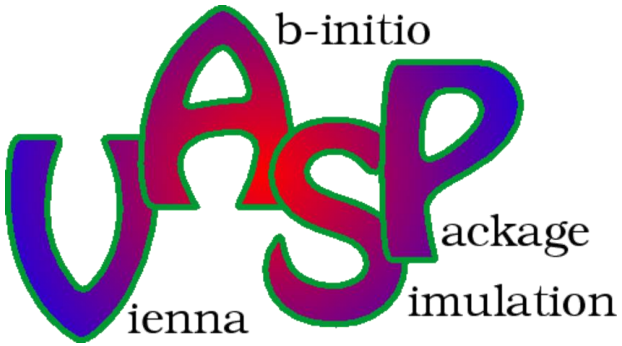
Vienna Ab Initio Package – Crash course

3rd Lecture – 16/09/21

Dr. Federico Dattila
fdattila@iciq.es



Structure of the course

Day / September	Hours / Madrid time	Location	Topic
Monday 6th	10:00-12:00	E4 / Zoom	Introduction + Handson 1 (molecules; frequencies; molecular dynamics)
Tuesday 7th	12:00-13:00	E4 / Zoom	Tutorial Handson 1
Wednesday 8th	10:00-12:00	E4 / Zoom	Correction exercises 1 + Handson 2 (bulk optimization and electronic properties) + Instructions for python / bash project
Thursday 9th	10:00-11:00	E3 / Zoom	Tutorial Handson 2
Friday 10th/ Wednesday 15th	Python / bash project		
Thursday 16th	10:00-12:00	E4 / Zoom	Correction exercises 2 and python / bash project + Handson 3 (surface optimization and electronic properties)
Friday 17th	10:00-11:00	E4 / Zoom	Tutorial Handson 3
Monday 20th	10:00-12:00	E4 / Zoom	Correction exercises 3 + Handson 4 (magnetic properties and Hubbard correction)
Tuesday 21st	10:00-11:00	E4 / Zoom	Tutorial Handson 4
Wednesday 22nd	10:00-11:00	E4 / Zoom	Correction exercises 4

Materials

- Materials available on OneDrive;
- All lectures and tutorials will be registered and later available on OneDrive;
- Detailed explanation online. The current course gives only an introduction!
- Save the link to the VASP manual online: https://www.vasp.at/wiki/index.php/The_VASP_Manual

Today’s class

1. Few tips
2. Update on status of python / bash project;
3. Correction of exercises of Handson 2;
4. Lecture 3 and instructions for Handson 3.

Based on:

- 1_optionic (ionic optimization)
- 2_optelectron (electronic optimization)

Further materials:

- 3_performance (install and compile VASP)

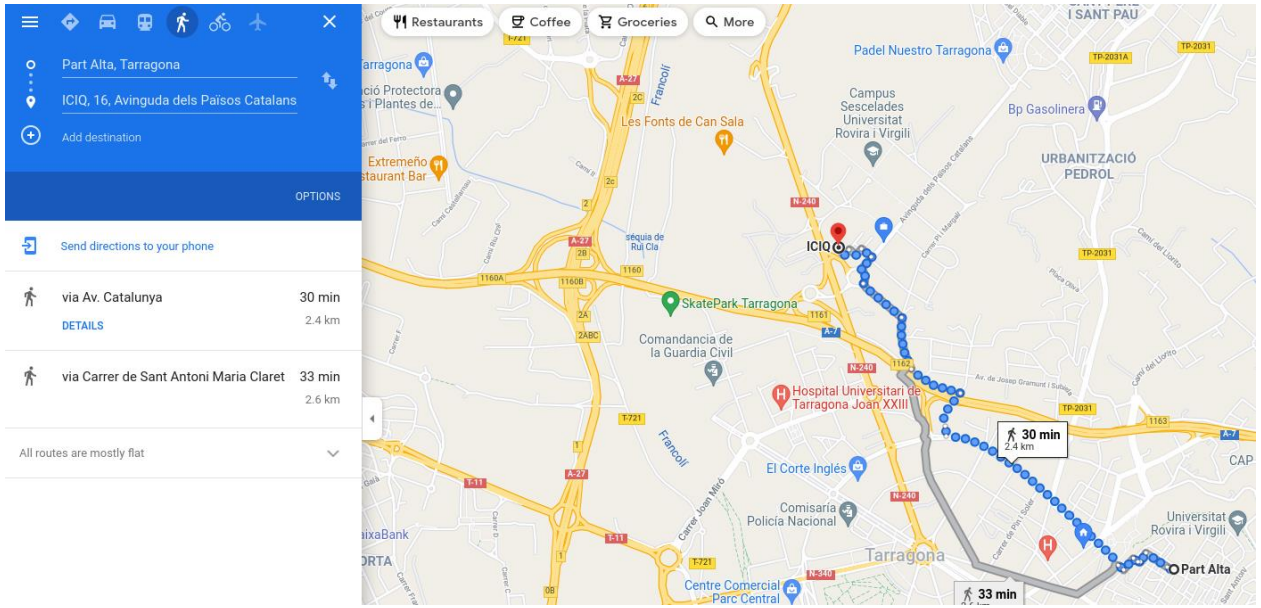
Related handson session:
(3) Surface optimization and electronic properties

1st tip: Take it easy!

Can you walk 1000 km?

1st tip: Take it easy!

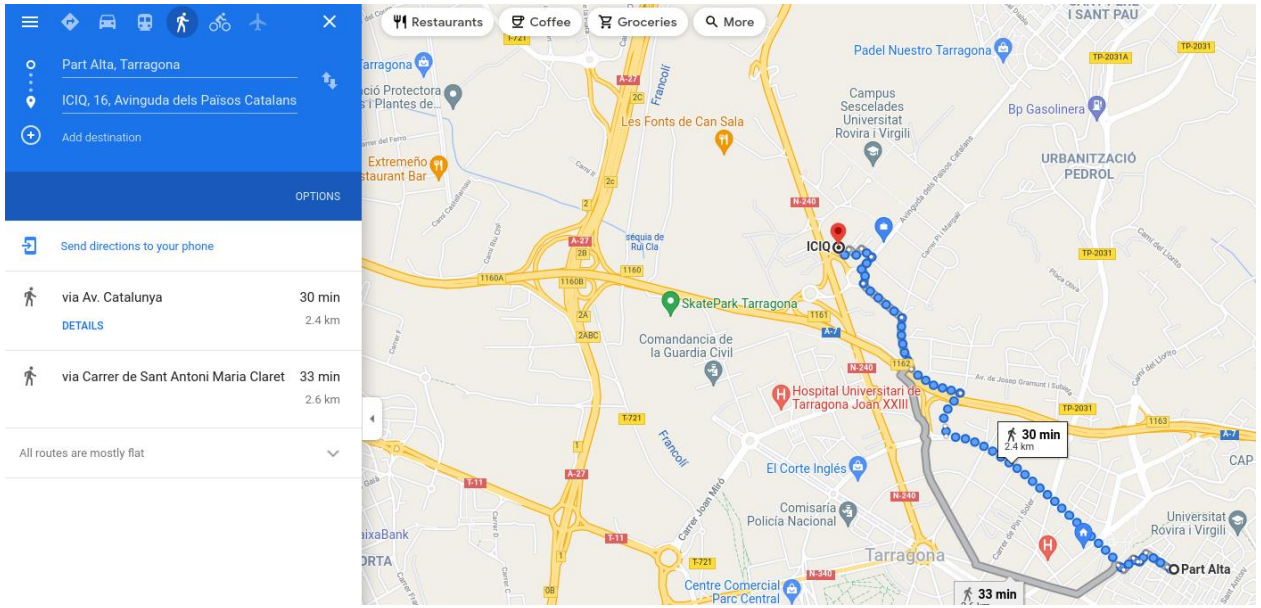
Can you walk 1000 km?



