VASP Tutorial:
A bit of surface science

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Setting up a VASP calculation

VASP requires 4 input files to run a calculation:

- INCAR
- POSCAR
- KPOINTS
- POTCAR

I: The INCAR file

The INCAR file contains the input parameters that steer the calculation:

- The default values set by VASP itself are a clever choice for most standard calculations

- These standard settings may be modified to specify:

  - What kind of calculation you want to do:
    SCF calculation, DOS, dielectric properties, …

  - Basic inputs concering the required precision, the requested level of convergence, ...

For a list of all INCAR-tags have a look at:

- The VASP manual: http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html
  Index: http://cms.mpi.univie.ac.at/vasp/vasp/Index.html
- The VASP wiki: http://cms.mpi.univie.ac.at/wiki/index.php/Main_page
  INCAR-tags: http://cms.mpi.univie.ac.at/wiki/index.php/Category:INCAR

II: The POSCAR file

In the POSCAR file you specify the structure (Bravais lattice and basis):

fcc: Ni	Header (comment)
3.53	Overall scaling constant
0.5 0.5 0.0 0.0 0.5 0.5 0.5 0.0 0.5	Bravais matrix
Ni	Name(s) of atomic type(s)
1	Number of atoms (of each type)
Selective Dynamics	(optional: selective dynamics)
Cartesian	Cartesian or Direct coordinates
0 0 0 (T T T)	positions of the atoms

III: The KPOINTS file

In the KPOINTS file you specify the points VASP will use to sample the first Brillouin zone in reciprocal space

Automatic mesh	Header (comment)
0	N_k=0: automatic mesh generation
G (M)	**Γ**-centered (G) mesh or Monkhorst-Pack (M) grid
4 4 4	# of subdivisions N_i along $\vec{b}_i$
0. 0. 0.	Optionally shift the mesh (s_i)

IV: The POTCAR file

The POTCAR file has to contain the PAW datasets for all atomic types you have specified in your POSCAR file:

VASP comes with a library of PAW datasets, (one or more) for most elements of the periodic table:

- Each individual PAW data set starts with a descriptive section, specifying amongst other things:
  - Parameters that were required to generate the dataset:
  - Number of valence electrons
  - Atomic mass
  - Default energy cutoffs

- When your unit cell contains more than one type of atom you have to concatenate the corresponding PAW datasets in the same order as you have specified the different atomic types in your POSCAR file.

- You should not mix PAW datasets generated with different exchange-correlation functionals.

OUTPUT files

OUTCAR

- detailed output of a VASP run, including:
  - a summary of the input parameters
  - information about the individual electronic steps: total energy, Kohn-Sham eigenvalues, Fermi-energy.
  - stress tensors
  - forces in the atoms
  - local charges, magnetic moments
  - dielectric properties
  - ... and a great many things more ...
- The amount of output written onto OUTCAR can be chosen by means of the NWRITE-tag in the INCAR file.

OSZICAR & stdout

- give a short summary of the self-consistency-cycle
  - chosen SCF algorithm
  - convergence of energy and charge density
  - free energies, total magnetic moment of the cell

OUTPUT files

CONTCAR & XDATCAR

- CONTCAR: updated geometry data *at the end of a run*
  - lattice parameter
  - Bravais matrix
  - ionic positions
  - velocities
- the format of the CONTCAR is the same as for POSCAR:
  It can be directly be used for a continuation run (copy CONTCAR to POSCAR)
- XDATCAR: updated ionic positions of each ionic step

DOSCAR, CHGCAR & WAVECAR

- DOSCAR: total DOS and integrated DOS, (local partial DOS)
- CHGCAR: the charge density
- WAVECAR: plane wave coefficients of the orbitals.
  Can be used to restart from a previous run

Documentation

- The VASP manual (http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html)
  Index: http://cms.mpi.univie.ac.at/vasp/vasp/Index.html

- The VASP wiki (http://cms.mpi.univie.ac.at/wiki/index.php/Main_page)
  INCAR-tags: http://cms.mpi.univie.ac.at/wiki/index.php/Category:INCAR

A bit of surface science

Examples:

Ni(100):

- surface relaxation
- surface energy
- LDOS
- surface bandstructure

Ni(111)

- clean surface
- CO adsorption
- LDOS
- workfunction (change)
- frequencies

STM of graphite and graphene

Ni(100) surface relaxation (ex.: Ni100clean_rel)

POSCAR:

fcc (100) surface	Header (comment)
3.53	Ni lattice constant
.50000 .50000 .00000 -.50000 .50000 .00000 .00000 .00000 5.00000	lattice vector a(1) lattice vector a(2) lattice vector a(3)
5	Number of atoms
Selective Dynamics	Switch on "selective dynamics"
Cartesian	Positions in cartesian coordinates
.00000 .00000 .000000 F F F .00000 .50000 .500000 F F F .00000 .00000 1.00000 F F F .00000 .50000 1.50000 T T T .00000 .00000 2.00000 T T T	positions of the atoms, and the specfications whether or not they are allowed to move during the relaxation.

- A $p(1 \times 1)$ surface cell: 1 Ni atom per layer
- 5 Ni layers
- first two layers (on one side) are relaxed
- $3 \times 3.53 = 10.59$ Å vacuum

POTCAR:
Ni GGA PAW potential

Ni(100) surface relaxation (ex.: Ni100clean_rel)

INCAR:

SYTEM = clean Ni(100) surface	Name of the calculation
ISTART = 0 ICHARG = 2	initial wave functions: random numbers initial charge density: overlapping atoms
ENCUT = 270	cutoff energy 270 eV (from POTCAR)
ALGO = Fast EDIFF = 1E-6	use RMM-DIIS for electronic optimization electronic convergence: energy change < 10^{-6} eV
ISMEAR = 2 SIGMA = 0.2	2nd order Methfessel-Paxton smearing (metal!) smearing width $\sigma = 0.2$ eV
ISPIN = 2 MAGMOM = 5*1	spin-polarized calculation initial magnetic moment on each Ni = 1 μ_B
IBRION = 1 NSW = 100 POTIM = 0.8	ionic relaxation

KPOINTS:

K-Points	Header (comment)
0	N_k=0: automatic mesh generation
Monkhorst-Pack	Monkhorst-Pack grid
9 9 1	# of subdivisions N_i along $\vec{b}_i$ (odd: centered on **Γ**)
0. 0. 0.	Optionally shift the mesh (s_i)

- 15 **k**-points in the IBZ
- 1 **k**-point along the *z*-direction!

Ni(100) surface relaxation (ex.: Ni100clean_rel)

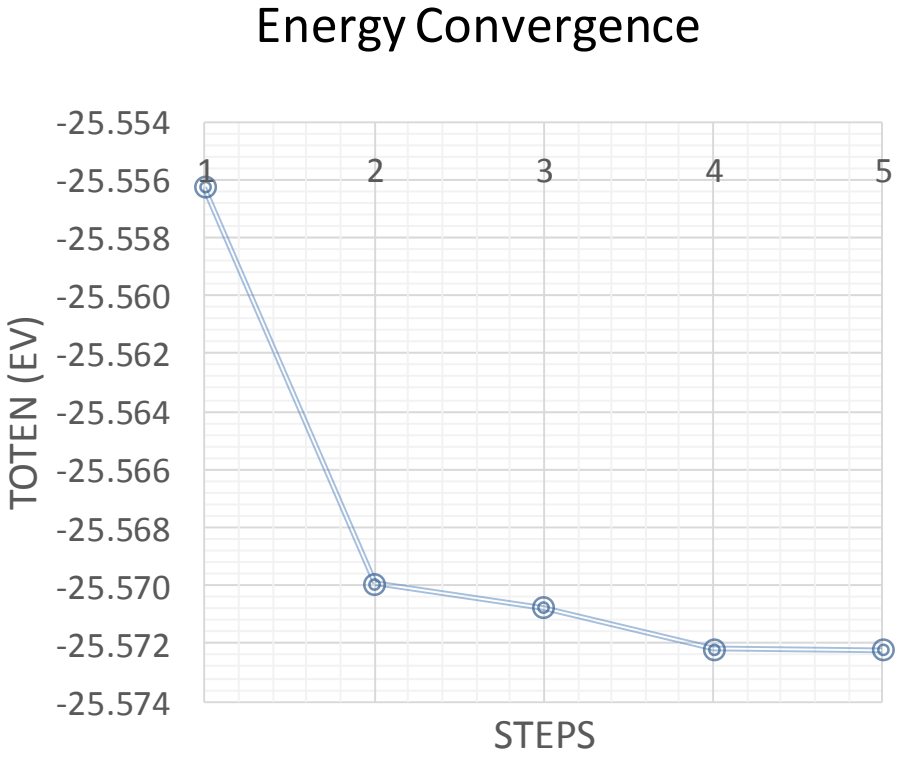
Forces in the first and last step of the relaxation (in OUTCAR)

```
POSITION                                       TOTAL-FORCE (eV/Angst)
-----------------------------------------------------------------------------------
     0.00000      0.00000      0.00000         0.000000      0.000000      0.391783
     0.00000      1.76500      1.76500         0.000000      0.000000     -0.397182
     0.00000      0.00000      3.53000         0.000000      0.000000      0.005392
     0.00000      1.76500      5.29500        -0.000000     -0.000000      0.390888
     0.00000      0.00000      7.06000         0.000000      0.000000     -0.390881
-----------------------------------------------------------------------------------
   total drift:                                 0.000000     -0.000000      0.016601


POSITION                                       TOTAL-FORCE (eV/Angst)
-----------------------------------------------------------------------------------
     0.00000      0.00000      0.00000        -0.000000      0.000000      0.396242
     0.00000      1.76500      1.76500         0.000000      0.000000     -0.394948
     0.00000      0.00000      3.53000         0.000000     -0.000000      0.000021
     0.00000      1.76500      5.30249         0.000000      0.000000     -0.000262
     0.00000      0.00000      6.98837        -0.000000     -0.000000     -0.001054
-----------------------------------------------------------------------------------
   total drift:                                 0.000000     -0.000000      0.000212
```

