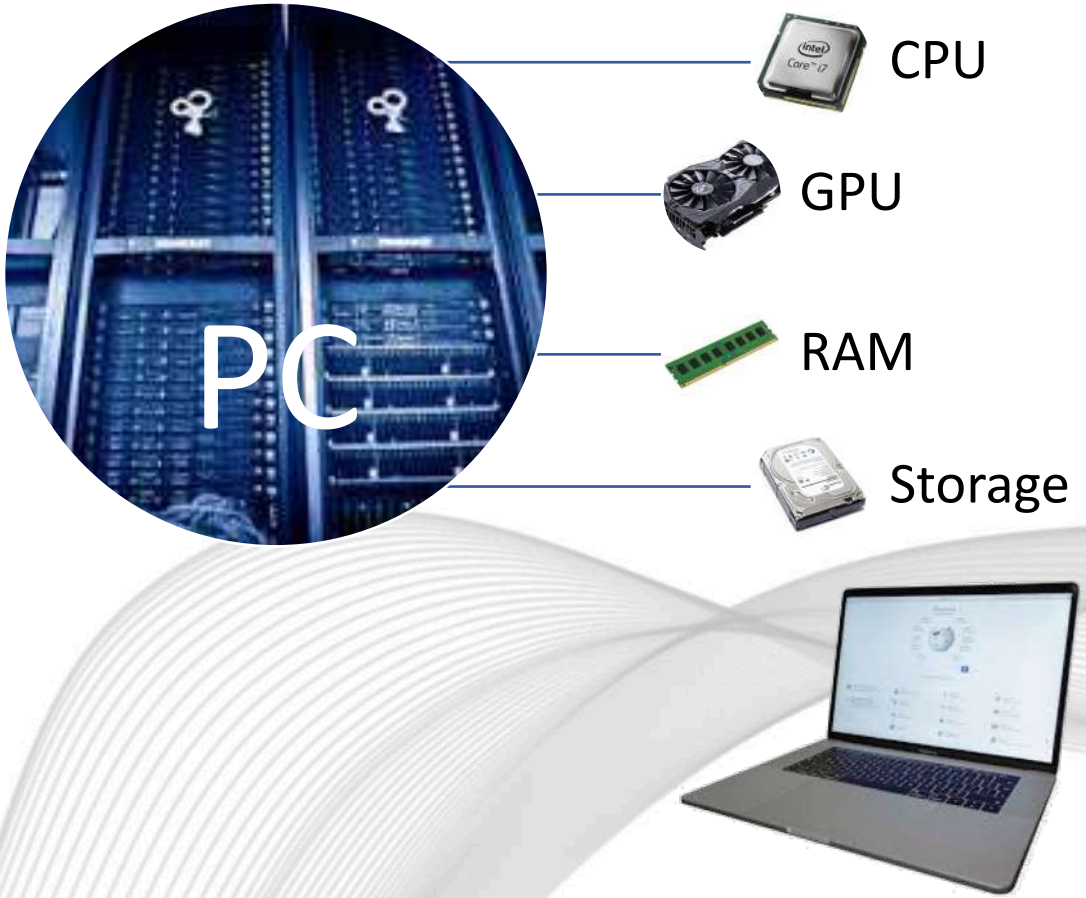
Hartree potential

Exchange-correlation potential



DFT tools


Software
Crystals (DFT)
Molecule (MD)
QUANTUMESPRESSO
b-initio
VASP
ienna
ackage
imulation
CASTEP
Gaussian
LAMMPS


PC
CPU
GPU
RAM
Storage

Why is DFT so popular?

- **Mudah ditransfer**

  Kode atau metode DFT yang sama dapat dipakai untuk material yang berbeda
- **Sederhana**

  Persamaan Kohn-Sham menyederhanakan Persamaan Schrödinger untuk elektron banyak
- **Reliabel**

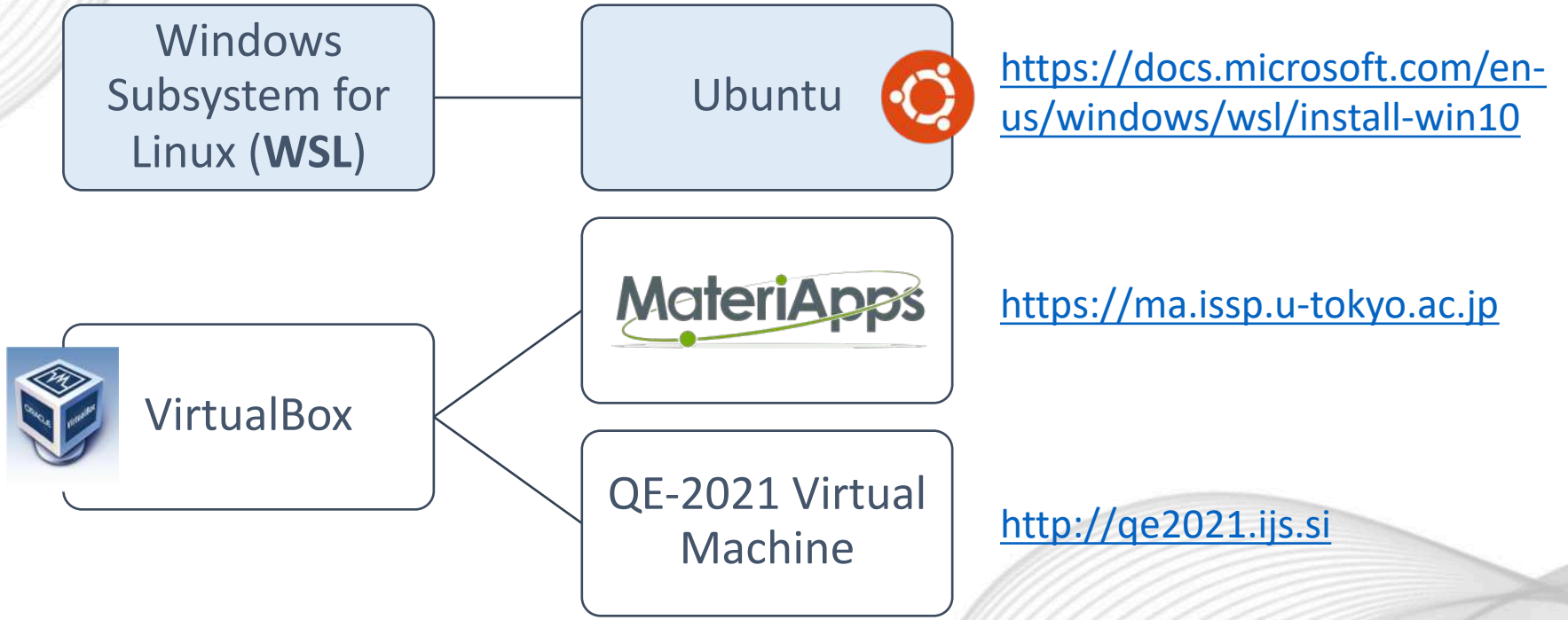
  Dapat memprediksi properti material dengan akurasi tinggi hingga bahkan sebelum eksperimen
- **Mudah dibagikan**

  DFT telah menjadi perusahaan global (pengembangan software dengan kolaborasi global dan open source)
- **Platformnya kokoh**

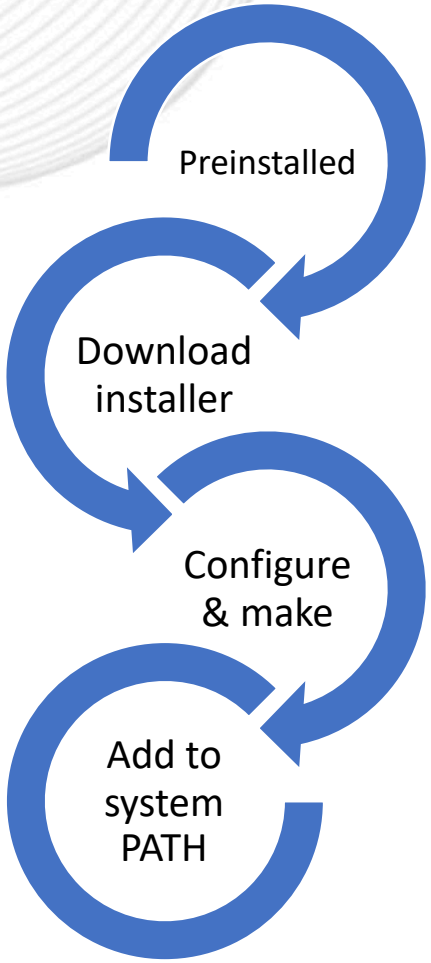
  Sering kali kelemahan pada DFT dapat diatasi dengan mengembangkan metode yang lebih kompleks, tetapi tetap berdasar pada DFT. Contoh: Metoda GW

QE Installation

QE installation on Windows



QE installation on Ubuntu




```
$ sudo apt install build-essential gfortran libopenmpi-dev
$ sudo apt install libblas-dev liblapack-dev libfftw3-dev
```

```
$ wget https://github.com/QEF/q-e/archive/qe-6.8.0.tar.gz
$ tar -zxvf qe-6.7.0.tar.gz
```

```
$ cd qe-6.8
$ ./configure
$ make all
```

Try your self:

```
$ make w90
$ make epw
$ make yambo
```

```
$ export PATH=$PATH:/home/username/qe-6.8/bin/
```

Useful Resources

- **How to obtain CIF File**
  - AFLOW (http://aflowlib.org)
  - Materials Project (https://materialsproject.org)
- **How to generate QE Input**
  - PWgui (http://www-k3.ijs.si/kokalj/pwgui/)
  - BURAI (https://nisihara.wixsite.com/burai)
  - Materials Cloud (https://www.materialscloud.org/home)
- **How to Running QE**
  - AiiDA (https://www.materialscloud.org/work/aiidalab)
  - Exabyte (https://exabyte.io)
  - HPC LIPI (https://hpc.lipi.go.id)

Tools

- **Text editor**
  - Notepad++
  - Gedit, Emacs, dll..
- **Graph plot**
  - Gnuplot
  - Origin, Excel
- **Crystal visualization**
  - VESTA
  - XCrysden

QE INPUT

Kohn-Sham equations

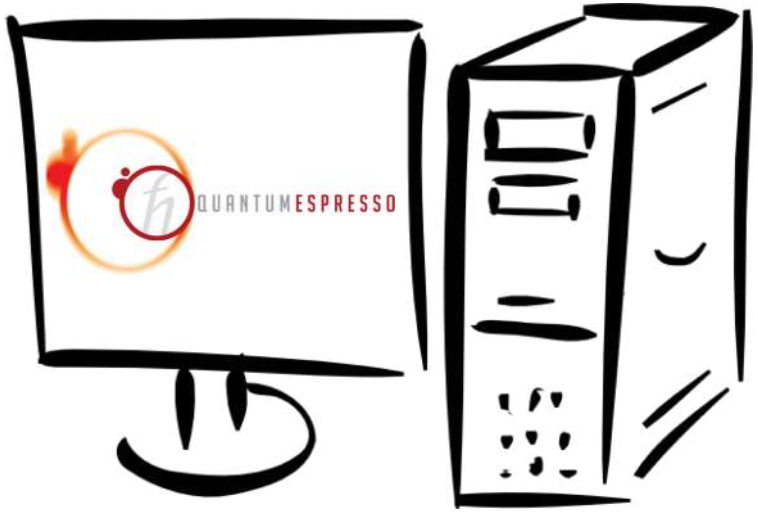
INPUT

Model:
unit cell
lattice vectors
basis

Physical approx:
xc-approximation
GGA, LDA, …

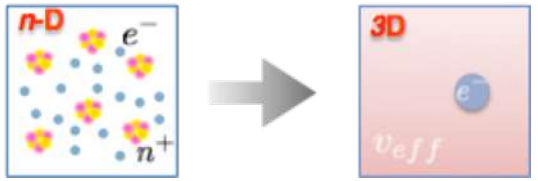
Numerical approx:
energy cut-off
k-points grid
SCF procedure

