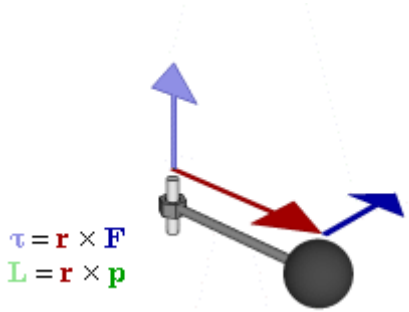
Femtosecond spin dynamics in two- and three-magnetic-center molecules

W. Hübner and G. Lefkidis

Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Box 3049, 67653 Kaiserslautern, Germany



Targoviste, 31 August 2011

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

OPTIMAS

Outline

1. History: theoretical achievements in spin dynamics
2. Introduction: theoretical and background aspects
3. Clusters with two magnetic centers
4. Clusters with three magnetic centers: magnetic logic
5. Role of bridging atoms
6. Conclusions

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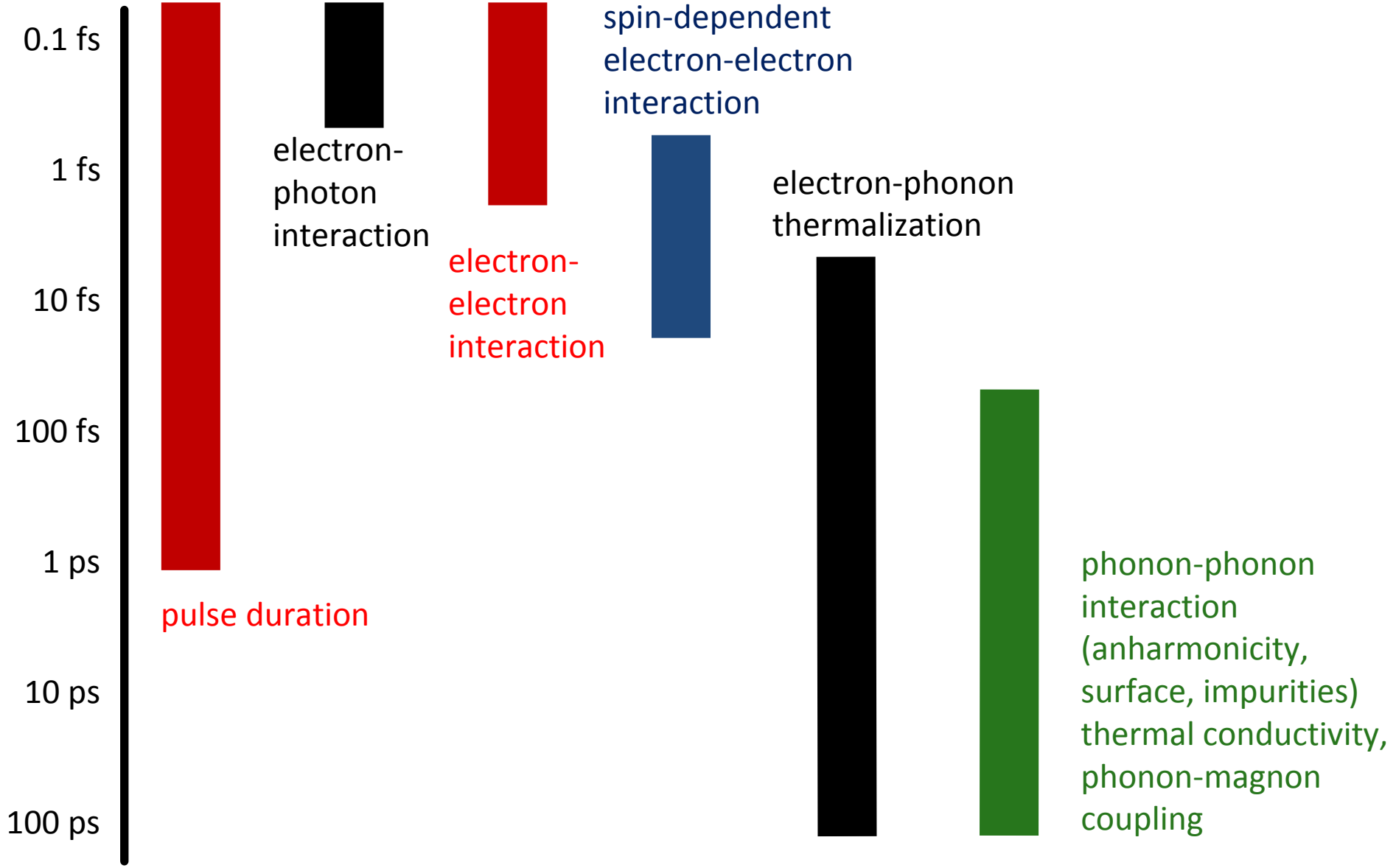
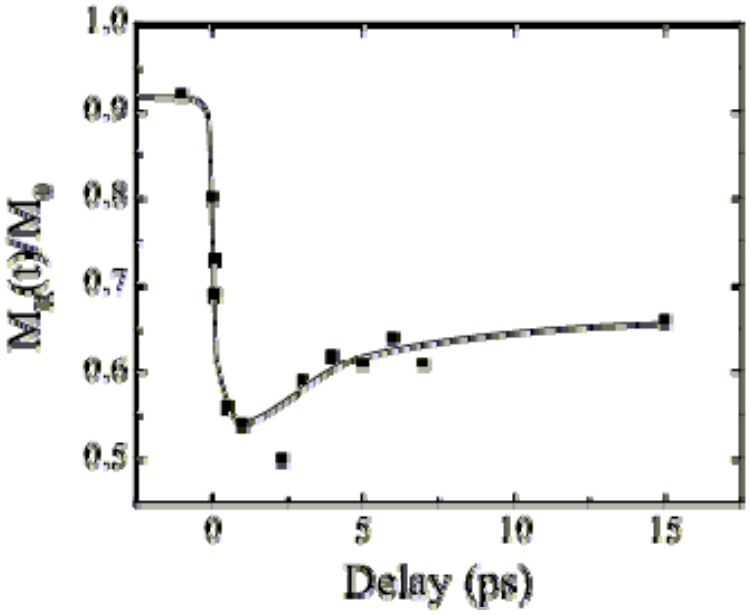
Relevant time scales for the laser control of magnetism



Femtosecond pump-probe (magneto-) optics



- Reflectivity
- MOKE
- $\tau_{spin} < 1$ ps

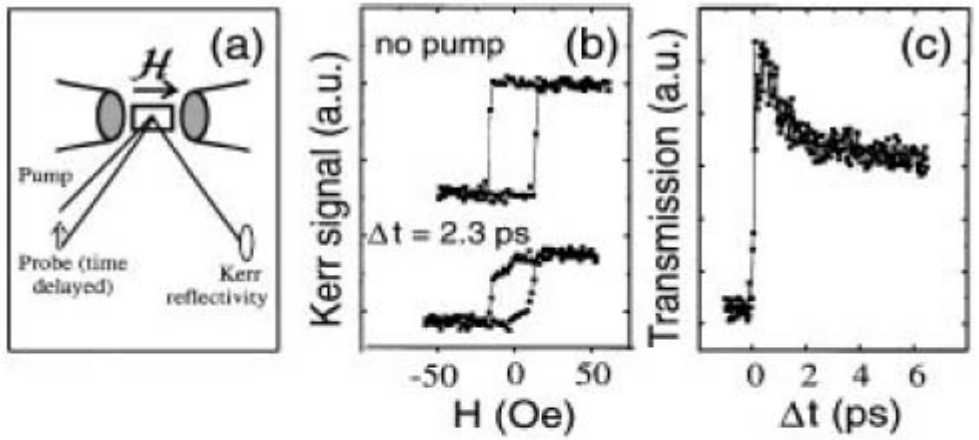
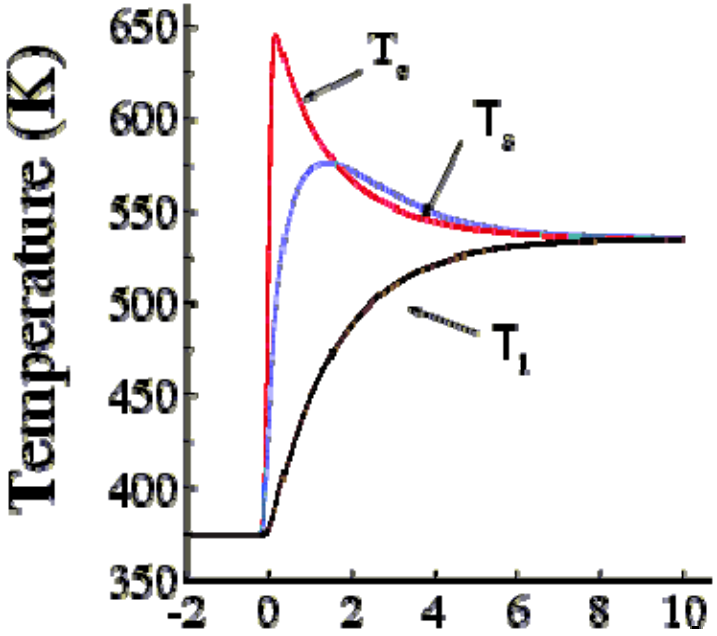
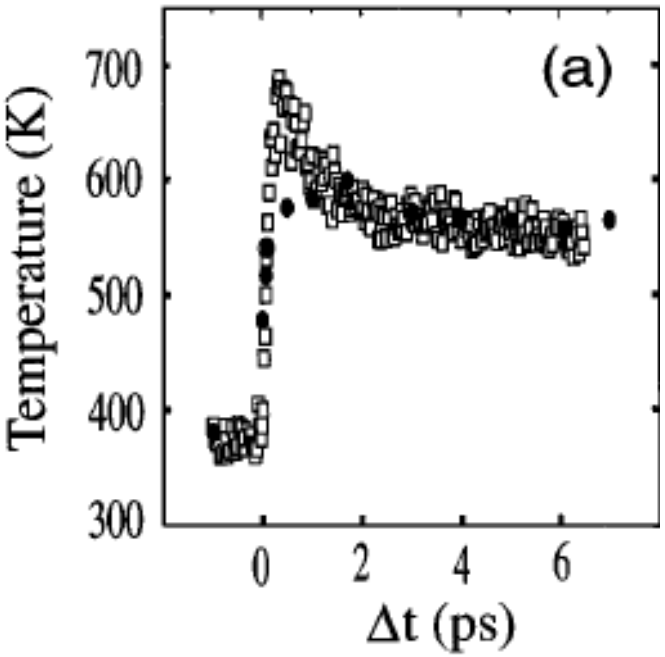


FIG. 1. (a) Experimental pump-probe setup allowing dynamic longitudinal Kerr effect and transient transmissivity or reflectivity measurements. (b) Typical Kerr loops obtained on a 22 nm thick Ni sample in the absence of pump beam and for a delay $\Delta t = 2.3$ ps between the pump and probe pulses. The pump fluence is 7 mJ cm^{-2}. (c) Transient transmissivity [same experimental condition as (b)].

E. Beaurepaire, J.-L. Marle, A. Daunois and J.-Y. Bigot, Phys. Rev. Lett. **76**, 4250 (1996)

3-Temperature model



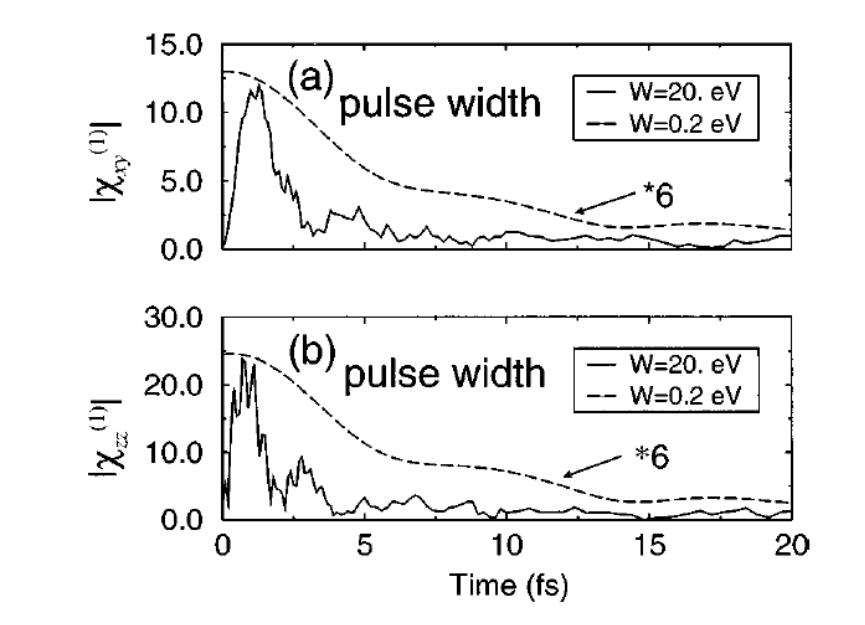


$$
\begin{aligned}
C_e(T_e)dT_e/dt &= -G_{el}(T_e - T_l) \\
&\quad - G_{es}(T_e - T_s) + P(t), \\
C_s(T_s)dT_s/dt &= -G_{es}(T_s - T_e) - G_{sl}(T_s - T_l) \\
C_l(T_l)dT_l/dt &= -G_{el}(T_l - T_e) - G_{sl}(T_l - T_s)
\end{aligned}
$$

- Good agreement with experiment
- Uniform temperature profile

E. Beaurepaire, J.-L. Marle, A. Daunois and J.-Y. Bigot, Phys. Rev. Lett. **76**, 4250 (1996)

History: theoretical achievements I
Spectral width → bleaching in Ni



Wide pulse (in frequency domain)
populates target states
→ transition paths blocked
→ bleaching

Affects both charge and spin dynamics

G. P. Zhang and W. Hübner, Phys. Rev. B **58**, R5920 (1998)

History: theoretical achievements I
Bleaching effect → magnetization dynamics in FM

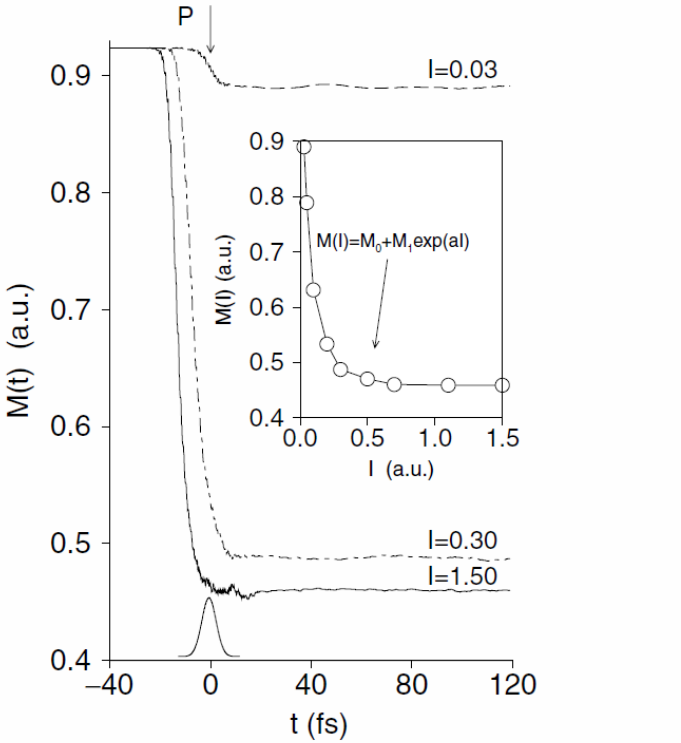


FIG. 2. With the presence of the spin-orbit coupling, the laser field can effectively influence the demagnetization. The intensity I (a.u.) is 0.03 (long-dashed line), 0.3 (dot-dashed line), and 1.50 (solid line). Inset: the exponential dependence of $M(I)$ on the laser intensity I.

Time-dependent problem

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

Ni

- Explicit dependence of magnetic moment on laser intensity
- Saturation for I > 0.5 (bleaching effect)
- τ < 10 fsec

G. P. Zhang and W. Hübner, J. Appl. Phys. **85**, 5657 (1999)

History: theoretical achievements II
Coherent dephasing intrinsic vs extrinsic quantities

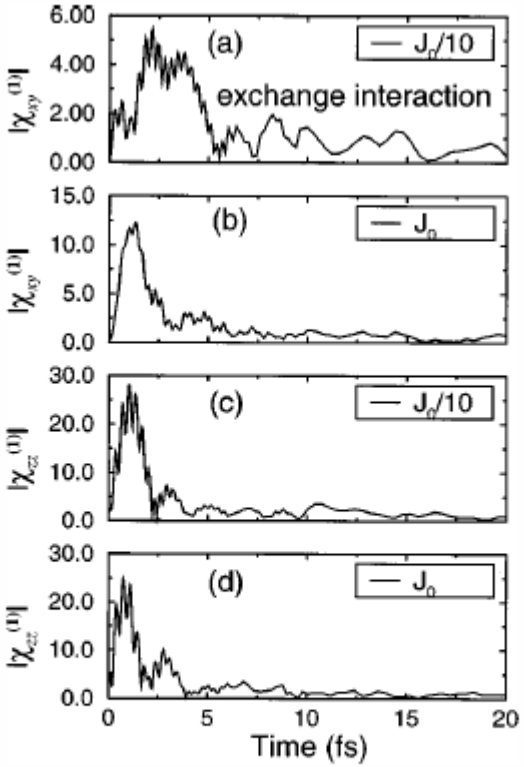


FIG. 1. Effect of exchange interaction J ($J=J_0/10$ and J_0) on spin [(a) and (b)] and charge dynamics [(c) and (d)]. Exchange interaction dominates the spin decay.

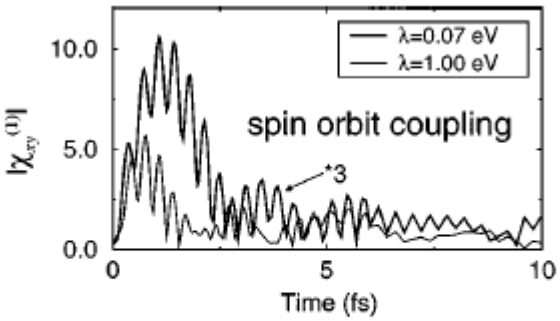
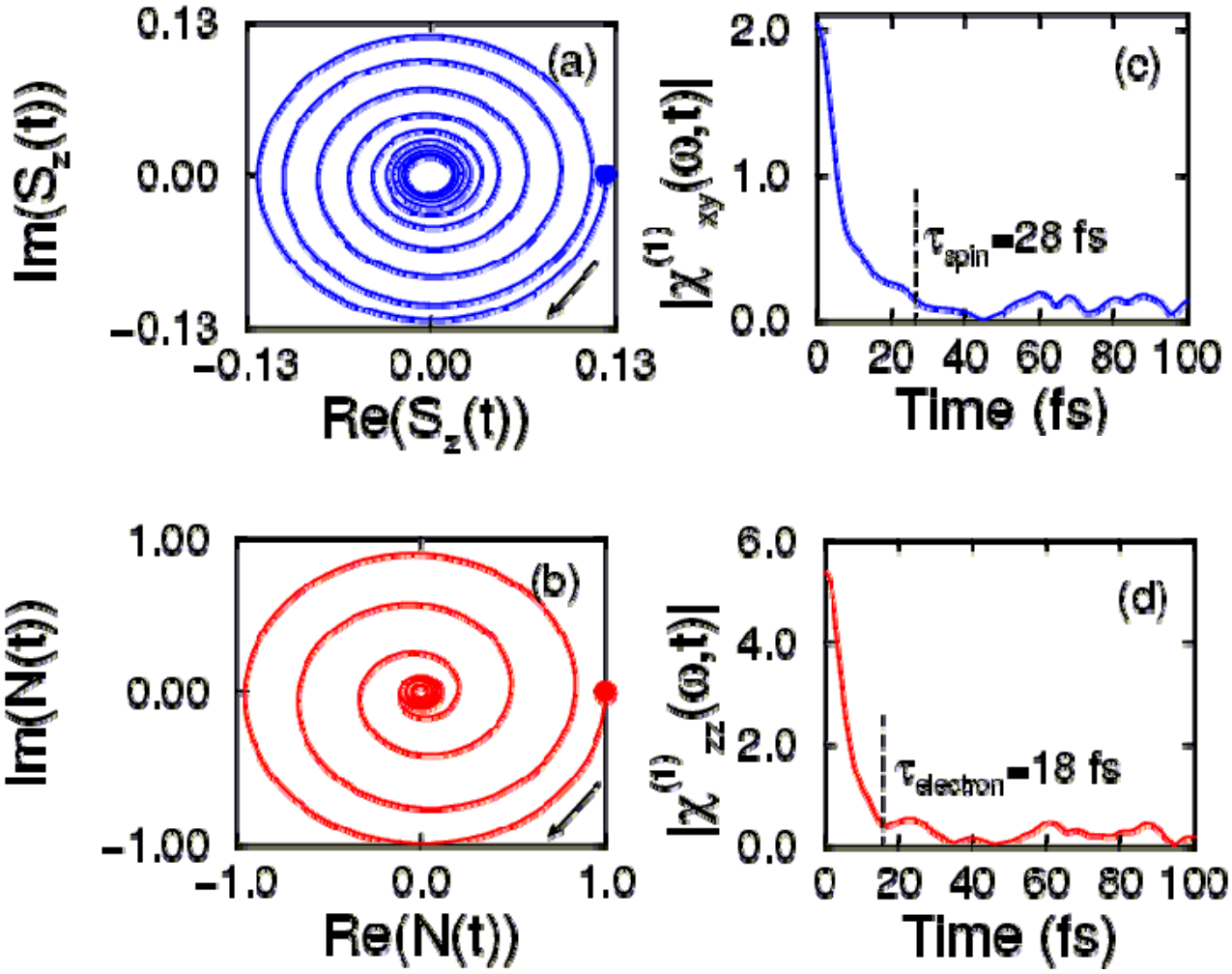


FIG. 2. Effect of spin-orbit coupling λ on spin dynamics. The solid curve is for λ=0.07 eV while the dashed curve is for λ=1 eV. SOC may speed up the spin dynamics only in heavy elements.

