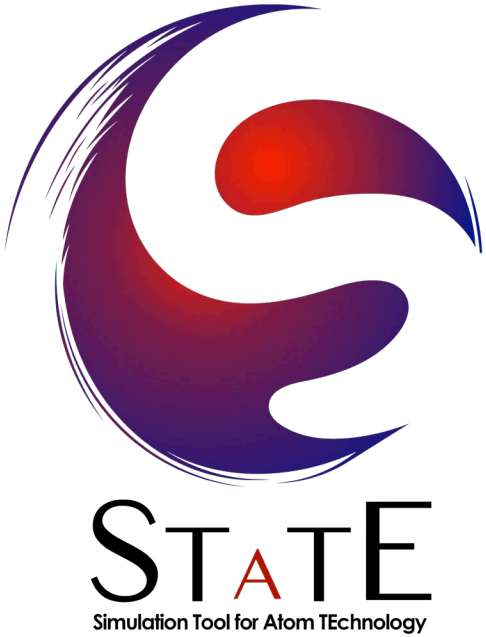
STATE tutorial



Online resources

- STATE wiki
  http://www-cp.prec.eng.osaka-u.ac.jp/puki_state/
- STATE document@Read the Docs
  https://state-doc.readthedocs.io/en/latest/index.html
- STATE examples
  https://github.com/ikuhamada/state-examples

Outline

- Introduction
  - Overview of STATE
- Compilation and configuration
  - Obtaining the code
  - Compiling the code
  - Preparing the job script
- Tutorial
  - Running the code
  - Analysis and post-processing of the results

What is STATE?

- Total energy code based on density functional theory
  - Plane-wave basis set
  - Pseudopotentials (normconserving & ultrasoft)
  - Iterative diagonalization (Davidson/RMM-DIIS)
  - Various exchange-correlation functionals
    - Semilocal functional (LDA/GGA)
    - vdW inclusive functional (DFT-D2/vdW-DF)
    - On-site Hubbard correction (DFT+U)
- Written in Fortran90
- Parallelized with MPI & openMP
- Parallelized over bands/k-points/G-vectors/images

People

- Developers
  - Yoshitada Morikawa (Osaka University)
  - Kouji Inagaki (Osaka University)
  - Yuji Hamamoto (Osaka University)
  - Ikutaro Hamada (Osaka University)
- Contributors
  - Zhong Fang (CAS)
  - Takashi Ikeda (JAEA)
  - Osamu Sugino (University of Tokyo)
  - Minoru Otani (AIST)
  - Makoto Haraguchi (System Numeric)
  - Teruo Hirakawa (Osaka University)

    … and many more

What can STATE compute?

- Total energy
- Hellmann-Feynman force
  - Geometry optimization
  - Reaction path search by nudged elastic band (NEB) method
  - Finite temperature molecular dynamics
  - Constraint molecular dynamics
  - Metadynamics
  - Vibrational mode analysis

What can STATE do?

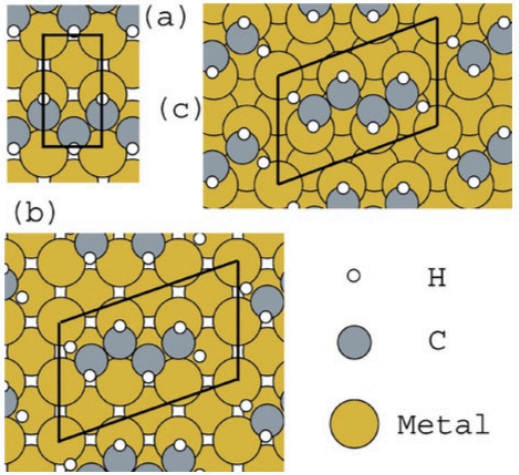
- Effective screening medium (ESM) method
  - Accurate slab calculation
  - Charged slab calculation
  - Constant charge & constant potential calculation

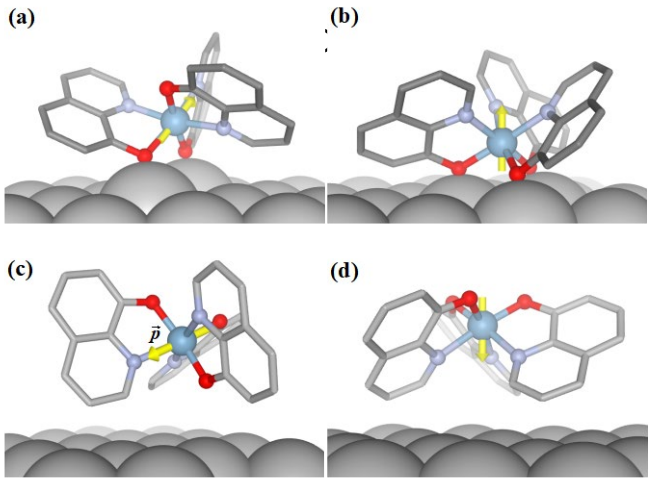
What can STATE do?

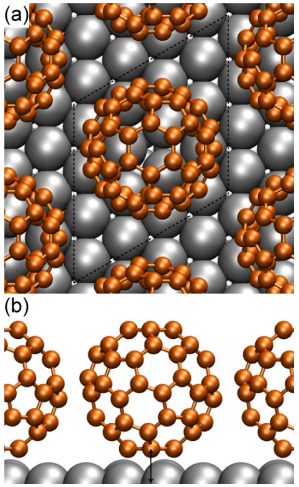
- Electronic structure analysis
  - Density of states
  - Band structure
  - Charge density / wave function plot
  - Bader charge analysis via the Bader program
- STM simulation
- XPS (core level shift) simulation

What can STATE do?

Organic metal interfaces







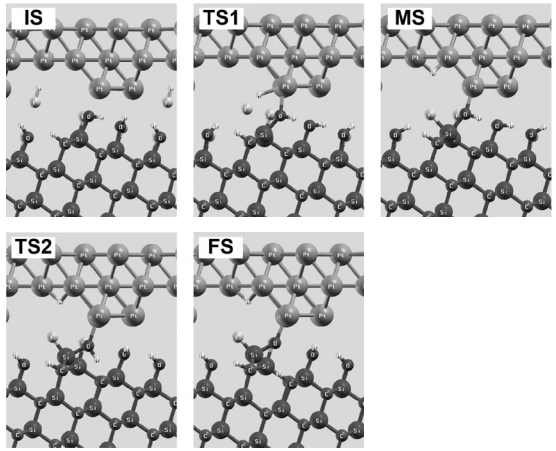
Morikawa, *et al.*, *Phys. Rev. B.* **69**, 041403 (2004).

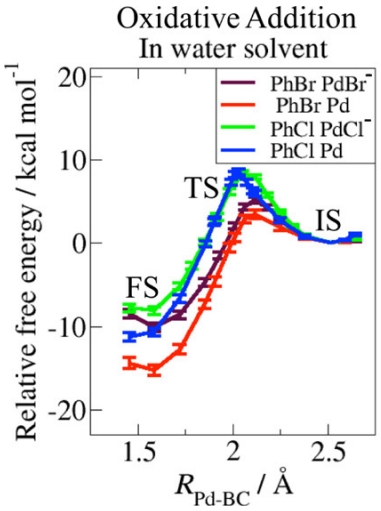
Yanagisawa, *et al.*, *Phys. Rev. B.* **83**, 235412 (2011).

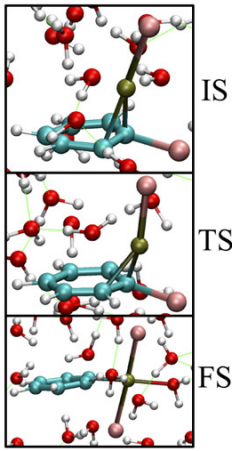
Yoshida, *et al.*, *Nano Lett.*. **13**, 481 (2013).
Hamada et al., *Phys. Rev. B* **85**, 121401(R) (2012).

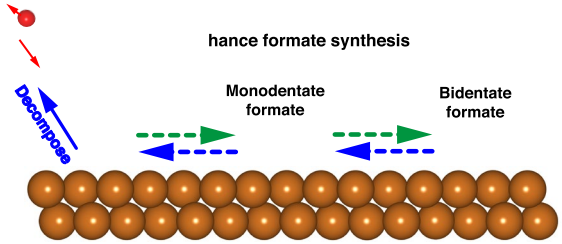
What can STATE do?

