

# Spin-Orbit Coupling in SIESTA

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**First steps with SIESTA**  
from zero to hero

October 5<sup>th</sup>, 2023

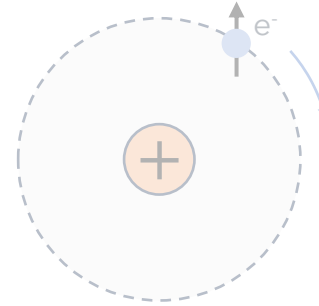
## Spin-orbit coupling (SOC)

- *relativistic effect*  
interaction of the electron spin  $\hat{\mathbf{S}}$  and its own orbital momentum  $\hat{\mathbf{L}}$

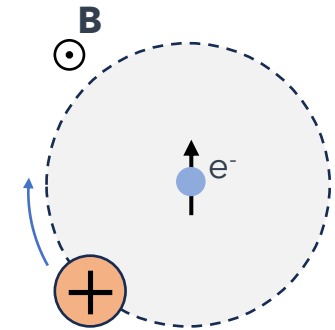
$$\hat{H}_{SO} \sim \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}$$

- **Isolated atom:**  
split energy levels in *atomic fine structure*
- **General:**  
couples real space and spin space  
→ also spins & crystal lattice

Rest frame of the nucleus



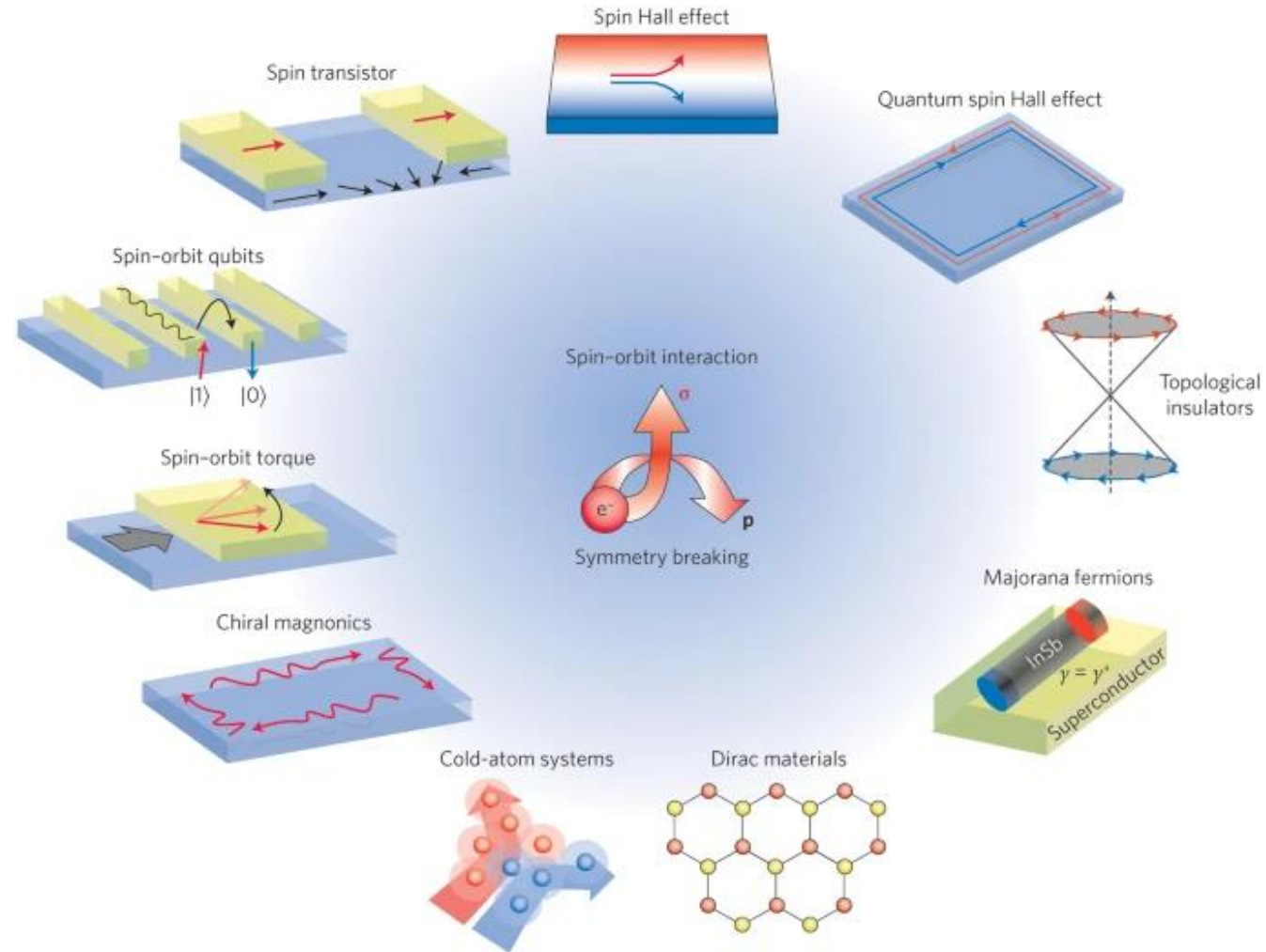
Rest frame of the electron



- Nucleus motion creates magnetic field  $\hat{\mathbf{B}} \sim \hat{\mathbf{L}}$
- Electron spin couples to  $\hat{\mathbf{B}}$   
→ Zeemann-like correction:  $\hat{H}_{SO} \sim \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{B}} \sim \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}$
- without SOC:  
 $(l, m)$  and spin ( $s$ ) are good quantum numbers
- with SOC:  
use  $(l_J, m_J)$  quantum numbers related to  $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$

SOC: small correction leading to rich physics

- Giant Magneto Resistance (Nobel prize 2007)  
→ read heads for hard drives
- Spin transfer torque  
→ electrically changing the magnetic configuration of a device
- Topological insulators
- ... and many more ...



*So far: SIESTA only without spin*

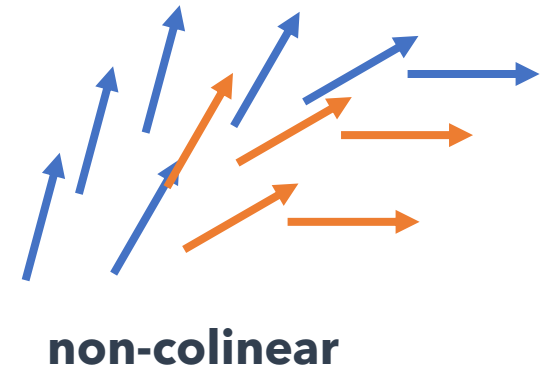
