

Hands on Session: Atoms and molecules

Overview

- discussion of the required files
- lot's of examples
 - O atom
 - O₂ dimer
 - CO
 - H₂O
- tasks
 - relaxation
 - vibrational frequencies
 - MD

The very first step: a single atom

- files required to do all calculations presented in this session can be found in the section

Atoms and molecules

of the list of examples in the vaspwiki.

- required files INCAR, KPOINTS, POSCAR, POTCAR
 - POTCAR pseudopotential file
generated by concatenation of individual POTCAR files from the data-base
 - KPOINTS Brillouin zone sampling
describes which k-points are used
 - POSCAR structural data
basis vectors and positions
 - INCAR steering the calculations
- let's start with the example O atom.

The POTCAR file

- what information can be found in the POTCAR file:
 - pseudopotential description
 - **data that is required to regenerate the potential**
 - number of valence electrons
 - atomic mass
 - required energy cutoff

The KPOINTS file

- determines how many k-points are used to sample the Brillouin zone
- for molecules or atoms **only a single k-point is required**

KPOINTS file:

Gamma-point only

1 ! one k-point

rec ! in units of the reciprocal lattice vector

0 0 0 1 ! 3 coordinates and weight

- for atoms and molecules the Bloch theorem does not apply, hence there is no need to use more than one single k-point
when more k-points are used, only the interaction between the atoms (which should be zero) is described more accurately

The POSCAR and INCAR files

- determines the lattice vectors (Bravais lattice) and the coordinates (position of the atoms)
- a single atom POSCAR file:

```
0 atom in a box
```

```
1.0          ! universal scaling parameters
```

```
8.0 0.0 0.0  ! lattice vector a(1)
```

```
0.0 8.0 0.0  ! lattice vector a(2)
```

```
0.0 0.0 8.0  ! lattice vector a(3)
```

```
1           ! number of atoms
```

```
cart       ! positions in cartesian coordinates
```

```
0 0 0
```

- INCAR steers the calculations:

```
SYSTEM = 0 atom in a box
```

```
ISMEAR = 0
```

Running vasp

vasp.4.6.2 07Jul02

POSCAR found : 1 types and 1 ions

LDA part: xc-table for Pade appr. of Perdew

POSCAR, INCAR and KPOINTS ok, starting setup

WARNING: wrap around errors must be expected

entering main loop

	N	E	dE	d eps	ncg	rms	rms(c)
DAV:	1	0.39156E+02	0.39157E+02	-0.95953E+02	14	0.335E+0	
DAV:	2	0.39499E+01	-0.35207E+02	-0.34385E+02	28	0.480E+0	
DAV:	3	-0.15830E+00	-0.41082E+01	-0.39042E+01	14	0.376E+0	
DAV:	4	-0.31026E+00	-0.15195E+00	-0.13836E+00	14	0.660E+0	
DAV:	5	-0.31321E+00	-0.29544E-02	-0.29502E-02	28	0.907E-0	0.286E-01
DAV:	6	-0.31407E+00	-0.86398E-03	-0.18767E-03	14	0.397E-0	0.142E-01
DAV:	7	-0.31422E+00	-0.14198E-03	-0.21862E-04	14	0.149E-0	0.480E-02
DAV:	8	-0.31427E+00	-0.55085E-04	-0.26453E-05	14	0.469E-0	

1 F= -.31427624E+00 E0= -.16001392E+00 d E =-.308525E+00

writing wavefunctions

OSZICAR *and* stdout file

initial charge corresponds to the charge of isolated overlapping atoms (POTCAR)
for 4 steps the charge remains fixed, then the charge is updated (rms (c) column)

N	iteration count
E	total energy
dE	change of total energy
d eps	change of the eigenvalues (fixed potential)
ncg	number of optimisation steps $\mathbf{H}\psi$
rms	total residual vector $\sum_{nk} w_k f_{nk} (\mathbf{H} - \epsilon_{nk}) \psi_{nk}$
rms (c)	charge density residual vector

OUTCAR *file*

individual parts are separated by lines

- first part: reading INCAR, POTCAR, POSCAR
- nearest neighbor distances and analysis of symmetry
- information on what was parsed from INCAR
- verbose job information
- information on lattice, k-points and positions
- information on the basis set (number of plane waves)
- non local pseudopotential information
- information for each electronic step (one line in OSZICAR)

```
POTLOK: VPU time    0.93: CPU time    0.93
SETDIJ: VPU time    0.01: CPU time    0.01
EDDAV  : VPU time    0.82: CPU time    0.83
DOS    : VPU time    0.00: CPU time    0.00
```

```
-----
LOOP:   VPU time    1.76: CPU time    1.76
```

```
eigenvalue-minimisations :    14
total energy-change (2. order) : 0.3915659E+02 (-0.9595269E+02)
number of electron      6.0000000 magnetization
augmentation part      6.0000000 magnetization
```

