

# Density functional theory in solid state physics

## Lecture 10

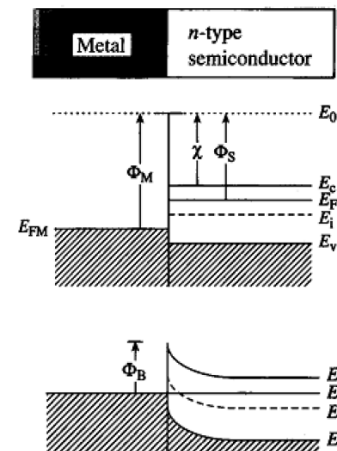
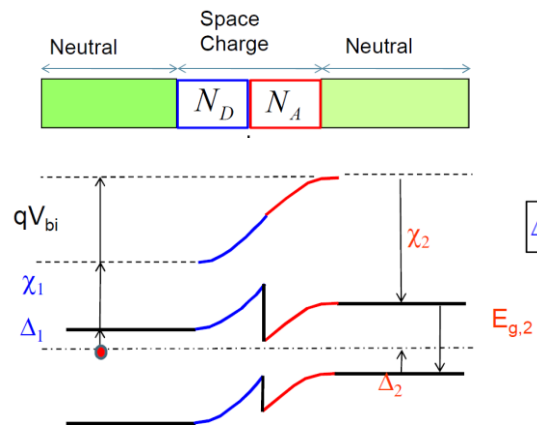
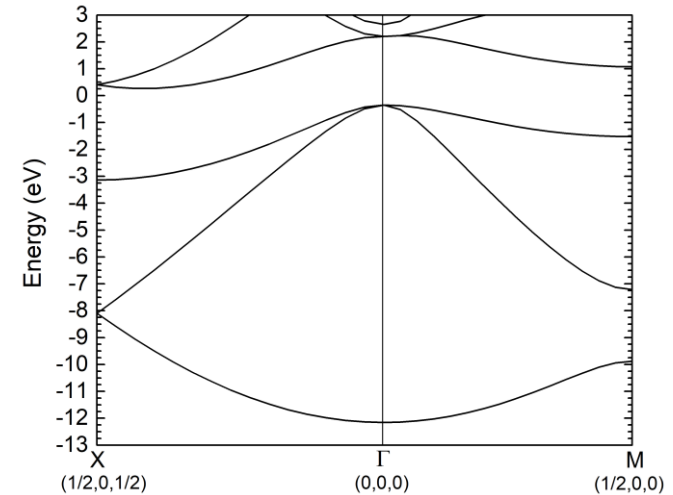
- Electronic structure of a material can be derived from DFT, using the single-particle energies obtained from solution of the KS Equations
- Often more k-points needed for good description of electronic properties than for obtaining ground-state electron density
  - non-selfconsistent calculations for a set of k-points and bands of interest, while keeping electron density and Kohn-Sham potential fixed
- Density-of-states: use a dense Monkhorst-Pack sampling of the Brillouin zone. The tetrahedron method can be very useful
- Electronic bandstructures: sample k-points along high-symmetry paths of interest
- Standard 'task' of DFT in solid state physics; electronic properties are reproduced reasonably well
- Hybrid functionals: NSCF not possible, use Wannier interpolation instead (or similar)

# Band structures and band alignment

- Typically, band structure plots shifted energies, such that the zero-of-energy is convenient

For example: Fermi energy, valence band maximum

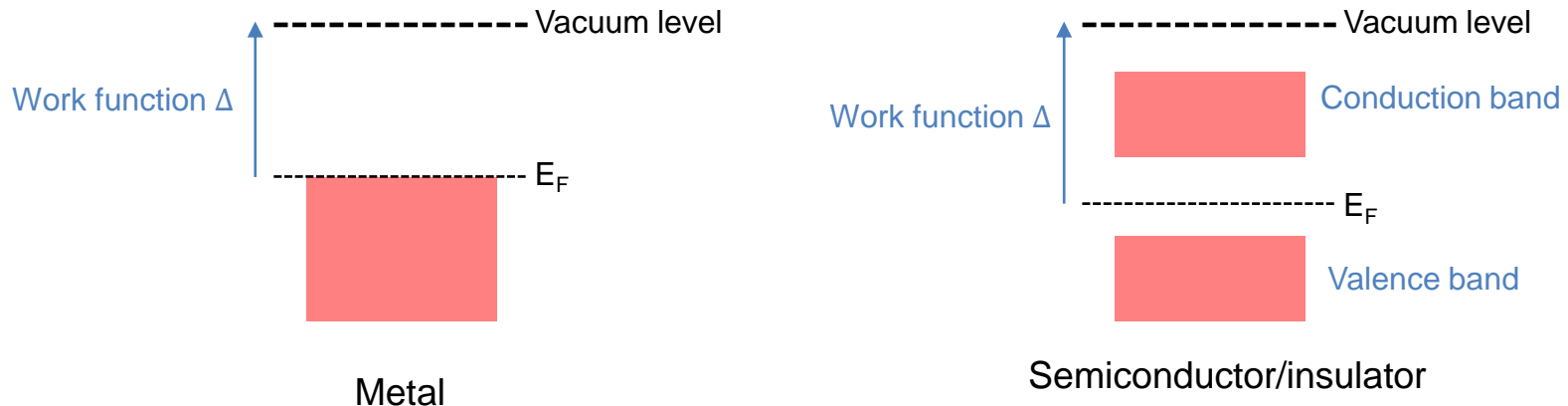
- Problem with DFT: energies and eigenvalues usually contain shift due to basis set
- Comparison of absolute energies between two materials difficult, needs common energy scale
- For example: Band alignment in p-n junctions or Schottky diodes