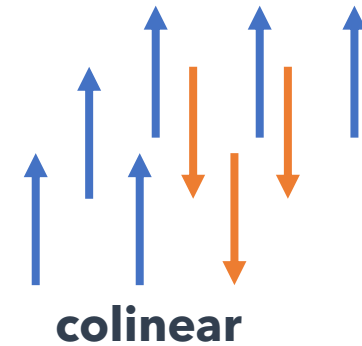
- *How do we include spins?*
- *How do we include spin-orbit coupling?*

Manchon, *Nature Mater* **14** (2015).

## How can we control the spins in SIESTA?

### Flag **Spin**

- **non-polarized**: no spins (default)
- **polarized**: colinear spins
- **non-colinear**: non-colinear spins no spin-orbit coupling
- **spin-orbit**: non-colinear spins with spin-orbit coupling



What does it mean?

Two Hamiltonians  $\hat{H} \rightarrow \hat{H}_{\uparrow}, \hat{H}_{\downarrow}$

Two sets of wavefunctions  $|\psi\rangle \rightarrow |\psi_{\uparrow}\rangle, |\psi_{\downarrow}\rangle$

Two density matrices  $\hat{\rho} \rightarrow \hat{\rho}_{\uparrow}, \hat{\rho}_{\downarrow}$

Spin-channels fully decoupled? **No!**

- Only in the Schrödinger equation.
- Exchange-correlation functional couples both spin-channels:

$$E_{XC}[\rho] \rightarrow E_{XC}[\rho_{\uparrow}, \rho_{\downarrow}] \neq E_{XC}[\rho_{\uparrow}] + E_{XC}[\rho_{\downarrow}]$$

Colinear spin calculation:

no SOC

→ spin and real space decoupled

→ polarization axis: arbitrary  
in SIESTA always **z-axis**

How do SIESTA outputs change?

- Information printed each SCF step:
  - includes (x,y,z) component of the spin moment of the whole cell and total spin.
  - in collinear case x and y components always zero.

	iscf	Eharris(eV)	E_KS(eV)	FreeEng(eV)	dDmax	Ef(eV)	dHmax(eV)
scf:	1	-2153.257209	-2198.764140	-2198.764152	3.041441	-3.686948	23.600408
		spin moment: {S} ,  S  = { 0.0 0.0 2.53181 } 2.53181					

How do SIESTA outputs change?

