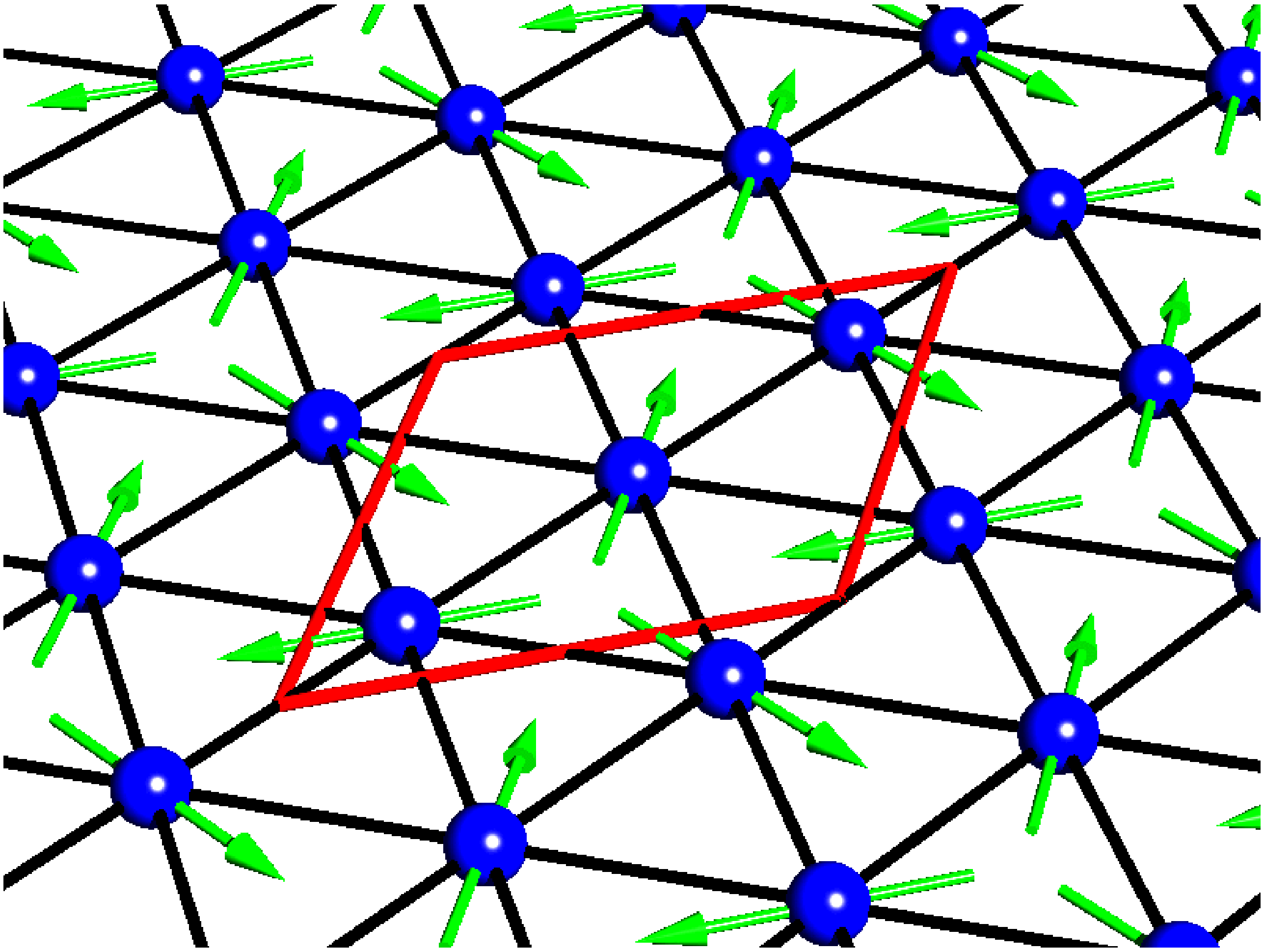
Non-collinear spins in electronic structure theory

Basic theory and some simple examples



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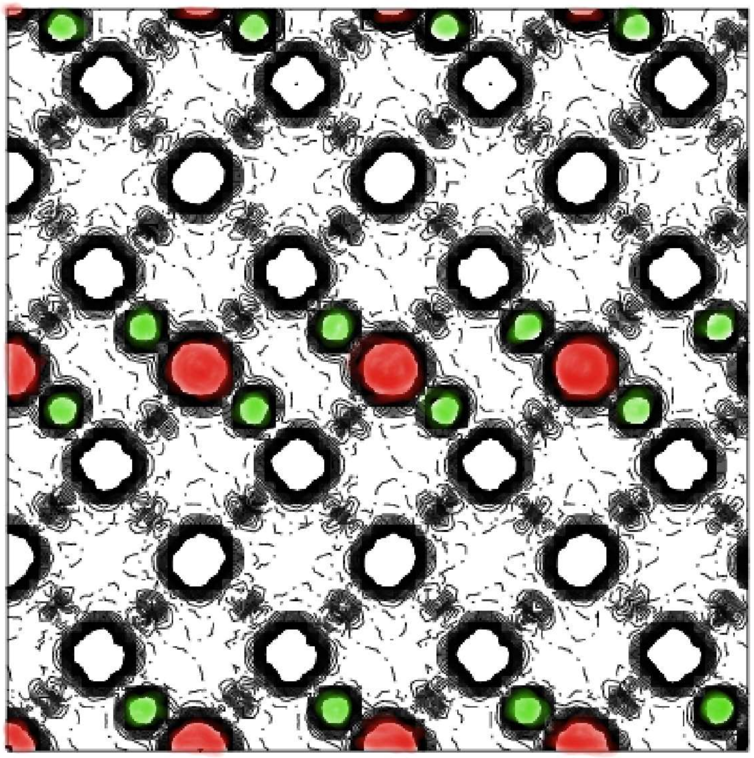
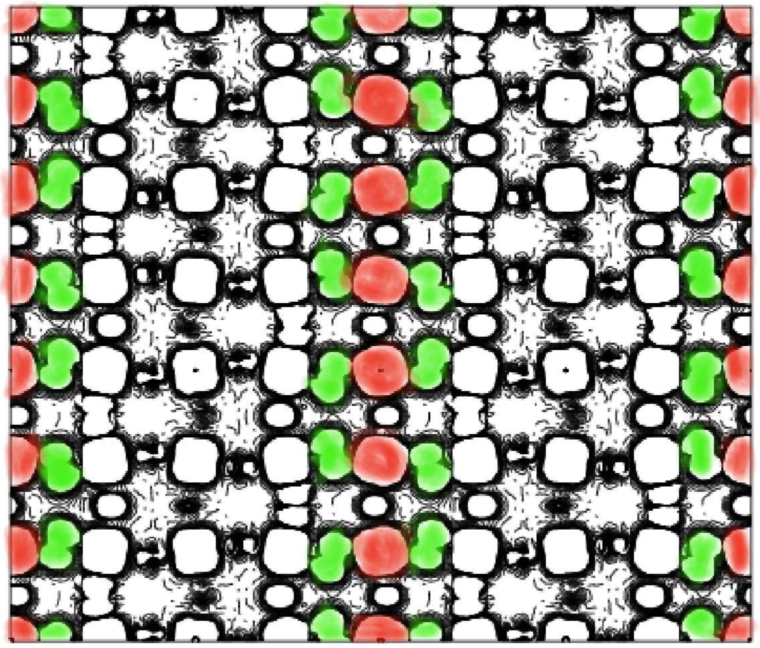
$La_{0.5}Ca_{0.5}MnO_3$ spin density

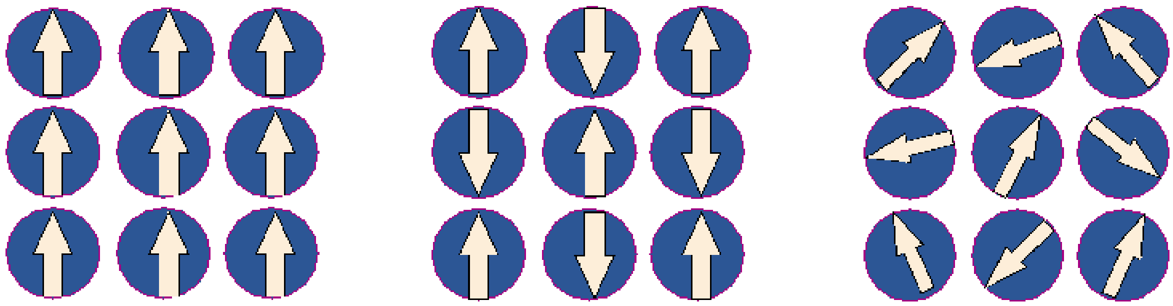
xz plane



xy plane



Non-collinear spins



• Many magnetic materials can be superficially characterized by atomic moments (or electron spins, in an itinerant picture) all aligned, parallel or antiparallel to some direction in space (the global quantization axis).

