Hands on Session II:

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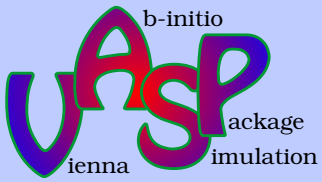


Outline

- `KPOINTS` file (DOS and Bandstructure)
- searching the optimal lattice parameter
- interpreting the `OUTCAR` file
- electronic density of states and band–structure
- relaxing the structure
- relaxing internal degrees of freedom

Getting Started

todays worklist:

- **Si**
  - setup bulk calculation for different crystal structures
  - find the optimal volume / lattice parameter (automated volume scan)
  - DOS and Bandstructure
  - Crystal Structure Optimization
- **Ni**
  - setup fcc Ni (spinpolarized)
  - determine optimal lattice parameter
  - DOS

files required for this session can be found in

```
~vw/2_1_description_of_job1
~vw/2_2_description_of_job2
```

Basics

POTCAR

- all calculations use GGA
- Potential–file `POTCAR` from
  `~vw/potpaw_GGA/Si`
  (`~vw/potpaw_PBE/Ni`)
  from the vasp potential database

- **Si** `PAW_PBE Si 05Jan2001`
  `Si:  s2p2, ENMAX = 245.345;`
  `EAUG = 322.069`
- **Ni** `PAW_PBE Ni 06Sep2000`
  `Ni:  ENMAX = 269.533;`
  `EAUG = 544.565`

insulators: fcc Si

```
general:
 System = fcc Si
 ISTART = 0 ; ICHARG=2
 ENCUT  =    240
 ISMEAR = 0; SIGMA = 0.1;



 K-Points
  0
 Monkhorst Pack
  11 11 11
  0  0  0
```

INCAR

- startjob; initial charge-density from overlapping atoms
- energy cut-off: 240 eV (from POTCAR)

KPOINTS

- equally spaced mesh
- odd $\rightarrow$ centered on Γ
- results in 56 k-points in IBZ

insulators: fcc Si continued

```
fcc Si:
 3.9
 0.5 0.5 0.0
 0.0 0.5 0.5
 0.5 0.0 0.5
   1
cartesian
0 0 0
```

files used in this example:

`POTCAR KPOINTS INCAR`

`POSCAR`

POSCAR

- fcc Si lattice constant 3.9 Å
- 1 atom in cell

groundstate volume ?

- calculate energy for different lattice parameters
- fit to some equation of states to obtain the equilibrium volume

automated volume scan

searching the optimal lattice parameter

- automated batch job: write a script
- store energy vs lattice parameter (Volume)
- very fast
- use one of those famous visualization tools like `Mma`
  to find optimum lattice parameter

```
#! /bin/bash
BIN=~vw/bin/vasp.4.6
rm WAVECAR
for i in  3.5 3.6 3.7 3.8 3.9 4.0 4.1 4.2 4.3 ; do
cat >POSCAR <<!
fcc:
   $i
 0.5 0.5 0.0
 0.0 0.5 0.5
 0.5 0.0 0.5
   1
cartesian
0 0 0
!
echo "a= $i" ; $BIN
E=‘tail -1 OSZICAR‘ ; echo $i $E  >>SUMMARY.fcc
done
cat SUMMARY.fcc
```

loop.sh

- Unix `bash script`
- use lattice parameters from 3.5 to 4.3 Å
- Result in `SUMMARY.fcc`

automated volume scan (continued)

```
3.4 1 F= -.40916606E+01 E0= -.40915302E+01 d E =-.260877E-03
3.5 1 F= -.44301421E+01 E0= -.44278642E+01 d E =-.455582E-02
3.6 1 F= -.46635511E+01 E0= -.46621165E+01 d E =-.286909E-02
3.7 1 F= -.47986983E+01 E0= -.47966436E+01 d E =-.410940E-02
3.8 1 F= -.48654598E+01 E0= -.48639627E+01 d E =-.299421E-02
3.9 1 F= -.48784931E+01 E0= -.48769634E+01 d E =-.305944E-02
4.0 1 F= -.48498418E+01 E0= -.48492073E+01 d E =-.126898E-02
4.1 1 F= -.47865540E+01 E0= -.47857796E+01 d E =-.154878E-02
4.2 1 F= -.46948550E+01 E0= -.46934142E+01 d E =-.288164E-02
4.3 1 F= -.45840107E+01 E0= -.45820708E+01 d E =-.387967E-02
4.4 1 F= -.44618699E+01 E0= -.44599101E+01 d E =-.391948E-02
```

