EPFL THEOS THEORY AND SIMULATION OF MATERIALS QUANTUMESPRESSO

Lab 3

Advanced topics in first-principles electronic structure calculations

Marnik Bercx & Nataliya Paulish
marnik.bercx@psi.ch *nataliya.paulish@psi.ch*

Paul Scherrer Institut - École Polytechnique Fédérale de Lausanne

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Outline

1. Band structure and density of states (DOS)

2. Standard GGA vs vdW density functionals

3. Magnetic stability and phase transitions

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1. Band structure and density of states (DOS)

2. Standard GGA vs vdW density functionals

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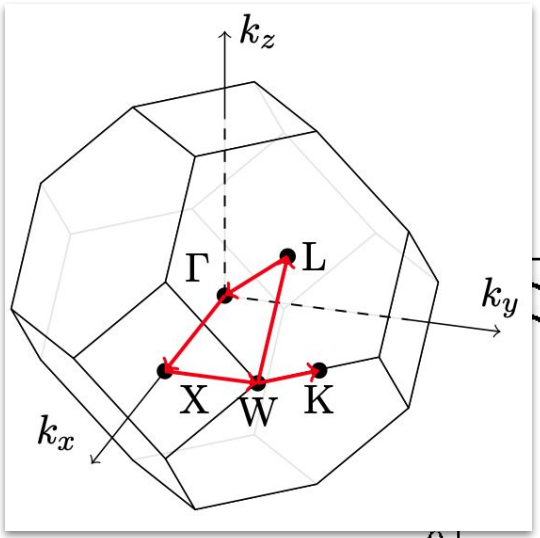
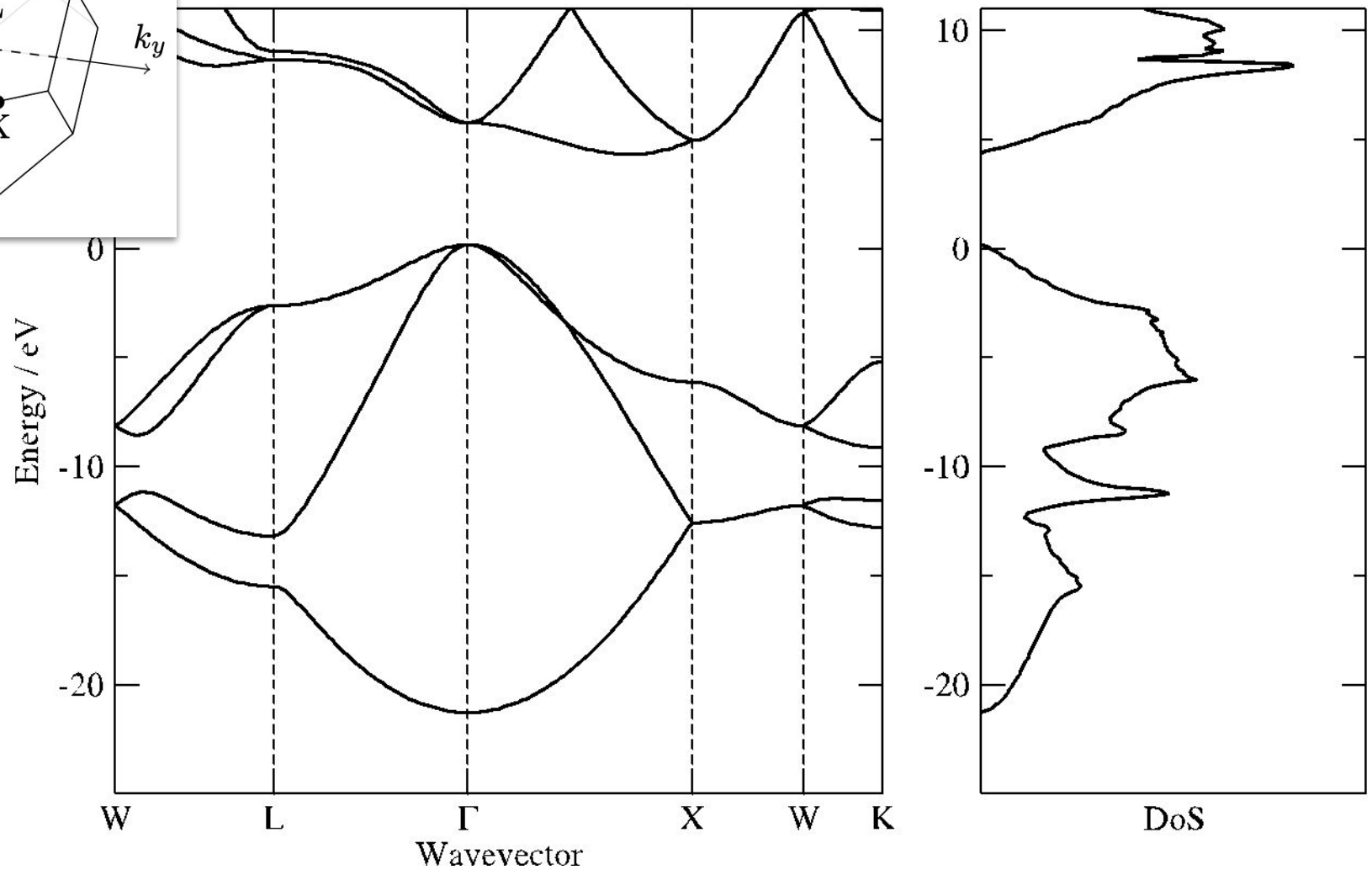
Band Structure and DOS