No contact

After contact

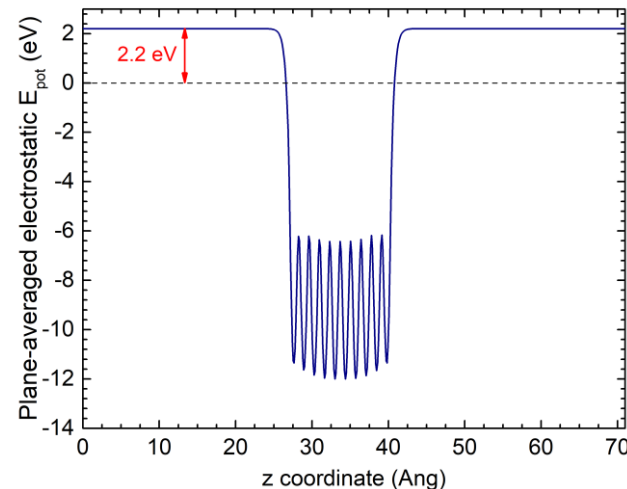
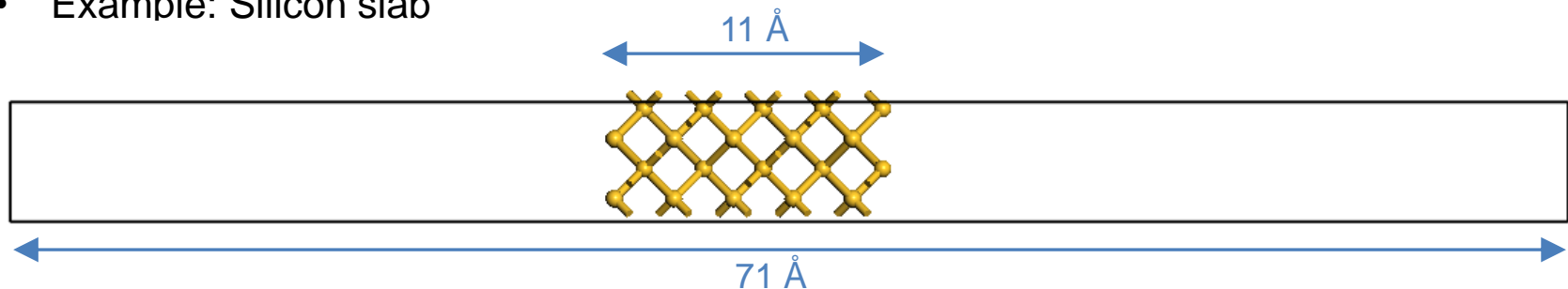
- One such scale: Work functions of metals and semiconductors (also of general interest)



- Vacuum level: potential from material should vanish sufficiently far away from material  
→ usually defined as 0 eV, such that  $\Delta = -E_F$
- Task: need to find vacuum level in order to derive work function (and band alignment)
- In DFT: Kohn-Sham potential decays rapidly from a surface into vacuum and saturates (see Exercise sheet 2)
- Saturated potential energy far away from material surface is the vacuum level

# Derivation of vacuum levels

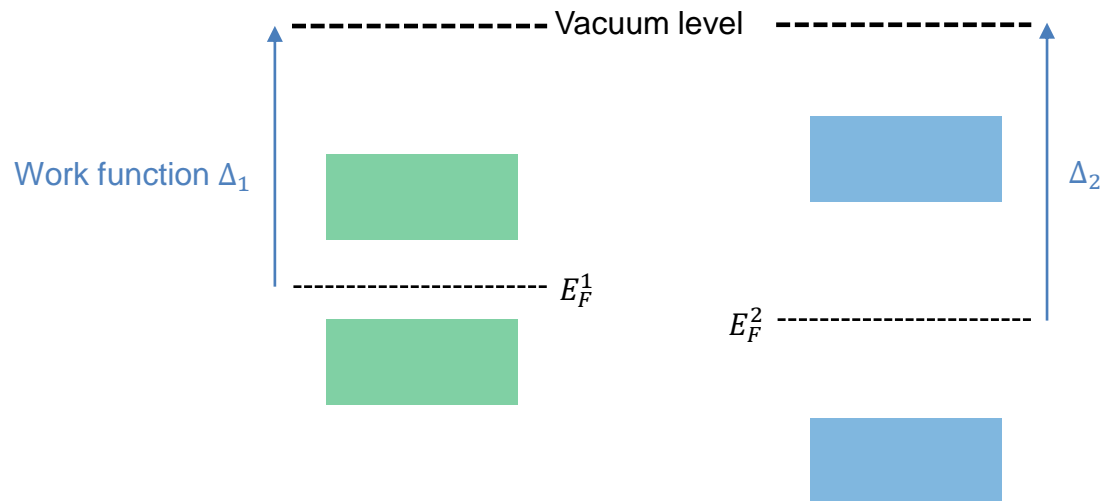
- Approach: 1. Build a surface with a large enough vacuum layer („slab“)
- 2. calculate potential, extract saturated potential energy
- Example: Silicon slab



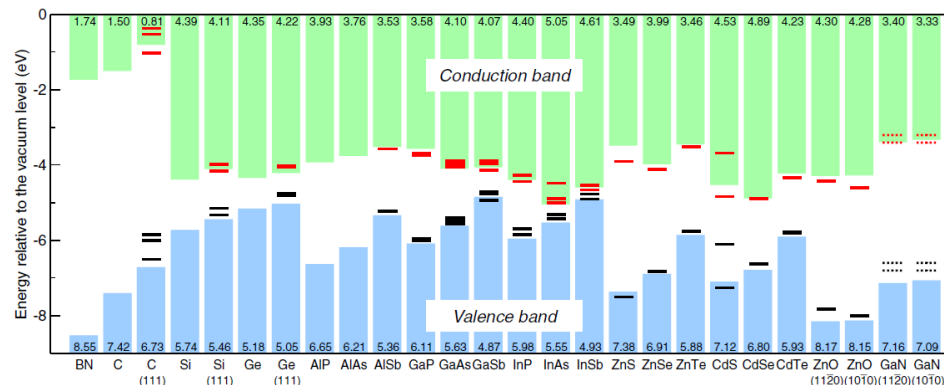
- From QE:  $E_F = -3.2 \text{ eV}$
- Work function:  $\Delta = -(-3.2 \text{ eV} - 2.2 \text{ eV}) = 5.4 \text{ eV}$
- Experiment:  $\Delta^{exp} = 4.85 \text{ eV}$
- Method especially easy for 1D or 2D materials (Exercise sheet 3)

# Band alignment between materials

- From workfunction we can guess band alignment
- Without contact between materials, alignment of vacuum level



