First-principles simulations of materials with SIESTA

Spin-Orbit Coupling

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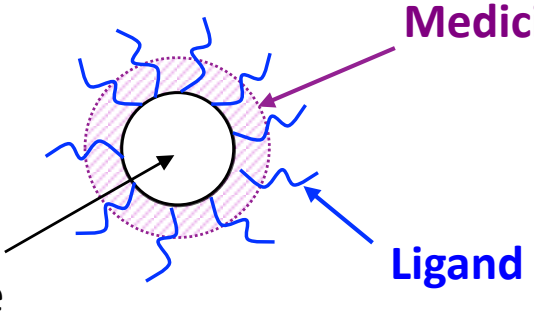
Summary

- Motivation
- What does the Spin-Orbit coupling mean?
- Pseudopotentials and Spin-Orbit
- SIESTA and Spin-Orbit (scalar vs. fully relativistic approx.)
- Some examples

Nano-devices:

- Medical applications
- Catalytic reactions
- Magnetic recording
- Biological sensors
- Optoelectronics, etc

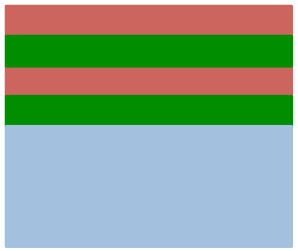


High density magnetic recording

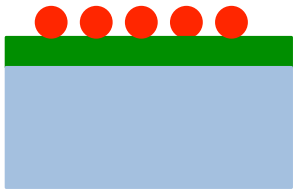
- State-of-the-art 1-2 Tbit/in^2

- Goal 10 Tbit/in^2

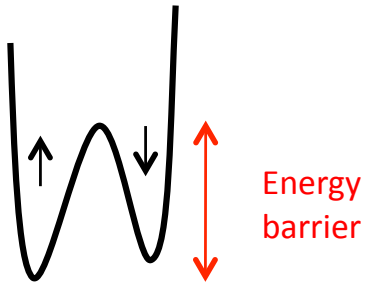
Multilayers, thin films



Magnetic nanoparticles onto a surface:



Major obstacle:
Superparamagnetic limit



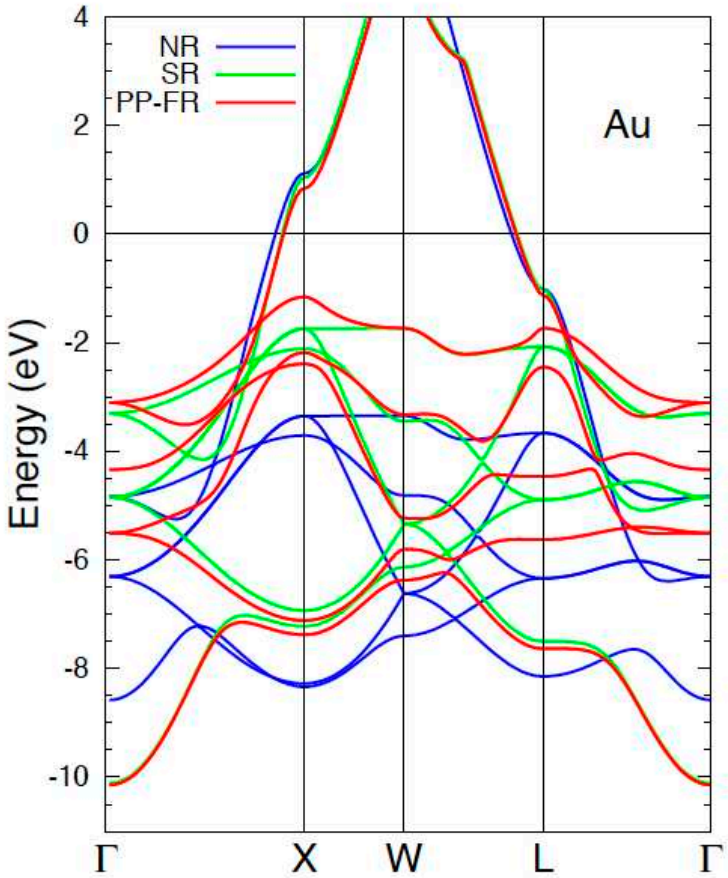
$$\tau_N = \tau_0 \exp(KV / k_B T)$$

Neel relaxation law

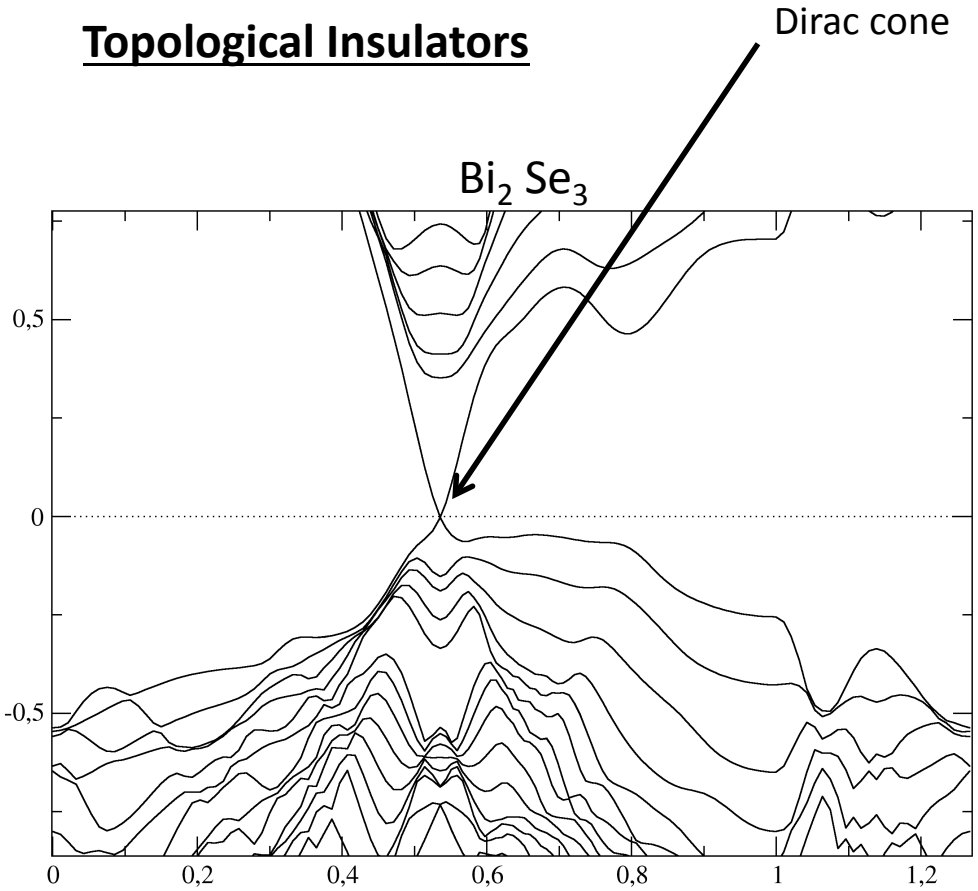
K : Anisotropy

V: NP volume

Au fcc:

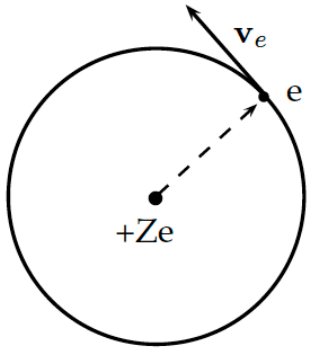


Topological Insulators

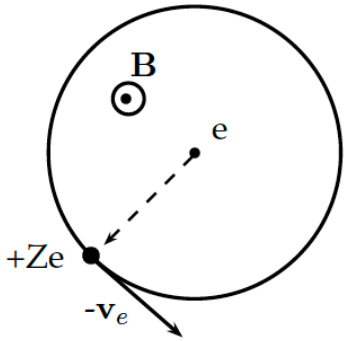


What does the Spin-Orbit physically represent?

