Density Functional Theory (DFT) Applied to Magnetism

Stefan Blügel

Peter Grünberg Institut and Institute for Advanced Simulation,
Forschungszentrum Jülich and JARA

MULTISCALE MODELING

Long wave length limit

$$\mathbf{m}_j = \mathbf{m}_i + \sum_\alpha \mathcal{R}_{ij,\alpha}\, \partial_\alpha \mathbf{m}_i + \ldots$$

- Spin Stiffness: $A \propto \sum_{j>0} J_{0j} R_{0j}^2$
- Spiralization: $\underline{\mathbf{D}} \propto \sum_{j>0} \mathbf{D}_{0j} \otimes \mathbf{R}_{0j}$

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$$E(\mathbf{m}) = \int_{\mathbb{R}^2} \left[A\,|\nabla \mathbf{m}|^2 + \underline{\mathbf{D}} : (\nabla \mathbf{m} \times \mathbf{m}) + \mathbf{m} \cdot \underline{\mathbf{K}} \cdot \mathbf{m} - B\,\mathbf{m} \cdot \hat{\mathbf{e}}_z \right] d\mathbf{r}$$

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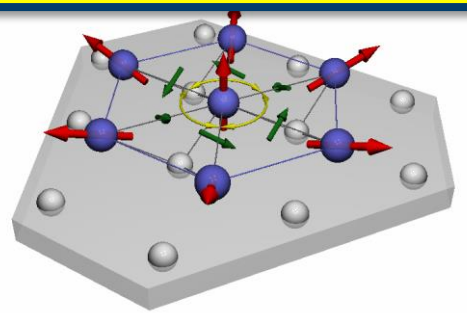

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$$E_{\text{tot}}^{\text{DFT}}(\mathbf{q}, \hat{e}_{\text{rot}}) = E_{\text{noSOC}}^{\text{DFT}}(\mathbf{q}) + \Delta E_{\text{SOC}}^{\text{DFT}}(\mathbf{q}, \hat{e}_{\text{rot}})$$

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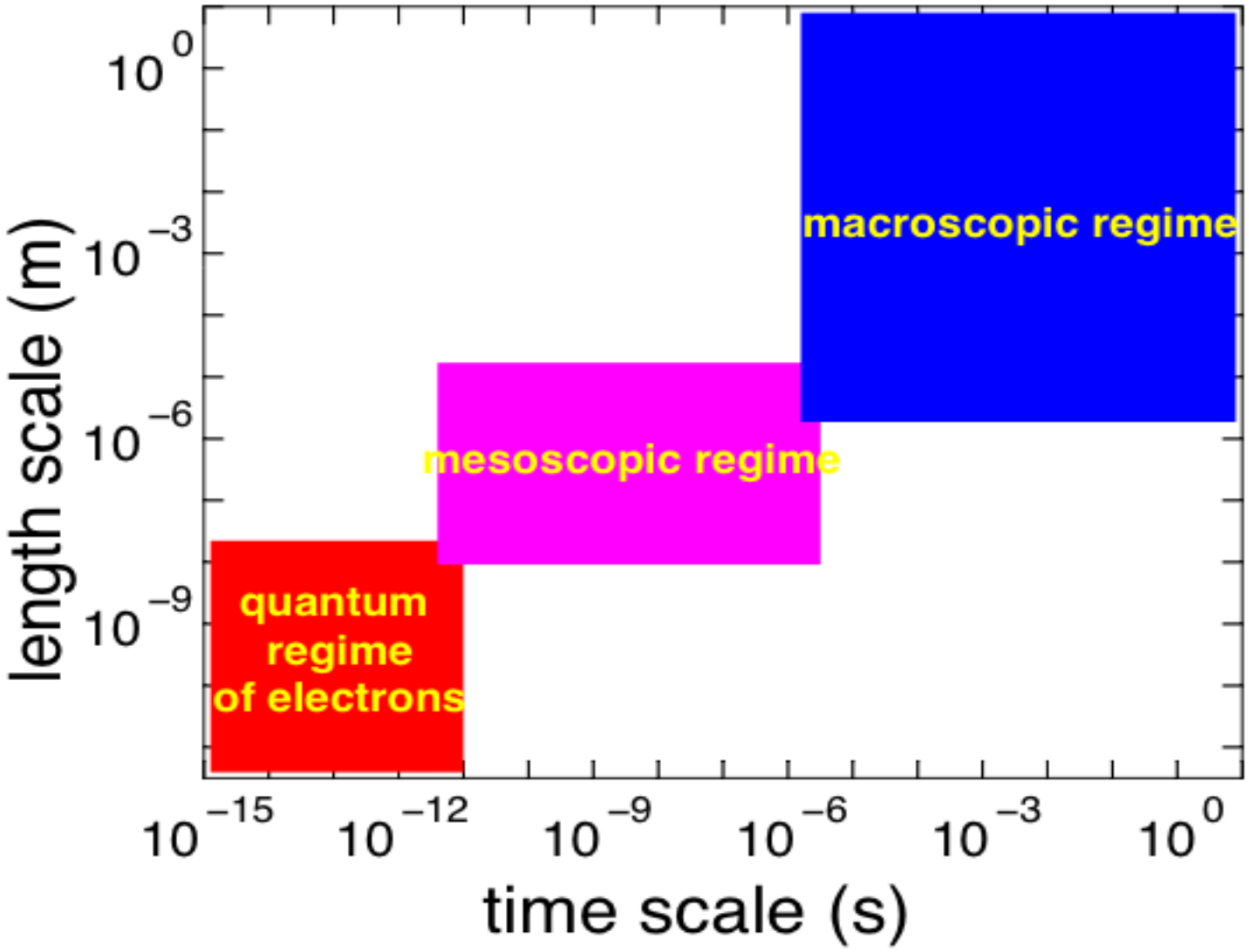

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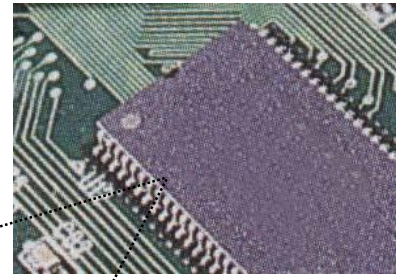
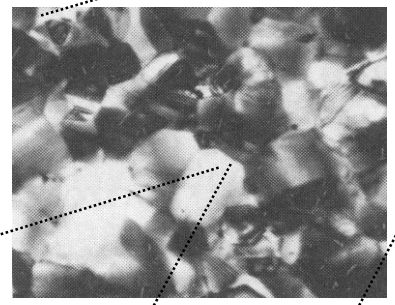
THE TOP TO DOWN CHALLENGE

Connection of atomistic and macroscopic scales



MACRO

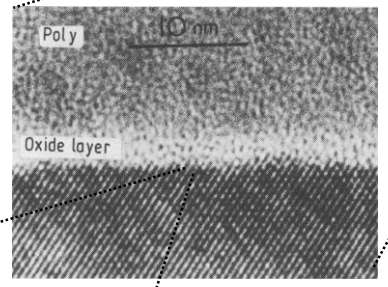
10^{-2}m, 10^{8}s



MESO

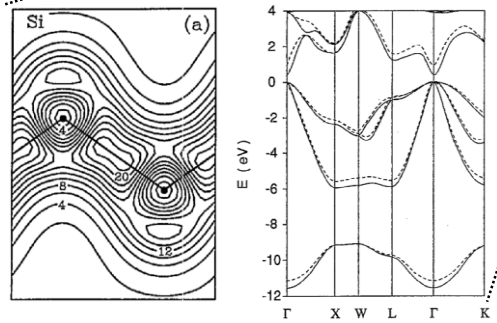
10^{-6}m, 10^{0}s

10 nm



ATOMS

10^{-9}m, 10^{-12}s



ELECTRONS

10^{-10}m, 10^{-15}s

With courtesy of materialscience.com

s.bluegel@fz-juelich.de

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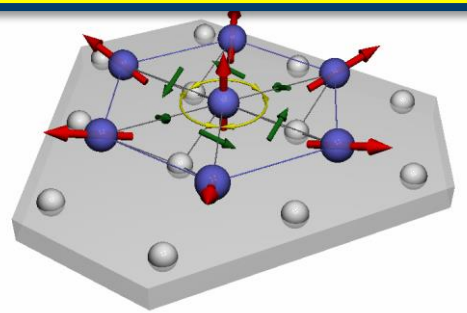

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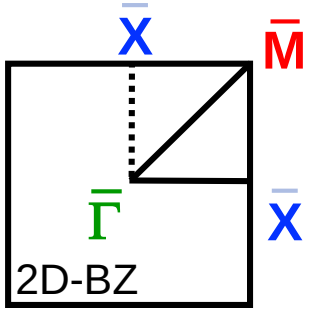
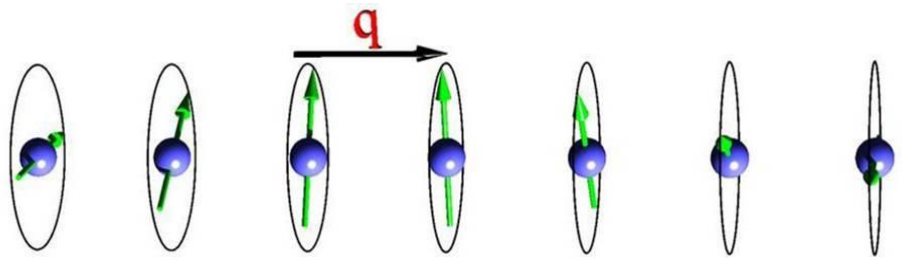
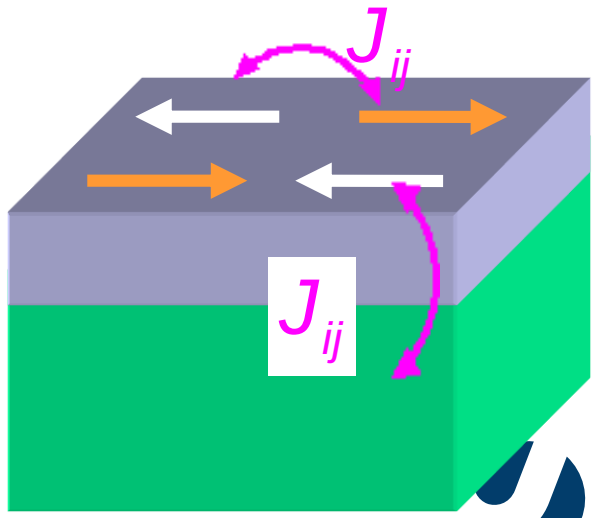
Spin spirals **q**







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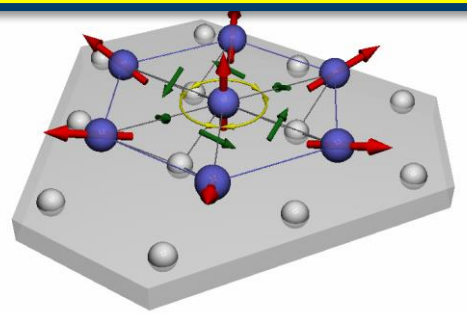

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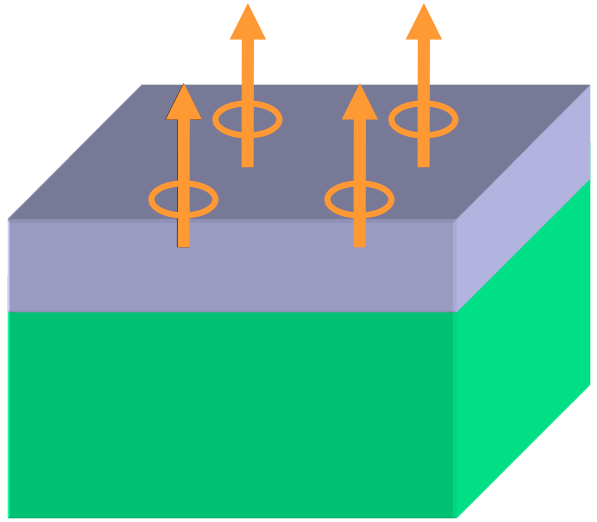
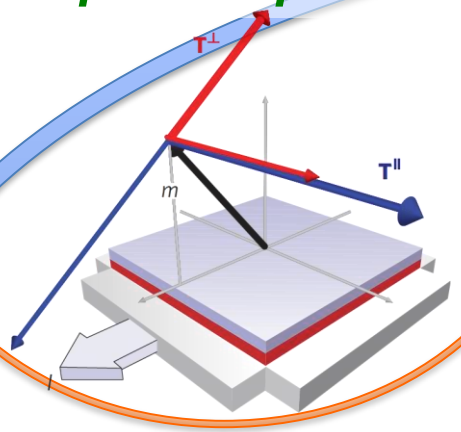


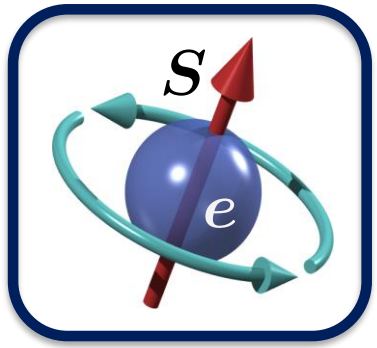
SPINTRONICS : MAGNETISM + SPIN-ORBIT + TOPOLOGY + TRANSPORT

Spin Torques

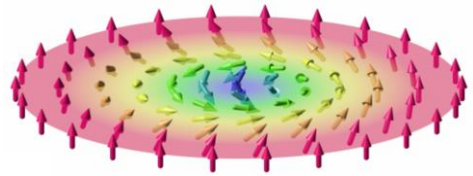


- Efficient switching
- Device scalability
- Reduced power

Garello et al., Nature Nano. ’13
Freimuth, Geranton, et al., ’14-’17



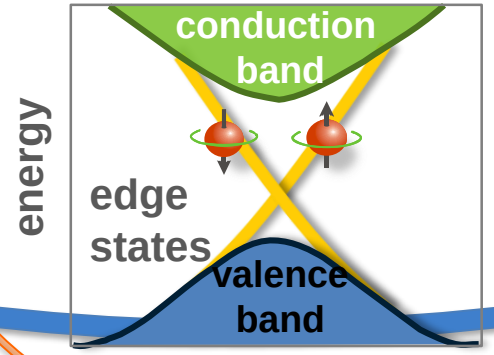
chiral spin textures



- particle-like
- ultra-robust
- efficient dynamics

A. Fert *et al.,* Nat. Nano ‘13

topological materials



- low-dissipation
- topological robustness

- Majorana fermions
- quantum computing

Hasan & Kane, RMP ‘10

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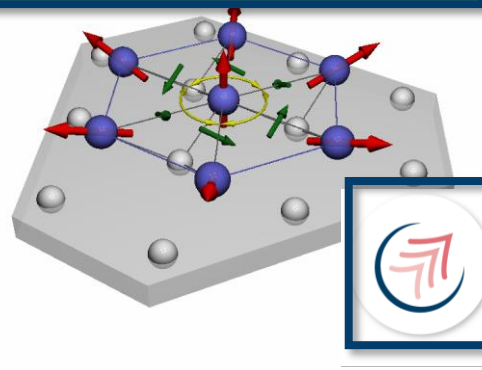


