Magnetism

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Outline

- (Non)collinear spin-density-functional theory
- On site Coulomb repulsion: L(S)DA+U
- Spin Orbit Interaction
- Spin spiral magnetism

Spin-density-functional theory

wavefunction $\rightarrow$ spinor

$$|\Phi\rangle = \begin{pmatrix} |\Psi^{\uparrow}\rangle \\ |\Psi^{\downarrow}\rangle \end{pmatrix}$$

density $\rightarrow 2\times 2$ matrix, $\overleftrightarrow{n}(\mathbf{r})$

$$n^{\alpha\beta}(\mathbf{r}) = \sum_n f_n \langle \Psi_n^{\beta} | \mathbf{r} \rangle \langle \mathbf{r} | \Psi_n^{\alpha} \rangle$$

$$n^{\alpha\beta}(\mathbf{r}) = \left(n_{\mathrm{Tr}}(\mathbf{r})\delta_{\alpha\beta} + \vec{m}(\mathbf{r})\cdot\vec{\sigma}_{\alpha\beta}\right)/2$$

$$\vec{m}(\mathbf{r}) = \sum_{\alpha\beta} n^{\alpha\beta}(\mathbf{r})\cdot\vec{\sigma}_{\alpha\beta} \qquad n_{\mathrm{Tr}}(\mathbf{r}) \equiv \mathrm{Tr}\left[n^{\alpha\beta}(\mathbf{r})\right] = \sum_{\alpha} n^{\alpha\alpha}(\mathbf{r})$$

Pauli spin matrices, $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$

$$\sigma_{\mathbf{x}} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \sigma_{\mathbf{y}} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \sigma_{\mathbf{z}} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The Kohn-Sham density functional becomes

$$E = \sum_{\alpha}\sum_{n} f_n \langle \Psi_n^{\alpha} | -\frac{1}{2}\Delta | \Psi_n^{\alpha} \rangle + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n_{\text{Tr}}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}' \frac{n_{\text{Tr}}(\mathbf{r}) n_{\text{Tr}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\text{xc}}[\overleftrightarrow{n}(\mathbf{r})]$$

and the Kohn-Sham equations

$$\sum_{\beta} H^{\alpha\beta} |\Psi_n^{\beta}\rangle = \varepsilon_n S^{\alpha\alpha} |\Psi_n^{\alpha}\rangle$$

with the 2×2 Hamilton matrix

$$H^{\alpha\beta} = -\frac{1}{2}\Delta\delta_{\alpha\beta} + V_{\text{ext}}(\mathbf{r})\delta_{\alpha\beta} + \int d\mathbf{r}' \frac{n_{\text{Tr}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\delta_{\alpha\beta} + V_{\text{xc}}^{\alpha\beta}[\overleftrightarrow{n}(\mathbf{r})](\mathbf{r})$$

$$\begin{pmatrix} H^{\alpha\alpha} & V_{\rm xc}^{\alpha\beta} \\ V_{\rm xc}^{\beta\alpha} & H^{\beta\beta} \end{pmatrix} \begin{pmatrix} |\Psi_n^{\alpha}\rangle \\ |\Psi_n^{\beta}\rangle \end{pmatrix} = \varepsilon_n \begin{pmatrix} |\Psi_n^{\alpha}\rangle \\ |\Psi_n^{\beta}\rangle \end{pmatrix}$$

$|\Psi_n^{\alpha}\rangle$ and $|\Psi_n^{\beta}\rangle$ couple over $V_{\rm xc}^{\alpha\beta}$ and $V_{\rm xc}^{\beta\alpha}$

$$V_{\rm xc}^{\alpha\beta}[\overleftrightarrow{n}(\mathbf{r})](\mathbf{r}) = \frac{\delta E_{\rm xc}[\overleftrightarrow{n}(\mathbf{r})]}{\delta n^{\beta\alpha}(\mathbf{r})}$$

unfortunately, only in case $\vec{m}(\mathbf{r}) = m_z(\mathbf{r}) \Leftrightarrow \overleftrightarrow{n}(\mathbf{r})$ diagonal , a reliable approximation to $E_{\rm xc}[\overleftrightarrow{n}(\mathbf{r})]$ is known

density matrix can be diagonalized

$$\sum_{\alpha\beta} U_{i\alpha}(\mathbf{r}) n^{\beta\alpha}(\mathbf{r}) U^{+}_{\beta j}(\mathbf{r}) = \delta_{ij} n_i(\mathbf{r})$$

where U(**r**) are spin-1/2 rotation matrices

$$V_{\rm xc}^{\alpha\beta}(\mathbf{r}) = \frac{1}{2}\left[\frac{\delta E_{\rm xc}}{\delta n_1(\mathbf{r})} + \frac{\delta E_{\rm xc}}{\delta n_2(\mathbf{r})}\right]\delta_{\alpha\beta} + \frac{1}{2}\left[\frac{\delta E_{\rm xc}}{\delta n_1(\mathbf{r})} - \frac{\delta E_{\rm xc}}{\delta n_2(\mathbf{r})}\right]\left(U^{+}(\mathbf{r})\sigma_z U(\mathbf{r})\right)_{\alpha\beta}$$

