Code FPSEID^{21} for excited state molecular dynamics

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Special thanks to Prof. Yayama at KOGAKUIN Univ.

FPSEID stands for '**F**irst-**P**rinciples **S**imulation tool for **E**lectron **I**on **D**ynamics
Named by Prof. Osamu Sugino ISSP (The Tokyo University)

Density functional theory for excited states

- The time-dependent density functional theory (TDDFT)
  - History in short
    - 1964 Hohenberg Kohn: many-body interaction as a functional of charge density → one-to-one relation between $V_{ext}(\boldsymbol{r})$ and $\rho(\boldsymbol{r})$
      → 1965 Kohn Sham equation $H^{KS}(\boldsymbol{r})\psi_n(\boldsymbol{r}) = \epsilon_n\psi_n(\boldsymbol{r})$
    - 1984 Runge Gross: proof of one-to-one relation between $V_{ext}(\boldsymbol{r},t)$ and $\rho(\boldsymbol{r},t)$
      → The time-dependent Kohn-Sham equation $i\frac{\partial}{\partial t}\psi_n(\boldsymbol{r},t) = H^{KS}(\boldsymbol{r},t)\psi_n(\boldsymbol{r},t)$

- Application of TDDFT
  - Optical response (within linear or non-linear)
  - Excited state molecular dynamics within Ehrenfest approximation

How one can know the “one-to-one relation” between charge and potential in TDDFT?

- First, we can derive one-to-one relation between

  $\frac{\partial}{\partial t}\boldsymbol{J}(\boldsymbol{r},t)$ and $\frac{\partial}{\partial \boldsymbol{r}}V_{ext}(\boldsymbol{r},t)$ in analogy of Newton’s equation

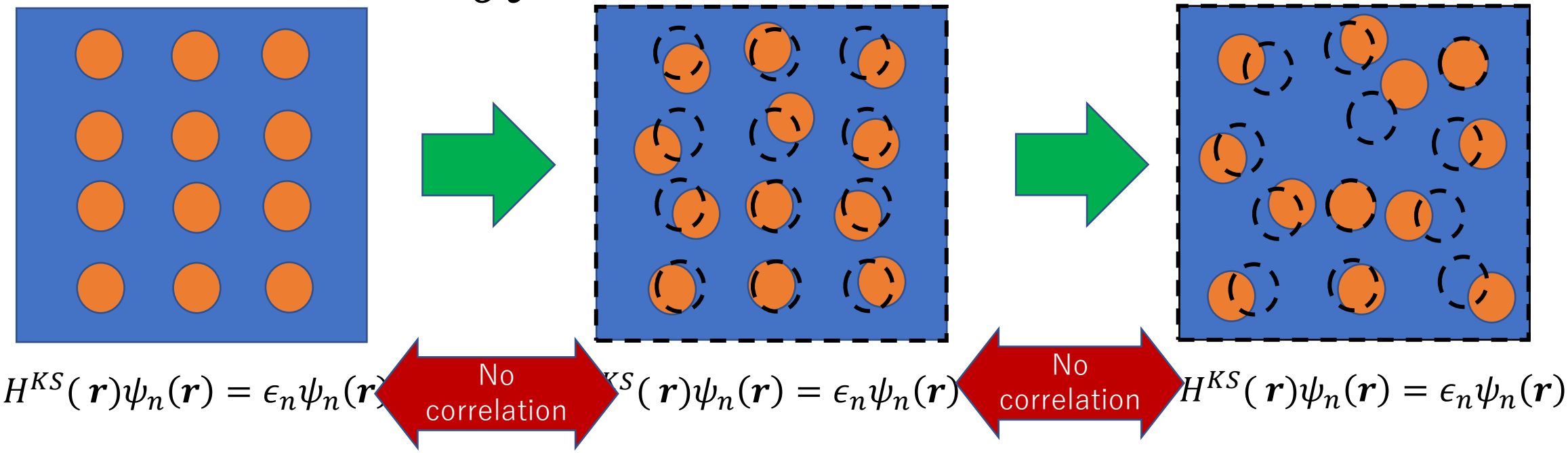
- Then, we can derive following relation

  $$\boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{r},t)=-\frac{\partial}{\partial t}\rho(\boldsymbol{r},t)$$

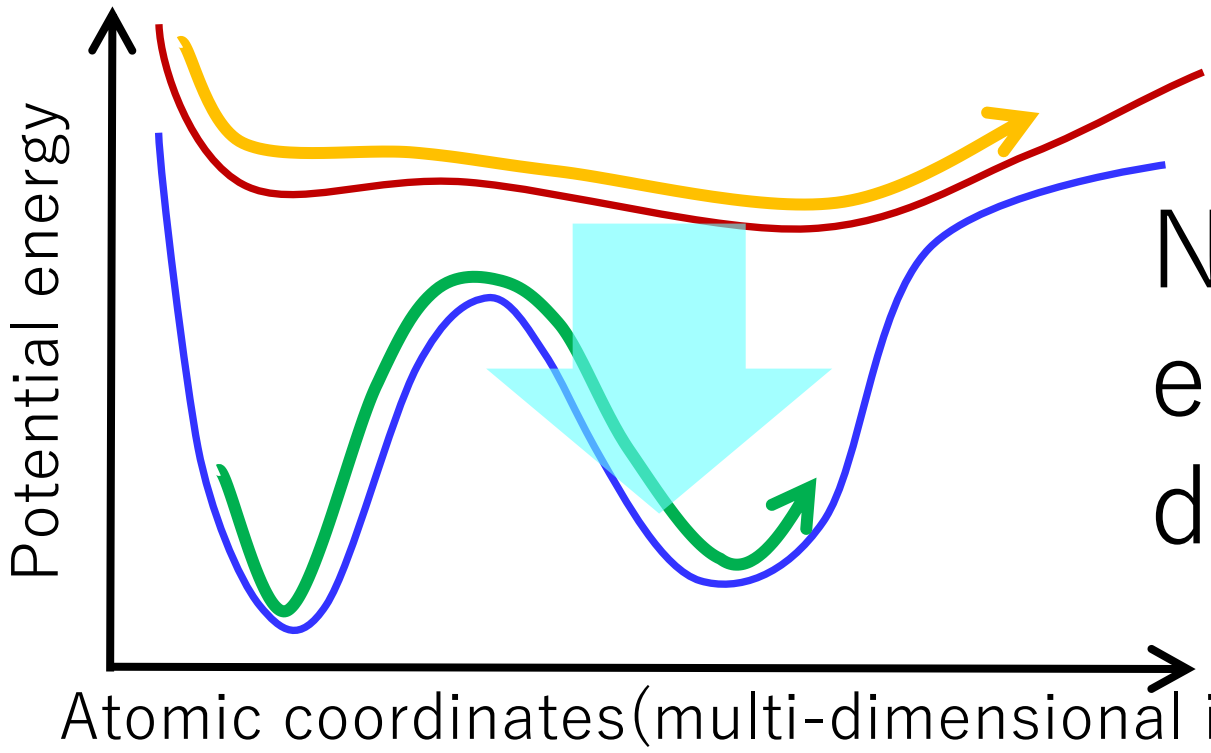
  derived from the time-dependent Schrödinger equation which guarantee the continuum condition of mass-flow.

Basic concept of ab-inito molecular dynamics (conventional scheme by 'Born-Oppenheimer')

$$M_I \frac{\partial^2}{\partial t^2} \boldsymbol{R}_I(t) = \boldsymbol{F}_I(t)$$



From ground state to excited state MD

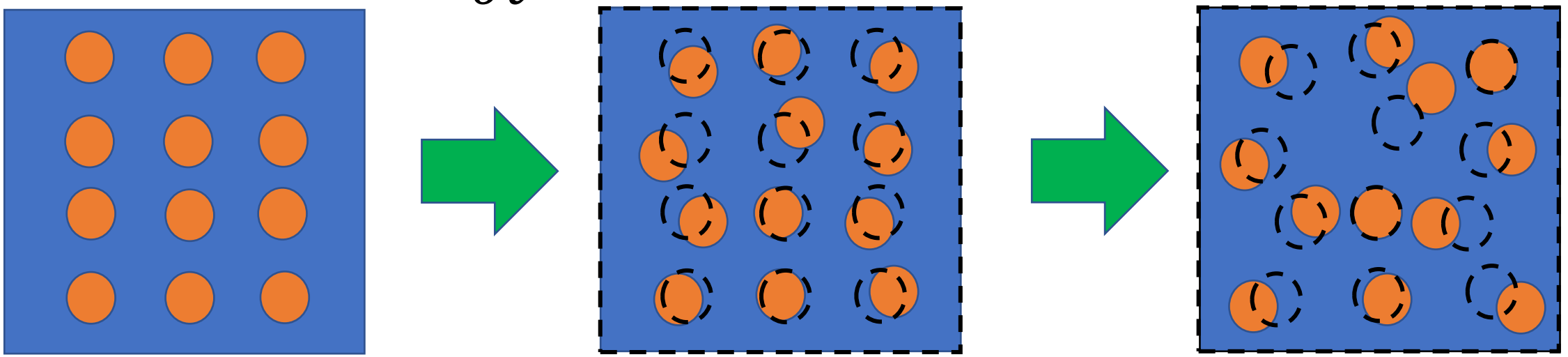


Need of tracing electron dynamics

Q: Can excited state continue forever? → finite lifetime of excited state

Basic concept of ab-inito molecular dynamics (Combination of electron-ion dynamics)

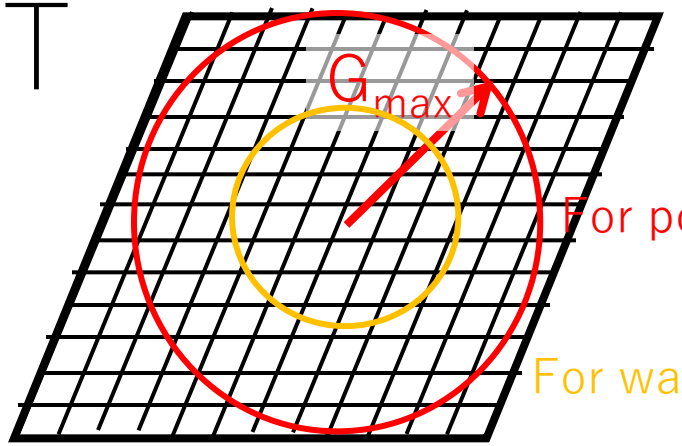
$$M_I \frac{\partial^2}{\partial t^2} \boldsymbol{R}_I(t) = \boldsymbol{F}_I(t)$$



$$H^{KS}(\boldsymbol{r},t)\psi_n(\boldsymbol{r},t) = i\frac{\partial}{\partial t}\psi_n(\boldsymbol{r},t)$$

The dynamics of ions and electrons correlate to each other

The different plane-wave basis set between DFT and TDDFT



For potential and charge

$|G_{max}|^2 \propto E_{cut}$

For wave functions

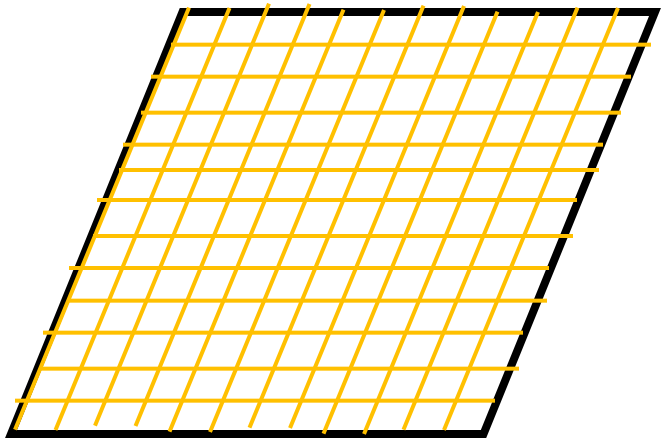
- DFT : a compact sphere for wavefunctions

$$\rho(\boldsymbol{r}) = \sum_{\boldsymbol{G}}^{|\boldsymbol{G}|<G_{cut}} \rho(\boldsymbol{G})\ e^{-i\boldsymbol{G}\cdot\boldsymbol{r}}$$

$$\rho(\boldsymbol{r}) = \sum_{n} \psi_n^*(\boldsymbol{r})\psi_n(\boldsymbol{r}) = \sum_{n} \sum_{\boldsymbol{G},\boldsymbol{G}'}^{|\boldsymbol{G}-\boldsymbol{G}'|<G_{cut}} C_n^*(\boldsymbol{G}')C_n(\boldsymbol{G})e^{i(\boldsymbol{G}-\boldsymbol{G}')\cdot\boldsymbol{r}}$$

- TDDFT: a full grid for wavefunctions (due to application of the time-evolution operator

$$e^{-i\int dt H^{KS}(\boldsymbol{r},t)}$$



The FPSEID[21] code

Please visit https://staff.aist.go.jp/yoshi-miyamoto

You can find this URL by Google with 'TDDFT AIST.'