- Dephasing results from exchange interaction and spin-orbit coupling
- High-speed limit of intrinsic spin dynamics ~ 10 fsec

W. Hübner and G. P. Zhang, Phys. Rev. B **58**, R5920 (1998)

History: theoretical achievements II
Coherent dephasing intrinsic vs extrinsic quantities

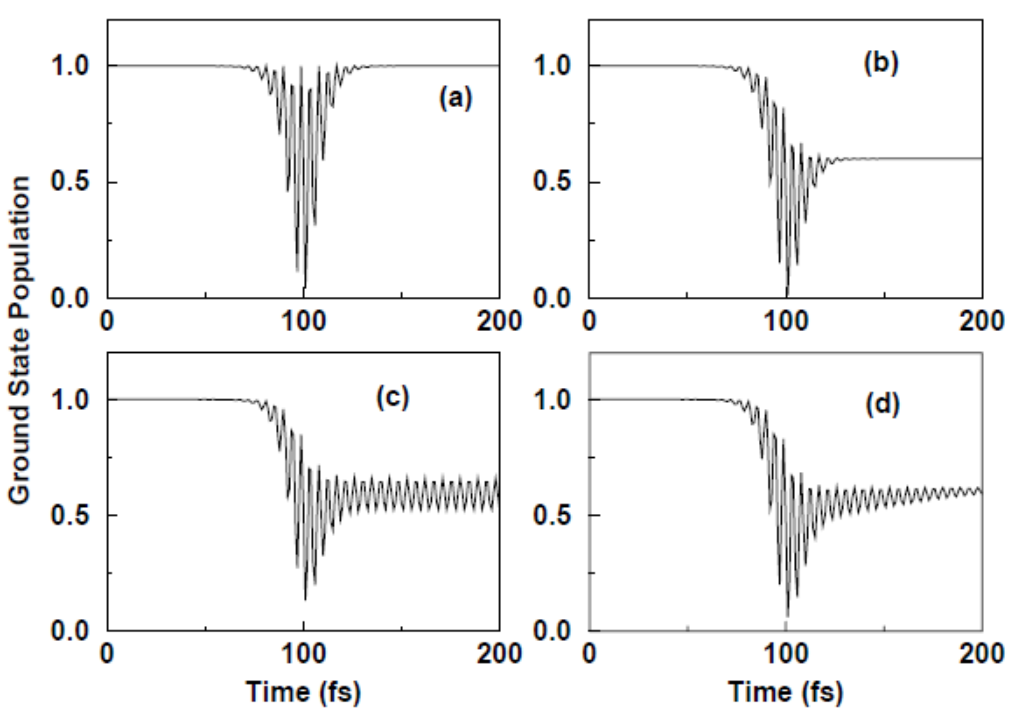


Ni

- Charge dynamics preceeds spin dynamics -> spin memory time
- Fast decay results from loss of coherence
- Increased exchange interaction speeds up spin (rather than charge) dynamics
- ~10 fsec

G. P. Zhang and W. Hübner, Appl. Phys. B **68**, 495 (1999)

4 Types of dynamics



a) Adiabatic solution of Hartree-Fock

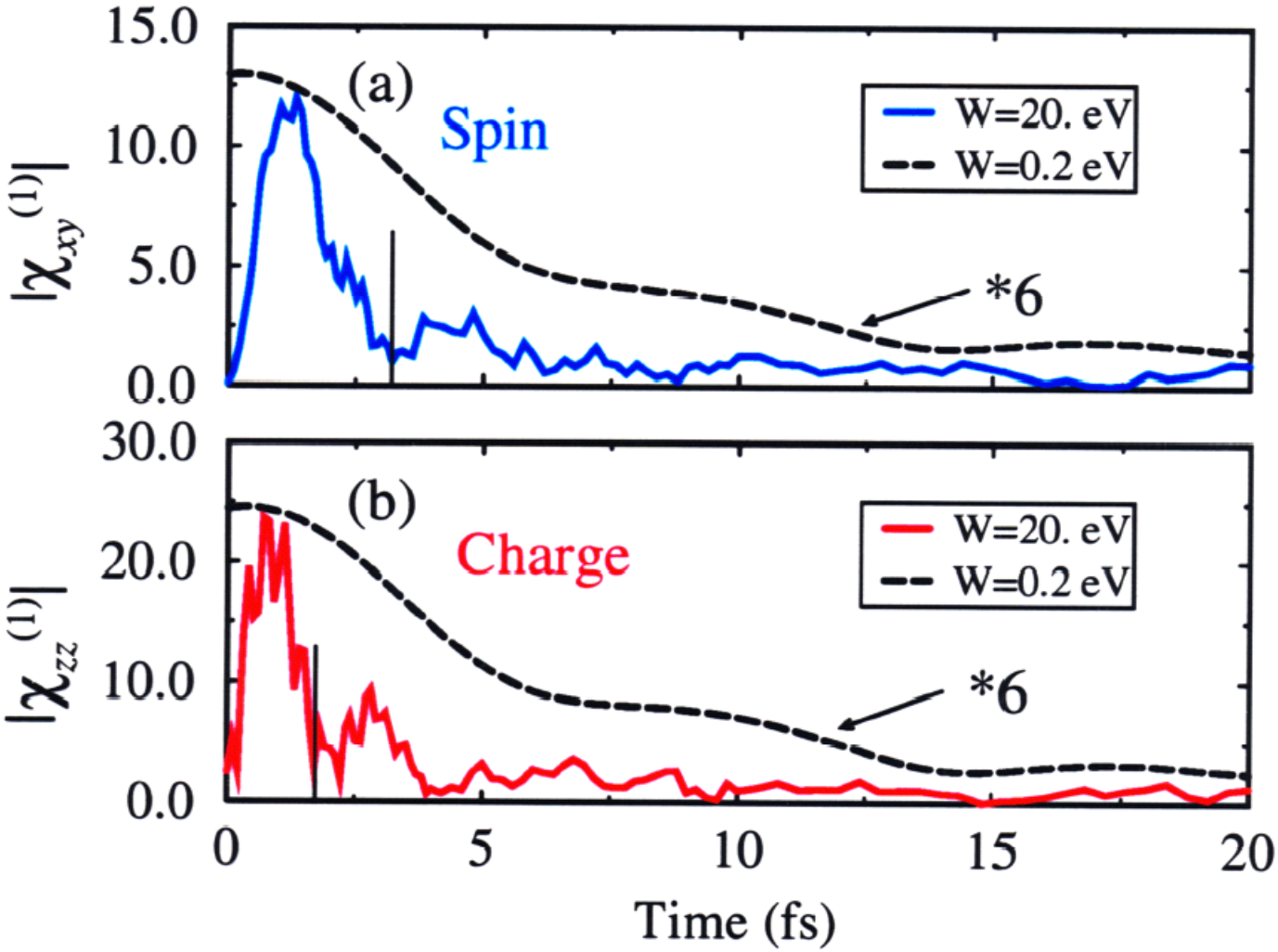
b) Evolution of matrix Hamiltonian

c) Solution of the TD-HF equation

d) Full quantum kinetic solution

Y. Pavlyukh and W. Hübner, Eur. Phys. J. D **21**, 239 (2002)

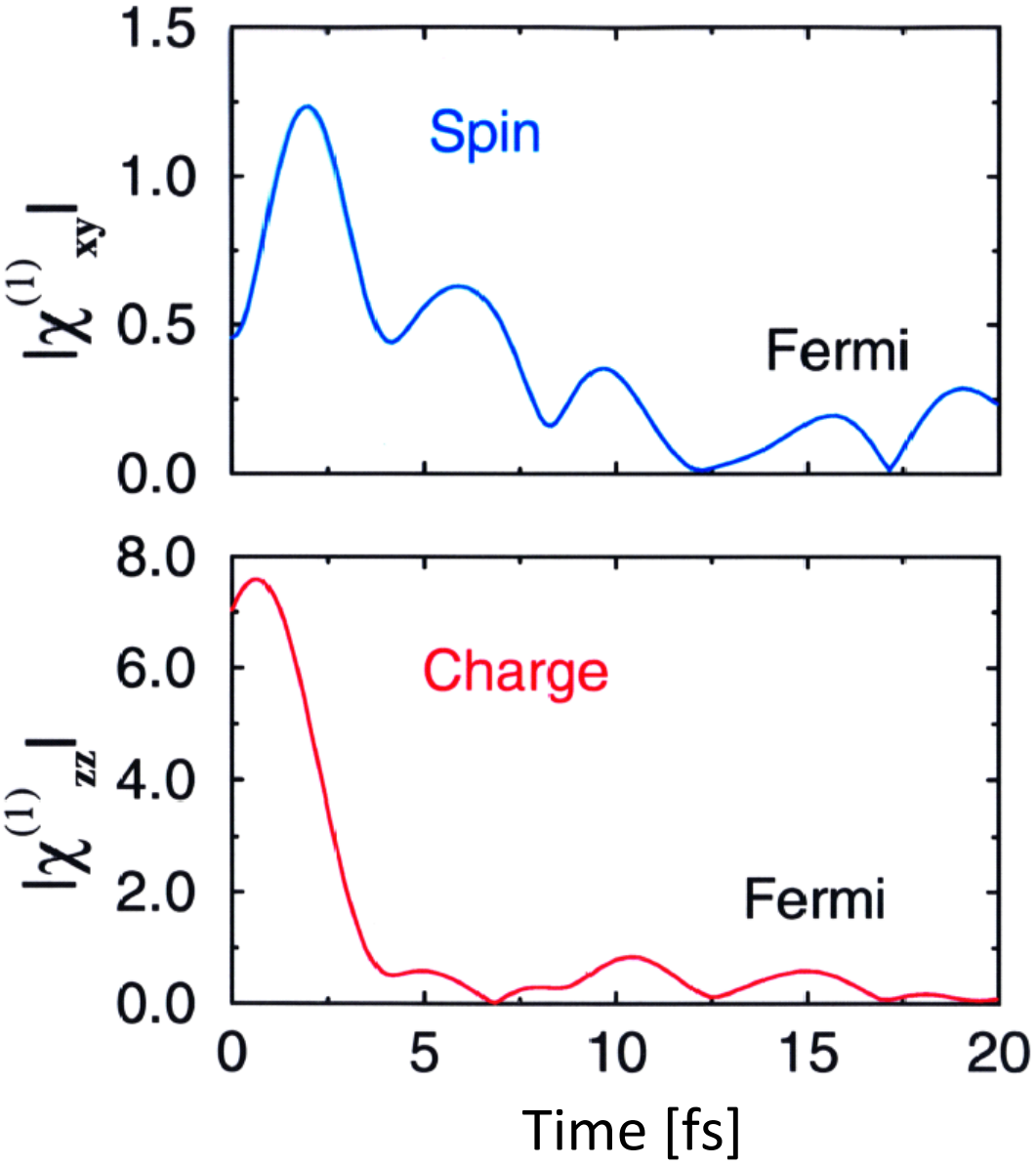
Effects of Gaussian Distribution Width W



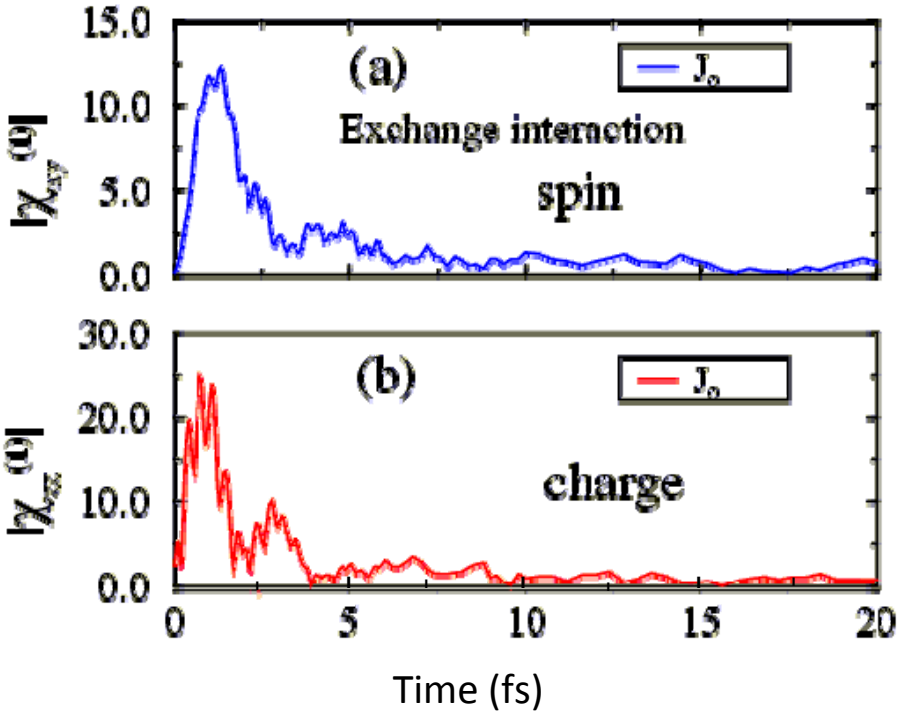
Dynamics depends on spectral width → bleaching

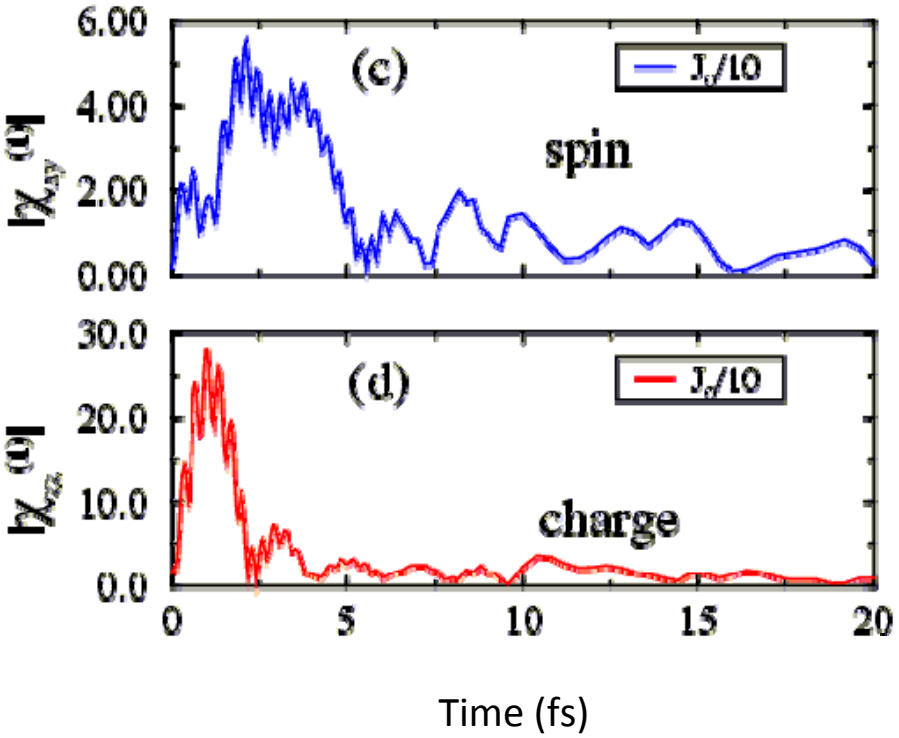
W. Hübner & G. P. Zhang, Phys. Rev. B **58**, R5920 (1998)

Spin Effects of Excited-State Distibution



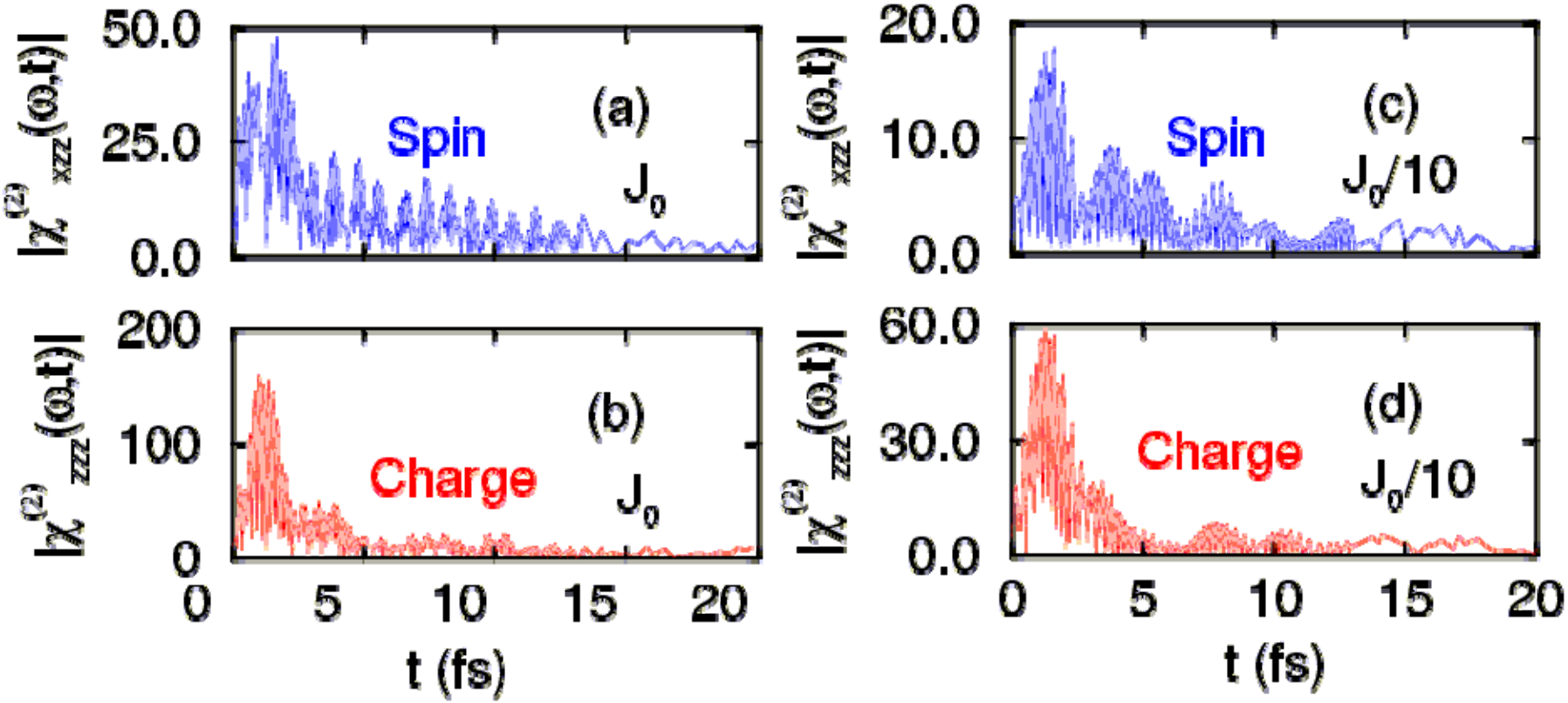
Magneto (-optical) Response in Ferromagnetic Ni





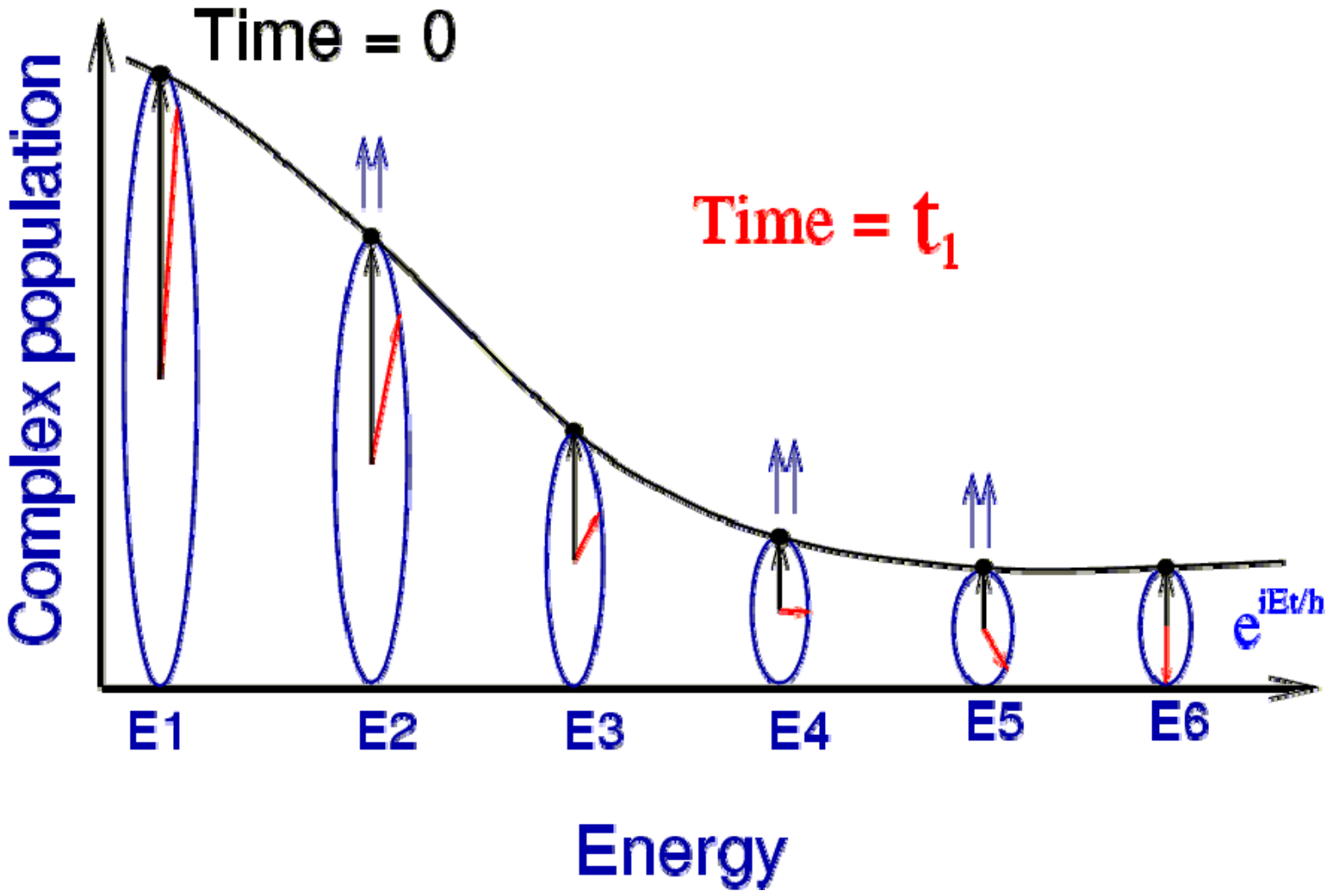
W. Hübner and G. P. Zhang, Phys. Rev. B **58**, R5920 (1998)

Nonlinear Magneto (-optical) Response in Ni



G. P. Zhang and W. Hübner, Appl. Phys. B **68**, 495 (1999)

Dephasing of the Excited State



Ingredients of the Electronic Theory for Ni

- **Hamiltonian:**

$$H = H_{band}(E_{\mathbf{k}}) + H_{electron-electron}(U, J, \Delta J) + H_{spin-orbit}(\lambda_{s.o.})[+H_{laser}(E_{el.mag.})]$$

- diagonalization of Hamiltonian: Schrödinger equation

$$H\psi_{\mathbf{k},n}(0) = E_{\mathbf{k},n}\psi(0)_{\mathbf{k},n}$$

- time evolution of states according to eigenvalues

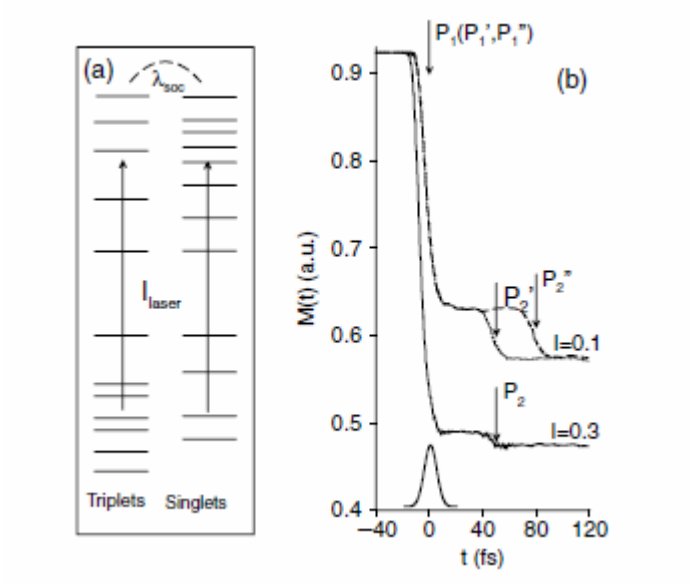
$$\psi_{\mathbf{k},n}(t) = \psi_{\mathbf{k},n}(0)e^{iE_{\mathbf{k},n}t/\hbar}$$

- pump pulse: preparation of initial state distribution

$$\Psi(0) = \sum_{\mathbf{k},n} p_{\mathbf{k},n}\psi(0)_{\mathbf{k},n}$$

- probe pulse: real-time monitoring of **spin and charge dynamics** from 100 as to 1 ps

History: theoretical achievements III
Population dynamics → magnetization dynamics in FM