Catalytic reactions





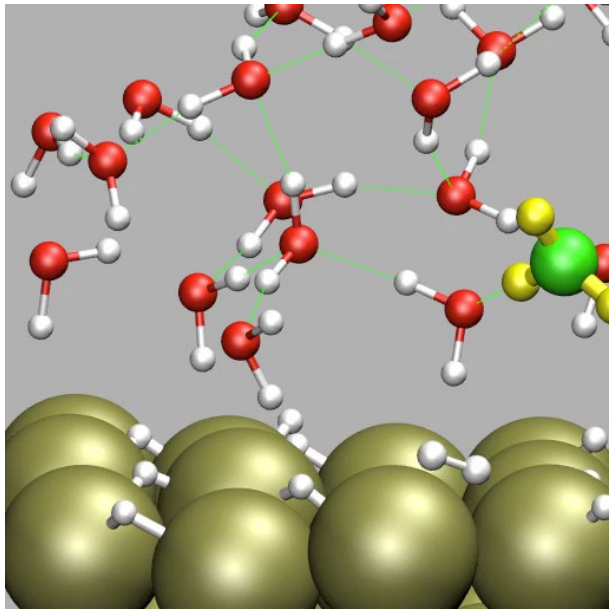




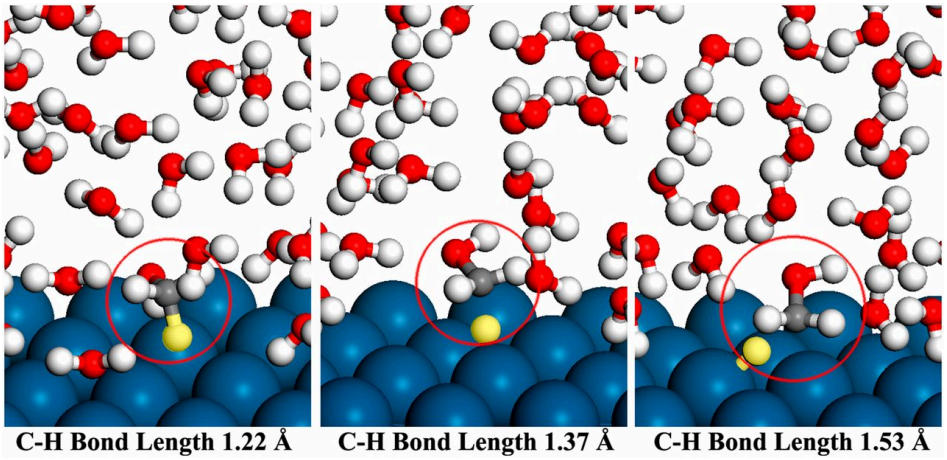
Bui, *et al*., *Appl. Phys. Lett.* **107**, 201601 (2015). Hirakawa, *et al*., *J. Phys. Chem. B.* **121**, 164 (2017). Muttaqien, *et al*., *Chem. Comm.* **53**, 9222 (2017).

What can STATE do?

Electrochemical reactions

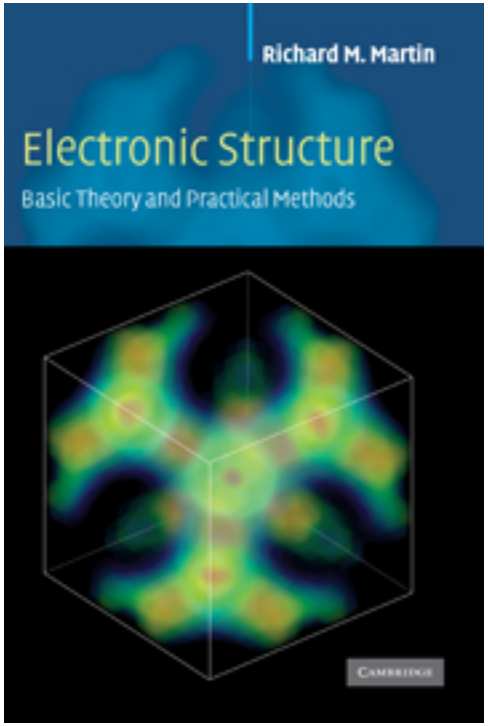


Otani, *et al*., *J. Phys. Soc. Jpn.* **77**, 024802 (2008).
Hamada and Sugino *HYOMEN KAGAKU* 34, 638 (2013).



Herron, Morikawa, Mavrikakis, *Proc. Natl. Acad. Sci. USA* **113**, E4937 (2016).

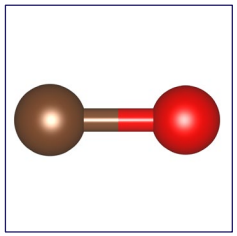
Recommended textbook



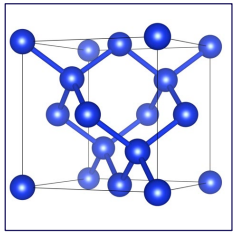
Electronic Structure
Basic Theory and Practical Methods
(Cambridge University Press)
Richard M. Martin

Tutorial

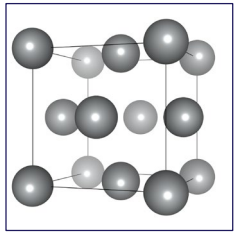
Outline



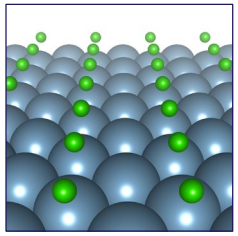
Carbon monoxide (CO) & ethylene (C_2H_4)



Silicon (Si)



Aluminum (Al) and nickel (Ni)



Chlorine atom on an Aluminum (100) surface [Cl/Al(100)]

Setup

Login

```
$ ssh –Y [your_userID]@cmd2.phys.sci.Osaka-u.ac.jp
```

Setup of STATE (for CMD workshop)

In the home directory, type:

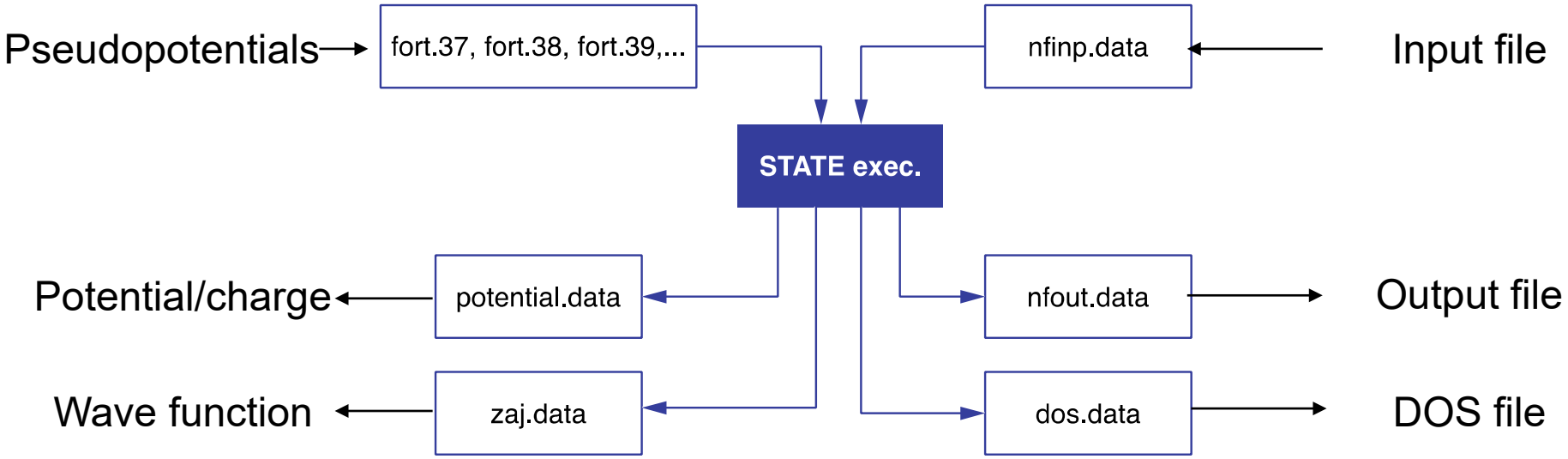
```
$ ~teac21/STATE/util/setup-state-cmd.sh
$ source ~/.bashrc
```

Type:

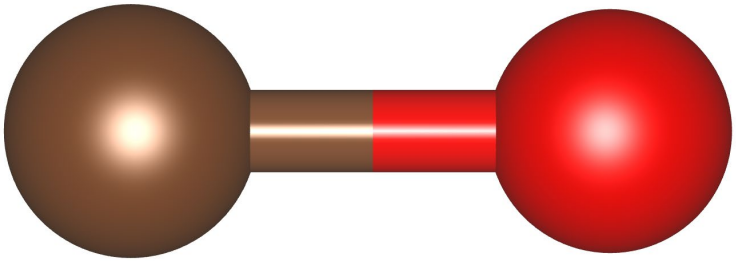
```
$ ls
STATE/
$ cd STATE
$ ls
examples/  gncpp@  src/
$ cd examples
$ ls
Al/  C2H4/  ClonAl100/ CO/  Ni/  README.md  Si/  util/
```

Input/output files

Ground state (SCF or single-point) calculation



CO molecule



Input file (nfinp_scf)

