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

13th: Density Functional Theory (6)
Jan. 11 (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) Density functional theory 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)
   - Magnetics
6. Jan. 11 (Fri) Practice

Today's Schedule

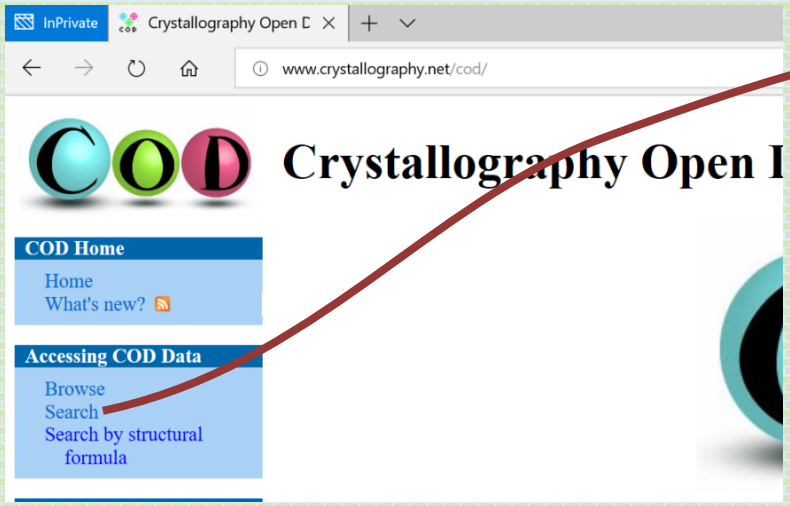
- Structure database
  - Crystallography Open Database
- Crystallographic Information Format (CIF) file
- Practice

