DE LA RECHERCHE À L'INDUSTRIE

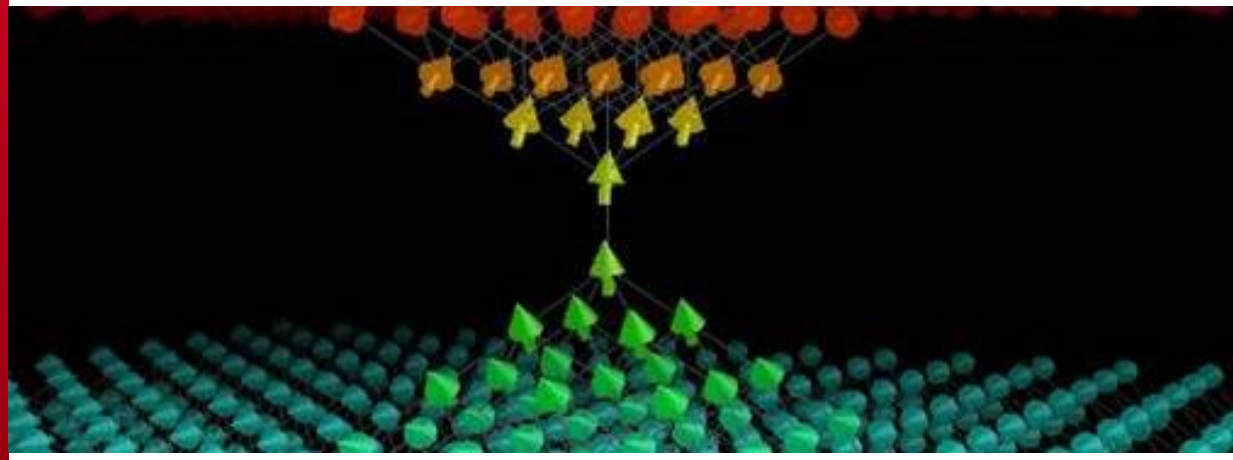
(Paris, France)

Saclay

(Copenhagen, Denmark)

Lyngby

MAGNETISM IN DFT
FROM THEORY TO PRACTICE



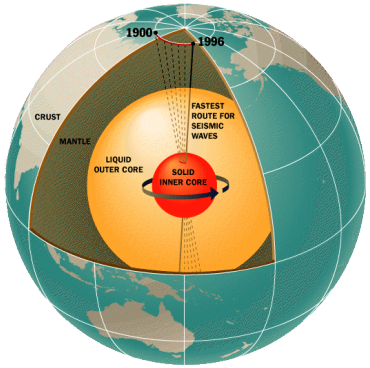
Cyrille Barreteau

CEA Saclay

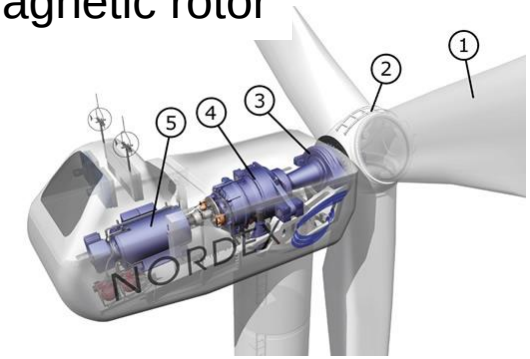
MAGNETISM

From the atomic nucleus to the inner core of Earth

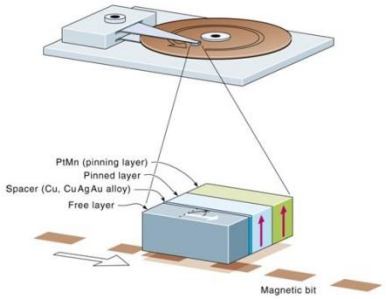
time

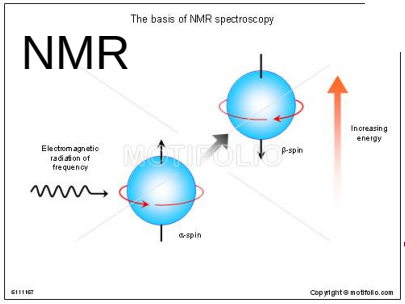


Magnetic rotor



GMR Read Head





length

MAGNETISM

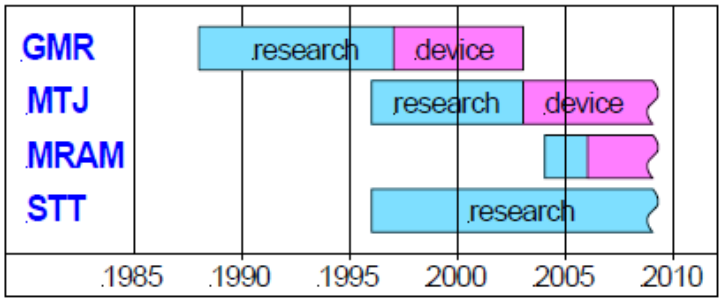
Intense activity in which **nanomagnetism** plays a crucial role

Search for permanent hard magnets without rare earth

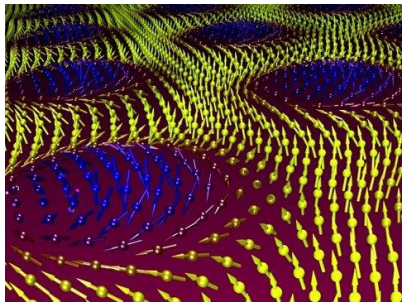
Replace Samarium-Cobalt, Neodyum by nanostructured « cheap » TM magnets

