Magnetism

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Outline

- **How does magnetism appear?**
  - From atoms and molecules to solids
  - Anderson and Stoner models
- **Magnetic order**
  - Exchange interaction and its mechanisms
- **Magnetism in spin density functional theory**
- **Mapping the Heisenberg model**
  - Fitting of different magnetic structures
  - Linear response technique
  - Noncollinear magnetic structures, spin spirals, generalized Bloch theorem
- **Implementation in FLEUR**
- **Practical issues and a couple examples**

Atomic magnetism: Hund's rule

- Fill the single-electron orbitals observing the Pauli principle
- Degenerate orbitals: Hund's rule (maximum multiplicity)
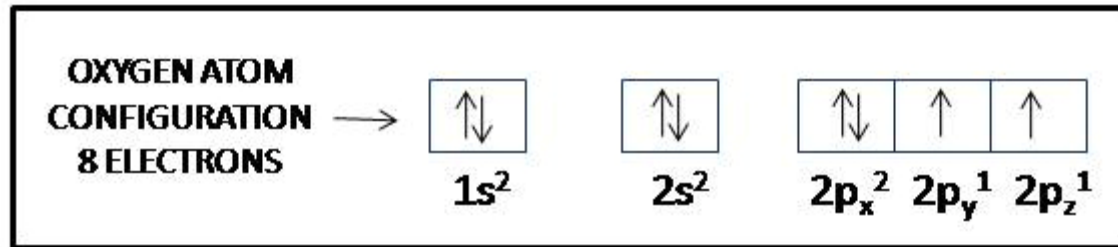
- Many-electron effects become important for partially filled shells
- Many-electron $\Psi(1, \ldots, N)$ is antisymmetric for all permutations
- Non-relativistic H does not affect spin,
  hence $\Psi(1, \ldots, N) = \chi(\sigma_1, \ldots, \sigma_N)\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$
- Permutation symmetry of χ determines the total spin and matches the symmetry of the coordinate $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$
- Coulomb energy is minimal when the electrons in the degenerate shell avoid each other, i.e. for antisymmetrized ψ and hence symmetrized χ; maximal spin of the unfilled shell (Hund's rule)

Magnetism of molecules

- Similar to atoms:
  - Fill the single-electron (SCF) orbitals observing the Pauli principle
  - Degenerate orbitals: Hund's rule (maximum multiplicity)
- Example: O_2 and N_2 molecules
  - Ground state
    O_2: triplet
    N_2: singlet
  - Dissociation energy
    O_2: 5.13 eV
    N_2: 9.78 eV
  - Singlet-triplet splitting
    O_2: 0.98 eV
- Hund exchange is "small"
- **Note the degeneracy!**

❑ Delocalization reduces the magnetic moment on the O atom from 2 to $1\mu_B$

❑ Most molecules have singlet ground state

2p-Orbitale

σ_p^*

$\pi_x^* \ \pi_y^*$

$\pi_x \ \pi_y$

σ_p

σ_s^*

2s-Orbitale

σ_s
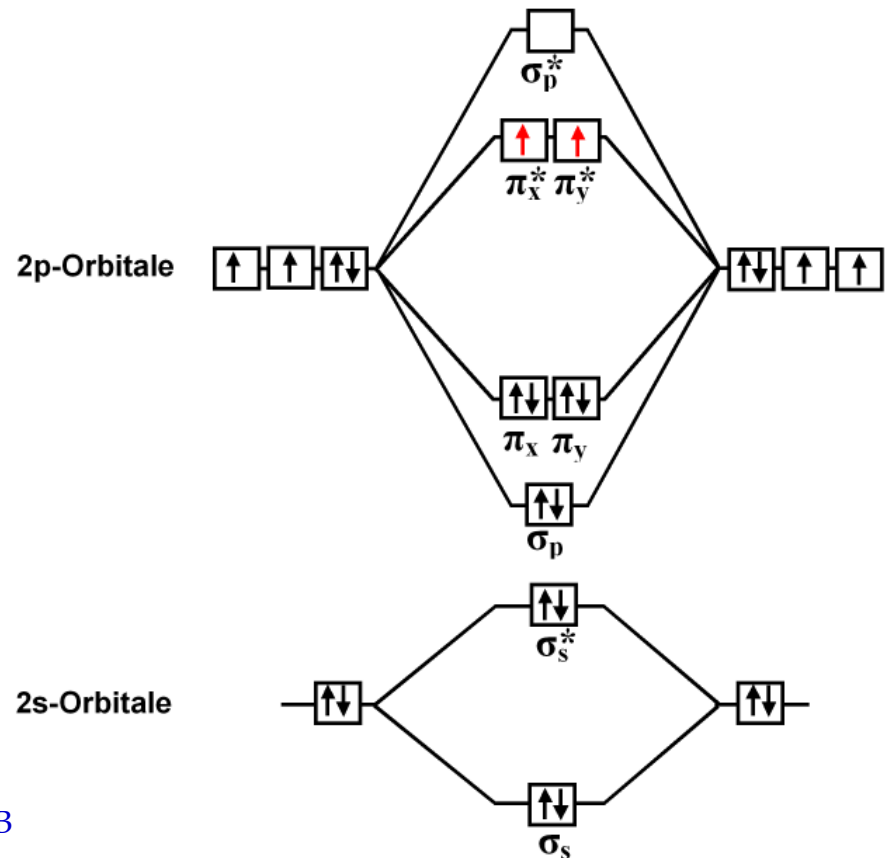
Magnetism of solids

- From molecules to solids:
  - Bonding/antibonding orbitals become energy bands, degeneracy lifted
  - Fractional filling of bands is possible (metals)
- Band filling with orbital-independent SCF: non-magnetic state
- Effects of on-site exchange and correlation:
  - On-site Coulomb repulsion – penalizes electrons for occupying the same site

$$E_C\left(n_{3d}\right) = \frac{1}{2}U_{3d}n_{3d}\left(n_{3d}-1\right)$$

  - On-site exchange J – favors electrons on the same site to have parallel spins
  - These are important for $3d$ and $4f$ orbitals
- Magnetism appears if correlation energy wins over the band energy
- Competing energy contributions:
  - On-site repulsion U promotes integer n_{3d}, hence local moments for odd n_{3d}
  - On-site (Hund) exchange directly promotes local moments
  - Hybridization promotes delocalization, tends to destroy local moments

Anderson model: 3*d* impurity in a metal

$$\mathcal{H} = \sum_{k\sigma} \varepsilon_k a_{k\sigma}^\dagger a_{k\sigma} + \sum_\sigma E_d a_{d\sigma}^\dagger a_{d\sigma} + \sum_{k\sigma} (V_{kd} a_{k\sigma}^\dagger a_{d\sigma} + V_{dk} a_{d\sigma}^\dagger a_{k\sigma})$$
$$+ U a_{d\uparrow}^\dagger a_{d\uparrow} a_{d\downarrow}^\dagger a_{d\downarrow} .$$

Hartree-Fock: $n_{d\uparrow,\downarrow} = \langle n_{d\uparrow,\downarrow}\rangle + (n_{d\uparrow,\downarrow} - \langle n_{d\uparrow,\downarrow}\rangle)$
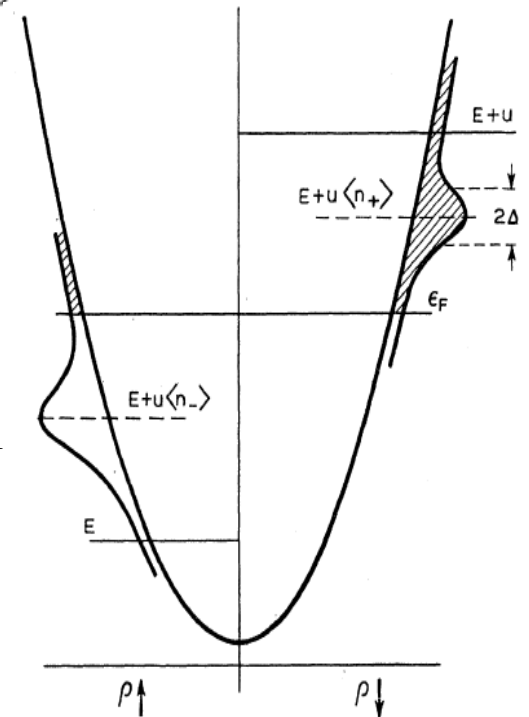
$$\mathcal{H}_{\mathrm{HF}} = \sum_{k\sigma} \varepsilon_k a_{k\sigma}^\dagger a_{k\sigma} + \sum_\sigma (E_d + U\langle n_{d-\sigma}\rangle) a_{d\sigma}^\dagger a_{d\sigma}$$
$$+ \sum_{k\sigma} (V_{kd} a_{k\sigma}^\dagger a_{d\sigma} + V_{dk} a_{d\sigma}^\dagger a_{k\sigma}) .$$