Short description

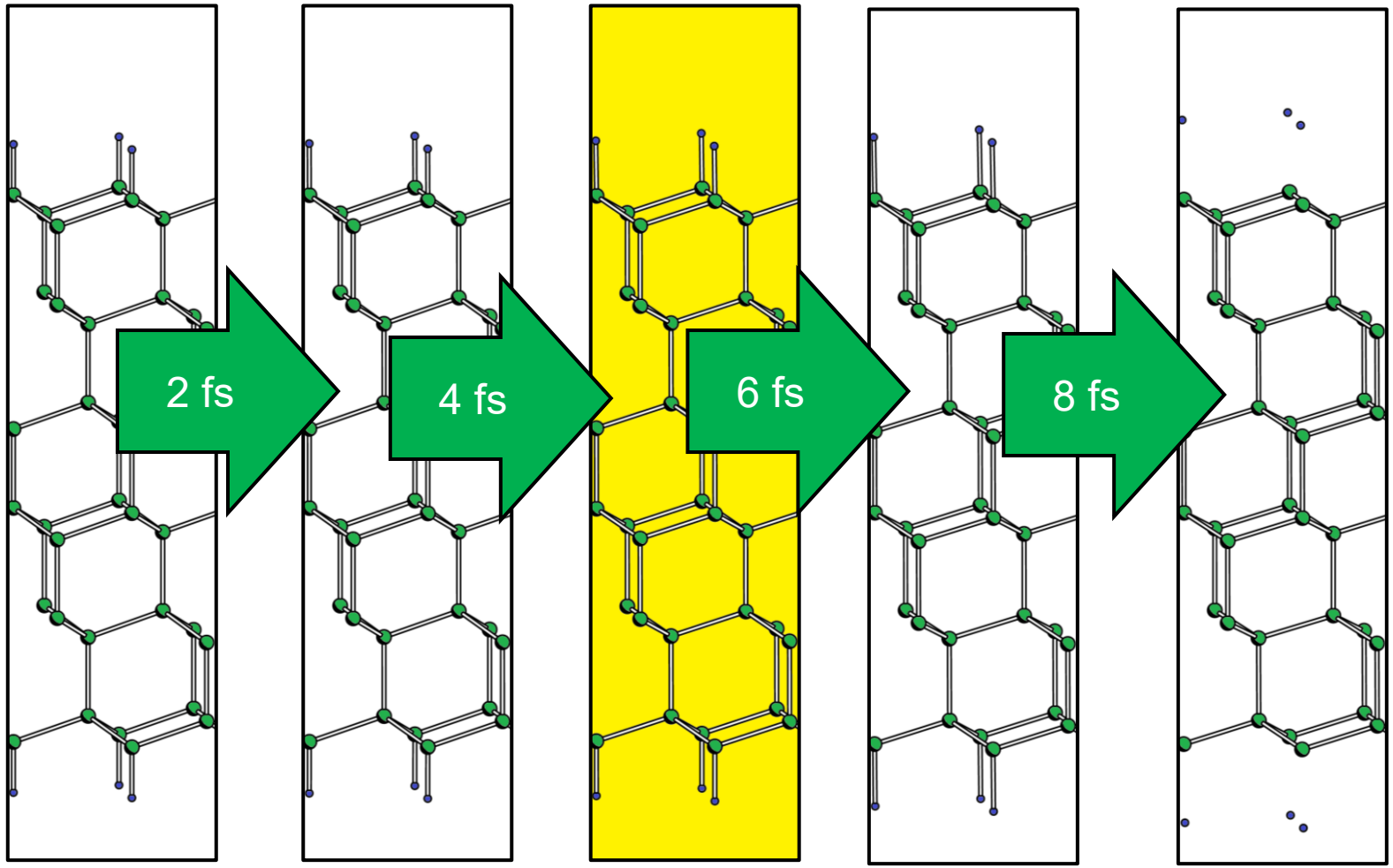
- On a basis of TDDFT (Runge, Gross, PRL **52**, 997 (1984)
- Plane wave basis set
- Norm conserving pseudopotentials: (so far, available for colored elements in a periodic table below)
- MD with Hellman-Feynman force (Ehrenfest approximation)
- Numerical details are written in Sugino, Miyamoto PRB**59**, 2579 (1999).

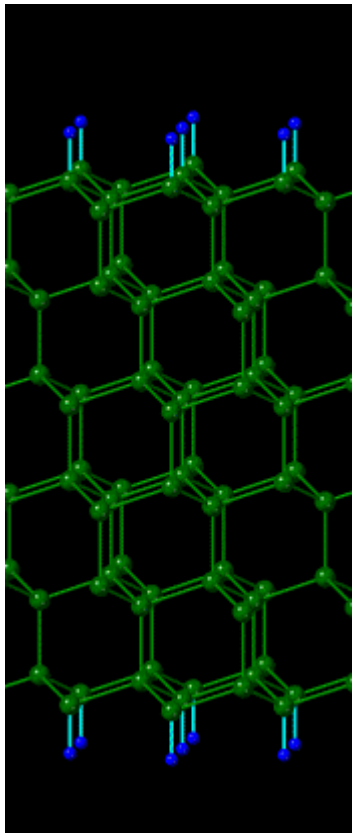
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

Today's exercise

- Si(111) 1x1 surface with Hydrogen termination

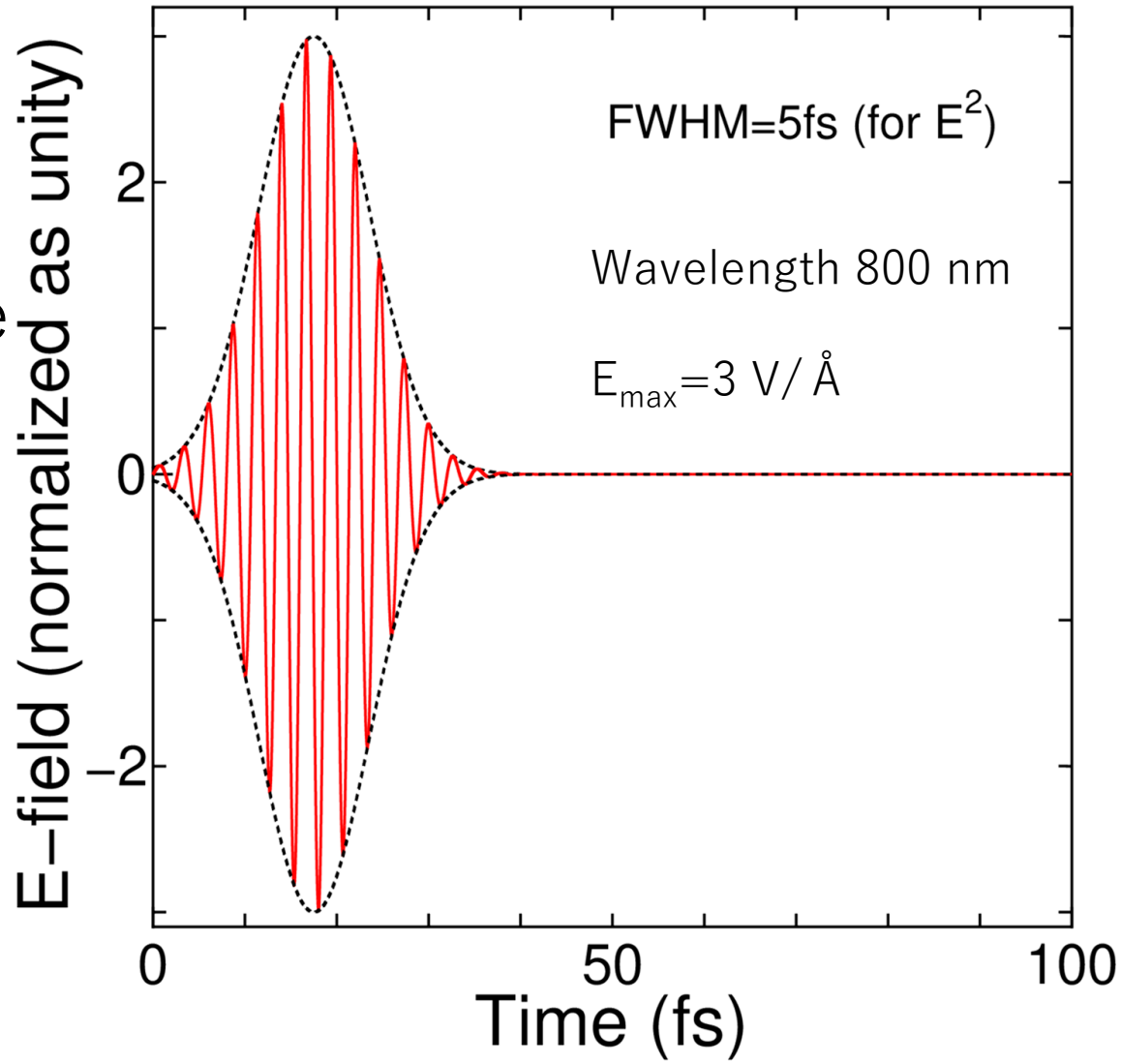
We will shine ultra short-pulse laser on it and see H-desorption





We will design shape of laser

Wavelength – see the frequent pitch
FWHM – see envelope shape
E-field intensity – see envelope shape



Now practice on you account ‘stud** ’
Please login.

First of all, copy three directories as follows

```
$cp –r /home/teac28/lm .
$cp –r /home/teac28/TR .
$cp –r /home/teac28/Si111-1x1H .
```

executing modules

pseudopotentials

Input data and job-scripts

The account and IP address are teac28@133.1.100.216

Check what you copied

- In the directory ‘lm’

  cg_exe
  sd_exe
  structure_view
  tddft_exe
  wf_decomp1d_input.x
  wfp2cube_watom.x

- In the directory ‘TR’

  TR.C95g_asci
  TR.H99g_asc
  TRLDA.Al18e_asci
  TRLDA.Al18g_asci
  TR.O94sp_asc.txt
  TR.Si93e_asci
  TR.Si93g_asci

  - In the directory ‘Si111-1x1H’

    Avec_begin
    Eext_begin
    Etot_begin
    Ework_begin
    Exec_cg.sh
    Exec_sd.sh
    FWHM=2fs-5.0VpA
    Si111-H.in
    Si111-H_sd.in
    Si111-H_tm.in_begin
    size.dat
    sym.C1

See next page

Check what you copied (continued)

- Go sub directory ‘FWHM=2fs-5.0VpA’

```
Exec_tm.sh
ChgDen.sh
laser.dat
Si111-H_tm.in
size.dat
sym.C1
```

Now go back to the directory ‘Si111-1x1H’

First step: run ordinary plane-wave code with given atomic geometry – ‘Si111-1x1H.in’

Use compact sphere for wavefunctions

Before running, let's visualize the input data with use of the VESTA

Please type following in the directory 'Si111-1x1H'

```
~/lm/structure_view Si111-H.in
```

Then you get prompt message

```
 # of element type=          2
name of 1-st type element?
```

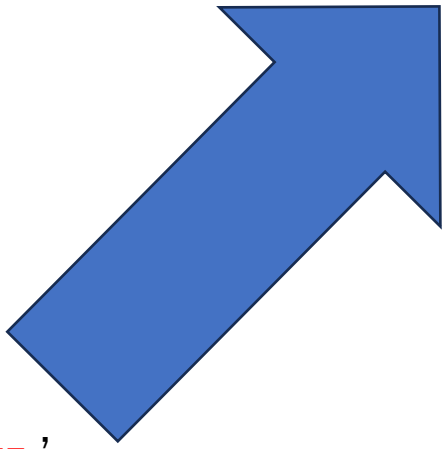
Please type 'Si,' then you get

```
Si is read
name of 2-nd type element?
```

Please type 'H', then you get

```
H is read
```

Then you find a new file 'structure.xyz.'