• In reality the direction of the magnetization can vary from point to point in space. This is not taken into account in most implementations of density functional theory.

• There are all sorts of interesting phenomena one could calculate using generalized theories which account for the possibility of vector magnetization fields.

When are non-collinear calculations useful?

Some examples

- Coherent helical, spiral and canted structures e.g. spiral spin phases in fcc iron, chromium and various lanthanides arising due to competing exchange interactions from different neighbours and/or spin-orbit effects. Also seen in finite systems such as metal clusters.

- Complex structures occuring in topologically frustrated antiferromagnets e.g. triangular lattice of Mn in ultrathin films on Cu(111).

- Amorphous systems, disordered crystals, spin glasses

- Magnetic excitations such as spin waves

- Intermetallics: Mn_3Sn, γ-FeMn, $RhMn_3$, $PtMn_3$, Mn_3GaN, Fe_3Pt

- Domain walls and magnetic multilayers

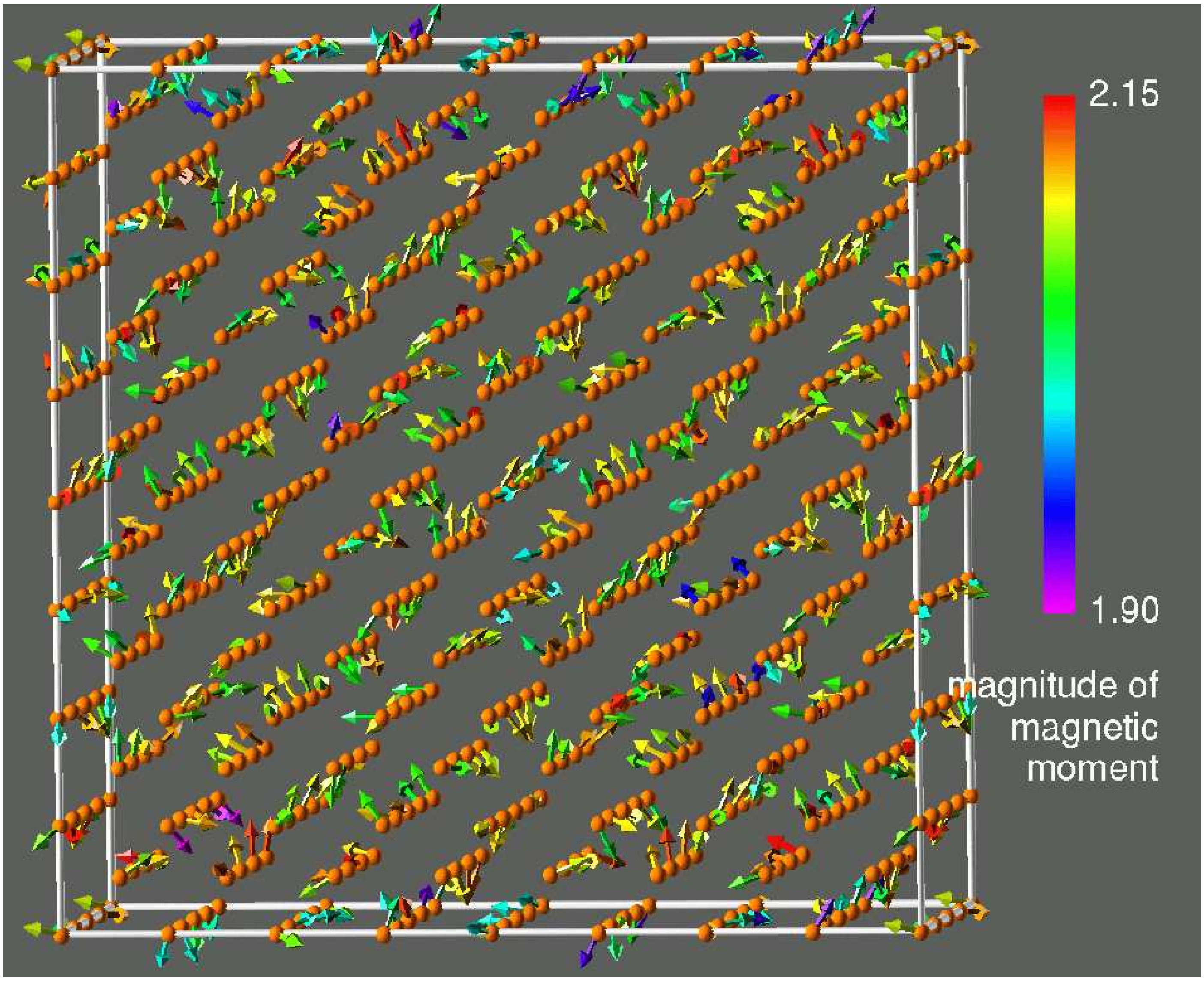
- Spin fluctuations at finite temperatures. Paramagnetic phases of e.g. iron above the Curie temperature.

- Ground state of free electron gas in HF approximation is static helical spin density wave (Overhauser 1960).

