DE LA RECHERCHE À L'INDUSTRIE

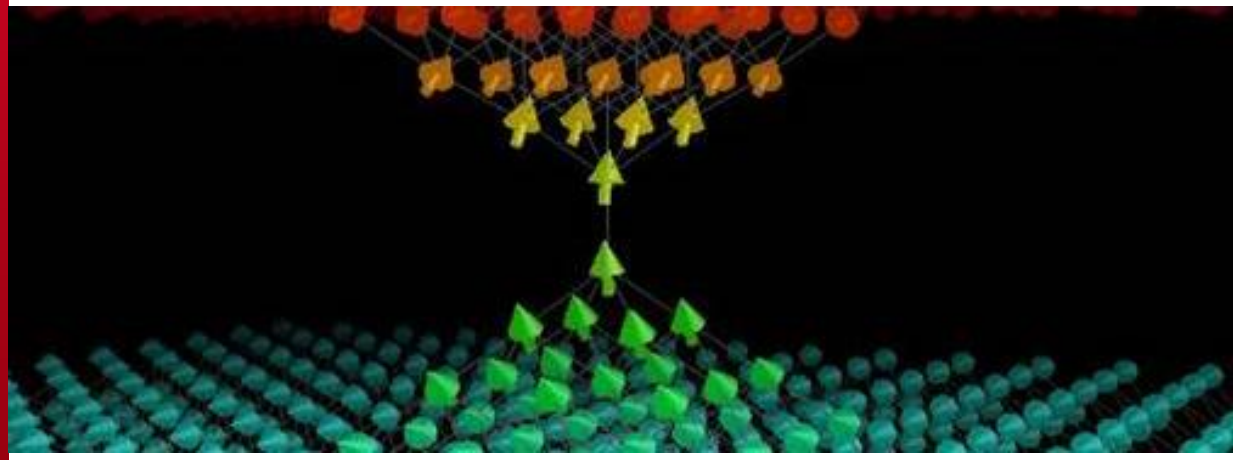
(Paris, France)

Saclay

(Copenhagen, Denmark)

Lyngby

# MAGNETISM IN DFT
# FROM THEORY TO PRACTICE



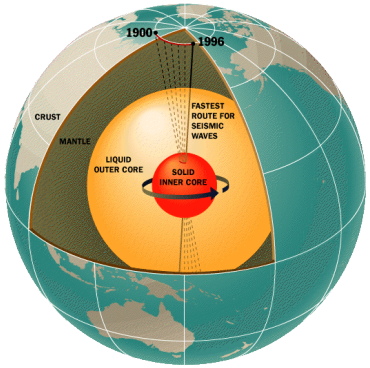
**Cyrille Barreteau**

**CEA Saclay**

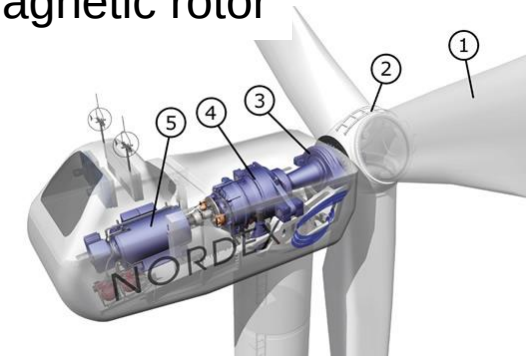
# MAGNETISM

From the atomic nucleus to the inner core of Earth

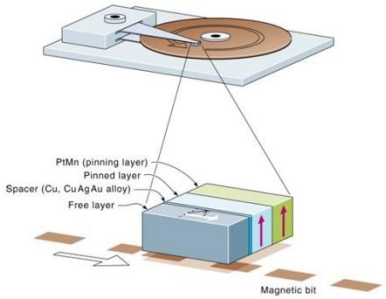
time

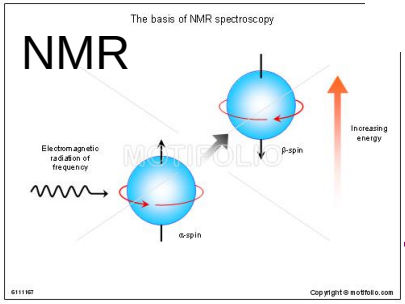



Magnetic rotor




GMR Read Head




length

# MAGNETISM

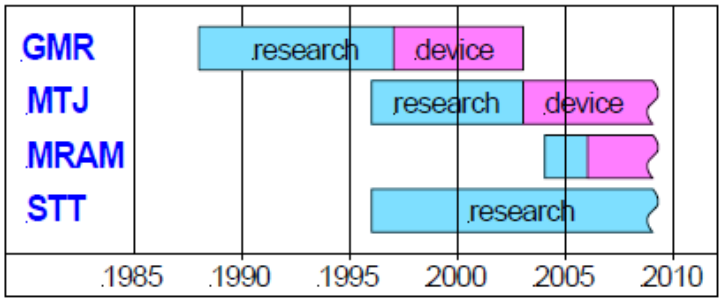
Intense activity in which **nanomagnetism** plays a crucial role

Search for permanent hard magnets without rare earth

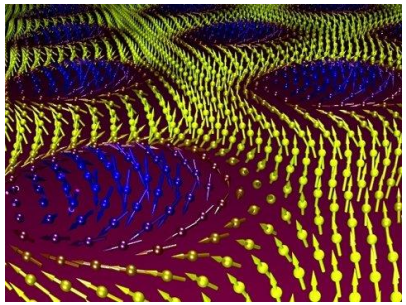
Replace Samarium-Cobalt, Neodyum by nanostructured « cheap » TM magnets

Spintronics

From Fundamentals to applications




micromagnetics



DFT is the perfect tool to adress (at least partly) most of these problems

# DENSITY FUNCTIONAL THEORY

Hohenberg & Kohn (1964) + Kohn Sham (1965)

$$E[n] = T_0[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r + \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' + E_{I-I} + E_{xc}[n]$$

$$\underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)}_{H_{KS}} \psi_\alpha(r) = \varepsilon_\alpha \psi_\alpha(\mathbf{r})$$

$$V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_\sigma \sum_{\alpha \text{occ}} |\psi_{\alpha,\sigma}(\mathbf{r})|^2 = 2\sum_{\alpha \text{occ}} |\psi_\alpha(\mathbf{r})|^2$$

if $\uparrow = \downarrow$

$$V_{\text{Hartree}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' \qquad V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

$V_{\text{ext}}(\mathbf{r})$ *(pseudo)-potental describing the interaction of valence electrons with the ions (nucleus+core electrons)*
*Can also include a « true » external potential*

# Local density approximation (LDA)

$$E_{xc}[n] = \int n(\mathbf{r})\varepsilon_{xc}(n(\mathbf{r}))d^3r$$

$\varepsilon_{xc}(n)$: exchange correlation energy (per particle) of homogenous gas

$$\varepsilon_{xc}(n) = \varepsilon_x(n) + \varepsilon_c(n)$$

$$\varepsilon_x(n) = -\frac{3}{4}\left(\frac{3n}{\pi}\right)^{\frac{1}{3}}$$ Hartree Fock in an homogenous jellium

$$\varepsilon_c(n) = F(n)$$ Parametrized from QMC

$$V_{\mathrm{xc}}(\mathbf{r}) = \left[\frac{d}{dn}(\mathrm{n}\,\varepsilon_{xc}(n))\right]_{n=n(\mathbf{r})}$$

## Generalized Gradient approximation (GGA)

$$E_{xc}[n] = \int n(\mathbf{r})\varepsilon_{xc}(n(\mathbf{r}), \nabla \mathrm{n(r)})d^3r$$

$$E_{xc}[n] = \int n(\mathbf{r})\varepsilon_{xc}^{\mathrm{hom}}(\mathrm{n}(\mathbf{r}))\,\mathrm{F}_{xc}(n(\mathbf{r}), \nabla \mathrm{n(r)})d^3r$$

$\varepsilon_{xc}^{\mathrm{hom}}(n)$: exchange correlation energy (per particle) of homogenous gas

$\mathrm{F}_{xc}(n(\mathbf{r}), \nabla \mathrm{n(r)})$: dimensionless enhancement factor

Some important sum rules and other relevant conditions should be verified…
But still a large variety of functionals

Most popular
- Perdew and Wang (PW91)
- Perdew Burke and Enzerhof (PBE)
- ……

# DFT implementation diagram

Kohn Sham algorithm

Initial guess
$n(\mathbf{r})$

Combination of atomic densities

Effective potential
$V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{xc}(\mathbf{r})$

Solve Poisson equation
but not in Harris Functional scheme

Solve KS equation
$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)\psi_\alpha(\mathbf{r}) = \varepsilon_\alpha \psi_\alpha(\mathbf{r})$

charge mixing

Determine the Fermi level

electron density and total energy
$n(\mathbf{r}) = 2\sum_{\alpha\ \text{occ}} |\psi_\alpha(\mathbf{r})|^2 \qquad E_{tot}[n(\mathbf{r})]$

$\langle T \rangle = E_{\text{band}} - E_{\text{dc}}$

Converged?

Analayse results

## Spin polarization

Spin moment operator

$$\mu_s = -g_s \mu_B \frac{\mathbf{S}}{\hbar}_{g_s=2} = -\mu_B \boldsymbol{\sigma}$$

(collinear case)

$$\boldsymbol{\sigma} = \sigma_z$$

spin moment

$$\mu_z^{spin} = \left\langle \mu_{s,z} \right\rangle = -\mu_B \sum_{\alpha occ} \left\langle \Psi_\alpha \left| \sigma_z \right| \Psi_\alpha \right\rangle$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\left| \Psi_\alpha \right\rangle = \begin{pmatrix} \left| \psi_\alpha^\uparrow \right\rangle \\ \left| \psi_\alpha^\downarrow \right\rangle \end{pmatrix} = \underbrace{\begin{pmatrix} \left| \psi_\alpha^\uparrow \right\rangle \\ 0 \end{pmatrix} \text{ or } \begin{pmatrix} 0 \\ \left| \psi_\alpha^\downarrow \right\rangle \end{pmatrix}}_{\text{in collinear case}}$$

$$m_z^{spin}(\mathbf{r}) = \sum_{\alpha occ} \left| \psi_\alpha^\uparrow(\mathbf{r}) \right|^2 - \sum_{\alpha occ} \left| \psi_\alpha^\downarrow(\mathbf{r}) \right|^2 = n^\uparrow - n^\downarrow$$

## Orbital polarization

orbital moment operator

$$\vec{\mu}_L = -\mu_B \frac{\vec{L}}{\hbar} = -\mu_B \vec{l}$$

orbital moment

$$\mathbf{m}^{orb}(\mathbf{r}) = \sum_{\alpha occ} \left\langle \Psi_\alpha \left| \mathbf{L} \right| \Psi_\alpha \right\rangle$$

*Average orbital moment: usually small (quenched) in bulk and strictly null if spin-orbit coupling (SOC) is ignored.*

# Local Spin density approximation (LSDA)

$$\varepsilon_{xc}(n^{\uparrow},\mathrm{n}^{\downarrow}) = \varepsilon_{x}(n^{\uparrow},\mathrm{n}^{\downarrow}) + \varepsilon_{c}(n^{\uparrow},\mathrm{n}^{\downarrow})$$

Alternative formulation $\quad n = n^{\uparrow} + n^{\downarrow} \qquad m = n^{\uparrow} - n^{\downarrow} \qquad \xi = \frac{m}{n}$

$$\varepsilon_{x}(n,\xi) = \varepsilon_{x}(n,0) + \left[\varepsilon_{x}(n,1) - \varepsilon_{x}(n,0)\right] f_{x}(\xi)$$

$$f_{x}(\xi) = \frac{1}{2}\frac{(1+\xi)^{4/3} + (1-\xi)^{4/3} - 2}{2^{1/3} - 1} = \begin{cases} 1 \text{ if } \zeta = 1 \\ 0 \text{ if } \zeta = 0 \end{cases}$$

$$\varepsilon_{c}(n,\xi) = \varepsilon_{c}(n,0) + \left[\varepsilon_{c}(n,1) - \varepsilon_{c}(n,0)\right] f_{c}(\xi) \qquad f_{c}(\xi) = f_{x}(\xi) \text{ (Perdew Zunger)}$$

Spin dependent potential

$$V_{\text{eff}}^{\sigma} = V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{xc}(n(\mathbf{r}), m(\mathbf{r})) - \sigma B_{xc}(\mathbf{r})$$

$$V_{xc}(r) = \varepsilon_{xc}(n^{\uparrow},\mathrm{n}^{\downarrow}) + n(r)\left[\frac{\partial \varepsilon_{xc}(n(r),\mathrm{m(r)})}{\partial n(r)}\right] \qquad B_{xc}(r) = -n(r)\left[\frac{\partial \varepsilon_{xc}(n(\mathrm{r}),\mathrm{m(r)})}{\partial m(r)}\right]$$

$B_{xc}(r)$ exchange correlation magnetic field

$B_{ext}(r)$ external magnetic field can be added

# Spin polarized DFT implementation diagram

Initial guess

$n_\sigma(r) = \frac{1}{2}(n(r) + \sigma m(r))$

$\sigma = \pm 1$

Combination of atomic densities
+ initial moment (symmetry breaking)

Spin dependent potential

$V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{xc}^{\sigma}(\mathbf{r})$

$\sigma = \pm 1$

Solve the two KS equation

$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}^{\sigma}(r)\right)\psi_\alpha^\sigma(r) = \varepsilon_\alpha^\sigma \psi_\alpha^\sigma(r)$

$\sigma = \pm 1$

charge mixing

Determine the common Fermi level

$E_F = E_F^{\uparrow} = E_F^{\downarrow}$

electron and spin density, total energy

$n^\sigma(\mathbf{r}) = \sum_{\alpha occ} \left|\psi_\alpha^\sigma(\mathbf{r})\right|^2$

$n(\mathbf{r}) = n^{\uparrow}(\mathbf{r}) + n^{\downarrow}(\mathbf{r})$

$\mathrm{m}(\mathbf{r}) = n^{\uparrow}(\mathbf{r}) - n^{\downarrow}(\mathbf{r})$

$E_{tot}\left[n(\mathbf{r}), \mathrm{m}(\mathbf{r})\right]$

Converged?

