Spin Orbit coupling implementation in SIESTA

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Summary

- **Motivation**
- **Relativistic approximations in SIESTA and magnetism**
- **Non-collinear magnetism**
- **Pseudopotential approximation**
- **Non-local pseudopotential operators and Spin-Orbit Coupling**
  - ➡ Scalar Relativistic calculations
  - ➡ Fully Relativistic calculations
- **Practical issues**
- **Some results**

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Nano-devices (DFT cappabilities):

- Medical applications
- Catalytic reactions
- High density magnetic recording
- Biological sensors
- Optoelectronics, etc

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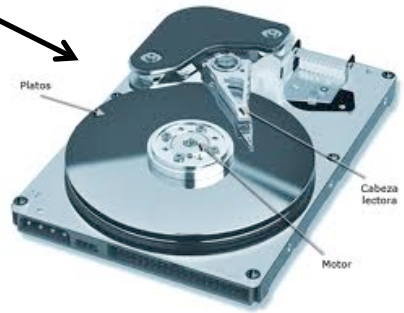

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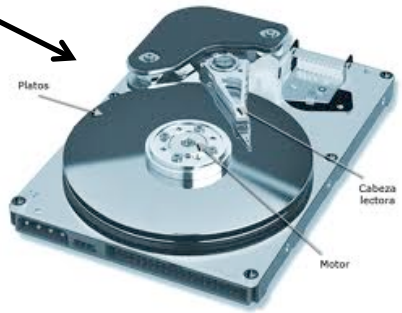
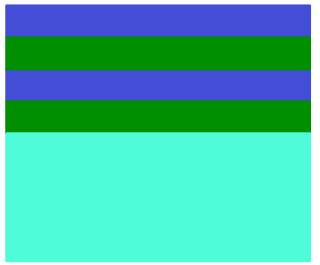
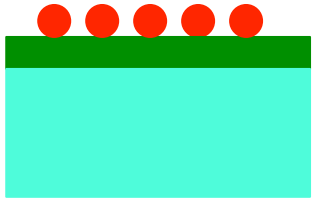


Multilayers, thin films



Magnetic nanoparticles onto a surface:



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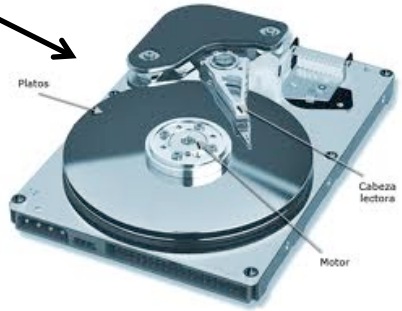

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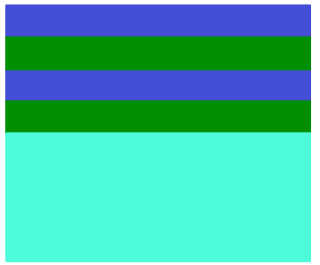

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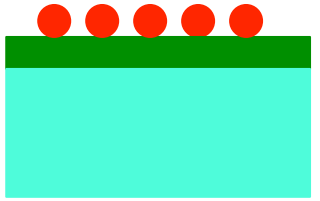
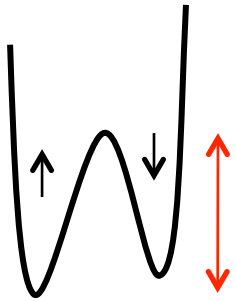
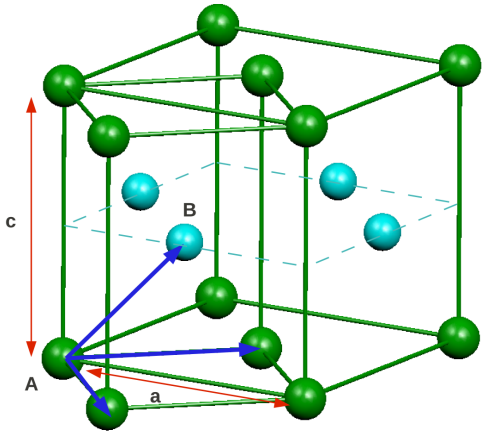
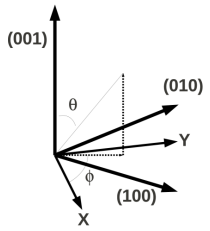