Solve the impurity problem by Green's function method, minimize the HF total energy

Result:

Stable solution with $\left\langle n_{d\uparrow}\right\rangle \neq \left\langle n_{d\downarrow}\right\rangle$ if $U\rho_d(E_F) > 1$

Impurities with resonant d levels near Fermi level develop local moments

Delocalization: kinetic energy gain   *vs*   Localization: potential energy gain

Stoner model

- Band electrons with short-range Coulomb interaction (Slater; Stoner)
- Originally $H_C = I\,\delta(\mathbf{r}_i - \mathbf{r}_j)$, but let's take the Hubbard model instead

$$H = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}\, \hat{c}^{\dagger}_{\mathbf{k}\sigma}\hat{c}_{\mathbf{k}\sigma} + U\sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} - \frac{g\mu_B H}{2}\sum_i \left(\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow}\right)$$

- Denote
$$n_i = \left\langle \hat{n}_{i\uparrow}\right\rangle + \left\langle \hat{n}_{i\downarrow}\right\rangle, \quad m_i = \left\langle \hat{n}_{i\uparrow}\right\rangle - \left\langle \hat{n}_{i\downarrow}\right\rangle$$

- Assume homogeneous n and m, use Hartree-Fock:

$$\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \approx \hat{n}_{i\uparrow}\left\langle \hat{n}_{i\downarrow}\right\rangle + \hat{n}_{i\downarrow}\left\langle \hat{n}_{i\uparrow}\right\rangle - \left\langle \hat{n}_{i\downarrow}\right\rangle\left\langle \hat{n}_{i\uparrow}\right\rangle$$

- In the magnetic state, energy bands are shifted:

$$\varepsilon_{\mathbf{k}\sigma} = \varepsilon_{\mathbf{k}} + Un_{-\sigma} - \frac{g\mu_B H}{2}\sigma$$

This can also come from Hund exchange J for denegerate bands

- Total energy:
$$\Delta E(m) = \frac{m^2}{4\rho(\varepsilon_F)} - \frac{Um^2}{4} - \frac{g\mu_B H}{2}m$$

- Susceptibility:
$$\chi = \frac{g\mu_B m}{2H} = \frac{\chi_0}{1 - U\rho(\varepsilon_F)}$$
diverges at $U\rho(\varepsilon_F) = 1$

Stoner criterion

Degeneracy favors magnetism (cf. O_2)

Interatomic exchange interaction… which is not really exchange

- Suppose that local moments exist
- How do they arrange themselves in the crystal?
- Magnetic ordering is driven by kinetic energy gain (interatomic exchange integrals are small and irrelevant)

Various mechanisms

- Direct exchange (virtual hopping between two magnetic sites)
- Superexchange (hopping through an intermediary anion)
- Zener double exchange (mixed valence manganites, etc.)
- Indirect exchange
  - Rare earth metals and compounds
  - RKKY (Ruderman-Kittel-Kasuya-Yosida): its linear response regime
- Exchange in metals
  - Interplay of many mechanisms
  - Local moments may depend on magnetic ordering

Exchange interaction in insulators

- Stable local moments
- Treat the hybridization perturbatively:

$$H = H_0 + H' = \sum_i H_i + \sum_{ij} t_{ij} c_i^\dagger c_j$$

Eigenstates $|\psi_i\rangle$ of H_i (single band):

$$|0\rangle, \quad E_0$$

$$|\uparrow\rangle, \quad E_0 + \varepsilon$$

$$|\downarrow\rangle, \quad E_0 + \varepsilon$$

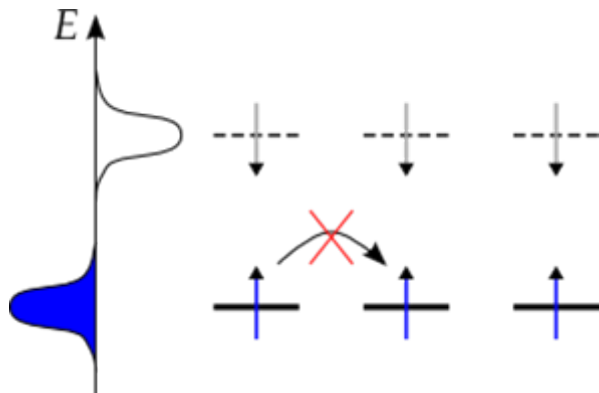$$|\uparrow\downarrow\rangle, \quad E_0 + 2\varepsilon + U$$

Eigenstates of H_0:

$$|\Psi_N\rangle = |\psi_1\rangle \otimes \ldots \otimes |\psi_N\rangle$$

Antiferromagnetic direct exchange

Half-filled band

Ferromagnetic

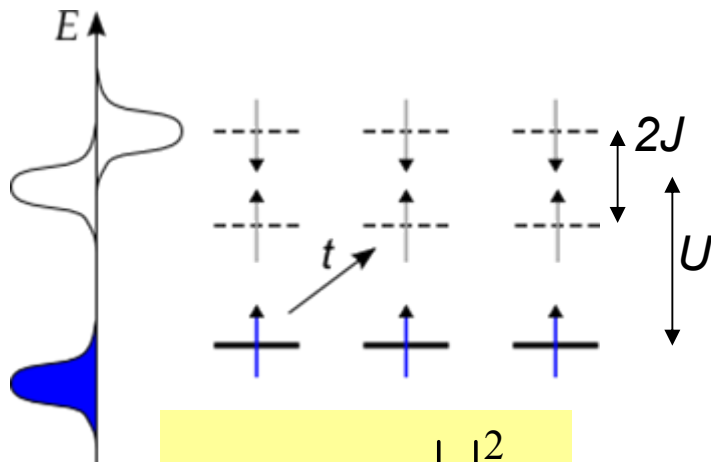**Antiferromagnetic**

$$\Delta E = 0$$
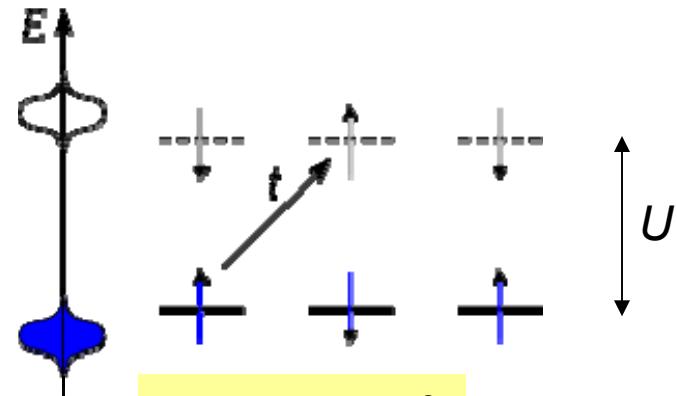
$$\Delta E = -\frac{|t|^2}{U}$$

- Hopping is possible only for antiferromagnetic pairs

- Energy is reduced for AFM (second-order perturbation theory)

- Band picture: in AFM state the occupied and empty states hybridize and repel each other; occupied states are pushed down
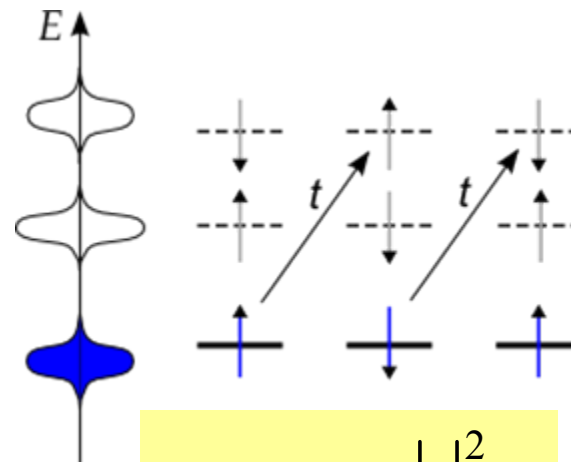
Ferromagnetic direct exchange

Half-filled orbital to empty orbital

Ferromagnetic
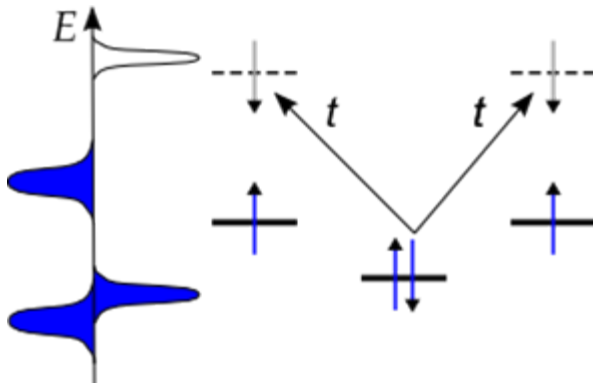
$$\Delta E = -\frac{|t|^2}{U - J}$$