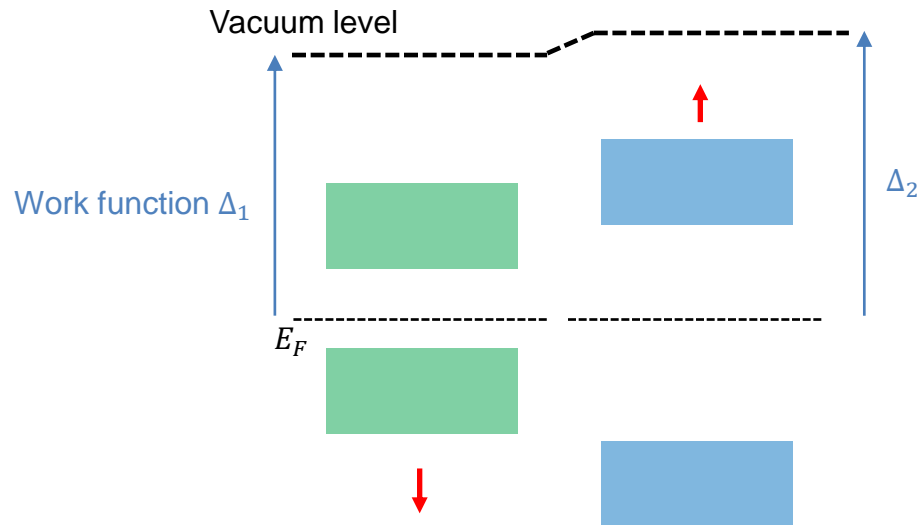
- From this, we can guess how the bands between two unknown materials will align



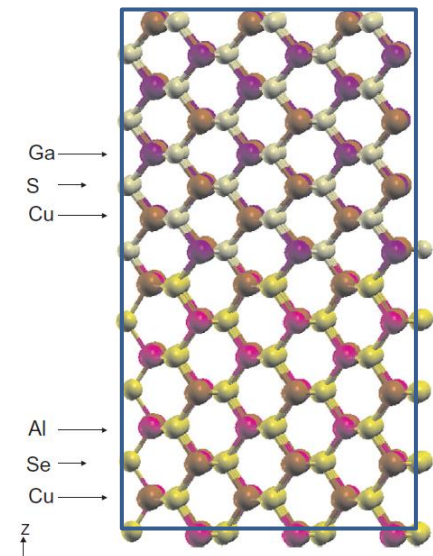
Phys. Rev. B 90, 155405 (2014)

# Band alignment between materials

- In contact: Fermi energy over the formed heterojunction will equalize in thermal equilibrium, possibly bonding between two materials



- Formation of potential at the interface causes relative shift of vacuum levels
- Of course, interface potential and correct band alignment can be deduced from explicit DFT calculation



- So far: neglected spin degree of freedom  
→ only spin-unpolarized systems
- Did this because then we only have to consider half the bands, each band occupied by two electrons

$$\left( -\frac{1}{2} \nabla^2 + v(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{XC}(\vec{r}) \right) \varphi_{kn}(\vec{r}) = \varepsilon_{kn} \varphi_{kn}(\vec{r})$$

spin-effects included here in a mean-field way

- This obviously makes sense if we do not require spin-polarization effects to describe the system
- For example in covalently or ionic-bonded materials, materials without *d* or *f* electrons etc.

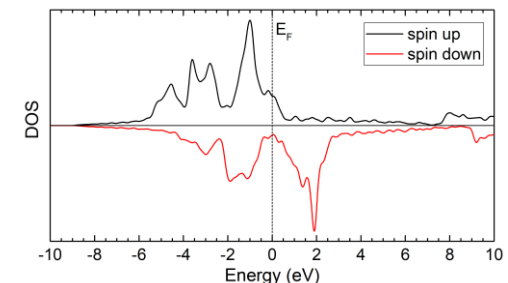
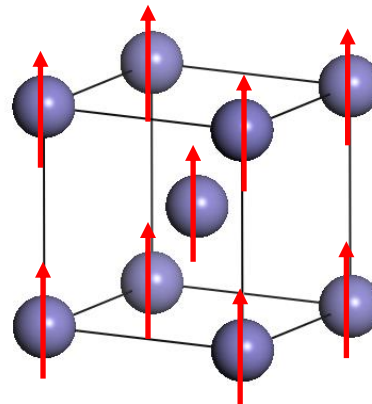


- Obviously does not make sense to do if we need spin-polarization effects
- For instance in
  - magnetic systems, i.e. a long-range spin-order

Exchange and correlation interaction effects can give rise to magnetic spin ordering

- Example: Iron

Exchange interaction favours ferromagnetic alignment of  $d$  electron spins (Stoner criterion)



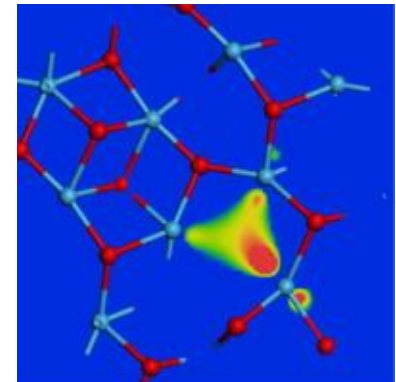
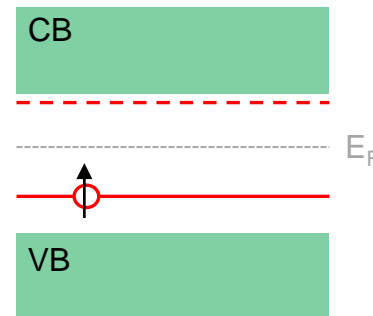
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Exchange and correlation interaction effects can give rise to magnetic spin ordering

- Non-magnetic systems with localized spin-momenta, e.g. defects
- Example: O vacancy in  $\text{HfO}_2$ :

Localized „defect state“, occupied with 1 electron

(Also see exercise sheet 4)



*Microelectr. Eng.* 88, 1464 (2011)

- Usual approximation: Collinear spin.

- Most relevant for ferro- and antiferromagnetism, works for many materials
- Each electron is characterized by quantum number  $\sigma = \uparrow$  or  $\sigma = \downarrow$
- Electron spins point along the same axis

The axis has to be defined in the DFT code, usually z-axis

- Local magnetization  $m(\vec{r})$  can be described by  $m(\vec{r}) = n^{\uparrow}(\vec{r}) - n^{\downarrow}(\vec{r})$  ( $= \zeta(\vec{r})n(\vec{r})$ )

„spin density“ of spin-up electrons

spin-polarization

# KS Equation with spin polarization

- Actually the assumption underlying the previously given KS-Equation:

$$\left( -\frac{1}{2} \nabla^2 + v_{KS}^{\sigma}(\vec{r}) \right) \varphi_{nk\sigma}(\vec{r}) = \varepsilon_{nk\sigma} \varphi_{nk\sigma}(\vec{r})$$

- Spin-dependent Kohn-Sham potential  $v_{KS}^{\sigma}$ :

$$v_{KS}^{\sigma}(\vec{r}) = v(\vec{r}) + v_H(\vec{r}) + v_{xc}^{\sigma}(\vec{r}) - \sigma B_{xc}(\vec{r})$$

