36th Computational Material Design Workshop

Friday, 21 February 2020
at Graduate School of Science and Technology, Osaka University

Hands-on

First step in first-principles calculation.
- Precision Criterion for DFT simulation -

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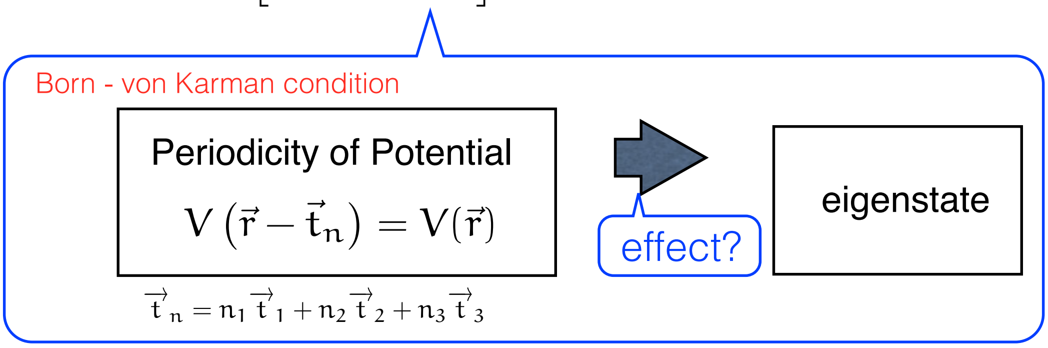
Translational Symmetry

Bloch State, Bloch function

1-electron Schrödinger Equation

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$



1-electron Schrödinger Equation

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \quad \Leftarrow \quad O_{(\epsilon|\vec{t}_n)}$$

Hamiltonian Operator: $-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})$; Eigenvalue: E; Eigenfunction: $\psi(\vec{r})$

$$O_\xi \psi(\vec{r}) \equiv \psi(\xi^{-1}\vec{r})$$

Born - von Karman condition

Periodicity of Potential

$$V(\vec{r} - \vec{t}_n) = V(\vec{r})$$

$$\vec{t}_n = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right]\psi(\vec{r} - \vec{t}_n) = E\psi(\vec{r} - \vec{t}_n)$$

Hamiltonian Operator; Eigenvalue: E (same eigenvalue); Eigenfunction: $\psi(\vec{r} - \vec{t}_n)$

$O(\epsilon|\vec{t}_n)$ $(= \psi(\vec{r} - \vec{t}_n))$ also is Eigenfunction whose eigenvalue is E

Bloch Theorem

$$O_{(\epsilon|\vec{t}_n)}\psi_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{t}_n}\psi_{\vec{k}}(\vec{r})$$ Bloch condition

phase factor: $e^{-i\vec{k}\cdot\vec{t}_n}$

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$$ **Bloch function**

periodic function $u_{\vec{k}}(\vec{r} - \vec{t}_n) = u_{\vec{k}}(\vec{r})$

Bloch state is characterized by $\vec{k}$

Key Point

Born-Karmann Condition

Periodic Potential

$$V(\vec{r}-\vec{t}_n) = V(\vec{r})$$

same periodicity

Wave function must be written as Bloch Function

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

plane wave

periodic function

$$u_{\vec{k}}(\vec{r}-\vec{t}_n) = u_{\vec{k}}(\vec{r})$$

$\psi_{\vec{k}}(\vec{r})$ = (plane wave) x (periodic function)

complex mathematical functional form…

summation of simple mathematical function

Bloch function and basis set

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

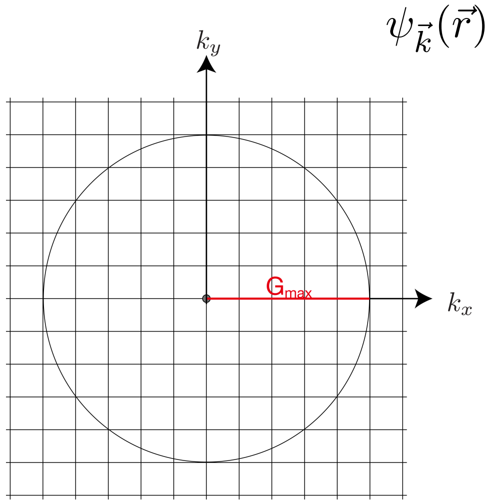
How do we represent the periodic function?