In the STATE directory

```
$ cd examples/CO
```

STATE legacy input (nfinp_dav)

```
  0  0  0  0  0  0                       : INPUT_CTRL (dummy line, 6 integers)
  5.50 20.00  2  2  2                    : GMAX GMAXP NTYP NATM NATM2
  1  0                                   : NUM_SPACE_GROUP TYPE
  6.00  4.00  4.00  90.00  90.00  90.00 : A B C ALPHA BETA GAMMA
  1  1  1  1  1  1                       : N1 N2 N3 M1 M2 M3
  1  0                                   : NCORD NINV
  0.0000  0.0000  0.0000  1  1  1        : CPS(1,1:3) IWEI IMDTYP ITYP
  2.2000  0.0000  0.0000  1  1  2        : CPS(2,1:3) IWEI IMDTYP ITYP
  6  0.1500  12.01 3 1 0.D0              : IATOMN ALFA AMION ILOC IVAN ZETA1
  8  0.1500  16.00 3 1 0.D0              : IATOMN ALFA AMION ILOC IVAN ZETA1
  0  0  0  0  0                         : ICOND INIPOS INIVEL ININOSE INIACC
  0  1                                   : IPRE IPRI
  200   200   0    57200.00  0          : NMD1 NMD2 ITER_LAST CPUMAX IFSTOP
  3  1                                   : WAY_MIX MIX_WHAT
  0  8  0.8                             : ITER_START KBXMIX MIX_ALPHA
  0.60  0.50  0.60  0.70  1.00          : DTIM1 DTIM2 DTIM3 DTIM4 DTIM
  30.00 2     1     0.1D-08             : DTIO IMDALG IEXPL EDELTA
  0.0010  0.10D+02    0                 : WIDTH FORCCR ISTRESS
ggapbe        1                         : XCTYPE NSPIN
  1.00                                  : DESTM
  102                                   : NBZTYP
  0  0  0                              : NKX NKY NKZ (dummy)
  0  0  0                              : NKX2 NKY2 NKZ2(dummy)
  8                                     : NEG
  1                                     : NEXTST (1: G-space, 0: R-space)
  0                                     : (dummy line)
  2                                     : IMSD (2: Davidson, 1: RMM)
  0                                     : EVALUATE_EKO_DIFF
  0                                     : NPDOSAO
  0  0.0                                : SM_N DOPING
```

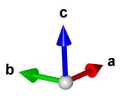
Input file (nfinp_scf)

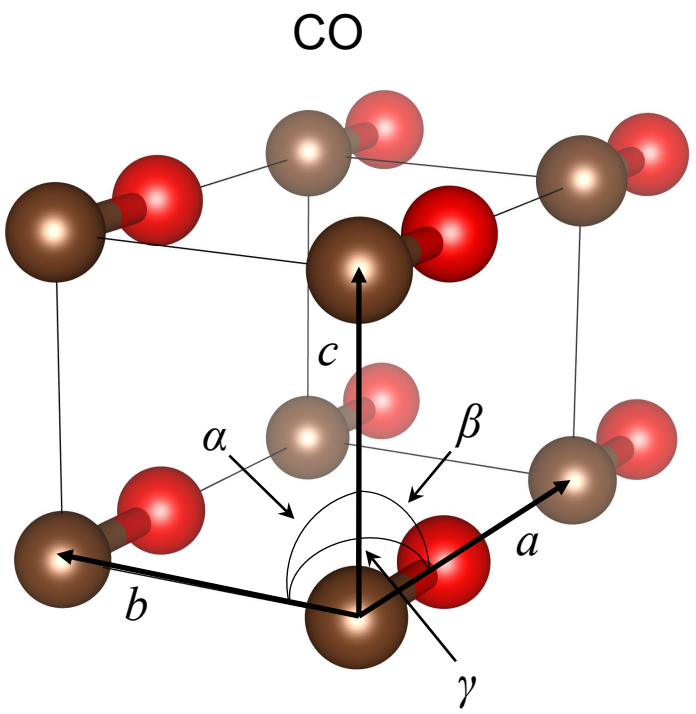
$ cat nfinp_scf

```
#
# CO molecule in a box
#
WF_OPT     DAV          ← Wave function optimization
NTYP       2            ← # of atomic species
NATM       2            ← # of atoms
GMAX       5.50         ← Cutoff wave vector for the wave function (GMAX²=E_cut^wf (Ry))
GMAXP      20.00        ← Cutoff wave vector for the augmented charge (GMAXP²=E_cut^den (Ry))
NSCF       200          ← Max # of SCF steps
WAYMIX     3
KBXMIX     8
MIX_ALPHA  0.8          ← Mixing parameter for SCF
WIDTH      0.0010       ← Smearing parameter for insulators (small number)
EDELTA     0.1000D-09   ← Convergence threshold for the total energy (Hartree/atom)
NEG        8            ← Number of bands
CELL       6.00  4.00  4.00  90.00  90.00  90.00   ← Cell parameters
                                                    A, B, C, ALPHA, BETA, GAMMA
&ATOMIC_TYPE
 6.00  0.1500  51577.50 3 1  0.0000
 8.00  0.1500  51577.50 3 1  0.0000
&END                        ← Atomic types (NTYP lines) (legacy format)
&ATOMIC_COORDINATES CARTESIAN
  0.0000  0.0000  0.0000  1  1  1
  2.2000  0.0000  0.0000  1  1  2
&END                        ← Atomic coordinates (NTYP lines) (legacy format)
```

Lattice parameters

```
CELL        6.00   4.00   4.00   90.00   90.00   90.00
```





A
Length of the first lattice vector *a*

B
Length of the second lattice vector *b*

C
Length of the third lattice vector *c*

ALPHA
Angle between lattice vectors *b* and *c*

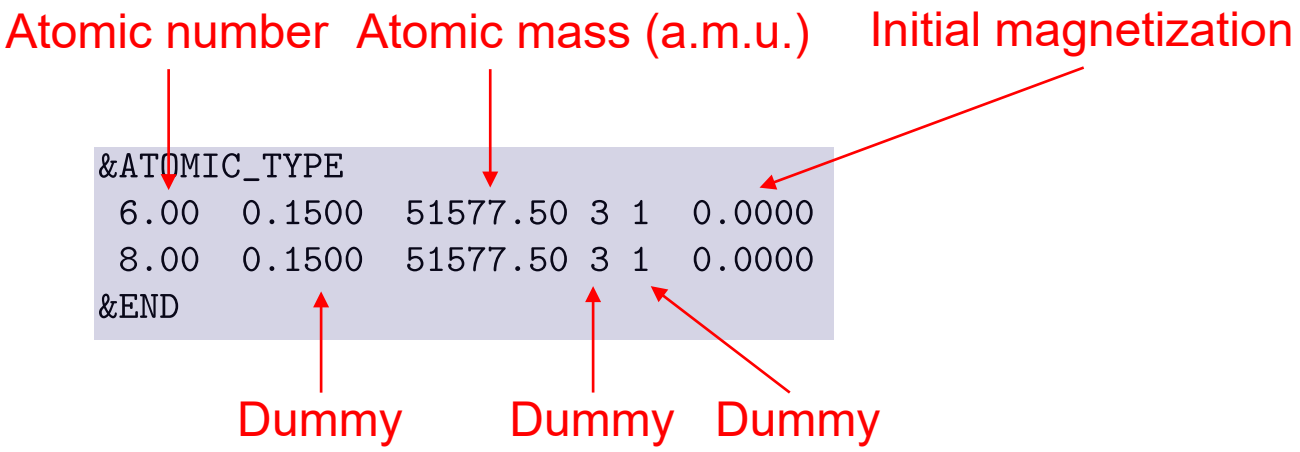
BETA
Angle between lattice vectors *c* and *a*

GAMMA
Angle between lattice vectors *a* and *b*

Input file (nfinp_scf)

```
#
# CO molecule in a box
#
WF_OPT    DAV
NTYP      2
NATM      2
GMAX      5.50
GMAXP     20.00
NSCF      200
WAYMIX    3
KBXMIX    8
MIX_ALPHA 0.8
WIDTH     0.0010
EDELTA    0.1000D-09
NEG       8
CELL      6.00  4.00  4.00  90.00  90.00  90.00
&ATOMIC_TYPE
 6.00  0.1500  51577.50 3 1  0.0000
 8.00  0.1500  51577.50 3 1  0.0000
&END
&ATOMIC_COORDINATES CARTESIAN
  0.0000  0.0000  0.0000  1  1  1
  2.2000  0.0000  0.0000  1  1  2
&END
```

Atomic types



Input file (nfinp_scf)

