Spins & Spin-Orbit Coupling in SIESTA

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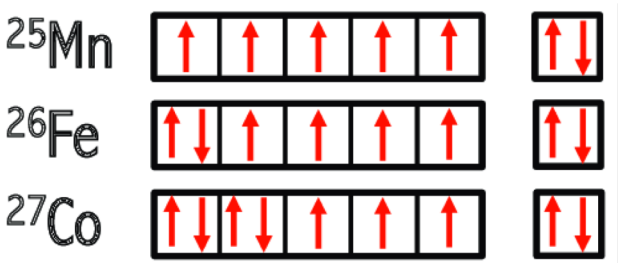
Magnetism

- Magnetism is an intrinsic property of some materials
- Origin: electron spin
- Typically, electrons are paired (with spin ↑ & spin ↓): no magnetism
- Sometimes: unpaired electron (only spin ↑ or spin ↓): then magnetism

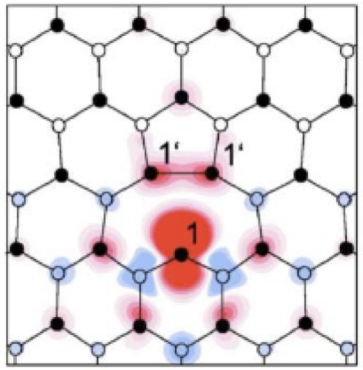
Magnetic Atoms
partially filled core shells



filling of orbital shells
according to Hund's rule
→ magnetic atoms

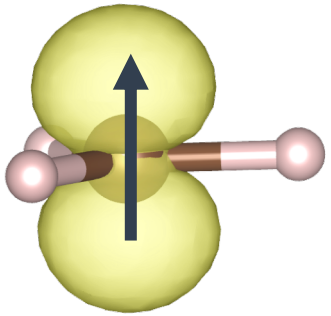
Solids and Molecules with unpaired electrons

C vacancy in graphene



Unpaired electron localized
near the defect side
→ local magnetic field

Methyl radical



Unpaired electron of C
→ magnetic field

Spin-Orbit Coupling

Spin-orbit coupling (SOC)

- *relativistic effect*

  interaction of the electron spin $\hat{\boldsymbol{S}}$ and its own orbital momentum $\hat{\boldsymbol{L}}$

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

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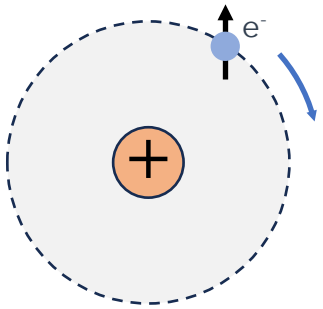
Rest frame of the nucleus



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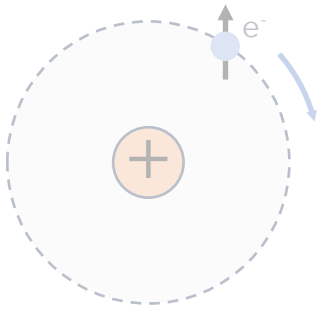
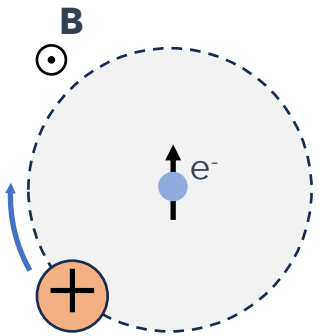


Rest frame of the electron



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

Spin-Orbit Coupling

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  interaction of the electron spin $\hat{\boldsymbol{S}}$ and its own orbital momentum $\hat{\boldsymbol{L}}$

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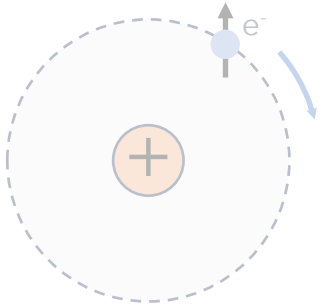