$$H\psi_{nk}(r) = E_n(k)\psi_{nk}(r)$$



$$D(E) = 2\frac{V}{(2\pi)^3}\sum_n \int_{\text{B.Z.}} \delta(E - E_n(k))\ dk$$

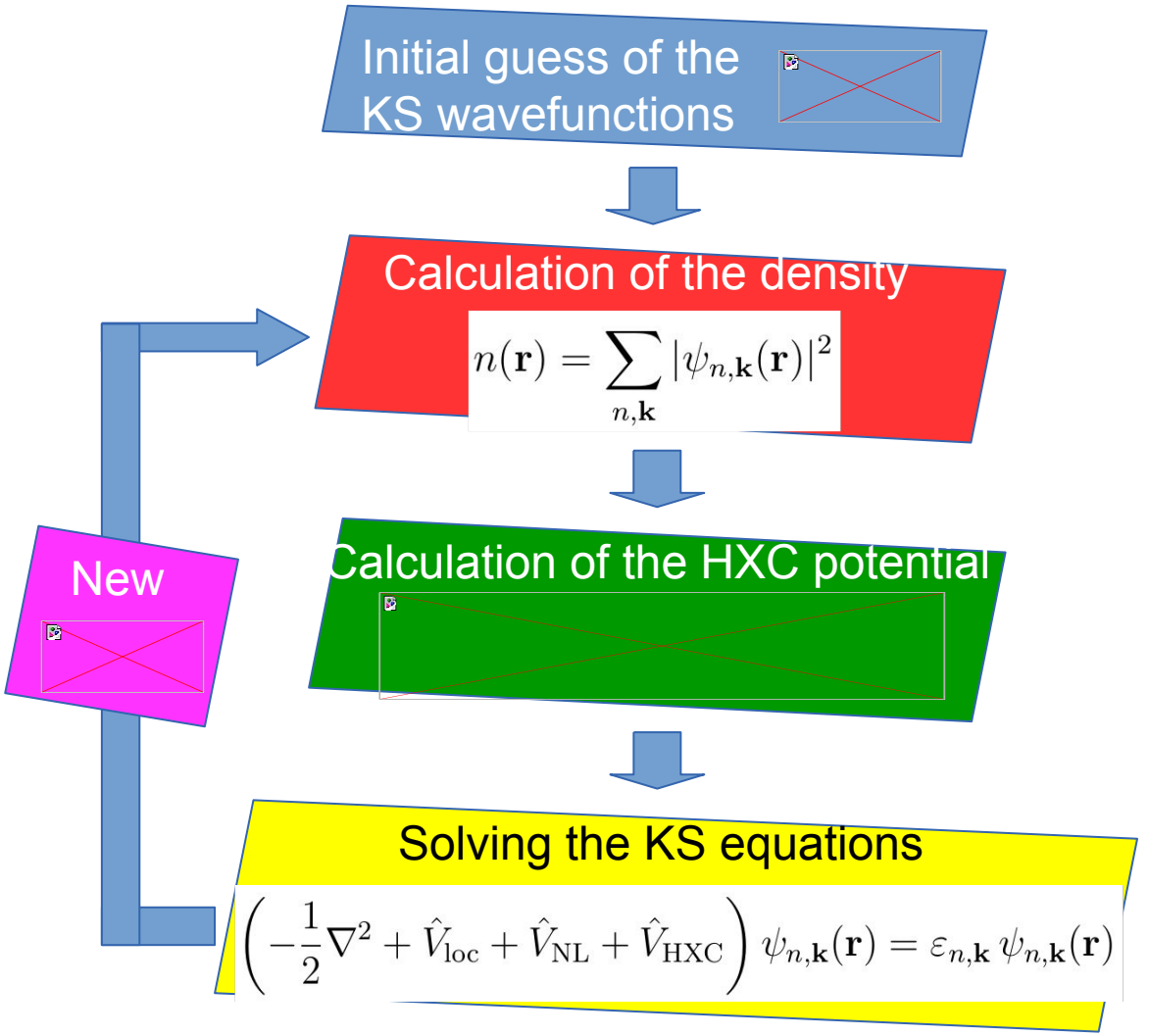
QE calculations: pseudopotentials

Preliminary step: choice of cutoffs for PP

MgO **self-consistent** calculation with **pw.x** (see e.g. **lab3/MgO/scf.in**)

```
&control
    calculation = 'scf'
    restart_mode = 'from_scratch'
    prefix = 'MgO'
    pseudo_dir = '< TO COMPLETE >'
    outdir = '../tmp'
/
&system
    ibrav = 2
    celldm(1) = 8.0374557182
    nat = 2
    ntyp = 2
    ecutwfc = < TO COMPLETE >
    ecutrho = < TO COMPLETE >
/
&electrons
    diagonalization = 'david'
    mixing_mode = 'plain'
    mixing_beta = 0.7
    conv_thr = 1.0d-8
/
ATOMIC_SPECIES
    Mg  24.0350
Mg.pbe-n-kjpaw_psl.0.3.0.UPF
    O   15.9994
O.pbe-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS (alat)
Mg      0.000000000  0.000000000
0.000000000
O       0.500000000  0.500000000
0.500000000
K_POINTS  {automatic}
 8 8 8 0 0 0
```

