Hands on Session III

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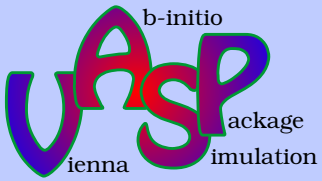
UNIVERSITÄT  WIEN



Overview

- Ni(100)
  - surface relaxation
  - surface energy
  - LDOS
  - surface band-structure
- Ni(111)
  - clean surface
  - CO adsorption
  - adsorption-energy
  - LDOS
  - work-function (change)
  - frequencies

Ni(100) - surface relaxation

```
 fcc (100) surface
 3.53
   .50000    .50000    .00000
  -.50000    .50000    .00000
   .00000    .00000   5.00000
  5
Selective Dynamics
Cartesian
   .00000    .00000    .00000 F F F
   .00000    .50000    .50000 F F F
   .00000    .00000   1.00000 F F F
   .00000    .50000   1.50000 T T T
   .00000    .00000   2.00000 T T T
```

POSCAR

- Ni lattice constant 3.53 Å
- 1 atom per layer $\Rightarrow p(1 \times 1)$ cell
- 5 nickel layers
- first two layers (of one side) relaxed
- $3 \cdot 3.53 = 10.59$Å vacuum

POTCAR

PAW-GGA potential for Ni

```
 general:
   SYSTEM = clean Ni(100) surface
   ISTART = 0 ; ICHARG=2
   ENCUT  =    270
   ISMEAR =    2  ; SIGMA = 0.2
 spin:
   ISPIN=2
   MAGMOM = 5*1
 dynamic:
   IBRION = 1
   NSW    = 100
   POTIM = 0.2

K-Points
 0
Monkhorst-Pack
9 9 1
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
- ionic relaxation

KPOINTS

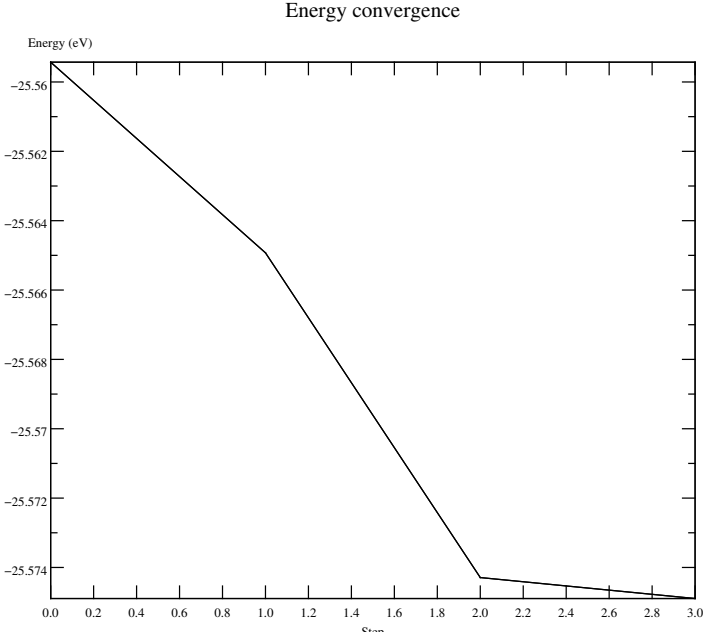
- equally spaced mesh
- odd $\rightarrow$ centered on Γ
- results in 15 k-points in IBZ
- 1 in z-direction !

the relaxation run

forces in the first and last step (in OUTCAR)