2.4 km × 2 times × 230 working days = 1100 km

1st tip: Take it easy!

Can you walk 1000 km?



2.4 km × 2 times × 230 working days = 1100 km

Your Ph.D. / Research project

- Understand properly the basics;
- Read the state-of-the-art;
- Plan your simulations;
- ….
- ….
- Submit simulations / Write paper.

2nd tip: Master degree vs Ph.D. degree

Master degree

- Established knowledge;
- Exercises: application of this established knowledge;
- Correction of exercises because there is already a defined solution.

Ph.D. degree

- New science;
- Exercises: try to apply your knowledge to solve the puzzle of this new science;
- Update (~~correction~~) on the status of the exercises since there is not yet a solution. You need to find your own and this takes time!

Python / Bash projects – How is it going?

Maryam / Santiago – Python

- Cut surface facets from bulk (input: POSCAR: output: POSCAR_xyz)

In case you finish the first (or it is too complex):

- Calculate the surface energy *γ* for a facet in J m^{-2} or eV $Å^{-2}$ (input: POSCAR surface/bulk, OUTCAR surface/bulk; output: the value of *γ*)

Enric / Sichen – bash

- Order a surface and fix bulk layer (input: POSCAR; output: POSCAR);
- Generate *k*-points mesh (input: POSCAR; output: KPOINTS);

In case you finish the first two:

- Add a molecule on top of an ordered POSCAR (input: CONTCAR; output: POSCAR)

```
fdattila@tekla2:~/00-vasp-course/scripting> for i in bash python ; do echo $i ; cd $i ; ls ; cd .. ; done
bash
add-mol  k-gen  ordtor
python
get-surface-energy  slab-gen
```

Handson 2

Question:

What is the most stable crystal structure of Si? Does your prediction agree with experiments?

Handson 2

Question:

What is the most stable crystal structure of Si? Does your prediction agree with experiments?

Crystal structure	Atom per unit cell	Energy / eV	Energy per atom / eV
fcc Si	2	–4.9	–2.4
Diamond Si	**2**	**–10.8**	**–5.4**
Beta-tin Si	2	–10.2	–5.1

https://en.wikipedia.org/wiki/Silicon

Handson 2

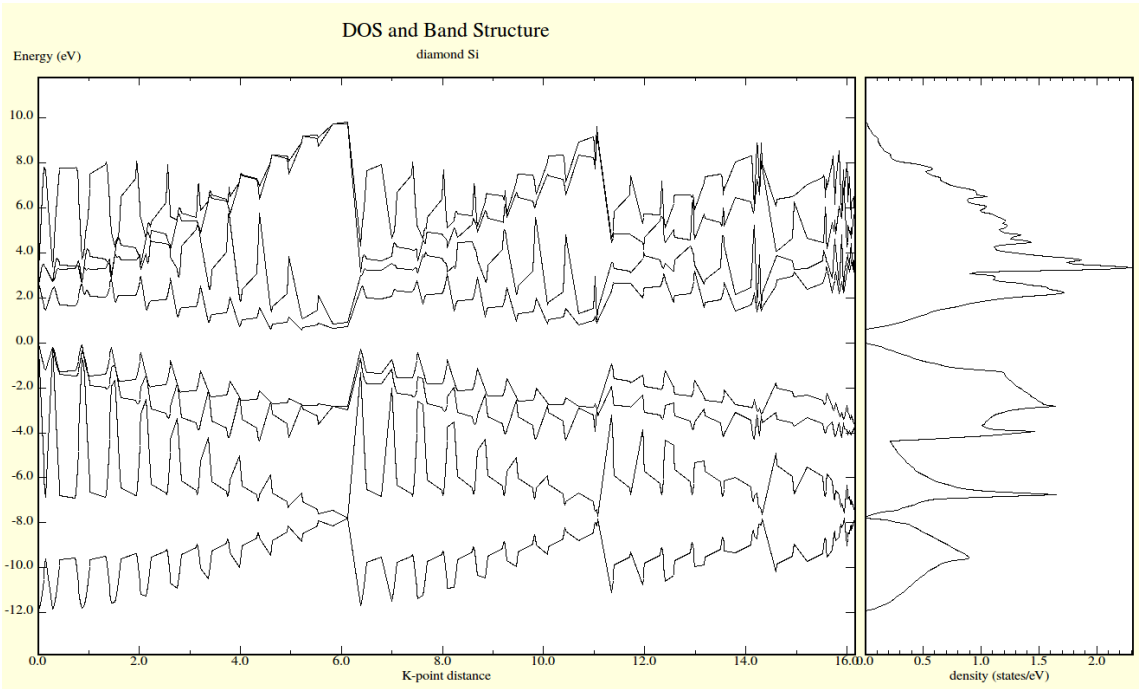
Question:

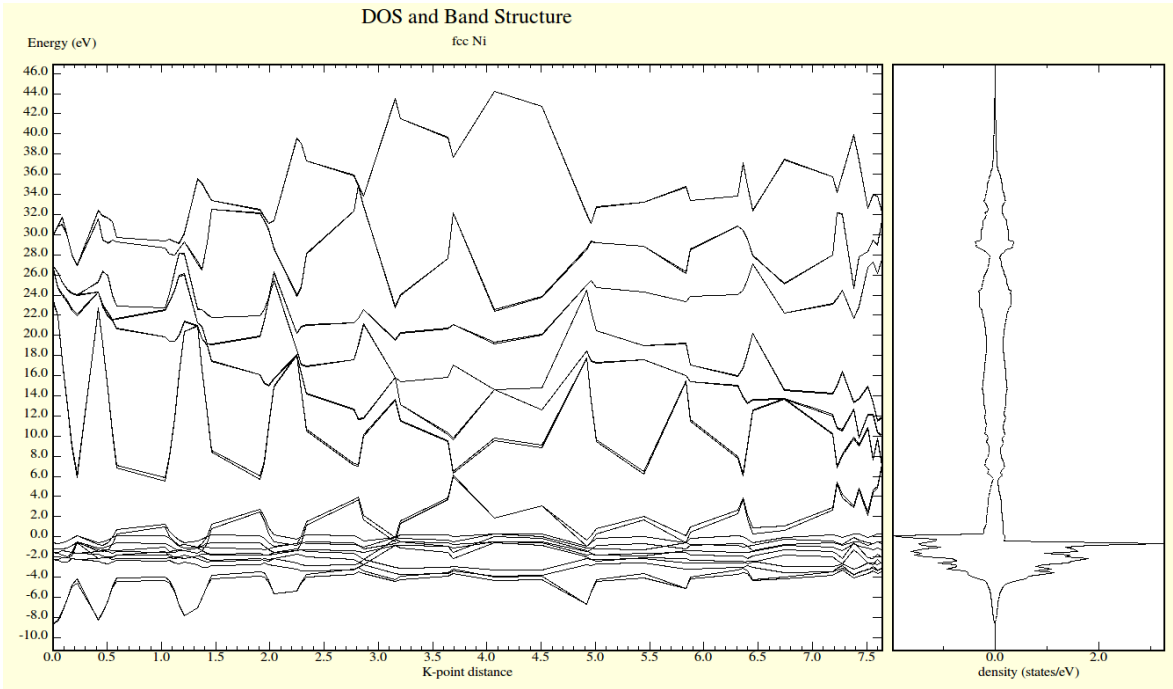
From the density of states, do you consider Si and Ni metals or semiconductors? Motivate the answer.

Handson 2

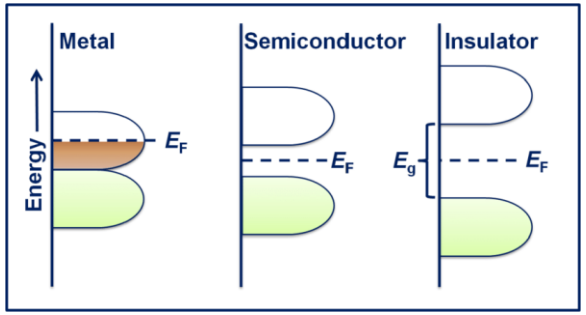
Question:

From the density of states, do you consider Si and Ni metals or semiconductors? Motivate the answer.





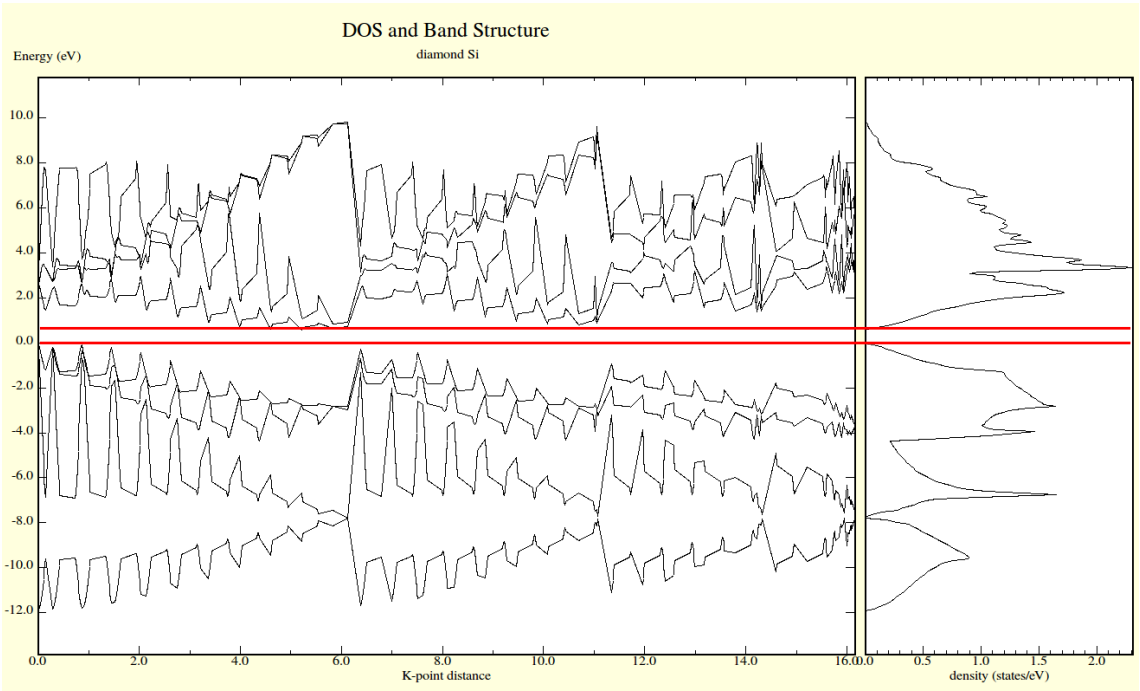
Handson 2



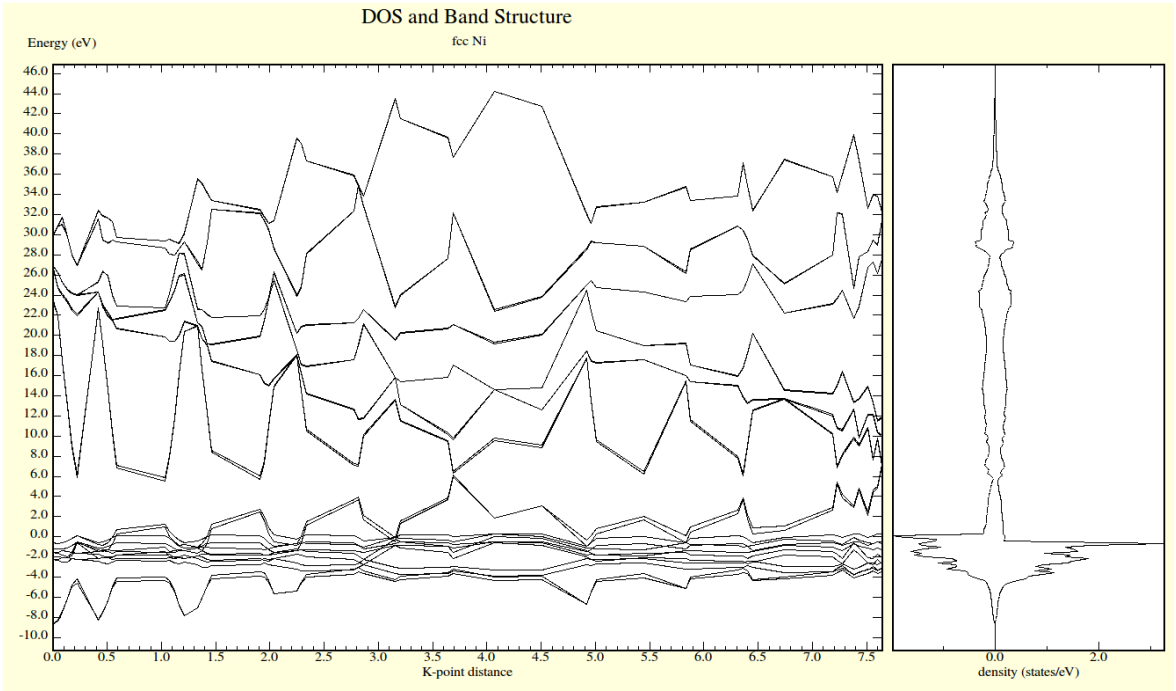
Question:

From the density of states, do you consider Si and Ni metals or semiconductors? Motivate the answer.