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

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

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

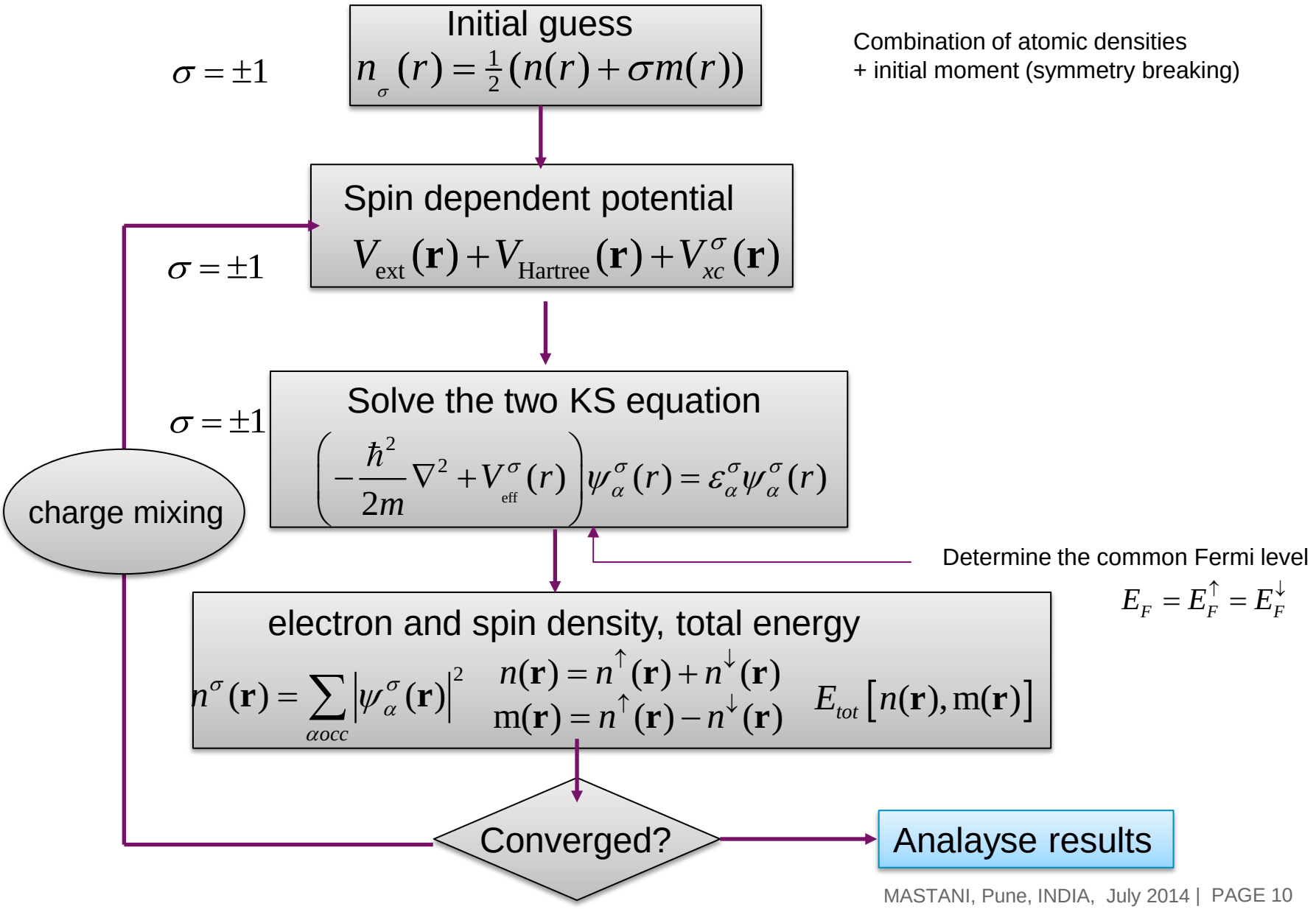
$$V_{\text{eff}}^{\sigma} = V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{xc}(n(\mathbf{r}), m(\mathbf{r})) - \sigma B_{xc}(\mathbf{r})$$

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

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

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

Spin polarized DFT implementation diagram



ANALYSE RESULTS

What do we get out of spin-polarized DFT calculation

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

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

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

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

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

DOS

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

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

Local moment

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

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

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

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

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

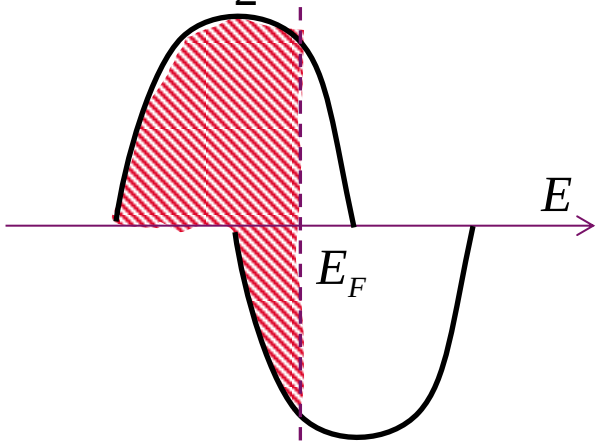
M : magnetic moment per atom

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

Rigid shift of up and down eigenvalues

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

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



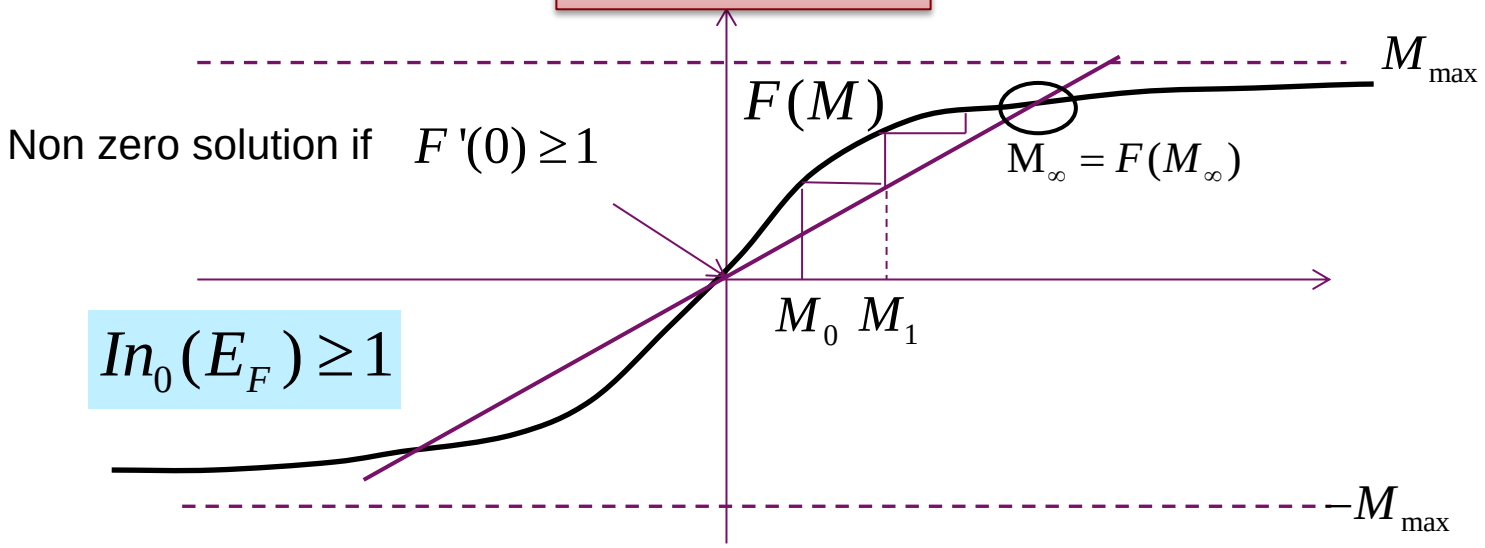
$$n^{\downarrow}(E) = n^{0}(E - \frac{\sigma}{2}IM)$$

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

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

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

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

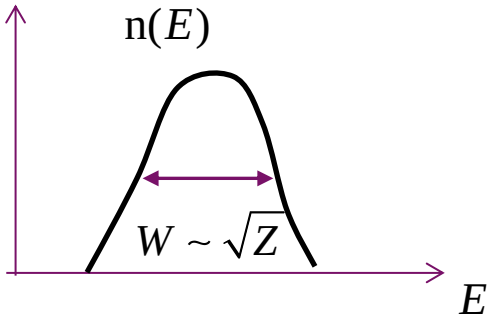
- magnetic susceptibility $\chi = \frac{\partial M}{\partial H} = \frac{\chi_0}{(1 - In_0(E_F))}$
- Total energy $E_{tot} = \sum_{\alpha occ} \varepsilon_\alpha + \frac{1}{2} \sum_i Im_i^2$