The Spin-Orbit coupling is a relativistic effect



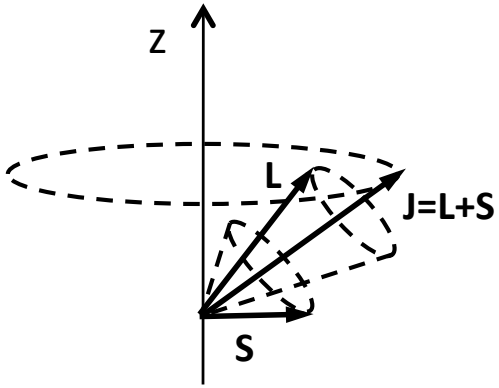
Nucleus rest frame



Electron rest frame

$$H_{total} = \overbrace{H_{NR} + \underbrace{H_{SR} + H_{SO}}_{\text{Relativistic corrections}}}^{\text{Dirac}}$$

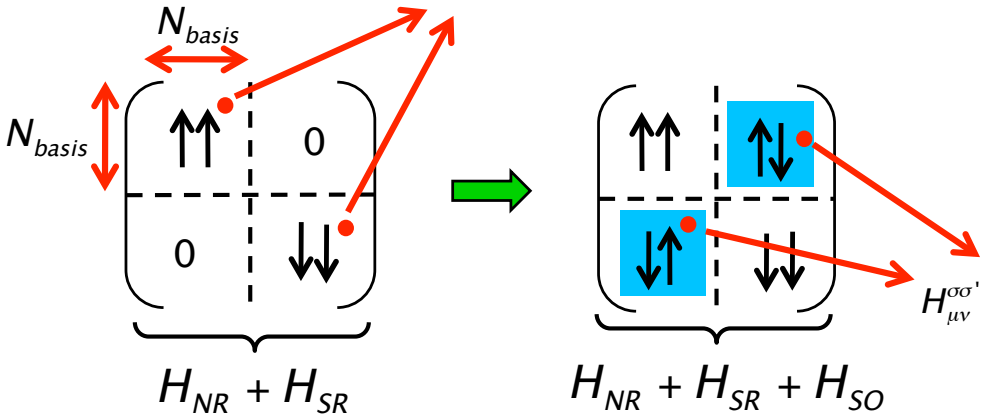
Schrödinger +



$$J_{\pm} = l \pm 1/2 \quad \downarrow \quad m_J = -J,\ldots,+J$$

Degeneracy $2J+1$

$$H^{\sigma\sigma}_{\mu\nu} = \left\langle \phi_\mu, \sigma \middle| \hat{H}_{NR} + \hat{H}_{SR} \middle| \phi_\nu, \sigma \right\rangle$$



$$H^{\sigma\sigma'}_{\mu\nu} = \left\langle \phi_\mu, \sigma \middle| \hat{H}_{TOTAL} \middle| \phi_\nu, \sigma' \right\rangle$$

$$|l,\sigma\rangle \rightarrow |J,m_J\rangle = \begin{pmatrix} C^l \middle| lm,\uparrow \rangle \\ C^l \middle| lm,\downarrow \rangle \end{pmatrix}$$

espinors

$\sigma, \sigma' = \uparrow, \downarrow$

How we can introduce the SO contribution within the total Hamiltonian in SIESTA?