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$$v_{KS}^{\sigma}(\vec{r}) = v(\vec{r}) + v_H(\vec{r}) + v_{xc}^{\sigma}(\vec{r}) - \sigma B_{xc}(\vec{r})$$

$$v_{xc}^{\sigma}(\vec{r}) = \varepsilon_{xc}[n, m] + n(\vec{r}) \frac{\partial \varepsilon_{xc}[n, m]}{\partial n(\vec{r})}$$

e.g. from local spin density approximation (LSDA)

$$B_{xc}(\vec{r}) = -n(\vec{r}) \frac{\partial \varepsilon_{xc}[n, m]}{\partial m(\vec{r})} \quad \text{exchange-correlation magnetic field}$$

- External magnetic field  $B_{ext}(\vec{r})$  can in principle be added seamlessly

# KS Equation with spin polarization

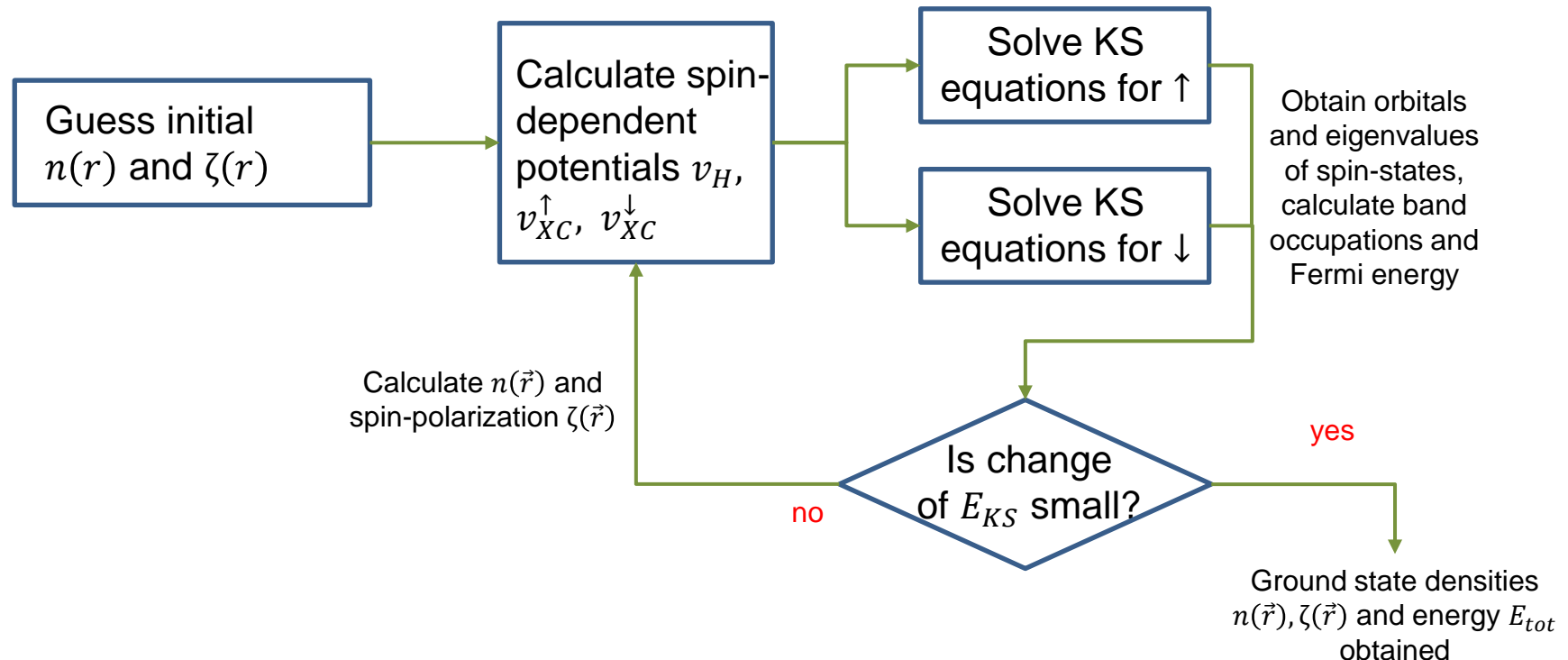
- Collinear spin leads to a block-structured Hamiltonian, if we use spinors

$$H_{KS} = \begin{pmatrix} H_{\uparrow\uparrow} & 0 \\ 0 & H_{\downarrow\downarrow} \end{pmatrix} \quad \text{Spinor: } \varphi_{nk}(\vec{r}) = \begin{pmatrix} \varphi_{nk,\uparrow}(\vec{r}) \\ 0 \end{pmatrix} \text{ or } \begin{pmatrix} 0 \\ \varphi_{nk,\downarrow}(\vec{r}) \end{pmatrix}$$

- One KS Equation per spin quantum number
- no direct coupling between states with opposite spin, indirect coupling through electron density
- Have to use 1 band per electron and spin  
→ computational effort twice as large as for spin-unpolarized calculations

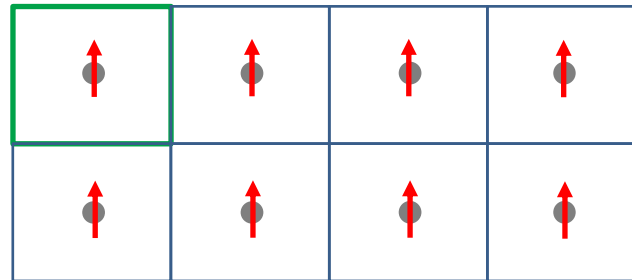
# SCF with collinear spin

- SCF for spin-polarized calculations
- Do not only mix electron density  $n(r)$ , but also spin-polarization  $\zeta(\vec{r}) = \frac{n^\uparrow(\vec{r}) - n^\downarrow(\vec{r})}{n(\vec{r})}$
- SCF convergence can be greatly slowed down by changes in spin densities  
 $n^\sigma(\vec{r}) = \sum_{n,k,\sigma} |\varphi_{nk\sigma}(\vec{r})|^2$