or equivalently, using

$$n_{\uparrow}(\mathbf{r}) = \frac{1}{2}[n_{\rm Tr}(\mathbf{r}) + |\vec{m}(\mathbf{r})|], \qquad n_{\downarrow}(\mathbf{r}) = \frac{1}{2}[n_{\rm Tr}(\mathbf{r}) - |\vec{m}(\mathbf{r})|], \quad \text{and} \quad \hat{m}(\mathbf{r}) = \frac{\vec{m}(\mathbf{r})}{|\vec{m}(\mathbf{r})|}$$

we can write

$$V_{\rm xc}^{\alpha\beta}(\mathbf{r}) = \frac{1}{2}\left[\frac{\delta E_{\rm xc}}{\delta n_{\uparrow}(\mathbf{r})} + \frac{\delta E_{\rm xc}}{\delta n_{\downarrow}(\mathbf{r})}\right]\delta_{\alpha\beta} + \frac{1}{2}\left[\frac{\delta E_{\rm xc}}{\delta n_{\uparrow}(\mathbf{r})} - \frac{\delta E_{\rm xc}}{\delta n_{\downarrow}(\mathbf{r})}\right]\hat{m}(\mathbf{r})\cdot\vec{\sigma}_{\alpha\beta}$$

where

$$E_{\rm xc} = \int n_{\rm Tr}(\mathbf{r})\varepsilon_{xc}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})]d\mathbf{r}$$

- Collinear (spins along z direction):

$$\begin{pmatrix} H^{\alpha\alpha} & \\ & H^{\beta\beta} \end{pmatrix} \begin{pmatrix} |\Psi_n^{\alpha}\rangle \\ |\Psi_n^{\beta}\rangle \end{pmatrix} = \varepsilon_n \begin{pmatrix} |\Psi_n^{\alpha}\rangle \\ |\Psi_n^{\beta}\rangle \end{pmatrix}$$

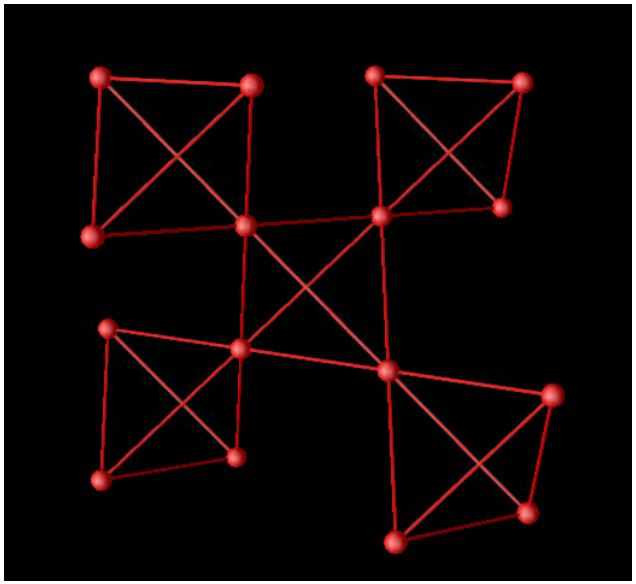
- Noncollinear:

$$\begin{pmatrix} H^{\alpha\alpha} & V_{\mathrm{xc}}^{\alpha\beta} \\ V_{\mathrm{xc}}^{\beta\alpha} & H^{\beta\beta} \end{pmatrix} \begin{pmatrix} |\Psi_n^{\alpha}\rangle \\ |\Psi_n^{\beta}\rangle \end{pmatrix} = \varepsilon_n \begin{pmatrix} |\Psi_n^{\alpha}\rangle \\ |\Psi_n^{\beta}\rangle \end{pmatrix}$$

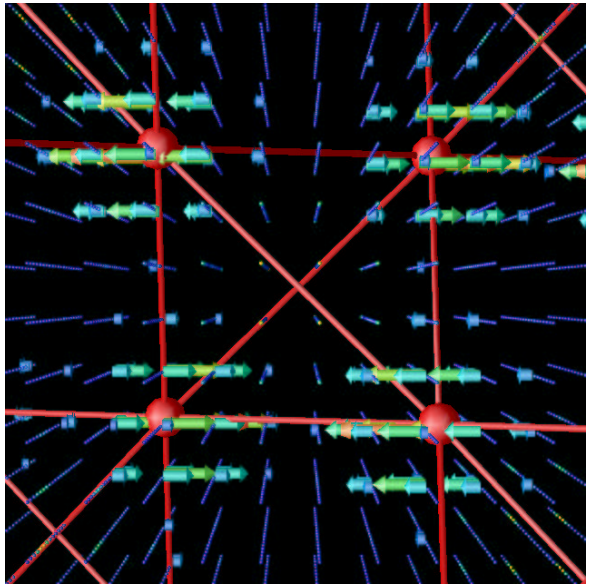
In the absence of Spin Orbit Interaction (SOI) the spin directions are not linked to the crystalline structure, i.e., the system is invariant under a general common rotation of all spins