By means of the PPs term

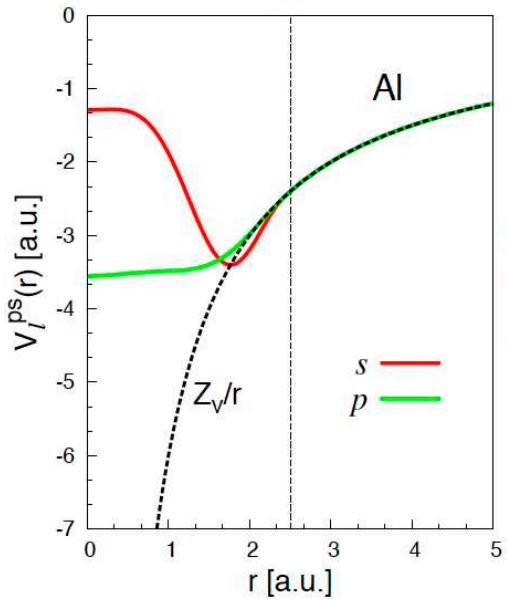
$$\left[\hat{T}_e + \hat{V}_{el}^{ps} + \hat{V}_H + \hat{V}_{XC}^{\sigma}\right]\psi_i^{KS,\sigma} = \varepsilon_i^{KS,\sigma}\psi_i^{KS,\sigma}$$

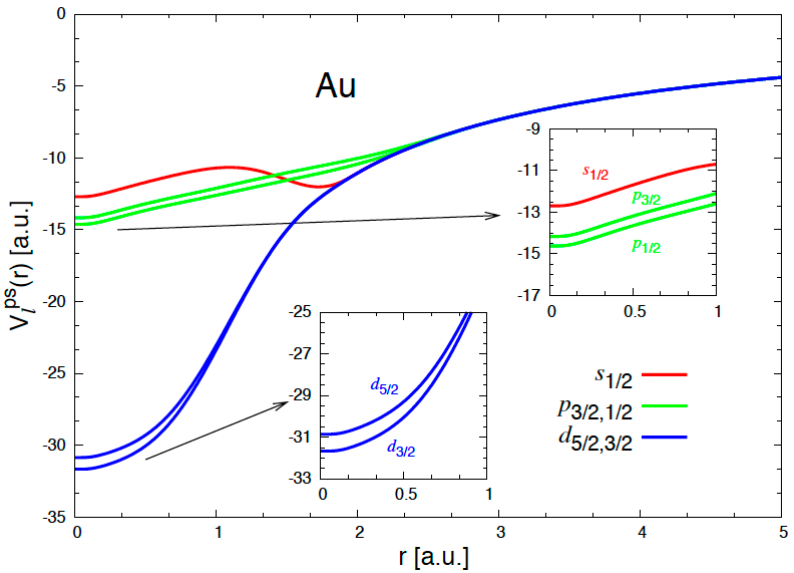
ATOM (PPs generator by means of Dirac eq.)

Scalar relativistic: $V_l(r)$

Fully Relativistic: $V_{l+1/2}(r), V_{l-1/2}(r)$

split





What does ATOM give us after solve the Dirac eq.?

$$V_{dn} = V_l^{ion} = \frac{1}{2l+1}\left[(l+1)V_{l+1/2} + lV_{l-1/2}\right]$$

$$V_{up} = V_l^{so} = \frac{2}{2l+1}\left[V_{l+1/2} - V_{l-1/2}\right]$$

#.psf

$$\hat{V}_I^{ps} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} V_{l,I}^{ps}(r)|lm\rangle\langle lm| = \sum_{l=0}^{\infty} V_{l,I}^{ps}(r)\hat{P}_l,$$

ATOM PROGRAM: https://departments.icmab.es/leem/siesta/Pseudopotentials/index.html

We want substitute the scalar relativistic operator V^{ps} by its fully relativistic version:

$$\hat{V}_I^{ps} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} V_{l,I}^{ps}(r)|lm\rangle\langle lm| = \sum_{l=0}^{\infty} V_{l,I}^{ps}(r)\hat{P}_l, \quad \Rightarrow \quad \hat{V}_I^{ps} = \sum_{l,J} V_{lJ}^{ps}(r)\hat{P}_J = \sum_{l,J,m_J} |Jm_J\rangle V_{lJ}^{ps}(r)\langle Jm_J|$$