Analayse results

# ANALYSE RESULTS

What do we get out of spin-polarized DFT calculation

Pw(scf) → $E_{\mathrm{tot}}\left[n_{\mathrm{eq}}, m_{\mathrm{eq}}\right]$ Total energy → find most stable structure! (not always easy..)

Pw(scf) → Total (and absolute) spin magnetic moment

$$M = \int \left(n^{\uparrow}(\mathbf{r}) - \mathrm{n}^{\downarrow}(\mathbf{r})\right) d^3r \qquad M_{\mathrm{abs}} = \int \left|n^{\uparrow}(\mathbf{r}) - \mathrm{n}^{\downarrow}(\mathbf{r})\right| d^3r$$

Pw(nscf) → Spin polarized band structure (for up and down spins)

Pw(scf) → Local analysis (many options…)
+projwf.x
+pp;x

DOS

$$n_{i\lambda\sigma}(E) = \sum_{\alpha} \left|\left\langle \phi_{i,\lambda}^{\mathrm{at}} \middle| \psi_{\alpha}^{\sigma} \right\rangle\right|^2 \delta\left(E - \varepsilon_{\alpha}^{\sigma}\right)$$

$$n_{\sigma}(E, r) = \sum_{\alpha} \left|\psi_{\alpha}^{\sigma}(r)\right|^2 \delta\left(E - \varepsilon_{\alpha}^{\sigma}\right)$$

Local moment

$$m_{i\lambda} = \sum_{\alpha \mathrm{occ}} \left|\left\langle \phi_{i,\lambda}^{\mathrm{at}} \middle| \psi_{\alpha}^{\uparrow} \right\rangle\right|^2 - \left|\left\langle \phi_{i,\lambda}^{\mathrm{at}} \middle| \psi_{\alpha}^{\downarrow} \right\rangle\right|^2$$ Atomic moment

$$m(r) = \sum_{\alpha \mathrm{occ}} \left|\psi_{\alpha}^{\uparrow}(\mathbf{r})\right|^2 - \left|\psi_{\alpha}^{\downarrow}(\mathbf{r})\right|^2$$ Spin density

# PHYSICAL INSIGHT

DFT is a very powerful tool but there is still a need for simpler phenomenological models and local analysis to get a deeper physical understanding of the phenomena

- Stoner model
- Heisenberg/Ising model
- Local analysis $\vec{m}_i$

# LSDA and the Stoner model

$$\varepsilon_{xc}(n,\xi) \approx \varepsilon_{xc}(n,0) + \tfrac{1}{2}\varepsilon_{xc}^{''}(n,0)\xi^2 + o(\xi^2)$$

$$B_{xc}(\mathbf{r}) = -\frac{1}{n(\mathbf{r})}\varepsilon_{xc}^{''}(n(\mathbf{r}),0)m(\mathbf{r})$$

$$V_{\text{eff}}^{\sigma} \approx V_{\text{eff}}^{0} - \frac{\sigma}{2}\text{IM}$$

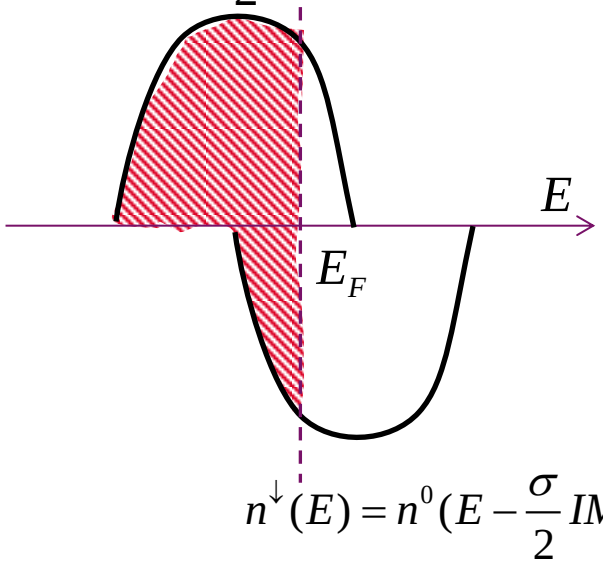
$M$ : magnetic moment per atom

$$M = \int_{\Omega} m(\mathbf{r})d^3r \qquad I = -\frac{1}{\Omega}\int_{\Omega}\frac{\varepsilon_{xc}^{''}(n(\mathbf{r}),0)}{n(\mathbf{r})}d^3r > 0$$

Rigid shift of up and down eigenvalues

$$\varepsilon_{\alpha}^{\sigma} = \varepsilon_{\alpha}^{0} - \frac{\sigma}{2}IM$$

$$n^{\uparrow}(E) = n^{0}(E + \frac{\sigma}{2}IM)$$



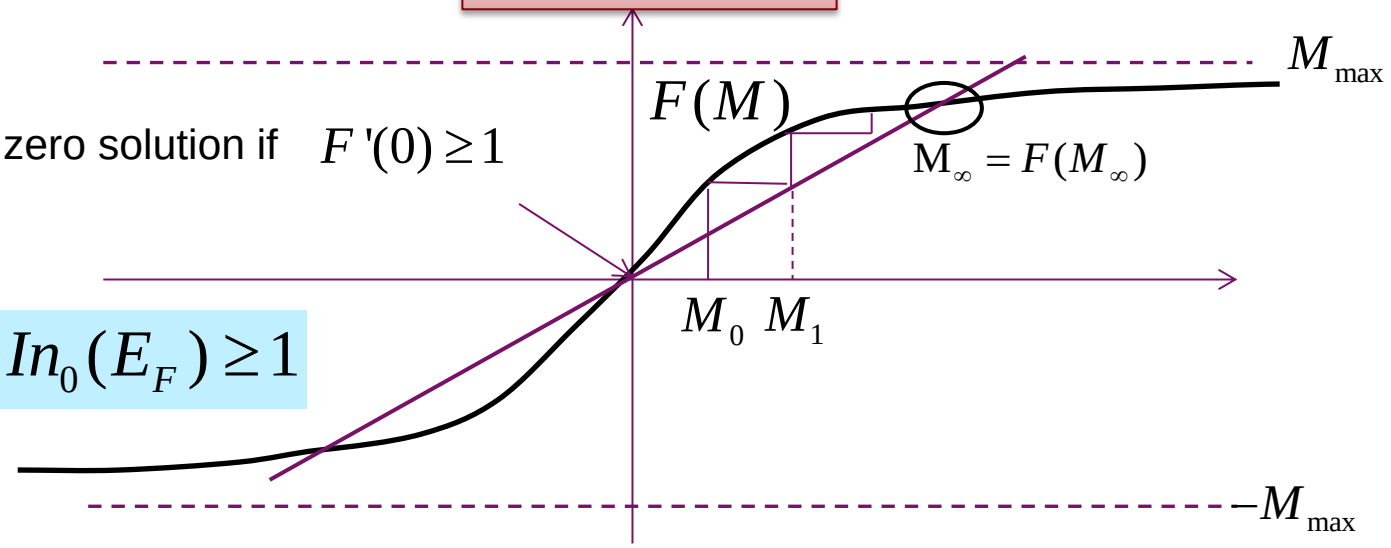

$$n^{\downarrow}(E) = n^{0}(E - \frac{\sigma}{2}IM)$$

$$N = \int^{E_F} (\mathrm{n}^0(E + \tfrac{1}{2}IM) + n^0(E - \tfrac{1}{2}IM))\,\mathrm{dE} \Rightarrow E_F(M)$$

$$M = \int^{E_F} (\mathrm{n}^0(E + \tfrac{1}{2}IM) - n^0(E - \tfrac{1}{2}IM))\,\mathrm{dE}$$

$$\Leftrightarrow F(M) = M$$

## Stoner criterion




$I \sim 1eV$ In most elements $\Rightarrow$ $n_0(E_F)$ plays a crucial role in magnetic susceptibility and onset of magnetism

Criterion can be also derived by analyzing

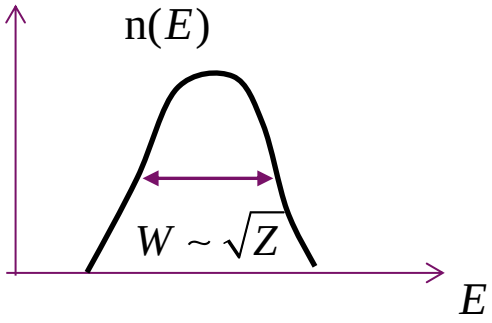
- magnetic susceptibility $\chi = \frac{\partial M}{\partial H} = \frac{\chi_0}{(1 - In_0(E_F))}$
- Total energy $E_{tot} = \sum_{\alpha occ} \varepsilon_\alpha + \frac{1}{2} \sum_i Im_i^2$

Nowadays Stoner model often used in parametrized Tight-Binding models

$$H_{ij}^\sigma = H_{ij}^0 - \frac{\sigma}{2} IM_i \delta_{ij}$$

# General trends

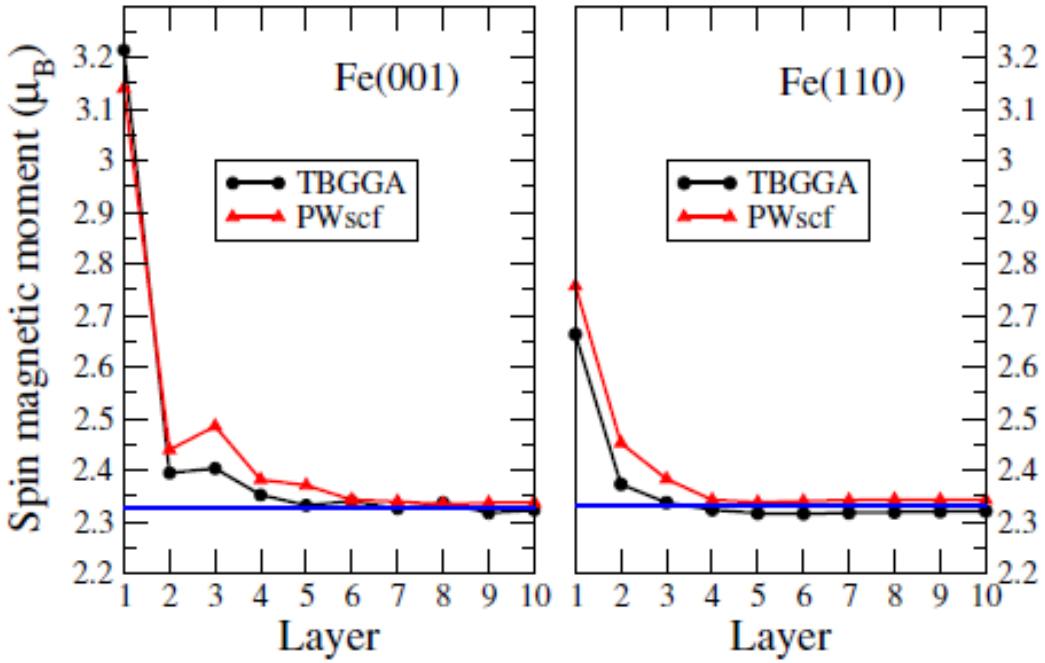
- Low coordination favors magnetism




$Z$ : number of neigbors

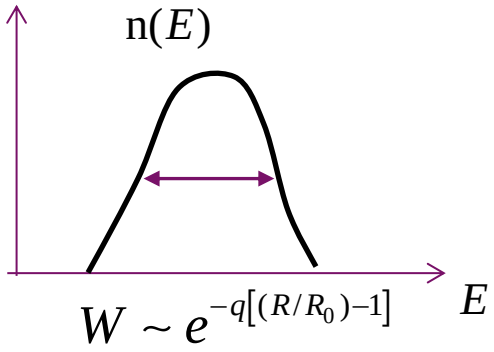
$$Z \searrow \Rightarrow \mathrm{n}(E_F) \nearrow$$