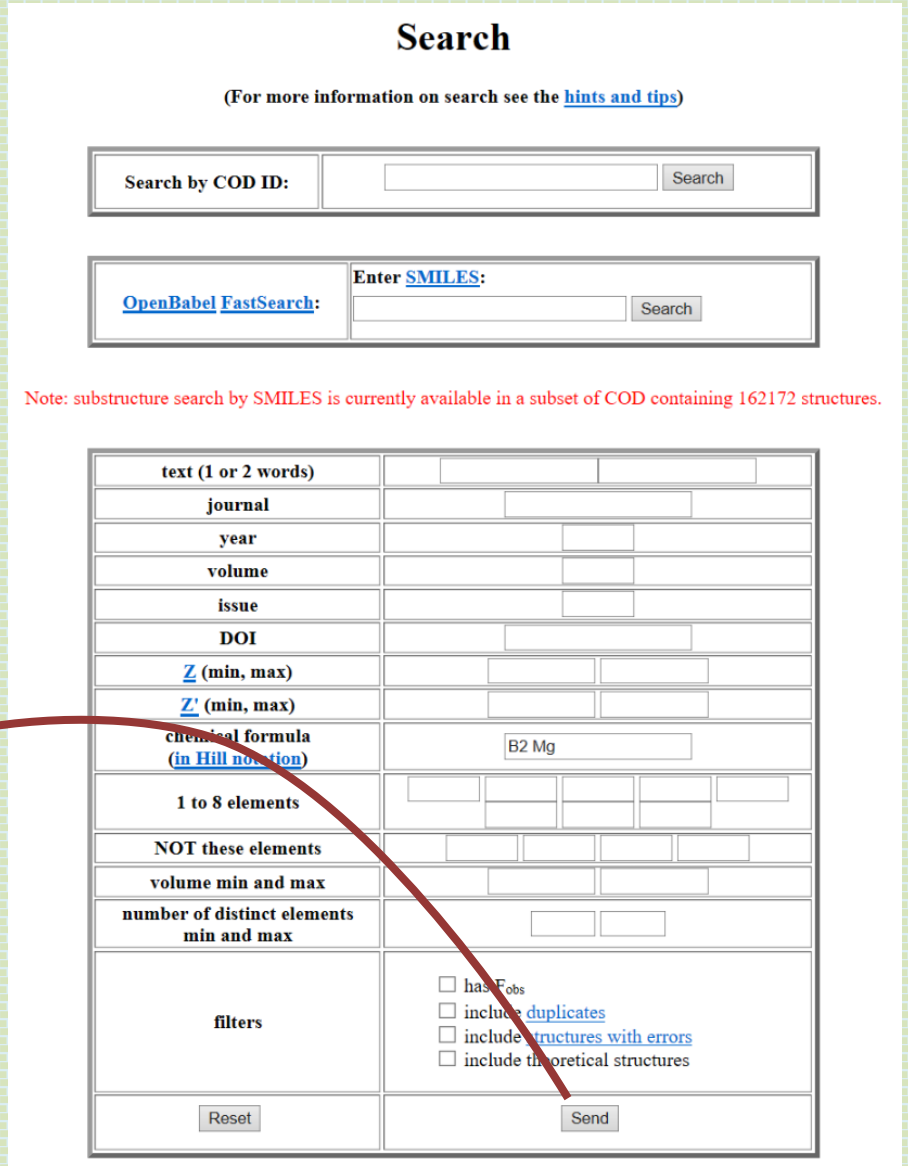
How to obtain crystalline structure

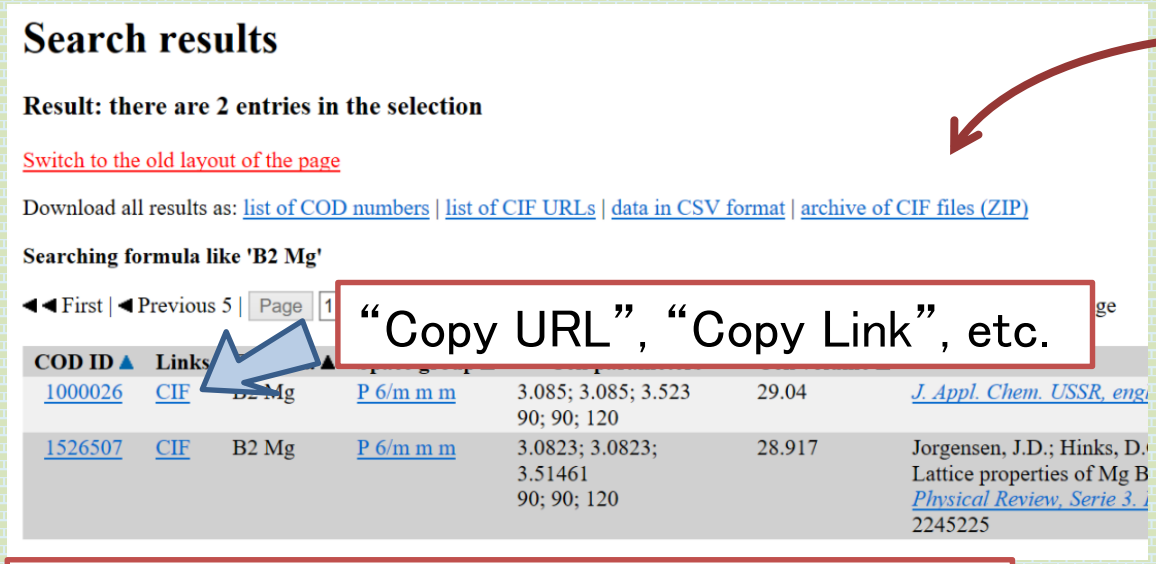
- Get from someone (e.g. experimental researcher)
- Generate by ourselves (e.g. theoretical prediction)
- Crystalline structure databases
  - Inorganic Crystallographic Structure Database (ICSD)
    - Commercial
  - AtomWorks by NIMS
    - https://crystdb.nims.go.jp/
    - Needs sign-up (we have to create account)
  - Crystallographic Open Database (COD)
    - http://www.crystallography.net/cod/search.html

Get CIF file from COD

http://www.crystallography.net/cod/search.html







"Copy URL", "Copy Link", etc.

"B2 Mg" into "chemical formula"

Alphabetic order

```
$ mkdir ~/MgB2
$ cd ~/MgB2
$ wget paste-url-here
$ vesta 1000026.cif
```

Crystallographic Information Format (CIF)

Various kind of information of a material

- Chemical formula
- Lattice constants
- Space group (Symmetry)
- Symmetry operator
- Structure
- Fractional occupancy (e.g. solid boron, please check it with COD)
- Information of article in which that structure is reported.
- Etc.

Parse CIF file (1)

```
$ cd ~/pwdft/
$ git checkout master
$ git pull
$ pip3.7 install spglib pymatgen seekpath pybtex --user
```

Python modules

- Spglib
  - https://atztogo.github.io/spglib/
  - Handling crstal symmetries
- pymatgen
  - http://pymatgen.org/
  - Library for Material Genomics
  - Parse CIF file
- SeeK-path
  - https://seekpath.readthedocs.io/en/latest/
  - Finding appropriate k-point path for band structure plot

Generate input files

```
$ cd ~/
$ wget https://www.materialscloud.org/discover/data/discover/sssp/downloads/SSSP_efficiency_pseudos.tar.gz
$ tar xzvf SSSP_efficiency_pseudos.tar.gz
$ wget https://www.materialscloud.org/discover/data/discover/sssp/downloads/sssp_efficiency.json ¥
-P SSSP_efficiency_pseudos/
$ cd ~/MgB2/
$ python3.7 ~/pwdft/tool/cif2qe.py 1000026.cif ~/SSSP_efficiency_pseudos/
```

- Usage

$ python3.7 ~/pwdft/tool/cif2qe.py *CIF-file* *Pseudo-dir*

- Products
  - scf.in : Input file for SCF calculation (pw.x)
  - nonscf.in : Input file for band-structure calculation (pw.x)
  - bands.in : Input file for post-process for band-structure (bands.x)
  - band.gp : Gnuplot script to plot the band structure
  - pp.in : Input file for displaying Kohn-Sham orbitals (pp.x)
  - dense.in : Input file for the dense-k-grid calculation for PDOS (pw.x)
  - proj.in : Input file for PDOS calculation (projwfc.x)

Magnetism is not considered (Not spin-DFT) in these input.