Self-consistent field (SCF) iterative solution of the Kohn-Sham (KS) equations:



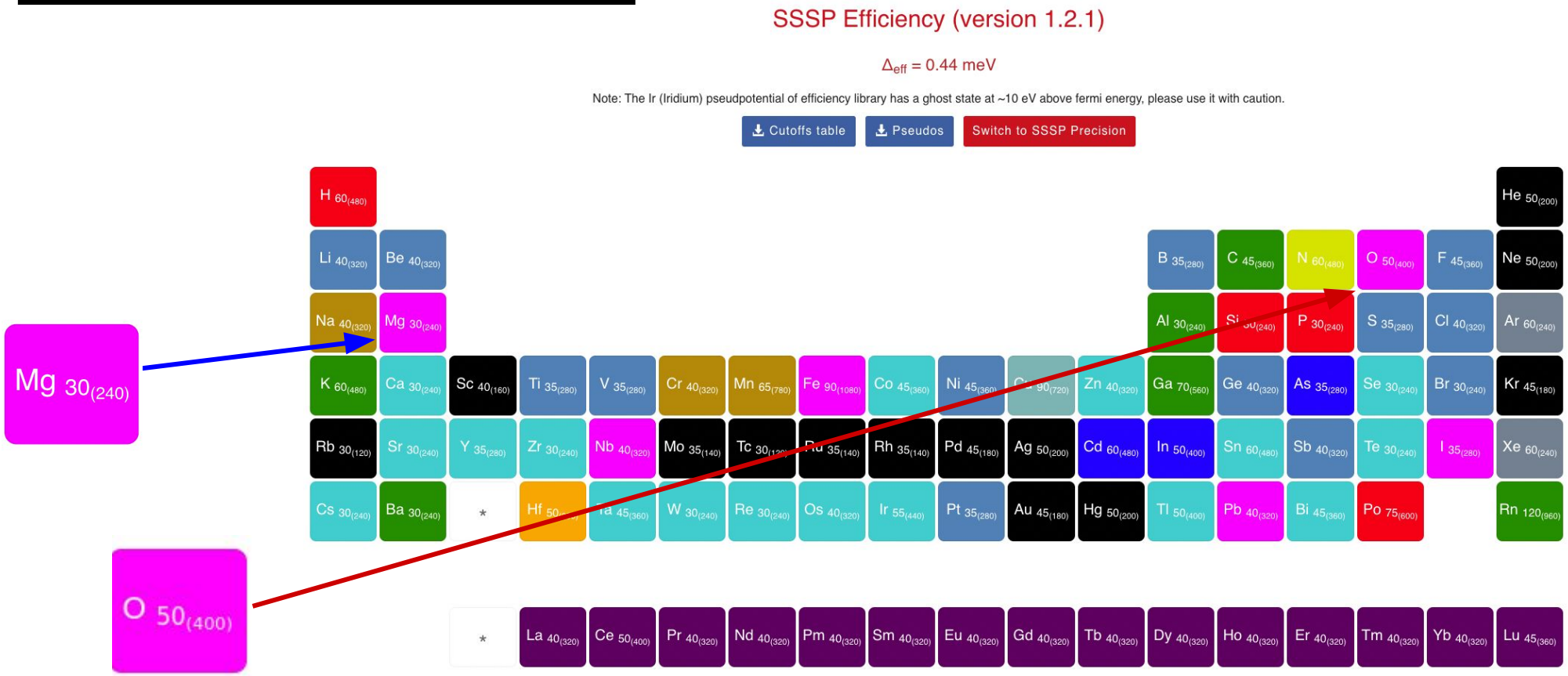
QE calculations: ultrasoft pseudopotentials

Preliminary step: choice of cutoffs for PP

MgO **self-consistent** calculation with **pw.x** (see e.g. **lab3/MgO/scf.in**)

```
&system
    ibrav = 2
    celldm(1) = 8.0374557182
    nat = 2
    ntyp = 2
    ecutwfc = < TO COMPLETE >
    ecutrho = < TO COMPLETE >
/
```