Spin magnetic moment is generally enhanced on low coordinated atoms



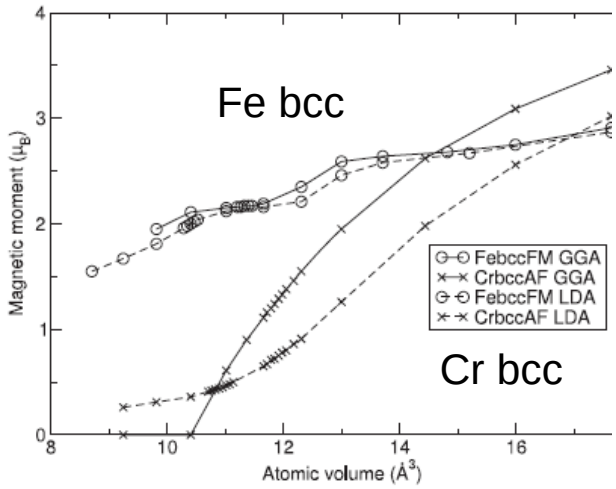
# General trends

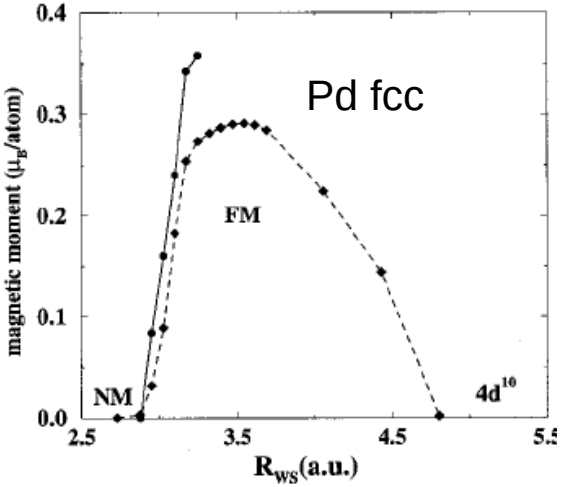
- Lattice expansion generally favors magnetism and vice versa…



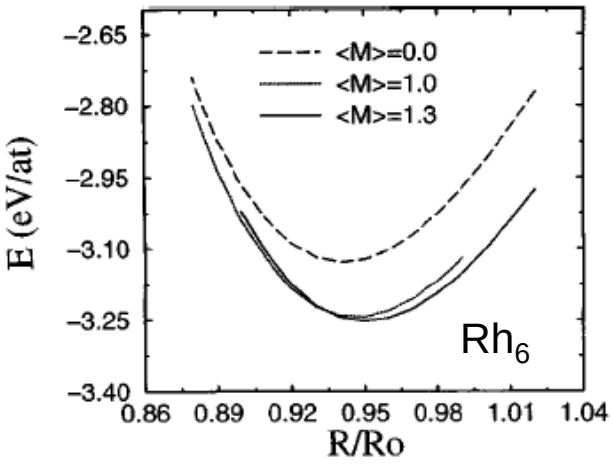

$$R\nearrow \Rightarrow \mathrm{W}\searrow \Rightarrow \mathrm{n}(E_F)\nearrow$$

$M(d)$



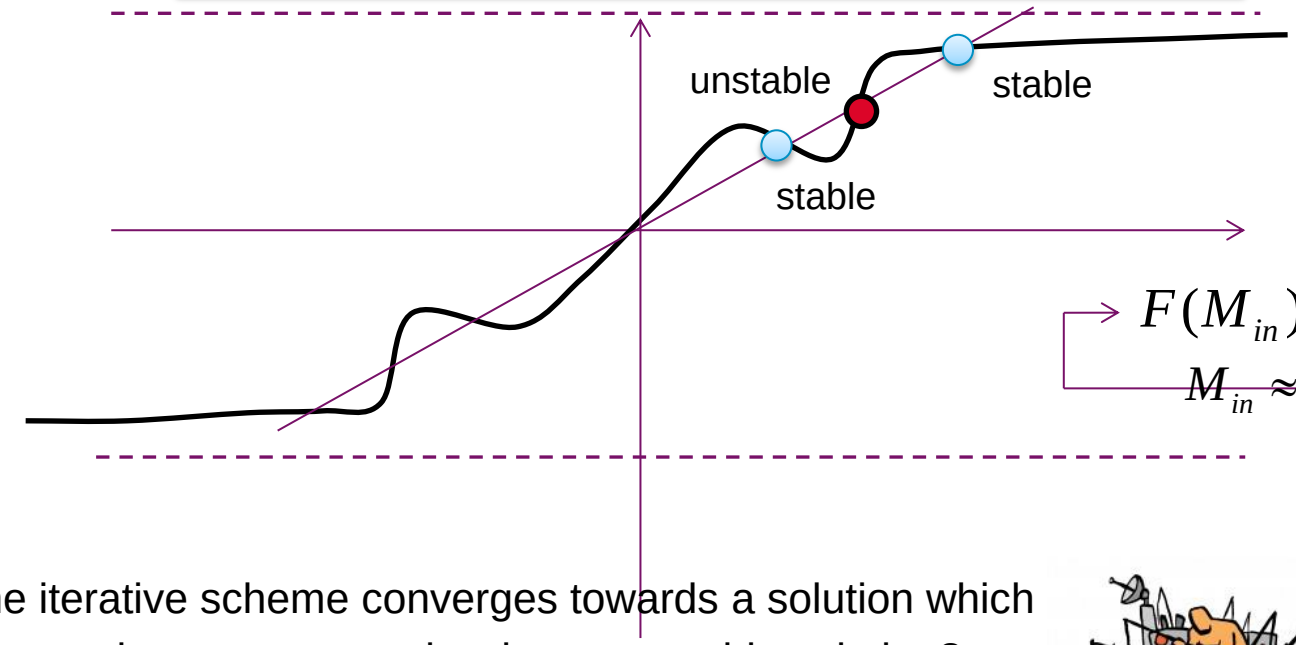




E($d$)



# Multiple magnetic solutions

## Stoner criterium does not tell the whole story




$$F(M_{in}) = M_{out}$$

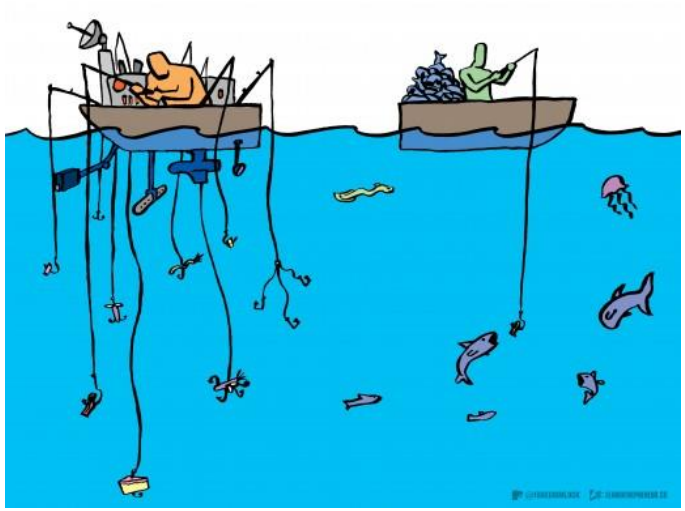
$$M_{in} \approx M_{out} \; ?$$

The iterative scheme converges towards a solution which

How to be sure not to miss the most stable solution?

- Several starting magnetization (fishing strategy)

- Fix spin moment (FSM) calculation allow to explore E(V,M) energy surface

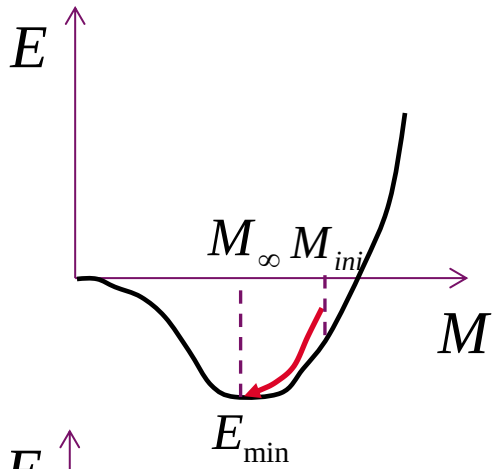


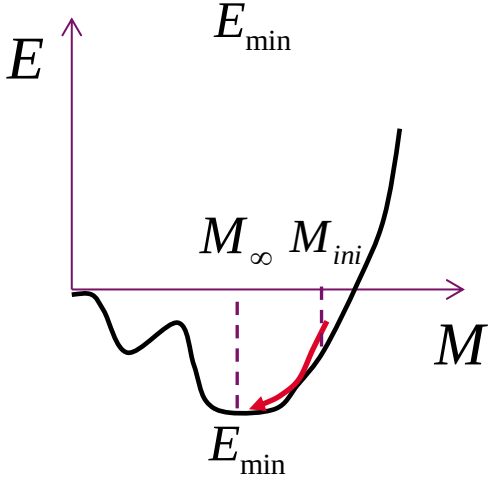
# Fixed Spin moment

## Conventional scheme

$E_F^{\uparrow} = E_F^{\downarrow}$ $N = N^{\uparrow} + N^{\downarrow}$ $M_{\text{ini}} \rightarrow M_{\infty}$

one scf loop

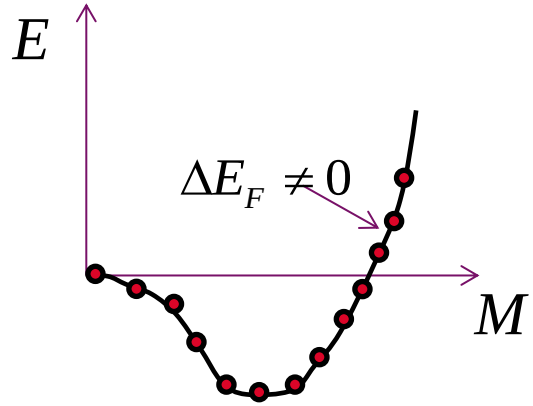


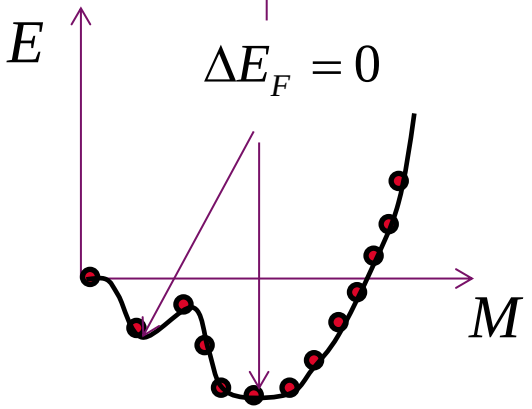

## FSM

$E_F^{\uparrow} \neq E_F^{\downarrow}$ $N = N^{\uparrow} + N^{\downarrow}$ $M = N^{\uparrow} - N^{\downarrow}$

many calculations




$\Delta E_F = 2H(M)$



# Penalization technique

Add a penalization term to the total energy functional to impose a given condition

- DFT

$$E_\lambda[n,m] = E_{tot}[n,m] + \lambda \int_\Omega (\mathrm{m}(\mathbf{r}) - \mathrm{m}_0(\mathbf{r}))^2 d^3r$$

Minimization → modified KS Hamiltonian

$$H_\lambda = H + 2\lambda (m(r) - m_0(r))\big|_\Omega .\sigma$$

- TB

$$E_\lambda[\{c_i\}] = E_{tot}[\{c_i\}] + \lambda (m_i - m_0)^2 \qquad |\psi\rangle = \sum_i c_i |\phi_i^{at}\rangle$$

$$H_{ij}^\lambda = H_{ij} + 2\lambda(m_i - \mathrm{m}_0).\sigma\delta_{ij}$$

# SOME IMPORTANT TECHNICAL POINTS

Before running (or trusting) a DFT calculation you should be aware of several important technicalities