Antiferromagnetic

$$\Delta E = -\frac{|t|^2}{U + J}$$

- Excited state is lower if the local moments are parallel

- Band picture: in the FM state the occupied band shifts down further in the ferromagnetic state

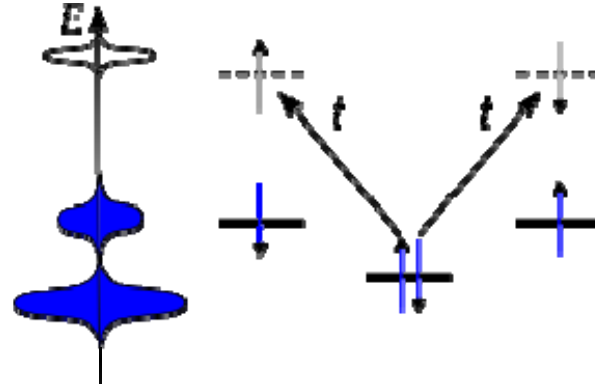# Superexchange

Half-filled orbitals and a filled anion band

**Ferromagnetic**   **Antiferromagnetic**

- Fourth-order virtual process in t
    AFM state is lower in energy by $\sim t^4/\Delta^3$
    AFM also wins away from half-filling for like cation orbitals

- Band picture: Less gain from hybridization in the FM state

- Goodenough-Kanamori rules describe the sign of interaction

Description in terms of spin rotations

- Consider a pair of spins at an angle
- Different unperturbed basis

$$\chi_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_j = \begin{pmatrix} \cos\dfrac{\theta}{2} e^{-i\varphi} \\ \sin\dfrac{\theta}{2} e^{i\varphi} \end{pmatrix},$$
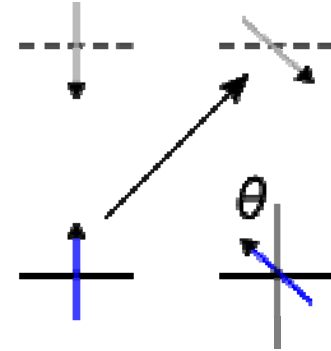
- The amplitude for the hopping is now

$$\langle i \,|\, H' \,|\, j \rangle = t_{ij} \langle \chi_i \,|\, T\chi_j \rangle = t_{ij} \sin\frac{\theta}{2} e^{i\varphi}$$

- Second-order correction to total energy:

$$\delta E_{ij} = -2\frac{|t_{ij}|^2}{U}\sin^2\frac{\theta}{2} \rightarrow \frac{|t_{ij}|^2}{U}\cos\theta \rightarrow -J_{ij}\mathbf{e}_i\mathbf{e}_j$$

- J_{ij}: exchange parameter (AFM in this case)
- Heisenberg model appears in second-order in t_{ij}

Magnetism in density functional theory

Hohenberg-Kohn theorem:

External potential V enters as $\quad H = H_0 + V(\mathbf{r})$

It follows that the GS charge density uniquely determines $V(\mathbf{r})$

The proof is based on the fact that $\quad \langle \Psi | H_1 - H_2 | \Psi \rangle = \int (V_1 - V_2) \rho \, d^3 r$

Now add external magnetic field $\boldsymbol{B}$:

$$H = H_0 + V(\mathbf{r})\hat{1} + \mu_B \mathbf{B}(\mathbf{r})\hat{\boldsymbol{\sigma}} = H_0 + \begin{pmatrix} V + \mu_B B_z & \mu_B B_- \\ \mu_B B_+ & V - \mu_B B_z \end{pmatrix} \triangleq H_0 + \hat{V}$$

where $\quad B_\pm = B_x \pm i B_y$

But $\quad \langle \Psi | \hat{V} | \Psi \rangle = \int \mathrm{Tr}\left(\hat{V} \hat{\rho} \right) d^3 r \quad$ where $\quad \rho_{\alpha\beta}(\mathbf{r}) = \langle \Psi | \hat{\psi}_\alpha^\dagger(\mathbf{r}) \hat{\psi}_\beta(\mathbf{r}) | \Psi \rangle$

The GS *spin density matrix* $\rho_{\alpha\beta}$ uniquely determines V and $\boldsymbol{B}$

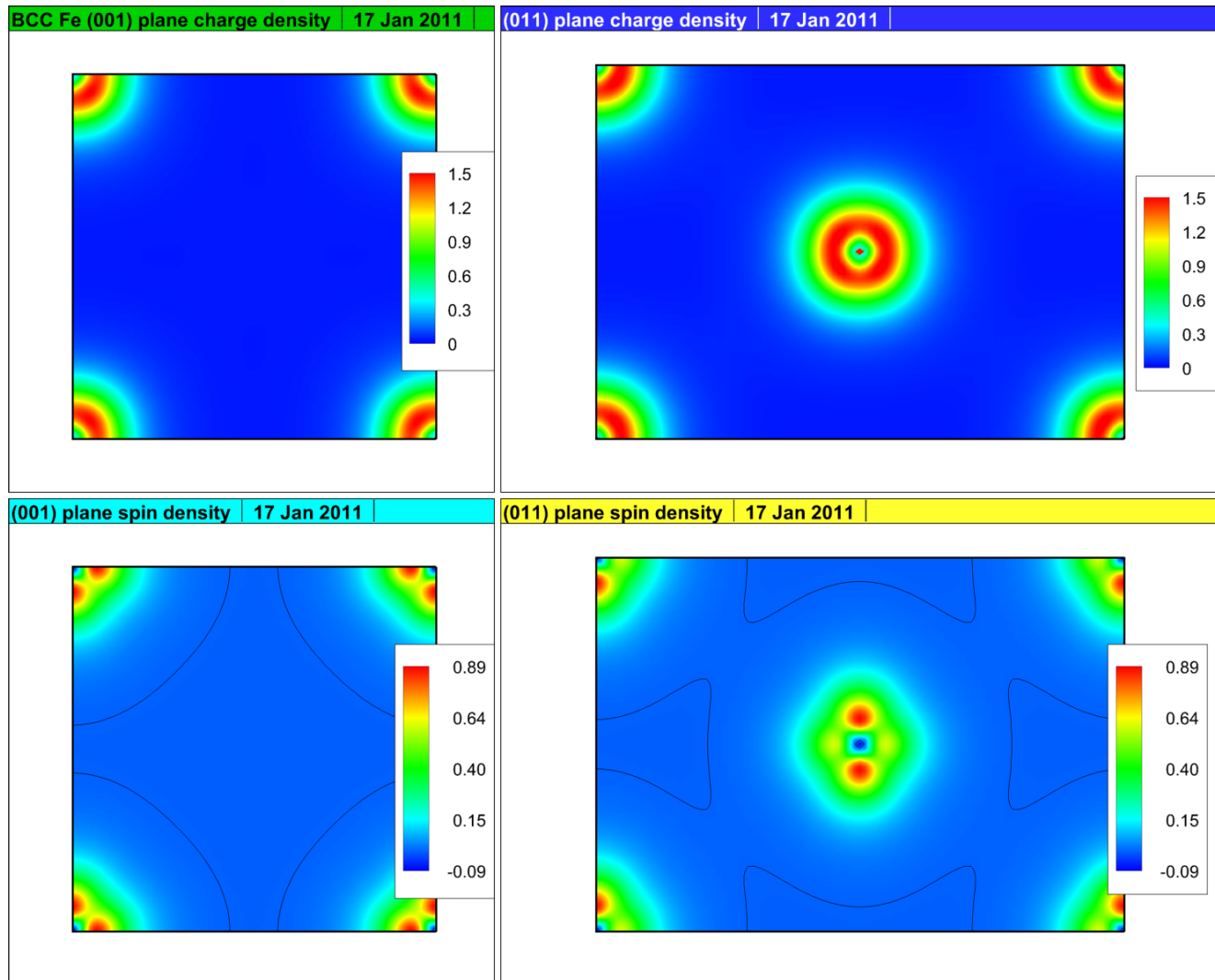$$\hat{\rho} = \frac{1}{2} \begin{pmatrix} n + m_z & m_- \\ m_+ & n - m_z \end{pmatrix} \qquad \text{or in Kohn-Sham:} \quad \rho_{\alpha\beta} = \sum_{i \in occ} \psi_{i\alpha}^*(\mathbf{r}) \psi_{i\beta}(\mathbf{r})$$