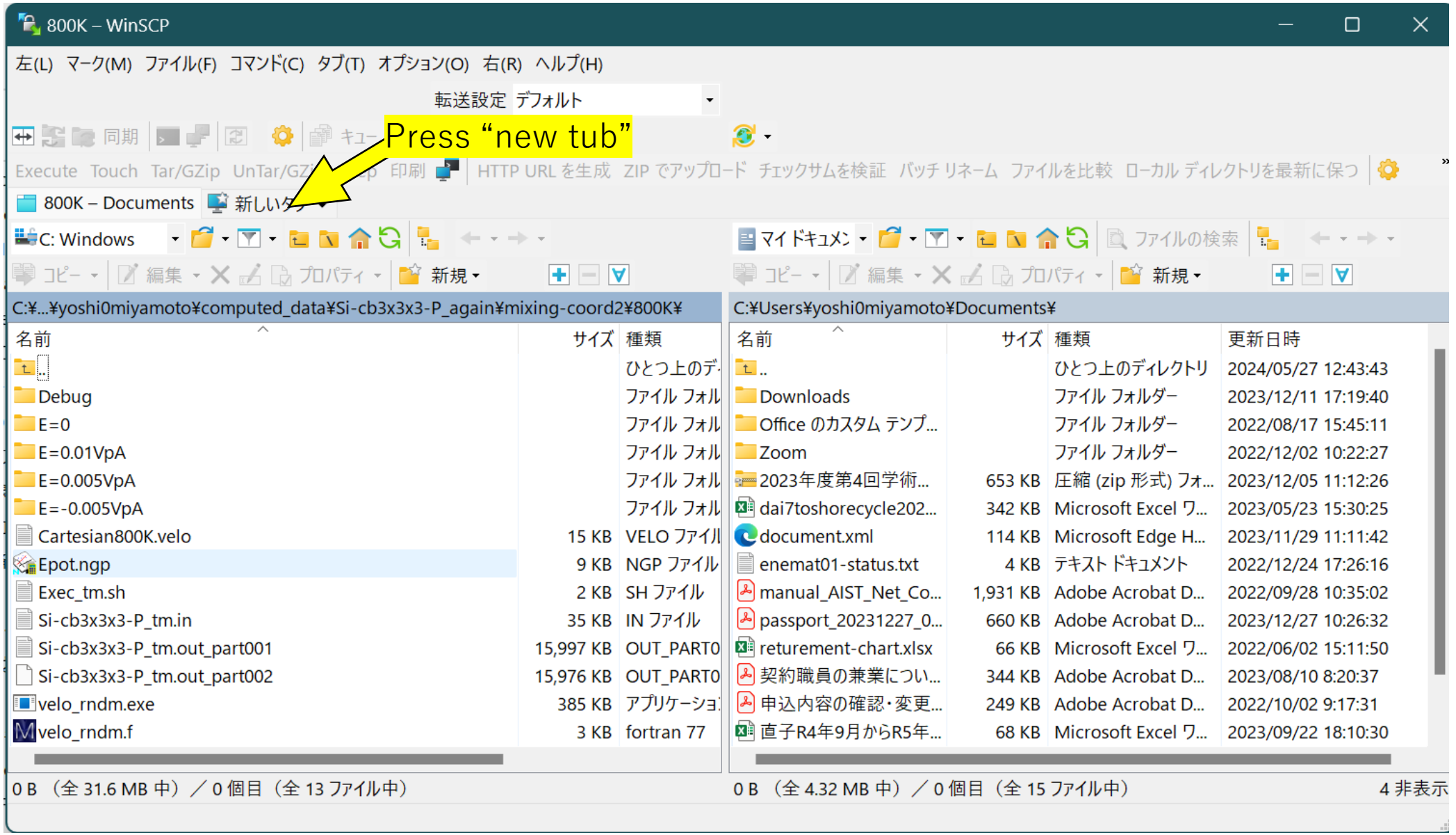


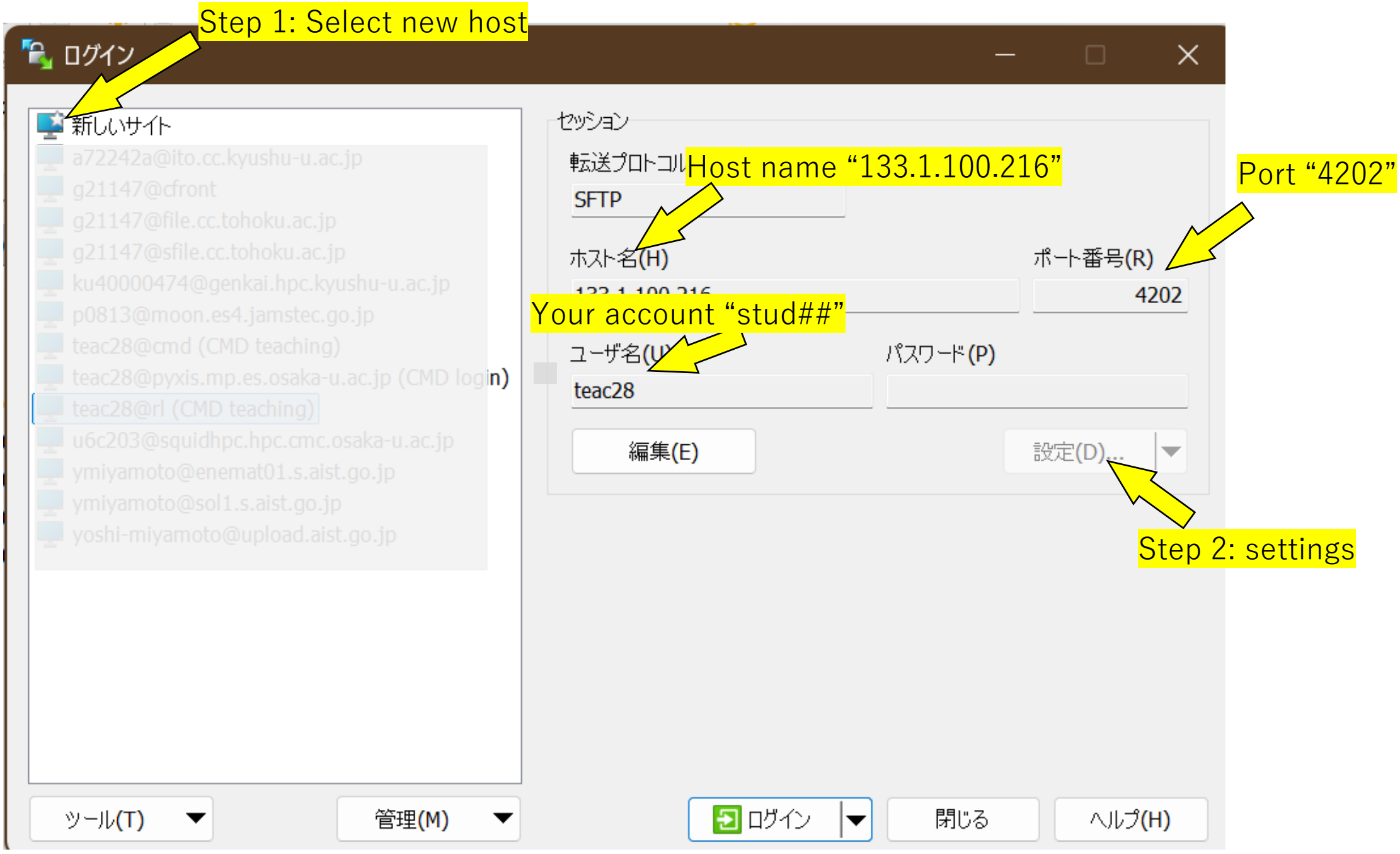
When you can use X-window from your terminal, you can activate VESTA

If you are Windows user and NOT able to use X-window on your terminal

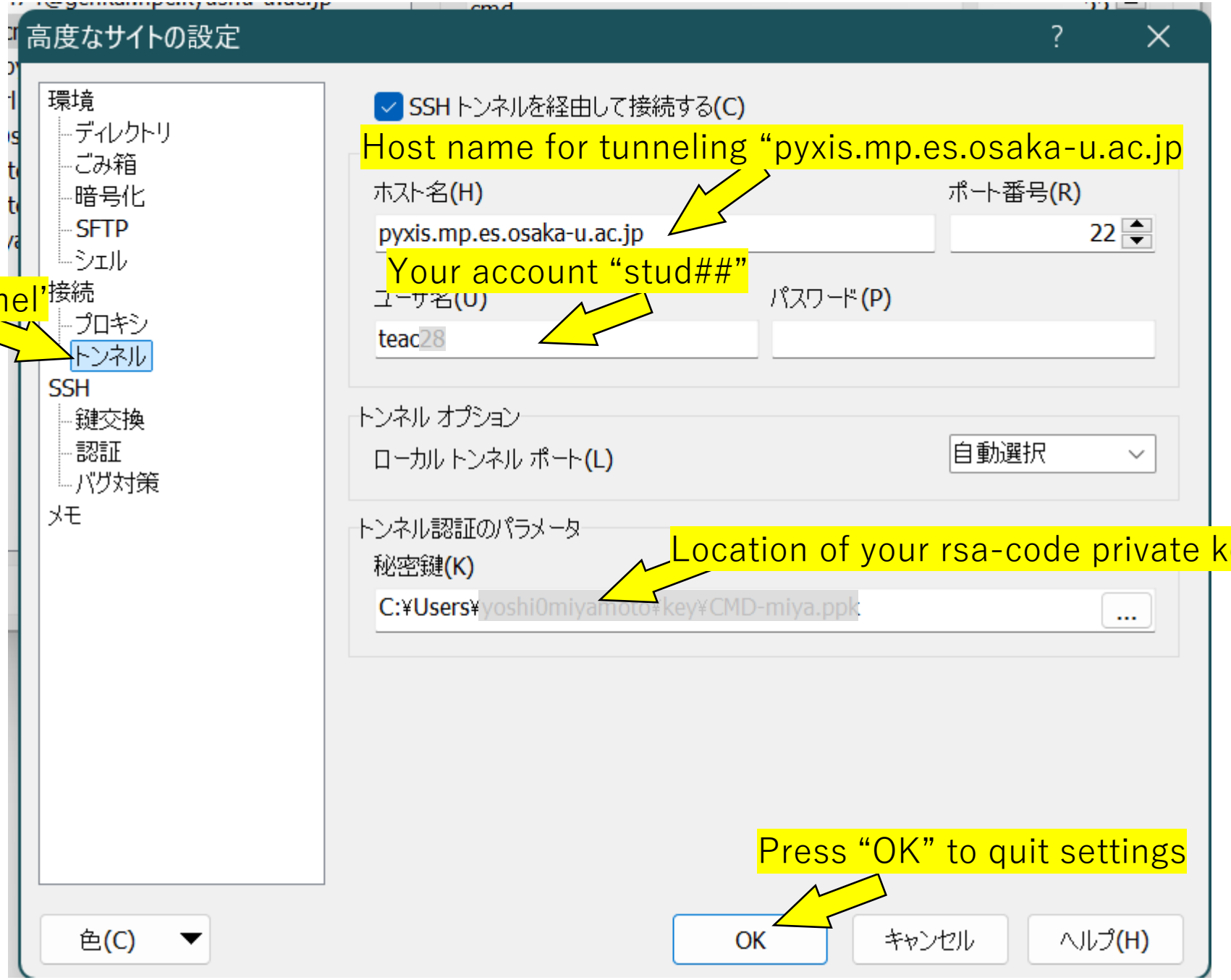
1. Install “VESTA” for Windows on your PC.
2. Transfer “Si111-H.in” file from ‘cmd’ server to your local PC using WinSCP software.

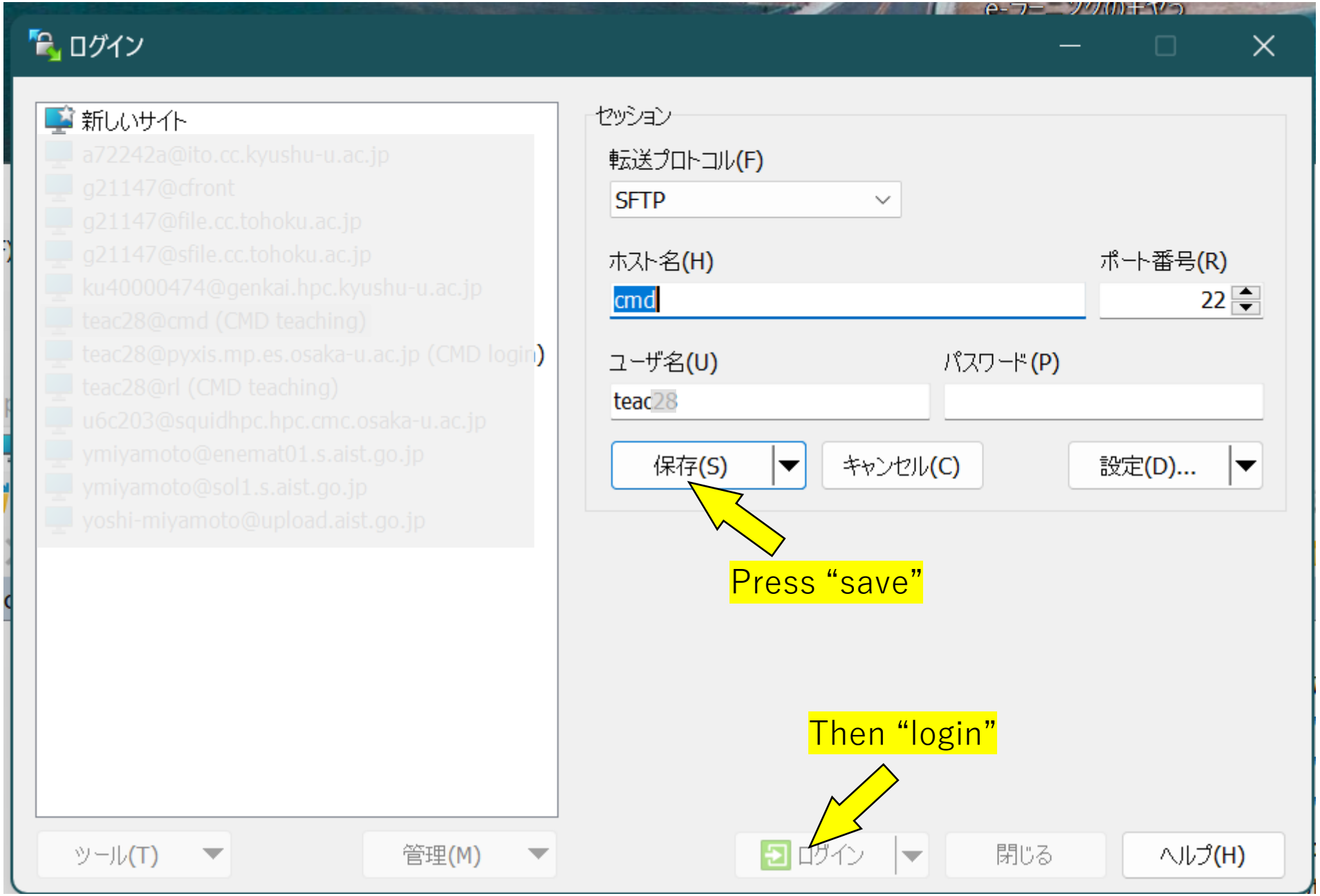
Activate WinSCP




Step 1: Select new host
ログイン
新しいサイト
a72242a@ito.cc.kyushu-u.ac.jp
g21147@cfront
g21147@file.cc.tohoku.ac.jp
g21147@sfile.cc.tohoku.ac.jp
ku40000474@genkai.hpc.kyushu-u.ac.jp
p0813@moon.es4.jamstec.go.jp
teac28@cmd (CMD teaching)
teac28@pyxis.mp.es.osaka-u.ac.jp (CMD login)
teac28@rl (CMD teaching)
u6c203@squidhpc.hpc.cmc.osaka-u.ac.jp
ymiyamoto@enemat01.s.aist.go.jp
ymiyamoto@sol1.s.aist.go.jp
yoshi-miyamoto@upload.aist.go.jp
セッション
転送プロトコル
SFTP
Host name “133.1.100.216”
Port “4202”
ホスト名(H)
ポート番号(R)
4202
Your account “stud##”
ユーザ名(U)
パスワード(P)
teac28
編集(E)
設定(D)...
Step 2: settings
ツール(T)
管理(M)
ログイン
閉じる
ヘルプ(H)

For settings




ログイン
新しいサイト
a72242a@ito.cc.kyushu-u.ac.jp
g21147@cfront
g21147@file.cc.tohoku.ac.jp
g21147@sfile.cc.tohoku.ac.jp
ku40000474@genkai.hpc.kyushu-u.ac.jp
teac28@cmd (CMD teaching)
teac28@pyxis.mp.es.osaka-u.ac.jp (CMD login)
teac28@rl (CMD teaching)
u6c203@squidhpc.hpc.cmc.osaka-u.ac.jp
ymiyamoto@enemat01.s.aist.go.jp
ymiyamoto@sol1.s.aist.go.jp
yoshi-miyamoto@upload.aist.go.jp
セッション
転送プロトコル(F)
SFTP
ホスト名(H)
cmd
ポート番号(R)
22
ユーザ名(U)
teac28
パスワード(P)
保存(S)
キャンセル(C)
設定(D)...
Press “save”
Then “login”
ツール(T)
管理(M)
ログイン
閉じる
ヘルプ(H)

Practical way in case of trouble with VESTA especially for Mac users.

