Hands on Session: VASP

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Overview

1. atoms: O
2. small molecules: O_2 (relaxation, vibrational frequencies)
3. bulk Ni: determination of the bulk lattice parameter
4. clean surfaces: Ni (001) and (111):
5. adsorption of H on Ni(001), subsurface H
6. the NEB method: subsurface diffusion of H into Ni (001):
7. magnetic structures: Ni (001) ML: E_{MCA}
8. LSDA+U: NiO

Required input files

POTCAR

1.
```
PAW_PBE O 08Apr2002
6.00000000000000000
parameters from PSCTR are:
  VRHFIN =O: s2p4
  LEXCH  = PE
  EATOM  =   432.3788 eV,   31.7789 Ry
  TITEL  = PAW_PBE O 08Apr2002
  .....
  POMASS =   16.000; ZVAL   =    6.000    mass and valenz
  RCORE  =    1.520    outmost cutoff radius
  RWIGS  =    1.550; RWIGS  =     .820    wigner-seitz radius (au A)
  ENMAX  =  400.000; ENMIN  =  300.000 eV
  ICORE  =        2    local potential
  ....
  EAUG   =  605.392
  .....
```


in `POTCAR` the basic default settings are given for

- the PP type (US or PAW)
- data that is required to regenerate the potential:
- the XC-type (`LEXCH`)
- the atomic mass (`POMASS`)
- the number of valence electrons (`ZVAL`),
  check V_RHFIN for the configuration of the ground state
- core- and Wigner-Seitz radii, (`RCORE, RWIGS`)
- required energy cutoffs (`ENMAX, ENMIN, EAUG`)

for cells built of different atom types, `POTCAR` is generated by concatenation (`cat`) of the individual atoms' `POTCAR` files from the data-base
the sequence has to correspond to the one in `POSCAR`

KPOINTS

2. : Brillouin zone sampling

   describes which k-points are used: $\vec{k}$-mesh densities, special grids (eg for generating band structures), centering on or around Γ,... (alternatively, `IBZKPT` can be read as well)

POSCAR

3. : structural data

   lattice parameter, basis vectors, number of ions (and their types) and positions, (initial MD-velocities)

INCAR

4. steering the calculations ...

The KPOINTS file

determines how many $\vec{k}$-points are used to sample the Brillouin zone

molecules or atoms:

only a single $\vec{k}$-point is required: atoms and molecules the Bloch theorem does not apply, hence there is no need to use more then one single $\vec{k}$-point when more $\vec{k}$-points are used, only the interaction between the atoms (which should be zero) is described more accurately

bulk and surface systems:

the $\vec{k}$-point mesh should be converged

single atoms, molecules:

```
Gamma-point only
 1        ! one k-point
rec       ! units: recip. latt. vector
 0 0 0 1  ! 3 coordinates and weight
```

bulk and surface calculations:

```
K-Points
 0
Monkhorst Pack
 9 9 9
 0  0  0
```

special k-grids along high symmetry lines of the BZ (band structures)

```
kpoints for bandstructure Gamma-Delta-X-M
 10             ! number of intersections along a line
line
reciprocal
  0.000 0.000 0.000    1
  0.500 0.000 0.000    1

  0.500 0.000 0.000    1
  0.500 0.500 0.000    1
```


The very first step: a single atom

required files: `1_free_atom/1_cub_spin1`

a single atom POSCAR file: unit cell, coordinates of the atoms

```
O atom in a box
 1.0          ! universal scaling parameters
 7.0 0.0 0.0  ! lattice vector  a(1)
 0.0 7.0 0.0  ! lattice vector  a(2)
 0.0 0.0 7.0  ! lattice vector  a(3)
1             ! number of atoms
cartesian     ! positions in cart. coordinates
 0 0 0
```

INCAR steers the calculations:

```
SYSTEM=O_free_atom
ISMEAR=0
SIGMA=0.01    #no broadening of atomic levels
```

Running vasp

```
/usr/local/chem/src/vasp/VASP-4.6/src/vasp.4.6/vasp_ngx
```

```
vasp.4.6.26 15Dec04 complex
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
FFT: planning ...           1
reading WAVECAR
entering main loop
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1     0.403646613230E+02    0.40365E+02   -0.11519E+03    14   0.377E+02
DAV:   2     0.425839128055E+01   -0.36106E+02   -0.36106E+02    28   0.470E+01
DAV:   3     0.812025174985E-01   -0.41772E+01   -0.41772E+01    14   0.533E+01
DAV:   4    -0.144676343307E-01   -0.95670E-01   -0.81393E-01    14   0.662E+00
DAV:   5    -0.167857530928E-01   -0.23181E-02   -0.22929E-02    14   0.928E-01    0.292E-01
DAV:   6    -0.169791154268E-01   -0.19336E-03   -0.32285E-03    28   0.468E-01    0.140E-01
DAV:   7    -0.171290537399E-01   -0.14994E-03   -0.11127E-04    14   0.126E-01    0.559E-02
DAV:   8    -0.171509103978E-01   -0.21857E-04   -0.26974E-05    14   0.666E-02
   1 F= -.17150910E-01 E0= -.94377944E-02  d E =-.154262E-01
 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 $\sum_{nk} w_k f_{nk} (\mathbf{H} - \varepsilon_{nk})\psi_{nk}$
`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
- timing information
- information for each electronic step (one line in OSZICAR)

- . . . last part (converged results)