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_n C_n \phi_n(\vec{r})$$

basis set

e.g., planewave basis set

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}(\vec{r})$$



cut-off energy is defined as

$$E_{\text{cut-off}} = \frac{\hbar^2 G_{\text{max}}^2}{2m_e}$$

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{n} C_n \phi_n(\vec{r})$$

basis set

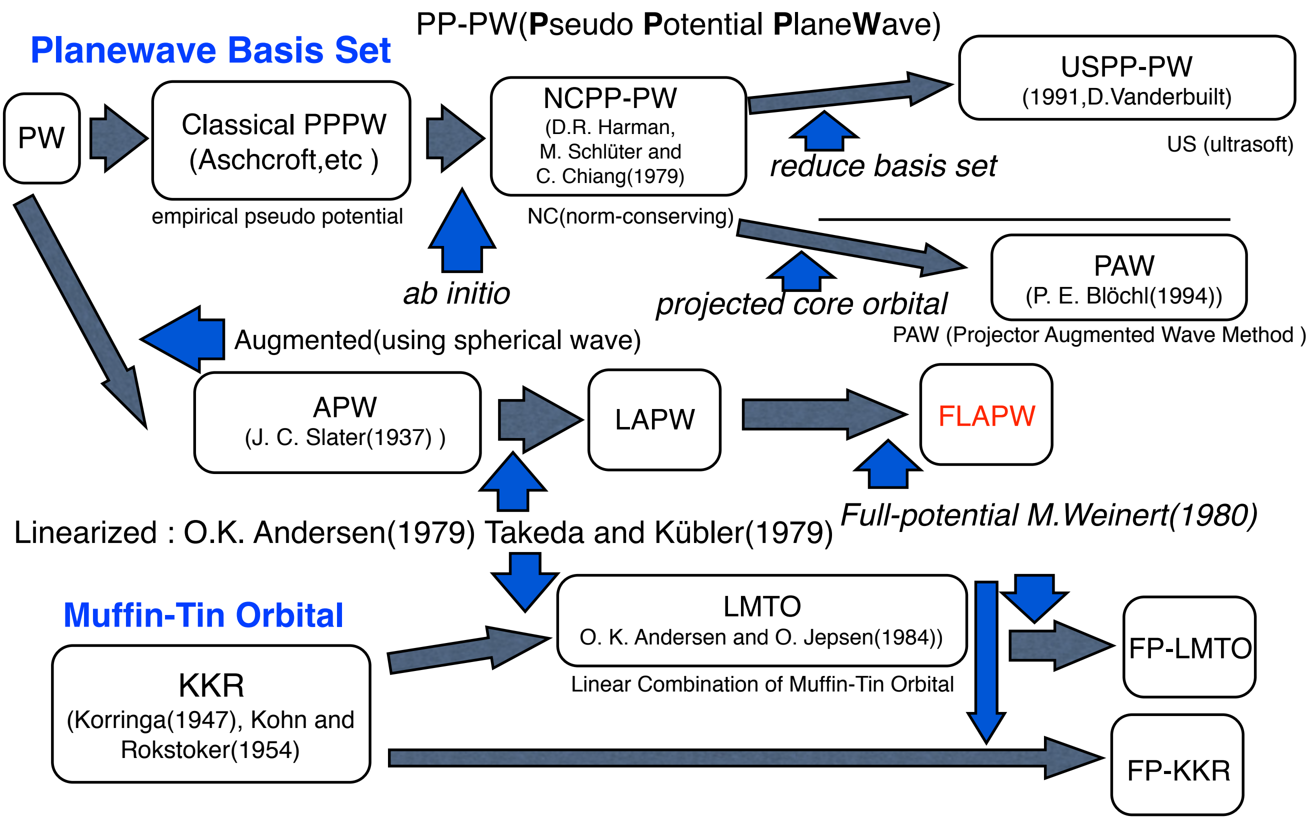
In generally speaking, Mathematics requires an **infinite** number of bases!

$0 \leq n \leq \infty$ **Ideal**

$0 \leq n \leq n_{max}$ **realistic calculation**

Cutoff

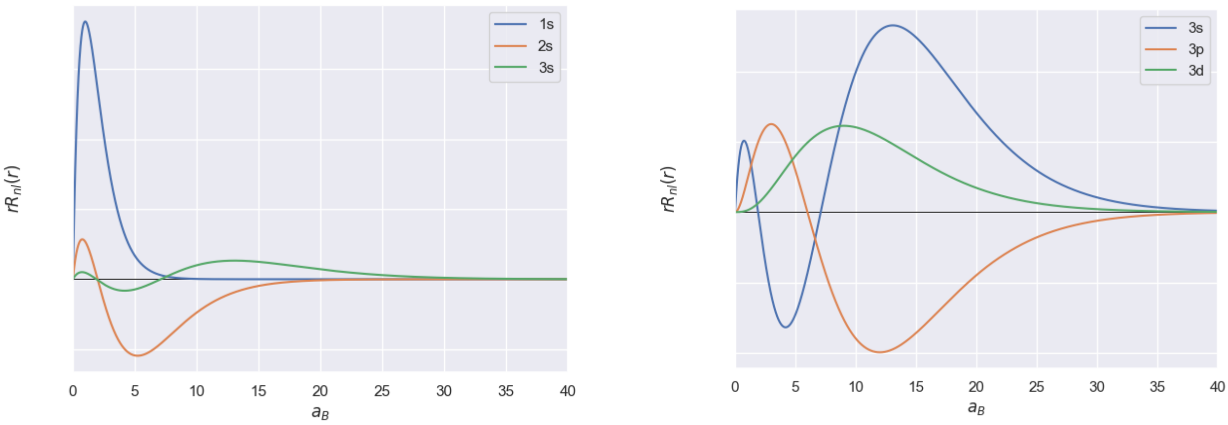
genealogy of DFT calculation



Computational Experiment 1

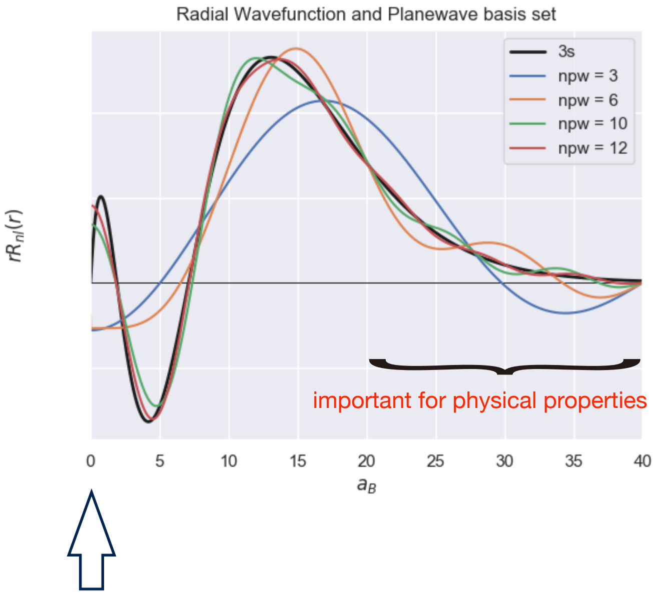
To simplify, we try to visualize the plane wave expansion for Hydrogen Radial wave function.(In this case, angular part is neglected)