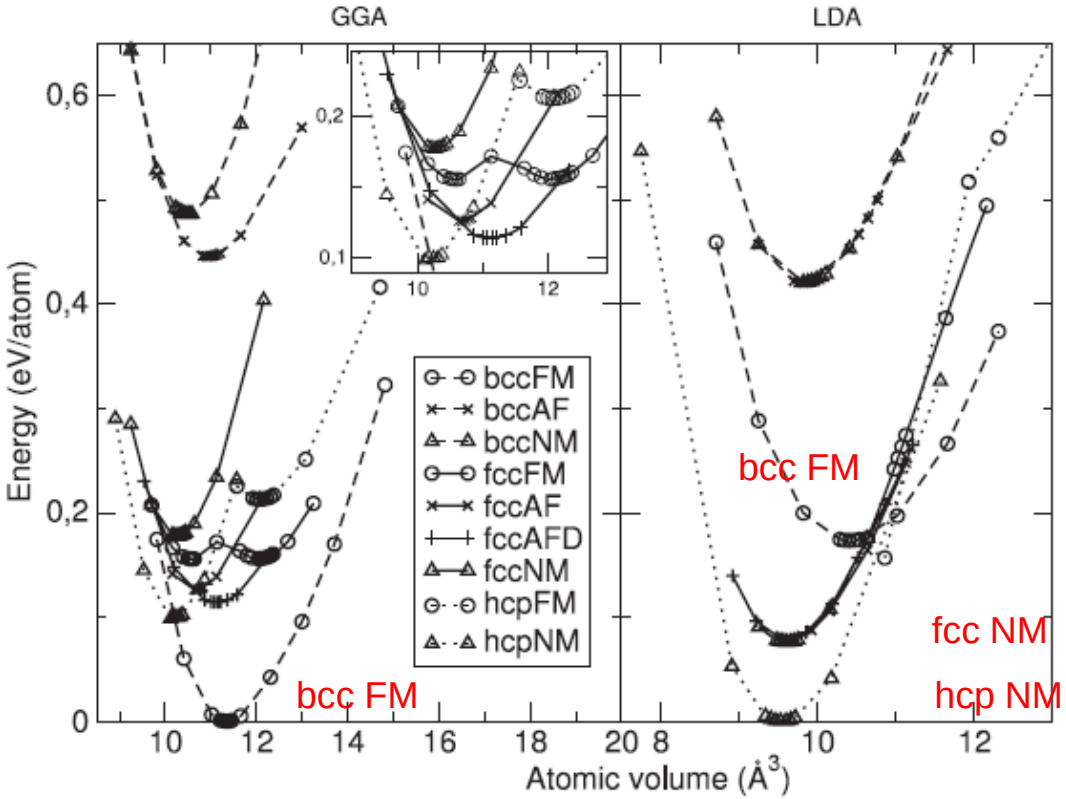
- Pseudopotential (`LDA pz /GGA pw91, pbe`)
- Energy cut-off (`ecutwfc, ecutrho≥8ecutwfc for US pseudo`)
- K-points sampling: denser mesh for metals
  note that in QE the #k points is doubled in spin-polarized system
- Smearing (`smearing, degausss`) Marzari Vanderbilt recommended
- Initial magnetization (`starting_magnetization`)
- Number of computed eigenvalues (`nbnd`) often needs to be increased
- Convergence threshold (`conv_thr`)

pseudopotential

As a rule of thumb: $a_{LDA} < a_{exp} < a_{GGA}$

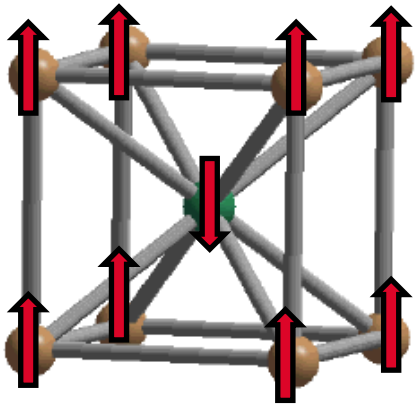
LDA bad for 3d but OK for 5d→ problematic for alloys (FePt, CoPt)

E(V)



## Initial magnetization

Cr bcc AF

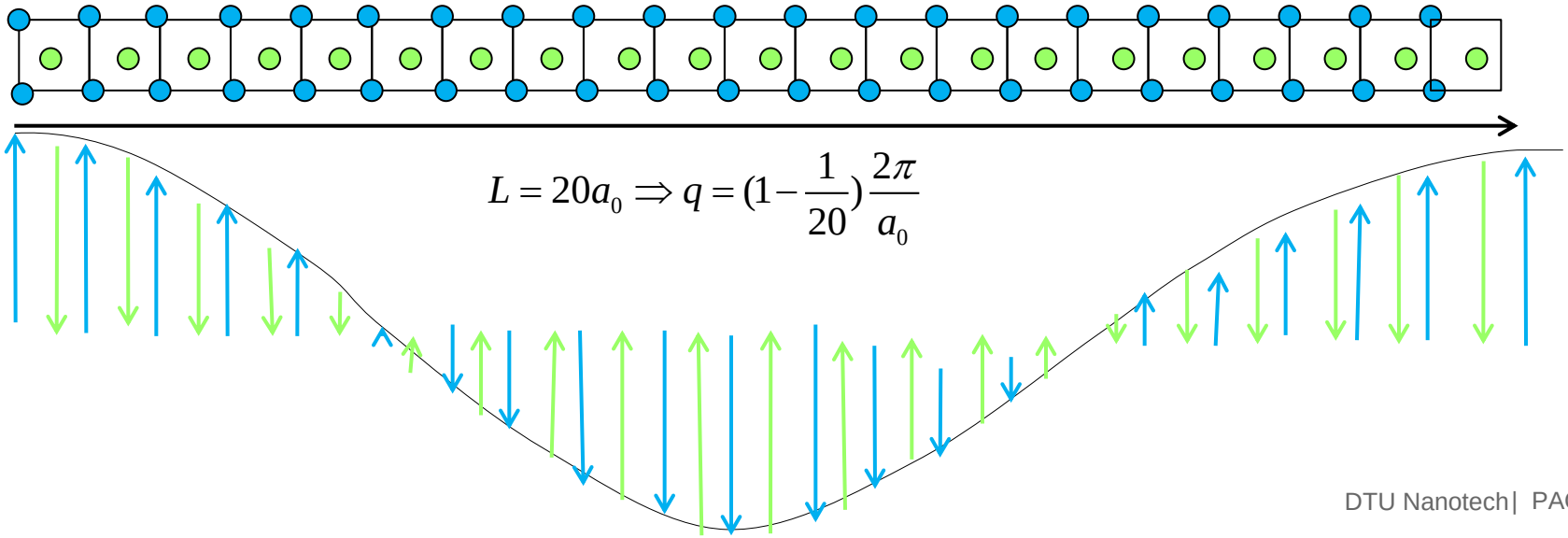


Define the system as **simple cubic** with 2 types of atoms per unit cell and opposite starting magnetization

```
ibrav=1
                starting_magnetization(1)= 0.5
nat=2           starting_magnetization(2)=-0.5
ntyp=2
```

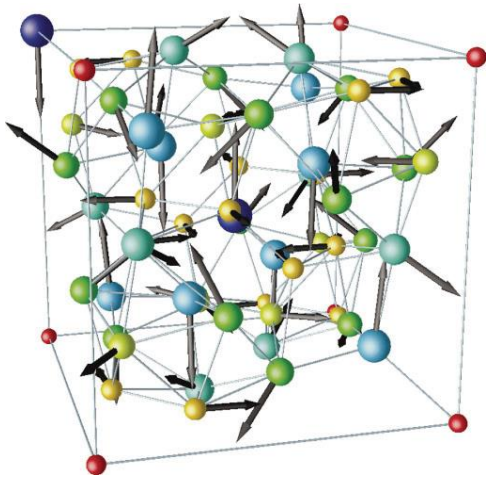
Cr SDW

$$m = m_0 \cos(\mathbf{q}.\mathbf{R}) \qquad q = 0.953 \sim 0.95 \text{ in unit of } \frac{2\pi}{a_0}$$



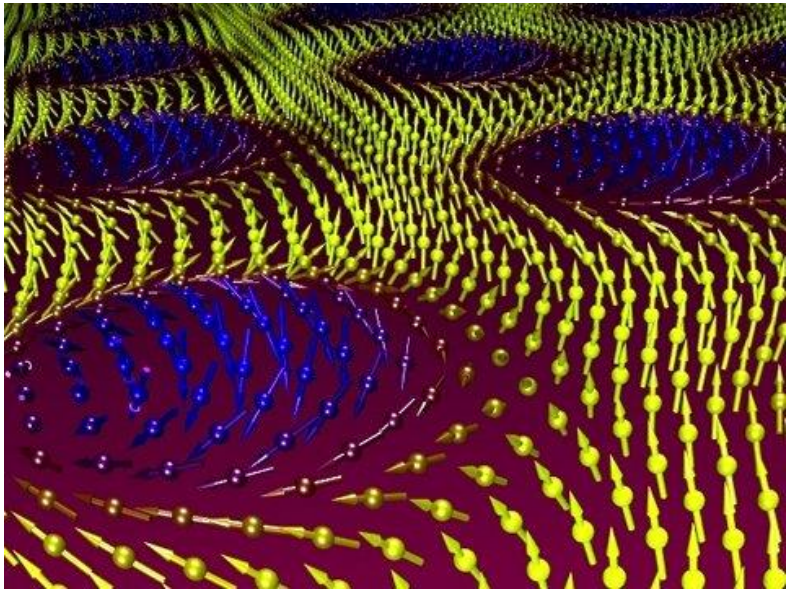
# NON COLLINEAR MAGNETISM

Why should we care about non collinearity?

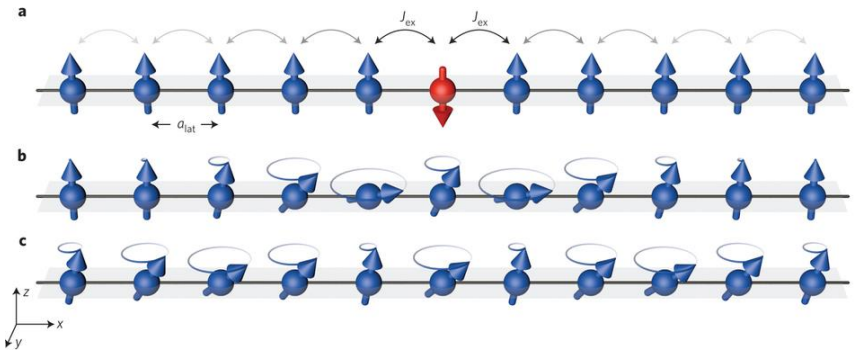


$\alpha - Mn$

Non-collinearity does exist!

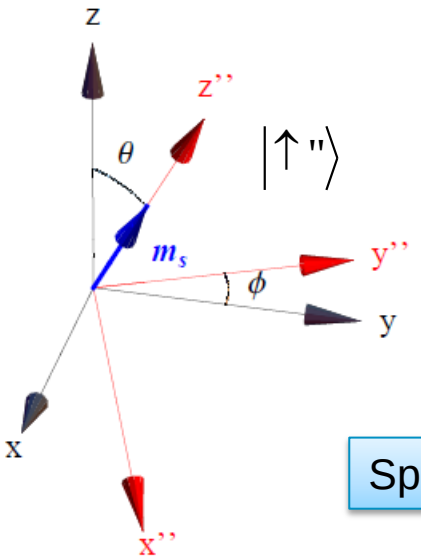


The future is in skyrmions ☺




Spin excitation

## Spin gymnastics




$(x, y, z)$ global axis $\qquad$ $(x'', y'', z'')$ local axis

$$\mathbf{m} = m\begin{pmatrix}\sin\theta\cos\phi\\ \sin\theta\sin\phi\\ \cos\theta\end{pmatrix} \qquad \mathbf{m}'' = m\begin{pmatrix}0\\0\\1\end{pmatrix}$$

### Spin ½ rotation matrix

$$U(\theta,\phi) = \begin{array}{c} \quad |\uparrow''\rangle \qquad\qquad |\downarrow''\rangle \\ \begin{pmatrix} e^{-i\frac{\phi}{2}}\cos(\frac{\theta}{2}) & -e^{-i\frac{\phi}{2}}\sin(\frac{\theta}{2}) \\ e^{-i\frac{\phi}{2}}\sin(\frac{\theta}{2}) & e^{i\frac{\phi}{2}}\cos(\frac{\theta}{2}) \end{pmatrix} \end{array} = e^{-i\frac{\phi}{2}\sigma_z} e^{-i\frac{\theta}{2}\sigma_y}$$

$$\boldsymbol{\sigma}_{i''} = U(\theta,\phi)\boldsymbol{\sigma}_i U^{\dagger}(\theta,\phi)$$