Major obstacle:
Superparamagnetic limit



Energy barrier





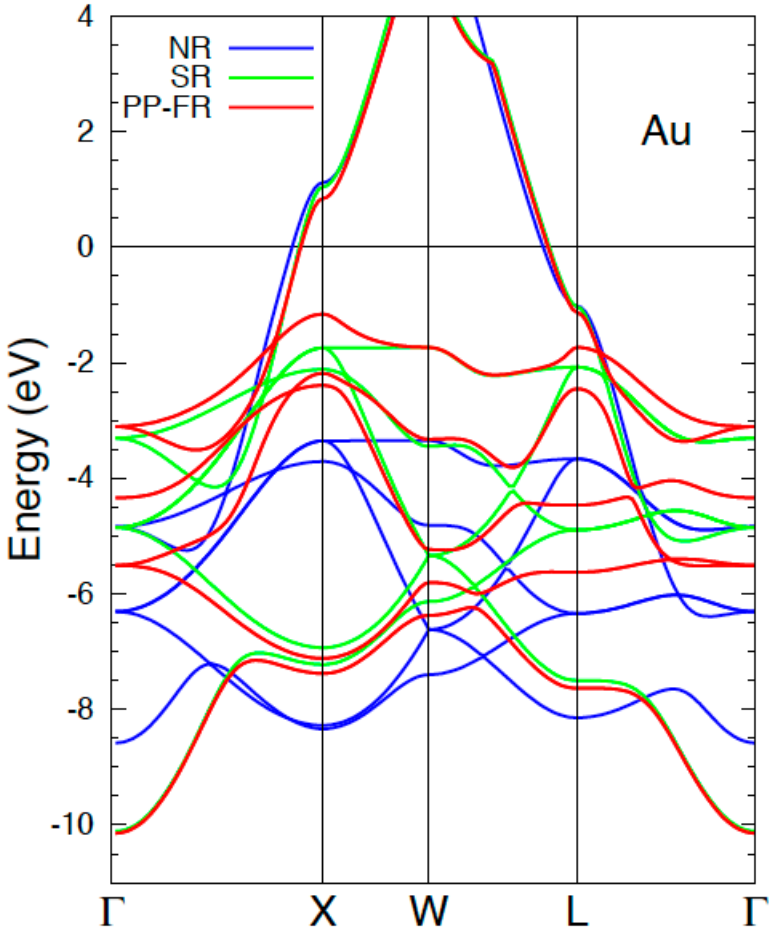
$$\tau_N = \tau_0 \exp(K_u V / k_B T)$$

Neel relaxation law

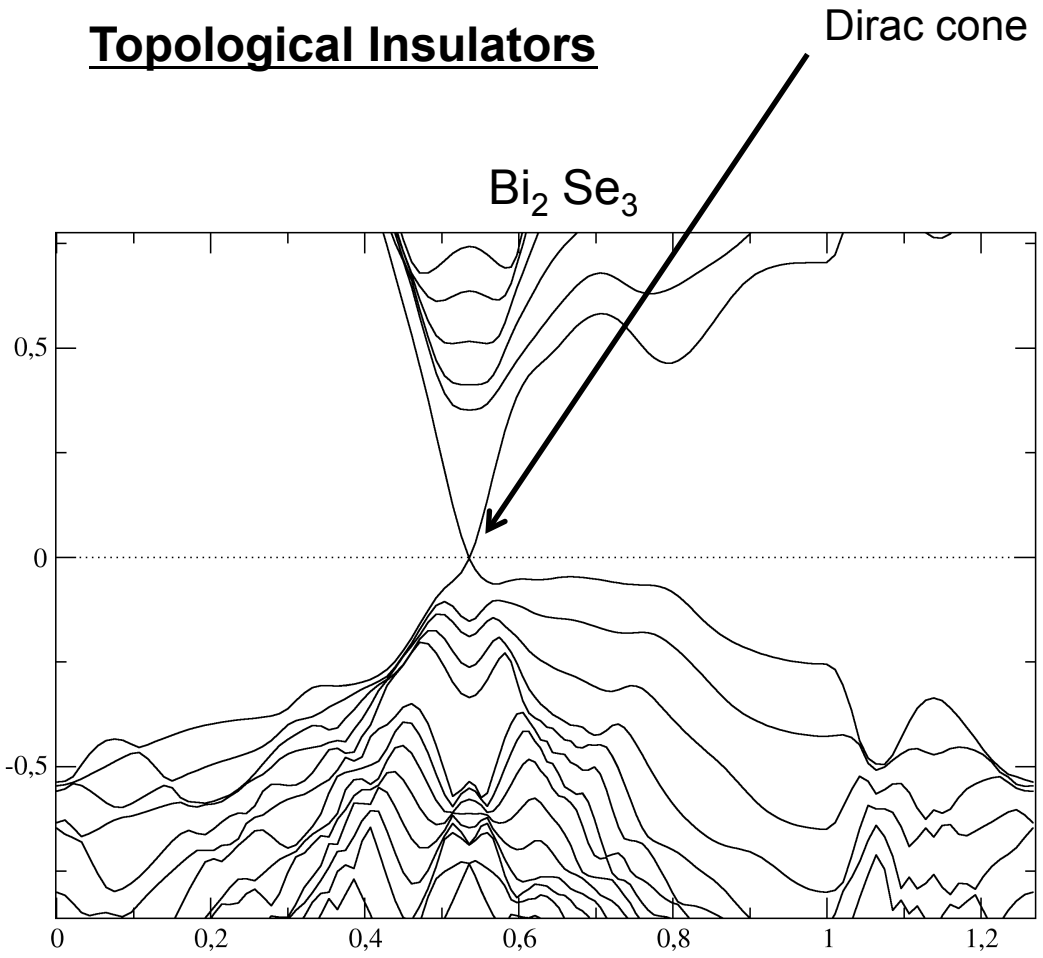
K_u : Anisotropy

V : NP volume

Au fcc:



Topological Insulators



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$$\left[\hat{T}_e + \hat{V}_{eI}^{ps} + \hat{V}_H + \hat{V}_{XC}^{\sigma}\right]$$

Darwin and velocity corrections terms

- Scalar Relativistic Hamiltonian: $H_{TOTAL}^{SR} = H_{NR} + H_{SR} \Leftrightarrow H_{SIESTA}^{SR} = H_{KS}^{SR}$

  - magnetic systems

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$$H^{KS} = \begin{pmatrix} h_{\mu\nu}^{KS,\uparrow} & 0 \\ 0 & h_{\mu\nu}^{KS,\downarrow} \end{pmatrix}$$

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- Fully relativistic Hamiltonian: $H_{TOTAL} = H_{NR} + H_{SR} + H_{SO} \Leftrightarrow H_{SIESTA}^{FR} = H_{KS}^{SR} + H_{SO}$

  - Spin – orbit coupling

H_{NR}: No relativistic KS Hamiltonian

$H_{SR} + H_{SO}$: Relativistic corrections

$H_{SO} \propto \mathbf{L} \cdot \mathbf{S}$

$$H^{KS} = \begin{pmatrix} h_{\mu\nu}^{KS,\uparrow} & 0 \\ 0 & h_{\mu\nu}^{KS,\downarrow} \end{pmatrix}$$

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H_{SR}: Relativistic corrections

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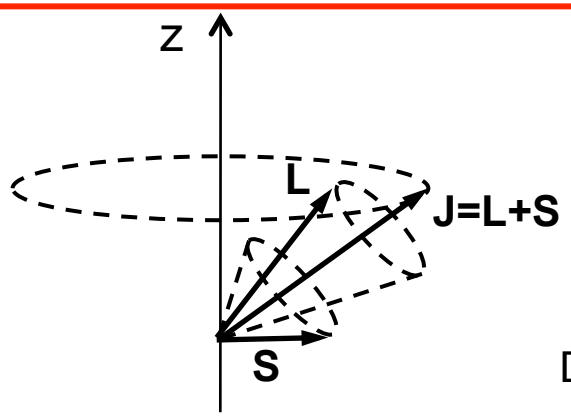
$$H^{KS} = \begin{pmatrix} h^{KS,\uparrow}_{\mu\nu} & 0 \\ 0 & h^{KS,\downarrow}_{\mu\nu} \end{pmatrix} \rightarrow H^{FR} = \begin{pmatrix} \uparrow\uparrow & \uparrow\downarrow \\ \downarrow\uparrow & \downarrow\downarrow \end{pmatrix}$$



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

Degeneracy $2J+1$

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SIESTA non-collinear:

- LSDA: colineal (common quatization axis) ↑↑↑↑↑

$$H^{\sigma}_{TOTAL} = \left[\hat{T}_e + \hat{V}^{\sigma}_{ps} + \hat{V}_H + \hat{V}^{\sigma}_{XC} \right]$$

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- SO: no-colineal (quatization axis varies with **r**) ↖↑↑↗↗↗ $H^{\sigma\sigma'}_{TOTAL} = \left[\hat{T}_e + \hat{V}^{\sigma\sigma'}_{ps} + \hat{V}_H + \hat{V}^{\sigma\sigma'}_{XC}\right]$

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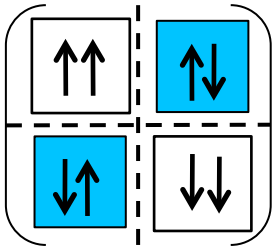
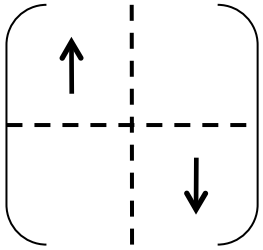
$\rho =$  $\xrightarrow[\text{locally}]{U\rho U^{\dagger}}$ $\tilde{\rho} =$ 

$\Rightarrow \tilde{V}^{\sigma}_{XC}\left[\tilde{\rho}^{\sigma}\right] \xrightarrow{\mathbf{U}^{\dagger}(\mathbf{r})\tilde{V}_{XC}(\mathbf{r})\mathbf{U}(\mathbf{r})}$

$$\hat{V}^{\sigma\sigma'}_{XC}(\mathbf{r}) = \frac{1}{2}(\tilde{V}^{\uparrow}_{XC} + \tilde{V}^{\downarrow}_{XC})\mathbb{1} + \frac{1}{2}(\tilde{V}^{\uparrow}_{XC} - \tilde{V}^{\downarrow}_{XC})\,\sigma\cdot\hat{\mathbf{m}}(\mathbf{r})$$