RUN



OUTPUT

Physical quantities:
charge density
total energy
KS wavefunctions
KS energies



Solve Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H[n(r)] + V_{XC}[n(r)] \right] \psi_i(r) = \varepsilon_i \psi_i(r)$$

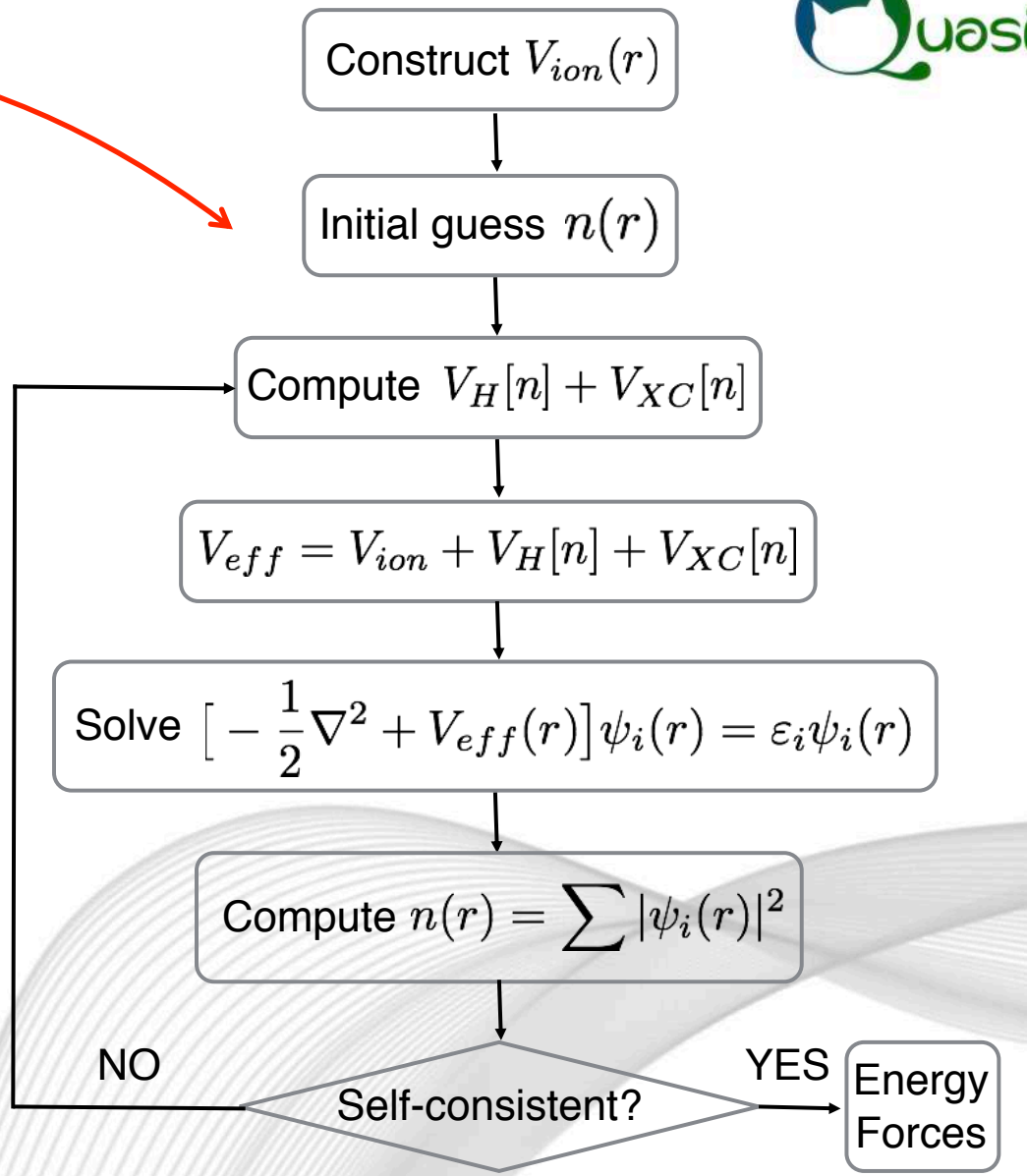
External nuclear potential

Hartree potential

Exchange-correlation potential

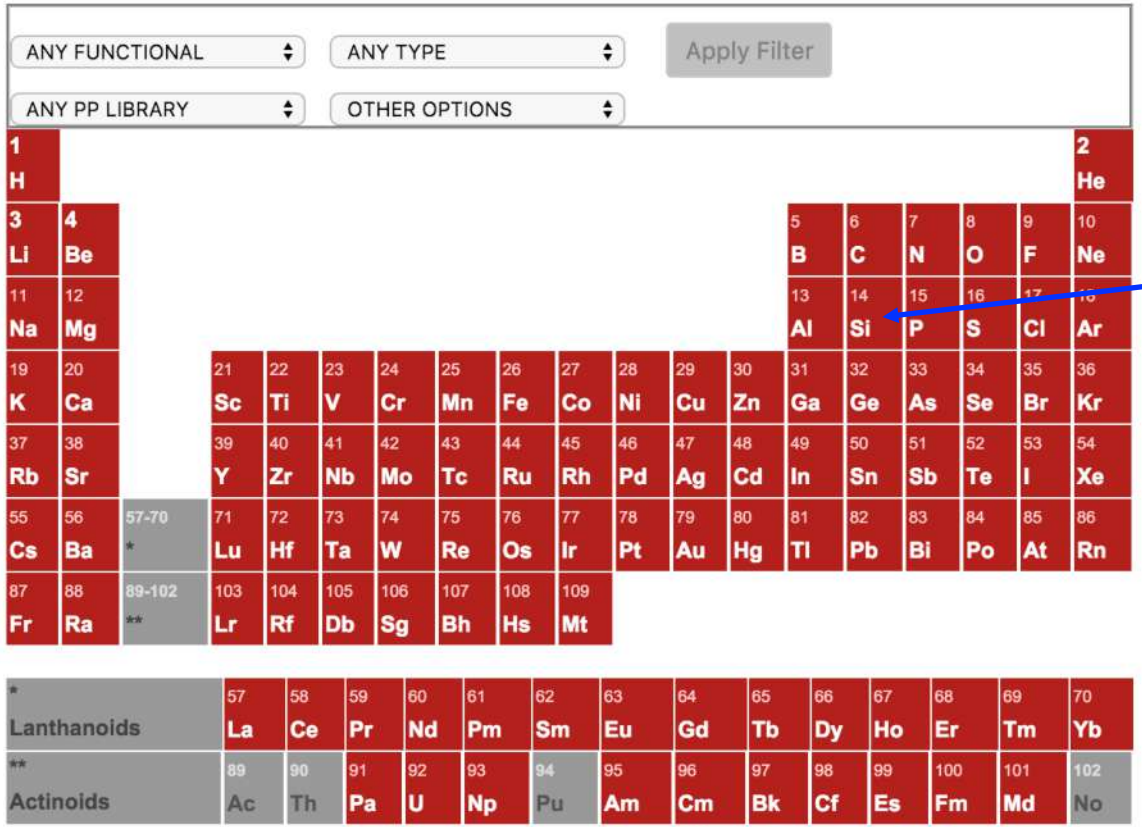
Structure of QE input file

```
&CONTROL
 calculation='scf',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../tmp/',
/
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 ecutrho=720.0,
/
&ELECTRONS
 mixing_beta=0.7,
 conv_thr=1d-8,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```



How to get pseudopotential

http://www.quantum-espresso.org/pseudopotentials/



PSEUDO SEARCH RESULTS

Pseudopotential File

Si.blyp-hgh.UPF

```
Pseudopotential type: NORMCONS
Method: Goedecker-Hartwigsen-Hutter-Teter
Functional type: Becke-Lee-Yang-Parr (BLYP) exch-corr
non relativistic

Origin: Hartwigsen-Goedeker-Hutter PP
Author: Goedecker/Hartwigsen/Hutter/Teter
Generated in analytical, separable form. Converted from CPMD format using cpmd2upf v.5.0.1.
Uploaded by marsamos
Classification unverified
```

Si.pbe-rrkj.UPF

```
Pseudopotential type: NORMCONS
Method: Rappe Rabe Kaxiras Joannopoulos
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
scalar relativistic

Origin: Original QE PP library
Author: Andrea Dal Corso
Generated by Andrea Dal Corso code (rrkj3)
Uploaded by Erica Vidal
Classification controlled by Paolo Giannozzi
```

Si.pbe-van_gipaw.UPF

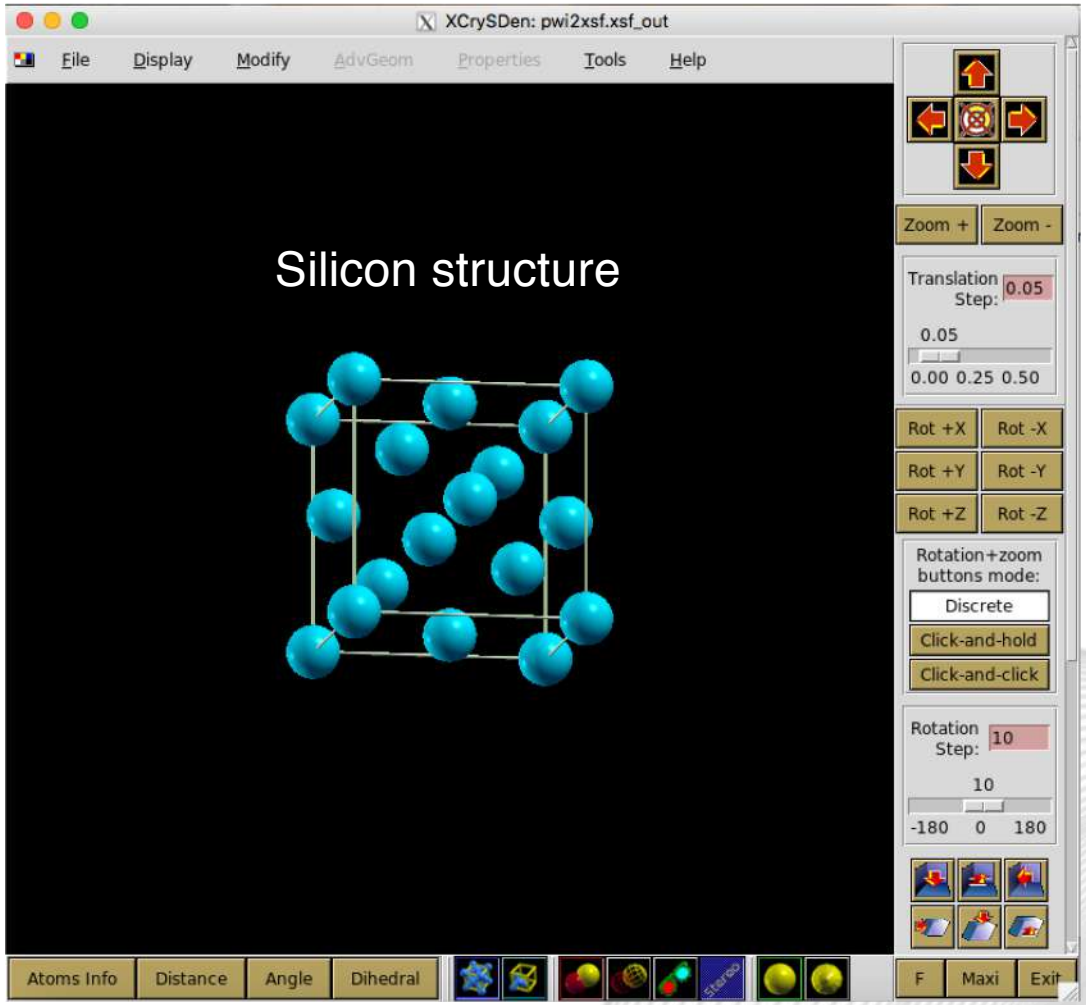
```
Pseudopotential type: ULTRASOFT
Method: Rappe Rabe Kaxiras Joannopoulos
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
Is Gipaw
scalar relativistic