Representation for Hydrogen Radial Wave function
as Summation of Plane wave Basis set



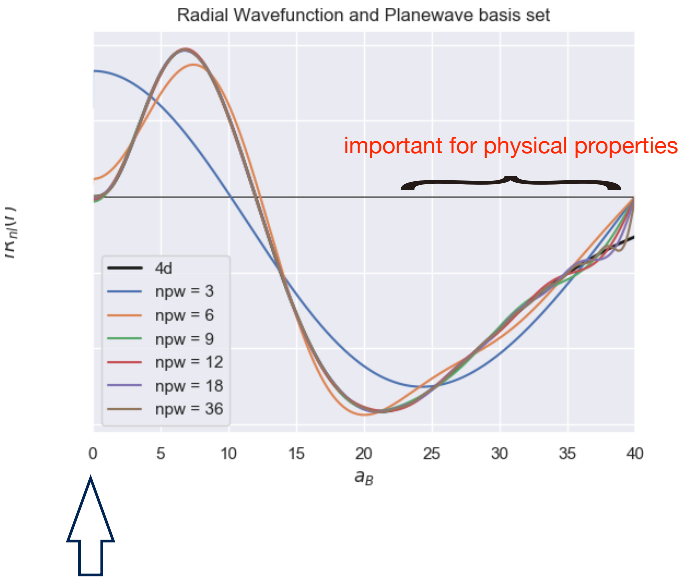
Reproducibility of Radial Wave function

Case: 3s orbital



center of Atom

Case: 4d orbital



center of Atom

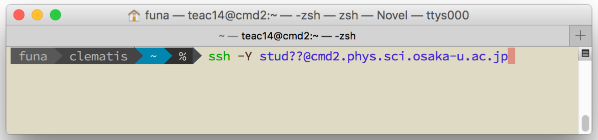
Practice 1

relation between number of plane wave bases and reproducibility of radial wave function

(1) login to *cmd2*

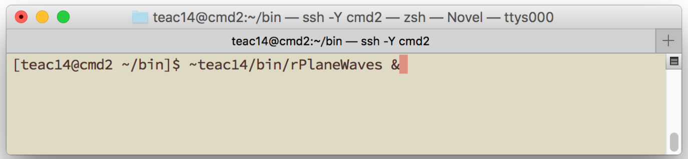
```
ssh -Y stud??@cmd2.phys.sci.osaka-u.ac.jp
```

your id



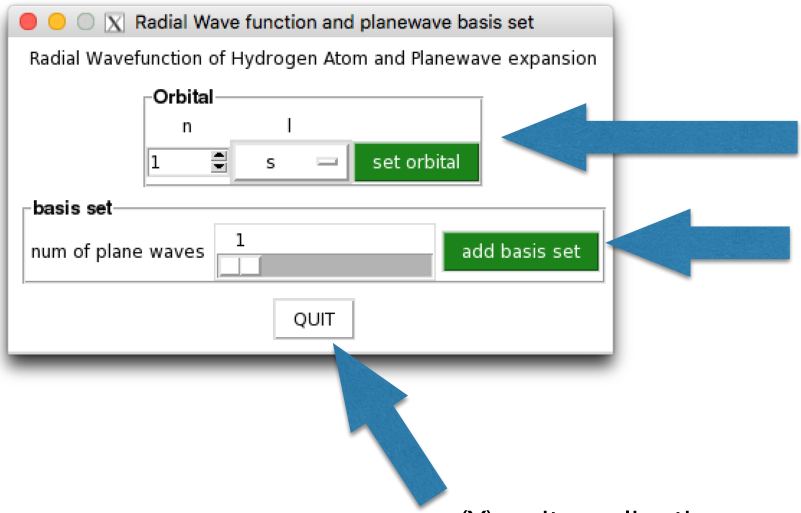
(2) launch App ``rPlaneWaves”

```
~teac14/bin/rPlaneWaves &
```



(wait few second…)

