



# HANDS-ON WORKSHOP ON DENSITY FUNCTIONAL THEORY

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Day 2  
02/10/2021

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# **EXERCISE 1 — STRUCTURE OPTIMIZATION**

# EXERCISE 1 — STRUCTURE OPTIMIZATION

- At a (local) minimum of a crystal structure:
  1. The forces on all atoms are 0
  2. The pressure is equal to the barostat (given) pressure
- QE has procedures for optimization (relaxation) of atomic positions and cell parameters until the above conditions are achieved

# EXERCISE 1 — STRUCTURE OPTIMIZATION

- *calculation = 'relax'* → optimize atomic positions
- *calculation = 'vc-relax'* → optimize atomic positions *and* cell parameters
  
- An optimization cycle consists of two steps:
  1. The forces and pressure are calculated from an SCF calculation
  2. The atom positions (and cell parameters) are varied using a suitable algorithm (BFGS)
  
- The above steps are repeated until the various convergence thresholds are satisfied:
  - Look at *etot\_conv\_thr*, *forc\_conv\_thr* and *press\_conv\_thr* in [pw.x documentation](#)

## **EXERCISE 2 – PHONONS**

# EXERCISE 2 — PHONONS

➤ This exercise consists of two examples:

1. Calculating the phonon frequencies at  $\Gamma$  point and determining LO-TO splitting
2. Plotting the phonon dispersion and DOS

➤ The basic program for phonon calculations is [ph.x](#)

➤ An additional program [dynmat.x](#) is used for (e.g.) calculating LO-TO splitting

➤ Programs *q2r.x* and *matdyn.x* are used for interatomic force constant calculations

## EXERCISE 2 – PHONONS ( $\Gamma$ )

```
freq ( 1) = -0.196663 [THz] = -6.559986 [cm-1]
freq ( 2) = -0.196663 [THz] = -6.559986 [cm-1]
freq ( 3) = -0.196663 [THz] = -6.559986 [cm-1]
freq ( 4) = 4.549038 [THz] = 151.739587 [cm-1]
freq ( 5) = 4.549038 [THz] = 151.739587 [cm-1]
freq ( 6) = 4.549038 [THz] = 151.739587 [cm-1]
```

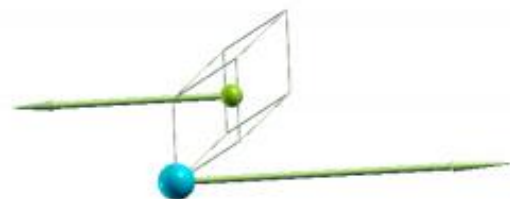
- We have  $3 * N_{atoms}$  frequencies, one per displacement
- Small (negative) values of the 3 acoustic modes are numerical artefacts (can be regarded as 0)
- The optical modes are degenerate  $\rightarrow$  should not happen for an ionic crystal such as NaCl

## EXERCISE 2 – PHONONS ( $\Gamma$ )

- After adding the non-analytical term to the dynamical matrix and imposing the acoustic sum rule:

```
freq ( 1) = -0.000000 [THz] = -0.000000 [cm-1]
freq ( 2) = 0.000000 [THz] = 0.000003 [cm-1]
freq ( 3) = 0.000000 [THz] = 0.000003 [cm-1]
freq ( 4) = 4.555892 [THz] = 151.968191 [cm-1]
freq ( 5) = 4.555892 [THz] = 151.968191 [cm-1]
freq ( 6) = 7.399029 [THz] = 246.805025 [cm-1]
```

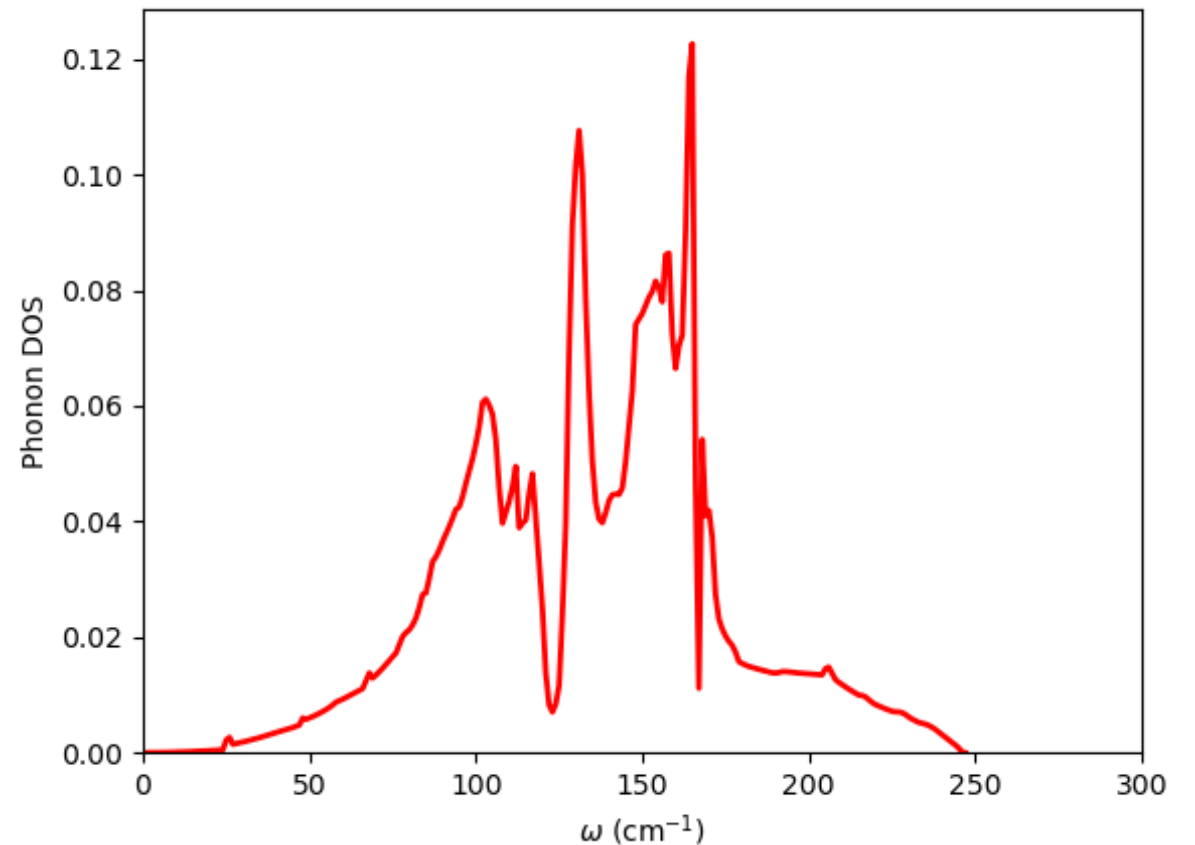
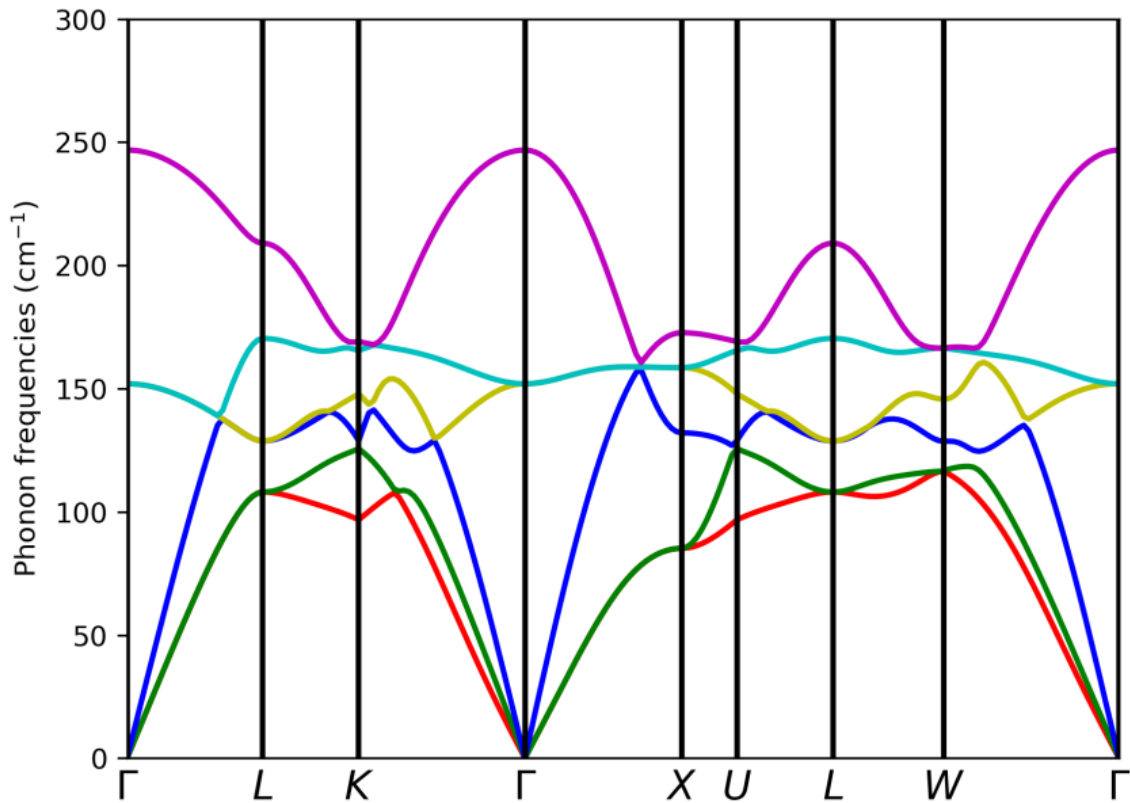