https://www.materialscloud.org/discover/sssp/table/efficiency

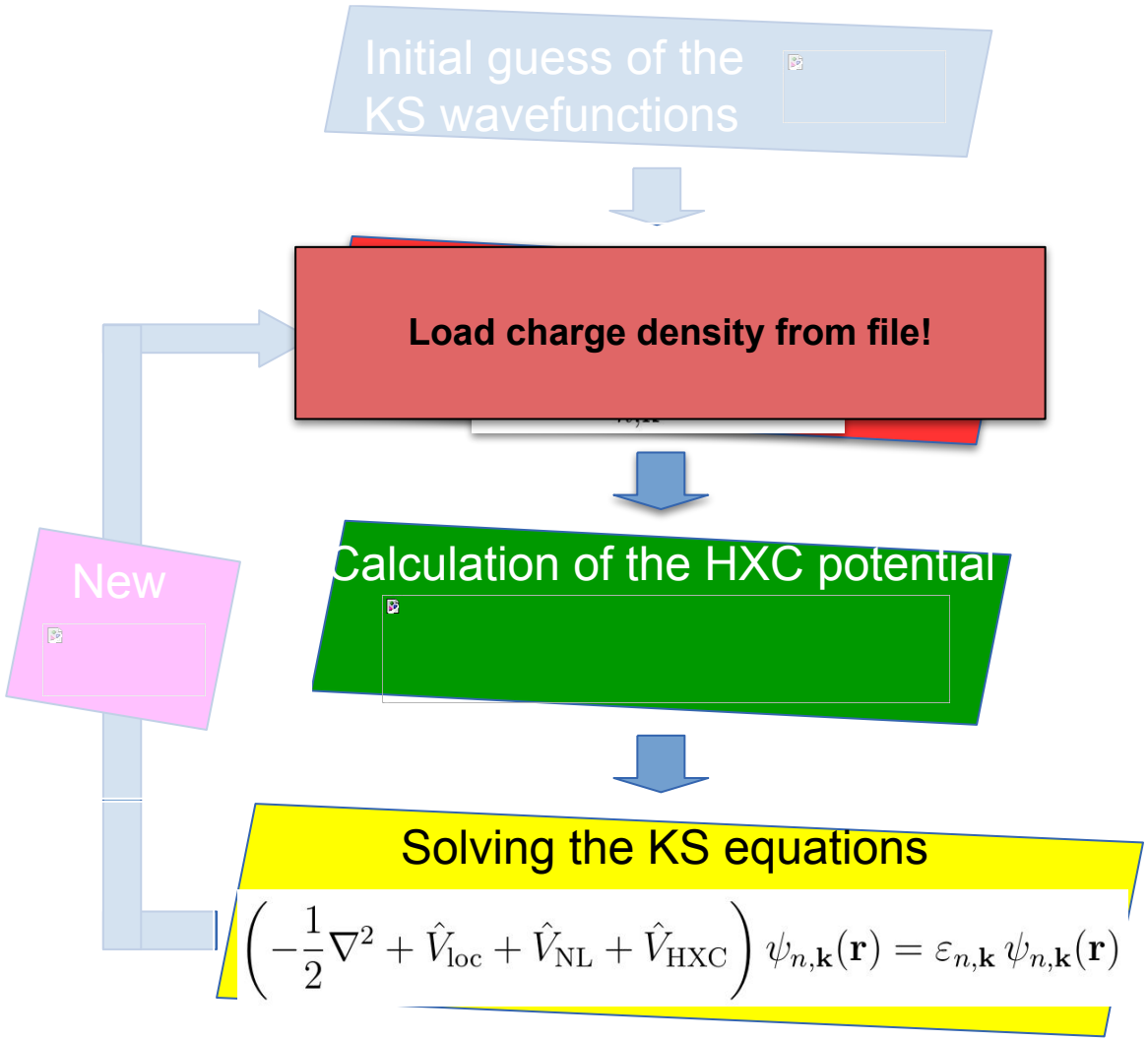


QE calculations: Band Structure and DoS (II)

The 2nd step is a **non-self-consistent** calculation with **pw.x** (see **lab3/MgO/pwbands.in**)

```
&control
    calculation = 'bands'
    restart_mode = 'from_scratch'
    prefix = 'MgO'
    pseudo_dir = '< TO COMPLETE >'
    outdir = '../tmp'
/
&system
    ibrav = 2
    celldm(1) = 8.0374557182
    nat = 2
    ntyp = 2
    ecutwfc = < TO COMPLETE >
    ecutrho = < TO COMPLETE >
    nbnd = < TO COMPLETE >
/
&electrons
    diagonalization = 'david'
    mixing_mode = 'plain'
    mixing_beta = 0.7
    conv_thr = 1.0d-8
/
ATOMIC_SPECIES
    Mg  24.0350
Mg.pbe-n-kjpaw_psl.0.3.0.UPF
    O   15.9994
O.pbe-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS (alat)
Mg      0.000000000  0.000000000
0.000000000
O       0.500000000  0.500000000
0.500000000
K_POINTS  tpiba_b
< TO COMPLETE >
```

Non-self-consistent field (NSCF) solution
of the Kohn-Sham (KS) equations from input density

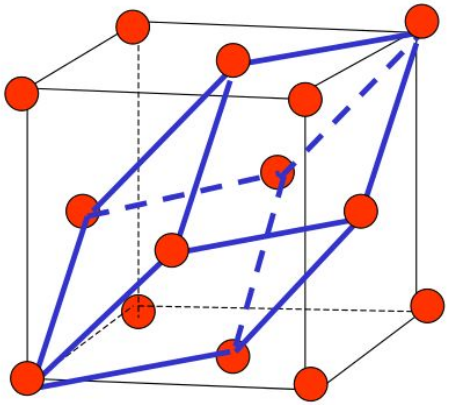


QE calculations: Band Structure and DoS (III)

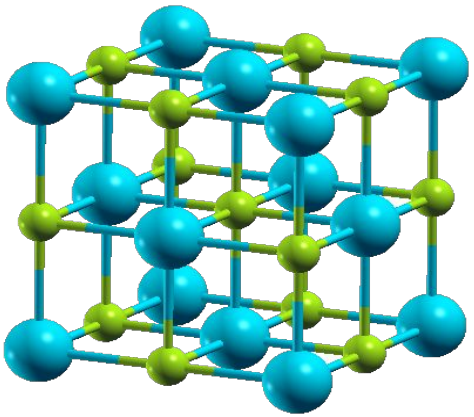
The 2nd step is a **non-self-consistent** calculation with **pw.x** (see **lab3/MgO/pwbands.in**)