Dwonload VESTA for Mac version on your PC and install this
See for latest version (scroll down on the URL below)
https://jp-minerals.org/vesta/en/download.html

Then download the ‘structure.xyz’ file from ‘cmd ‘workstation to your PC, and run VESTA

```
scp  -P 4202  stud24@133.1.100.216:Si111-1x1H/structure.xyz .
```

Your account

~~scp -P 4202 -oProxyCommand='ssh -W %h:%p stud##@pyxis.mp.es.osaka-u.ac.jp' stud##@133.1.100.216:Si111-1x1H/structure.xyz .~~

Prepare to run ‘cg_exe’ (ordinary plane-wave code) check the contents of input data ‘Si111-H.in’

```
%%% Si(111)1x1 H-term cell %%%%
STND KPOINT=MESH ALAT=4.4427103214141699 ZVAL=50 RCUT=845 GCUT=12.0
PP=(KB,SOFT) CD=ATOM WF=INIT CG=(5,8,3) SCF=60 EXT=PANDEY
OUTWF=23 METAL=(25,0) KCONT=0 FFTWF
RMIX=0.03 CONV=1.D-7 MAXFN=0 OKSTEP=0.1D0/
  1.4142135623730951   -0.8164965809277260    0.0000000000000000
  1.4142135623730951    0.8164965809277260    0.0000000000000000
  0.0000000000000000    0.0000000000000000   13.1042541360369356
 2   Si12H2   # of Atomic types
12   2  28.0855
   0.0000000000000000    0.0000000000000000    0.0380725996019826   TAU(   1)
   0.3333333333333333    0.3333333333333333    0.0628830683197726   TAU(   2)
   0.3333333333333333    0.3333333333333333    0.1388370510257218   TAU(   3)
  -0.3333333333333333   -0.3333333333333333    0.1638618412213989   TAU(   4)
  -0.3333333333333333   -0.3333333333333333    0.2398223878715089   TAU(   5)
  -0.0000000000000000   -0.0000000000000000    0.2642651909875856   TAU(   6)
  -0.0000000000000000   -0.0000000000000000   -0.0380725996019826   TAU(   7)
  -0.3333333333333333   -0.3333333333333333   -0.0628830683197726   TAU(   8)
  -0.3333333333333333   -0.3333333333333333   -0.1388370510257218   TAU(   9)
   0.3333333333333333    0.3333333333333333   -0.1638618412213989   TAU(  10)
   0.3333333333333333    0.3333333333333333   -0.2398223878715089   TAU(  11)
   0.0000000000000000    0.0000000000000000   -0.2642651909875856   TAU(  12)
-2   0   1.0
  -0.0000000000000000   -0.0000000000000000    0.3131888120278811   TAU(  13)
   0.0000000000000000    0.0000000000000000   -0.3131888120278811   TAU(  14)
30.0     Rcut for LVGENX
 4
 1  1  0
 2  2  4
 1  0  0    just these three lines
 0  1  0
 0  0  1
 0  0  0
10 10 10    NDX NDY NDZ for DOS
2.0  2.0    for type 1 -- #s of electrons on s- and p-orbitals
1.0  0.0
```

Type 1 atom ‘Si’

Type 2 atom ‘H’

```
4
1  1  0
2  2  4
```

This will be discussed later

Input data‘sym.C1’

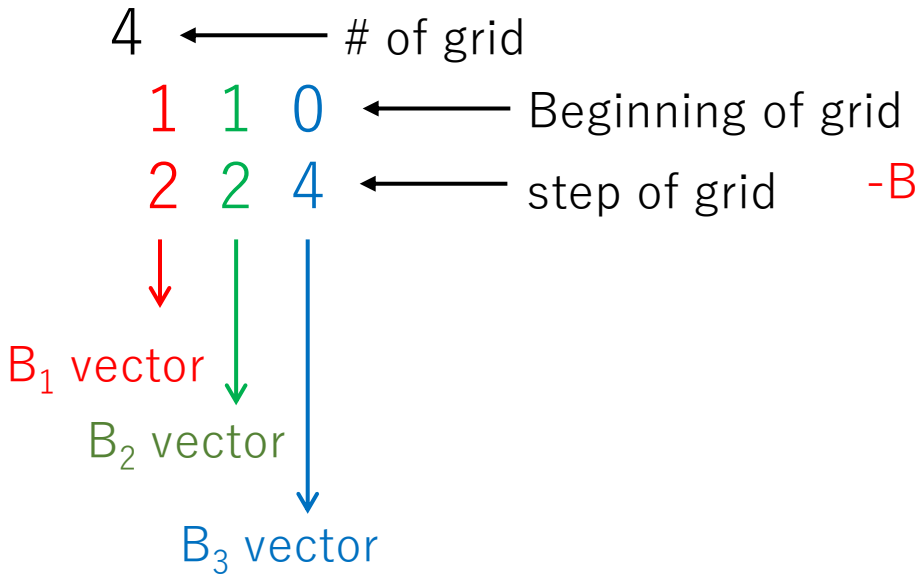
```
1
  1    1 0 0    0 1 0    0 0 1
```

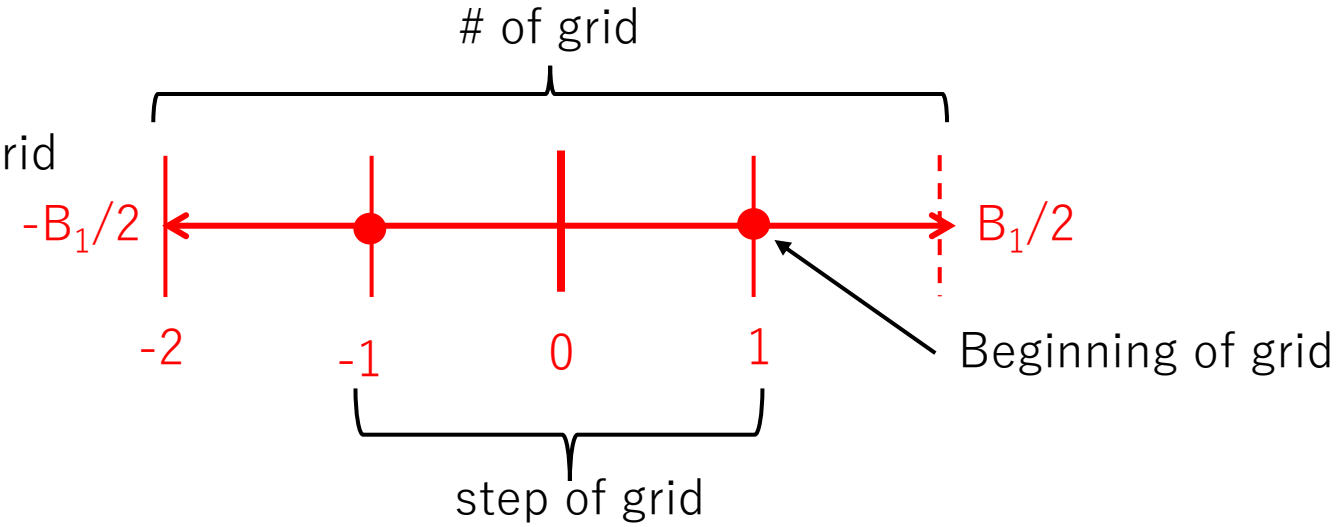
Input data ‘size.dat’

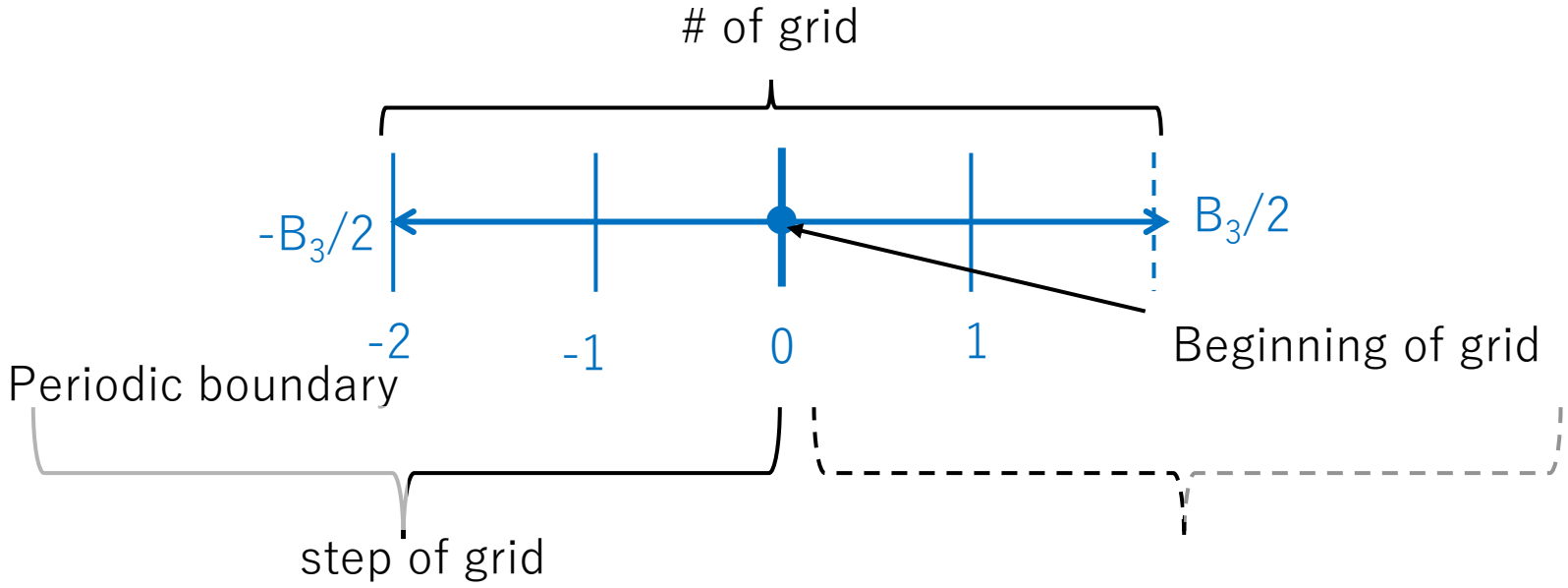
```
15   15  129 for FFT mesh grids
      18628        2328 for NG and NG2 : G for potential and wf
 2 # of irreducible k-points
 25    7 # of occupied and empty bands
 14   2 # of atoms and atomic types per cell
```

The ‘size.dat’ gives necessary size for arrays needed to perform calculations

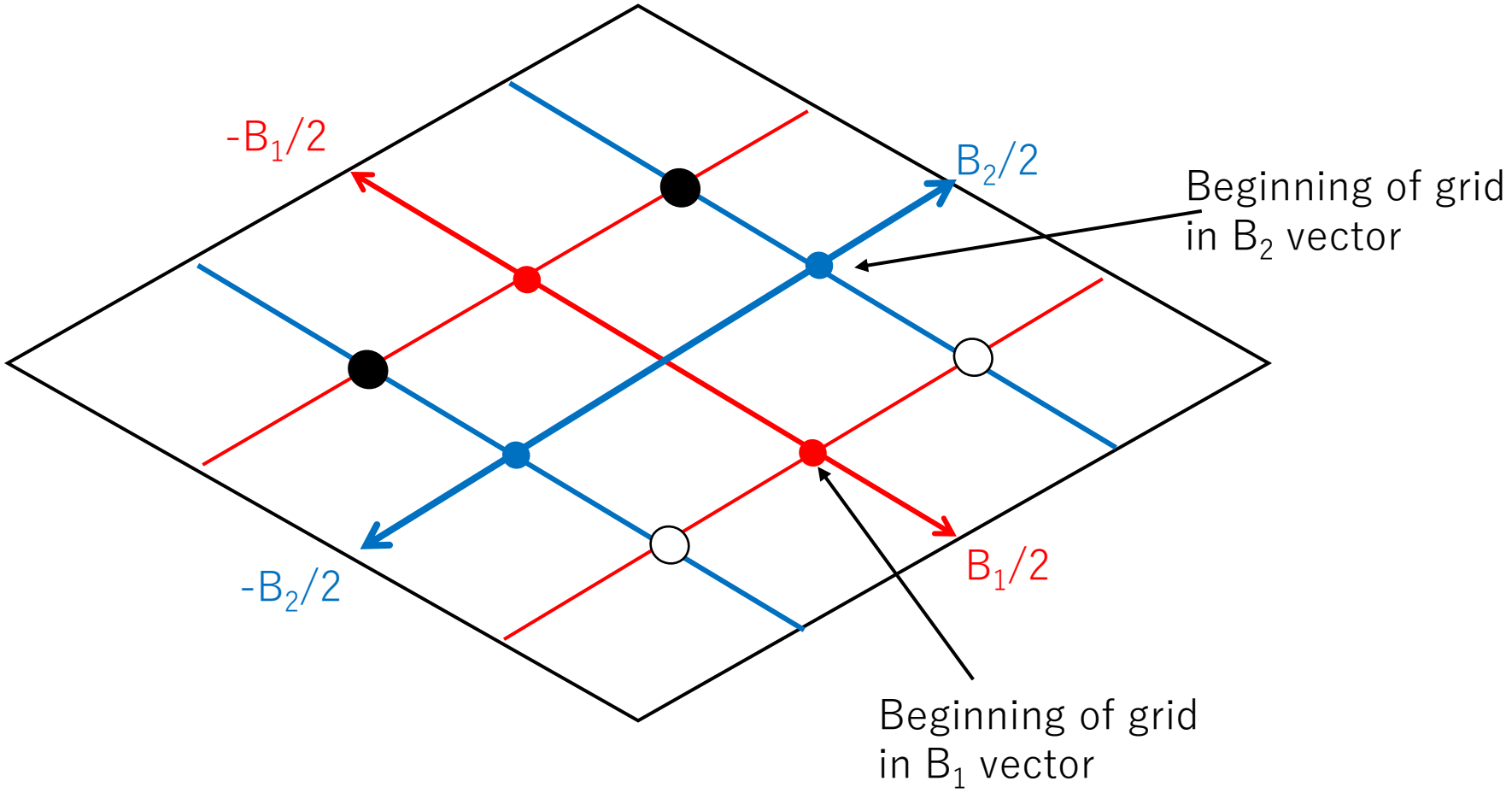
Rule of k-points generation







Rule of k-points generation (continued)



Prepare to run ‘cg_exe’ (ordinary plane-wave code)
Please see a job-script ‘Exec_cg.sh’, the template of which is

```
#!/bin/csh -f
#$ -N Si111-H-1x1H
#$ -q rl.q
#$ -cwd
#$ -j y
#$ -e std.err
#$ -o std.out
#$ -pe smp 1
### --- input files
setenv FORT41 ~/TR/TR.Si93g_asci
setenv FORT46 ~/TR/TR.Si93e_asci
setenv FORT42 ~/TR/TR.H99g_asc
setenv FORT54 size.dat
setenv FORT55 sym.C1
####
setenv FORT20 rh.Si111-H
setenv FORT22 wf.Si111-H
### --- output files
###
setenv FORT23 wf.Si111-H_new
setenv FORT88 wf_real.Si111-H
setenv FORT90 Vall.Si111-H
setenv FORT24 rh.Si111-H_new
setenv FORT25 Vint.temp
setenv FORT77 tau.Si111-H
setenv FORT78 need
setenv OMP_NUM_THREADS 1
~/lm/cg_exe  < Si111-H.in >& Si111-H.out
```

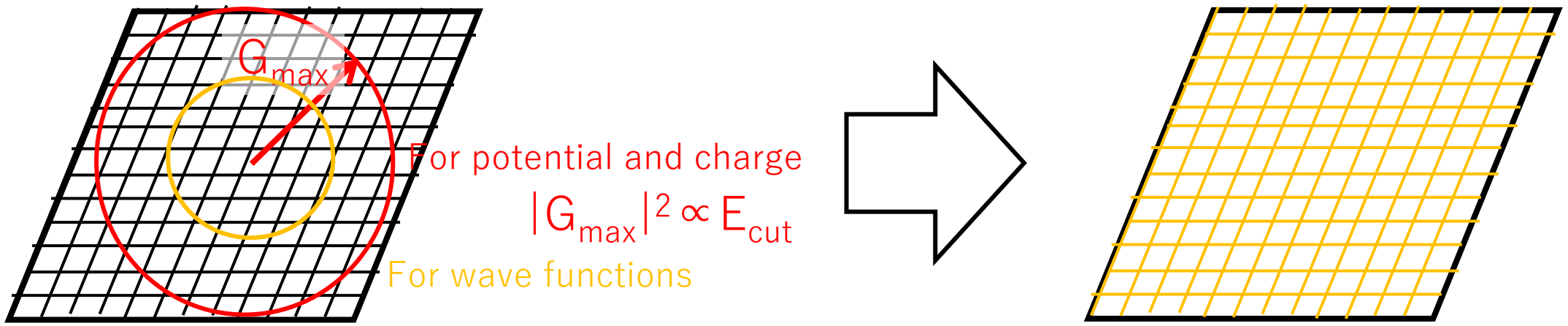
For type 1 atom ‘Si’
(Files are separated into two)