Menu Window for rPlaneWaves



(3) Select Orbital

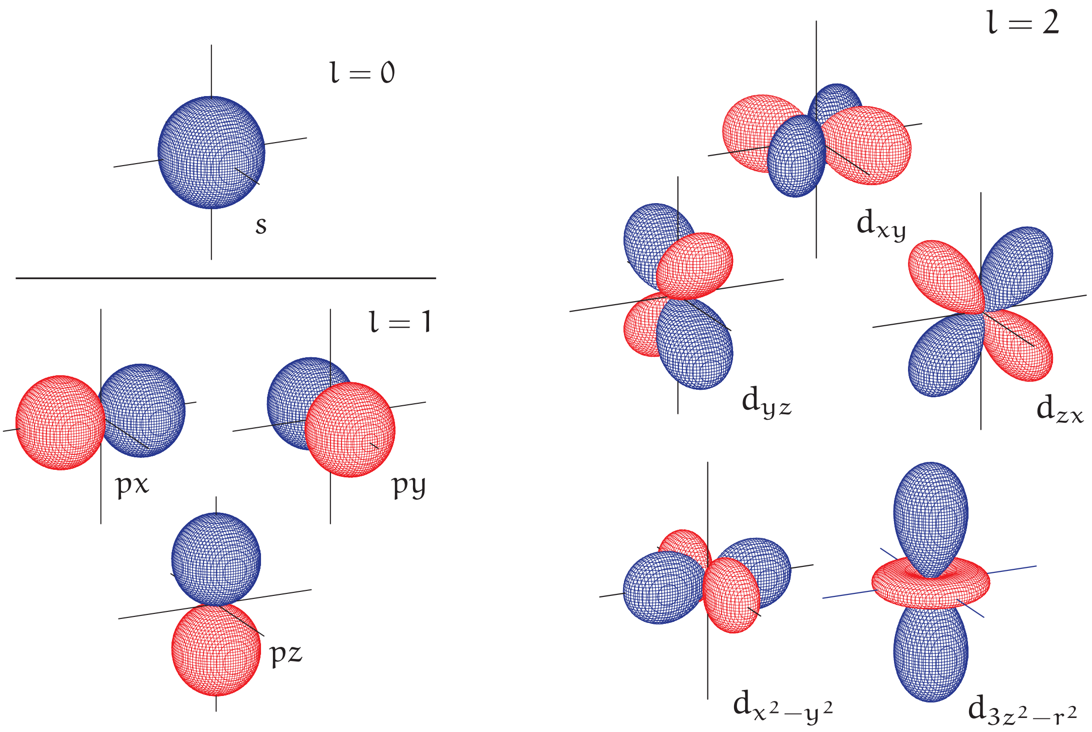
(4) Select num of Plane wave basis set

(5) Select num of Plane wave basis set

⋮

(X) quit application

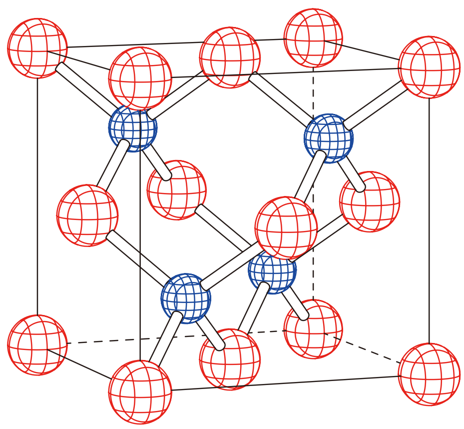
Actually, wave function has angular part, we are required *much* number of bases…



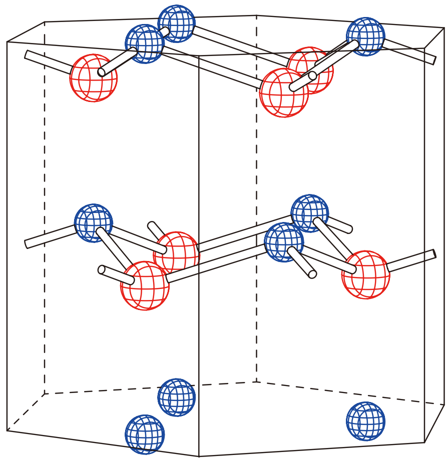
Computational Experiment 2

k-dependency and cutoff Energy dependency for real material in DFT calculation using FLAPW method(ABCAP code)

GaN



c-GaN(zincblende structure)



h-GaN(wurtzite structure)

Which is the most stable phase??

$$\Delta E_{\text{total}} = 1.73910^{-2}(eV)$$ (calc. FLAPW; DFT-LDA)

Does your calculation results have enough precision to compare total energy?

In these calculation, we vary *2 parameters*
to determine the precision of DFT Calculation Results,

- number of k-point mesh(grid)
- cutoff energy to expand wave function

We perform to the 2-type of calculation.

(1) check k-point mesh dependency(cutoff energy is static)

(2) check cutoff dependency(k-point mesh is static)

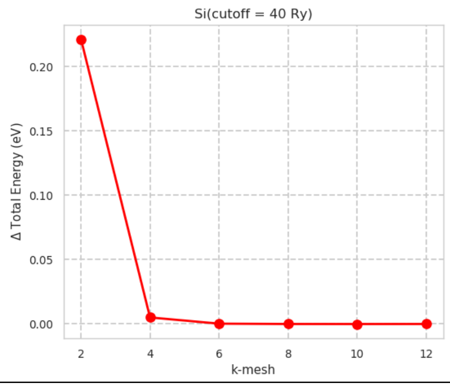
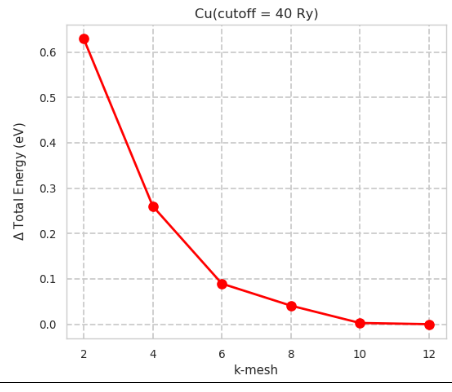
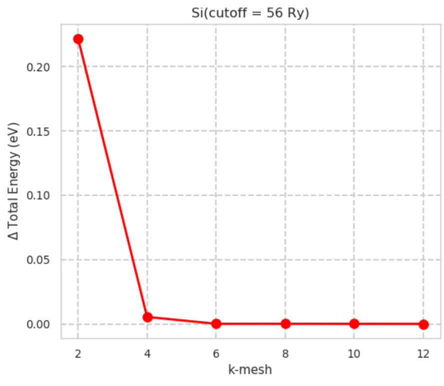
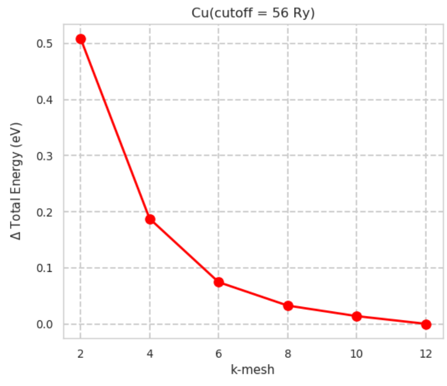
status for Si