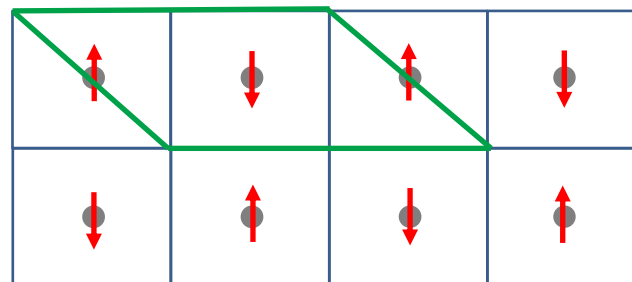


# Magnetic unit cells

- Spin-polarized calculations are straight-forward to do in most DFT codes
- Careful: „Magnetic unit cell“ might not be the same as the „geometric“ unit cell
- Simple: Ferromagnetic spin order



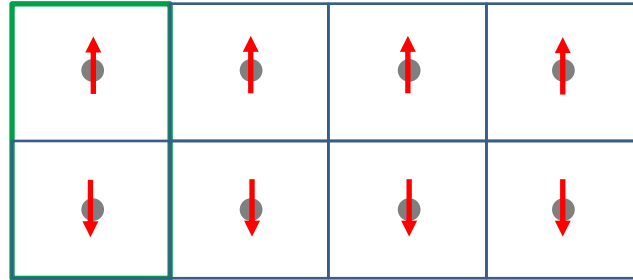
- More complex: antiferromagnetic order. Need to choose a „supercell“



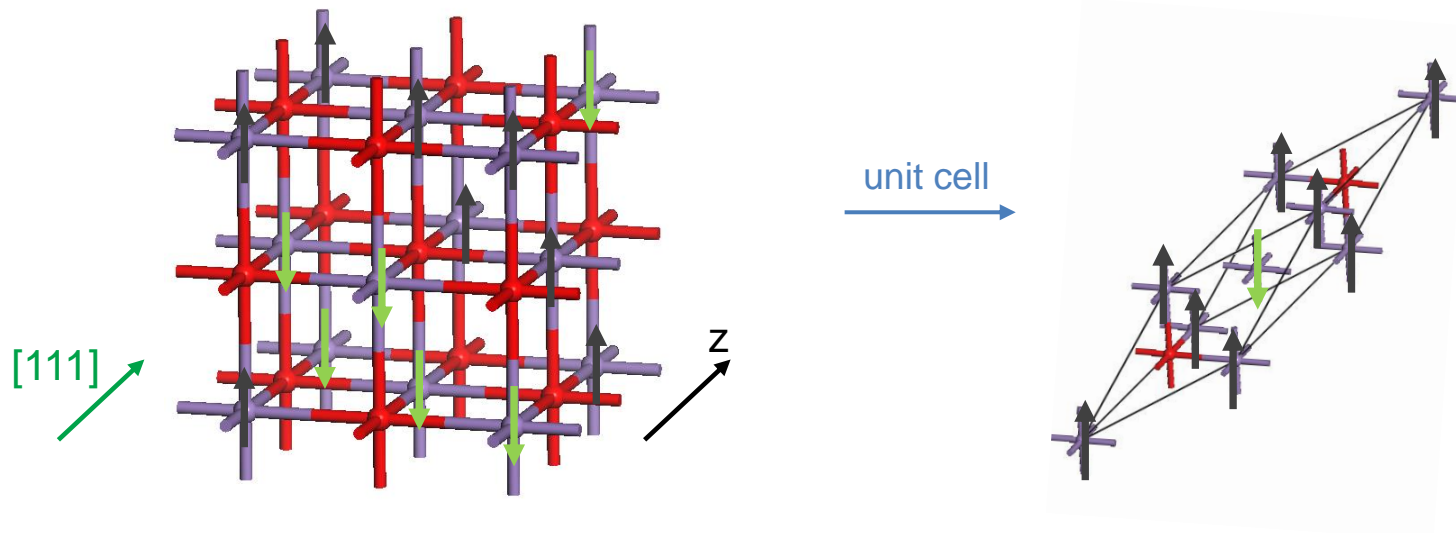


# Magnetic unit cells

- Could also have „mixed“ order



- Supercells have to be chosen such that atoms in the cell can adopt desired spin ordering
- Example: MnO, antiferromagnetic spin order in  $[111]$  direction



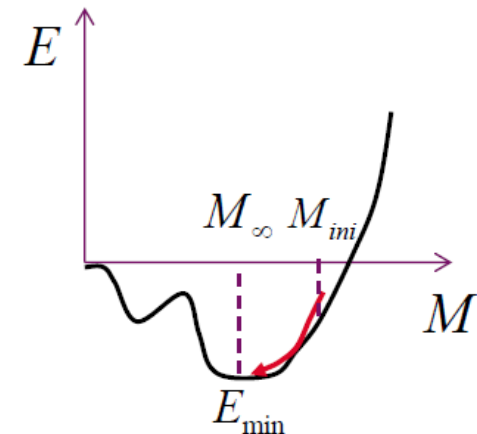
- Can get a number of interesting properties
  - Total and absolute spin magnetic moment in the unit cell

$$M_{tot} = \int_{unitcell} (n^{\uparrow}(\vec{r}) - n^{\downarrow}(\vec{r})) dr \quad M_{abs} = \int_{unitcell} |n^{\uparrow}(\vec{r}) - n^{\downarrow}(\vec{r})| dr$$

- Spin-polarized bandstructure for up and down spins
- Spin-resolved density of states (See exercise sheet 3)
- Spin densities  $n^{\uparrow}(\vec{r})$  and  $n^{\downarrow}(\vec{r})$ , and the local magnetization  $m(\vec{r})$

