Radboud Universiteit

# *Quantitative theory of magnetic interactions in solids*

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# *Epigraphs*

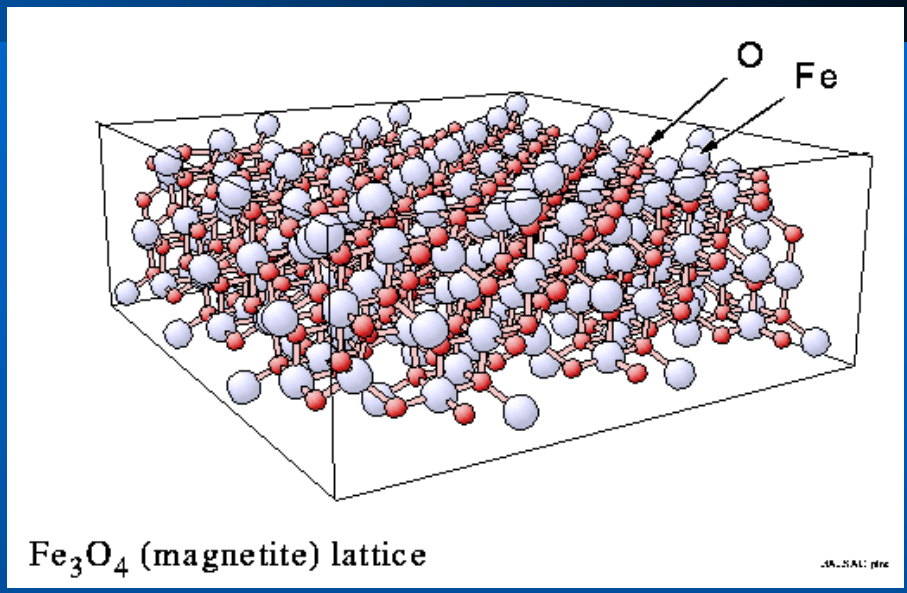
*To the theoretical physicists, ferromagnetism presents a number of very interesting, unsolved and beautiful challenges. Our challenge is to understand why it exists at all.*

*(Feynman Lectures on Physics)*

*Make things as simple as possible but not simpler*

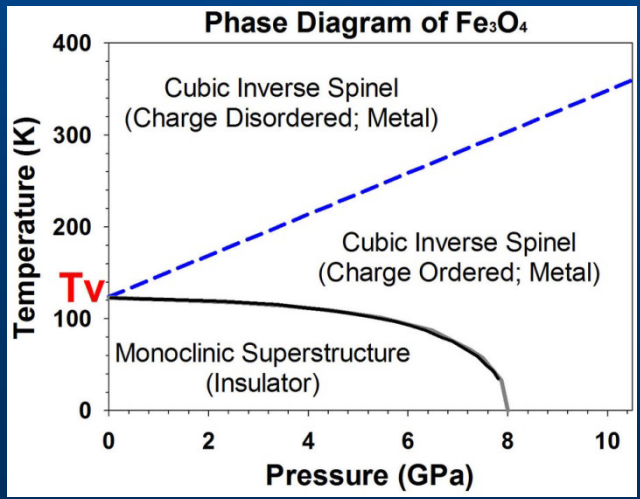
*(A. Einstein)*

# Magnetite – first known magnet



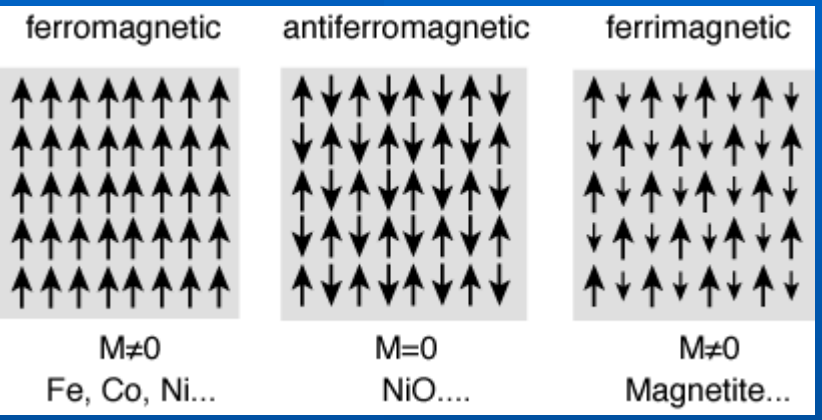

*Very complicated structure, still a lot of open questions*

*Two types of Fe sites (tetra and octa);*
*Metal-insulator transition;*
*Charge ordering;*
*Role of orbital degrees of freedom;*
*Half-metallicity…*



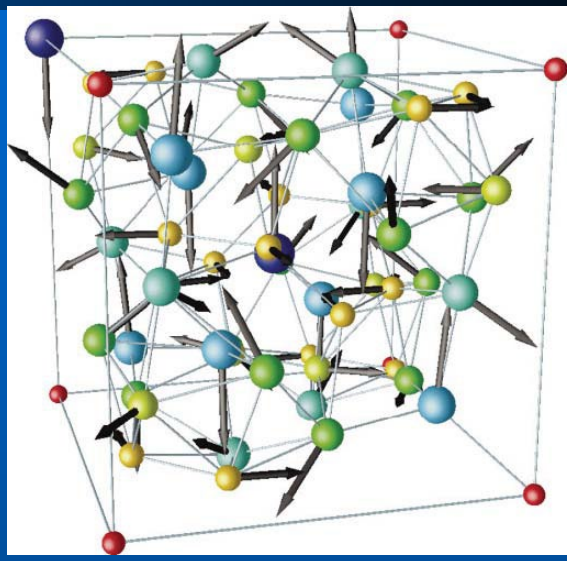
# Types of magnetic ordering

*Textbook wisdom*

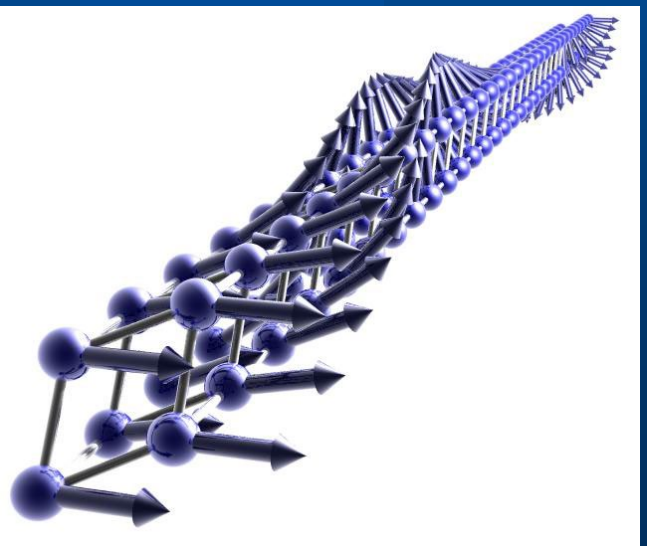



*Sometimes very complicated*

*α-Mn*

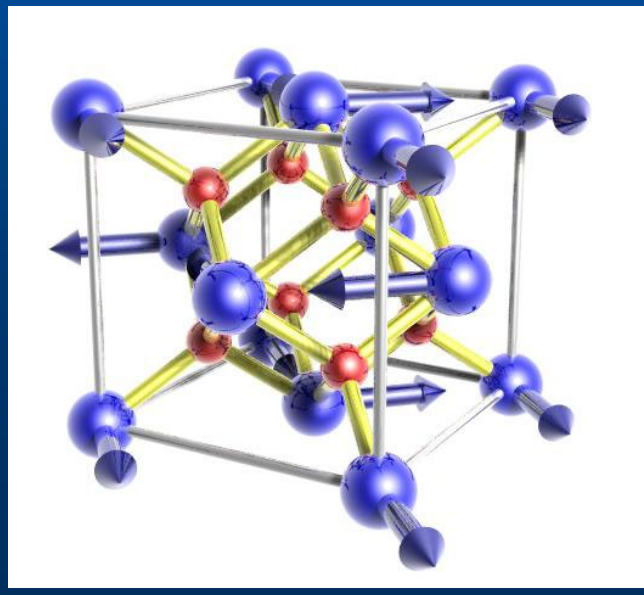


*Spin spirals*

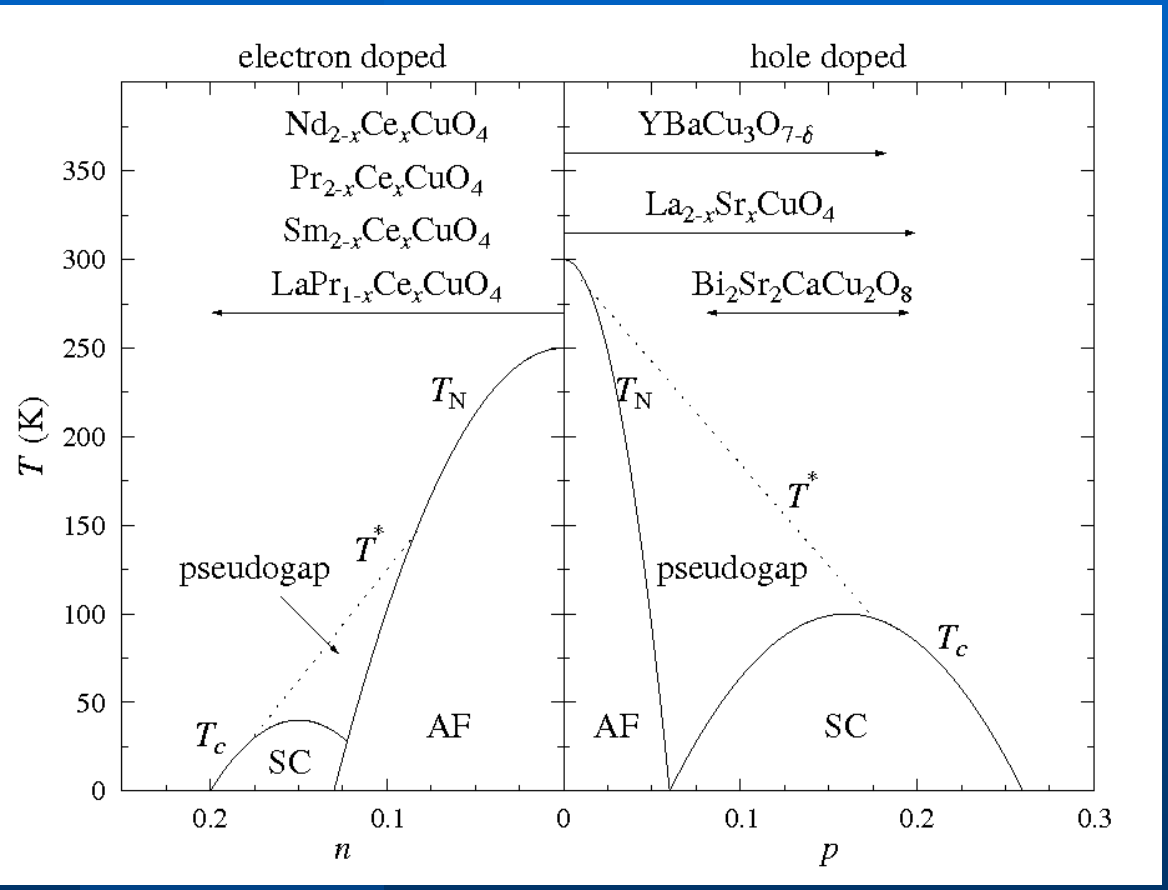


*γ-Fe*

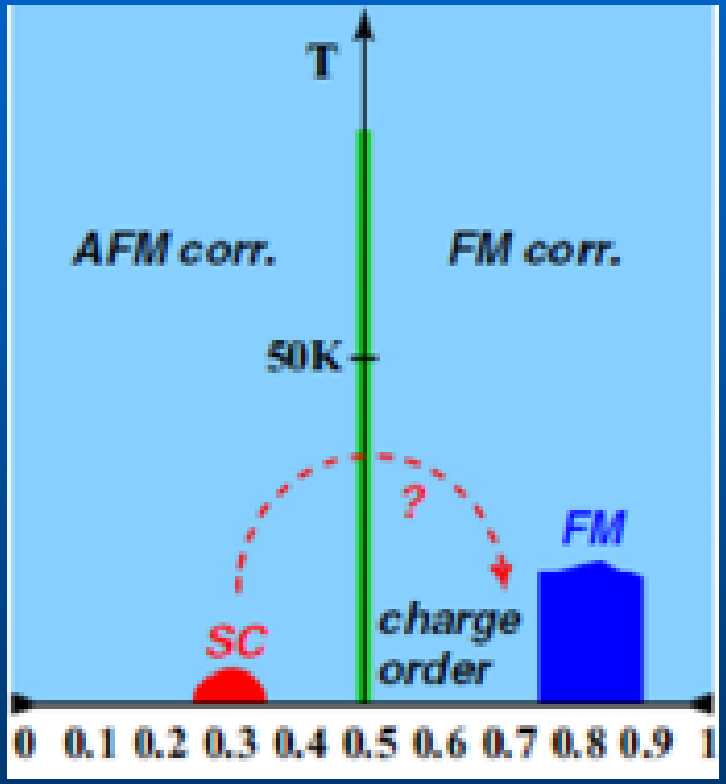
*$UO_2$*



# Relation to superconductivity and other phenomena




Simplified phase diagram of Cu-O high-Tc superconductors




Layered cobaltates $Na_xCoO_2$

# Types of magnetic interactions

$$\hat{H} = \sum_{ij} J_{ij} \hat{\vec{S}}_i \hat{\vec{S}}_j + \sum_{i\mu\nu} \hat{S}_i^{\mu} A_i^{\mu\nu} \hat{S}_i^{\nu} + \sum_{ij} \vec{D}_{ij} [\hat{\vec{S}}_i \times \hat{\vec{S}}_j]$$

*The first term: exchange interactions (Heisenberg model)*
*Quantum, nonrelativistic (Coulomb interaction plus Pauli principle). Determine the type of magnetic ordering (mostly)*

*The second term: magnetic anisotropy*
*Quantum, relativistic (due to spin-orbit interaction). At least, second-order in SOC. Determine "practical" magnetism (hard and soft magnetic materials, hysteresis loop, etc.)*

*The third term: Dzyaloshinskii-Moriya interactions*
*Quantum, relativistic (due to spin-orbit interaction). First-order in SOC but require broken inversion symmetry. Responcible for weak FM, skyrmiones etc.*

# *Levels of description*

- Macroscopic (LLG equations + temperature balance, etc.)