Origin: Original QE PP library
Generated by "atomic" code by A. Dal Corso (QE distribution)
Uploaded by Erica Vidal
Classification controlled by Paolo Giannozzi
```

Si.pbe-rrkj.UPF

- type of exchange-correlation functional
- type of pseudopotential

How to check the structure

XCrySDen: http://www.xcrysden.org



QUANTUM ESPRESSO CONVERGENCY

HANDS-ON #1

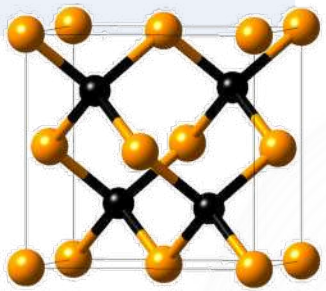
QE Convergency

- Basic self consistent calculation (**scf**)
- Convergence of total energy & plane waves cut-off (**ecut**)
- Convergence of total energy & BZ sampling (**k-point**)
- Lattice constant (**vc-relax**)

SCF

- Ecut
- K-point

vc-relax

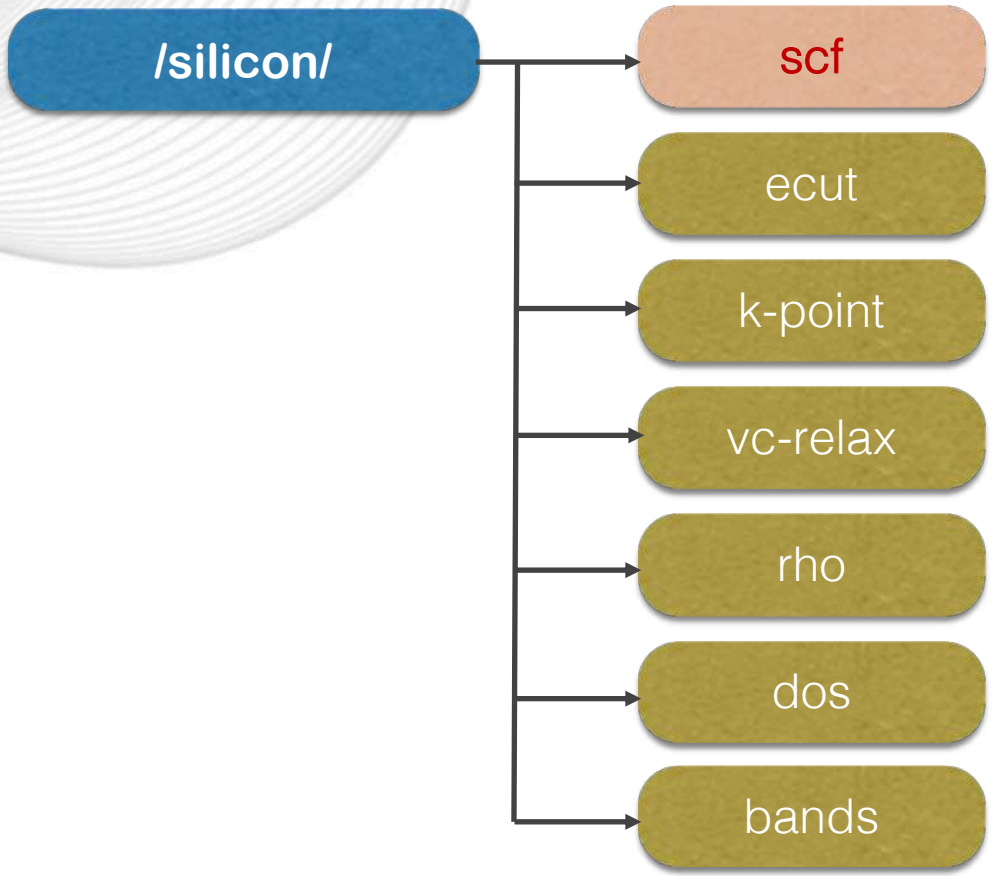
- 

nscf

- Bands
- DOS
- Wavefunction
- …

SCF

Files for self consistent calculation



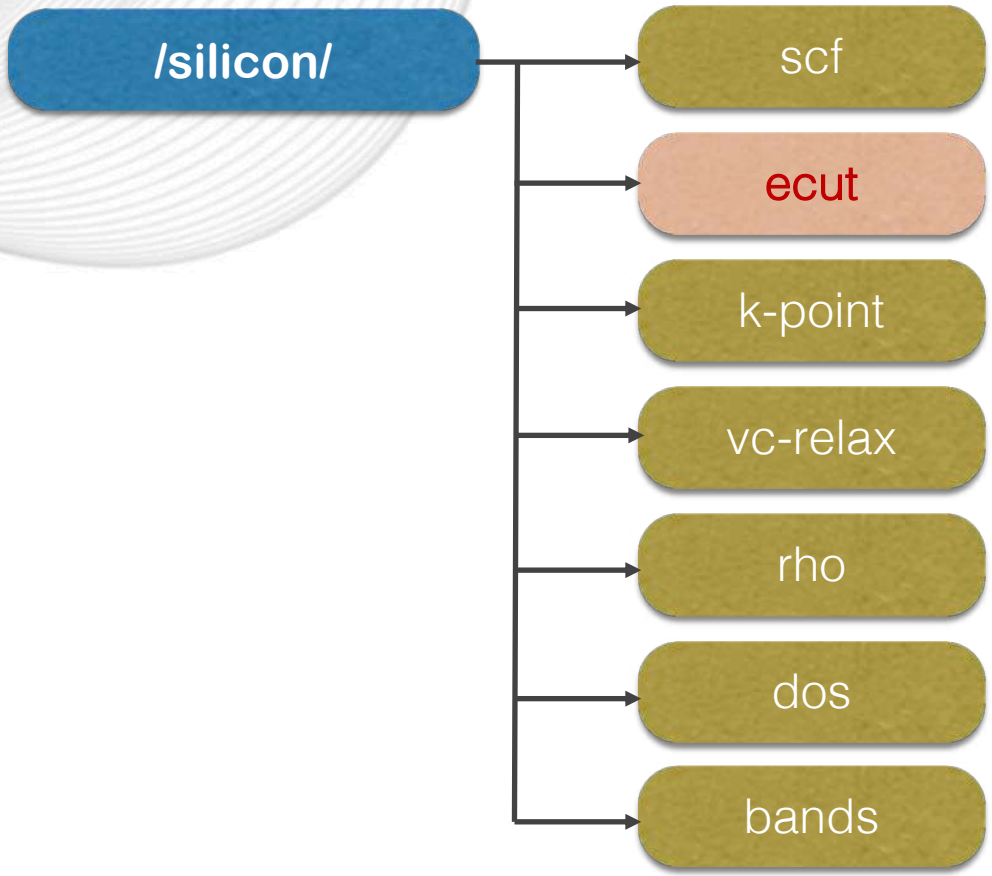
- Basic self consistent calculation (**scf**)

```
command:
$ pw.x <Si.scf.in> Si.scf.out &
$ grep ! Si.scf.out
```

```
     highest occupied level (ev):     5.9399

!    total energy              =     -15.74122935 Ry
     Harris-Foulkes estimate   =     -15.74122935 Ry
     estimated scf accuracy    <          8.8E-09 Ry

     The total energy is the sum of the following terms:

     Parallel routines
     fft_scatter  :      0.16s CPU      0.24s WALL (    2061 calls)