# EXERCISE 2 — PHONONS (DISPERSION & DOS)

- Phonon frequencies for any wavenumber can be calculated in two ways:
  1. Explicitly list a path in 1 BZ at the end of *ph.x* input file and calculate as we did for  $\Gamma$
  2. Calculate frequencies for a finite wavenumber grid and extract interatomic force constants (IFC)
- Method 1 is rather slow
- Once IFCs are known, calculating frequencies at any wavenumber is very fast

# EXERCISE 2 – PHONONS (DISPERSION & DOS)



## **EXERCISE 3 — MAGNETIC SYSTEMS**

# EXERCISE 3 — MAGNETIC SYSTEMS

➤ This exercise consists of two examples:

1. Ferromagnetic system (Fe)
2. Antiferromagnetic system (NiO)

➤ The total charge density becomes a sum of densities of subsystems with different spins

➤ Calculations on magnetic systems take *at least* twice as long compared to nonmagnetic

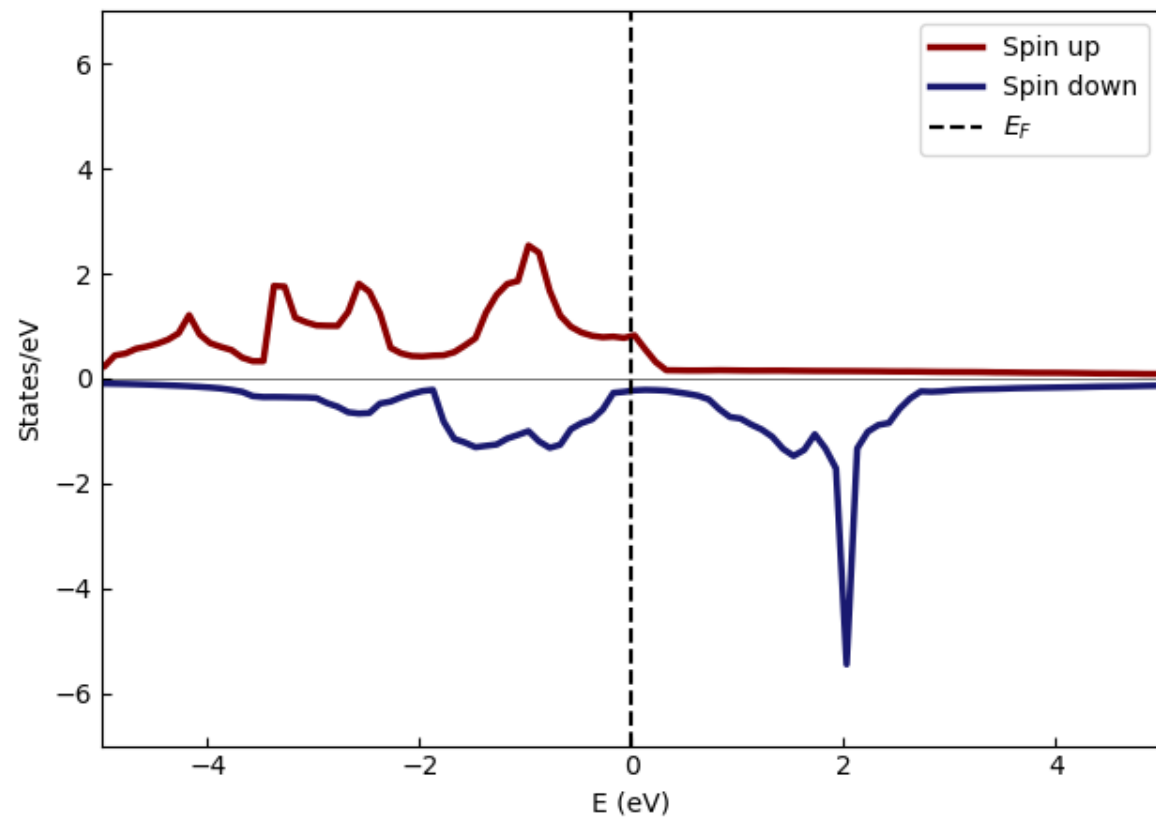
# EXERCISE 3 — MAGNETIC SYSTEMS (FM)

- Notice the appearance of two new variables in the SCF input file:
  1. *nspin* = tell QE to make a spin polarized calculation
  2. *starting\_magnetization(i)* = starting spin polarization on atomic type *i*
- SCF calculation will determine the final value of the magnetic moment
- The magnetic moment can also be fixed with the *tot\_magnetization* variable

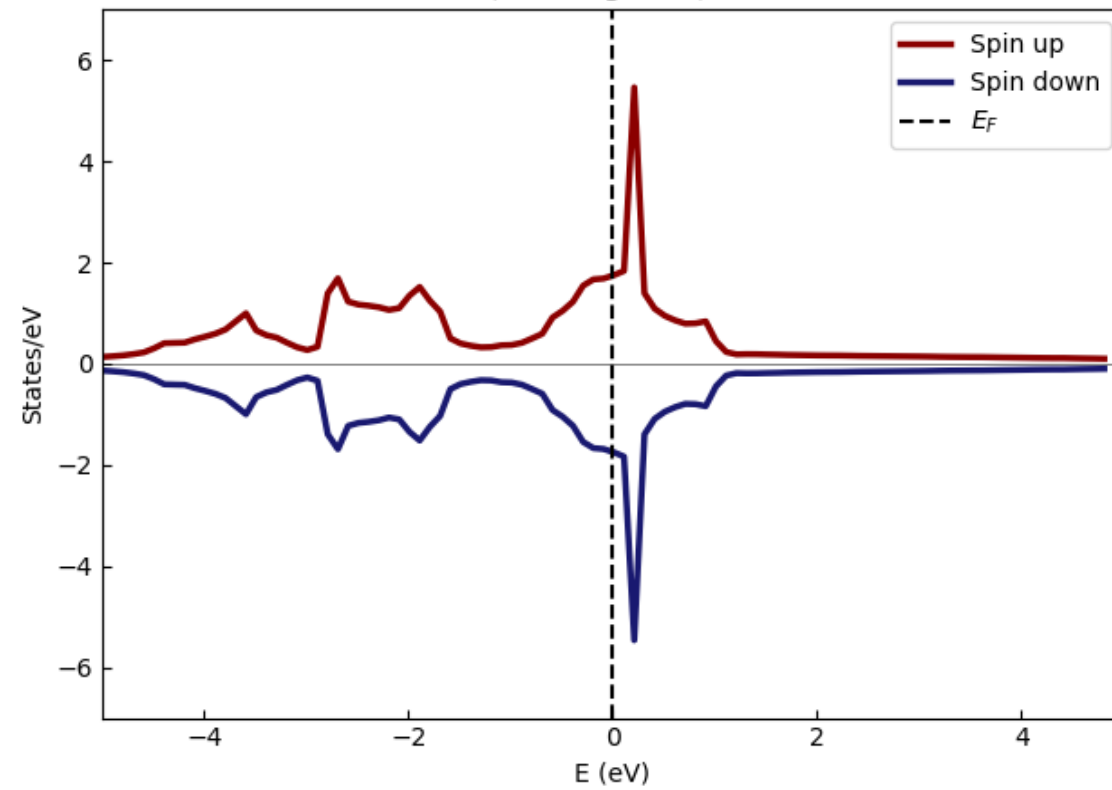
## EXERCISE 3 — MAGNETIC SYSTEMS (FM)