- Microscopic, classical Heisenberg model

- Microscopic, quantum itinerant-electron model

-Ab initio, time-dependent density functional or Green function functional (GW, DFT+DMFT, …)

Multiscale problem

# *LDA (DFT)+DMFT versus DFT*

(Lichtenstein & MIK 1997, 1998,1999; Anisimov et al 1997)

| LSDA | LDA++ |
|---|---|
| Density functional | Baym-Kadanoff functional |
| Density $\rho(\mathbf{r})$ | Green-Function $G(\mathbf{r},\mathbf{r}',E)$ |
| Potential $V_{xc}(\mathbf{r})$ | Self-energy $\Sigma_i(E)$ |
| $E_{tot} = E_{sp} - E_{dc}$ | $\Omega = \Omega_{sp} - \Omega_{dc}$ |
| $E_{sp} = \sum_{\lambda<\lambda_F} \varepsilon_\lambda$ | $\Omega_{sp} = -Tr\ln[-G^{-1}]$ |
| $E_{dc} = E_H + \int \rho V_{xc} d\mathbf{r} - E_{xc}$ | $\Omega_{dc} = Tr\Sigma G - \Phi_{LW}$ |
| Temperature: | Matsubara frequencies: real-T |
| in the Fermi function | for collective excitations |

# How to map fully microscopic description to magnetic Hamiltonians?

*The talk is based on theory developed for about 40 years, first of all, with Sasha Lichtenstein, and with other friends and colleagues*

J. Phys. F: Met. Phys. **14** (1984) L125–L128. Printed in Great Britain

LETTER TO THE EDITOR

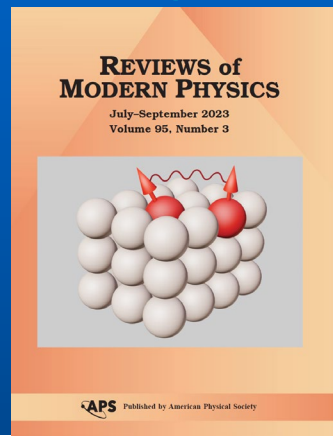
**Exchange interactions and spin-wave stiffness in ferromagnetic metals**

A I Liechtenstein†, M I Katsnelson‡ and V A Gubanov†

Journal of Magnetism and Magnetic Materials 67 (1987) 65–74
North-Holland, Amsterdam

**LOCAL SPIN DENSITY FUNCTIONAL APPROACH TO THE THEORY OF EXCHANGE INTERACTIONS IN FERROMAGNETIC METALS AND ALLOYS**

A.I. LIECHTENSTEIN, M.I. KATSNELSON [+], V.P. ANTROPOV [+] and V.A. GUBANOV




PHYSICAL REVIEW B VOLUME 61, NUMBER 13 1 APRIL 2000-I

**First-principles calculations of magnetic interactions in correlated systems**

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(Received 13 April 1999; revised manuscript received 28 October 1999)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **16** (2004) 7439–7446 PII: S0953-8984(04)80755-0

**Magnetic susceptibility, exchange interactions and spin-wave spectra in the local spin density approximation**

**M I Katsnelson[1,2] and A I Lichtenstein[2,3]**

REVIEWS OF MODERN PHYSICS, VOLUME 95, JULY–SEPTEMBER 2023

**Quantitative theory of magnetic interactions in solids**

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(published 11 September 2023)

# The first step: adiabatic approximation

In condensed matter physics we know the basic laws, it is laws of quantum mechanics

**Time-dependent Schrödinger equation** *(general)*

$$i\hbar\frac{\partial}{\partial t}|\Psi(\mathbf{r},t)\rangle = \hat{H}|\Psi(\mathbf{r},t)\rangle$$

In solids/liquids/molecules/clusters...

$$\hat{H} = \hat{T}_n + V_{nn}\left(\vec{R}_l\right) + \hat{H}_e\left(\vec{R}_l\right)$$

$$\hat{T}_n = \sum_l \frac{\hat{\vec{P}}_l^2}{2M_l}$$

$$V_{nn}\left(\vec{R}_l\right) = \frac{1}{2}\sum_{l\neq l'}\frac{Z_l Z_{l'} e^2}{\left|\vec{R}_l - \vec{R}_{l'}\right|}$$

$$\hat{H}_e\left(\vec{R}_l\right) = \sum_i \frac{\hat{\vec{p}}_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} - \sum_{il}\frac{Z_l e^2}{\left|\vec{r}_i - \vec{R}_l\right|}$$

*Adiabatic approximation: small parameter*

$$\kappa = \left(\frac{m}{M}\right)^{1/4}$$

*allows to separate electron and lattice degrees of freedom*

# *Adiabatic approximation for spins*

*Spin variables are not separated at the level of Hamiltonian; some serious work is needed but at the end it can be done quite rigorously*

*The basic idea: dual boson approach, collective variables are introduced into the fermionic action*

Dual boson approach to collective excitations in correlated fermionic systems

A.N. Rubtsov [a], M.I. Katsnelson [b], A.I. Lichtenstein [c,*]

Annals of Physics 327 (2012) 1320–1335

*Applications to spin degrees of freedom*

PHYSICAL REVIEW LETTERS **121,** 037204 (2018)

**Effective Heisenberg Model and Exchange Interaction for Strongly Correlated Systems**

E. A. Stepanov,[1,2] S. Brener,[3] F. Krien,[3] M. Harland,[3] A. I. Lichtenstein,[3,2] and M. I. Katsnelson[1,2]

PHYSICAL REVIEW B **105**, 155151 (2022)

**Spin dynamics of itinerant electrons: Local magnetic moment formation and Berry phase**

E. A. Stepanov,[1,*] S. Brener,[2,3] V. Harkov,[2,4] M. I. Katsnelson,[5] and A. I. Lichtenstein[2,3,4]

# *The main conceptual results*

1. *Mapping of interacting electrons onto effective spin Hamiltonians is possible only locally, near given equilibrium spin configuration; distinction of local and global spin models*
2. *Even locally, ambiguity in definition of exchange parameters: magnon energies (poles of dynamic susceptibility) vs energy of static magnetic configurations (static susceptibility)*
3. *In two cases the mapping is unambiguous: (3a) small wave vectors (spin-wave stiffness constant is unique) and (3b) well-localized magnetic moments (Stoner splitting is much larger than characteristic magnon energy)*

# Magnetic force theorem

*Initial idea: to calculate the change of thermodynamic potential under small spin rotations with respect to equilibrium spin configuration*

*Works both for density functionals and for Green function functionals; to be specific, consider the latter case.*

$$\Omega = \Omega_{sp} - \Omega_{dc},$$
$$\Omega_{sp} = -\mathrm{Tr}\{\ln[\Sigma - G_0^{-1}]\},$$
$$\Omega_{dc} = \mathrm{Tr}\Sigma G - \Phi, \qquad (5.57)$$

where $G$, $G_0$, and $\Sigma$ are an exact Green's function, its bare value, and its self-energy, respectively; $\Phi$ is the Luttinger generating functional (the sum of all connected skeleton diagrams without free legs); $\mathrm{Tr} = \mathrm{Tr}_{\omega i L\sigma}$ is the sum over Matsubara frequencies $\mathrm{Tr}_\omega \cdots = T\sum_\omega \cdots$, $\omega = \pi T(2n+1)$, and $n = 0, \pm 1, \ldots$; and $T$ is the temperature. Furthermore, $iL\sigma$ represents site numbers ($i$), orbital quantum numbers ($L = l, m$), and spin projections $\sigma$, respectively. The two Green's functions are related via the Dyson equation as

$$G^{-1} = G_0^{-1} - \Sigma, \qquad (5.58)$$

with the important variational identity

$$\delta\Phi = \mathrm{Tr}\Sigma\delta G. \qquad (5.59)$$

# Magnetic force theorem II

*Variation of thermodynamic potential under e.g. spin rotations*

$$\delta\Omega = \delta^*\Omega_{\rm sp} + \delta_1\Omega_{\rm sp} - \delta\Omega_{\rm dc}, \qquad (5.60)$$

where $\delta^*$ is the variation without taking into account the change of the "self-consistent potential" (i.e., self-energy) and $\delta_1$ is the variation due to this change of $\Sigma$.

$$\delta_1\Omega_{\rm sp} = \delta\Omega_{\rm dc} = {\rm Tr} G\delta\Sigma$$

and hence

$$\delta\Omega = \delta^*\Omega_{\rm sp} = -\delta^*{\rm Tr}\ln\left[\Sigma - G_0^{-1}\right]$$

*For local self-energy (e.g. DFT+DMFT)*

$$\Sigma_i = \Sigma_i^c + \vec{\Sigma}_i^s\vec{\sigma},$$
$$G_{ij} = G_{ij}^c + \vec{G}_{ij}^s\vec{\sigma},$$

$$\Sigma_i^{(c,s)} = (1/2)(\Sigma_i^{\uparrow} \pm \Sigma_i^{\downarrow}) \text{ and } \vec{\Sigma}_i^s = \Sigma_i^s\vec{e}_i$$

*Decomposing the expression for local torque into pair terms we find expression for exchange parameters*

$$J_{ij} = 2{\rm Tr}_{\omega L}\left(\Sigma_i^s G_{ij}^{\uparrow}\Sigma_j^s G_{ji}^{\downarrow}\right)$$

*Nomenclature:*

$$\mathcal{H}_H = \sum_{\langle ij\rangle} J_{ij}\vec{e}_i\cdot\vec{e}_j$$

*Expressed in terms of self-energy and Green functions*

# Magnetic force theorem III

DFT analog

$$J_{ij}^{(2)} = -\frac{2}{\pi}\Im \int \mathrm{Tr}_L(B_i G_{ij}^{\uparrow} B_j G_{ji}^{\downarrow}) d\varepsilon$$

(B – exchange-correlation field, integration over occupied energy states)

Substituting

$$G(z) = \sum_{\mu} \frac{|\varphi_\mu\rangle\langle\varphi_\mu|}{z - \varepsilon_\mu}$$

Transformation to RKKY-like shape

$$J(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mu\nu} \frac{f_{\mu\uparrow} - f_{\nu\downarrow}}{\omega - \varepsilon_{\mu\uparrow} + \varepsilon_{\nu\downarrow}} \star \psi_{\mu\uparrow}^*(\mathbf{r}) B_{\mathrm{xc}}(\mathbf{r}) \psi_{\nu\downarrow}(\mathbf{r}) \psi_{\nu\downarrow}^*(\mathbf{r}') B_{\mathrm{xc}}(\mathbf{r}') \psi_{\mu\uparrow}(\mathbf{r}')$$

$f_{\mu\sigma} = f(\varepsilon_{\mu\sigma})$ is the Fermi distribution

(contains also Stoner damping); corresponds to the poles of dynamic susceptibility in adiabatic approximation for xc field

$$\omega = \Omega(\mathbf{r},\mathbf{r}',\omega)$$

$$\Omega(\mathbf{r},\mathbf{r}',0) = \frac{4}{m(\mathbf{r})} J(\mathbf{r},\mathbf{r}',0) - 2B_{\mathrm{xc}}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$$

# Comparison to alternative approaches

*Difference of total energies of magnetic configurations? – but it assumes Heisenberg shape of the Hamiltonian which is rarely true*
*Energy of spin spiral magnetic configurations? – much better, but it does not give magnon energy, contrary to local force theorem*

*With explicit formula we can study general tendencies*

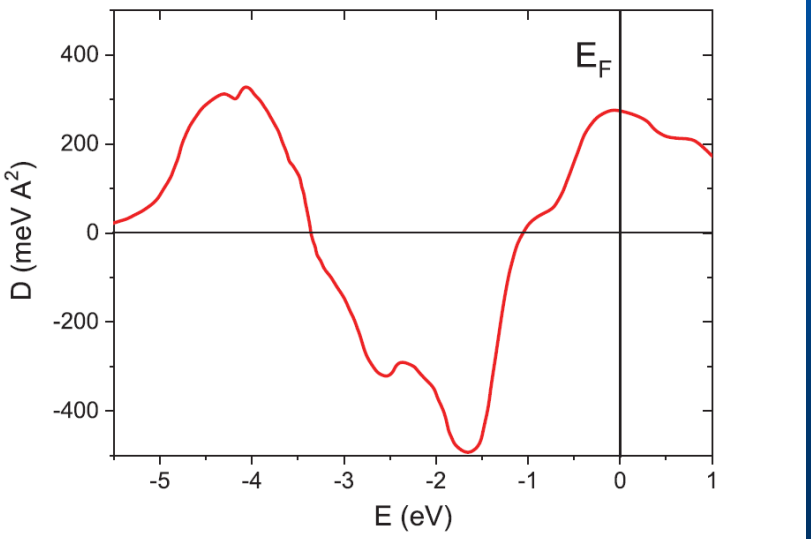



FIG. 8. Spin-wave stiffness in bcc Fe as a function of the upper integration limit. Adapted from Liechtenstein, Katsnelson, and Gubanov, 1984.