```
 POSITION                                       TOTAL-FORCE (eV/Angst)
 -----------------------------------------------------------------------------------
      0.00000      0.00000      0.00000         0.000000      0.000000      0.397218
      0.00000      1.76500      1.76500         0.000000      0.000000     -0.391340
      0.00000      0.00000      3.53000         0.000000      0.000000     -0.001868
      0.00000      1.76500      5.29500         0.000000      0.000000      0.392187
      0.00000      0.00000      7.06000         0.000000      0.000000     -0.396197
 -----------------------------------------------------------------------------------
    total drift:                                 0.000000      0.000000      0.000485
.
 POSITION                                       TOTAL-FORCE (eV/Angst)
 -----------------------------------------------------------------------------------
      0.00000      0.00000      0.00000         0.000000      0.000000      0.403512
      0.00000      1.76500      1.76500         0.000000      0.000000     -0.382356
      0.00000      0.00000      3.53000         0.000000      0.000000      0.111374
      0.00000      1.76500      5.32841         0.000000      0.000000     -0.063214
      0.00000      0.00000      7.02095         0.000000      0.000000     -0.069316
 -----------------------------------------------------------------------------------
    total drift:                                 0.000000      0.000000      0.007076
```

surface energy



- energy changes during relaxation
  from -25.560 to -25.575 eV
  $\Rightarrow$ relaxation energy $E^{\text{rel}} = -15$ meV
- surface energy of (unrelaxed) surface according
  $$\sigma = \frac{1}{2}(E_{\text{surf}} - N_{\text{atoms}} \cdot E_{\text{bulk}})$$
  $\Rightarrow \sigma^{\text{unrel}} = \frac{1}{2}(-25.560 - 5 \cdot (-5.457)) = 0.86$ eV
- $\sigma = \sigma^{\text{unrel}} + E^{\text{rel}} = 0.71$ eV

geometry

from CONTCAR (or OUTCAR) file

```
 Phonons - (100)-direction
   3.53000000000000
     0.5000000000000000    0.5000000000000000    0.0000000000000000
    -0.5000000000000000    0.5000000000000000    0.0000000000000000
     0.0000000000000000    0.0000000000000000    5.0000000000000000
   5
Selective dynamics
Direct
  0.0000000000000000  0.0000000000000000  0.0000000000000000   F   F   F
  0.5000000000000000  0.5000000000000000  0.1000000000000014   F   F   F
  0.0000000000000000  0.0000000000000000  0.2000000000000028   F   F   F
  0.5000000000000000  0.5000000000000000  0.3018929055424291   T   T   T
  0.0000000000000000  0.0000000000000000  0.3977878031170696   T   T   T
```

- inward relaxation of surface layers

  $\Rightarrow \Delta d_{12} = (0.3978 - 0.3019)/0.1 = -4.1\%$

  $\Rightarrow \Delta d_{12} = (0.3019 - 0.2000)/0.1 = +1.9\%$

Ni(100) - local density of states