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- **.bands** file: twice as many eigenvalues for each k point first channel 1 then channel 2

```

-3.58228951613775
0.000000000000000000E+000    4.14093362787451
-13.8419785400988    68.6417154298812
      24          2          351
0.000000    -13.8420  -10.1800  -9.8289  -7.3976  -7.3976  -6.7511  -6.0972  -5.8342  -4.5706
      -4.4758   5.2572  19.1906  19.5233  27.6085  27.6085  31.6350  34.5379  37.6186
      50.6420  56.7901  61.3181  61.3181 -13.5977  -9.5698  -9.4133  -6.2825  -6.2825
-4.5791  -3.2974  -2.1377  -2.1377  -2.1064   6.2058  20.0516  20.3546  28.3583
      32.2540  35.4856  38.8661  43.4723  52.7600  57.5402  62.4527  62.4527
0.008768  -13.8407  -10.1792  -9.8285  -7.3971  -7.3971  -6.7516  -6.0970  -5.8347  -4.5708
    
```

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  - use option **-s** to select spin up (1) or spin down (2)
  - or nothing: adds third column to output with 1 and 2 to identify spin up and spin down

```
0.000000 -10.259710 1
0.008768 -10.258410 1
0.017536 -10.254510 1
...
0.000000 -10.259710 2
0.008768 -10.258410 2
0.017536 -10.254510 2
...
```



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- **DOS** file:
  - one additional column per energy point: energy, DOS(up), DOS(down)

-9.99999	1.00971	0.63864
-9.98497	1.04733	0.66864
-9.96996	1.04293	0.64380
...		

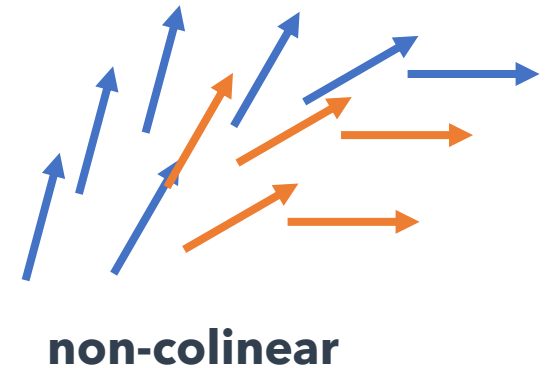
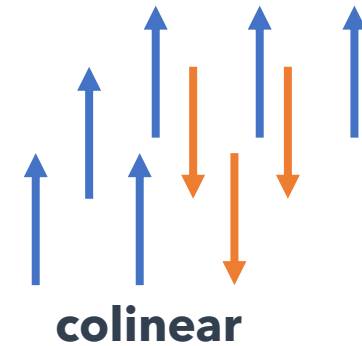
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- **... quantities** separately for up and down channel

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Spinor wavefunction  $|\psi\rangle \rightarrow \begin{pmatrix} |\psi_{\uparrow}\rangle \\ |\psi_{\downarrow}\rangle \end{pmatrix}$

Spin dependent operators

$$\hat{H} \rightarrow \begin{pmatrix} \hat{H}_{\uparrow\uparrow} & \hat{H}_{\uparrow\downarrow} \\ \hat{H}_{\downarrow\uparrow} & \hat{H}_{\downarrow\downarrow} \end{pmatrix} \quad \hat{\rho} \rightarrow \begin{pmatrix} \hat{\rho}_{\uparrow\uparrow} & \hat{\rho}_{\uparrow\downarrow} \\ \hat{\rho}_{\downarrow\uparrow} & \hat{\rho}_{\downarrow\downarrow} \end{pmatrix}$$

What do the values of  $\hat{\rho}_{\sigma\sigma'}$  indicate?