*One can see that close to half-filling exchange is not ferromagnetic (therefore it is so difficult to have FMs with high magnetization @RT)*

# Non-Heisenberg exchange

## Almost obvious for itinerant-electron magnets

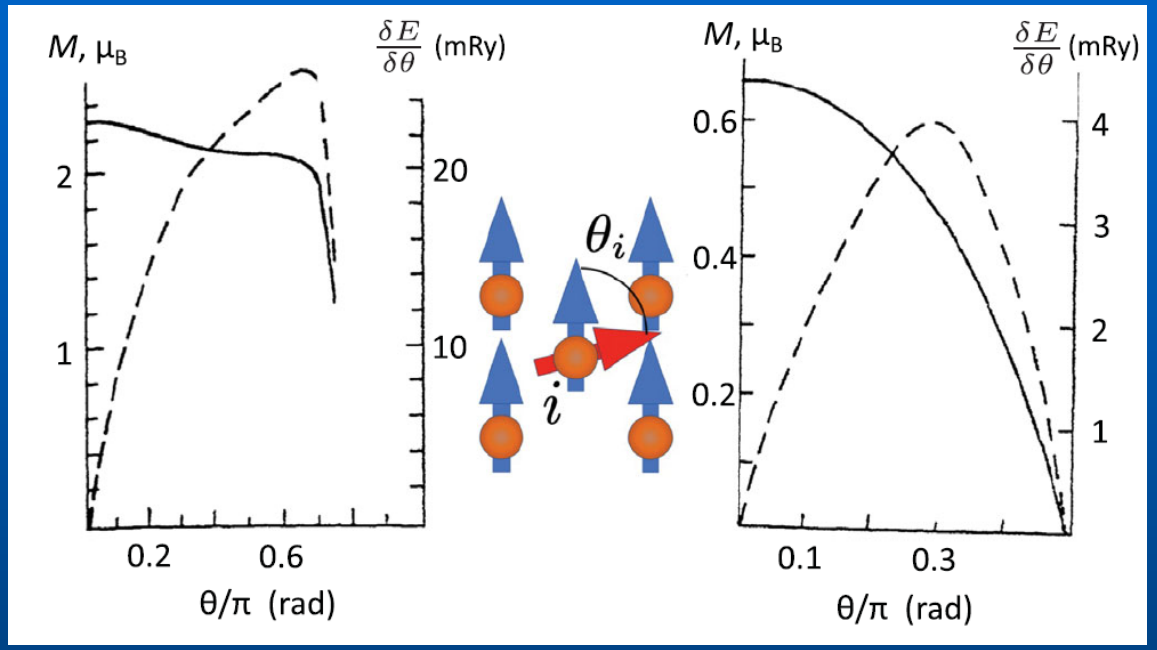



FIG. 13. Magnetic moment in $\mu_B$ (solid lines) and the first derivative of the energy ($\Omega$) with respect to angle $\theta_i$ (dashed lines) for the cases of bcc Fe (left) and fcc Ni (right) when one spin is rotated with a finite $\theta_i$ in a ferromagnetic background (Turzhevskii, Liechtenstein, and Katsnelson, 1990), as shown in the added schematic.


Turzhevskii, S., A. I. Liechtenstein, and M. I. Katsnelson, 1990, "Degree of localization of magnetic moments and the non-Heisenberg nature of exchange interactions in metals and alloys," Sov. Phys. Solid State **32**, 1138–1142, https://www.mathnet.ru/eng/ftt/v32/i7/p1952.

# Non-Heisenberg exchange II

## Even for insulating metal-oxide compounds

J. Phys.: Condens. Matter **29** (2017) 335801 (9pp) https://doi.org/10.1088/1361-648X/aa7b00

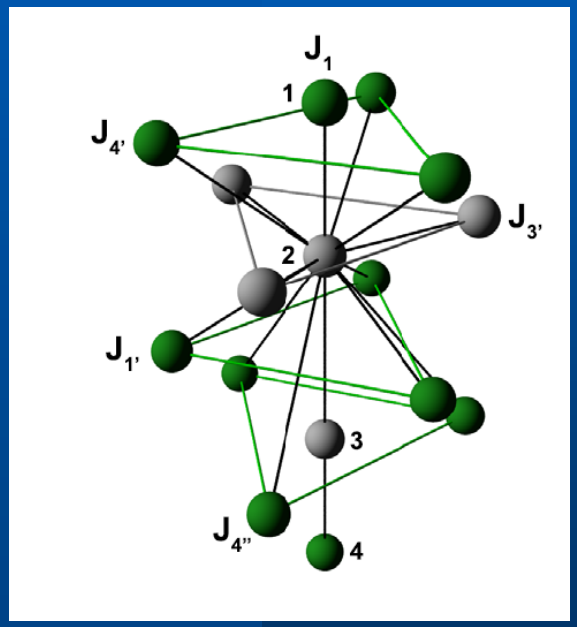
**Exchange interactions in transition metal oxides: the role of oxygen spin polarization**

R Logemann, A N Rudenko, M I Katsnelson and A Kirilyuk

*Nomenclature*

$$H = -\sum_{i>j} 2J_{ij}\boldsymbol{s}_i \cdot \boldsymbol{s}_j$$

$\boldsymbol{s}_i$ ($\boldsymbol{s}_j$) is the unit vector




*Fe atoms in elementary cell of hematite; green spins down*

*LDA+U calculations*

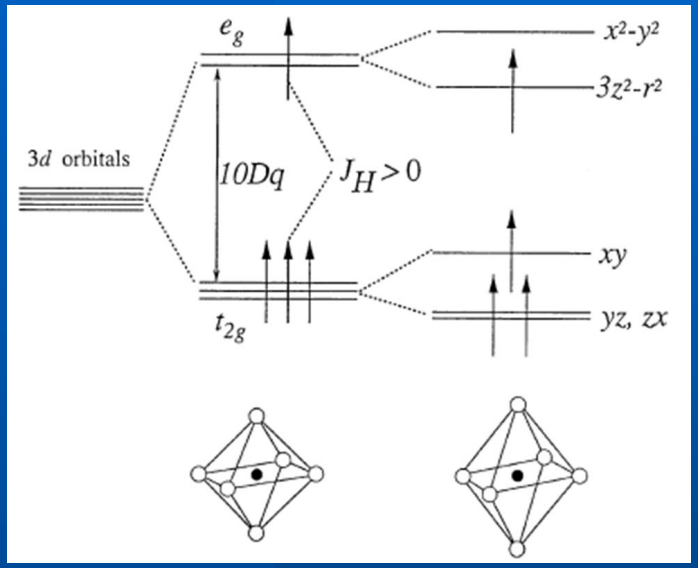
**Table 6.** Effective exchange parameters (in meV) in hematite calculated using (13) for the AFM and FM magnetic configurations and their relative difference (= (AFM − FM)/FM).

| | AFM | FM | Difference (%) |
|---|---|---|---|
| $J_{1'}^{\text{eff}}$ | −13.9 | −10.4 | 34 |
| $J_{4'}^{\text{eff}}$ & $J_{4''}^{\text{eff}}$ | −9.8 | −9.0 | 9 |
| $J_{1}^{\text{eff}}$ | −3.5 | 7.8 | −144 |
| $J_{3'}^{\text{eff}}$ | −3.1 | 6.8 | −146 |

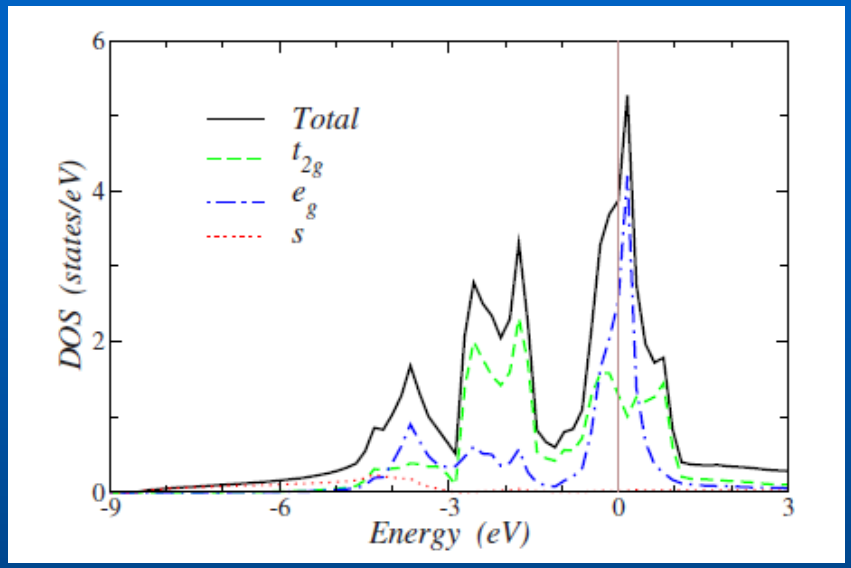
*Polarization of oxygen effects essentially on superexchange*

# Orbital decomposition

*bcc Fe as an example: different role of different orbitals*




*Crystal field splitting*




*DOS for non magnetic Fe*

*Stoner criterion is fulfilled due to $e_g$ states only; they should play a special role in magnetism*

(Irkhin, Katsnelson, Trefilov, JPCM 5, 8763 (1993))

# Orbital decomposition II

PRL 116, 217202 (2016) PHYSICAL REVIEW LETTERS week ending 27 MAY 2016

**Microscopic Origin of Heisenberg and Non-Heisenberg Exchange Interactions in Ferromagnetic bcc Fe**

Y. O. Kvashnin,[1] R. Cardias,[2] A. Szilva,[1] I. Di Marco,[1] M. I. Katsnelson,[3,4] A. I. Lichtenstein,[4,5] L. Nordström,[1] A. B. Klautau,[2] and O. Eriksson[1]

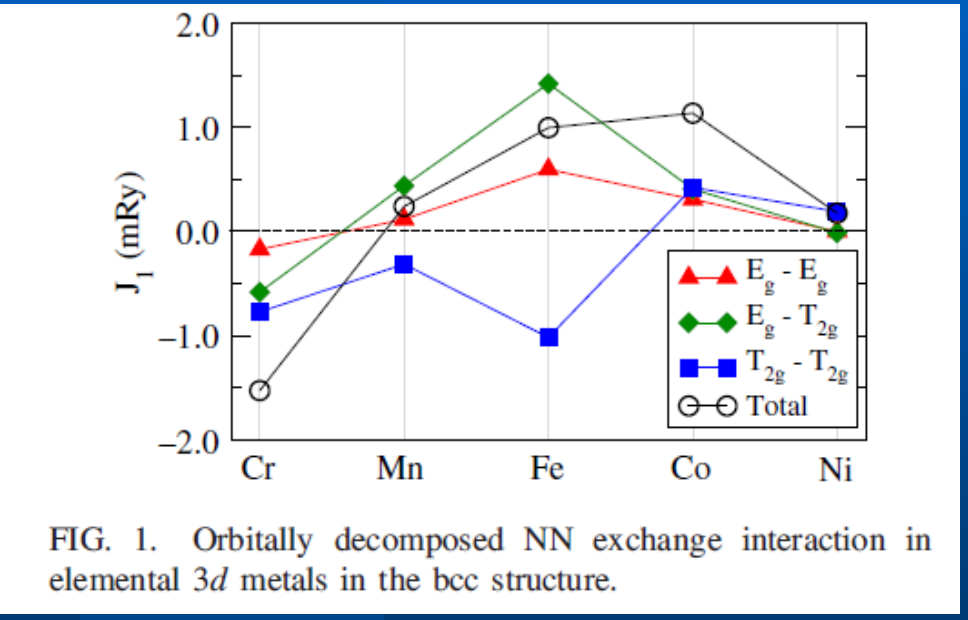
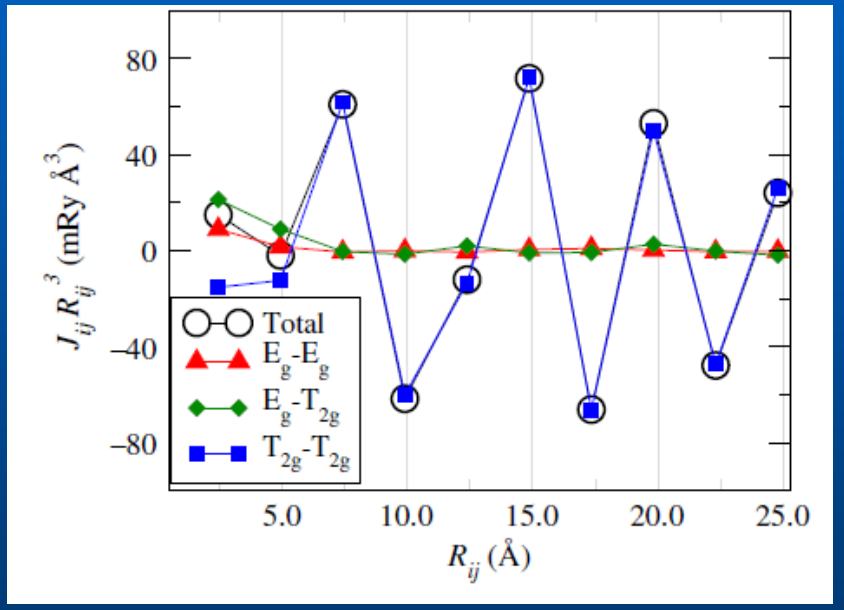



FIG. 1. Orbitally decomposed NN exchange interaction in elemental 3*d* metals in the bcc structure.