- Invar effect in e.g. fcc alloys of iron and nickel

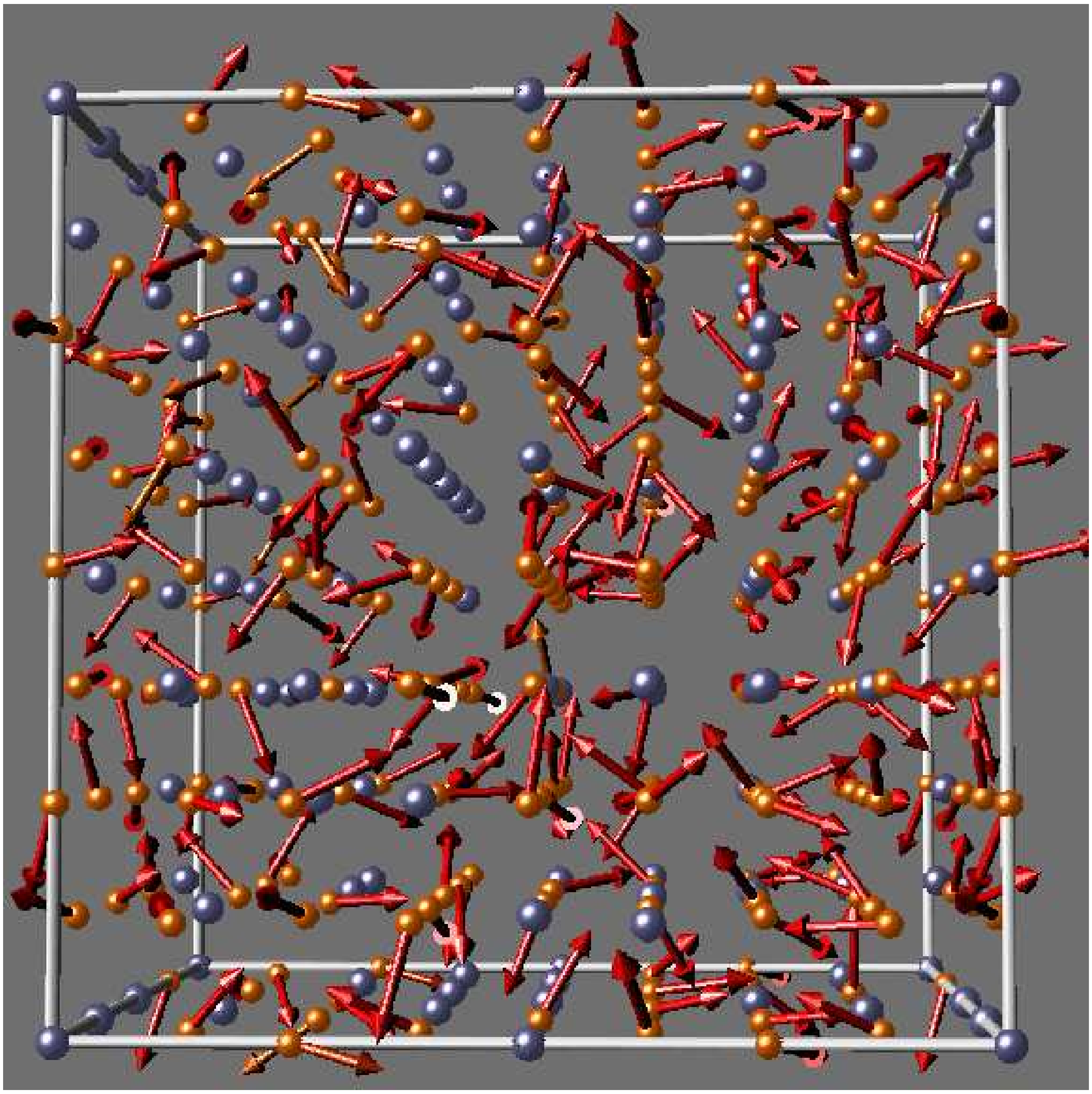
Paramagnetic bcc Fe

512 atoms

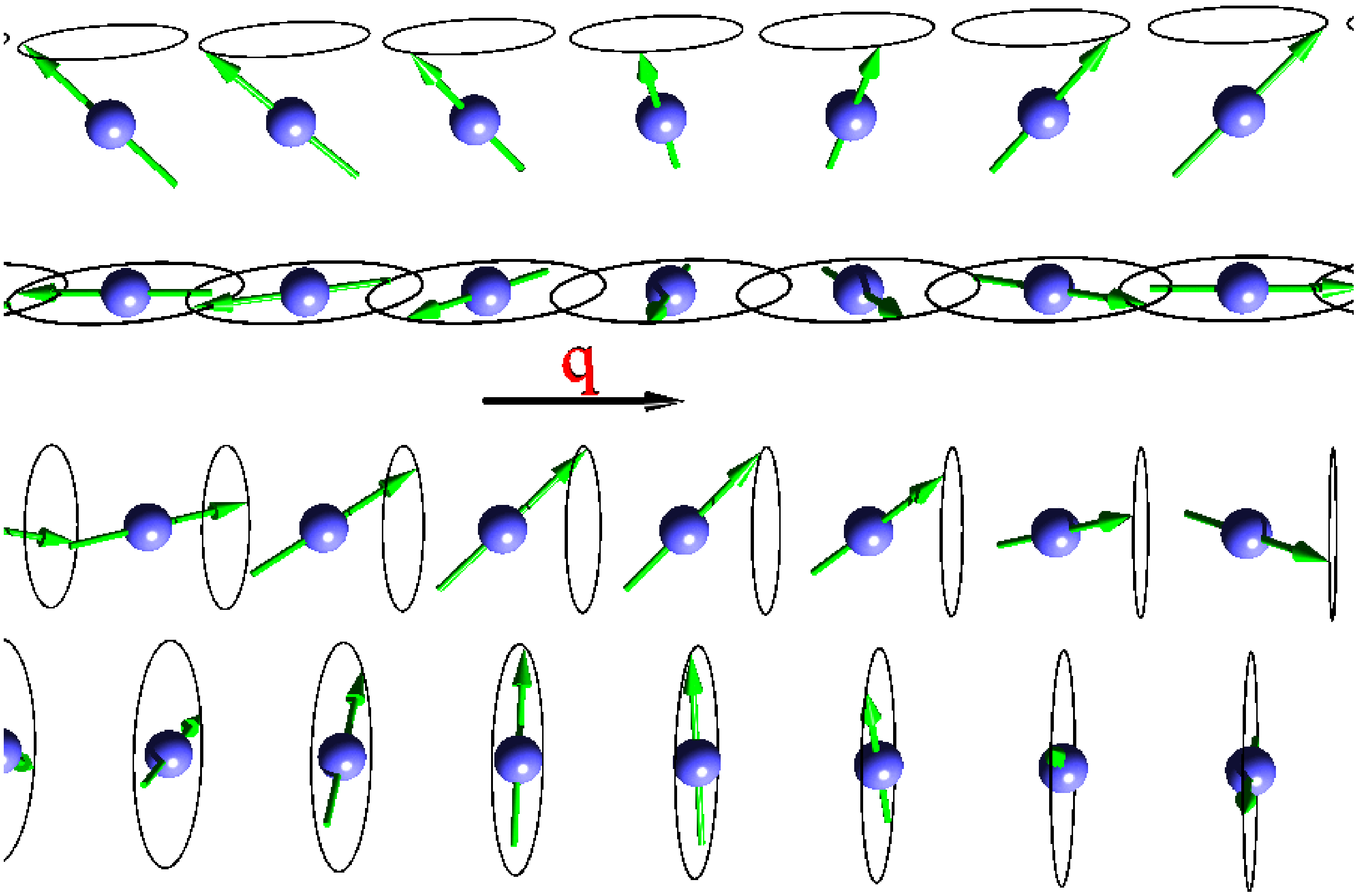


Disordered $Fe_{65}Ni_{35}$ alloy

Invar effect

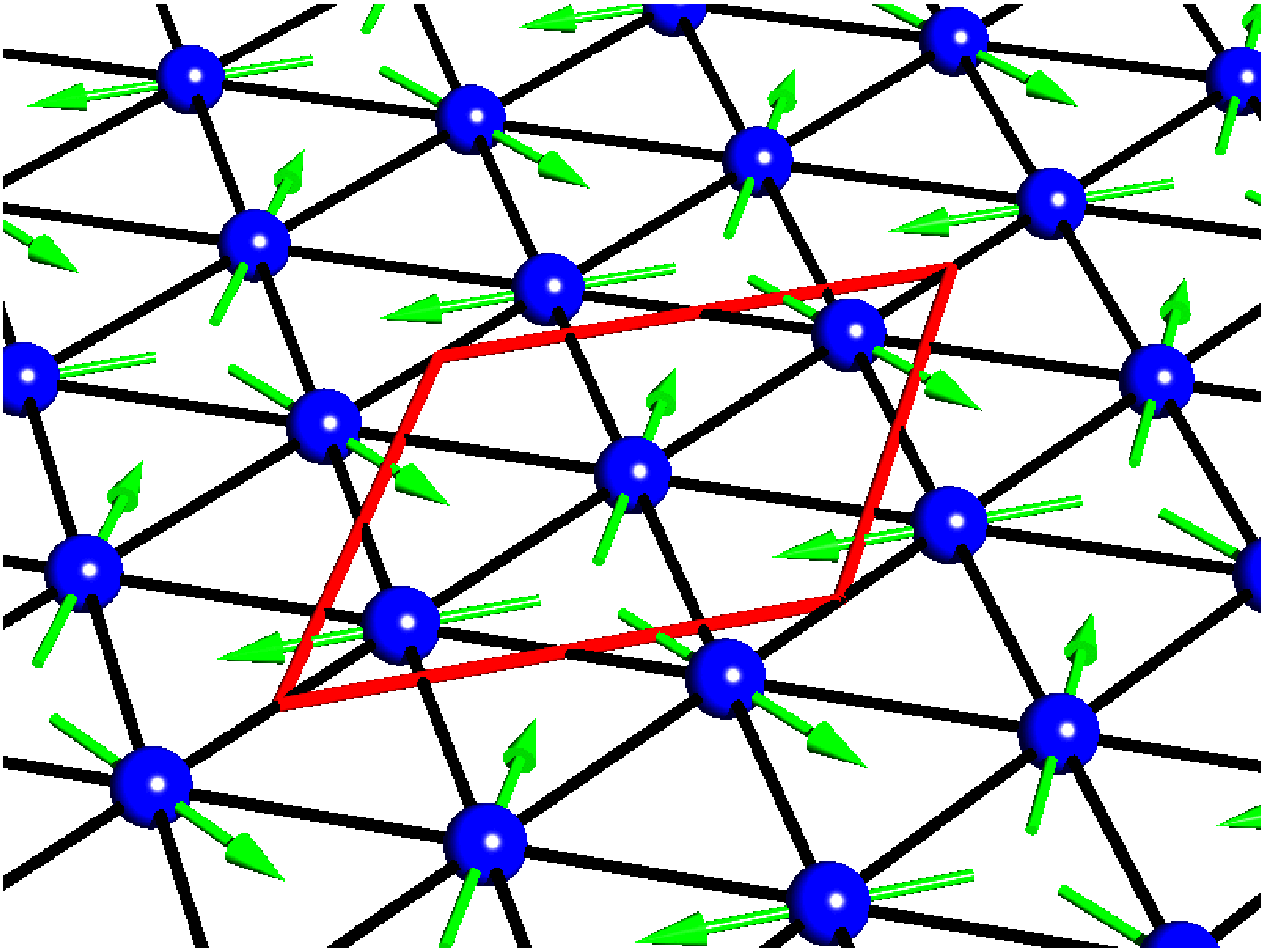


Spin waves



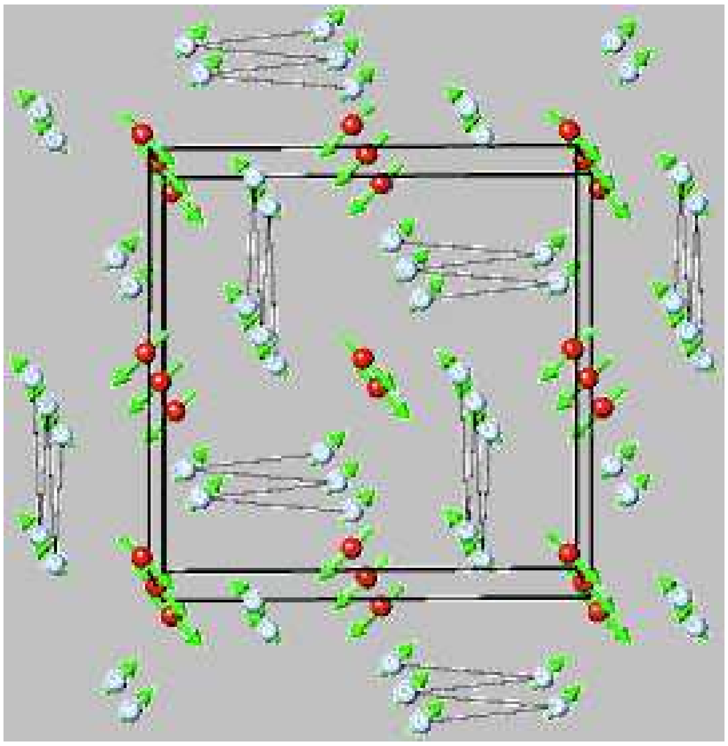
Spin frustration

e.g. Mn or Cr layers on Cu(111) surface



Competing exchange and spin-orbit effects

CuB_2O_4



Model Hamiltonians

Until recently non-collinear problems were investigated theoretically mostly with model Hamiltonians of localized magnetic moments:

Heisenberg model

$$\hat{H}_{Heisenberg} = -\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$$

Assumes localized moments represented by vector observables of constant length firmly attached to a given atom in the crystal and coupled by exchange constants.

Ising model

$$\hat{H}_{Ising} = -\sum_{ij} J_{ij} S_z^i S_z^j$$

Spin-up/spin-down only. Obviously analagous to standard spin-polarized DFT/UHF cases. Can show (e.g. in simplest case with one coupling constant and z neighbours): $\Delta E(\uparrow\uparrow - \uparrow\downarrow) = 2S^2Jz$

$\boxed{\text{First-principles equivalent of the Heisenberg model?}}$

Non-collinear spins in practice

• Until recently, most modern electronic structure codes have been completely incapable of treating problems involving non-collinear spins. We can do spin-polarized calculations, but these deal with the *spin density* which can be loosely defined as "excess of up-spin electrons compared with down-spin electrons", or, "density of spin angular momentum around the z axis". There is no sense in which this has a vector nature.

• Often not clear *a priori* how full vector magnetization will affect results assuming collinear magnetism, since not much work done. More research required.

• None of the codes used in TCM (CASTEP, CRYSTAL, PARATEC, ONES, CASINO, GAUSSIAN, CPMD) can do this. Codes which can include:

- ABINIT (pseudopotential plane-wave DFT)

www.mapr.ucl.ac.be/ABINIT/

- WIEN (FLAPW DFT)

www.wien2k.at/index.html

- FLEUR (FLAPW DFT)

www.flapw.de

- SIESTA ($\mathcal{O}(N)$ DFT)

www.uam.es/departamentos/ciencias/fismateriac/siesta/

- VASP (pseudopotential plane-wave/PAW DFT)

cms.mpi.univie.ac.at/vasp/

- LMTART (LMTO DFT)

www.mpi-stuttgart.mpg.de/andersen/activities/95-00.html

Spin operators

Three basic properties for spin-$\frac{1}{2}$ particles:

- Have intrinsic vector property that does not depend on space coordinates

- This vector has the characters of an angular momentum

- If one of the components of the spin is measured, the result can be only one of its two eigenvalues, $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$.

These properties can be described using a two component wave function and corresponding 2×2 matrices to represent the spin operators.