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

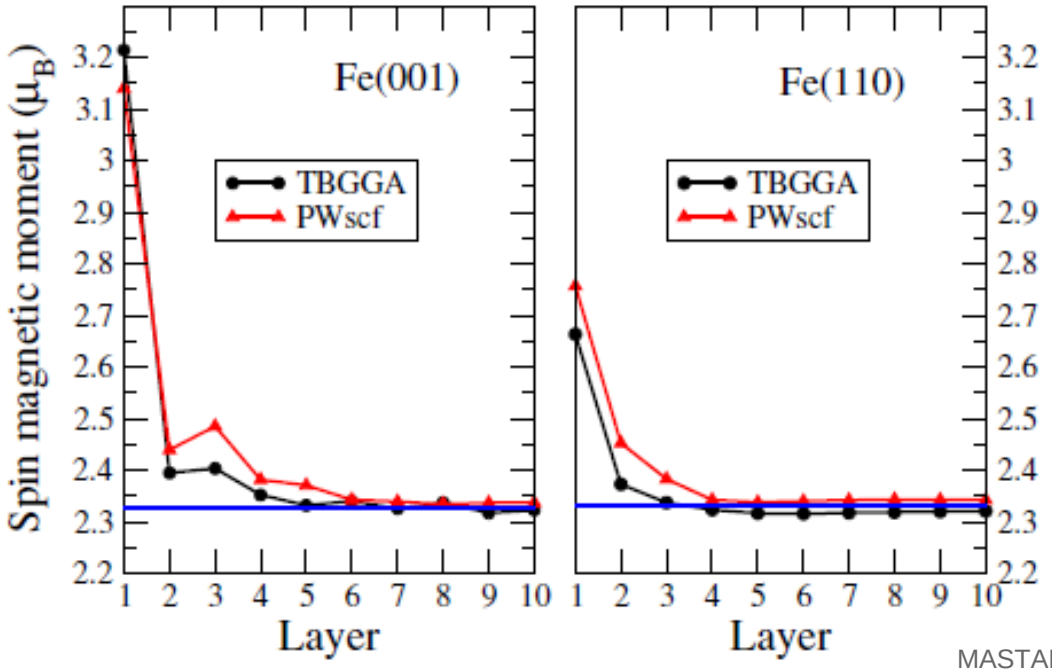
- Low coordination favors magnetism



Z : number of neigbors

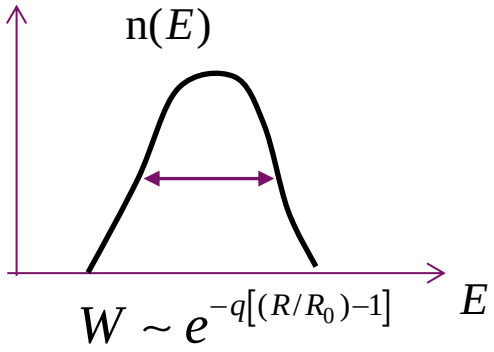
$$Z \searrow \Rightarrow \mathrm{n}(E_F) \nearrow$$

Spin magnetic moment is generally enhanced on low coordinated atoms



General trends

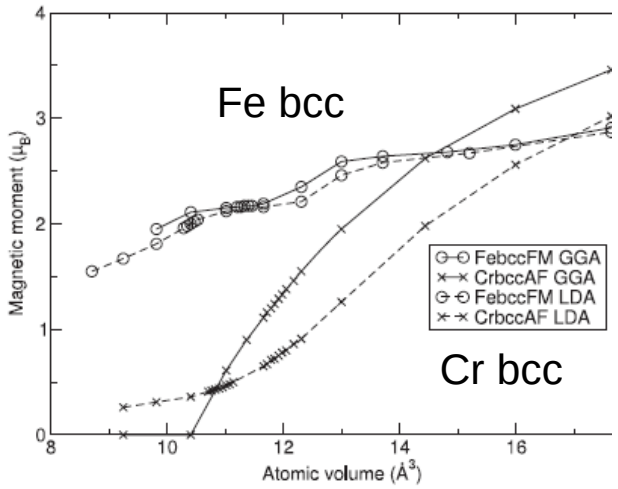
- Lattice expansion generally favors magnetism and vice versa…

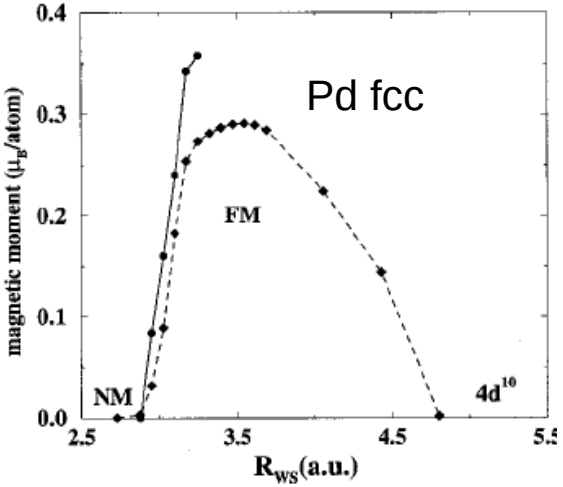


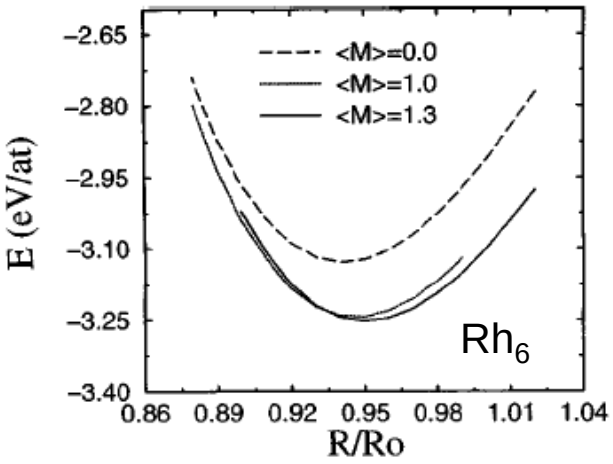
$$R \nearrow \Rightarrow W \searrow \Rightarrow n(E_F) \nearrow$$

$M(d)$

E(d)