$\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ also transforms like a space vector

$$\boldsymbol{\sigma}_{i''} = R_{ij}\boldsymbol{\sigma}_j$$

## 2x2 matrices algebra

$$\mathbf{M} \in M_2(\mathbb{C})$$

$$\mathbf{M} = a\mathbf{I} + \mathbf{b}.\boldsymbol{\sigma} \qquad a = \tfrac{1}{2}Tr(\mathbf{M}) \qquad \mathbf{b} = \tfrac{1}{2}Tr(\mathbf{M}.\boldsymbol{\sigma})$$

If $\mathbf{M}$ is hermitian then $a$ and $\mathbf{b}$ are real numbers

diagonalization

2 eigenvalues $a \pm \|\mathbf{b}\|$

$$\mathbf{b} = \|\mathbf{b}\|\mathbf{n} \qquad \mathbf{n} = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}$$

$$\mathbf{M} = U \begin{pmatrix} a + \|\mathbf{b}\| & 0 \\ 0 & a - \|\mathbf{b}\| \end{pmatrix} U^{\dagger}$$

$$U = \begin{pmatrix} e^{-i\frac{\phi}{2}}\cos(\frac{\theta}{2}) & -e^{-i\frac{\phi}{2}}\sin(\frac{\theta}{2}) \\ e^{-i\frac{\phi}{2}}\sin(\frac{\theta}{2}) & e^{i\frac{\phi}{2}}\cos(\frac{\theta}{2}) \end{pmatrix}$$

# From electron density/magnetization vector to the Density matrix

$n, \mathbf{m}$

$$n(\mathbf{r}) = \sum_{\alpha,\sigma} f_\alpha \psi_\alpha^{\sigma *}(\mathbf{r}) \psi_\alpha^{\sigma}(\mathbf{r}) \quad \mathbf{m}(\mathbf{r}) = \sum_{\alpha} f_\alpha \mathbf{\Psi}_\alpha^{\dagger}(\mathbf{r}) \boldsymbol{\sigma} \mathbf{\Psi}_\alpha(\mathbf{r}) = \sum_{\alpha,\sigma,\sigma'} f_\alpha \psi_\alpha^{\sigma' *}(\mathbf{r}) \boldsymbol{\sigma}_{\sigma\sigma'} \psi_\alpha^{\sigma}(\mathbf{r})$$

$$\left| \mathbf{\Psi}_\alpha \right\rangle = \begin{pmatrix} \left| \psi_\alpha^{\uparrow} \right\rangle \\ \left| \psi_\alpha^{\downarrow} \right\rangle \end{pmatrix}$$

Density matrix

$$\rho^{\sigma\sigma'}(\mathbf{r}) = \sum_{\alpha} f_\alpha \psi_\alpha^{\sigma' *}(\mathbf{r}) \psi_\alpha^{\sigma}(\mathbf{r}) \qquad \boldsymbol{\rho}(\mathbf{r}) = \begin{pmatrix} \rho^{\uparrow\uparrow} & \rho^{\uparrow\downarrow} \\ \rho^{\downarrow\uparrow} & \rho^{\downarrow\downarrow} \end{pmatrix}$$

n,**m** → ρ

$$\boldsymbol{\rho}(\mathbf{r}) = \frac{1}{2}\left( n(\mathbf{r})\, \mathrm{I} + \boldsymbol{\sigma}.\mathbf{m}(\mathbf{r}) \right) = \frac{1}{2} \begin{pmatrix} n + m_z & m_x - i m_y \\ m_x + i m_y & n - m_z \end{pmatrix}$$

ρ → n,**m**

$$n = Tr(\boldsymbol{\rho}) \qquad \mathbf{m} = Tr(\boldsymbol{\rho}\boldsymbol{\sigma})$$

# The non-collinear Stoner Hamiltonian

Local spin axis

$$H^{"}_{\text{Stoner}} = -\frac{I}{2} m \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = -\frac{I}{2} m \sigma_{z"}$$

Global spin axis

$$H_{\text{Stoner}} = U H^{"}_{Stoner} U^{\dagger} = -\frac{I}{2} m \begin{pmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{pmatrix}$$

$$H_{\text{Stoner}} = -\frac{I}{2} m \left[ \sin\theta\cos\phi \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \sin\theta\sin\phi \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \cos\theta \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right]$$

$$H_{\text{Stoner}} = -\frac{I}{2} \mathbf{m}.\boldsymbol{\sigma}$$

A lot of fuss for a straightforward result!

## Kohn Sham Hamiltonian

$$H_{KS}^{\sigma\sigma'} = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}^{\sigma\sigma'}(r)$$

$$V_{\text{eff}}^{\sigma\sigma'}(\mathbf{r}) = \left( V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' \right)\delta_{\sigma\sigma'} + \underbrace{V_{xc}^{\sigma\sigma'}[\boldsymbol{\rho}(r)]}_{\frac{\partial E_{xc}[\boldsymbol{\rho}(\mathbf{r})]}{\partial \rho_{\sigma\sigma'}}}$$

$$V_{\text{eff}}^{\sigma\sigma'}(\mathbf{r}) = \left( V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + \frac{\partial E_{xc}[\boldsymbol{\rho}(\mathbf{r})]}{\partial n(r)} \right)\delta_{\sigma\sigma'} - \underbrace{\boldsymbol{\sigma}.\mathbf{B}_{xc}}_{\frac{\partial E_{xc}[\boldsymbol{\rho}(\mathbf{r})]}{\partial \mathbf{m}(r)}}$$

In LDA $\quad \varepsilon_{xc}(\mathrm{n}) = f(\mathrm{n})$

diagonalization of $\boldsymbol{\rho} \Rightarrow$ diagonalization of $\varepsilon_{xc}(\boldsymbol{\rho}) = \begin{pmatrix} \varepsilon_{xc}(\mathrm{n}^{\uparrow}) & 0 \\ 0 & \varepsilon_{xc}(\mathrm{n}^{\downarrow}) \end{pmatrix}$

$\Rightarrow (m(\mathbf{r}), \theta(\mathbf{r}), \varphi(\mathbf{r}))$ at each position $\mathbf{r}$ in space

$\Rightarrow$ rotate "back" with matrix $\mathbf{U}$ to get $\varepsilon_{xc}(\boldsymbol{\rho}(\mathbf{r}))$

In GGA $\quad \varepsilon_{xc}(\mathrm{n}) = f(\mathrm{n}, \nabla n)$

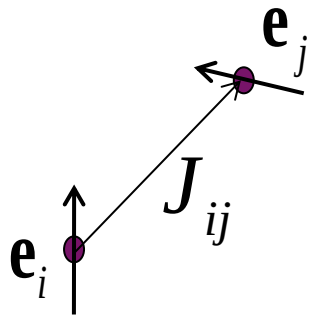
Additional complication since $\boldsymbol{\rho}$ and $\nabla\boldsymbol{\rho}$ cannot be diagonalized in the same basis

off diagonal terms of $\nabla\rho$ are neglected

# PHYSICAL INSIGHT

Classical Heisenberg Hamiltonian

$$E = -\frac{1}{2}\sum_{\langle i,j \rangle} J_{ij}\mathbf{e}_i\mathbf{e}_j$$

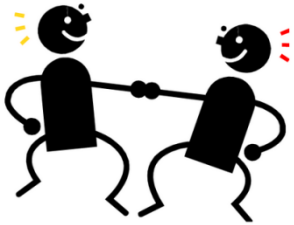


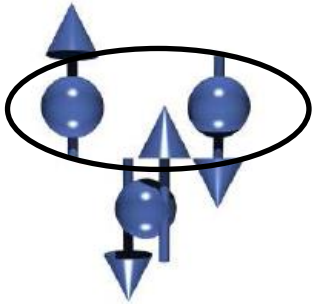

$J_{ij}$ Can be obtained by various approaches from DFT (not yet available in QE)

$J_{ij} > 0$ Favors FM order

$J_{ij} < 0$ Favors AF order

Frustration



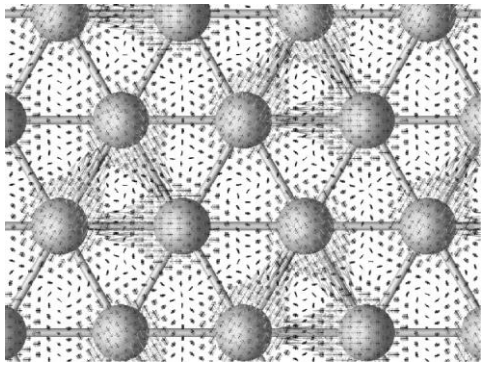



Fairly happy

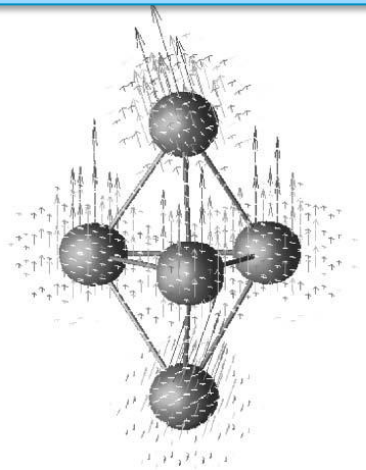
Remark: without SOC system is invariant under global rotation of the spins

# Some examples

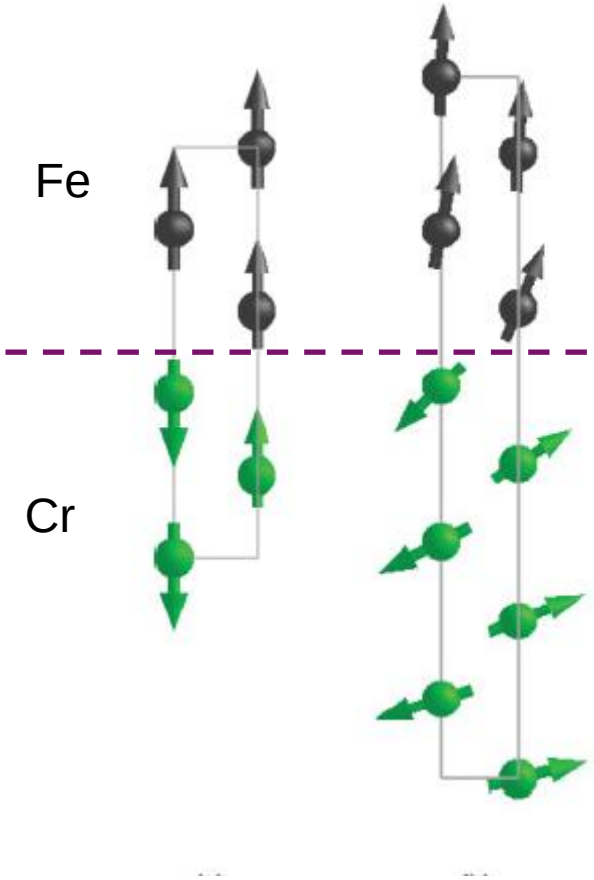
Cr/Cu(111)



Fe bibyramidal cluster

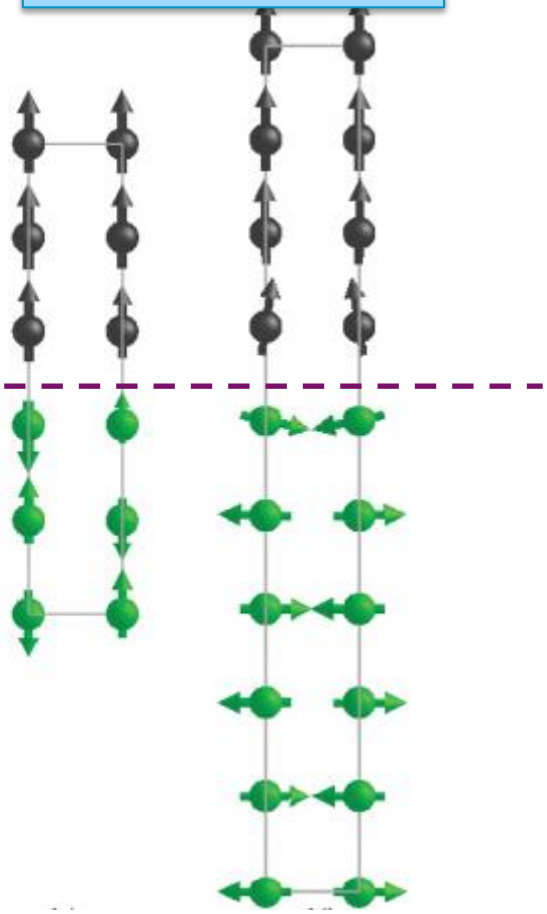


Fe/Cr(001) interface




$E_{\mathrm{col}} < E_{\mathrm{ncol}}$

Fe/Cr(110) interface



$E_{\mathrm{col}} > E_{\mathrm{ncol}}$

# SPIN-ORBIT COUPLING

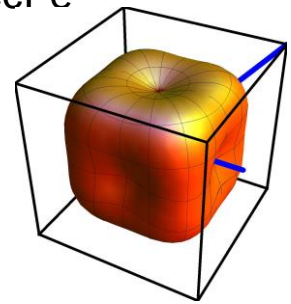
Why should we care about SOC?