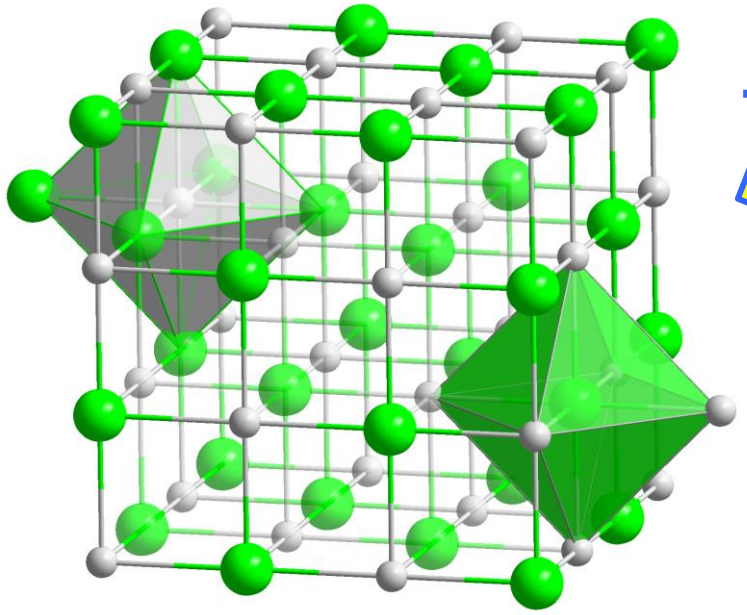
❖ Its all in the Schrödinger equation :

$$\left[-\frac{\hbar^2}{2m} \Delta + V(x) \right] \Psi(x) = E \Psi(x)$$

E. Schrödinger (1926), Annalen der Physik, 361-377

➢ Wavefunction based theory

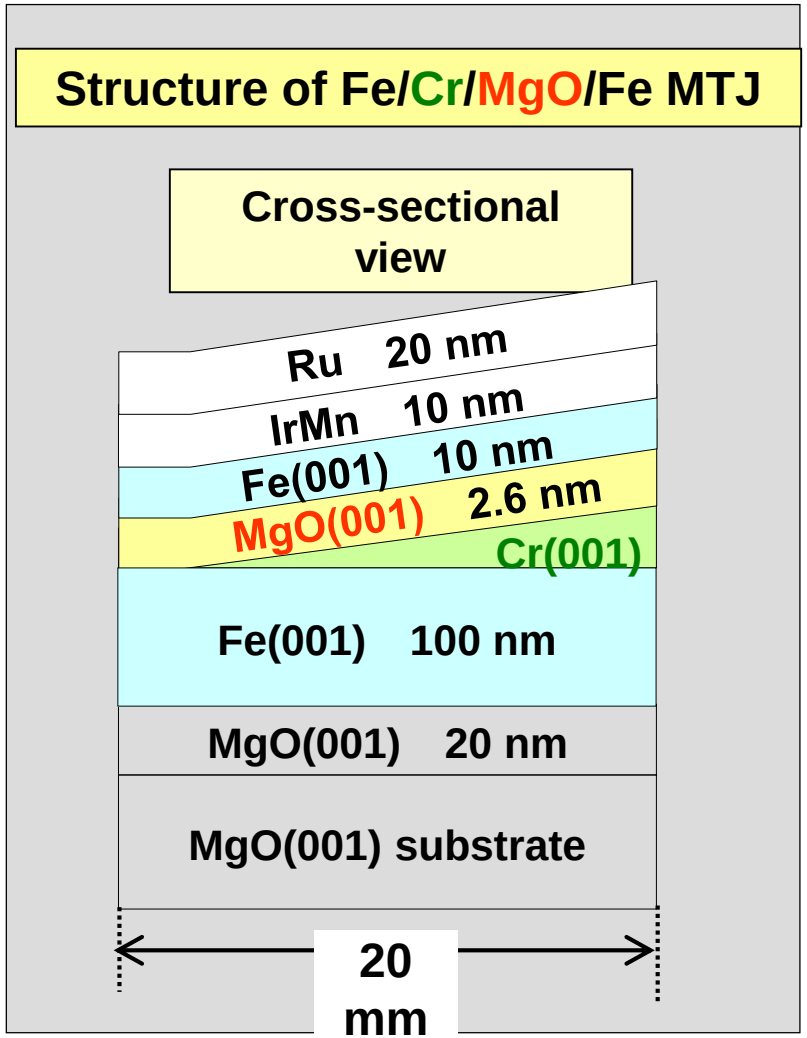
SOLID – PROPERTY RELATION



$$\mathcal{H}\Psi = E\Psi$$

- Dzyaloshinskii Moriya interaction
- vibrational properties
- multiferroicity
- structural stability
- van der Waals
- phase diagrams
- orbital ordering
- magnetism & magnetic order
- workfunction
- Elliot Yafet
- chemical reactivity
- superconductivty
- electrical polarization
- Kondo physics
- ferroelectricity
- heavy fermion systems
- chemical reactivity
- Mott transition
- ionization energies
- topological insulator
- compressibilities
- quantum Hall effect
- elastic modules
- Dresselhaus effect
- giant & colossal magneto resistance

INVERSE RELATION: PROPERTY - MATERIALS



$\mathcal{H}\psi = E\psi$

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High Tc
Magnetoresistivity
High sensitivity

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THE QUANTUM MANY-BODY PROBLEM

$$H\Psi = E\Psi, \qquad \Psi(x_1, x_2, \cdots, x_n)$$

iron (Fe) atom: $\Psi(r_1,\ldots r_{26})$

Example: Expressing the wavefunction:

1) Hydrogen H : n=1, exact or num. : 10^3 grid points ⟹ 16 KB
2) Helium He: n=2, exact or num. : 10^6 grid points ⟹ 16 MB < 1 CD
3) Lithium Li : n=3, num. : 10^9 grid points ⟹ 16 GB ~ 4 DVD

• • •
• • •
• • •

6) Carbon C : n=6, num. : 10^{18} grid points ⟹ ~ 16 Mill TB = 40000 Hard Discs = 1000 Trucks

MODELS, APPROXIMATIONS, PHYSICS

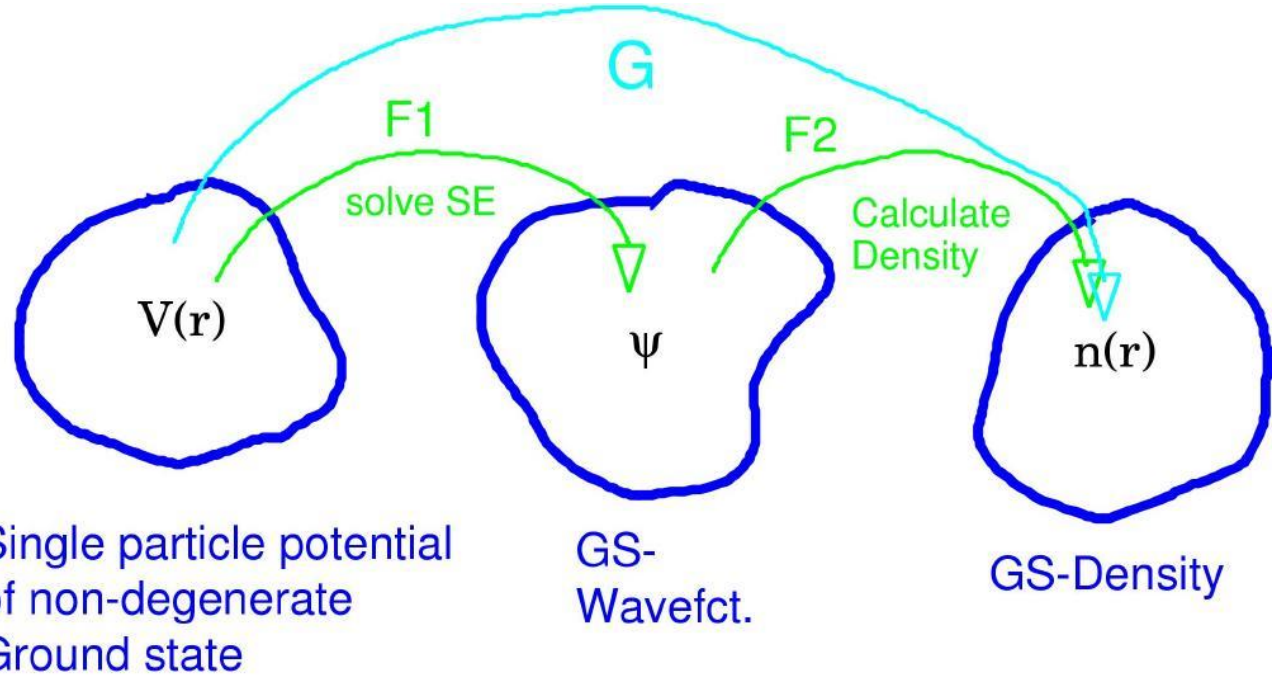
P.M.A. Dirac

The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.M.A. Dirac, Proceedings of the Royal Society **A 123**, 714(1929)

DENSITY FUNCTIONAL THEORY (DFT)

Maps interacting many body problem onto noninteracting electrons ineffective Potential



Hohenberg-Kohn-Theorem (1964):
G is invertable

$$\left.\begin{aligned} F_1 &: V(\mathbf{r}) \longmapsto \psi \\ F_2 &: \psi \longmapsto n(\mathbf{r}) \end{aligned}\right\}$$ per construction surjective

$$F_1 \circ F_2 := G \quad : \quad V(\mathbf{r}) \longmapsto n(\mathbf{r})$$

THE KOHN-SHAM (KS) ANSATZ

- From Hohenberg-Kohn the ground state energy is a functional of the electron density $E_0[n]$, minimum at $n = n_0$
- From Kohn-Sham

➢Kohn Sham Total Energy:

$$E_{\mathrm{KS}}[n|\{\mathbf{R}\}] = E_{\mathrm{kin}}[n] + E_{\mathrm{H}}[n] + E_{\mathrm{ext}}[n|\{\mathbf{R}\},] + E_{\mathrm{ion}}[\{\mathbf{R}\}] + E_{\mathrm{xc}}[n]$$

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact theory but **unknown** functional!

➢Electron Density: $n(\mathbf{r}) = \sum_{i(occ)}^{M} |\psi_i(\mathbf{r})|^2$

- **The new paradigm – find useful, approximate functionals**

EXCHANGE-CORRELATION FUNCTIONALS

Local Density Approximation (LDA): depends on one variable since uses only $n(r)$ at point r.

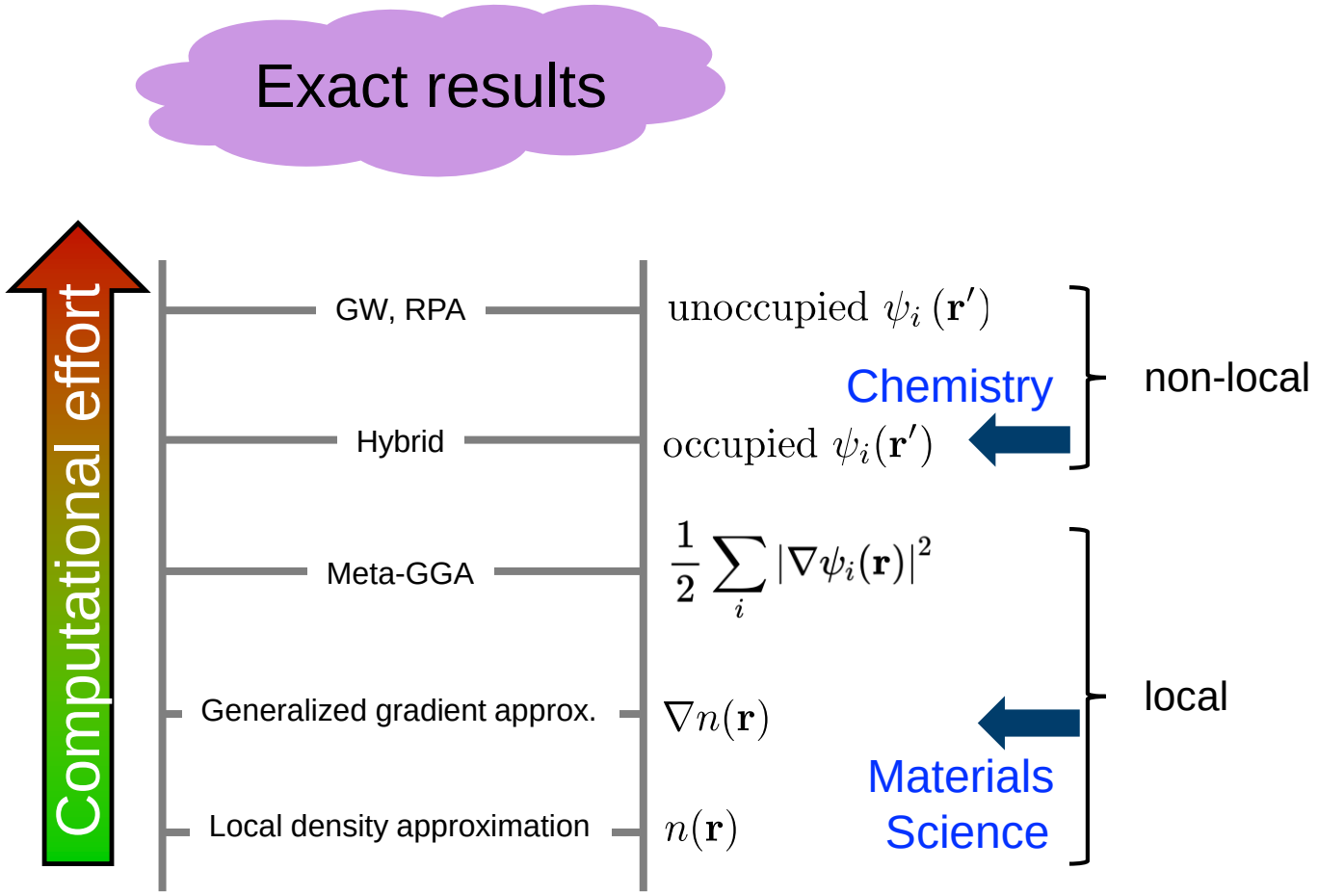
Should be good for slowly varying electron density

$$E_{xc}^{LDA}[n] = \int \varepsilon_{xc}^{\mathrm{hom\,og}}(n(\vec{r}))n(\vec{r})d^3r$$

Quantity	Deviation from Exp.
• Bond lengths in Molecules	< 5.0%
• Lattice constants	< 2%
• Magnetic moments	some %
• Atomic & molecular GS Energy	< 0.5 %

Inaccurate for molecular systems (too short bond lengths), Fe bulk has wrong x-tal structure (fcc instead of bcc), overestimates binding energies, band gaps much too small

BEYOND LDA/GGA DFT



Known failures of LDA/GGA:

- Insulator / Semiconductor
- Bandgap calculations
- Localization of wavefunctions

Hybrid functionals:

- Mix-in Hartree-Fock
- Exact treatment of exchange

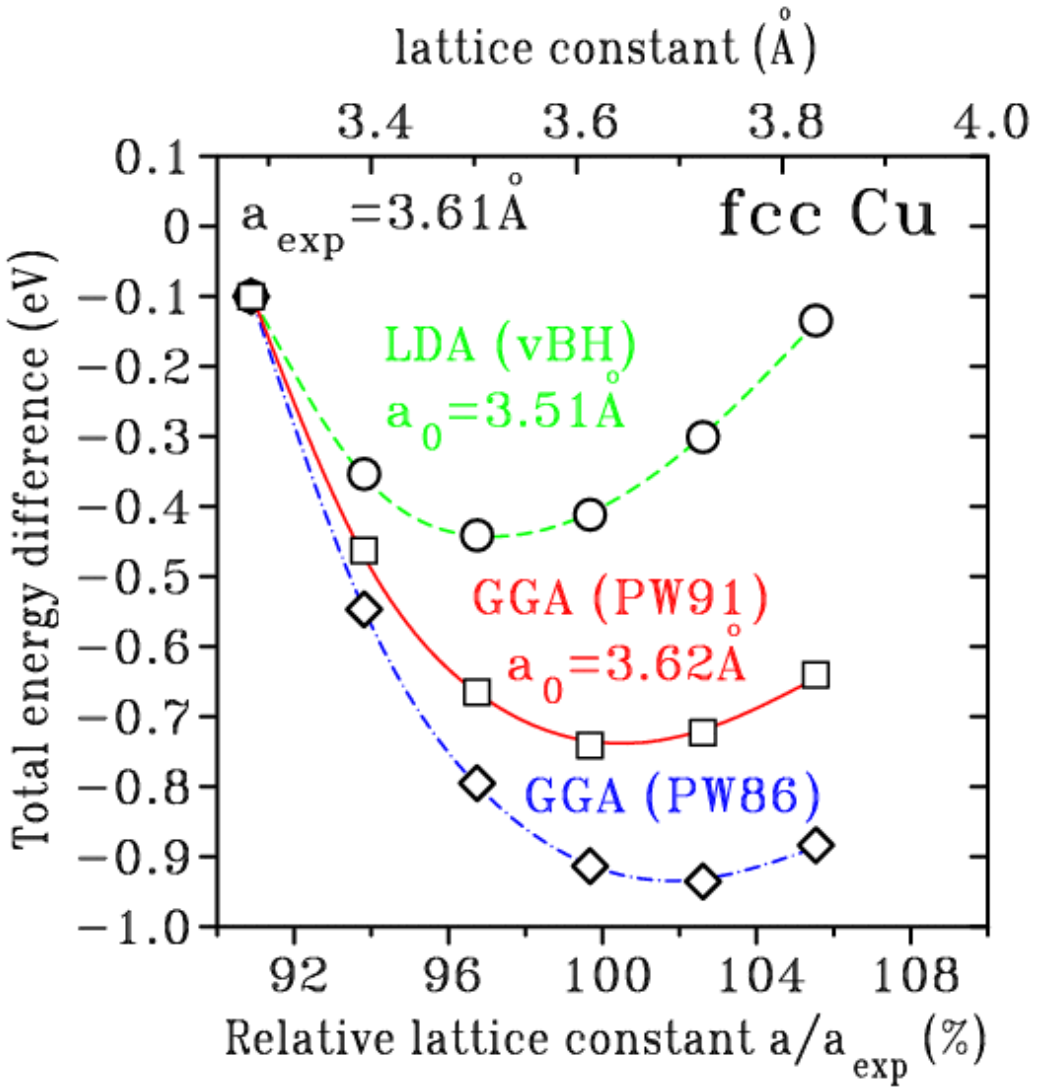
$$E_{\mathrm{x}}^{\mathrm{exact}} = -\frac{1}{2}\sum_{i,j}^{N_{\mathrm{occ}}} \iint \frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d\mathbf{r}d\mathbf{r}'$$

More complex levels of theory:

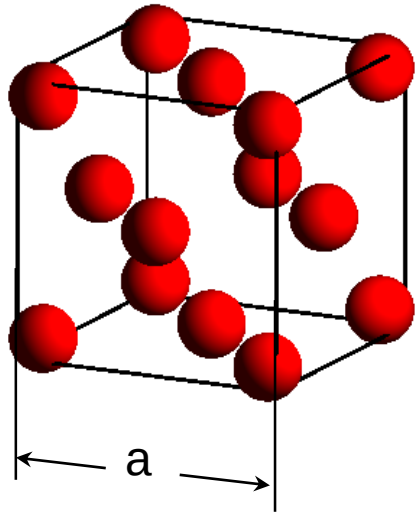
- RPA total energy
- Many-body perturbation theory

Computational effort: O(#atoms^4) vs O(#atoms^3)

EXAMPLE: LATTICE CONSTANT OF Cu



$$E[\mathrm{a}, S = fcc, n_0^a]$$



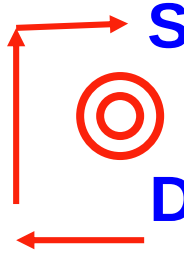
THE KOHN-SHAM STANDARD MODEL

"**The** Computational Approach"

For: Physics, Chemistry, Nanoscience, Materials Science, Bio-Physics, Minerology, Geology,…

Total Energy: $E = E[n, \{R_I\}, a, \ldots]$

Energy is functional of electron density n and external parameters such as lattice constants, atoms positions, magnetization direction…



Secular Equation: $\hat{H}[n]\,\psi_i[n] = \varepsilon_i[n]\,\psi_i[n]$

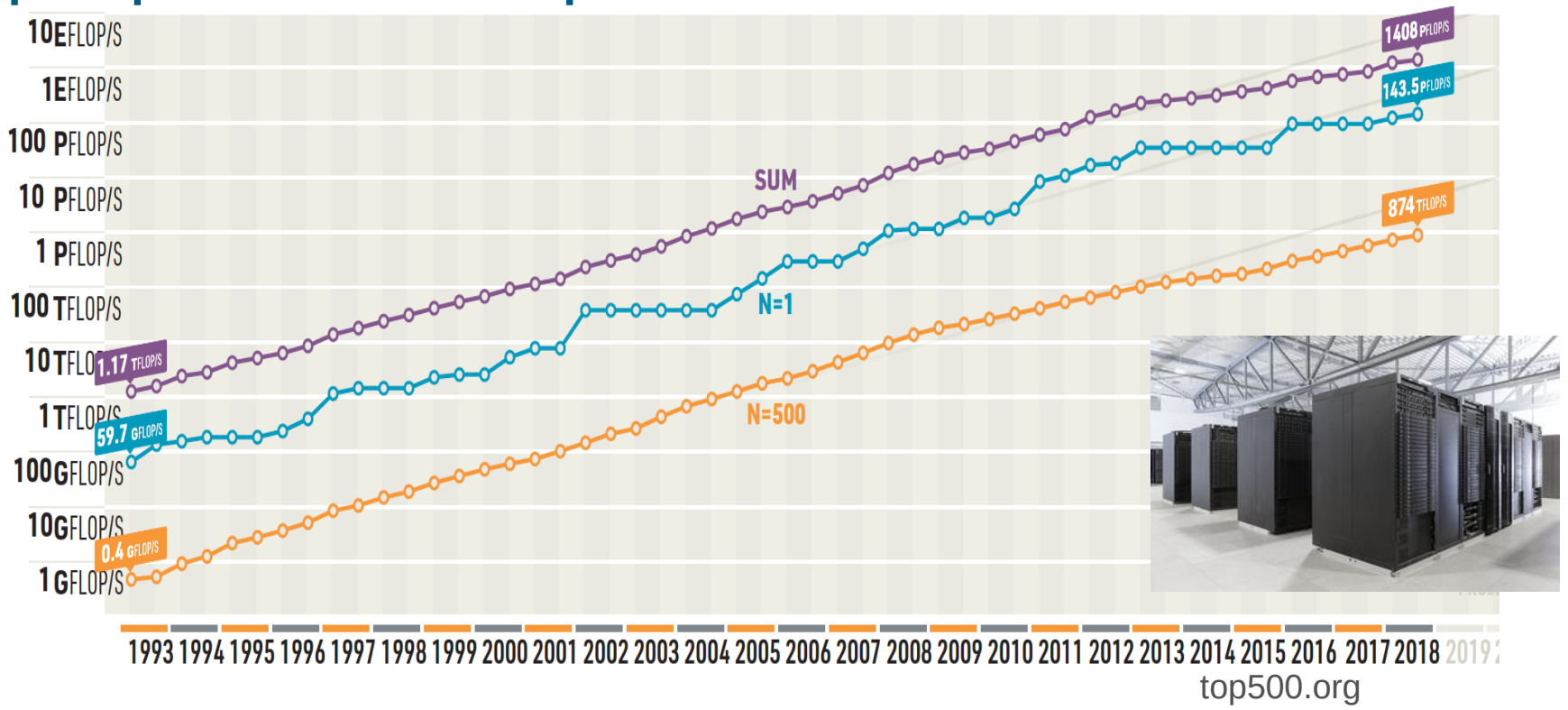
Selfconsistency loop

Density: $n(\mathbf{r}) = \sum_{i(occ)}^{M} |\,\psi_i(\mathbf{r})\,|^2$

CPU-Time scaling: ≈ N^3_{atom} ≈ Volume^3, ≈ Precision^3

THE DIGITAL SPACE

- **Evolution of peak performance on Top500 list**



- If brick-and-mortar laboratories were to follow this pace, an experiment that took **one year in 1989** would take **one second in 2018** (30-million-fold increase)
- CPUs AND THROUGHPUT CAPACITY DOUBLE EVERY 14 MONTHS

➔ **Virtualization of Materials Exploration and Design**

DOWNLOAD A CODE OF CHOICE

https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software

Numerical details

Package	License[1]	Language	MPI	OpenMP	GPU	I/O libraries	Parallel I/O
ABINIT	Free, GPL	Fortran	Yes	Yes	Yes, CUDA	Yes, HDF5, NetCDF	Yes, Fortran and HDF5
ACES[1]	Free, GPL	Fortran, C++	Yes	No	Yes	Unknown	Unknown
ADF, Amsterdam Modeling Suite	Commercial	Fortran	Unknown	Unknown	Yes, CUDA	Yes, HDF5, custom	Unknown
AMPAC	Academic	Unknown	Unknown	Unknown	No	Unknown	Unknown
Atomistix ToolKit (QuantumATK)	Commercial	C++, Python	Yes	Yes	Yes, CUDA	Yes, HDF5, NetCDF	Yes, HDF5
BigDFT	Free, GPL	Fortran	Yes	Yes	Yes	Yes, HDF5, NetCDF	Yes, HDF5, NetCDF
CADPAC	Academic	Fortran	Unknown	Unknown	No	Unknown	Unknown
CASINO (QMC)	Academic	Fortran 2003	Yes	Yes	Yes, OpenACC	No	No
CASTEP	Academic, commercial	Fortran 95, Fortran 2003	Yes	Yes	No	Unknown	Unknown
COLUMBUS	Free, LGPL	Fortran	Yes	No	No	No	No
CONQUEST	Free, MIT	Fortran 90	Unknown	Unknown	No	Unknown	Unknown
CP2K	Free, GPL	Fortran 95	Yes	Yes	Yes, CUDA and OpenCL	Unknown	Unknown
CPMD	Academic	Fortran	Yes	Yes	No	Unknown	Unknown
CRYSTAL	Academic (UK), Commercial (IT)	Fortran	Yes	Yes	No	Unknown	Unknown
Dalton	Free, LGPL	Fortran	Yes	Yes, LSDalton	No	Unknown	Unknown
DIRAC	Free, LGPL	Fortran 77, Fortran 90, C	Yes	No	No	Unknown	Unknown
DMol3	Commercial	Fortran 90	Yes	Unknown	No	Unknown	Unknown
FLEUR[2]	Free, MIT	Fortran 95	Yes	Yes	Yes, OpenACC, CuBLAS	Yes, HDF5, custom	Yes, HDF5
FHI-aims	Academic, commercial	Fortran	Yes	Unknown	Yes	Unknown	Unknown
FreeON (formerly MondoSCF)	Free, GPL	Fortran 95	Unknown	Unknown	No	Unknown	Unknown
Firefly (formerly PC GAMESS)	Academic	Fortran, C, Assembly	Unknown	Unknown	Yes	Unknown	Unknown
GAMESS (UK)	Academic UK, Commercial	Fortran	Unknown	Unknown	Yes	Unknown	Unknown
GAMESS (US)	Academic	Fortran	Yes	Yes	Yes	Unknown	Unknown
Gaussian	Commercial	Fortran	Unknown	Unknown	Yes, CUDA	Unknown	Unknown
Jaguar	Commercial	Fortran, C	Unknown	Unknown	No	Unknown	Unknown
MADNESS	Free, GPL	C++	Unknown	Unknown	No	Unknown	Unknown
MOLCAS / OpenMolcas	Academic, commercial[3] / LGPL	Fortran, C, C++, Python, Perl	Yes	Yes	Yes	Yes, HDF5	Unknown
MOLPRO	Commercial	Fortran	Yes	Yes	Yes	Unknown	Unknown
MOPAC	Free, LGPL[4]	Fortran	Unknown	Unknown	Yes	Unknown	Unknown

https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software Page 1 of 5

+ INPUT PHYSICS:

Crystal structure/Structure Model

Atom positions

Nuclear Numbers

+ INPUT ACCURACY INFO:

Choice of XC functional

Number of Basis functions

Number of Bloch vectors

Validation of codes:

- Kurt Lejaeghere *et al.*, Science **351**, 3000 (2016)
- Emanuele Bosoni *et al.*, Nat. Rev. Phys. **6** 45 (2024)

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SUMMARY DFT

Quantum Space of electrons

$$\left[-\frac{\hbar^2}{2m}\Delta + V(x)\right]\Psi(x) = E\Psi(x)$$

Schrödinger Equation

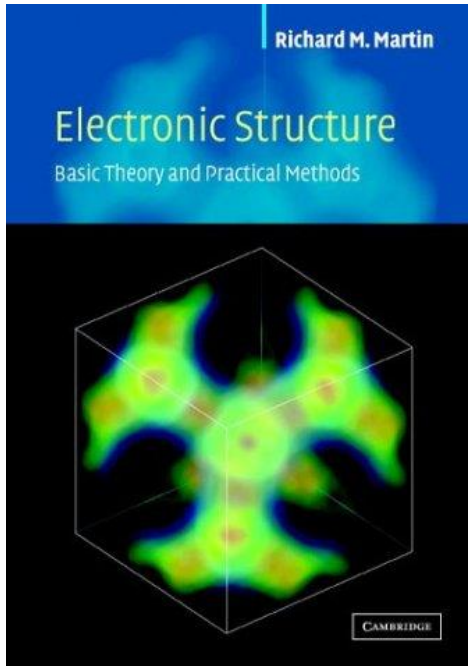
Density functional theory (DFT)

$$\left[-\frac{\hbar^2}{2m}\Delta + V[n](x)\right]\Psi(x) = E\Psi(x)$$

Selfconsistency loop

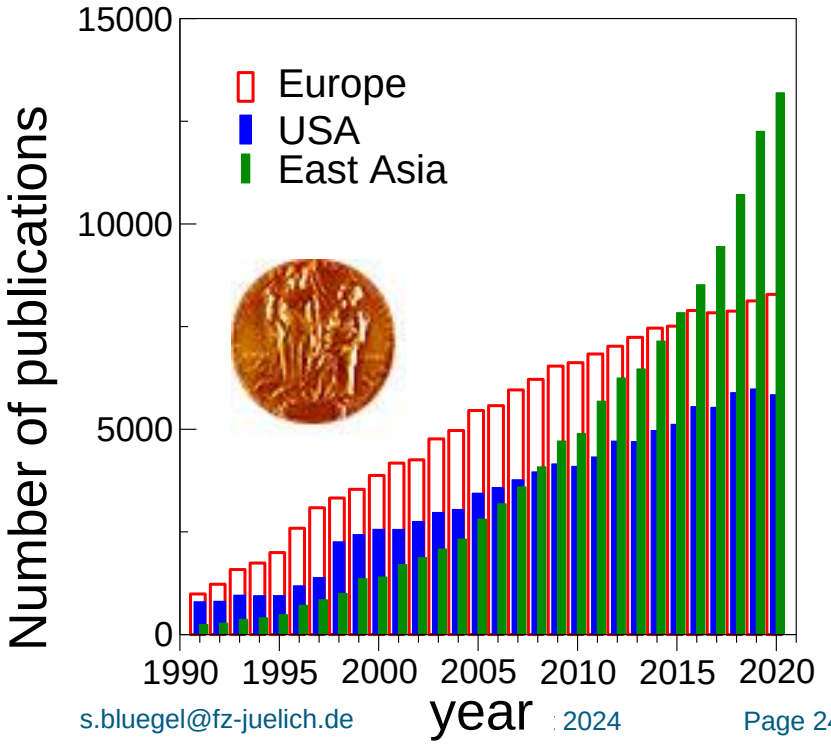
Density: $n(x) = \sum_i^{\text{occ}} |\Psi_i(x)|^2$