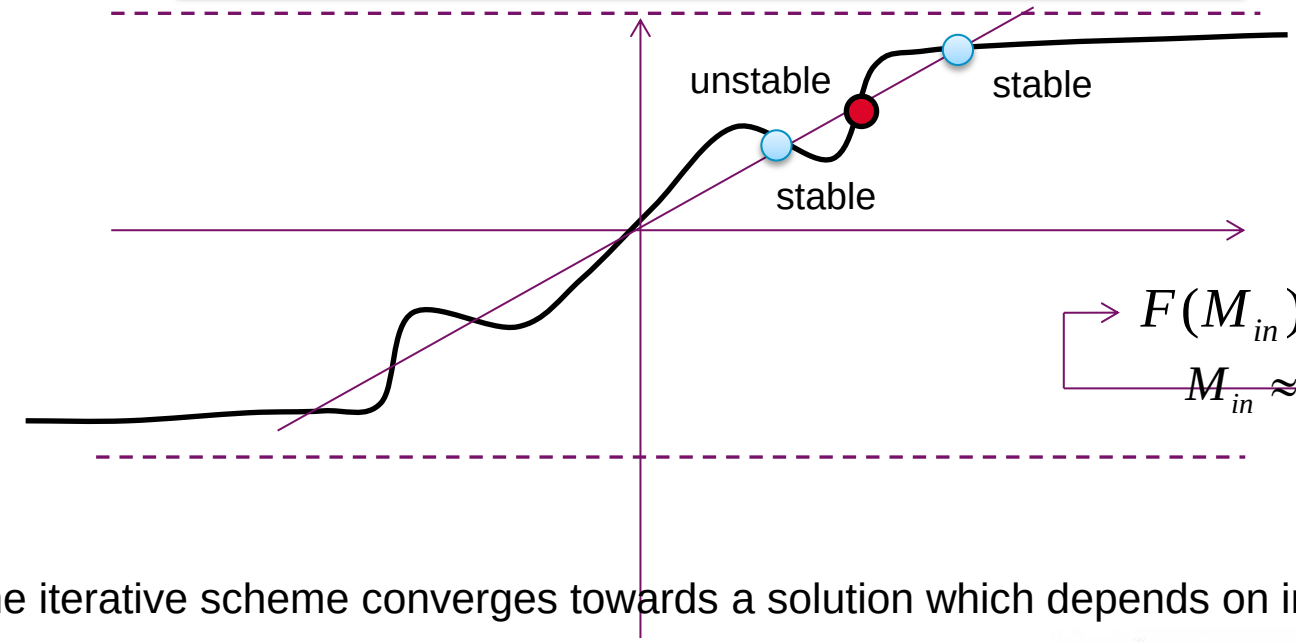






Multiple magnetic solutions

Stoner criterium does not tell the whole story



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

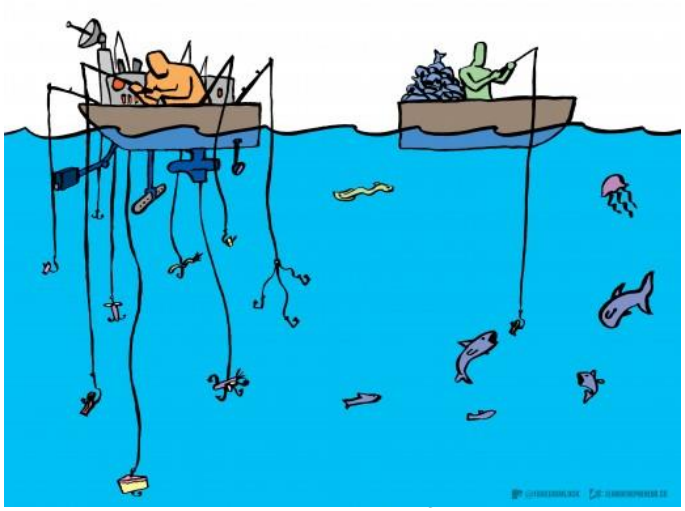
$$M_{in} \approx M_{out} \; ?$$

The iterative scheme converges towards a solution which depends on initial spin moment

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

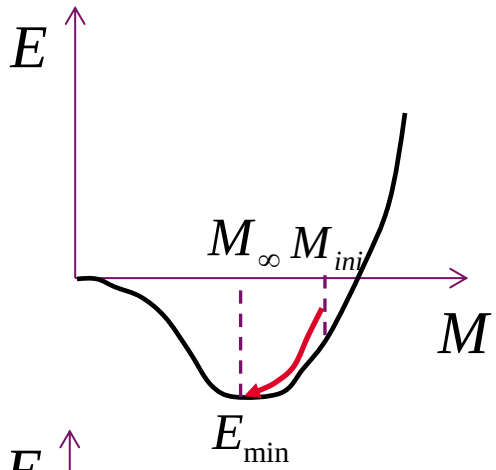


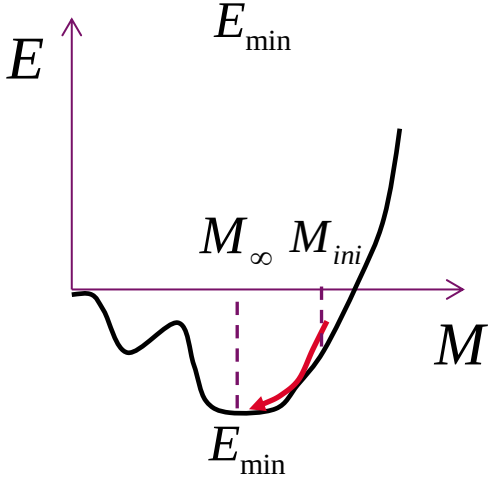
Fixed Spin moment

Conventional scheme

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

one scf loop

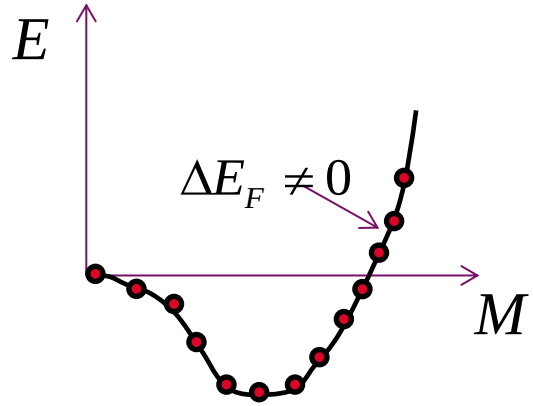




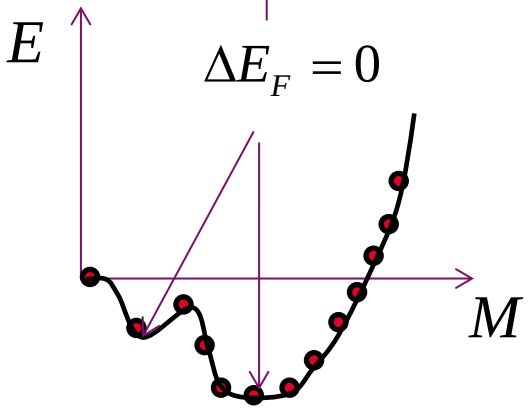
FSM

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

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

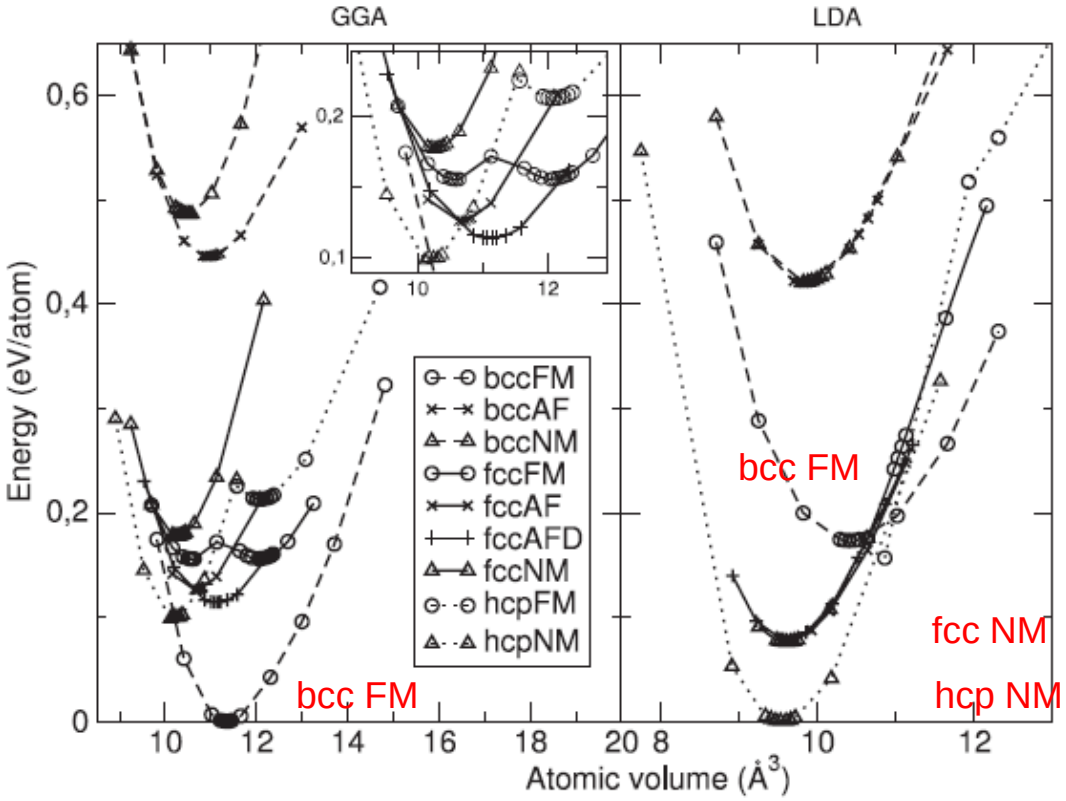
Before running (or trusting) a DFT calculation you should be aware of several important technicalities