- $\hat{\rho}_{\uparrow\uparrow} + \hat{\rho}_{\downarrow\downarrow}$  : related to charge
- $\hat{\rho}_{\uparrow\uparrow} - \hat{\rho}_{\downarrow\downarrow}$  : related to spin polarization z-axis
- $\text{Re}\{\hat{\rho}_{\uparrow\downarrow}\}$ : related to spin polarization along x axis
- $\text{Im}\{\hat{\rho}_{\uparrow\downarrow}\}$ : related to spin polarization along y-axis

$$Q = \text{Tr}\{ (\hat{\rho}_{\uparrow\uparrow} + \hat{\rho}_{\downarrow\downarrow}) \mathbf{S} \}$$

$$M_z = \mu_B \frac{1}{2} \text{Tr}\{ (\hat{\rho}_{\uparrow\uparrow} - \hat{\rho}_{\downarrow\downarrow}) \mathbf{S} \}$$

$$M_x = \mu_B \text{Tr}\{ \text{Re}\{ \hat{\rho}_{\uparrow\downarrow} \} \mathbf{S} \}$$

$$M_y = \mu_B \text{Tr}\{ \text{Im}\{ \hat{\rho}_{\uparrow\downarrow} \} \mathbf{S} \}$$

How can  $\hat{H}_{\uparrow\downarrow}$  be non-zero?

1. If not all spins are align along z, then

$$\hat{\rho}_{\uparrow\downarrow} \neq \mathbf{0} \rightarrow$$

To calculate  $E_{XC}$

a) the density is locally (i.e. for each point on the grid) rotated along z

b)  $E_{XC}[\rho_{\uparrow}, \rho_{\downarrow}]$  is calculated

c) the corresponding term in the Hamiltonian is rotated back according to original direction

$$\rightarrow \hat{H}_{\uparrow\downarrow} \neq \mathbf{0}$$

2. If we include spin-orbit coupling:

$$\hat{H}_{SO} \sim \hat{L} \cdot \hat{S}$$

$$\rightarrow \hat{H}_{\uparrow\downarrow} \neq \mathbf{0}$$

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      -6.3620  -6.0184  -5.7102  -4.8477  -4.7915  -4.4688  -4.3186  -4.2566  -3.2346
      -2.0978  -2.0153   5.2669   6.2161  19.1865  19.5289  20.0456  20.3643  27.5877
      28.3833  28.3866  31.6409  32.2675  34.5233  35.4643  37.6469  38.8891  42.3467
      50.6597  52.7767  56.7916  57.5425  61.3260  61.3262  62.4743  62.4752
0.008768    -13.8448  -13.5988  -10.2396  -9.9184  -9.6636  -9.5332  -7.4535  -7.4032  -6.8076
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- **DOS** file:
  - two additional columns: *energy*,  $DOS(\uparrow\uparrow)$ ,  $DOS(\downarrow\downarrow)$ ,  **$\text{Re}\{DOS(\uparrow\downarrow)\}$** ,  **$\text{Im}\{DOS(\uparrow\downarrow)\}$**

**Siesta Documentation**  
0.1

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**Tutorials**

- Setting up the local working environment for the tutorial exercises
- Basics of Siesta
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  - Molecular Dynamics
  - Spin-Orbit coupling**
    - Performing calculations with different spin configuration.
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## Spin-Orbit coupling

**Author** Ramón Cuadrado (University of Southampton) & Nils Wittemeier (ICN2)

The main goal of this tutorial is to cover the basic notions to perform calculations using the spin and spin-orbit coupling (SOC) in Siesta.

### Performing calculations with different spin configuration.

#### Hint

Please move to directory *Example-1*.

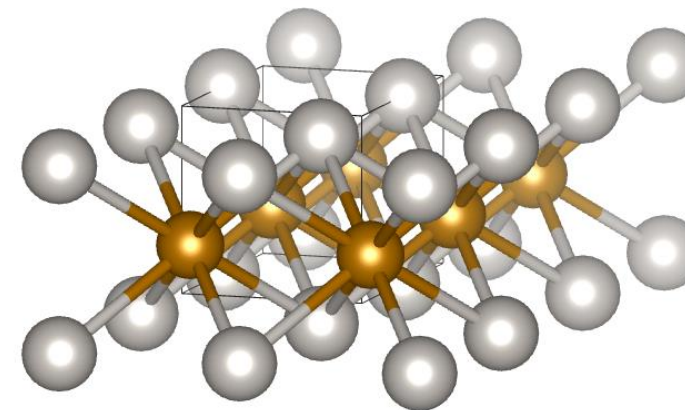
#### Note

The original fdf for this example can be found in *example\_1.fdf.original*. We have made some changes (can you see them?) to speed the calculation while maintaining reasonable quality results.

In this example you will calculate the band structure, density-of-states (DOS), and Mulliken charges of bulk FePt using different spin options.