Ni(100) surface relaxation (ex.: Ni100clean_rel)

- Energy changes during relaxation from -25.556 eV to -25.572 eV

  $\Longrightarrow E^{\mathrm{rel}} = -16\ \mathrm{meV}$



- Surface energy:

$$\sigma = \tfrac{1}{2}\left(E_{\mathrm{surf}} - N_{\mathrm{atoms}} \times E_{\mathrm{bulk}}\right)$$

- Surface energy of unrelaxed surface:

$$\Longrightarrow \sigma^{\mathrm{unrel}} = \tfrac{1}{2}\left(-25.556 - 5 \times (-5.458)\right) = 0.867\ \mathrm{eV}$$

- $\sigma = \sigma^{\mathrm{unrel}} + E^{\mathrm{rel}} = 0.867 - 0.016 = 0.851\ \mathrm{eV}$

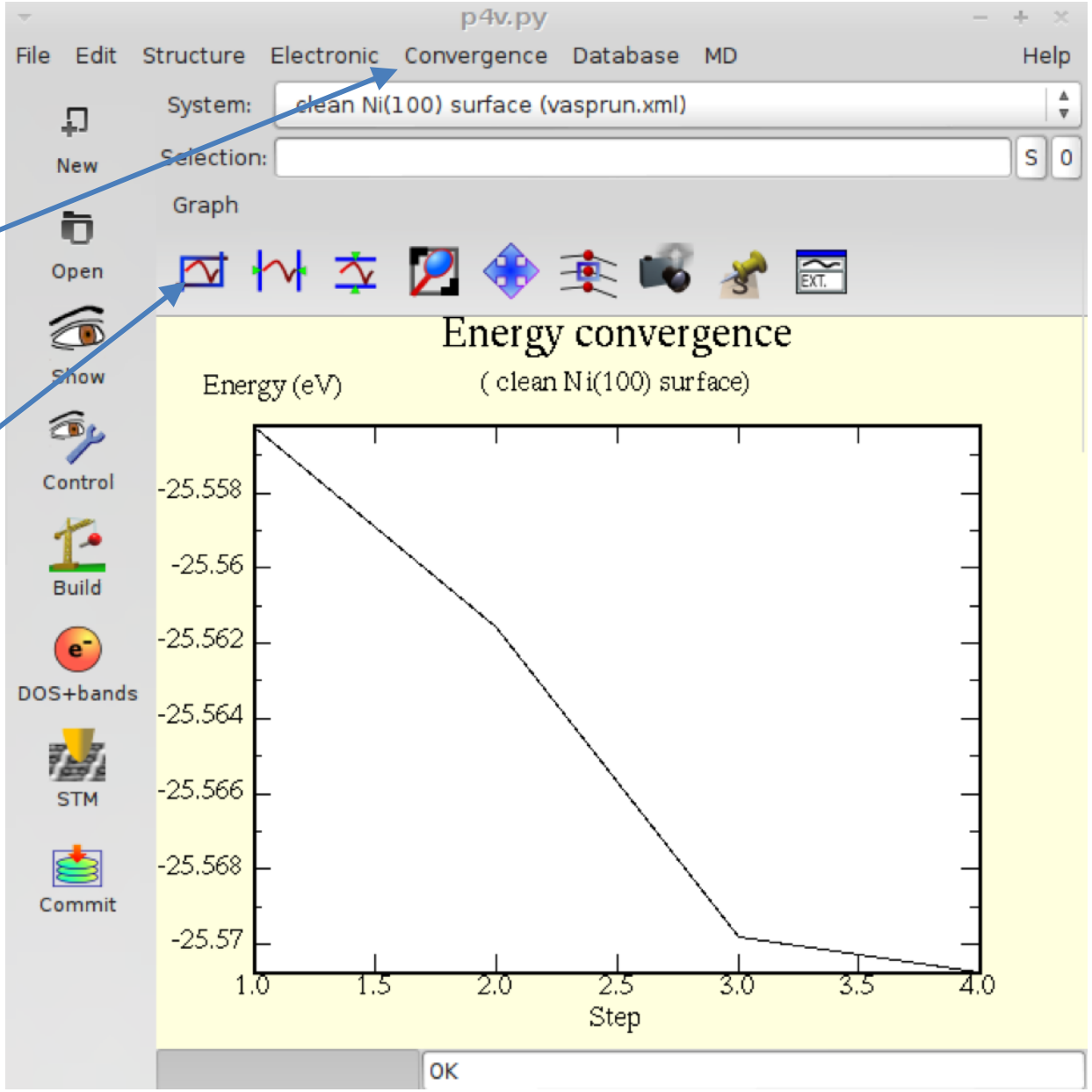
N.B.: you will find the setup for the calculation of the "bulk" energy in the `Ni100clean_rel/bulk` subdirectory.

Ni(100) surface relaxation (ex.: Ni100clean_rel)

Start p4vasp:
> p4v [vasprun.xml]

Step. 1) Go to:
Convergence/Energy

Step. 2) “update” graph



Ni(100) surface relaxation (ex.: Ni100clean_rel)

Final geometry from CONTCAR (or OUTCAR) file:

```
fcc (100) surface
   3.53000000000000
     0.5000000000000000    0.5000000000000000    0.0000000000000000
    -0.5000000000000000    0.5000000000000000    0.0000000000000000
     0.0000000000000000    0.0000000000000000    5.0000000000000000
   Ni
     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  0.3004245271852446   T   T   T
  0.0000000000000000 -0.0000000000000000  0.3959414474619545   T   T   T

  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00
```

- Inward/outward relaxation of the surface layers:

$$\Delta d_{54} = \big((0.3959 - 0.3004) - 0.1\big)/0.1 \times 100 = -4.5\%$$

$$\Delta d_{43} = \big((0.3004 - 0.2000) - 0.1\big)/0.1 \times 100 = +0.4\%$$

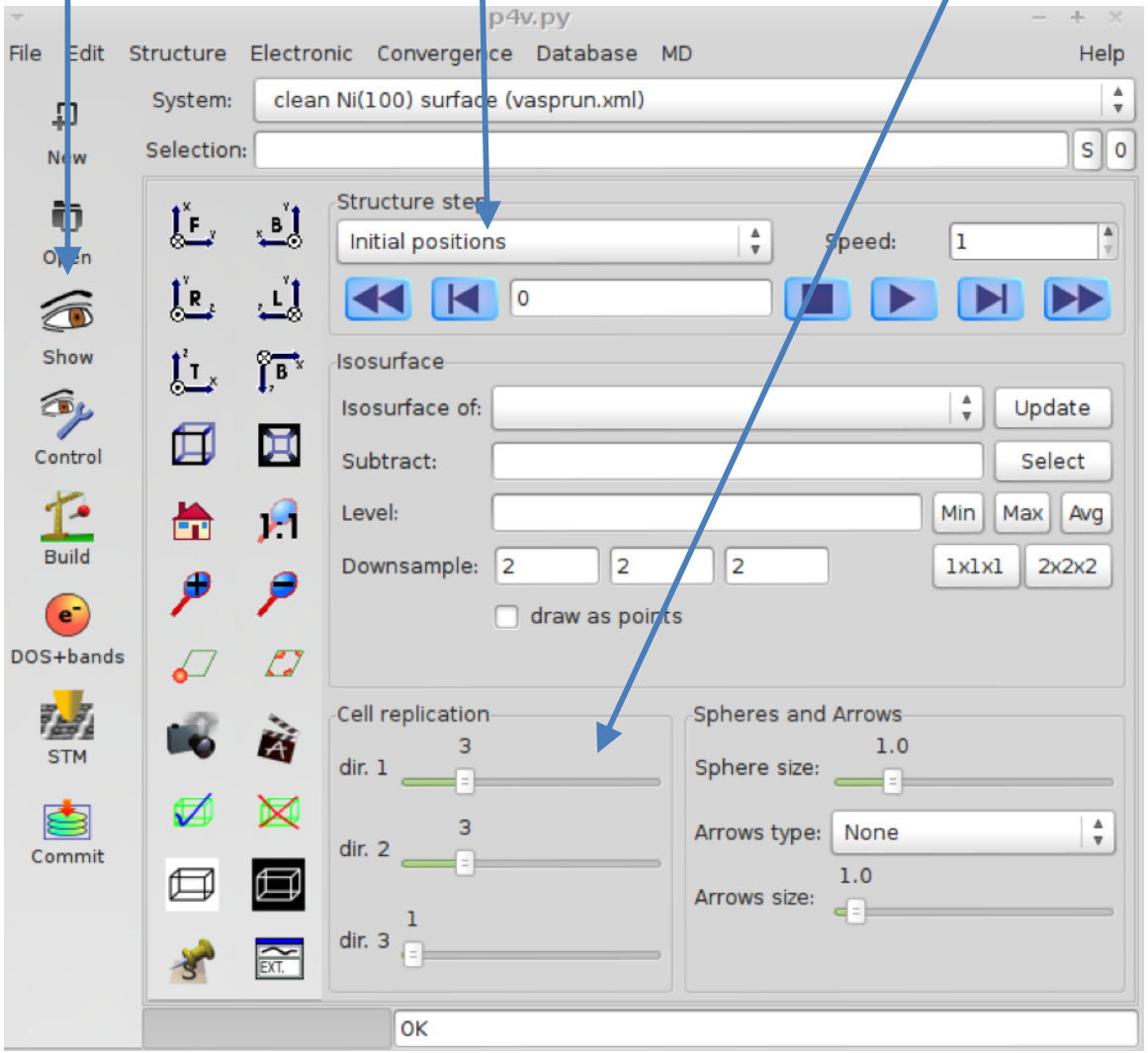
Ni(100) surface relaxation (ex.: Ni100clean_rel)