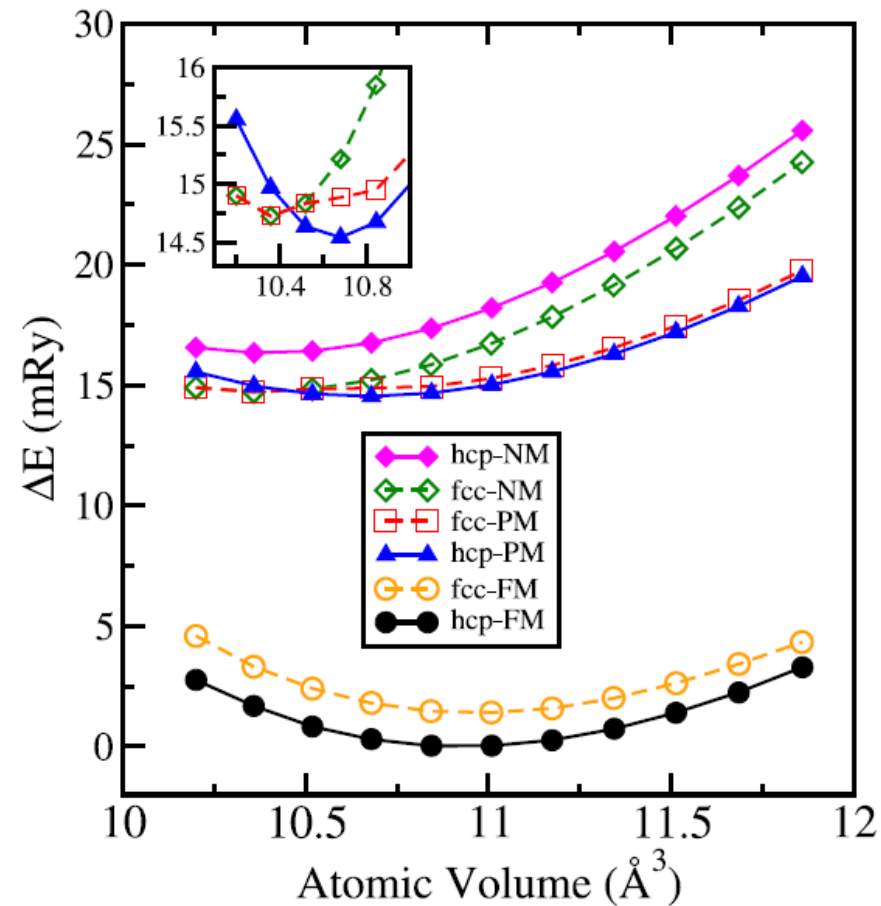
# Magnetic order and DFT

- Magnetic orderings correspond to minima in the potential energy surface
- Total energy differences between magnetic states small, so have to be careful in what minimum calculation ends up in
- Usually use desired spin order as starting guess for calculation
- Can try different spin orders to learn about ground state magnetic properties
- Also possible to fix magnetic state magnetic structure, for example for calculating paramagnetic states



# Magnetic order and DFT

- Example: magnetic ordering and phase-transition in metallic Co



*Sci. Rep. 7, 3778 (2017)*

# The Heisenberg model and DFT

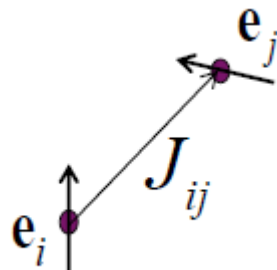
- DFT can help understand magnetism, for example by providing parameters for Heisenberg model

$$H^{\text{Heisenberg}} = J \sum_{\langle i,j \rangle} \vec{s}_i \cdot \vec{s}_j$$

Spin vectors with unit length

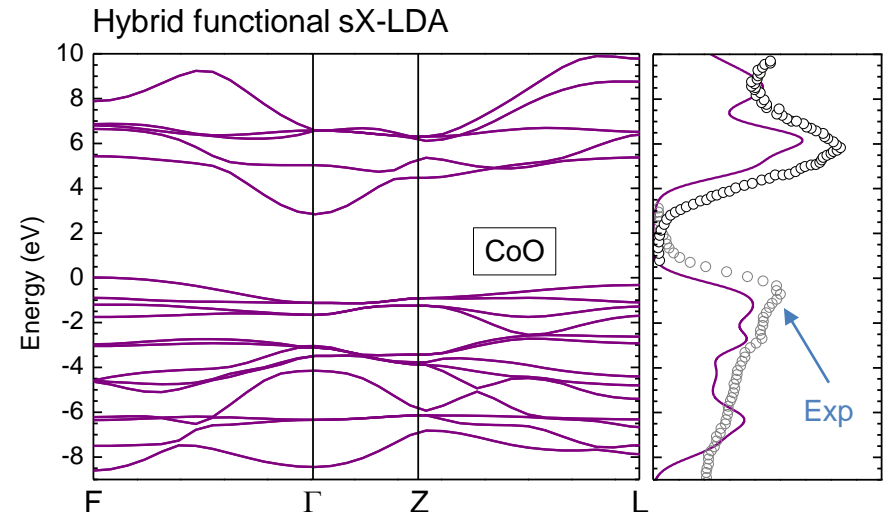
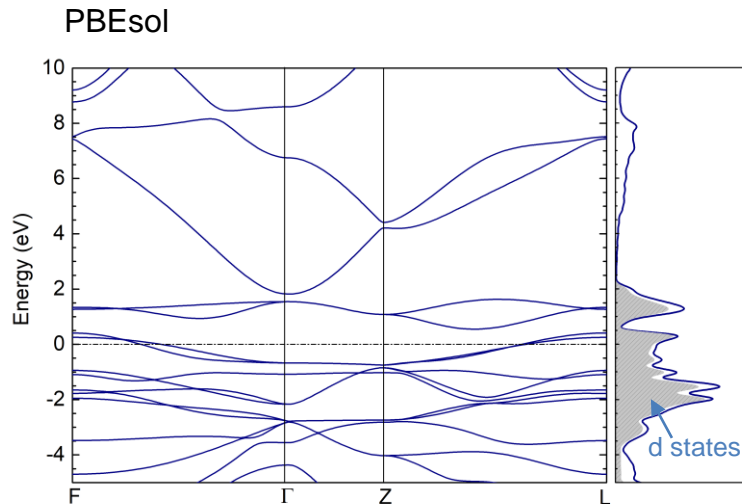
Sum over nearest neighbours

Exchange coupling,  $J = \begin{cases} > 0, & \text{ferromagnetic} \\ < 0, & \text{antiferromagnetic} \end{cases}$