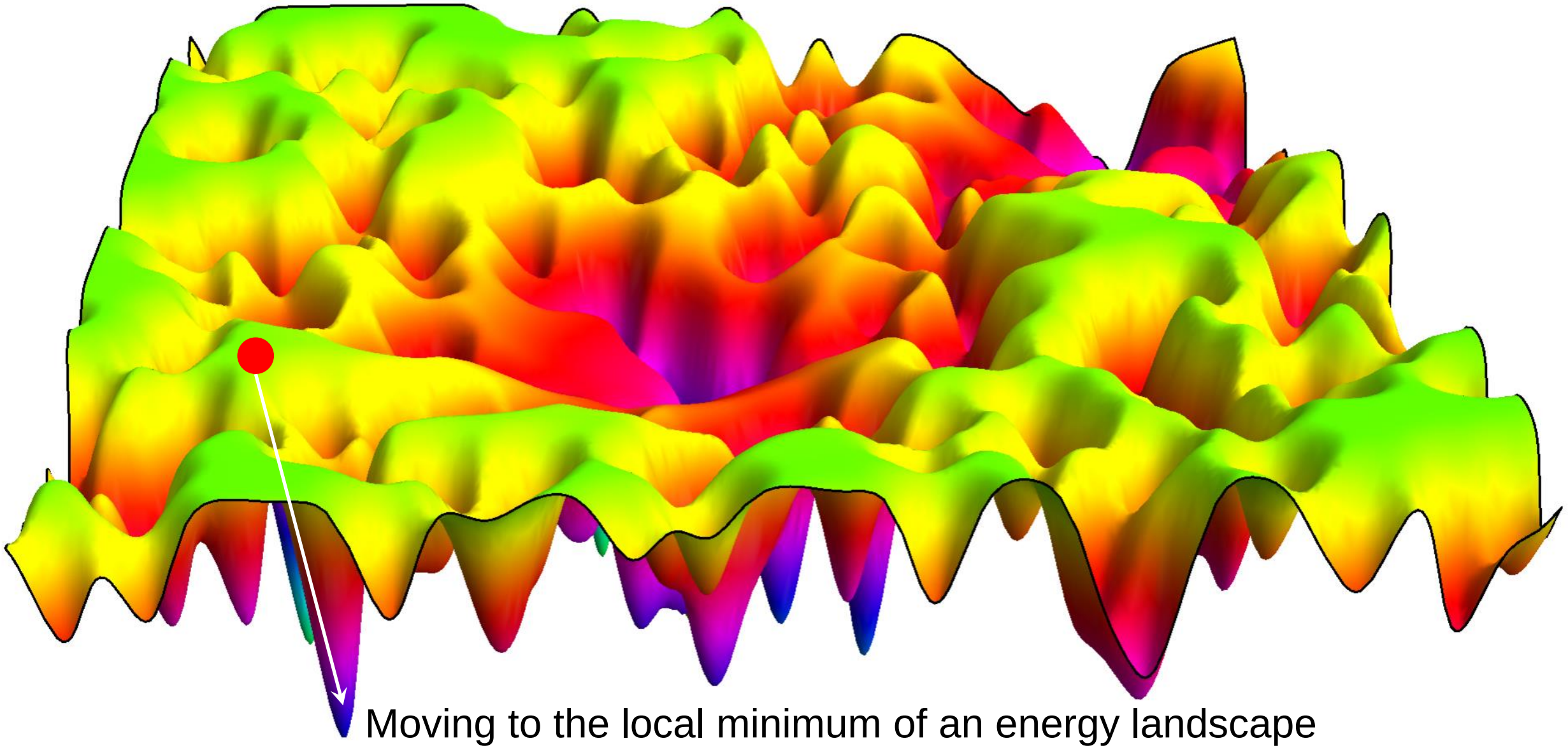
Diamond Si: Semiconductor



Ni fcc: Metal



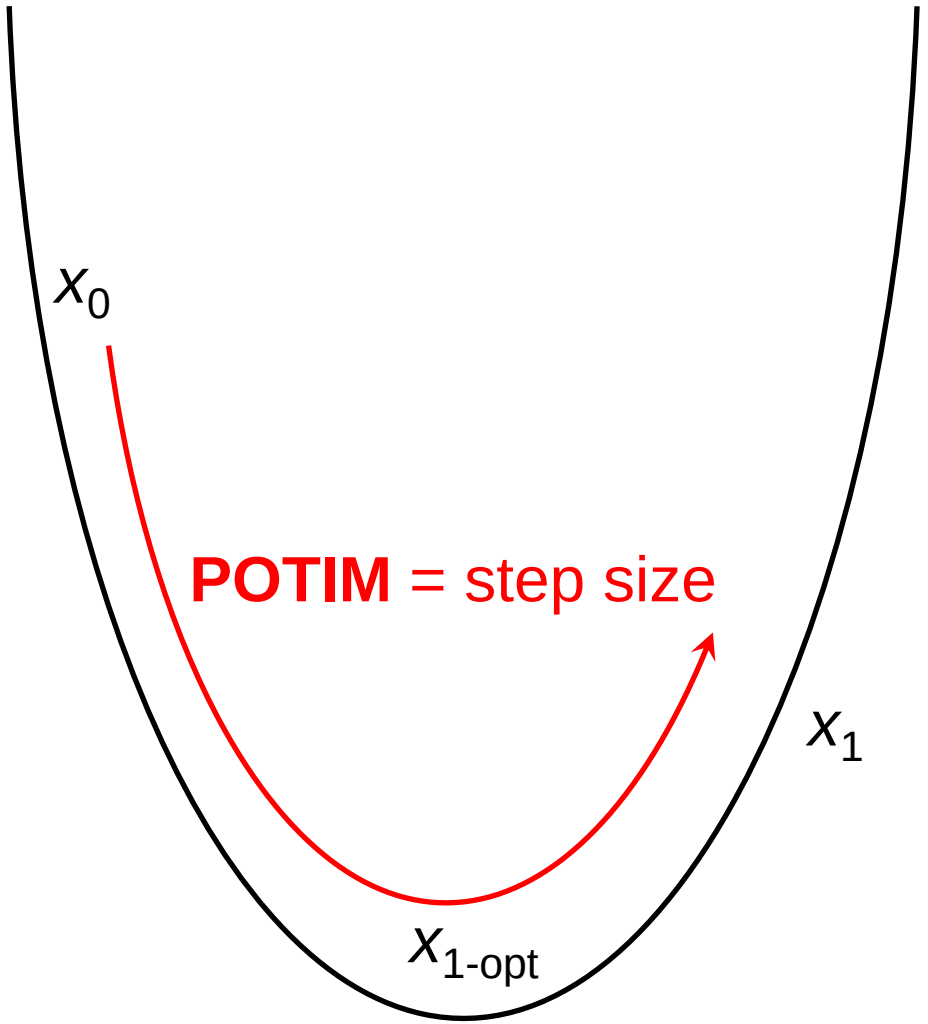
Ionic optimization algorithms



Moving to the local minimum of an energy landscape

Full DIIS algorithm – IBRION = 1

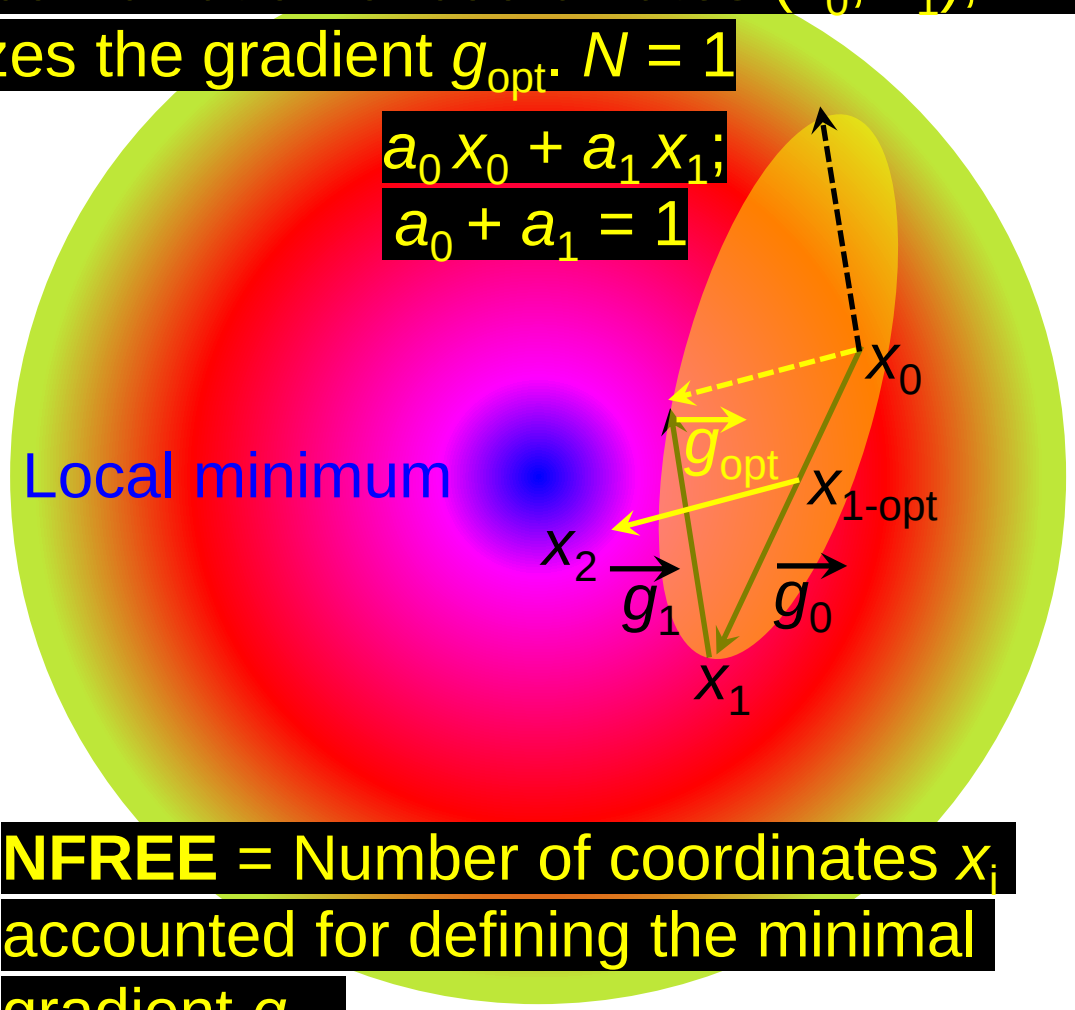