### Getting started

To get started inspect the input file *example\_1.fdf* file, and make sure that you are familiar with all options in the input file. Refer to the user manual to clarify any doubts. Alongside the input file you will find two pseudopotential files one for Fe and one for Pt (*Fe\_fept\_SOC.psf*, *Pt\_fept\_SOC.psf*)



**Perform and analyze calculations of FePt with all different option for *Spin***

How can we include SO in SIESTA? - **Pseudo potentials.**

## Pseudo potential generation

*Scalar relativistic case:*

1. Solve **Schrödinger** equation  
*including scalar relativistic corrections*
2. Smoothen wavefunction
3. Construct potential

$$\hat{V}_{PP} = V_{\text{local}}(r) + \sum_l \delta V_l(r) \hat{P}_l$$

*Fully relativistic pseudo potential:*

1. Solve **Dirac** equation
2. Smoothen wavefunction
3. Construct potential
  - $\mathbf{j} = \mathbf{l} \pm \frac{1}{2}$  instead  $\mathbf{l}$  ( $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ )  
$$\hat{V}_{PP} = V_{\text{local}}(r) + \sum_j \delta V_j(r) \hat{P}_j$$
  - Twice the number projectors and PP components

R Cuadrado and J I Cerdá 2012 *J. Phys.: Condens. Matter* **24** 086005

How can we include SO in SIESTA? - **Pseudo potentials.**

## Pseudo potentials

Scalar relativistic

1. Solve **Sc**  
including
2. Smooth
3. Construct

How do you get your hands on fully relativistic pseudo potentials?

- Generate with **Atom**:

<https://siesta-project.org/siesta/Pseudopotentials/index.html>

- Use database, e.g. **Pseudo Dojo**:

<http://www.pseudo-dojo.org/>

$\hat{V}_{PP}$

components

$\hat{S}$ )

id PP

R Cuadrado and J I Cerdá 2012 *J. Phys.: Condens. Matter* **24** 086005

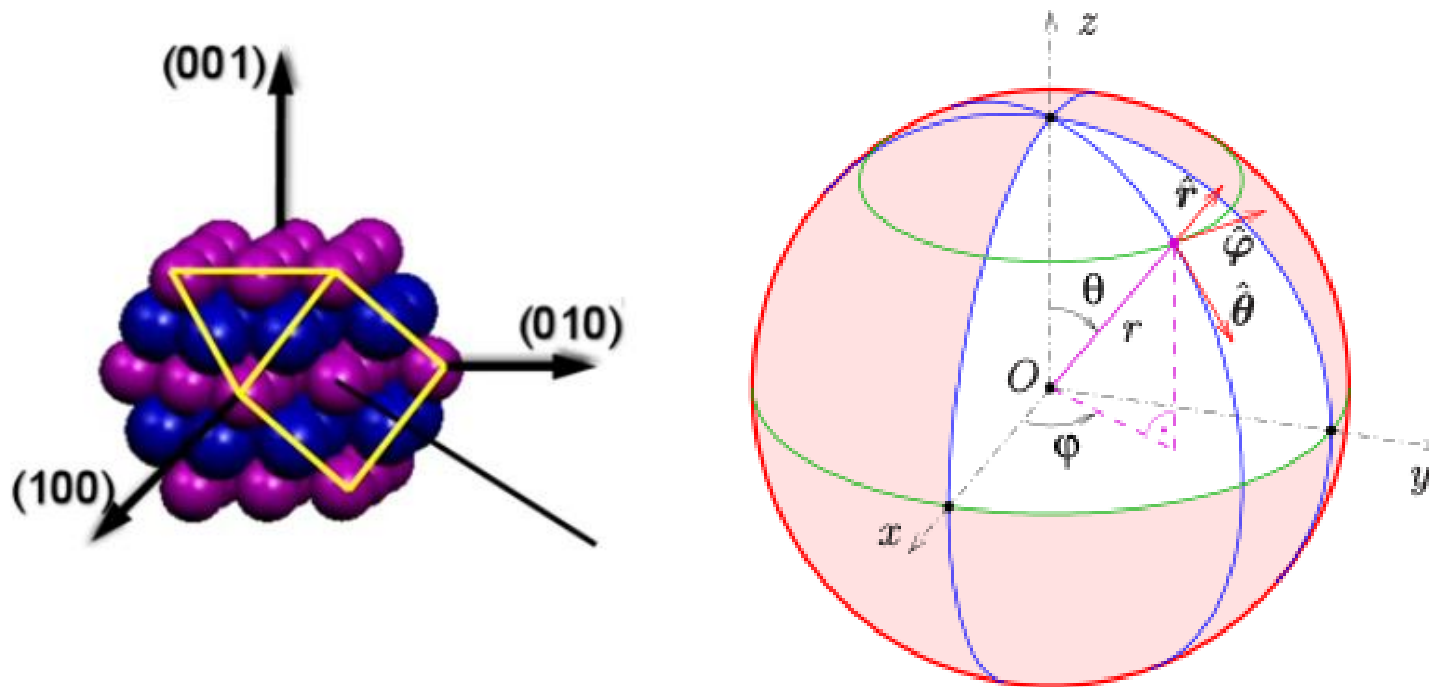
## How to run SIESTA with spin-orbit coupling