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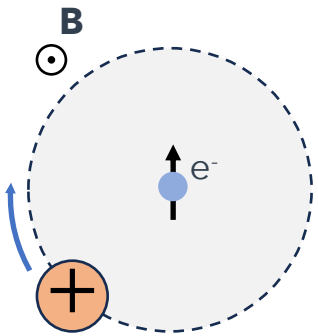

- **Isolated atom:**
  split energy levels in *atomic fine structure*
- **General:**
  couples real space and spin space
  → also spins & crystal lattice

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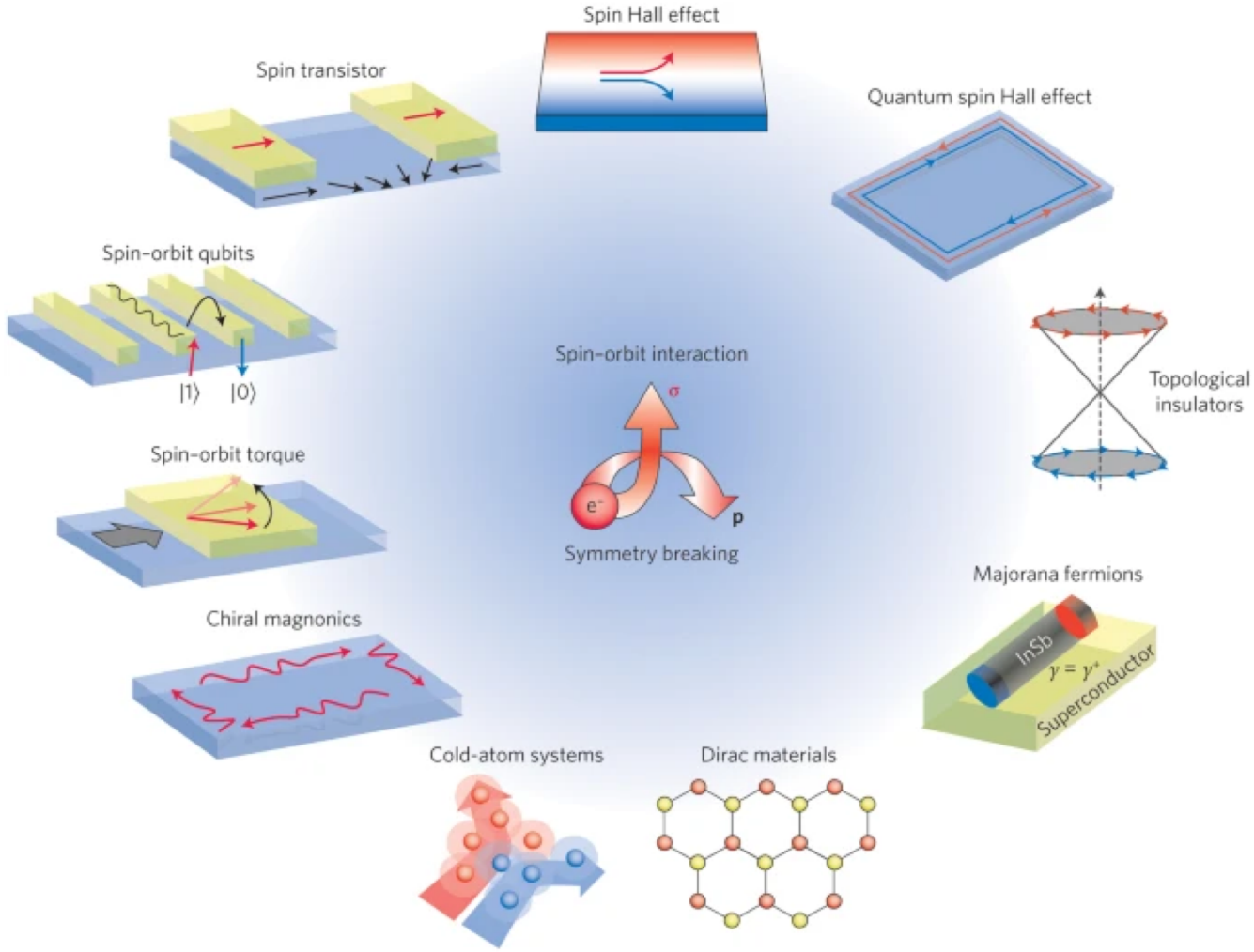
Spin-Orbit Coupling