Side view



Top view

Linear combination of coordinates (x_0, x_1), which minimizes the gradient g_{opt}. $N = 1$

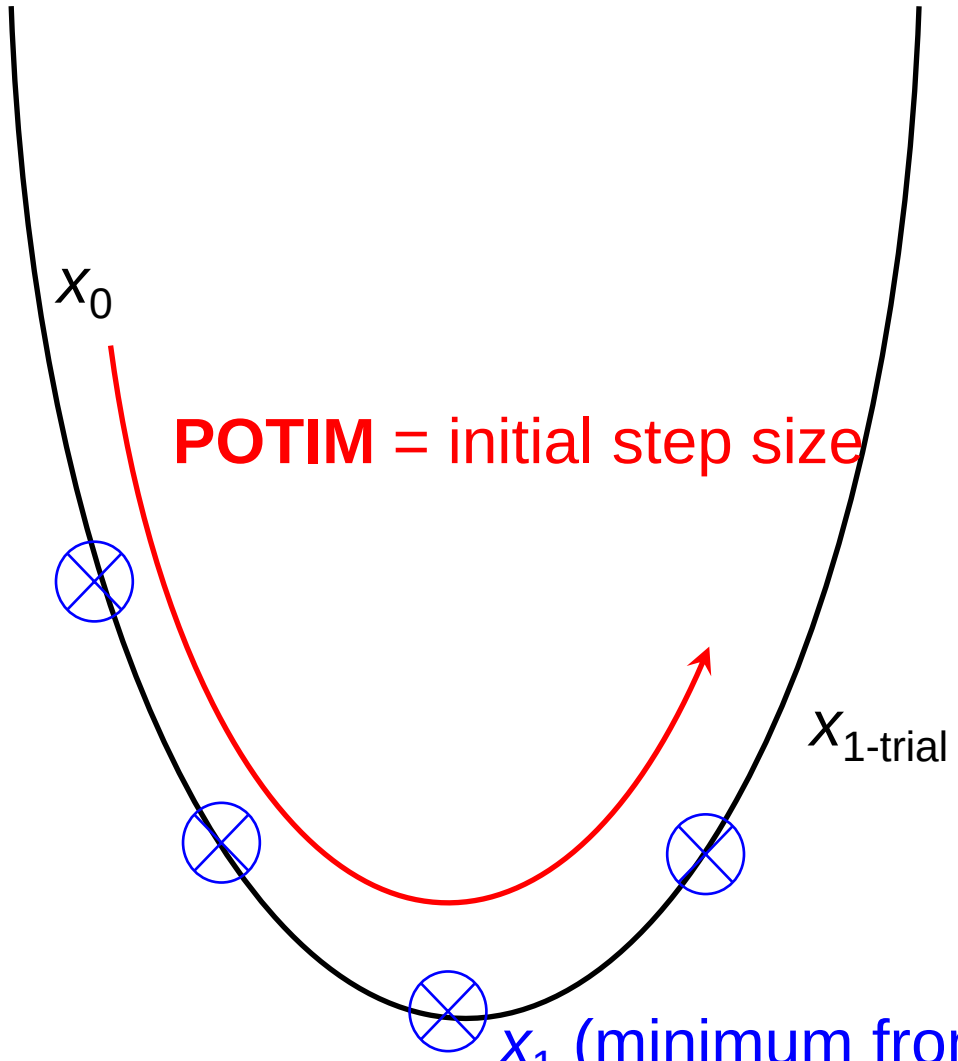
$a_0 x_0 + a_1 x_1$;
$a_0 + a_1 = 1$



NFREE = Number of coordinates x_i accounted for defining the minimal gradient g_{opt}