```
----------------------------------------- Iteration    1(    8)  ----------------------------

    POTLOK:  VPU time    0.32: CPU time    0.82
    SETDIJ:  VPU time    0.00: CPU time    0.00
    EDDAV :  VPU time    0.21: CPU time    0.50
    DOS   :  VPU time    0.00: CPU time   -0.09
    ------------------------------------------
      LOOP:  VPU time    0.53: CPU time    1.41

 eigenvalue-minimisations  :    14
 total energy-change (2. order) :-0.2185666E-04  (-0.2697382E-05)
 number of electron    5.9999867 magnetization
 augmentation part     0.5073932 magnetization

 Free energy of the ion-electron system (eV)
  ---------------------------------------------------
  alpha Z        PSCENC =         0.40505152
  Ewald energy   TEWEN  =      -105.05952003
  -1/2 Hartree   DENC   =      -269.12295617
  -V(xc)+E(xc)   XCENC  =        26.10973322
  PAW double counting   =       249.71494682     -251.52585908
  entropy T*S    EENTRO =        -0.01542623
  eigenvalues    EBANDS =       -82.78631698
  atomic energy  EATOM  =       432.26319604
  ---------------------------------------------------
```

```
free energy    TOTEN  =        -0.01715091 eV
energy without entropy =       -0.00172468  energy(sigma->0) =       -0.00943779
```

- E_F eigenvalues and level occupancies (at each $\vec{k}$-point)

```
E-fermi :  -8.8145     XC(G=0):  -1.1783     alpha+bet : -0.2183
  add alpha+bet to get absolut eigen values

k-point   1 :       0.0000    0.0000    0.0000
 band No.  band energies     occupation
     1      -23.7580      2.00000
     2       -8.8176      1.33334
     3       -8.8176      1.33334
     4       -8.8176      1.33332
     5       -0.5864      0.00000
     6        2.4381      0.00000
     7        2.4381      0.00000
```

- information on the stress tensor

```
FORCE on cell =-STRESS in cart. coord.  units (eV/reduce length):
Direction    X        Y        Z        XY       YZ       ZX
--------------------------------------------------------------------------------------
Alpha Z      0.41      0.41      0.41
Ewald      -35.02    -35.02    -35.02      0.00      0.00      0.00
Hartree     89.72     89.72     89.72      0.00      0.00      0.00
E(xc)      -27.94    -27.94    -27.94      0.00      0.00      0.00
Local     -139.44   -139.44   -139.44      0.00      0.00      0.00
n-local    -20.55    -20.55    -20.55      0.00      0.00      0.00
```



```
augment      5.55      5.55      5.55      0.00      0.00      0.00
Kinetic    126.51    126.51    126.51      0.00      0.00      0.00
--------------------------------------------------------------------------------------
Total       -0.77     -0.77     -0.77      0.00      0.00      0.00
in kB       -3.59     -3.59     -3.59      0.00      0.00      0.00
external pressure =       -3.59 kB  Pullay stress =        0.00 kB
```

- final relaxed positions and forces on the atoms

```
POSITION                                       TOTAL-FORCE (eV/Angst)
-----------------------------------------------------------------------------------
     0.00000      0.00000      0.00000         0.000000      0.000000      0.000000
-----------------------------------------------------------------------------------
   total drift:                                0.000000      0.000000      0.000000
-----------------------------------------------------------------------------------
```

- summary of timing for this job:

```
General timing and accounting informations for this job:
========================================================
                 Total CPU time used (sec):       13.920
                           User time (sec):       13.040
                         System time (sec):        0.880
                        Elapsed time (sec):       28.312
                  Maximum memory used (kb):           0.
                  Average memory used (kb):           0.
                         Minor page faults:       117804
                         Major page faults:          888
                Voluntary context switches:            0
```


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 if the default smearing (`SIGMA=0.2`) is used (not shown),

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

  reducing the smearing to `SIGMA=0.01` (this run) reduces it, but may slow down convergence.

```
entropy T*S    EENTRO =        -0.01542623
```

  `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

Spin polarized calculation of an O atom

required files: in `1_free_atom/2_cub_spin2`

- the O atom is an open shell system with **2 unpaired electrons**
- add `ISPIN=2` to the INCAR file (remove WAVECAR) and restart vasp

```
 vasp.4.6.26 15Dec04 complex
 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
 FFT: planning ...           1
 reading WAVECAR
 entering main loop
       N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1     0.369427908623E+02    0.36943E+02   -0.91941E+02    32   0.265E+02
.....
DAV:   9    -0.151509746037E+01   -0.38102E-01   -0.67209E-03    32   0.417E-01    0.875E-02
DAV:  10    -0.152146059451E+01   -0.63631E-02   -0.21071E-03    48   0.244E-01    0.195E-02
DAV:  11    -0.152148983035E+01   -0.29236E-04   -0.45622E-05    32   0.432E-02
   1 F= -.15214898E+01 E0= -.15176333E+01  d E =-.771312E-02  mag=     1.9998
 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 μ_B

```
 spin component 1
 k-point   1 :       0.0000    0.0000    0.0000
  band No.  band energies     occupation
      1     -25.0062      1.00000
      2     -10.0004      1.00000
      3     -10.0004      1.00000
      4     -10.0004      1.00000
      5      -0.5590      0.00000
      6       2.4255      0.00000
      7       2.4255      0.00000
      8       2.6047      0.00000

 spin component 2
 k-point   1 :       0.0000    0.0000    0.0000
  band No.  band energies     occupation
      1     -21.7596      1.00000
      2      -6.9730      0.33333
      3      -6.9730      0.33333
      4      -6.9730      0.33333
      5      -0.4999      0.00000
      6       2.5612      0.00000
      7       2.5613      0.00000
      8       2.5613      0.00000
---------------------------------------------
```