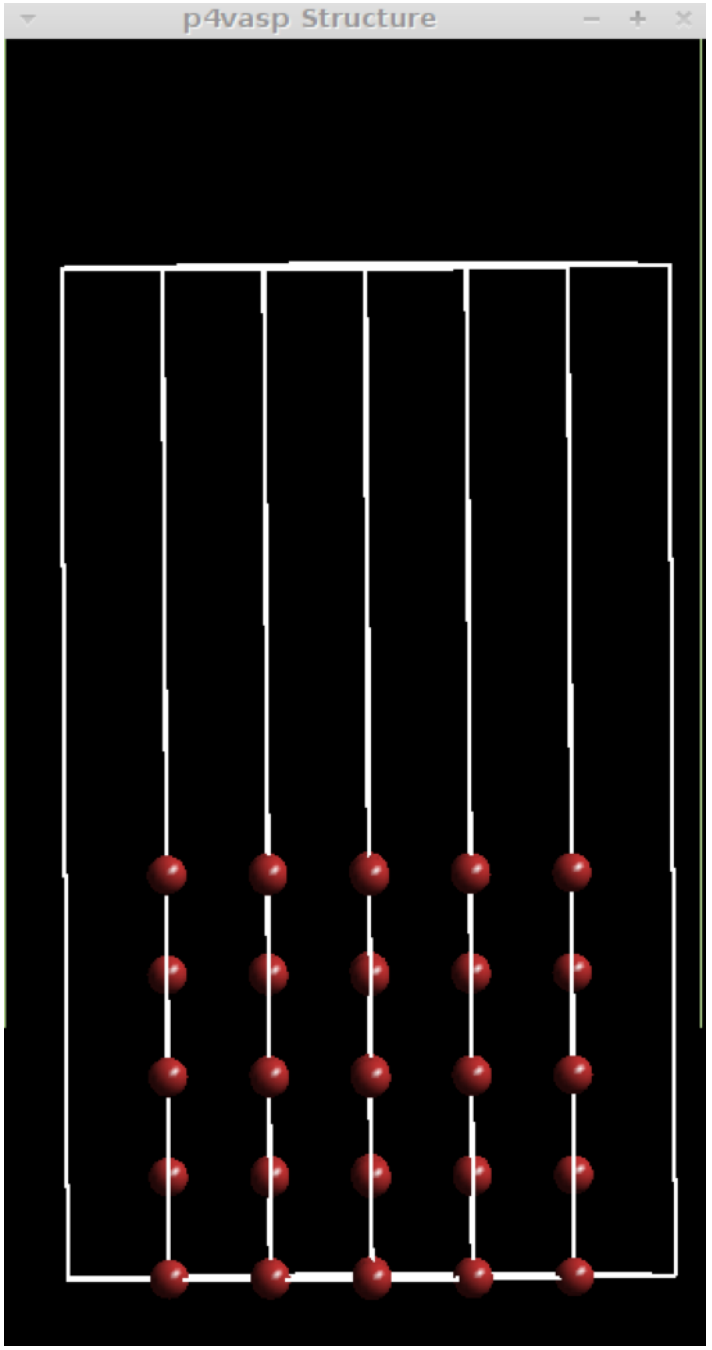
Start p4vasp:> p4v [vasprun.xml]

Step 1.) Show structure

Step 2.) Select “initial” or “final” positions

Possibly “replicate” cells





Ni(100) LDOS (ex.: Ni100clean_LDOS)

INCAR:

`SYTEM = clean Ni(100) surface`	`Name of the calculation`
`ENCUT = 270`	`cutoff energy 270 eV (from POTCAR)`
`ALGO = Normal`	`use block-Davidson for electronic minimization`
`ISMEAR = -5`	`Tetrahedron method with Blöchl corrections`
`ISPIN = 2` `MAGMOM = 5*1`	`spin-polarized calculation` `initial magnetic moment on each Ni = 1` μ_B
`LORBIT = 11`	`LM-decomposed site resolved density of states`

N.B.: we want to use the optimized structure from Ni100clean_rel:

Normally this would mean copying `Ni100clean_rel/CONTCAR` to POSCAR in the directory where you want to run Ni100clean_LDOS.

In this case, however, that has already been taken care of, and the POSCAR file in Ni100clean_LDOS is the correct one.

Ni(100) LDOS (ex.: Ni100clean_LDOS)

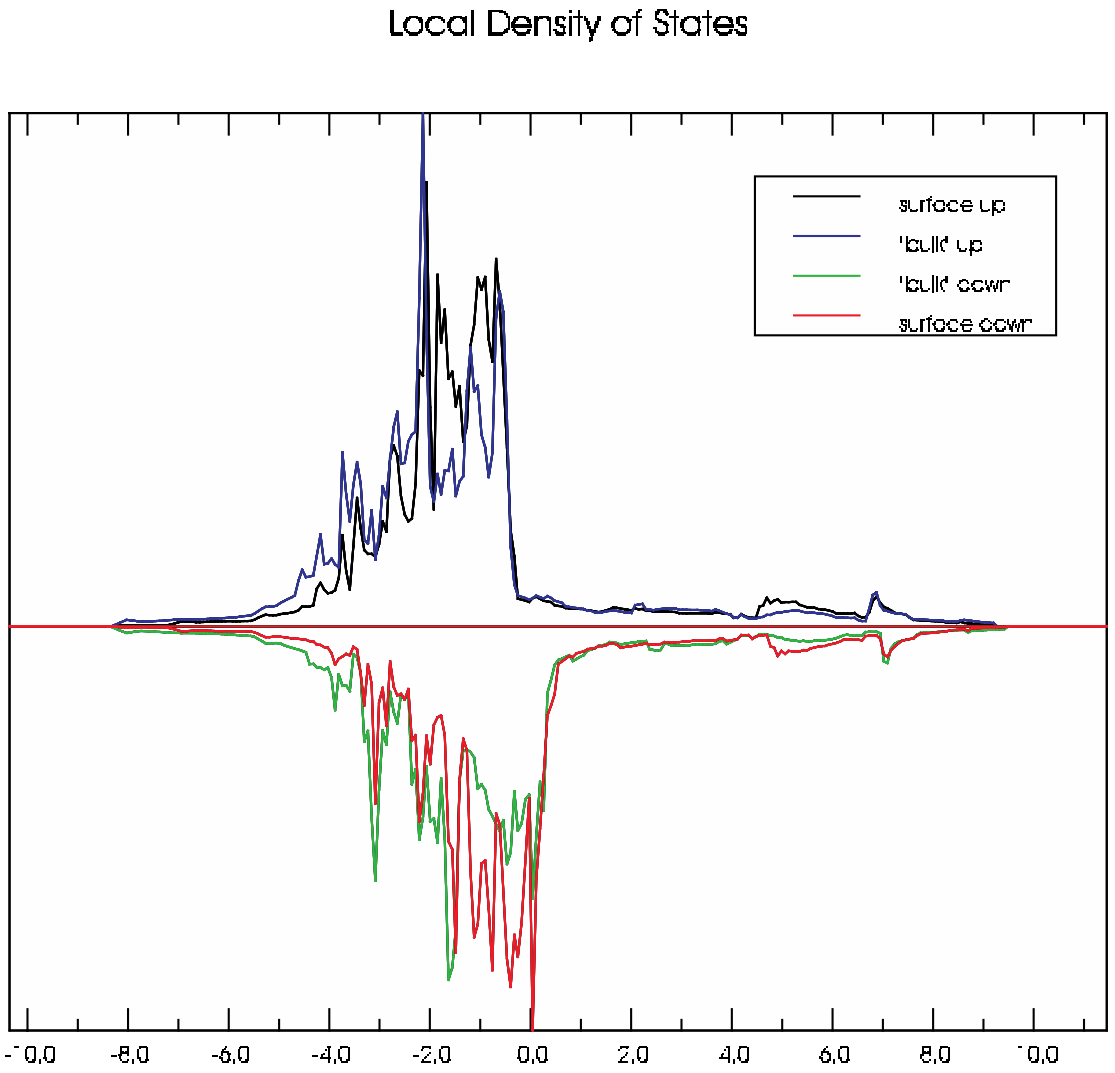
```
 total charge
# of ion       s       p       d       tot
--------------------------------------------
    1        0.466   0.326   8.314   9.106
    2        0.490   0.481   8.333   9.304
    3        0.494   0.482   8.338   9.313
    4        0.500   0.501   8.350   9.351
    5        0.478   0.346   8.345   9.169
--------------------------------------------
tot          2.427   2.135  41.681  46.244
```

```
 magnetization (x)
# of ion       s       p       d       tot
--------------------------------------------
    1       -0.003  -0.019   0.725   0.703
    2       -0.008  -0.024   0.613   0.582
    3       -0.008  -0.024   0.611   0.579
    4       -0.008  -0.024   0.605   0.573
    5       -0.004  -0.020   0.703   0.680
--------------------------------------------
tot         -0.030  -0.111   3.257   3.116
```

- At the end of the OUTCAR file information on local charge and magnetization is given.
- Instead of `LORBIT=11`, one might use `LORBIT=1` and set `RWIGS` appropriately.
- As is clearly shown, the local magnetic moments at the surface are enhanced.
- The central layers behave “bulk”-like.

Ni(100) LDOS (ex.: Ni100clean_LDOS)

- Projection onto surface and bulk layers.
- Each spin component is plotted separately.
- Band narrowing at the surface.
- Exchange splitting is larger at the surface.