YMn_2

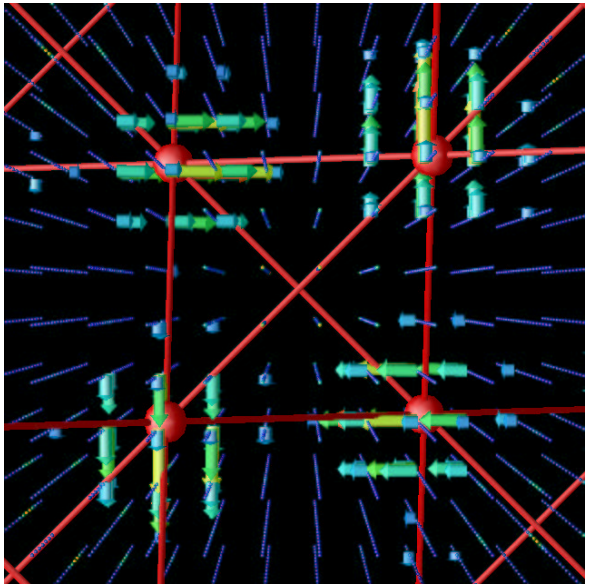
Mn sublattice



collinear



noncollinear



On site Coulomb repulsion

- L(S)DA fails to describe systems with localized (strongly correlated) d and f electrons $\rightarrow$ wrong one-electron energies
- Strong intra-atomic interaction is introduced in a (screened) Hartree-Fock like manner $\rightarrow$ replacing L(S)DA on site

$$E_{\mathrm{HF}} = \frac{1}{2}\sum_{\{\gamma\}}(U_{\gamma_1\gamma_3\gamma_2\gamma_4} - U_{\gamma_1\gamma_3\gamma_4\gamma_2})\hat{n}_{\gamma_1\gamma_2}\hat{n}_{\gamma_3\gamma_4}$$

determined by the PAW on site occupancies

$$\hat{n}_{\gamma_1\gamma_2} = \langle \Psi^{s_2} \mid m_2\rangle\langle m_1 \mid \Psi^{s_1}\rangle$$

and the (unscreened) on site electron-electron interaction

$$U_{\gamma_1\gamma_3\gamma_2\gamma_4} = \langle m_1 m_3 \mid \frac{1}{|\mathbf{r}-\mathbf{r}'|} \mid m_2 m_4\rangle \delta_{s_1 s_2}\delta_{s_3 s_4}$$

($|m\rangle$ are the spherical harmonics)

- $U_{\gamma_1\gamma_3\gamma_2\gamma_4}$ given by Slater's integrals F^0, F^2, F^4, and F^6 (f-electrons)
- Calculation of Slater's integrals from atomic wave functions leads to a large overestimation because in solids the Coulomb interaction is screened (especially F^0).
- In practice treated as fitting parameters, i.e., adjusted to reach agreement with experiment: equilibrium volume, magnetic moment, band gap, structure.
- Normally specified in terms of effective on site Coulomb- and exchange parameters, U and J.

  For $3d$-electrons: $U = F^0$, $J = \frac{1}{14}(F^2 + F^4)$, and $\frac{F^4}{F^2} = 0.65$
- U and J sometimes extracted from constrained-LSDA calculations.

Total energy and double counting

Total energy

$$E_{\mathrm{tot}}(n,\hat{n}) = E_{\mathrm{DFT}}(n) + E_{\mathrm{HF}}(\hat{n}) - E_{\mathrm{dc}}(\hat{n})$$

Double counting

LSDA+U $\quad E_{\mathrm{dc}}(\hat{n}) = \frac{U}{2}\hat{n}_{\mathrm{tot}}(\hat{n}_{\mathrm{tot}}-1) - \frac{J}{2}\sum_{\sigma}\hat{n}^{\sigma}_{\mathrm{tot}}(\hat{n}^{\sigma}_{\mathrm{tot}}-1)$

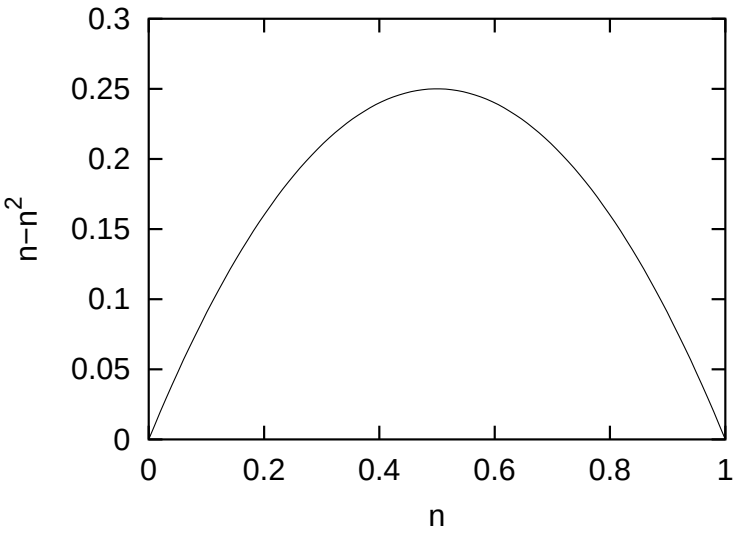
LDA+U $\quad E_{\mathrm{dc}}(\hat{n}) = \frac{U}{2}\hat{n}_{\mathrm{tot}}(\hat{n}_{\mathrm{tot}}-1) - \frac{J}{4}\hat{n}_{\mathrm{tot}}(\hat{n}_{\mathrm{tot}}-2)$