cutoff\kmesh	2	4	6	8	10	12
40	finished	finished	finished	finished	finished	finished
44	finished	finished	finished	finished	finished	finished
48	finished	finished	N/A	finished	N/A	N/A
52	finished	finished	N/A	finished	N/A	N/A
56	finished	finished	finished	finished	finished	finished
60	finished	finished	N/A	finished	N/A	N/A
64	finished	finished	N/A	finished	N/A	N/A
68	finished	finished	N/A	finished	N/A	N/A
72	finished	finished	N/A	finished	N/A	N/A

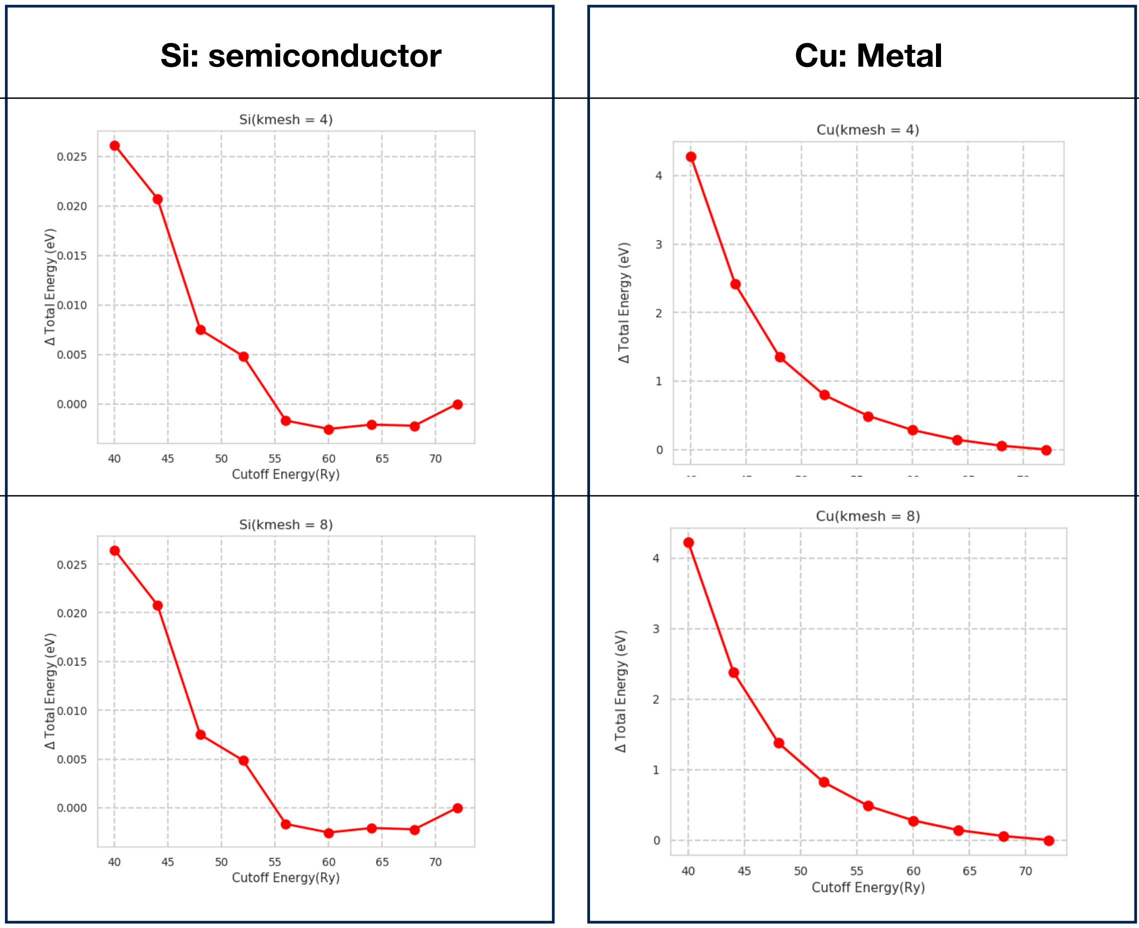
ok

Insulator(semiconductor) vs. Metal

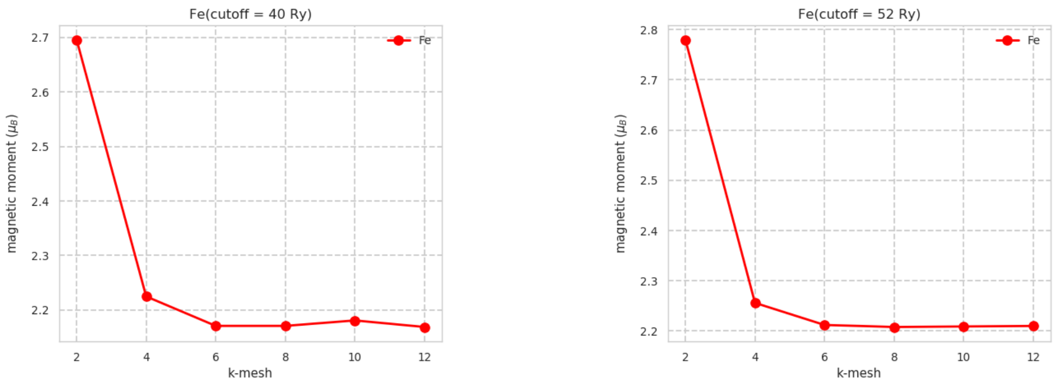
Precision for total energy (k-point mesh dependency)