Fully relativistic operator V^{ps} and Spin-Orbit:

#.psf

$$V_{dn} = V_l^{ion} = \frac{1}{2l+1}\left[(l+1)V_{l+1/2} + lV_{l-1/2}\right]$$

$$V_{up} = V_l^{so} = \frac{2}{2l+1}\left[V_{l+1/2} - V_{l-1/2}\right]$$

$$V_{l+1/2}(r) = V_{dn,l}(r) + \frac{l}{2}V_{up,l}(r)$$

$$V_{l-1/2}(r) = V_{dn,l}(r) - \frac{(l+1)}{2}V_{up,l}(r)$$

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J. Phys.: Condens. Matter **24** (2012) 086005 (15pp) doi:10.1088/0953-8984/24/8/086005

Fully relativistic pseudopotential formalism under an atomic orbital basis: spin–orbit splittings and magnetic anisotropies

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$$\hat{V}_I^{ps} = \sum_{l,J} V_{lJ}^{ps}(r)\hat{P}_J = \sum_{l,J,m_J} |Jm_J\rangle V_{lJ}^{ps}(r)\langle Jm_J|$$

Fully non-local Kleinman-Bylander (KB) op.

$$\delta\hat{V}^{\mathrm{ps}} \approx \hat{V}^{\mathrm{KB}} = \sum_{lJ_\pm m_{J_\pm}} |v_{lJ_\pm}; lJ_\pm, m_{J_\pm}\rangle\langle v_{lJ_\pm}; lJ_\pm, m_{J_\pm}|$$

$$\hat{V}_I^{ps}(\mathbf{r}) = \hat{V}^{SR}(\mathbf{r}) + \hat{V}^{SO}(\mathbf{r})$$

Magnetic Anisotropy Energy of CoPt-L1$_0$ NP

PHYSICAL REVIEW B **86**, 224415 (2012)

Electronic and magnetic properties of bimetallic $L1_0$ cuboctahedral clusters by means of fully relativistic density-functional-based calculations