Symmetry broken O atom

required files: in `1_atoms/3_noncub_spin2`

- 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 7.5 and 8.0 in the POSCAR file

```
 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)
```

- rerunning VASP you will find a lower energy

```
 vasp.4.6.26 15Dec04 complex
.....
DAV:  15    -0.163749782903E+01   -0.33870E-03   -0.44909E-05    64   0.382E-02    0.660E-03
DAV:  16    -0.163756138433E+01   -0.63555E-04   -0.83733E-06    32   0.174E-02
   1 F= -.16375614E+01 E0= -.16347404E+01  d E =-.564190E-02  mag=     2.0003
 writing wavefunctions
```


small molecules: O_2

required files: in `2_molecules/O2/1_relax`

POSCAR:

```
O 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
selective     ! relax the bond length only
cartesian     ! positions in cart. coord.
 0 0 0      F F T   ! first atom
 0 0 1.22   F F T  ! second atom
```

INCAR:

```
SYSTEM=O2 molecule
ISMEAR=0
ISPIN = 2          !correct spin ground state
EDIFF=1e-04
ENMAX=400.0

#ionic relaxation
 IBRION=2
 NSW=7
 POTIM =0.1
 EDIFFG=-1e-03
```


Relaxing the O_2 dimer

- geometry relaxation: in this case at most 7 ionic steps (`NSW = 7`)
  for the relaxation a conjugate gradient algorithm is used `IBRION = 2`
  - 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

OSZICAR

```
...
DAV:   1    -0.986091413654E+01   -0.98609E+01   -0.29647E-06    30   0.157E-02    0.542E-04
DAV:   2    -0.986091414525E+01   -0.87175E-08   -0.76886E-08    33   0.274E-03
   7 F= -.98609141E+01 E0= -.98609141E+01  d E =-.480019E-06  mag=     2.0000
```

OUTCAR

```
 POSITION                                       TOTAL-FORCE (eV/Angst)
-----------------------------------------------------------------------------
 0.00000      0.00000     -0.00714          0.000000      0.000000      0.000290
 0.00000      0.00000      1.22714          0.000000      0.000000     -0.000290
```

O_2 molecule vibrations

required files: in 2_molecules/O2/2_vibrations

- start from the relaxed geometry:

  cp ../1_relax/CONTCAR ./POSCAR

  cp ../1_relax/WAVECAR ./.

INCAR

```
SYSTEM= O2 vibration
 PREC = Normal    ! standard precision
 ENMAX = 400
 ISMEAR = 0 ; SIGMA = 0.1
 ISTART=1         !read WAVECAR of the rel. geom.
 IBRION = 5       !calculate vibrat. spectrum
 NFREE = 2        !2 independent deg. of freedom
POTIM=0.02        !keep in the harmonic regime!
 NSW = 1          ! 1 ionic step
EDIFF=1e-05
```

```
\rot{{\tt POSCAR}}
O2 molecule
   1.0
     8.00    0.00    0.00
     0.00    8.00    0.00
     0.00    0.00    8.00
   2
Selective dynamics
Direct
  0.00  0.00 -0.0009   F   F   T
  0.00  0.00  0.1534   F   F   T
```


OUTCAR

```
 Eigenvectors and eigenvalues of the dynamical matrix
 ----------------------------------------------------


   1 f  =   46.840406 THz   294.306949 2PiTHz 1562.427709 cm-1   193.716417 meV
             X         Y         Z           dx          dy          dz
      0.000000  0.000000  7.992925            0           0   -0.176866
      0.000000  0.000000  1.227075            0           0    0.176687

   2 f/i=    0.023681 THz     0.148792 2PiTHz    0.789910 cm-1     0.097936 meV
             X         Y         Z           dx          dy          dz
      0.000000  0.000000  7.992925            0           0   -0.176687
      0.000000  0.000000  1.227075            0           0   -0.176866
```

- the atoms' coordinates which are displaced are given in POSCAR (T/F)
- the vibration modes are given in OUTCAR

Determining the bulk lattice parameter

1. doing it step by step

   required files: in 3_bulk/E_vs_V

   run the script a_bulk.sh

KPOINTS

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

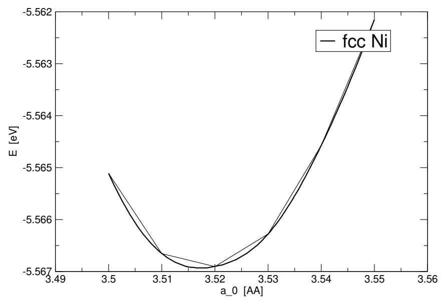
POSCAR (generated in the script)

```
fcc-Ni
   3.530
     0.50    0.50    0.00
     0.00    0.50    0.50
     0.50    0.00    0.50
   1
Direct
  0.00  0.00  0.00
```


INCAR

```
SYSTEM=Ni
PREC=High
EDIFF=1e-05
ISMEAR=1
SIGMA=0.2
ISPIN=2
MAGMOM=1
ENCUT=270.0
```

→ interpolated to a_0=3.517Å.