- 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`)

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

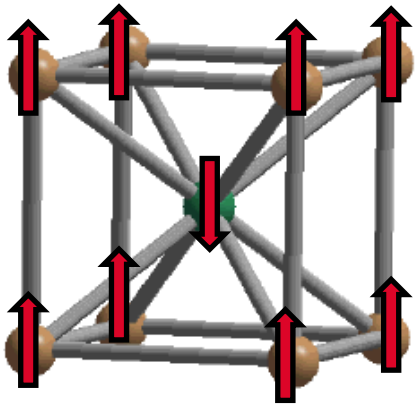
LDA bad for 3d but OK for 5d→ problematic for alloys (FePt, CoPt)

E(V)



Initial magnetization

Cr bcc AF

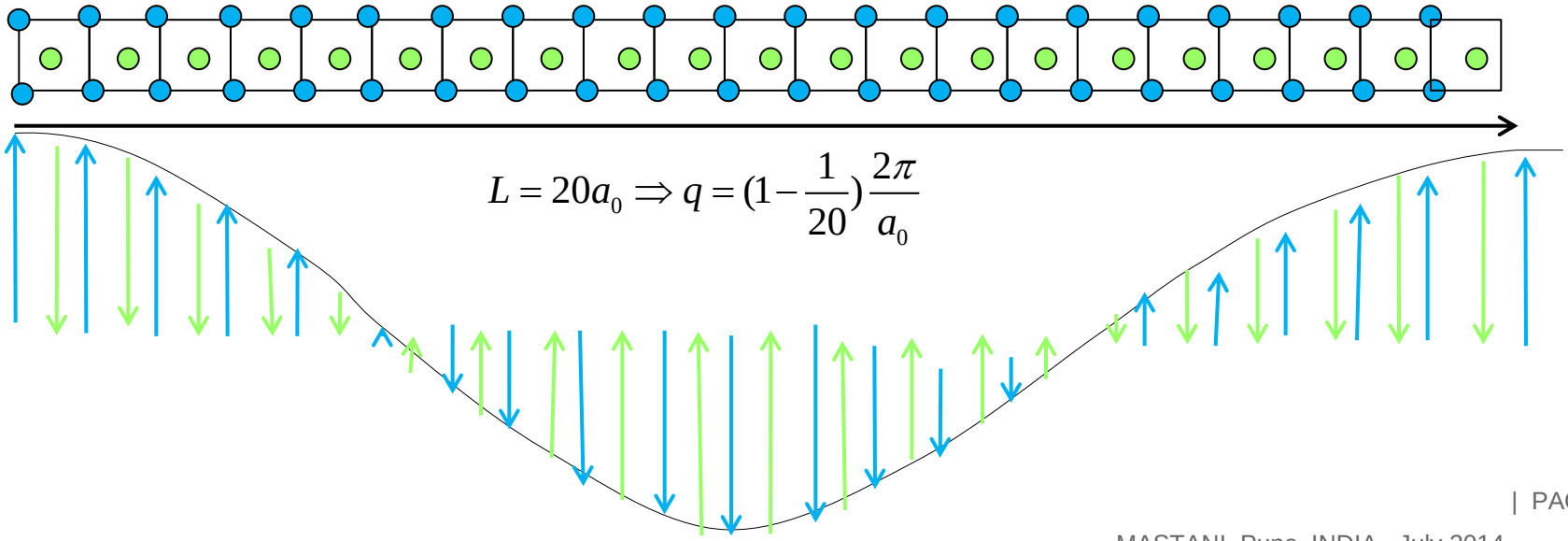


Define the system as **simple cubic** with 2 types of atoms per unit cell and opposite starting magnetization

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

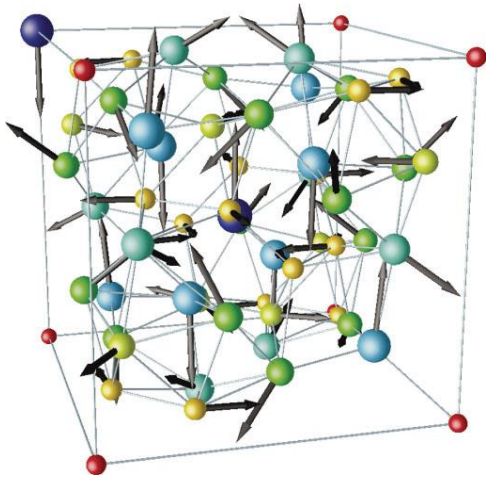
Cr SDW

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



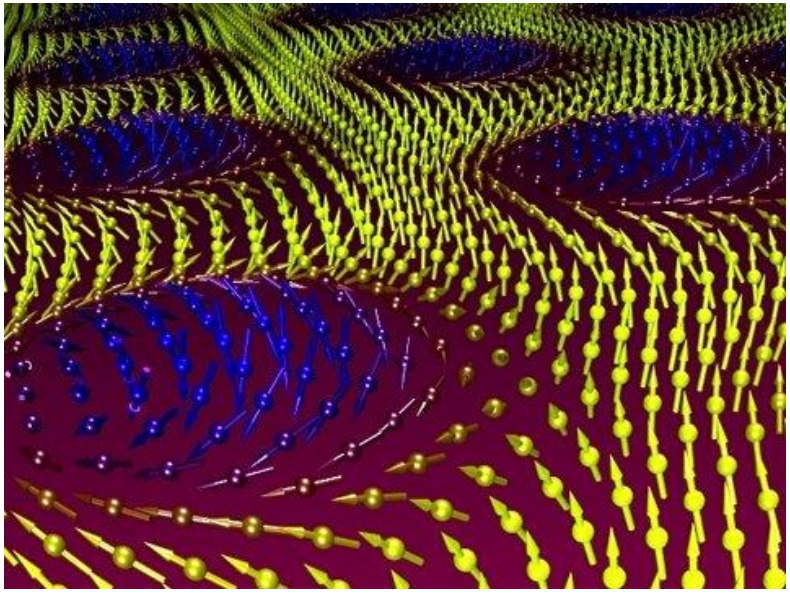
NON COLLINEAR MAGNETISM

Why should we care about non collinearity?