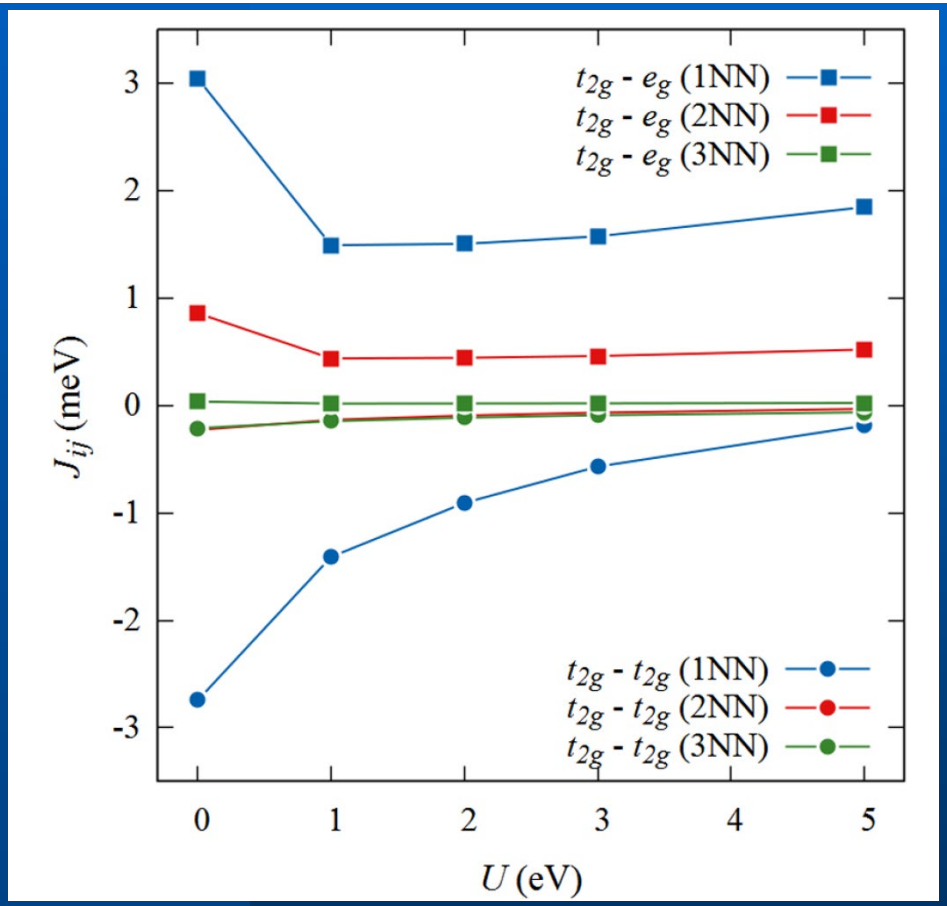

*$t_{2g}$ are itinerant electrons providing (Heisenberg-like) RKKY exchange with Friedel oscillations; $e_g$ are more correlated providing (non-Heisenberg) "double exchange" typical for narrom-band systems*

# Orbital decomposition III

Orbitally-resolved ferromagnetism of monolayer $CrI_3$

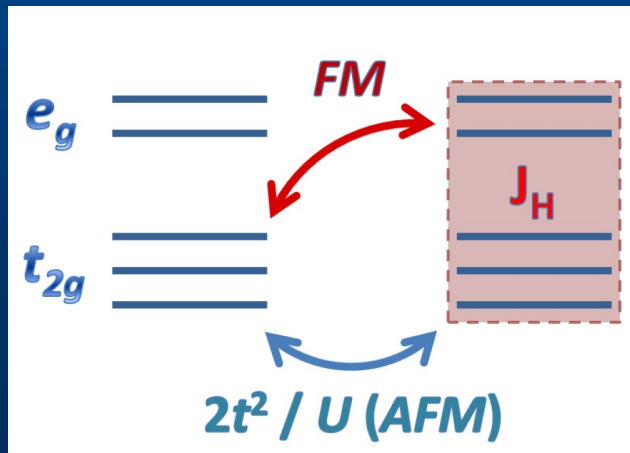
I V Kashin[1], V V Mazurenko[1], M I Katsnelson[1,2] and A N Rudenko[3,2,1]

*2D Mater.* **7** (2020) 025036




*LDA+U results: competing FM and AFM contributions to superexchange*

*Qualitative explanation within Kugel-Khomskii model*



# Applications to various systems: Alloys

## Invar problem

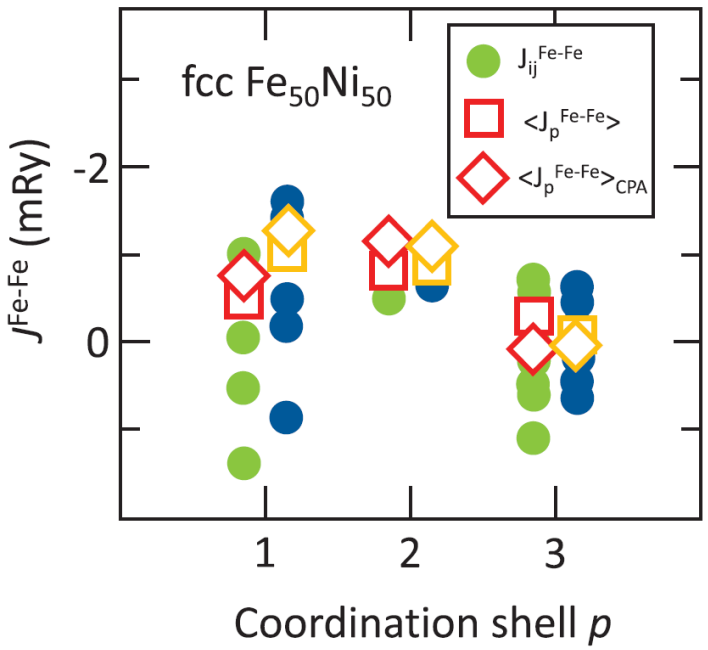



FIG. 15. Calculated Fe-Fe exchange interactions with first three coordination shells in fcc $Fe_{0.5}Ni_{0.5}$ for two different unit cell volumes ($V$) (Ruban *et al.*, 2005). The 16-atom supercell-based results for $V = 73.6$ a.u.$^3$ and $V = 70.3$ a.u.$^3$ are shown with blue (dark gray) and green (light gray) circles, respectively. Supercell- and CPA-averaged $J_{ij}$'s are shown for comparison.


Ruban, A. V., M. I. Katsnelson, W. Olovsson, S. I. Simak, and I. A. Abrikosov, 2005, "Origin of magnetic frustrations in Fe-Ni Invar alloys," Phys. Rev. B **71**, 054402.


## Heussler alloys

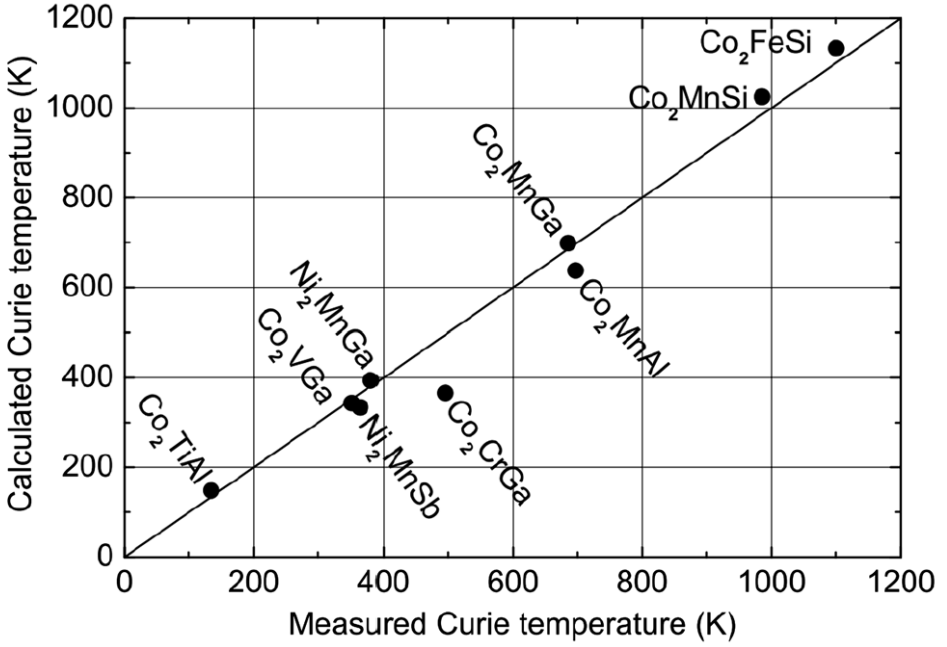



FIG. 16. Calculated vs measured $T_c$'s in the series of $L2_1$ Heusler alloys. From Thoene *et al.*, 2009.


Thoene, Jan, Stanislav Chadov, Gerhard Fecher, Claudia Felser, and Jürgen Kübler, 2009, "Exchange energies, Curie temperatures and magnons in Heusler compounds," J. Phys. D **42**, 084013.


*Mean-field estimate of Curie temperature*

# Applications to various systems: Magnetic monolayers

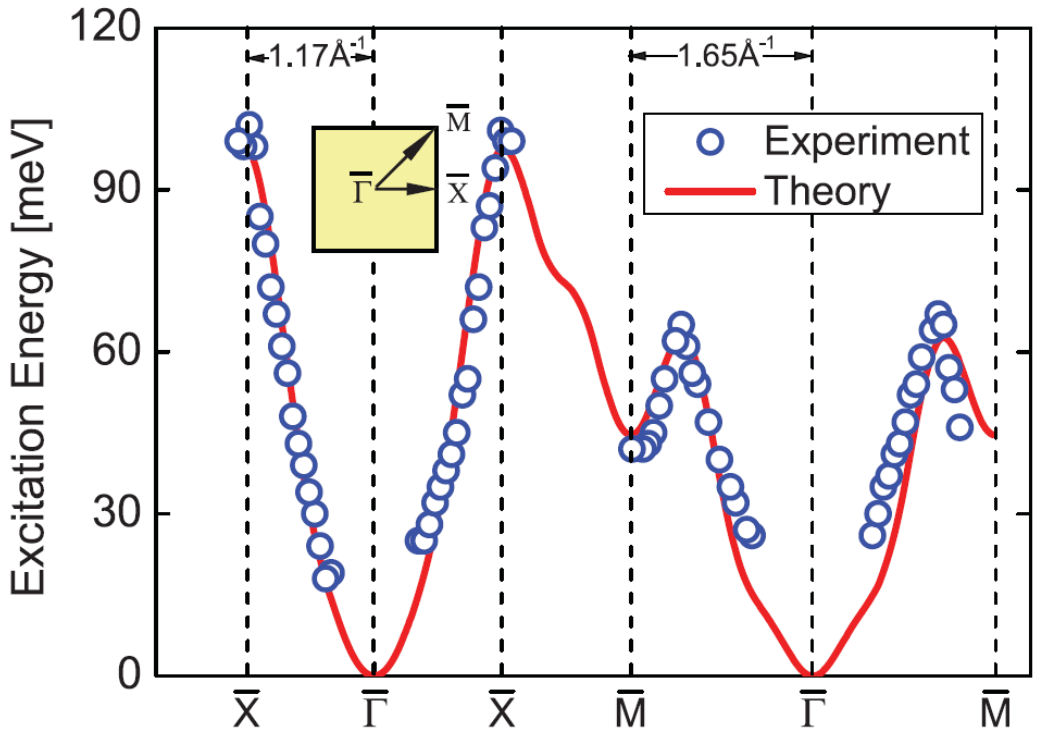



FIG. 19. Computed and measured acoustic magnon dispersions in Fe/Rh(001). Inset shows the parts of the Brillouin zone used in the plot. From Meng *et al.* 2014

Meng, Y., Kh. Zakeri, A. Ernst, T.-H. Chuang, H. J. Qin, Y.-J. Chen, and J. Kirschner, 2014, "Direct evidence of antiferromagnetic exchange interaction in Fe(001) films: Strong magnon softening at the high-symmetry $\bar{M}$ point," Phys. Rev. B **90**, 174437.