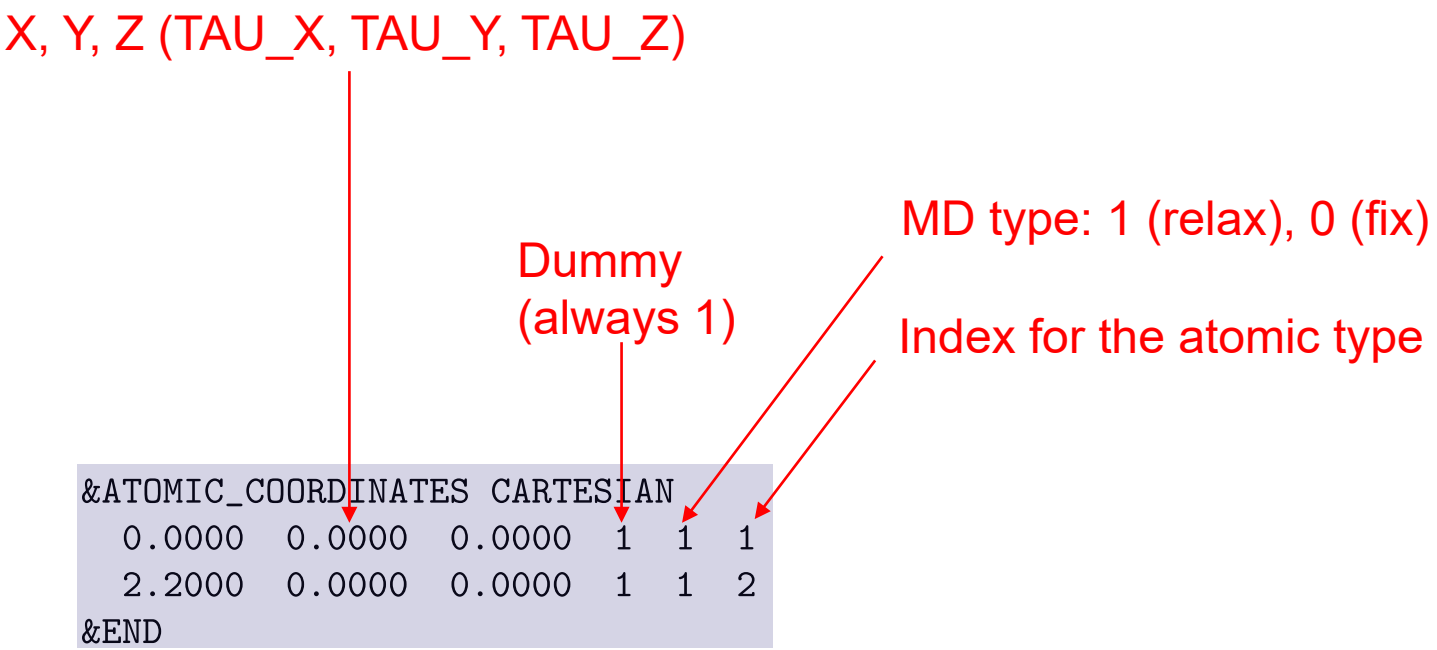
```
#
# CO molecule in a box
#
WF_OPT    DAV
NTYP      2
NATM      2
GMAX      5.50
GMAXP     20.00
NSCF      200
WAYMIX    3
KBXMIX    8
MIX_ALPHA 0.8
WIDTH     0.0010
EDELTA    0.1000D-09
NEG       8
CELL      6.00  4.00  4.00  90.00  90.00  90.00
&ATOMIC_TYPE
 6.00  0.1500  51577.50 3 1  0.0000
 8.00  0.1500  51577.50 3 1  0.0000
&END
&ATOMIC_COORDINATES CARTESIAN
  0.0000  0.0000  0.0000  1  1  1
  2.2000  0.0000  0.0000  1  1  2
&END
```

Atomic coordinates

```
&ATOMIC_COORDINATES CARTESIAN
  0.0000   0.0000   0.0000   1   1   1
  2.2000   0.0000   0.0000   1   1   2
&END
```

CARTESIAN or CRYSTAL

Input file (nfinp_scf)



Checking the input file

```
$ chkinpf nfinp_scf
```

```
PROGRAM chkinpf VERSION 1.5.4
READING nfinp_1...DONE.
GENERATING CO.xsf...DONE.
*INFO: ESTIMATED NUMBER OF VALENCE ELECTRONS:   10
*INFO: PRIM. CELL VOLUME:  0.960000E+02 BOHR**3 =     14.225715 ANGSTROM**3
```

```
$ VESTA CO.xsf
```

Job script (qsub_cmd.sh)

$ cat qsub_cmd.sh

```
#!/bin/sh
#$ -cwd
#$ -pe fillup 6
#$ -N CO
#
setenv OMP_NUM_THREADS 1
#
# Execuable of the STATE code
ln -fs ${HOME}/STATE/src/state/src/STATE .
#
# Pseudopotential data
ln -fs ${HOME}/STATE/gncpp/pot.C_pbe1 fort.37
ln -fs ${HOME}/STATE/gncpp/pot.O_pbe1 fort.38
#
# Run!
mpirun -np $NSLOTS ./STATE < nfinp_scf > nfout_scf
```

← # of cores to be used

← STATE executable

← Pseudos.

$ qsub qsub_cmd.sh

STATE output

$ less nfout_1

```
*************************************************************************
*                                                                       *
*                                                                       *
*                                                                       *
*              ******  ********    **    ******** ********            *
*             ******** ********   ****   ******** ********            *
*             **          **     **  **     **    **                   *
*              ***        **    ********    **    ******               *
*                ***      **   **********   **    ******               *
*                   **    **  **        **  **    **                   *
*             ********    ** **          ** **    ********             *
*              ******     ** VERSION 5.6.6  **    ********             *
*                              RICS-AIST                                *
*                           OSAKA UNIVERSITY                            *
*                                                                       *
*************************************************************************

PROGRAM STATE STARTED AT: Aug 31 13:29:59 2020

THIS JOB RUNS ON            :cmd406
THE CURRENT DIRECTORY IS    :/home/CMD/teac21/STATE/work/state-exampl
THE PROCESS ID IS           :    415338
THE JOB WAS SUBMITTED BY    :teac21
THE NUMBER OF PROCESSORS    :     6
```

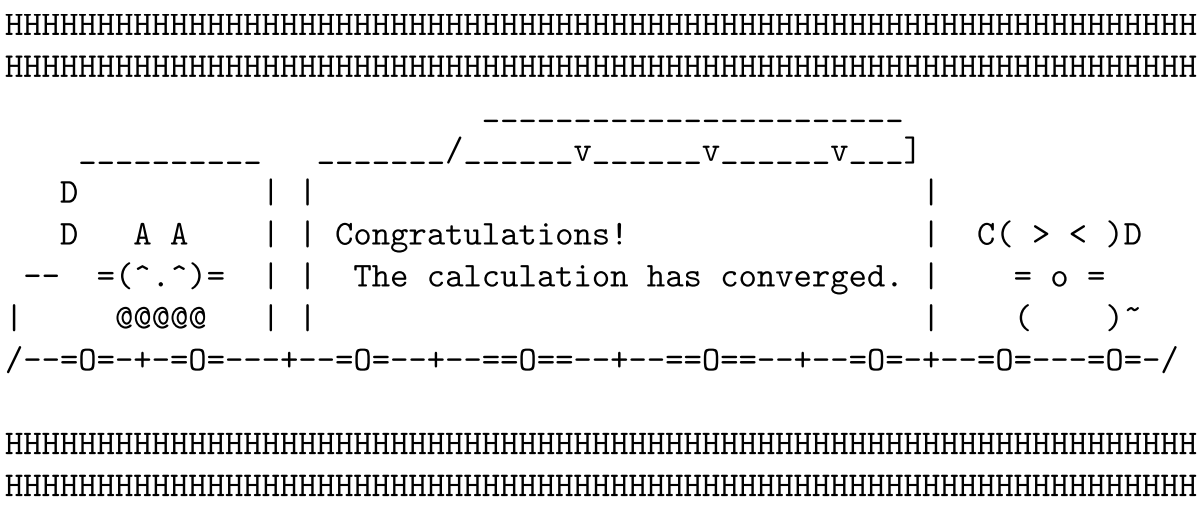
STATE output

When SCF converges, following information is printed

```
                    TOTAL CHARGE DENSITY =      9.9999966

      TOTAL ENERGY AND ITS COMPONENTS
   TOTAL ENERGY     =         -22.21942426 A.U.
 KINETIC ENERGY     =           9.92111407 A.U.
 HARTREE ENERGY     =           5.12121800 A.U.
      XC ENERGY     =          -5.89585641 A.U.
   LOCAL ENERGY     =         -20.23161605 A.U.
NONLOCAL ENERGY     =           6.73686141 A.U.
   EWALD ENERGY     =         -17.87114528 A.U.
      PC ENERGY     =           0.00000000 A.U.
ENTROPIC ENERGY     =           0.00000000 A.U.

                          FERMI ENERGY =       0.43248213
```