     PWSCF        :     1.96s CPU         4.47s WALL


   This run was terminated on:  19: 3:24  14Feb2016

=------------------------------------------------------------------------------=
   JOB DONE.
=------------------------------------------------------------------------------=
```

ECUT

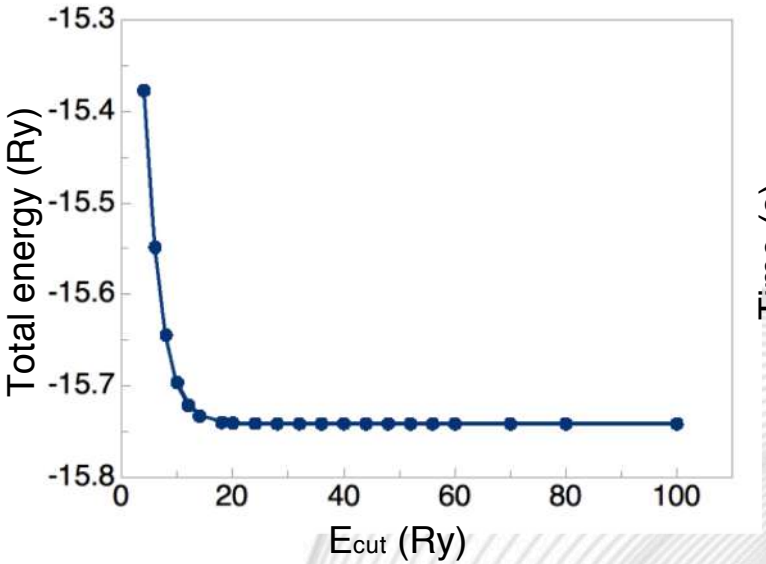
Files for cutoff energy

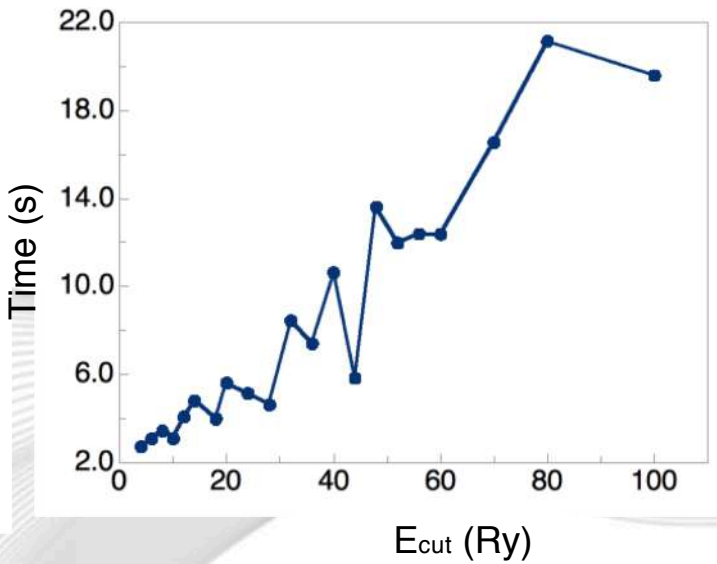


Convergence of total energy & plane waves cutoff (**ecut**)

Command:

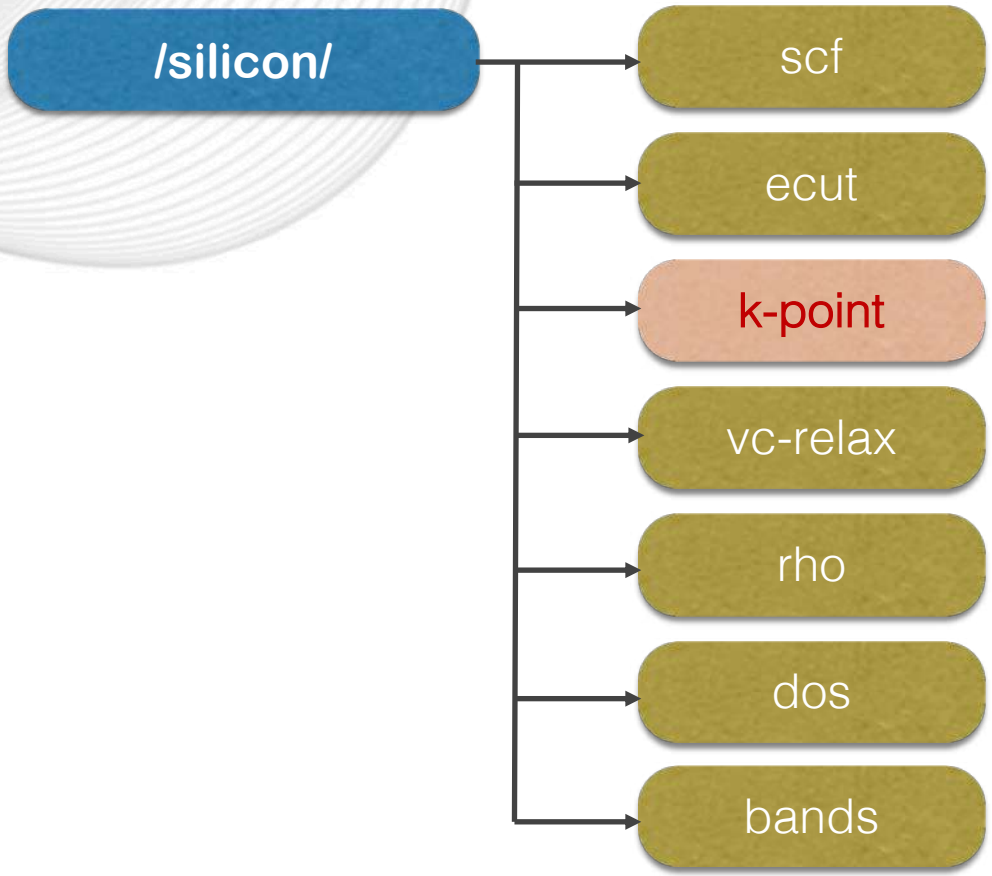
```
$ pw.x <Si.ecut.#.in> Si.ecut.#.out
```





K-POINT

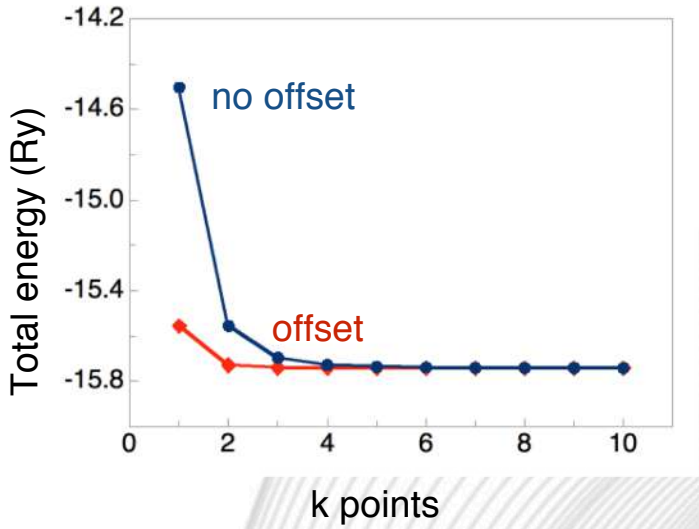
Files for k-point sampling

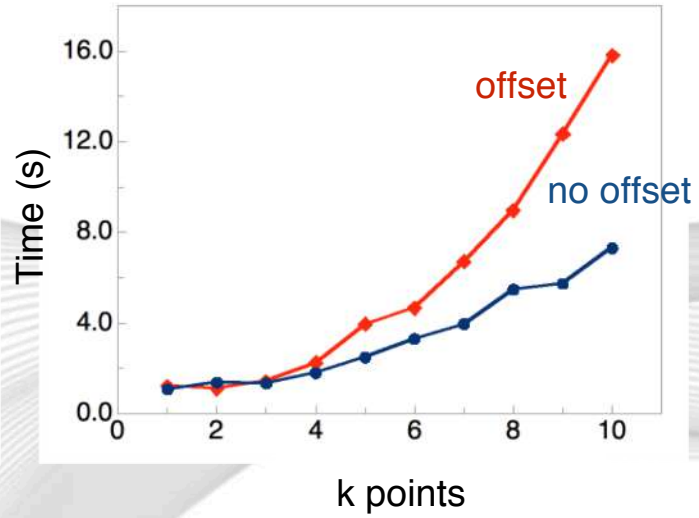


Convergence of total energy & BZ sampling (**k-point**)

Command:

```
$ pw.x <Si.k-point.#.in> Si.k-point.#.out
```

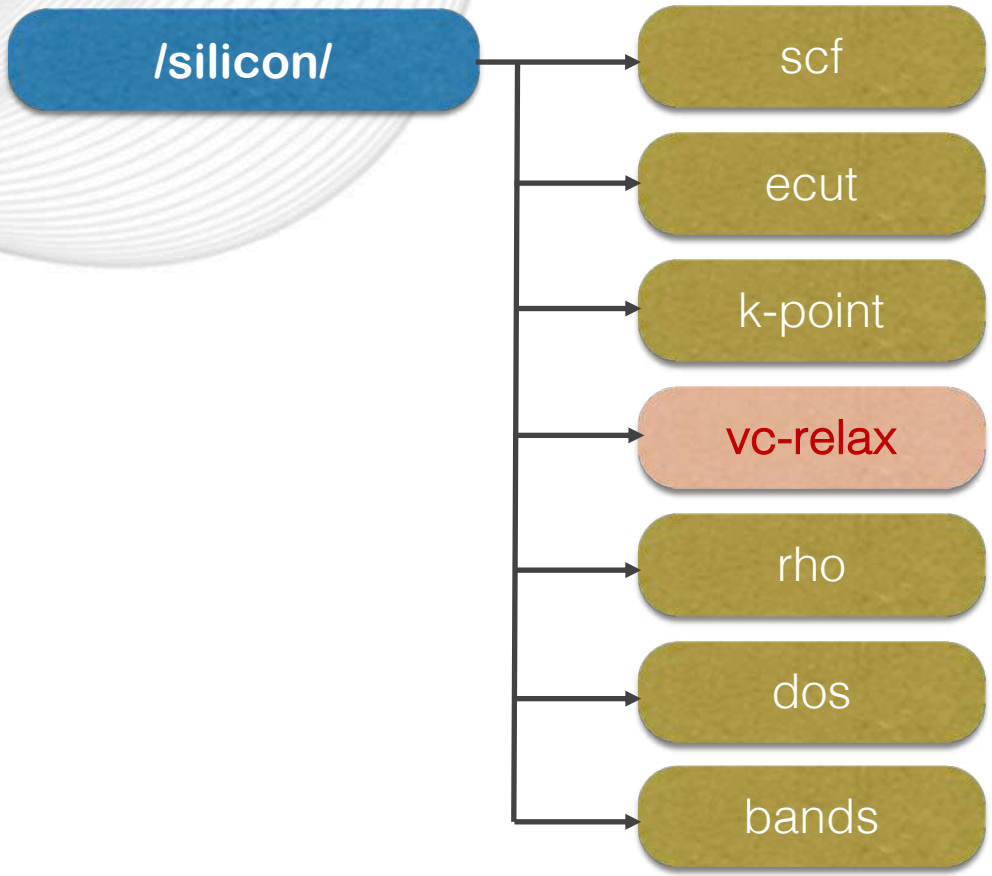


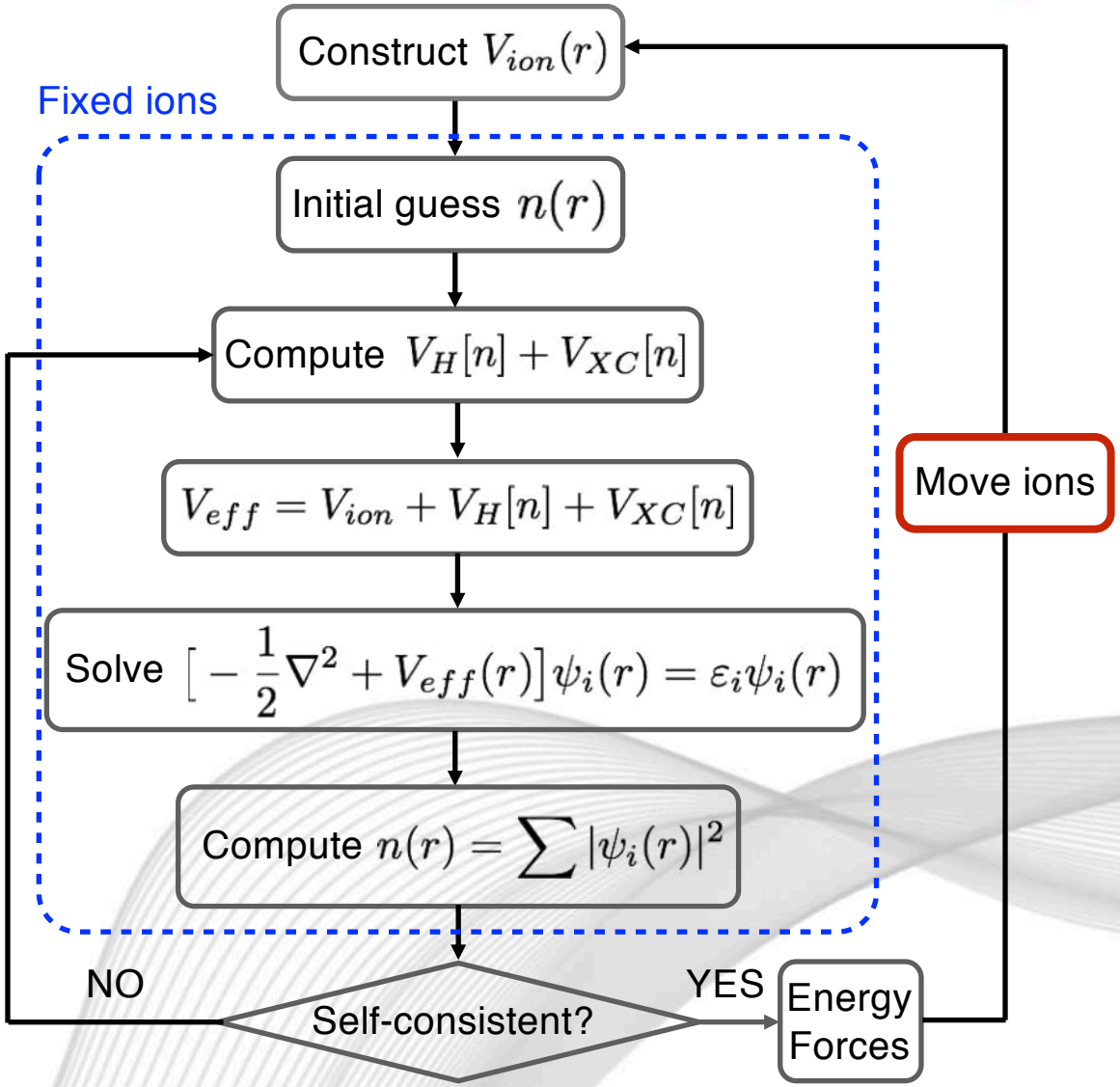


VC-RELAX

VC-RELAX

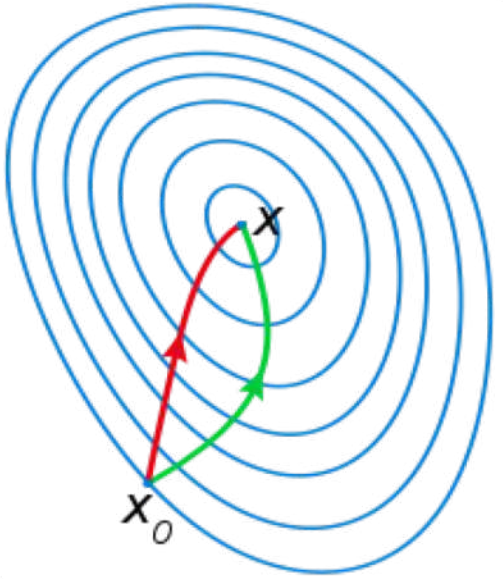
Files for vc-relax





Structure optimization

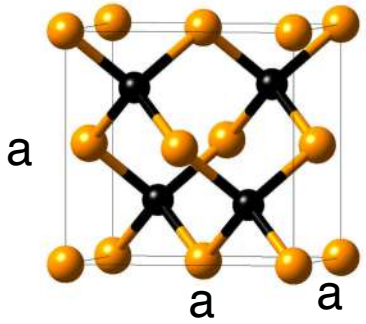
```
&CONTROL
 calculation='vc-relax',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../tmp/',
 forc_conv_thr=1d-5,
/
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 ecutrho=720.0,
/
&ELECTRONS
 mixing_beta=0.7,
 conv_thr=1d-8,
/
&IONS
 ion_dynamics='bfgs',
/
&CELL
 cell_dynamics='bfgs',
 press=0.0,
 press_conv_thr=0.5,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```