2. doing it automatically via the stress tensors ISIF=3

INCAR

```
SYSTEM=Ni lattice parameter via ISIF3
ISTART=0
EDIFF=1e-04
ISMEAR=1        !metal: MP method
SIGMA=0.2       !default metal smearing
ISPIN=2         !magnetic
MAGMOM=1        !start guess for the magnetic moment
ENCUT=350.0     !increase cutoff by 30%
IBRION=1        !DIIS
NSW=10          !10 ionic steps
ISIF=3          !cell shape and volume relaxation via stress tensors
EDIFFG=-0.001   !geometry relaxation criterium
```

OUTCAR (last ionic step)

```
  FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)
  ---------------------------------------------------
  free  energy   TOTEN  =        -5.575289 eV
  energy  without entropy=       -5.572884  energy(sigma->0) =       -5.574488

  FORCE on cell =-STRESS in cart. coord.  units (eV/reduce length):
  Direction    X        Y        Z        XY       YZ       ZX
  ---------------------------------------------------------------------------
  Alpha Z     92.47     92.47     92.47
```



```
 Ewald     -312.61   -312.61   -312.61      0.00      0.00      0.00
 Hartree     74.99     74.99     74.99      0.00      0.00      0.00
 E(xc)      -55.05    -55.05    -55.05      0.00      0.00      0.00
 Local      102.84    102.84    102.84      0.00      0.00      0.00
 n-local    -32.53    -33.49    -32.36     -1.64      0.66      1.56
 augment     52.21     52.21     52.21      0.00      0.00      0.00
 Kinetic     77.18     79.95     76.72      1.44     -1.35     -1.17
 -------------------------------------------------------------------------------
 Total       -0.01     -0.01     -0.01      0.00      0.00      0.00
 in kB       -1.17     -1.17     -1.17      0.00      0.00      0.00
 external pressure =       -1.17 kB  Pullay stress =        0.00 kB

VOLUME and BASIS-vectors are now :
-----------------------------------------------------------------------------
 energy-cutoff  :      350.00
 volume of cell :       10.90
     direct lattice vectors                 reciprocal lattice vectors
    1.759962620  1.759962620  0.000000000     0.284096943  0.284096943 -0.284096943
    0.000000000  1.759962620  1.759962620    -0.284096943  0.284096943  0.284096943
    1.759962620  0.000000000  1.759962620     0.284096943 -0.284096943  0.284096943

 length of vectors
    2.488963006  2.488963006  2.488963006     0.492070339  0.492070339  0.492070339
```

$\longrightarrow$ interpolated vale of the lattice parameter: a_0=3.520Å.

clean surfaces: Ni (001) and Ni(111): I equilibrium geometry

- relax the surface layers
  - always use the calculated equilibrium bulk lattice parameter
  - test the thickness of the vacuum layer
  - for polar surfaces set IDIOPL=3

files: in 4_surfaces/Ni_001/1_relax
and 4_surfaces/Ni_111/1_relax

KPOINTS

```
K-Points
 0
Monkhorst Pack
 9 9 1
 0  0  0
```

- for the long axis along the surface normal, 1 $\vec{k}$-point is sufficient

INCAR

```
SYSTEM=clean Ni surface, 1x1
ISTART = 0; ICHARG = 2
ENCUT=270.0
 electronic relaxation
EDIFF=1e-04
ISMEAR=2
SIGMA=0.2
ALGO = V
 spins
ISPIN=2
MAGMOM= 5*1.0
 ionic relaxation
IBRION=1
NSW=20
EDIFFG=-0.01
```

- new start
- for small systems, it is safe to use the RMM-DIIS algorithm for electronic convergence ALGO=V
- the magnetic moment is set for each atom
- converge to maximum remaining force of 0.01 eV/Å

the POSCAR files:

Ni-(001)

```
fcc Ni (100) surface
 3.52
   .50000   .50000   .00000
  -.50000   .50000   .00000
   .00000   .00000  5.00000
  5
Selective Dynamics
Kartesisch
   .00000   .00000   .00000 F F F
   .00000   .50000   .50000 F F F
   .00000   .00000  1.00000 T T T
   .00000   .50000  1.50000 T T T
   .00000   .00000  2.00000 T T T
```

Ni-(111)

```
fcc Ni (111) surface
  3.52
   .70710678  .0000000  .000000
 -0.35355339 0.6123724  .000000
   .000000    .000000  5.1961524
    5
selective dynamics
direct
   .00000   .00000   .00000  F  F  F
   .33333   .66667   .11111  F  F  F
   .66667   .33333   .22222  T  T  T
   .00000   .00000   .33333  T  T  T
   .33333   .66667   .44444  T  T  T
```


001

OSZICAR

```
RMM:   1    -0.261262553262E+02   -0.26126E+02   -0.25276E-03  1934   0.277E-01    0.170E-02
RMM:   2    -0.261262999521E+02   -0.44626E-04   -0.58734E-05  1045   0.714E-02
   6 F= -.26126300E+02 E0= -.26126916E+02  d E =-.611527E-04  mag=     3.1905
```

OUTCAR

```
 E-fermi :   0.0284     XC(G=0):  -7.7144     alpha+bet : -5.9349
   add alpha+bet to get absolut eigen values
 POSITION                                              TOTAL-FORCE (eV/Angst)
 -----------------------------------------------------------------------------------
      0.00000      0.00000      0.00000         0.000000      0.000000      0.330313
      0.00000      1.76000      1.76000         0.000000      0.000000     -0.336351
      0.00000      0.00000      3.53362         0.000000      0.000000     -0.000389
      0.00000      1.76000      5.31219         0.000000      0.000000      0.007966
      0.00000      0.00000      7.00586         0.000000      0.000000     -0.001539
 -------------------------------------------------------------------------------
```