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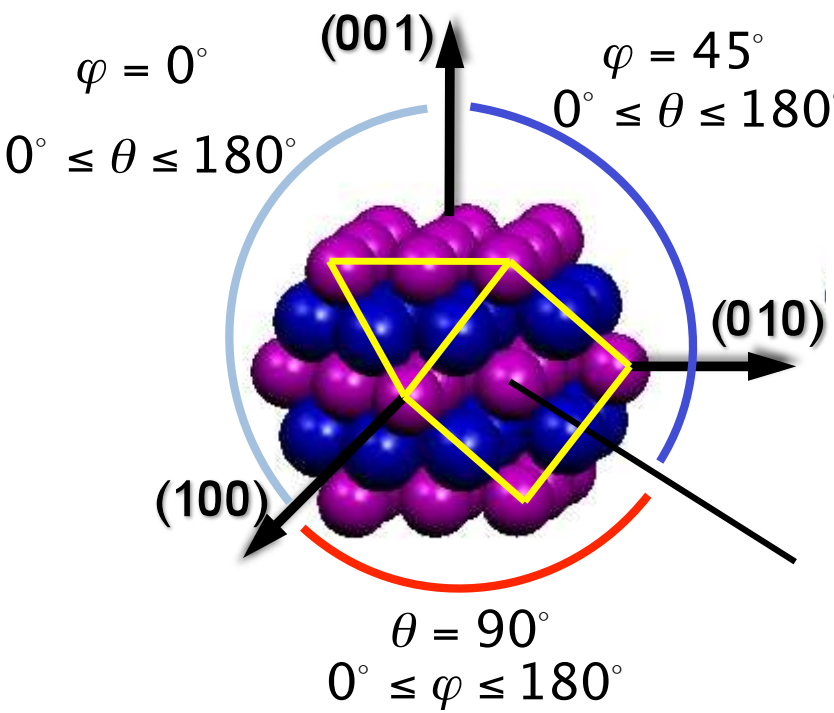
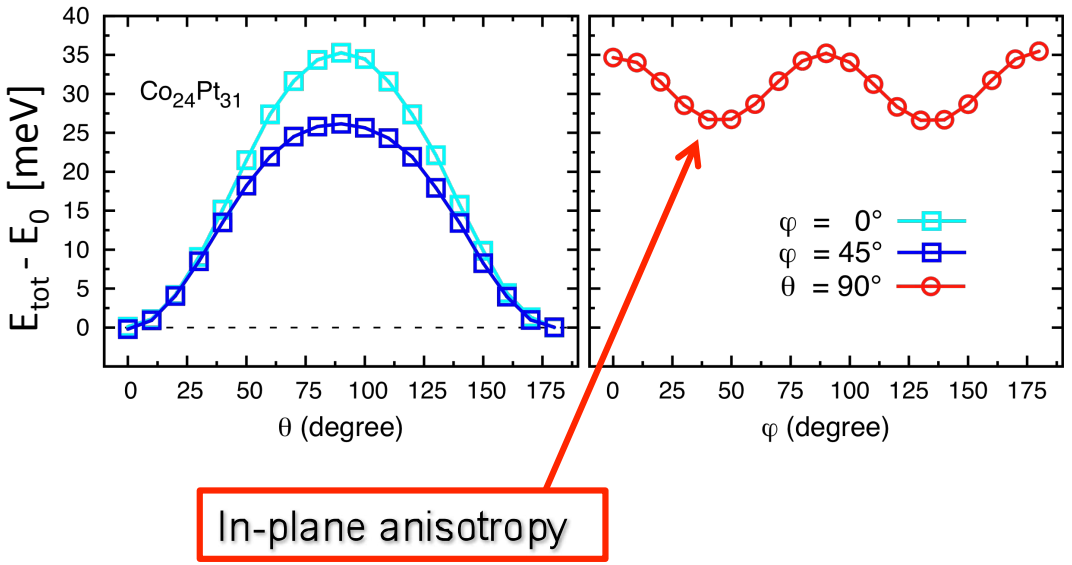
Total energy vs. magnetizations angles





SIESTA manual and Spin-Orbit:

6.8 Spin-Orbit coupling

SIESTA includes the posibility to perform fully relativistic calculations by means of the inclusion in the total Hamiltonian not only the Darwin and velocity correction terms (Scalar–Relativistic calculations), but also the spin-orbit (SO) contribution. There are two approaches regarding the SO formalism: on-site and off-site. Within the on-site approximation only the intra-atomic SO contribution is taken into account. In the off-site scheme additional neighboring interactions are also included in the SO term. By default, the off-site SO formalism is switched on, being necessary to change the **Spin** flag in the input file if the on-site approximation wants to be used. See **Spin** on how to handle the spin-orbit coupling.

The on-site spin-orbit scheme in this version of SIESTA has been implemented by Dr. Ramón Cuadrado based on the original on-site SO formalism and implementation developed by Prof. Jaime Ferrer and his collaborators *et al* (L Fernández–Seivane, M Oliveira, S Sanvito, and J Ferrer, Journal of Physics: Condensed Matter, **18**, 7999 (2006); L Fernández–Seivane and Jaime Ferrer, Phys. Rev. Lett. **99**, 183401 (2007)).

The off-site scheme has been implemented by Dr. Ramón Cuadrado and Dr. Jorge I. Cerdá based on their initial work (R. Cuadrado and J. I. Cerdá "Fully relativistic pseudopotential formalism under an atomic orbital basis: spin-orbit splittings and magnetic anisotropies", J. Phys.: Condens. Matter **24**, 086005 (2012); "In-plane/out-of-plane disorder influence on the magnetic anisotropy of $Fe_{1-y}Mn_yPt$-L1(0) bulk alloy", R. Cuadrado, Kai Liu, Timothy J. Klemmer and R. W. Chantrell, Applied Physics Letters, **108**, 123102 (2016)).