- k-points are written twice in the output because they are separately calculated for the two subsystems
- The total and absolute magnetization are now written in the output files
- If we put *starting\_magnetization(1)* = 0.0 we always end up with a nonmagnetic state
- The magnetic state is lower in energy by 0.04 Ry

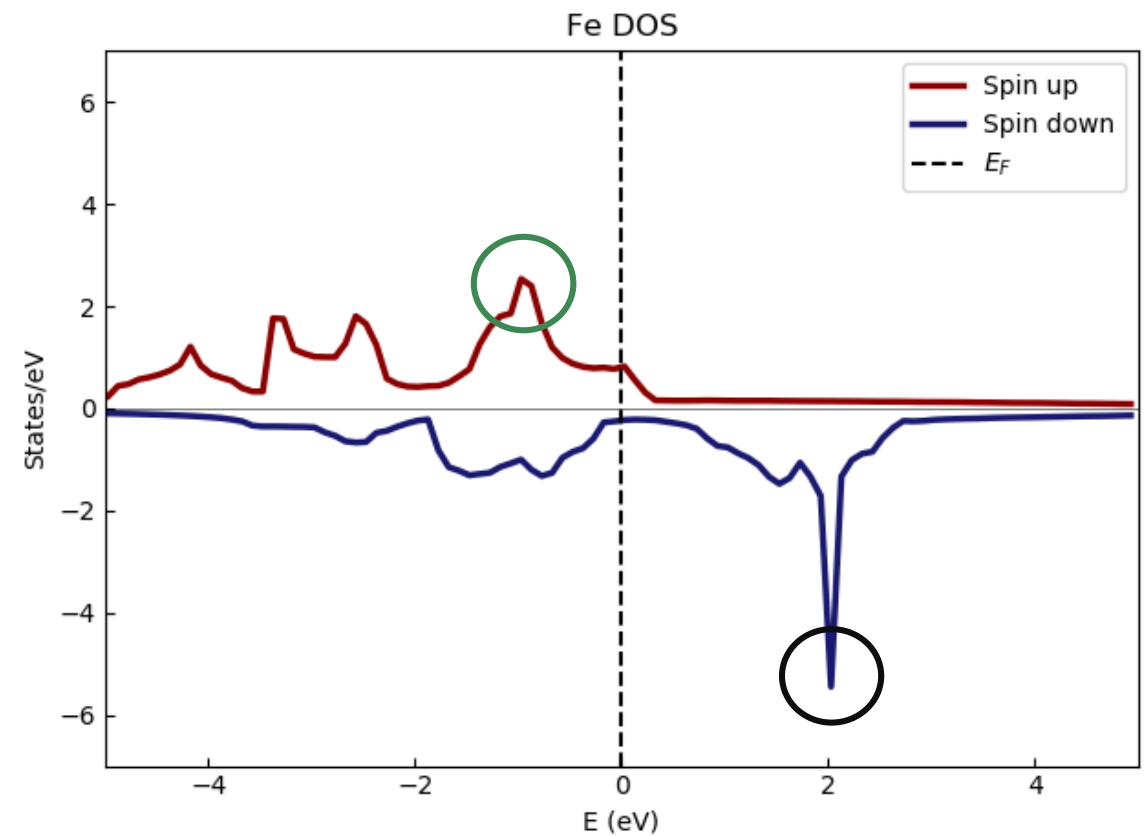
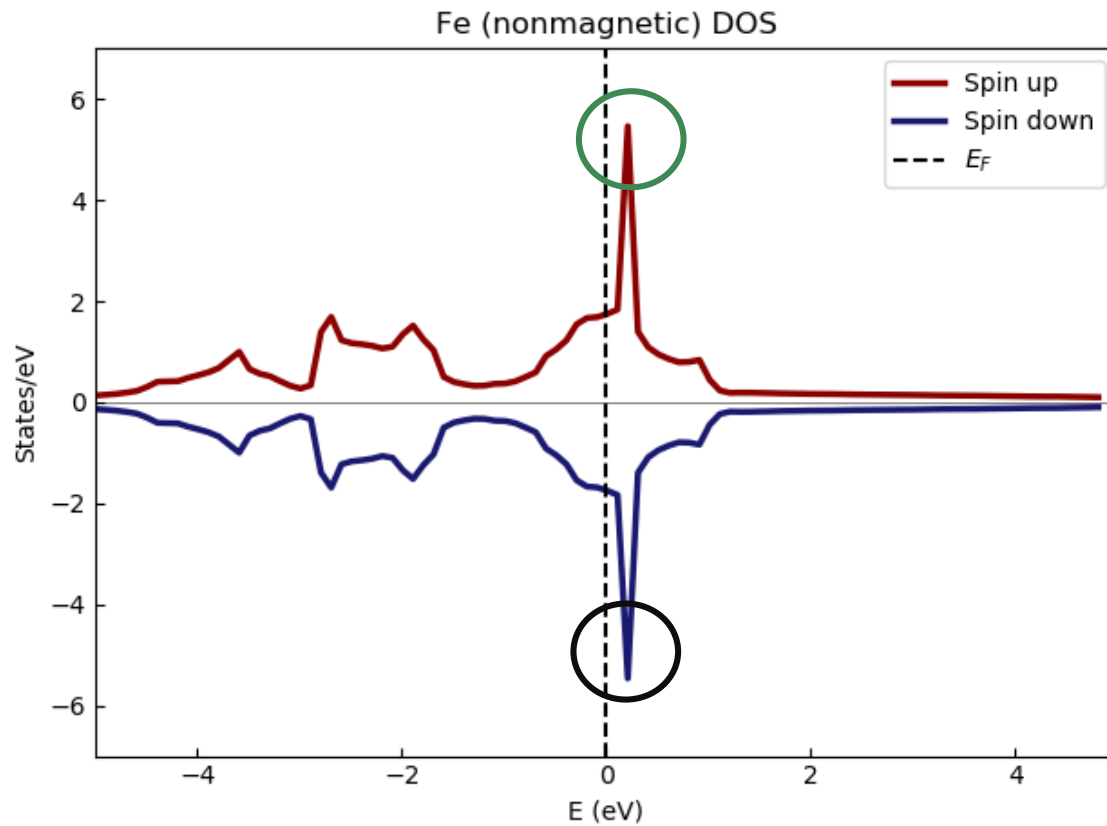
Fe DOS



Fe (nonmagnetic) DOS







- Hund rule: some d-orbitals of an isolated Fe atom are occupied only with electrons of the same spin orientation (broken spin degeneracy of the d-orbitals)
- Let's see how the crystal field (other Fe atoms) affects the d-orbitals hybridization