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 …



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

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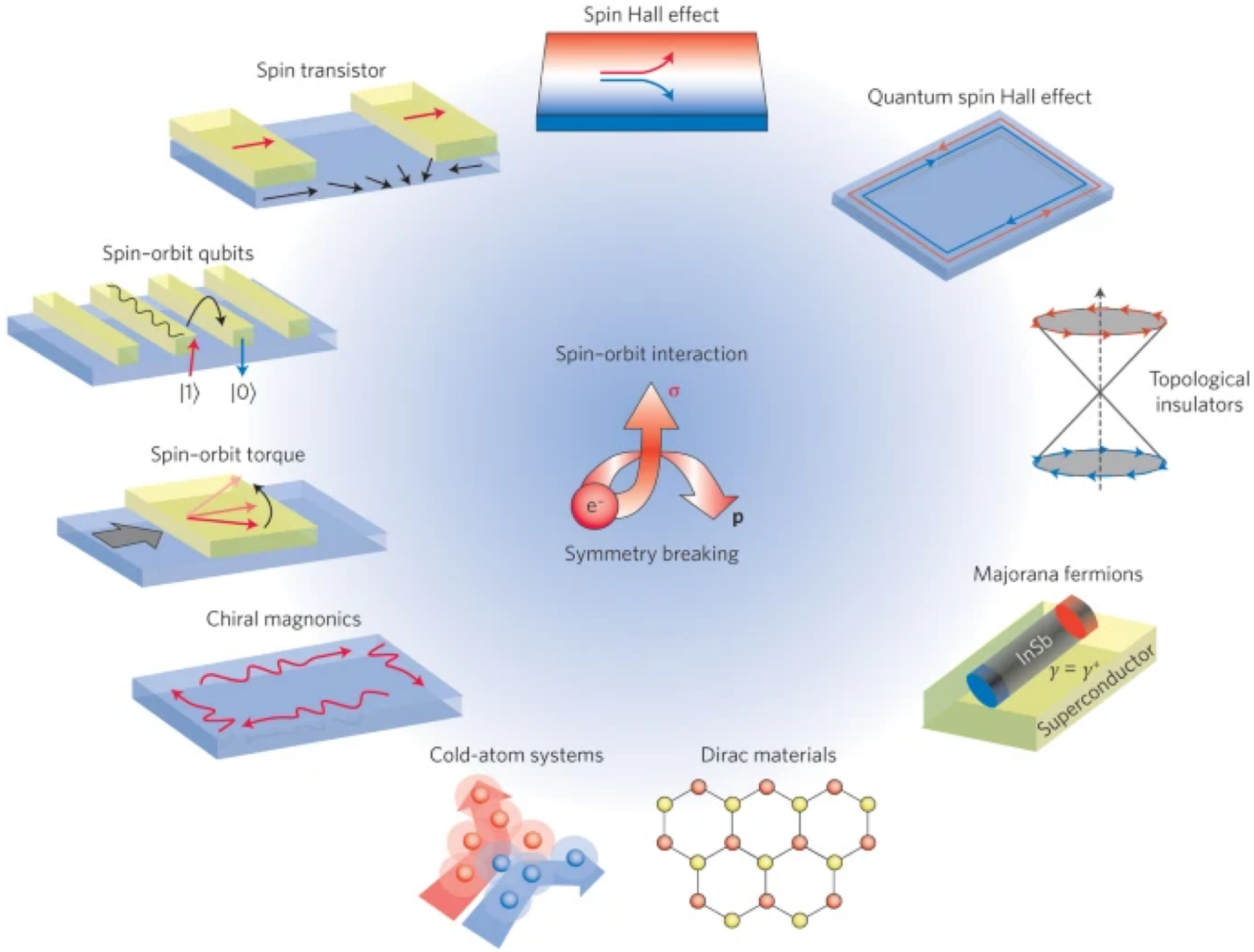