For type 2 atom ‘H’

After ‘qsub Exec_cg.sh’, please check new files (denoted in red in the script) appear.

rh.Si111-H_new
wf.Si111-H_new
wf_real.Si111-H
Si111-H.out

Second step: expand plane-waves from compact sphere to full-grid by running extended plane wave code with the same atomic geometry – ‘Si111-1x1H_sd.in’



Check a new input data ‘Si111-H_sd.in’ for the ‘sd_exe’ code

```
%%% Si(111)1x1 H-term cell %%%%
STND KPOINT=MESH ALAT=4.4427103214141699 ZVAL=50 RCUT=845 GCUT=12.0
PP=(KB,SOFT) CD=FILE WF=FFT SD=(5,8,3) SCF=60 EXT=PANDEY
OUTWF=23 METAL=(25,0) KCONT=0
RMIX=0.03 CONV=1.D-7 MAXFN=0 OKSTEP=0.1D0/
  1.4142135623730951   -0.8164965809277260    0.0000000000000000
  1.4142135623730951    0.8164965809277260    0.0000000000000000
  0.0000000000000000    0.0000000000000000   13.1042541360369356
 2   Si12H2   # of Atomic types
 12   2  28.0855
   0.0000000000000000    0.0000000000000000    0.0380725996019826   TAU(   1)
   0.3333333333333333    0.3333333333333333    0.0628830683197726   TAU(   2)
   0.3333333333333333    0.3333333333333333    0.1388370510257218   TAU(   3)
  -0.3333333333333333   -0.3333333333333333    0.1638618412213989   TAU(   4)
  -0.3333333333333333   -0.3333333333333333    0.2398223878715089   TAU(   5)
  -0.0000000000000000   -0.0000000000000000    0.2642651909875856   TAU(   6)
  -0.0000000000000000   -0.0000000000000000   -0.0380725996019826   TAU(   7)
  -0.3333333333333333   -0.3333333333333333   -0.0628830683197726   TAU(   8)
  -0.3333333333333333   -0.3333333333333333   -0.1388370510257218   TAU(   9)
   0.3333333333333333    0.3333333333333333   -0.1638618412213989   TAU(  10)
   0.3333333333333333    0.3333333333333333   -0.2398223878715089   TAU(  11)
   0.0000000000000000    0.0000000000000000   -0.2642651909875856   TAU(  12)
-2   0   1.0
  -0.0000000000000000   -0.0000000000000000    0.3131888120278811   TAU(  13)
   0.0000000000000000    0.0000000000000000   -0.3131888120278811   TAU(  14)
 30.0     Rcut for LVGENX
  4
  1  1  0
  2  2  4
  1  0  0    just these three lines
  0  1  0
  0  0  1
  0  0  0
 10 10 10    NDX NDY NDZ for DOS
 2.0  2.0    for type 1 -- #s of electrons on s- and p-orbitals
 1.0  0.0
```

Different line from ‘Si111-H.in’

Before run ‘sd_exe’ mv

‘rh.Si111-H_new’ to ‘rh.Si111-H’
‘wf.Si111-H_new’ to ‘wf.Si111-H’

Prepare to run ‘sd_exe’ full-grid plane-wave code
Check the job-script ‘Exec_sd.sh’ which is almost the same as ‘Exec_cg.sh’

```
#!/bin/csh -f
#$ -N Si111-H-1x1H
#$ -q rl.q
#$ -cwd
#$ -j y
#$ -e std.err
#$ -o std.out
#$ -pe smp 1
### --- input files
setenv FORT41 ~/TR/TR.Si93g_asci
setenv FORT46 ~/TR/TR.Si93e_asci
setenv FORT42 ~/TR/TR.H99g_asc
setenv FORT54 size.dat
setenv FORT55 sym.C1
####
setenv FORT20  rh.Si111-H
setenv FORT22 wf_fft.Si111-H
### --- output files
###
setenv FORT23 wf_fft.Si111-H_new
setenv FORT88 wf_real.Si111-H
setenv FORT90 Vall.Si111-H
setenv FORT24 rh.Si111-H_new
setenv FORT25 Vint.temp
setenv FORT77 tau.Si111-H
setenv FORT78 need
setenv OMP_NUM_THREADS 1
~/lm/sd_exe  < Si111-H_sd.in >& Si111-H_sd.out
```

Now this file becomes an input file.

After ‘qsub Exec_sd.sh’, please check new files (denoted in red) appear.
rh.Si111-H_new
wf_fft.Si111-H_new
Si111-H_sd.out

The next step is preparation for TDDFT calculation ‘tddft_exe’

Please move the created files of ‘sd_exe’ ended as ‘*_new’, to those ended as ‘*_begin’ for initial condition of ‘tddft_exe’

```
$mv rh.Si111-H_new rh.Si111-H_begin
$mv wf_fft.Si111-H_new wf_fft.Si111-H_begin
```

Protect all files ended as ‘*_begin’ from overwirting by using chmod command as

```
$chmod 444 *_begin
```

to avoid accidental update of the data for the initial condition,

Also note we already have other ‘*_begin’ files as

```
Avec_begin
Eext_begin
Etot_begin
Ework_begin
Si111-H_tm.in_begin
```

Check what are written in ‘Si111-H_tm.in_begin’

PP=(KB,SOFT) CD=FILE WF=32 CG=(5,8,3) SCF=10 EXT=PANDEY
OUTWF=23 METAL=(25,0) KCONT=0
dt=0.40 tstep=1000 TMOD=50 SUZUKI=4
RMIX=0.03 CONV=1.D-5 MAXFN=0 OKSTEP=0.1D0/

```
%%% Si(111)1x1 H-term cell %%%%
STND KPOINT=MESH ALAT=4.4427103214141699 ZVAL=50 RCUT=845 GCUT=12.0
PP=(KB,SOFT) CD=FILE WF=32 CG=(5,8,3) SCF=10 EXT=PANDEY
OUTWF=23 METAL=(25,0) KCONT=0
dt=0.40 tstep=1000 TMOD=50 SUZUKI=4
RMIX=0.03 CONV=1.D-5 MAXFN=0 OKSTEP=0.1D0/
  1.4142135623730951   -0.8164965809277260    0.0000000000000000
  1.4142135623730951    0.8164965809277260    0.0000000000000000
  0.0000000000000000    0.0000000000000000   13.1042541360369356
 2   Si12H2   # of Atomic types
 12   2  28.0855
   0.0000000000000000   0.0000000000000000   0.0380725996019826   TAU(   1)
   0.3333333333333333   0.3333333333333333   0.0628830683197726   TAU(   2)
   0.3333333333333333   0.3333333333333333   0.1388370510257218   TAU(   3)
  -0.3333333333333333  -0.3333333333333333   0.1638618412213989   TAU(   4)
  -0.3333333333333333  -0.3333333333333333   0.2398223878715089   TAU(   5)
  -0.0000000000000000  -0.0000000000000000   0.2642651909875856   TAU(   6)
  -0.0000000000000000  -0.0000000000000000  -0.0380725996019826   TAU(   7)
  -0.3333333333333333  -0.3333333333333333  -0.0628830683197726   TAU(   8)
  -0.3333333333333333  -0.3333333333333333  -0.1388370510257218   TAU(   9)
   0.3333333333333333   0.3333333333333333  -0.1638618412213989   TAU(  10)
   0.3333333333333333   0.3333333333333333  -0.2398223878715089   TAU(  11)
   0.0000000000000000   0.0000000000000000  -0.2642651909875856   TAU(  12)
-2   0   1.0
  -0.0000000000000000  -0.0000000000000000   0.3131888120278811   TAU(  13)
   0.0000000000000000   0.0000000000000000  -0.3131888120278811   TAU(  14)
 30.0     Rcut for LVGENX
  4
  1  1  0
  2  2  4
  1  0  0    just these three lines
  0  1  0
  0  0  1
  0  0  0
 10 10 10    NDX NDY NDZ for DOS
 2.0  2.0    for type 1 -- #s of electrons on s- and p-orbitals
 1.0  0.0
   0.0   0.0   0.0
   0.0   0.0   0.0
....  ....  ......
   0.0   0.0   0.0
   0.0   0.0   0.0
   0.0   0.0   0.0
   0.0   0.0   0.0
   0.0   0.0   0.0
 0.0
```

Velocities for 14 atoms

time

Now we obtained initial conditions for ‘tddft_exe’

Exercise for TDDFT calculation:

Laser conditions FWHM=2 fs, wavelength 800 nm, max of E-field strength 5 V/ Å

Go to subdirectory ‘FWHM=2fs-5.0VpA’

Input files are

```
laser.dat
size.dat
sym.C1
```

Here, ‘sym.C1’ and ‘size.dat’ are the same.

The new data here is ‘laser.dat’ which is as follows

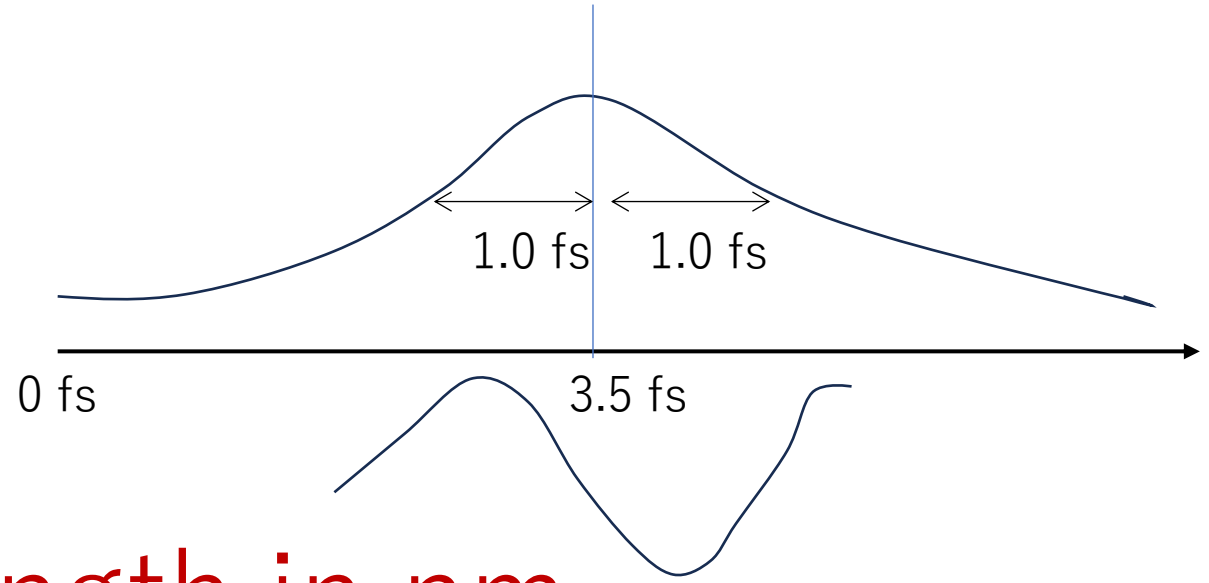
```
800   ! wavelength in nm
 3.5   ! peak position in fs
 1.0   ! half of FWHM in fs
 5.0d0   0.0  0.0   ! (Ex Ey Ez) in V/A
```

You can design these parameters!
But be careful to set red colored ones
as these take time.

The last line is E-field strength in (V/ Å) unit: In this case, E-field is polarized in the x-direction.

FWHM=2fs

laser.dat




```
800   ! wavelength in nm
  3.5   ! peak position in fs
  1.0   ! half of FWHM in fs
  5.0d0   0.0  0.0   ! (Ex Ey Ez) in V/A
```

In subdirectory ‘FWHM=2fs-5.0VpA’

Copy all ‘*_begin’ files from upper directory

```
$cp ../*_begin .
```

Move all ‘*_begin’ files to those without ‘_begin’ by following procedure

Firstly, please type

```
$ls –l *begin
```

Then you see all *_begin files. So please use ‘mv’ command like as

```
$mv Avec_begin Avec
$mv Etot_begin Etot
$mv Eext_begin Eext
$mv Ework_begin Ework
$mv rh.Si111-H_begin rh.Si111-H
$mv wf_fft.Si111-H_begin wf_fft.Si111-H
$mv Si111-H_tm.in_begin Si111-H_tm.in
```

```
#!/bin/csh -f
#$ -N Si111-H-1x1H
#$ -q rl.q
#$ -cwd
#$ -j y
#$ -e std.err
#$ -o std.out
#$ -pe fillup  6
### --- input files
setenv FORT41 ~/TR/TR.Si93g_asci
setenv FORT46 ~/TR/TR.Si93e_asci
setenv FORT42 ~/TR/TR.H99g_asc
####
setenv FORT53 laser.dat
setenv FORT54=size.dat
####
setenv FORT18 Eext
setenv FORT28 Etot
setenv FORT60 Avec
setenv FORT62 Ework
##
setenv FORT55 sym.C1
####
setenv FORT20 rh.Si111-H
setenv FORT22 wf_fft.Si111-H
### --- output files
setenv FORT19 Eext_new
setenv FORT29 Etot_new
setenv FORT61 Avec_new
setenv FORT63 Ework_new
###
setenv FORT23 wf_fft.Si111-H_new
setenv FORT88 wf_real.Si111-H
setenv FORT90 Vall.Si111-H
setenv FORT24 rh.Si111-H_new
setenv FORT30 rh.Si111-H_1000steps
setenv FORT25 Vint.temp
setenv FORT77 tau.Si111-H
setenv FORT78 need
setenv OMP_NUM_THREADS 1
mpirun –np 6 ~/lm/tddft_exe  < Si111-H_tm.in >& Si111-H_tm.out_1000steps
```

Check the script ‘Exec_tm.sh’ to run ‘tddft_exe’

$tail Si111-H_tm.out_1000steps

→ How to get results for MD?