Broyden–Fletcher–Goldfarb–Shanno (**BFGS**) algorithm is an iterative method for solving unconstrained nonlinear optimization problems

Structure optimization

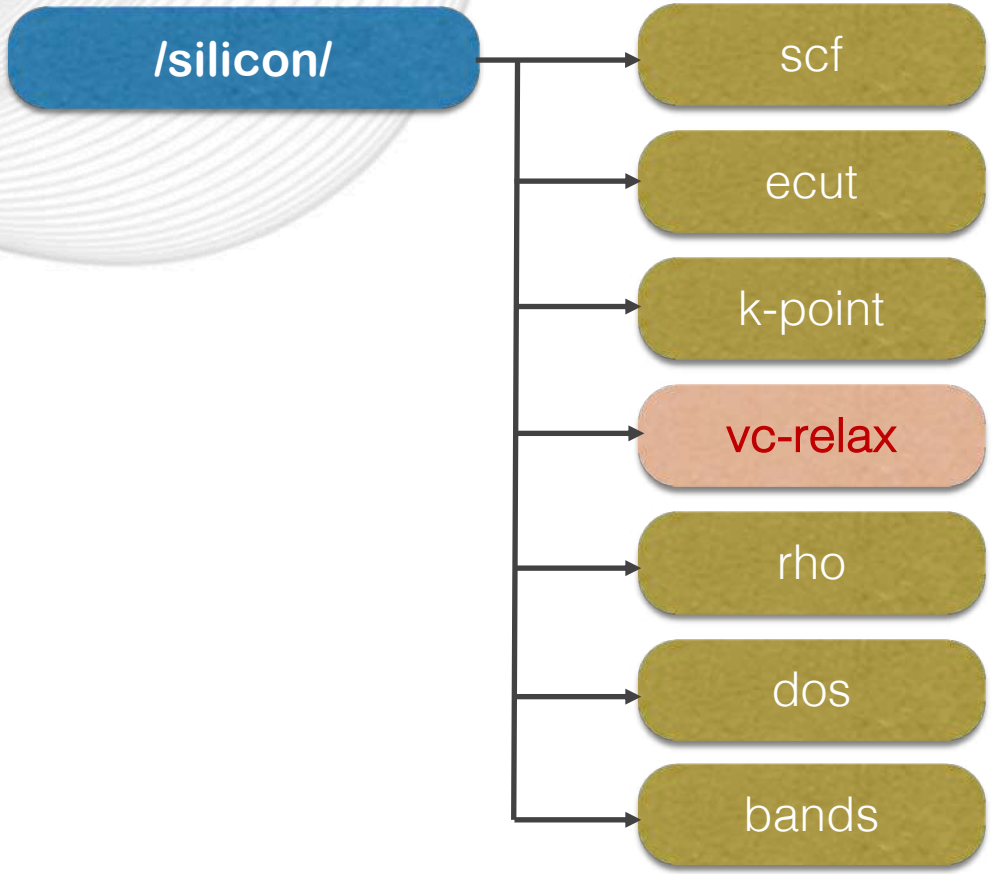
```
&CONTROL
 calculation='vc-relax',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../tmp/',
 forc_conv_thr=1d-5,
/
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 ecutrho=720.0,
/
&ELECTRONS
 mixing_beta=0.7,
 conv_thr=1d-8,
/
&IONS
 ion_dynamics='bfgs',
/
&CELL
 cell_dynamics='bfgs',
 press=0.0,
 press_conv_thr=0.5,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

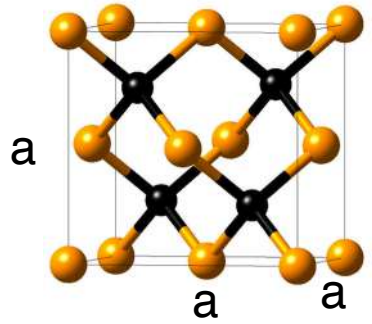


Cell lattice parameters and free (internal) coordinates of the atoms may be changed by relaxation

VC-RELAX

Files for vc-relax





- Lattice constant (**vc-relax**)

Command:

```
$ pw.x <Si.vc-relax.in> Si.vc-relax.out
```

```
     bfgs converged in   4 scf cycles and   3 bfgs steps
     (criteria: energy <  1.0E-04, force <  1.0E-05, cell <  5.0E-01)

     End of BFGS Geometry Optimization

     Final enthalpy =     -15.7417268079 Ry
Begin final coordinates
     new unit-cell volume =    276.89334 a.u.^3 (    41.03136 Ang^3 )

CELL_PARAMETERS (alat= 10.25000000)
  -0.504704263   0.000000000   0.504704263
  -0.000000000   0.504704263   0.504704263
  -0.504704263   0.504704263   0.000000000