SUMMARY.fcc

- Energy vs. lattice parameter

DOS (fcc Si)

- perform a static (`NSW=0, IBRION=-1`) self-consistent calculation $\rightarrow$ DOS in `DOSCAR`
- large system
  1. convergence with a small number of kpoints
  2. for DOS; increase the number of kpoints
     and set `ICHARG=11`, charge–density (`CHGCAR`) from the last self-consistent run
  - `ICHARG=11` treats all k-points independently
  - charge density and the potential fixed
  - $\rightarrow$ Bandstructure

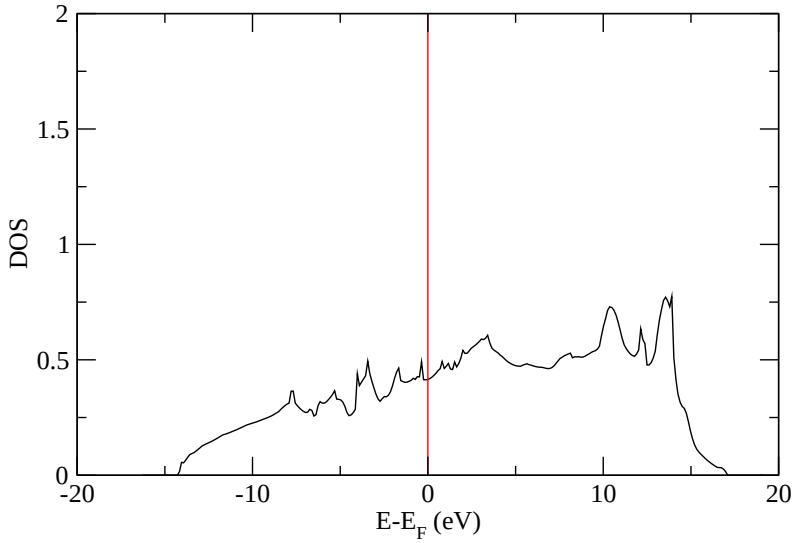
DOS (fcc Si)

```
 general:
  System = fcc Si
  ICHARG=11 #charge read file
  ENCUT  =    240
  ISMEAR = -5 #tetrahedron

K-Points
 0
Monkhorst Pack
 21 21 21
 0  0  0
```

INCAR

- read `CHGCAR` from previous run
- set smearing to fit the problem

KPOINTS

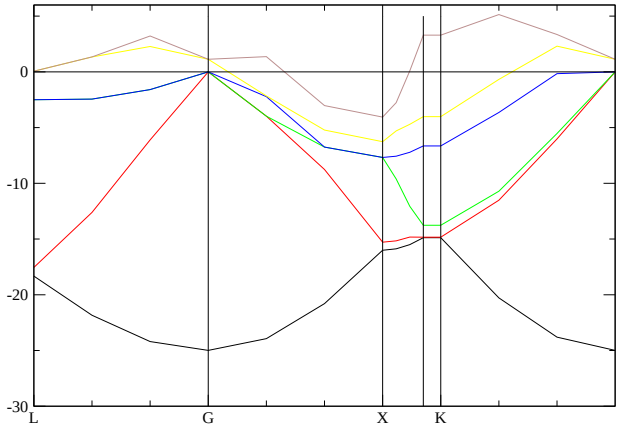


Bandstructure (fcc Si)

```
 kpoints from kgen
kpoints for bandstructure L-G-X-U K-G
 10
line
reciprocal
  0.50000  0.50000  0.50000    1
  0.00000  0.00000  0.00000    1

  0.00000  0.00000  0.00000    1
  0.00000  0.50000  0.50000    1

  0.00000  0.50000  0.50000    1
  0.25000  0.62500  0.62500    1

  0.37500  0.7500   0.37500    1
  0.00000  0.00000  0.00000    1
```