Time-dependent problem

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

Ni

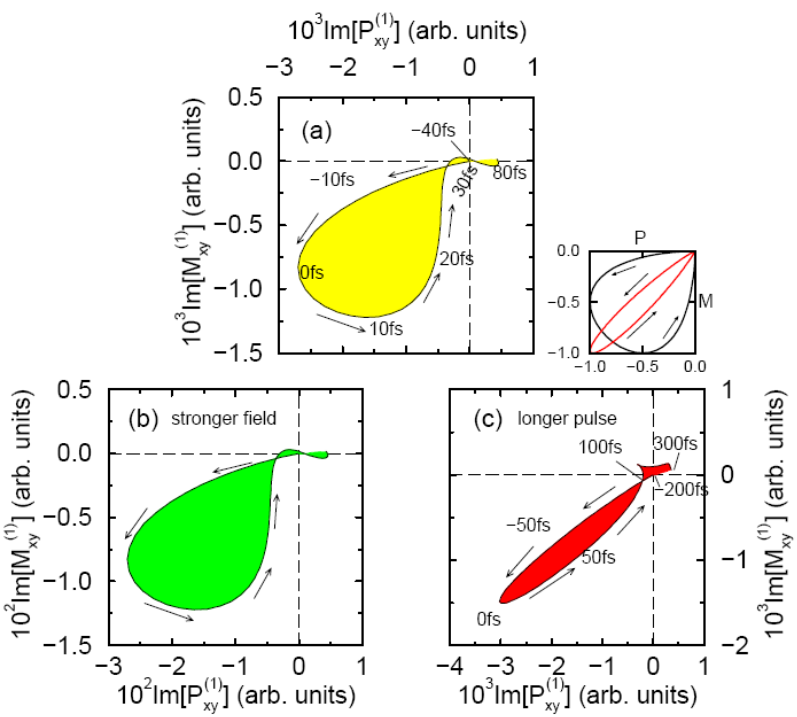
- Cooperative effect of laser pulse and SOC
- Controllable process!
- τ_1 ~ 40 fsec

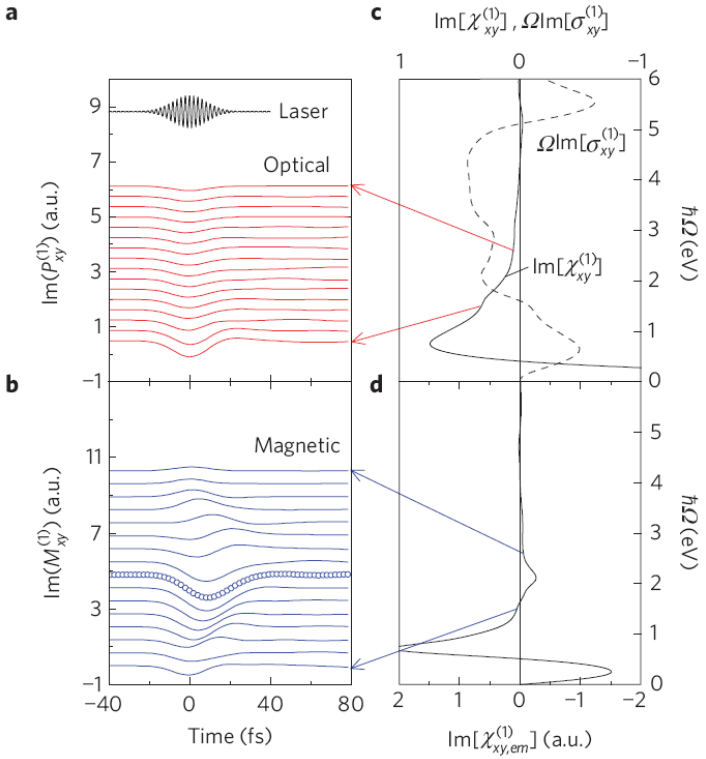
G. P. Zhang and W. Hübner, Phys. Rev. Lett. **85**, 3025 (2000)

History: theoretical achievements III
Separability of spin and charge dynamics in Ni

TR dynamical Kerr-effect, as probe for magnetism

one center, theory: separability of spin and charge dynamics

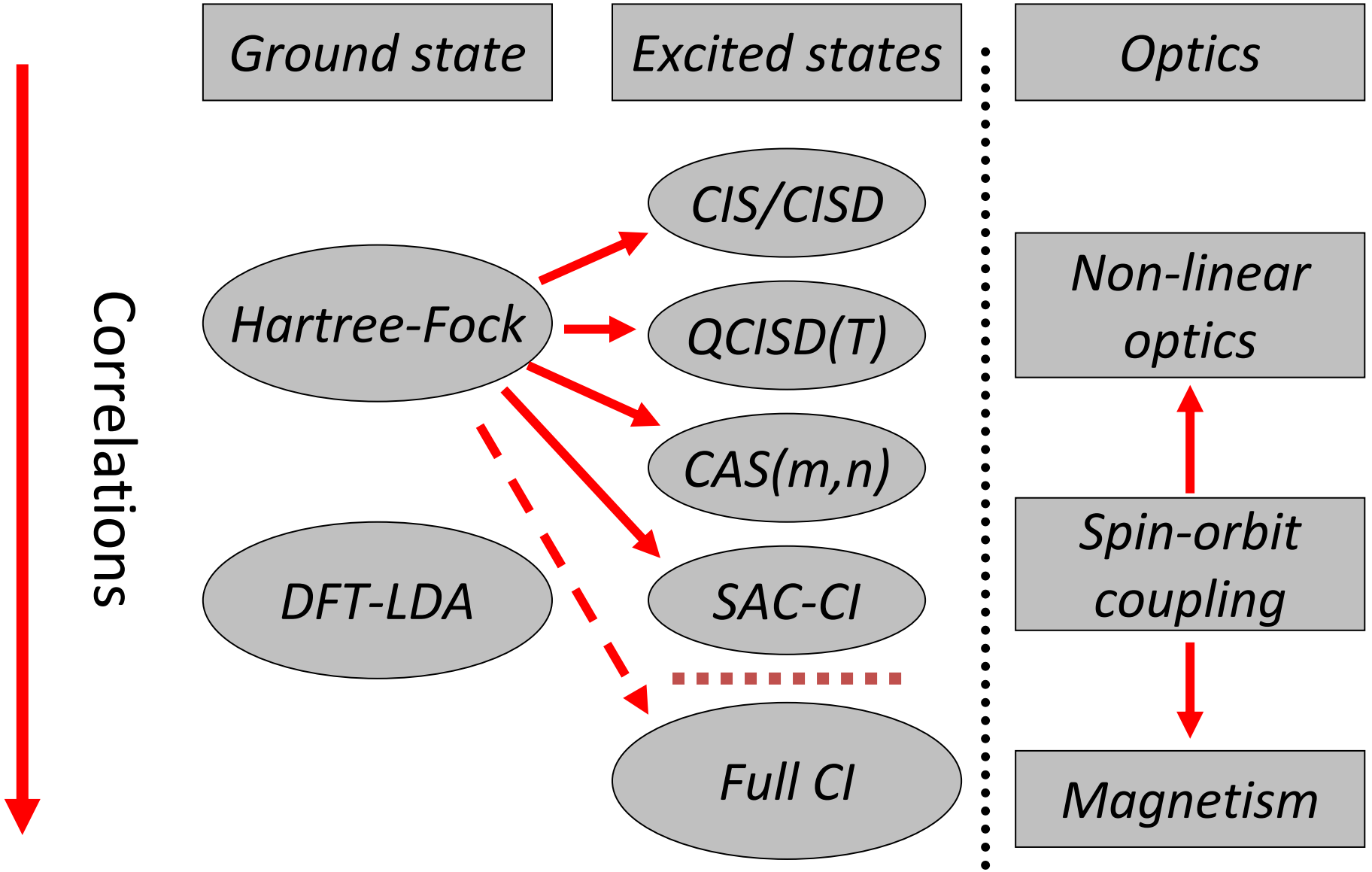




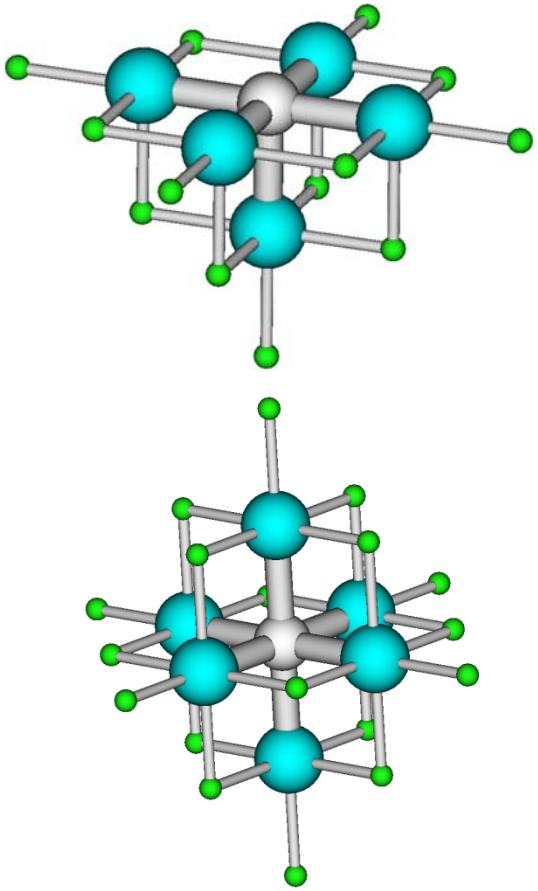
- For short laser pulses charge dynamics preceeds spin dynamics
- Magnetically nonimportant higher excited states dominate dynamics on first few femtoseconds

G. P. Zhang, W. Hübner, G. Lefkidis, Y. Bai, and T. F. George, Nature Physics **5**, 499 (2009)

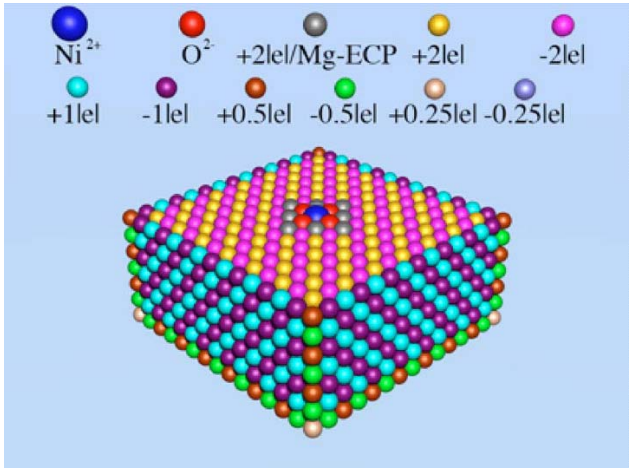
Quantum Chemical Methods



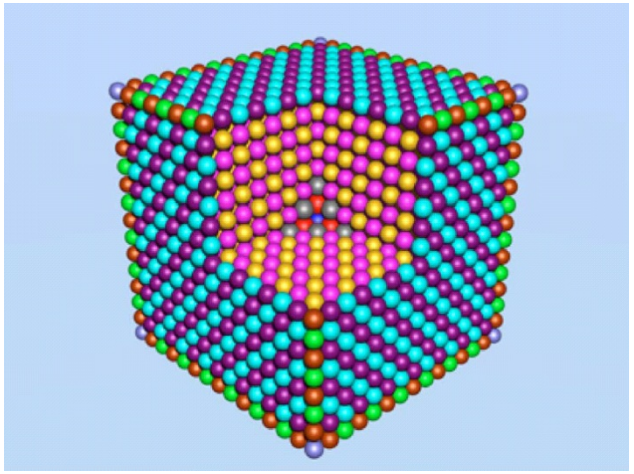
Doubly Embedded Cluster Models



$(NiO_5)^{8-}$



$(NiO_6)^{10-}$

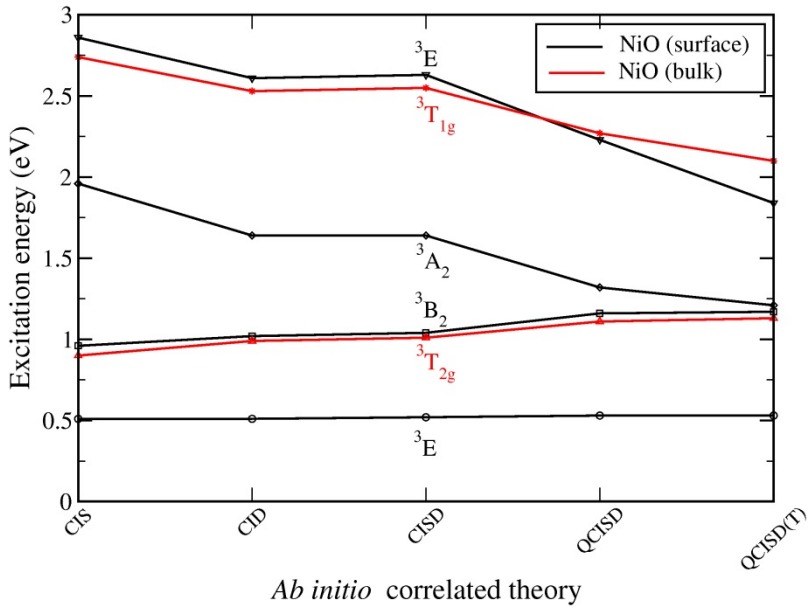


1st embedding shell: ECPs for better description of environment of O atoms
2nd embedding shell: Madelung potential

K. Satitkovitchai, Y. Pavlyukh, and W. Hübner, Phys. Rev. B **72**, 045116 (2005)

Theory for NiO [bulk and (001) surface]

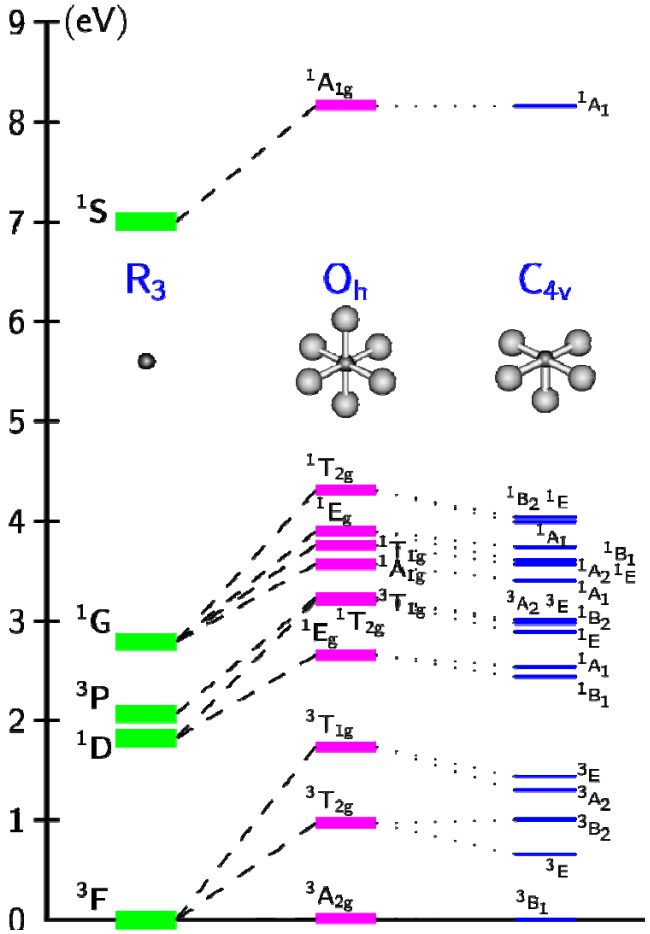
Quantum chemistry for NiO



+ Laser pulse → electron dynamics

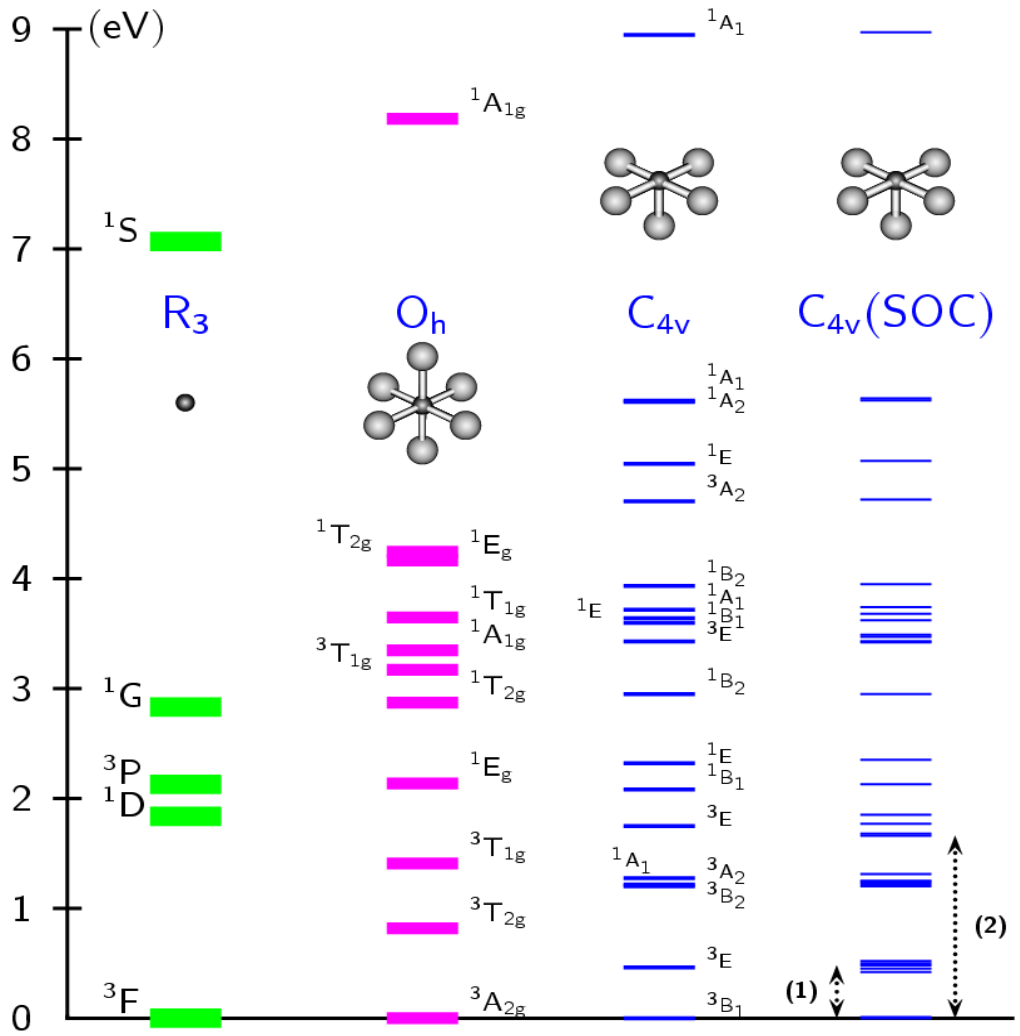
+ SOC → spin dynamics

QCISD(T)



K. Satitkovitchai, Y. Pavlyukh and W. Hübner, Phys. Rev. B **67**, 165413 (2003)

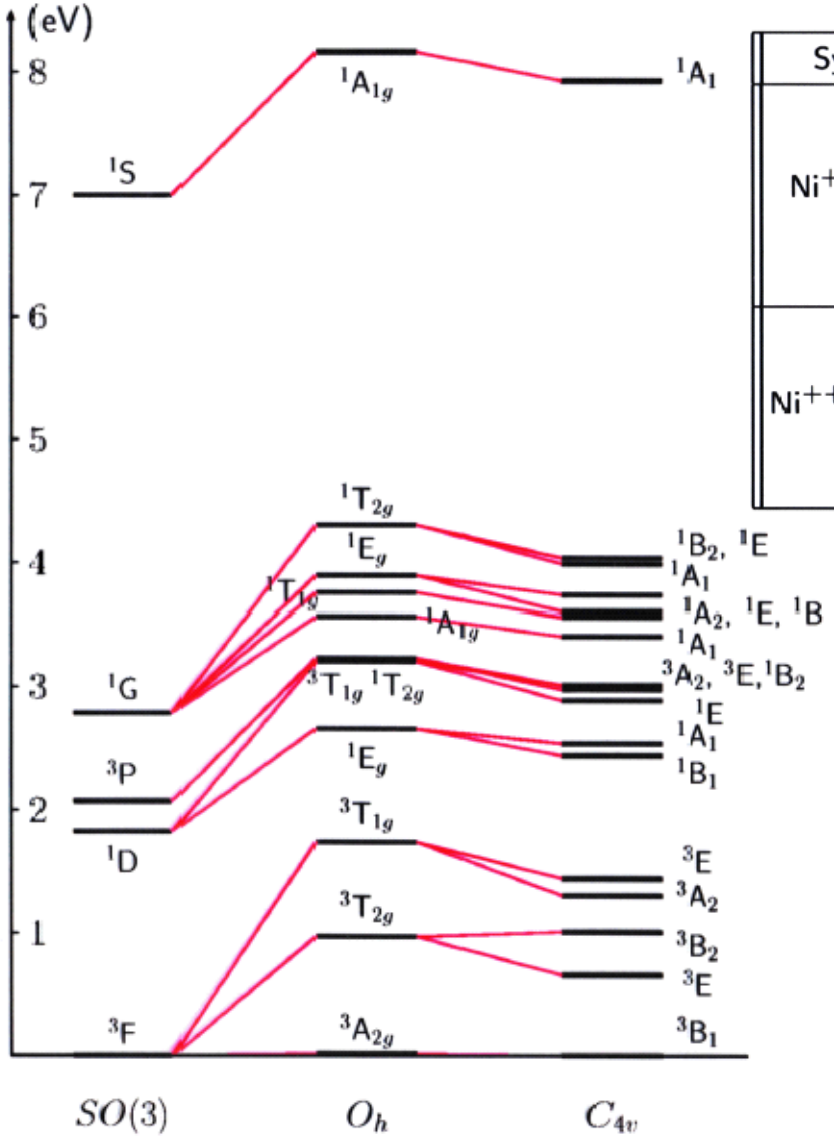
NiO Cluster – *d*-Level Splitting



- Discrete intragap levels
  - Lower four levels by QCISDT
  - Upper levels fitted with Ligand Field Theory
  - Perturbative inclusion of SOC
- Possibility to address states selectively

O. Ney, Ph. D. thesis, Martin-Luther-Universität Halle-Wittenberg (2003)
R. Gómez-Abal, O. Ney, K. Satitkovitchai and W. Hübner, Phys. Rev. Lett. **92**, 227402 (2004)