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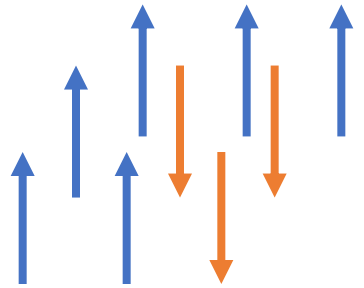
So far: SIESTA only without spin

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

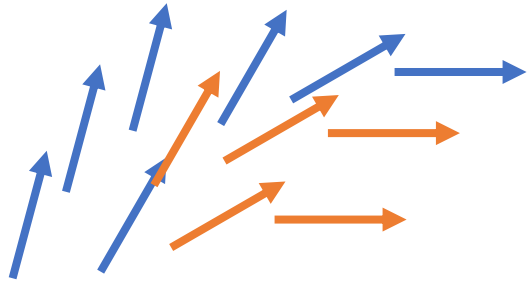
How can we control the spins in SIESTA?

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



colinear



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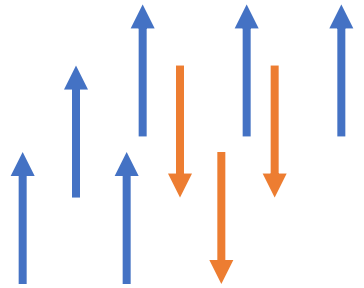

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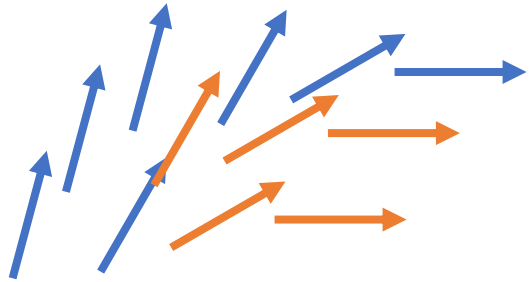

non-colinear

Colinear Spins in SIESTA (1/2)

What does it mean?

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

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

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

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

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

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

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Colinear spin calculation:

no SOC

→ spin and real space decoupled

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

Colinear Spins in SIESTA (2/2)

How do SIESTA outputs change?

- Information printed each SCF step:
  - includes (x,y,z) components and magnitude of the spin per cell
  - 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
```

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- **.bands** file: twice as many eigen values for each k point: spin up, spin down

```
  -3.58228951613775
  0.000000000000000E+000    4.14093362787451
  -13.8419785400988         68.6417154298812
           24           2          351                    # Number of spin channels 2
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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- **gnubands**:
  - 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
...
```

Colinear Spins in SIESTA (2/2)

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- **DOS** file:
  - one additional column per energy point: energy, DOS(up), DOS(down)
- **… quantities** separately for up and down channel

Mulliken charges (1/2)

How can we tell the magnetic moment of each atom?

- Calculate Mulliken charges (or Voronoi/Hirschfeld)
- Example Mulliken charges:

```
<input.fdf>
Charges.Mulliken         end   # Calculate Mulliken charges at the end (using final DM)
Charges.Mulliken.Format 1      # Calculate atomic and orbital populations
```