LSDA: $\quad \mathbf{B}_{xc}(\mathbf{r}) = B_{xc}\left[m(\mathbf{r})\right] \dfrac{\mathbf{m}(\mathbf{r})}{m(\mathbf{r})}$

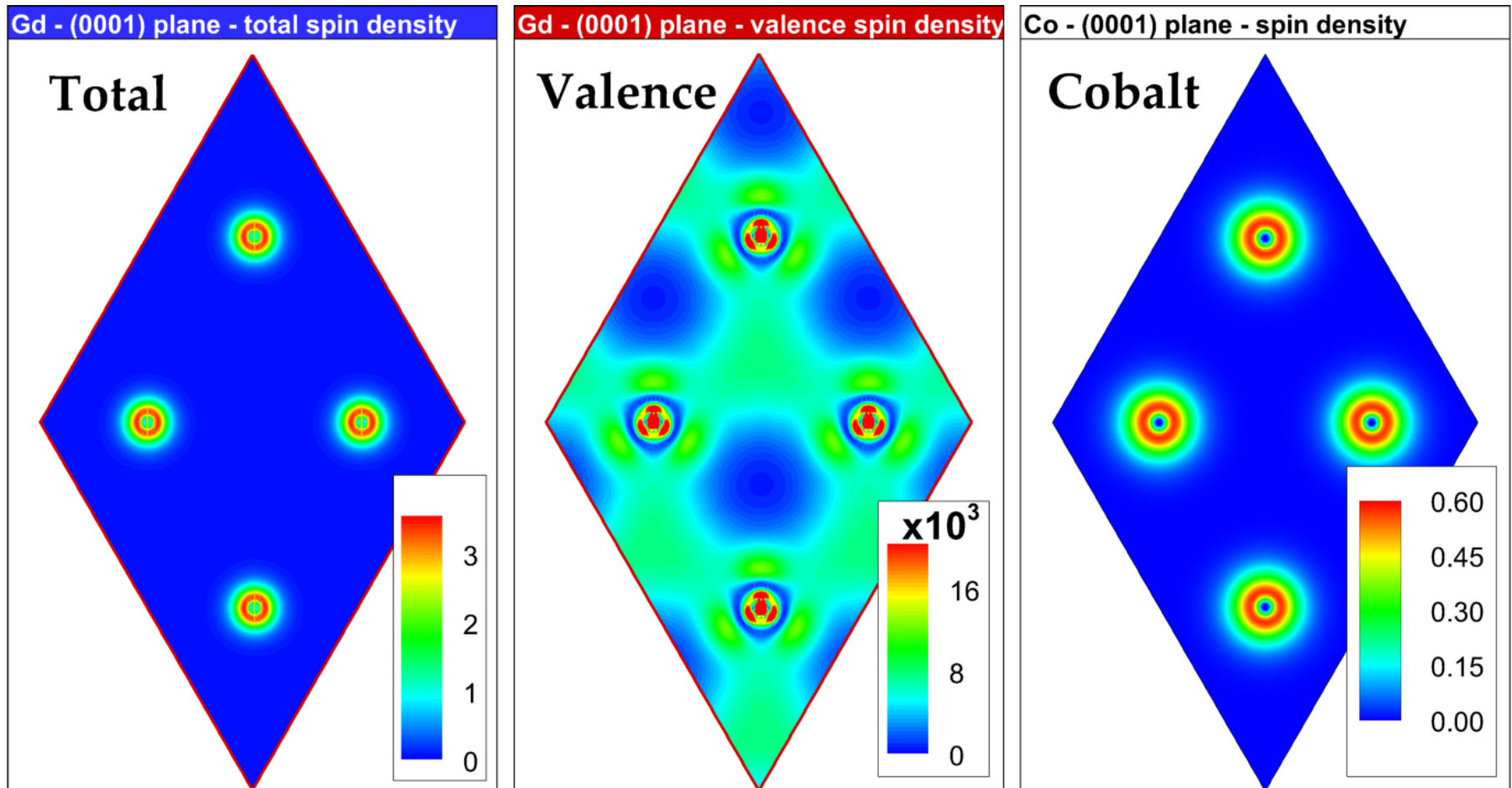- Ground state may be collinear or noncollinear

This is what drives magnetism in LSDA

Charge and spin density in b.c.c. Fe

- Magnetization is formed within a 0.7 Å atomic sphere (3d wavefunction range)

Spin density in Gd compared to Co

Gd - (0001) plane - total spin density — Total

Gd - (0001) plane - valence spin density — Valence

Co - (0001) plane - spin density — Cobalt

- The 4*f* part ("open core" here) of the magnetization (~7 μ_B) is strongly localized
- The valence part (mainly 5*d*) is delocalized (~0.4 μ_B in and 0.3 μ_B out of the MT)
- Valence band is polarized by the 4*f* shell, otherwise would be non-magnetic

Exchange interaction from DFT

- Many practical options for systems with stable local moments
- Fitting of total energies for different orderings
  - Usually Heisenberg model
- Linear response calculations with respect to the ground state
  - Directly applicable to spin wave spectra
  - Rigid spin approximation: valid in many cases, easy
- Spin spirals
  - Total energies for noncollinear "spin-spiral" configurations
  - Applicable both to spin waves and beyond linear response
  - Alternative to the supercell method
- Thermodynamics
  - Given a mapping to Heisenberg model, thermodynamic properties can be studied; however, poorly justified assumptions are needed about the character of magnetic fluctuations (e.g. classical spins)
  - Mean field theory or Monte Carlo

Heisenberg model

- Map the total energies of a solid onto an effective spin model

$$E = -\sum_{i<j} J_{ij} \mathbf{S}_i \mathbf{S}_j$$

- $\mathbf{S}_i$ are classical vector spin variables (with DFT - what else?)
- Mapping works well in most insulators and in some metals
- Adiabatic approximation ("slow" effective spin variables)

Fitting of a collinear set

- Straightforward way: fit the total energies of a number of collinear spin configurations in supercells (i. e. treat $\mathbf{S}_i$ as Ising σ_i)
- Similar to Connolly-Williams method in alloy theory, but odd powers of $\mathbf{S}$ are not allowed (can't make a scalar)
- Some higher-order terms can not be extracted
  For example, $(\mathbf{S}_i \mathbf{S}_j)^2 = S^4 =$ const for all collinear configurations

Constrained DFT for noncollinear states

- Imagine that the low-lying spin excitations are classical adiabatic rotations of local moments (not well justified, but still…)
- We wish to stabilize (muffin-tin) local moments $\langle \mathbf{m} \rangle_i = M_i \mathbf{e}_i$
- Introduce constraining fields in DFT as Lagrange multipliers

$$\tilde{E}\left[\rho_{\alpha\beta}(\mathbf{r})\right] = E\left[\rho_{\alpha\beta}(\mathbf{r})\right] + \sum_i \boldsymbol{\lambda}_i \cdot \mathbf{e}_i \times \langle \mathbf{m} \rangle_i, \quad \text{with } \boldsymbol{\lambda}_i \parallel \mathbf{e}_i \times \langle \mathbf{m} \rangle_i$$

- Denote $\mathbf{e}_i \times \boldsymbol{\lambda}_i = \mathbf{B}_{ci}$ (constraining fields), then

$$\tilde{E}[\hat{\rho}] = E[\hat{\rho}] - \sum_i \mathbf{B}_{ci} \langle \mathbf{m} \rangle_i, \quad \text{with } \mathbf{B}_{ci} \cdot \mathbf{e}_i \times \langle \mathbf{m} \rangle_i = 0$$

- This is well-defined in DFT, and one can use $E[\mathbf{e}_i]$ to map out the spin configuration space
- In practice, $\mathbf{B}_{ci}$ are iteratively adjusted to achieve $\langle \mathbf{m} \rangle_i \parallel \mathbf{e}_i$ in parallel with DFT iterations
- In LSDA one can also use $\mathbf{B}_{ci}(\mathbf{r}) = B_i^{xc}(\mathbf{r}) \delta \mathbf{e}_i$ to keep the total $\mathbf{B}_i$ collinear

$\langle \mathbf{m} \rangle_i$

$\mathbf{e}_i$

$\mathbf{B}_{ci}$

(complanar)
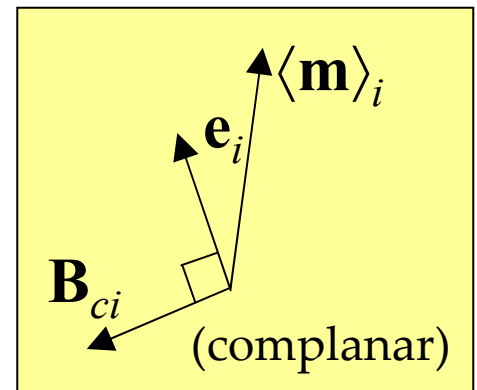
Exchange parameters: Linear response