Literature



- **R. Martin,** "Electronic Structure: Basic Theory and Practical Applications", Cambridge University Press, 2004

The Crowd



Web of Science
Key words:
- First-principles
- Ab initio
- Density functional

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DFT FOR NON-COLLINEAR MAGNETS

❖ Two-component spinor in general form: $\Psi(\mathbf{r}) = \begin{pmatrix} \psi_1(\mathbf{r}) \\ \psi_2(\mathbf{r}) \end{pmatrix}$

❖ Density → **Density Matrix** in spinor space

$$\underline{\mathbf{n}}(\mathbf{r}) = \begin{pmatrix} \psi_1^*(\mathbf{r})\psi_1(\mathbf{r}) & \psi_1^*(\mathbf{r})\psi_2(\mathbf{r}) \\ \psi_2^*(\mathbf{r})\psi_1(\mathbf{r}) & \psi_2^*(\mathbf{r})\psi_2(\mathbf{r}) \end{pmatrix}$$

➢ Density $n(\mathbf{r}) = \langle \Psi(\mathbf{r}) | \underline{\mathbf{1}}_2 | \Psi(\mathbf{r}) \rangle$

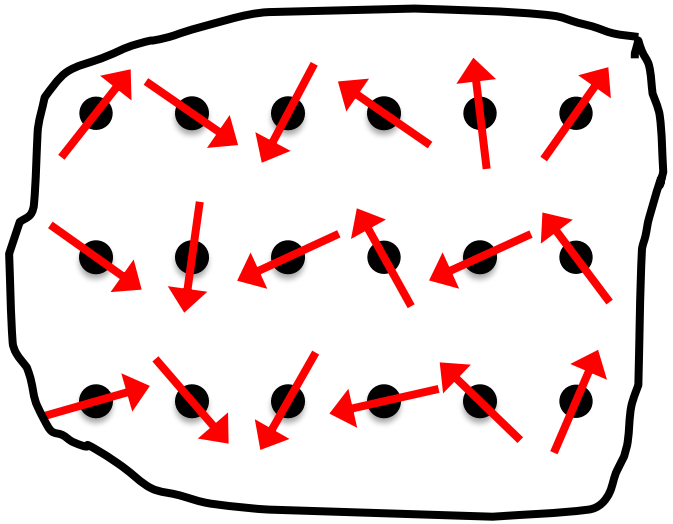
➢ **Vector-spin density** $\mathbf{m}(\mathbf{r}) = \langle \Psi(\mathbf{r}) | \underline{\sigma} | \Psi(\mathbf{r}) \rangle$

$$\underline{\mathbf{n}}(\mathbf{r}) = \frac{1}{2} \begin{pmatrix} n(\mathbf{r}) + m_z(\mathbf{r}) & m_x(\mathbf{r}) + i\, m_y(\mathbf{r}) \\ m_x(\mathbf{r}) - i\, m_y(\mathbf{r}) & n(\mathbf{r}) - m_z(\mathbf{r}) \end{pmatrix}$$

off-diagonal elements hermitian !

$$\underline{\mathbf{n}}(\mathbf{r}) = \frac{1}{2} \left(n(\mathbf{r})\underline{\mathbf{1}}_2 + \mathbf{m}(\mathbf{r})\underline{\sigma} \right)$$

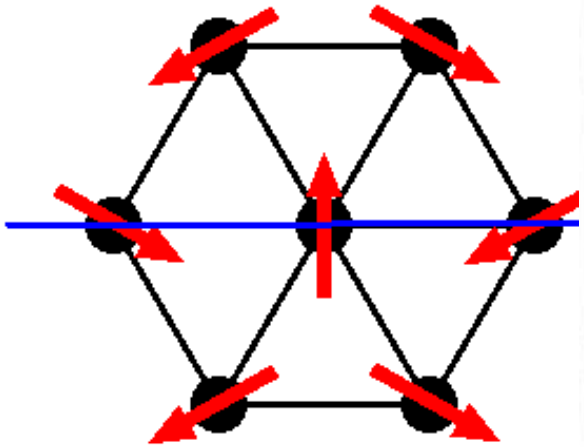
We work here with 4 densities !



Solid

GROUND STATE PROPERTIES

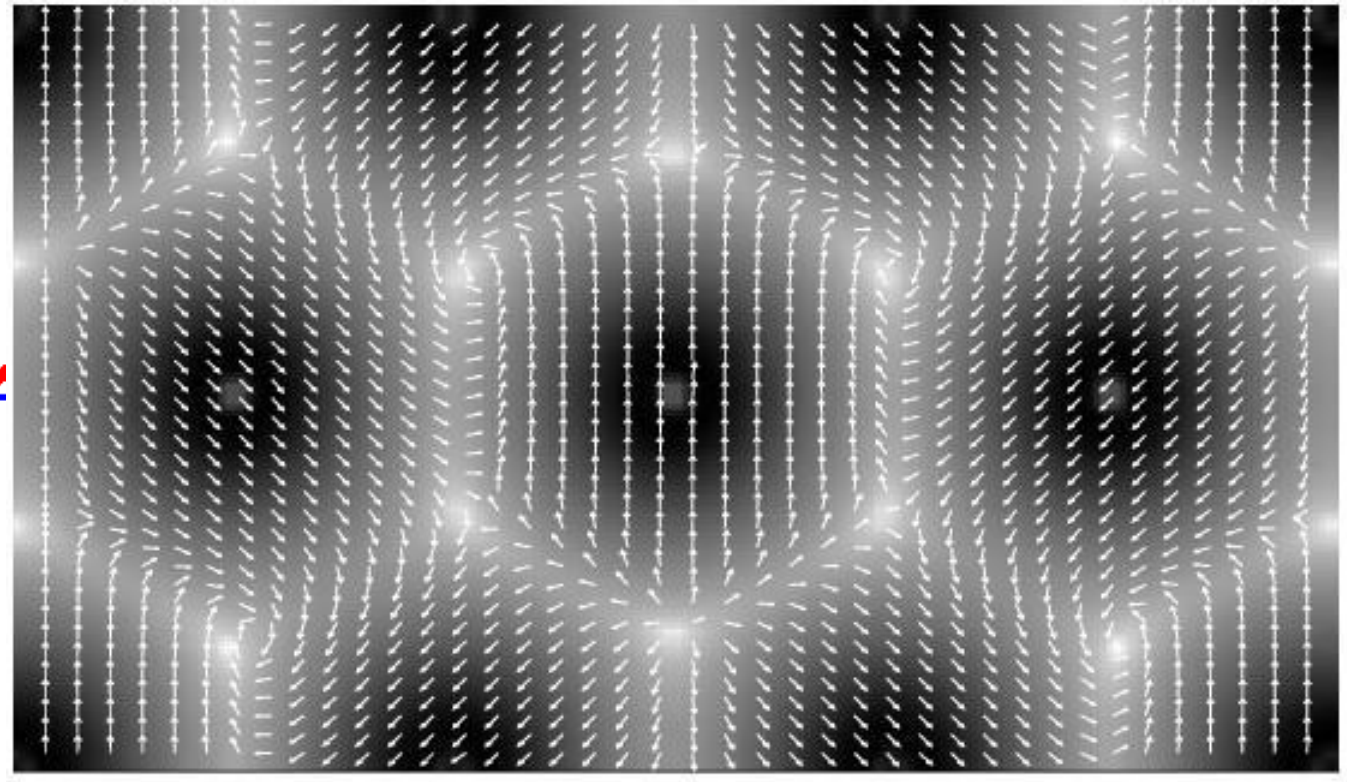
- Self-consistent calculation of:
  1) charge density
  2) size of magnetic moments
  3) direction of magnetic moments
  4) Total energy



Mn/Cu(111)

- Vector spin density:

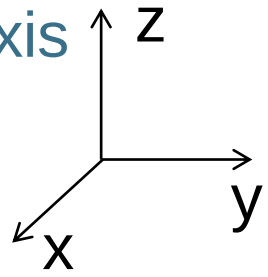
120° Neel Structure on hexagonal lattice



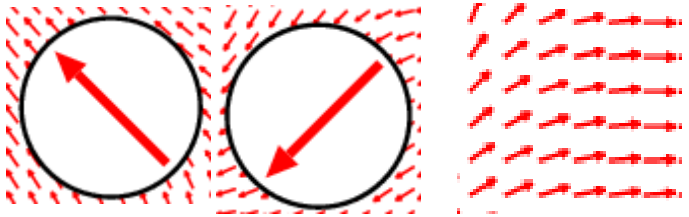
VECTOR-SPIN DENSITY WITH LOCAL QUANTIZATION AXIS

- Vector-spin-density formulation:
  full magnetisation density in interstitial $\mathbf{m}(\mathbf{r})$
  projected collinear density in the MT-spheres $m(\mathbf{r})\,\hat{\mathbf{e}}_M$

- Global quantization axis

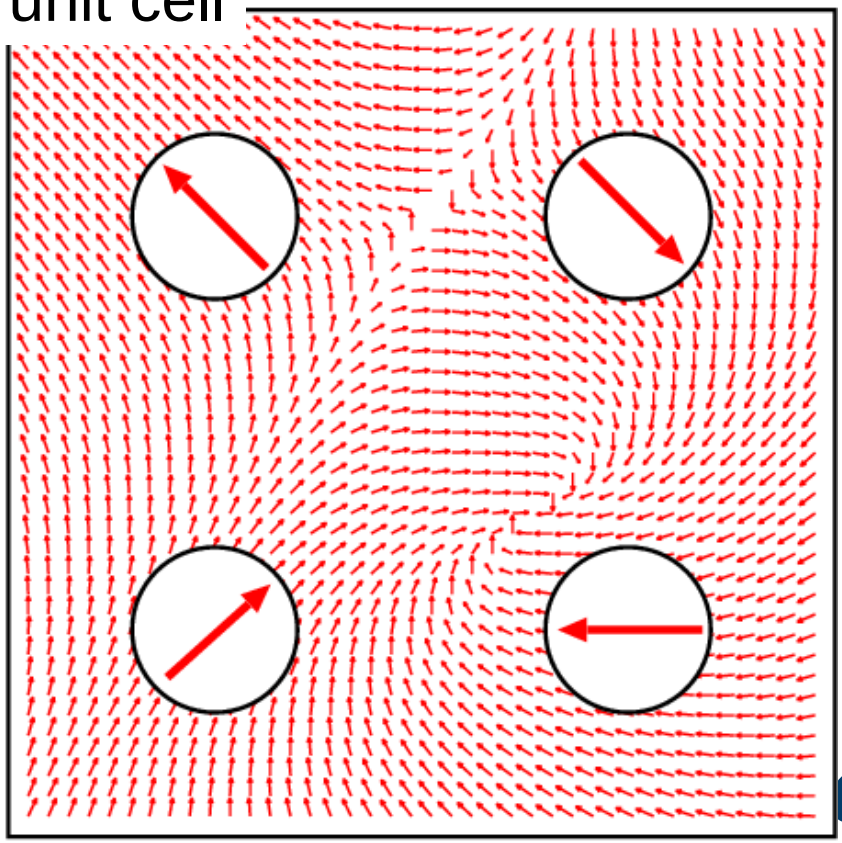


- Local quantization axes

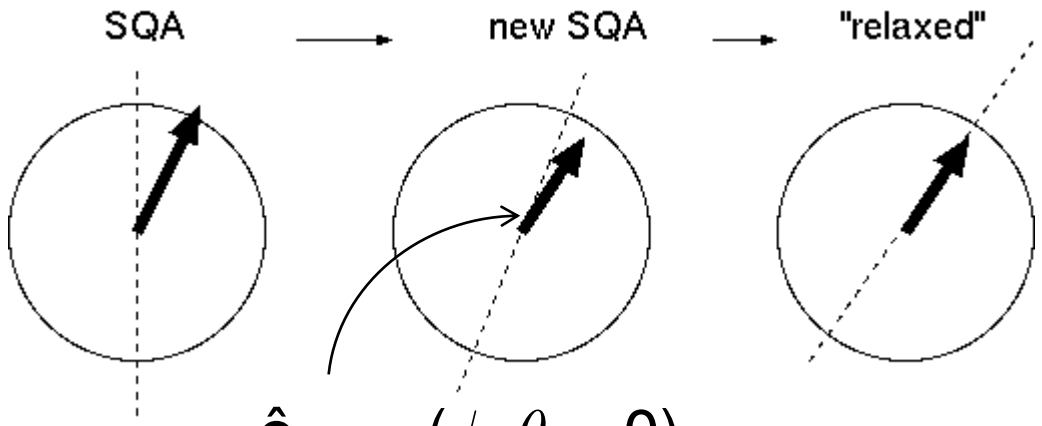


$m(\mathbf{r})\,\hat{\mathbf{e}}_M$ $\mathbf{m}(\mathbf{r})$

unit cell



RELAXATION OF MAGNETIC MOMENTS



$$\hat{\mathbf{e}}_M = (\phi, \theta = 0)$$

❖ Straight relaxation of angle:

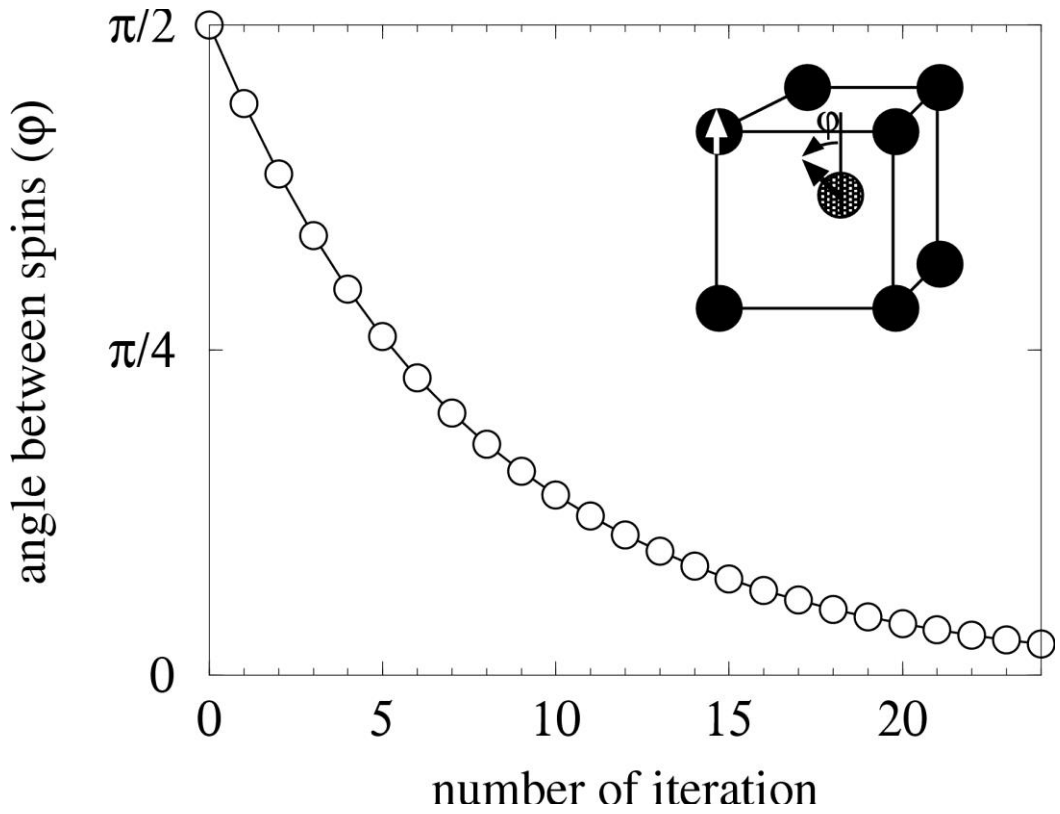
$$\phi^{(i+1)} = \phi^{(i)} + \beta \left(\phi^{(\text{out})} - \phi^{(i)} \right)$$

Can be quite large

$$\beta \approx 100 \text{ to } 300$$

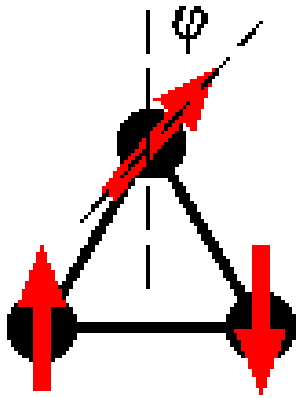
In general: (ϕ, θ)

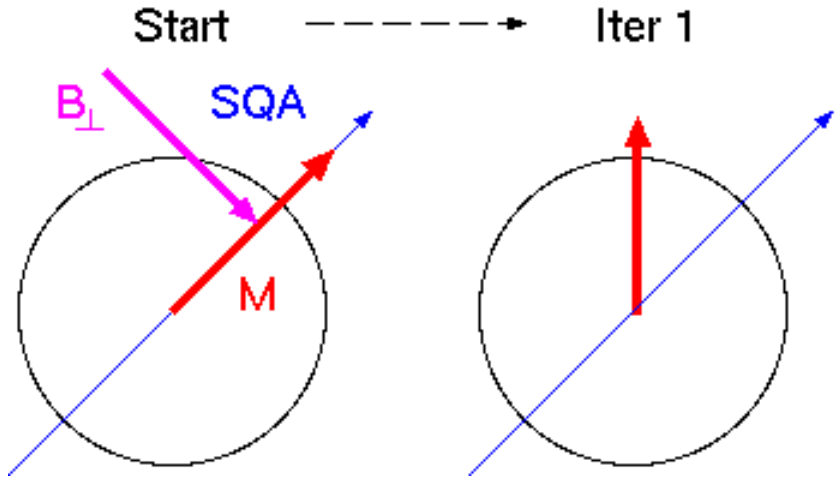
Relaxation of bcc-Fe



EXTERNAL CONSTRAINING FIELDS

AIM: $E(\hat{e}_M) = E(\varphi)$



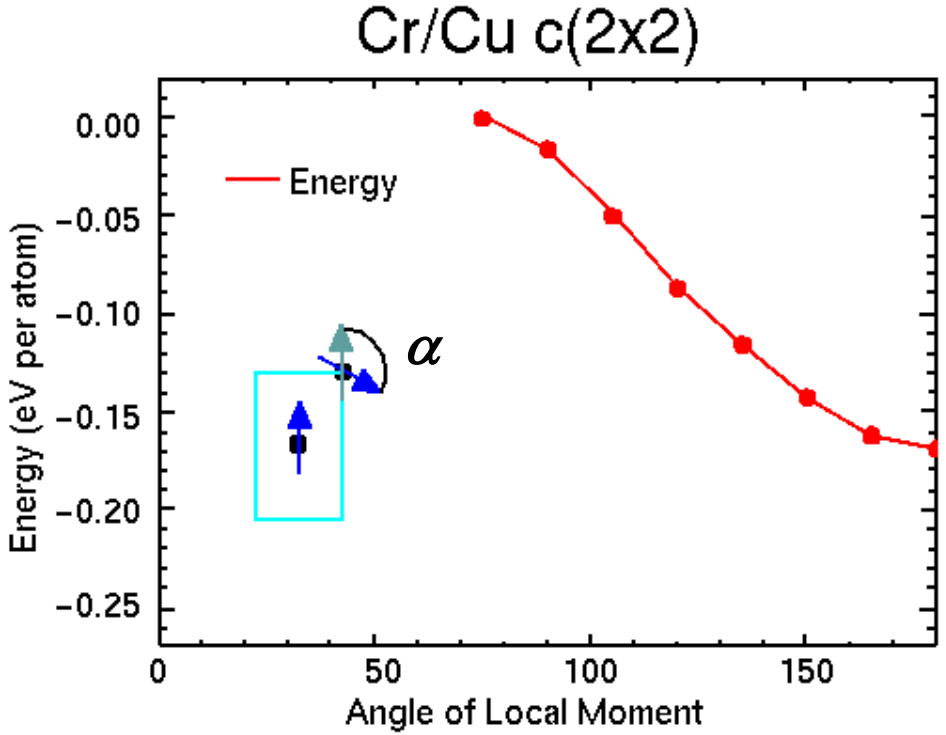


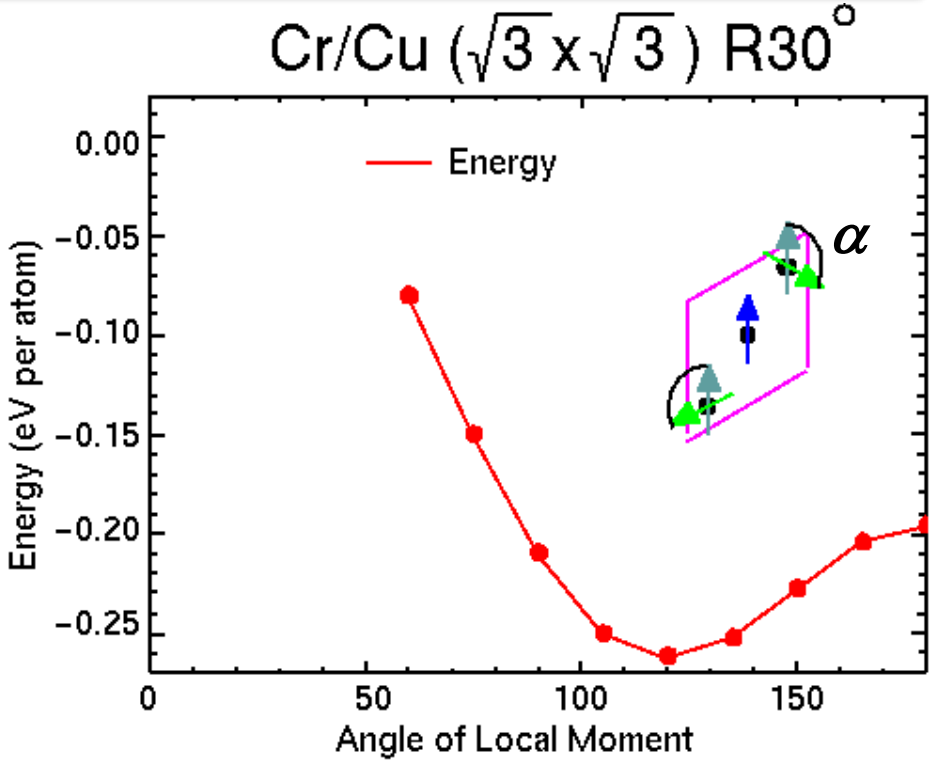
Constraint DFT

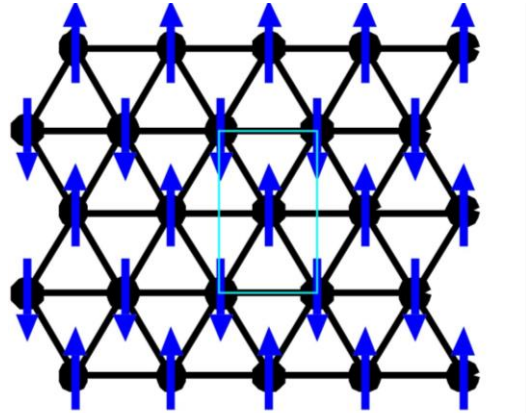
$$E(\{\hat{\mathbf{e}}_M^\alpha\}) = \min\left\{E[n(\mathbf{r}),\mathbf{m}(\mathbf{r})] + \sum_\alpha \mathbf{B}_\perp^\alpha \langle \mathbf{m}^\alpha \rangle \times \hat{\mathbf{e}}_M^\alpha\right\}$$

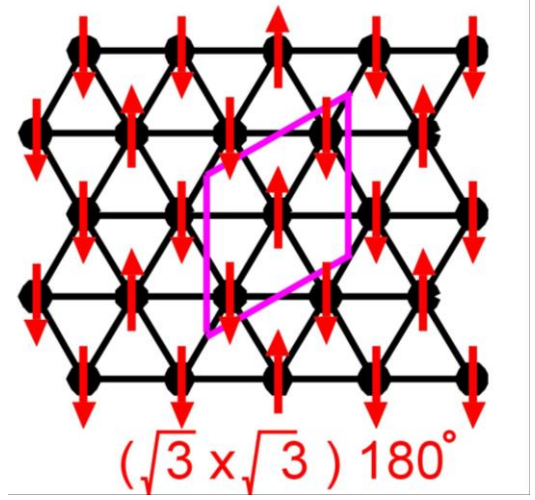
TEST HEISENBERG SYSTEMS? UML Cr/Cu(111)

- Calculate total energy path of rotating non-collinear magnetic moments
- Constraint DFT $E^{\mathrm{DFT}}(\hat{\mathbf{e}}_M^{(i)}) = \min\left\{E[n(\mathbf{r}),\mathbf{m}(\mathbf{r})] + \mathbf{B}_\perp^\alpha \langle \mathbf{m}^{(i)}\rangle \times \hat{\mathbf{e}}_M^{(i)}\right\}$
- Compare with Heisenberg model





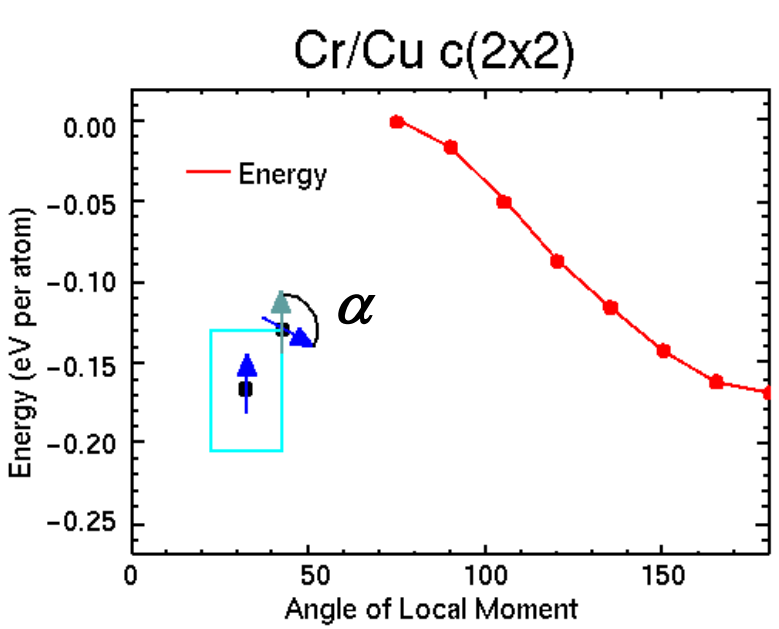


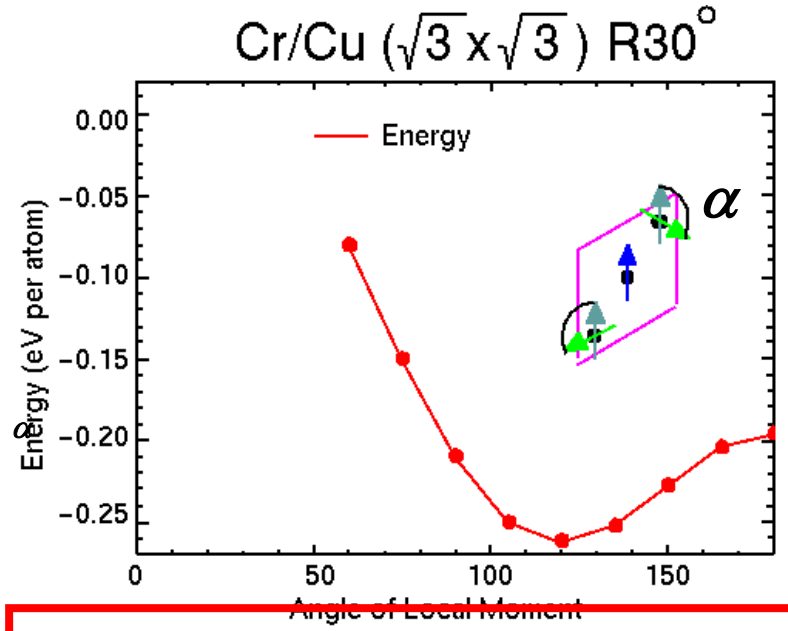


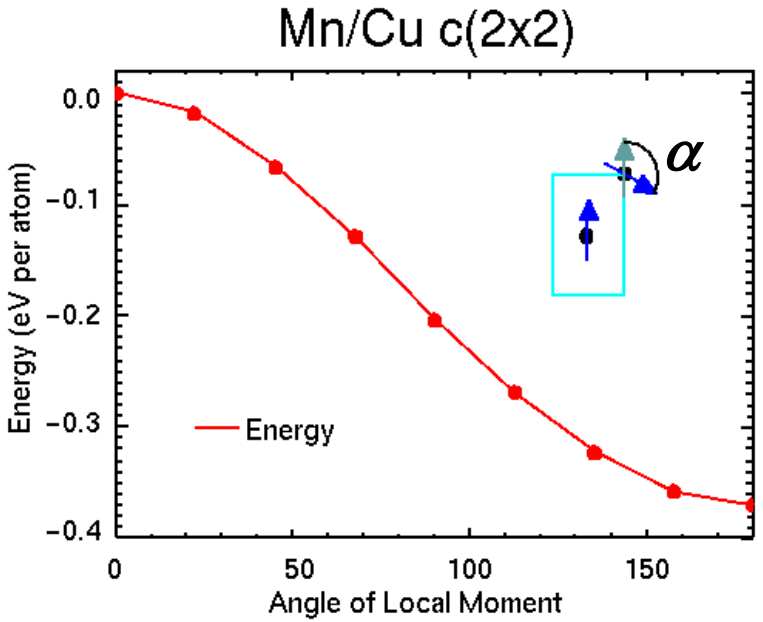
Heisenberg: $E(\alpha) = -2J_1(1 + 2\cos\alpha)$