Small quantity (at least in 3d) with huge physical consequences

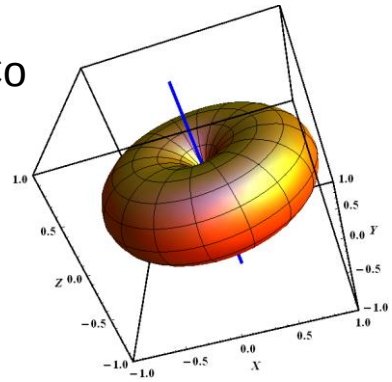
- At the origin of magneto-crystalline anisotropy …..and therefore of the stability of magnets!

$E(\theta,\varphi)$

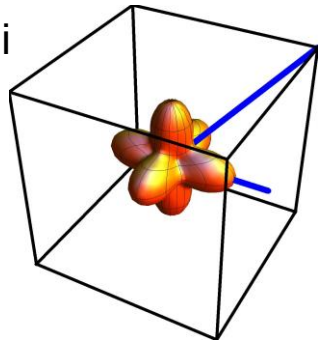
bccFe



hcpCo

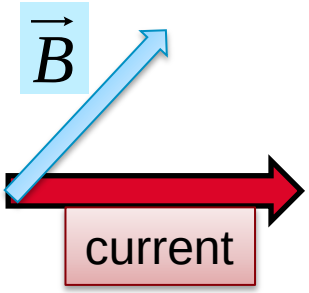


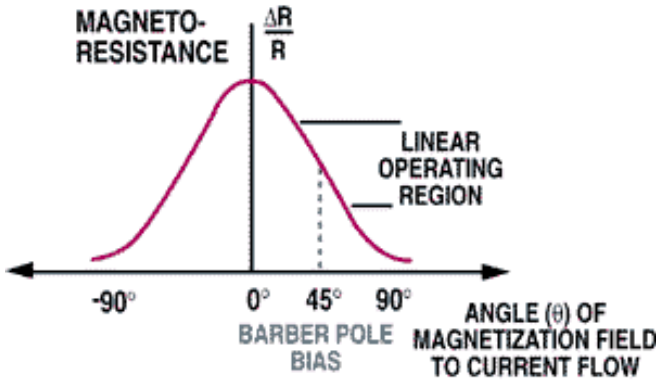
fccNi



- At the origin Anisotropic Magneto-Resistance

$R(\theta)$



# Relativistic effects

## Dirac equation

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t}=\left(c\boldsymbol{\alpha}.\mathbf{p}+\boldsymbol{\beta}mc^2+V\right)\Psi(r,t)$$

$$\boldsymbol{\alpha}_i=\begin{pmatrix}0 & \sigma_i\\ \sigma_i & 0\end{pmatrix}\qquad \boldsymbol{\beta}=\begin{pmatrix}\mathbf{I} & 0\\ 0 & -\mathbf{I}\end{pmatrix}\qquad \Psi(r,t)=\begin{pmatrix}\begin{pmatrix}\psi_1(r,t)\\ \psi_2(r,t)\end{pmatrix}\\ \begin{pmatrix}\psi_3(r,t)\\ \psi_4(r,t)\end{pmatrix}\end{pmatrix}$$

$\psi(r,t)$ Large component

$\chi(r,t)$ Small component

## Scalar relativistic

Small v/c limit $\chi(r,t)\sim\frac{v}{c}\psi(r,t)$

$$H=\left[-\frac{\hbar^2}{2m}\nabla^2+V(r)\right]+\frac{\mu_B}{\hbar}(\mathbf{L}+2\mathbf{S}).B$$

Schrödinger + Zeeman

$$-\frac{p^4}{8m^3c^2}$$

Mass-velocity

*Contraction and stabilization of s and p shells + expansion and destabilization of d and f*

$$\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{L}.\mathbf{S}=\xi(r)\hat{\mathbf{l}}.\hat{\mathbf{s}}=\tfrac{1}{2}\xi(r)\hat{\mathbf{l}}.\boldsymbol{\sigma}$$

Spin-Orbit Coupling

*Splitting of orbitals with angular momentum.*

$$-\frac{\hbar^2}{8m^2c^2}\nabla^2V$$

Darwin

# The good basis

- Without SOC: $\vec{L}$ et $\hat{\vec{S}}$ commute with $H$

Basis diagonalizing $L^2, L_z, \hat{S}^2, \hat{S}_z \longrightarrow |l,m\rangle \otimes |\varepsilon\rangle$

$$L^2|l,m\rangle = l(l+1)\hbar^2|l,m\rangle \qquad \hat{S}^2|\varepsilon\rangle = \frac{3}{4}\hbar^2|\varepsilon\rangle$$

$$L_z|l,m\rangle = m\hbar|l,m\rangle \qquad \hat{S}_z|\varepsilon\rangle = \varepsilon\hbar|\varepsilon\rangle$$

- With SOC: $\vec{L}$ et $\hat{\vec{S}}$ no longer commute with $H + H_{so}$

we consider $\hat{\vec{J}} = \vec{L} + \hat{\vec{S}}$

Basis diagonalizing $\hat{J}^2, \hat{J}_z \longrightarrow |j,m_j\rangle$

$$\hat{J}^2|j,m_j\rangle = j(j+1)\hbar^2|j,m_J\rangle \qquad |l-s| \le j \le l+s$$

$$\hat{J}_z|j,m\,j\rangle = m_j\hbar|j,m_j\rangle \qquad m_j = \underbrace{-j,-j+1,\ldots,j}_{2j+1}$$

$$L.\hat{S}|j,m_j\rangle = \frac{1}{2}\left[\langle\hat{J}^2\rangle - \langle L^2\rangle - \langle\hat{S}^2\rangle\right]|j,m_j\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]|j,m_j\rangle$$

- From one basis to the other = Clebsh Gordan

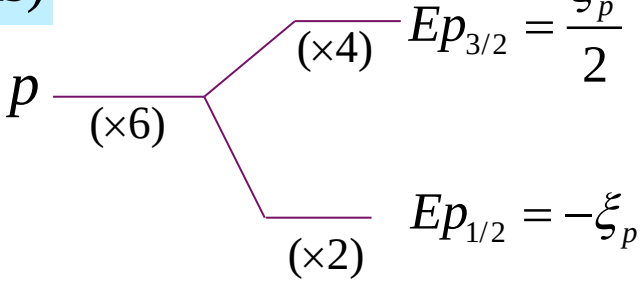
## Removal of degeneracies

$$s = \frac{1}{2}$$

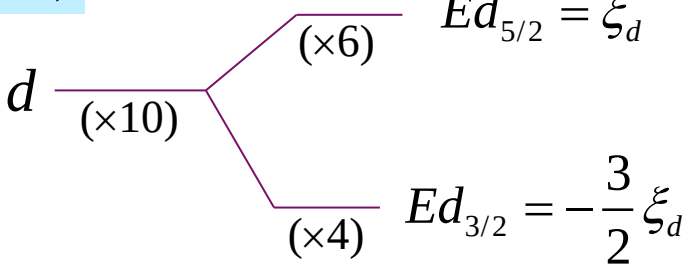
$$j = \begin{cases} l+\frac{1}{2} & (2l+2) \\ l-\frac{1}{2} & (2l) \end{cases} \quad 2(2l+1)$$

$$\xi \hat{l}.\hat{s} \left| j, m_j \right\rangle = \frac{\xi}{2}\left[ \left\langle \hat{\mathbf{j}}^2 \right\rangle - \left\langle \hat{\mathbf{l}}^2 \right\rangle - \left\langle \hat{\mathbf{s}}^2 \right\rangle \right] \left| j, m_j \right\rangle = \frac{\xi}{2}\left[ j(j+1) - l(l+1) - \tfrac{1}{2}(\tfrac{1}{2}+1) \right] \left| j, m_j \right\rangle$$

$l = 1$ (p orbitals)




$l = 2$ (d orbitals)



# Relativistic pseudo-potentials

- Without SOC

*But including other (scalar) relativistic effects*

$$V_{\text{pseudo}} = V_{\text{loc}}(r) + \underbrace{\sum_I \sum_{l,m_l} E_l^I \left|\beta_l^I Y_{l,m_l}^I\right\rangle\left\langle\beta_l^I Y_{l,m_l}^I\right|}_{\delta V_{NL}}$$

```
Fe.pbe-nd-rrkjus.UPF

Pseudopotential type: ULTRASOFT
Method: Rappe Rabe Kaxiras Joannopoulos
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
Nonlinear core correction
scalar relativistic
```

- With SOC

*For technical details please contact Andrea dal Corso….*

$$V_{\text{pseudo}} = V_{\text{loc}}(r) + \sum_{j=l\pm\frac{1}{2}} \delta V_{NL}^j = \sum_{lm} \left(V_l \mathbf{Id} + V_l^{SO} \mathbf{L.S}\right) \left|Y_{lm}\right\rangle\left\langle Y_{lm}\right|$$

```
Fe.rel-pbe-spn-rrkjus_psl.0.2.1.UPF

Pseudopotential type: ULTRASOFT
Method: Rappe Rabe Kaxiras Joannopoulos
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
Semi-core state in valence
Nonlinear core correction
full relativistic
```

# SOME IMPORTANT TECHNICAL POINTS

⟹ Relativistic Pseudopotential (`LDA pz /GGA pw91, pbe`)

⟹ $\left(\mathbf{L.S}\right)_{\sigma\sigma'}$ Is **not** diagonal in spins → impossible to split up and down spins
= drastic increase of the computational cost

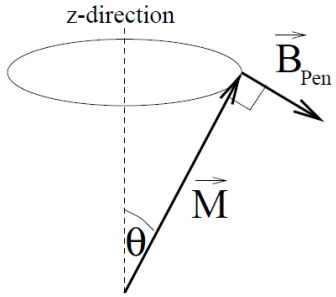
collinear $\begin{pmatrix} \uparrow\uparrow & 0 \\ 0 & \downarrow\downarrow \end{pmatrix}$ Non-collinear $\begin{pmatrix} \uparrow\uparrow & \uparrow\downarrow \\ \downarrow\uparrow & \downarrow\downarrow \end{pmatrix}$

⟹ Very dense K-points mesh

⟹ Check very carefully the influence of « Fermi » broadening

⟹ Use penalization when necessary)

$$E_{pen} = \lambda(\theta - \theta_0)^2 = \lambda\left(\arccos\left(\frac{M_z}{M}\right) - \theta_0\right)^2$$




$E(\theta,\varphi)$

⟹ Very strict convergence threshold

# A FEW THINGS ABOUT SOC

- $\xi(r)$ Is short range (atomic-like) in TB (or LCAO) on site term $\sum_I \xi_I \left(\mathbf{L}.\mathbf{S}\right)_I$
- $\xi(r) \sim \mathrm{Z}^4$ Increases drastically with atomic number

$$\xi_{ll'} = \int_0^\infty R_l^{at}(r) R_{l'}^{at}(r) \xi(\mathrm{r})\, \mathrm{r}^2\, dr$$

$\xi_d \sim 0.05eV$ for $3d$

$\xi_d \sim 0.5eV$ for $5d$

- SOC removes degeneracies (splitting)
- The band structure depends on the magnetization axis
- SOC is at the origin of the magnetocrystalline anisotropy $E(\theta,\varphi)$