- Small deviations from the ground state
- *In the lattice model*: Apply external fields $\mathbf{B}_{ci}$, linear response:

$$\delta M_i^\alpha = \sum_j \chi_{ij}^{\alpha\beta} B_{ci}^\beta, \quad \delta^2 E = \frac{1}{2} \sum_{ij} B_{ci}^\alpha \chi_{ij}^{\alpha\beta} B_{cj}^\beta$$

- Inverse susceptibility: $\quad B_{ci}^\alpha = \sum_j \left(\chi^{-1}\right)_{ij}^{\alpha\beta} \delta M_j^\beta$

- Energy in terms of local moments:

$$\delta^2 E = \frac{1}{2} \sum_{ij} \delta M_i^\alpha \left(\chi^{-1}\right)_{ij}^{\alpha\beta} \delta M_j^\beta$$

- Exchange parameters (collinear reference state, only rotations):

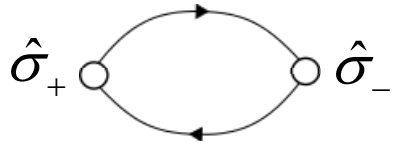$$J_{ij} = M_i \left(\chi^{-1}\right)_{ij}^{+-} M_j$$

- Thus, one needs to calculate the inverse transverse susceptibility

Calculating the susceptibility in DFT

- In general, $\delta\hat{V}_{KS} = \hat{V}_{ext} + \delta\hat{V}_{int}, \quad \hat{\rho} = \hat{\rho}\left[\hat{V}_{KS}\right]$

- Assuming zero charge response to transverse magnetic field:

$$\delta\mathbf{B}_{KS} = \mathbf{B}_{ext} + \delta\mathbf{B}_{xc}, \quad \delta\mathbf{m}(\mathbf{r}) = \hat{\chi}^0_{+-}\delta\mathbf{B}_{KS} = \hat{\chi}_{+-}\mathbf{B}_{ext}$$

- Result: $\hat{\chi}^{-1} = \hat{\chi}_0^{-1} - \hat{I}, \quad \text{where} \quad \hat{I}(\mathbf{r},\mathbf{r}') = \delta\mathbf{B}_{xc}(\mathbf{r})/\delta\mathbf{m}(\mathbf{r}')$

$$\hat{\sigma}_+ \qquad \hat{\sigma}_- \qquad \hat{\chi}^0_{+-}(\mathbf{r},\mathbf{r}') = \frac{1}{\pi}\text{Im}\int^{\varepsilon_F} G^{KS}_\uparrow(\mathbf{r},\mathbf{r}',z)G^{KS}_\downarrow(\mathbf{r}',\mathbf{r},z)dz$$

$$\delta^2 E = \frac{1}{2}\sum_{ij}\int_{V_i,V_j} \delta\mathbf{B}_{KS}(\mathbf{r}_i)\chi^0_{+-}(\mathbf{r}_i,\mathbf{r}_j)\delta\mathbf{B}_{KS}(\mathbf{r}_j)d^3r_id^3r_j - \frac{1}{2}\sum_i\int_{V_i}\delta m_i\hat{I}\delta m_i d^3r d^3r'$$

- **How to turn this into a reasonable Heisenberg model-like form?**

- We may ask for the softest mode producing the given $\delta\mathbf{M}_i$

- Then we need to calculate χ^0 and I in a complete basis, use matrix inversion to obtain χ^{-1}, find its lowest eigenvalue

- This is likely a good approach to calculate the spin wave spectrum (as long as the adiabatic approximation is valid)

Rigid spin approximation

- Drastic simplification: assume that when $\mathbf{M}_i$ are rotated, the total $\mathbf{B}_{KS}$ rotate rigidly with them:

$$\delta\mathbf{B}^i_{KS}(\mathbf{r}) = B^i_{xc}(\mathbf{r})\,\delta\mathbf{e}_i, \quad \delta\mathbf{m}_i = M_i\delta\mathbf{e}_i$$

- Then for $i \neq j$ in second-order

$$\delta^2 E_{ij} = \frac{1}{2}\delta\mathbf{e}_i \cdot \delta\mathbf{e}_j \underbrace{\int_{V_i}\int_{V_j} B_{xc}(\mathbf{r}_i)\,\chi^0_{+-}(\mathbf{r}_i,\mathbf{r}_j)\,B_{xc}(\mathbf{r}_j)\,d^3r_i d^3r_j}_{-J_{ij}}$$

- Easy to implement in KKR or LMTO (very popular)

$$J_{ij} = \frac{1}{4\pi}\,\mathrm{Im}\int^{\varepsilon_F}\mathrm{Tr}\,\Delta t_i^{-1}T_{ij}^{\uparrow}\Delta t_j^{-1}T_{ji}^{\downarrow}\,dz \qquad \text{Liechtenstein } et\ al.,\ 1984$$

- How come we have $J \sim \chi$, while we are supposed to have $J \sim \chi^{-1}$?

Long-wave or rigid spin approximation

- To generate a large-angle rotation:
  - Constraining fields are of order Weiss field $J_0 M$, where $J_0 = \sum_j J_{ij}$
  - Exchange-correlation field of order IM (exchange splitting)
- Therefore
  $$\hat{\chi}_0^{-1} = \frac{\partial B_{KS}^i}{\partial M_j} = I \cdot \hat{1} + \hat{J} = I\left(\hat{1} + \frac{\hat{J}}{I}\right) \qquad \text{close to diagonal}$$

  $$\hat{\chi}_0 \approx \frac{1}{I} \cdot \hat{1} - \frac{1}{I^2}\hat{J} \qquad \chi_{ij}^0 = -\frac{1}{I^2}\left(\chi^0\right)_{ij}^{-1}$$

- Or, in **q**-space at small q ("long-wave approximation)

  $$\hat{\chi}_0^{-1}(\mathbf{q}) - \hat{\chi}_0^{-1}(\mathbf{0}) \approx \hat{\chi}_0^{-1}(\mathbf{0})\left[\hat{\chi}_0(\mathbf{0}) - \hat{\chi}_0(\mathbf{q})\right]\hat{\chi}_0^{-1}(\mathbf{0})$$

- Generally valid for small q (long-wavelength magnons)
- At high q it is invalid in strongly itinerant metals (e.g. Ni)

  Antropov, 2003; Bruno, 2003

- Non-adiabatic effects (damping of higher-q spin waves, longitudinal spin fluctuations; no consistent treatment available)

Spin spirals

- Finite rotations - alternative to linear response
  - Mapping to a Heisenberg model (plus higher-order terms) possible
- Small deviations from ground state require large supercells
- Solution: Spin spirals
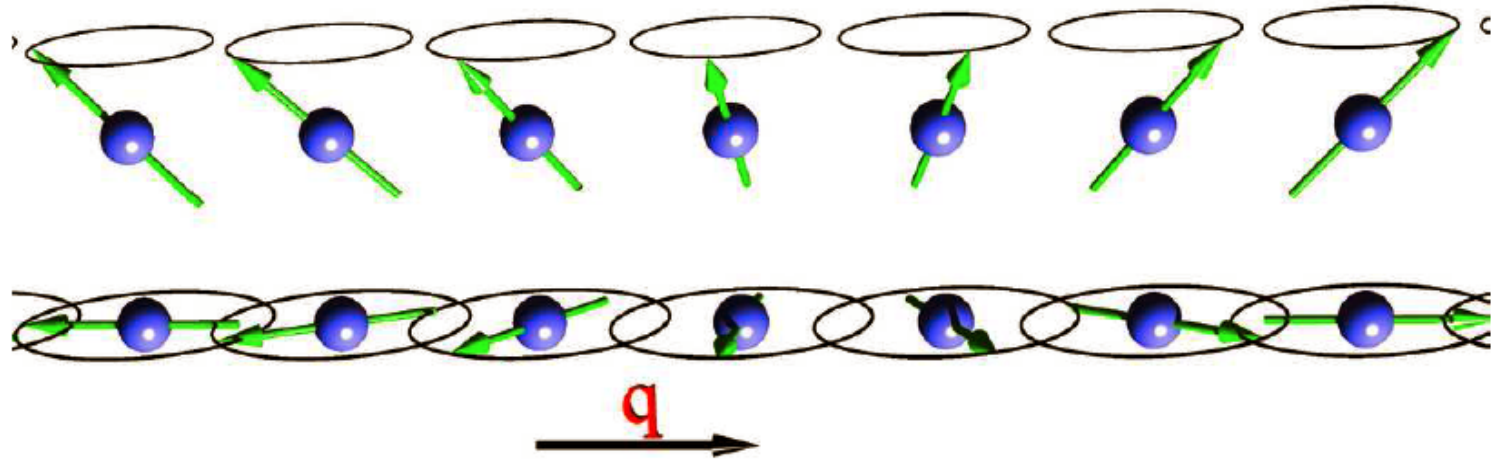
Using "twisted" boundary conditions, total energies of such spirals are accessible without increasing the unit cell size beyond that at $\mathbf{q} = 0$.