Ab Initio Theory of NiO Clusters

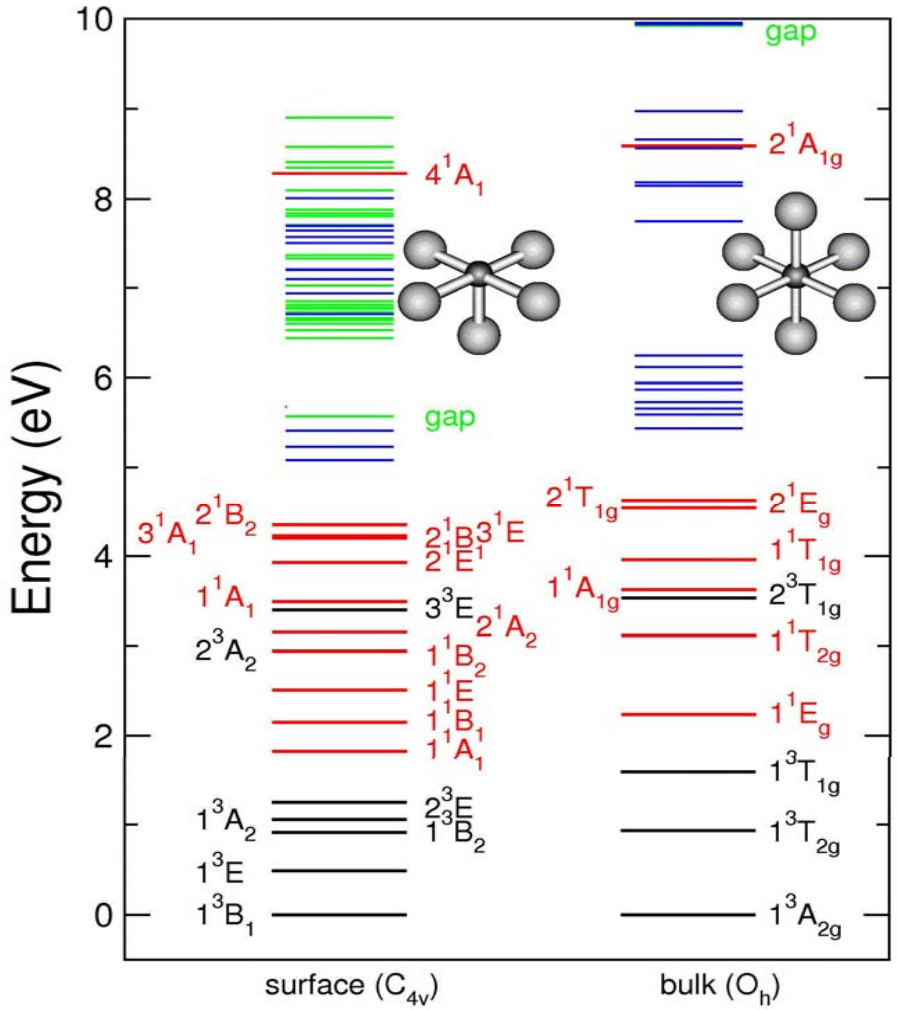


System	Transition	Experiment ♯	QCISD	QCISD(T)
Ni^{++} bulk	$^3A_{2g} \rightarrow {}^3T_{2g}$	1.05, 1.08, 1.10, 1.13, 1.16	1.11	1.13
	$^3A_{2g} \rightarrow {}^3T_{1g}$	1.79, 1.86, 1.87, 1.95	2.27	2.10
Ni^{++} surface	$^3B_1 \rightarrow {}^3E$	0.57,0.90,0.60	0.53	0.53
	$^3B_1 \rightarrow {}^3B_2$	1.10	1.16	1.17
	$^3B_1 \rightarrow {}^3A_2$	1.30	1.32	1.21
	$^3B_1 \rightarrow {}^3E$	1.62, 1.75	2.23	1.84

Excellent agreement with experiment

♯ W. C. Mackrodt and C. Noguera, Surf. Sc. Lett. **457**, L386 (2000)

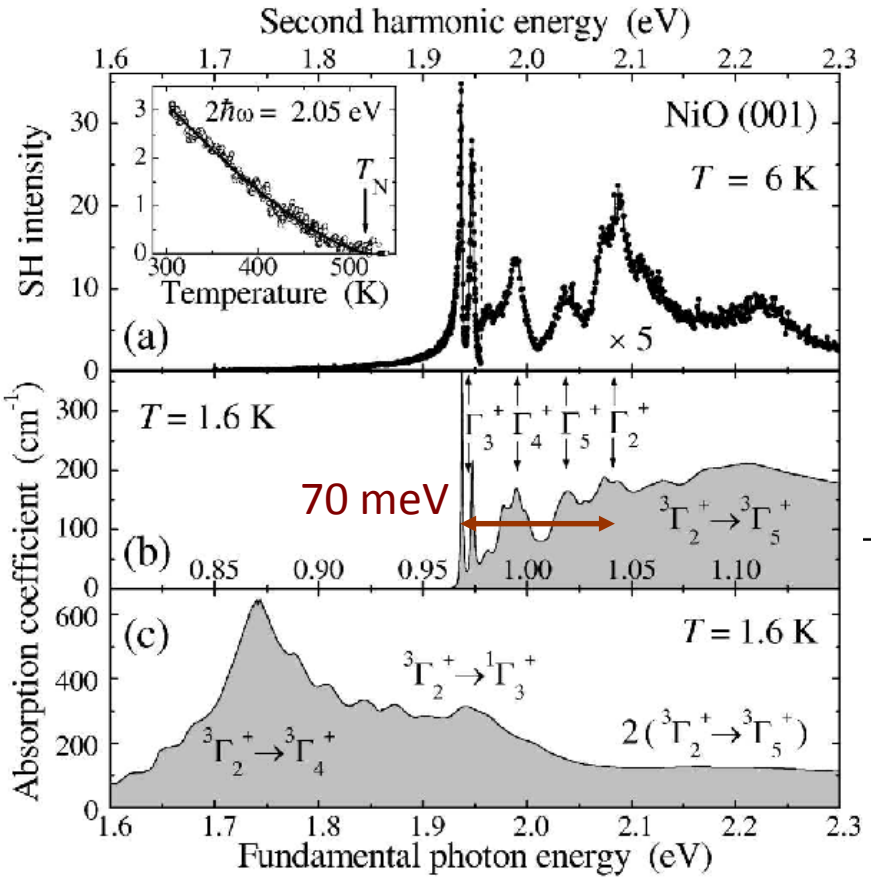
MC-SCF CAS: Levels for NiO (001) & bulk



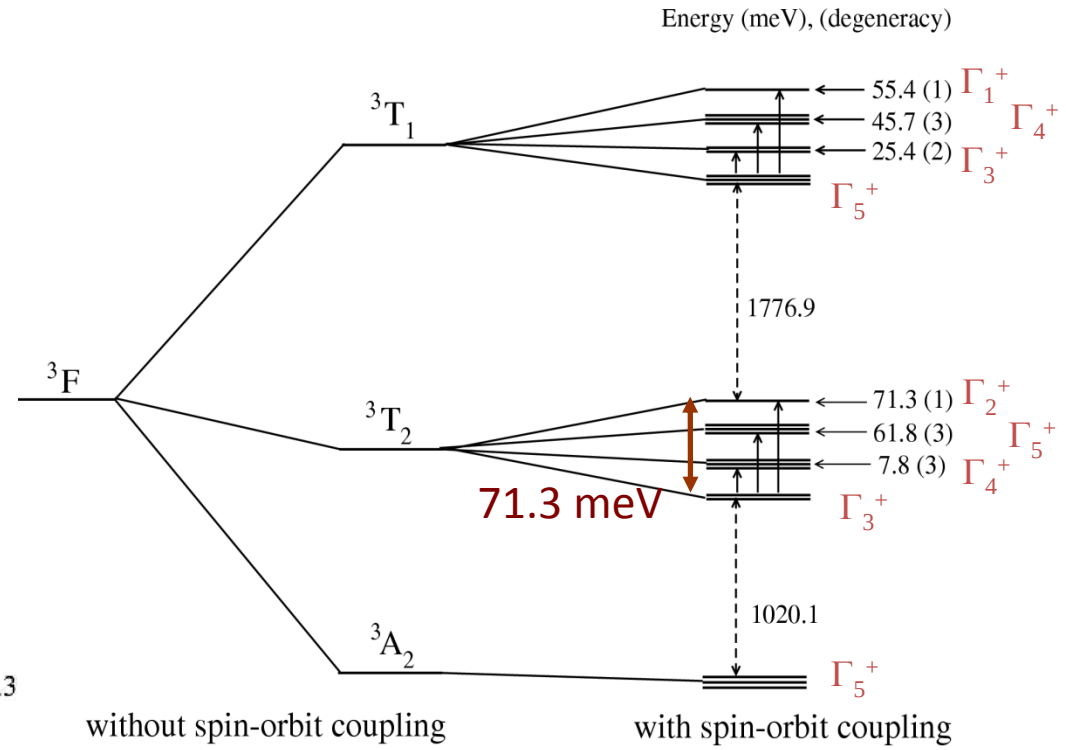
- Highly correlated system
- High spin density
- Localized discrete intragap *d*-levels
- Agreement with experiment

G. Lefkidis & W. Hübner, Phys. Rev. Lett. 95, 77401 (2005)
Bulk: R. Newman & R. M. Chrenko, Phys. Rev. 114, 1507 (1959)
Surface: B. Fromme et al., Phys. Rev. Lett. 77, 1548 (1996)

Results: Spin-Orbit Coupling NiO (bulk)

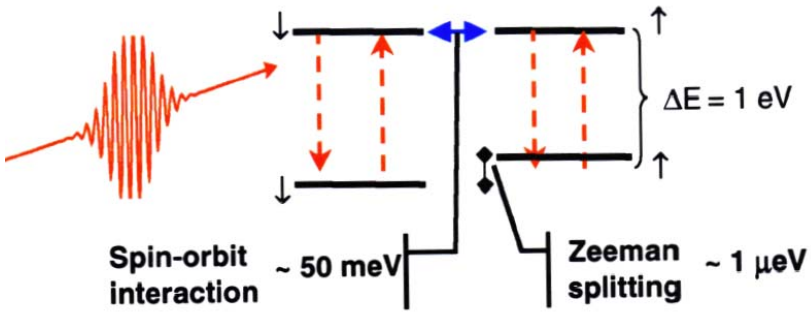


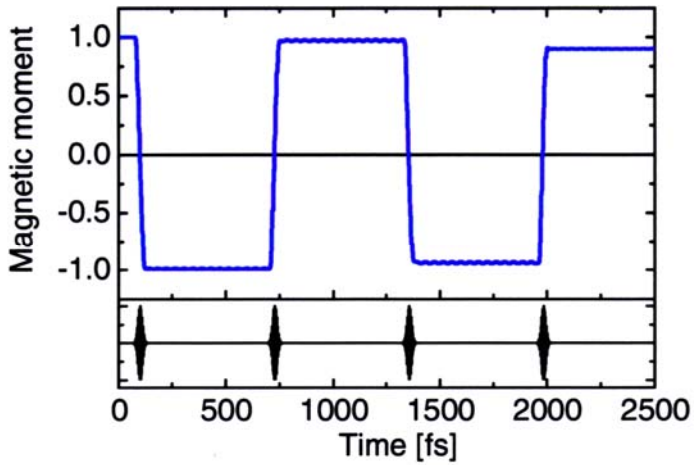
Relativistic effects in the low-lying excited states of bulk NiO



Experiment: M. Fiebig et al., Phys. Rev. Lett. **87**, 137202 (2001)
K. Satitkovitchai, Y. Pavlyukh and W. Hübner, Phys. Rev. B **67**, 165413 (2003)

Four-Level System





PROs:

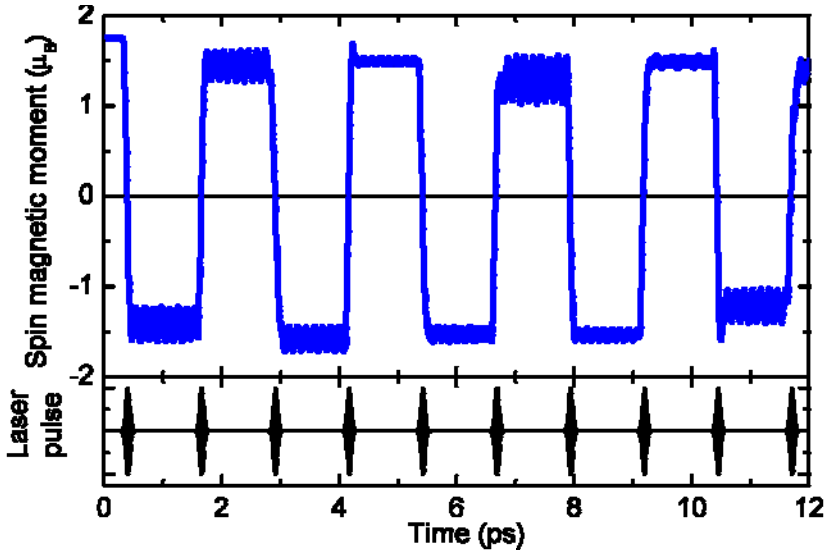
- Faster (50 fs) than present methods
  (wall motion, precession and current switching)
- A variety of possible materials
  (magnetic semiconductors, metallic and nonmetallic nanostructures, magnetic oxides)
- Near field optics is conceptually very similar to passing switching currents through leads on nanowires
- Externally tunable
  - fast and dissipative for static devices.
  - less dissipative and slower for mobile devices.

CONs:

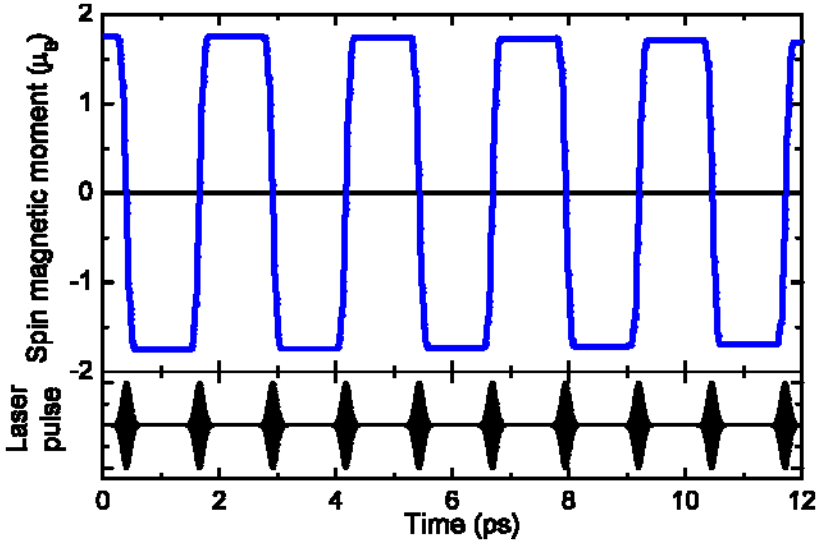
- No experimentally demonstrated... Yet!!

Results: NiO (001)

- First results for NiO, showing the possibility of all optical spin switching in the subpicosecond regime
- Tuning photon energy, intensity and width of the laser pulse



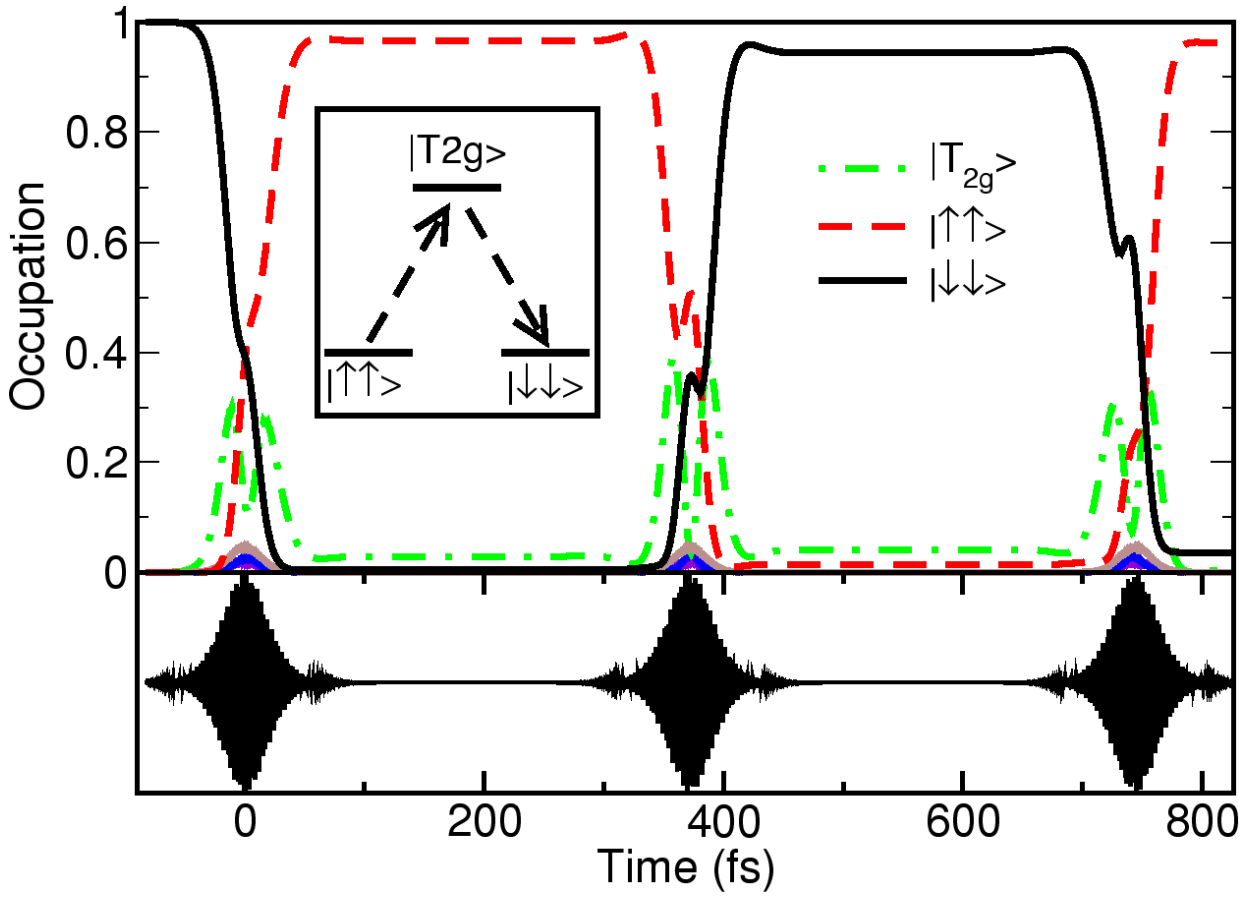
$\hbar\omega 0$ = 0.422 eV, l = 2933 nm
FWHM = 59 fs, Imax ≈ 1014 W/cm2



$\hbar\omega 0$ = 1.645 eV, l = 752 nm
FWHM = 117 fs, Imax ≈ 1.2·1014 W/cm2

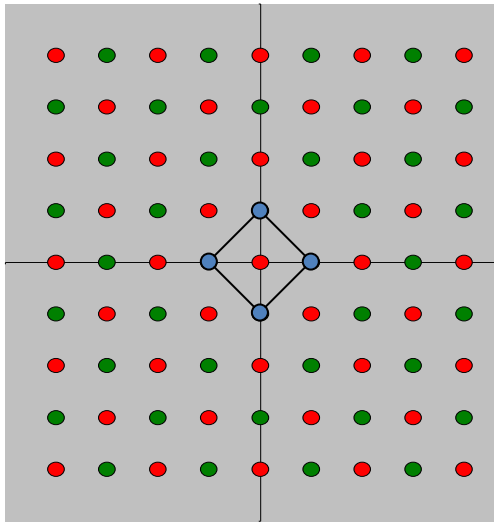
R. Gómez-Abal et al., Phys. Rev. Lett. **92**, 227402 (2004)

Results: NiO (001) with CAS-SCF + SOC

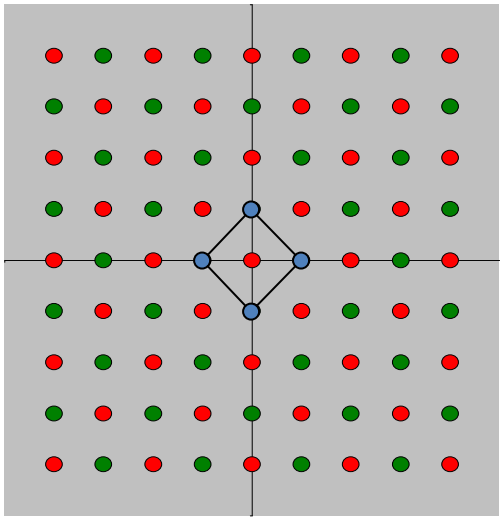


- Control up to more then 10 duty cycles
- Phase between states important
- Damping between cycles leads to total magnetization reversal?