Free energy of the ion-electron system (eV)

```
-----
alpha Z      PSCENC =          0.27135287
Ewald energy TEWEN =         -91.92708002
-1/2 Hartree DENC  =        -281.84385690
-V(xc)+E(xc) XCENC =          26.11949869
PAW double counting =         245.99840262      -247.84808825
entropy T*S   EENTRO =         -0.18330906
eigenvalues   EBANDS =         -43.69352752
atomic energy EATOM =          432.26319604
```

```
-----
free energy   TOTEN  =          39.15658846 eV
```

```
energy without entropy =          39.33989752  energy(sigma->0) =          39.24824299
```

- eigenvalues

```
k-point 1 :      0.0000      0.0000      0.0000
band No.  band energies      occupation
   1      -23.8345      2.00000
   2       -8.8952      1.33333
   3       -8.8952      1.33333
   4       -8.8952      1.33333
   5       -0.4860      0.00000
   6        1.8485      0.00000
   7        1.8486      0.00000
```

- information on charge + some more timing informations

```
soft charge-density along one line, spin component      1
      0      1      2      3      4      5      6      7      8
x      5.4925      5.1765      4.3721      3.3741      2.4214      1.6318      1.0341      0.6112      0.3290
```

- information on the energy and stress tensor

FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)

 free energy TOTEN = -0.314276 eV

energy without entropy= -0.005752 energy(sigma->0) = -0.160014

FORCE on cell =-STRESS in cart. coord. units (eV/reduce length):

Direction	X	Y	Z	XY	YZ	ZX
Alpha Z	0.27	0.27	0.27			
Ewald	-30.64	-30.64	-30.64	0.00	0.00	0.00
Hartree	93.89	93.89	93.89	0.00	0.00	0.00
E(xc)	-27.94	-27.94	-27.94	0.00	0.00	0.00
Local	-147.85	-147.85	-147.85	0.00	0.00	0.00
n-local	-20.54	-20.54	-20.54	0.00	0.00	0.00
augment	5.55	5.55	5.55	0.00	0.00	0.00
Kinetic	126.50	126.50	126.50	0.00	0.00	0.00
Total	-0.77	-0.77	-0.77	0.00	0.00	0.00
in kB	-2.41	-2.41	-2.41	0.00	0.00	0.00
external pressure =	-2.41 kB		Pullay stress =	0.00 kB		

- final timing information

Some comments on this particular run

- the relevant energy for molecules and atoms is `energy without entropy`

```
energy without entropy= -0.005752 energy(sigma->0) = -0.160014
```

three degenerate p orbitals are occupied by 2/3 electrons causing a unphysical electronic entropy

```
entropy T*S EENTRO = -0.30852464
```

- a tiny value for SIGMA=0.01 would reduce the entropy but might slow convergence (default is SIGMA=0.2)

SIGMA controls the electronic temperature, which is not a very meaningful quantity for molecules and atoms

- the total energy is found to be essentially zero

VASP subtracts from any calculated energy the energy of the atom in the configuration for which the pseudopotential was generated

all pseudopotentials were generated using non spin polarized reference atoms

Restart vasp in same directory

vasp.4.6.2 07Jul02

POSCAR found : 1 types and 1 ions

LDA part: xc-table for Pade appr. of Perdew

found WAVECAR, reading the header

POSCAR, INCAR and KPOINTS ok, starting setup

WARNING: wrap around errors must be expected

the WAVECAR file was read successfully

initial charge from wavefunction

entering main loop

	N	E	dE	d eps	ncg	rms	rms(c)
DAV:	1	-0.314277E+00	-0.31428E+00	-0.14320E-06	14	0.899E-03	0.157E-03
DAV:	2	-0.314277E+00	0.64237E-07	-0.19000E-07	7	0.353E-03	
1 F=		-.31427731E+00	E0=	-.16001499E+00	d E =	-.308525E+00	

writing wavefunctions

when vasp is restarted the **WAVECAR** file is read and the run is continued from the previous wavefunctions (converging rapidly)

Spin polarized calculation

- the O atom is an open shell system with 2 unpaired electrons
- add ISPIN=2 to the INCAR file remove WAVECAR and restart vasp
(alternatively download the input files from O atom spinpolarized)

```
vasp.4.6.2 07Jul02
```

```
POSCAR found : 1 types and 1 ions
```

```
...
```

```
entering main loop
```

	N	E	dE	d eps	ncg	rms	rms(c)
DAV:	1	0.38975372E+02	0.38975E+02	-0.10098E+03	32	0.259E+02	
DAV:	2	0.31791299E+01	-0.35796E+02	-0.35789E+02	64	0.438E+01	
DAV:	3	-0.11905610E+01	-0.43697E+01	-0.36660E+01	32	0.327E+01	
DAV:	4	-0.12616637E+01	-0.71103E-01	-0.69167E-01	32	0.508E+00	
DAV:	5	-0.12625234E+01	-0.85968E-03	-0.85961E-03	48	0.504E-01	0.653E+00

```
...
```

```
DAV: 11 -0.16719490E+01 0.16543E-04 -0.47746E-04 32 0.131E-01  
1 F= -.16719490E+01 E0= -.15948179E+01 d E =-.154262E+00 mag= 1.9986
```

```
writing wavefunctions
```