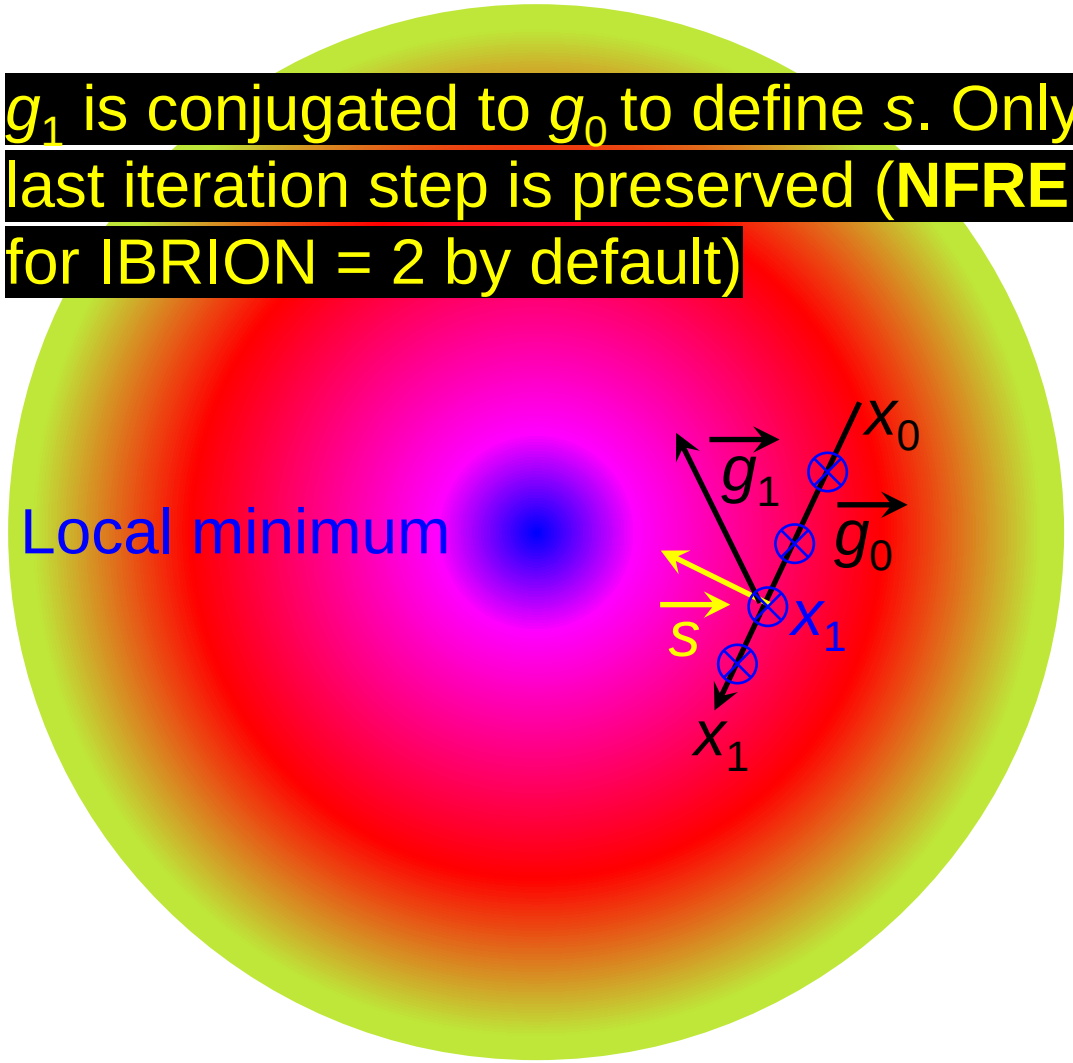
Conjugate gradient algorithm – IBRION = 2