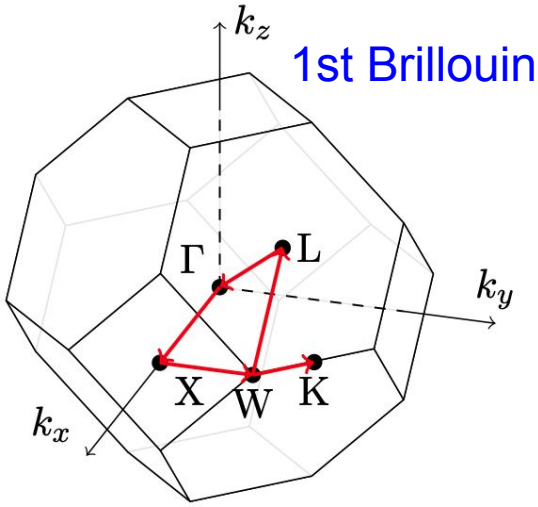
```
&control
    calculation = 'bands'
    restart_mode = 'from_scratch'
    prefix = 'MgO'
    pseudo_dir = '< TO COMPLETE >'
    outdir = '../tmp'
/
&system
    ibrav = 2
    celldm(1) = 8.0374557182
    nat = 2
    ntyp = 2
    ecutwfc = < TO COMPLETE >
    ecutrho = < TO COMPLETE >
    nbnd = < TO COMPLETE >
/
&electrons
    diagonalization = 'david'
    mixing_mode = 'plain'
    mixing_beta = 0.7
    conv_thr = 1.0d-8
/
ATOMIC_SPECIES
    Mg  24.0350
Mg.pbe-n-kjpaw_psl.0.3.0.UPF
    O   15.9994
O.pbe-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS (alat)
Mg      0.000000000  0.000000000
0.000000000
O       0.500000000  0.500000000
0.500000000
K_POINTS  tpiba_b
< TO COMPLETE >
```

FCC unit cell



MgO structure





Choose k-points along a desired path in reciprocal space

```
K_POINTS  tpiba_b
6
1.000 0.500 0.000  n1 !W
0.500 0.500 0.500  n2 !L
...
```

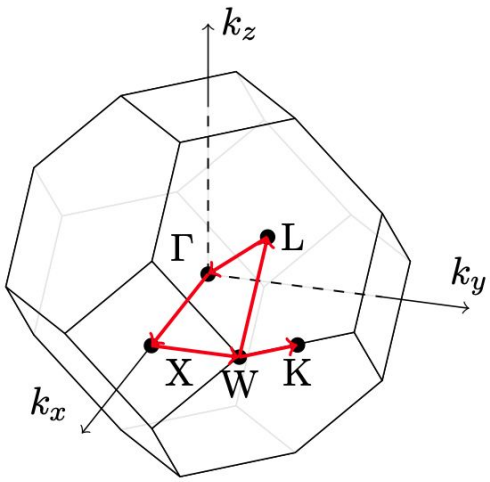
QE calculations: Band Structure and DoS (III)

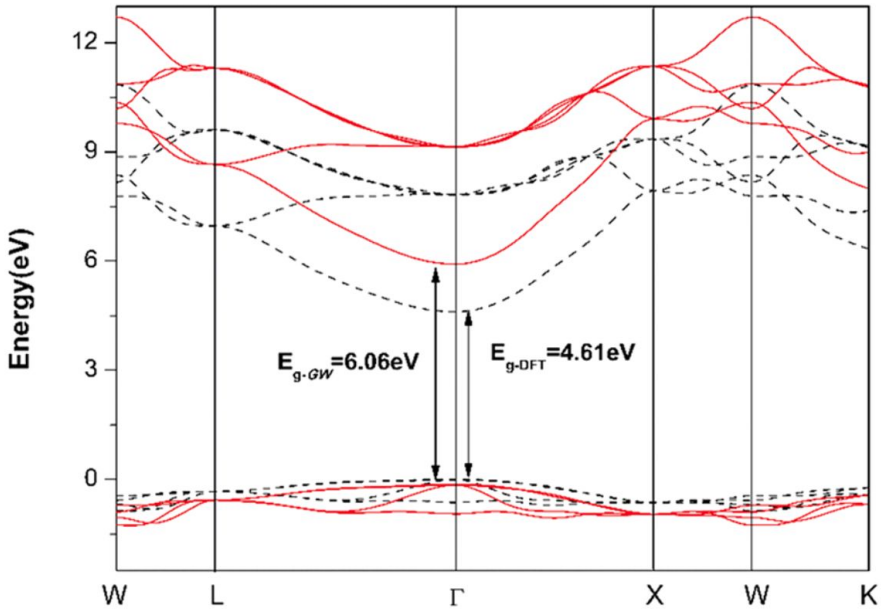
The 2nd step is a **non-self-consistent** calculation with **pw.x** (see **lab3/MgO/pwbands.in**)

```
&control
    calculation = 'bands'
    restart_mode = 'from_scratch'
    prefix = 'MgO'
    pseudo_dir = '< TO COMPLETE >'
    outdir = '../tmp'
/
&system
    ibrav = 2
    celldm(1) = 8.0374557182
    nat = 2
    ntyp = 2
    ecutwfc = < TO COMPLETE >
    ecutrho = < TO COMPLETE >
    nbnd = < TO COMPLETE >
/
&electrons
    diagonalization = 'david'
    mixing_mode = 'plain'
    mixing_beta = 0.7
    conv_thr = 1.0d-8
/
ATOMIC_SPECIES
    Mg  24.0350
Mg.pbe-n-kjpaw_psl.0.3.0.UPF
    O   15.9994
O.pbe-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS (alat)
Mg      0.000000000  0.000000000
0.000000000
O       0.500000000  0.500000000
0.500000000
K_POINTS  tpiba_b
< TO COMPLETE >
```