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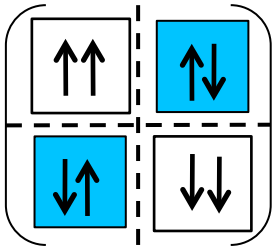
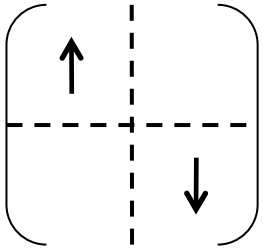
$\rho =$  $\xrightarrow[\text{locally}]{U\rho U^{\dagger}}$ $\tilde{\rho} =$ 

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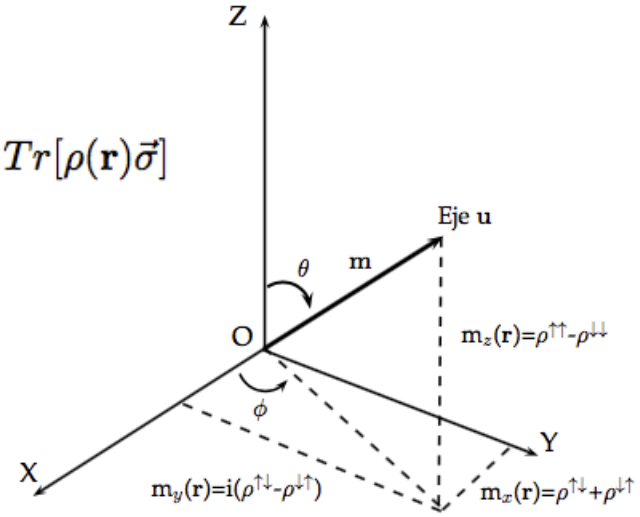
$\mathbf{m}(\mathbf{r}) = Tr[\rho(\mathbf{r})\vec{\sigma}]$



$$|\mathbf{m}| = \sqrt{(\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow})^2 + 4(Re\{\rho^{\uparrow\downarrow}\}^2 + Im\{\rho^{\uparrow\downarrow}\}^2)}$$

$$\tan\theta(\mathbf{r}) = \frac{2\{[Re\,\rho^{\uparrow\downarrow}]^2 + [Im\,\rho^{\uparrow\downarrow}]^2\}^{1/2}}{[\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow}]}$$

$$\tan\phi(\mathbf{r}) = -\frac{Im\,\rho^{\uparrow\downarrow}}{Re\,\rho^{\uparrow\downarrow}}$$

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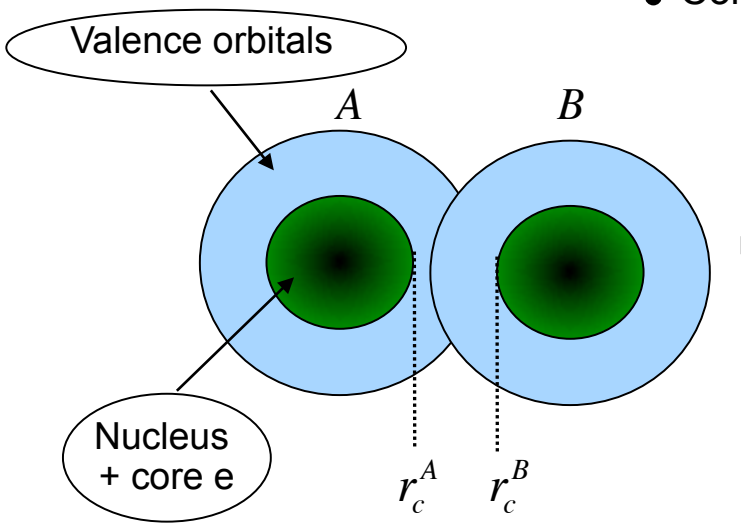
Bond between atoms

- Core e$^-$ are independent



Join the effect of nucleus + inner e$^-$

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

$$\hat{V}_{eI}^{ps}(\mathbf{r}) = \sum_{lm} V_l^{ps}(r)\,|lm\rangle\langle lm|$$

Depend of each l

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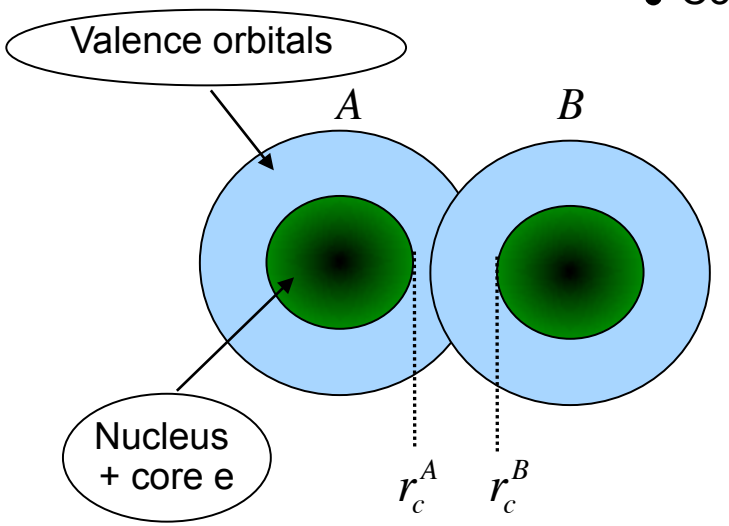

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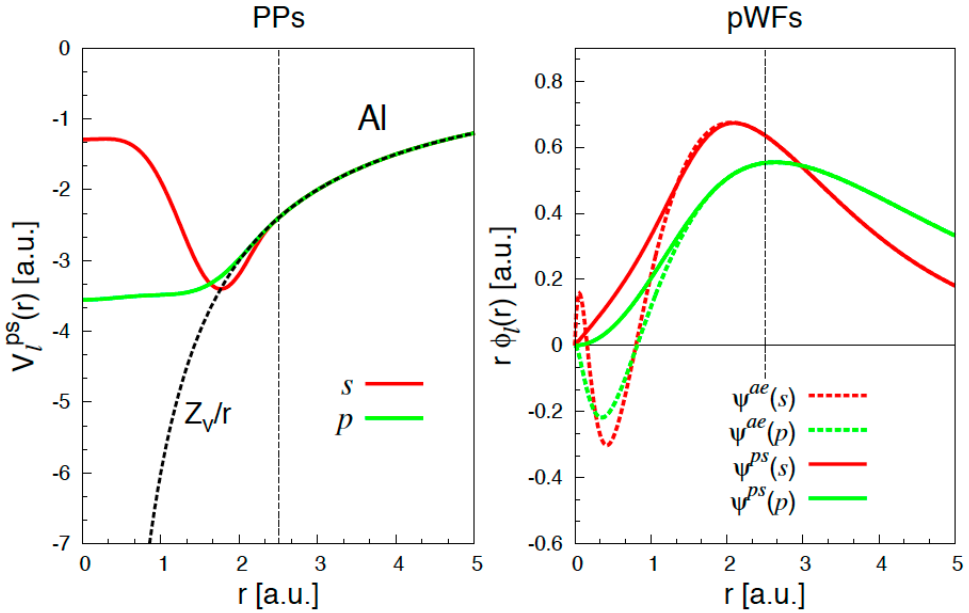

- Exact potential from a radius
- PPs must be smooth → Simplify the integrals
- Are generated for each atom using different XC functionals
- Troullier-Martins scheme
- Reduction of the matrix elements N_c+N_v to N_v

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Spin - orbit coupling (SO): Non-local Pseudopotential operators

ATOM (PPs generator)

- Spin Polarized: Schrödinger eq.
- Fully Relativistic: Dirac: $\underbrace{V_{l+1/2}(r)}_{J_+}, \underbrace{V_{l-1/2}(r)}_{J_-}$

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

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

Semi-local op.: Acts in different way on each l but in the same fashion on the radial parts.