```
<siesta output>

mulliken: Qtot =        4.000

Mulliken Atomic Populations:
Atom #   charge [q] valence [e]      Sz [e]  Species
     1     0.000000    8.000000    0.000000  Fe
-----------------------------------------
 Total     0.000000                0.000000
```

Mulliken charges (2/2)

```
<siesta output>
mulliken: Atomic and Orbital Populations:

mulliken: Spin UP

Species: Fe
Atom  Qatom  Qorb
               4s       4s       3dxy     3dyz     3dz2     3dxz     3dx2-y2 3dxy
               3dyz     3dz2     3dxz     3dx2-y2 4Ppy     4Ppz     4Ppx
   1  4.000  -0.195    0.336    0.687    0.687    0.697    0.687    0.697   -0.040
             -0.040   -0.068   -0.040   -0.068    0.219    0.219    0.219

mulliken: Qtot =        4.000

mulliken: Spin DOWN

Species: Fe
Atom  Qatom  Qorb
               4s       4s       3dxy     3dyz     3dz2     3dxz     3dx2-y2 3dxy
               3dyz     3dz2     3dxz     3dx2-y2 4Ppy     4Ppz     4Ppx
   1  4.000  -0.195    0.336    0.687    0.687    0.697    0.687    0.697   -0.040
             -0.040   -0.068   -0.040   -0.068    0.219    0.219    0.219
```

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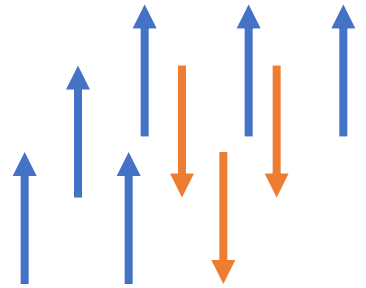
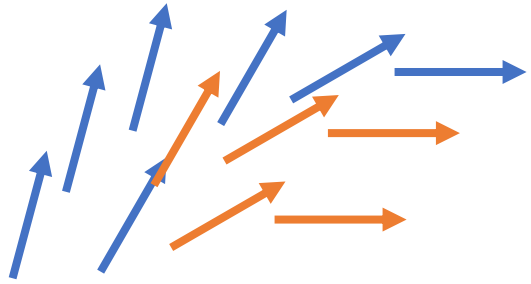


colinear



non-colinear

Non-collinear Spins in SIESTA (1/4)

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

Spin dependent operators

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

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

- $\hat{\rho}_{\uparrow\uparrow} + \hat{\rho}_{\downarrow\downarrow}$: related to charge $\quad \mathrm{Q} = \mathrm{Tr}\{ (\hat{\rho}_{\uparrow\uparrow} + \hat{\rho}_{\downarrow\downarrow}) \boldsymbol{S} \}$
- $\hat{\rho}_{\uparrow\uparrow} - \hat{\rho}_{\downarrow\downarrow}$: related to spin polarization *z-axis* $\quad \mathrm{M}_z = \mu_B \frac{1}{2} \mathrm{Tr}\{ (\hat{\rho}_{\uparrow\uparrow} - \hat{\rho}_{\downarrow\downarrow}) \boldsymbol{S} \}$
- $\mathrm{Re}\{\hat{\rho}_{\uparrow\downarrow}\}$: related to spin polarization along *x axis* $\quad \mathrm{M}_x = \mu_B \, \mathrm{Tr}\{ \mathrm{Re}\{\hat{\rho}_{\uparrow\downarrow}\} \boldsymbol{S} \}$
- $\mathrm{Im}\{\hat{\rho}_{\uparrow\downarrow}\}$: related to spin polarization along *y-axis* $\quad \mathrm{M}_y = \mu_B \, \mathrm{Tr}\{ \mathrm{Im}\{\hat{\rho}_{\uparrow\downarrow}\} \boldsymbol{S} \}$

Non-collinear Spins in SIESTA (2/4)

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

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

   $\rightarrow \hat{\rho}_{\uparrow\downarrow} \neq 0$ **initial guess!**

   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

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

2. If we include spin-orbit coupling:

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

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