The inclusion of the SO term in the Hamiltonian (and in the Density Matrix) causes an increase in the number of non-zero elements in their off-diagonal parts, i.e., for some (μ,ν) pair of basis orbitals, $\mathbf{H}^{\sigma\sigma'}_{\mu\nu}$ ($\mathbf{DM}^{\sigma\sigma'}_{\mu\nu}$) $[\sigma,\sigma' = \uparrow,\downarrow]$ will be $\neq 0$. This is mainly due to the fact that the $\mathbf{L}\cdot\mathbf{S}$ operator will promote the mixing between different spin-up/down components. In addition, these $\mathbf{H}^{\sigma\sigma'}_{\mu\nu}$ (and $\mathbf{DM}^{\sigma\sigma'}_{\mu\nu}$) elements will be complex, in contrast with typical polarized/non-polarized calculations where these matrices are purely real. Since the spin-up and spin-down manifolds are essentially mixed, the solver has to deal with matrices whose dimensions are twice as large as for the collinear (unmixed) spin problem. Due to this, we advise to take special attention to the memory needed to perform a spin-orbit calculation.

Unless explicitly advised the following type of calculation can be carried out regardless of whether on-site or off-site approximation is employed:

- Selfconsistent calculations for gamma point as well as for bulks.
- Structure optimizations
- Magnetic Anisotropy Energy (MAE) can be easily calculated. From first principles it is obtained after subtracting the total selfconsistent energy calculated for two different magnetic orientations. In SIESTA it is possible to perform calculations with different initial magnetic orderings by means of the use of the block **DM.InitSpin** in the fdf file. In doing so one will be able to include the initial orientation angles of the magnetization for each atom, as well as an initial value of its net magnetic moments.
- By means of Mulliken analysis, after the selfconsistent procedure, local spin and orbital moments can be calculated by means of the flags **WriteMullikenPop** and **WriteOrbMom**.

Note: Due to the small SO contribution to the total energy, the level of precision required to perform a proper fully relativistic calculation during the selfconsistent process is quite demanding. The following values must be carefully converged and checked for each specific system to assure that the results are accurate enough: **SCF.H.Tolerance** during the selfconsistency (typically between 10^{-3} eV – 10^{-4} eV), **ElectronicTemperature**, k–point sampling and high values of **MeshCutoff** (specifically for extended solids). In general, one can say that a good calculation will have high number of k–points, low **ElectronicTemperature**, extremely small **SCF.H.Tolerance** and high values of **MeshCutoff**. We encourage the user to test carefully these options for each system. An additional point to take into account is the mixing scheme employed. You are encouraged to use **SCF.Mix Hamiltonian** (currently this is the default) instead of density matrix mixing, since it speeds up the convergence. The pseudopotentials have to be properly generated and tested for each specific system and they have to be in their fully relativistic form, together with the non-linear core corrections. Finally it is worth to mention that the selfconsistent convergence for some non-highly symmetric magnetizations directions with respect to the physical symmetry axis could still be difficult.

Spin.OrbitStrength 1.0 *(real)*

It allows to vary the strength of the spin-orbit interaction from zero to any positive value. It can be used for both the on-site and off-site SOC flavors, but only for debugging and testing purposes, as the only physical value is 1.0. Note that this feature is implemented by modifying the SO parts of the semilocal potentials read from a `.psf` file. Care must be taken when re-using any `.ion` files produced.

WriteOrbMom false *(logical)*

If **true**, a table is provided in the output file that includes an estimation of the vector orbital magnetic moments, in units of the Bohr magneton, projected onto each orbital and also onto each atom. The estimation for the orbital moments is based on a two-center approximation, and makes use of the Mulliken population analysis.

If **MullikenInScf** is **true**, this information is printed at every scf step.