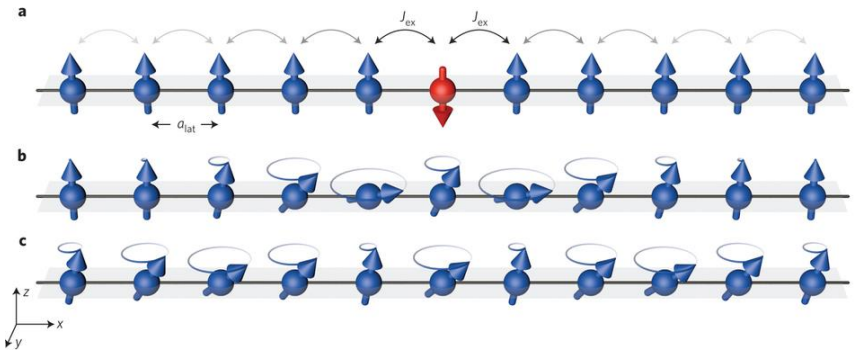


$\alpha - Mn$

Non-collinearity does exist!

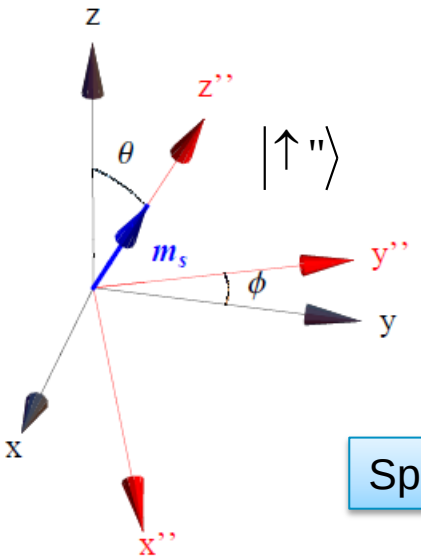


The future is in skyrmions ☺



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

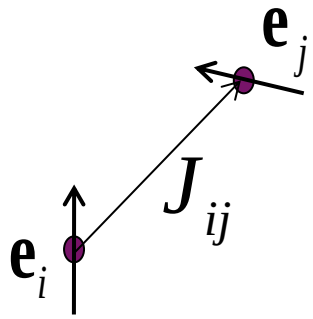
Additional complication since $\boldsymbol{\rho}$ and $\nabla\boldsymbol{\rho}$ cannot be diagonalized in the same basis

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

PHYSICAL INSIGHT

Classical Heisenberg Hamiltonian

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

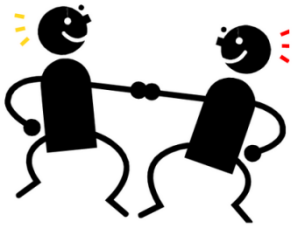


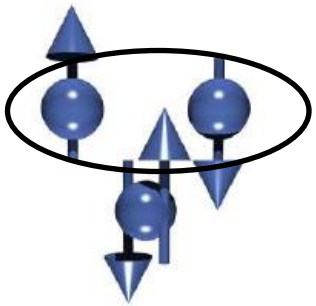
J_{ij} Can be obtained by various approaches from DFT (not yet available in QE)

$J_{ij} > 0$ Favors FM order

$J_{ij} < 0$ Favors AF order

Frustration

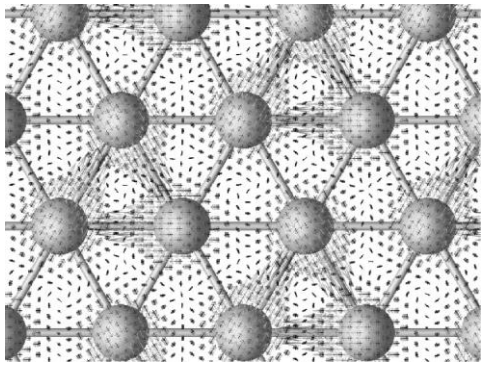




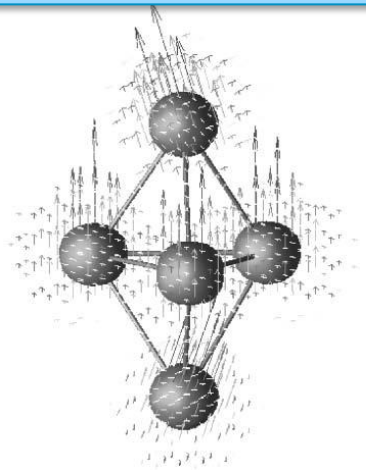
Fairly happy

Some examples

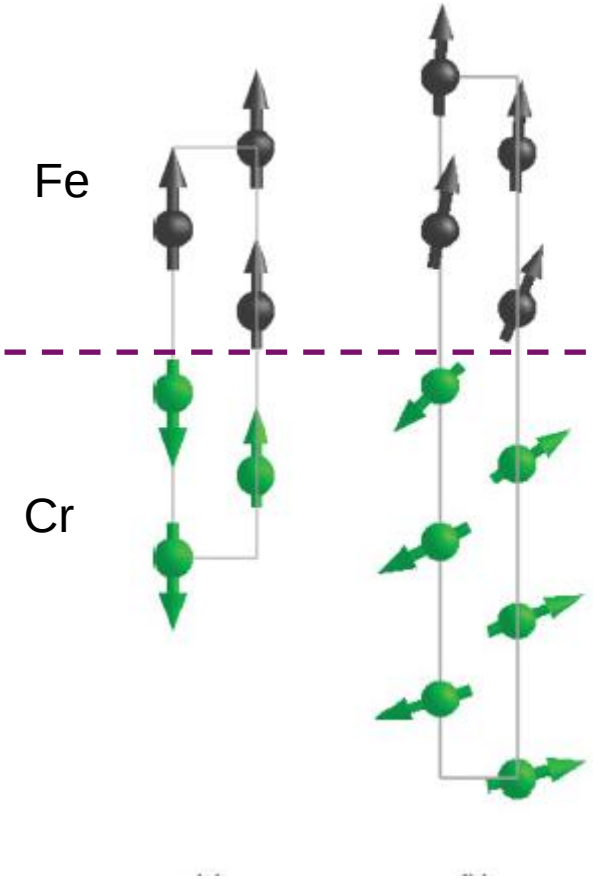
Cr/Cu(111)



Fe bibyramidal cluster

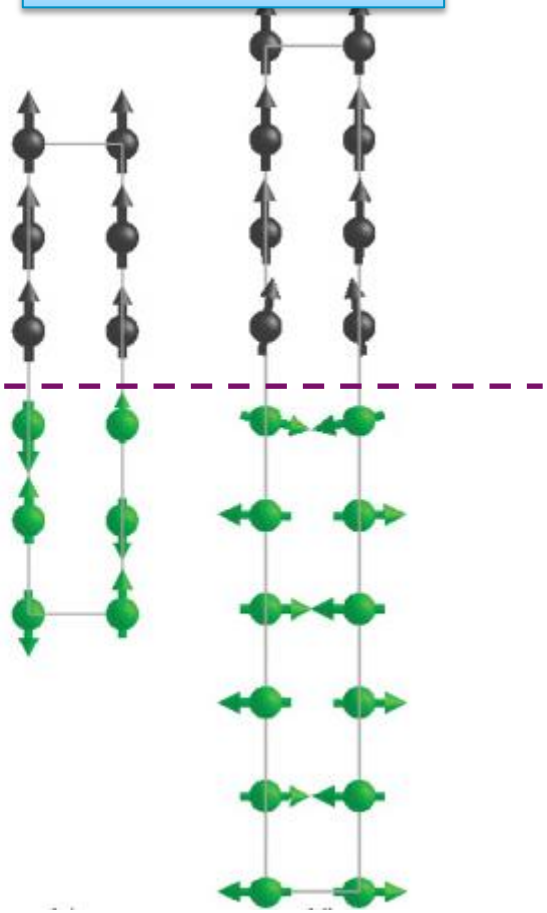


Fe/Cr(001) interface



$E_{col} < E_{ncol}$

Fe/Cr(110) interface



$E_{col} > E_{ncol}$

SPIN-ORBIT COUPLING

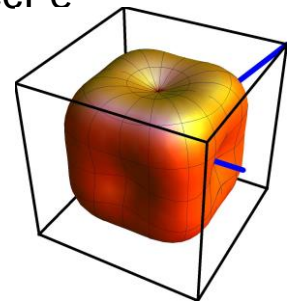
Why should we care about SOC?