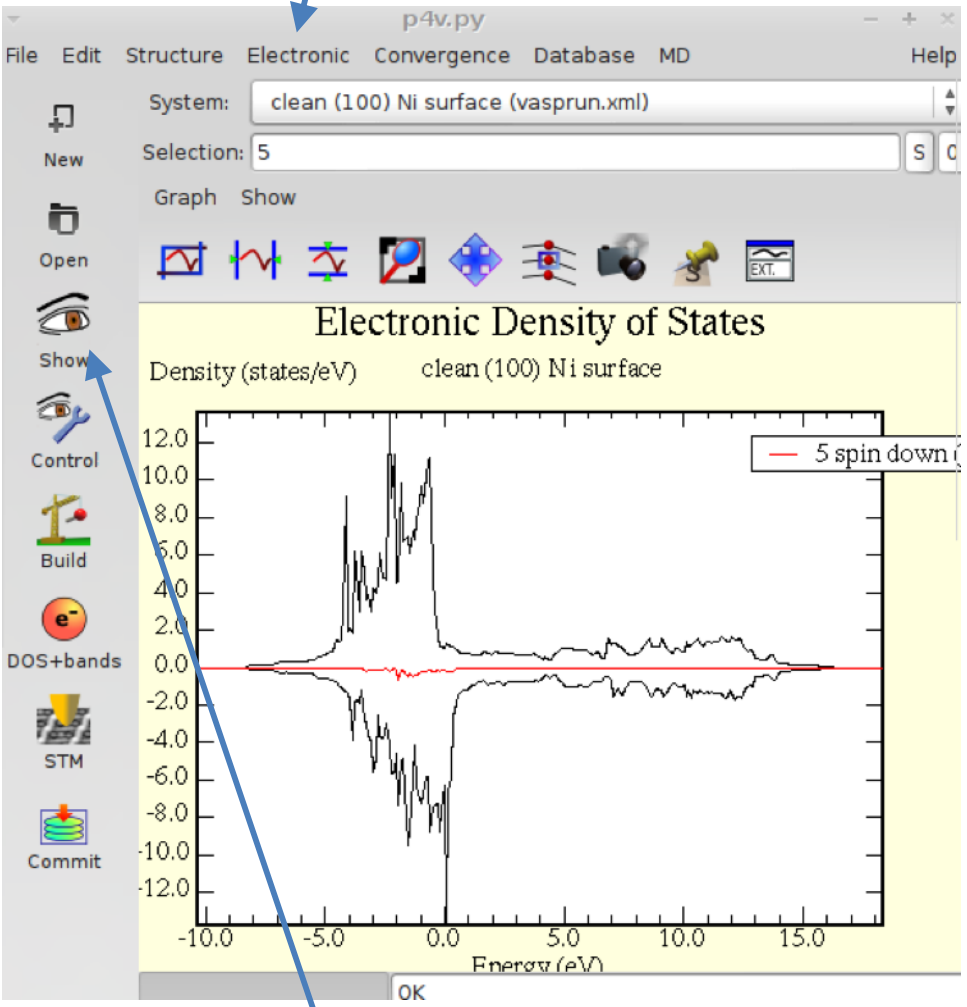


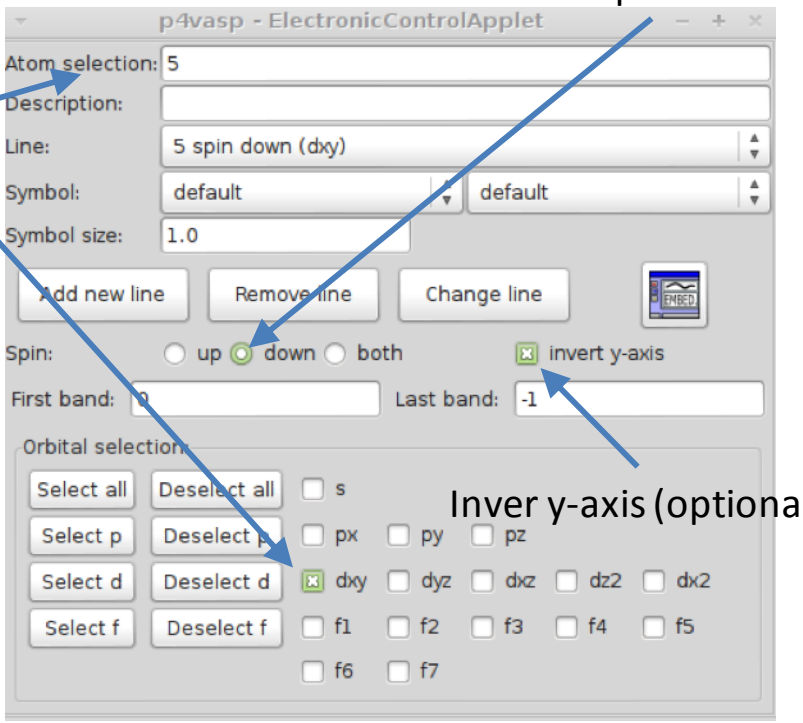
Ni(100) LDOS (ex.: Ni100clean_LDOS)

Select: “Electronic/Local DOS+Bands control”

Select atom,
and orbital character

Select spin channel



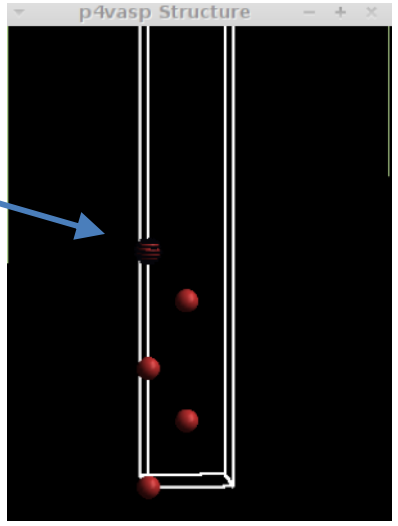


Inver y-axis (optional)

Press “Show” to show structure

Place pointer over atom, and press space to select/deselect.

The selection should appear in the Electronic Control applet above



Ni(100) surface bandstructure (ex.: Ni100clean_band)

INCAR:

SYTEM = clean Ni(100) surface	Name of the calculation
ENCUT = 270	cutoff energy 270 eV (from POTCAR)
ALGO = Normal	use block-Davidson for electronic minimization
ISMEAR = 2 SIGMA = 0.2	2nd order Methfessel-Paxton smearing (metal!) smearing width $\sigma = 0.2$ eV
ISPIN = 2 MAGMOM = 5*1	spin-polarized calculation initial magnetic moment on each Ni = 1 μ_B
LORBIT = 11	LM-decomposed site resolved density of states
ICHARG = 11	Read initial charge from CHGCAR (ICHARG=1), and keep it fixed (ICHARG=ICHARG+10) during the subsequent calculation

N.B.: You need to copy the self-consistent charge density (CHGCAR) from Ni100clean_LDOS to the directory where you want to run Ni100clean_band.

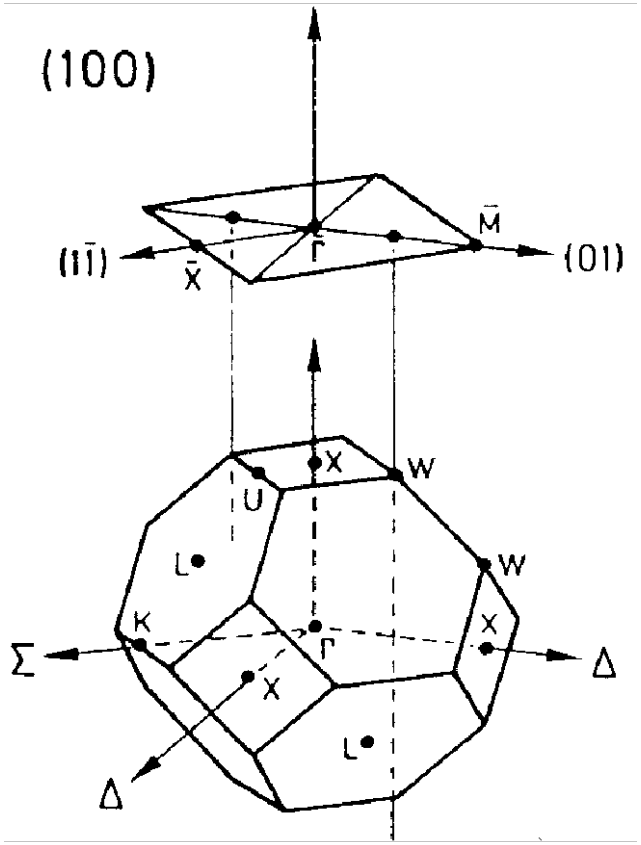
You need to do this: if VASP can not read the CHGCAR file, the run will terminate.