```
general:
  SYSTEM = clean (100) Ni surface
  ISMEAR =   -5
  ALGO=V

spin:
  ISPIN=2
  MAGMOM = 5*1

  NPAR  = 1
  RWIGS = 1.4
```

INCAR

- tetrahedron method
- Wigner-Seitz radius of 1.4 Å
- NPAR=1 necessary for parallel run

POSCAR

- copy CONTCAR (optimized!) to POSCAR

total charge

# of ion	s	p	d	tot
1	0.522	0.390	8.449	9.361
2	0.551	0.577	8.463	9.591
3	0.551	0.571	8.464	9.586
4	0.559	0.595	8.470	9.624
5	0.535	0.415	8.461	9.411
tot	2.72	2.55	42.31	47.57

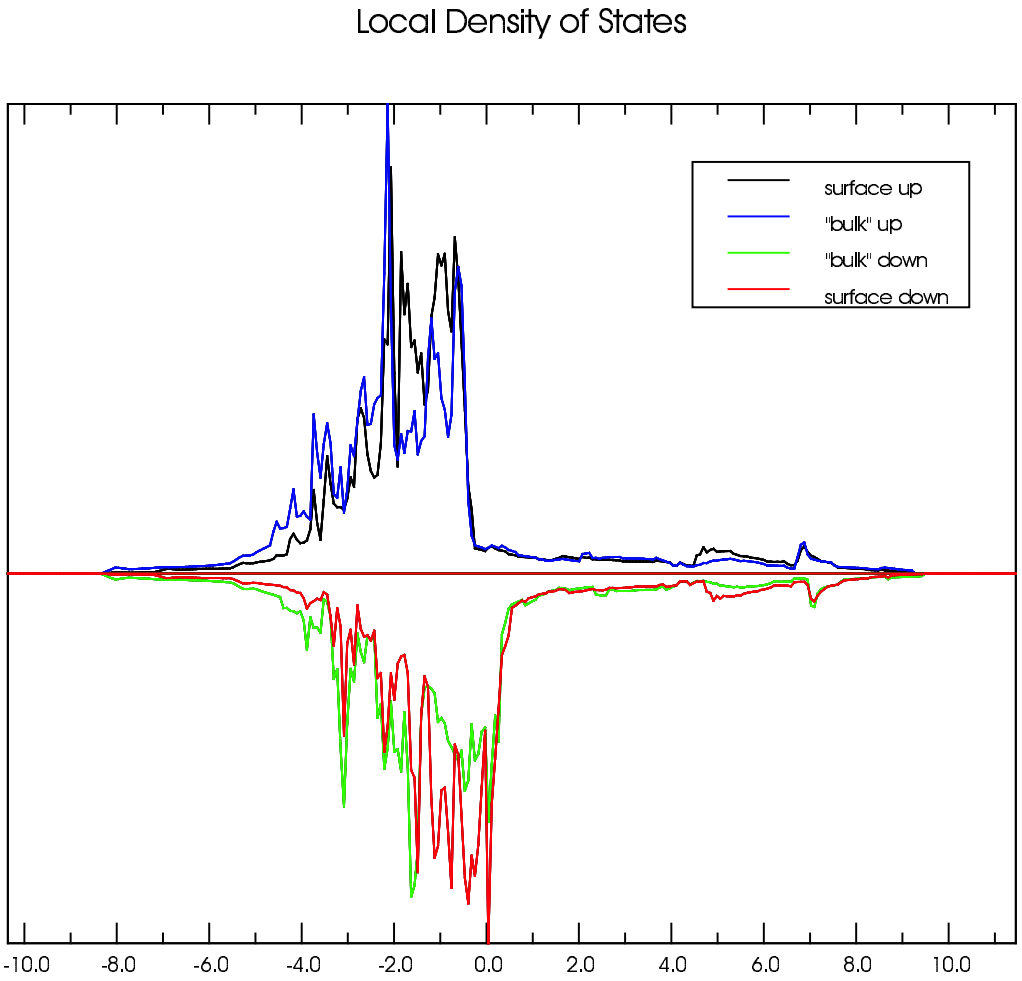
magnetization (x)

# of ion	s	p	d	tot
1	-0.003	-0.023	0.715	0.689
2	-0.008	-0.028	0.618	0.582
3	-0.008	-0.029	0.618	0.582
4	-0.008	-0.028	0.621	0.585
5	-0.004	-0.024	0.705	0.678
tot	-0.03	-0.13	3.28	3.12

partial charge - magnetization

- at the end of the OUTCAR file information on local charge and magnetization is given
- by changing RWIGS the total number of electrons within the spheres could be adapted (nickel pseudo-potential has a valence of 10)
- enhancement of the magnetic moment at the surface
- in the center “bulk like

LDOS



- projection onto surface layer and bulk layer
- each spin component is plotted separately
- band narrowing at surface
- exchange splitting larger at surface

Ni(100) - band structure

```
  ICHARG = 11
general:
  SYSTEM = clean (100) nickel surface
  ENMAX  = 270
  ISMEAR =   2 ; SIGMA = 0.2
  ALGO=V

spin:
  ISPIN=2
  MAGMOM = 5*1

  NPAR=1
  RWIGS = 1.4

for consistency with parallel run:
 NGX =  10 ; NGY =  10 ; NGZ =  72
 NGXF=  18 ; NGYF=  18 ; NGZF= 140
```

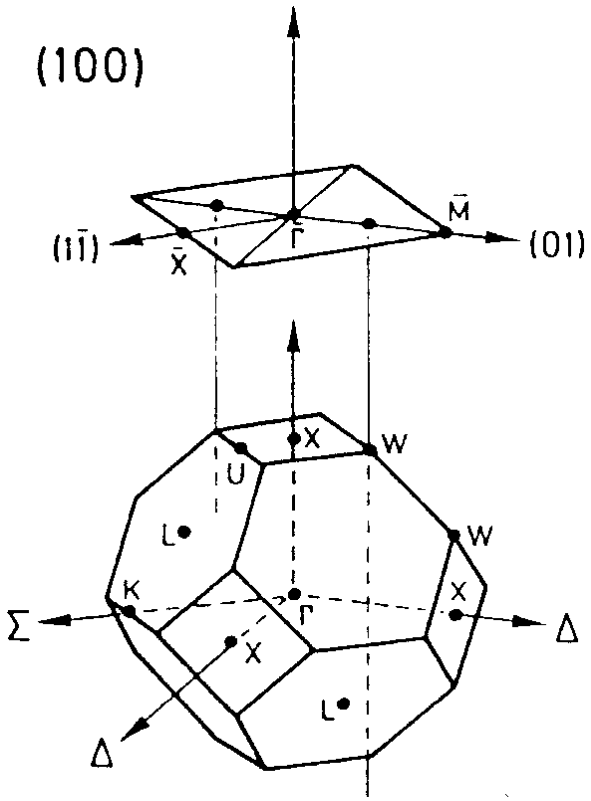
INCAR

- read in charge density (1) and do not update it (+10) $\Rightarrow$ non-selfconsistent run!
- set FFT grid parameters manually to same values, to make sure that CHGCAR file is read properly