Si: semiconductor	Cu: Metal
	
	

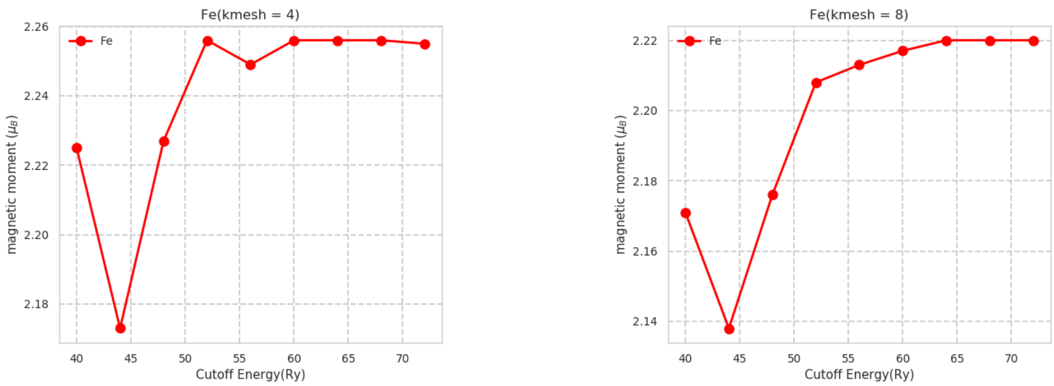
Precision for total energy (cutoff energy)



Precision for magnetic moment (k-point mesh)

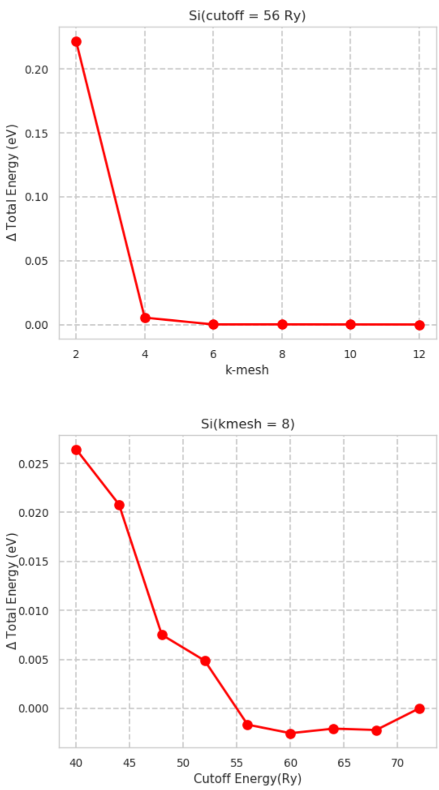


Precision for magnetic moment (cutoff energy)

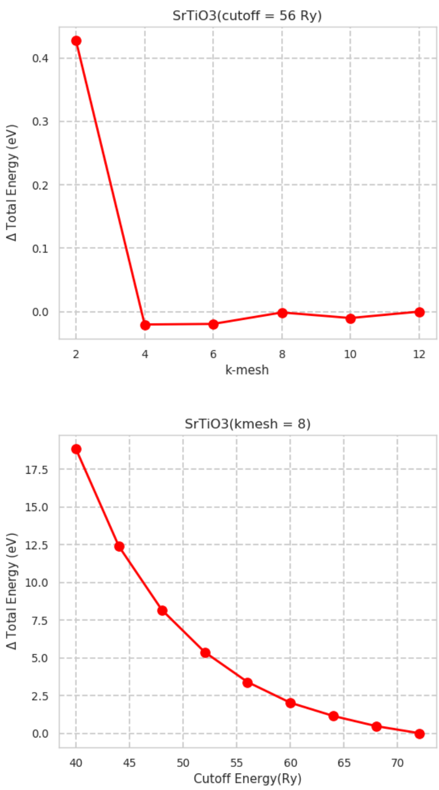


small cell vs. large cell

Si (2atoms / unit cell)



$SrTiO_3$ (5atoms / unit cell)



translational lattice vector in real space

$$\vec{t}_n = n_1 \vec{t}_1 + n_2 \vec{t}_2 + n_3 \vec{t}_3$$

$\vec{t}_1, \vec{t}_2, \vec{t}_3$:primitive translational lattice vector

primitive reciprocal vector

$$\vec{g}_1 = \frac{2\pi(\vec{t}_2 \times \vec{t}_3)}{\vec{t}_1(\vec{t}_2 \times \vec{t}_3)}$$

$$\vec{g}_2 = \frac{2\pi(\vec{t}_3 \times \vec{t}_1)}{\vec{t}_1(\vec{t}_2 \times \vec{t}_3)}$$

$$\vec{g}_3 = \frac{2\pi(\vec{t}_1 \times \vec{t}_2)}{\vec{t}_1(\vec{t}_2 \times \vec{t}_3)}$$

reciprocal lattice

$$\vec{g}_l = l_1 \vec{g}_1 + l_2 \vec{g}_2 + l_3 \vec{g}_3$$

orthogonality

$$\vec{g}_i \cdot \vec{t}_j = 2\pi\delta_{i,j}$$

$$e^{i\vec{g}_l \cdot \vec{t}_n} = e^{2\pi n i} = 1 \quad (n\text{:integer})$$

$$e^{-i(\vec{k}+\vec{g}_l)\cdot\vec{t}_n} = e^{-i\vec{k}\cdot\vec{t}_n}$$

(periodicity in k-space)