Ni(100) surface bandstructure (ex.: Ni100clean_band)

KPOINTS:

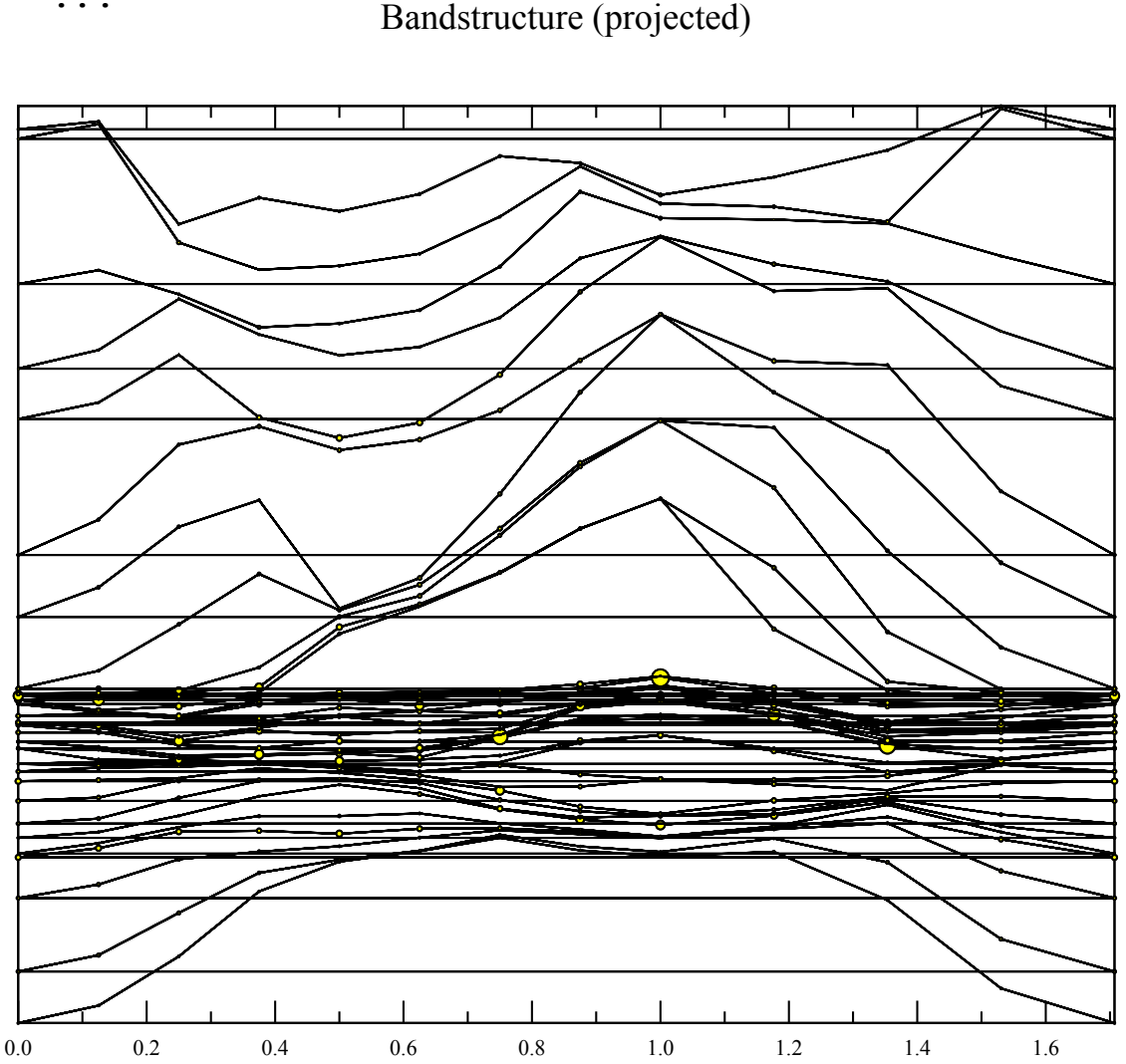
```
kpoints for band-structure G-X-M-G
  13
reziprok
   .00000   .00000   .00000    1
   .12500   .00000   .00000    1
   .25000   .00000   .00000    1
   .37500   .00000   .00000    1
   .50000   .00000   .00000    1

   .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
```

- 13 **k**-points along $\bar{\Gamma} - \bar{X} - \bar{M} - \bar{\Gamma}$
- Explicitly specfied, in reciprocal coordinates
- All points with weight 1



Ni(100) surface bandstructure (ex.: Ni100clean_band)

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

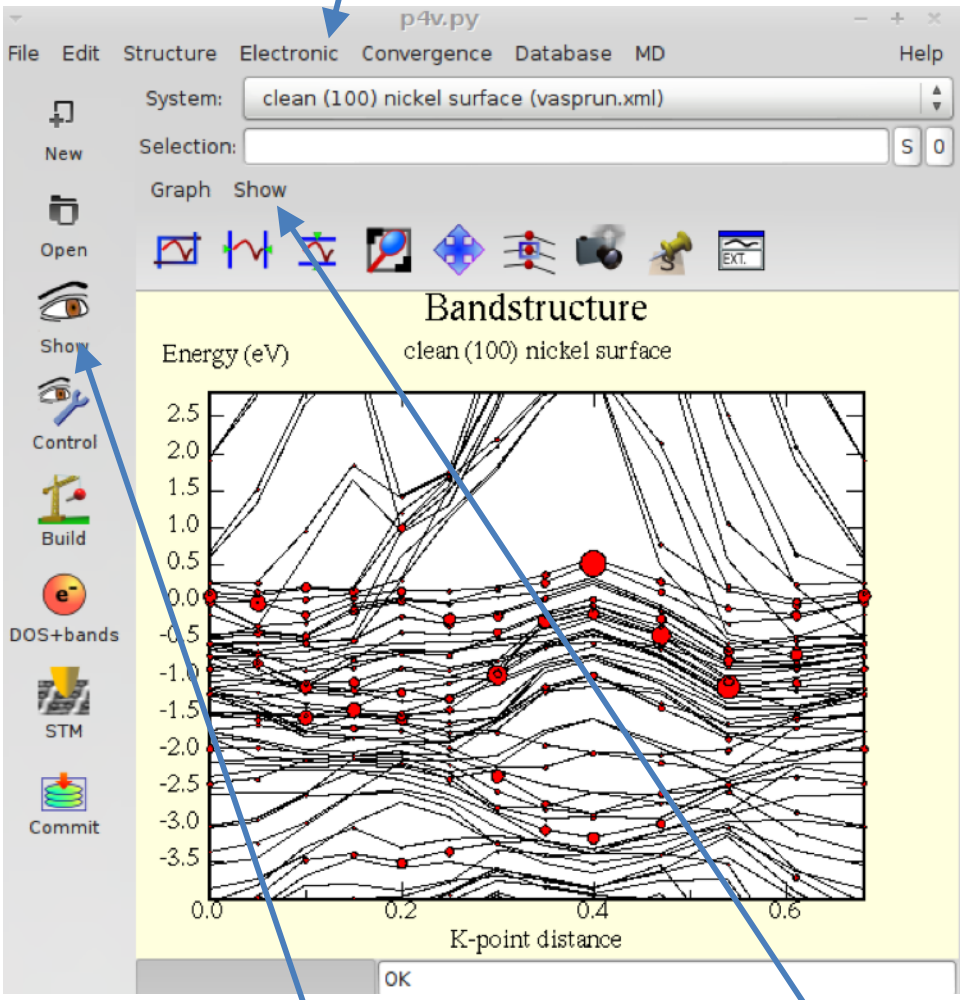


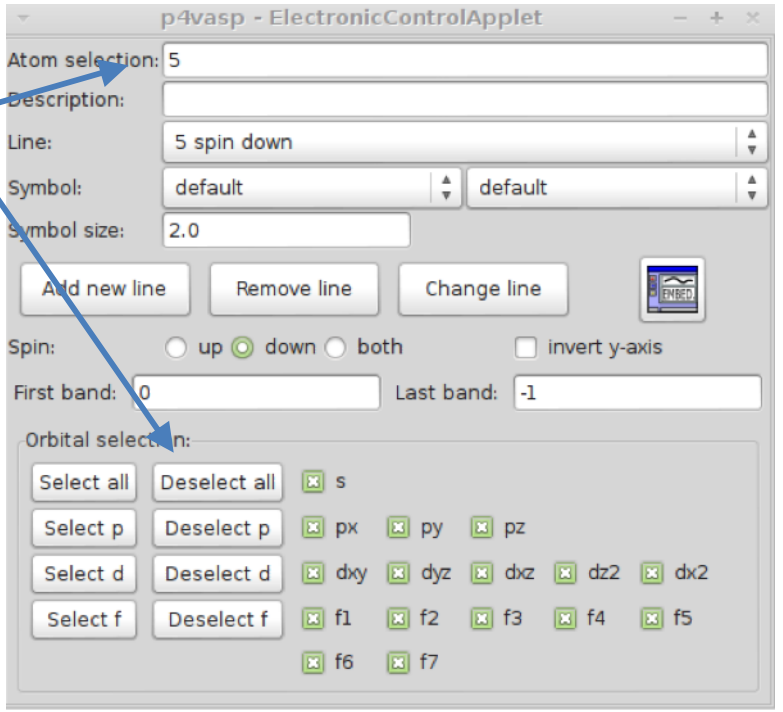
- status message in OUTCAR on actual job:
  ⇒ non-selfconsistent calc.
- Bandstructure consist mainly of bulk-like bands.
- Dots mark localization at surface layer.

Ni(100) surface bandstructure (ex.: Ni100clean_band)

Select: “Electronic/Local DOS+Bands control”

Select atom,
and orbital character



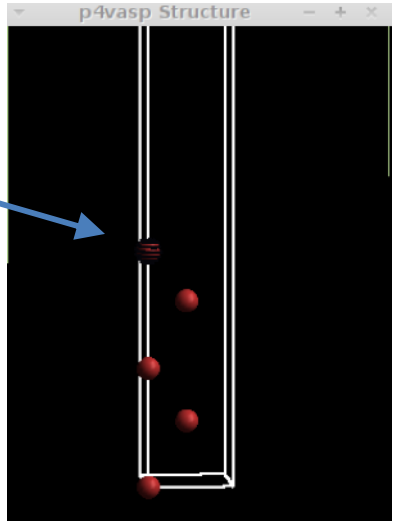


Press “Show” to show structure

Select “Bands”

Place pointer over atom, and press space to select/deselect.

The selection should appear in the Electronic Control applet above



Ni(111) surface relaxation (ex.: Ni111clean_rel)

INCAR:

SYTEM = clean Ni(100) surface	Name of the calculation
ISTART = 0 ICHARG = 2	initial wave functions: random numbers initial charge density: overlapping atoms
ENCUT = 270	cutoff energy 270 eV (from POTCAR)
ALGO = Fast EDIFF = 1E-6	use RMM-DIIS for electronic optimization electronic convergence: energy change < 10^{-6} eV
ISMEAR = 2 SIGMA = 0.2	2nd order Methfessel-Paxton smearing (metal!) smearing width $\sigma = 0.2$ eV
IBRION = 1 NSW = 100 POTIM = 0.8	ionic relaxation

- Essentially the same INCAR file as used in Ni100clean_rel.
- Spin polarization neglected.