Hartree-Fock Hamiltonian can be simply added to the AE part of the PAW Hamiltonian

- Orbital dependent potential that enforces Hund's first and second rule
  - maximal spin multiplicity
  - highest possible azimuthal quantum number L_z
    (when SOI included)

Dudarev's approach to LSDA+U

$$E_{\mathrm{LSDA+U}} = E_{\mathrm{LSDA}} + \frac{(U-J)}{2} \sum_{\sigma} \left[\left(\sum_{m_1} n^{\sigma}_{m_1,m_1} \right) - \left(\sum_{m_1,m_2} \hat{n}^{\sigma}_{m_1,m_2} \hat{n}^{\sigma}_{m_2,m_1} \right) \right]$$



- Penalty function that forces idempotency of the onsite occupancy matrix,
  $\hat{n}^{\sigma} = \hat{n}^{\sigma}\hat{n}^{\sigma}$
- real matrices are only idempotent, if their eigenvalues are either 1 or 0
  (fully occupied or unoccupied)

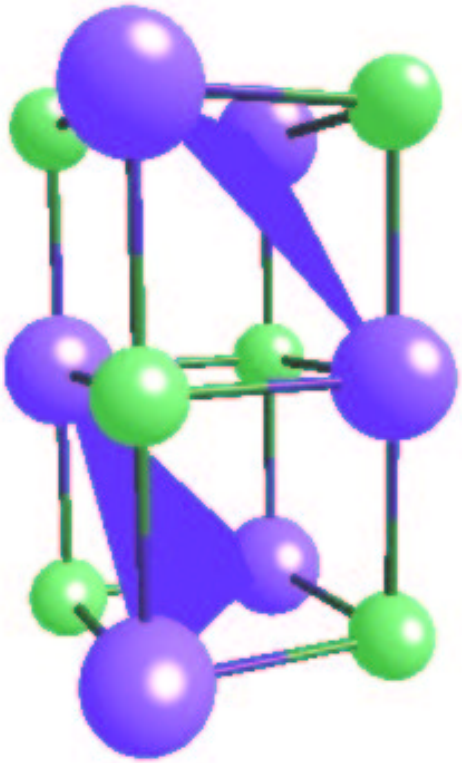
$$E_{\mathrm{LSDA+U}} = E_{\mathrm{LSDA}}(\{\varepsilon_i\}) + \frac{(U-J)}{2} \sum_{\sigma,m_1,m_2} \hat{n}^{\sigma}_{m_1,m_2} \hat{n}^{\sigma}_{m_2,m_1}$$

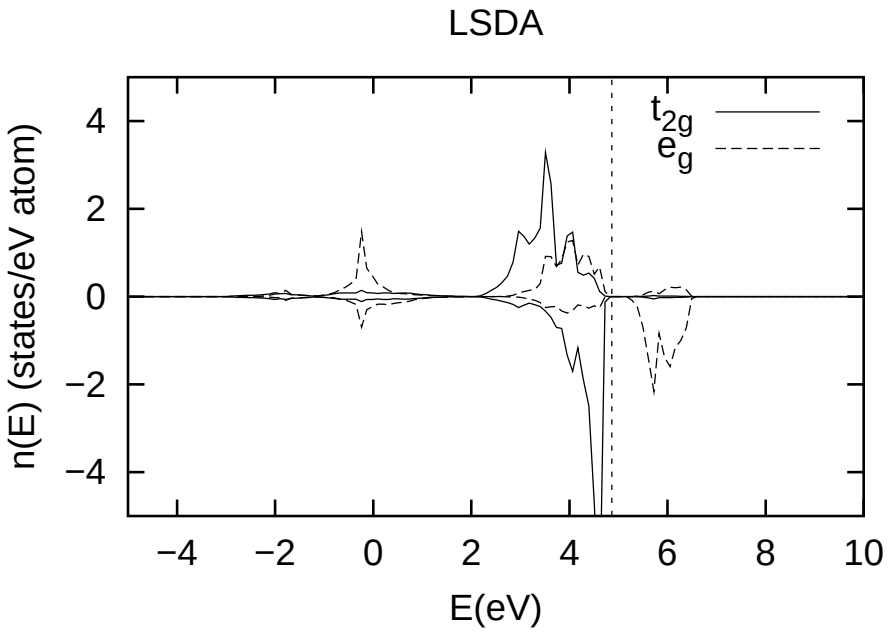
An example: NiO, a Mott-Hubbard insulator