Global magnetization rotation

- Let's drop spin-orbit coupling from the Hamiltonian
- Then, H does not contain spin operators, and the wavefunctions look like $\Psi\left(r_i, \sigma_i\right) = \chi\left(\sigma_i\right)\varphi\left(r_i\right)$
- The total spin operator effects a global rotation of the spin wavefunction, preserves its permutation symmetry
- Hence, the total spin operator applied to an eigenstate from the Fock space produces a degenerate eigenstate within the Fock space
- This is preserved in DFT (*xc* functional is invariant under rotation of the magnetization density)
- **How does this help us map the energies of noncollinear spin configurations?**

Generalized Bloch theorem

- One can attach an operator rotating $\mathbf{m}(\mathbf{r})$ (denote it D_φ) to any space group operator g, and then all gD_φ commute with H

$$D_\varphi = \begin{pmatrix} e^{-i\varphi} & 0 \\ 0 & e^{i\varphi} \end{pmatrix}$$

- Generalized translation group:
  - Select a common rotation axis (usually chosen as the z axis)
  - Attach D_φ to all translations $T_\mathbf{R}$ with $\varphi = \mathbf{q}\mathbf{R}$, i.e. redefine $T_\mathbf{R} \rightarrow D_{\mathbf{q}\mathbf{R}} T_\mathbf{R}$
  - The generalized translation group is Abelian (and commutes with H)
- Generalized Bloch theorem follows:
  - We can find all wavefunctions as eigenstates of generalized translations with a given $\mathbf{q}$, and thereby a state with $\mathbf{M}(\mathbf{r})$ invariant under them
- These are spin spirals; ground states under a constraint
- In general constraining fields are needed (otherwise such eigenstates generally do not exist!)

Magnetic symmetry

Magnetic space (or point) group can contain regular symmetry operations plus their combinations with time reversal R
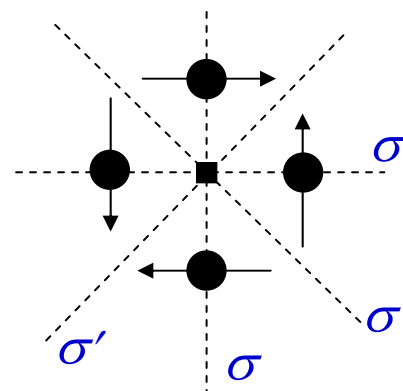
(1) R is in the group – non magnetic or AFM (for point groups)

(2) R does not appear at all

(3) Index-2 subgroup H of a regular space group G:
Magnetic point group is formed as $M = H + Rg_1H$
2 cosets – one without R (includes E), another one with R
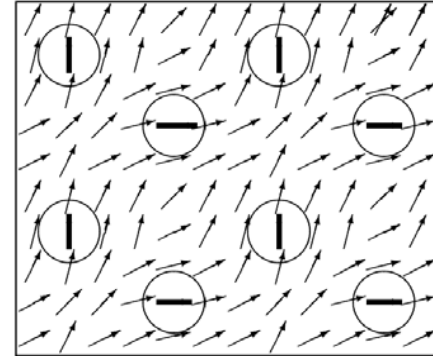
Magnetic symmetry is not implemented in FLEUR

Examples

4mm

$H = C_{2v}$

4'mm'
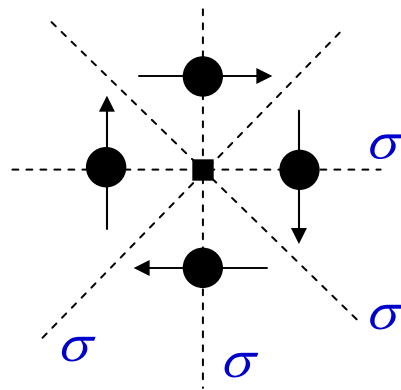
Non-collinear magnetism in FLEUR

- "Hybrid approach"
  - General $\mathbf{m}(\mathbf{r})$ outside the MT spheres
  - Collinear $\mathbf{m}(\mathbf{r}) = m(\mathbf{r})\,\mathbf{e}_i$ inside the MT spheres
- Augmentation orbitals in MT's:
  - Local frame with spin quantization axis along $\mathbf{e}_i$
  - V_{xc} is diagonal in this frame ($\mathbf{B}_{xc} \parallel \mathbf{e}_i$)
  - Orbitals $\psi_{lm\sigma}(\mathbf{r}) = \varphi_{l\sigma}(r)Y_{lm}$ and $\dot{\varphi}_{l\sigma}(r)Y_{lm}$ in each MT
- Interstitial region:
  - Plane waves $e^{i(\mathbf{k}+\mathbf{G})}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $e^{i(\mathbf{k}+\mathbf{G})}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ in the global frame
- Basis function:
  - Plane wave augmented by a linear combination of $\psi_{lm\sigma}(\mathbf{r})$ with both spins; both Ψ and $\partial\Psi/\partial r$ matched at the MT boundary
- Hamiltonian matrix off-diagonal; both spins mix
- Spin density matrix $\rho_{\alpha\beta} = \sum_{v \in occ} \psi_{v\alpha}^*(\mathbf{r})\psi_{v\beta}(\mathbf{r})$
- Magnetization $\mathbf{m}(\mathbf{r})$ in MT's projected onto $\mathbf{e}_i$; collinear $\mathbf{B}_{xc}(\mathbf{r})$ in MT

Non-collinear magnetism in FLEUR: Options

- Constraining fields
  - Effective field $\mathbf{B}_{eff}(\mathbf{r}) = \mathbf{B}_{xc}(r) + \mathbf{B}_{ci}$ in MT approximated as collinear
  - $\mathbf{B}_{ci}$ adjusted to enforce the local moment directions specified by user
- Relaxation of the spin configuration
  - User defines initial local moment directions (not local minimum of E)
  - Output spin density used to find the transverse components of $\mathbf{M}_i$
  - Spin directions are rotated (mixing specified by user)
  - Repeated until self-consistent directions $\mathbf{e}_i$ are found (minimum of E)
- If neither $\mathbf{B}_c$'s nor relaxation is used, self-consistency is incomplete (except for special symmetric configurations), and energy is wrong
- Spin spirals
  - Spin rotation around the z axis (user must align rotation axis with z)
  - User specifies the spiral $\mathbf{q}$-vector
  - $\mathbf{B}_c$'s not implemented (thus not self-consistent except for a planar spiral)
- Calculation of Heisenberg model parameters
  - Automated calculation through spin spirals with many $\mathbf{q}$'s
  - "Force theorem" is used (not self-consistent)
  - **Results are valid only if the rigid spin approximation is valid**

Practical issues for magnetic insulators

- LSDA is always bad (small band gap or wrong ground state)
- LSDA+U often reasonable, but needs to be validated
- Exchange is sensitive to U and J parameters!

Example: Cr_2O_3

U	J_1	J_2	J_3	J_4	J_5
2.5	30.9	21.9	−0.60	−1.83	4.92
3.0	23.9	17.3	−1.26	−2.36	3.72
3.5	18.6	13.8	−1.74	−2.72	2.84
4.0	14.6	11.1	−2.11	−2.96	2.16
4.5	11.1	9.04	−2.41	−3.11	1.64
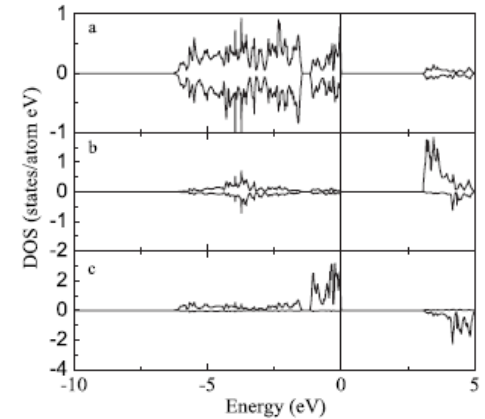
- U needs to be either carefully calculated (difficult) or adjusted to experimental data (band gap, structure, etc.)
- Manipulate the band positions to explore mechanisms of exchange

Cr_2O_3: Shifting the O-p states down has little effect on exchange parameters, hence superexchange is ruled out

V	U	Δ	++++	++−−	+−−+
0	3.5	4.5	130	124	66
−12	3.5	5.8	115	102	59
−12	2.5	5.6	154	128	74
−24	3.5	7.9	102	80	51
−24	2.15	7.7	145	110	71