Ni(111) surface relaxation (ex.: Ni111clean_rel)

POSCAR:

`Ni - (111)`	`Header (comment)`
`3.53`	`Ni lattice constant`

`  .70710678  .0000000  .000000`
`-0.35355339 0.6123724  .000000`
`  .000000    .000000  5.196152`
	`lattice vector a(1)`
	`lattice vector a(2)`
	`lattice vector a(3)`

` 5`	`Number of atoms`
`selective dynamics`	`Switch on "selective dynamics"`
`direct`	`Positions in cartesian coordinates`

`.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`
	`positions of the atoms, and the specfications whether or not they are allowed to move during the relaxation.`

Similar setup as for (100) surface:

- again 5 layers, 2 relaxed
- $(1 - .444) \times 5.196 \times 3.53 \approx 10.2$ Å of vacuum

Ni(111) surface relaxation (ex.: Ni111clean_rel)

Geometry and surface energy:

POSITION			TOTAL-FORCE (eV/Angst)		
0.00000	0.00000	0.00000	0.000000	-0.000000	0.179780
-0.00000	1.44112	2.03805	0.000000	-0.000000	-0.064012
1.24804	0.72056	4.07609	-0.000000	0.000000	-0.116688
0.00000	-0.00000	6.09140	0.000000	0.000000	0.000253
-0.00000	1.44112	8.09550	-0.000000	0.000000	0.000667
total drift:			-0.000032	0.000002	-0.018784

- Forces at the beginning already rather small
  $\Longrightarrow$ small relaxations for compact surfaces

- For surface energy we need non-spin-polarized bulk nickel as reference: the setup for the calculation of the “bulk” energy you’ll find in the *Ni111clean_rel/bulk* subdirectory.

$$\sigma^{\mathrm{unrel}} = \tfrac{1}{2}\left(-25.737 - 5 \times (-5.407)\right) = 0.649$$

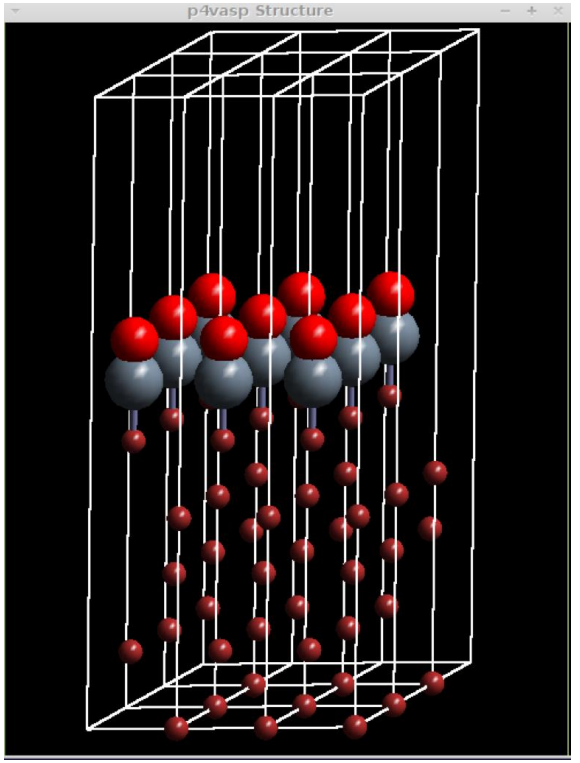
- (111) surface more stable than the (100) surface

CO@Ni(111) (ex.: COonNi111_rel)

POSCAR:

```
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
```

- Compared to previous examples, we now have two additional atomic types (C & O) ⟹ change POTCAR!
- Concatenate nickel, carbon, and oxygen PAW datasets.



CO molecule put above surface atom ⟹ “on-top”:

- $z_C = (.540 - .444) \times 5.196 \times 3.53 \approx 1.76$ Å
- $z_{CO} = (.603 - .540) \times 5.196 \times 3.53 \approx 1.16$ Å

CO@Ni(111) (ex.: COonNi111_rel)

Geometry

POSITION			TOTAL-FORCE (eV/Angst)		
0.00000	0.00000	0.00000	0.000000	-0.000000	0.174586
-0.00000	1.44112	2.03805	0.000000	-0.000000	-0.107681
1.24804	0.72056	4.07609	-0.000000	-0.000000	-0.073588
-0.00000	0.00000	6.10111	0.000000	-0.000000	-0.000361
-0.00000	1.44112	8.15449	-0.000000	-0.000000	-0.002450
-0.00000	1.44112	9.91089	0.000000	-0.000000	0.014846
-0.00000	1.44112	11.06589	-0.000000	0.000000	-0.005352
total drift:			-0.000177	-0.000361	0.013511

- Small outward relaxation of the surface due to adsorption:
  $\Delta d_{12} = (8.154 - 6.101)/2.038 \times 100 - 100 = 0.74\%$

- CO geometry:

  $d_{CO} = 11.066 - 9.911 = 1.155$ Å

  $z_{CNi} = 9.911 - 8.154 = 1.757$ Å

Ni(111) with higher cutoff (ex.: Ni111clean_400eV)

- the PAW datasets for carbon and oxygen used in example COonNi111_rel require a plane wave energy cutoff of 400 eV (see C and O POTCAR files).
- The previous calculation of the Ni(111) clean surface was done with an energy cutoff of 270 eV

$\Longrightarrow$ To be able to calculate the adsorption energy we need to run a single point calculation for the Ni(111) clean surface at a higher cutoff (400eV).

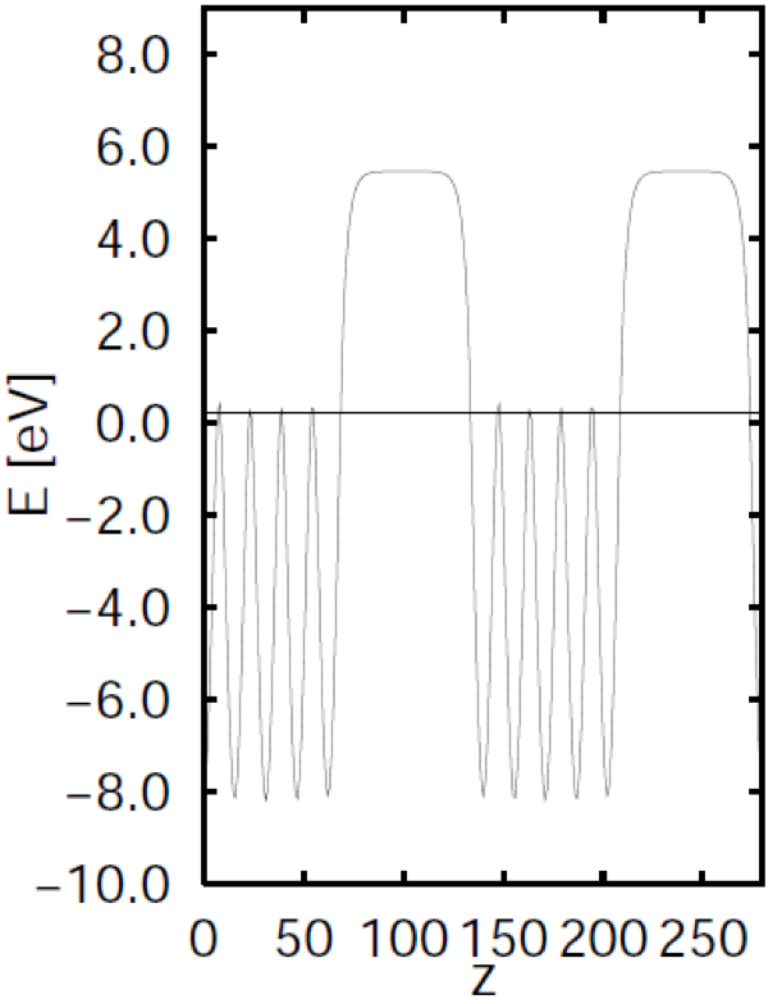
`SYTEM = clean Ni(111) surface`	`Name of the calculation`
`ISTART = 0` `ICHARG = 2`	`initial wave functions: random numbers` `initial charge density: overlapping atoms`
`ENMAX = 400`	`cutoff energy 400 eV`
`ALGO = Fast` `EDIFF = 1E-6`	`use RMM-DIIS for electronic optimization` `electronic convergence: energy change < 10`$^{-6}$ `eV`
`ISMEAR = 2` `SIGMA = 0.2`	`2`nd `order Methfessel-Paxton smearing (metal!)` `smearing width` $\sigma = 0.2$ `eV`
`LVHAR = .TRUE.` `# LVTOT = .TRUE.`	`Write electrostatic potential to LOCPOT file, needed to calculate the work function`

- Change in cutoff lowers total energy:
  ENCUT=270 eV: $E(\sigma \to 0) = -25.737$
  ENCUT=400 eV: $E(\sigma \to 0) = -25.742$
- Adsorption energy: $E_{\text{ads}} = E_{\text{total}} - E_{\text{clean}} - E_{\text{CO}}$
  $E_{\text{ads}} = -40.829 + 25.742 + 14.835 = -0.252$ eV

N.B.: the setup for the calculation of "E_{CO}", you will find in the Ni111clean_400eV/CO subdirectory

Ni(111) with higher cutoff (ex.: Ni111clean_400eV)

- Use `p4vasp` to show the planar average of the potential (LOCPOT).
- vacuum-potential $E^{\mathrm{vac}} = 5.45$ eV
- Fermi-level $\varepsilon_F = 0.226$ eV (in OUTCAR)
- $\Phi = E^{\mathrm{vac}} - \varepsilon_F = 5.22$ eV



Ni(111) with higher cutoff (ex.: Ni111clean_400eV)