Spin vector operator: $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$

Define Pauli matrices $\hat{\sigma}_i$ where e.g. $\hat{S}_z = \frac{1}{2}\hbar\hat{\sigma}_z$.

Pauli matrices in the $\hat{\sigma}_z$ representation

Choose z-direction as the 'direction of quantization' i.e. the axis which the orientation of the spin is related to. Then the spin functions are eigenfunctions of $\hat{\sigma}_z$, which is diagonal with eigenvalues (1,-1).

$$\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Then, from angular momentum commutation relations, can derive:

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Unit vectors $\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\beta = \begin{pmatrix} 0 \\ -1 \end{pmatrix}$

So $\hat{\sigma}_z\alpha = \alpha$, $\hat{\sigma}_z\beta = -\beta$, and e.g. $\hat{\sigma}_y\alpha = i\beta$ etc. in terms of eigenfunctions of $\hat{\sigma}_z$

Normally we choose a global spin quantization axis to describe the whole system. In a crystal with non-collinear spins, we consider that the axis can rotate from point to point $\Longrightarrow$ the orbitals are no longer eigenfunctions of the $\hat{S}_z$ operator.

Spinor orbitals

Basic difference between collinear and non-collinear magnets is the absence in the non-collinear case of a natural spin quantization axis for the whole crystal. As a result each one-electron state must be treated as a 2-component spinor function.

Standard spin-$\frac{1}{2}$ rotation matrix

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

Represent spinor wave function as

$$\begin{pmatrix} \Psi_1(\mathbf{r}) \\ \Psi_2(\mathbf{r}) \end{pmatrix} = \mathbf{U}(\theta(\mathbf{r}),\phi(\mathbf{r})) \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

where the angles determine the direction of the spin moment of the given state at point $\mathbf{r}$.

Orbitals

Single determinants of one-electron spin orbitals.

- Restricted form All orbitals Ψ_n are pure space-spin products of the form $\phi_n(\mathbf{r})\alpha$ or $\phi_n(\mathbf{r})\beta$ and are occupied in pairs with a common orbital factor $\phi_n(\mathbf{r})$. This is what is generally done in electronic structure calculations of spin-unpolarized systems.

- Unrestricted form Spin orbitals Ψ_n no longer occupied in pairs but still pure space-spin products $\phi_n(\mathbf{r})\alpha$ or $\bar{\phi}_n(\mathbf{r})\beta$. However, now have different spatial factors $\phi_n(\mathbf{r})$ and $\bar{\phi}_n(\mathbf{r})$ for different spins. This is what is usually done in electronic structure calculations of spin-polarized systems.

- General unrestricted form No longer restrict to simple product form. Each spin orbital now a 2-component complex spinor function: $\psi_n(\mathbf{r}) = \phi_n^\alpha(\mathbf{r})\alpha + \phi_n^\beta(\mathbf{r})\beta$.