ATOMIC_POSITIONS (alat)
Si       -0.000000000  -0.000000000  -0.000000000
Si        0.252352132   0.252352132   0.252352132
End final coordinates
```

Input:

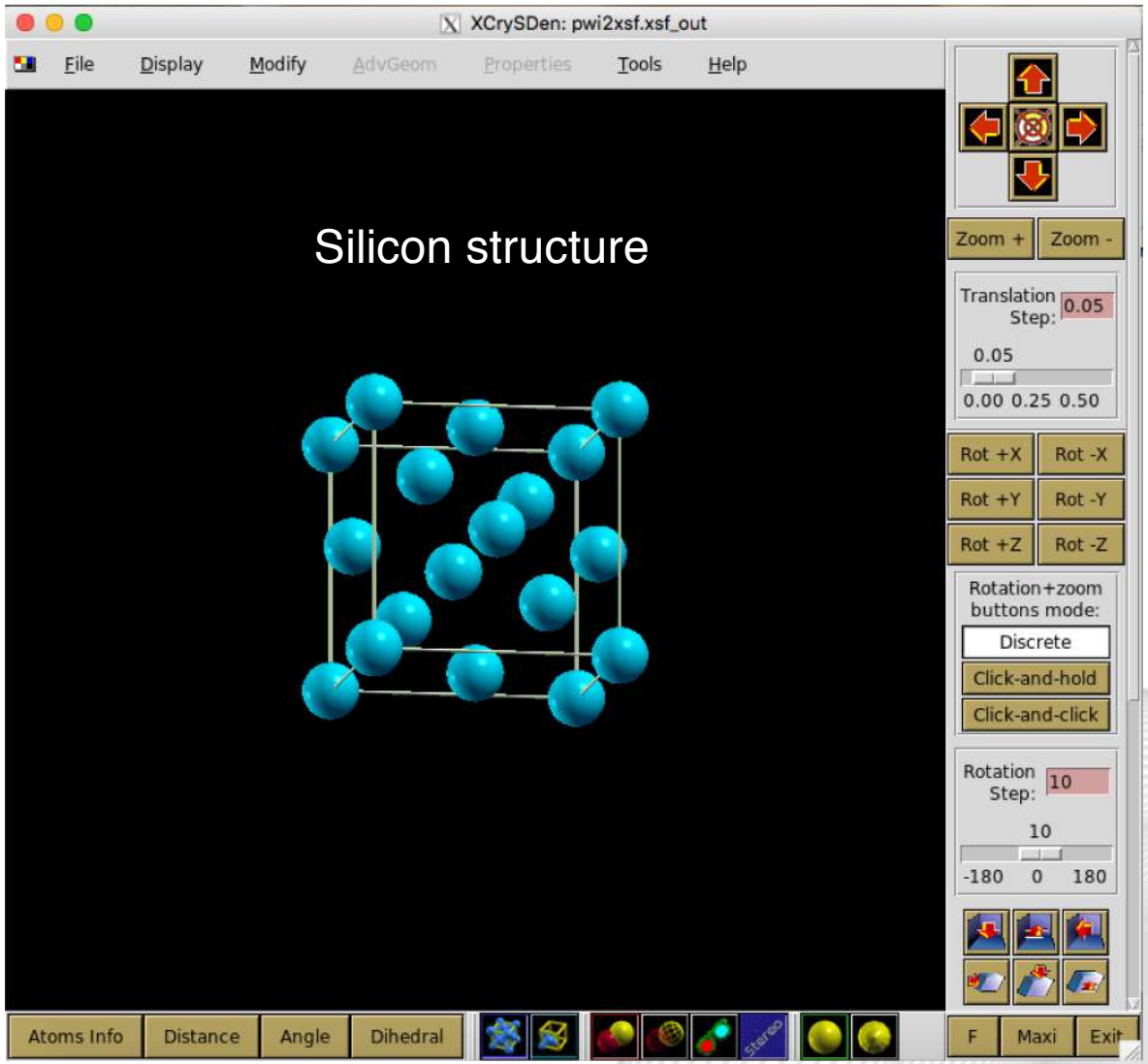
a = 10.2500 Bohr

Output:

a = 10.3464 Bohr

How to check the structure

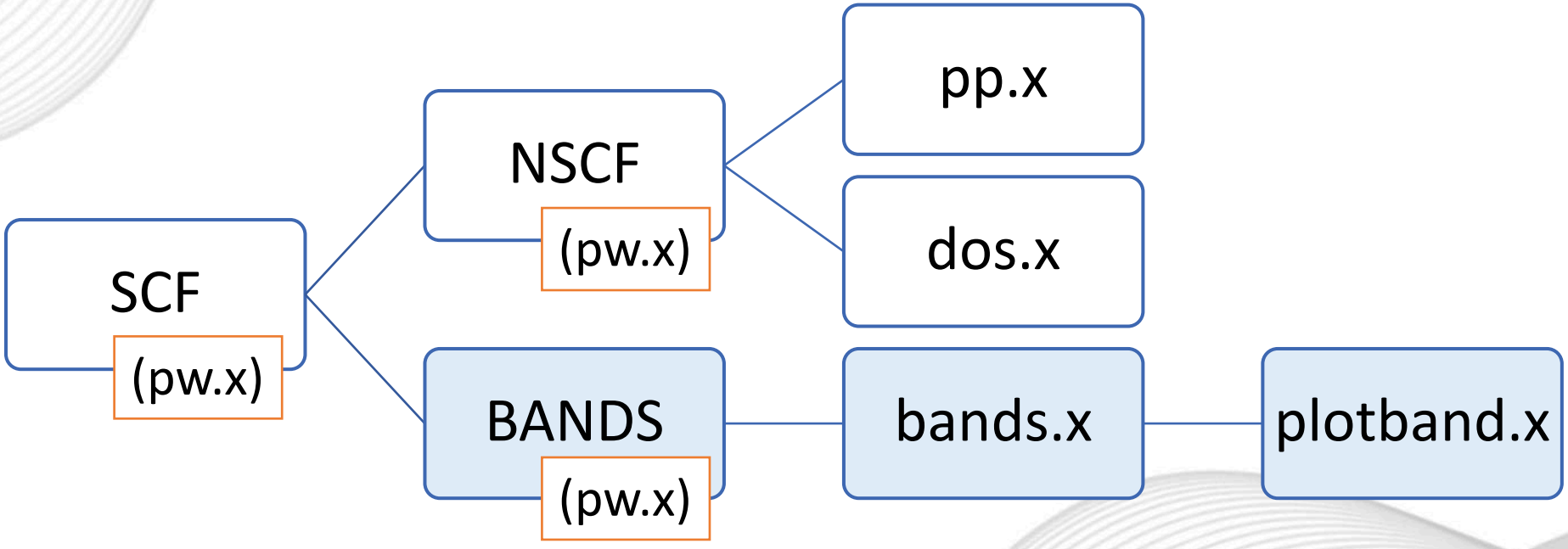
XCrySDen: http://www.xcrysden.org



QUANTUM ESPRESSO BAND STRUCTURE & DOS

HANDS-ON #2

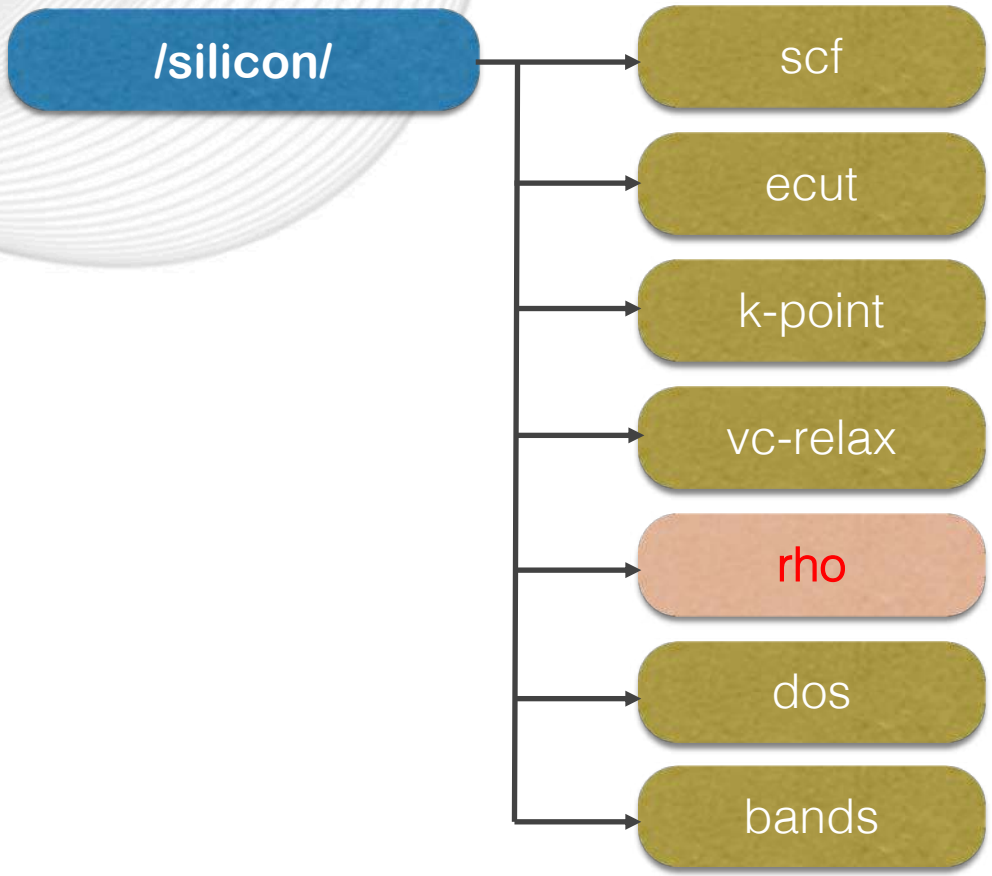
QE Post Processing



Charge Density

Charge density

Files for charge density



Step 1: SCF calculation (Hands-on #1)
Step 2: post processing charge density
Step 3: Visual charge density

Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pp.x < Si.pp.in > Si.pp.out
```

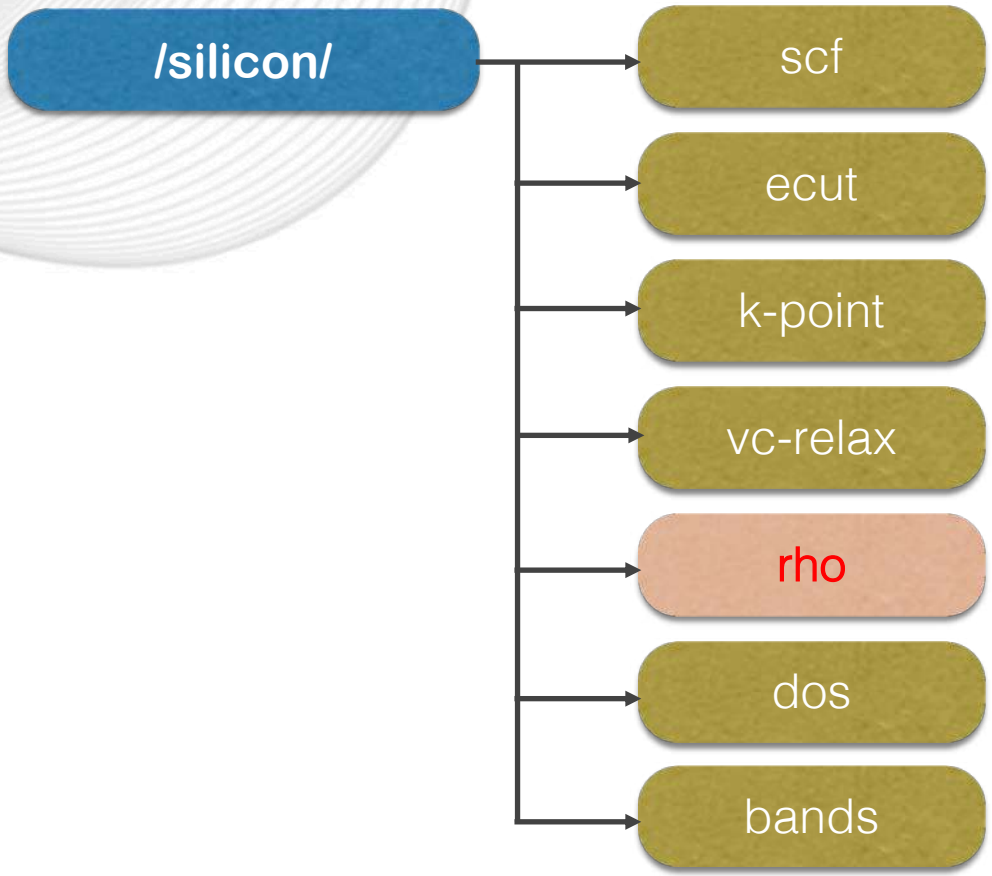
The electronic density n(r):

$$n(r) = \frac{1}{\Omega_{BZ}} \sum_i \int_{BZ} |\Psi_{i,k}(r)|^2 f(\epsilon_{i,k} - \epsilon_F) d(k)$$

Charge density

Step 1: SCF calculation (Hands-on #1)
Step 2: post processing charge density
Step 3: Visual charge density

Files for charge density



Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pp.x < Si.pp.in > Si.pp.out
```

Si.pp.in