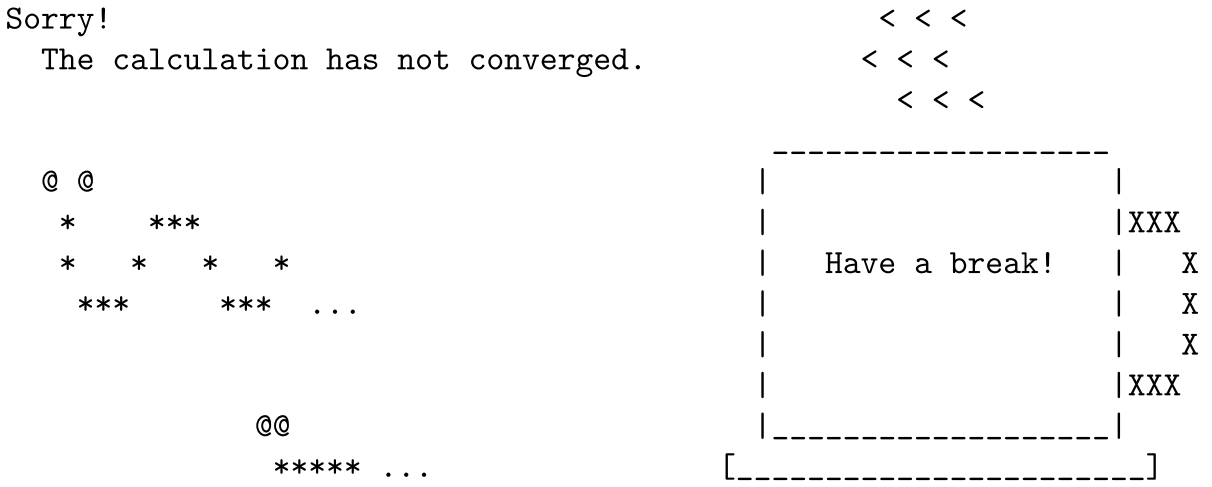
STATE output

and also …



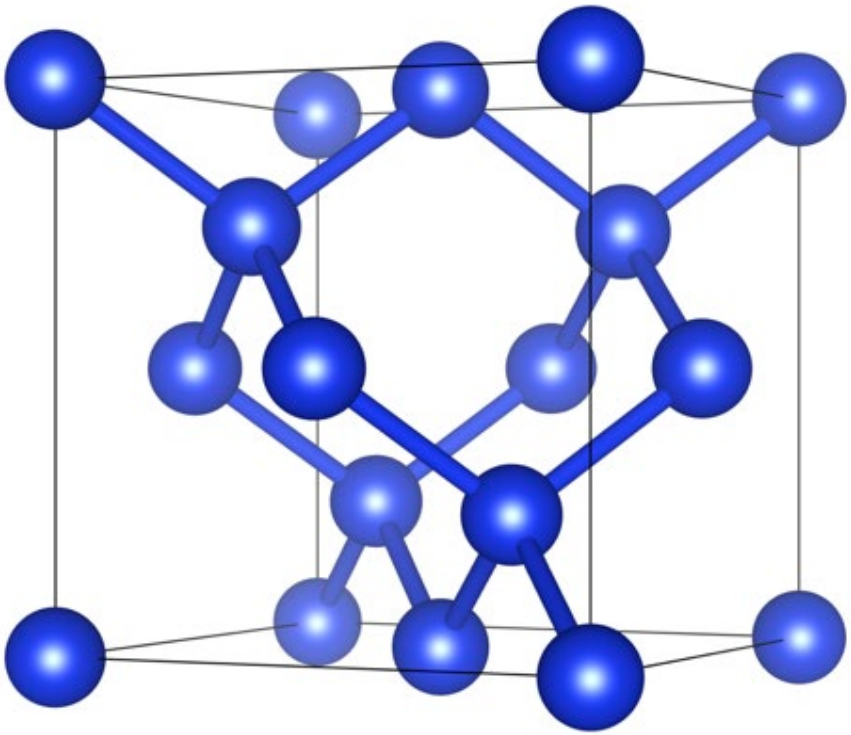
STATE output

If NOT SCF converged …



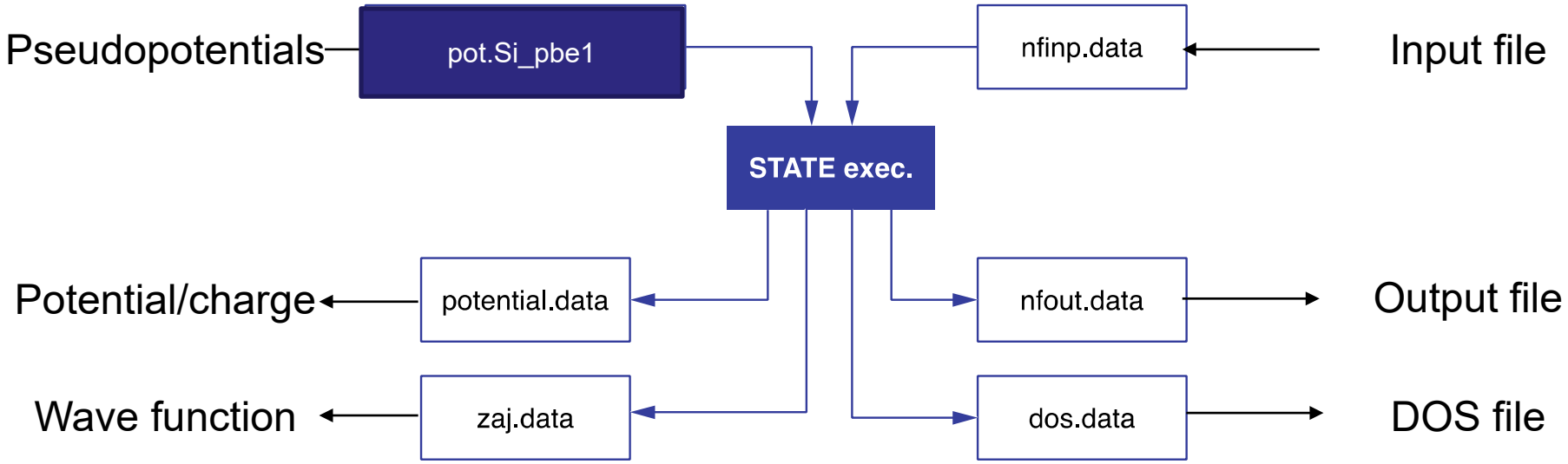
- Change the mixing parameter and restart when SCF convergence is not achieved.
- Change time step and restart when structural optimization is not achieved.

Silicon in the diamond structure



Input/output files

Ground state (SCF or single-point) calculation



Name of the pseudopotential can be arbitrary with new input interface

Input file (nfinp_scf)

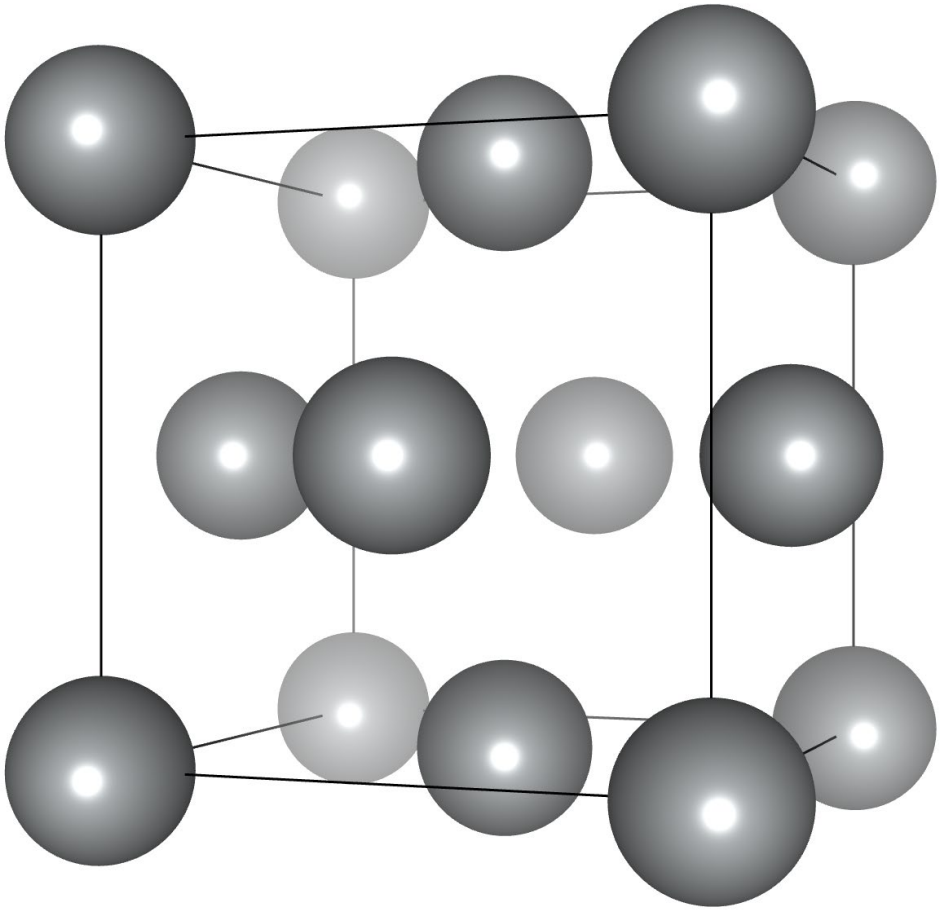
```
#
# Crystalline silicon in the diamond structure
#
WF_OPT     DAV
NTYP       1
NATM       2
TYPE       2
NSPG       227   ← Space group number
GMAX       4.00
GMAXP      8.00
KPOINT_MESH     8    8    8     ← K-point mesh
KPOINT_SHIFT    OFF  OFF  OFF   ← K-point shift (1: OFF, 2: ON)
WIDTH      0.0002
EDELTA     0.5000D-09
NEG     8
CELL    10.30   10.30   10.30   90.00   90.00   90.00
&ATOMIC_SPECIES
 Si 28.0900 pot.Si_pbe1 ← Atomic species
&END
&ATOMIC_COORDINATES CRYSTAL   ← Atomic coordinates in the crystal coordinate
      0.000000000000      0.000000000000      0.000000000000     1     1     1
      0.250000000000      0.250000000000      0.250000000000     1     1     1
&END
```