Practice 2

relation between number of plane wave bases and reproducibility of radial wave function

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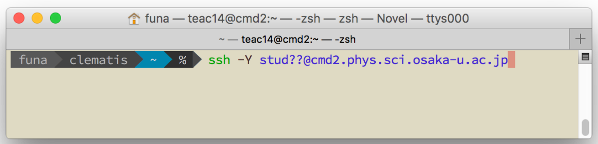
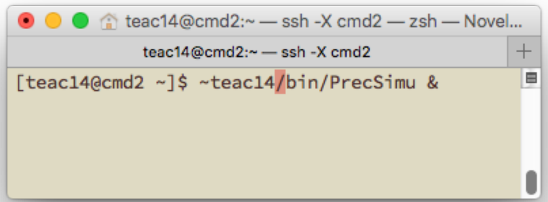
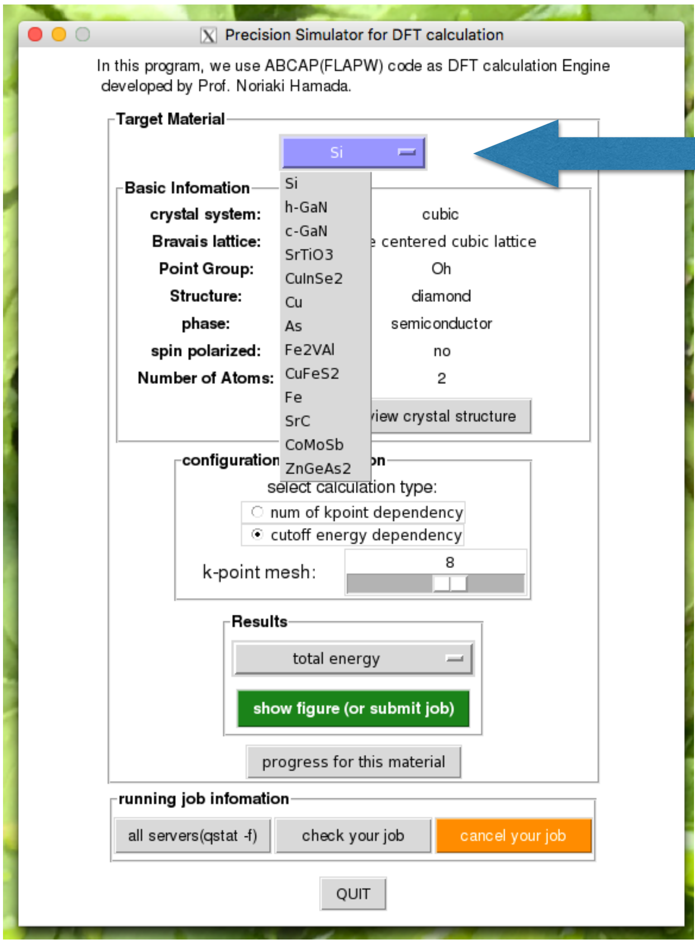


(2) launch App ``PrecSimu”

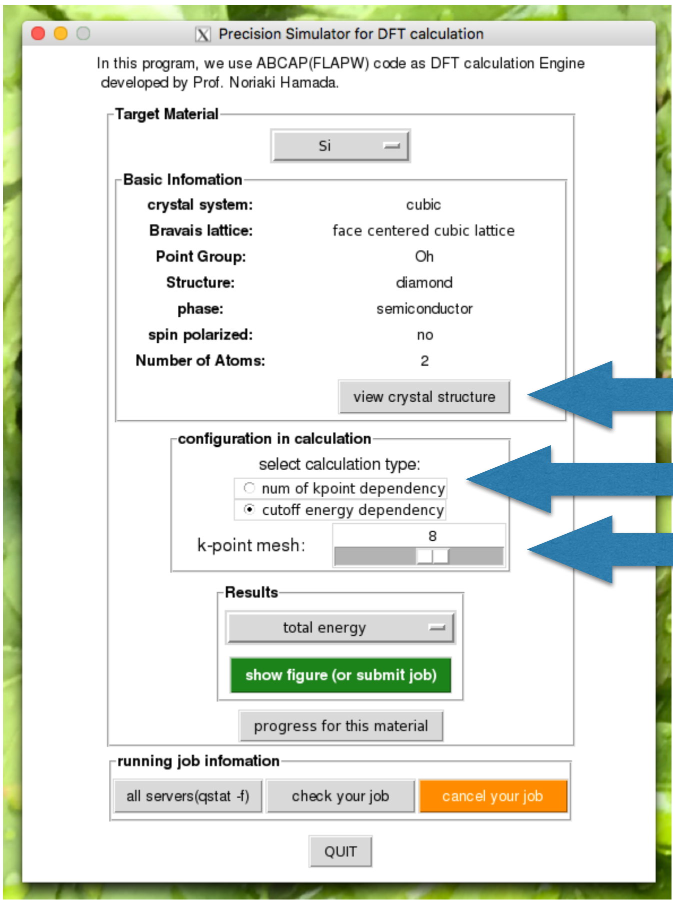
```
~teac14/bin/PrecSimu &
```



(wait few second…)