# Applications to various systems: rare-earth elements

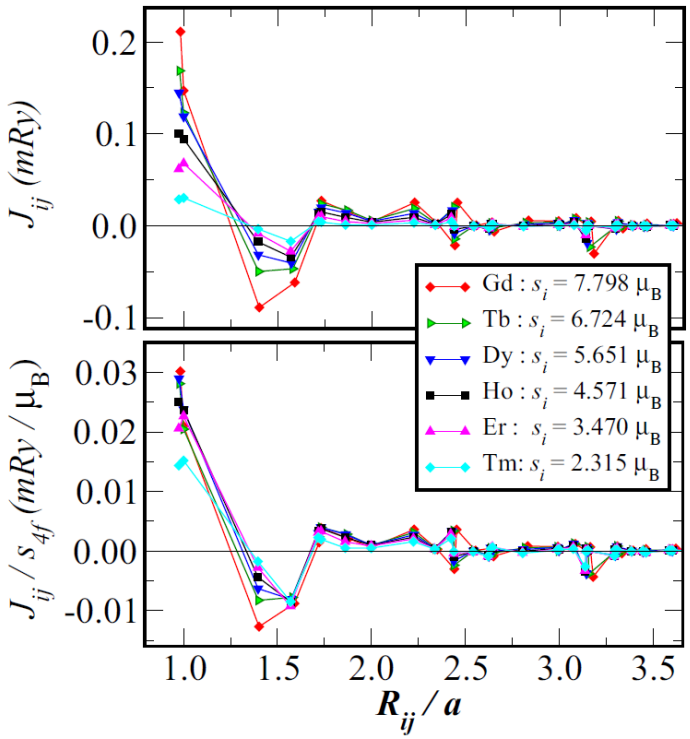
PHYSICAL REVIEW B **94**, 085137 (2016)

**Standard model of the rare earths analyzed from the Hubbard I approximation**

I. L. M. Locht,[1,2] Y. O. Kvashnin,[1] D. C. M. Rodrigues,[1,3] M. Pereiro,[1] A. Bergman,[1] L. Bergqvist,[4,5] A. I. Lichtenstein,[6] M. I. Katsnelson,[2] A. Delin,[1,4,5] A. B. Klautau,[3] B. Johansson,[1,7] I. Di Marco,[1] and O. Eriksson[1]

## Nomenclature

$$H = -\sum_{i \neq j} J_{ij}\, \mathbf{e}_i \cdot \mathbf{e}_j$$



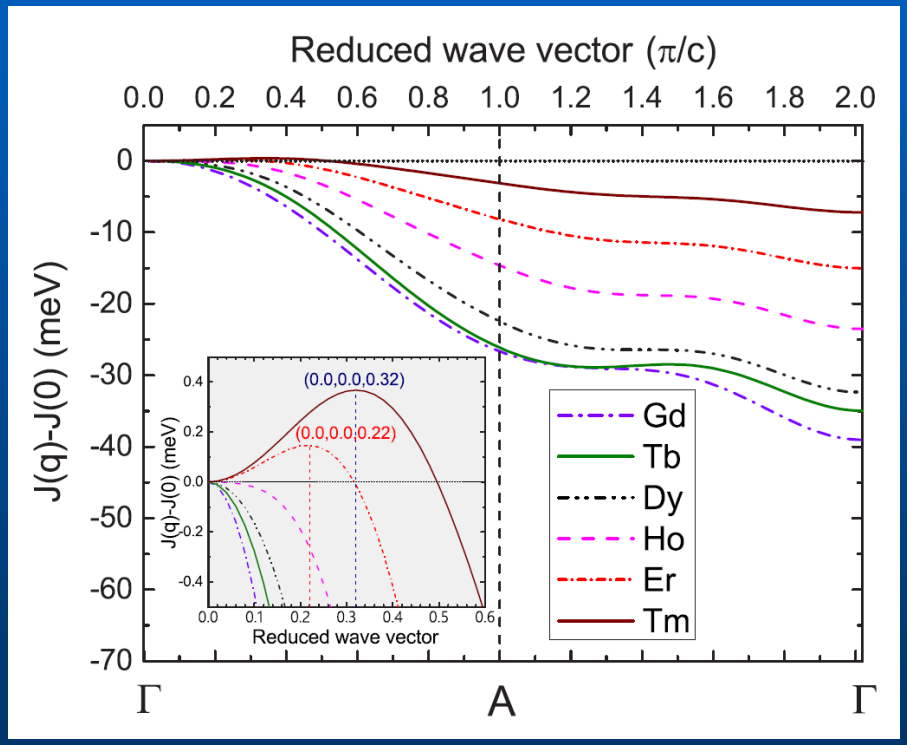




FIG. 23. Fourier transform of the exchange interaction $J(\vec{q}) - J(0)$ in heavy elemental lanthanides (Locht *et al.*, 2016). If the minimum corresponds to the Γ point, the ferromagnetic order is preferable.

# *Dzialoshinskii-Moriya interactions*

MIK, Kvashnin, Mazurenko & Lichtenstein, PRB 82, 100403 (2010)

*LDA+U*

$$\begin{aligned}\hat{H} &= \hat{H}_t + \hat{H}_u \\ &= \sum_{12} c_1^+ t_{12} c_2 + \frac{1}{2} \sum_{1234} c_1^+ c_2^+ U_{1234} c_3 c_4\end{aligned}$$

*DM interactions (weak FM, etc.)*

$$H_{DM} = \sum_{ij} \vec{D}_{ij} [\vec{e}_i \times \vec{e}_j]$$

*Small rotations*

$$\hat{R}_i = e^{i\delta\vec{\varphi}_i \vec{J}}$$

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

# Dzialoshinskii-Moriya interactions II

Starting from collinear configuration

$$\delta\hat{H}_t = \sum_{ij} c_i^+ (\delta\hat{R}_i^+ \hat{t}_{ij} + \hat{t}_{ij}\delta\hat{R}_j) c_j$$

$$= -i \sum_{ij} c_i^+ (\delta\vec{\varphi}_i \hat{\vec{J}}\hat{t}_{ij} - \hat{t}_{ij}\hat{\vec{J}}\delta\vec{\varphi}_j) c_j$$

$$= -\frac{i}{2} \sum_{ij} c_i^+ (\delta\vec{\varphi}_i - \delta\vec{\varphi}_j)(\hat{\vec{J}}\hat{t}_{ij} + \hat{t}_{ij}\hat{\vec{J}}) c_j$$

$$\vec{D}_{ij} = -\frac{i}{2} Tr_{m,\sigma} \langle c_i^+ [\hat{\vec{J}}, \hat{t}_{ij}]_+ c_j \rangle = -\frac{i}{2} Tr_{m,\sigma} N_{ji} [\hat{\vec{J}}, \hat{t}_{ij}]_+$$

$$N_{ji} = \langle c_i^+ c_j \rangle = -\frac{1}{\pi} \int_{-\infty}^{E_f} ImG_{ji}(E) dE$$

# $FeBO_3$

LETTERS
PUBLISHED ONLINE: 9 FEBRUARY 2014 | DOI: 10.1038/NPHYS2859
nature physics

## Measuring the Dzyaloshinskii–Moriya interaction in a weak ferromagnet

V. E. Dmitrienko[1], E. N. Ovchinnikova[2], S. P. Collins[3*], G. Nisbet[3], G. Beutier[4], Y. O. Kvashnin[5], V. V. Mazurenko[6], A. I. Lichtenstein[7] and M. I. Katsnelson[6,8]

*A novel exper. technique to measure DM vector and not only canting angle (resonant X-ray scattering)*

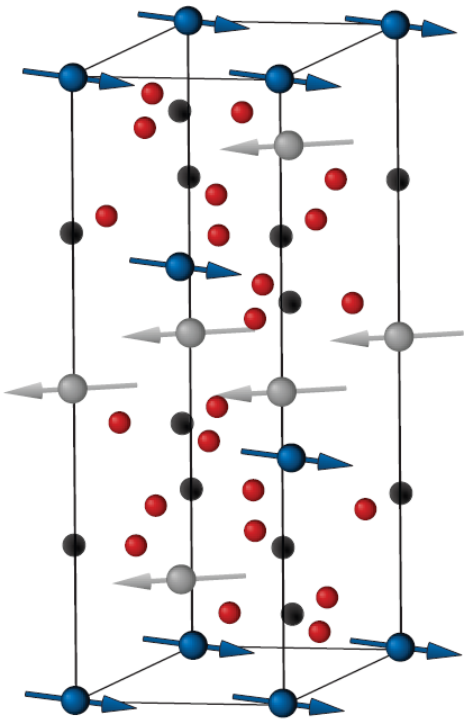


TABLE I. Calculated values of isotropic exchange interactions between magnetic moments in $FeBO_3$ (in meV). The number in parentheses denotes the coordination sphere.

| $Fe^{(1)}$ | $Fe^{(2)}$ | $Fe^{(3)}$ | $Fe^{(4)}$ | $Fe^{(5)}$ | $Fe^{(6)}$ | $Fe^{(7)}$ |
|---|---|---|---|---|---|---|
| 10.28 | 0.21 | 0 | 0.54 | -0.08 | 0 | 0.02 |

TABLE III. Parameters of Dzyaloshinskii-Moriya interaction (in meV) calculated by using Eq. (6).

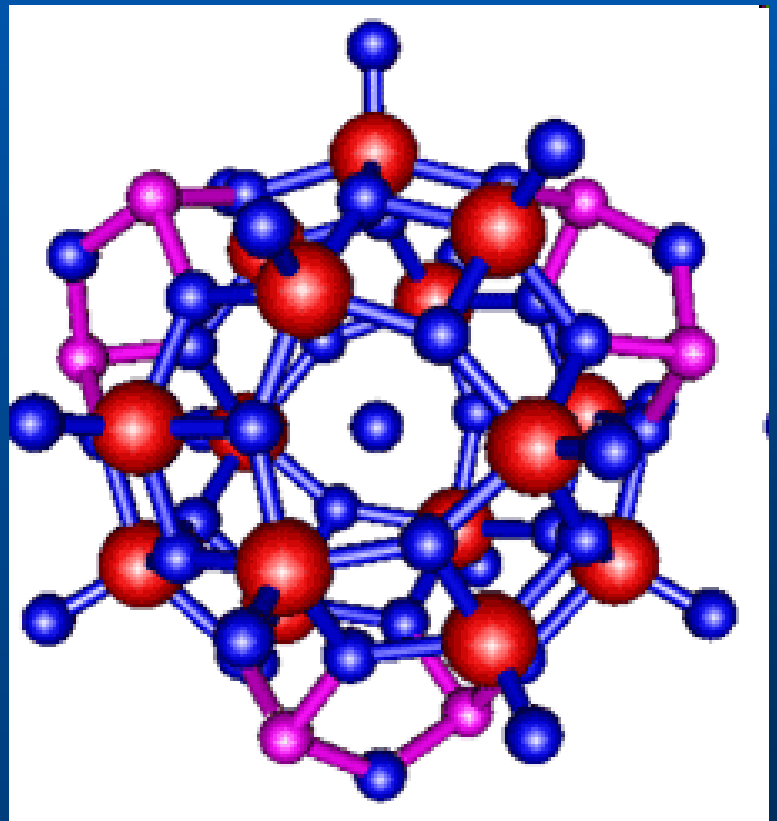
| Bond $m-n$ | $\mathbf{R}_{mn}$ | $\mathbf{D}_{mn}$ (meV) |
|---|---|---|
| 0-1 | (1.0 ; 0.0 ; -0.904) | (-0.25; 0.0; -0.24) |
| 0-2 | (-0.5 ; $-\sqrt{3}/2$ ; -0.904) | (0.12 ; 0.22 ; -0.24) |
| 0-3 | (-0.5 ; $\sqrt{3}/2$ ; -0.904) | (0.12 ; -0.22 ; -0.24) |
| 0-4 | (-1.0 ; 0.0 ; 0.904) | (-0.25; 0.0 ; -0.24) |
| 0-5 | (0.5 ; $-\sqrt{3}/2$ ; 0.904) | (0.12 ; -0.22 ; -0.24) |
| 0-6 | (0.5 ; $\sqrt{3}/2$ ; 0.904) | (0.12 ; 0.22 ; -0.24) |