```
&INPUTPP
 outdir='../tmp/',
 prefix='si',
 plot_num=0,
/
&PLOT
 iflag=3,
 output_format=6,
 fileout='si_rho.cube',
 nx=64,ny=64,nz=64,
/
```

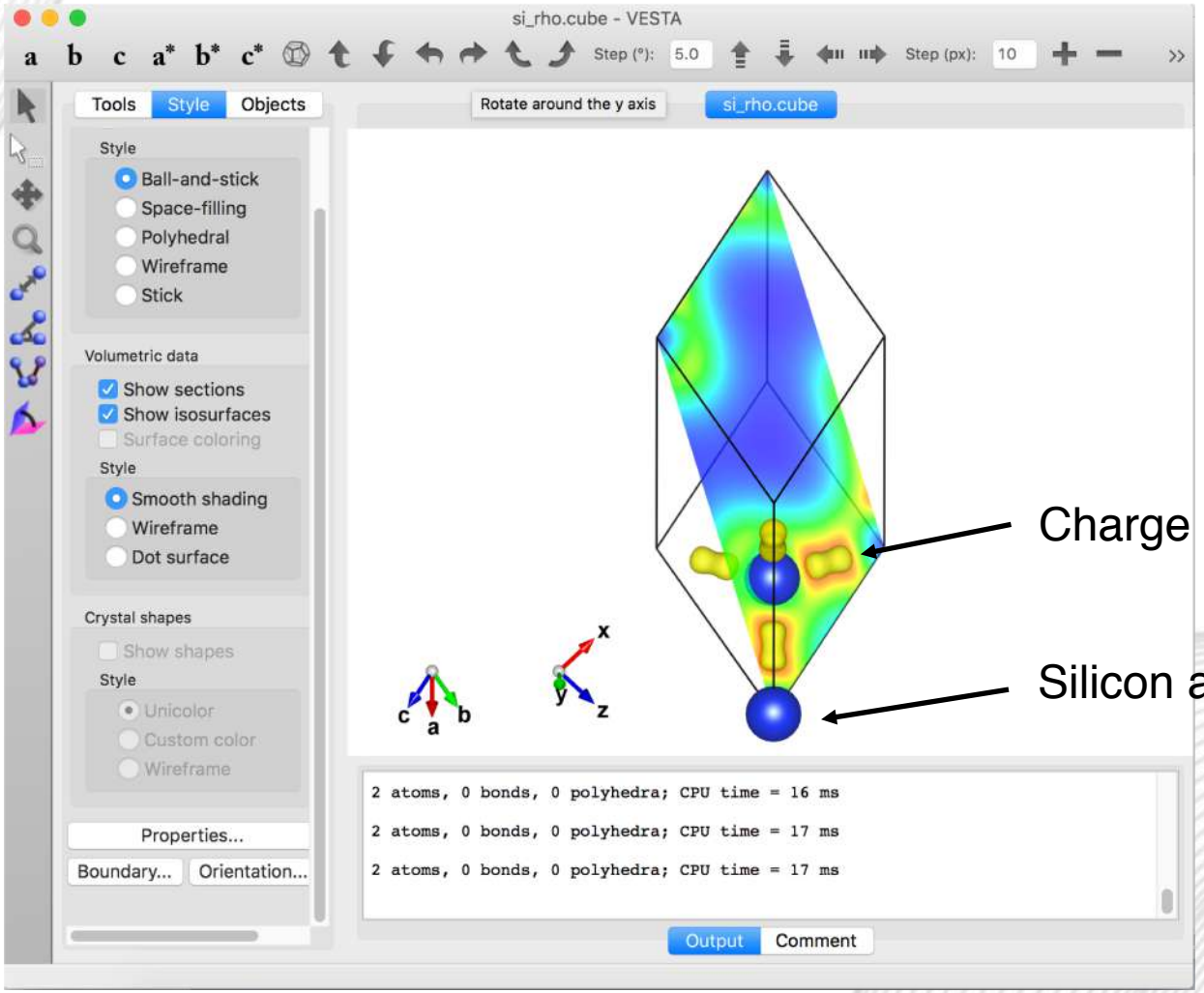
Data of wavefunctions in step SCF

Data of charge density

http://web.mit.edu/espresso_v6.1/i386_linux26/qe-6.1/Doc/INPUT_PP.html

Visual Charge density

VESTA: http://jp-minerals.org/vesta/en/

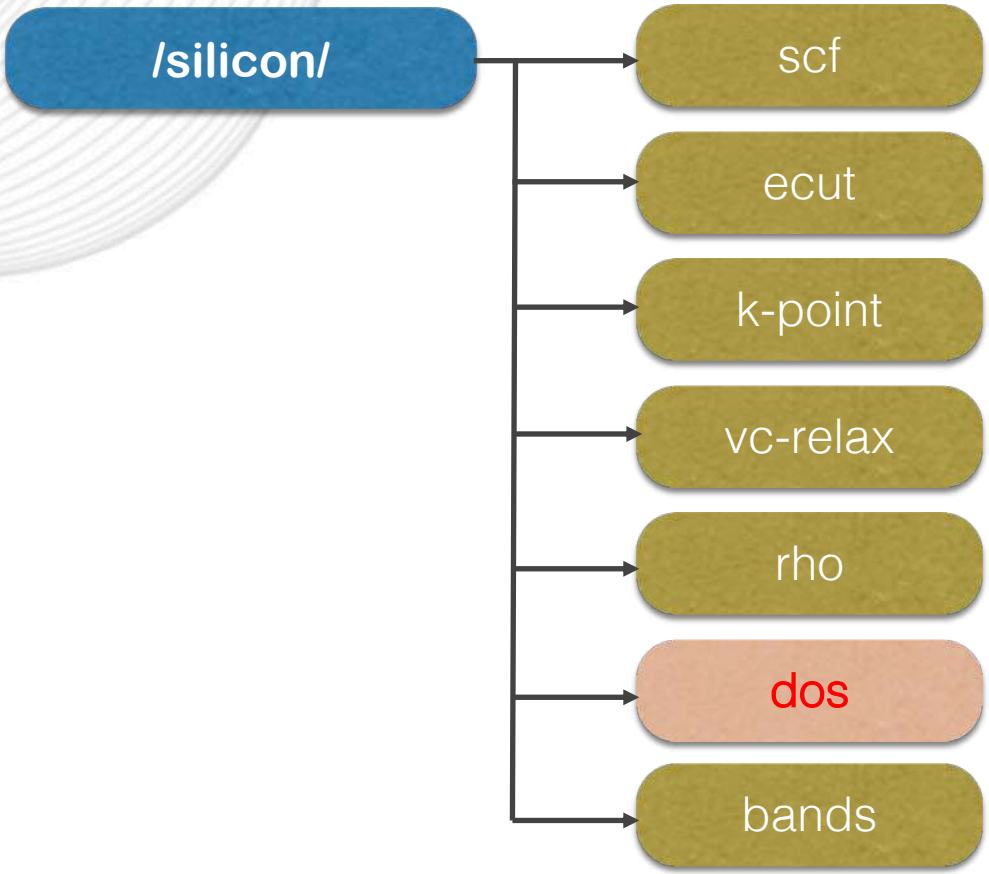


Step 1: SCF calculation (Hands-on #1)
Step 2: post processing charge density
Step 3: Visual charge density

Density of States

Density of states (DOS)

Files for density of states



Step 1: SCF calculation (Hands-on #1)
Step 2: Non-SCF calculation
Step 3: Plot DOS

Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pw.x < Si.nscf.in > Si.nscf.out
$ dos.x < Si.dos.in > Si.dos.out
```

Density of states (DOS)

Si.nscf.in

```
&CONTROL
 calculation='nscf',
 verbosity = 'high',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../tmp/',
/
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 ecutrho=720.0,
 nbnd=8,
 occupations='tetrahedra',
/
&ELECTRONS
 mixing_beta=0.7,
 conv_thr=1d-8,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
12 12 12 1 1 1
```

non-SCF calculation

Linear tetrahedron method

High density k-point

Step 1: SCF calculation (Hands-on #1)
Step 2: Non-SCF calculation
Step 3: Plot DOS

Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pw.x < Si.nscf.in > Si.nscf.out
$ dos.x < Si.dos.in > Si.dos.out
```

Density of states (DOS)

Step 1: SCF calculation (Hands-on #1)
Step 2: Non-SCF calculation
Step 3: Plot DOS

Si.dos.in

```
&DOS
  prefix='si',
  outdir='../tmp/',
  fildos='si.dos'
  emin=-9.0,
  emax=16.0,
/
```

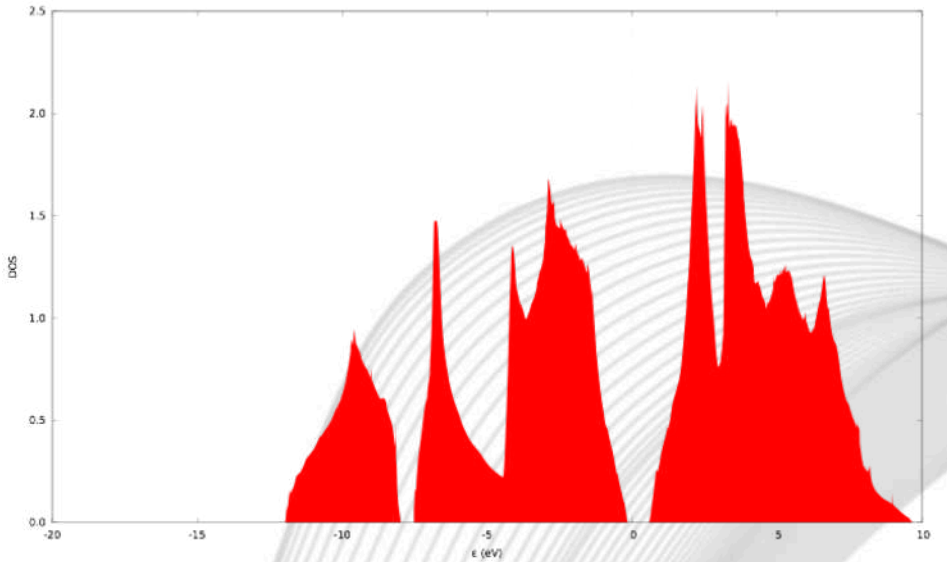
→ Data file of DOS (state/eV)

Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pw.x < Si.nscf.in > Si.nscf.out
$ dos.x < Si.dos.in > Si.dos.out
```

Command:

```
$ gnuplot < si_dos.gnu
```



Projected Density of States (PDOS)

Step 1: SCF calculation (Hands-on #1)
Step 2: Non-SCF calculation
Step 3: Plot PDOS

Si.projwfc.in

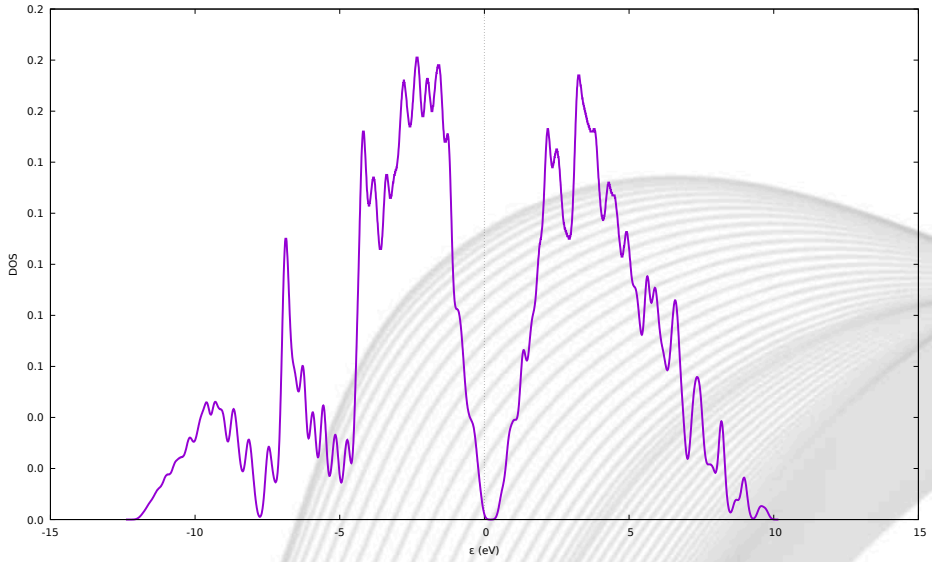
```
&projwfc
  prefix='si',
  outdir='../tmp/',
  degauss = 0.01,
/
```

Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pw.x < Si.nscf.in > Si.nscf.out
$ projwfc.x < Si.projwfc.in > Si.projwfc.out
```

Command:

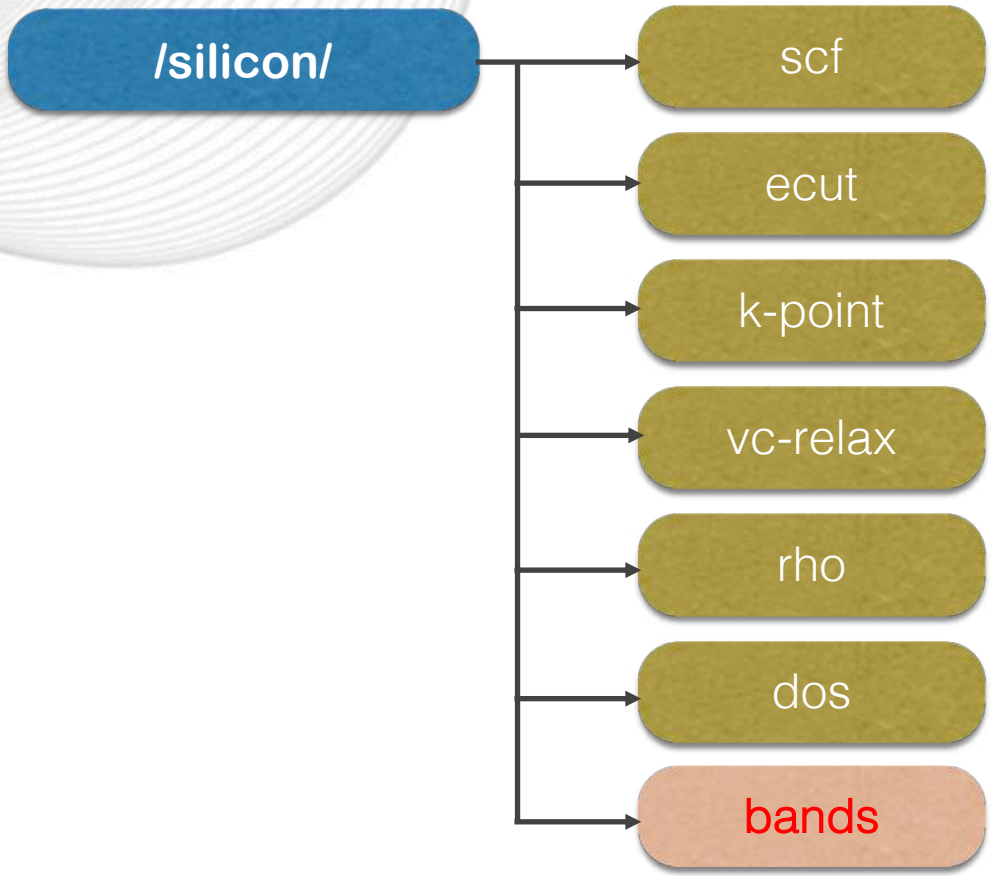
```
$ gnuplot < si_pdos.gnu
```



Band Structure

Band structure

Files for band structure



Step 1: SCF calculation (Hands-on #1)
Step 2: Non-SCF calculation
Step 3: Data of bands structure
Step 4: Plot band structure

Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pw.x < Si.nscf.in > Si.nscf.out
$ bands.x <Si.bands.in > Si.bands.out
$ plotband.x <Si.plotband
```