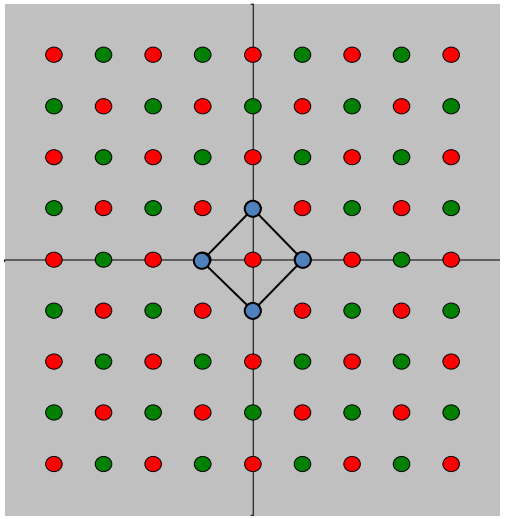
Phonons: local symmetries in NiO bulk



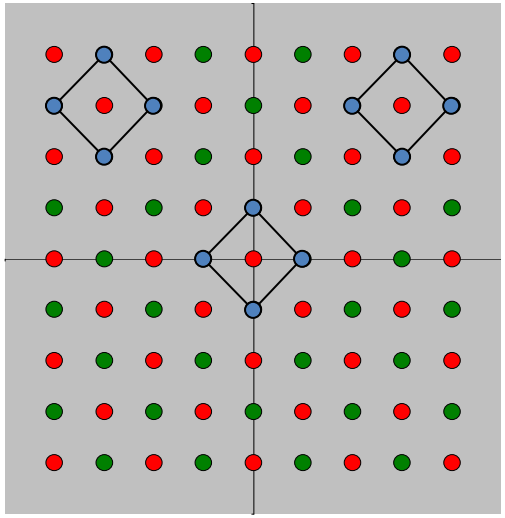
Γ-Acoustic
O_h



X-Acoustic
C_{4v}

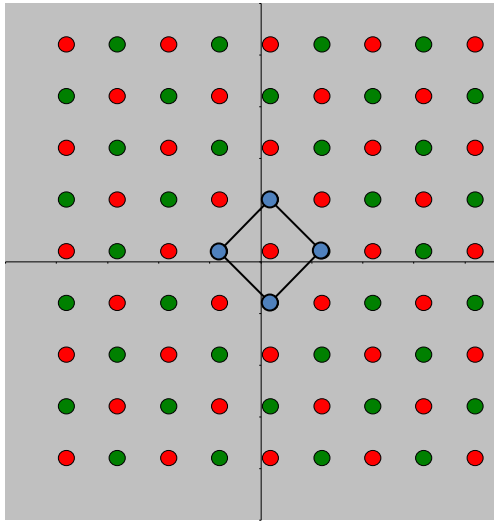


Γ-Optical
C_s

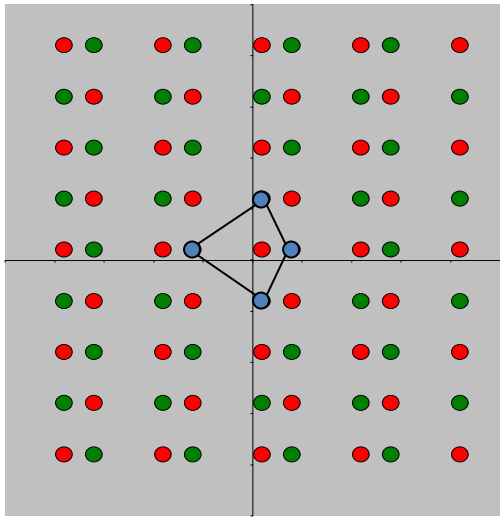


Δ-Optical
O_h / D_{4h} / C_s

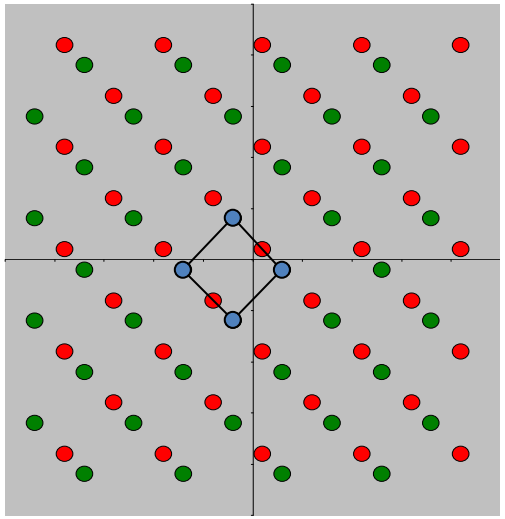
Phonons: local symmetries in NiO bulk



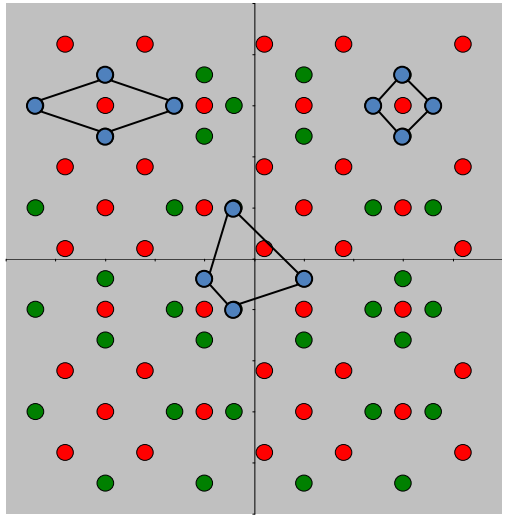
Γ-Acoustic
O_h



X-Acoustic
C_{4v}



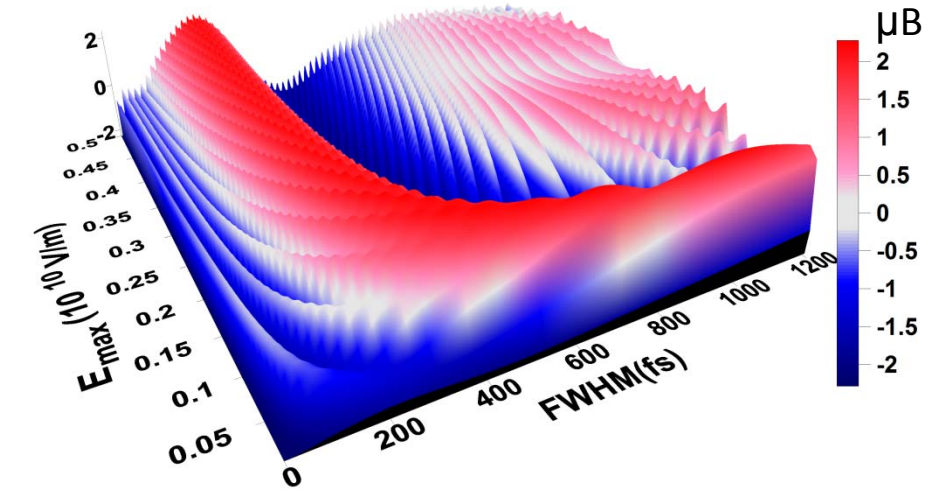
Γ-Optical
C_s



Δ-Optical
O_h / D_{4h} / C_s

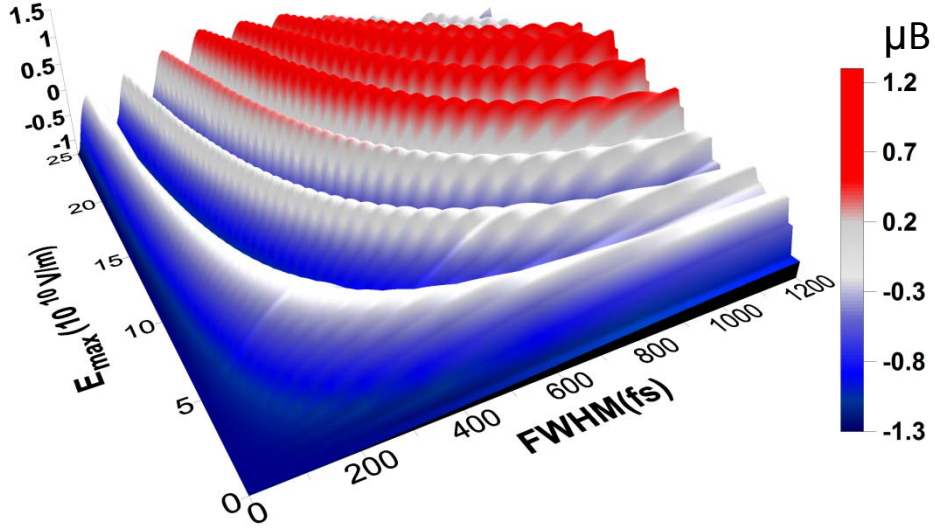
Historic achievements IV
Electron-phonon coupling in NiO

force matrix → normal modes → quantization → electron-phonon interaction



no phonons

- phonons affect symmetry
  ⇒ different selection rules
- lattice temperature dependence



phonons

G. Lefkidis and W. Hübner, J. Mag. Mag. Mater. **321**, 979 (2009)

History: theoretical achievements V
Spin-lattice relaxation time $\tau_{SL} \approx 48$ psec for Gd

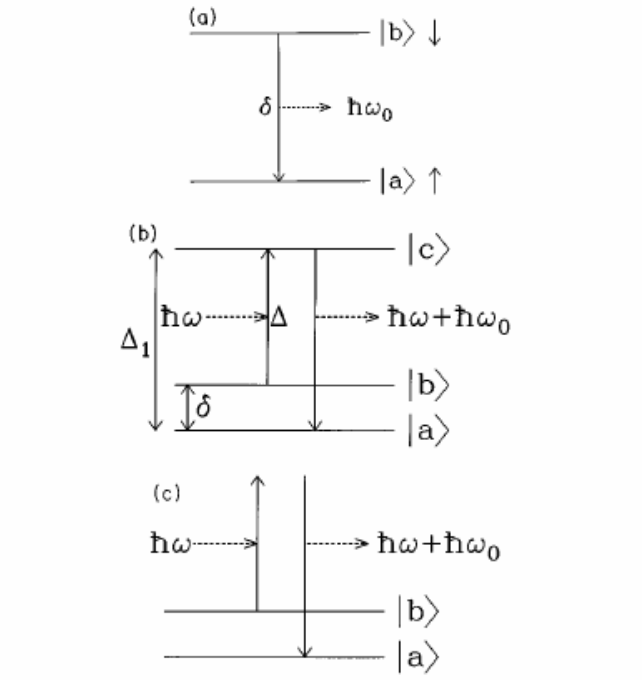


FIG. 1. (a) Direct process, (b) Orbach process, and (c) Raman process.

- Good agreement with experiment
- Time given by spin-orbit induced magnetocrystalline anisotropy energy
- Three phonon involving processes
  - Direct process (one-phonon scattering, very low T)
  - Orbach process (crystal-field splitting, low T)
  - Raman process (two-phonon scattering, moderate T)
- Phonon-magnon coupling
- 2-phonon processes → high-temperature theory (for low-temperature plateau)

rate equation $$\dot{N}_b = \frac{9\Sigma_{mn}|\langle a|v_n^m|b\rangle|^2}{8\rho^2\pi^3\hbar^7 v_s^{10}} \int [N_a\bar{p}_0(\delta_2)[\bar{p}_0(\delta_1)+1] - N_b\bar{p}_0(\delta_1)[\bar{p}_0(\delta_2)+1]]\delta_1^6 d\delta_1$$

W. Hübner and K. H. Bennemann, Phys. Rev. B **53**, 3422 (1996)

History: theoretical achievements summary

a. Bleaching (<10 fsec)

b. Dephasing (10 fsec)

c. Population dynamics (40-80 fsec)

d. Electron-phonon coupling (<1 psec)

e. Spin-lattice relaxation (48 psec)

Outline

1. History: theoretical achievements in spin dynamics
2. Introduction: theoretical and background aspects
3. Clusters with two magnetic centers
4. Clusters with three magnetic centers: magnetic logic
5. Role of bridging atoms
6. Conclusions

Which materials?

Why molecular magnets: motivation

- Ferromagnets → fast dynamics but no selective control possible
  (many broad bands i.e. no addressability of excited states)
- Antiferromagnets → narrow bands → good addressability
- Molecular magnets → few discrete levels → even better addressability
- AF and molecular magnets allow coherent control
  → active spin control → functionalization (applications)

Which materials?

Molecular magnets: three different experimental environments

•ligand-stabilized complexes (fluid phase/pellets)
(+) conventional wet chemistry
(+) exist already
(-) far from application devices

•Gas phase of bare clusters (nozzle expansion)
(+) few atomes
(+) larger active-center/total-atoms ratio
(+) charged particles → control through mass-selection
(-) far from application devices

•Clusters on surfaces
(+) close to application devices
(-) exploit of additional features needed for selectivity
(resonance selection/magnetic field gradient)
(-) bottom-up preparation: good but not excellent structures, e.g. on (111) surfaces)
magnetically fair

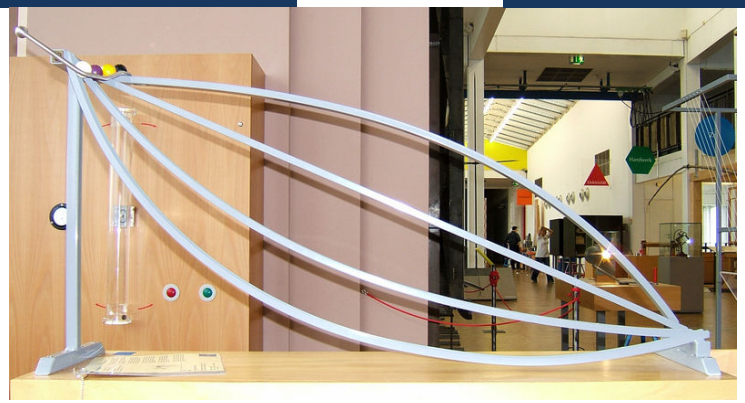
Logic operations: the need for speed
shortest ≠ fastest

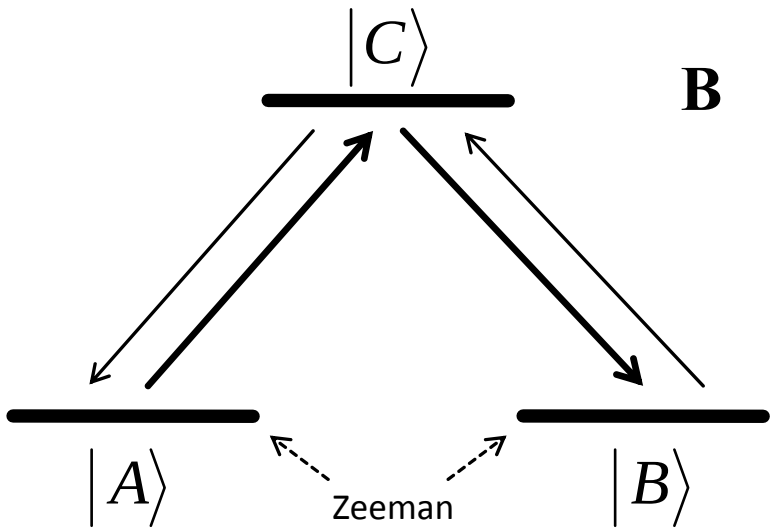
macro

micro

U Giselastraße

U Universität





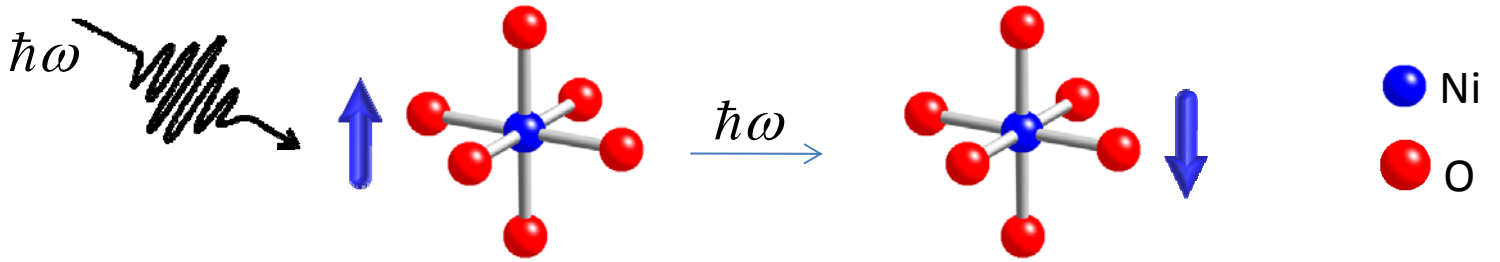
time minimization (brachistochrone)

Optical Λ process

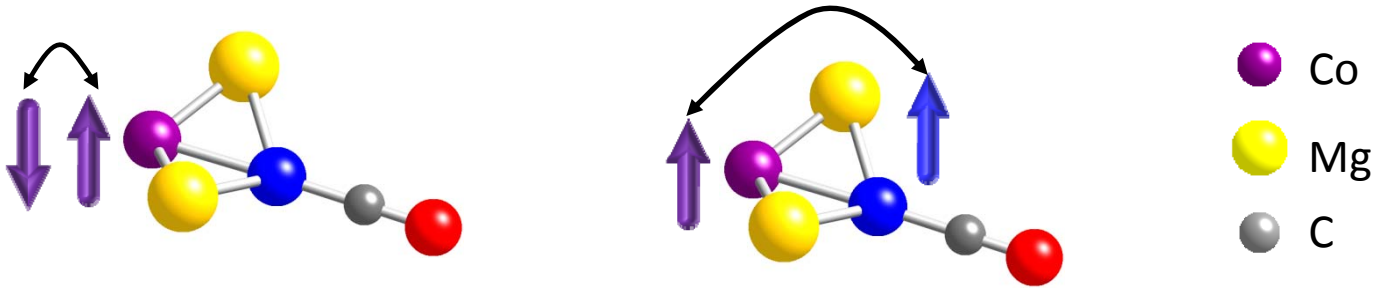
- Two optical transitions faster than one magnetic transition
- Best results with
  - slightly tilted linearly polarized light σ_0
  - transition matrix elements almost equal
  - intermediate excited state consisting 50% of $|\uparrow\uparrow\rangle$ and 50 % of $|\downarrow\downarrow\rangle$

From one to more centers

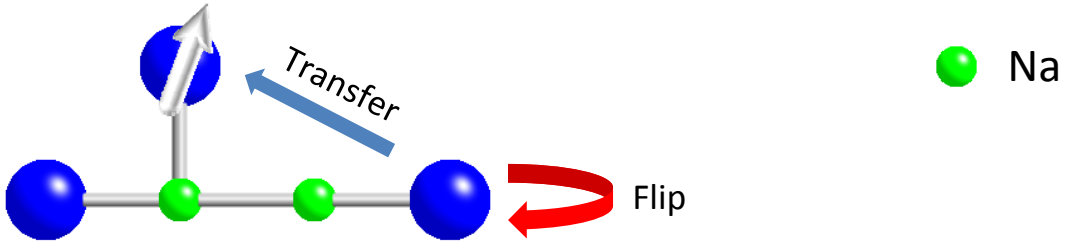
One active center → Spin flip



Two active centers → Spin flip and transfer (minimum requirement)



More active centers → Logic functionalization



How many centers?

1 center

local switch

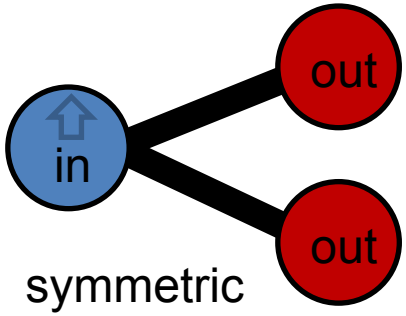
information carrier

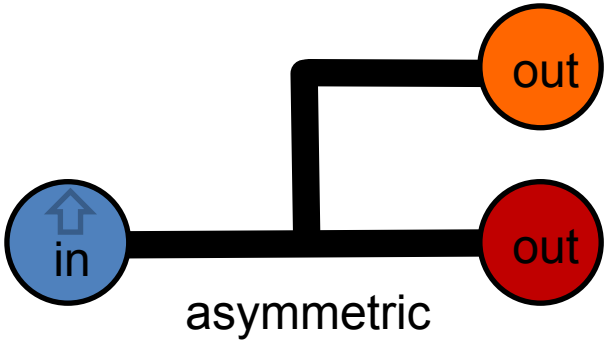
2 centers

…+ transfer

decoupling input/output and propagation of information

3 centers

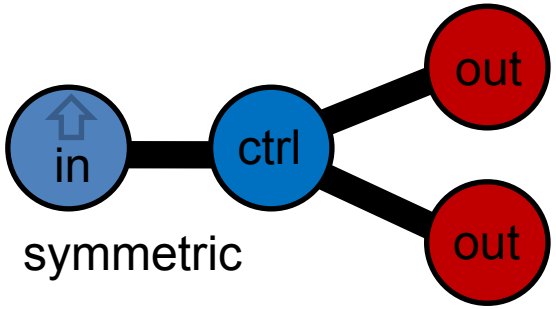


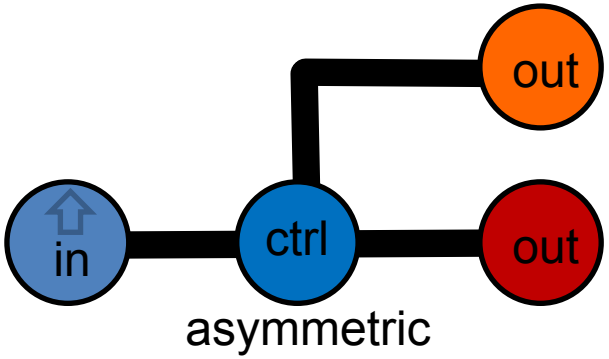


…+ branching

direction of information propagation, interference

4 centers

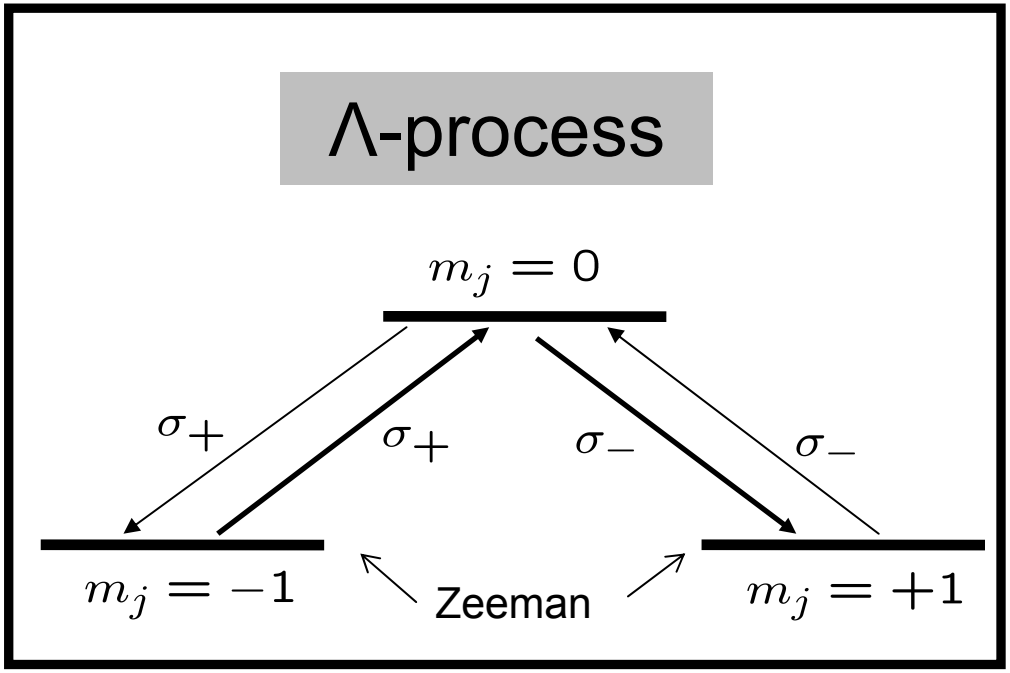




…+ control

logic

Concept

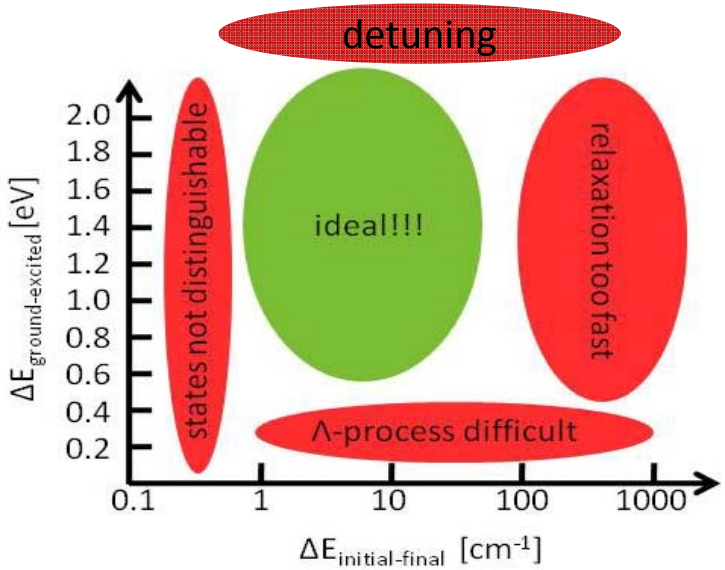


spin-orbit coupling AND laser →
spin dynamics AND functionalization !

in silico: time minimization (< 1 psec)

propagation process $|A\rangle \xrightarrow{\hbar\omega} |B\rangle$

the spins of the states can have **different**
- magnitude → demagnetization
- orientation → spin flip
- localization → spin transfer



Energy differences

Hamiltonian

$$\hat{H}^{(0)} = -\frac{1}{2}\sum_{i=1}^{N_{\text{el}}}\nabla^2 - \sum_{i=1}^{N_{\text{el}}}\sum_{a=1}^{N_{\text{at}}}\frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|} + \sum_{i=1}^{N_{\text{el}}}\sum_{j=1}^{N_{\text{el}}}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{a=1}^{N_{\text{at}}}\sum_{b=1}^{N_{\text{at}}}\frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}$$