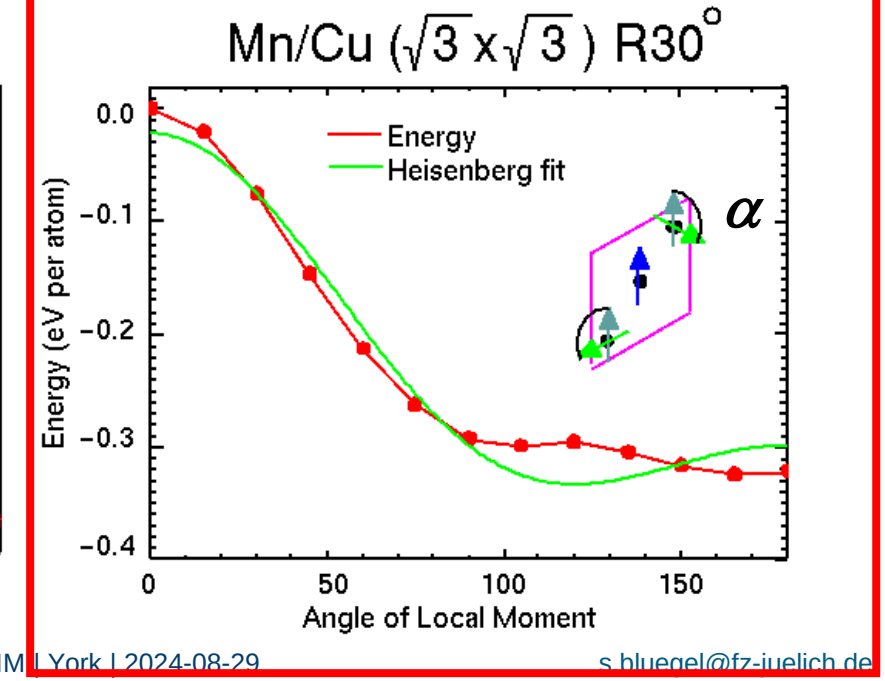
$E(\alpha) = -J_1(4\cos\alpha + 2\cos 2\alpha)$

TEST HEISENBERG SYSTEMS: UML Cr/Cu(111) + Mn/Cu(111)









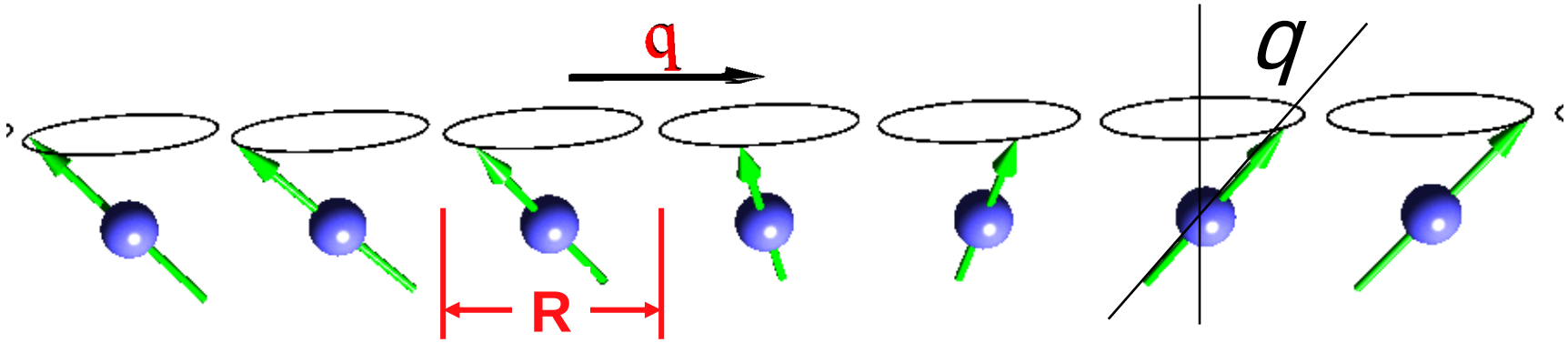
Heisenberg fit:

$$H_{2\text{-spin}} = -\sum_{ij} J_{ij}\left(\mathbf{S}_i \cdot \mathbf{S}_j\right)$$

$$E(\alpha) = -J_1(4\cos\alpha + 2\cos 2\alpha) + 6J_2$$

→ Missing Term $\propto \cos 3\alpha$

INCOMMENSURATE SPIN SPIRALS



- Spiral magnetic structure: $\mathbf{m}(\mathbf{R}^\alpha) = m \begin{pmatrix} \sin\theta\cos(\mathbf{q}\mathbf{R}^\alpha) \\ \sin\theta\sin(\mathbf{q}\mathbf{R}^\alpha) \\ \cos\theta \end{pmatrix}$

$$\mathbf{m}(\mathbf{R}^\beta) = m \begin{pmatrix} \sin\theta\cos(\mathbf{q}\mathbf{R}^\beta) \\ \sin\theta\sin(\mathbf{q}\mathbf{R}^\beta) \\ \cos\theta \end{pmatrix} = m \begin{pmatrix} \sin\theta\cos(\mathbf{q}(\mathbf{R}^\alpha + \mathbf{R}^{\beta-\alpha})) \\ \sin\theta\sin(\mathbf{q}(\mathbf{R}^\alpha + \mathbf{R}^{\beta-\alpha})) \\ \cos\theta \end{pmatrix}$$

$$= m\,\underline{\mathcal{R}}(\mathbf{q}\mathbf{R}^{\beta-\alpha})\,\hat{\mathbf{m}}(\mathbf{R}^\alpha - \mathbf{R}^{\beta-\alpha}) = \mathcal{T}_{\beta-\alpha}\mathbf{m}(\mathbf{R}^\alpha)$$

- Generalized Translation = Rotation + Translation:

$$\mathcal{T}_{\mathbf{q}\alpha;\hat{z}} = \underline{\mathcal{R}}(\mathbf{q}\mathbf{R}^\alpha;\hat{z})\,T_\alpha$$

GENERALIZED BLOCH THEOREM

- Generalized Translation applied to wave function

$$\mathcal{T}_{\mathbf{q}\alpha;\hat{z}} = \underline{\mathcal{R}}(\mathbf{q}\mathbf{R}^{\alpha};\hat{z})\,T_{\alpha} \Longrightarrow \mathcal{T}_{\mathbf{q}\alpha;\hat{z}}\,\Psi_{\mathbf{k}\nu}(\mathbf{r}) = \underline{\mathbf{U}}(\mathbf{q}\mathbf{R}^{\alpha};\hat{z})\,T_{\alpha}\,\Psi_{\mathbf{k}\nu}(\mathbf{r})$$

- Wave function is lattice periodic function times phase factors

$$\Psi_{\mathbf{k}\nu}(\mathbf{r}) = e^{-i\,\mathbf{k}\cdot\mathbf{r}} \begin{pmatrix} e^{-i\,\frac{1}{2}\,\mathbf{q}\cdot\mathbf{r}} & 0 \\ 0 & e^{+i\,\frac{1}{2}\,\mathbf{q}\cdot\mathbf{r}} \end{pmatrix} \cdot \begin{pmatrix} u^{(\uparrow)}_{\mathbf{k}\nu}(\mathbf{r}) \\ u^{(\downarrow)}_{\mathbf{k}\nu}(\mathbf{r}) \end{pmatrix}$$

with

$$\mathbf{k}, \mathbf{q} \in \mathrm{BZ}$$

spin rotation

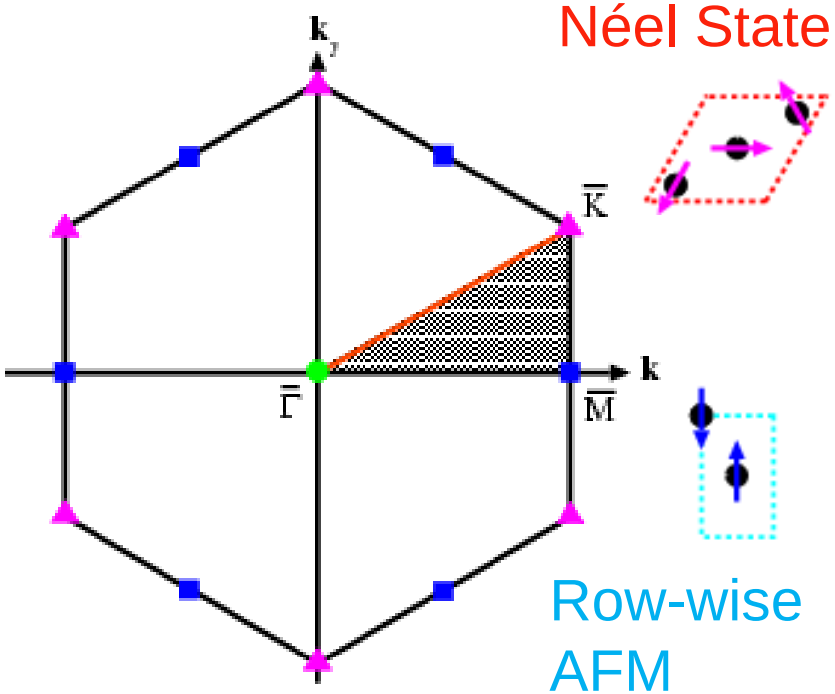
periodicity of **chemical** lattice

Herring, *Academic*, New York (1966)
Sandratskii, *J. Phys.: Condens. Matter* **3**, 8565 (1991)
P. Kurz *etal,* PRB **69,** 024415 (2004)

SSDW E(Q): UML CR AND MN ON CU (111)

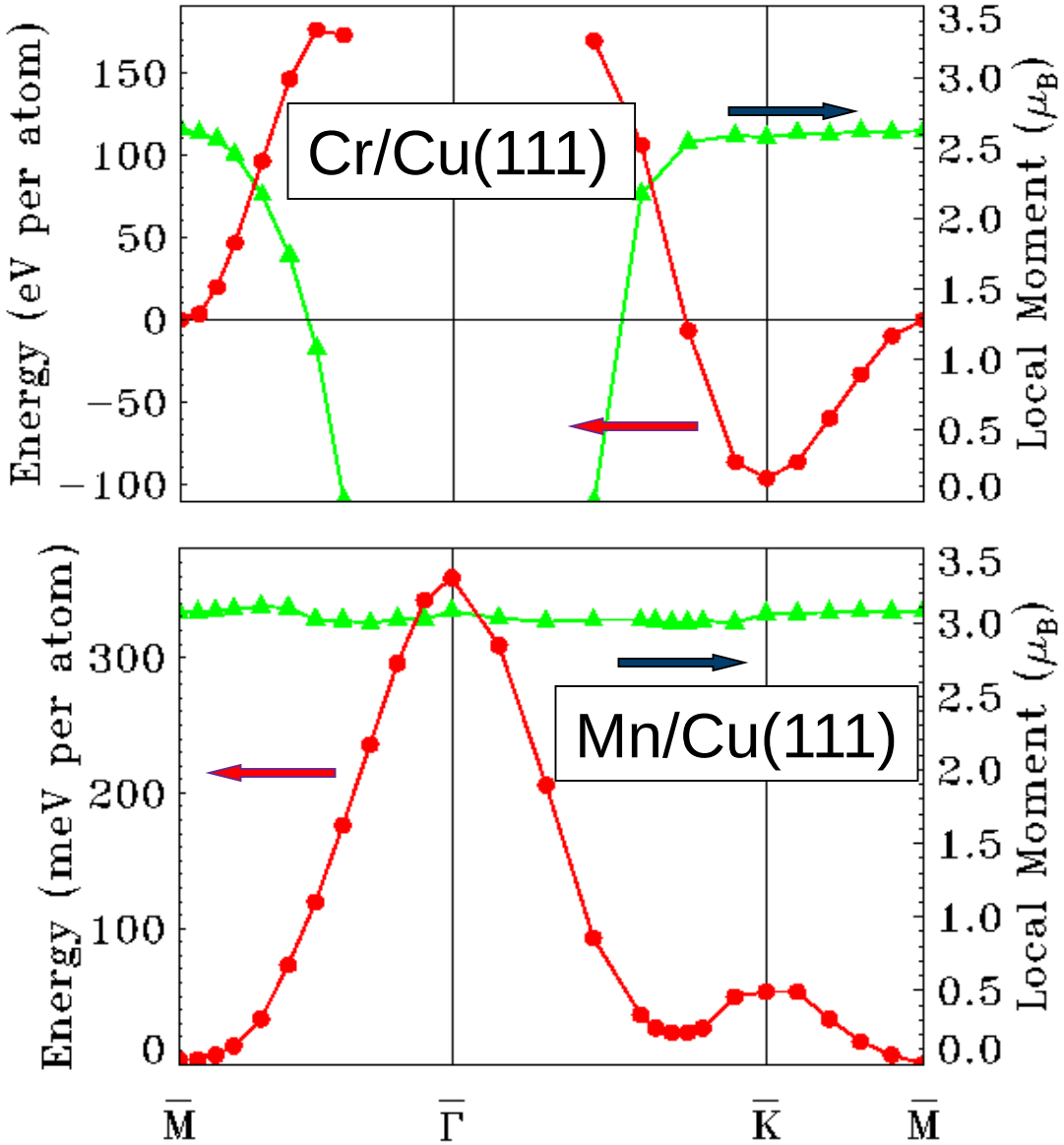
❖ DFT-model:

ab initio total energy $E^{DFT}(\mathbf{q})$



Néel State

Row-wise AFM (1Q-state)



SSDW E(q): UML Cr AND Mn ON Cu (111)

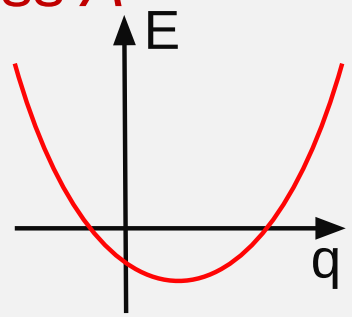
❖ DFT-model:

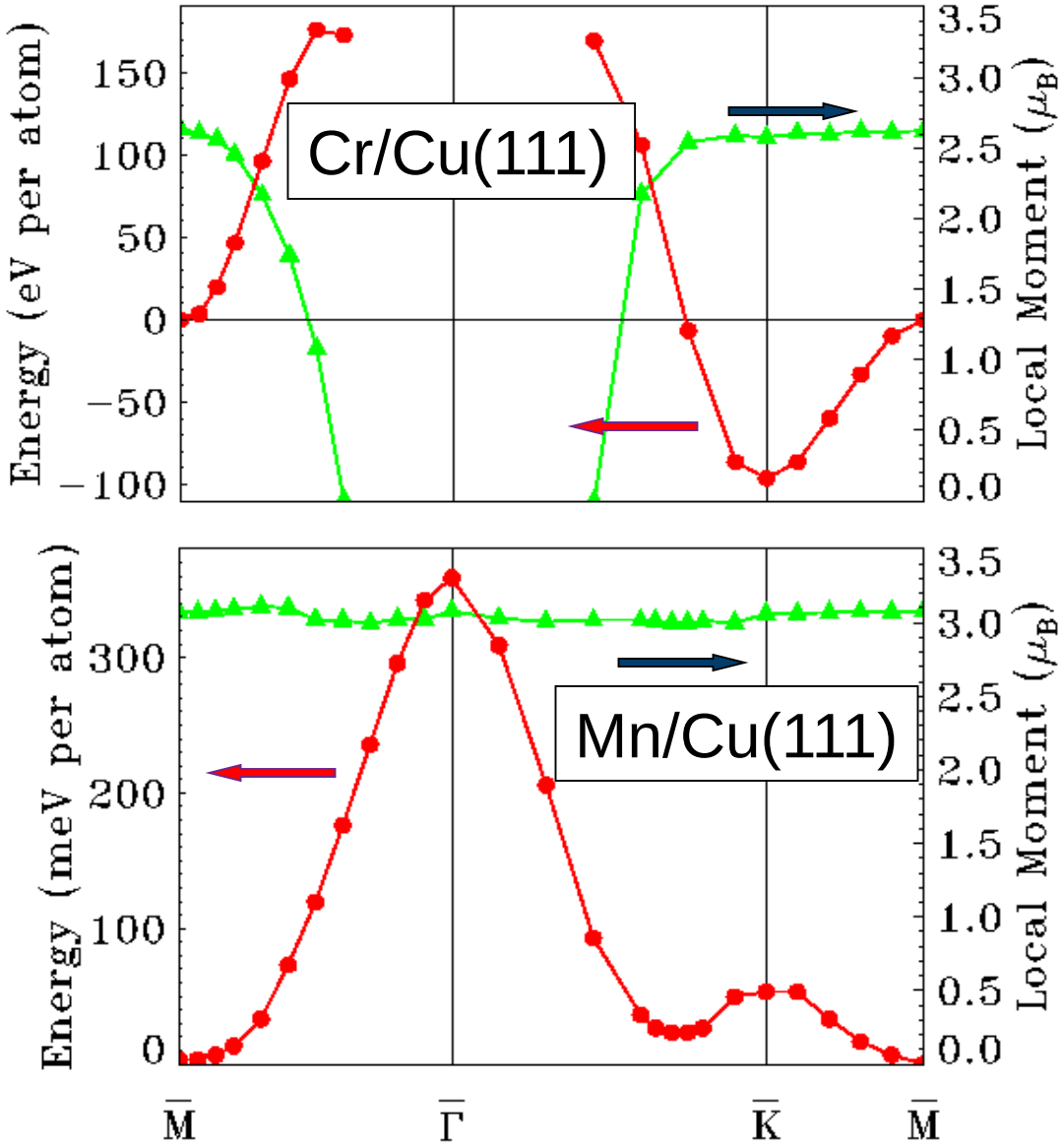
ab initio total energy $E^{\mathrm{DFT}}(\mathbf{q})$

➢ Spin-stiffness A

$E(q) = Aq^2$

$$\mathcal{A} = \left.\frac{d^2 E(\mathbf{q})}{d\mathbf{q}d\mathbf{q}}\right|_{\mathbf{q}\to 0}$$





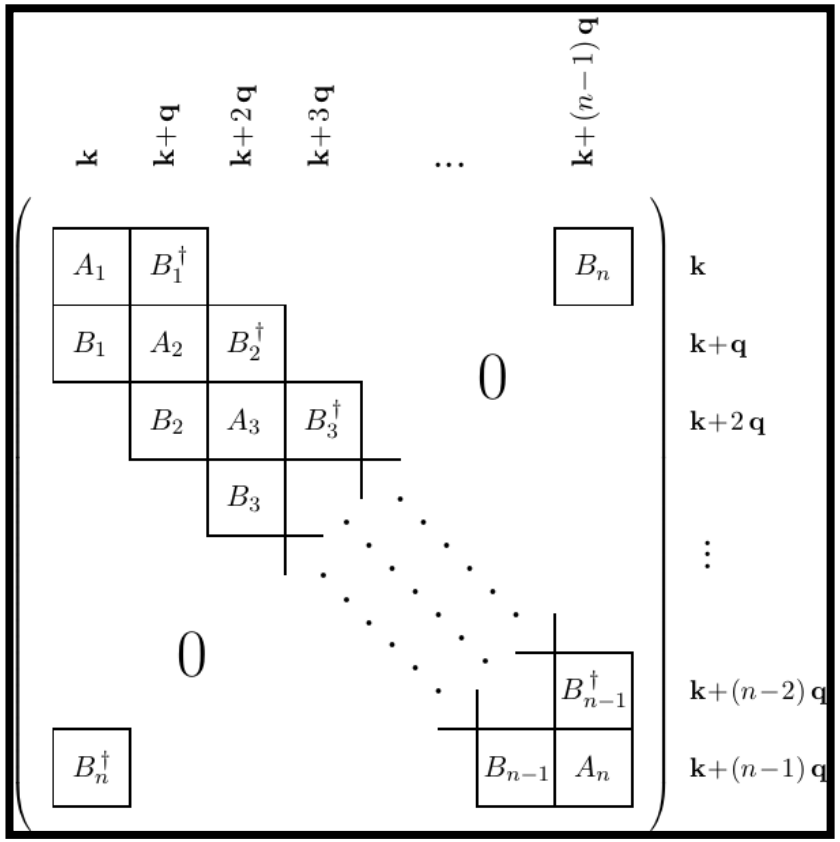
M. Heide, G. Bihlmayer, and S. Blügel, Physica B **404**, 2678 (2009)
B. Zimmermann, M. Heide, G. Bihlmayer, and S. Blügel, PRB **90**, 115427 (2014)
B. Schweflinghaus, B. Zimmermann, G. Bihlmayer and S. Blügel, PRB **94**, 024403 (2016)

COMPUTATIONAL APPROACH TO DMI

(DZYALOSHINSKII-MORIYA INTERACTION)

Unperturbed states: generalized Bloch theorem

$$\psi_\mu(\mathbf{r}) = \psi_{\mathbf{k},j}(\mathbf{r}) = \exp(i\,\mathbf{k}\cdot\mathbf{r}) \begin{pmatrix} \exp(-i\,\frac{1}{2}\,\mathbf{q}\cdot\mathbf{r}) & 0 \\ 0 & \exp(+i\,\frac{1}{2}\,\mathbf{q}\cdot\mathbf{r}) \end{pmatrix} \begin{pmatrix} u^{(\uparrow)}_{\mathbf{k},j}(\mathbf{r}) \\ u^{(\downarrow)}_{\mathbf{k},j}(\mathbf{r}) \end{pmatrix}$$



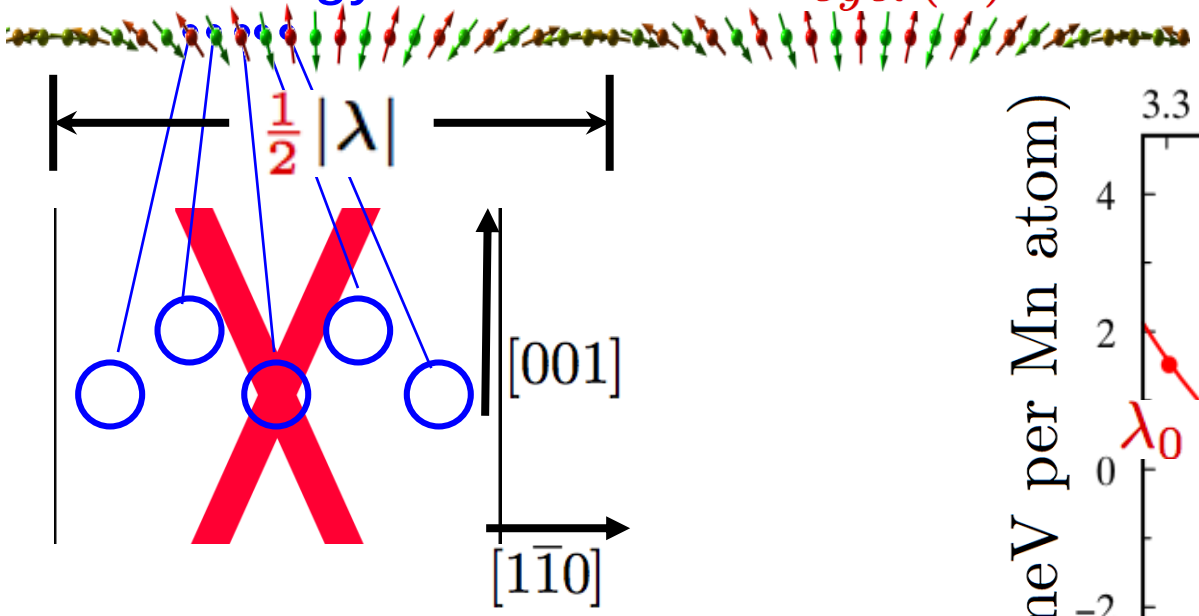
Spin-Orbit Coupling $\mathcal{H}_{\rm so} = \sum_\alpha \frac{1}{r_\alpha}\frac{\mathrm{d}V_\alpha(r_\alpha)}{\mathrm{d}r_\alpha}\,\boldsymbol{\sigma}\cdot\hat{\mathbf{L}}_\alpha = \begin{pmatrix} \mathcal{H}^{(\uparrow,\uparrow)}_{\rm so} & \mathcal{H}^{(\uparrow,\downarrow)}_{\rm so} \\ \mathcal{H}^{(\downarrow,\uparrow)}_{\rm so} & \mathcal{H}^{(\downarrow,\downarrow)}_{\rm so} \end{pmatrix}$ Hamiltonian Matrix

Sparse Matrix: $H_{\{\mathbf{k}\}} = \left(\delta_{\mu,\mu'}\,\epsilon_\mu + \langle\psi_{\mu'}|\mathcal{H}_{\rm so}|\psi_\mu\rangle \right)_{\mu,\mu'}$

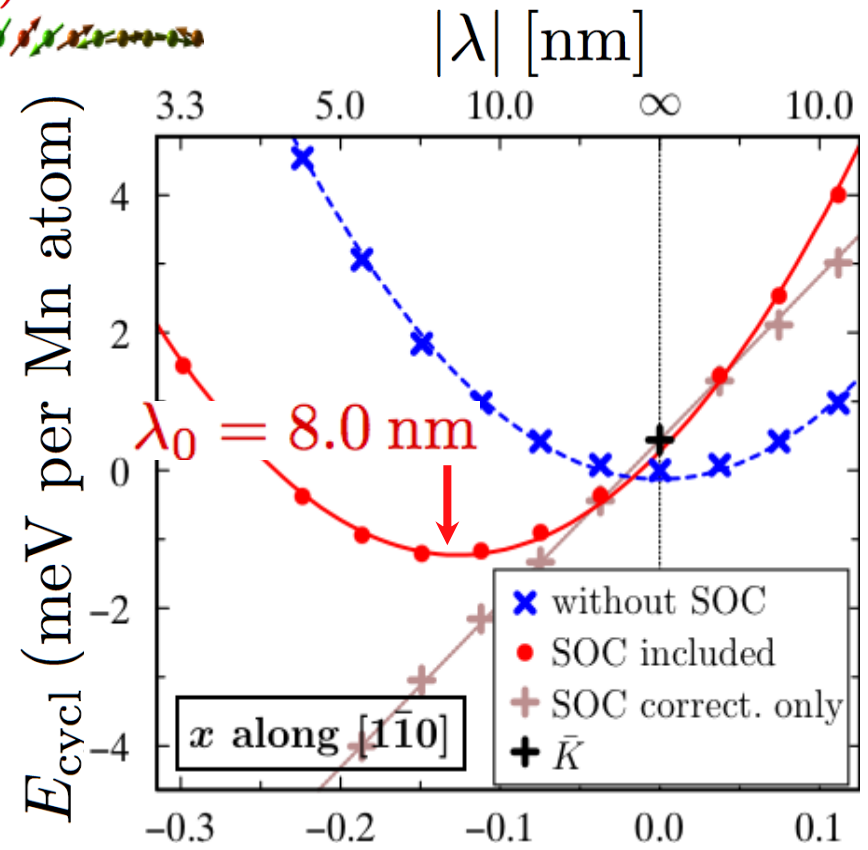
SEARCH FOR CYCLOIDAL SPIRAL: Mn/W(110)

Magnetic Configuration:

Total Energy Calculation: $E_{cycl}(\lambda)$



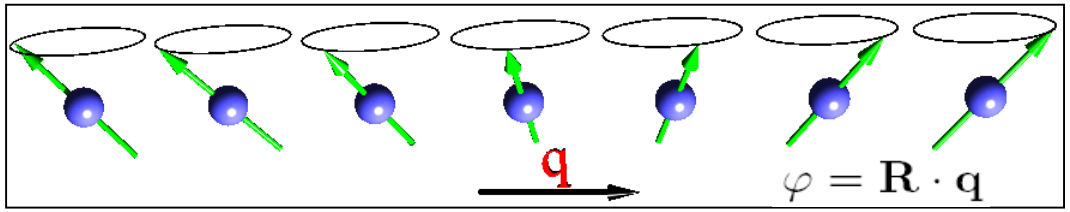
$$E_{\text{cycl}}\left[\frac{2\pi}{\lambda}\right] = J\left(\frac{2\pi}{\lambda}\right)^2$$



$J = 95.6 \frac{\text{meV}}{\text{Mn atom}}$ $D = -17.0 \frac{\text{meV}}{\text{Mn atom}}$ $\overline{K} = 0.6 \frac{\text{meV}}{\text{Mn atom}}$

SPIN-SPIRALS WITH SMALL CONE ANGLE

Approximation: Frozen magnons as spin spirals

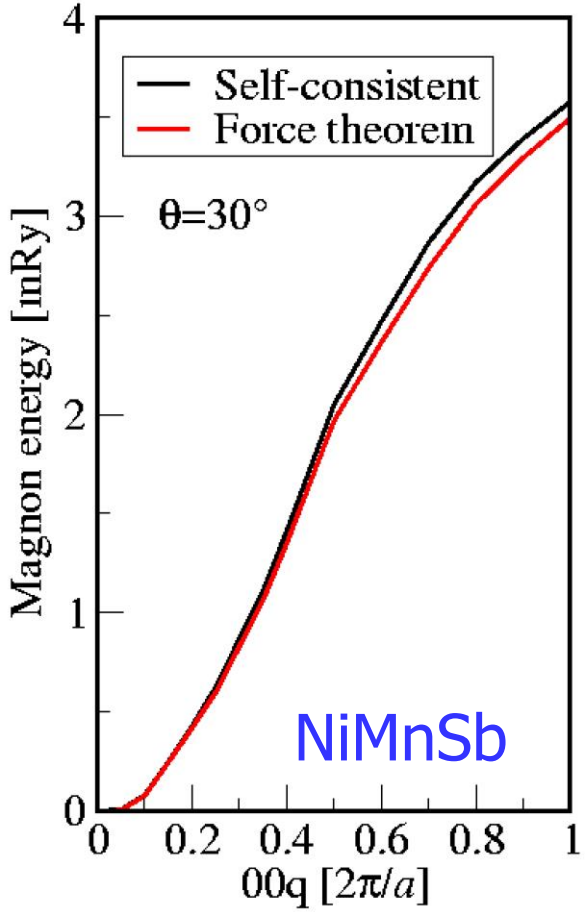


$$\mathbf{M}^n = M(\cos(\mathbf{q}\cdot\mathbf{R}^n)\sin\theta, \sin(\mathbf{q}\cdot\mathbf{R}^n)\sin\theta, \cos\theta)$$