Band structure

Si.nscf.in

```
&CONTROL
 calculation='bands',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../tmp/',
/
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 ecutrho=720.0,
 nbnd=8,
/
&ELECTRONS
 mixing_beta=0.7,
 conv_thr=1d-8,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF

ATOMIC_POSITIONS (alat)
Si   0.00   0.00   0.00
Si   0.25   0.25   0.25

K_POINTS {crystal_b}
5
    0.0000000000     0.0000000000    -0.5000000000      20
    0.0000000000     0.0000000000     0.0000000000      30
   -0.5000000000     0.0000000000    -0.5000000000      10
   -0.3750000000     0.0000000000    -0.6250000000      30
    0.0000000000     0.0000000000     0.0000000000      20
```

non-SCF calculation

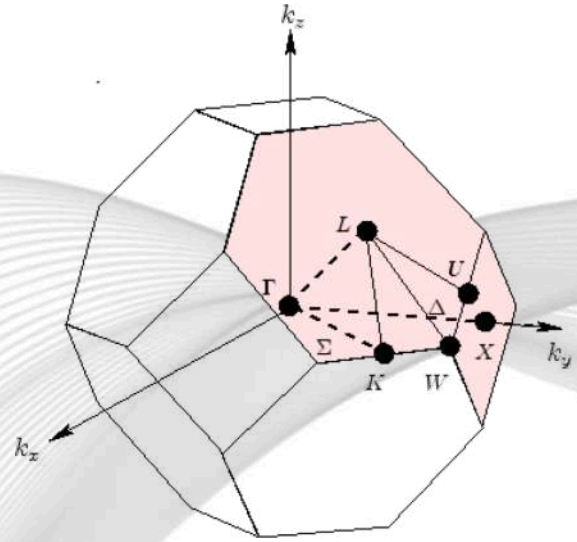
Selected special k-point coordinates

L
Γ
X
U
Γ

Step 1: SCF calculation (Hands-on #1)
Step 2: Non-SCF calculation
Step 3: Data of bands structure
Step 4: Plot band structure

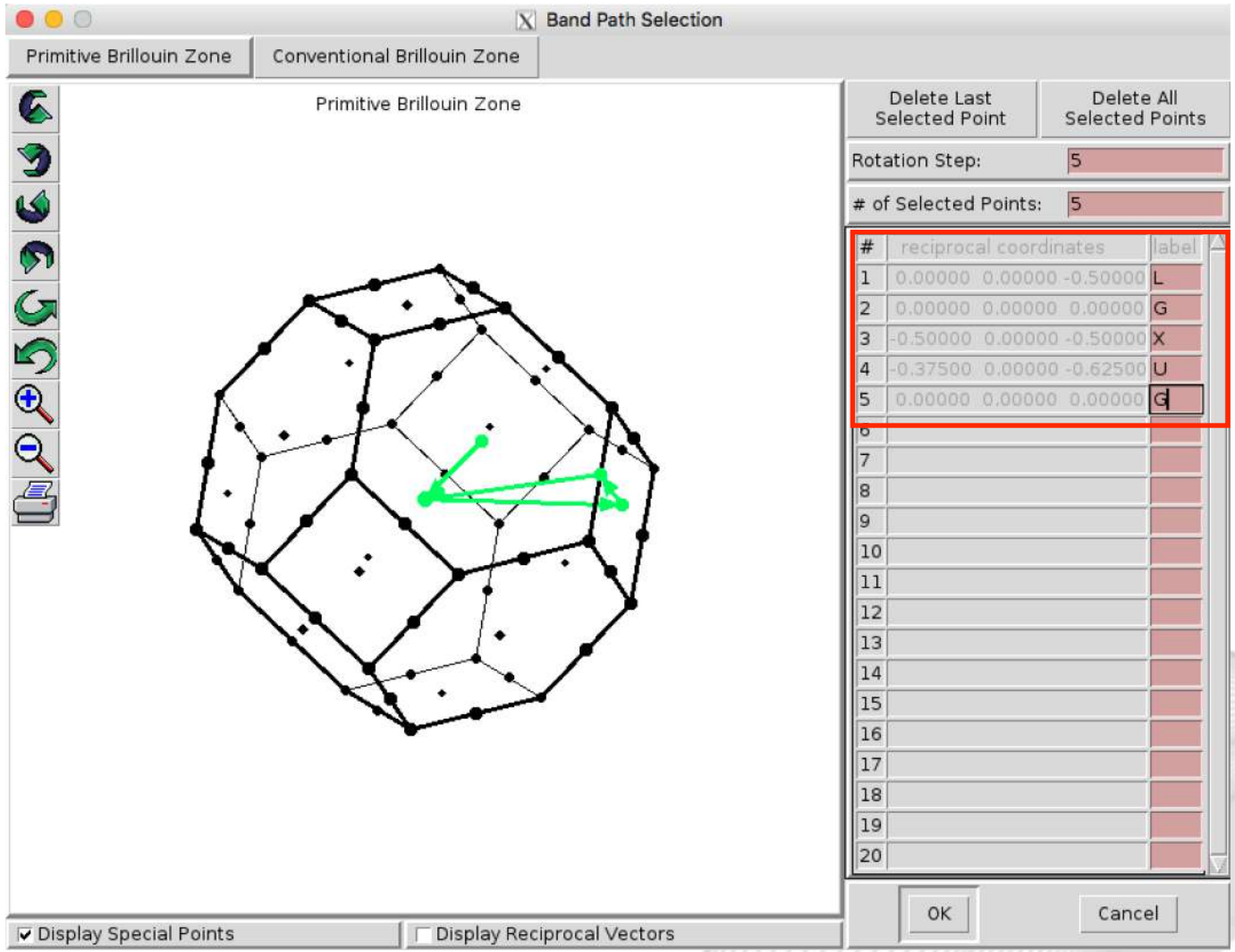
Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pw.x < Si.nscf.in > Si.nscf.out
$ bands.x <Si.bands.in > Si.bands.out
$ plotband.x <Si.plotband
```



XCrySDen k-path

XCrySDen: http://www.xcrysden.org



Band structure

Si.bands.in

```
&BANDS
 outdir='../tmp/',
 prefix='si',
 filband='si.bands',
/
```

→ Name of data file

Step 1: SCF calculation (Hands-on #1)
Step 2: Non-SCF calculation
Step 3: Data of bands structure
Step 4: Plot band structure

Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pw.x < Si.nscf.in > Si.nscf.out
$ bands.x <Si.bands.in > Si.bands.out
$ plotband.x <Si.plotband
```

Band structure

Step 1: SCF calculation (Hands-on #1)
Step 2: Non-SCF calculation
Step 3: Data of bands structure
Step 4: Plot band structure

Si.bands.in

```
&BANDS
 outdir='../tmp/',
 prefix='si',
 filband='si.bands',
/
```

→ Name of data file

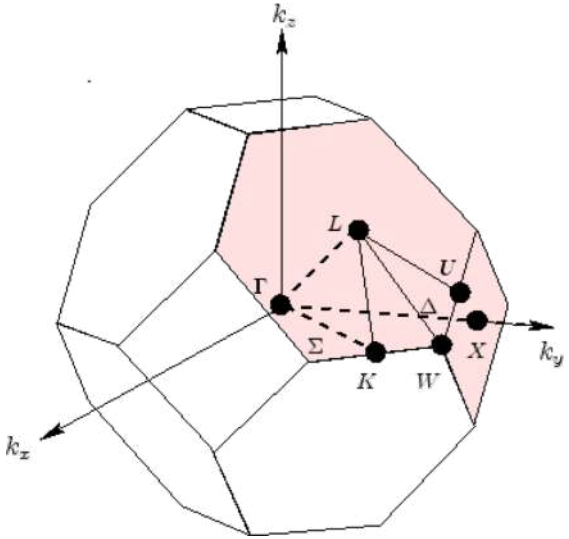
Si.plotband

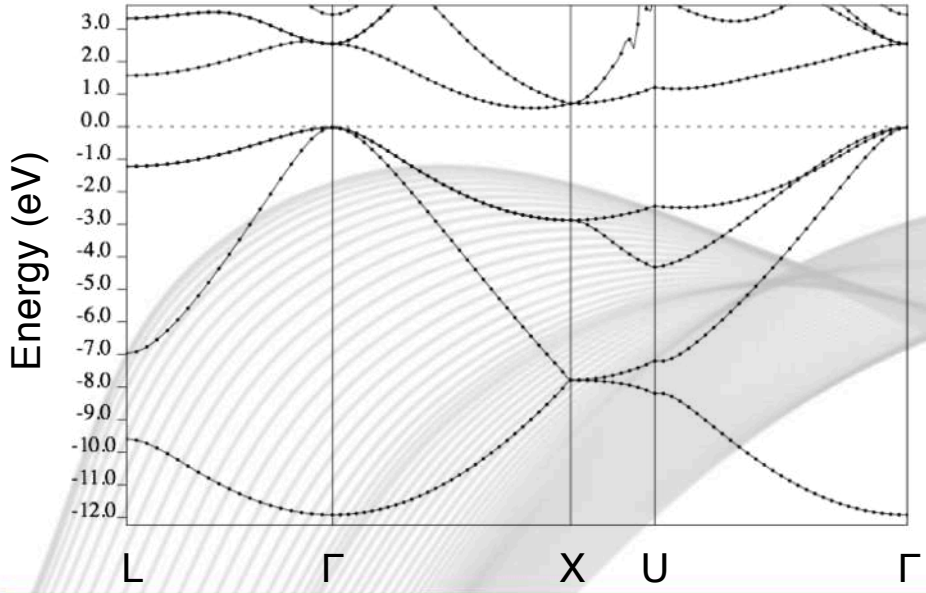
```
si.bands
-6.0 10
si.bands.xmgr
si.bands.ps
6.255
1.0 6.255
```

← Data file

Command:

```
$ pw.x < Si.scf.in > Si.scf.out
$ pw.x < Si.nscf.in > Si.nscf.out
$ bands.x <Si.bands.in > Si.bands.out
$ plotband.x <Si.plotband
```





Any Questions?

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