Post-processing steps will get you to the actual plots

```
&bands
    prefix = 'MgO'
    outdir = '../tmp'
    filband = 'MgO-bands.dat'
/
```





J. Comput. Electron **15**, 1521–1530 (2016)

QE calculations: Band Structure and DOS (IV)

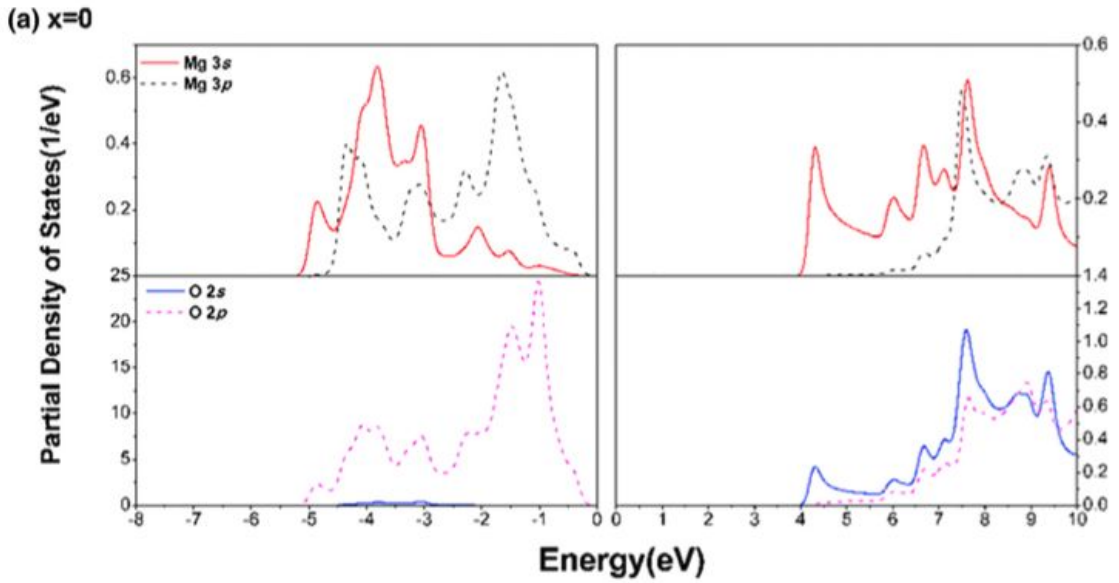
Obtaining (P)DOS starts with another type of **NSCF** calculation (see **lab3/MgO/nscf.in**)

```
&control
    calculation = 'nscf'
    prefix='MgO'
    pseudo_dir = '< TO COMPLETE >'
    outdir = '../tmp'
/
&system
    ibrav = 2
    celldm(1) = 8.0374557182
    nat = 2
    ntyp = 2
    ecutwfc = < TO COMPLETE >
    ecutrho = < TO COMPLETE >
    occupations='tetrahedra'
    nbnd = < TO COMPLETE >
/
&electrons
/
ATOMIC_SPECIES
    Mg  24.0350
Mg.pbe-n-kjpaw_psl.0.3.0.UPF
    O   15.9994
O.pbe-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS (alat)
Mg      0.000000000  0.000000000
0.000000000
O       0.500000000  0.500000000
0.500000000
K_POINTS  {automatic}
 16 16 16 0 0 0
```

Then a few post-processing steps will give the actual (P)DOS

```
&dos
    prefix = 'MgO'
    outdir = '../tmp'
    fildos = 'MgO-dos.dat'
    Emin =  0.0
    Emax = 32.0
    DeltaE = 0.1
/
```

```
&projwfc
    prefix = 'MgO'
    outdir = '../tmp'
    filpdos = 'MgO-pdos.dat'
    lwrite_overlaps = .true.
/
```