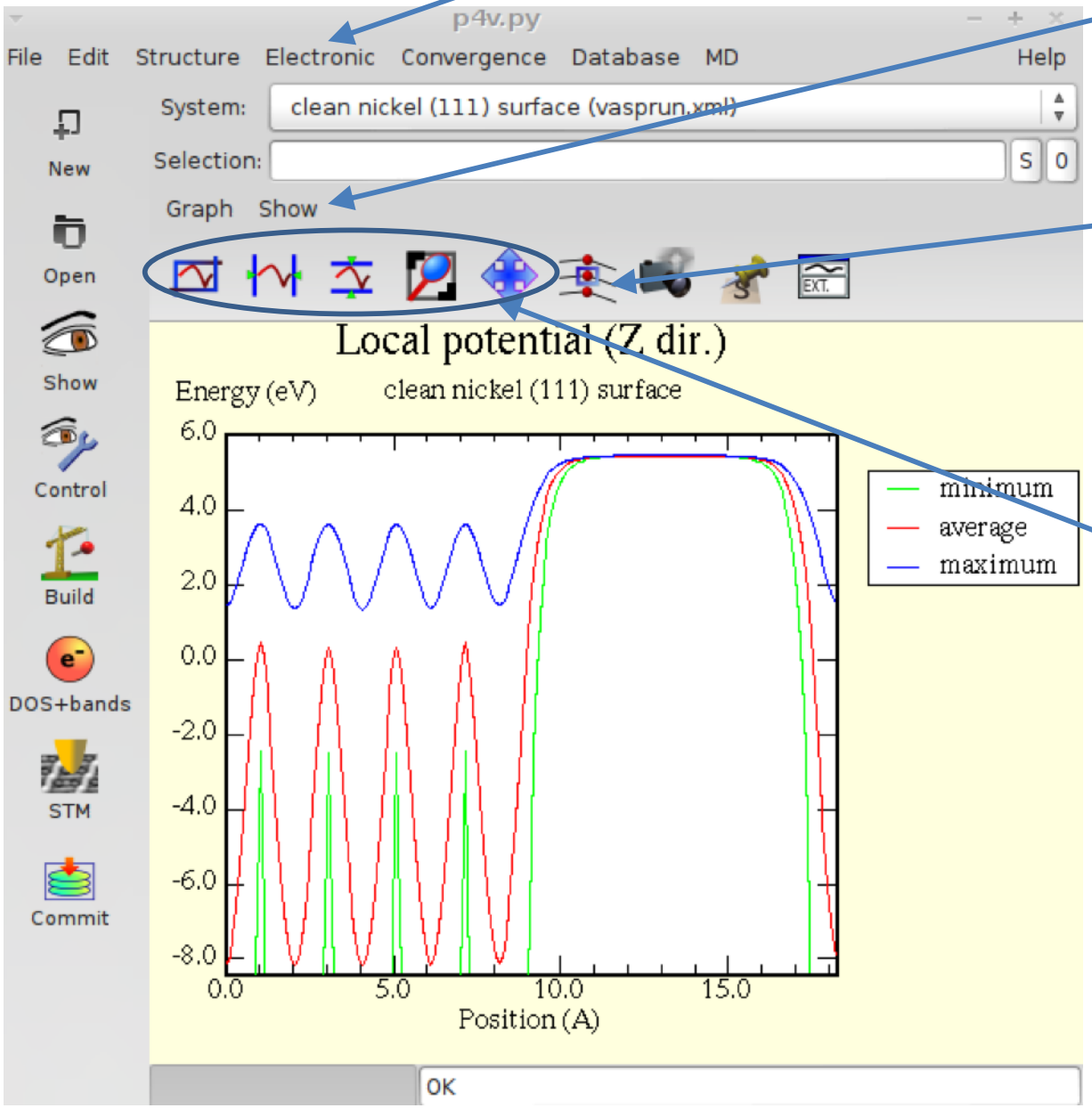
Go to “Electronic/Local potential”

Select “Z - direction”

“Measure” point in graph

Zoom to area of interest

Start p4vasp:
> p4v [vasprun.xml]



CO@Ni(111) LDOS&Workfunction (ex.: COonNi111_LDOS)

INCAR:

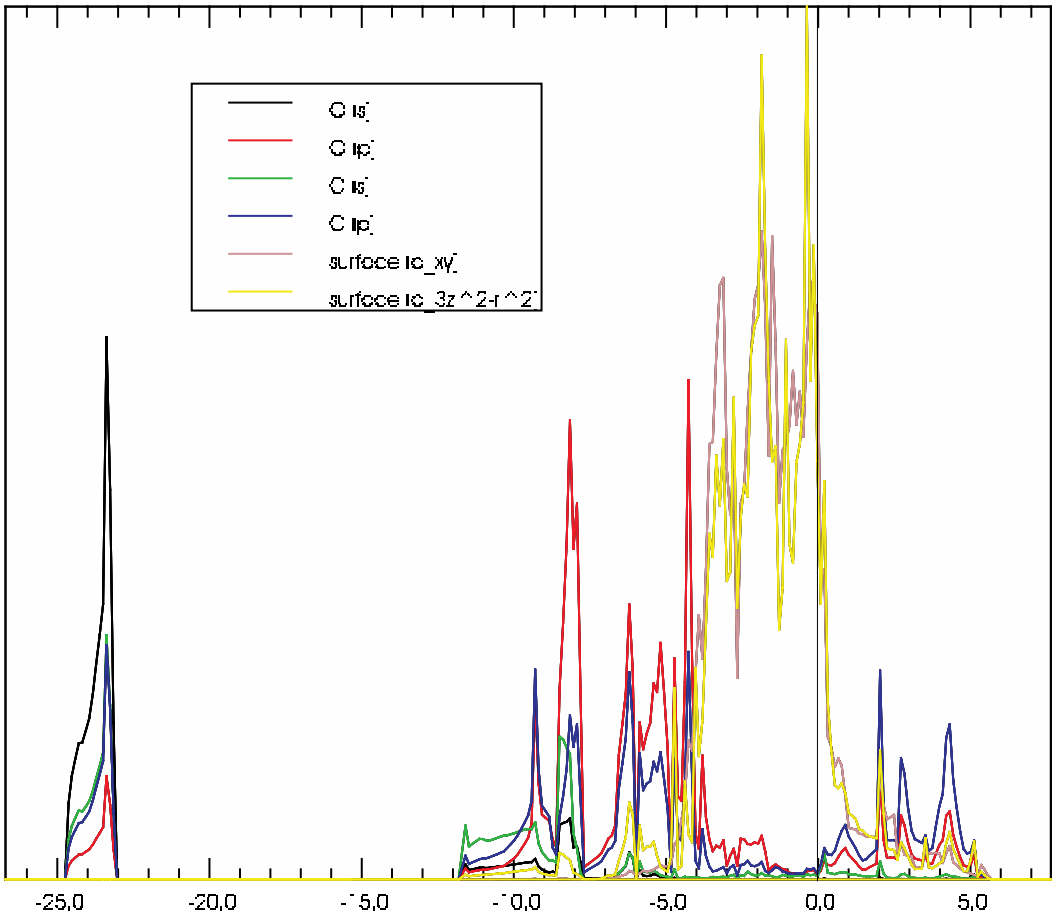
SYSTEM = CO adsorption on Ni(111)	Name of the calculation
ENMAX = 400	cutoff energy 400 eV
ISMEAR = -5	tetrahedron method with Blöchl corrections
ALGO = Fast	use RMM-DIIS for electronic optimization
LORBIT = 11	LM-decomposed site resolved density-of-states
IDIPOL = 3 LDIPOL = .TRUE. LVHAR = .TRUE. #LVTOT = .TRUE.	Enable dipole corrections in direction 3 Switch on dipole corrections to potential (=diplole layer) Write Hartree part of local potential to LOCPOT Write total local potential to LOCPOT

N.B.: We want to use the optimized structure of COonNi111_rel:
In principle this would mean copying the CONTCAR of COonNi111_rel to POSCAR in the directory where you want to run COonNi111_LDOS.
This, however, has already been taken care of, and the POSCAR file in COonNi111_LDOS is already the correct one.

CO@Ni(111) LDOS&Workfunction (ex.: COonNi111_LDOS)

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

  $\Longrightarrow$ from symmetry



Visualisation: use p4vasp as explained for example Ni100clean_LDOS.

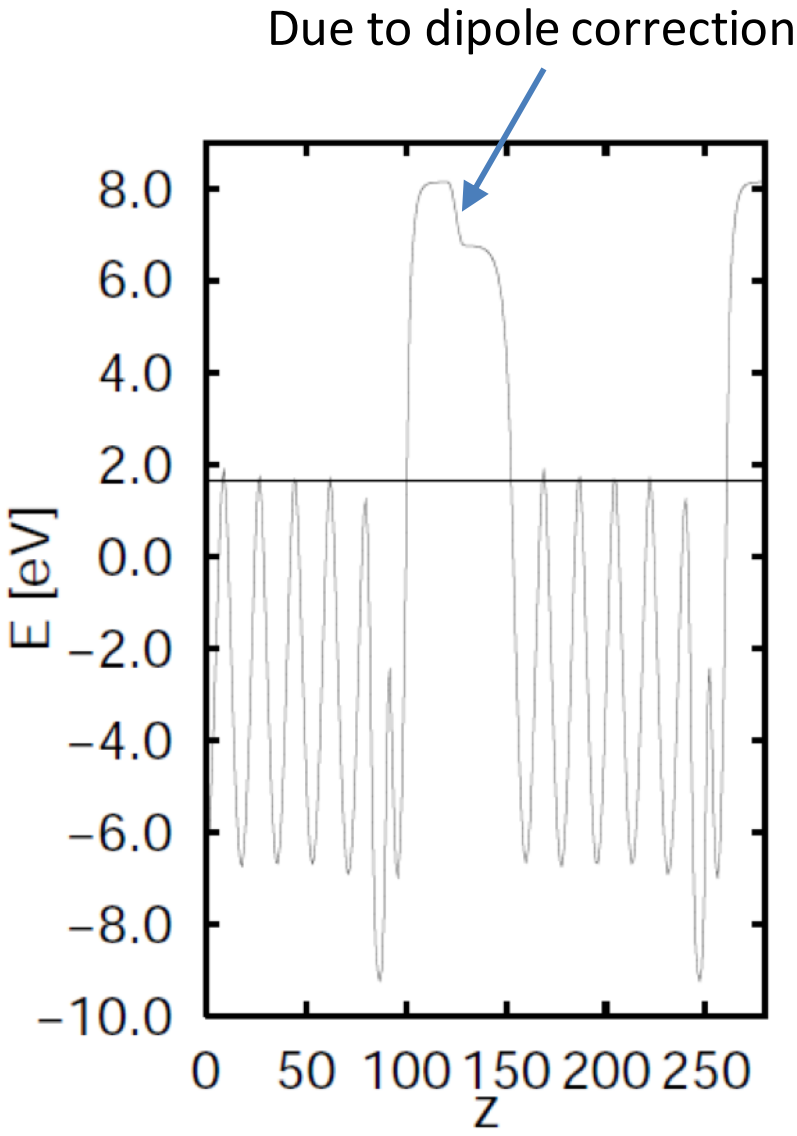
CO@Ni(111) LDOS&Workfunction (ex.: COonNi111_LDOS)