```
kpoints for band-structure G-X-M-G
  13
reziprok
    .00000    .00000    .00000    1
    .12500    .00000    .00000    1
    .25000    .00000    .00000    1
    .37500    .00000    .00000    1
    .50000    .00000    .00000    1

    .50000    .12500    .00000    1
    .50000    .25000    .00000    1
    .50000    .37500    .00000    1
    .50000    .50000    .00000    1

    .37500    .37500    .00000    1
    .25000    .25000    .00000    1
    .12500    .12500    .00000    1
    .00000    .00000    .00000    1
```

KPOINTS

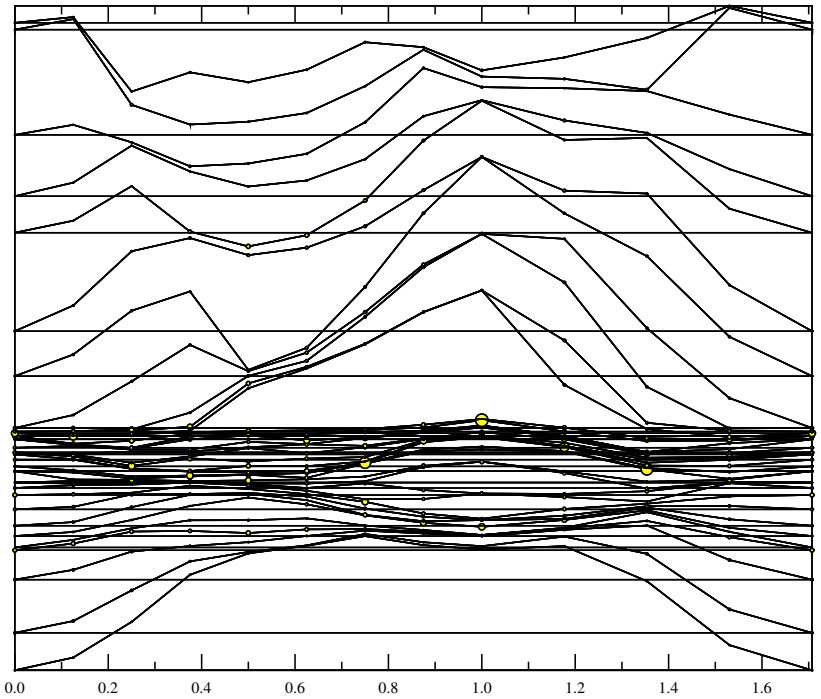
- 13 k-points along line $\bar{\Gamma} - \bar{X} - \bar{M} - \bar{\Gamma}$
- in reciprocal coordinates
- all points with weight 1



surface bandstructure

```
...
Static calculation
charge density remains constant during run
spin polarized calculation
...
```

Bandstructure (projected)



- in OUTCAR status message on actual job
  $\Rightarrow$ non-selfconsistent calculation

- bandstructure consists mainly out of bulk-like bands
- dots mark localization at surface layer

Ni(111) - surface relaxation

```
general:
  ISTART = 0;   ICHARG = 2
  SYSTEM = clean (111) surface
  ENMAX  = 270
  ISMEAR =    2  ; SIGMA = 0.2
  ALGO=V

dynamic:
  NSW=100
  POTIM = 0.2
  IBRION = 1
```

INCAR

- same INCAR file as previously for (100) surface
- spin-polarization neglected