$MCA \sim 10^{-2} - 10^{-3} meV$ / atom in bulk Fe, Co, Ni

Much larger in nanostructures

$MCA \sim meV$ / atom in bulk FePt L10

- SOC is at the origin of the anisotropic magneto_resistance $R(\theta)$

$AMR \sim 1\%$ in bulk

larger in atomic wires

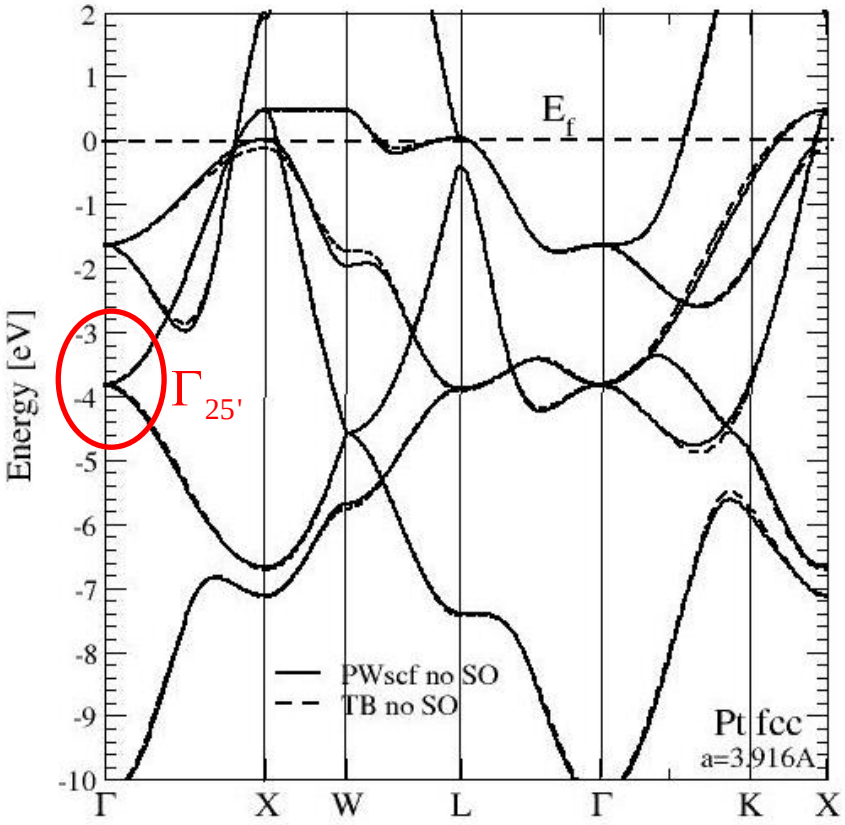
- SOC is at the origin of the orbital moment

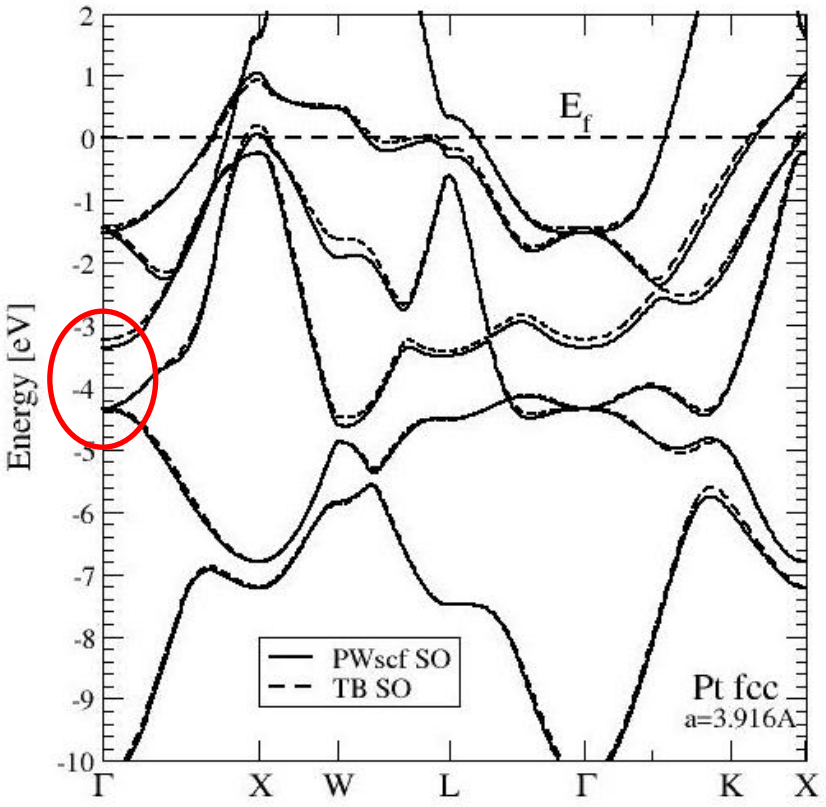
# Removal of degeneracies in non magnetic systems

•Without SOC

Pt bandstructure

•With SOC




$\Gamma_{25'}$ sixfold degenerate → twofold, fourfold

$$\Delta \approx \frac{3}{2}\xi$$

# Rashba splitting

Time reversal

$$\varepsilon_{\uparrow}(k) = \varepsilon_{\downarrow}(-k)$$

Inversion symmetry

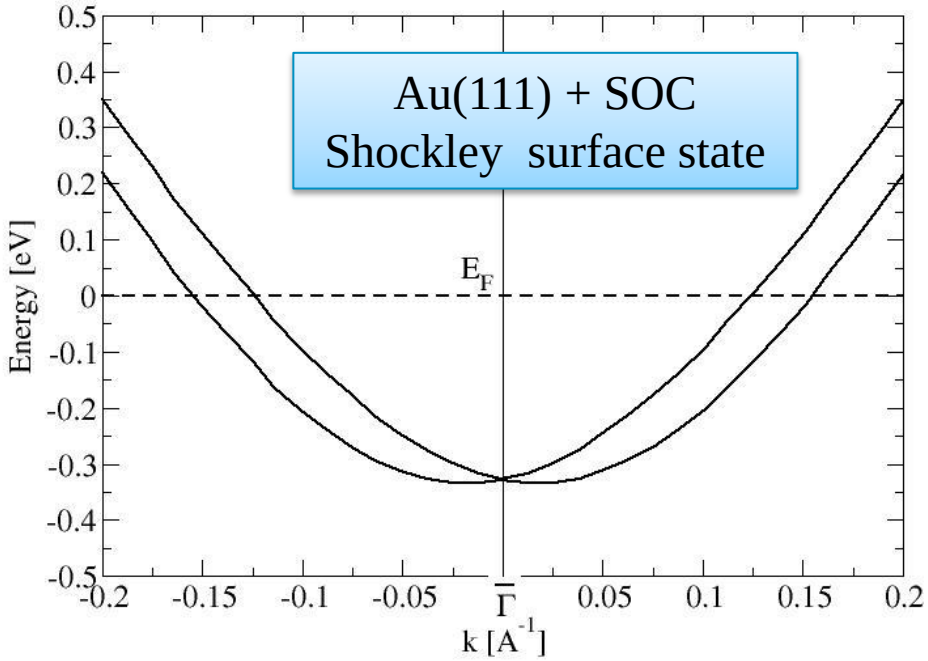
$$\varepsilon_{\sigma}(k) = \varepsilon_{\sigma}(-k)$$

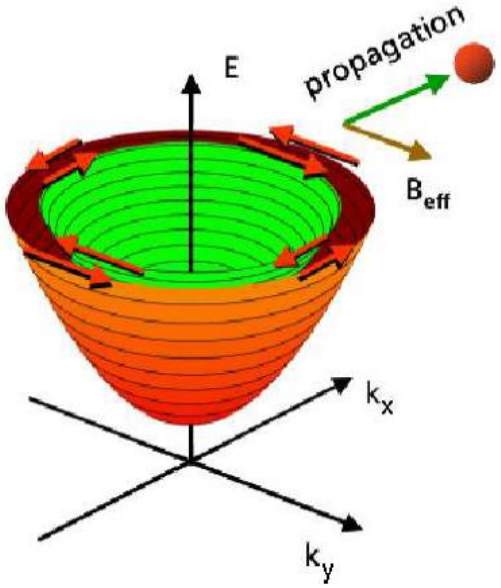
Time reversal + inversion

$$\varepsilon_{\uparrow}(k) = \varepsilon_{\downarrow}(k)$$

Breaking of Inversion symmetry $\varepsilon_{\uparrow}(k) \neq \varepsilon_{\downarrow}(k)$

$$E_{\pm} = E_0 + \frac{\hbar^2}{2m^*} k_{\parallel}^2 \pm \gamma_{SO} k_{\parallel}$$



# MAGNETOCRSYTALLINE ANISOTROPY

How to calculate MCA?

•Brute force method (self-consistent)

$$E_{MCA} = E_{\text{tot}}^{\mathbf{n}_1} - E_{\text{tot}}^{\mathbf{n}_2}$$

where $E_{\mathbf{n}_1}$ and $E_{\mathbf{n}_2}$ are obtained from SCF calculation including SOC

*In principle « exact » but very time consuming and hard to converge*
*One should use penalization techniques to obtain $E_n$ for any direction*

•Force Theorem method

$$E_{MCA} = E_{\text{band}}^{\mathbf{n_1}} - E_{\text{band}}^{\mathbf{n_2}} = \int^{E_F^1} En^1(E)dE - \int^{E_F^2} En^2(E)dE$$

$E_{\text{band}}^{\mathbf{n_1}}$ and $E_{\text{band}}^{\mathbf{n_2}}$ are band energies of NSCF calculations including SOC

Initial density is obtained from a SCF spin-collinear calculation and spin-moment further rotated to appropriate spin direction

*Very stable numerically but cannot be applied to systems with too large SOC.*

# MCA: the local picture

- Force Theorem in grand canonical ensemble

$$\Delta E = \int^{E_F^1} En^1(E)dE - \int^{E_F^2} En^2(E)dE \approx \int^{E_F^0} (E - E_F^0)\Delta n(E)dE$$

$$\Delta E_{gc} = \int^{E_F^0} (E - E_F^0)\Delta n(E)dE$$

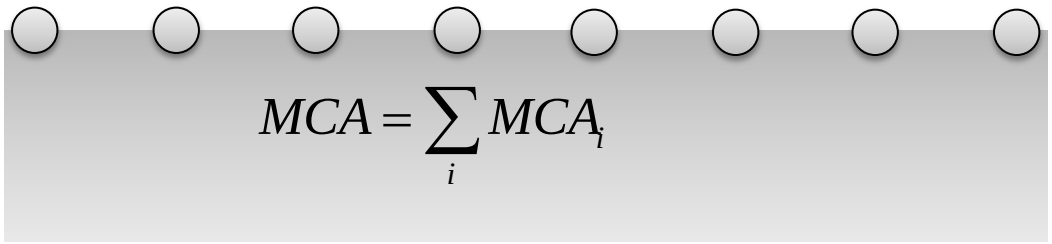
- Local decomposition

Projection onto atomic orbitals $\Delta E_i^{gc} = \int^{E_F^0} (E - E_F^0)\Delta n_i(E)dE$

Real space picture $\Delta E^{gc}(r) = \int^{E_F^0} (E - E_F^0)\Delta n(E,r)dE$

*The local decommposition in « canonical » picture leads to spurious oscillations due to long range Friedel-like charge oscillations.. But the total MCA value is kept due to charge conservation*