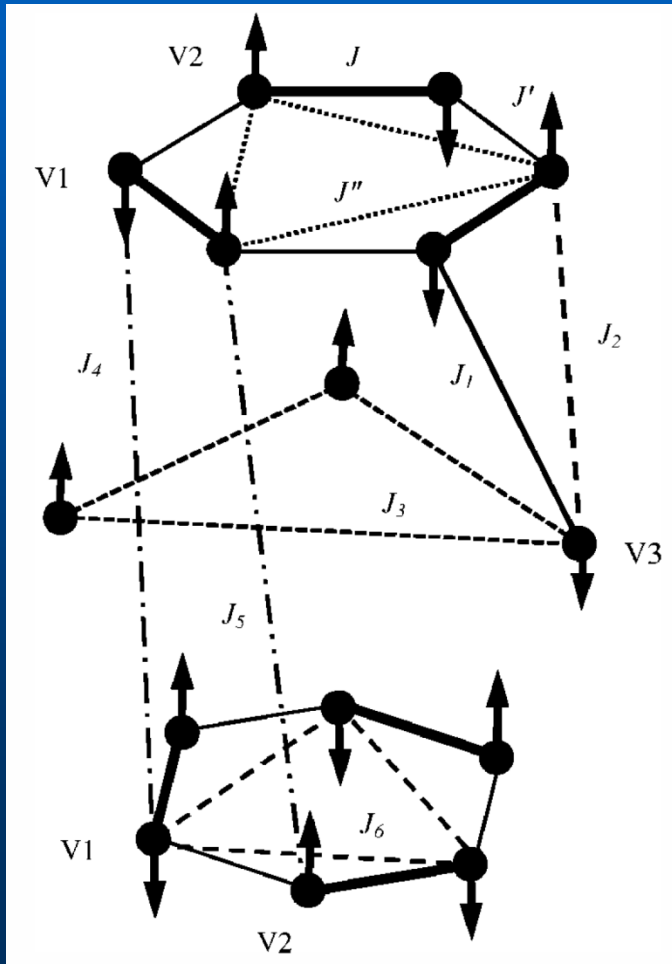
*Agrees well with exper.*

# *Molecular magnets*

Example: $V_{15}$ AFM ground state *S = 1/2*

$$V_{15}(K_6[V_{15}As_6O_{42}(H_2O)]\cdot 8H_2O)$$





# LDA+U calculations

PHYSICAL REVIEW B **70**, 054417 (2004)

## Electronic structure and exchange interactions in $V_{15}$ magnetic molecules: LDA+U results

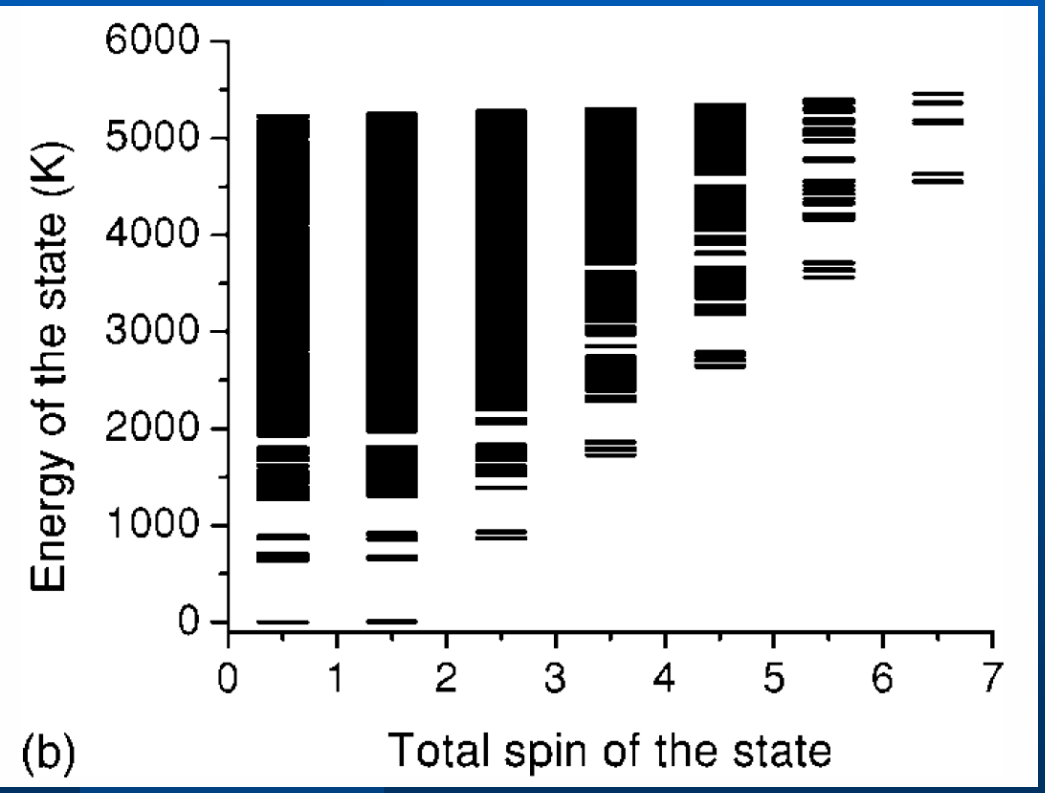
D. W. Boukhvalov,[1,2] V. V. Dobrovitski,[3] M. I. Katsnelson,[2,4] A. I. Lichtenstein,[5] B. N. Harmon,[3] and P. Kögerler[3]

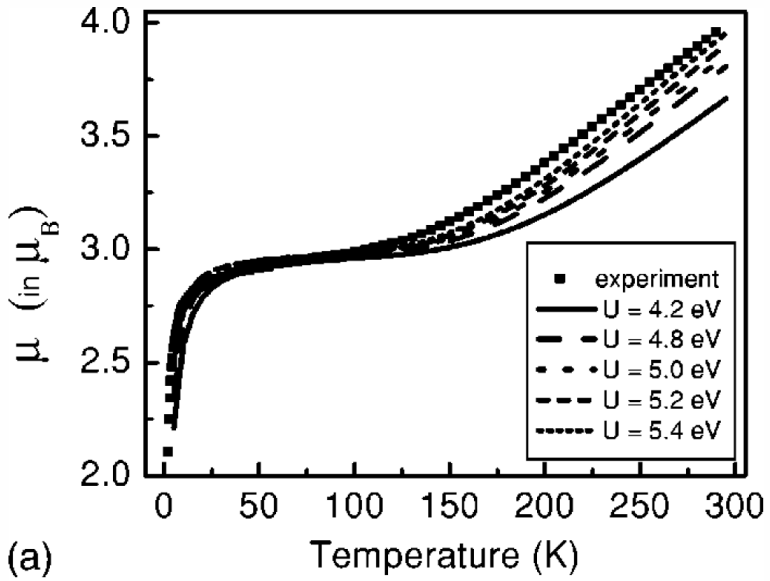
TABLE II. The exchange parameters (in Kelvin), electronic gap, and the magnetic moments of V ions for different magnetic structures of $V_{15}$. The calculations have been made for $U$=4 eV, $J$=0.8 eV.

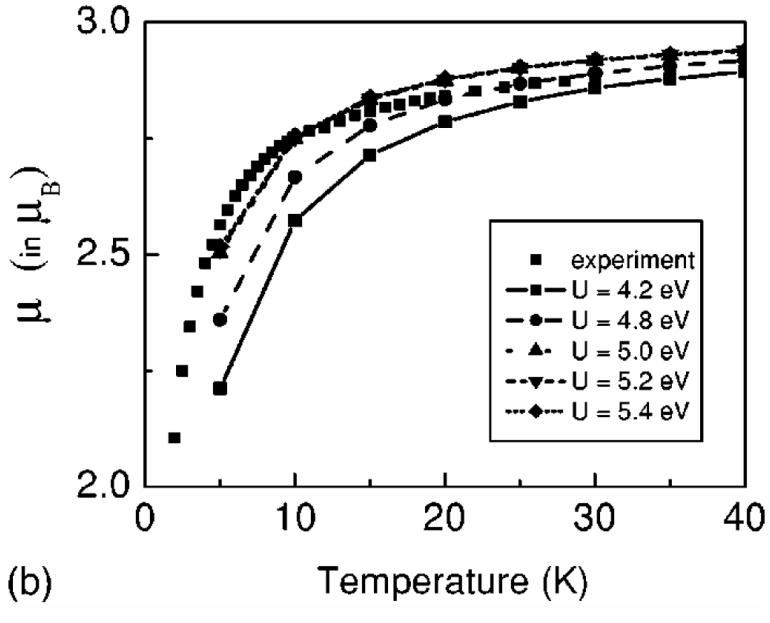
| parameter | AFM1 | AFM2 | FM |
|---|---|---|---|
| $J$ | −910 | −905 | −942 |
| $J'$ | −45 | −46 | −53 |
| $J''$ | −136 | −139 | −156 |
| $J_1$ | −219 | −247 | −255 |
| $J_2$ | −134 | −128 | −132 |
| $J_3$ | −5 | −5 | −6 |
| $J_4$ | −13 | −12 | −15 |
| $J_5$ | −3 | −3 | −3 |
| $J_6$ | −3 | −3 | −3 |
| gap | 1.08 | 1.02 | 1.16 |
| $\mu_{V1}$ | −0.94 | −0.93 | −0.99 |
| $\mu_{V2}$ | +0.91 | +0.92 | −0.97 |
| $\mu_{V3}$ | −1.00 | +0.97 | −1.00 |

# LDA+U calculations II

Exact diagonalization for Heisenberg model



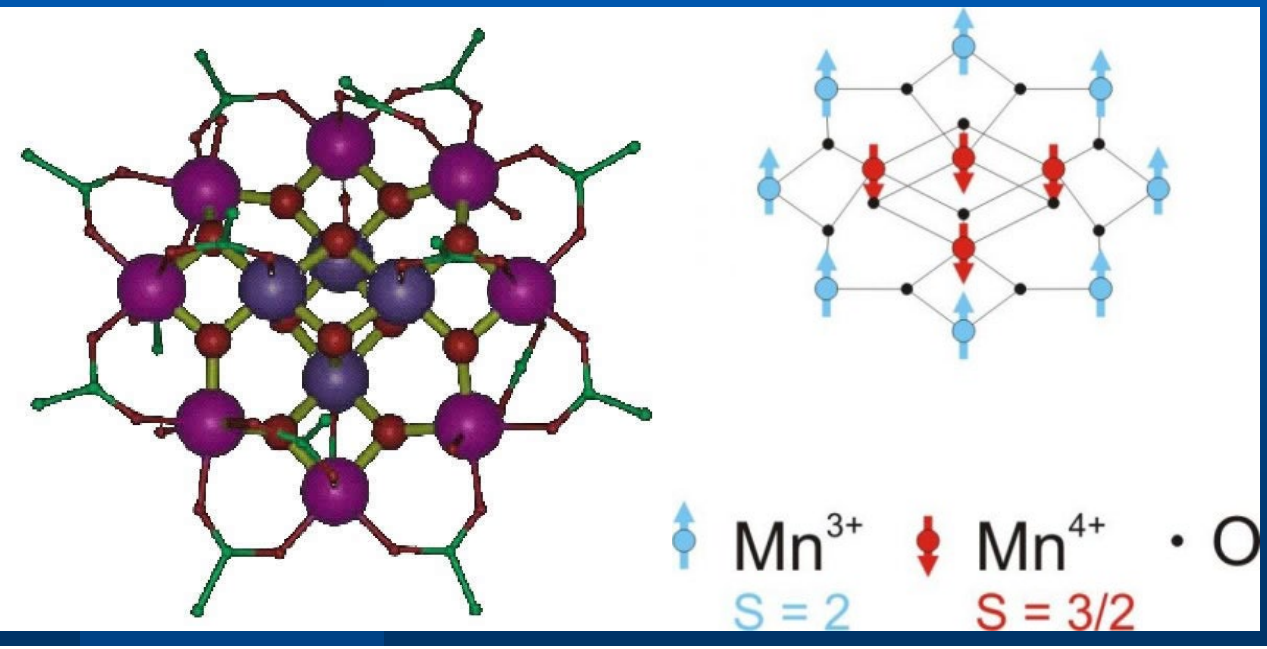
# $Mn_{12}$: full calculations

PHYSICAL REVIEW B **00**, 004400 (2014)

**First-principles modeling of magnetic excitations in $Mn_{12}$**

V. V. Mazurenko,[1] Y. O. Kvashnin,[2,3] Fengping Jin,[4] H. A. De Raedt,[5] A. I. Lichtenstein,[6] and M. I. Katsnelson[1,7]

## Motivation




*The prototype molecular magnet*

*Dimension of Hilbert space:*
$(2^x2+1)^8(2^x3/2+1)^4=10^8$

*A real challenge!*

$$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$$

# $Mn_{12}$: full calculations II

Inelastic netron scattering data: cannot be explained without strong DM interactions (MIK, Dobrovistki & Harmon, PRB 1999)

Eight-spin model: S = ½ dimers from S=2 and S=3/2
Dimensionality of Hilbert space decreases to $10^4$
Cannot be justified quantitatively!