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

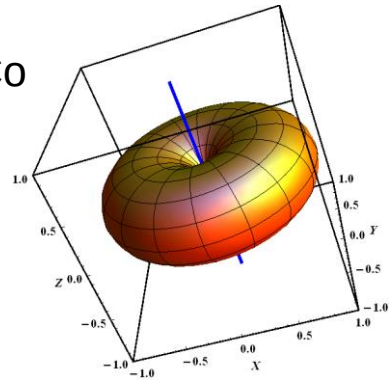
- At the origin of magneto-crystalline anisotropy …..and therefore of the stability of magnets!

$E(\theta,\varphi)$

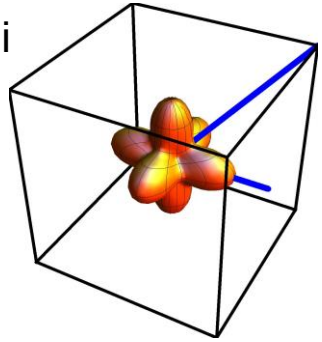
bccFe



hcpCo

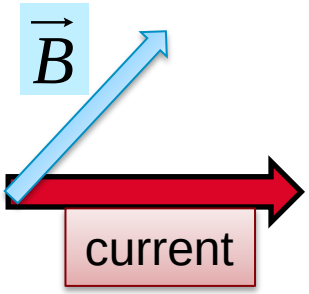


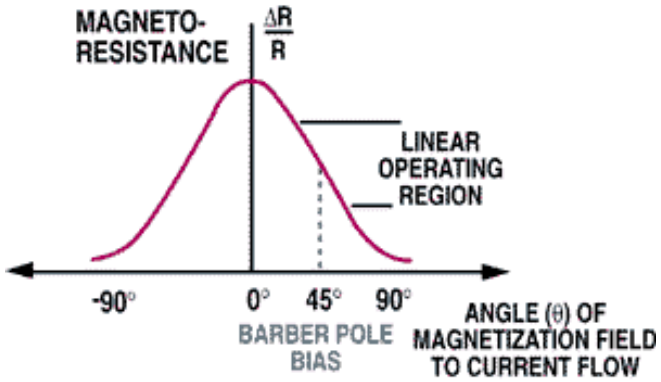
fccNi



- 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.

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

Darwin

The good basis

- Without SOC: $\vec{L}$ et $\vec{\hat{S}}$ 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 $\vec{\hat{S}}$ no longer commute with $H + H_{so}$

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

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

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

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

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

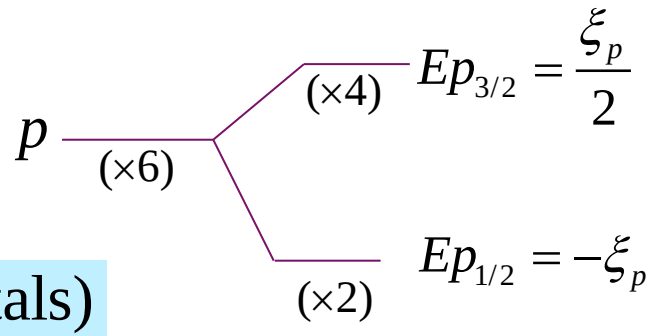
- From one basis to the other = Clebsh Gordan

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

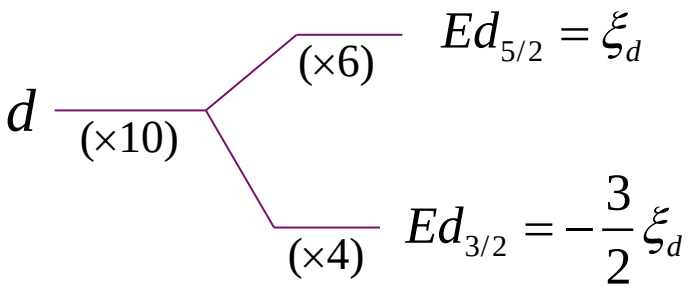
$$j = \begin{cases} l+\frac{1}{2} & (2l+2) \\ l-\frac{1}{2} & (2l) \end{cases} \quad 2(2l+1)$$

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

$l = 1$ (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 `degauss`

⟹ Use penalization when necessary (`constrained_magnetization`)

$$E(\theta,\varphi)$$

⟹ Very strict convergence threshold (`conv_thr`)

A FEW THINGS ABOUT SOC

- $\xi(r)$ Is short range (atomic-like) in TB (or LCAO) on site term $\sum_I \xi_I \left(\mathbf{L.S}\right)_I$