SIESTA and Spin-Orbit:

- **Total Energy calculations** including E^{SO}:

$$E^{SO} = \mathrm{Tr}(\hat{\rho}\hat{V}^{SO}) = \sum_{\mu\nu\sigma\sigma'} \rho_{\mu\nu}^{\sigma\sigma'} V_{\nu\mu}^{SO,\sigma'\sigma}$$

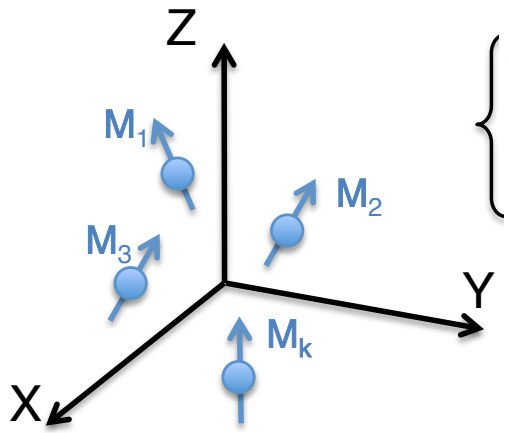
- SO contribution to the forces:

$$\mathbf{F}_I^{SO} = -\sum_{\sigma\sigma'} \frac{\partial E^{SO,\sigma\sigma'}}{\partial \mathbf{R}_I}$$

```
siesta: Program's energy decomposition (eV):
siesta: Ebs      =      -186.088668
siesta: Eions    =      2552.419586
siesta: Ena      =        75.153146
siesta: Ekin     =      4650.897453
siesta: Enl      =     -3816.826902
siesta: Eso(offS)=        -0.045988
siesta: Edau     =         0.000000
siesta: DEna     =       -21.150000
siesta: DUscf    =         7.867448
siesta: DUext    =         0.000000
siesta: Exc      =     -1614.095394
siesta: eta*DQ   =         0.000000
siesta: Emadel   =         0.000000
siesta: Emeta    =         0.000000
siesta: Emolmec  =         0.000000
siesta: Ekinion  =         0.000000
siesta: Eharris  =     -3270.509003
siesta: Etot     =     -3270.509003
siesta: FreeEng  =     -3270.520677
```

- **Bands structure.**

- **Mulliken analysis population**: Magnetic moments.



$$\begin{cases} M_k^x = Tr\left[\rho(\mathbf{r}) \cdot \sigma_x\right] \\ M_k^y = Tr\left[\rho(\mathbf{r}) \cdot \sigma_y\right] \\ M_k^z = Tr\left[\rho(\mathbf{r}) \cdot \sigma_z\right] \end{cases}$$

```
Species: Fe

Atom      Orb        Charge     Spin        Svec
--------------------------------------------------------------------
  25   1 4s        -0.18131   0.01610    0.000   0.000   0.016
  25   2 4s         0.61076   0.03126    0.000  -0.001   0.031
  25   3 3dxy       1.13211   0.54063   -0.003  -0.001   0.541
  25   4 3dyz       1.11510   0.59972    0.001   0.006   0.600
  25   5 3dz2       1.21548   0.49411   -0.003  -0.005   0.494
  25   6 3dxz       1.16038   0.39366   -0.003   0.000   0.394
  25   7 3dx2-y2    1.23344   0.48719    0.000  -0.002   0.487
  25   8 3dxy       0.11818   0.09901    0.000   0.000   0.099
  25   9 3dyz       0.12831   0.11494    0.000   0.000   0.115
  25  10 3dz2       0.12127   0.10262   -0.001   0.000   0.103
  25  11 3dxz       0.08961   0.07738    0.000   0.000   0.077
  25  12 3dx2-y2    0.11431   0.09747    0.000   0.000   0.097
  25  13 4Ppy       0.16868   0.02443    0.000   0.000   0.024
  25  14 4Ppz       0.17519   0.01665    0.000   0.000   0.017
  25  15 4Ppx       0.12020   0.02829    0.000   0.000   0.028
  25     Total      7.32171   3.12337   -0.009  -0.002   3.123
```

- **Projected density of states.**

Thank you very much for your attention