Spin polarized calculation

- eigenstates for spin up and spin down are calculated “separately”
in LSDA they interact only via the effective local potential
spin-up and spin-down potential
- in the OUTCAR file, one can see two spin components
- the spin component 1 has 2 more electrons corresponding the a magnetization of $2 \mu_B$

```
k-point 1 :      0.0000      0.0000      0.0000
band No.  band energies      occupation
   1      -25.0761      1.00000
   2      -10.0715      1.00000
   3      -10.0715      1.00000
   4      -10.0715      1.00000
   5       -0.3997      0.00000
   6       1.6965      0.00000
   7       1.9499      0.00000
   8       1.9499      0.00000
```

```
spin component 2
k-point 1 :      0.0000      0.0000      0.0000
band No.  band energies      occupation
   1      -21.8260      1.00000
   2       -7.0425      0.33333
   3       -7.0425      0.33333
   4       -7.0425      0.33333
   5       -0.4479      0.00000
   6       1.9043      0.00000
   7       1.9043      0.00000
   8       1.9043      0.00000
```


Symmetry broken O atom

- in the GGA, most atoms are characterized by a symmetry broken solution
VASP however symmetrizes the charge-density according to the determined symmetry of the cell
check the OUTCAR file, which symmetry is VASP using
- to lower the symmetry simply change the lattice parameters to 7.0 8.0 and 9.0 in the POSCAR file (alternatively download the input files from O atom spinpolarized low symmetry):

```
7.0 0.0 0.0 ! lattice vector a(1)
0.0 7.5 0.0 ! lattice vector a(2)
0.0 0.0 8.0 ! lattice vector a(3)
```

and reduce SIGMA to SIGMA=0.01 (INCAR file)

- rerunning VASP you will find a much lower energy

```
vasp.4.6.2 07Jul02
...
DAV: 17 -0.190131780202E+01 -0.53122E-04 -0.35327E-06 32 0.128E-02
1 F= -.19013178E+01 E0= -.19013178E+01 d E =-.938468E-52 mag= 1.9997
```

Let's add another atom: the O₂ dimer

- copy the required files and start VASP (see footnote)

- POSCAR:

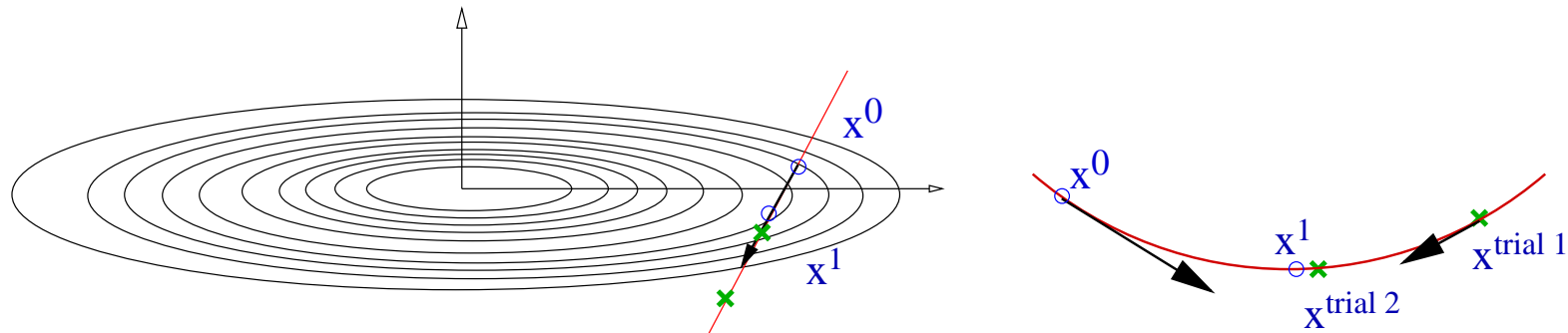
```
0 atom in a box
1.0          ! universal scaling parameters
8.0 0.0 0.0  ! lattice vector a(1)
0.0 8.0 0.0  ! lattice vector a(2)
0.0 0.0 8.0  ! lattice vector a(3)
2           ! number of atoms
cart       ! positions in cartesian coordinates
0 0 0      ! first atom
0 0 1.22   ! second atom
```

- INCAR:

```
SYSTEM = O2 dimer in a box
ISMEAR = 0 ! Gaussian smearing
ISPIN  = 2 ! spin polarized calculation
NSW    = 5  ! 5 ionic steps
IBRION = 2 ! use the conjugate gradient algorithm
```

Relaxing the O₂ dimer

- we have inserted that geometry relaxation should be performed:
in this case 5 ionic steps (NSW = 5) should be done at most
for the relaxation a conjugate gradient algorithm is used IBRION = 2
- CG requires a line minimizations along the search direction



this is done using a variant of Brent's algorithm

- trial step along search direction (gradient scaled by POTIM)
- quadratic or cubic interpolation using energies and forces at \vec{x}_0 and \vec{x}_1 allows to determine the approximate minimum
- continue minimization, if app. minimum is not accurate enough

Relaxing the O₂ dimer

DAV: 1 0.511277926223E+02 0.51128E+02 -0.31305E+03 60 0.528E+02

...