*Full LDA+U calculations plus Lanczos ED*

$$\hat{H} = \sum_{ij} J_{ij} \hat{S}_i \hat{S}_j + \sum_{i\mu\nu} \hat{S}_i^{\mu} A_i^{\mu\nu} \hat{S}_i^{\nu} + \sum_{ij} \vec{D}_{ij} [\hat{S}_i \times \hat{S}_j]$$

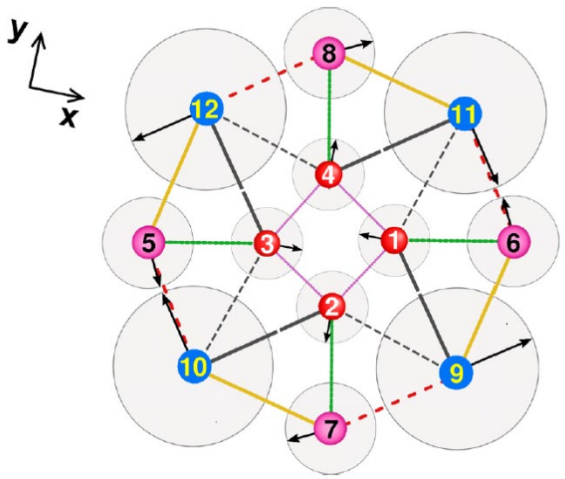



TABLE I. Intramolecular isotropic exchange interaction parameters (in meV) calculated by using the LDA + $U$ approach. Positive sign corresponds to the antiferromagnetic coupling.

| Bond $(i, j)$ | 1–6 | 1–11 | 1–9 | 6–9 | 7–9 | 1–4 | 1–3 |
|---|---|---|---|---|---|---|---|
| $J_{ij}$ (this work) | 4.6 | 1.0 | 1.7 | −0.45 | −0.37 | −1.55 | −0.5 |
| $J_{ij}$ (Ref. [4]) | 4.8 | 1.37 | 1.37 | −0.5 | −0.5 | −1.6 | −0.7 |
| $J_{ij}$ (Ref. [26]) | 7.4 | 1.72 | 1.72 | | | −1.98 | |

# $Mn_{12}$: full calculations III

TABLE II. Intramolecular anisotropic exchange interaction parameters calculated by using the LDA + $U$ approach. $\vec{R}_{ij}$ is a radius vector connecting $i$th and $j$th atoms (in units of $a = 17.31$ Å).

| Bond $(i, j)$ | $\vec{R}_{ij}$ | $\vec{D}_{ij}$ (meV) |
|---|---|---|
| 2–7 | (0.03; −0.16; 0.0) | (−0.008; −0.013; −0.002) |
| 4–8 | (−0.03; 0.16; 0.0) | (0.008; 0.013; −0.002) |
| 1–6 | (0.16; 0.03; 0.0) | (−0.013; 0.008; −0.002) |
| 3–5 | (−0.16; −0.03; 0.0) | (0.013; −0.008; −0.002) |
| 1–11 | (0.06; 0.18; 0.07) | (−0.020; 0.03; −0.055) |
| 3–10 | (−0.06; −0.18; 0.07) | (0.020; −0.03; −0.055) |
| 2–9 | (0.18; −0.06; −0.07) | (−0.03; −0.020; −0.055) |
| 4–12 | (−0.18; 0.06; −0.07) | (0.03; 0.020; −0.055) |
| 1–9 | (0.11; −0.16; 0.04) | (0.020; 0.014; 0.03) |
| 3–12 | (−0.11; 0.16; 0.04) | (−0.020; −0.014; 0.03) |
| 2–10 | (−0.16; −0.11; −0.04) | (−0.014; 0.020; 0.03) |
| 4–11 | (0.16; 0.11; −0.04) | (0.014; −0.020; 0.03) |
| 6–9 | (−0.04; −0.18; 0.04) | (−0.006; −0.004; −0.012) |
| 5–12 | (0.04; 0.18; 0.04) | (0.006; 0.004; −0.012) |
| 7–10 | (−0.18; 0.04; −0.04) | (0.004; −0.006; −0.012) |
| 8–11 | (0.18; −0.04; −0.04) | (−0.004; 0.006; −0.012) |
| 7–9 | (0.15; 0.1; −0.07) | (0.020; −0.004; 0.012) |
| 8–12 | (−0.15; −0.1; −0.07) | (−0.020; 0.004; 0.012) |
| 6–11 | (−0.1; 0.15; 0.07) | (−0.004; −0.020; 0.012) |
| 5–10 | (0.1; −0.15; 0.07) | (0.004; 0.020; 0.012) |
| 4–1 | (−0.10; 0.06; 0.11) | (−0.014; 0.005; −0.013) |
| 1–2 | (−0.06; −0.10; 0.11) | (−0.005; −0.014; −0.013) |
| 3–4 | (0.07; 0.1; 0.11) | (0.005; 0.014; −0.013) |
| 2–3 | (−0.10; 0.07; −0.11) | (0.014; −0.005; −0.013) |
| 1–3 | (−0.16; −0.03; 0.0) | (−0.006; 0.030; 0) |
| 2–4 | (−0.04; 0.17; 0.0) | (−0.030; −0.006; 0) |

Plus anisotropy tensors...

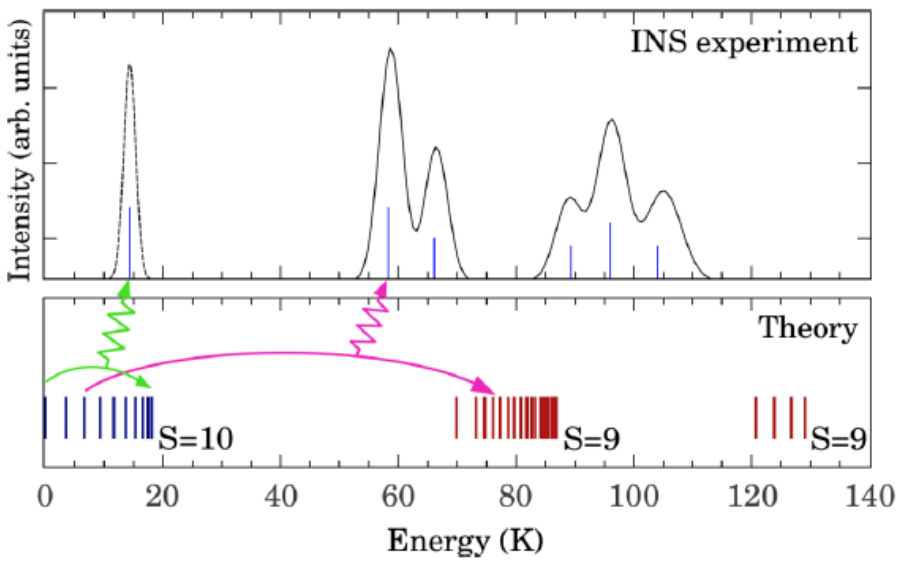



FIG. 2. (Color online) Schematic comparison of the theoretical spectrum obtained by diagonalizing Eq. (1) and INS spectrum taken from Ref. [12] (Figs. 6 and 8 therein). The arrows denote the intra- and interband transitions that correspond to the excitations observed in the INS experiment.

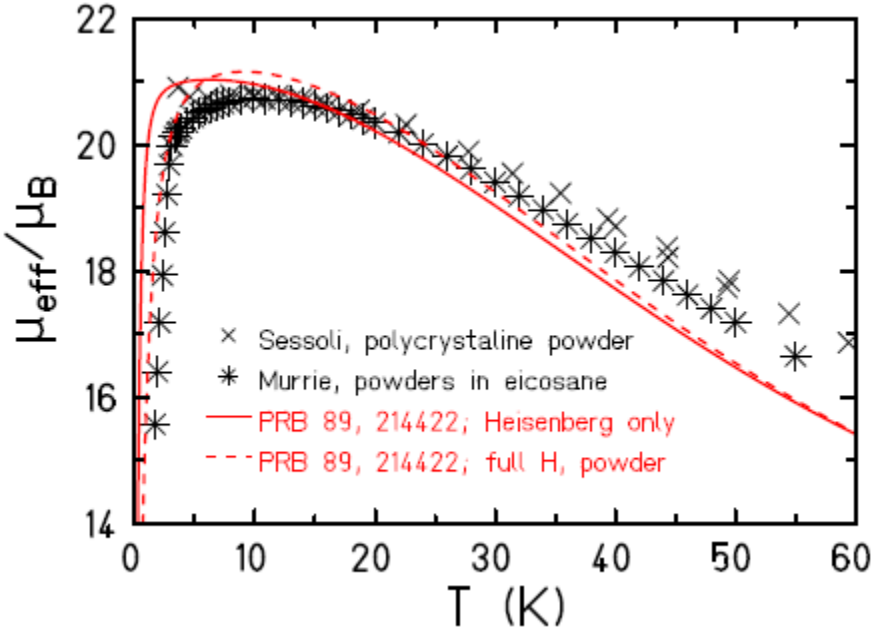
*No fitting parameters at all – not so bad!*

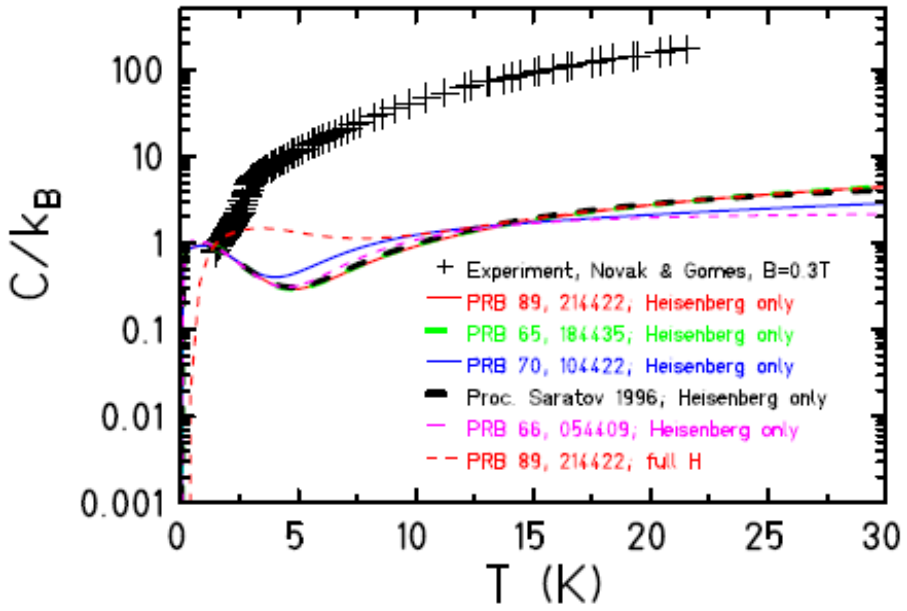
# $Mn_{12}$: full calculations IV

PHYSICAL REVIEW B **92**, 064424 (2015)