Denser k-point mesh
compared to the SCF calculation

Outline

1. Band structure and density of states (DOS)

2. Standard GGA vs vdW density functionals

3. Magnetic stability and phase transitions

Layered materials

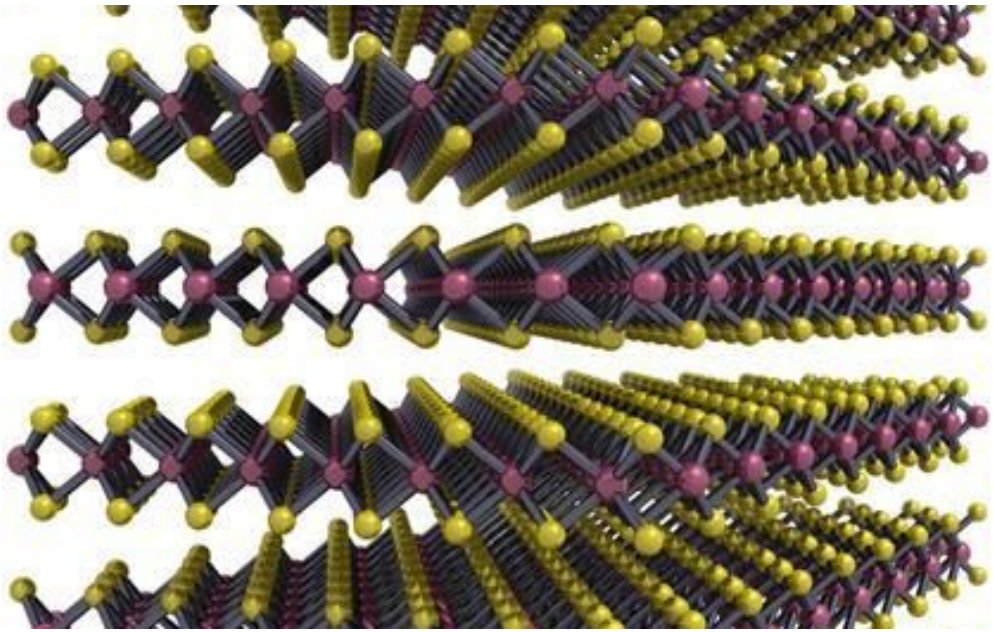
Strong chemical bonds within the layer
Between layers weak van der Waals (vdW) interactions

Behind vdW interactions are electric dipoles appearing due to charge fluctuations

=> typical $1/R^6$ decay

non-local effect => cannot be described using local (LDA) or semi-local (GGA) approximations

Molybdenum disulfide (bulk)



Layers of Mo atoms (pink), each sandwiched between two S layers (yellow)

Van der Waals Interaction in DFT

Non-local correlation term can be included in the exchange and correlation functional to correctly describe weakly-bound layered materials.

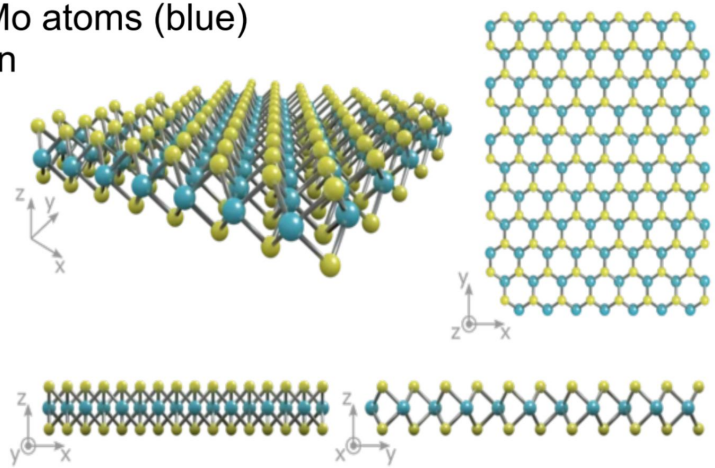
```
&control
  calculation  = 'scf'
  restart_mode = 'from_scratch'
  prefix       = 'MoS2'
  pseudo_dir   = '../PP'
  outdir       = './out'
 /
&system
  ibrav=4,
  celldm(1)= < TO COMPLETE >
  celldm(3)= < TO COMPLETE >
  nat=  6,
  ntyp= 2,
  ecutwfc = 40
  ecutrho = 600
  input_dft = 'VDW-DF2-C09',
/
&ELECTRONS
  conv_thr =   1.0000000000d-8,
  electron_maxstep = 200,
  mixing_beta =   3.0000000000d-01,
  mixing_mode = 'plain',
  startingwfc = 'atomic+random',
/
&IONS
/
K_POINTS automatic
8 8 4 0 0 0

ATOMIC_SPECIES
Mo  95.940000 Mo.pbe-spn-rrkjus-tested-pslib025.UPF
S   32.066000 S.pbe-n-rrkjus-tested-pslib025.UPF

ATOMIC_POSITIONS crystal
Mo  0.3333333333  0.6666666667  0.0000000000
S   0.6666666667  0.3333333333 -0.1278996622
S   0.6666666667  0.3333333333  0.1278996622
Mo  0.6666666667  0.3333333333  0.5000000000
S   0.3333333333  0.6666666667  0.3721003378
S   0.3333333333  0.6666666667  0.6278996622
```

Molybdenum disulfide

The crystal structure of monolayer MoS_2 showing a layer of Mo atoms (blue) sandwiched between two layers of S atoms (yellow)



- Use vdW-compliant density functional (vdW-DF)
- *"vdW_kernel_table"* file inside of PP

[Dion et al. Phys. Rev. Lett. 92, 246401 (2004)]
[Lee et al. Phys. Rev. B 82 081101 (2010)]
[Cooper V.R. Phys. Rev. B 81 161104 (2010)]

Summary of tasks

Warning: This is just a summary, tasks with all the questions to answer are formulated in the assignment document!