DAV: 11 -0.985454093746E+01 -0.88826E-04 -0.59757E-05 44 0.746E-02

1 F= -.98545409E+01 E0= -.98545409E+01 d E =-.985454E+01 mag= 2.0000

curvature: 0.00 expect dE= 0.000E+00 dE for cont linesearch 0.000E+00

trial: gam= 0.00000 g(F)= 0.111E+00 g(S)= 0.000E+00 ort = 0.000E+00 (trialstep = 0.100E+01)

search vector abs. value= 0.111E+00

bond charge predicted

...

2 F= -.96306943E+01 E0= -.96306943E+01 d E =0.223847E+00 mag= 2.0000

trial-energy change: 0.223847 1 .order 0.186756 -0.110518 0.484030

step: 0.1406(harm= 0.1859) dis= 0.00726 next Energy= -9.862210 (dE=-0.767E-02)

bond charge predicted

...

3 F= -.98624278E+01 E0= -.98624278E+01 d E =-.788682E-02 mag= 2.0000

curvature: -0.09 expect dE=-0.448E-05 dE for cont linesearch -0.448E-05

trial: gam= 0.00000 g(F)= 0.484E-04 g(S)= 0.000E+00 ort =-0.231E-02 (trialstep = 0.828E+00)

search vector abs. value= 0.484E-04

reached required accuracy - stopping structural energy minimisation

CG: What does all this mean?

- the quantity `trial-energy` change is the change of the energy in the trial step
- the first value after `1.order` is the expected energy change calculated from the forces $((\mathbf{F}(\text{start}) + \mathbf{F}(\text{trial}))/2 \times \text{change of positions})$

`central difference`

second and third value corresponds to $\mathbf{F}(\text{start}) \times \text{change of positions}$ and $\mathbf{F}(\text{trial}) \times \text{change of positions}$

- the value `step`: is the estimated size of the step leading to a line minimization along the current search direction

`harm` is the optimal step using a second order (or harmonic) interpolation

- the trial step size can be controlled by the parameter `POTIM`
the value `step`: times the present `POTIM` is usually optimal
- the final positions after the optimisation are stored in `CONTCAR`
you can copy `CONTCAR` to `POSCAR` and continue the relaxation

Let's add another species: the CO molecules

- copy required files and start VASP

- POSCAR:

```
...
1 1          ! number of atoms for each species
cart        ! positions in cartesian coordinates
0 0 0       ! first atom
0 0 1.12    ! second atom
```

- POTCAR is created by the concatenation of two individual POTCAR files corresponding to O and C; e.g.:

```
cat .../O/POTCAR .../C/POTCAR >POTCAR
```

- a similar relaxation as in the previous case is performed

but in this case more steps are required, since the first estimate for the minimum is not very accurate

the trial steps are much too long (POTIM parameter)

Relaxing the CO dimer

```
1 F= -.14764188E+02 E0= -.14764188E+02 d E =-.147642E+02
curvature: 0.00 expect dE= 0.000E+00 dE for cont linesearch 0.000E+00
trial: gam= 0.00000 g(F)= 0.822E+00 g(S)= 0.000E+00 ort = 0.000E+00 (trialstep = 0.100E+01)
search vector abs. value= 0.822E+00
...
2 F= -.12657048E+02 E0= -.12657048E+02 d E =0.210714E+01
trial-energy change: 2.107140 1 .order 1.312507 -0.821770 3.446784
step: 0.1925(harm= 0.1925) dis= 0.02710 next Energy= -14.843291 (dE=-0.791E-01)
...
3 F= -.14747873E+02 E0= -.14747873E+02 d E =0.163154E-01
curvature: -0.10 expect dE=-0.909E-01 dE for cont linesearch -0.909E-01
ZBRENT: interpolating
opt : 0.0929 next Energy= -14.802370 (dE=-0.382E-01)
...
4 F= -.14797047E+02 E0= -.14797047E+02 d E =-.328587E-01
curvature: -0.04 expect dE=-0.341E-03 dE for cont linesearch -0.341E-03
trial: gam= 0.00000 g(F)= 0.844E-02 g(S)= 0.000E+00 ort =-0.833E-01 (trialstep = 0.819E+00)
search vector abs. value= 0.844E-02
reached required accuracy - stopping structural energy minimisation
```

Vibrational frequencies of the CO dimer

- SYSTEM = CO dimer in a box
ISMEAR = 0 ! Gaussian smearing
IBRION = 5 ! vibrational spectrum
NFREE = 2 ! use central differences
POTIM = 0.02 ! 0.02 stepwidth
NSW = 1 ! ionic steps must be larger 0 (that's all)

- POSCAR:

```
sel          ! selective degrees of freedom are changed
cart        ! positions in cartesian coordinates
  0 0 0      F F T ! first atom
  0 0 1.143 F F T ! second atom
```

the selected degrees of freedom are displaced once in the direction \hat{x} and once $-\hat{x}$ by 0.02 \AA

in the present case this makes 4 displacements plus the equilibrium positions (i.e. a total of five ionic configurations)