See part of output file 'Si111-H_tm.out_1000steps' as below

```
Time (fsec) =     5.3240000000000007
 Positions
 -0.000023319445450 3   -0.000850271434070 8    0.039243251247306 5   TAU(  1)
  0.333408826792792 8    0.333036319122383 9    0.061350650178830 7   TAU(  2)
  0.332279733346478 5    0.332546565850942 4    0.140060911005488 5   TAU(  3)
 -0.332886092917295 7   -0.334492578090999 9    0.161989864576784 9   TAU(  4)
 -0.333170428838875 0   -0.332916360951341 1    0.240716630604600 3   TAU(  5)
 -0.000148467876287 1   -0.000271319891028 8    0.263141336814379 8   TAU(  6)
  0.000249645650970 2   -0.000390706789951 2   -0.039314568600173 9   TAU(  7)
 -0.333672964672216 1   -0.333415706253526 7   -0.061403261383194 2   TAU(  8)
 -0.333048522056190 2   -0.334535295447736 7   -0.140098019209296 6   TAU(  9)
  0.333339525101436 4    0.333328732127951 1   -0.162014992048004 5   TAU( 10)
  0.333577127111055 2    0.332226617834810 1   -0.240873826944240 5   TAU( 11)
 -0.000656564263128 9   -0.001094272064830 5   -0.263276972252446 7   TAU( 12)
 -0.007580507577339 9   -0.000398641838887 5    0.331318215667935 2   TAU( 13)
 -0.000457019257640 0    0.001812217879247 9   -0.330664797323335 7   TAU( 14)
```

The positions are the Whycoff coordinate, so you need data for the lattice vector to get the Cartesian coordinates.

But there will be easier way by using VESTA package as described in next page

Create '*.xyz' file for VESTA from TDDFT results

```
$ cp Si111-H_tm.in Si111-H_tm.in_1000steps
```

Then 'Si111-H_tm.in_1000steps' is as following

```
%%% Si(111)1x1 H-term cell %%%%
STND KPOINT=MESH ALAT=4.4427103214141699 ZVAL=50 RCUT=845 GCUT=12.0
PP=(KB,SOFT) CD=FILE WF=32 CG=(5,8,3) SCF=10 EXT=PANDEY
OUTWF=23 METAL=(25,0) KCONT=0
dt=0.40 tstep=1000 TMOD=50 SUZUKI=4
RMIX=0.03 CONV=1.D-5 MAXFN=0 OKSTEP=0.1D0/
  1.4142135623730951   -0.8164965809277260    0.0000000000000000
  1.4142135623730951    0.8164965809277260    0.0000000000000000
  0.0000000000000000    0.0000000000000000   13.1042541360369356
 2   Si12H2   # of Atomic types
 12   2  28.0855
   0.0000000000000000    0.0000000000000000    0.0380725996019826   TAU(   1)
   0.3333333333333333    0.3333333333333333    0.0628830683197726   TAU(   2)
   0.3333333333333333    0.3333333333333333    0.1388370510257218   TAU(   3)
  -0.3333333333333333   -0.3333333333333333    0.1638618412213989   TAU(   4)
  -0.3333333333333333   -0.3333333333333333    0.2398223878715089   TAU(   5)
  -0.0000000000000000   -0.0000000000000000    0.2642651909875856   TAU(   6)
  -0.0000000000000000   -0.0000000000000000   -0.0380725996019826   TAU(   7)
  -0.3333333333333333   -0.3333333333333333   -0.0628830683197726   TAU(   8)
  -0.3333333333333333   -0.3333333333333333   -0.1388370510257218   TAU(   9)
   0.3333333333333333    0.3333333333333333   -0.1638618412213989   TAU(  10)
   0.3333333333333333    0.3333333333333333   -0.2398223878715089   TAU(  11)
   0.0000000000000000    0.0000000000000000   -0.2642651909875856   TAU(  12)
 -2   0   1.0
  -0.0000000000000000   -0.0000000000000000    0.3131888120278811   TAU(  13)
   0.0000000000000000    0.0000000000000000   -0.3131888120278811   TAU(  14)
 30.0     Rcut for LVGENX
  4
…. (I skipped to show
```

Then edit 'Si111-H_tm.in_1000steps' by substituting position and vector by referring the lines of 'Si111-H_tm.out_1000steps'

```
Time (fsec) =     5.3240000000000007
 Positions
  -0.0000233194454503   -0.0008502714340708    0.0392432512473065   TAU(   1)
   0.3334088267927928    0.3330363191223839    0.0613506501788307   TAU(   2)
   0.3322797333464785    0.3325465658509424    0.1400609110054885   TAU(   3)
  -0.3328860929172957   -0.3344925780909999    0.1619898645767849   TAU(   4)
  -0.3331704288388750   -0.3329163609513411    0.2407166306046003   TAU(   5)
  -0.0001484678762871   -0.0002713198910288    0.2631413368143798   TAU(   6)
   0.0002496456509702   -0.0003907067899512   -0.0393145686001739   TAU(   7)
  -0.3336729646722161   -0.3334157062535267   -0.0614032613831942   TAU(   8)
  -0.3330485220561902   -0.3345352954477367   -0.1400980192092966   TAU(   9)
   0.3333395251014364    0.3333287321279511   -0.1620149920480045   TAU(  10)
   0.3335771271110552    0.3322266178348101   -0.2408738269442405   TAU(  11)
  -0.0006565642631289   -0.0010942720648305   -0.2632769722524467   TAU(  12)
  -0.0075805075773399   -0.0003986418388875    0.3313182156679352   TAU(  13)
  -0.0004570192576400    0.0018122178792479   -0.3306647973233357   TAU(  14)
```

Then do

```
$~/lm/structure_view Si111-H_tm.in_1000steps
```

structure.xyz → but do not download this now!

After doing ~/lm/structure_view input.dat

A new file ‘structure.xyz’ appears

Before you download a new ‘structure.xyz’, it is better to rename this for example ‘structure1000steps.xyz’ to keep information ‘Before’ running ‘tddft_exe.’

Apply VESTA to visualize atomic structure

Hope this manual works!

But we have more for visualization!

Now move to folder
Si111-1x1H/FWHM=2fs-5.0VpA

This time, we can also visualize the 3D charge distribution by VESTA

We have execution modules in ~/lm, as 'wf_decomp1d_input.x' and 'wfp2cube_watom.x' courtesy of Prof. Yayama (KOGAKUIN Univ.)

Let's draw charge using shell script 'ChgDen.sh' in the current directory.

Note we still keep beginning data 'Si111-1x1H_tm.in', 'rh.Si111-1x1H', which are data just before running 'tddft_exe'.

Then just simply

```
$qsub 'ChgDen.sh'
```

Then, you will get 'fort.1.cube' file

Just rename this file to avoid overwriting in later.

```
$mv fort.1.cube fort.1-0step.cube
```

Now we can also draw charge after running 'tddft_exe'

After 1000 time-steps, edit head of 'ChgDen.sh' as follows

```
#!/bin/csh -f
#$ -q rl.q
#$ -N VESTA_Si111-H
#$ -o std.out -e std.err
#$ -j y
#$ -cwd
#$ -pe smp 1
# set you directory and execution files
# you can also use these exe's with interactive format
###setenv DIR=/home/teac28
setenv EXE1 wf_decomp1d_input.x
setenv EXE2 wfp2cube_watom.x

# filename of your wavefunction
setenv FILENAME_WF rh.Si111-H
# filename of your input fil
setenv FILENAME_IN Si111-H_tm.in
# band numbers "FROM - TO" to extract
setenv FROM 1
setenv TO 1
…… (continuing) …..
```

Convert these filenames as

rh.Si111-H_1000steps

Si111-H_tm.in_1000steps

Then do again

```
$qsub ChgDen.sh
$mv fort.1.cube fort.1-1000steps.cube
```

Now we have ‘fort.1-0step.cube’ and ‘fort.1-1000steps.cube’ files

Please activate VESTA to see these files.

How about charge density between 0 step and 1000 steps?

We can monitor positions and charge density at 500 steps when we re-do the ‘tddft_exe calculation.

Let’s edit ‘Si111-H_tm.in’

```
PP=(KB,SOFT) CD=FILE WF=32 CG=(5,8,3) SCF=10 EXT=PANDEY
OUTWF=23 METAL=(25,0) KCONT=0
dt=0.40 tstep=500 TMOD=50 SUZUKI=4
RMIX=0.03 CONV=1.D-5 MAXFN=0 OKSTEP=0.1D0/
```

Edit ‘Exec_tm.sh’

```
setenv FORT23 wf_fft.Si111-H_new
setenv FORT88 wf_real.Si111-H
setenv FORT90 Vall.Si111-H
setenv FORT24 rh.Si111-H_new
setenv FORT30 rh.Si111-H_500steps
setenv FORT25 Vint.temp
setenv FORT77 tau.Si111-H
setenv FORT78 need
setenv OMP_NUM_THREADS 1
mpirun –np 6 ~/lm/tddft_exe  < Si111-H_tm.in >& Si111-H_tm.out_500steps
```

```
$qsub  Exec_tm.sh
```

After finish of 500 steps tddft calculation

```
$cp Si111-H_tm.in Si111-H_tm.in_500steps
```

Then edit ‘Si111-H_tm.in_500steps‘ revising its atomic coordinates with last position of ‘Si111-H_tm.out_500steps’

Now it is a time to modify laser parameters

Move to upper folder ‘Si111-1x1H’ first.

We consider different laser parameters:
For instance:
intensity of electric field
polarization
wavelength
pulse width

Depending on laser parameters: consider new folder’s name and do ‘mkdir *your-new-folder*’

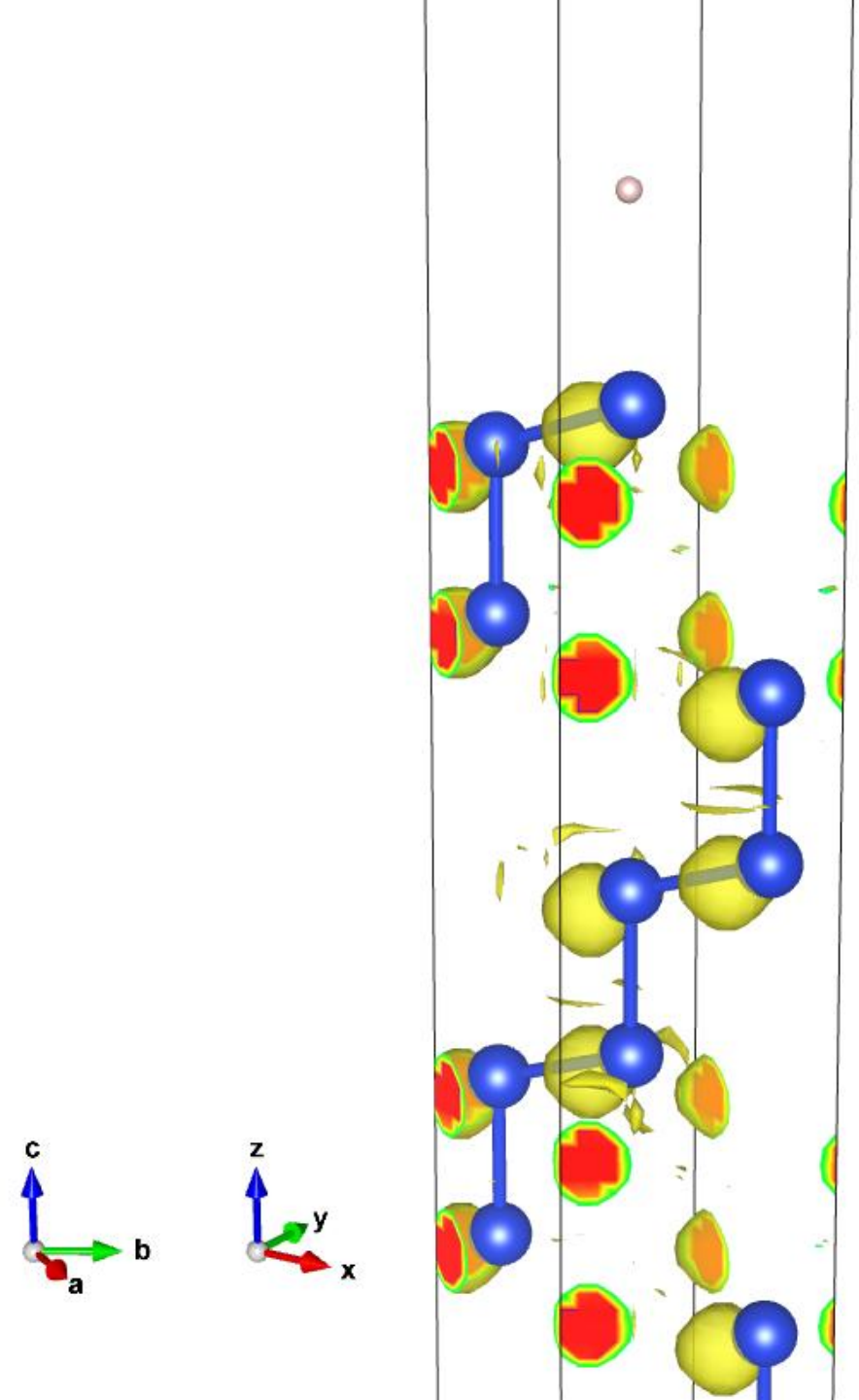
```
$cp FWHM=2fs-5.0VpA/*.dat your-new-folder/.
$cp FWHM=2fs-5.0VpA/Si111-1x1H_tm.in your-new-folder/.
$cp FWHM=2fs-5.0VpA/Exec_tm.sh your-new-folder/.
$cp FWHM=2fs-5.0VpA/rh* your-new-folder/.
$cp FWHM=2fs-5.0VpA/wf_fft* your-new-folder/.
$cp FWHM=2fs-5.0VpA/sym.C1 your-new-folder/.
$cp FWHM=2fs-5.0VpA/Avec your-new-folder/.
$cp FWHM=2fs-5.0VpA/E* your-new-folder/.
$cp FWHM=2fs-5.0VpA/ChgDen.sh your-new-folder/.
```

I will copy these on slack

Then in your new folder, edit ‘laser.dat’ as you like..