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↓ Matrix elements: M x N^2

$$V_{I,\mu\nu}^{ps} = \langle\phi_\mu|\hat{V}_I^{ps}|\phi_\nu\rangle = \sum_{l,m}\underbrace{\int \phi_\mu^*(\mathbf{r})V_{l,I}^{ps}(r)\phi_\nu(\mathbf{r})d^3\mathbf{r}}_{\text{Three center integrlas}}$$

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

$$\delta\hat{V}^{ps} \approx \hat{V}^{KB} = \sum_{l=0}^{l_{max}^{KB}}\sum_{m=-l}^{l}\sum_{n=1}^{N_l^{KB}} |\chi_{lmn}^{KB}\rangle v_{ln}^{KB}\langle\chi_{lmn}^{KB}|$$

$$v_{ln}^{KB} = \langle\varphi_{ln}|\delta V_l(r)|\varphi_{ln}\rangle^{-1}$$

$$\chi_{lmn}^{KB}(\mathbf{r}) = \delta V_l(r)\varphi_{ln}(r)\,Y_{lm}(\hat{\mathbf{r}})$$

$$H^{Total} = \begin{pmatrix} \uparrow\uparrow & 0 \\ 0 & \downarrow\downarrow \end{pmatrix}$$

- Matrix elements: M x N elements
- Products of two center integrals

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- **Fully relativistic** on-site Spin-Orbit (semi-local): **ON-SITE**

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

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- **Fully relativistic** on-site Spin-Orbit (semi-local): **ON-SITE**

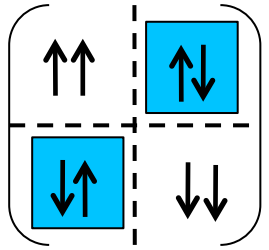
$$\hat{V}_I^{ps} = \sum_{l,J} V_{lJ}^{ps}(r)\hat{P}_J = \sum_{l,J,m_J} |Jm_J\rangle V_{lJ}^{ps}(r)\langle Jm_J|$$

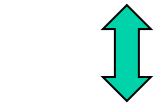
Changing basis from (J,m_J) to (l,m_l)

$$\hat{V}_I^{ps}(\mathbf{r}) = \sum_{l,m} |lm\rangle [V_l^{SR}(r) + V_l^{SO}(r)\mathbf{L}\cdot\mathbf{S}]\langle lm|$$

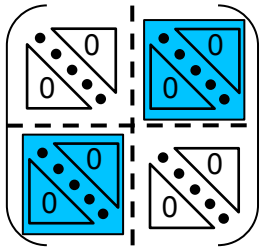
On-site SO approximation if only terms involving orbitals of the same atom are included

$V^{SO}_{on-site}$ =





$V^{SO}_{on-site}$ =



On-site approximation for spin–orbit coupling in linear combination of atomic orbitals density functional methods

L Fernández-Seivane[1], M A Oliveira[2], S Sanvito[2] and J Ferrer[1]

ATOM (PPs generator)

- Spin Polarized: Schrödinger eq.
- Fully Relativistic: Dirac: $V_{\underbrace{l+1/2}_{J_+}}(r), V_{\underbrace{l-1/2}_{J_-}}(r)$

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

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

#.psf

- **Fully relativistic and fully non-local** Off-Site Spin-Orbit implementation: **OFF-SITE**

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

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

ATOM (PPs generator)

- Spin Polarized: Schrödinger eq.
- Fully Relativistic: Dirac: $V_{\underbrace{l+1/2}_{J_+}}(r), V_{\underbrace{l-1/2}_{J_-}}(r)$

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

#.psf

- **Fully relativistic and fully non-local** Off-Site Spin-Orbit implementation: **OFF-SITE**

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

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

ATOM (PPs generator)

- Spin Polarized: Schrödinger eq.
- Fully Relativistic: Dirac: $V_{\underbrace{l+1/2}_{J_+}}(r), V_{\underbrace{l-1/2}_{J_-}}(r)$

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

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#.psf

- **Fully relativistic and fully non-local** Off-Site Spin-Orbit implementation: **OFF-SITE**

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

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

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

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

$$v_{lJ_\pm}(r) = \frac{\delta V_{lJ_\pm}^{\mathrm{ps}}(r) R_{lJ_\pm}^{\mathrm{ps}}(r)}{(\langle R_{lJ_\pm}^{\mathrm{ps}}|\delta V_{lJ_\pm}^{\mathrm{ps}}|R_{lJ_\pm}^{\mathrm{ps}}\rangle)^{1/2}}$$

Off-Site Spin Orbit Coupling

ATOM (PPs generator)

- Spin Polarized: Schrödinger eq.
- Fully Relativistic: Dirac: $V_{\underbrace{l+1/2}_{J_+}}(r), V_{\underbrace{l-1/2}_{J_-}}(r)$

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

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

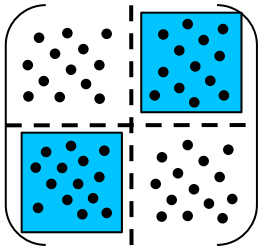
#.psf

- **Fully relativistic and fully non-local** Off-Site Spin-Orbit implementation: **OFF-SITE**

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

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

$V^{SO}{}_{off-site}$ =



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

$$\hat{V}^{SR}(\mathbf{r}) = \sum_{lm}\left[|v_{lm}^{SR}\rangle\langle v_{lm}^{SR}|\right]$$

$$\hat{V}^{SO}(\mathbf{r}) = \sum_{lm}\left[\frac{1}{4}l(l+1) - \frac{1}{2}\mathbf{L}\cdot\mathbf{S}\right]|v_{lm}^{SO}\rangle\langle v_{lm}^{SO}| + \sum_{lm}\mathbf{L}\cdot\mathbf{S}\left[|v_{lm}^{SR}\rangle\langle v_{lm}^{SO}| + |v_{lm}^{SO}\rangle\langle v_{lm}^{SR}|\right]$$

$$v_l^{SR}(r) = \frac{l+1}{2l+1}v_{lJ_+}(r) + \frac{l}{2l+1}v_{lJ_-}(r)$$

$$v_l^{SO}(r) = \frac{2}{2l+1}[v_{lJ_+}(r) - v_{lJ_-}(r)].$$

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

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

$$v_{lJ_\pm}(r) = \frac{\delta V_{lJ_\pm}^{ps}(r)R_{lJ_\pm}^{ps}(r)}{(\langle R_{lJ_\pm}^{ps}|\delta V_{lJ_\pm}^{ps}|R_{lJ_\pm}^{ps}\rangle)^{1/2}}$$

- Total Energy calculations including E_{SO}: $E^{SO} = \mathrm{Tr}(\hat{\rho}\hat{V}^{SO}) = \sum_{\mu\nu\sigma\sigma'} \rho_{\mu\nu}^{\sigma\sigma'} V_{\nu\mu}^{SO,\sigma'\sigma}$

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

- Calculation of band structures

- Mulliken analysis population. Magnetic moments, magnetization (S_x,S_y,S_z), etc.