- use **spin spin-orbit**
- use fully relativistic pseudopotentials
- carefully converge
  - k-points sampling & electronic temperature
  - mesh cutoff
- Use low tolerance for the
  - density matrix  $< 10^{-5}$  eV
  - And/or Hamiltonian  $< 10^{-4}$  eV

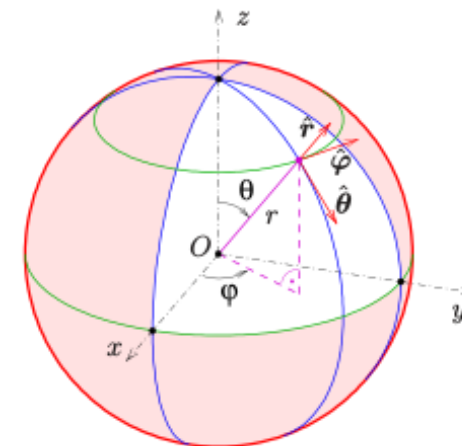
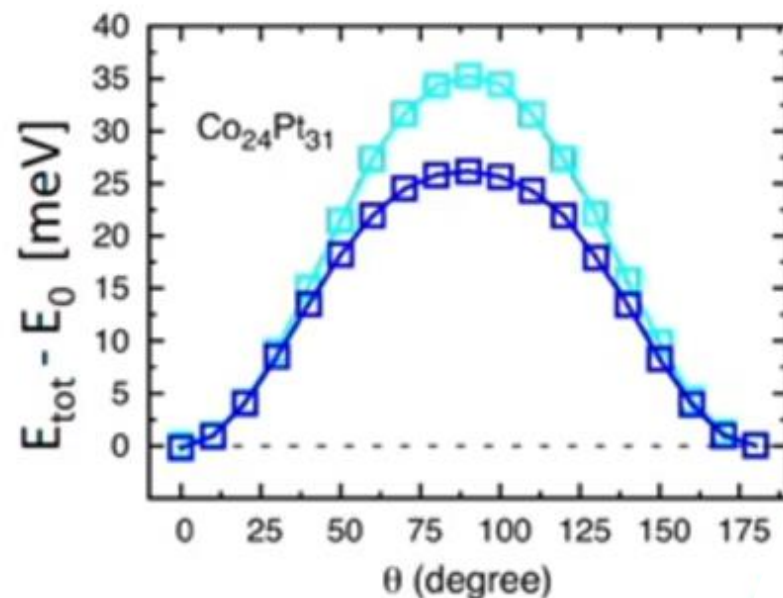
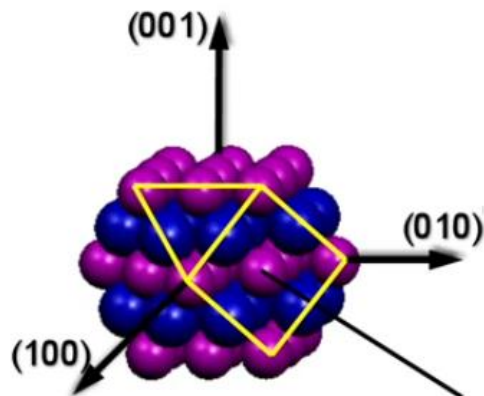
## Specific outputs:

- Energy decomposition:
  - **Eso**: spin-orbit energy
- Everything else like non-collinear case