```
%block DM.InitSpin
# ia   S[μB]   theta[deg]   phi[deg]
   1   3.0          90.0       45.0
   4   1.0          35.1       27.3
%endblock
```

Non-colinear Spins in SIESTA (3/4)

How do SIESTA outputs change?

- Information printed each SCF step:
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  - now all components can be non-zero

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- **.bands** file: twice as many eigenvalues for each k point, no separation by spin index

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  -13.8419785400988         68.6417154298812
           48           1          351
0.000000  -13.8461 -13.6001 -10.2404  -9.9188  -9.6644  -9.5335  -7.4540  -7.4037  -6.8073
           -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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Non-colinear Spins in SIESTA (3/4)

How do SIESTA outputs change?

- Information printed each SCF step:
  - includes spin moment and (x,y,z) component.
  - in collinear case x and y components always zero.
- **.bands** file: twice as many eigenvalues for each k point, no separation by spin index
- **gnubands**: like no-spin-case, but twice as many bands
- **DOS** file:
  - two additional columns: *energy, DOS(↑↑), DOS(↓↓),* ***Re{DOS(↑↓)}, Im{DOS(↑↓)}***

```
    -9.99999      1.00971      0.63864      0.00984      0.15962
    -9.98497      1.04733      0.66864      0.01432      0.19872
    -9.96996      1.04293      0.64380      0.00974      0.14875
...
```

Non-colinear Spins in SIESTA (4/4)

- **Mulliken charges**

```
mulliken: Atomic and Orbital Populations:

Species: Fe

Atom      Orb         Charge      Spin       Svec
--------------------------------------------------------------------
    1  1 4s         -0.40124   0.09699      0.000   0.000   0.097
    1  2 4s          0.68554   0.08028     -0.000  -0.000  -0.080
    1  3 3dxy        1.42547   0.33596      0.000   0.000   0.336
…
    1 15 4Ppx        0.44364   0.05058      0.000  -0.000  -0.051
    1     Total      8.00000   2.18666      0.000   0.000   2.187

--------------------------------------------------------------------
Total                8.00000   2.18666      0.000   0.000   2.187