111

OSZICAR

```
RMM:   3    -0.265547166451E+02    0.33578E-03   -0.40253E-05   858   0.604E-02    0.104E-01
RMM:   4    -0.265547159174E+02    0.72763E-06   -0.17306E-05   822   0.354E-02
   6 F= -.26554716E+02 E0= -.26553847E+02  d E =-.474081E-04  mag=     3.0241
```

OUTCAR

```
E-fermi :   0.4759     XC(G=0):  -8.3328     alpha+bet : -6.5943
   add alpha+bet to get absolut eigen values
...........
 POSITION                                              TOTAL-FORCE (eV/Angst)
 -----------------------------------------------------------------------------------
      0.00000      0.00000      0.00000         0.000000      0.000000      0.116955
      0.00000      1.43703      2.03227         0.000000      0.000000     -0.100203
      1.24451      0.71852      4.06757         0.000000      0.000000     -0.004065
      0.00000      0.00000      6.10511         0.000000      0.000000     -0.005409
      0.00000      1.43703      8.11508         0.000000      0.000000     -0.007278
 -------------------------------------------------------------------------------
```


Ni surfaces II: LDOS, surface energy (σ) and workfunction (φ)

files: in 4_surfaces/Ni_001/2_LDOS (and 4_surfaces/Ni_111/2_LDOS)

cp ../1_relax/CONTCAR ./POSCAR; cp ../1_relax/CHGCAR,WAVECAR ./.

INCAR for both surfaces

```
SYSTEM=clean Ni(xxx) surface, 1x1
ISTART = 1
ENCUT=270.0
 electronic relaxation
EDIFF=1e-04
ISMEAR=2
SIGMA=0.2
ALGO = V
 spins
ISPIN=2
MAGMOM= 5*1.0
 LDOS and workfunction
LORBIT=11
#NPAR=1
LVTOT=True
```

- continue from the relaxation run:
- : to calculate the local DOS `RWIGS` has to be defined, either from the POTCAR file (PAW PPs), or in INCAR (`RWIGS`=Wigner_Seitz_radius)
- if you run parallel, set `NPAR=1`

001

OUTCAR

magnetization (x)

# of ion	s	p	d	tot
1	-0.002	-0.019	0.747	0.726
2	-0.007	-0.025	0.645	0.614
3	-0.009	-0.026	0.646	0.612
4	-0.007	-0.025	0.647	0.614
5	-0.003	-0.019	0.735	0.713
tot	-0.028	-0.114	3.420	3.278

111

OUTCAR

magnetization (x)

# of ion	s	p	d	tot
1	-0.004	-0.021	0.652	0.628
2	-0.010	-0.026	0.667	0.630
3	-0.006	-0.023	0.618	0.588
4	-0.010	-0.026	0.666	0.630
5	-0.004	-0.021	0.650	0.625
tot	-0.034	-0.117	3.252	3.101

- the surface energy σ is defined with respect to the Ni atom in the bulk ground state (-5.567 eV, see results of excercise 3)

$$\boxed{\sigma = \frac{1}{2}[E_{tot} - N_{Ni}E_{Ni}]}$$

- the workfunction φ is defined with respect to $E = 0$ in the vacuum (E_{vac}).

$$\boxed{\varphi = E_{vac} - E_F}$$

in repeated slab methods, the vacuum level is only given to a constant energy offset.
$\Rightarrow$ the vacuum has to be large enough ($E_{vac} = const.$ in the center of the vacuum)

- calculation the vacuum level:
  - set `LVTOT=True` in INCAR: $\longrightarrow$ `LOCPOT`
  - compile vtotav.f in 4_surfaces: f77 vtotav.f -o vtotav
  - run `vtotav` $\longrightarrow$ `VLINE`

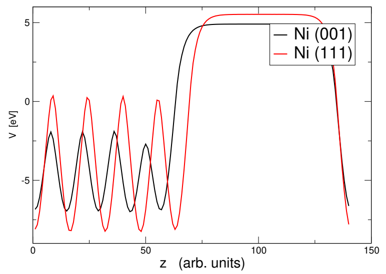
001

- φ=4.88 eV
- σ= 0.85 eV/cell

001

- φ= 5.076 eV
- σ= 0.64 eV/cell

$\Rightarrow$ the (111) surface is more stable for Ni



Adsorption: H on Ni(001)