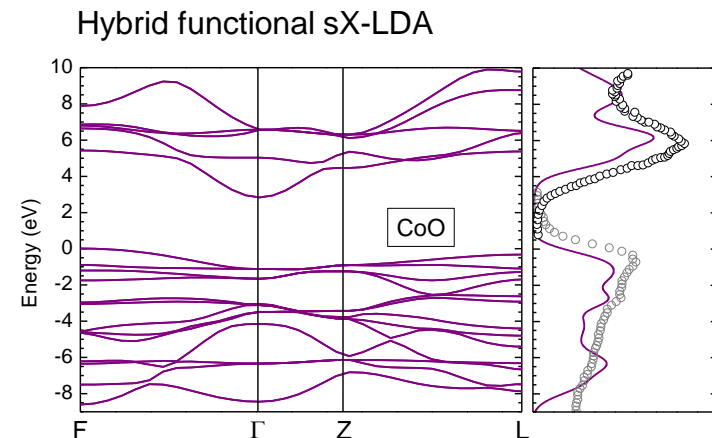
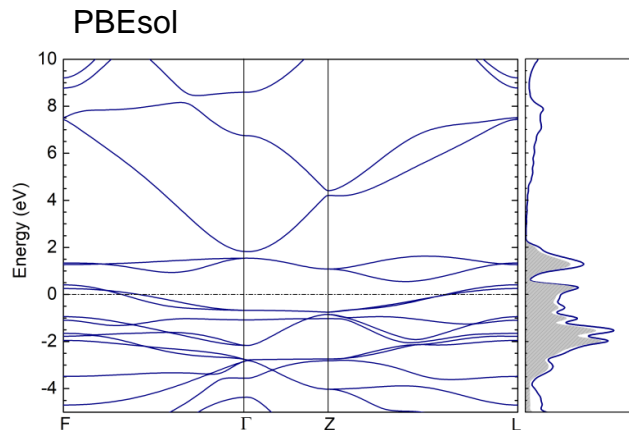
- Mapping of DFT  $E_{\text{tot}}$  to Heisenberg model:  $J = \frac{1}{N_{\text{nearest-neighbours}}} (E_{\text{tot}}^{\text{AFM}} - E_{\text{tot}}^{\text{FM}})$
- Can also do similar calculations for pair-specific  $J_{ij}$  and beyond nearest-neighbour approximation
- Néel and Curie temperatures can be derived from Heisenberg model based on DFT data

- LDA and GGA usually work well for predicting magnetic ground state and magnetizations
- LDA and GGA can be bad with *qualitatively* predicting band gaps in magnetic insulators
- Example: antiferromagnetic semiconducting CoO
  - PBEsol find correct geometry
  - PBEsol predicts antiferromagnetic GS
  - Correct crystal field splitting of *d* states
  - But predicts metallicity



*J. Phys. Cond. Mat.* 25, 165502 (2013)

- CoO (and similarly FeO, MnO and NiO etc) are Mott insulators
- They should be metals according to band theory as they contain incomplete  $d$  shells
- But Coulomb repulsion between the localized  $d$  electrons  $>$  kinetic energy  
→ system acts like an insulator
- LDA and GGA tend to over-delocalize electrons and underestimate this Coulomb repulsion
- Hybrid functionals better, but expensive



# A cheap way out: The DFT+U method

- Poor man's hybrid functionals: DFT+U

- Starting point: Hubbard model
 
$$H_{Hubbard} = t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + h.c.) + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow}$$

Hopping integral, proportional to band width
Coulomb repulsion strength
occupation number

- Minimal physics necessary to capture Mott insulator physics, i.e. when  $t \ll U$

- Idea: Write the total energy of a system as

$$E_{DFT+U} = E_{DFT}[n(r)] + E_{Hubbard-U}[\{\hat{n}_{m,m'}^{I\sigma}\}] - E_{dc}[\hat{n}^{I\sigma}]$$

Double-counting correction

Occupation numbers of localized orbitals :

$$\hat{n}_{m,m'}^{I\sigma} = \sum_{v,k} f_{vk}^\sigma \langle \varphi_{vk}^\sigma | \phi_m^I \rangle \langle \phi_{m'}^I | \varphi_{vk}^\sigma \rangle$$

- Compensate the underestimated Coulomb repulsion for localized states (like  $d$  or  $f$  electrons)



# A cheap way out: The DFT+U method

- Different formulations

- FLL: 
$$E_{DFT+U} = E_{DFT} + \sum_I \frac{U^I}{2} \sum_{m,\sigma \neq m',\sigma'} \hat{n}_m^{I\sigma} \hat{n}_{m'}^{I\sigma'} - \frac{U^I}{2} \hat{n}^I (\hat{n}^I - 1)$$

*J. Phys.: Cond. Mat.* 9, 767 (1997)

- Rotationally invariant: 
$$E_{DFT+U} = E_{DFT} + E_{Hubbard}[U, J, \{\hat{n}_{m,m'}^{I\sigma}\}] - E_{dc}[U, J, \hat{n}^{I\sigma}]$$

*Phys. Rev. B.* 52, R5467 (1995)

Exchange coupling  
strength

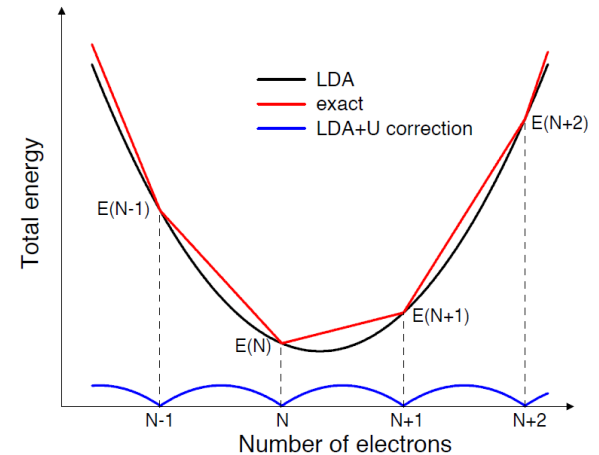
- Simplified: 
$$E_{DFT+U} = E_{DFT} + \sum_I \frac{1}{2} \underbrace{U_{eff}}_{U-J} \text{Tr}[\hat{n}^I - \hat{n}^I \hat{n}^I]$$

*Phys. Rev. B* 57, 1505 (1998)

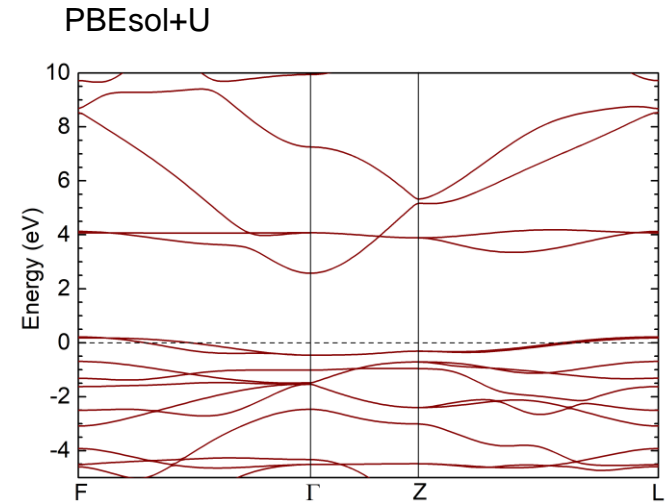
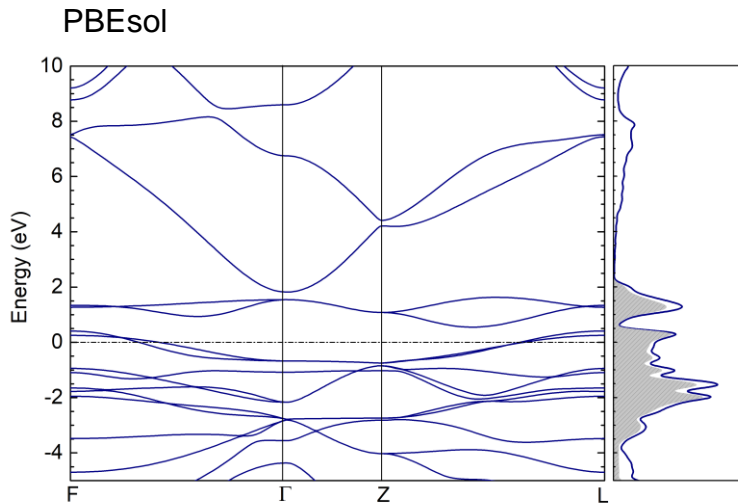
- The simplified method usually is in good agreement with the (more accurate) rotationally invariant method
- U (and maybe J) are usually chosen semiempirically by fitting to experimental data
- U between 3 eV and 6 eV seems to be good in most cases