Electronic correlations

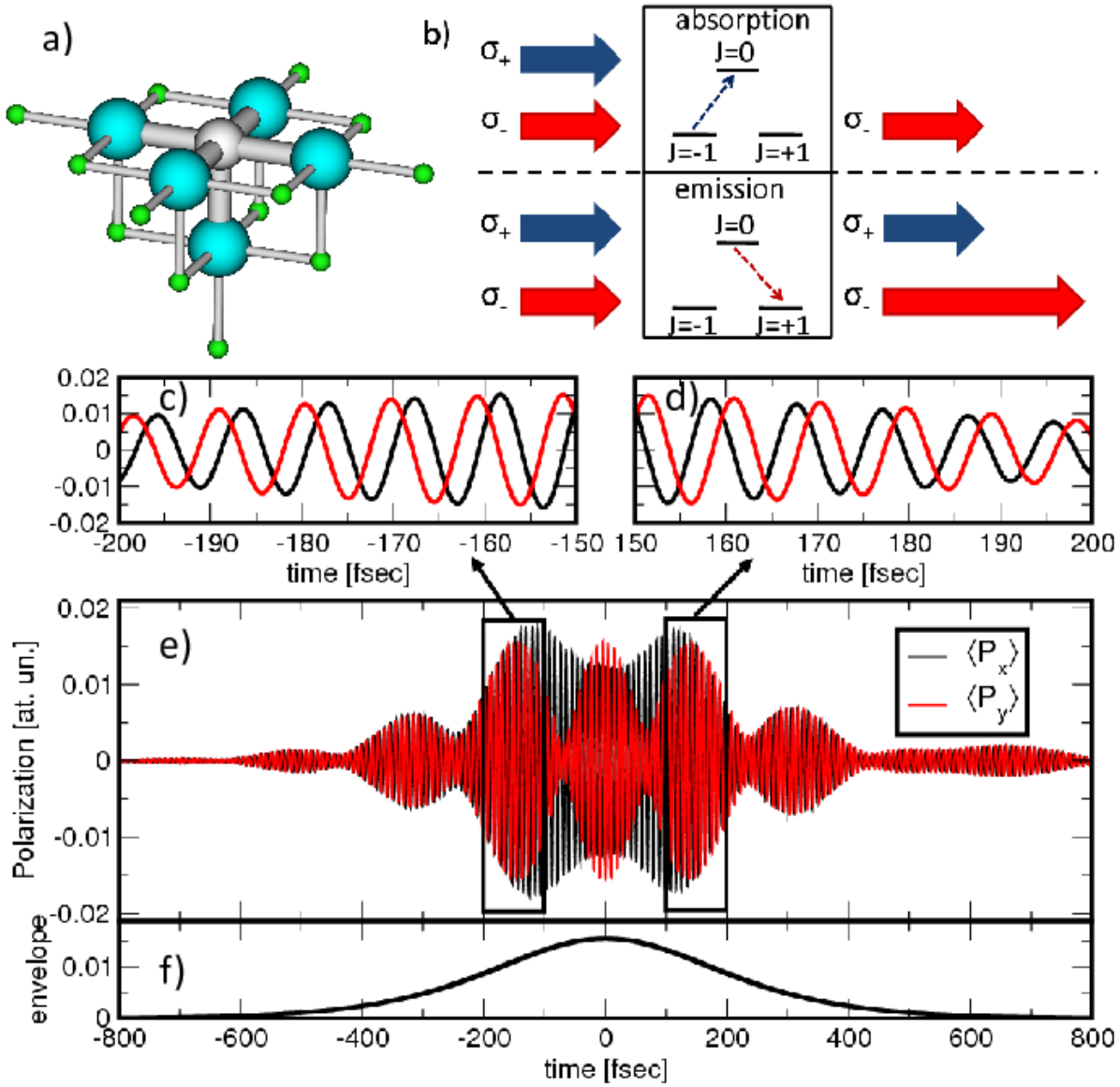
$$\hat{H}^{(1)} = +\sum_{i=1}^{N_{\text{el}}}\frac{Z_a^{\text{eff}}}{2c^2 R_i^3}\mathbf{L}\cdot\tilde{\mathbf{S}} + \sum_{i=1}^{N_{\text{el}}}\mu_L \mathbf{L}\cdot\mathbf{B}_{\text{stat}} + \sum_{i=1}^{N_{\text{el}}}\mu_S\tilde{\mathbf{S}}\cdot\mathbf{B}_{\text{stat}} + \sum_{i=1}^{N_{\text{el}}}\sum_{\mathbf{q}}\lambda_a^{\mathbf{q}}\langle\mathbf{q}\rangle$$

SOC — Static B-field — phonons

$$\hat{H}^{(2)} = \mathbf{p}^{(0+1)}\cdot\mathbf{A}_{\text{laser}}(t) + \tilde{\mathbf{S}}\cdot\mathbf{B}_{\text{laser}}(t)$$

laser

NiO: semiclassical approach



$$\langle \mathbf{P}(t) \rangle$$

x and y polarization shifted → circularly polarized light

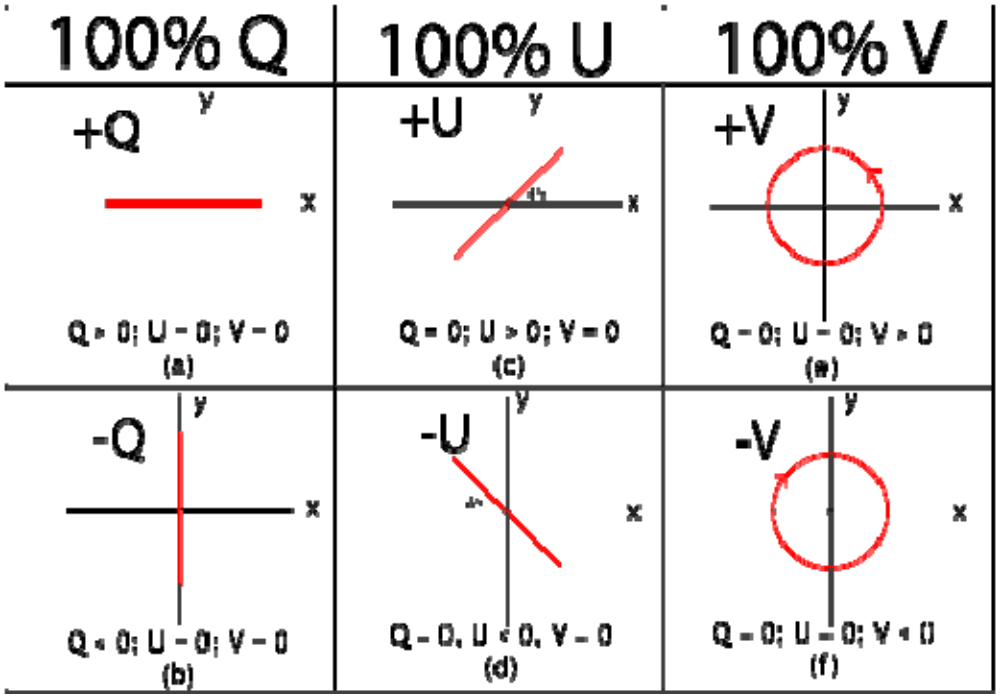
TD frequency analysis: semiclassical approach TD-FT

$$\tilde{\mathbf{P}}(\omega,t)=\int_{-\infty}^{+\infty}\mathbf{P}(t')g(t-t')e^{i\omega t}dt'$$

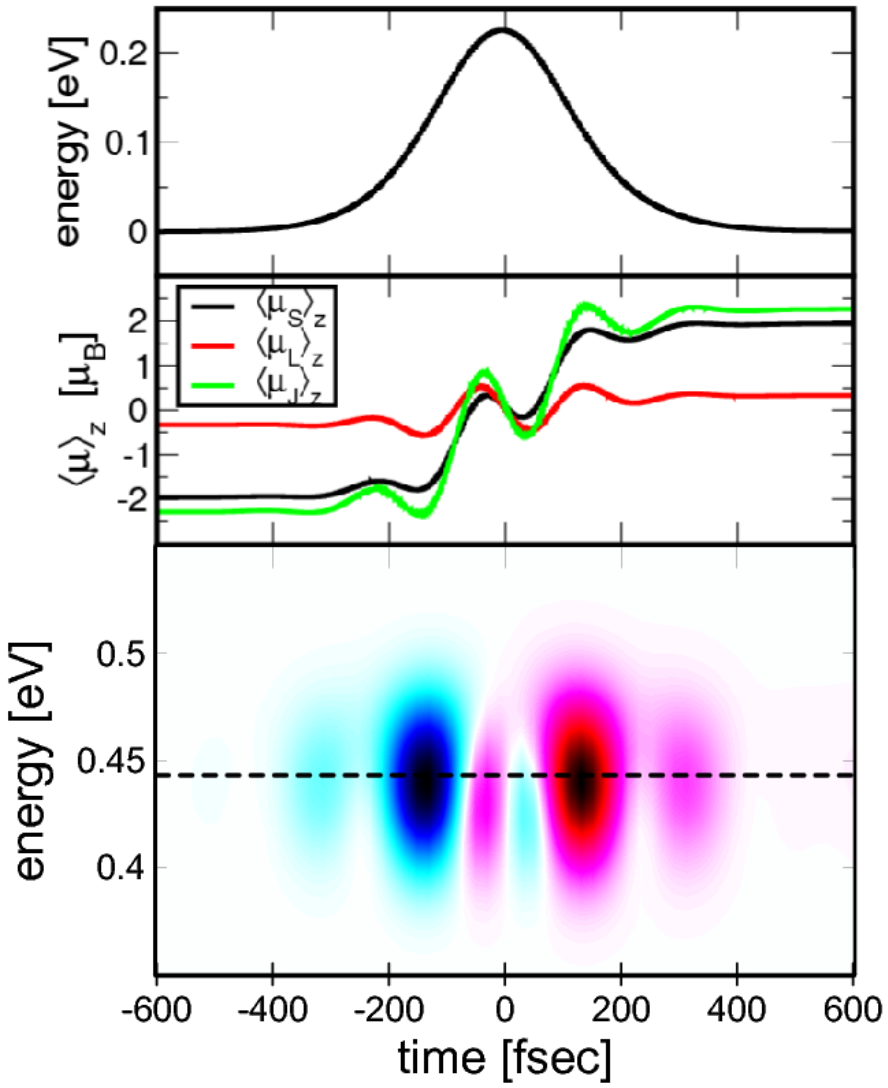
Stokes vector

$$\vec{S}=\begin{pmatrix}S_0\\S_1\\S_2\\S_3\end{pmatrix}=\begin{pmatrix}I\\Q\\U\\V\end{pmatrix}$$

$$\begin{aligned}
I &\equiv |E_x|^2+|E_y|^2,\\
&= |E_a|^2+|E_b|^2,\\
&= |E_l|^2+|E_r|^2,\\
Q &\equiv |E_x|^2-|E_y|^2,\\
U &\equiv |E_a|^2-|E_b|^2,\\
V &\equiv |E_l|^2-|E_r|^2,
\end{aligned}$$



NiO: semiclassical approach TD-FT



circular polarization

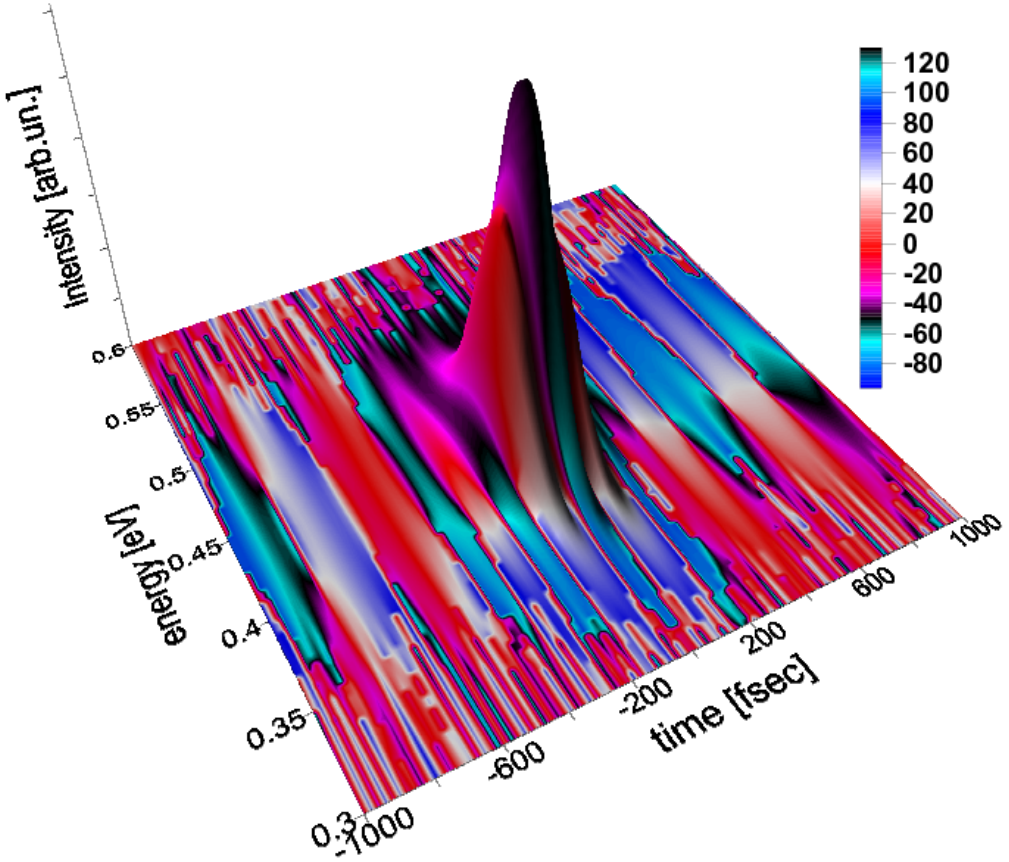
- Material absorbs or emits helicity as needed
- book keeping not possible
- alternative means of distinguishing necessary

$$\tilde{\mathbf{P}}(\omega,t) = \int_{-\infty}^{+\infty} \mathbf{P}(t')g(t-t')e^{i\omega t}dt'$$

G. Lefkidis, G. P. Zhang, and W. Hübner, Phys. Rev. Lett. **103**, 217401 (2009)

TD frequency analysis: semiclassical approach TD-FT

Linear polarization



- strong dynamical Kerr effect
- pump = probe
- **No** cw limit
- nonequilibrium

G. Lefkidis, G. P. Zhang, and W. Hübner, Phys. Rev. Lett. **103**, 217401 (2009)

Outline

1. History: theoretical achievements in spin dynamics
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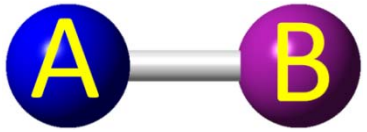
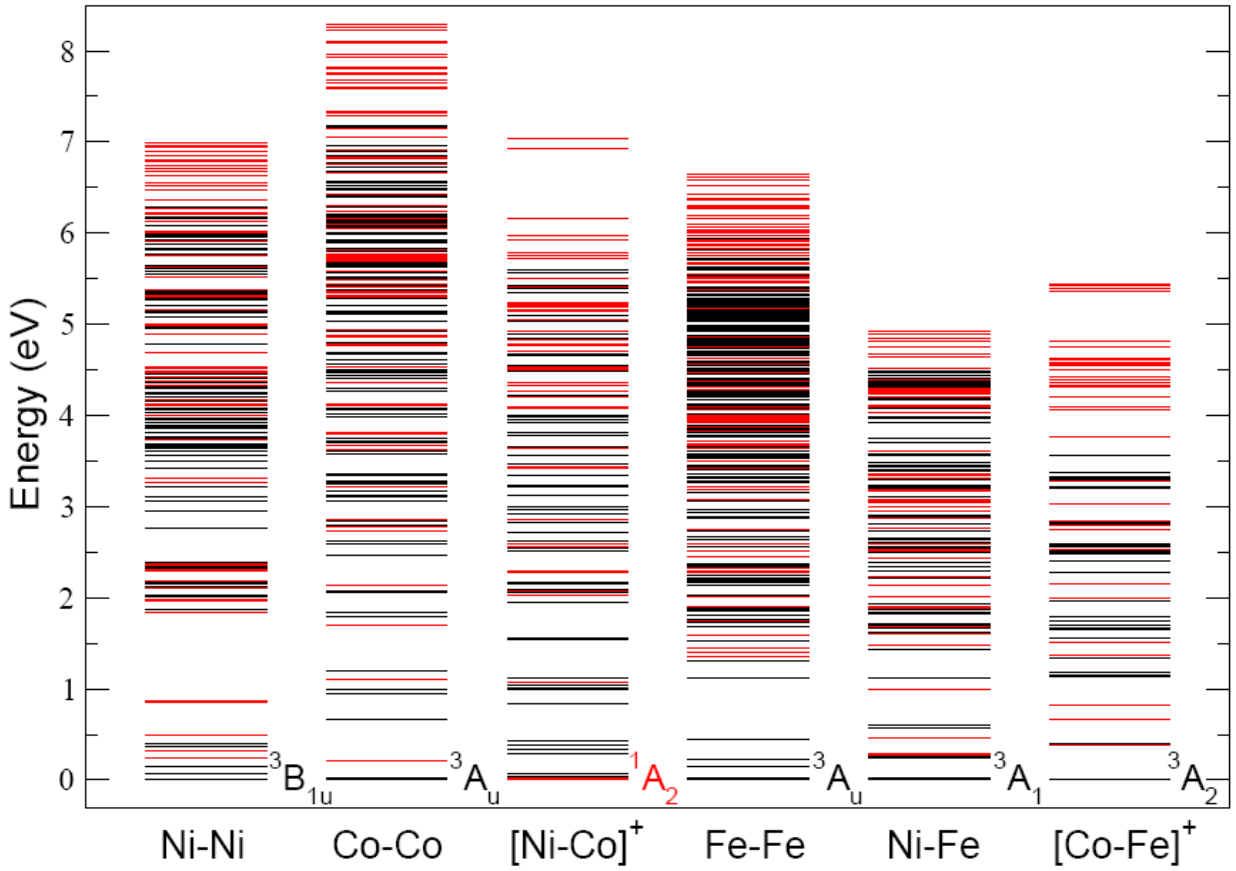
Two-magnetic-center nanostructures

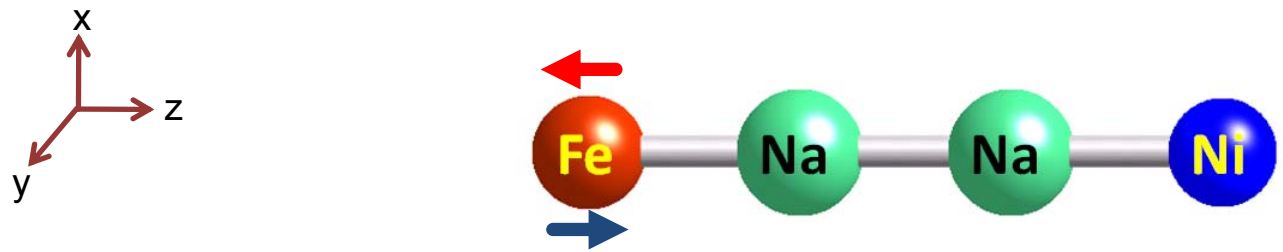


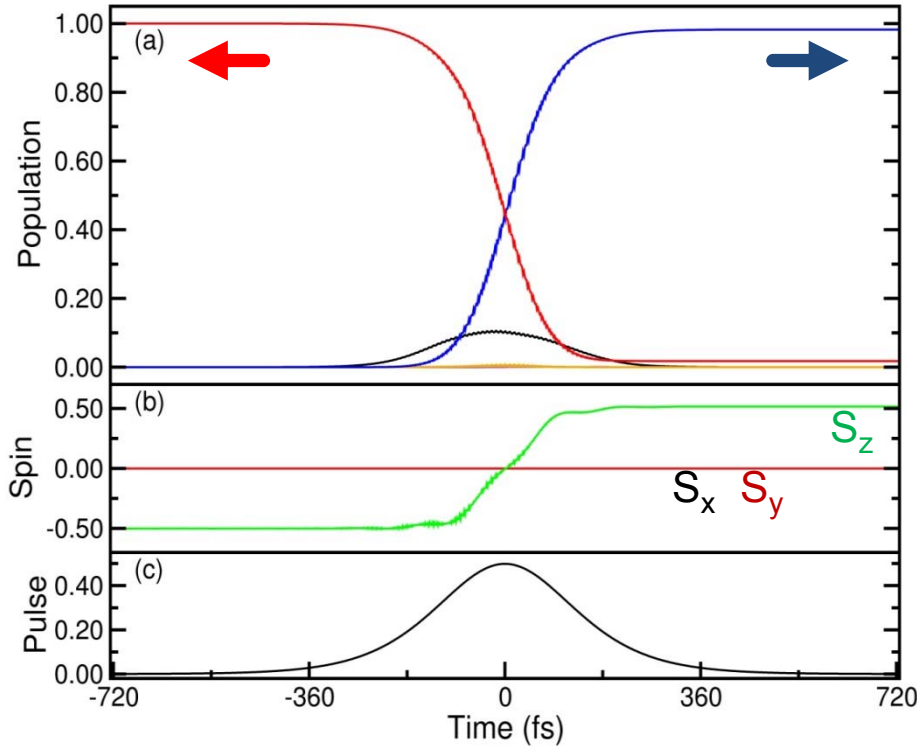
A, B = Fe, Co, Ni

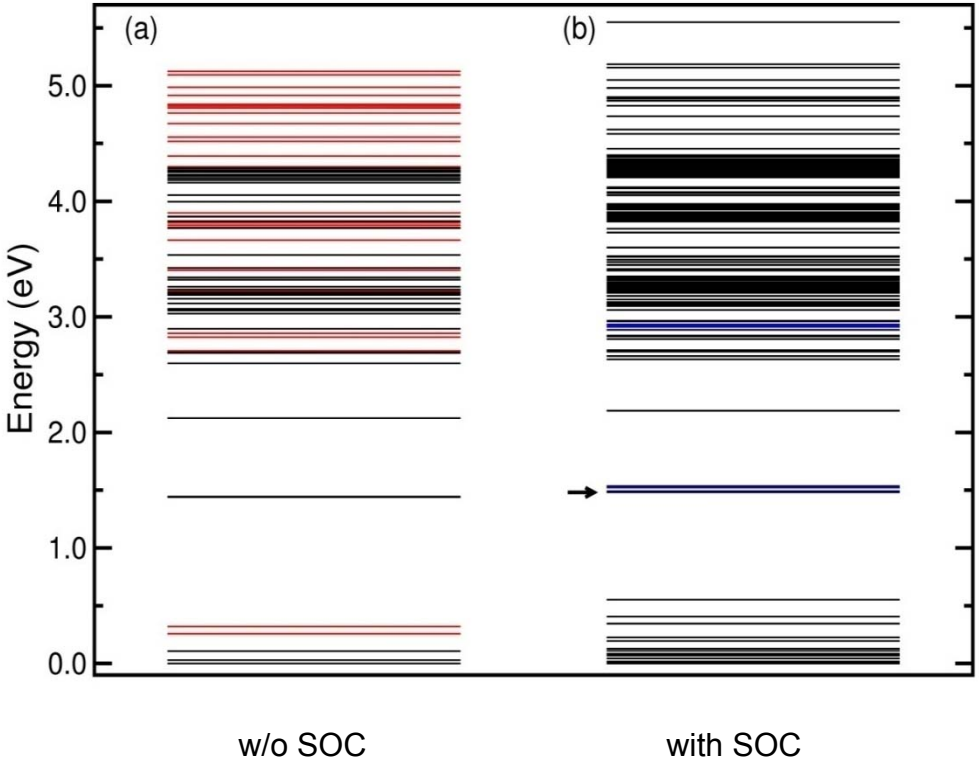


- Magnetic ground state
- Neutral & Charged
- Realistic systems
- Singlet & Triplet
- SAC-CI results (Lanl2dz)

Two centers: local spin flip on Fe in $FeNa_2Ni$



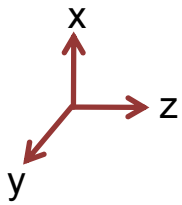


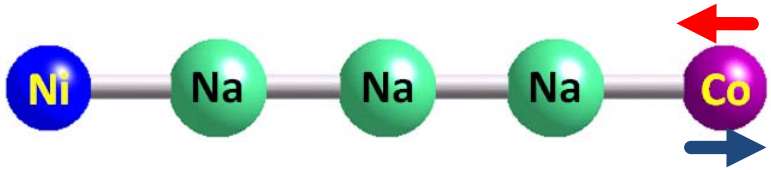


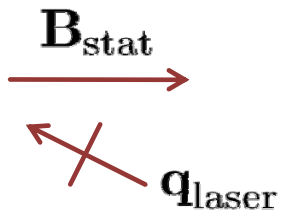
- States with spin localization (Mulliken)
- Genetic algorithm