## EXERCISE 3 — MAGNETIC SYSTEMS (FM)

- Kohn-Sham wave functions can be projected onto localized atomic orbitals using [projwfc.x](#)
- The orbitals are read from the pseudopotential files

Atomic states used for projection  
(read from pseudopotential files):

```
state # 1: atom 1 (Fe ), wfc 1 (l=0 m= 1)
state # 2: atom 1 (Fe ), wfc 2 (l=1 m= 1)
state # 3: atom 1 (Fe ), wfc 2 (l=1 m= 2)
state # 4: atom 1 (Fe ), wfc 2 (l=1 m= 3)
state # 5: atom 1 (Fe ), wfc 3 (l=2 m= 1)
state # 6: atom 1 (Fe ), wfc 3 (l=2 m= 2)
state # 7: atom 1 (Fe ), wfc 3 (l=2 m= 3)
state # 8: atom 1 (Fe ), wfc 3 (l=2 m= 4)
state # 9: atom 1 (Fe ), wfc 3 (l=2 m= 5)
state # 10: atom 1 (Fe ), wfc 4 (l=0 m= 1)
state # 11: atom 1 (Fe ), wfc 5 (l=1 m= 1)
state # 12: atom 1 (Fe ), wfc 5 (l=1 m= 2)
state # 13: atom 1 (Fe ), wfc 5 (l=1 m= 3)
```

```
k = 0.0000000000 0.0000000000 0.0000000000
```

```
==== e( 1) = -70.05016 eV ====
```

```
psi = 0.954*[# 1]+0.046*[# 10]
```

```
|psi|^2 = 1.000
```

```
==== e( 2) = -35.84389 eV ====
```

```
psi = 0.009*[# 2]+0.009*[# 3]+0.009*[# 4]
```

```
|psi|^2 = 0.026
```

```
==== e( 3) = -35.84389 eV ====
```

```
psi = 0.641*[# 2]+0.641*[# 3]+0.641*[# 4]+0.011*[# 11]+0.011*[# 12]
+0.011*[# 13]
```

```
|psi|^2 = 1.954
```

```
==== e( 4) = -35.84389 eV ====
```

```
psi = 0.334*[# 2]+0.334*[# 3]+0.334*[# 4]+0.006*[# 11]+0.006*[# 12]
+0.006*[# 13]
```

```
|psi|^2 = 1.019
```

```
==== e( 5) = 9.60552 eV ====
```

```
psi = 0.954*[# 10]+0.046*[# 1]
```

```
|psi|^2 = 1.000
```

```
==== e( 6) = 15.75113 eV ====
```

```
psi = 0.331*[# 6]+0.331*[# 7]+0.331*[# 9]
```

```
|psi|^2 = 0.994
```

```
==== e( 7) = 15.75113 eV ====
```

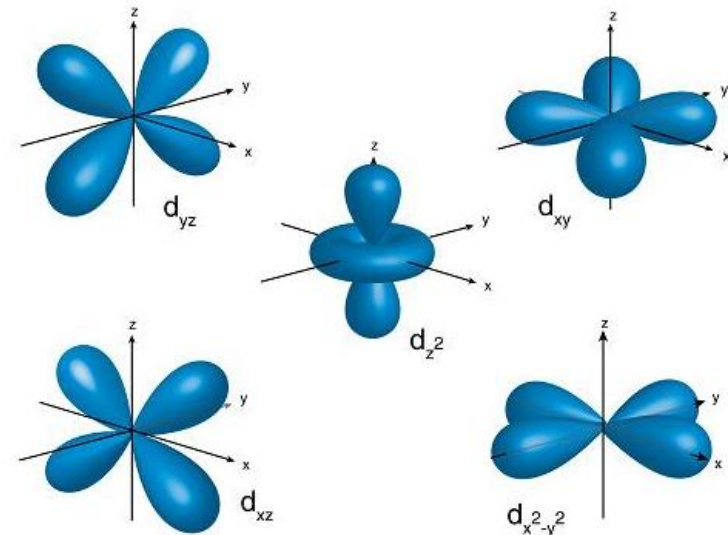
```
psi = 0.331*[# 6]+0.331*[# 7]+0.331*[# 9]
```

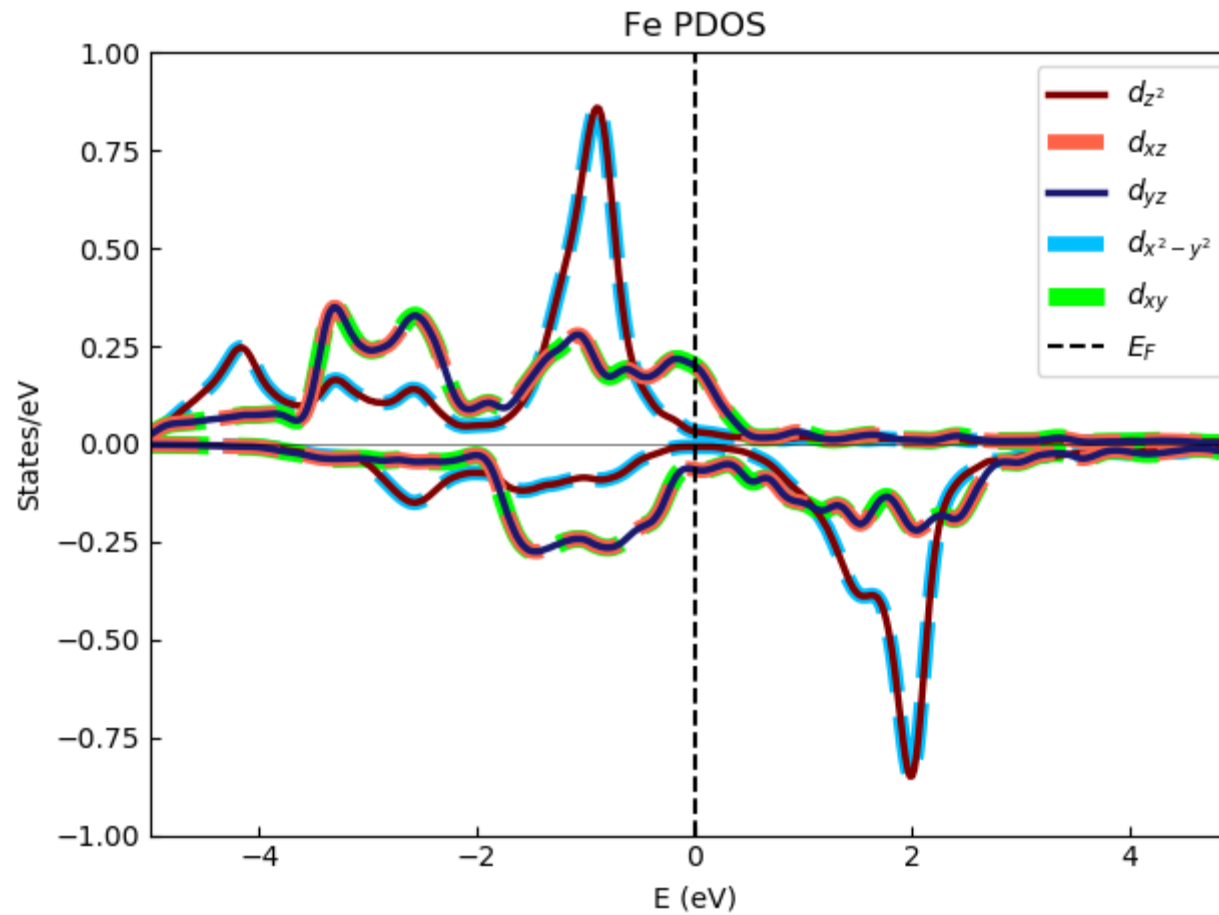
```
|psi|^2 = 0.994
```

# EXERCISE 3 — MAGNETIC SYSTEMS (FM)

- We are interested in d-orbitals ( $l = 2$ )
- In *PDOS/Fe.pdos\_atm#1 (Fe)\_wfc#3(d)* the projected density of states (PDOS(E)) is written for spin-up and spin-down components in the order:

1.  $d_{z^2}$
2.  $d_{xz}$
3.  $d_{yz}$
4.  $d_{x^2-y^2}$
5.  $d_{xy}$





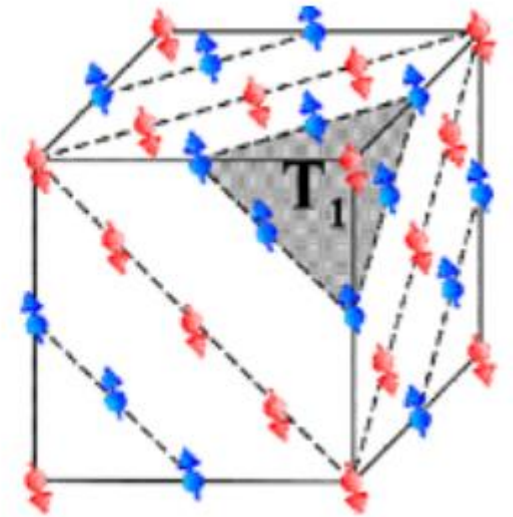
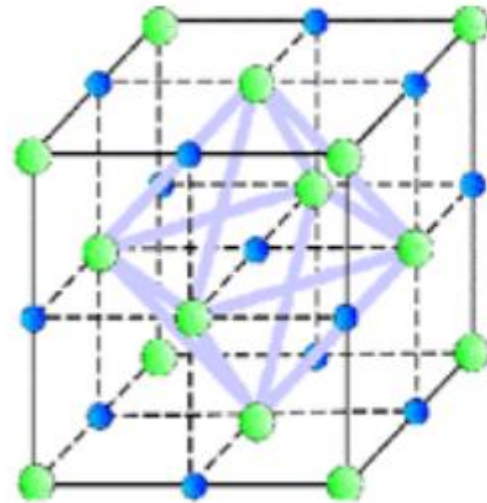
- $d_{z^2}$  and  $d_{x^2-y^2}$  are weakly hybridized (sharp peaks) so the Hund rules break spin degeneracy
- The other orbitals are strongly hybridized (wide peaks) because they point towards the other Fe atoms at the vertices of the BCC cube

# EXERCISE 3 — MAGNETIC SYSTEMS (AFM)

- **Note:** The calculations in this exercise (*ex2.afm*) take quite some time
- The results are therefore already prepared in the *reference* directory
- Following the instructions in *README.md*, you can copy those results and take a look at the input/output files

# EXERCISE 3 — MAGNETIC SYSTEMS (AFM)

- The Ni ions of the NiO crystal have alternating magnetic moment
- We have to treat them as different atom types with the same pseudopotential but different *starting\_magnetization*



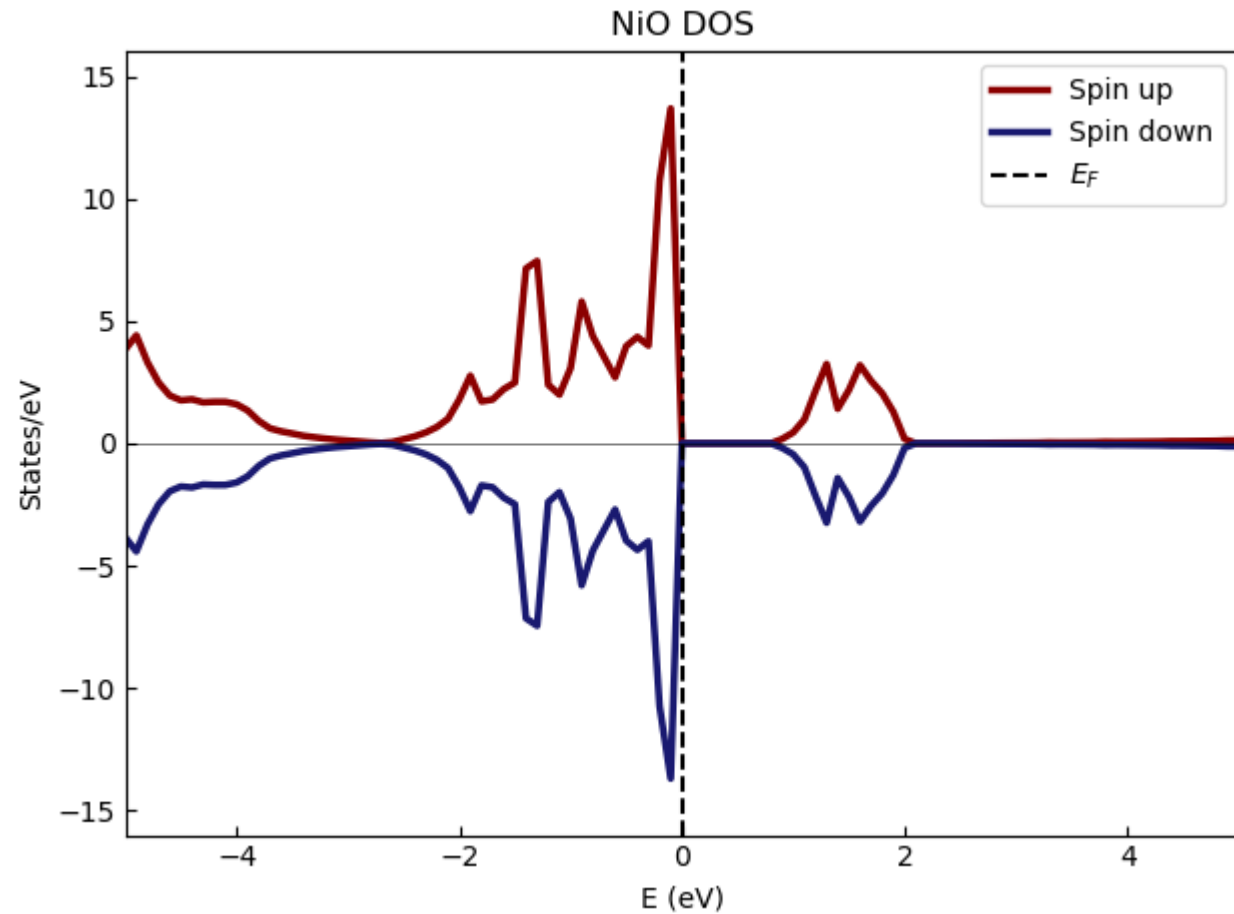
## EXERCISE 3 — MAGNETIC SYSTEMS (AFM)

```
Magnetic moment per site (integrated on atomic sphere of radius R)
atom  1 (R=0.206)  charge=  5.6606  magn= -0.0000
atom  2 (R=0.206)  charge=  5.6606  magn= -0.0000
atom  3 (R=0.206)  charge= 15.6783  magn=  1.3342
atom  4 (R=0.206)  charge= 15.6783  magn= -1.3342
```



# EXERCISE 3 — MAGNETIC SYSTEMS (AFM)

- The gap is about  $\sim 0.84$  eV
- The experimental gap is 3.6-4 eV
- A significant discrepancy!