KPOINTS

- k-points along line $\bar{L} - \bar{\Gamma} - \bar{X} - \bar{U}\bar{K} - \bar{\Gamma}$
- 10 points per line
- keyword `line` to generate bandstructure
- in reciprocal coordinates
- all points with weight 1



insulators: diamond Si

```
cubic diamond
   5.5
 0.0    0.5     0.5
 0.5    0.0     0.5
 0.5    0.5     0.0
  2
Direct
 -0.125 -0.125 -0.125
  0.125  0.125  0.125
```

POSCAR

- diamond Si lattice constant 5.5 Å
- fcc cell
- 2 atoms in cell
- calculate energy vs. lattice parameter
  - execute `~vw/2_4_diamondSi/loop`

insulators: diamond Si (continued)

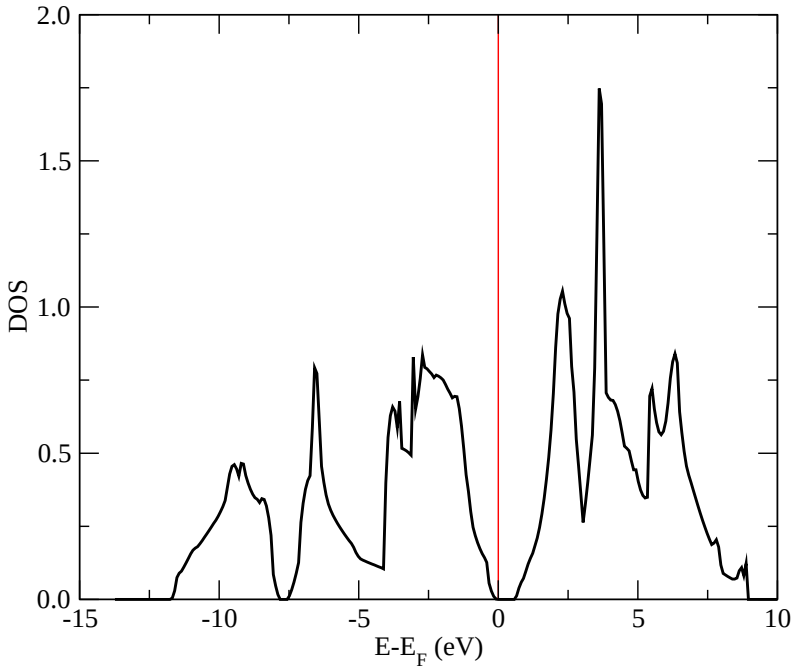
```
5.1 1 F= -.10222147E+02 E0= -.10221786E+02 d E =-.721447E-03
5.2 1 F= -.10517565E+02 E0= -.10517500E+02 d E =-.129988E-03
5.3 1 F= -.10704095E+02 E0= -.10704088E+02 d E =-.130462E-04
5.4 1 F= -.10797653E+02 E0= -.10797653E+02 d E =-.832225E-06
5.5 1 F= -.10814441E+02 E0= -.10814441E+02 d E =-.409086E-07
5.6 1 F= -.10766003E+02 E0= -.10766003E+02 d E =-.223801E-08
5.7 1 F= -.10664898E+02 E0= -.10664898E+02 d E =-.108197E-09
```

SUMMARY.diamond

- Energy vs. lattice parameter
  $a = 5.465$ Å
- for DOS and band-structure rounded to
  $a = 5.5$ Å