```
 Ni - (111)
  3.53
    .70710678   .0000000   .000000
  -0.35355339 0.6123724   .000000
    .000000     .000000   5.196152
     5
selective dynamics
direct
.00000000 .00000000 .00000000   F   F   F
.33333333 .66666667 .11111111   F   F   F
.66666667 .33333333 .22222222   F   F   F
.00000000 .00000000 .33333333   T   T   T
.33333333 .66666667 .44444444   T   T   T
```

POSCAR

- similar setup as for (100) surface
- again 5 layers, 2 relaxed
- $(1 - .444) \cdot 5.196 \cdot 3.53 =$
  ~ 10.2Å of vacuum

surface energy - geometry

POSITION			TOTAL-FORCE (eV/Angst)		
0.00000	0.00000	0.00000	0.000000	0.000000	0.173189
0.00000	1.44112	2.03805	0.000000	0.000000	-0.059921
1.24804	0.72056	4.07609	0.000000	0.000000	-0.004067
0.00000	0.00000	6.11414	0.000000	0.000000	0.064998
0.00000	1.44112	8.15219	0.000000	0.000000	-0.174199
total drift:			-0.000054	0.000104	-0.004855

- forces already at the beginning rather small
  $\Rightarrow$ small relaxations for compact surfaces
- for surface energy non-spin-polarized bulk nickel as reference !
  $\Rightarrow \sigma^{\text{unrel}} = \frac{1}{2}(-25.729 - 5 \cdot (-5.406)) = 0.65$ eV
  $\Rightarrow$ (111) surface more stable than (100) surface

Ni(111) - CO adsorption

```
 Ni - (111)
  3.53
    .70710678   .0000000   .000000
 -0.35355339 0.6123724    .000000
    .000000     .000000  5.1961524
     5 1 1
selective dynamics direct
.00000000 .00000000 .00000000  F  F  F
.33333333 .66666667 .11111111  F  F  F
.66666667 .33333333 .22222222  F  F  F
.00000000 .00000000 .33333333  T  T  T
.33333333 .66666667 .44444444  T  T  T
.33333333 .66666667 .54029062  T  T  T
.33333333 .66666667 .60298866  T  T  T
```

POSCAR

- two additional types (C+O)
  $\Rightarrow$ POTCAR!
- CO molecule put above surface atom
  $\Rightarrow$*on-top*
- $z_C = (.540 - .444) \cdot 5.196 \cdot 3.53 =$
  ~ 1.76Å
- $d_{CO} = (.603 - .540) \cdot 5.196 \cdot 3.53 =$
  ~ 1.16Å

POTCAR

- append carbon and oxygen potentials

geometry

POSITION			TOTAL-FORCE (eV/Angst)		
0.00000	0.00000	0.00000	0.000000	0.000000	0.170860
0.00000	1.44112	2.03805	0.000000	0.000000	-0.108390
1.24804	0.72056	4.07609	0.000000	0.000000	-0.030356
0.00000	0.00000	6.10874	0.000000	0.000000	-0.082039
0.00000	1.44112	8.15398	0.000000	0.000000	0.007561
0.00000	1.44112	9.90862	0.000000	0.000000	0.020113
0.00000	1.44112	11.06330	0.000000	0.000000	0.022250
total drift:			-0.000184	-0.000227	0.014065

- small outward relaxation of surface due to adsorption
  $\Rightarrow \Delta d_{12} = (8.154 - 6.109)/2.038 = 0.4\%$
- CO geometry
  $\Rightarrow d_{\mathrm{CO}} = 11.063 - 9.909 = 1.155\text{Å}$; $z_C = 9.909 - 8.154 = 1.755\text{Å}$.

Ni(111) - 400 eV

(for adsorption energy)

- potentials for oxygen and carbon require an energy cut-off of 400 eV.
  $\Rightarrow$ previous calculation for clean cannot be used as reference
  $\Rightarrow$ recalculate with same energy cut-off

INCAR

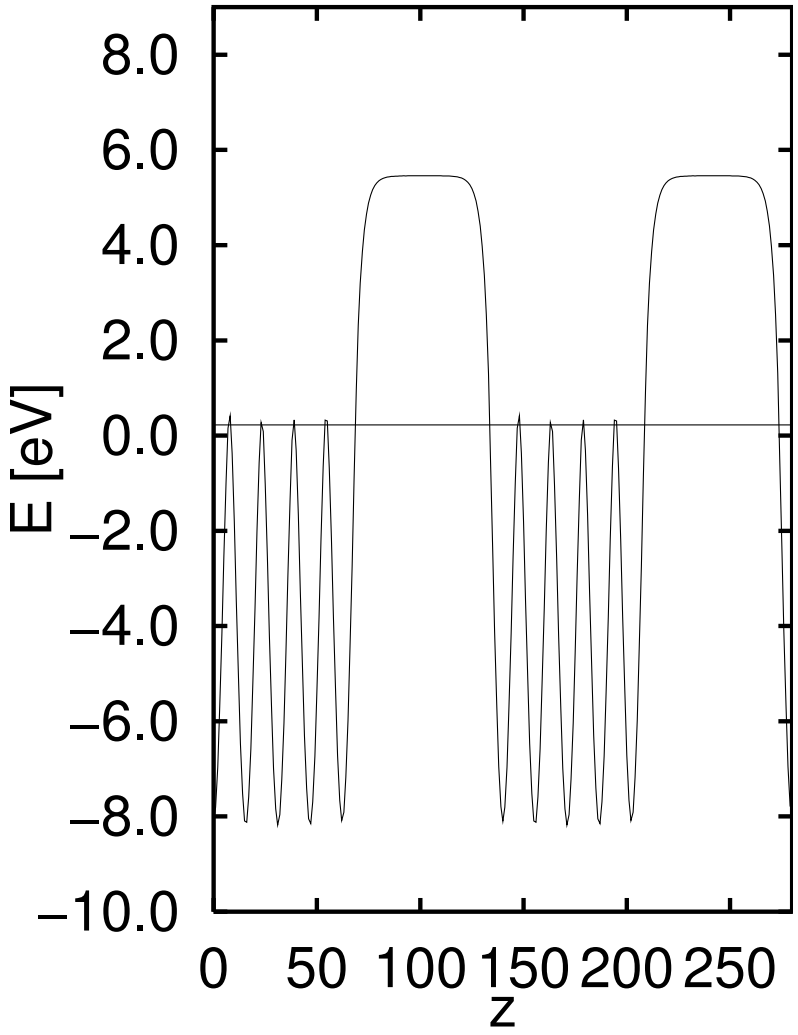
```
ENMAX = 400