# EXERCISE 3 – MAGNETIC SYSTEMS (AFM)

- The problem arises because PBE (GGA/LDA in general) underestimates band gaps
- Ways to deal with insulators/semiconductors:
  1. Band insulators (gap due to crystal potential) – GW approximation (YAMBO)
  2. Strongly correlated systems (Mott/charge-transfer insulators) – **DFT+U**
- A term representing the repulsion between electrons of different spins is added to the functional
- DFT+U favours integer orbital occupancy (localization)

Fundamental issues of DFT band gap calculations

*Physical Review B 44.3 (1991): 943.*

*Physical Review B 48.23 (1993): 16929.*

*Physical Review B 52.8 (1995): R5467*

# EXERCISE 3 — MAGNETIC SYSTEMS (AFM)

- DFT+U is included in the SCF calculation by the *lda\_plus\_u* and *Hubbard\_U(i)* variables
- Hubbard correction is applied to the states defined in *Modules/set\_hubbard\_n.f90* and *Modules/set\_hubbard\_l.f90*
- The values of *Hubbard\_U(i)* need to be separately computed:
  1. *Physical Review B* 71.3 (2005): 035105.
  2. *Physical Review B* 84.11 (2011): 115108

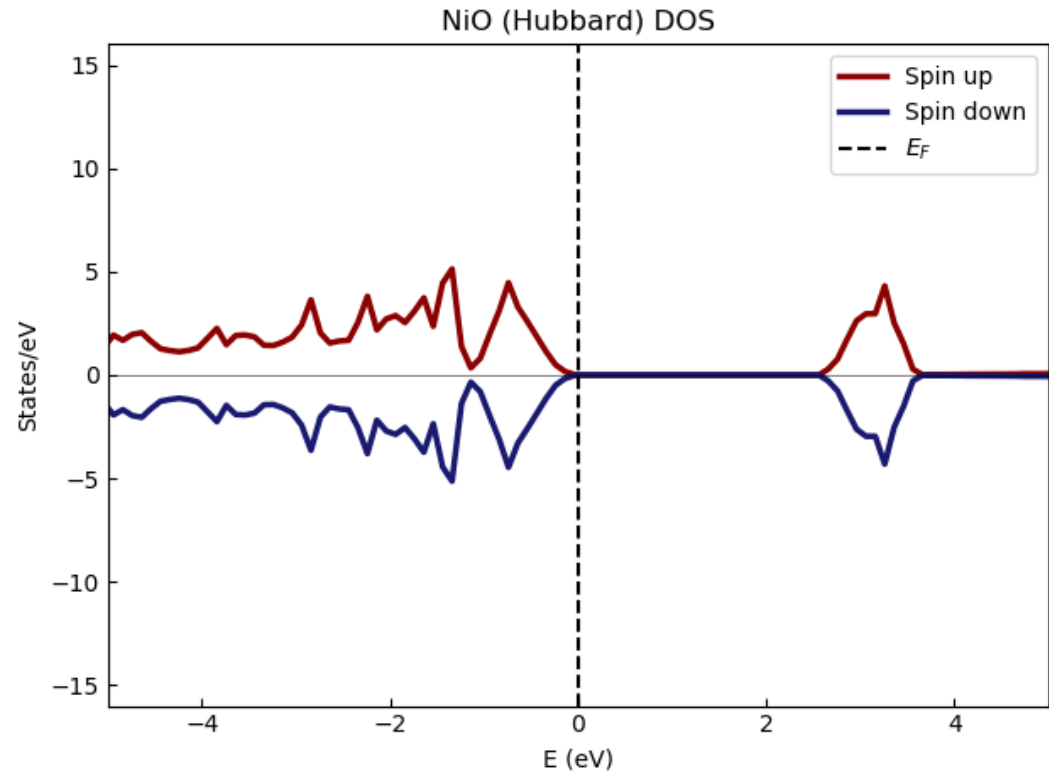
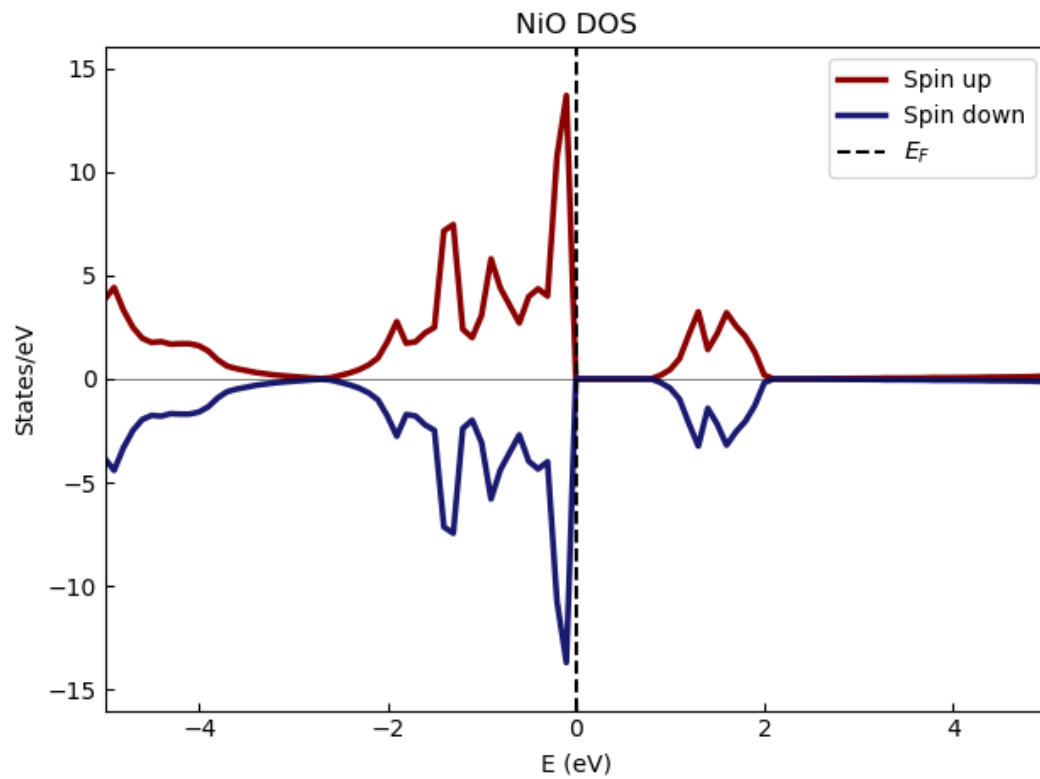
Fundamental issues of DFT band gap calculations