Spinor orbitals and GUHF theory

In Hartree-Fock theory, the requirement that energy be stationary subject to orthonormality of spin orbitals implies matrix GUHF equation:

$$\begin{pmatrix} \mathbf{F}_{\uparrow\uparrow} & \mathbf{F}_{\uparrow\downarrow} \\ \mathbf{F}_{\downarrow\uparrow} & \mathbf{F}_{\downarrow\downarrow} \end{pmatrix} = \begin{pmatrix} \mathbf{c}_{\uparrow} \\ \mathbf{c}_{\downarrow} \end{pmatrix} = \epsilon \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} \mathbf{c}_{\uparrow} \\ \mathbf{c}_{\downarrow} \end{pmatrix}$$

Get normal UHF equations by striking out all off diagonal blocks $(\uparrow\downarrow), (\downarrow\uparrow)$. There are then two sets of equations:

$$\mathbf{F}_{\uparrow}\mathbf{c}_{\uparrow} = \epsilon \mathbf{S}\mathbf{c}_{\uparrow}, \mathbf{F}_{\downarrow}\mathbf{c}_{\downarrow} = \epsilon \mathbf{S}\mathbf{c}_{\downarrow}$$

The only coupling between $\uparrow$-spin and $\downarrow$-spin solutions arises indirectly from the electron interaction matrices which involve contributions to the total density from both spins.

Vector magnetization density

The spin density as usually defined is just one component of a vector density:

$$\mathbf{m}(\mathbf{r}) = [m_x(\mathbf{r}), m_y(\mathbf{r}), m_z(\mathbf{r})].$$

For a spin eigenstate with spin quantized in the z-direction, m_x and m_y are identically zero at all points in space. So regular SDFT is a simplification of the full treatment with zero off-diagonal elements of the 2×2 spin-density matrix (see later).

Evaluate local magnetization self-consistently by calculating the expectation values of the Pauli spin matrices using the spinor orbitals

$$m_k(\mathbf{r}) = \sum_i^{occ} \psi_i^*(\mathbf{r}) \sigma_k \psi_i(\mathbf{r})$$

Generalized Hohenberg-Kohn theorem

Original Hohenberg-Kohn-Sham theory developed only for spinless case. Quantum mechanics guarantees that for a given interaction and particle number, the potential in which the particles move determines the ground state many-body wave function, which in turn determines the ground state density (by simple integration). Essence of first HK theorem is that this mapping is invertible:

$$v(\mathbf{r}) \Longleftrightarrow \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N) \Longleftrightarrow \rho(\mathbf{r})$$

Second HK theorem gives energy variational principle: the ground state energy of a many electron system can be obtained as the minimum of the energy functional:

$$E[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + F[\rho]$$

where $F[\rho] = T[\rho] + V_{ee}[\rho]$.

Particular approximations for $F[\rho]$ allow us to make a one-to-one mapping to a fictitious system of N non-interacting particles.

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V_{\text{eff}}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

Problem

The potentials of spin density funtional theory are not unique functionals of the spin densities, which implies that the exchange-correlation energy is not always a differentiable functional of the spin density.

Whole literature on this:

See e.g. Capelle/Vignale, Phys. Rev. Lett **86**, 5546 (2001).

Local spin density functional theory

Original LSDF theory (von Barth/Hedin 1972) was non-collinear in concept although most computations are limited to the collinear version of it. The Kübler group and the Sandratskii/Guletskii groups were the first to implement a simplified version of this in the late 1980s.

Instead of the density, the basic variable of DFT is a 2×2 density matrix $\rho(\mathbf{r})$ with elements $\rho_{\alpha\beta}(\mathbf{r})$.

$$\rho(\mathbf{r}) = \begin{pmatrix} \rho_{11}(\mathbf{r}) & \rho_{12}(\mathbf{r}) \\ \rho_{21}(\mathbf{r}) & \rho_{22}(\mathbf{r}) \end{pmatrix}$$

$\rho_{11} + \rho_{22}$: charge density
$\rho_{11} - \rho_{22}$: projection of the magnetization density on the global quantization axis
ρ_{12}, ρ_{21} : determine components of the magnetization density perpendicular to the quantization axis and are responsible for the non-collinearity of the magnetic structure
Can also express total density matrix as

$$\rho_{\alpha\beta}(\mathbf{r}) = \frac{Tr[\rho(\mathbf{r})]\delta_{\alpha\beta} + \mathbf{m}(\mathbf{r}) \cdot \sigma_{\alpha\beta}}{2}$$

Magnetization density

$$\mathbf{m}(\mathbf{r}) = \sum_{\alpha\beta} \rho_{\alpha\beta}(\mathbf{r}) \cdot \sigma_{\alpha\beta}$$

Methodologies

Get Kohn-Sham-like equations with a 2x2 potential matrix and 2-component spinor wave functions. The exchange-correlation potential is

$$V_{xc}^{\alpha\beta} = \frac{\delta E_{xc}[\rho_{\alpha\beta}]}{\delta \rho_{\alpha\beta}}$$

In the local approximation the spatial variation in the magnetization direction does not influence the exchange-correlation potential at a given point.

$$\begin{aligned} E_{xc}[\rho_{\alpha\beta}] &= \int \rho_{Tr}(\mathbf{r})\epsilon_{xc}[\rho_{\alpha\beta}(\mathbf{r})]d\mathbf{r} \\ &= \int \rho_{Tr}(\mathbf{r})\epsilon_{xc}[\rho_{Tr}(\mathbf{r}), |\mathbf{m}(\mathbf{r}|]d\mathbf{r} \end{aligned}$$

- Atomic sphere approximation Space is divided into spheres around each atom wherein there is only one local spin quantization axis and corresponding magnetization density. Stable magnetic structures are defined as the one that minimizes the total energy with respect to the quantization axes chosen as inputs to the calculation. Can't cope with intra-atomic non-collinear magnetism. Various ways to do this.

- General theory Fully unconstrained vector-field description of non-collinear magnetism : spin quantization axis of each state can vary with position.

Beyond simple local approximations

See e.g. Capelle/Oliveira, "Density functional theory for spin-density waves and antiferromagnetic systems", PRB **61**, 15228 (2000).

• In ferromagnetic state, local magnetization is on average same everywhere (and thus quite well described by a local approximation).
• Expect long-range spatial variation of the magnetic order in antiferromagnetic and non-collinear spin configurations implies strong *non-local* correlations, which are hard to account for in local or semi-local approximations to DFT.
• Incorporate this by extra variable, the staggered density, which supplements usual spin densities, and describes spin-dependent spatially non-local correlations between particles at sites $\mathbf{r}$ and $\mathbf{r}'$.

$$\rho_s(\mathbf{r},\mathbf{r}') = \langle \hat{\Psi}_\uparrow^\dagger(\mathbf{r}) \hat{\Psi}_\downarrow^\dagger(\mathbf{r}') \rangle$$

• Allows us to extract from the exchange-correlation energy one more term - the staggered Hartree term - as compared to conventional DFT or SDFT (which extract only non-interacting KE, T_s, and regular Hartree term U_H.
• Various levels of deriving functionals within this approach - see Capelle paper.