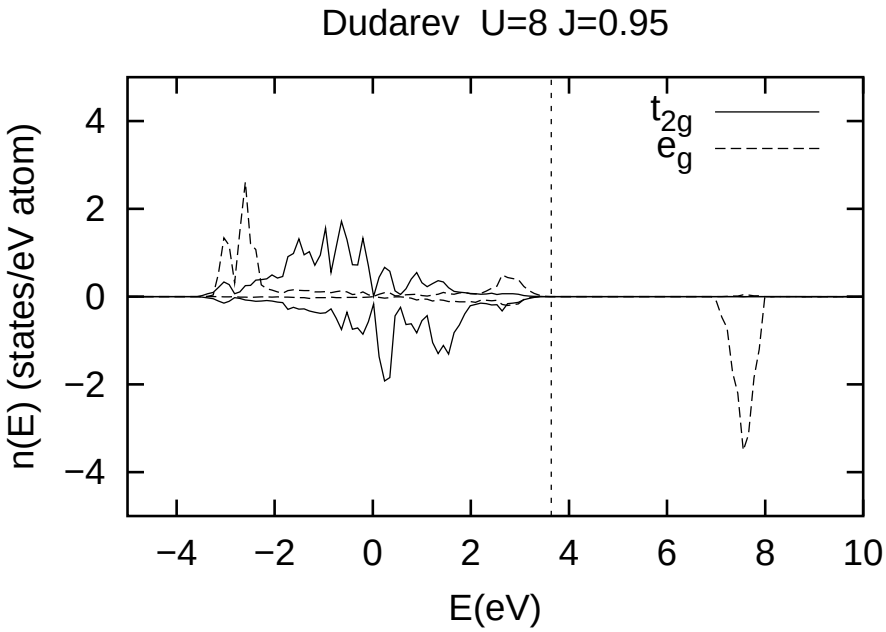
- Rocksalt structure
- AFM ordering of Ni (111) planes
- Ni 3d electrons in octahedral crystal field

  t_{2g} $(3d_{xy}, 3d_{xz}, 3d_{yz})$

  e_g $(3d_{x^2-y^2}, 3d_{z^2})$







$|m_{Ni}|$ = 1.15 μ_B

E_{gap} = 0.44 eV

$|m_{Ni}|$ = 1.71 μ_B

E_{gap} = 3.38 eV

Experiment

$|m_{Ni}|$ = 1.64 - 1.70 μ_B E_{gap} = 4.0 - 4.3 eV

Spin Orbit Interaction

Relativistic effects, in principle stemming from 4-component Dirac equation

- Pseudopotential generation: Radial wave functions are solutions of the scalar relativistic radial equation, which includes Mass-velocity and Darwin terms
- Kohn-Sham equations: Spin Orbit Interaction is added to the AE part of the PAW Hamiltonian (variational treatment of the SOI)

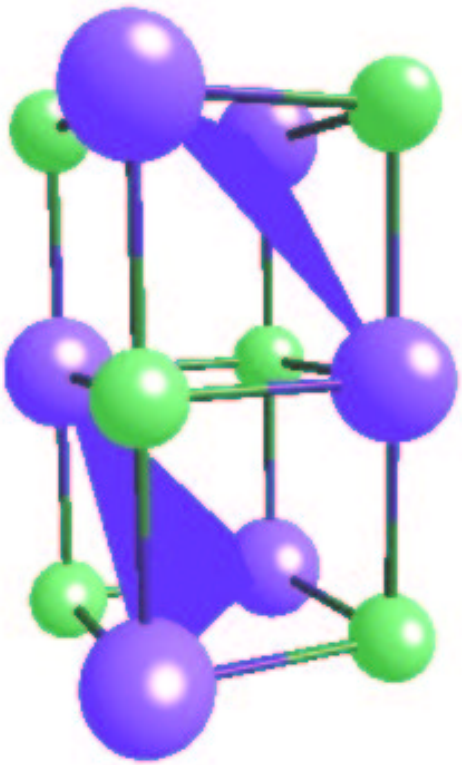
$$H^{\alpha\beta}_{\mathrm{SOI}} = \frac{\hbar^2}{(2m_e c)^2} \sum_{i,j} \langle \phi_i \mid \frac{1}{r} \frac{\mathrm{d}V_{\mathrm{spher}}}{\mathrm{d}r} \mid \phi_j \rangle \mid \tilde{p}_i \rangle \vec{\sigma}_{\alpha\beta} \cdot \vec{L}_{ij} \langle \tilde{p}_j \mid$$

Consequences:

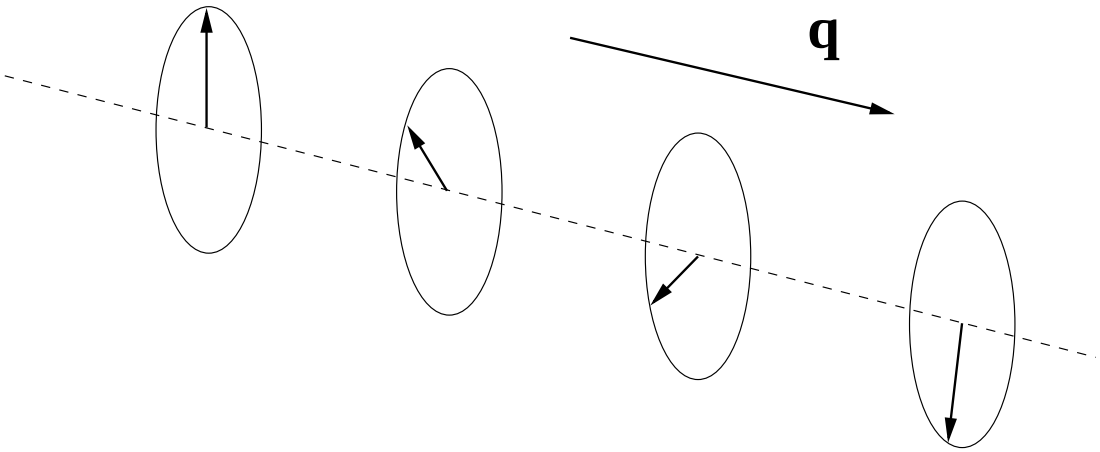
- Mixing of up- and down spinor components, noncollinear magnetism
- Spin directions couple to the crystalline structure, magneto-crystalline anisotropy
- Orbital magnetic moments

An example: CoO

- Rocksalt structure
- AFM ordering of Co (111) planes
- Experiment: $|m_{\mathrm{Co}}| \approx 3.8\ \mu_{\mathrm{B}}$ along $[\bar{1}\bar{1}2]$
- Orbital moment in t_{2g} manifold of Co^{2+} [$3d^7$] ion not completely quenched by crystal field
- LDA+U (U=8 eV, J=0.95 eV) + SOI
  $\Longrightarrow$ enforce Hund's rules
- Calculations yield correct easy axis,
  $|m_S| = 2.8\ \mu_{\mathrm{B}}$ $|m_L| = 1.4\ \mu_{\mathrm{B}}$
  and c/a ratio < 1 (magnetostriction)



Spin spirals



$$\mathbf{m}(\mathbf{r}+\mathbf{R}) = \begin{pmatrix} m_x(\mathbf{r})\cos(\mathbf{q}\cdot\mathbf{R}) - m_y(\mathbf{r})\sin(\mathbf{q}\cdot\mathbf{R}) \\ m_x(\mathbf{r})\sin(\mathbf{q}\cdot\mathbf{R}) + m_y(\mathbf{r})\cos(\mathbf{q}\cdot\mathbf{R}) \\ m_z(\mathbf{r}) \end{pmatrix}$$

Generalized Bloch condition

$$\begin{pmatrix} \Psi^{\uparrow}_{\mathbf{k}}(\mathbf{r}) \\ \Psi^{\downarrow}_{\mathbf{k}}(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} e^{-i\mathbf{q}\cdot\mathbf{R}/2} & 0 \\ 0 & e^{+i\mathbf{q}\cdot\mathbf{R}/2} \end{pmatrix} \begin{pmatrix} \Psi^{\uparrow}_{\mathbf{k}}(\mathbf{r}-\mathbf{R}) \\ \Psi^{\downarrow}_{\mathbf{k}}(\mathbf{r}-\mathbf{R}) \end{pmatrix}$$

keeping to the usual definition of the Bloch functions

$$\Psi^{\uparrow}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C^{\uparrow}_{\mathbf{kG}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad \text{and} \quad \Psi^{\downarrow}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C^{\downarrow}_{\mathbf{kG}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

the Hamiltonian changes only minimally

$$\begin{pmatrix} H^{\alpha\alpha} & V_{xc}^{\alpha\beta} \\ V_{xc}^{\beta\alpha} & H^{\beta\beta} \end{pmatrix} \rightarrow \begin{pmatrix} H^{\alpha\alpha} & V_{xc}^{\alpha\beta} e^{-i\mathbf{q}\cdot\mathbf{r}} \\ V_{xc}^{\beta\alpha} e^{+i\mathbf{q}\cdot\mathbf{r}} & H^{\beta\beta} \end{pmatrix}$$

where in $H^{\alpha\alpha}$ and $H^{\beta\beta}$ the kinetic energy of a plane wave component changes to

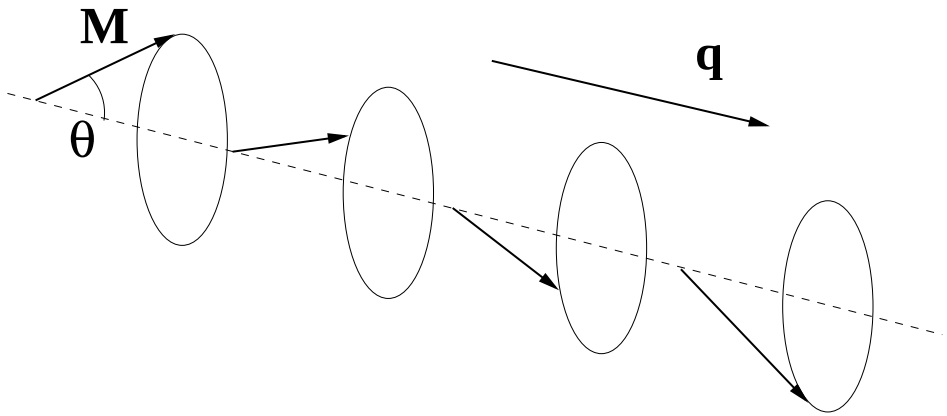
$$|\mathbf{k}+\mathbf{G}|^2 \rightarrow |\mathbf{k}+\mathbf{G}-\mathbf{q}/2|^2 \quad (\text{in } H^{\alpha\alpha})$$