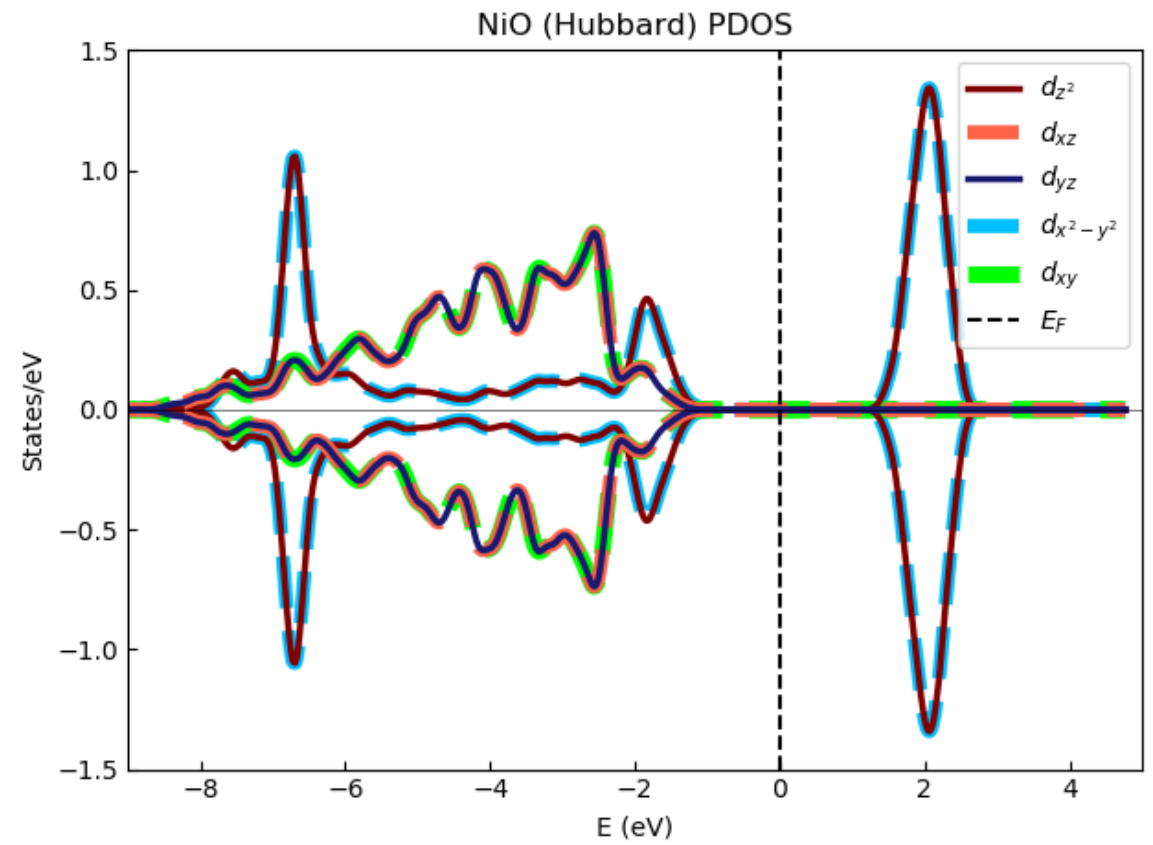
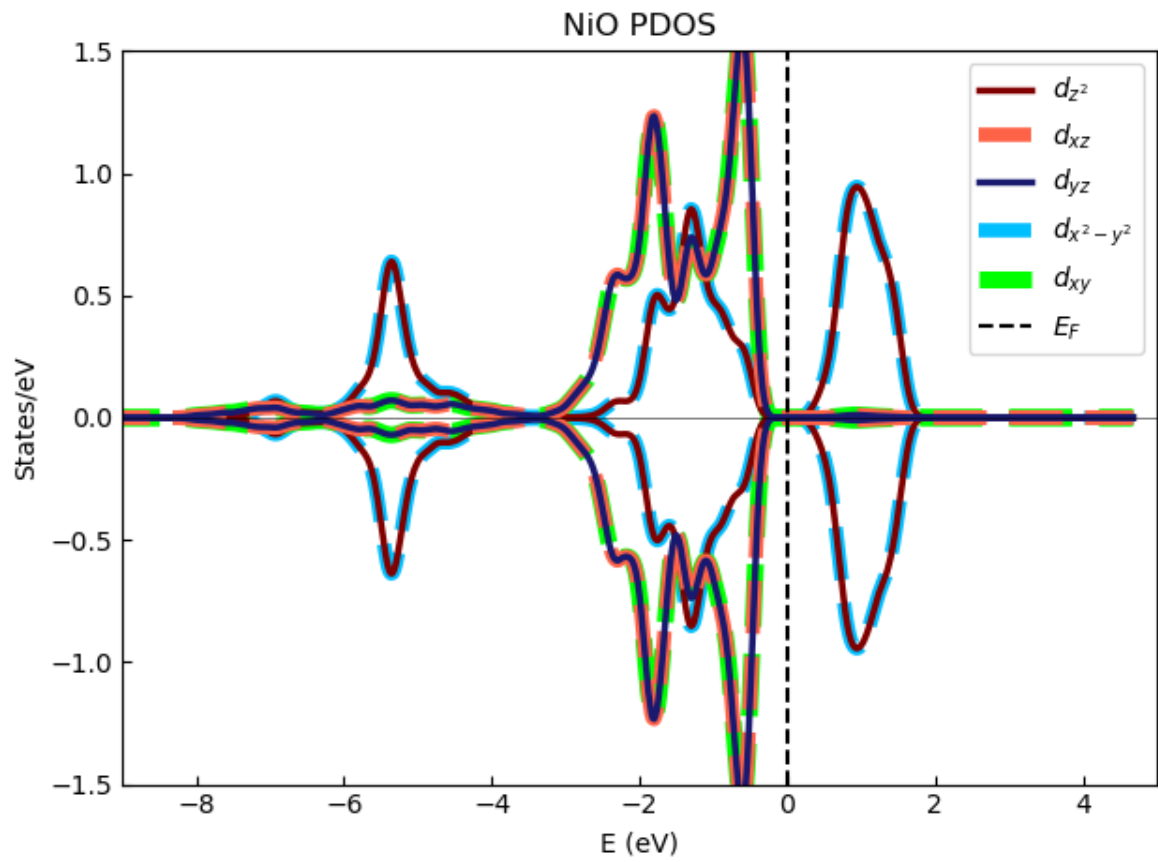
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# EXERCISE 3 — MAGNETIC SYSTEMS (AFM)