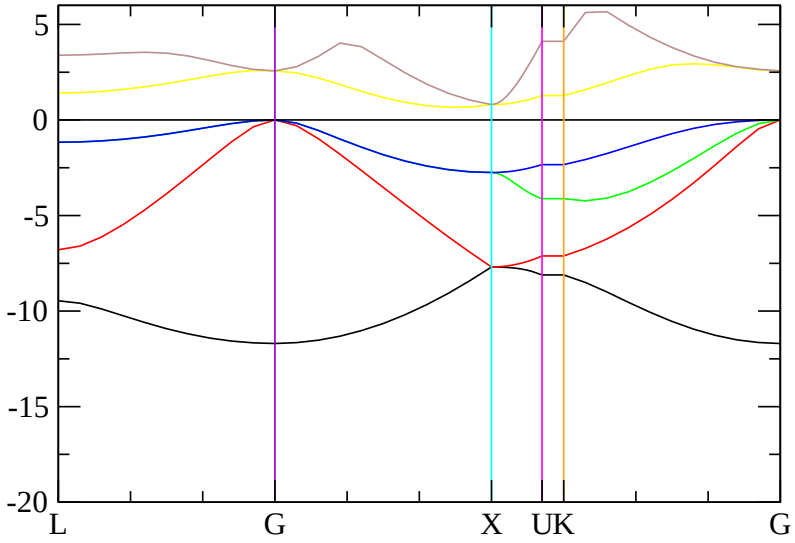
Density of States

Si diamond a=5.5A



Bandstructure

Bandstructure Si diamond



relaxing the structure

- fit the energy over a certain volume range to an equation of states
  (see last pages)
- relaxing the structure with vasp
  - `IBRION=2` conjugate-gradient algorithm
  - `ISIF=3` change internal parameters & shape & volume

```
System = diamond Si
ISMEAR = 0; SIGMA = 0.1;
ENMAX  =  240
IBRION=2; ISIF=3 ; NSW=15
EDIFF  = 0.1E-04
EDIFFG = -0.01
```

- `NSW=15` 15 steps of ionic relaxation
- increase accuracy of electronic steps
- forces on ions smaller than 0.01 eV/Å

relaxing the structure (cont)

```
-----------------------------------------------------------------------------
 Total        0.00      0.00      0.00      0.00      0.00      0.00
 in kB        0.05      0.05      0.05      0.00      0.00      0.00
 external pressure =        0.05 kB  Pullay stress =        0.00 kB

VOLUME and BASIS-vectors are now :
-----------------------------------------------------------------------
 energy-cutoff  :      240.00
 volume of cell :       40.81
```

- from equation of state $a = 5.488$ Å(volume scan)
- relaxing the structure $a = 5.465$ Å
- difference is is due to the Pulay stress
  - increase the plane wave cutoff by 30% (`ENMAX`)
  - use small `EDIFF`

Crystal Structure Optimization (Summary)

- calculation of the equilibrium volume
  - fit the energy over a certain volume range to an equation of states
  - when internal degrees of freedom exist (e.g. c/a), the structure must be optimized

    at each volume `IBRION = 2` conjugate-gradient algorithm
    `NSW = 10` e.g. 10 ionic steps
    `ISIF=4` change internal parameters & shape

- simpler but less reliable: relaxing all degrees of freedom including volume
  - to relax all degrees of freedom use:
    `ISIF=3` change internal parameters & shape & volume
  - mind Pulay stress problem (details in Section Accuracy)
    increase cutoff by 25-30% when the volume is allowed to change (e.g. Si `ENMAX = 300`)

Crystal Structure Optimization (cont.)

- files to watch during relaxations
  - STDOUT (Terminal), each electronic step is written to the terminal
  - `OSZICAR` a copy of the Terminal output
  - `OUTCAR` more detailed information on every electronic and ionic step
- other important files
  - `CONTCAR` holds the structure of the last ionic step,
    the structural result (also very important for restarting a relaxation)
  - `STOPCAR` stops a relaxation

diamond Si - relaxing internal degrees of freedom

```
general:
 System = diamond Si
 START = 0 ; ICHARG=2
 ENCUT  =    240
 ISMEAR = 0; SIGMA = 0.1;
 NSW    =  5; IBRION =  2
 ISIF   =  2
```

INCAR

- `NSW = 5` ionic relaxation, 5 steps
- `IBRION = 2`: conjugate-gradient algorithm
- `ISIF=2` relax internal parameters

diamond Si - relaxing internal degrees of freedom

```
fcc:
   5.5
 0.0    0.5     0.5
 0.5    0.0     0.5
 0.5    0.5     0.0
  2
Direct
 -0.125 -0.125 -0.125
  0.125  0.125  0.130
```

POSCAR

- standard diamond structure
  $\rightarrow$ break symmetry
- change z position
  from 0.125 $\rightarrow$ 0.130

after 1 step:

```
POSITION                                      TOTAL-FORCE (eV/Angst)
 -----------------------------------------------------------------------------------
     4.81250      4.81250      4.81250         0.173830      0.173830     -0.005889
     0.70125      0.70125      0.68750        -0.173830     -0.173830      0.005889
 -----------------------------------------------------------------------------------
   total drift:                                -0.000682     -0.000681     -0.000001
```

insulators: beta-tin Si

```
beta Sn
    4.9000000000000
 1.0    0.0     0.0
 0.0    1.0     0.0
 0.5    0.5     0.26
  2
Direct
 -0.125 -0.375  0.25
  0.125  0.375 -0.25
```