Shi, Wysocki, KB, 2009

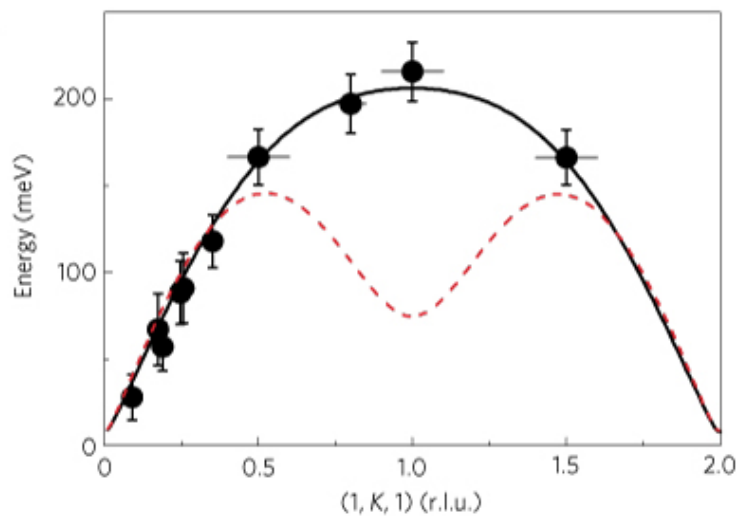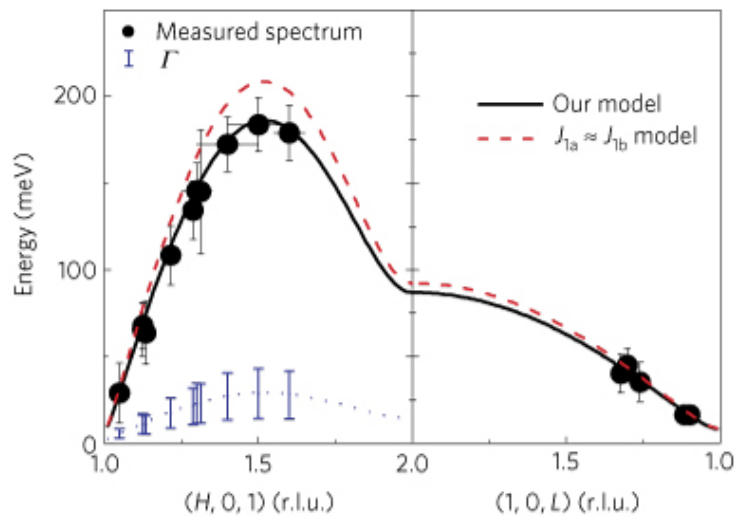# Ferropnictides (itinerant metals)

- New family of high-temperature superconductors, T_c up to 60 K
- Magnetism competes with superconductivity
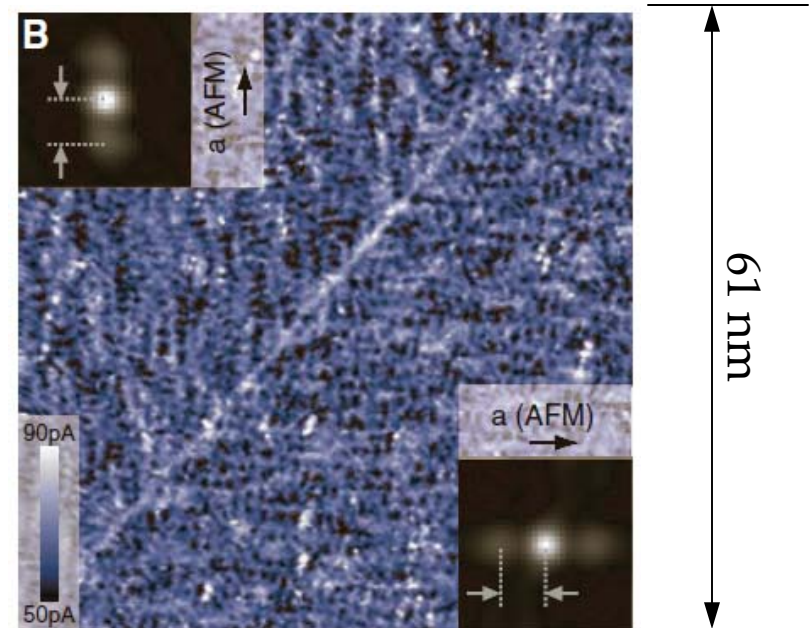- Pairing likely mediated by spin fluctuations
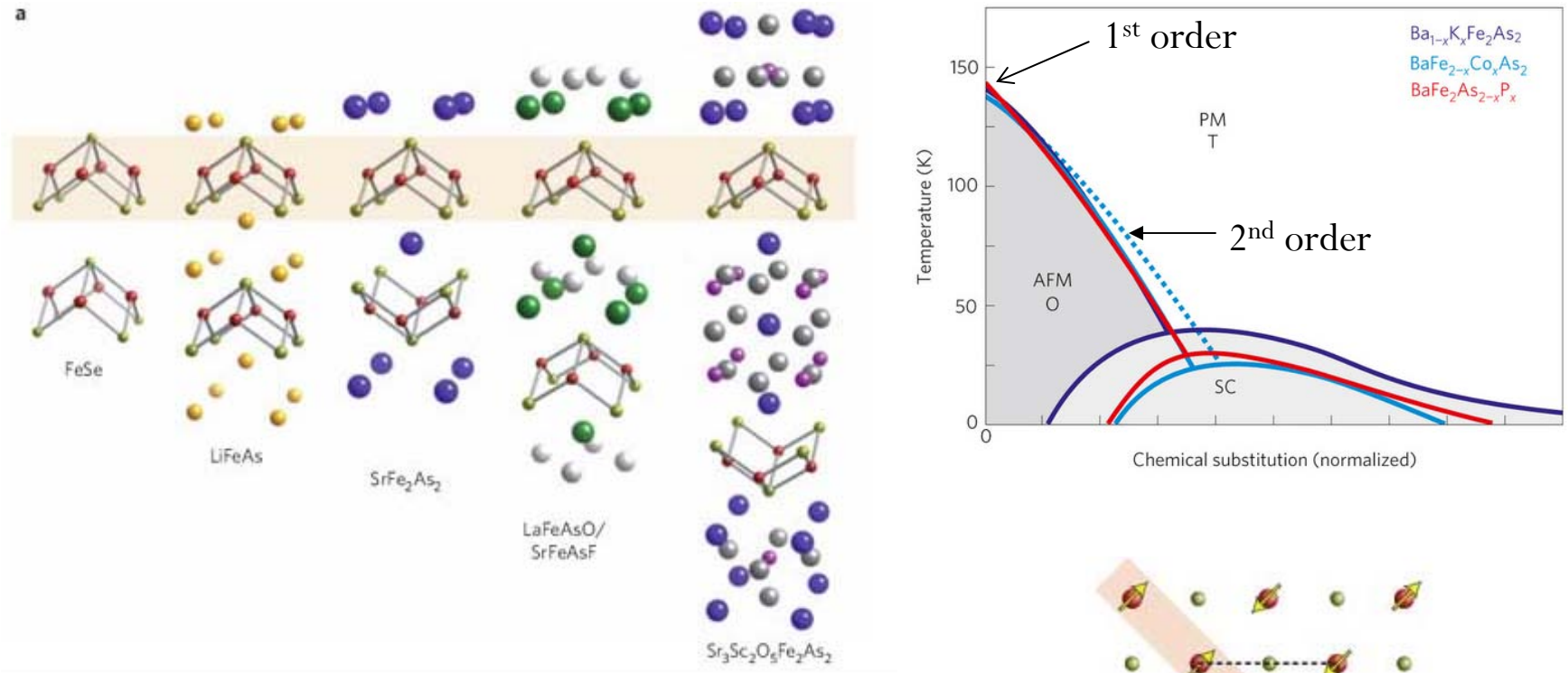
- **"Stripe" AFM ground state**
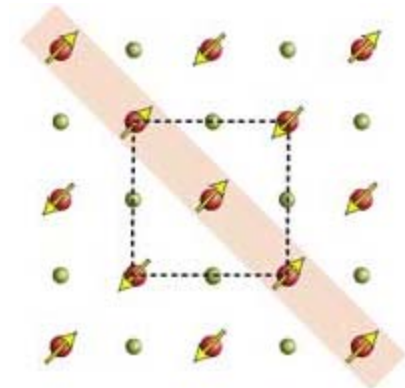
Heisenberg model fails! What is missing?