- Projected density of states

- LSDA + U

- Different vdW schemes.

- Motivation
- Relativistic approximations in SIESTA and magnetism
- Non-collinear magnetism
- Pseudopotential approximation
- Non-local pseudopotential operators and Spin-Orbit Coupling
  - ➡ Scalar Relativistic calculations
  - ➡ Fully Relativistic calculations
- **Practical issues**
- Some results

SIESTA manual

6.7 Spin polarization

Spin non-polarized *(string)*

Choose the spin-components in the simulation.

NOTE: this flag has precedence over **SpinOrbit**, **NonCollinearSpin** and **SpinPolarized** while these older flags may still be used.

non-polarized Perform a calculation with spin-degeneracy (only one component).

polarized Perform a calculation with collinear spin (two spin components).

non-collinear Perform a calculation with non-collinear spin (4 spin components), up-down and angles.

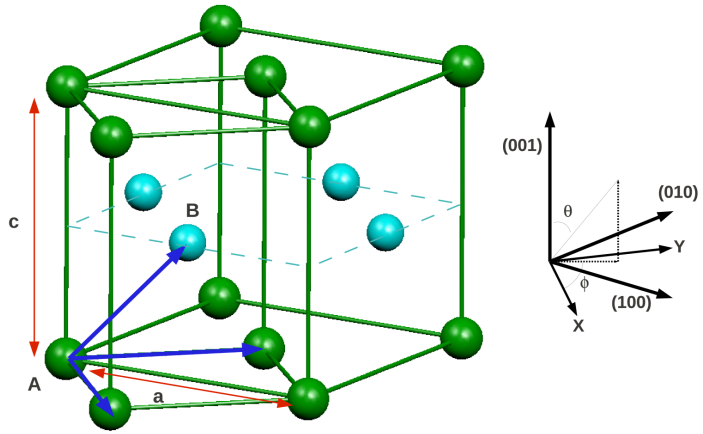
Refs: T. Oda et al, PRL, **80**, 3622 (1998); V. M. García-Suárez et al, Eur. Phys. Jour. B **40**, 371 (2004); V. M. García-Suárez et al, Journal of Phys: Cond. Matt **16**, 5453 (2004).

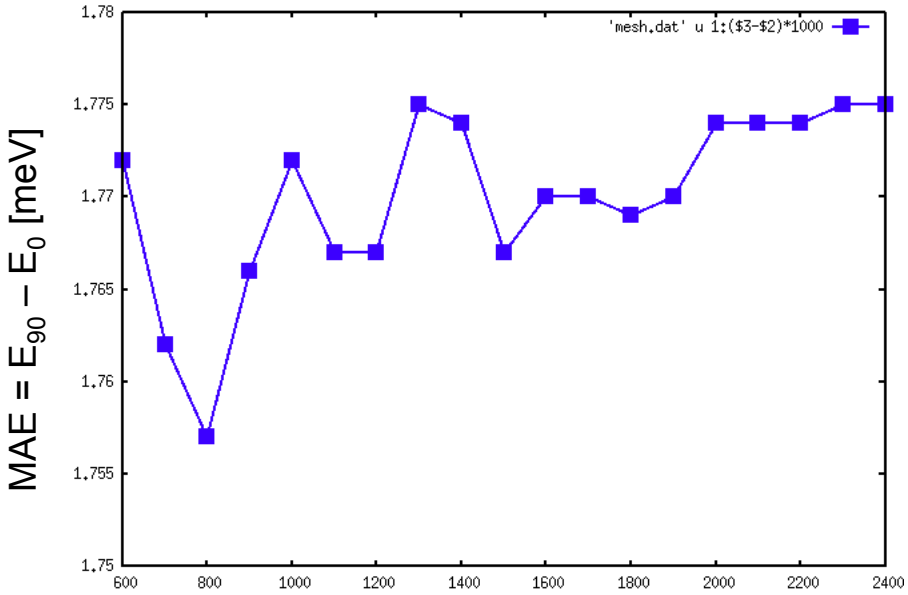
spin-orbit Performs calculations including the spin–orbit coupling. By default the off–site SO option is set up to **true**. To perform an on–site SO calculations this option has to be **spin-orbit+onsite**.

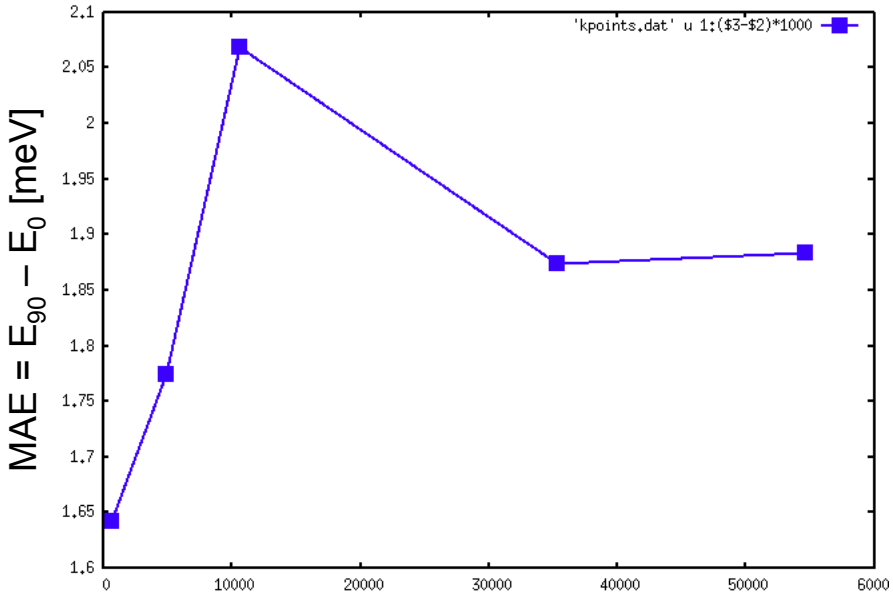
6.8 Spin–Orbit coupling

Note: Due to the small SO energy value contribution to the total energy, the level of precision requiered 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 **Mesh-Cutoff** (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.DM.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 is set up by default) instead of the density matrix, due to that 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–high symmetric magnetizations directions with respect to the physical symmetry axis could be coumbersome, however

FePt – $L1_0$


c
B
A
a
(001)
(010)
(100)
θ
ϕ
Y
X


'mesh.dat' u 1:($3-$2)*1000
MAE = E90 – E0 [meV]
Mesh cutoff [Ry]
1.78
1.775
1.77
1.765
1.76
1.755
1.75
600
800
1000
1200
1400
1600
1800
2000
2200
2400