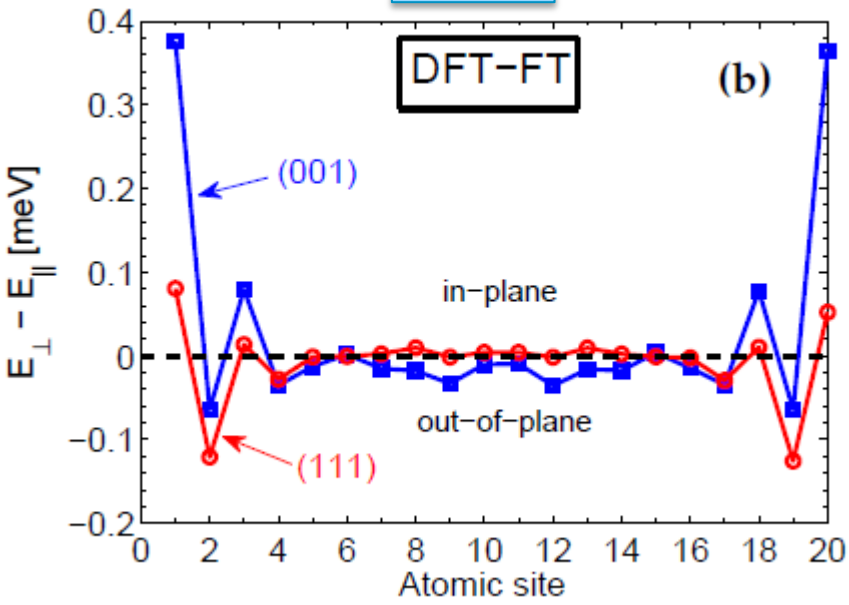
# MCA: the local picture



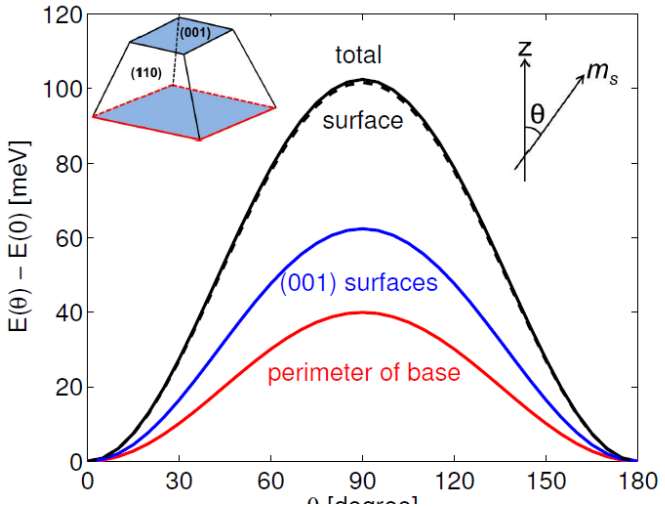
$$MCA = \sum_i MCA_i$$

MCA of a slab orginates from surface atoms of the outermost layers

## fccCo

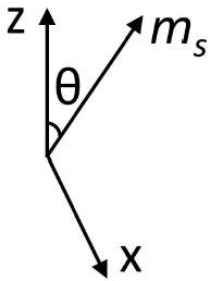


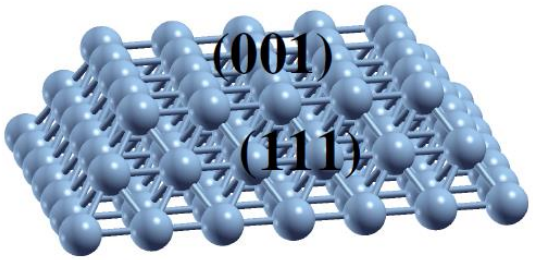

## Fe pyramid

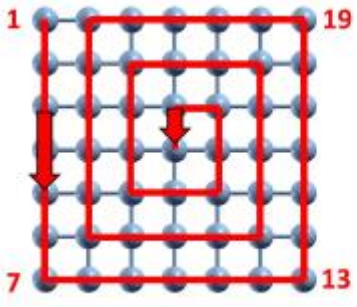


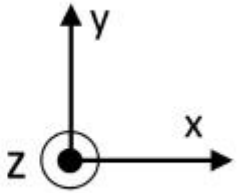
# MCA: the local picture

Co (N = 110)

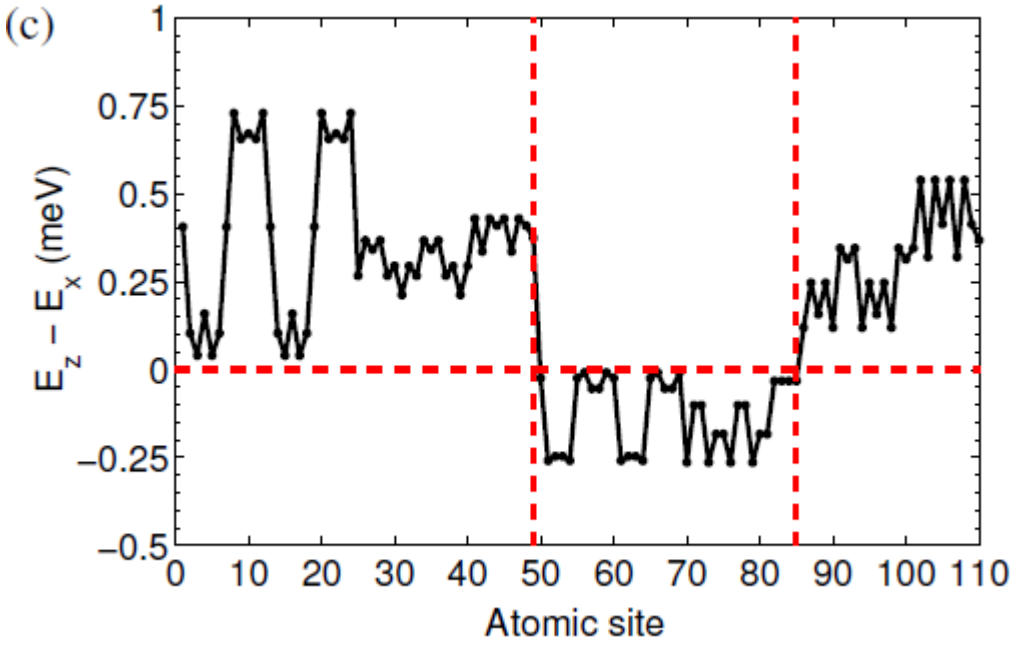



*l/h = 1.41*



# PHYSICAL INSIGHT

Extended Heisenberg Hamiltonian

$$E = -\frac{1}{2}\sum_{\langle i,j\rangle} J_{ij}\mathbf{e}_i\mathbf{e}_j + \sum_i F_i(\mathbf{e}_i) + \sum_{\langle ij\rangle} \mathbf{D}_{ij}.\mathbf{e}_i \times \mathbf{e}_j$$

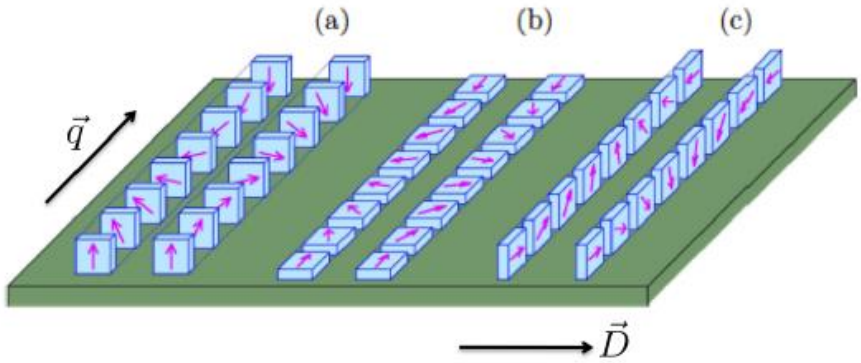
MCA

$$F_i(\mathbf{e}_i) = \mathbf{e}_i^t \underline{\underline{K}}_i \mathbf{e}_i$$

$$F(\mathbf{e}_i) = -K(\mathbf{n}.\mathbf{e}_i)^2$$ Uniaxial anisotropy

DM Dzyaloshinskii-Moriya interaction $\mathbf{D}$ only between first neighbours

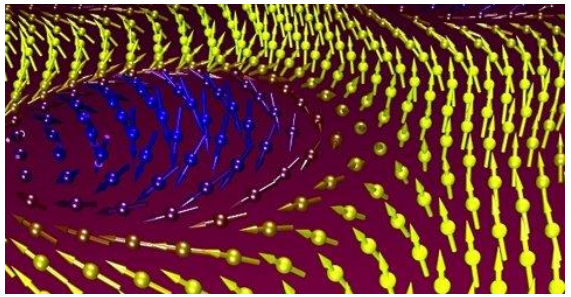
(only exists in the absence of inversion symmetry)




DM=0 DM=0 DM≠0

DM favors non-collinear configurations

At the origin of skyrmion structures



# SHAPE ANISOTROPY

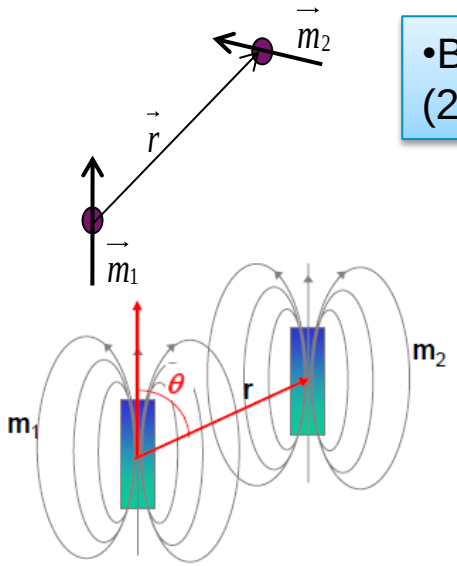
•Classical dipole-dipole interaction

$$E_{dip}(\vec{r}) = \frac{\mu_0}{4\pi r^3}\left[\vec{m}_1.\vec{m}_2 - \frac{3}{r^2}\left(\vec{m}_1.\vec{r}\right)\left(\vec{m}_2.\vec{r}\right)\right]$$

Colllinear magnetism

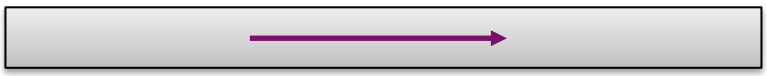
$$E_{dip}(\theta) = \frac{\mu_0}{4\pi r^3} m_1 m_2 \left[1 - 3\cos\theta\right]$$

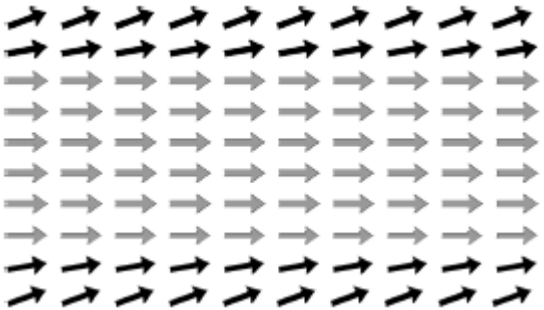
For θ<54.74° FM  For θ>54.74° AF




•Breit interaction
(2 body relativistic term)

In thin films: **in-plane** magnetization is always favored





$E_{MCA} \sim$ Surface

$E_{shape} \sim$ Volume

*For ultra-thin films MCA is generally dominant while the shape anisotropy always ends up by dominating for thicker films*

# IMPORTANT THINGS I DID NOT TALK ABOUT

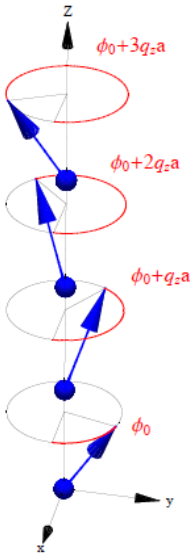
•Orbital moment

$$\mathbf{m}^{\mathrm{orb}}(\mathbf{r}) = \sum_{\alpha \mathrm{occ}} \left\langle \Psi_\alpha \left| \mathbf{L} \right| \Psi_\alpha \right\rangle \qquad \mathbf{m}_i^{\mathrm{orb}}(\mathbf{r}) = \sum_{\alpha \mathrm{occ}} \left\langle \Psi_\alpha \left| \mathbf{L} \right| \Psi_\alpha \right\rangle_i$$

*For modern theory of orbital magnetization see David Vanderbilt*

•DFT+U and orbital polarization

When using the rotationally invariant scheme of Liechtenstein (`lda_plus_u_kind=1`) the Racah B parameter plays a crucial role in orbital magnetization




•Spin-spirals and generalized Bloch theorem

•Mapping DFT on model Hamiltonian $J_{ij}$

•Spin dynamics etc.…

•Spin-polarized transport

# ACKNOWLEDGEMENTS


TEAM

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COLLEAGUES (Julich)

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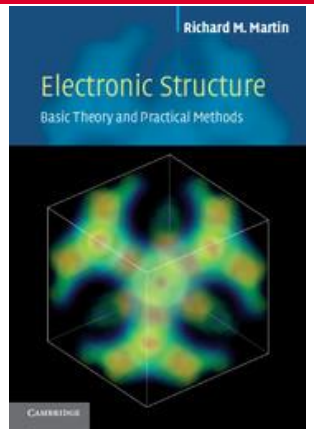
# BIBLIOGRAPHY

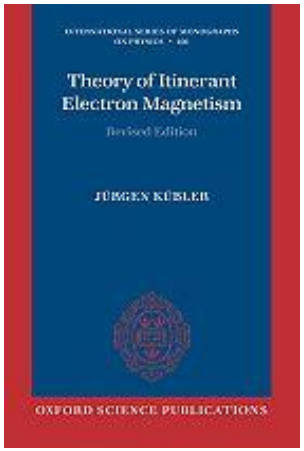



**Electronic Structure**

**Basic Theory and Practical Methods**

Richard Martin

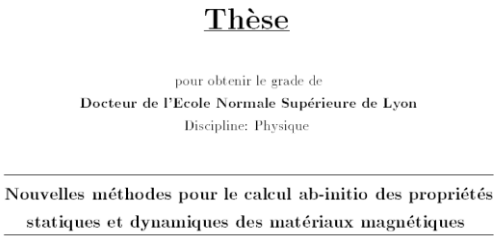
Cambridge University Press




**Theory of itinerant electron magnetism**

Jürgen Kübler

Oxford Science Publications


Thèse

pour obtenir le grade de
Docteur de l'École Normale Supérieure de Lyon
Discipline: Physique

Nouvelles méthodes pour le calcul ab-initio des propriétés statiques et dynamiques des matériaux magnétiques

**Nouvelles méthodes pour le calcul ab-initio des propriétés statiques et dynamiques des matériaux magnétiques.**

Ralph Gebauer PhD thesis 1999

(in english)

THANK YOU FOR YOUR ATTENTION

QUESTIONS?

COMMENTS?