Zhao *et al.*, Nature Physics 2009

- Spin waves need $J_{1a} \neq J_{1b}$ to fit

- First-principles LR calculations confirm this

- Heisenberg model gives a continuously degenerate ground state; contradicts first-principles calculations

- Thin domain walls are observed

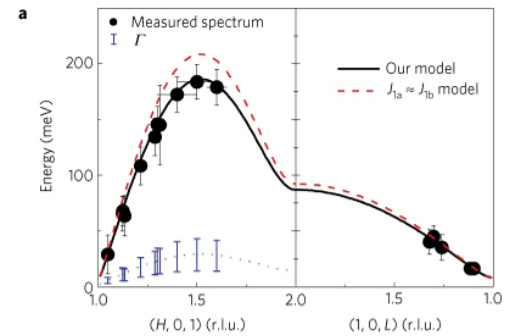Chuang *et al.*, Science 2010
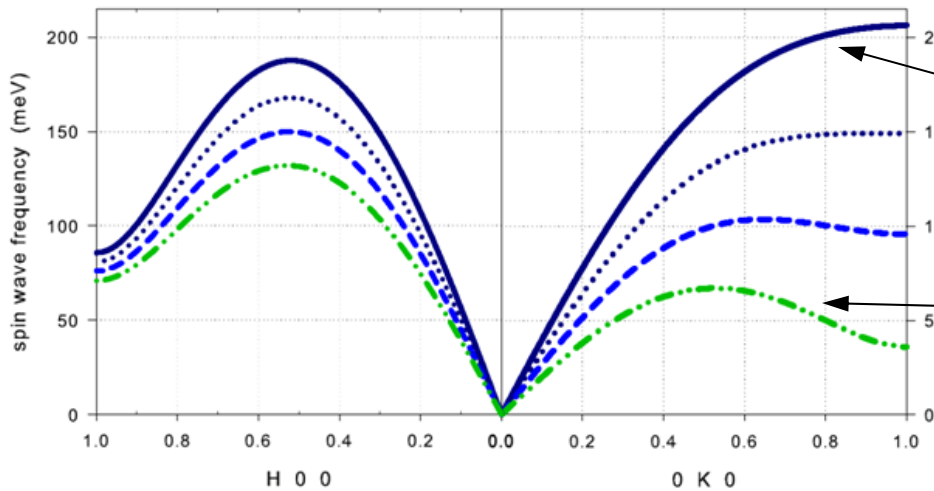
The solution: Biquadratic interaction

$$H = \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + K \sum_{ij}^{nn} (\mathbf{S}_i \cdot \mathbf{S}_j)^2$$

Reinterpretation of linear response results: $\tilde{J}_{ij} = -(\mathbf{S}_i \cdot \mathbf{S}_j)^{-1} \dfrac{\partial^2 H}{\partial \theta_{ij}^2} = J_{ij} - 2K_{ij}S^2 \mathbf{e}_i \cdot \mathbf{e}_j$
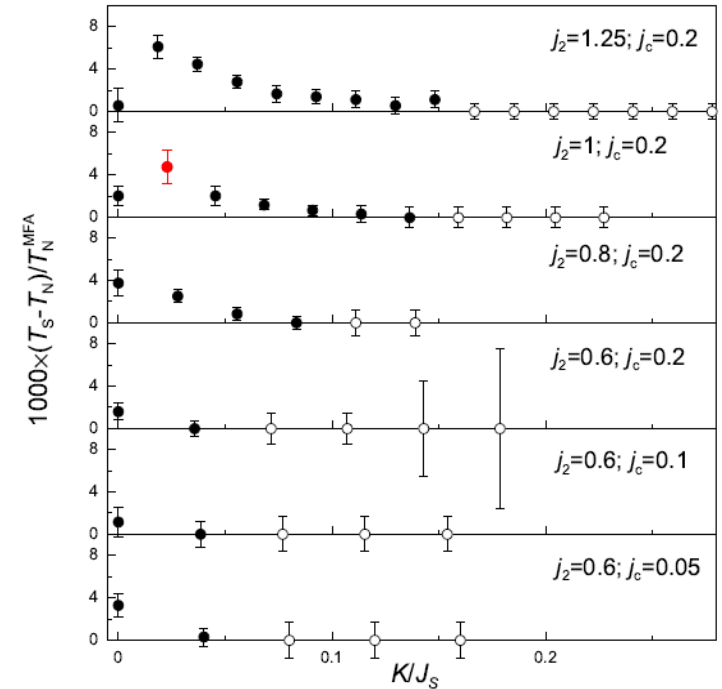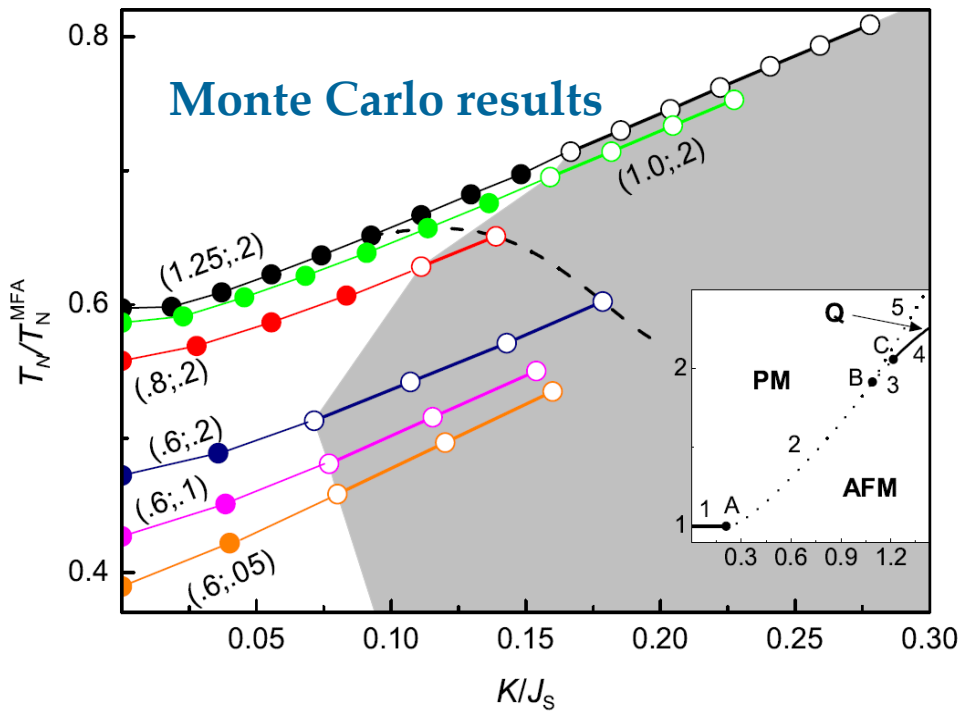
Explains dependence of J_{ij} on local moment
Restores energy barrier between stripe domains
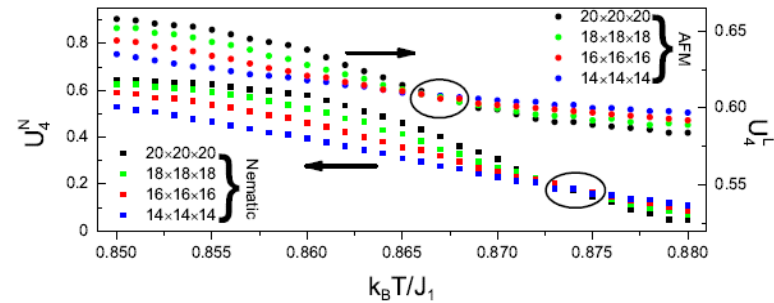Parameters from spin waves: J_1-K-J_2-J_c model
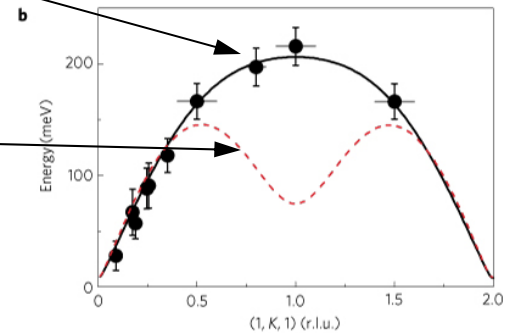
Thermodynamics of the J_1-K-J_2-J_c model

Monte Carlo results

T_c for CaFe$_2$As$_2$:   90 K predicted
                           170 K experiment

May indicate that the (bare) local moment is higher than (renormalized) measured

- **Consistent, satisfactory model of magnetism**
- **Large K indicates strong electron-spin fluctuation coupling: pairing mechanism?**

Nematic phase?

Wysocki, KB, Antropov, arXiv:1011.1715

Warnings

- Heisenberg model sometimes fails (sometimes miserably)
- Why classical spins? There is no good justification
- Thermodynamic properties of itinerant metals are inaccessible to current techniques
- "Good agreement with experiment" often coincidental