Side view



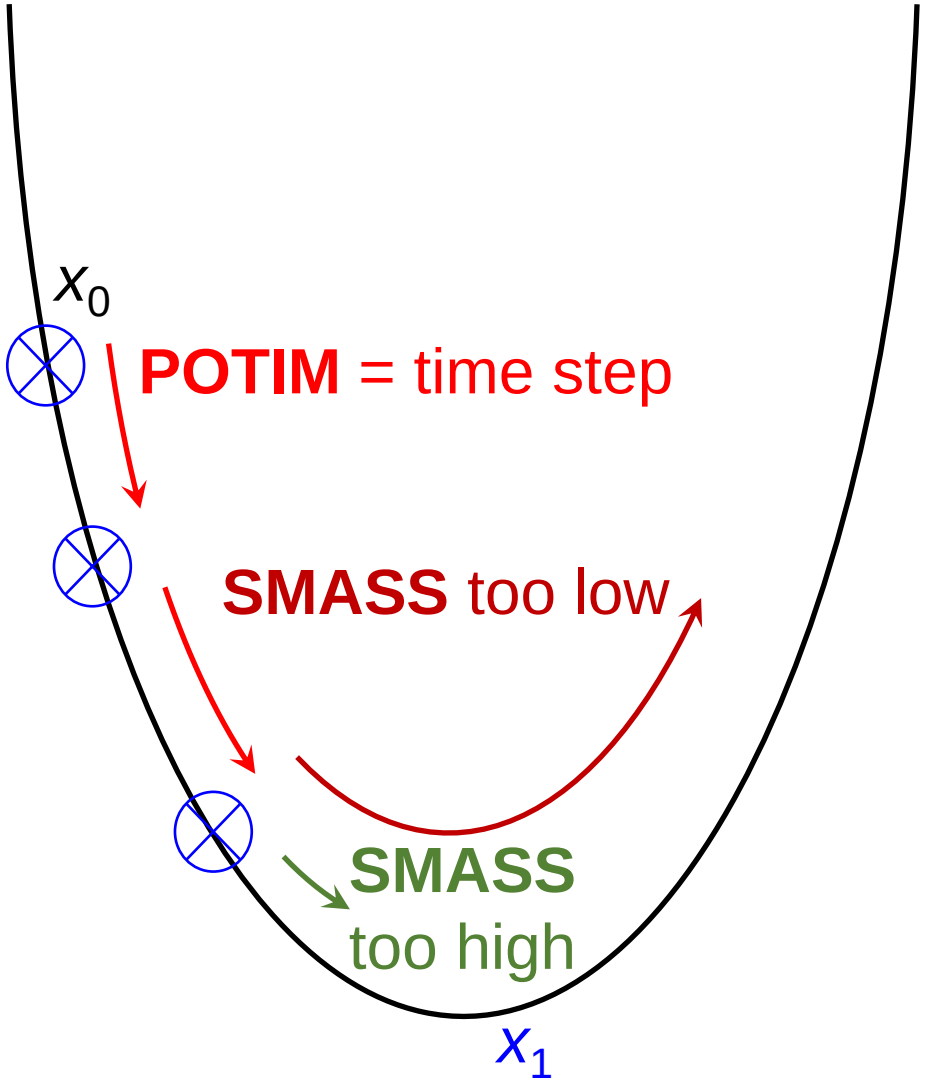
Top view

g_1 is conjugated to g_0 to define s. Only the last iteration step is preserved (**NFREE** = 1 for IBRION = 2 by default)

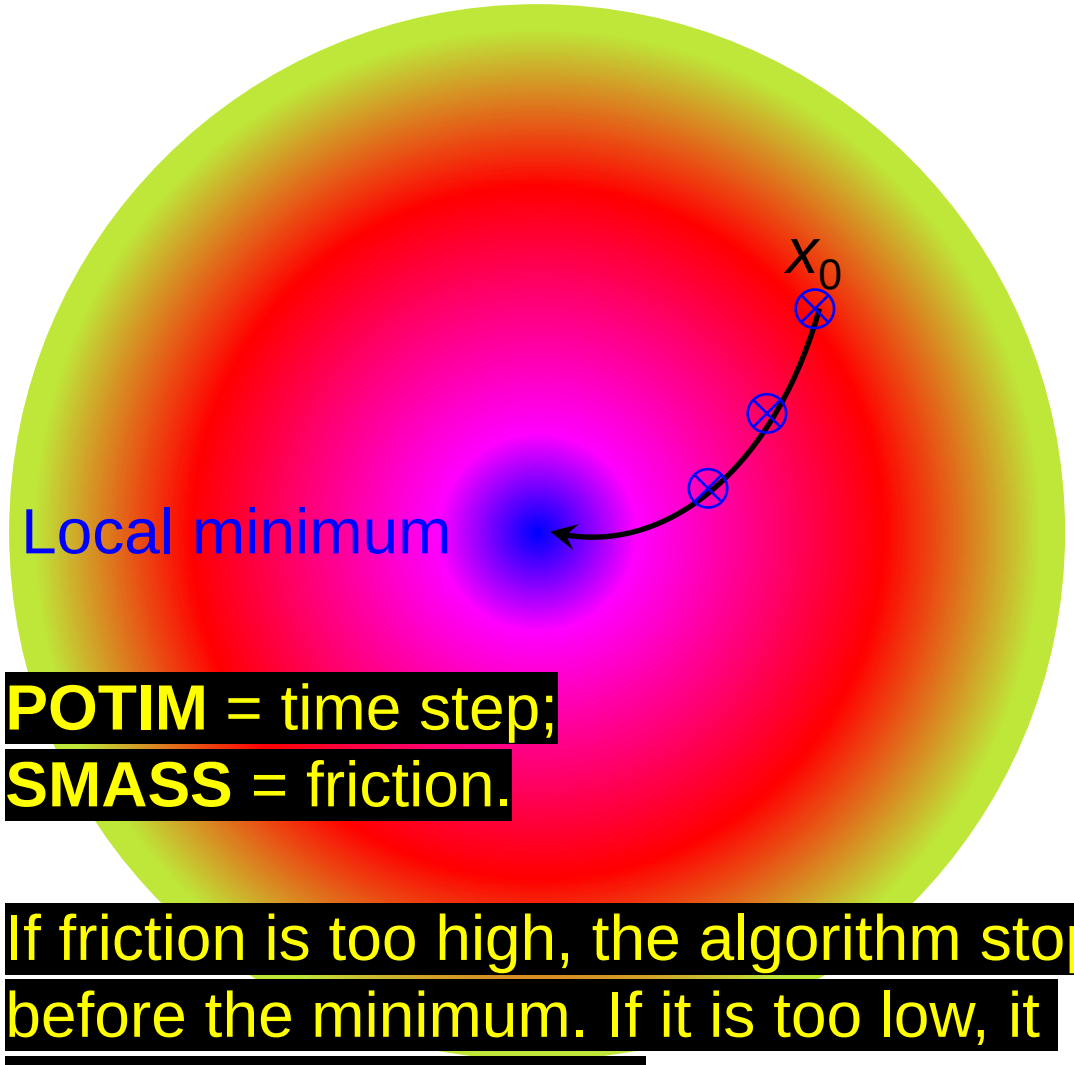


Damped molecular dynamics – IBRION = 3

Side view



Top view



POTIM = time step;
SMASS = friction.

If friction is too high, the algorithm stops before the minimum. If it is too low, it exceeds the minimum.

Handson 3

Exercises

- 3_1_Ni100clean_rel
- 3_2_Ni100clean_LDOS
- 3_3_Ni100clean_BAND
- 3_4_Ni111clean_rel
- 3_5_COonNi111_rel
- 3_6_Ni111clean_400eV
- 3_7_COonNi111_LDOS
- 3_8_COonNi111_freq

Investigations

- Most stable surface facets → most abundant in the experimental system
- Comparison with experimental surface energy;
- Bandgap;
- Density of states;
- Adsorption energy.
- Vibrational frequencies;

Handson 3

Ionic optimization of the surface

- 3_1_Ni100clean_rel
- 3_4_Ni111clean_rel

$$\gamma = \frac{1}{A}\left\{\frac{1}{2}\left[E_{\text{unrel}} - n \cdot (E_{\text{bulk}})\right] + \Delta E_{\text{rel}}\right\}$$

A = Area = $a_x \times b_y$
E_{unrel} = energy of the first ionic step
(*grep "energy w" OUTCAR | head –n 1*)
E_{rel} = energy of the last ionic step
(*grep "energy w" OUTCAR | tail –n 1*)
$\Delta E_{\text{rel}} = E_{\text{rel}} - E_{\text{unrel}}$
E_{bulk} = energy of the bulk crystal structure (2_7_fccNi_opt)
n = number of unit cell in the surface

Question:

Define the surface energies for Ni(100) and Ni(111). Which is the most stable crystalline facet between Ni(100) and Ni(111)? Compare with experimental values. Which facet is the most abundant on a Ni nanoparticle? Check paper below to answer.