POSCAR

- beta-tin Si lattice constant Å
- 2 atoms in cell
- use loop and determine ground-state volume
- 1 internal parameter, use relaxation method
  to determine c/a

metals: fcc Ni

```
general:
  SYSTEM = fcc Ni
  ISTART = 0 ; ICHARG=2
  ENCUT  =    270
  ISMEAR =    1  ; SIGMA = 0.2
spin:
  ISPIN=2
  MAGMOM = 1

  K-Points
   0
  Monkhorst-Pack
  11 11 11
  0 0 0
```

INCAR

- startjob; initial charge-density from overlapping atoms
- energy cut-off: 270 eV (default)
- MP-smearing (metal!)
- spinpolarized calculation initial moments of 1
- static calculation

KPOINTS

- equally spaced mesh, 56 kpoints
- odd $\rightarrow$ centered at Γ

metals: fcc Ni continued

```
fcc:
 3.53
 0.5 0.5 0.0
 0.0 0.5 0.5
 0.5 0.0 0.5
   1
cartesian
0 0 0
```

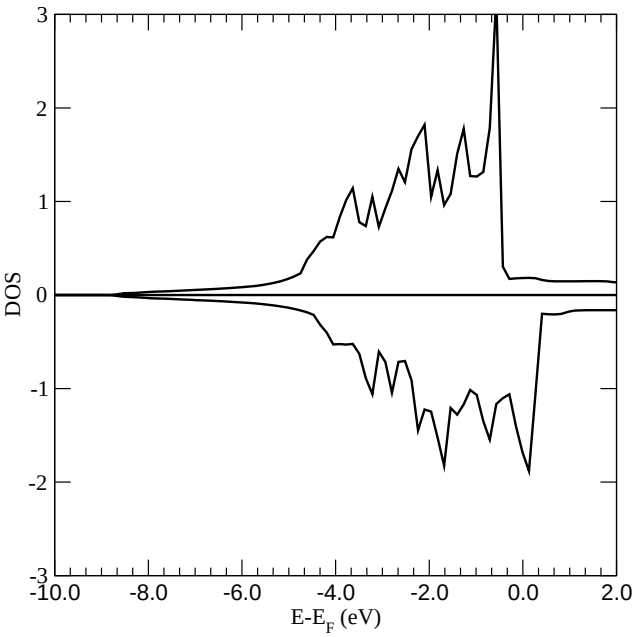
POSCAR

once again the fcc structure
for a the groundstate lattice
parameter of 3.53 Å
usually it is a good idea to start
from the experimental volume.

- start `vasp`
- result:

```
...
       N       E                     dE             d eps       ncg     rms         rms(c)
...
DAV:   9    -0.545983670040E+01    0.32312E-02   -0.60310E-03  2954   0.646E-01  0.891E-02
DAV:  10    -0.545982894631E+01    0.77541E-05   -0.31490E-05  1348   0.758E-02
   1 F= -.54598289E+01 E0= -.54598484E+01  d E =0.777759E-04  mag=     0.5683
```

fcc Ni



metals: fcc Ni continued

```
#! /bin/bash
BIN=~/bin/vasp.4.6
rm WAVECAR
for i in 3.0 3.1
...

....
   ISMEAR =   -5
   RWIGS = 1.4
```

loop.sh

our script to scan the volume

INCAR

- tetrahedron method
  $\rightarrow$ m=0.5704μ_B
- Wigner-Seitz radius of 1.4 Å

Summarize

Important: before starting any further analyses or relaxations:
perform a static (NSW=0, IBRION=-1) self-consistent calculation using a few k-points

- save the `CHGCAR` file from this run for the further steps
- the charge density and the effective potential converge rapidly with increasing number of k-points.
- important parameter: ICHARG=11
  all k-points can be treated independently, there is no coupling between them, because the charge density and the potential are kept fixed