Job script (qsub_cmd.sh)

```
#$ -S /bin/sh
#$ -cwd
#$ -pe fillup 6
#$ -N Si

#disable OPENMP parallelism
setenv OMP_NUM_THREADS 1

# execuable of the STATE code
ln -fs ${HOME}/STATE/src/state-5.6.6_beta/src/STATE .

# pseudopotential data
ln -fs ${HOME}/STATE/gncpp/pot.Si_pbe1

# launch STATE
mpirun -np $NSLOTS ./STATE < nfinp_scf > nfout_scf
```

$ qsub qsub_cmd.sh

Aluminum in the fcc structure

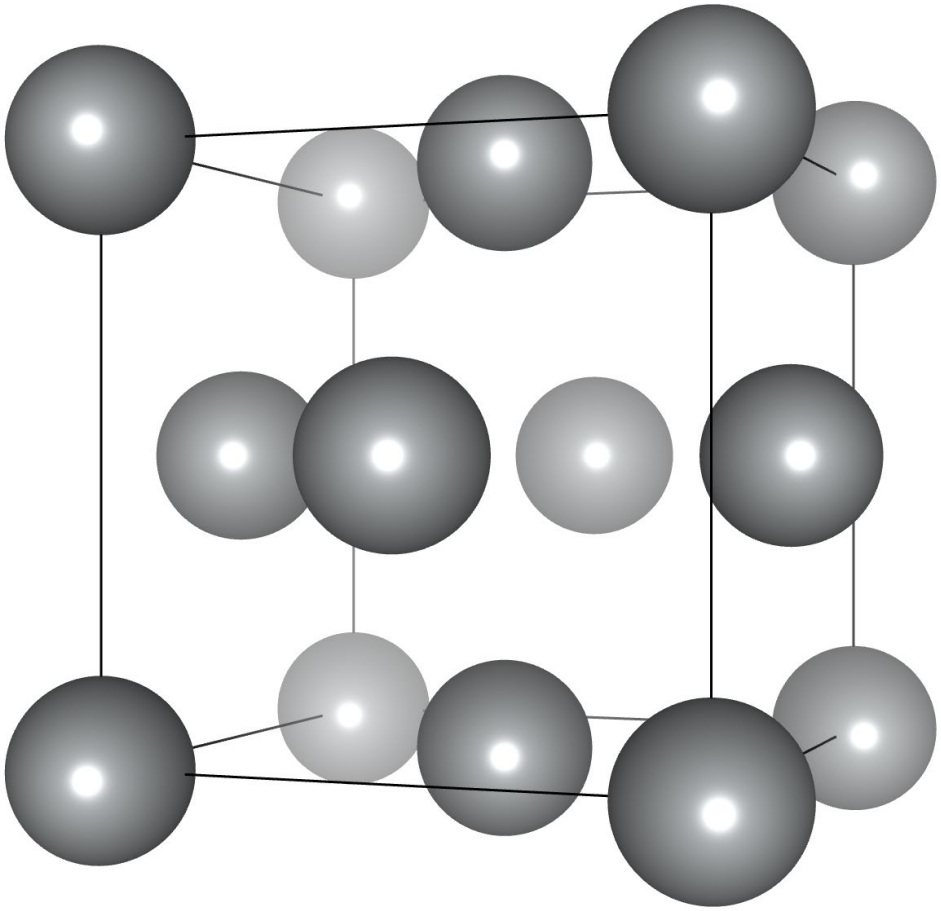


Input file (nfinp_scf)

```
#
# Crystalline aluminum in the face centered cubic structure
#
WF_OPT  DAV
NTYP    1
NATM    1
TYPE    2
NSPG    221
GMAX    4.00
GMAXP   8.00
KPOINT_MESH  12  12  12
KPOINT_SHIFT OFF OFF OFF
SMEARING MP
WIDTH   0.0020
EDELTA  0.5000D-09
NEG     6
CELL    7.50000000   7.50000000   7.50000000  90.00000000  90.00000000  90.00000000
&ATOMIC_SPECIES
Al 26.9815386 pot.Al_pbe1
&END
&ATOMIC_COORDINATES CRYSTAL
      0.000000000000      0.000000000000      0.000000000000    1    0    1
&END
```

← Smearing function for metals

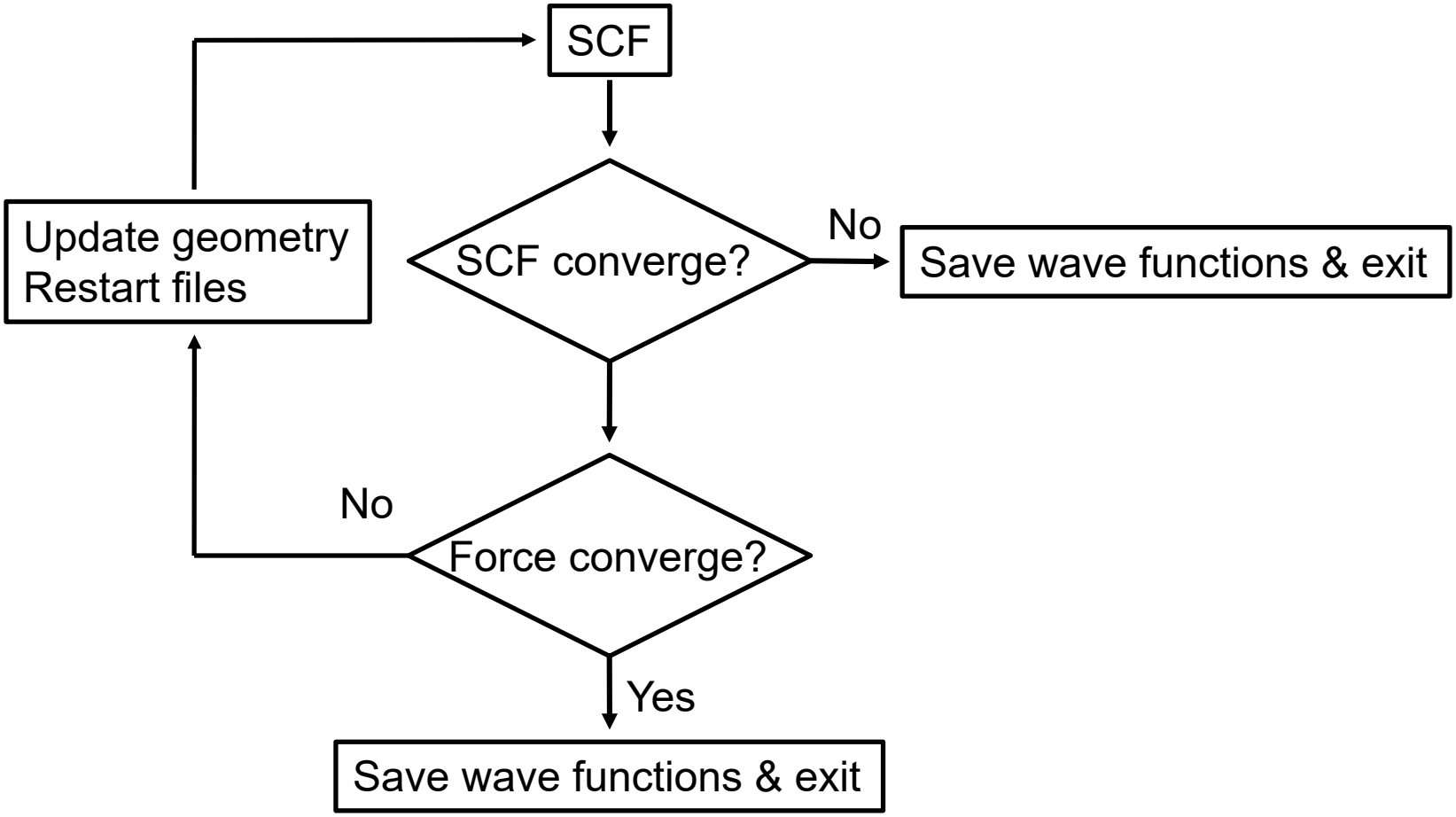
Ferromagnetic Ni in the fcc structure



Input file (nfinp_scf)

```
#
# Ferromagnetic Ni in the fcc structure
#
WF_OPT DAV
NTYP   1
NATM   1
TYPE   2
NSPG   221
GMAX    5.00
GMAXP  15.00
KPOINT_MESH   12  12  12
KPOINT_SHIFT  OFF OFF OFF
MIX_ALPHA 0.3
SMEARING MP
WIDTH  0.0020
EDELTA 0.5000D-09
NSPIN  2                    ← Spin polarization allowed
NBZTYP 102
NEG    10
CELL   6.70  6.70  6.70  90.00  90.00  90.00
&ATOMIC_SPECIES
 Ni 58.6900 pot.Ni_pbe4
&END
&INITIAL_ZETA
 0.20                       ← Initial magnetization
&END
&ATOMIC_COORDINATES CRYSTAL
      0.000000000000      0.000000000000      0.000000000000    1    1    1
&END
```