**Example:** Magnetic Anisotropy (CoPt nano particle)



## Example: Magnetic Anisotropy (CoPt nano particle)



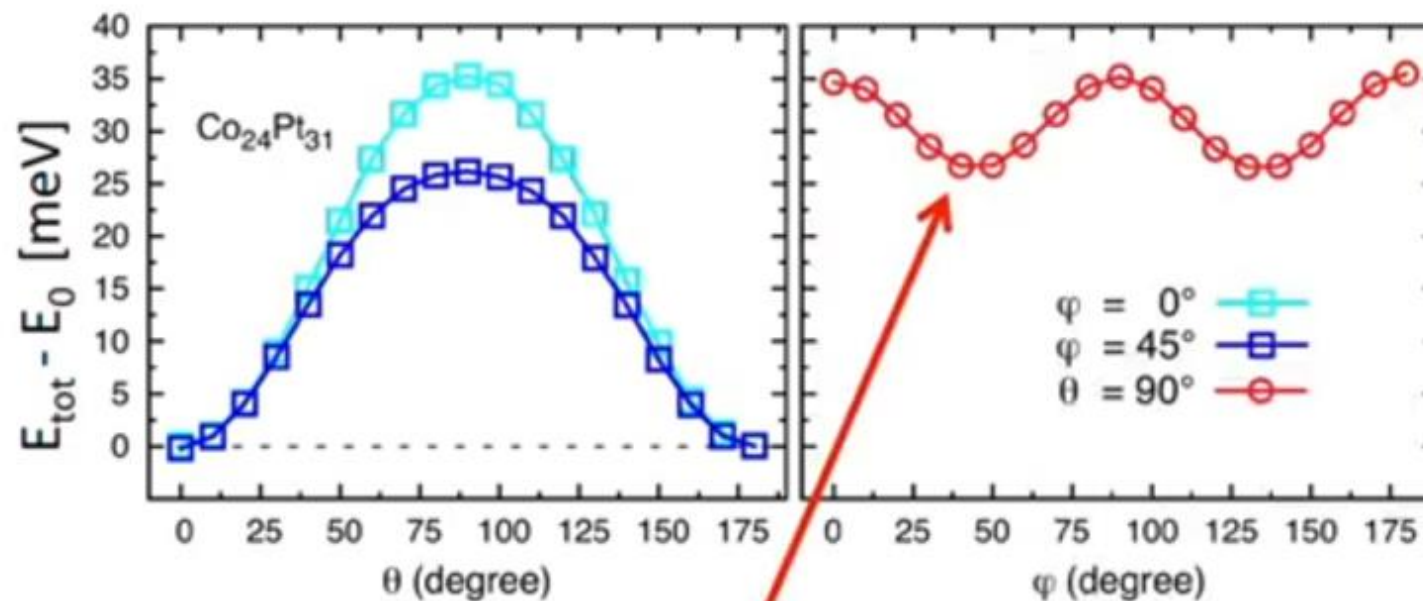
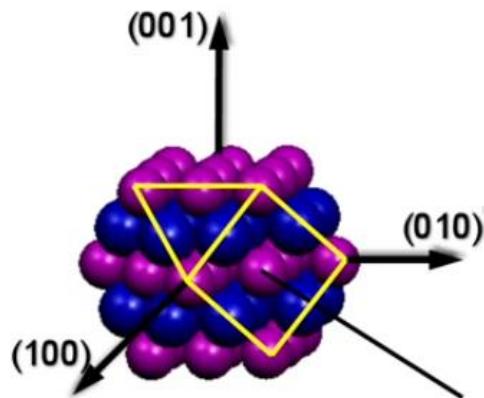
- As the angle between the magnetic moment and the z-axis increases, the total energy rises.
- When the **spin is (anti)parallel to the z-axis** the energy is the lowest, i.e. this is the **most stable** configuration.
- Magnetic anisotropy energy (MAE):

$$E_{\text{tot}}(\theta=0) - E_{\text{tot}}(\theta=90) \sim 36 \text{ meV}$$

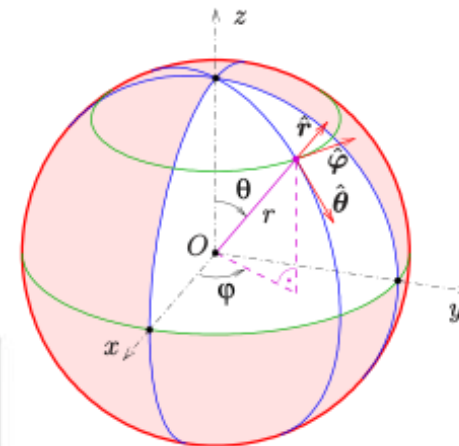


# What can we do with this?

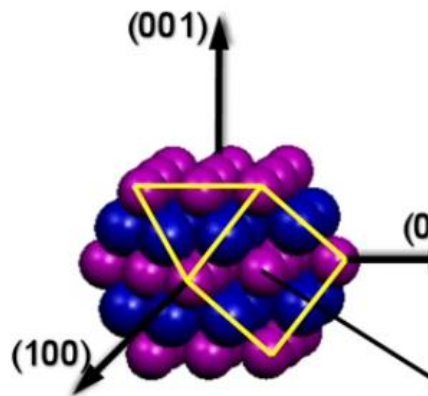
**Example:** Magnetic Anisotropy (CoPt nano particle)