general:
  SYSTEM = Ni(100)
  ISTART = 0
  ICHARG = 2
  ISMEAR = 2
  SIGMA = 0.2
  ALGO=V

special:
  LVTOT = .TRUE.
```

- change of cut-off lowers total energy
  $\Rightarrow$ –25.730 eV (270 eV) $\rightarrow$ –25.741 eV at 400 eV
  $\Rightarrow$ becomes more important for larger cells!
- $E_{\text{ads}} = E_{\text{total}} - E_{\text{clean}} - E_{\text{CO}}$

  $\Rightarrow E_{\text{ads}} = -40.830 + 25.741 + 14.833 = -0.256$ eV
- we use this run also to calculate the work-function of Ni(111)

work-function

- usage of simple utility `vtotav` gives planar average of the potential
- vacuum-potential $E^{\text{vac}} = 5.46$ eV
- Fermi-level $\varepsilon_F = 0.225$ eV (from OUTCAR)
- $\Phi = E^{\text{vac}} - \varepsilon_F = 5.24$ eV



LDOS, workfunction

```
general:
  ENMAX = 400
  SYSTEM = CO adsorption on Ni(100)
  ISMEAR = -5
  ALGO=V

LDOS:
  LORBIT = 1 ; NPAR  = 1
  RWIGS = 1.40 1.29  1.11

workfunction:
  IDIPOL=3
  LDIPOL= .TRUE.
  LVTOT = .TRUE.
```

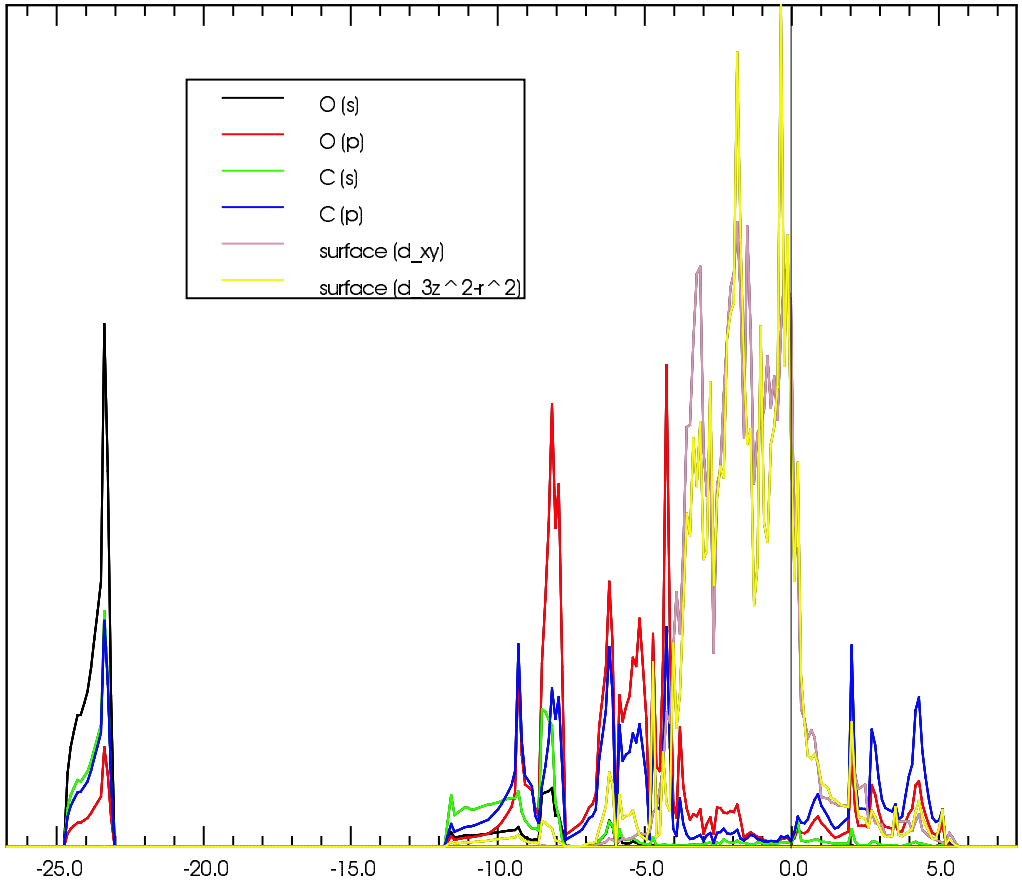
INCAR

- for DOS calculation ISMEAR=-5
- two additional WS-radii
- LVTOT writes local potential into LOCPOT file
- IDIPOL enables dipole correction in direction 3
- active dipole corrections to potential (=dipole layer)

POSCAR

- copy CONTCAR (optimized!) to POSCAR

LDOS

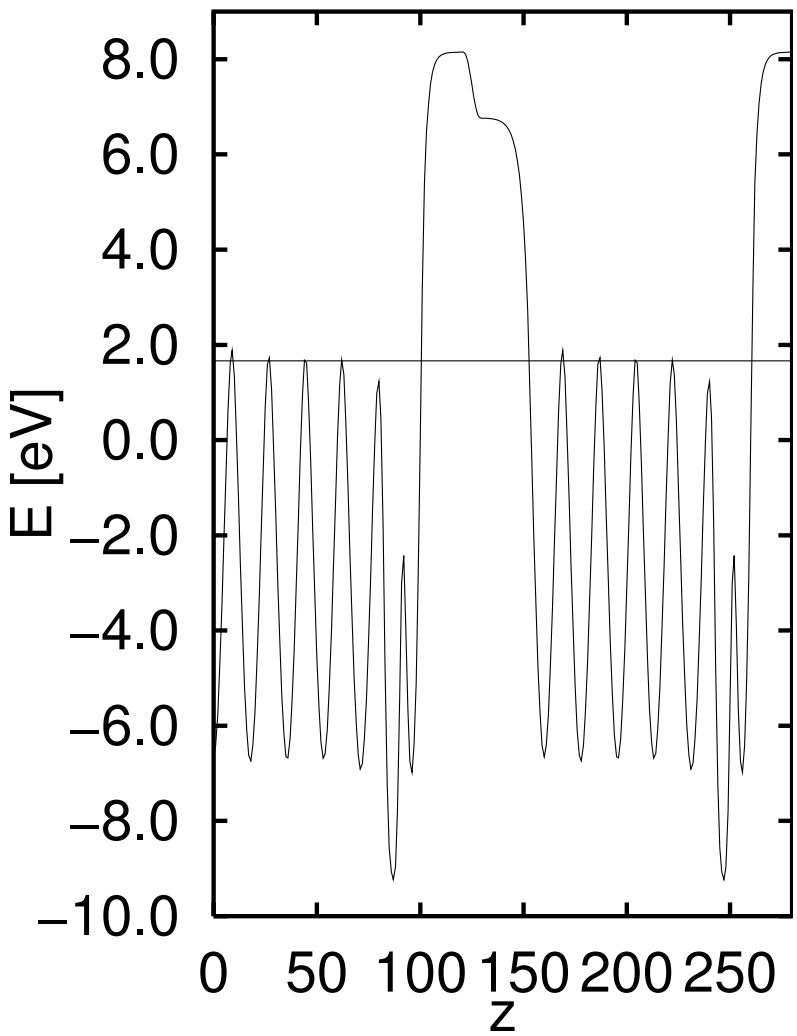


- lm-decomposed DOS helps to analyze the bonding
- CO $5\sigma,1\pi,2\pi^*$
- from comparison with substrate LDOS
  - hybridization with Ni-$d_{3z^2-r^2}$
  - no interaction with d_{xy}

    $\Rightarrow$ from symmetry

workfunction

- $\varepsilon_F = 1.66$ eV (from OUTCAR)
- vacuum-potential at 8.15 / 6.76 eV
  $\Rightarrow \Phi_{CO} = 6.49, \Phi_{clean} = 5.10$ eV
- too small result for clean surface due to too small vacuum ...



frequencies