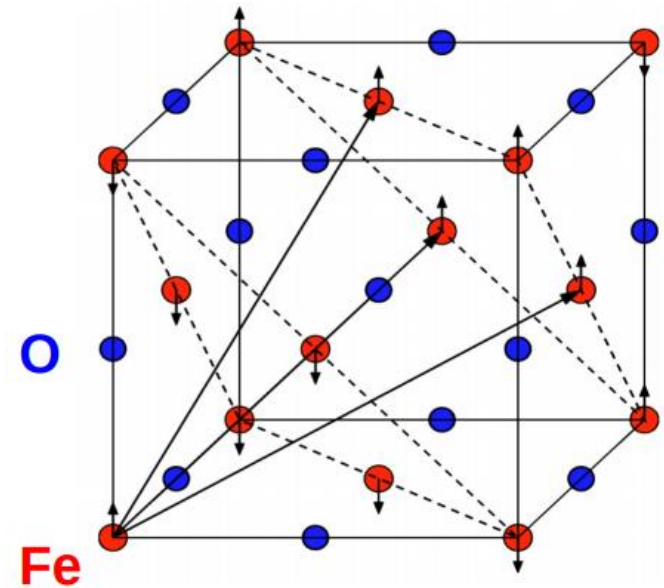




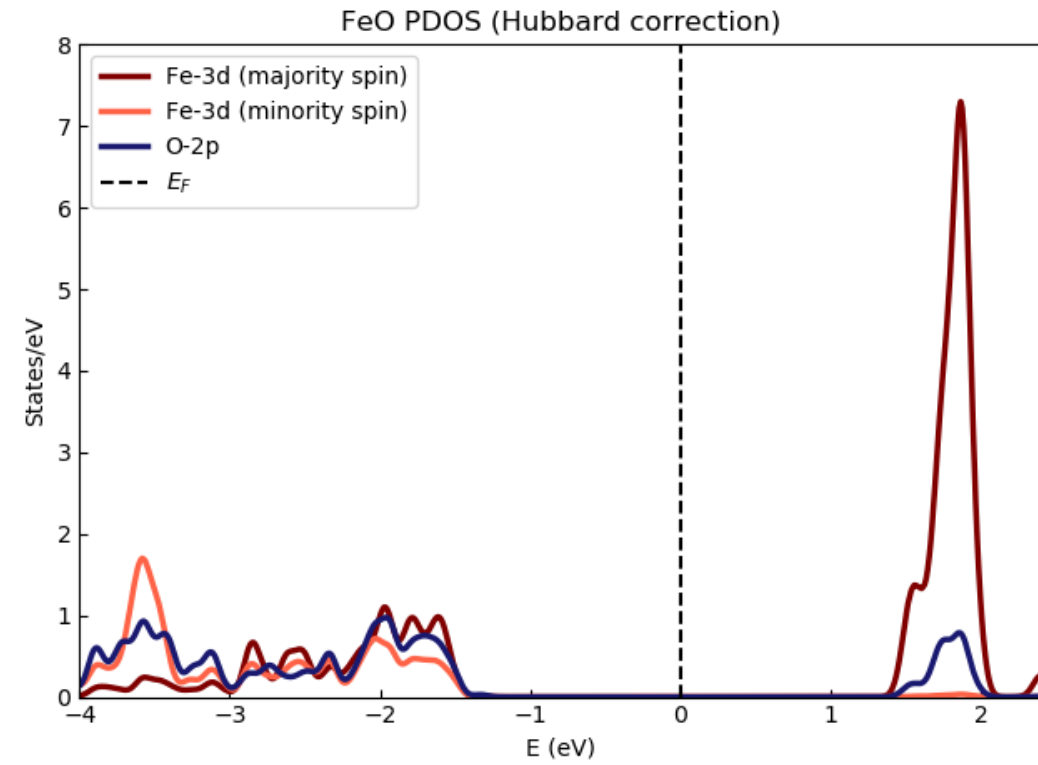
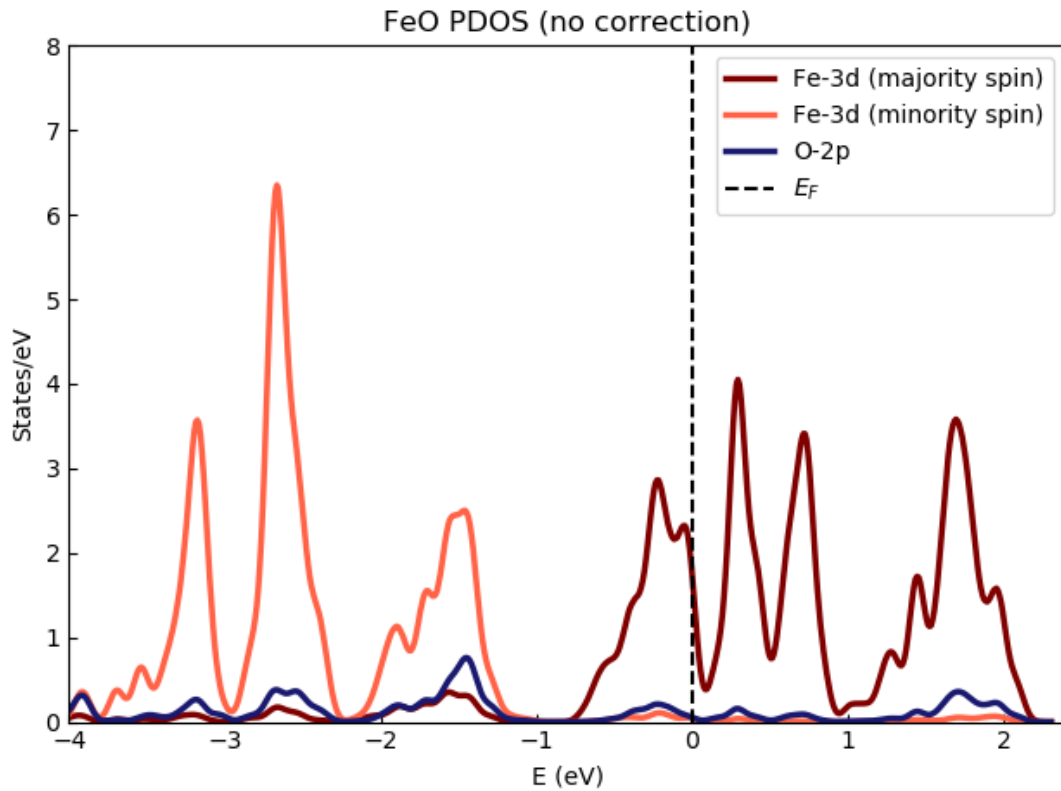
➤ The Hubbard correction changes the order of the d-orbitals and increases the gap

# EXERCISE 3 — MAGNETIC SYSTEMS (FeO)

- An even more drastic example of DFT gap underestimation is FeO
- The system is in reality **insulating**, but DFT predicts it to be a **metal**



# EXERCISE 3 — MAGNETIC SYSTEMS (FeO)



# EXERCISE 3 — MAGNETIC SYSTEMS (FeO)

- In older QE versions, a metallic state would be obtained even with DFT+U
- The DFT+U SCF would converge to a local minimum of state occupations
- In these cases, it's necessary to force starting occupations with the *starting\_ns\_eigenvalue* variable

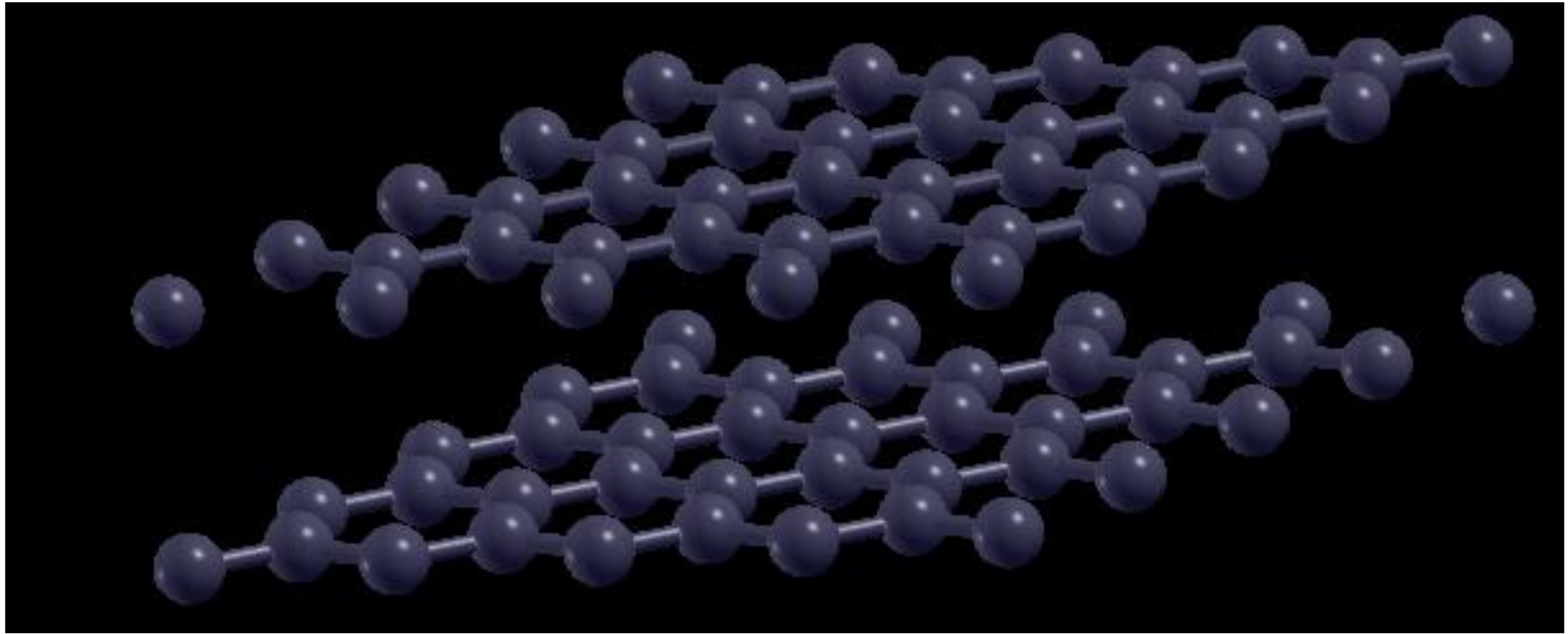


## **EXERCISE 4 — VDW FUNCTIONAL**

# EXERCISE 4 — VDW FUNCTIONAL

- The *input\_dft* variable controls the XC functional used in (N)SCF calculations
- The functional specified in pseudopotential files is used by default
- Available functionals are listed in *Modules/funct.f90*
- In this exercise we will use the nonlocal ‘vdw-df-cx’ functional
- We use the pseudopotential for the closest GGA (PBE)
- There are no PPs for non-local functionals

## EXERCISE 4 — VDW FUNCTIONAL



# EXERCISE 4 — VDW FUNCTIONAL

➤ The optimized interlayer distances are:

1. PBE = 3.55 Å
2. vdw-df-cx = 3.22 Å
3. LDA = 3.19 Å

➤ The experimental interlayer distance is 3.336 Å



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