- $\xi(r) \sim \mathrm{Z}^4$ Increases drastically with atomic number

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

$$\xi_d \sim 0.05eV \text{ for } 3d$$

$$\xi_d \sim 0.5eV \text{ for } 5d$$

- 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

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

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

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

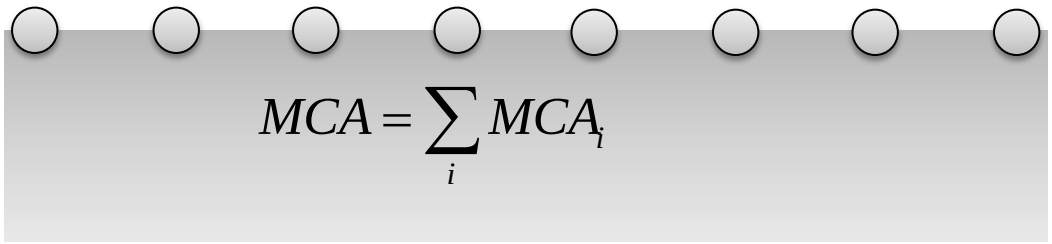
- Local decomposition

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

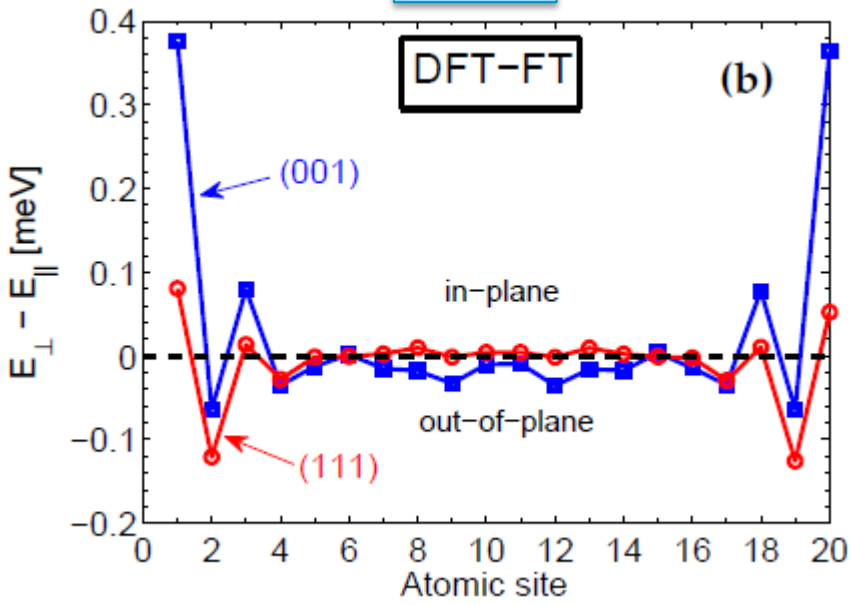
MCA: the local picture



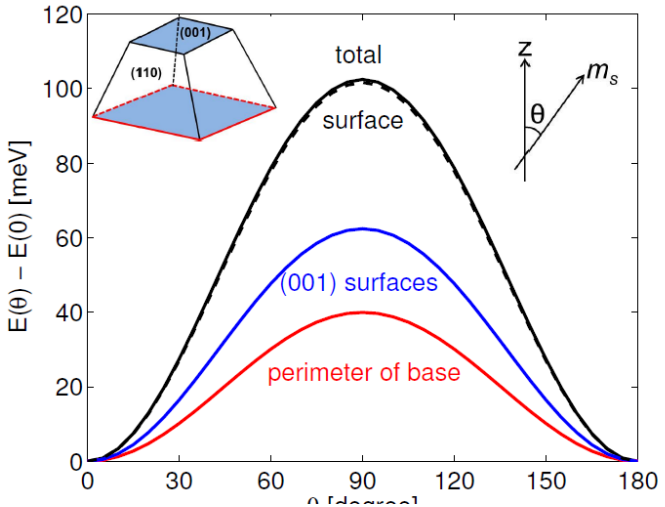
$$MCA = \sum_i MCA_i$$

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

fccCo



Fe pyramid



PHYSICAL INSIGHT

Extended Heisenberg Hamiltonian

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

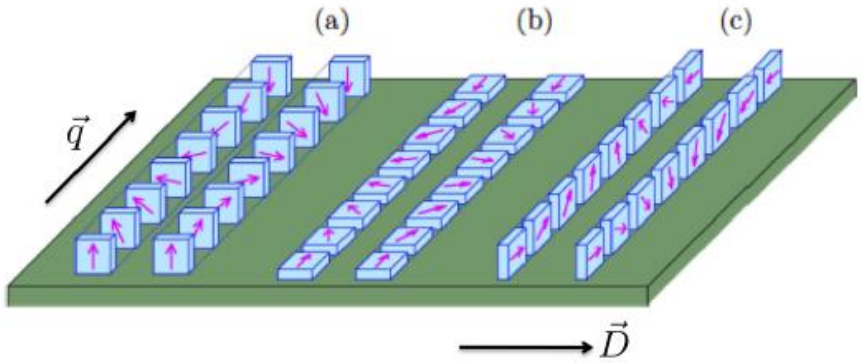
MCA

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

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

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

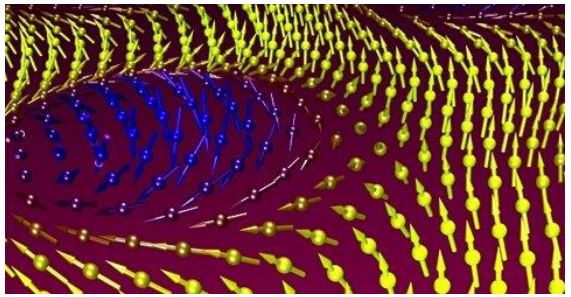
(only exists in the absence of inversion symmetry)



DM=0 DM=0 DM≠0

DM favors non-collinear configurations

At the origin of skyrmion structures



SHAPE ANISOTROPY

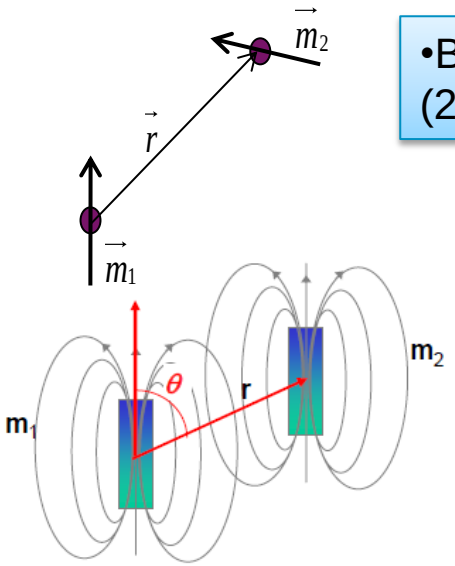
•Classical dipole-dipole interaction

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

Colllinear magnetism

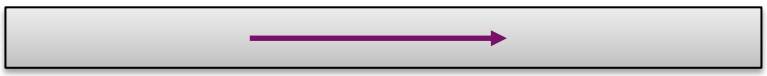
$$E_{dip}(\theta) = \frac{\mu_0}{4\pi r^3} m_1 m_2 \left[1 - 3\cos\theta\right]$$

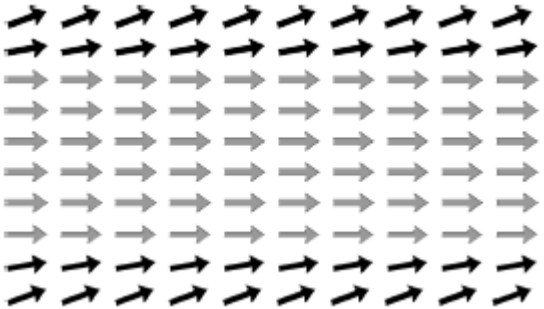
For θ<54.74° FM For θ>54.74° AF



•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

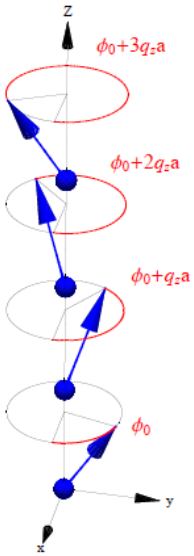
•Orbital moment

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

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

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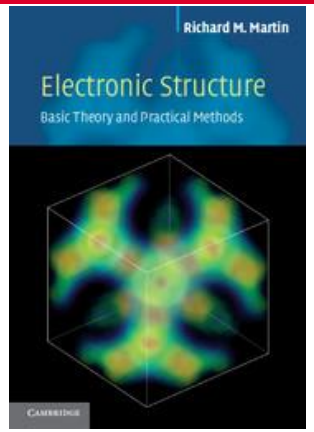
BIBLIOGRAPHY



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Basic Theory and Practical Methods
Richard Martin
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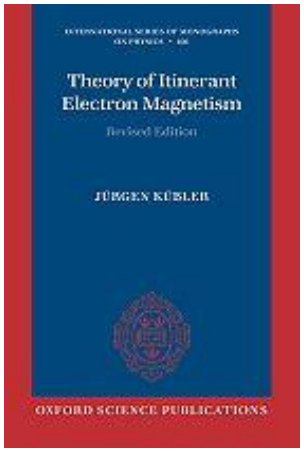

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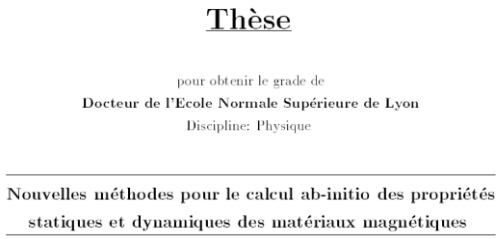
Oxford Science Publications


Thèse

pour obtenir le grade de
Docteur de l'Ecole 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?