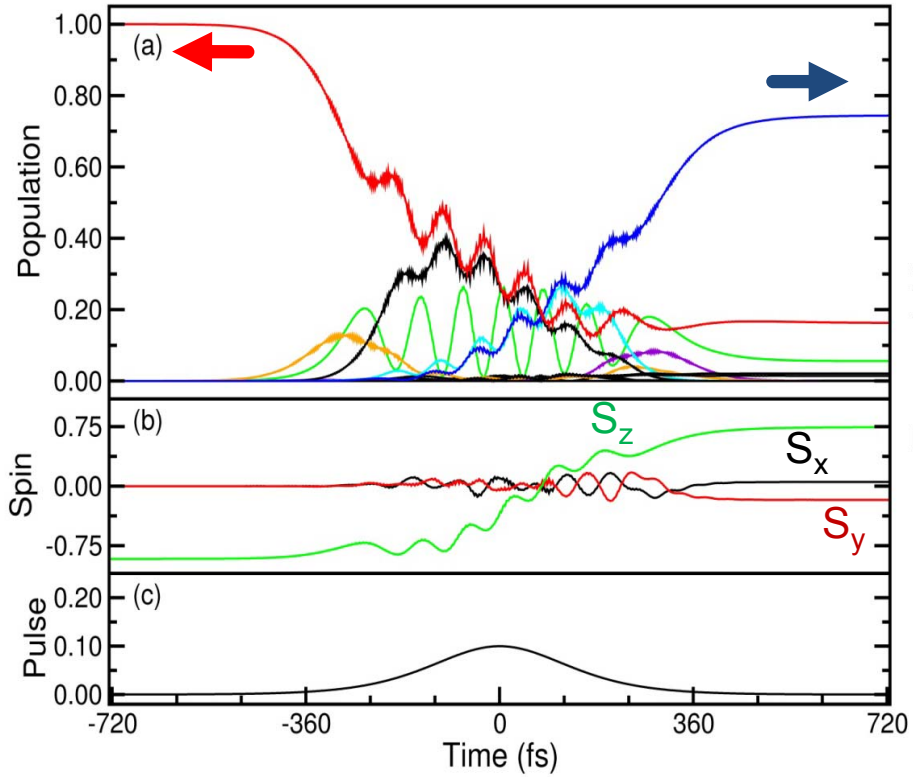
T. Hartenstein, G. Lefkidis, W. Hübner, G. P. Zhang, and Y. Bai, J. Appl. Phys. **105**, 07D305 (2009)

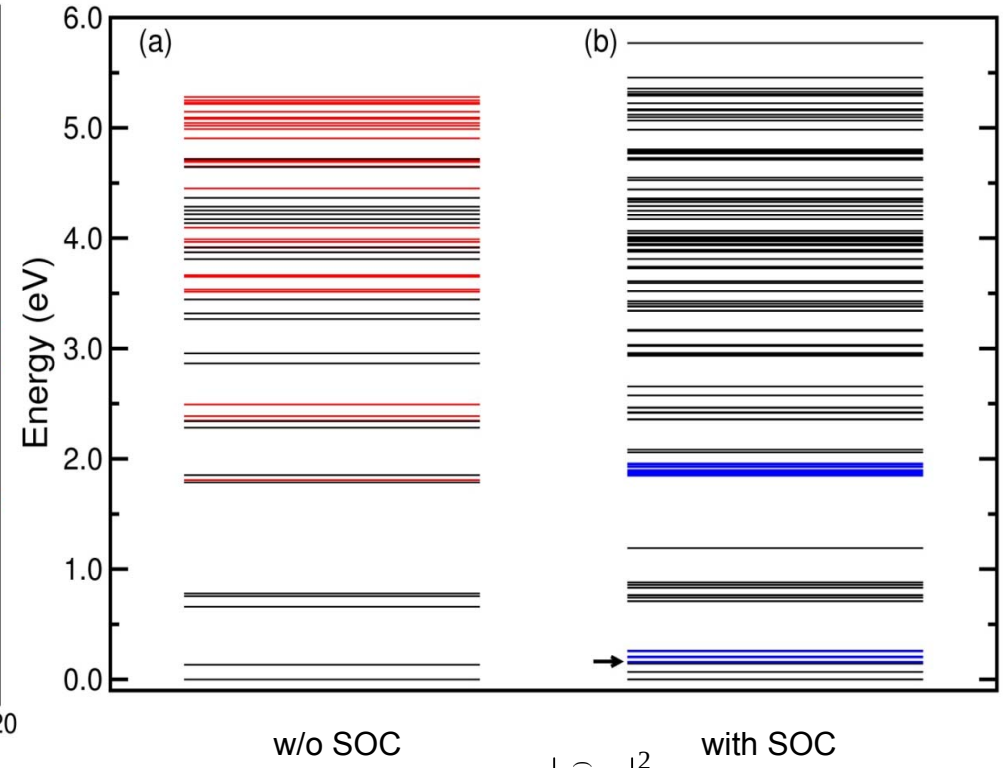
Two centers: local spin flip on Co in $FeNa_3Co$









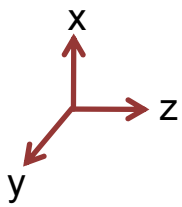


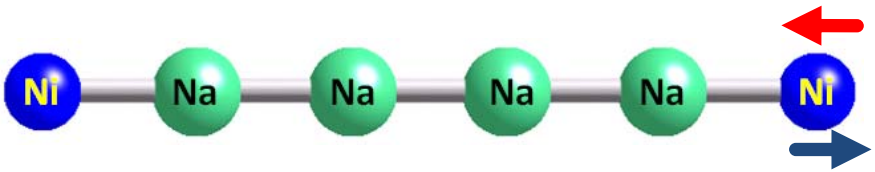
- Cascade-like behavior ⇔ low-field regime
- Large frequency ⇔ small maximum probability:

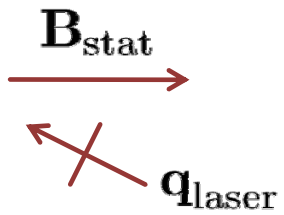
$$\left(P_{n\to k}\right)_{\max} = \frac{4\left|\widehat{H}_{nk}\right|^2}{\left|\Delta\Omega\right|^2 + 4\left|\widehat{H}_{nk}\right|^2}$$

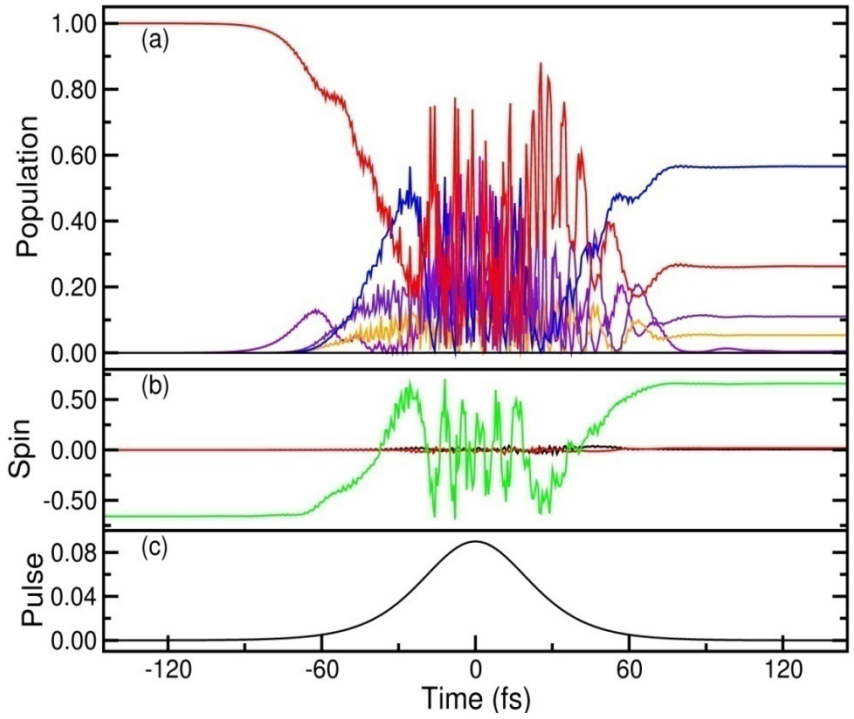
T. Hartenstein, G. Lefkidis, W. Hübner, G. P. Zhang, and Y. Bai, J. Appl. Phys. **105**, 07D305 (2009)

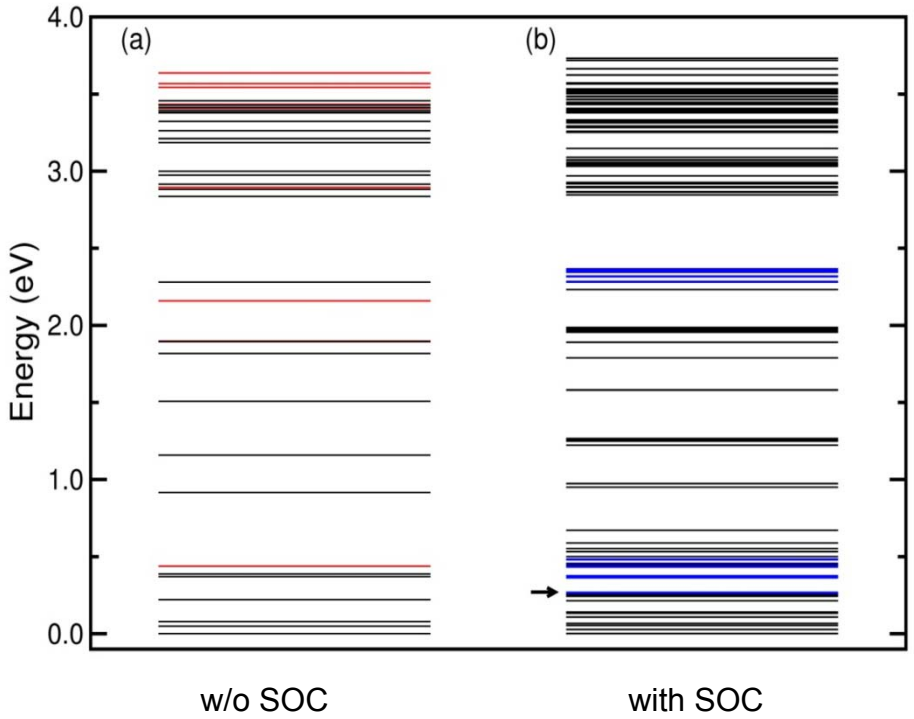
Two centers: local spin flip on Ni in $NiNa_4Ni$











- NOT a chaotic behavior, one process dominates!

(compare: J. Kasparian, B. Krämer, J. P. Dewitz, S. Vajda, P. Rairoux, B. Vezin, V. Boutou, T. Leisner, W. Hübner, J. P. Wolf, L. Wöste, and K. H. Bennemann, PRL **78**, 2952 (1997))

T. Hartenstein, G. Lefkidis, W. Hübner, G. P. Zhang, and Y. Bai, J. Appl. Phys. **105**, 07D305 (2009)

CO frequency calculation

Coordinates Matrix

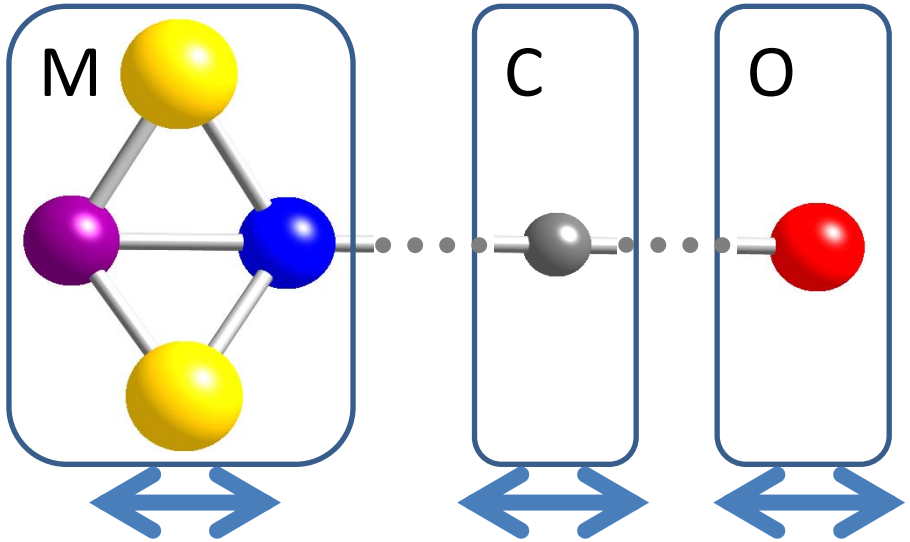
Forces Matrix

Force constant matrix

$$\begin{array}{c|ccc} & M & C & O \\ M & \frac{k_{xx}^{MM}}{\sqrt{m_M}\sqrt{m_M}} & \frac{k_{xx}^{MC}}{\sqrt{m_M}\sqrt{m_C}} & \frac{k_{xx}^{MO}}{\sqrt{m_M}\sqrt{m_O}} \\ C & \frac{k_{xx}^{CM}}{\sqrt{m_C}\sqrt{m_M}} & \frac{k_{xx}^{CC}}{\sqrt{m_C}\sqrt{m_C}} & \frac{k_{xx}^{CO}}{\sqrt{m_C}\sqrt{m_O}} \\ O & \frac{k_{xx}^{OM}}{\sqrt{m_O}\sqrt{m_M}} & \frac{k_{xx}^{OC}}{\sqrt{m_O}\sqrt{m_C}} & \frac{k_{xx}^{OO}}{\sqrt{m_O}\sqrt{m_O}} \end{array}$$

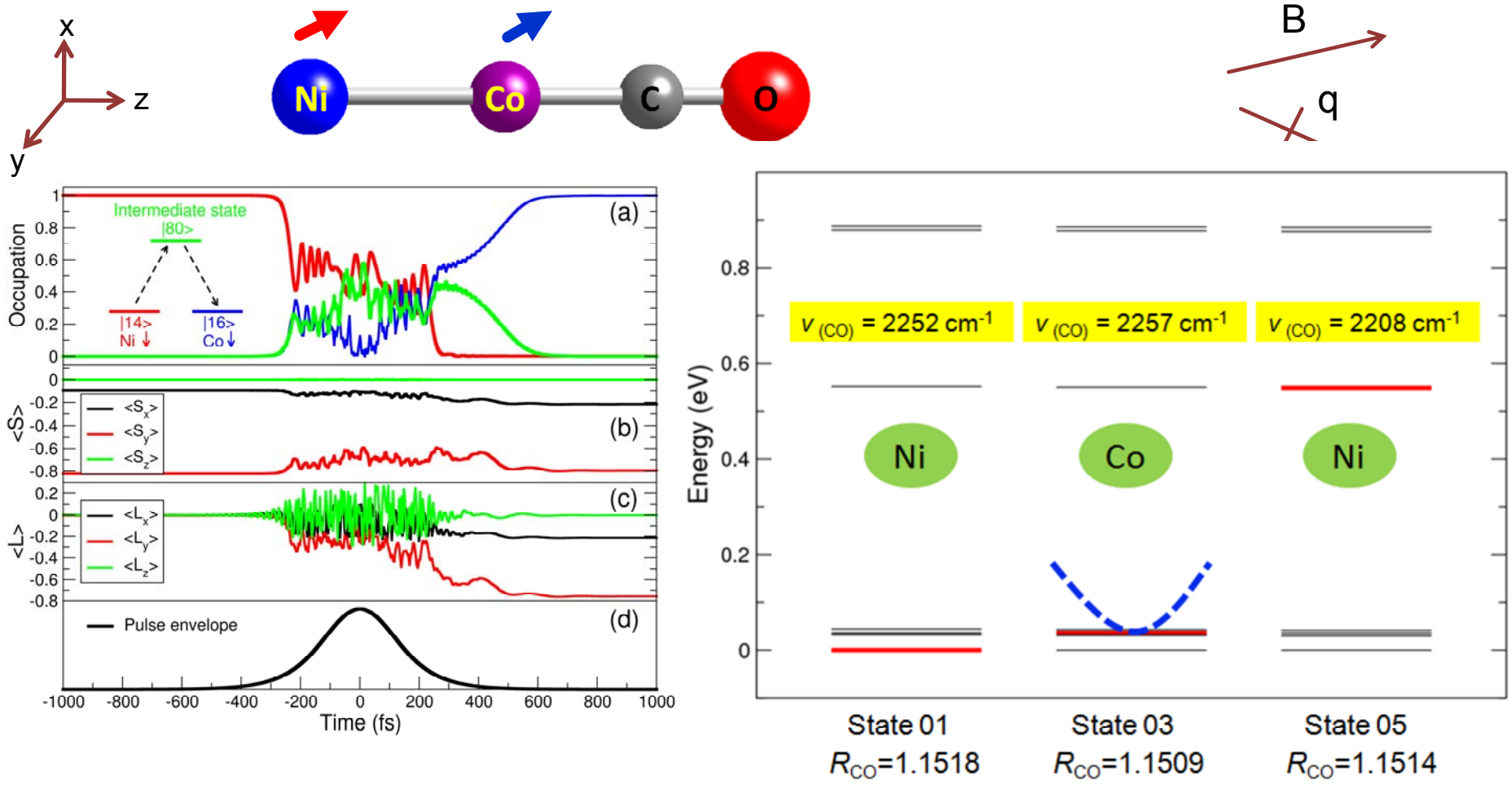
Extract the eigenvalues

C-O bond stretching frequency



Cluster	State	Bond length (Å)	Frequency (cm^{-1})
$[CoMg_2Ni\text{-}CO]^+$	1	1.1561	2080
	3	1.1550	2100
	5	1.1467	2264
$[Co\text{-}Ni\text{-}CO]^+$	1	1.1532	2149
	3	1.1545	2363
	5	1.1518	2160
$[Ni\text{-}Co\text{-}CO]^+$	1	1.1518	2252
	3	1.1509	2257
	5	1.1514	2208

Two centers: local flip and transfer in [CoNi-Co]$^{+}$

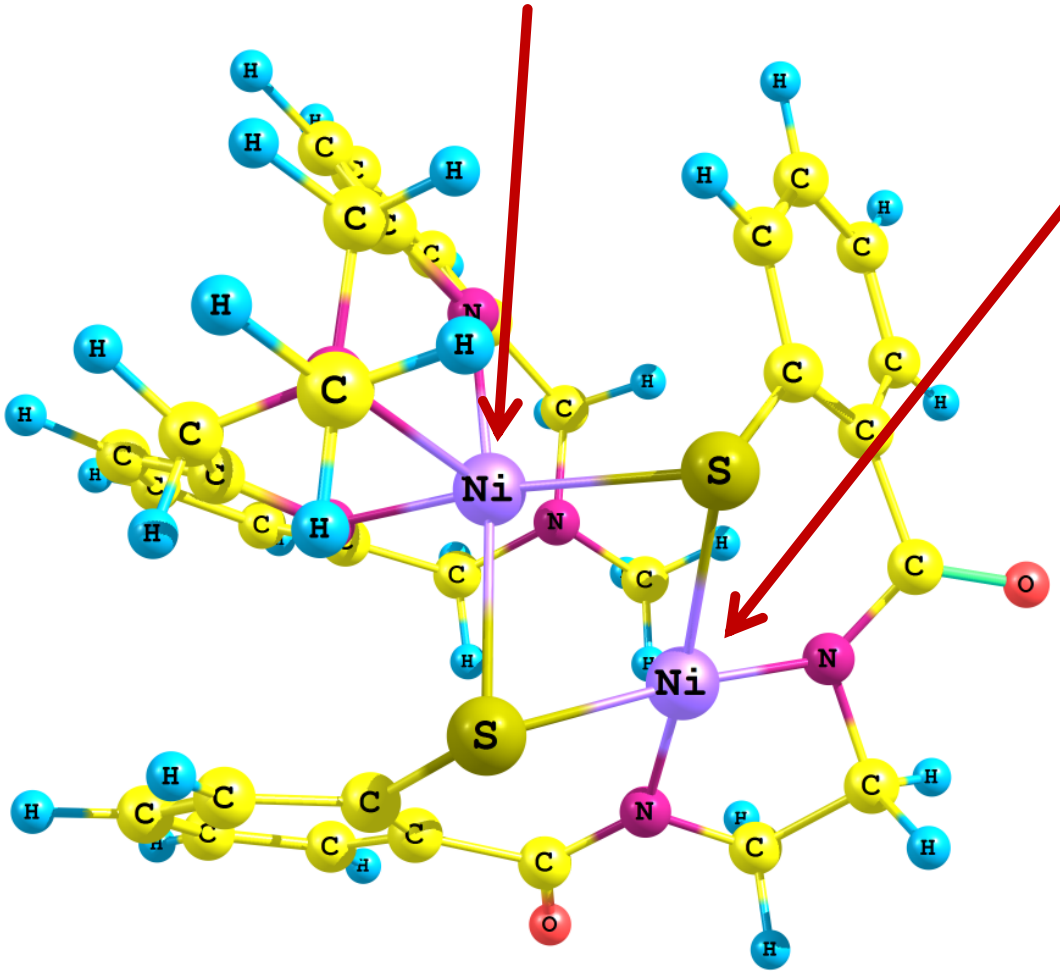


- States with spin localization (Mulliken)
- Both flip and transfer possible (but not simultaneously)
- IR Spectrum of CO as marker of the magnetic state (phonon-magnon coupling)

C. Li, T. Hartenstein, G. Lefkidis and W. Hübner, Phys. Rev. B **79**, 180413(R) (2009)

Synthesized structure: $[Ni^{II}_2(L\text{-}N_4Me_2)(emb)]$

octahedral Ni: high spin (*S=1*) vs. square planar Ni: low spin (*S=0*)



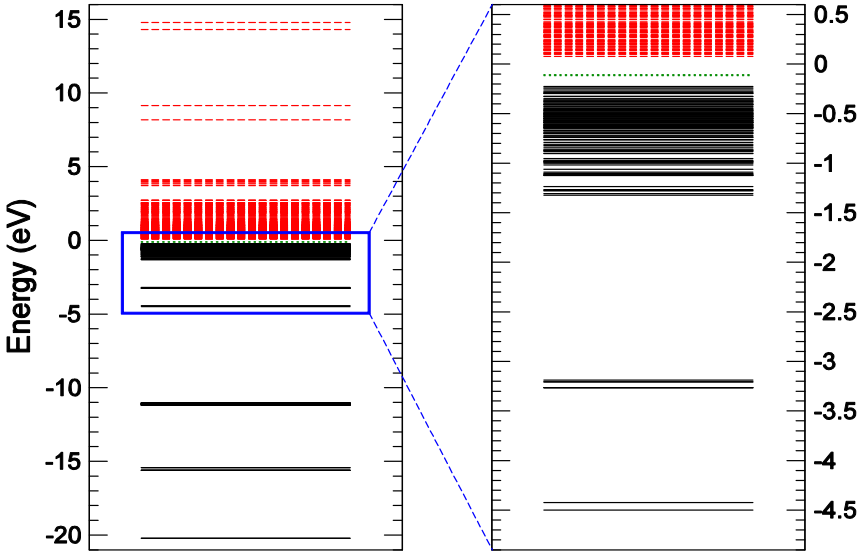
- synthesizability
- calculability
- spin localization
- discrete levels
- vibrational modes