**Thermodynamic observables of $Mn_{12}$-acetate calculated for the full spin Hamiltonian**

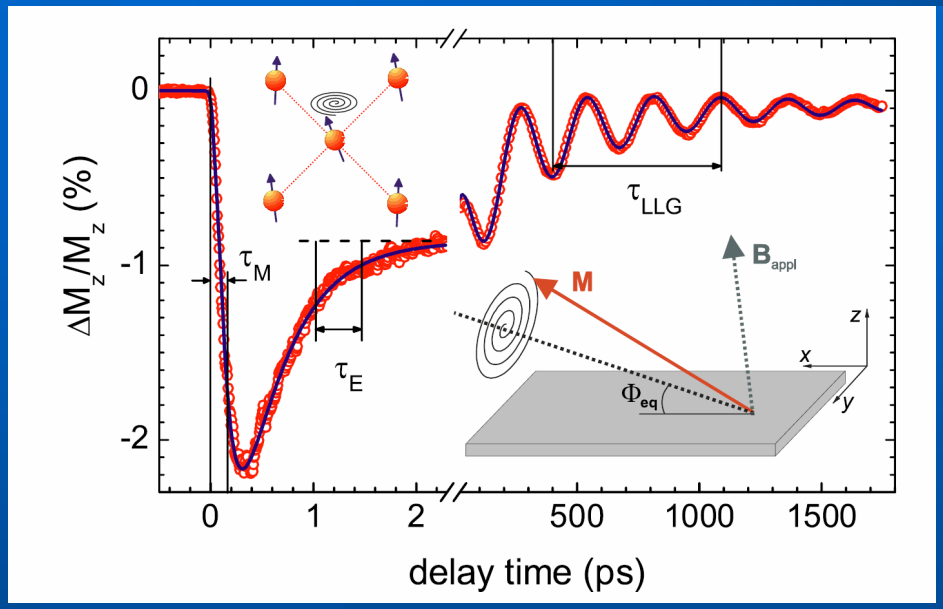
Oliver Hanebaum and Jürgen Schnack*



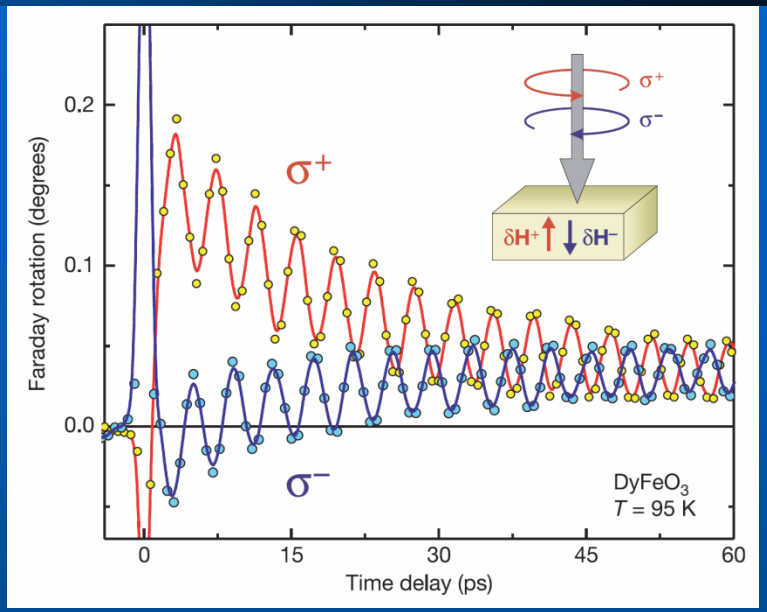




*Also, thermodynamic quantities can be calculated*

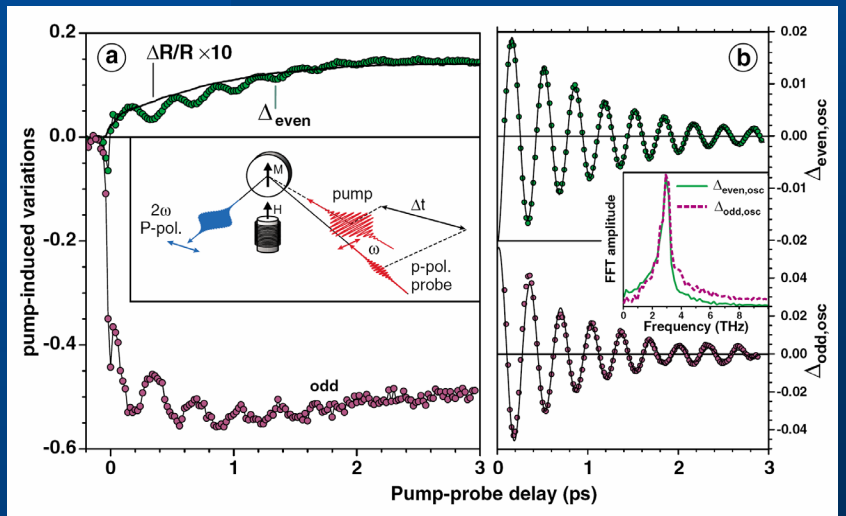
# Ultrafast magnetism: Examples




Nickel Koopmans et al PRL 2005




Orthoferrites Kimel et al Nature 2005




Gadolinium Melnikov et al PRL 2003

# Ultrafast magnetism: a theory

Non-equilibrium magnetic interactions in strongly correlated systems

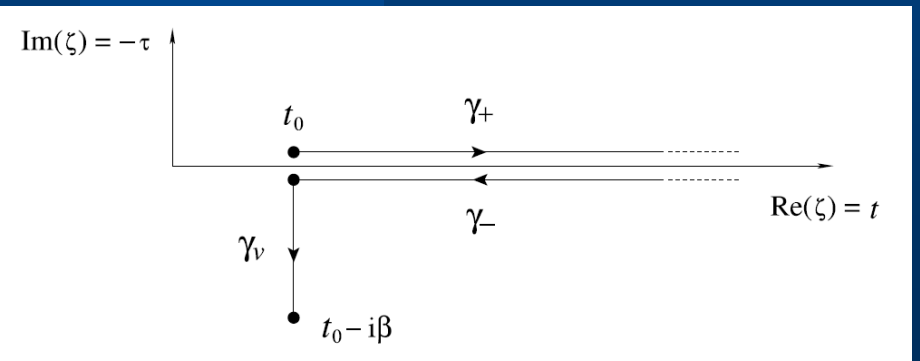
Annals of Physics 333 (2013) 221–271

A. Secchi [a,*], S. Brener [b], A.I. Lichtenstein [b], M.I. Katsnelson [a]

$$\hat{H}(t) \equiv \hat{H}_T(t) + \hat{H}_V \quad \hat{H}_T(t) \equiv \sum_{i_a\lambda_a} \sum_{i_b\lambda_b} T_{i_a\lambda_a, i_b\lambda_b}(t) \sum_{\sigma} \hat{\phi}^{\dagger}_{i_a\lambda_a\sigma} \hat{\phi}_{i_b\lambda_b\sigma}$$

$$\hat{H}_V \equiv \frac{1}{2} \sum_{i} \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \sum_{\sigma\sigma'} V_{\lambda_1\lambda_2\lambda_3\lambda_4} \hat{\phi}^{\dagger}_{i\lambda_1\sigma} \hat{\phi}^{\dagger}_{i\lambda_2\sigma'} \hat{\phi}_{i\lambda_3\sigma'} \hat{\phi}_{i\lambda_4\sigma}$$

Consider dynamics of Baym-Kadanoff-Keldysh countour




*Path integral over Grassmann variables*

$$\mathcal{Z} = \int \mathcal{D}\left[\bar{\phi}, \phi\right] e^{iS\left[\bar{\phi}, \phi\right]}$$

# Ultrafast magnetism: a theory II

*Introduce rotations*

$$\bar{\phi}_{a\pm}(t) = \bar{\psi}_{a\pm}(t) \cdot R^{\dagger}_{a\pm}(t), \qquad \phi_{a\pm}(t) = R_{a\pm}(t) \cdot \psi_{a\pm}(t)$$

$$\bar{\phi}_{av}(\tau) = \bar{\psi}_{av}(\tau) \cdot R^{\dagger}_{av}(\tau), \qquad \phi_{av}(\tau) = R_{av}(\tau) \cdot \psi_{av}(\tau)$$

$$R_i(z) \equiv \begin{pmatrix} \sqrt{1 - |\xi_i(z)|^2} & \xi_i^*(z) \\ -\xi_i(z) & \sqrt{1 - |\xi_i(z)|^2} \end{pmatrix}$$

*Expand effective actions up to the second order in "Holstein-Primakoff" fields ξ, ξ**

$$\xi_i(z) \equiv -\mathrm{e}^{\mathrm{i}\varphi_i(z)} \sin\left[\theta_i(z)/2\right]$$

$$\mathcal{Z} = \int \mathcal{D}\left[\bar{\psi}, \psi\right] \mathrm{e}^{\mathrm{i}S\left[\bar{\psi}, \psi\right]} \int \mathcal{D}\left[\theta, \varphi\right] \mathrm{e}^{\mathrm{i}S'\left[\bar{\psi}, \psi, \xi^*(\theta,\varphi), \xi(\theta,\varphi)\right]}$$

*Integrate over Grassman variables neglecting vertex corrections*

# Ultrafast magnetism: a theory III

*General expression of nonlocal in time exchange interactions in terms of Beym-Kadanoff-Keldysh Green's functions. E.g., time-dependent stiffness constant:*

$$D_{\alpha\beta}(t) \equiv -\frac{\mathrm{i}}{2M}\sum_{\eta}\eta\sum_{\sigma}\int_{t_0}^{\infty}\mathrm{d}t'\,\mathrm{sign}(t'-t)\,\overline{\Sigma}^{S}(t)\,\overline{\Sigma}^{S}(t')$$

$$\times\frac{1}{n}\sum_{\boldsymbol{k}}\frac{\partial G_{\boldsymbol{k}}^{\eta\sigma}(t',t)}{\partial k_\alpha}\,\frac{\partial G_{\boldsymbol{k}}^{\bar{\eta}\bar{\sigma}}(t,t')}{\partial k_\beta}.$$

*Additional terms (twist exchange) of the structure* $\propto (\boldsymbol{\sigma}_1 \times \boldsymbol{\sigma}_2)\cdot\boldsymbol{\sigma}_3$

*(at equilibrium forbidden by time-reversal symmetry)*

*The first step is done, a lot of things to do*

# High-frequency limit

Quickly oscillating strong electric field: quickly oscillating effective hopping

$$t_{ij} \to t_{ij} \exp\left\{ \frac{ie}{\hbar c} \int_{\vec{R}_j}^{\vec{R}_i} d\vec{r}\,' \vec{A}(\vec{r}\,', t) \right\}$$

At very high frequency effective static Hamiltonian should exist

## Classical analog: Kapitza pendulum

One needs to develop efficient perturbative theory in inverse frequency of the laser field

In classical mechanics:
Bogoliubov, Krylov ...

Development for matrix Hamiltonians:
A. P. Itin & A. I. Neishtadt, Phys. Lett. A 378, 822 (2014)

# High-frequency limit II

## Perturbation expansion: general scheme

A.P. Itin & MIK, PRL115, 075301 (2015); C. Dutreix & MIK, PRB 95, 024306 (2017)

The time-periodic Hamiltonian $H(t)$ of the initial problem obeys the time-dependent Schrödinger equation

$$i\partial_t \Psi(\lambda, t) = H(t)\Psi(\lambda, t). \tag{8.9}$$

One can introduce a dimensionless parameter $\lambda = \delta E/\Omega$ that compares a certain energy scale $\delta E$ of the system to the frequency $\Omega$ of the applied field. One then tries to find a unitary transformation $\Psi(\lambda, \tau) = \exp\{-i\Delta(\tau)\}\psi(\lambda, \tau)$ that removes the time dependence of the Hamiltonian. Here we introduce $\tau = \Omega t$ and also impose the condition that $\Delta(\tau) = \sum_{n=1}^{+\infty} \lambda^n \Delta_n(\tau)$, with $\Delta_n(\tau)$ a $2\pi$ periodic function. The Schrödinger equation (8.9) can then be rewritten as

$$i\partial_t \psi(\lambda, \tau) = \lambda \overline{\mathcal{H}} \psi(\lambda, \tau) \tag{8.10}$$

with an effective Hamiltonian

$$\bar{\mathcal{H}} = e^{i\Delta(\tau)} \bar{H}(\tau) e^{-i\Delta(\tau)} - i\lambda^{-1} e^{i\Delta(\tau)} \partial_\tau e^{-i\Delta(\tau)}. \tag{8.11}$$

In Eqs. (8.10) and (8.11) the bar over the Hamiltonian indicates a normalization on the energy scale $\delta E$: $\bar{H}(\tau) = H(\tau)/\delta E$. Using the series representation $\bar{\mathcal{H}} = \sum_{n=1}^{+\infty} \lambda^n \tilde{H}_n$, one can determine operators $\tilde{H}_n$ and $\Delta_n(\tau)$ iteratively in all orders in $\lambda$. The zeroth-order term in this representation is given by the time average over the period of the driving $\tilde{H}_0 = \langle \bar{H}(\tau) \rangle = \bar{H}_0$ defined as $\bar{H}_m = \int_{-\pi}^{+\pi} (d\tau/2\pi) e^{im\tau} \bar{H}(\tau)$. The first- and second-order terms $\lambda$ in the effective Hamiltonian are given by the following equations:

$$\tilde{H}_1 = -\frac{1}{2} \sum_{m \neq 0} \frac{[\bar{H}_m, \bar{H}_{-m}]}{m}, \tag{8.12}$$

$$\tilde{H}_2 = \frac{1}{2} \sum_{m \neq 0} \frac{[[\bar{H}_m, \bar{H}_0], \bar{H}_{-m}]}{m^2} + \frac{1}{3} \sum_{m \neq 0} \sum_{n \neq 0, m} \frac{[[\bar{H}_m, \bar{H}_{n-m}], \bar{H}_{-n}]}{mn}, \tag{8.13}$$

*Application to magnetism:* E. A. Stepanov, C. Dutreix & MIK, PRL 118, 157201 (2017)

# High-frequency limit III

*Effective superexchange in narrow-band half-filled Hubbard model*

$$J^{D}_{\mathrm{ind}} = 2t^2 U \sum_{m=1}^{+\infty} \frac{\mathcal{J}^2_m(\mathcal{E})}{m^2\Omega^2 - U^2}$$

$$\mathcal{E} = eE_0 a/\Omega$$

strength of the laser field $E_0$

*One can change sign of effective exchange interaction*


Itin, A. P., and M. I. Katsnelson, 2015, "Effective Hamiltonians for Rapidly Driven Many-Body Lattice Systems: Induced Exchange Interactions and Density-Dependent Hoppings," Phys. Rev. Lett. **115**, 075301.

Bukov, Marin, Michael Kolodrubetz, and Anatoli Polkovnikov, 2016, "Schrieffer-Wolff Transformation for Periodically Driven Systems: Strongly Correlated Systems with Artificial Gauge Fields," Phys. Rev. Lett. **116**, 125301.

# Beyond the talk

- *Spin dynamics (including lattice + spin dynamics);*
- *Application to nonmagnetic systems (analogs for superconductors and for charge-ordered systems;*
- *Finite-temperature effects*

*Collaboration with many people, especially Nijmegen, Hamburg, Uppsala, and Ekaterinburg groups*

*Thank you for your attention*