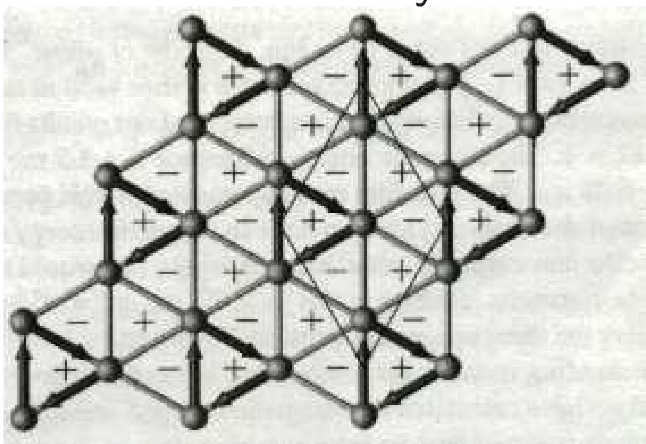
Other interesting things I don't have time to talk about

- spin-orbit coupling + relativistic
- symmetry and space-spin groups
- orbital moments
- spin dynamics
- magnetic susceptibility
- diamagnetic effects
- Dzyaloshinksii-Moriya interaction
- magnon spectra

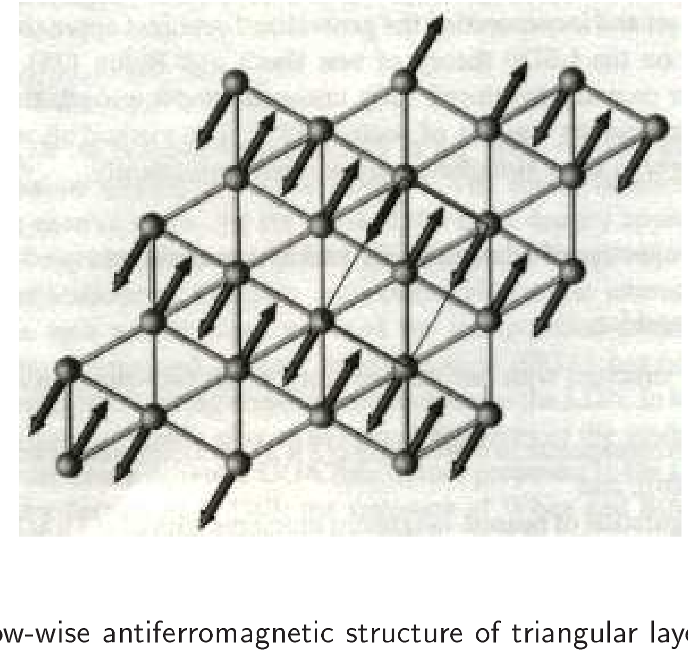
Example: triangular lattice spin frustration

"Fully unconstrained non-collinear magnetism in triangular Cr and Mn monolayers and overlayers on Cu(111) substrates"

Hobbs/Hafner, J. Phys.:Cond. Mat **12**, 7025 (2000)