- Fermi-level $\varepsilon_F = 1.68$ eV (in OUTCAR)
- vacuum-potential at 8.24/6.77 eV:

$\Phi_{\mathrm{CO}} = 8.24 - 1.68 = 6.56$ eV
$\Phi_{\mathrm{clean}} = 6.77 - 1.68 = 5.09$ eV

From Ni111clean_400eV, however:
$\Phi_{\mathrm{clean}} = 5.22$ eV

This discrepancy is due to a too small vacuum!



Visualisation: use p4vasp as explained for example Ni111clean_400eV.

CO@Ni(111) vibrational frequencies (ex.: COonNi111_freq)

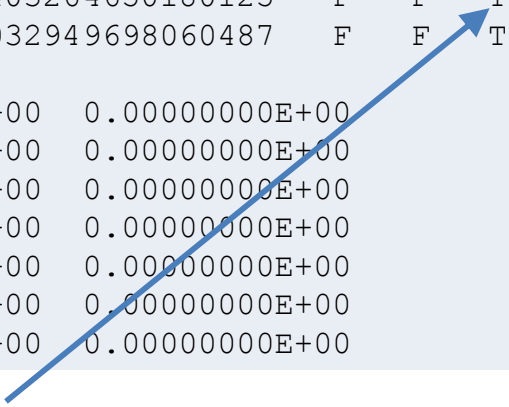
INCAR:

SYSTEM = CO on Ni (111) frequencies	
ENMAX = 400	cutoff energy 400 eV
ISMEAR = 2 SIGMA = 0.2	2nd order Methfessel-Paxton smearing smearing width $\sigma = 0.2$ eV
ALGO = Fast	use RMM-DIIS for electronic optimization
EDIFF = 1E-6	tight convergence needed to compute vibrational properties
MAXMIX = 60	(Default: MAXMIX=45) Store more mixing steps, save time but costs memory
NSW = 100	
IBRION = 5	Compute vibrational spectrum using finite differences (displacements: 0.015 Å)
NFREE = 2	Use two displacements per degree-of-freedom (i.e., a 2nd order finite difference stencil)

CO@Ni(111) vibrational frequencies (ex.: COonNi111_freq)

POSCAR:

```
Ni - (111) + CO on-top
   3.53000000000000
     0.7071067800000000    0.0000000000000000    0.0000000000000000
    -0.3535533900000000    0.6123724000000000    0.0000000000000000
     0.0000000000000000    0.0000000000000000    5.1961523999999999
   Ni    C    O
      5     1     1
Selective dynamics
Direct
  0.0000000000000000  0.0000000000000000  0.0000000000000000   F   F   F
  0.3333333300000021  0.6666666699999979  0.1111111100000031   F   F   F
  0.6666666699999979  0.3333333300000021  0.2222222199999990   F   F   F
 -0.0000000000000000  0.0000000000000000  0.3326227833039623   F   F   F
  0.3333333300000021  0.6666666699999979  0.4445699380869117   F   F   F
  0.3333333300000021  0.6666666699999979  0.5403264650180125   F   F   T
  0.3333333300000021  0.6666666699999979  0.6032949698060487   F   F   T

  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
```



- Frequencies only for CO molecule, and only in the *z*-direction (*z* and (*x*,*y*) are independent).

Use the POSCAR file in COonNi111_freq, or copy COonNi111_rel/CONTCAR to POSCAR

CO@Ni(111) vibrational frequencies (ex.: COonNi111_freq)

Additional output in the OUTCAR file for frequency calculations via finite differences, e.g.:

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

- After the initial calculation for the equilibrium geometry, NFREE displacements (±POTIM) are performed for each degree of freedom; from the forces that are induced by 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.

CO@Ni(111) vibrational frequencies (ex.: COonNi111_freq)

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

  1 f  =   63.847137 THz   401.163391 2PiTHz 2129.711174 cm-1   264.050627 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  6.101106             0            0            0
    -0.000000  1.441116  8.154488             0            0            0
    -0.000000  1.441116  9.910894             0            0   -0.781357
    -0.000000  1.441116 11.065888             0            0    0.624084

  2 f  =   12.457302 THz    78.271540 2PiTHz  415.530869 cm-1    51.519280 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  6.101106             0            0            0
    -0.000000  1.441116  8.154488             0            0            0
    -0.000000  1.441116  9.910894             0            0   -0.624084
    -0.000000  1.441116 11.065888             0            0   -0.781357
```

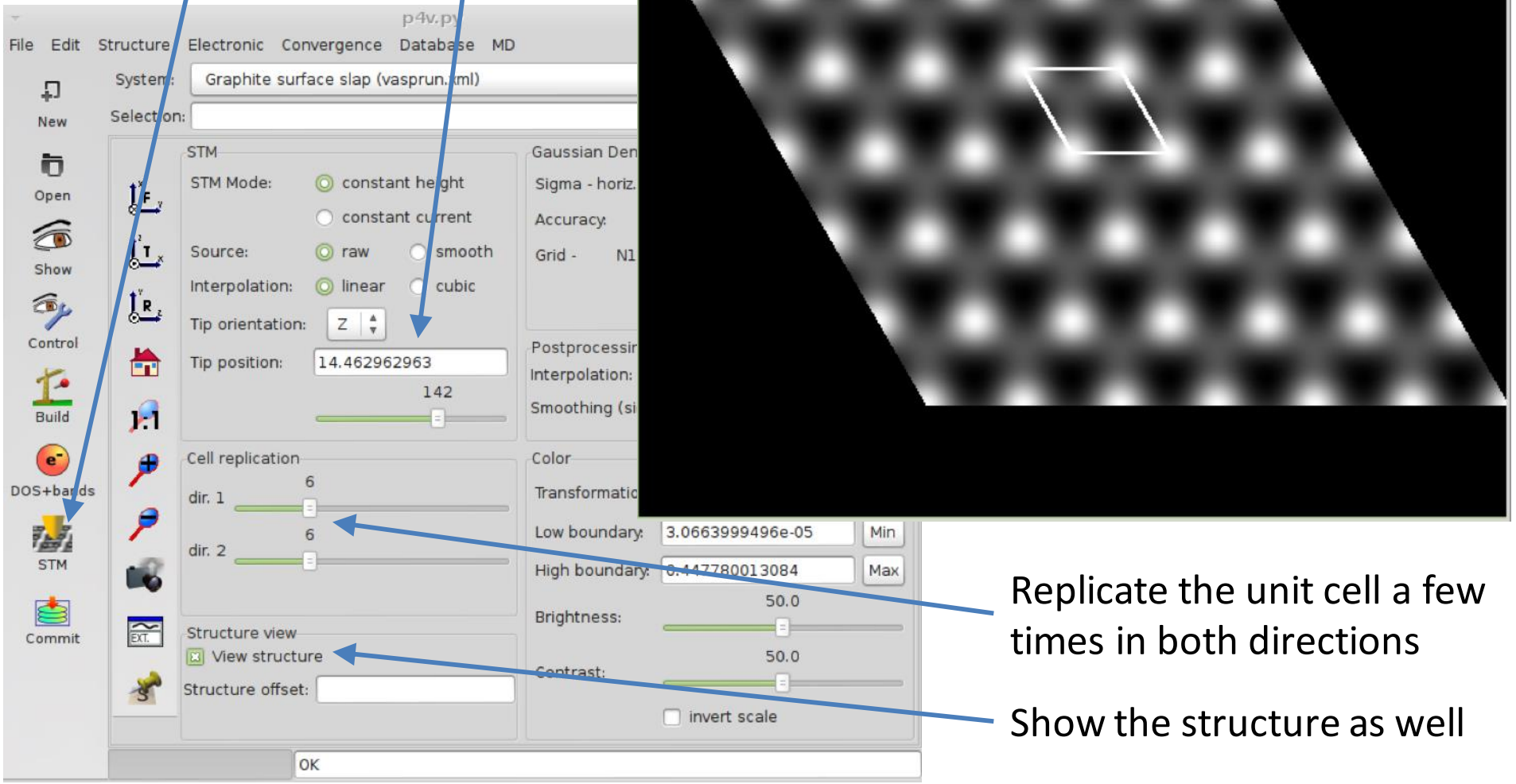
CO stretch

CO-metal

STM (ex.: Graphite_STM and Graphene_STM)

Chose a plane roughly 1 Å above the surface atoms

Step 1.) select “STM”



Replicate the unit cell a few times in both directions

Show the structure as well

STM (ex.: Graphite STM and Graphene STM)