- H adsorption on the hollow site (h):
  required files: in `5_adsorption/hH-Ni001/1_relax/`
  inputs for alternative (less favored) bridge and top adsorption sites can be found in `5_adsorption/bH-Ni001/` and `5_adsorption/tH-Ni001/`
- subsurface H below the t-site : required files: in `5_adsorption/H-sub_t/`
  inputs for alternative (less stable) subsurface sites (below b) can be found in `5_adsorption/H-sub_b`
- the chosen supercells correspond to a coverage of Θ=1ML,
- for $\Theta < 1$ML,
  - the supercell has to be increased (eg to (2×2)) for Θ=0.25 ML)
  - always check different adsorbate configurations for relative stabilities

hH-adsorption

POSCAR

```
h-H / Ni(001)
   3.52
     0.50 0.50 0.00
    -0.50 0.50 0.00
     0.00 0.00 5.00
 1   5
Selective dynamics
Direct
  0.50  0.50  0.4353  T T T
  0.00  0.00  0.0000  F F F
  0.50  0.50  0.1000  F F F
  0.00  0.00  0.2029  T T T
  0.50  0.50  0.3037  T T T
  0.00  0.00  0.4085  T T T
```

subsurface H

POSCAR

```
H sub t / Ni(001)
   3.52
     0.50 0.50 0.00
    -0.50 0.50 0.00
     0.00 0.00 5.00
 1   5
Selective dynamics
Direct
  0.00  0.00  0.3100  T T T
  0.00  0.00  0.0000  F F F
  0.50  0.50  0.1000  F F F
  0.00  0.00  0.2006  T T T
  0.50  0.50  0.3015  T T T
  0.00  0.00  0.3976  T T T
```


hH/Ni(001)

OSZICAR

```
RMM:   4    -0.300682136562E+02    0.13391E-03   -0.62212E-05  1043   0.615E-02    0.558E-02
RMM:   5    -0.300682137429E+02   -0.86672E-07   -0.15949E-05   998   0.332E-02
  20 F= -.30068214E+02 E0= -.30066392E+02  d E =-.202591E-04  mag=     2.7476
```

OUTCAR

```
POSITION                                       TOTAL-FORCE (eV/Angst)
 -----------------------------------------------------------------------------------
      0.00000      1.76000      7.55771         0.000000      0.000000     -0.000171
      0.00000      0.00000      0.00000         0.000000      0.000000      0.307386
      0.00000      1.76000      1.76000         0.000000      0.000000     -0.297695
      0.00000      0.00000      3.53501         0.000000      0.000000     -0.002309
      0.00000      1.76000      5.28961         0.000000      0.000000     -0.006670
      0.00000      0.00000      7.10989         0.000000      0.000000     -0.000539
 -----------------------------------------------------------------------------------
```


rerun with LORBIT=11 (5_adsorption/hH-Ni001/2_LDOS) ⟶ magnetic moments

OUTCAR

```
 magnetization (x)
# of ion     s       p       d       tot
----------------------------------------
  1       -0.002  -0.001   0.000  -0.002
  2       -0.002  -0.021   0.759   0.736
  3       -0.009  -0.026   0.673   0.638
  4       -0.007  -0.026   0.686   0.653
  5       -0.006  -0.019   0.622   0.597
  6       -0.003  -0.010   0.249   0.236
------------------------------------------------
```


H below t of Ni(001)

OSZICAR

```
   0.207E-01
RMM:   3    -0.293844262307E+02    0.10913E-03   -0.29297E-05  1115   0.456E-02    0.433E-02
RMM:   4    -0.293844256638E+02    0.56697E-06   -0.10673E-06   519   0.486E-03
  40 F= -.29384426E+02 E0= -.29383556E+02  d E =-.715932E-05  mag=     2.5558
```

OUTCAR

```
 POSITION                                       TOTAL-FORCE (eV/Angst)
 -----------------------------------------------------------------------------------
      0.00000      0.00000      5.31742         0.000000      0.000000      0.000365
      0.00000      0.00000      0.00000         0.000000      0.000000      0.326847
      0.00000      1.76000      1.76000         0.000000      0.000000     -0.329500
      0.00000      0.00000      3.51465         0.000000      0.000000      0.002358
      0.00000      1.76000      5.46676         0.000000      0.000000      0.000285
      0.00000      0.00000      7.29204         0.000000      0.000000     -0.000354
 -----------------------------------------------------------------------------------
```

Interpretation of the results:

- adsorption of H quenches the magnetic moments of Ni in the surface layer ($0.713\mu_B \longrightarrow 0.236\mu_B$)
- adsorption energy E_{ads}

$$E_{ads} = E_{H/Ni} - (E_{Ni} + E_{1/2H_2})$$

  with $E_{1/2H_2}$=3.3544 eV,
  $E_{ads}(h)$= -30.0664 - (-26.1269 -3.3544) = -0.5851 eV/atom
  $\Rightarrow$ exothermic reaction
- other adsorption types give E_0 = -29.857799eV (b) and E_0 = -29.300837eV (t)
  $\Rightarrow$: relative adsorption strength: $h > b > t$
- subsurface H is less stable than adsorbed H by 0.683eV/atom.
- barrier for the diffusion of H into the subsurface: Nudged Elastic Band (NEB) method

Diffusion barriers: The Nudged Elastic Band method

required files: in `6_NEB`
NEB runs HAVE to be done parallel, please use the job script `run_NEB` for this excercise

How to do....