'kpoints.dat' u 1:($3-$2)*1000
MAE = E90 – E0 [meV]
K-points sampling
2.1
2.05
2
1.95
1.9
1.85
1.8
1.75
1.7
1.65
1.6
0
10000
20000
30000
40000
50000
60000

Summary

- Motivation
- Relativistic approximations in SIESTA and magnetism
- Non-collinear magnetism
- Pseudopotential approximation
- Non-local pseudopotential operators and Spin-Orbit Coupling
  - ➡ Scalar Relativistic calculations
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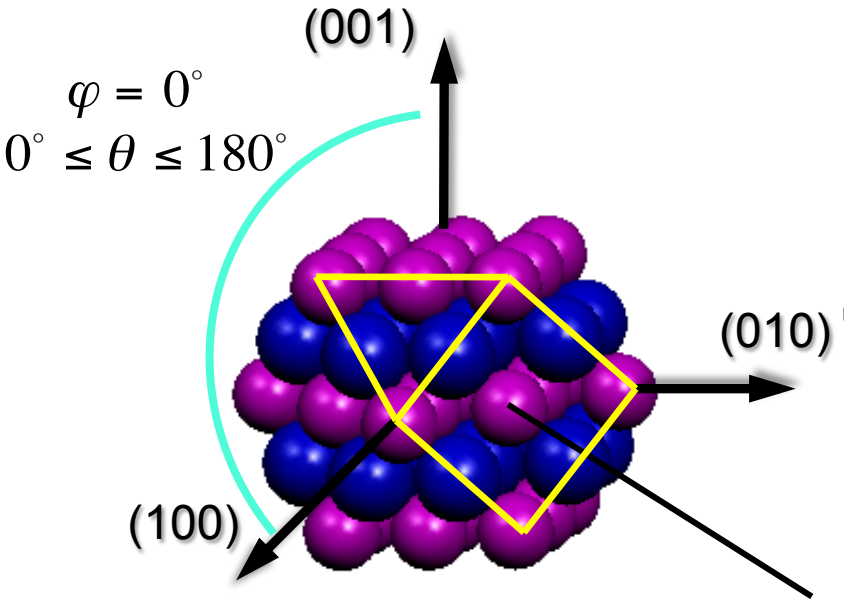
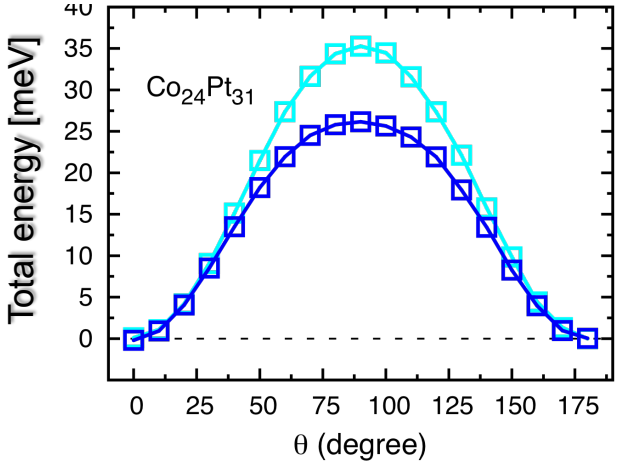
PHYSICAL REVIEW B **86**, 224415 (2012)

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

R. Cuadrado and R. W. Chantrell
Department of Physics, University of York, York YO10 5DD, United Kingdom
(Received 25 July 2012; revised manuscript received 6 November 2012; published 18 December 2012)

Total energy vs. magnetizations angles





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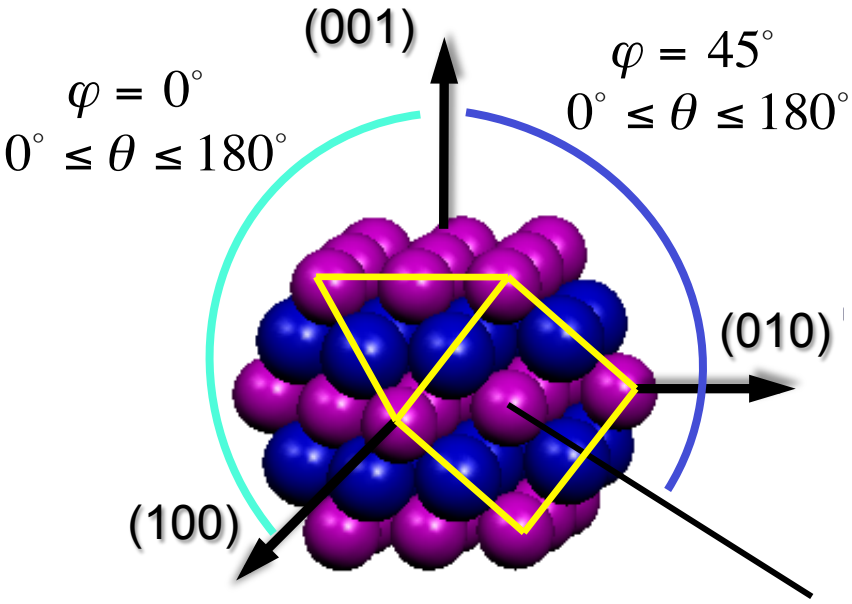