Mulliken Atomic Populations:
Atom #   charge [q] valence [e]          S      Sx [e]      Sy [e]      Sz [e]  Species
     1     0.000000    8.000000    2.186656    0.000000    0.000000    2.186656  Fe
-------------------------------------------------------------------------------
 Total     0.000000                2.186656    0.000000    0.000000    2.186656
```

Detailed break-down

- *One row for each orbital/atom*
- *Total population (charge)*
- *Magnitude of spin moment*
- *Spin vector (S_x, S_y, S_z)*

Summary for each atom

Spin-Orbit coupling in SIESTA

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

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

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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
   - $\mathbf{j} = \boldsymbol{l} \pm \frac{\mathbf{1}}{\mathbf{2}}$ instead $\boldsymbol{l}$ $\quad (\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}})$

     $$\hat{V}_{PP} = V_{\text{local}}(r) + \sum_{j} \delta V_j(r)\hat{P}_j$$

   - Twice the number projectors and PP components

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Spin-Orbit coupling in SIESTA

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

Pseudo poten

Scalar relati

1. Solve ***Sc***
   includin
2. Smooth
3. Constru

$\hat{S}$)

$\hat{V}_{PP}$

d PP

components

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/

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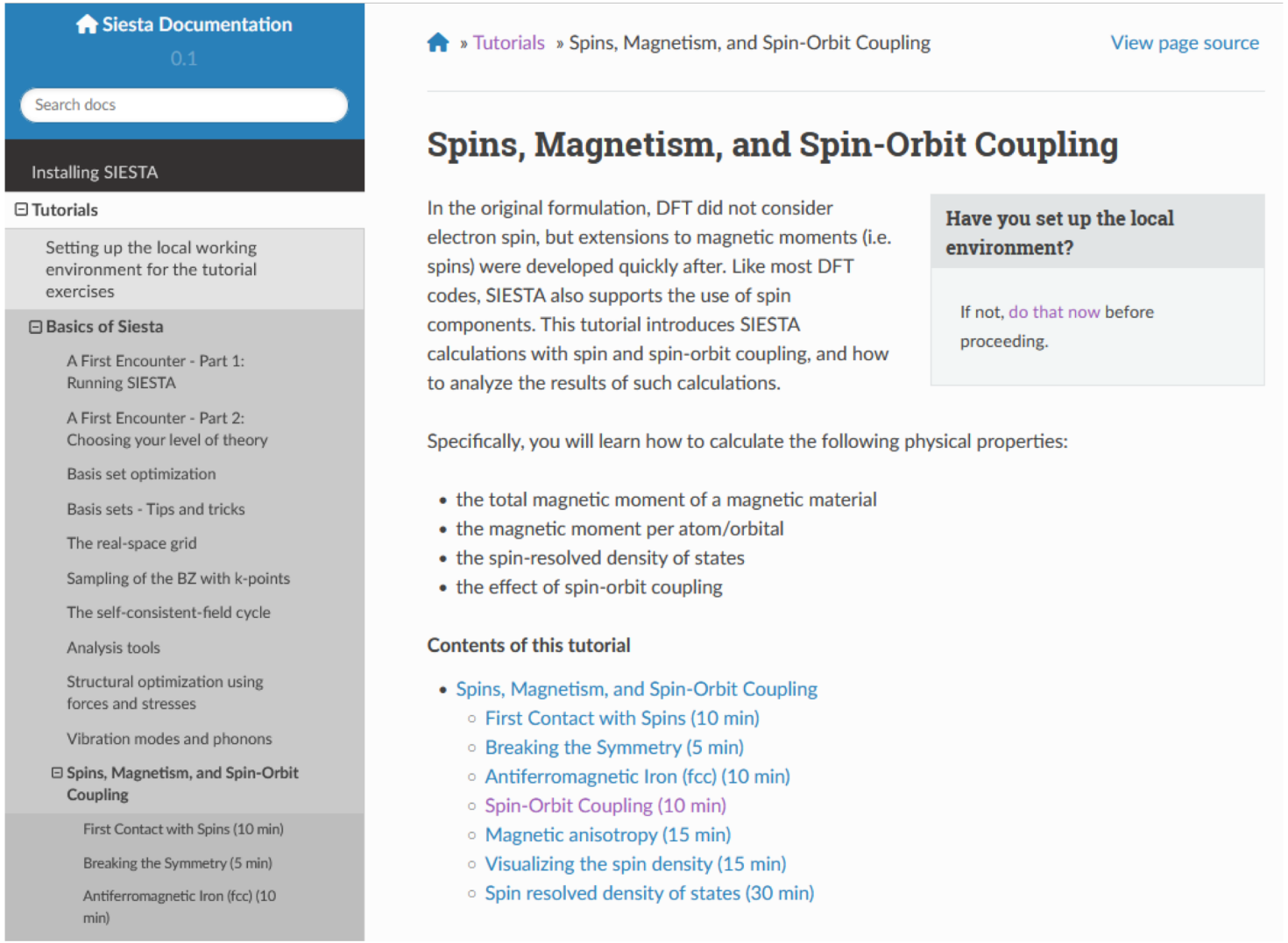
Tutorials



Time to try it for yourself!

Instructions:

» Tutorials » Spins, Magnetism, and Spin-Orbit Coupling

https://docs.siesta-project.org/projects/siesta/en/latest/tutorials/basic/magnetism

On MareNostrum5:

Find input files in

day4/magnetism/02.SpinMagnetism