1. calculate the equilibrium geometries of the initial and the final state (hH/Ni(001) and H-sub_t in this excercise)
2. choose the number of interpolated steps (`IMAGES`, usually 4)
3. make subdirectories 00 – 0(IMAGES+1): each of these subdirectories contains one `POSCAR` file,
   `POSCAR`(initial state): in 00
   `POSCAR`(final state): in 05
4. concatenate the POSCARS of initial and final state and run the script


```
interpolatePOSCAR

      cat  00/POSCAR > POSCAR_if
      cat  05/POSCAR >> POSCAR_if
      interpolatePOSCAR POSCAR_if
```

   the `POTCAR`s of the intermediate steps are written into subdirectories 01 – 0(IMAGES)

5. `INCAR, KPOINTS, POTCAR` are in the parent directory
6. start the NEB run,....
7. the calculation may be refined in the region around the barrier by taking the results adjacent to the transition state as new initial and final states and re-starting from 1

INCAR

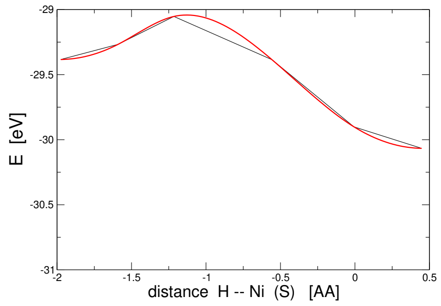
```
SYSTEM= NEB
ENCUT=270.0

SPRING=-5
IMAGES=4
POTIM=0.1

 electronic relaxation
EDIFF=1e-04
ALGO = N
ISMEAR= 1

 spins
ISPIN=2

 ionic relaxation
IBRION=2
NSW=20
EDIFFG=-1e-02
```

NEB Results

from a very first run (14 ionic steps, far from being converged....)

```
00  energy(sigma->0) =      -30.066392
     (converged adsorbate state E of 5_adsorption/hH-Ni001/1_relax)
01  energy(sigma->0) =      -30.042384
02  energy(sigma->0) =      -29.495075
03  energy(sigma->0) =      -29.078264
04  energy(sigma->0) =      -29.283778
05  energy(sigma->0) =      -29.383556
     (converged subsurface state E of  5_adsorption/H-sub_t/)
```


- first estimation of the diffusion barrier height: E_{barr}=0.314 eV/H atom
- (1×1) cell: simultaneous diffusion of 1ML of H through the surface
- PATIENCE required to achieve convergence



Noncollinear Magnetism: E_{MCA} of a Ni (001) ML

required files: in `7_magnetics/Ni_001_x/` and in `7_magnetics/Ni_001_z/`
for all excercises following, the executables
/usr/local/chem/vasp/VASP.4.6/src/vasp.4.6/vasp or
/usr/local/chem/vasp/VASP.4.6/src/vasp.4.6/mpi_vasp are needed

- for certain magnetic systems (thin films, layered structures,...) two spin states can be stabilized, like in-plane ($||$) or out of plane ($\perp$) orientation of the spin moment with respect to a surface.
- the magneto-crystalline anisotropy energy E_{MCA} shows the difference in their stabilities.

$$E_{MCA} = E(m_{\perp}) - E(m_{||})$$

INCAR

```
SYSTEM         = Ni (100) ML mag(x/z)
ISTART         = 0
ENCUT          = 270.00
LNONCOLLINEAR = .TRUE.
MAGMOM    = 1.0 0.0 0.0      (x)
#MAGMOM   = 0.0 0.0 1.0      (z)
LSORBIT        = .TRUE.
ISYM= -1
LMAXMIX        = 4
```

- start with `MAGMOM` set sufficiently high to avoid converging into a low-spin solution
- switch on non-collinear magnetism (`LNONCOLLINEAR`) and `LSORBIT` to allow for non-equivalent solutions of spin quantisation directions
- `LMAXMIX` has to be increased to ensure proper mixing of high-l components of the charge densities
- switch off all symmetries (`ISYM=-1`)

Results:

m_x

OSZICAR

```
DAV:  16    -0.383032411096E+01   -0.20284E-03   -0.12318E-04  3504   0.511E-02    0.106E-02
DAV:  17    -0.383033088832E+01   -0.67774E-05   -0.34754E-05  2824   0.258E-02
   1 F= -.38303309E+01 E0= -.38310174E+01  d E =0.205965E-02  mag=     0.9059     0.0000     0.0001
```

m_z

OSZICAR

```
DAV:  16    -0.382923246223E+01   -0.12216E-03   -0.65859E-05  3240   0.380E-02    0.982E-03
DAV:  17    -0.382925970954E+01   -0.27247E-04   -0.16318E-05  2968   0.180E-02
   1 F= -.38292597E+01 E0= -.38301244E+01  d E =0.259401E-02  mag=     0.0000     0.0000     0.9033
```

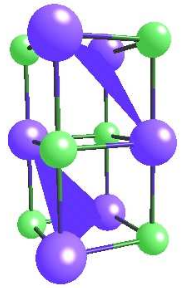
$E_{MCA} = E(m_z) - E(m_x) = 0.9$ meV/Ni atom

$\Rightarrow$ the in-plane axis is the easy axis of fcc-Ni(001) monolayers

NiO

required files: in `8_LDApU/NiO_LSDA`

- Rocksalt structure
- AFM ordering of Ni (111) planes



POSCAR

```
NiO AFM
 4.17
 1.0 0.5 0.5
 0.5 1.0 0.5
 0.5 0.5 1.0
 2 2
Cartesian
 0.0 0.0 0.0
 1.0 1.0 1.0
 0.5 0.5 0.5
 1.5 1.5 1.5
```

KPOINTS

```
k-points
0
Gamma
  4   4   4
  0   0   0
```

POSCAR

- AFM coupling:
  4 atoms in the basis (instead of 2)

KPOINTS

- 4×4×4 Γ-centered
  Monkhorst-Pack grid

INCAR

```
SYSTEM   = NiO

ISPIN    = 2
MAGMOM   = 2.0 -2.0 2*0

ENMAX    = 250
EDIFF    = 1E-3

ISMEAR   = -5

AMIX     = 0.2
BMIX     = 0.00001
AMIX_MAG = 0.8
BMIX_MAG = 0.00001

LORBIT   = 11
```