Conditions : VASP code, DFT (GGA), plane-wave basis (270 eV), all-electron from PAW, fully-unconstrained non-collinearity ; atomic, electronic, and magnetic structures relaxed simultaneously and self-consistently.



Non-collinear magnetic structure of triangular layers : Heisenberg models with nearest-neighbour interactions (+ and - signs indicate helicities in the elementary triangles).



Row-wise antiferromagnetic structure of triangular layers.

Monolayer results

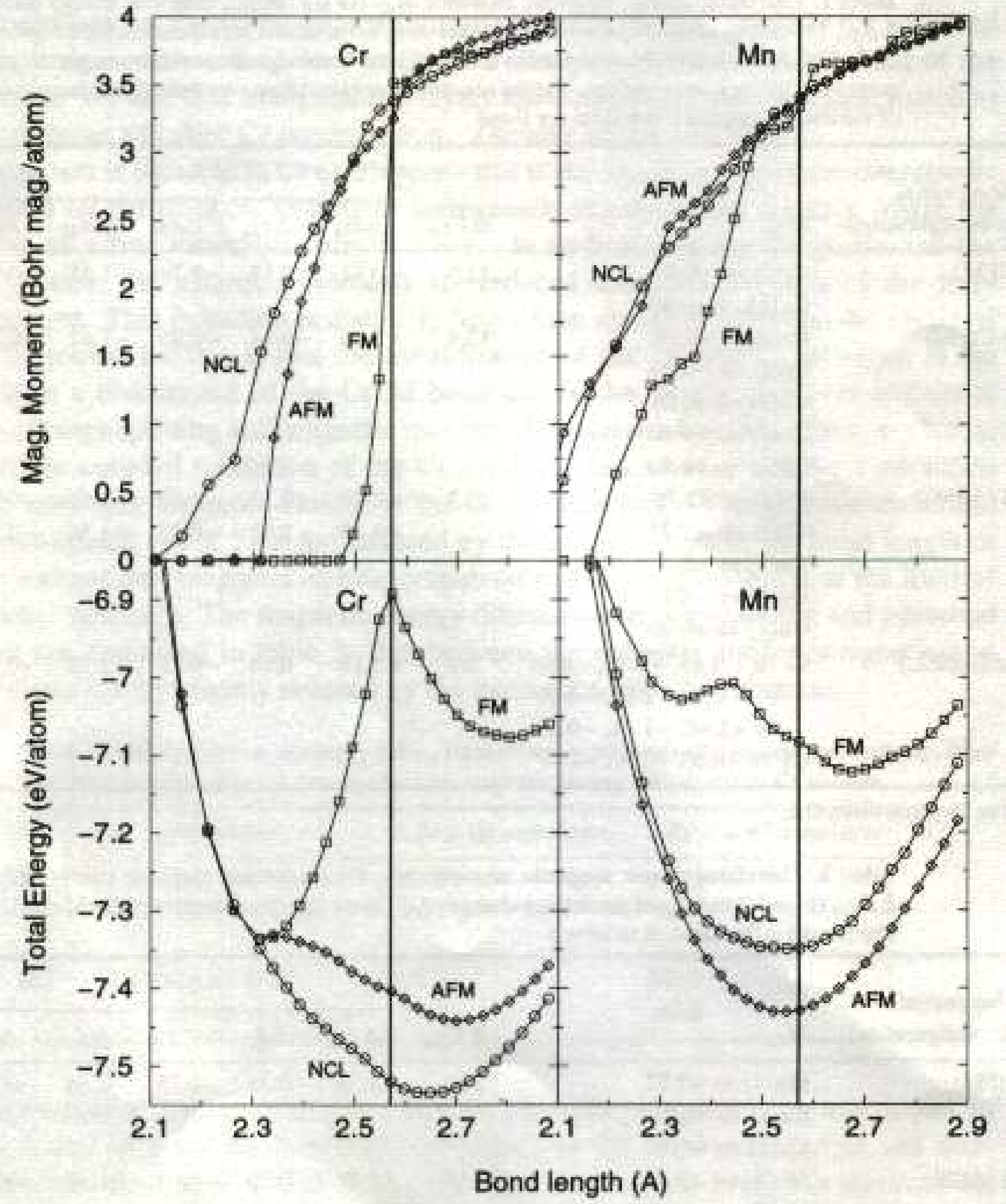
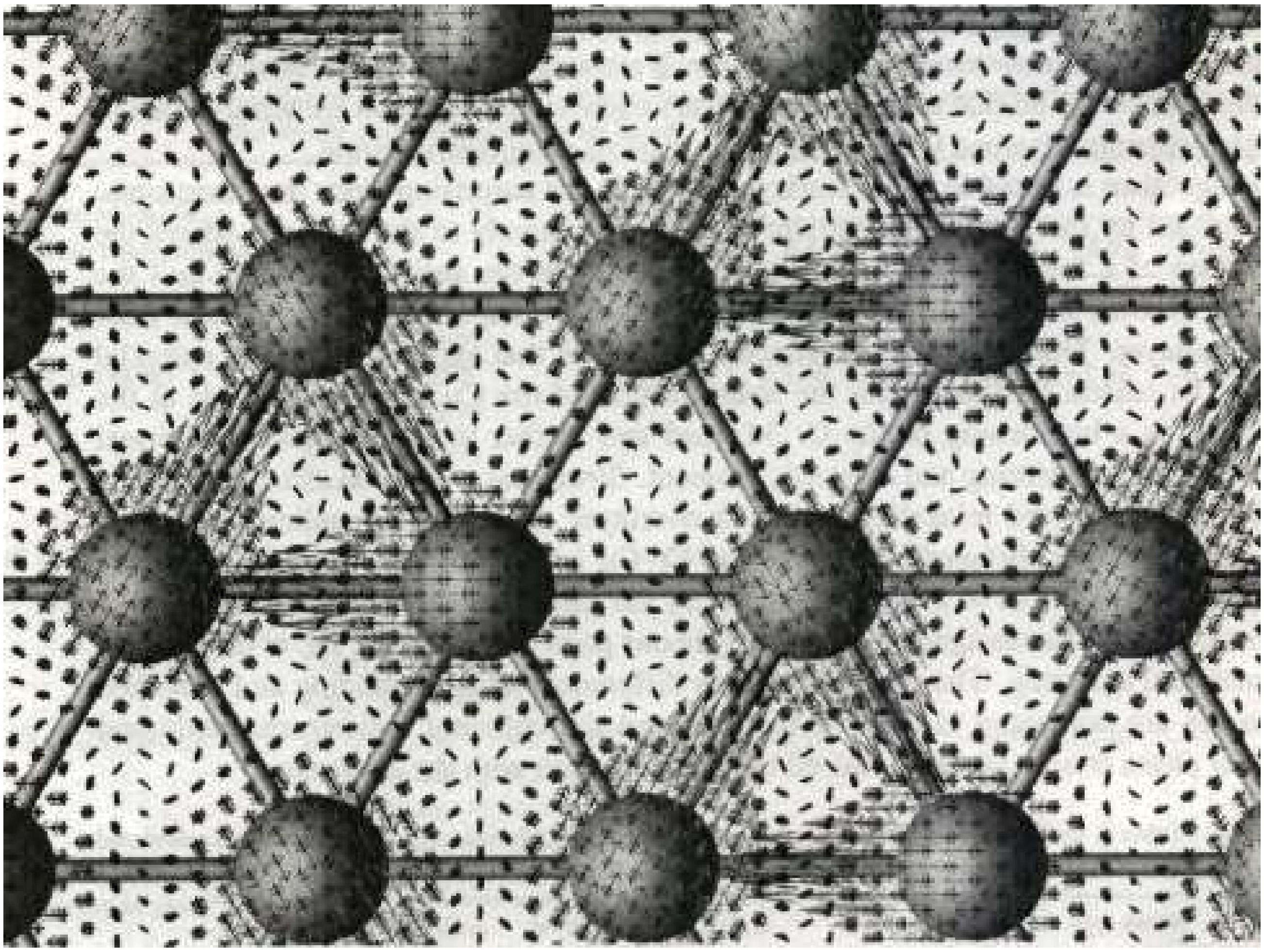
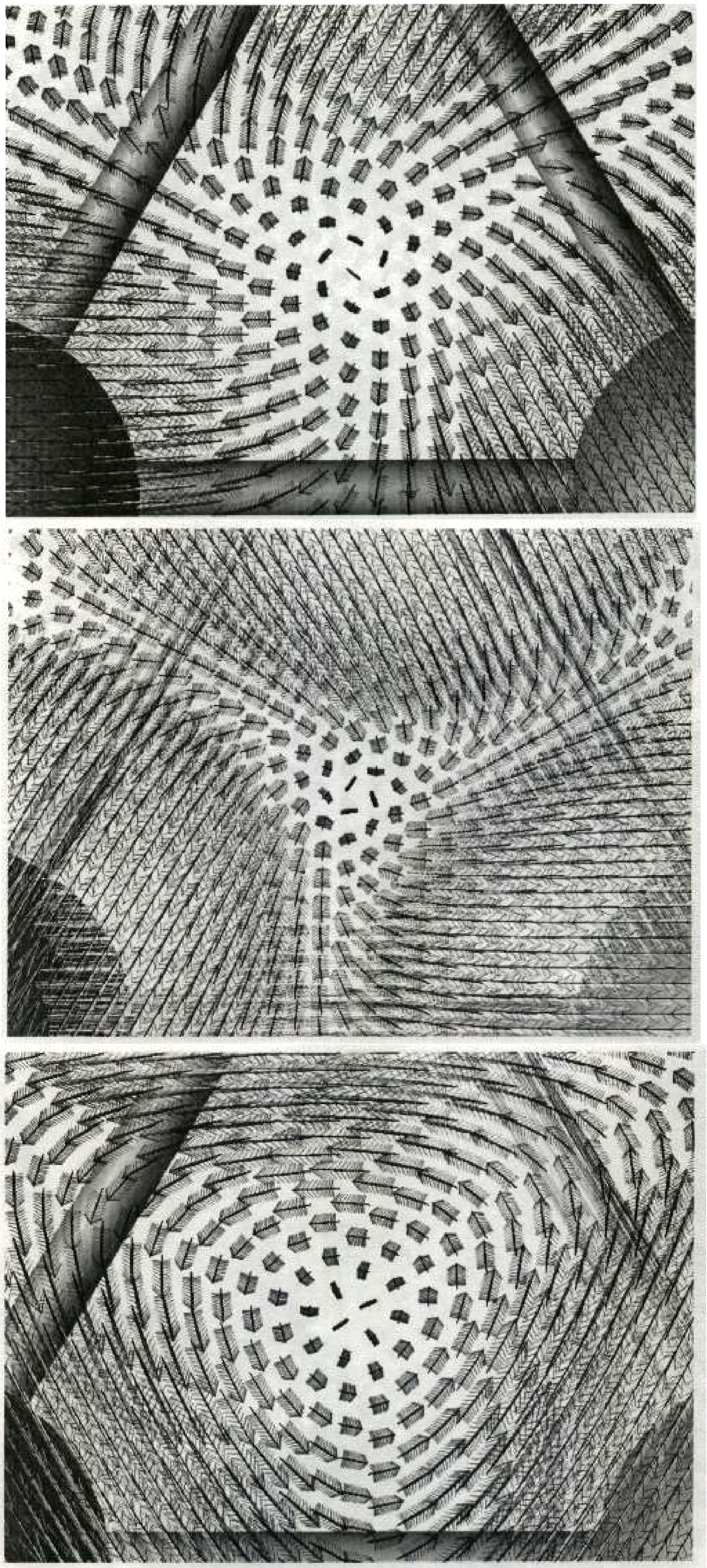