# A cheap way out: The DFT+U method

- Can also calculate  $U$  from ab initio, using linear-response theory, implemented in many codes
- For example: try to find  $U$  that reproduces derivative discontinuity
- CoO with PBEsol+U ( $U=6$  eV):



<https://www.cond-mat.de/events/correl12/manuscripts/cococcioni.pdf>



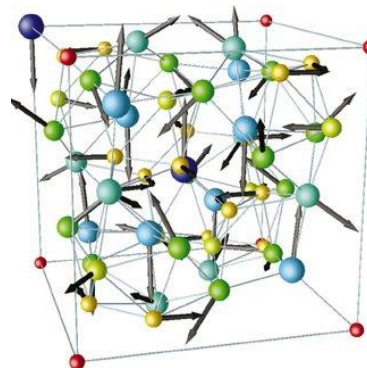
# Non-collinear spin

- Non-collinear spin: spins of different electrons can point along different axes
- Concept of spin quantum number not good anymore, Kohn-Sham states are *spinors*

$$\varphi_{ik}(\vec{r}) = \begin{pmatrix} \varphi_{ik+}(\vec{r}) \\ \varphi_{ik-}(\vec{r}) \end{pmatrix}$$

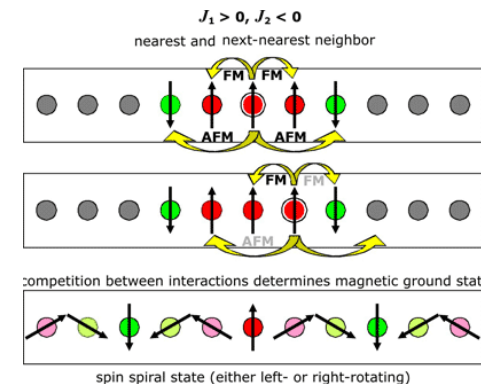
- Kohn-Sham Hamiltonian:  $H_{KS} = \begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix}$
- Can now not separate up spin and down spin anymore

- Examples:



Non-collinear  
spin structure  
in  $\alpha$ -Mn

Phys. Rev. B 68, 014407 (2003)



Spin spirals

[http://www.nanoscience.de/HTML/research/noncollinear\\_spins.html](http://www.nanoscience.de/HTML/research/noncollinear_spins.html)

- Standard Kohn-Sham describes *non-relativistic* electrons

- Relativistic treatment: Dirac Equation  $i\hbar \frac{\partial}{\partial t} \varphi_{nk} = (c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + V)\varphi_{nk} = H\varphi_{nk}$
- Dirac matrices
Spinor

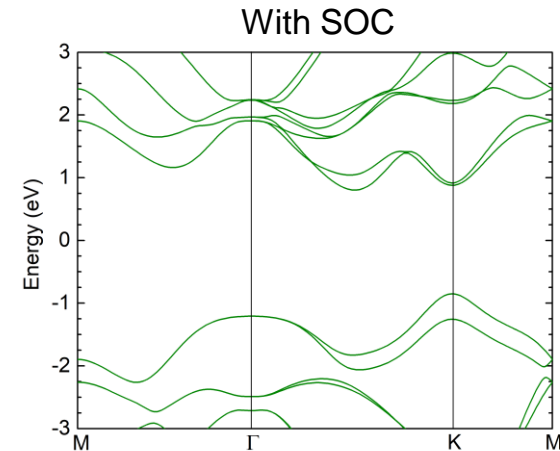
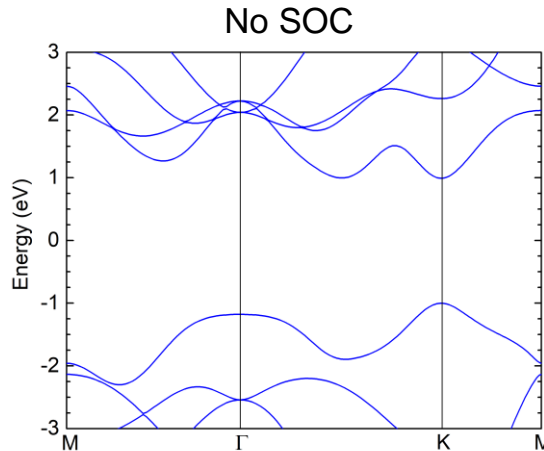
- In the non-relativistic limit:

$$H = \left[ \frac{p^2}{2m} + V \right] + \underbrace{\frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) \cdot \vec{B} - \frac{p^4}{8m^3c^2} - \frac{\hbar^2}{8m^2c^2} \nabla^2 V}_{\text{scalar-relativistic correction}} - \underbrace{\frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \vec{L} \cdot \vec{S}}_{\text{spin-orbit coupling}}$$

Splitting of orbitals with  
angular momentum

- Spin-orbit coupling has crucial effects on the electronic structure of materials containing heavy elements
- Effect is (almost) localized to region near the core, where  $\frac{dV}{dr}$  is large

- Example: Monolayer  $\text{WS}_2$



- Relativistic formulations of Kohn-Sham Equation have been developed and implemented
- In planewave codes, spin-orbit coupling enters through the pseudopotentials
- This requires use of pseudopotentials, which have been generated using the Dirac Eq.
- Twice as many bands as unpolarized calculation and each electron has 2 „spin channels“  
→ computational effort 4x larger than for unpolarized calculation