In-plane anisotropy



## Example: Magnetic Anisotropy (CoPt nano particle)

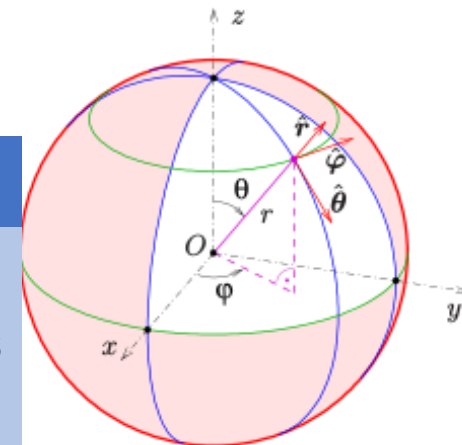


### Disclaimer

During the SCF cycle, the magnetic moments may change. **Spin directions are not fixed.** As such the final and initial spin moments may differ. The final moments should converge to a local minimum on the energy surface. In practice, the spin moments often do not fully converge and it is possible to explore different spin configurations. However, **always check the final spin moments!**

Ideally, one should use **non-collinear spin-constrained DFT\*** calculations. This feature was already implemented in SIESTA but is not publicly available, yet.

\*R Cuadrado *et al* 2018 *J. Phys. Mater.* **1** 015010



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  - The Lua scripting engine
  - Calculation of optical properties
  - Computing magnetic interaction parameters with TB2J
  - Simulation of STM images

## Calculation of the magnetic anisotropy of Pt<sub>2</sub>.

In this example, you will calculate the magnetic anisotropy of a Pt<sub>2</sub> dimer. This means you will have to run multiple SIESTA calculations each with magnetic moments aligned along different directions and extract the total energy.

To get started inspect the input file *example\_2z.fdf* file. Use this input file and the pseudopotential of Pt atom, *Pt\_pt2\_SOC.psf* (note that the pseudo for Pt is different from the one used in the first example), and calculate the total self-consistent energy *Etot* for three highly symmetric orientations of the initial magnetization, namely, X, Y and Z, keeping fixed the physical dimer (the (x,y,z) coordinates of each atom).

Each calculation has to be initialized modifying the `DM.InitSpin`, updating the orientation of each atomic magnetization. As a result one has to have three different energy values for each (θ,φ) pair.

Remember to rename each one of the *.fdf* files, change the `SystemLabel` flag inside for each magnetic orientation and do not re-use the density matrix (*.DM* file) obtained in other orientations. Reading the density matrix will cause SIESTA to ignore the `DM.InitSpin`. To calculate the total energy for each specific magnetic configuration you need to start from scratch.

## Calculation of the magnetic anisotropy of FePt bulk

In this example, you will calculate the magnetic anisotropy bulk FePt.

You will find the *example\_3z.fdf* file and the PPs of Fe and Pt: *Fe\_fept\_SOC.psf* and *Pt\_fept\_SOC.psf*. Each calculation has to be initialized modifying the `DM.InitSpin` block, as above, updating the orientation of each atomic magnetization. As a result one has to have different energy values for each (θ,φ) pair.

- A) Obtain the *Etot* for three highly symmetric orientations of the initial magnetization, namely, X, Y and Z, keeping fixed the atoms in their unit cell. Again do not use the same density matrix for same calculations. Allow SIESTA to calculate it from scratch.
- B) Create a magnetization curve changing the angles at intervals of 20 degrees from the Z-axis initial orientation, to finalize along the X axis. Plot the resulting energy as a function of the varied angle. Check the orientation of the final magnetic moment in each output file. Does it coincide with the initial one?

- In addition to the first exercise, We prepared two more exercise, in which we walk through the **calculation of the magnetic anisotropy of**

- a Pt<sub>2</sub> dimer**
- bulk FePt**