Ref. 1: *Top. Catal.* **2013**, *56*, 1262–1272

Handson 3

Electronic properties

- 3_2_Ni100clean_LDOS
- 3_3_Ni100clean_BAND

- Use the CONTCAR from 3_1_Ni100clean_rel as POSCAR;
- For 3_3_Ni100clean_BAND use the CHGCAR from 3_1_Ni100clean_rel and adapt the INCAR accordingly

```
fdattila@tekla2:~/00-vasp-course/handson3/3_3_Ni100clean_BAND> cat INCAR
   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 consistence with parallel run:
    NGX =    10 ; NGY =   10 ; NGZ =   72
    NGXF=    TBD ; NGYF=   TBD ; NGZF=  TBD # Retrieve these values from the CHGCAR of 3_1_Ni100clean_rel
```

Adapt the INCAR

Check the structure of CHGCAR and retrieve these values

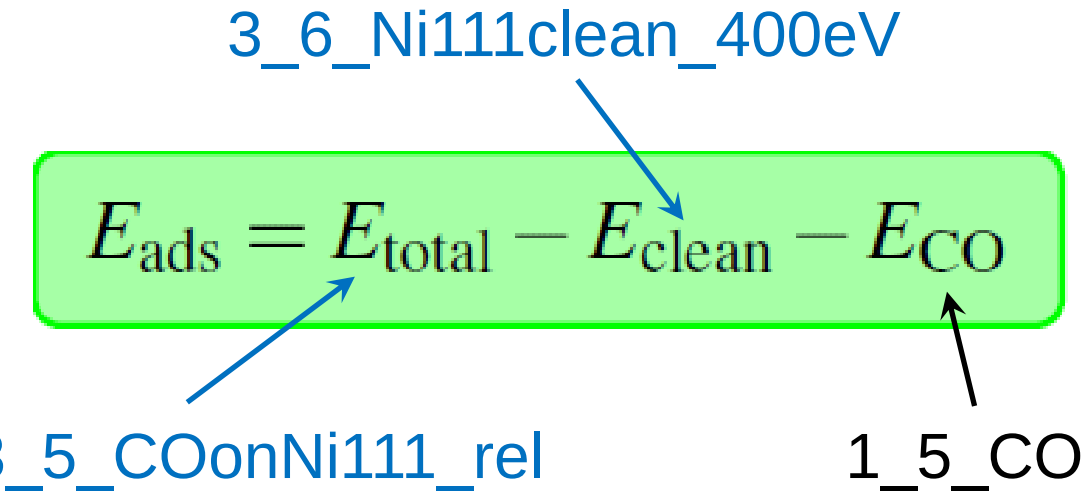
```
clean (100) nickel surface
   3.530000000000000
     0.500000    0.500000    0.000000
    -0.500000    0.500000    0.000000
     0.000000    0.000000    5.000000
   Ni
     5
Direct
  0.000000  0.000000  0.000000
  0.500000  0.500000  0.100000
  0.000000  0.000000  0.200000
  0.500000  0.500000  0.301807
  0.000000  0.000000  0.397925

  20   20  144
```

Handson 3

Adsorption energy for CO

- 3_5_COonNi111_rel
- 3_6_Ni111clean_400eV



Question:

How much is CO adsorption energy (E_{ads}) on Ni(111)? Compare with experimental values (Thermal desorption spectroscopy)

Handson 3

Exercises

- 3_7_COonNi111_LDOS
- 3_8_COonNi111_freq

- Use the CONTCAR from 3_5_COonNi111_rel as POSCAR;
- For 3_8_COonNi111_freq fix the coordinates accordingly

```
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  0.3330387119385086   F   F   F
  0.3333333300000021  0.6666666699999979  0.4445350284187818   F   F   F
  0.3333333300000021  0.6666666699999979  0.5402086464236896   F   F   T
  0.3333333300000021  0.6666666699999979  0.6031625865481731   F   F   T
```

Question:

List Ni-CO vibrational frequencies and compare with experimental values.

Handson 3

Questions:

1. Define the surface energies for Ni(100) and Ni(111). Which is the most stable crystalline facet between Ni(100) and Ni(111)? Compare with experimental values. Which facet is the most abundant on a Ni nanoparticle?

2. How much is CO adsorption energy (E_{ads}) on Ni(111)? Compare with experimental values (Thermal desorption spectroscopy)

3. List Ni-CO vibrational frequencies and compare with experimental values.

Handson 3 – copy the exercises (supercomputer)

- Enter the virtual machine (password: guest1$) or AnyDesk;
- Open a terminal: *Ctrl* + *Alt* + *t*
- Enter teklahome (from ICIQ workstation): *ssh tekla2.iciq.es*
- From outside ICIQ: enable Betelgeuse tunnel and then enter teklahome
  ssh -p2004 -X yourusername@betelgeuse.iciq.es
  ssh tekla2.iciq.es
- Make a directory *handson* and a subdirectory *3*
  mkdir handson ; mkdir handson/3
- Copy the exercises from my teklahome to yours
  cp –r /home/fdattila/00-vasp-course/handson3/ ~/handson/3*
- Enter the folder and check to have successfully copied the files
  cd handson/3 ; ls –lt ; cd ../..

Handson 3 – check the exercises

Check the VASP input (supercomputer / locally)

- Enter each simulation and check INCAR / KPOINTS
  cd handson/3 ; cd simulation-folder ; vi INCAR ; cd .. ; cd ../..

- Use the VASP manual to understand properly all the tag of the INCAR.

Handson 3 – submit simulation (supercomputer)

Only for Maryam!

- Create a bin directory and copy the rungen file
  mkdir /home/yourusername/bin ; cp –r /home/fdattila/bin/rungen ~/bin/.
- Check the file with the vi editor. Change all the fdattila to yourusername through the editor
  vi ~/bin/rungen ;
- Alternatively, replace all the fdattila in rungen with yourusername automatically
  sed –i "s/fdattila/yourusername/g" ~/bin/rungen

- Enter the handson/3 folder and create a run.sh file in each simulation to be run (e.g. 3_1_O_atom)
  cd handson/3/simulation-folder; ~/bin/rungen name-of-sim 4 4 5.3.5 ; sed –i "s/vasp_std/vasp/g" run.sh ; cd ../../..
- Enter the handson folder, check that you have INCAR, KPOINTS, POTCAR, POSCAR and run.sh, submit the simulation.
  cd handson/3/simulation-folder; qsub run.sh; cd ../../..

Tip: consider iterating the creation of run.sh file and the submission of each simulation with the for command. E.g. *cd handson/3 ; for i in 3_* ; do cd $i ; action-to-be-performed ; cd .. ; done ; cd ../..*

Handson 3 – check the VASP output (locally)

- Only if you access through virtual machine. Run the commands tunnel1 and tunnel2 in 2 terminals
  tunnel1 yourusername (terminal 1)
  tunnel2 yourusername (terminal 2)

- Open a new terminal and enter the teklahome folder
  cd ~/teklahome

- Enter a simulation and check the structure through the p4v utility
  cd handson/3 ; cd simulation-folder; p4v vasprun.xml ; cd .. ; cd ../..