SECOND DERIVATIVES (NOT SYMMETRIZED)

```
-----
          1Z          2Z
1Z -114.847733  114.847733
2Z  114.305971 -114.305971
```

Eigenvectors and eigenvalues of the dynamical matrix

```
-----
1 f = 63.876494 THz  401.347846 2PiTHz 2130.690412 cm-1  264.172038 meV
      X          Y          Z          dx          dy          dz
0.000000  0.000000  0.000000          0          0  -0.655709
0.000000  0.000000  1.143000          0          0   0.755014
2 f/i= 0.074763 THz   0.469753 2PiTHz   2.493841 cm-1   0.309197 meV
      X          Y          Z          dx          dy          dz
0.000000  0.000000  0.000000          0          0  -0.755014
0.000000  0.000000  1.143000          0          0  -0.655709
```

Eigenvectors after division by SQRT(mass)

Eigenvectors and eigenvalues of the dynamical matrix

```
-----
1 f = 63.876494 THz  401.347846 2PiTHz 2130.690412 cm-1  264.172038 meV
      X          Y          Z          dx          dy          dz
0.000000  0.000000  0.000000          0          0  -0.163927
0.000000  0.000000  1.143000          0          0   0.217854
2 f/i= 0.074763 THz   0.469753 2PiTHz   2.493841 cm-1   0.309197 meV
      X          Y          Z          dx          dy          dz
```

...

H₂O molecules

- POSCAR

```
H2O _2
0.52918 ! scaling parameter
 15 0 0
 0 15 0
 0 0 15
1 2
select
cart
      0.00      0.00      0.00 F F F
      1.10     -1.43      0.00 T T F
      1.10      1.43      0.00 T T F
```

all coordinates are scaled by the factor 0.529

- INCAR:

```
PREC = Normal      ! standard precision
ENMAX = 400        ! cutoff should be set manually
ISMEAR = 0 ; SIGMA = 0.1
IBRION = 1         ! use DIIS algorithm to converge
NFREE = 2          ! 2 independent degrees of freedom
NSW = 10           ! 10 ionic steps
EDIFFG = -0.02    ! forces smaller 0.02 A/eV
```

H₂O molecules: comments

- `PREC = Normal` should be used in `vasp.4.6`
slightly more balanced setup than the default `PREC = Medium`
- I strongly urge to set the `energy cutoffs manually in the INCAR file`, as it gives you more control over the calculations
- for the ionic optimisation the DIIS algorithm is used
this algorithm builds an approximation of the Hessian matrix and converges usually faster than the conjugate gradient algorithm
it is however recommended to set the independent degrees of freedom manually
`EDIFFG` determines when to terminate relaxation
positive values: energy change between steps must be less than `EDIFFG`
negative values: $|\vec{F}_i| < |\text{EDIFFG}| \quad \forall i = 1, N_{ions}$

Interpreting the eigenstates of CO

- the PROCAR file gives valuable information of the character of the one electron states
 - LORBIT 10 DOSCAR and l decomposed PROCAR file
 - LORBIT 11 DOSCAR and lm decomposed PROCAR file
- we use LORBIT=11 to distinguish p_x and p_z states
- copy the required input files, and check them using an editor
execute vasp again

PROCAR file:

band 3 # energy -11.46549527 # occ. 2.00000000

ion	s	py	pz	px	dxy	dyz	dz2	dxz	dx2	tot
1	0.000	0.546	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.546
2	0.000	0.157	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.157
tot	0.000	0.703	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.703

band 4 # energy -11.46549510 # occ. 2.00000000

ion	s	py	pz	px	dxy	dyz	dz2	dxz	dx2	tot
1	0.000	0.000	0.000	0.546	0.000	0.000	0.000	0.000	0.000	0.546
2	0.000	0.000	0.000	0.157	0.000	0.000	0.000	0.000	0.000	0.157
tot	0.000	0.000	0.000	0.703	0.000	0.000	0.000	0.000	0.000	0.703

band 5 # energy -8.76451122 # occ. 2.00000000

ion	s	py	pz	px	dxy	dyz	dz2	dxz	dx2	tot
1	0.001	0.000	0.135	0.000	0.000	0.000	0.000	0.000	0.000	0.136
2	0.172	0.000	0.261	0.000	0.000	0.000	0.000	0.000	0.000	0.433
tot	0.173	0.000	0.396	0.000	0.000	0.000	0.000	0.000	0.000	0.569

Let's do some a MD for H₂O

- **INCAR:**

```
PREC = Normal      ! standard precision
ENMAX = 400        ! cutoff should be set manually
ISMEAR = 0 ; SIGMA = 0.1
```

```
IBRION = 0         ! molecular dynamics
NSW = 100          ! 100 steps
POTIM = 1.0        ! timestep 1 fs
```