INCAR

- Initial magnetic moment:
  $\pm 2\,\mu_B$ (Ni), $0\,\mu_B$ (O)
- `AMIX=0.2` and `AMIX_MAG=0.8` (default)
  `BMIX` and `BMIX_MAG` practically zero,
  i.e. linear mixing

The magnetic moment

In OSZICAR (total magnetic moment = **0!**):

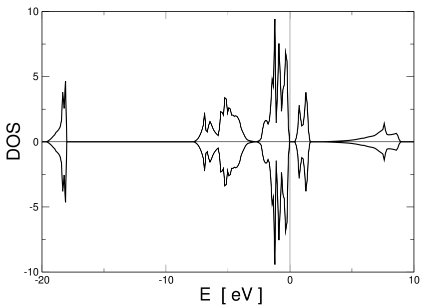
```
       N       E                     dE             d eps       ncg     rms          rms(c)
...
DAV:  10    -0.267638479978E+02    0.79765E-02   -0.28771E-02  1304   0.351E+00    0.233E-01
DAV:  11    -0.267640848017E+02   -0.23680E-03   -0.14141E-03   568   0.684E-01
   1 F= -.26764085E+02 E0= -.26764085E+02  d E =0.000000E+00  mag=     0.0000
```

in OUTCAR (integration of magnetic moment in the PAW sphere):

```
 magnetization (x)

# of ion     s       p       d       tot
----------------------------------------
  1       -0.012  -0.014   1.237   1.211
  2        0.012   0.014  -1.237  -1.211
  3        0.000   0.000   0.000   0.000
  4        0.000   0.000   0.000   0.000
------------------------------------------------
tot        0.000   0.000   0.000   0.000
```


DOS

- $|m_{\mathrm{Ni}}| = 1.21\ \mu_B$ (exp. $1.70\ \mu_B$)
- $E_{\mathrm{gap}} = 0.44$ eV (exp. 4.0 eV)



LSDA+U; Dudarev's approach

required files: in 8_LDApU/NiO_LSDApU

```
...
LDAU      = .TRUE.
LDAUTYPE  = 2
LDAUL     = 2 -1
LDAUU     = 8 00   0.00
LDAUJ     = 0.95   0.00
LDAUPRINT = 2
```

addition to INCAR of NiO calc.

- Switch on L(S)DA+U
- Select Dudarev's approach (LSDA+U Type 2)
- L quantum number for which on site interaction is added (-1 = no on site interaction)
- U parameter
- J parameter
- Print occupation matrices in OUTCAR

L,U, and J must be specified for all atomic types!

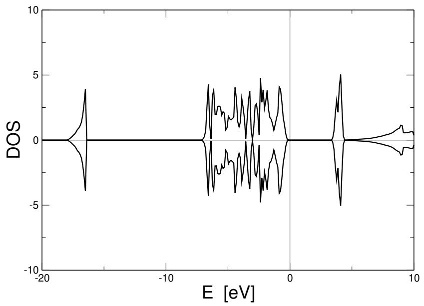
The Ni d-LDOS and local magnetic moment

$$E_{\mathrm{LSDA+U}} = E_{\mathrm{LSDA}} + \frac{(U-J)}{2}\sum_{\sigma}\left[\left(\sum_{m_1} n^{\sigma}_{m_1,m_1}\right) - \left(\sum_{m_1,m_2} \hat{n}^{\sigma}_{m_1,m_2}\hat{n}^{\sigma}_{m_2,m_1}\right)\right]$$

S.L.Dudarev et.al., Phys.Rev.**B 57**, 1505 (1998)

OUTCAR

```
 magnetization (x)
# of ion     s       p       d       tot
----------------------------------------
  1       -0.003  -0.006   1.718   1.709
  2        0.003   0.006  -1.718  -1.709
  3        0.000   0.000   0.000   0.000
  4        0.000   0.000   0.000   0.000
------------------------------------------------
tot        0.000   0.000   0.000   0.000
```



Total Energy

On site occupancy matrix is NOT idempotent →
Total energy contains penalty contribution!

```
...
  0.144E-01
DAV:  12    -0.229082558960E+02   -0.16637E-02   -0.19890E-03   692   0.109E+00    0.485E-02
DAV:  13    -0.229085645284E+02   -0.30863E-03   -0.11911E-03   568   0.366E-01
   1 F= -.22908565E+02 E0= -.22908565E+02  d E =0.000000E+00  mag=     0.0000
```

The total energy for $(U - J) > 0$ is in that case always higher than for $(U - J) = 0$ (just LSDA, see below):

```
...
DAV:  10    -0.267638479978E+02    0.79765E-02   -0.28771E-02  1304   0.351E+00    0.233E-01
DAV:  11    -0.267640848017E+02   -0.23680E-03   -0.14141E-03   568   0.684E-01
   1 F= -.26764085E+02 E0= -.26764085E+02  d E =0.000000E+00  mag=     0.0000
```

Comparing the total energies from calculations with different $(U - J)$ is meaningless

Thank You.....

- Patrick Norman for
  - his kind invitation to this workshop,
  - giving me access to `green.nsc.liu.se` to prepare this excercise session and
  - his valuable hints to re-write the NEB jobscript
- YOU for your attention
- all the people at CMS