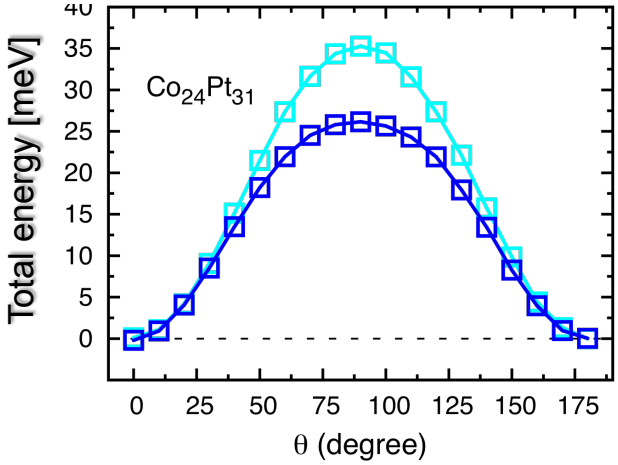

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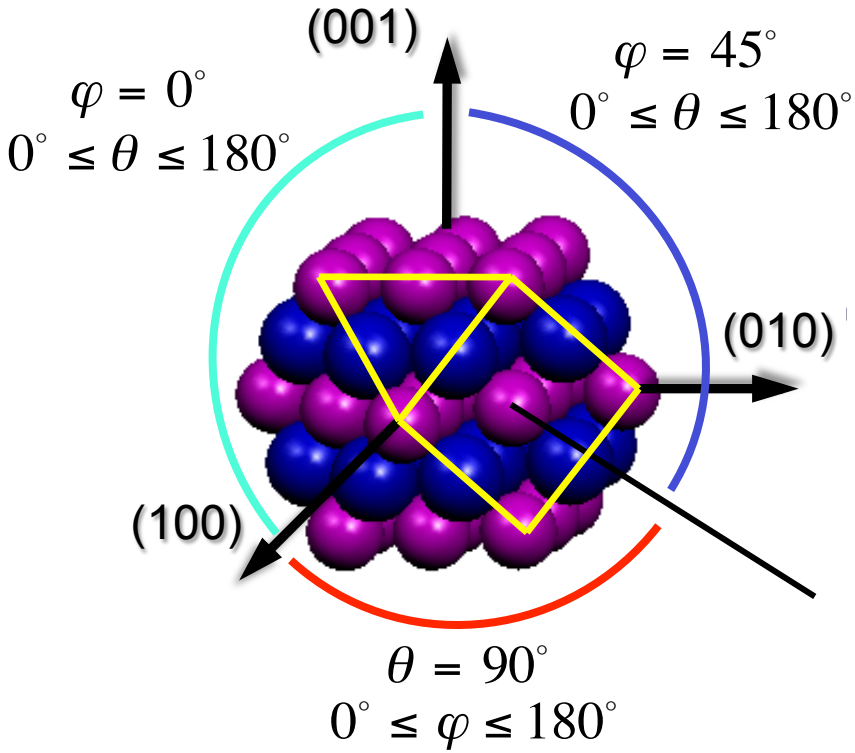
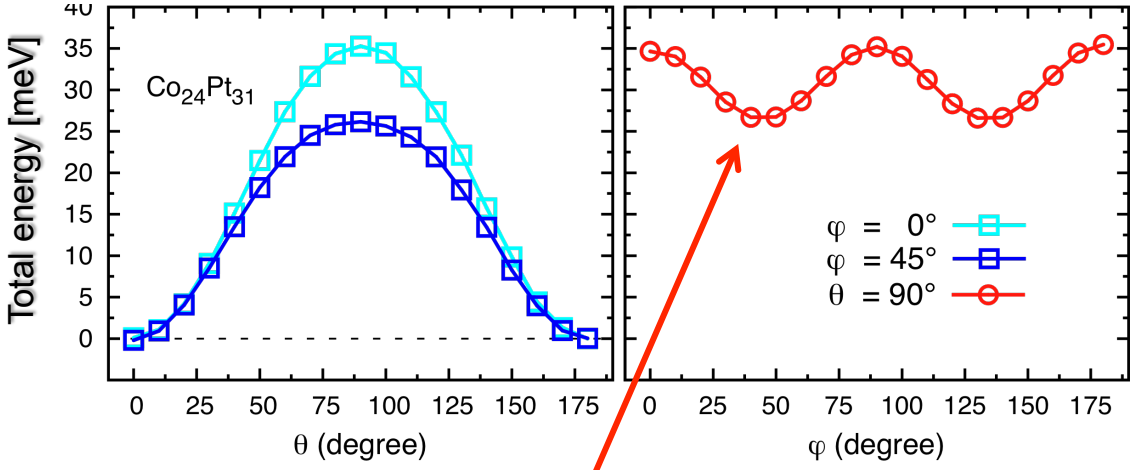
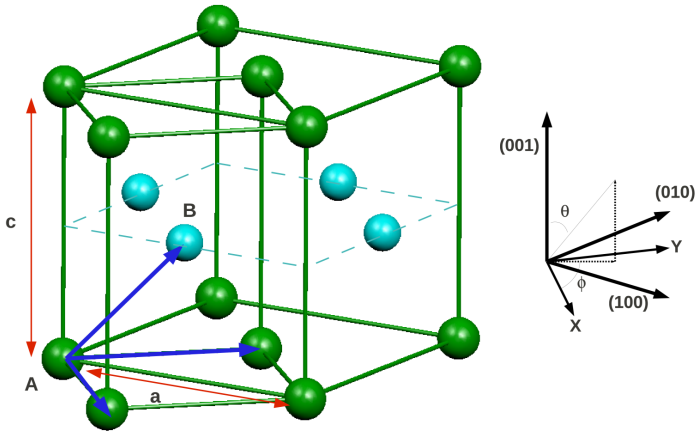




In-plane anisotropy

Metalic alloys $L1_0$



A: M

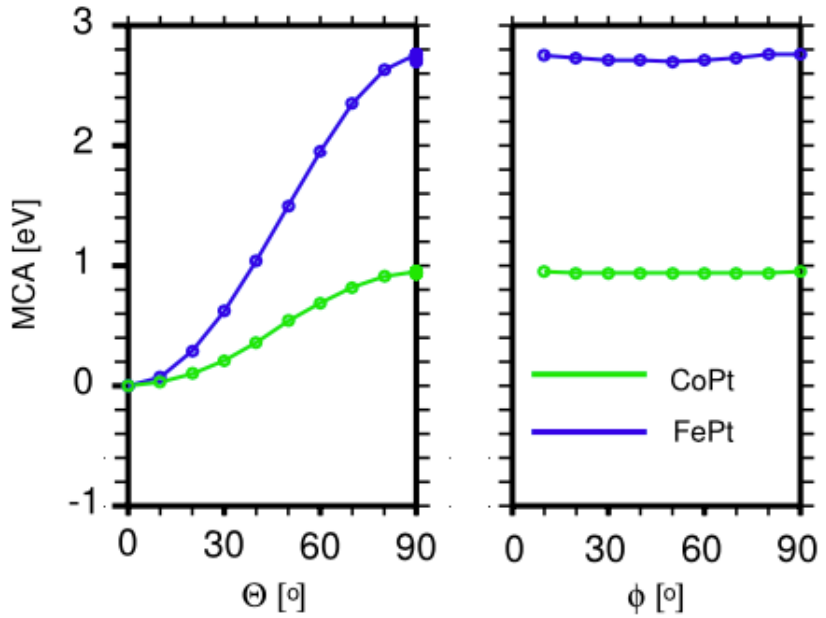
B: NM

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **24** (2012) 086005 (15pp) doi:10.1088/0953-8984/24/8/086005