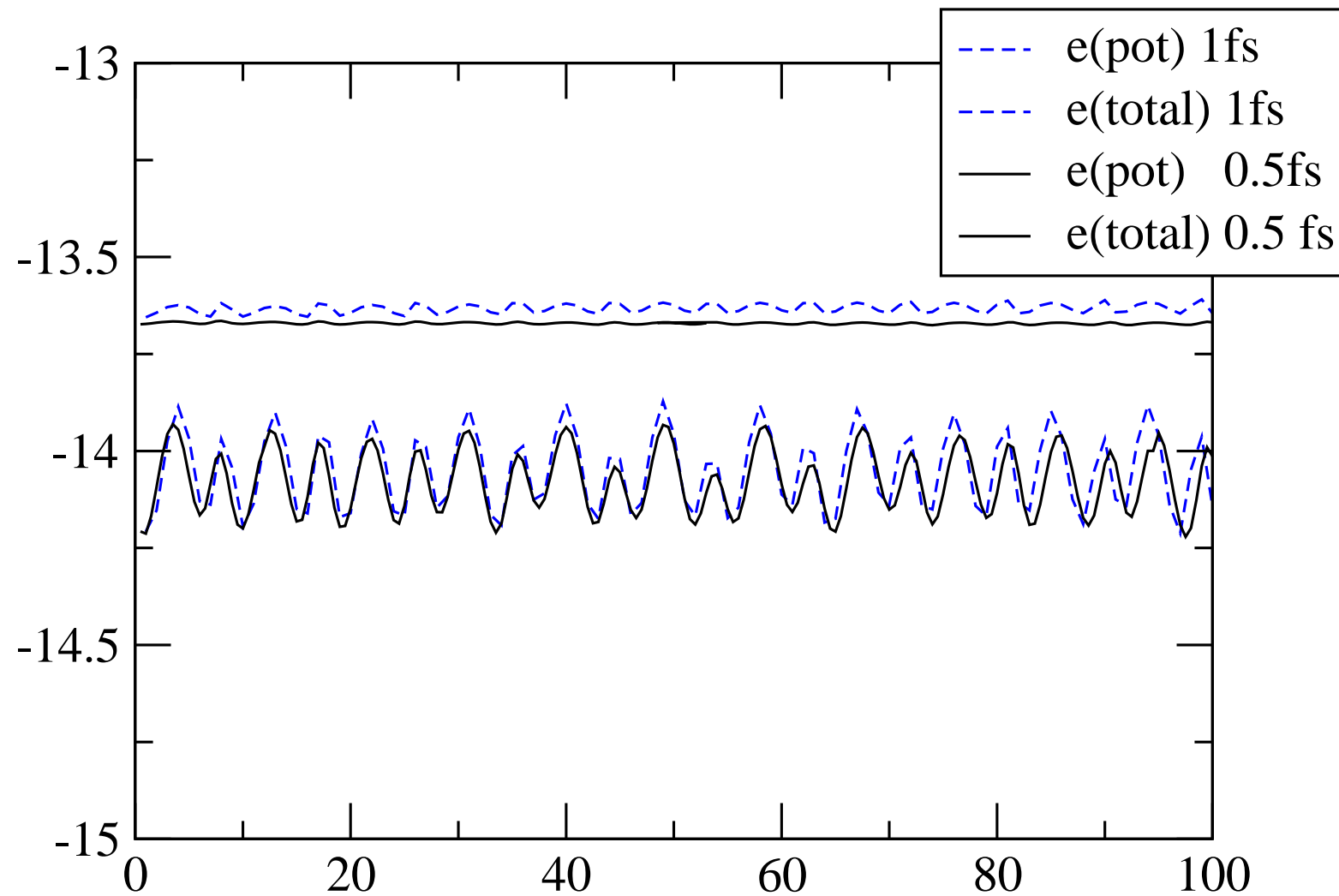
```
SMASS = -3        ! micro-canonical ensemble
TEBEG = 2000 ; TEEND = 2000 ! temperature
```

time step for this system should be around 0.5-0.7 fs

- **POSCAR:** to save time the box size is reduced to 12 a.u.

- **OSZICAR:**

```
1 T= 2134. E= -.13655511E+02 F= -.14207209E+02 E0=.. EK= 0.55170E+00 SP= 0.00E+00 SK= 0.00E+00
2 T= 1971. E= -.13643254E+02 F= -.14152912E+02 E0=.. EK= 0.50966E+00 SP= 0.00E+00 SK= 0.00E+00
3 T= 1336. E= -.13629241E+02 F= -.13974630E+02 E0=.. EK= 0.34539E+00 SP= 0.00E+00 SK= 0.00E+00
4 T= 1011. E= -.13624149E+02 F= -.13885486E+02 E0=.. EK= 0.26134E+00 SP= 0.00E+00 SK= 0.00E+00
5 T= 1307. E= -.13629772E+02 F= -.13967549E+02 E0=.. EK= 0.33778E+00 SP= 0.00E+00 SK= 0.00E+00
```



Excercises

- How does the energy change when you decrease SIGMA to 0.01 in the INCAR file starting from O atom ? Why ?
- Try to copy CONTCAR to POSCAR after running the example O dimer. Why is the calculation so fast ?
- Try to play with the parameter POTIM for the example O dimer. What is the optimal value ?
- What is the reason for the imaginary frequency in the example CO vibration. Does the behavior improve when the step width (smaller or larger) is changed. Also try to improve the precision to which the groundstate is converged (EDIFF=1E-5). What happens if the accuracy of the calculations is improved (PREC=Accurate).
- Try to use the conjugate gradient algorithm to the H₂O molecule (example H2O).
- Calculate the vibrational frequencies of the H₂O molecule (example H2O) after relaxation (example H2Ovib). Why does one find 3 modes that have small frequencies. Try EDIFF=1E-5 instead of EDIFF=1E-4.