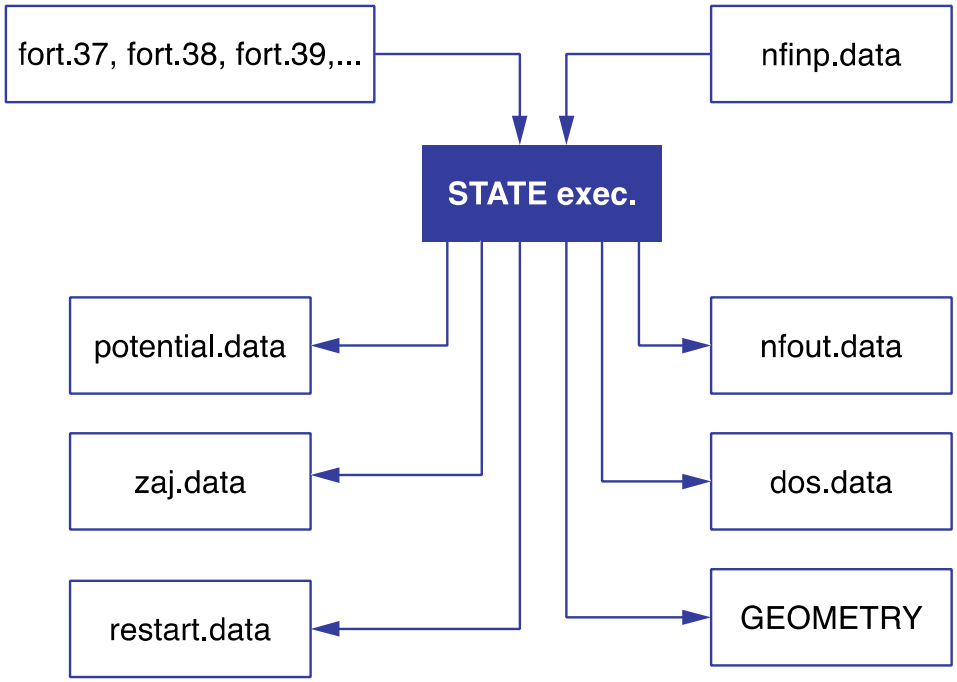
Geometry optimization



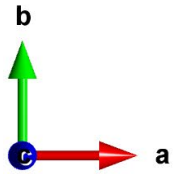
No restart file generated if 1st SCF does not converge

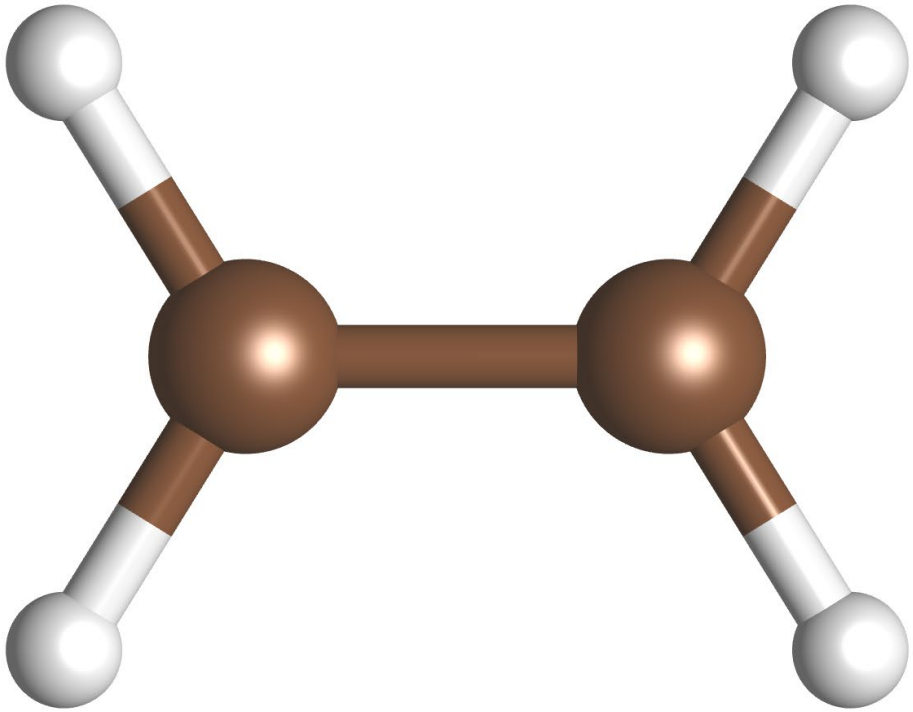
Input/output files

Geometry optimization



C_2H_4 molecule



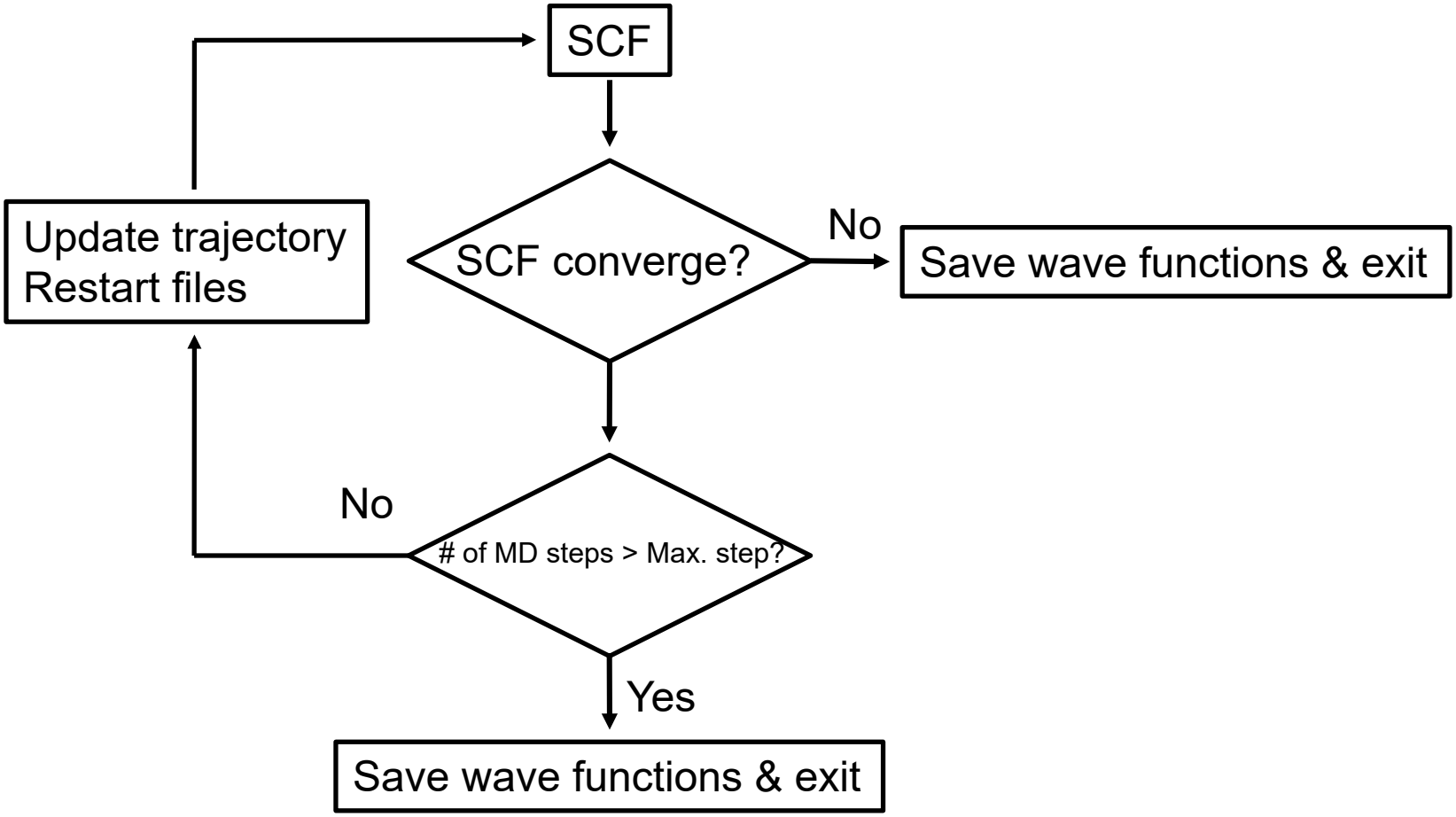


Structural optimization

Input file (nfinp_gdiis)