(3) target material



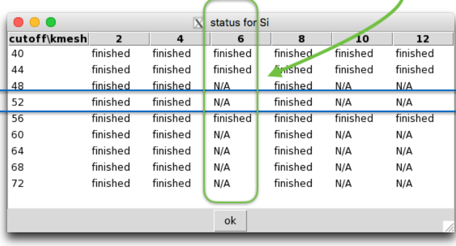
(4:optional) check crystal structure

(5) select calculation type

(6) select fixed value

(1) check k-point mesh dependency(cutoff energy is static)

(2) check cutoff dependency(k-point mesh is static)



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60	finished	finished	N/A	finished	N/A	N/A
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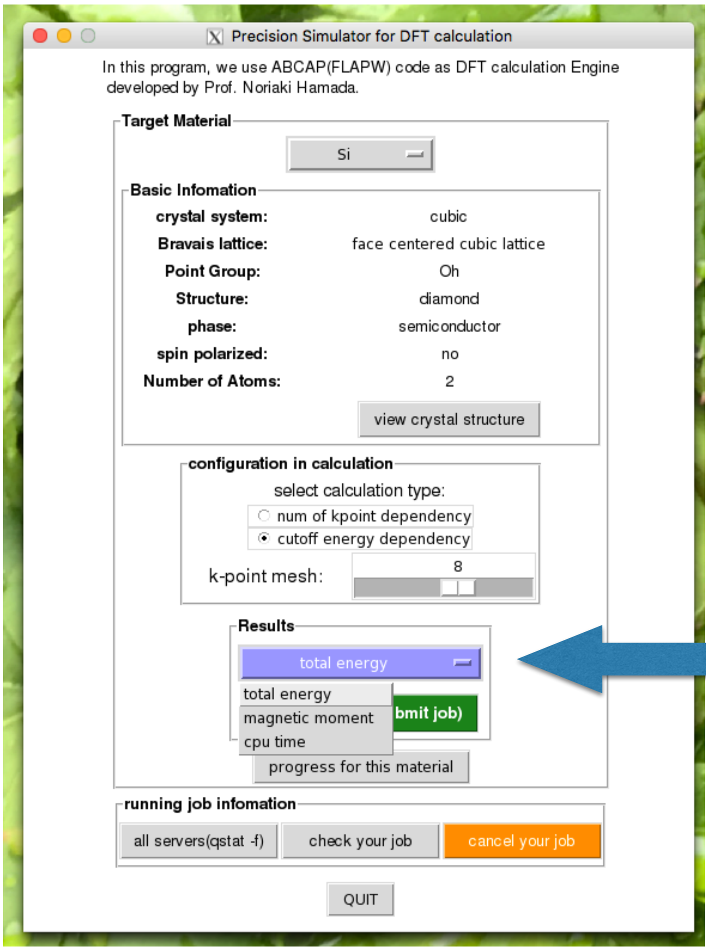
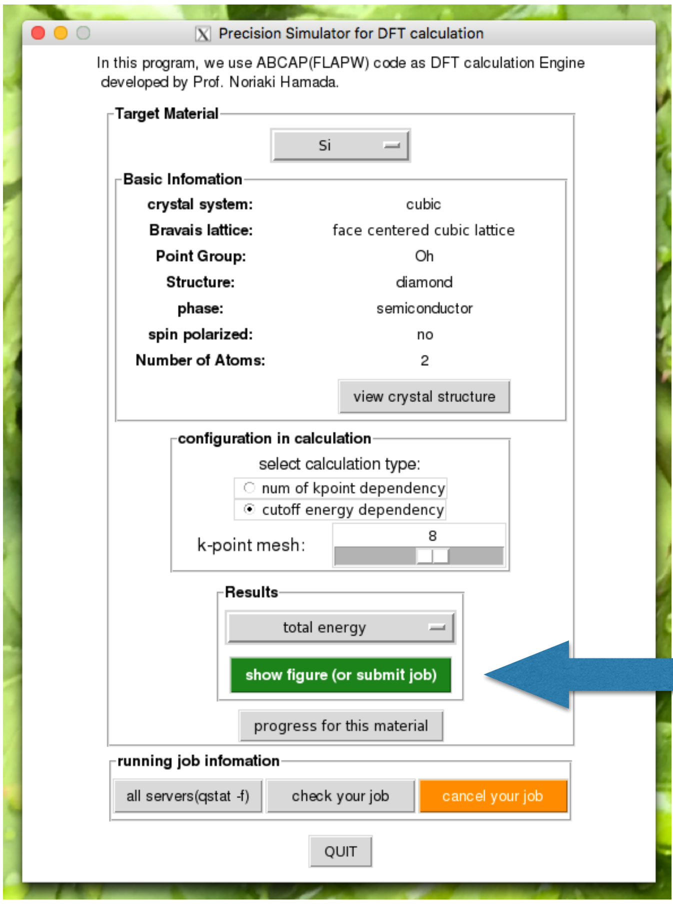
68	finished	finished	N/A	finished	N/A	N/A
72	finished	finished	N/A	finished	N/A	N/A

ok



(7)select graph type



(7) plot graph
(if you don't have DFT calculation results, you submit the job to calculate electronic structure)