Simple bulk systems

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

- **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 the section

Simple bulk systems

of the list of examples in the vaspwiki

Basics

POTCAR

- all calculations use GGA

- **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

loop.sh

```
#!/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
```

- 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 → 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
 - → Bandstructure

DOS (fcc Si)

general:

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

K-Points

0

Monkhorst Pack

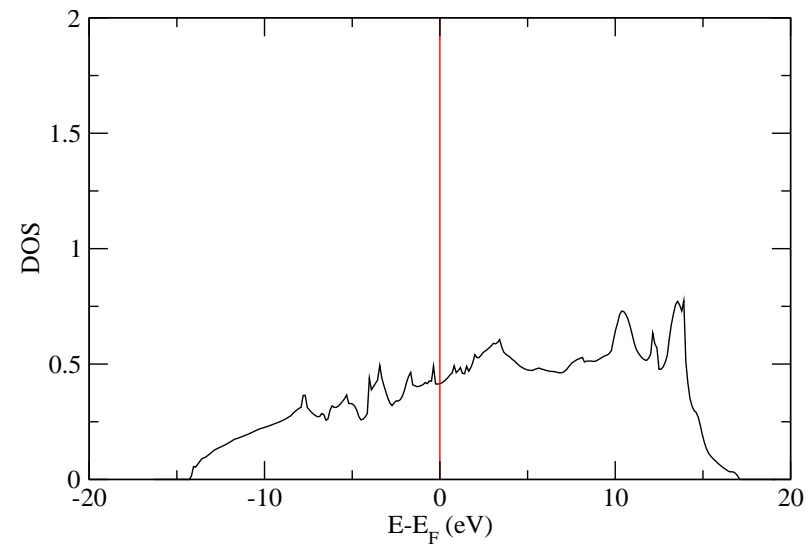
21 21 21

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

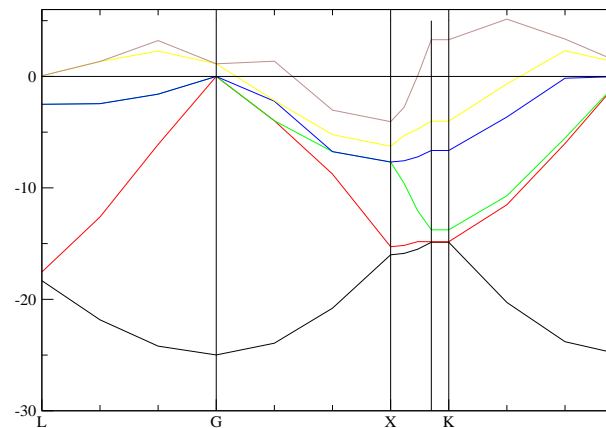
0.00000 0.00000 0.00000 1
0.00000 0.50000 0.50000 1

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

POSCAR

```
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
```

- 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)