Calculations give the dispersion E(q).
Excitation energy of the magnon: E(q)-E(q=0).

cone angle: q

Smallness parameter: $q = 0$ ferromagnetic state



Lezaic *et al*, PRB **88**, 134403 (2013)

Use of frozen force theorem $E(q) - E(0) = \sum_{kn}^{E_F(q)} e_{kn}(q) - \sum_{kn}^{E_F(0)} e_{kn}(q=0)$

LOCAL FORCE THEOREM

- Total energy for state given by θ and **q**: $E[n, \mathbf{m}](\theta, \mathbf{q})$
- Energy of magnetic state 1: $E[n_1, \mathbf{m}_1](\theta_1, \mathbf{q}_1)$
- Energy of magnetic state 2: $E[n_2, \mathbf{m}_2](\theta_2, \mathbf{q}_2)$
- Energy difference $\Delta E = E[n_2, \mathbf{m}_2](\theta_2, \mathbf{q}_2) - E[n_1, \mathbf{m}_1](\theta_1, \mathbf{q}_1)$
- If the density and vector-spin density are hardly unchanged between the state 1 and 2 the local force theorem says:

$$\Delta E = \sum_{\mathbf{k}\nu} \varepsilon_{\mathbf{k}\nu}(\theta_2, \mathbf{q}_2) - \varepsilon_{\mathbf{k}\nu}(\theta_1, \mathbf{q}_1) + \mathcal{O}\left((\delta n)^2, (\delta m)^2\right)$$

- Only 1 self-consistent calculation is necessary , rest is single shot.

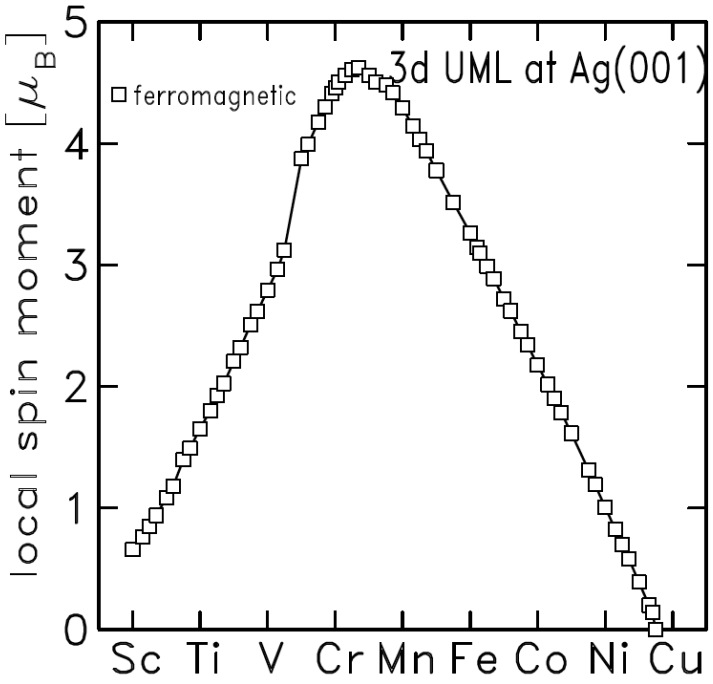
- Smallness parameter θ !

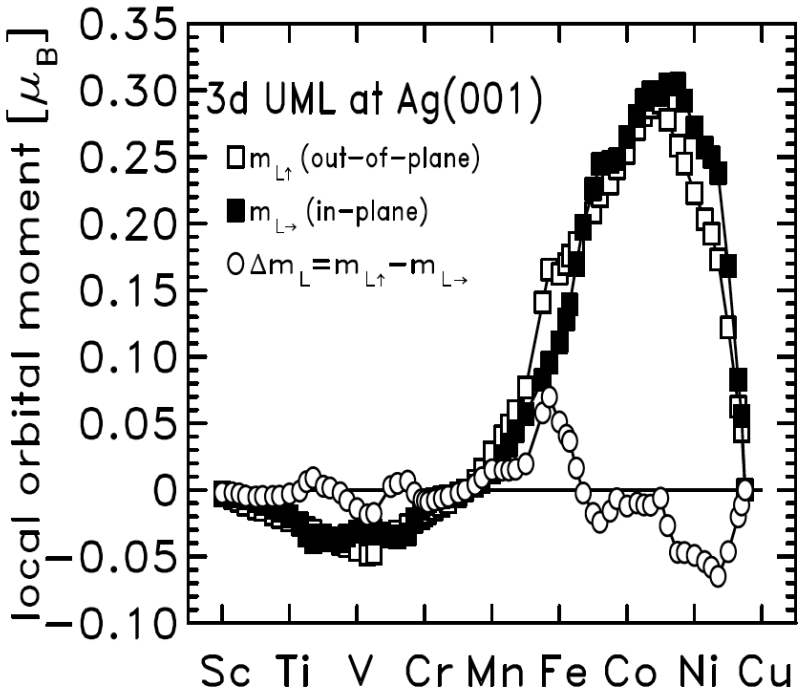
CALCULATION OF MAGNETIC ANISOTROPY

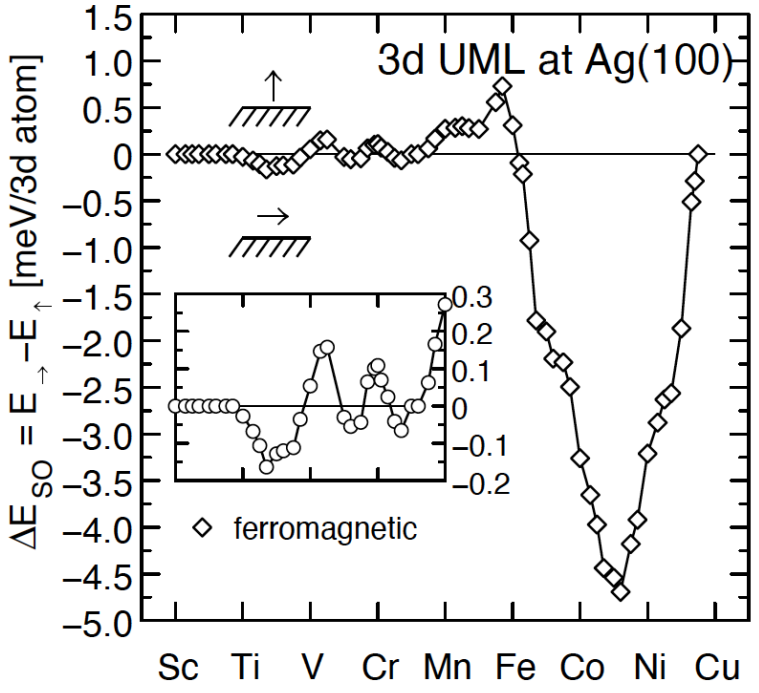
E_{MCA}

$$\Delta E = \sum_{\mathbf{k}\nu} \varepsilon_{\mathbf{k}\nu}(\Uparrow) - \varepsilon_{\mathbf{k}\nu}(\Rightarrow) + \mathcal{O}\left((\delta n)^2, (\delta m)^2\right)$$

EXAMPLE 3D MONOLAYER LATTICE OF Ag(100)







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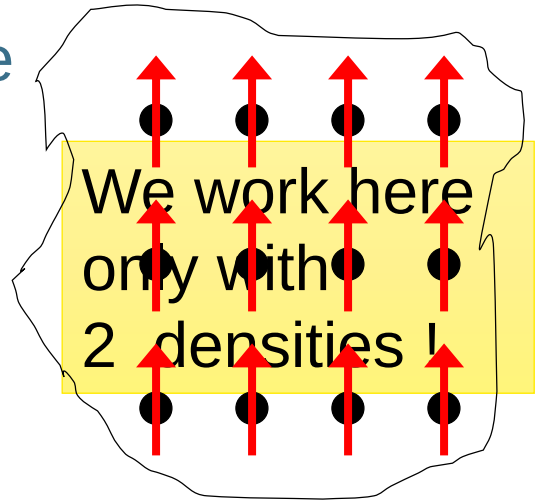
COLLINEAR MAGNETIC STRUCTURE

❖ Two-component spinor in general form: $\Psi(\mathbf{r}) = \begin{pmatrix} \psi_1(\mathbf{r}) \\ \psi_2(\mathbf{r}) \end{pmatrix}$

❖ Density → **Density Matrix** in spinor space

$$\underline{\mathbf{n}}(\mathbf{r}) = \begin{pmatrix} \psi_1^*(\mathbf{r})\psi_1(\mathbf{r}) & \psi_1^*(\mathbf{r})\psi_2(\mathbf{r}) \\ \psi_2^*(\mathbf{r})\psi_1(\mathbf{r}) & \psi_2^*(\mathbf{r})\psi_2(\mathbf{r}) \end{pmatrix}$$



➢ Density $n(\mathbf{r}) = \langle \Psi(\mathbf{r}) | \underline{\mathbf{1}}_2 | \Psi(\mathbf{r}) \rangle$

➢ ~~Vector-~~spin density $\mathbf{m}(\mathbf{r}) = \langle \Psi(\mathbf{r}) | \underline{\sigma} | \Psi(\mathbf{r}) \rangle \Longrightarrow m_z(\mathbf{r}) = \langle \Psi(\mathbf{r}) | \underline{\sigma_z} | \Psi(\mathbf{r}) \rangle$

$$\underline{\mathbf{n}}(\mathbf{r}) = \frac{1}{2} \begin{pmatrix} n(\mathbf{r}) + m_z(\mathbf{r}) & m_x(\mathbf{r}) + i m_y(\mathbf{r}) \\ m_x(\mathbf{r}) - i m_y(\mathbf{r}) & n(\mathbf{r}) - m_z(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} n_\uparrow(\mathbf{r}) \\ n_\downarrow(\mathbf{r}) \end{pmatrix}$$

COLLINEAR MAGNETIC STRUCTURE

❖ Kohn-Sham Hamiltonian

$$\left[-\Delta + \begin{pmatrix} V_{11}(\mathbf{r}) & V_{12}(\mathbf{r}) \\ V_{21}(\mathbf{r}) & V_{22}(\mathbf{r}) \end{pmatrix}\right] \begin{pmatrix} \psi_{\mathbf{k}\nu\uparrow}(\mathbf{r}) \\ \psi_{\mathbf{k}\nu\downarrow}(\mathbf{r}) \end{pmatrix} = \varepsilon_{\mathbf{k}\nu} \begin{pmatrix} \psi_{\mathbf{k}\nu\uparrow}(\mathbf{r}) \\ \psi_{\mathbf{k}\nu\downarrow}(\mathbf{r}) \end{pmatrix}$$

❖ Kohn-Sham Hamiltonian for spin-up and -down

$$\begin{aligned} \left[-\Delta + V_{\uparrow}(\mathbf{r})\right] \psi_{\mathbf{k}\nu\uparrow}(\mathbf{r}) &= \varepsilon_{\mathbf{k}\nu\uparrow}\, \psi_{\mathbf{k}\nu\uparrow}(\mathbf{r}) \\ \left[-\Delta + V_{\downarrow}(\mathbf{r})\right] \psi_{\mathbf{k}\nu\downarrow}(\mathbf{r}) &= \varepsilon_{\mathbf{k}\nu\downarrow}\, \psi_{\mathbf{k}\nu\downarrow}(\mathbf{r}) \end{aligned}$$

❖ CPU – time : non-collinear vs collinear ⟹ x 100 CPU

Noncollinear:
- spin up and down coupled (x 4)
- hermitian (x 2)
- more k-points (x 4)
- lower symmetry due to spin-structure (x 4)

LOCAL SPIN-DENSITY APPROXIMATION

- Local **spin**-density approximation (LSDA)

$$E_{\mathrm{xc}}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})] \approx \int_V n(\mathbf{r})\, \epsilon_{\mathrm{xc}}^{hom}\left(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})\right)\, d\mathbf{r}$$

- Xα approximation: only exchange (Hartree-Fock)

$$E_{\mathrm{X}}^{\mathrm{hom}}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})] = -\alpha \frac{3e^2}{4}\left(\frac{6}{\pi}\right)^{1/3} \int_V \left[(n_\uparrow(\mathbf{r}))^{4/3} + (n_\downarrow(\mathbf{r}))^{4/3}\right] d\mathbf{r}$$

$$\Longrightarrow V_{\mathrm{X}}^{\uparrow,\downarrow}(\mathbf{r}) = -\alpha e^2 \left(\frac{6}{\pi}\right)^{1/3} \left(n_{\uparrow,\downarrow}(\mathbf{r})\right)^{1/3}$$

- better approximations: von Barth-Hedin (1972)
  Ceperley-Alder QMC (1980)
  Perdew-Wang GGA (1991)
  Perdew-Burke-Ernzerhof (1996)

WHY DOING DFT CALCULATIONS ?

- To get insight (not only numbers) , e.g. by calculating the chemical trend
- To complement or analyse experiments
- To predict new phenomena
- To design new materials with particular functionalities
- To use as digital twin to optimize complex physical infrastructures (e.g. synchrotron beam lines)
- To replace difficult, expensive or dangerous experiments
- To perform a virtual microscopy
- To explore the large number of configurations and chemical variations

THE QUANTUM MATERIALS SPACE

- **Quantum Space of electrons** (Hilbert Space):

$$\left[-\frac{\hbar^2}{2m}\Delta + V(x)\right]\Psi(x) = E\Psi(x)$$

DFT — Static + Dynamik

GW — Excitation

Kubo — Transport

Challenges

- Larger Systems
- More electron correlation
- Longer spin-dynamics simulation

Very different exascale challenges

- **Chemical Space** (Configuration Space):

Combining: quantum engine + autonomous high-throughput framework + data informatics

Challenges

- Making quantum engines resilient and robust (Error handling and recovery)
- Writing workflows
- Connecting high-throughput frameworks with Exascale computer considering securitu

JÜLICH DFT SIMULATION INFRASTRUCTURE

Computational Infrastructure for design & analyse of materials ϕ high-throughput calculations on Exascale

www.juDFT.de

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workshops
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SPEX

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All kinds of exotic transport properties

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Exascale

MAX DRIVING THE EXASCALE TRANSITION

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Pablo Picasso, Stier, 5.12.1945 - 17.1.1946 © Succession Picasso / VG Bild-Kunst, Bonn 2005

Thanks !