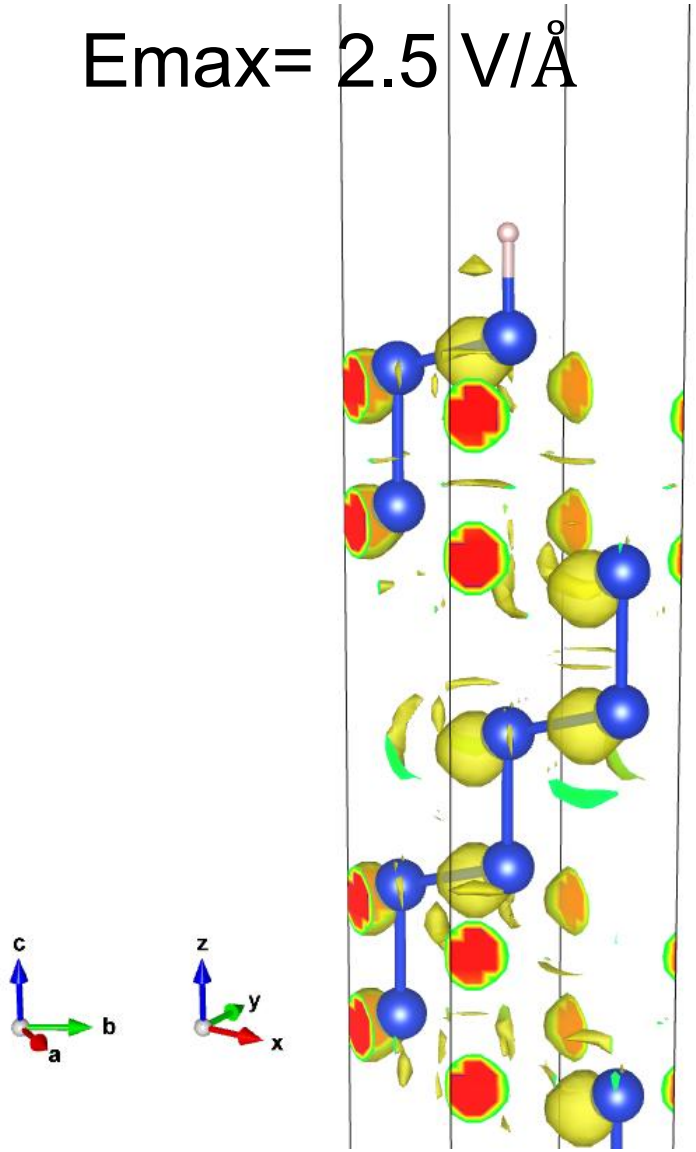
```
800   ! wavelength in nm
  3.5   ! peak position in fs   a) this should be more than 3*b)
  1.0   ! half of FWHM in fs  b)
  5.0d0   0.0  0.0   ! (Ex Ey Ez) in V/A
```

Example of change of charge density and ions' positions with laser condition FWHM=2fs, E=2.5 V/Å
(use 'slide show' and click to monitor each frame of the time evolution)

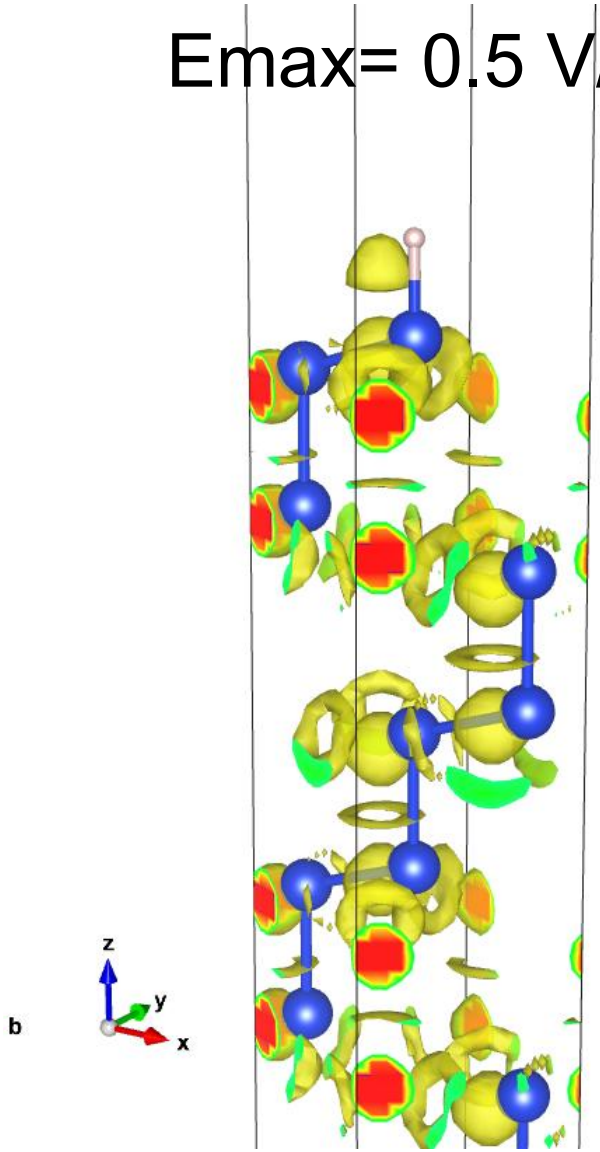


Compare the moment of laser irradiation at 500 steps

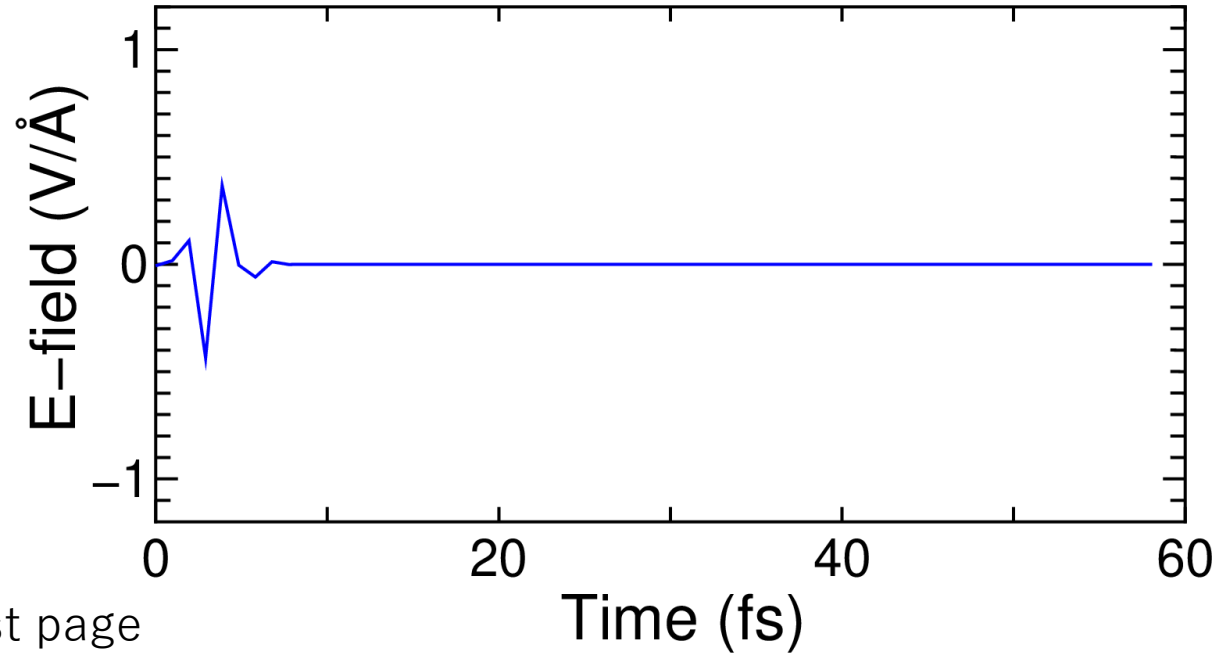
Emax= 2.5 V/Å



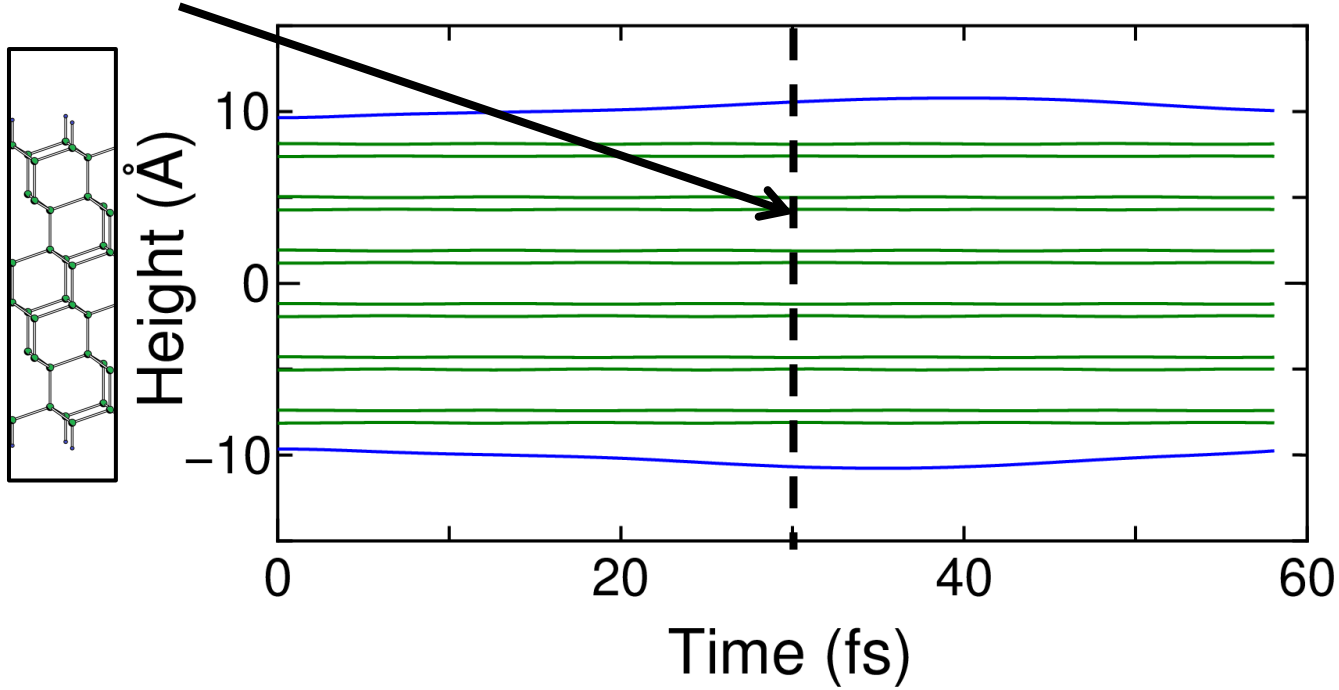
Emax= 0.5 V/Å

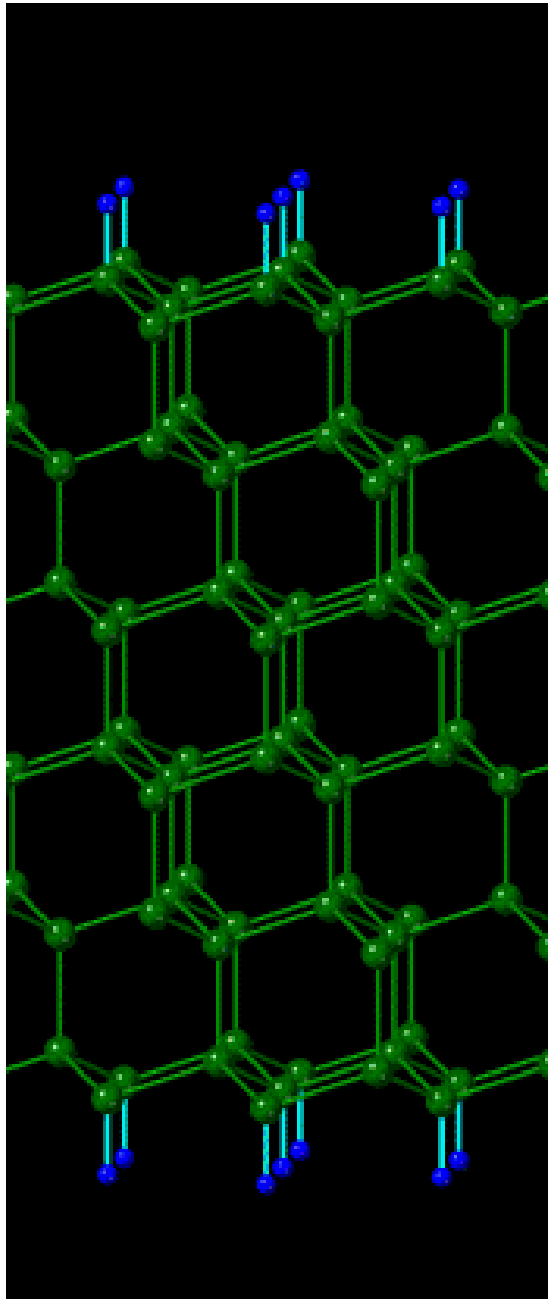


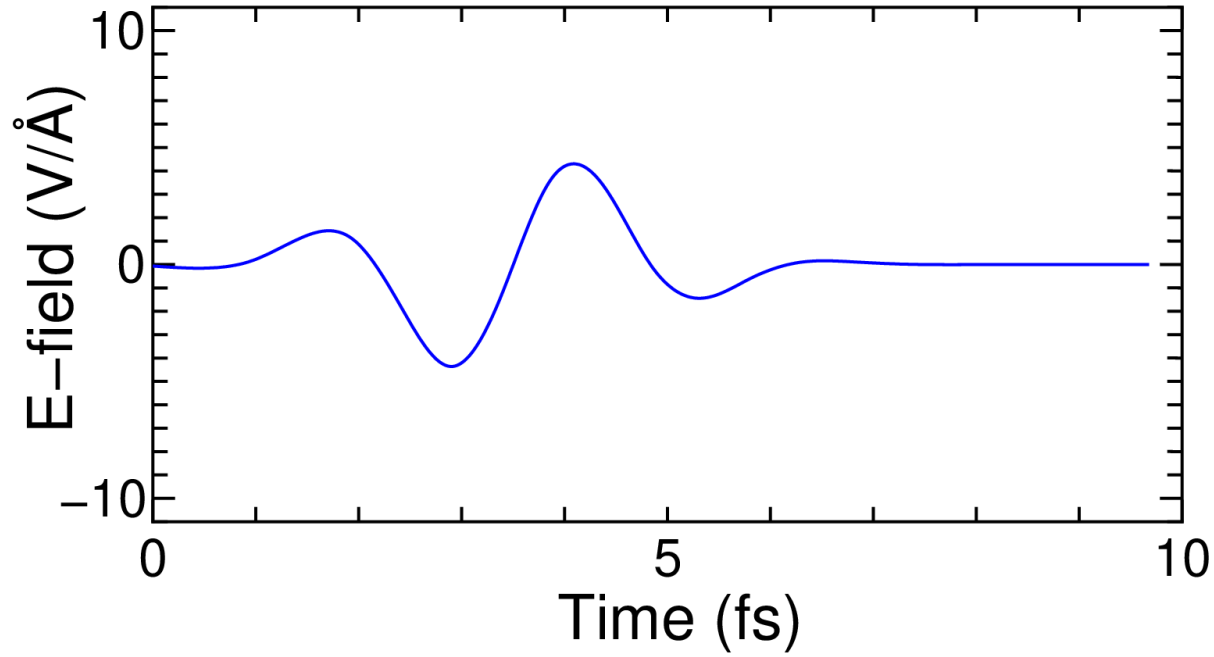
Let’s try!