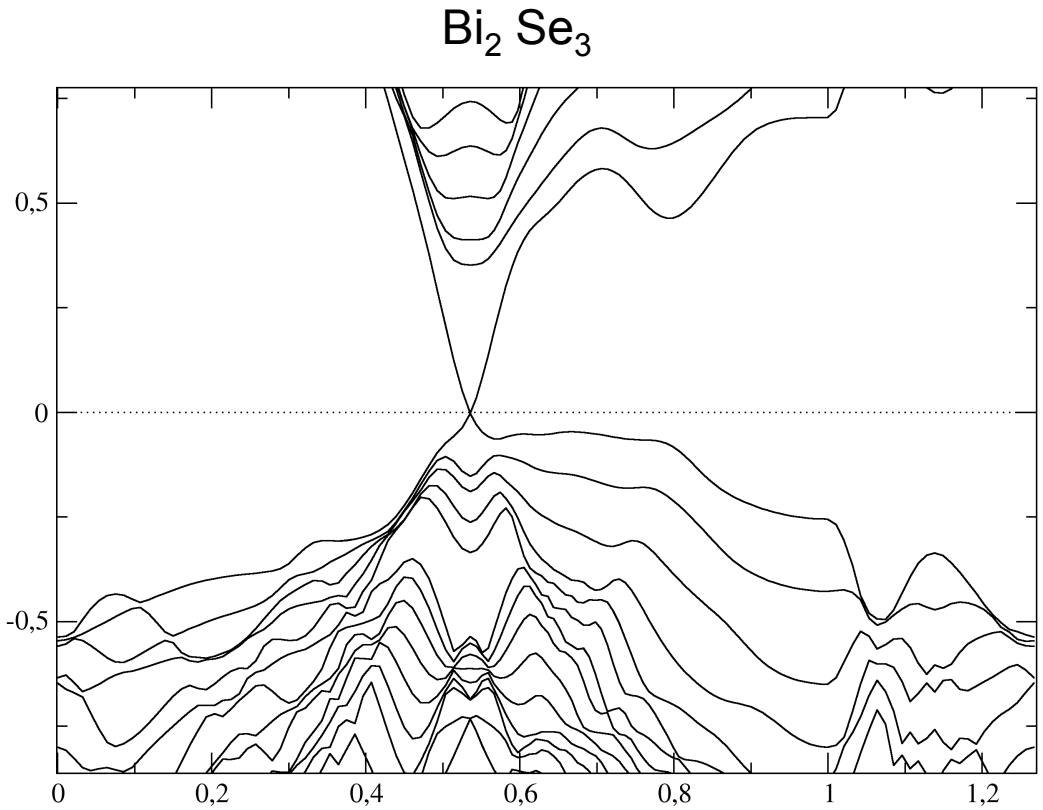
Fully relativistic pseudopotential formalism under an atomic orbital basis: spin–orbit splittings and magnetic anisotropies

R Cuadrado and J I Cerdá

Instituto de Ciencia de Materiales de Madrid ICMM-CSIC, Cantoblanco, 28049 Madrid, Spain



Topological Insulators



Thank you very much!

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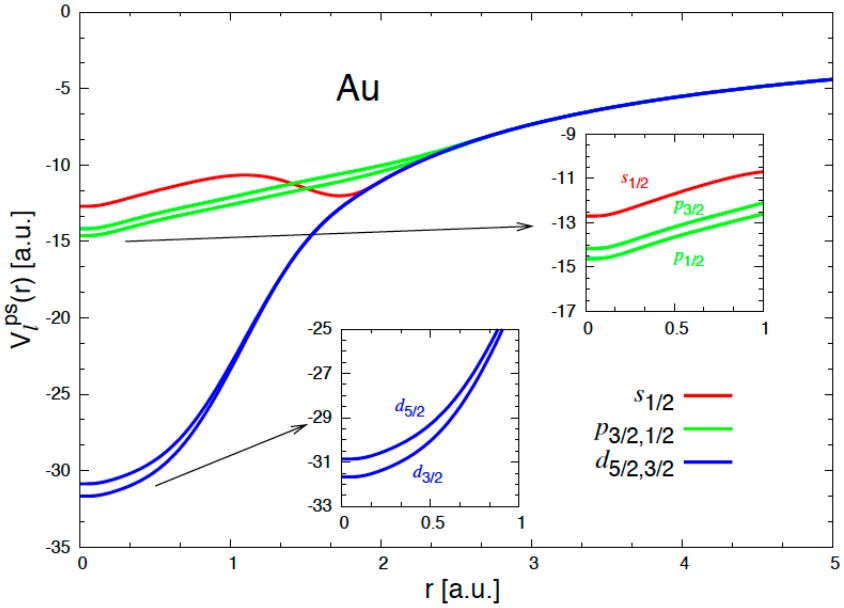
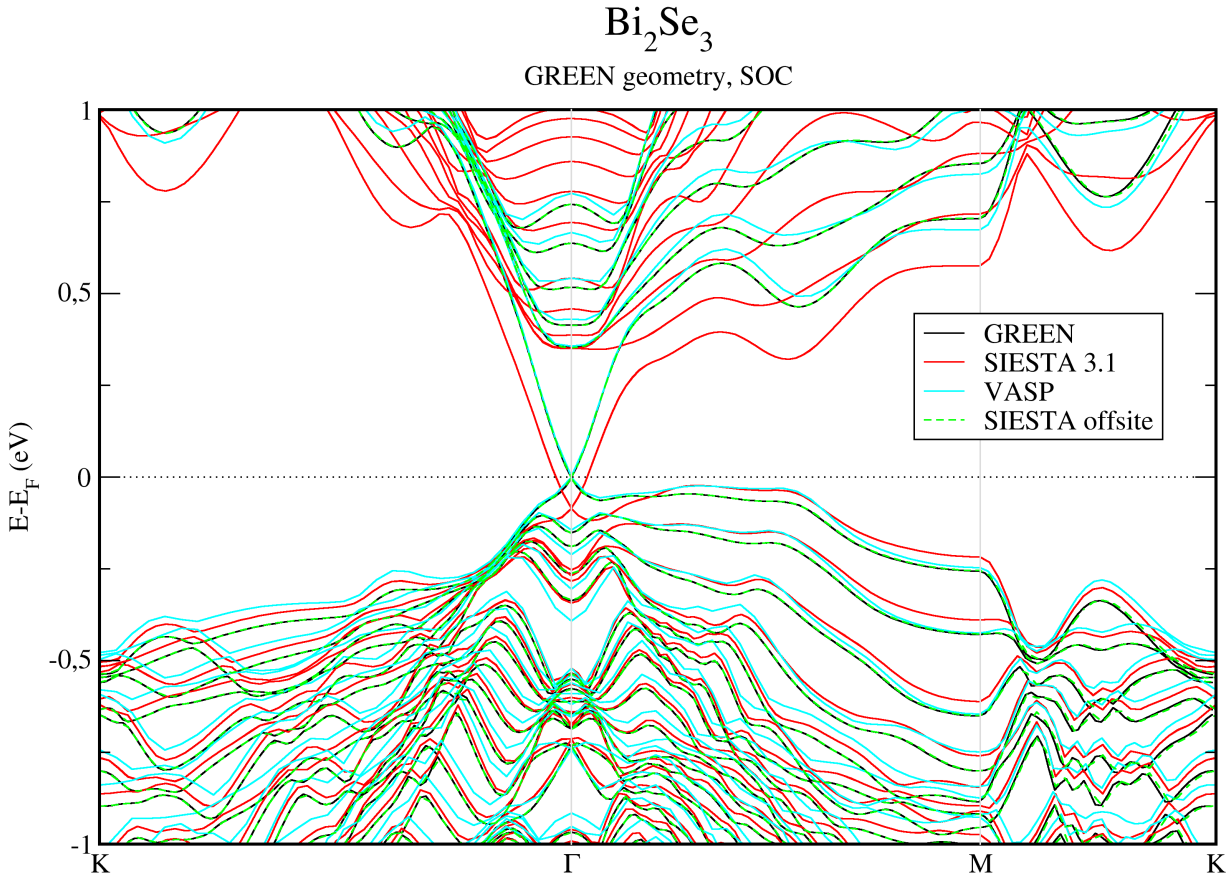
$$V_{dn} = V_l^{ion} = \frac{1}{2l+1}\left[(l+1)V_{l+1/2} + lV_{l-1/2}\right]$$

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

#.psf




Bi2Se3
GREEN geometry, SOC
E-EF (eV)
1
0,5
0
-0,5
-1
K
Γ
M
K
GREEN
SIESTA 3.1
VASP
SIESTA offsite