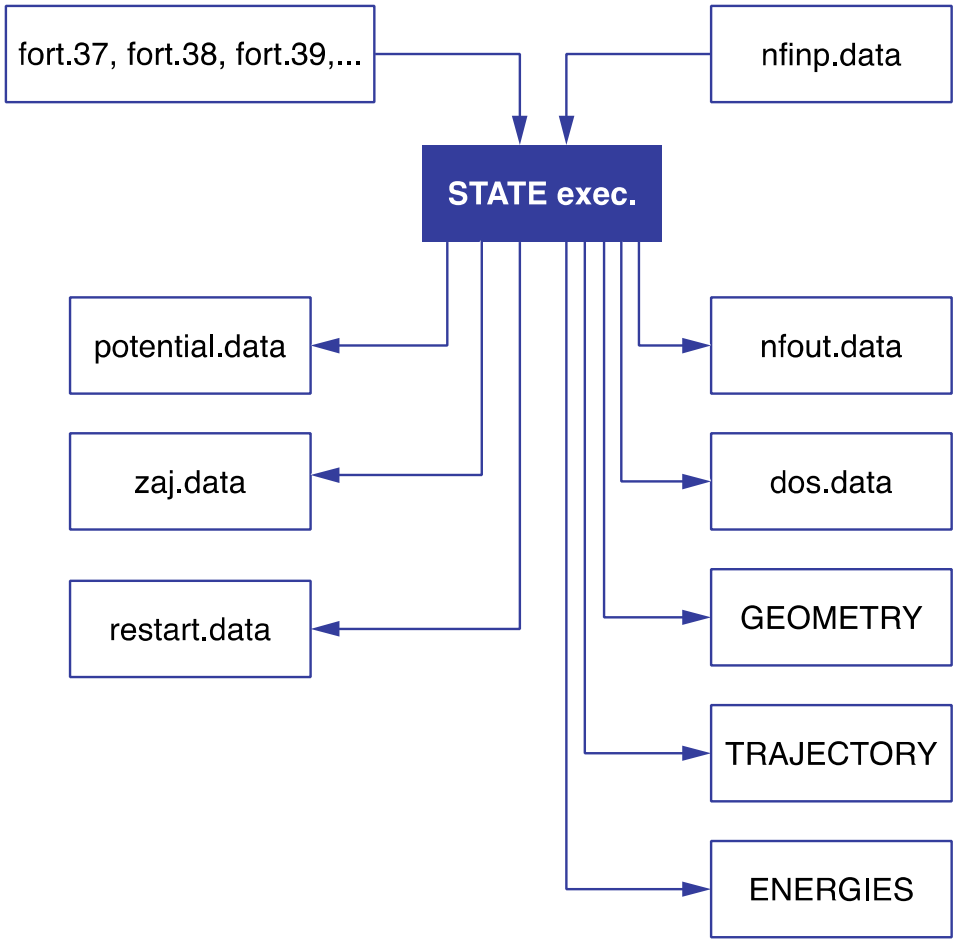
```
#
# Ethylene molecule in a box: geometry optimization with the GDIIS method
#
WF_OPT DAV
GEO_OPT GDIIS          ← Geometry optimization (GDIIS)
NTYP    2
NATM    6
TYPE    0
GMAX     5.00
GMAXP   15.00
MIX_ALPHA 0.8
WIDTH    0.0010
EDELTA   0.1000D-08
NEG      10
FMAX     0.5000D-03    ← Force threshold (Hartree/Bohr)
CELL    12.00   12.00   12.00   90.00   90.00   90.00
&ATOMIC_SPECIES
 C   12.0107   pot.C_pbe3
 H    1.0079   pot.H_lda3
&END
&ATOMIC_COORDINATES CARTESIAN
      1.262722983300      0.000000000000      0.000000000000    1    1    1
      2.348328846800      1.753458668500      0.000000000000    1    1    2
      2.348328846800     -1.753458668500      0.000000000000    1    1    2
     -1.262722983300      0.000000000000      0.000000000000    1    1    1
     -2.348328846800      1.753458668500      0.000000000000    1    1    2
     -2.348328846800     -1.753458668500      0.000000000000    1    1    2
&END
```

Molecular dynamics



Input/output files

Molecular dynamics simulation



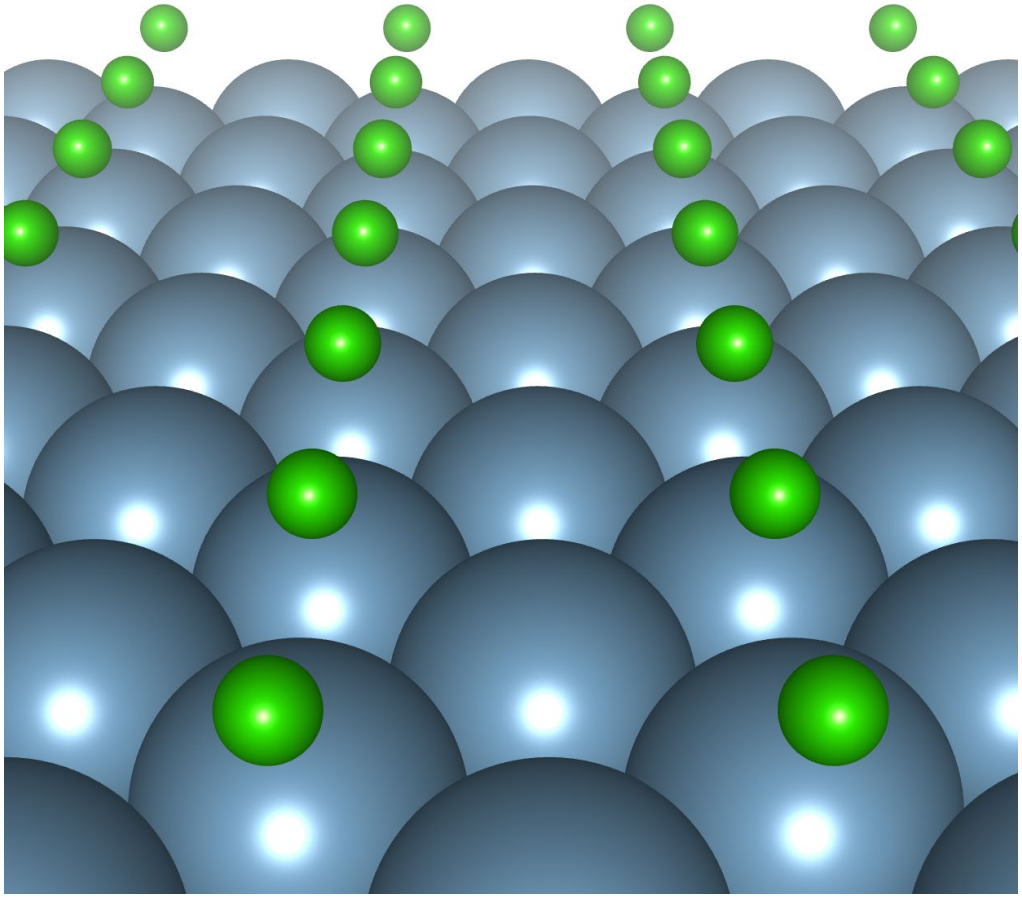
Input file (nfinp_nhc)

```
#
# Ethylene molecule in a box: geometry optimization with the GDIIS method
#
WF_OPT  DAV
ION_DYN FTMD
NTYP   2
NATM   6
TYPE   0
GMAX    5.00
GMAXP  15.00
MIX_ALPHA 0.8
WIDTH   0.0010
EDELTA  0.1000D-08
NEG     10
TEMP_CONTROL NHC
TEMPW   300.0D0
WNOSEP  500.0D0
NHC     8
NOSY    15
NDRT    1
CELL   12.00  12.00  12.00  90.00  90.00  90.00
&ATOMIC_SPECIES
 C  12.0107  pot.C_pbe3
 H   1.0079  pot.H_lda3
&END
&ATOMIC_COORDINATES CARTESIAN
      1.262722983300      0.000000000000      0.000000000000    1 1001    1
      2.348328846800      1.753458668500      0.000000000000    1 1001    2
      2.348328846800     -1.753458668500      0.000000000000    1 1001    2
     -1.262722983300      0.000000000000      0.000000000000    1 1001    1
     -2.348328846800      1.753458668500      0.000000000000    1 1001    2
     -2.348328846800     -1.753458668500      0.000000000000    1 1001    2
&END
```

← Finite temperature molecular dynamics

← Temperature (K)

Cl on Al(100) (optional)



Converting the input file format

Use the utility program “chkinpf” to convert the legacy input to the new input:

```
$ chkinpf --convert nfinp_1
```

Type the following for the available options:

```
$ chkinpf --help
```

Have fun with STATE!

大阪大学「ワニ博士」

Units used in STATE

- Hartree atomic unit
  - 1 Hartree (E_h) = 1 a.u.
  - 1 Rydberg = 0.5 a.u.
  - 1 Bohr radius (Bohr) = 1 a.u.
  - 1 electron rest mass (m_e) = 1 a.u.
  - 1 elementary charge (e) = 1 a.u.
  - 1 Planck's constant ($\hbar$) = 1 a.u.
  - 1 proton mass ≈ 1836 a.u.