Typical procedure

```
$ mpirun -np 2 ~/bin/pw.x -npool 2 -in scf.in | tee scf.out
$ mpirun -np 2 ~/bin/pw.x -npool 2 -in nonscf.in
$ mpirun -np 2 ~/bin/bands.x -npool 2 -in bands.in
$ grep Fermi scf.out
 the Fermi energy is     7.5595 ev
$ gnuplot -e "ef=7.5595;emin=-15;emax=15" band.gp
$ open -a Preview.app band.pdf
$ mpirun -np 1 ~/bin/pp.x -npool 1 -in pp.in
$ vesta tmp.pp_K001_B00*.xsf
$ mpirun -np 2 ~/bin/pw.x -npool 2 -in dense.in
$ mpirun -np 1 ~/bin/fermi_velocity.x -in dense.in
$ fermisurfer vfermi.frmsf
$ mpirun -np 2 ~/bin/projwfc.x -npool 2 -in pdos.in > pdos.out
$ ~/bin/sumpdos.x  pwscf.pdos_*¥(Mg¥)* > Mg
$ ~/bin/sumpdos.x  pwscf.pdos_*¥(B¥)* > B
$ mv pwscf.pdos_tot Total
$ bash ~/pwdft/tool/pdos.sh 7.5595 Total Mg B
$ gnuplot pdos.gp
$ open -a Preview.app pdos.pdf
Modify pdos.in for fermi_proj.x
$ mpirun -np 1 ~/bin/fermi_proj.x -in pdos.in
$ fermisurfer proj.frmsf
```

Input file format and usage

Input file format

- pw.x : https://www.quantum-espresso.org/Doc/INPUT_PW.html
- bands.x : https://www.quantum-espresso.org/Doc/INPUT_BANDS.html
- pp.x : https://www.quantum-espresso.org/Doc/INPUT_PP.html
- projwfc.x : https://www.quantum-espresso.org/Doc/INPUT_PROJWFC.html
- fermi_velocity.x : The same as that of pw.x
- fermi_proj.x :
  http://fermisurfer.osdn.jp/en/_build/html/fermisf_qe_en.html#compute-and-display-projection-onto-the-atomic-orbital (English)
  http://fermisurfer.osdn.jp/ja/_build/html/fermisf_qe_ja.html#id1 (日本語)

Usage

- VESTA : https://jp-minerals.org/vesta/archives/VESTA_Manual.pdf
- FermiSurfer :
  http://fermisurfer.osdn.jp/en/_build/html/fermisf_ops_en.html (English)
  http://fermisurfer.osdn.jp/ja/_build/html/fermisf_ops_ja.html (日本語)

Report problem 4

Download arbitrary structure from COD, compute the electronic structure with the script cif2qe.py, and explain that electronic properties in a (very short) article format.

Do not need to compute large size system. One ～ few atoms per unit cell is OK.

Sample

```
$ cd ~/pwdft/sample/report/
$ pdflatex report.tex
$ bibtex report.aux
$ pdflatex report.tex
$ pdflatex report.tex
$ open -a Preview.app report.pdf
```

- Only "Numerical conditions" and "Result" section.
- Including figures (for VESTA and FermiSurfer, screenshot is useful).
- Explanation of results does not have to be long. (a few sentence)
- Numerical condition and citation are important.

Numerical condition and citation

- Used programs with citation
  - Quantum ESPRESSO, VESTA, FermiSurfer
- Exchange-correlation functional (GGA-PBE, LDA, ・・・)
- Plane-wave cutoff for wavefunction
- Pseudopotential (Kind and Library)
  - Kind : Ultrasoft (US), PAW, Norm-conserving (NC)
  - SG15 (NC), GBRV (US), Pslibrary (rrkjus=US, kjpaw=PAW), Pseudo Dojo(NC), Wentzcovitch(PAW)
  - Verification (SSSP)
- Brillouin-zone integration method (tetrahedron) and k-point grids.

For citation, see report.bib which already has citations necessary for each case.

Today's summary

- Structure database
  - Crystallography Open Database
- Crystallographic Information Format (CIF) file
- Practice of calculation and writing paper.