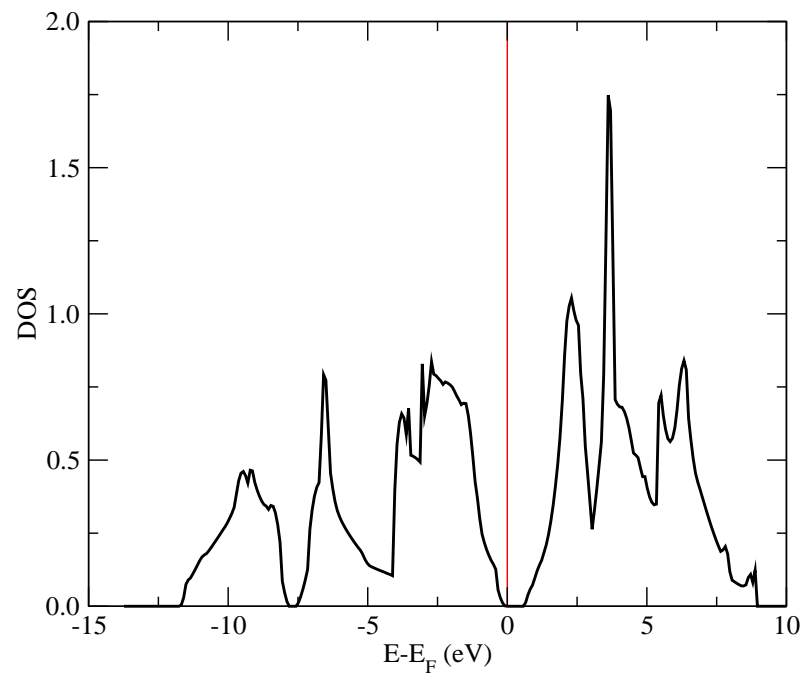
```
5.1 1 F= -.10222147E+02 E0= -.10221786E+02 d E =-.721447E-03
5.2 1 F= -.10517565E+02 E0= -.10517500E+02 d E =-.129988E-03
5.3 1 F= -.10704095E+02 E0= -.10704088E+02 d E =-.130462E-04
5.4 1 F= -.10797653E+02 E0= -.10797653E+02 d E =-.832225E-06
5.5 1 F= -.10814441E+02 E0= -.10814441E+02 d E =-.409086E-07
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
 $a = 5.465 \text{ \AA}$
- for DOS and band-structure rounded to
 $a = 5.5 \text{ \AA}$

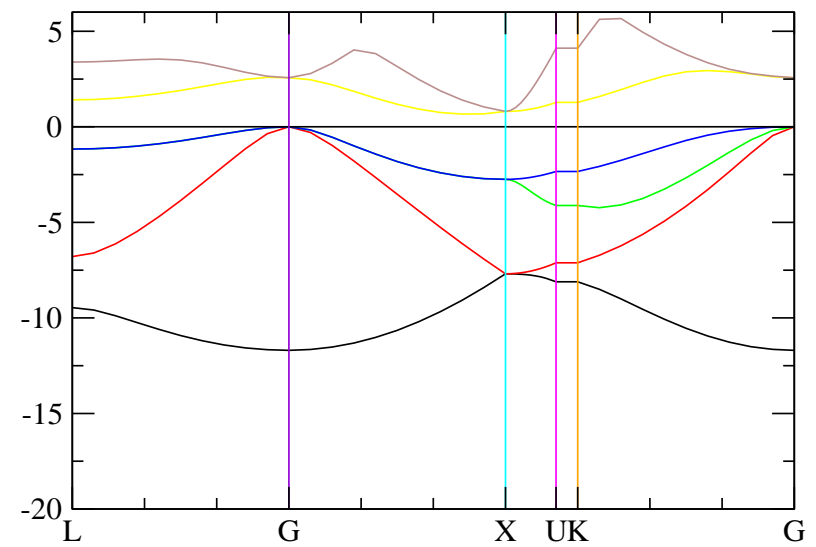
Density of States

Si diamond $a=5.5\text{\AA}$



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 Pulay stress = 0.00 kB

VOLUME and BASIS-vectors are now :

energy-cutoff : 240.00
volume of cell : 40.81

- from equation of state $a = 5.488 \text{ \AA}$ (volume scan)
- relaxing the structure $a = 5.465 \text{ \AA}$
- difference 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
 - IBRION = 2 conjugate-gradient algorithm
 - at each volume 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

POSCAR

```
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
```

- standard diamond structure
→ break symmetry
- change z position
from 0.125 → 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

POSCAR

```
beta Sn
  4.900000000000000
  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
```

- 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

INCAR

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

- 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 → centered at Γ

metals: fcc Ni continued

POSCAR

```
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
```

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.

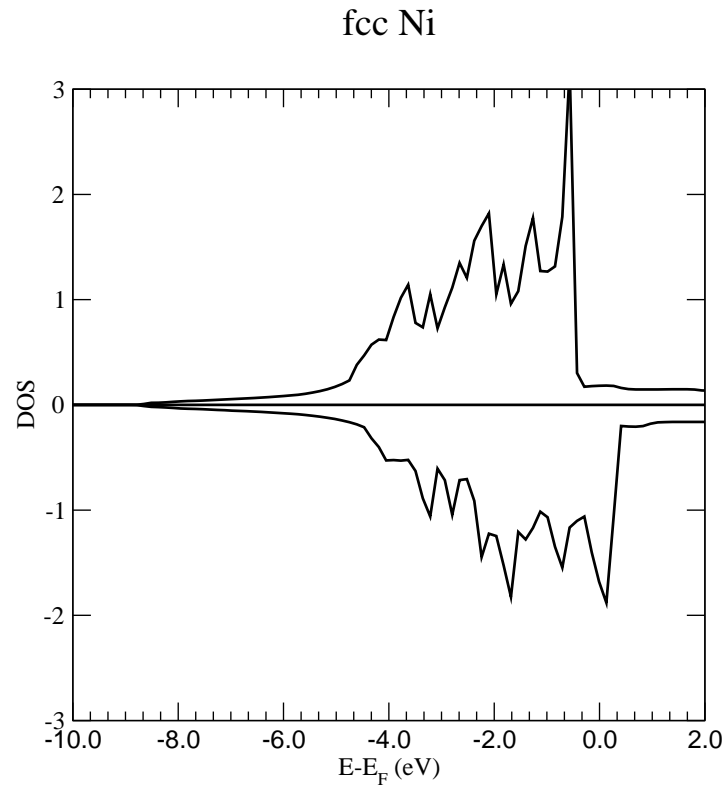
- start vasp
- result:

```

...
      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

```

- DOS



metals: fcc Ni continued

```
#!/bin/bash
BIN=~ /bin/vasp.4.6
rm WAVECAR
for i in 3.0 3.1
...
.....
    ISMEAR =    -5
    LORBIT = 11
```

loop.sh

our script to scan the volume

INCAR

- tetrahedron method
- s-, p-, d-projected DOS and local magnetic moments

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