Geometry optimization

- **optimize in-plane lattice parameter** while keeping interlayer distance fixed to the experimental value both **with and without accounting for vdW interactions**
- using optimized in-plane lattice parameter, **optimize the interlayer distance** both **with and without vdW correction**

Band structure of bulk

- using the optimized lattice constants compute and analyse **band structure of bulk** MoS_2

Band structure of the single layer

- using appropriate inter-layer distance to simulate a single layer of MoS_2, compute **band structure of monolayer** MoS_2. **Compare** bulk and monolayer band structures

Provided materials

Folder Structure:

- Exercise 2
  - geometry_optimization
    - pbe
      - **run_pbe_loop.sh**
    - vdw
      - **run_vdw_loop.sh**
  - bands
    - **run.sh**
    - scf.in
    - bands.in
    - bandsx.in
  - single_layer
    - **run.sh**
    - scf.in
    - bands.in
    - bandsx.in
  - PP
    - pseudopotentials and vdW kernel table

Outline

1. Band structure and density of states (DOS)

2. Standard GGA vs vdW density functionals

3. Magnetic stability and phase transitions

Magnetic Stability: Cobalt

```
&control
   calculation = 'scf'
   restart_mode = 'from_scratch'
   prefix = 'Co_fcc-fm'
   tstress = .true.
   tprnfor = .true.
   outdir = '../temp/'
   pseudo_dir = '../PP/'
/
&system
   ibrav = < TO COMPLETE >
   celldm(1) = < TO COMPLETE >
   nat = 1
   ntyp = 1
   ecutwfc = 45
   ecutrho = 360
   occupations = 'smearing'
   degauss = 0.01
   smearing = 'm-v'
   nspin = < TO COMPLETE >
   starting_magnetization(1) = < TO COMPLETE >
/
&electrons
   mixing_beta = 0.7
   conv_thr = 1.0d-8
/
ATOMIC_SPECIES
Co  58.933194  Co_pbe_v1.2.uspp.F.UPF
ATOMIC_POSITIONS crystal
Co  0.0 0.0 0.0
K_POINTS automatic
   12 12 12 0 0 0
```

<u>Co is a metal</u>

Fermi level (energy of the highest occupied state) falls on a point where there is a finite density of states.

Smearing is therefore needed to integrate the resulting discontinuous functions in the BZ without having to use an incredibly dense k-mesh

Magnetic Stability: Cobalt

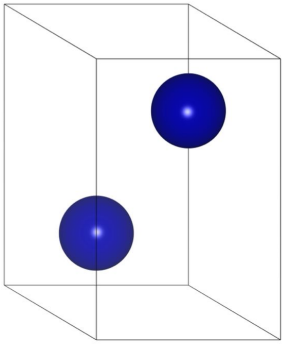
```
&control
  calculation = 'scf'
  restart_mode = 'from_scratch'
  prefix = 'Co_hcp-afm'
  tstress = .true.
  tprnfor = .true.
  outdir = '../temp/'
  pseudo_dir = '../PP/'
/
&system
  ibrav = < TO COMPLETE >
  celldm(1) = < TO COMPLETE >
  celldm(3) = < TO COMPLETE >
  nat = 2
  ntyp = 2
  ecutwfc = 45
  ecutrho = 360
  occupations = 'smearing'
  degauss = 0.01
  smearing = 'm-v'
  nspin = < TO COMPLETE >
  starting_magnetization(1) = < TO COMPLETE >
  starting_magnetization(2) = < TO COMPLETE >
/
&electrons
  mixing_beta = 0.7
  conv_thr =  1.0d-8
/
ATOMIC_SPECIES
CoU  58.933194  Co_pbe_v1.2.uspp.F.UPF
CoD  58.933194  Co_pbe_v1.2.uspp.F.UPF
ATOMIC_POSITIONS crystal
CoU  0.333333 0.666667 0.25
CoD  0.666667 0.333333 0.75
K_POINTS automatic
  12 12 6 0 0 0
```

Inputs that specify magnetic configuration

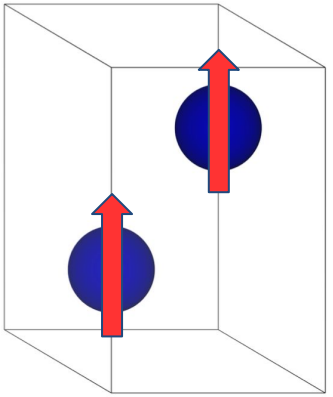
<u>Investigate magnetic ground state of Co-HCP</u>

Compare the energies of 3 magnetic configurations:

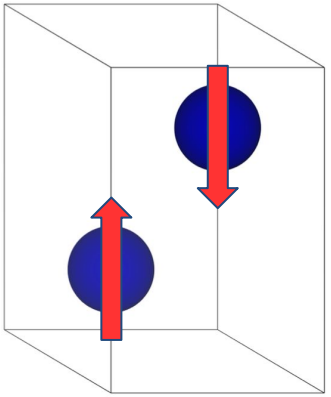
Non-magnetic



Ferromagnetic



Antiferromagnetic



Finally, calculate and compare the DoS of the non-magnetic and ferromagnetic configurations.

Plotting

- Use your favorite plotting tool (plotband.x, Python, Excel, …), as long as the plot is complete it won't affect your grade.
- Feel free to ask questions in case Quantum ESPRESSO output format is unclear!
- Example (not complete!!) plot script with Python:

```
import numpy as np
import matplotlib.pyplot as plt

bands_data = np.loadtxt('MgO-bands.dat.gnu')

plt.plot(bands_data[:, 0], bands_data[:, 1], '.')
```