Figure 2. Total energy and magnetic moments of the ferromagnetic p(1 × 1), the antiferromagnetic c(2 × 2), and the non-collinear ($\sqrt{3} \times \sqrt{3}$) phases of free-standing triangular Cr and Mn monolayers as functions of the nearest-neighbour bond length. The vertical lines mark the lateral interatomic distance of a Cu(111) substrate.

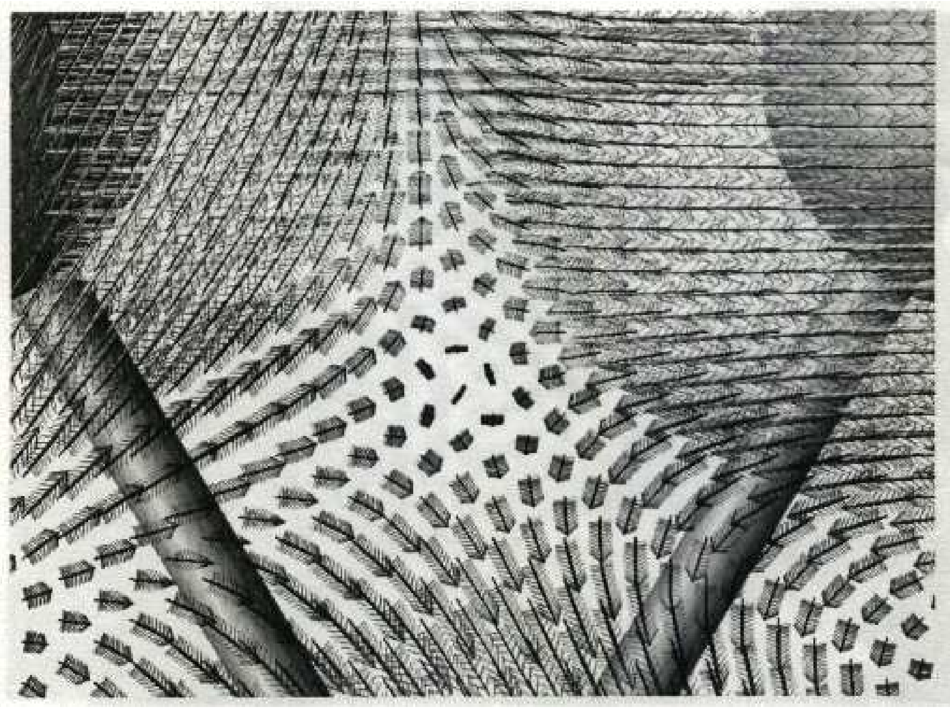
Magnetization densities



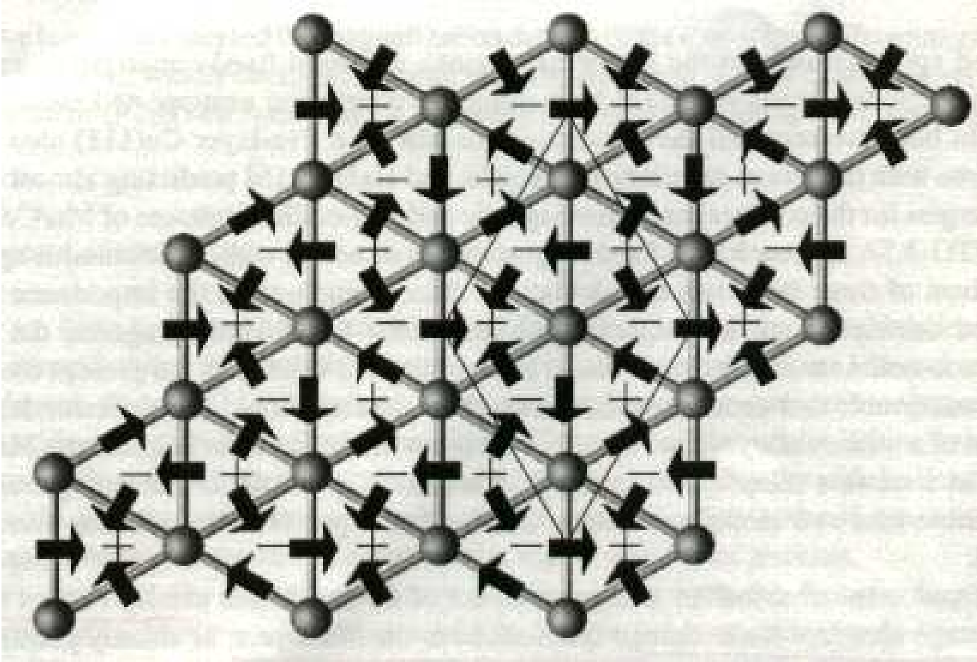
Vortices



Anti-vortex

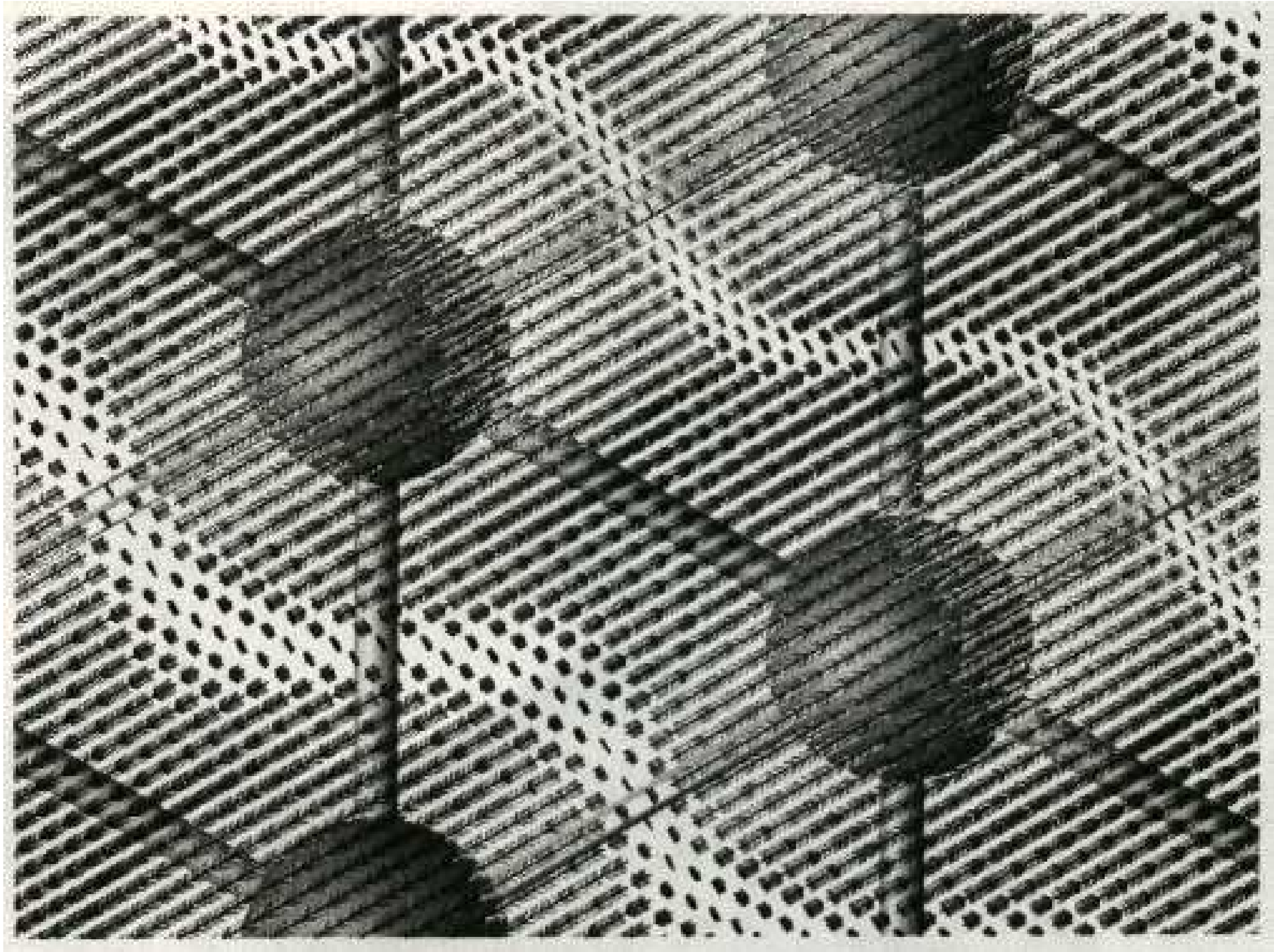


Direction of magnetic flux lines at the bond center



Thus, interesting symmetries in the vector field of magnetization densities, with three different types of vortex structure in the elementary triangles with positive helicity and anti-vortices in the triangles with negative helicities.

Row-wise antiferromagnetic state

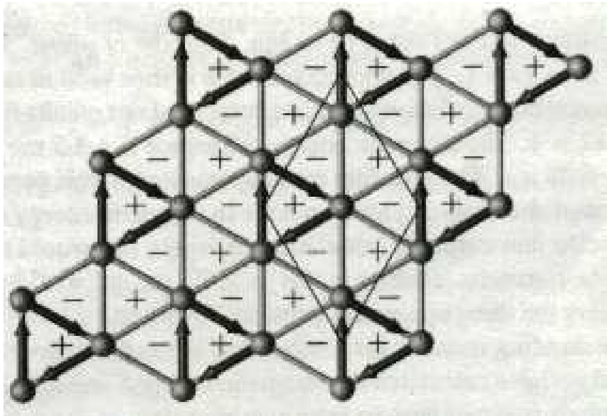


Basic points

As a whole the study clearly confirms the importance of relaxing the magnetization densities. Quite large effect on geometry and magnetic moments.

• For Cr, the ground state is non-collinear for both the free standing and adsorbed monolayers. However, for Mn the ground state is clearly the collinear antiferromagnetic (slightly surprising since contradicts Heisenberg model!).

• Difference in behaviour of Cr/Mn clearly related to the rather long-range nature of the exchange interactions in Mn layers.



• The existence of the three vortex types demonstrates the formation of a non-collinear magnetic structure in an *itinerant* system leads to a new type of broken symmetry unknown in the localized spin models.

Conclusions

• Problems involving non-collinear magnetism perfectly treatable with one-electron DFT methods. Large impetus to add this functionality to existing spin-polarized electronic structure codes.

Discussion points

• How can we get such a code in TCM? I presume it won't be in CASTEP any time soon..? Best code appears to be VASP - huge rivalry.. :-)

• Ongoing research : how we do formulate a quantum Monte Carlo theory of non-collinear magnetism?

$$\Psi = D^{\uparrow} D^{\downarrow} \exp\left(\mathcal{J}\right)$$

• Why are magnetization densities/non-collinear spins never mentioned in quantum chemistry? What is the analogy between the non-collinear DFT and the multireference quantum chemistry techniques?

• How much more expensive in terms of computer time is it to work with the spinor wave functions and to relax the magnetic structure self-consistently?