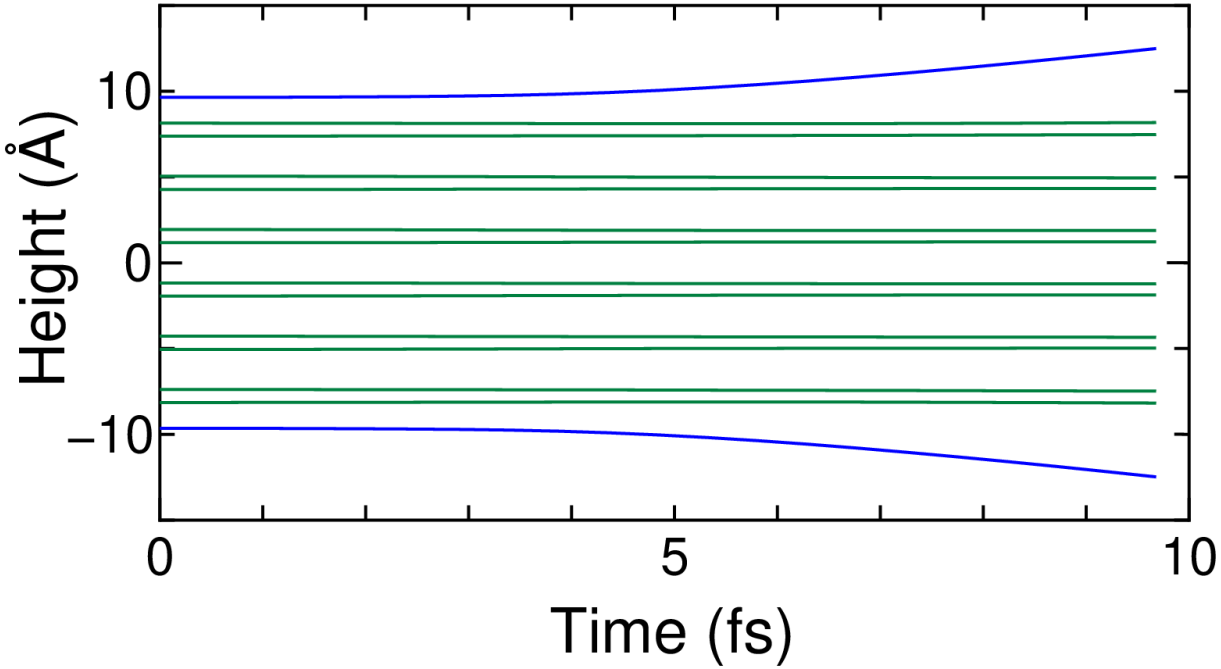


Amination in the last page






10
0
−10
E–field (V/Å)
0
5
10
Time (fs)


10
0
−10
Height (Å)
0
5
10
Time (fs)

Appendix

Appendix: How to obtain ‘size.dat’?

```
15   15  129 for FFT mesh grids
      18628         2328 for NG and NG2 : G for potential and wf
 2 # of irreducible k-points
 25    7 # of occupied and empty bands
 14    2 # of atoms and atomic types per cell
```

These values can be derived from input data ‘Si111-1x1H.in’ considering size-shape of the unit cell and plane wave cut-off energy etc.

For details, please visit https://staff.aist.go.jp/yoshi-miyamoto

Analytic solution of the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi_n(t) = H(t)\psi_n(t)$$

$$\psi_n(t) = \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 H(t_1)\psi_n(t_1) + \psi_n(t_0)$$

$$\psi_n(t_1) = \frac{1}{i\hbar}\int_{t_0}^{t_1} dt_2 H(t_2)\psi_n(t_2) + \psi_n(t_0)$$

$$\psi_n(t_2) = \frac{1}{i\hbar}\int_{t_0}^{t_2} dt_3 H(t_3)\psi_n(t_3) + \psi_n(t_0)$$

$$\psi_n(t) = \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 H(t_1)\frac{1}{i\hbar}\left(\int_{t_0}^{t_1} dt_2\psi_n(t_2) + \psi_n(t_0)\right) + \psi_n(t_0)$$

$$= \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 H(t_1)\frac{1}{i\hbar}\left(\int_{t_0}^{t_1} dt_2 H(t_2)\left(\frac{1}{i\hbar}\int_{t_0}^{t_2} dt_3 H(t_3)\psi_n(t_3) + \psi_n(t_0)\right) + \psi_n(t_0)\right) + \psi_n(t_0)$$

$$= \sum_{n=0}^{\infty}\left(\frac{1}{i\hbar}\right)^n \int_{t_0}^{t} dt_1 H(t_1)\int_{t}^{t_1} dt_2 H(t_2)\int_{t}^{t_2} d\,t_3 H(t_3)\cdots\int_{t}^{t_{n-1}} dt_n H(t_n)\psi_n(t_0)$$

$$= T\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{i\hbar}\right)^n \int_{t_0}^{t} dt_1 H(t_1)\int_{t}^{t} dt_2 H(t_2)\int_{t}^{t} d\,t_3 H(t_3)\cdots\int_{t}^{t} dt_n H(t_n)\psi_n(t_0) = Te^{\frac{1}{i\hbar}\int_{t_0}^{t} H(t')dt'}\psi_n(t_0)$$

With small interval of the time-step

$$\psi_n(t) = Te^{\frac{1}{i\hbar}\int_{t_0}^{t} H(t')dt'}\psi_n(t_0)$$

$$t = t_0 + \Delta t$$

p_j: value to divide time

$$\psi_n(t_0 + \Delta t) \cong e^{\frac{1}{i\hbar}\int_{t_0}^{t_0+\Delta t} H(t')dt'}\psi_n(t_0) \cong \prod_j e^{\frac{1}{i\hbar}H(t_0+p_j\Delta t)}\psi_n(t_0)$$

With the Hamiltonian $H(t)$ we have

$$H(t) = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2} + V_{ion}^{nonl} + V_{ion}^{loc} + V_H + V_{XC} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2} + \sum_\tau v_\tau^{nonl} + V_{loc}$$

Non commutable operator
$A_iA_j \neq A_jA_i$ when $i \neq j$

$$= A_1 + A_2 + \cdots A_{n-1} + A_n$$

What is exponential of $H(t)$, $e^{\frac{\Delta t}{i\hbar}H(t)}$?

$$H(t) = A_1 + A_2 + \cdots A_{n-1} + A_n \qquad x \equiv \frac{\Delta t}{i\hbar}$$

Approximation in second order

$$e^{xH(t)} \cong e^{\frac{x}{2}A_1}\ e^{\frac{x}{2}A_2} \cdots e^{\frac{x}{2}A_{n-1}} e^{xA_n} e^{\frac{x}{2}A_{n-1}} \cdots e^{\frac{x}{2}A_2}\ e^{\frac{x}{2}A_1} \equiv S_2(t)$$

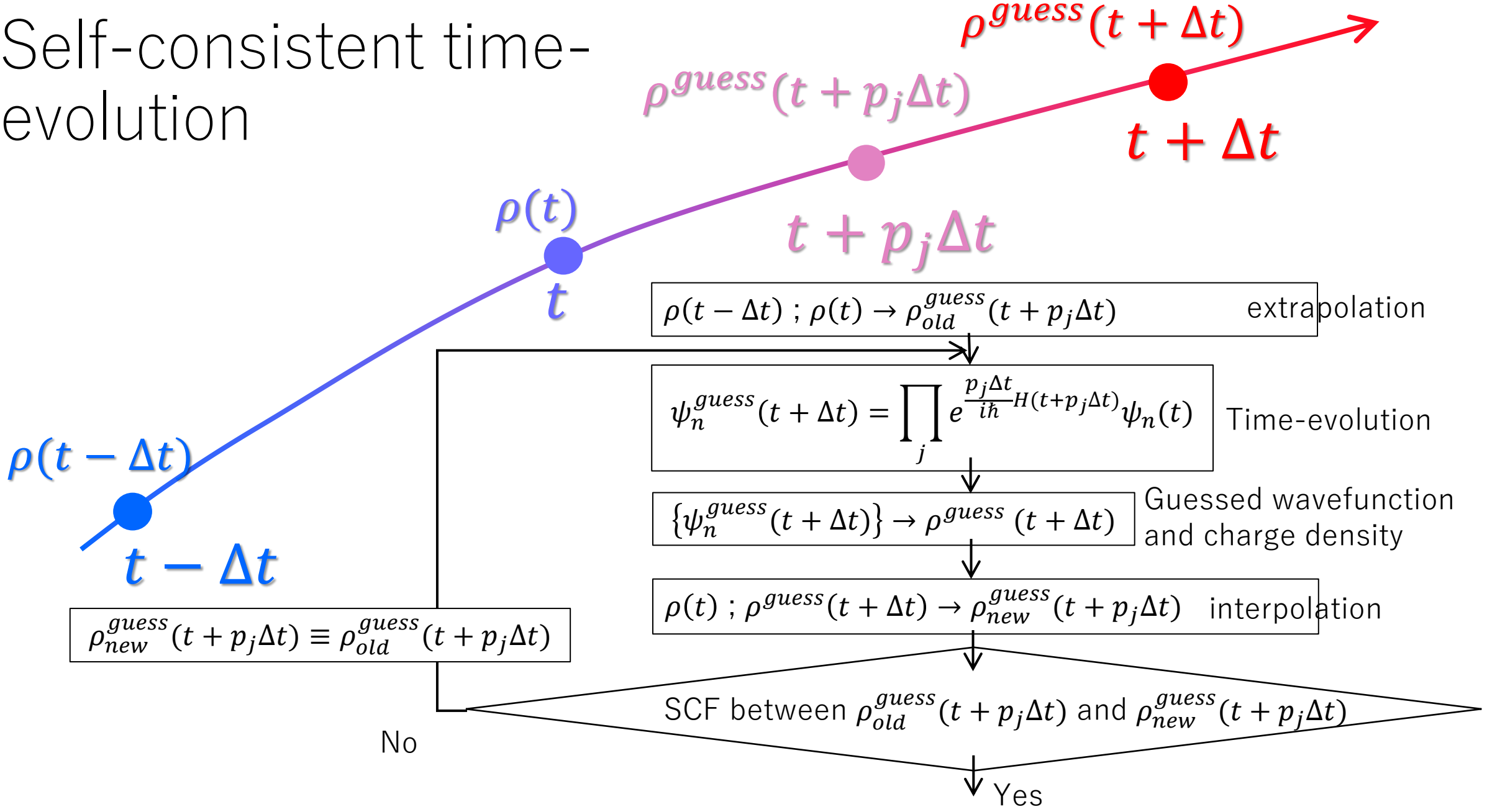
in 4th oeder

M. Suzuki, J. Phys. Soc. Jpn, 61, 3015 (1992)

$$e^{xH(t)} \cong S_2(p_1 t) S_2(p_2 t)\ S_2(p_3 t)\ S_2(p_2 t)\ S_2(p_1 t)$$

$$p_1 = p_2 = \frac{1}{4 - 4^{\frac{1}{3}}} \qquad p_3 = 1 - 4p_1$$

Self-consistent time-evolution



From Length gauge to velocity gauge

$$i\hbar\frac{\partial}{\partial t}\psi_n(\boldsymbol{r},t)=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2}+V_{ion}^{loc}(\boldsymbol{r},t)+V_{ion}^{nonloc}(\boldsymbol{r}',\boldsymbol{r},t)+V_{HXC}(\boldsymbol{r},t)+e\boldsymbol{E}(t)\cdot\boldsymbol{r}\right]\psi_n(\boldsymbol{r},t)$$

A Unitary transformation that preserve charge density but changes the phase.

$$e\boldsymbol{E}(t)=\frac{e}{c}\frac{\partial}{\partial t}\boldsymbol{A}(t)$$

$$\tilde{\psi}_n(\boldsymbol{r},t)=e^{-\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\psi_n(\boldsymbol{r},t)$$

$$i\hbar\frac{\partial}{\partial t}\tilde{\psi}_n(r,t)=e^{-\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\left\{-e\boldsymbol{E}(t)\cdot\boldsymbol{r}+i\hbar\frac{\partial}{\partial t}\right\}\psi_n(\boldsymbol{r},t)$$

$$=e^{-\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2}+V_{ion}^{loc}(\boldsymbol{r},t)+V_{ion}^{nonloc}(\boldsymbol{r}',\boldsymbol{r},t)+V_{HXC}(\boldsymbol{r},t)\right]\psi_n(\boldsymbol{r},t)$$

$$=e^{-\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2}+V_{ion}^{loc}(\boldsymbol{r},t)+V_{ion}^{nonl}(\boldsymbol{r}',\boldsymbol{r},t)+V_{HXC}(\boldsymbol{r},t)\right]e^{\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\tilde{\psi}_n(\boldsymbol{r},t)$$

Continued…

$$i\hbar\frac{\partial}{\partial t}\tilde{\psi}_n(r,t) = e^{-\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2} + V_{ion}^{loc}(\boldsymbol{r},t) + V_{ion}^{nonloc}(\boldsymbol{r}',\boldsymbol{r},t) + V_{HXC}(\boldsymbol{r},t)\right] e^{\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\,\tilde{\psi}_n(\boldsymbol{r},t)$$

$$= \left[\frac{1}{2m}\left\{\frac{\hbar}{i}\frac{\partial}{\partial \boldsymbol{r}} - \frac{1}{c}\boldsymbol{A}(t)\right\}^2 + V_{ion}^{loc}(\boldsymbol{r},t) + V_{HXC}(\boldsymbol{r},t) + e^{\frac{-\boldsymbol{A}(t)\cdot\boldsymbol{r}'}{i\hbar c}} V_{ion}^{nonloc}(\boldsymbol{r}',\boldsymbol{r},t) e^{\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\right]\tilde{\psi}_n(\boldsymbol{r},t)$$

As $\boldsymbol{A}(t)$ is uniform in real-space,

$$\frac{\hbar}{i}\frac{\partial}{\partial\,\boldsymbol{r}} e^{\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\tilde{\psi}_n(\boldsymbol{r},t) = e^{\frac{\boldsymbol{A}(t)\cdot\boldsymbol{r}}{i\hbar c}}\left(-\boldsymbol{A}(t) + \frac{\hbar}{i}\frac{\partial}{\partial \boldsymbol{r}}\right)\tilde{\psi}_n(\boldsymbol{r},t)$$

Operate $\frac{\hbar}{i}\frac{\partial}{\partial \boldsymbol{r}}$ to both side of above equation

can derives the top equation.