```
 SYSTEM= CO on Ni111 - frequencies

general:
  ENMAX  = 400
  ISMEAR =    2  ; SIGMA = 0.2
  ALGO   = V
  EDIFF  = 1E-6

dynamic:
  NSW=100
  POTIM = 0.04
  IBRION = 5
  NFREE  = 2
```

INCAR

- the very usual settings ...
- smaller termination criterion EDIFF
- automatic frequency calculation (displacement 0.04 Å)

```
 Ni - (111) + CO ontop
   3.53000000000000
     0.70710678 0.0000000 0.0000000
    -0.35355339 0.6123724 0.0000000
     0.00000000 0.0000000 5.1961524
   5   1   1
Selective dynamics
Direct
  0.0000000 0.0000000 0.0000000  F F F
  0.3333333 0.6666667 0.1111111  F F F
  0.6666666 0.3333333 0.2222222  F F F
  0.0000000 0.0000000 0.3314564  F F F
  0.3333333 0.6666667 0.4453762  F F F
  0.6666666 0.3333333 0.5177755  F F T
  0.6666666 0.3333333 0.5815997  F F T
```

POSCAR

- take CONTCAR from relaxed calculation
- frequencies only for CO molecule and z-direction
  (z- and (x,y) are independent!)

frequencies

Additional output in OUTCAR file for frequency calculation via finite difference:

```
Finite differences progress:
 Degree of freedom:   1/  2
 Displacement:        1/  2
 Total:               1/  4
```

- After the first calculation for the equilibrium geometry, NFREE displacements ($\pm$ POTIM) are performed for each degree of freedom; from these displacements the dynamical matrix is set up and diagonalized
- at the end of the OUTCAR file the
  - forces,
  - the dynamical matrix and finally
  - the eigenfrequencies and
  - eigenvectors (first normalized and then mass-weighted)

  are listed

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

  1 f  =   64.112970 THz   402.833672 2PiTHz 2138.578420 cm-1   265.150026 meV
            X         Y         Z           dx          dy          dz
     0.000000  0.000000  0.000000            0           0           0
     0.000000  1.441116  2.038046            0           0           0
     1.248043  0.720558  4.076093            0           0           0
     0.000000  0.000000  6.108743            0           0           0
     0.000000  1.441116  8.153979            0           0           0
     0.000000  1.441116  9.908620            0           0   -0.225414
     0.000000  1.441116 11.063296            0           0    0.156066

  2 f  =   12.362230 THz    77.674183 2PiTHz  412.359599 cm-1    51.126093 meV
            X         Y         Z           dx          dy          dz
     0.000000  0.000000  0.000000            0           0           0
     0.000000  1.441116  2.038046            0           0           0
     1.248043  0.720558  4.076093            0           0           0
     0.000000  0.000000  6.108743            0           0           0
     0.000000  1.441116  8.153979            0           0           0
     0.000000  1.441116  9.908620            0           0   -0.180127
     0.000000  1.441116 11.063296            0           0   -0.195303
```

CO stretch

CO-metal