$$|\mathbf{k}+\mathbf{G}|^2 \rightarrow |\mathbf{k}+\mathbf{G}+\mathbf{q}/2|^2 \quad (\text{in } H^{\beta\beta})$$

- Primitive cell suffices, no need for supercell that contains a complete spiral period
- Adiabatic spin dynamics: Magnon spectra
  for instance for elementary ferromagnetic metals (bcc Fe, fcc Ni)

$$\omega(\mathbf{q}) = \lim_{\theta \to 0} = \frac{4}{M} \frac{\Delta E(\mathbf{q}, \theta)}{\sin^2 \theta}$$

$$\Delta E(\mathbf{q}, \theta) = E(\mathbf{q}, \theta) - E(\mathbf{0}, \theta)$$



see for instance:

"Theory of Itinerant Electron Magnetism", J. Kübler, Clarendon Press, Oxford (2000).

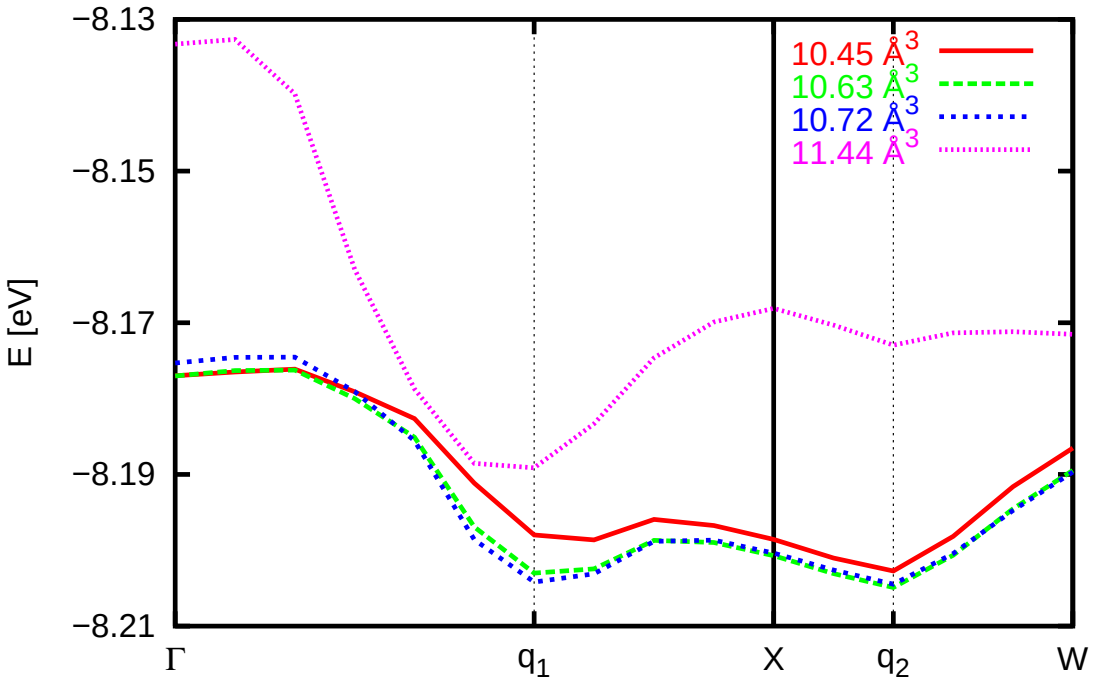
Spin spirals in fcc Fe

$$\Gamma\ (\mathrm{FM}) = \frac{2\pi}{a_0} \times (0,0,0)$$

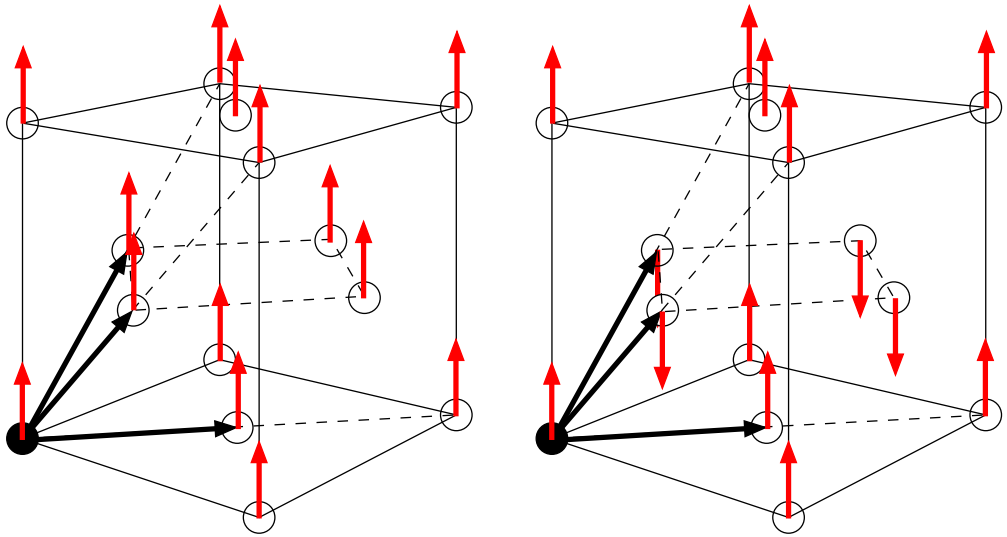
$$\mathbf{q_1} = \frac{2\pi}{a_0} \times (0,0,0.6)$$

$$\mathrm{X}\ (\mathrm{AFM}) = \frac{2\pi}{a_0} \times (0,0,1.0)$$

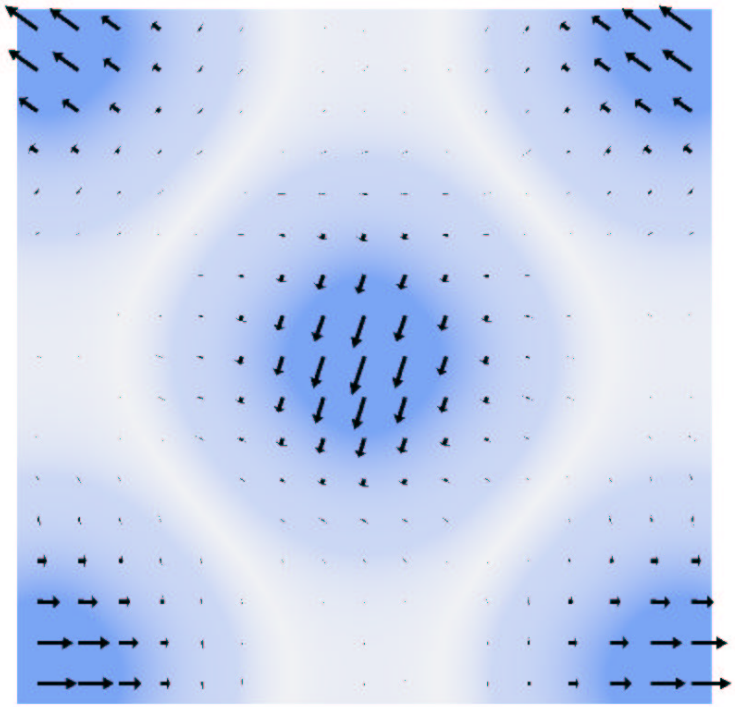
$$\mathbf{q_2} = \frac{2\pi}{a_0} \times (0.15,0,1.0)$$

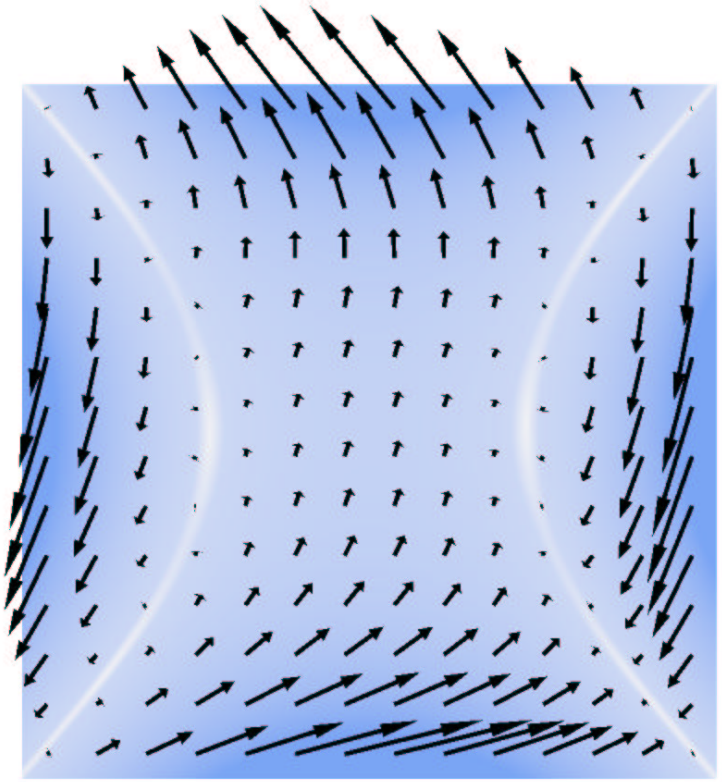


$$\mathbf{q}_{\mathrm{exp}} = \frac{2\pi}{a_0} \times (0.1,0,1.0)$$



Magnetization at $\mathbf{q_1}$





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