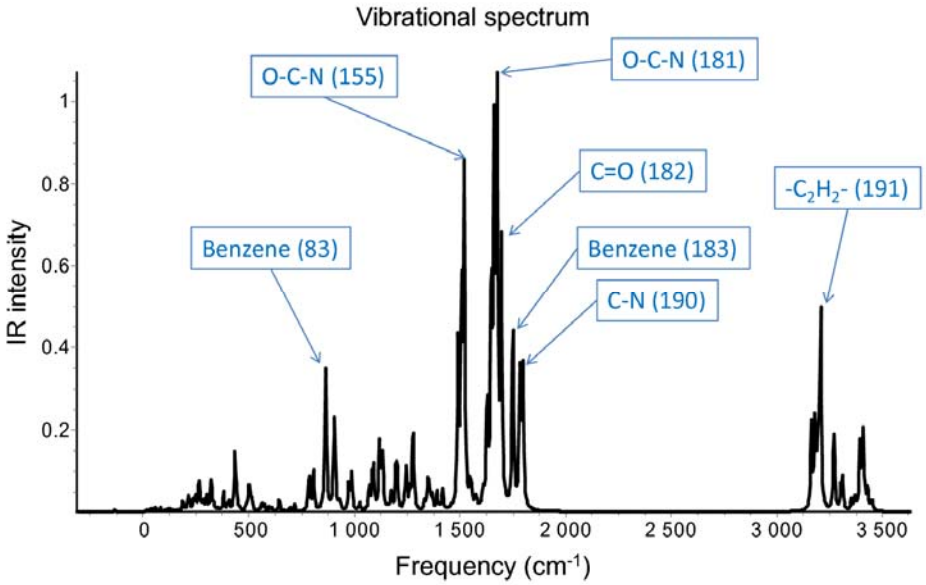
cooperation with synthetic chemistry

G. Lefkidis, M. Blug, H. Kelm, C. Li, G. Pal, H.-J. Krüger, and W. Hübner, J. Phys. Chem. A **115**, 1774 (2011)

Levels and vibrational spectrum: $[Ni^{II}_2(L\text{-}N_4Me_2)(emb)]$

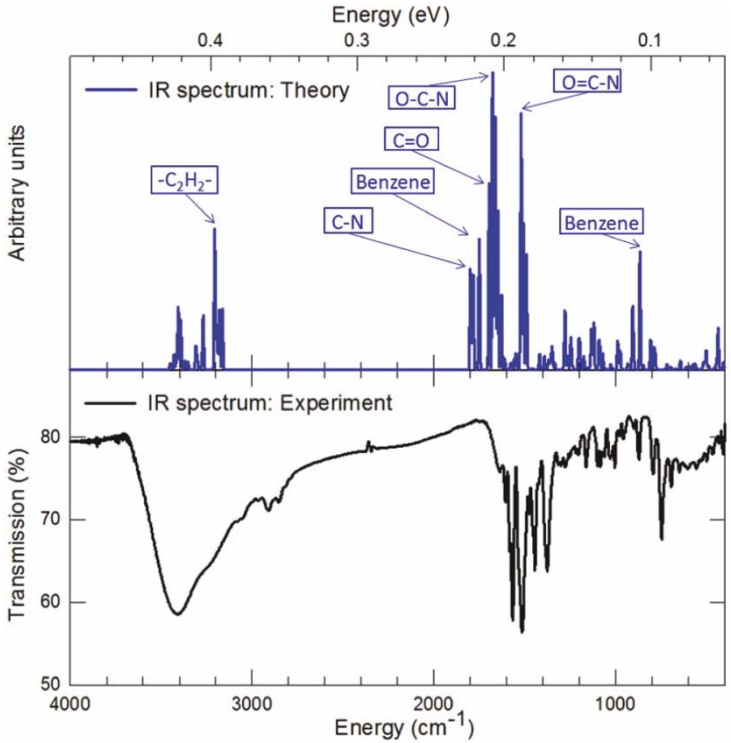
- first indications give bond-length results with **< 5%** error
- vibrational spectrum, deviaton **< 10 %**
- electronic spectrum, coincidence of main peaks in UV-Vis



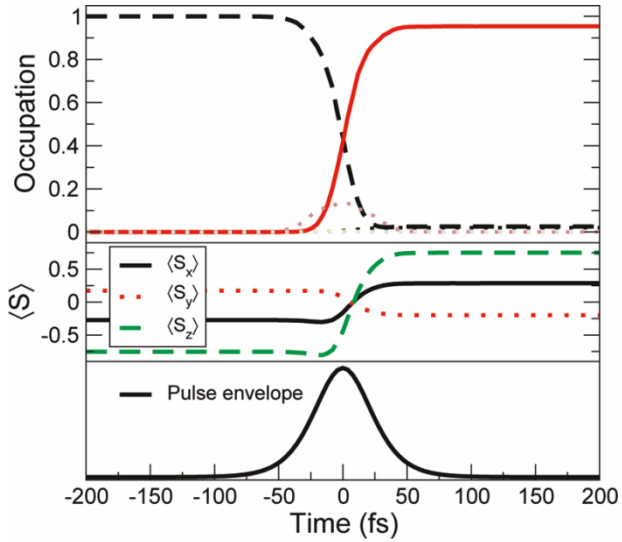


G. Lefkidis, M. Blug, H. Kelm, C. Li, G. Pal, H.-J. Krüger, and W. Hübner, J. Phys. Chem. A **115**, 1774 (2011)

Vibrational spectrum and spin flip
$[Ni^{II}_2(L\text{-}N_4Me_2)(emb)]$



Spin flip on octahedral Ni



- Good agreement theory – experiment (bond lengths, UV-Vis spectrum)
- Spin-flip scenario on an existing substance

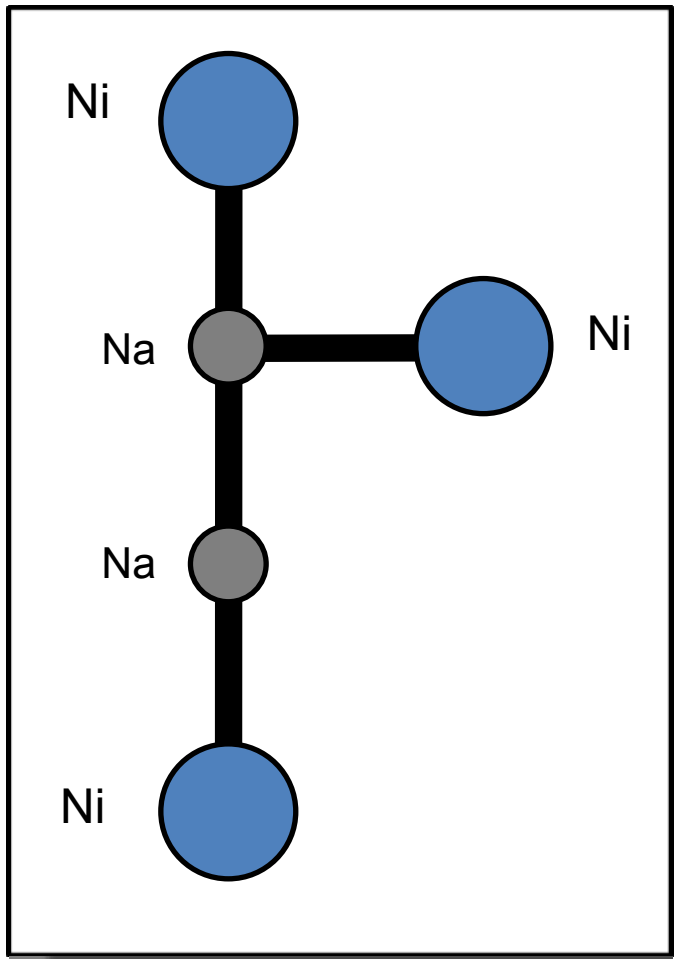
G. Lefkidis, M. Blug, H. Kelm, C. Li, G. Pal, H.-J. Krüger, and W. Hübner, J. Phys. Chem. A **115**, 1774 (2011)

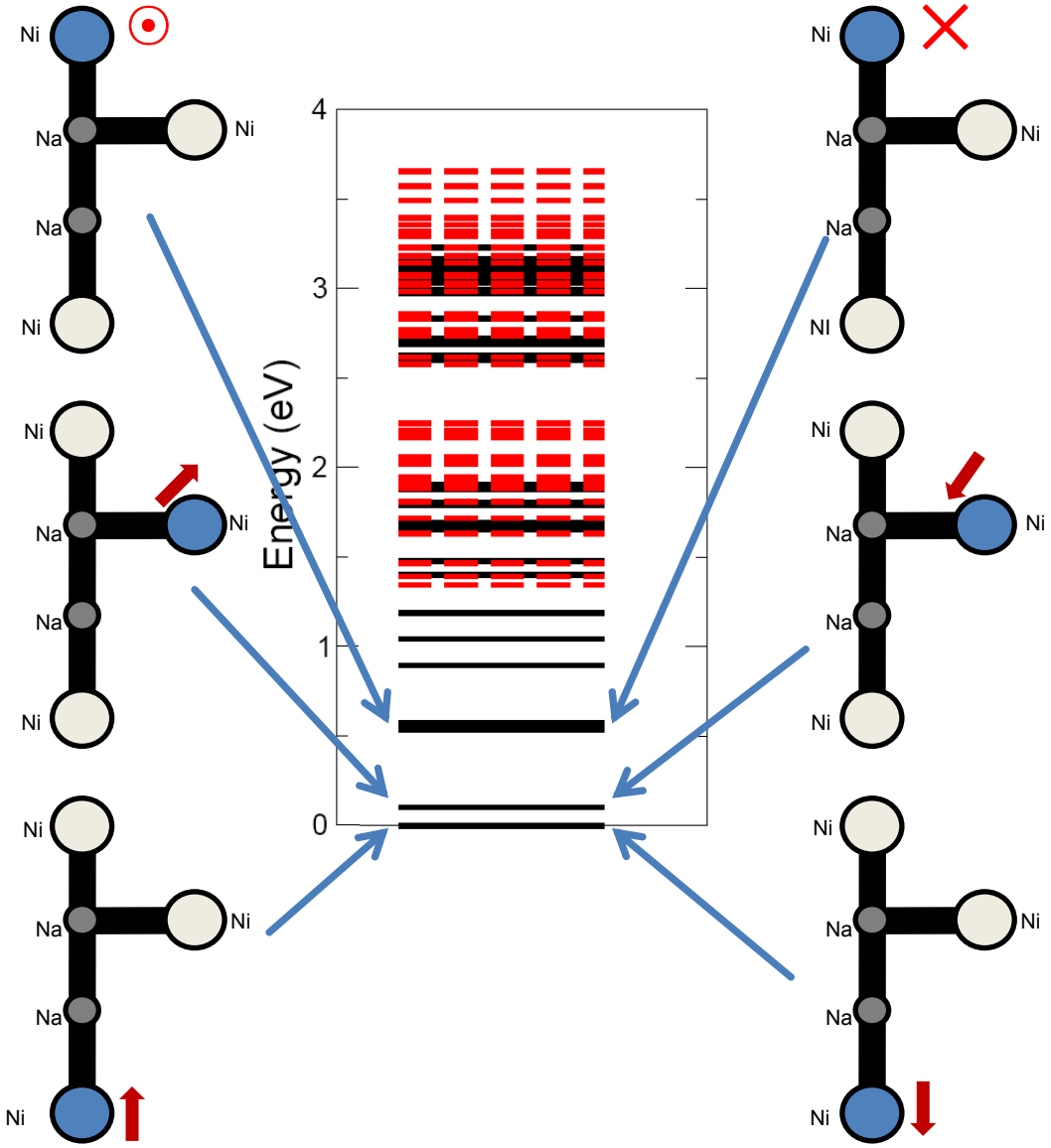
Outline

1. History: theoretical achievements in spin dynamics
2. Introduction: theoretical and background aspects
3. Clusters with two magnetic centers
4. Clusters with three magnetic centers: magnetic logic
5. Role of bridging atoms
6. Conclusions

Systems: Ni_3Na_2

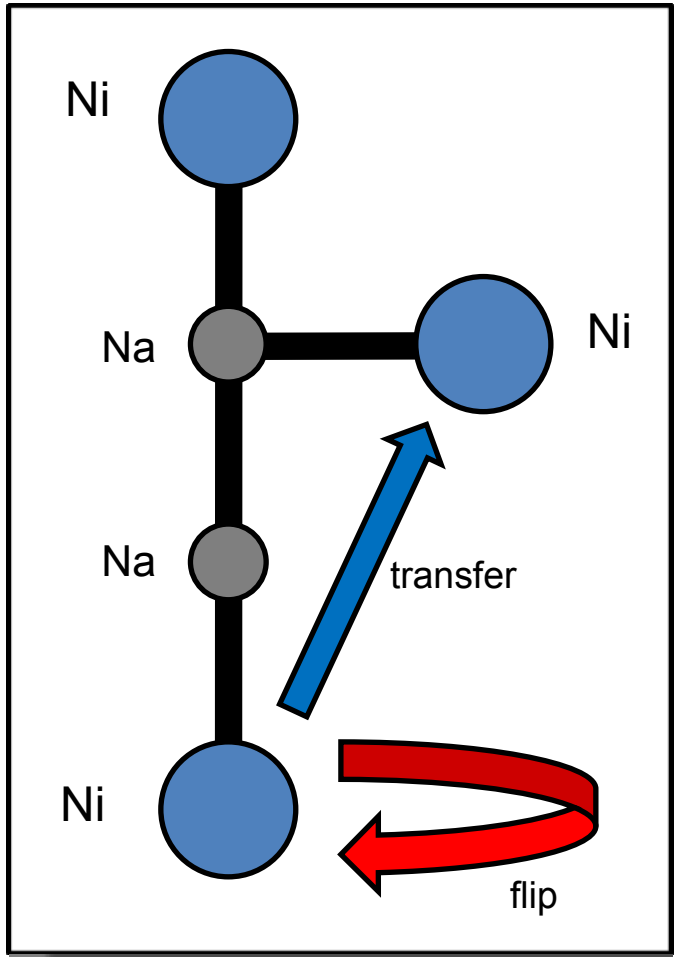
- local flip
- transfer

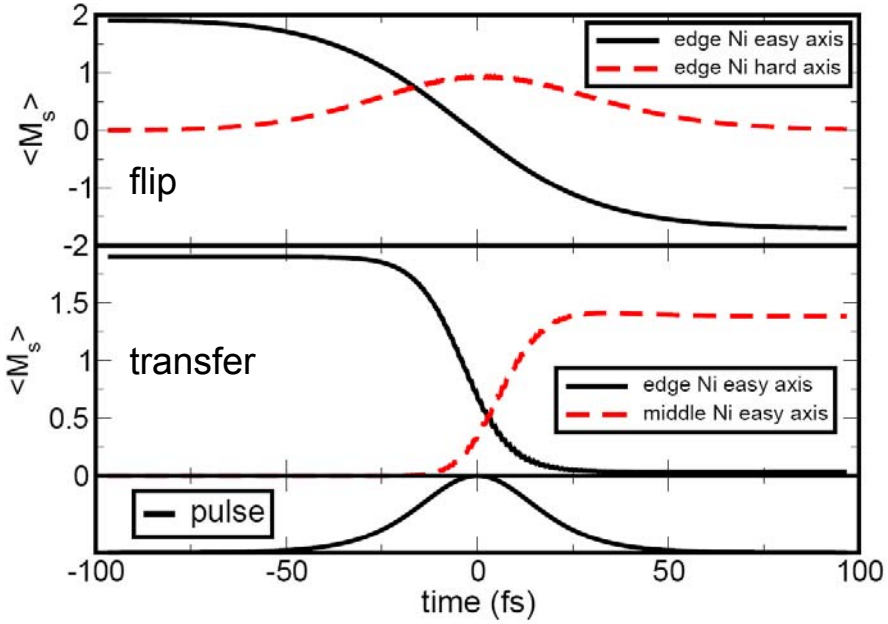


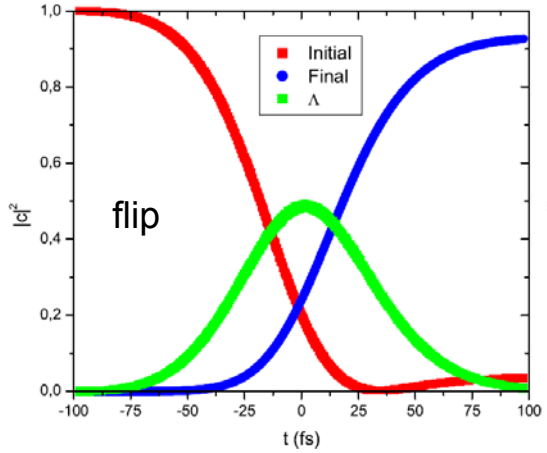


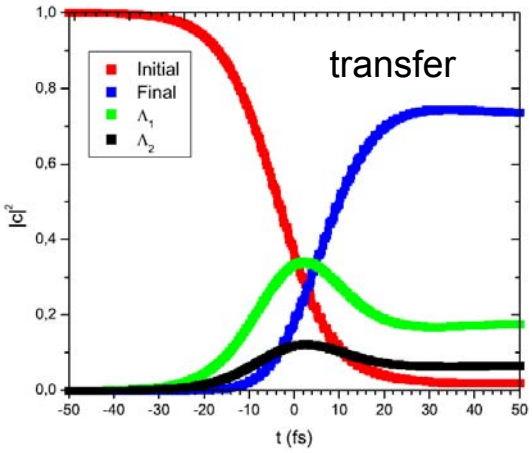
Systems: Ni_3Na_2

Success !

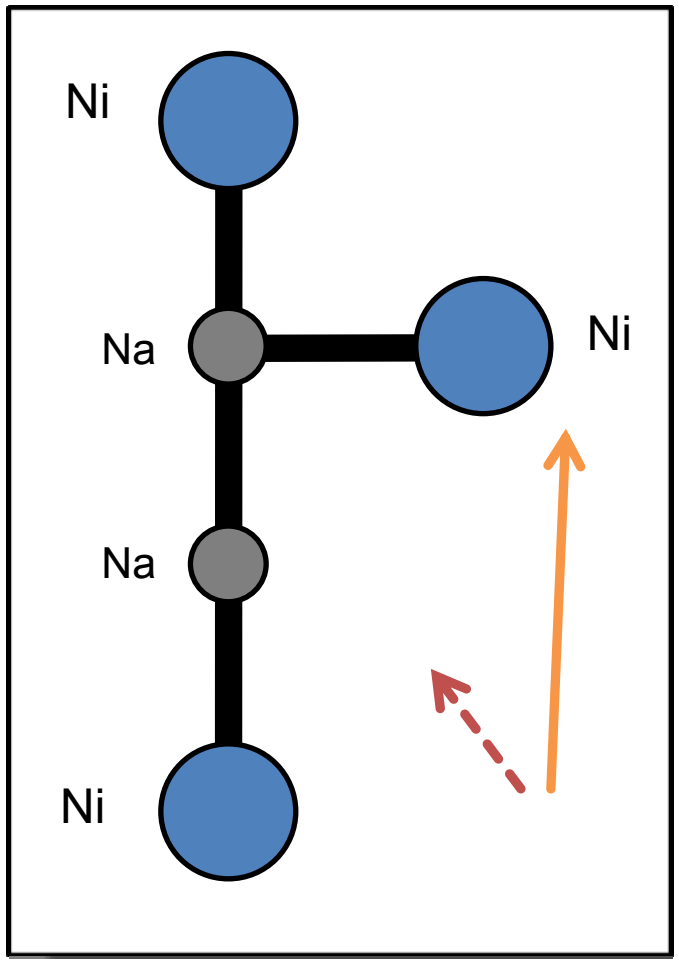


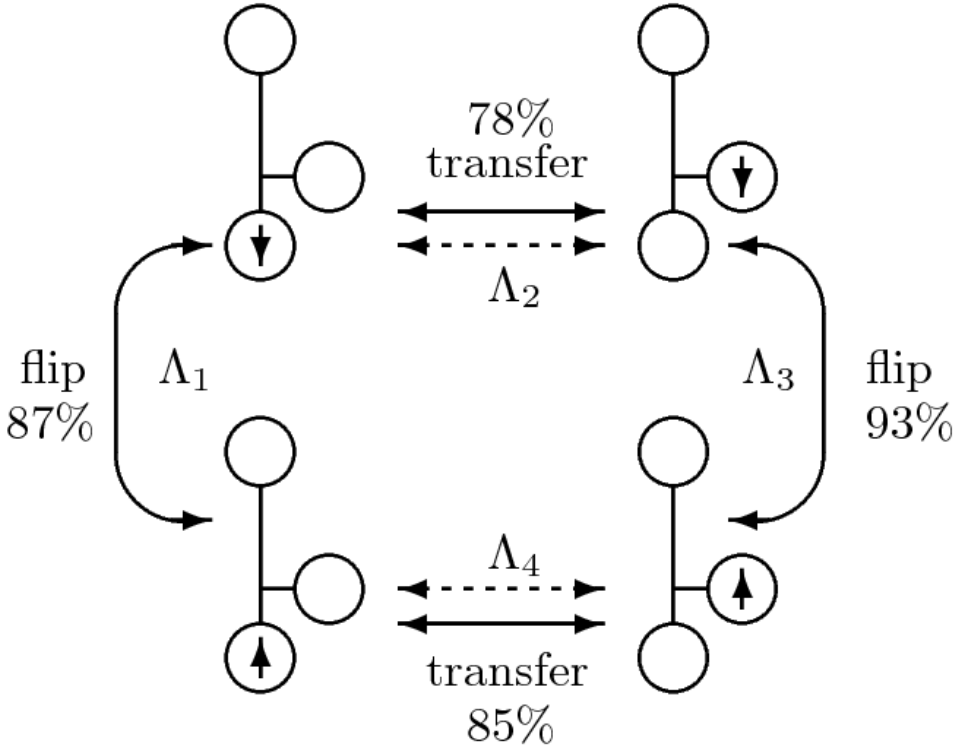






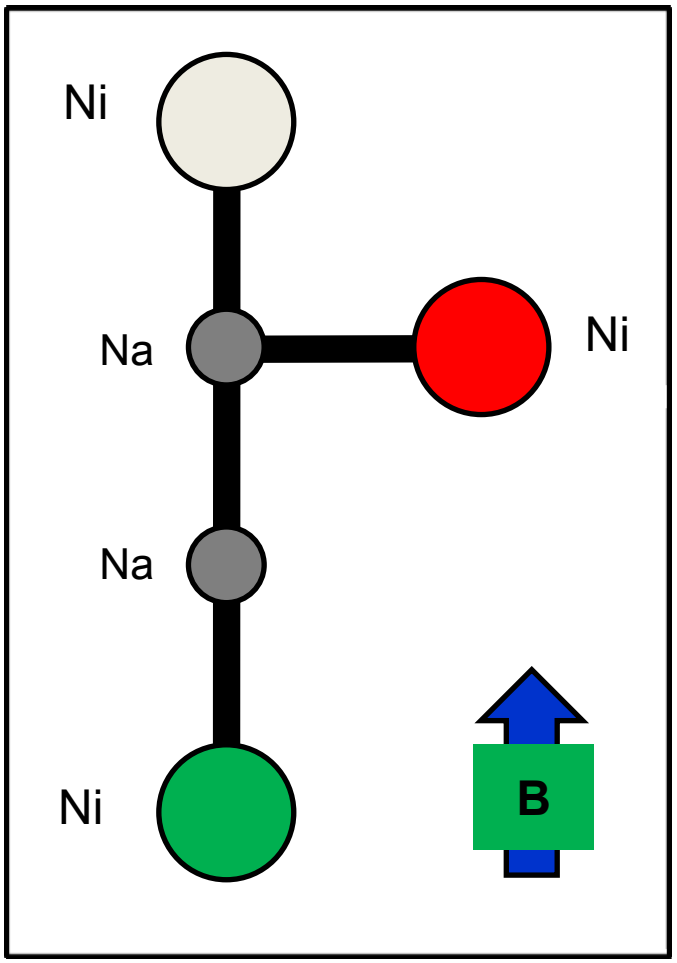
Systems: Ni_3Na_2 : possible mechanisms





Nevertheless transfer more difficult

Systems: Ni_3Na_2 : gates



AND gate

input 1 spin	input 2 **B**-field	output spin+position
1 (edge↑)	1 ($\theta = 0°$)	1 (middle↑)
0 (edge↓)	1 ($\theta = 0°$)	0 (middle↓)
1 (edge↑)	0 ($\theta = 78°$ and $\phi = 96°$)	0 (edge↑)
0 (edge↓)	0 ($\theta = 78°$ and $\phi = 96°$)	0 (edge↓)

OR gate

input 1 spin	input 2 **B**-field	output spin+position
0 (edge↑)	0 ($\theta = 0°$)	0 (middle↑)
1 (edge↓)	0 ($\theta = 0°$)	1 (middle↓)
0 (edge↑)	1 ($\theta = 78°$ and $\phi = 96°$)	1 (edge↑)
1 (edge↓)	1 ($\theta = 78°$ and $\phi = 96°$)	1 (edge↓)

XOR gate

input 1 spin	input 2 **B**-field	output spin
1 (edge↑)	1 ($\theta = 78°$ and $\phi = 96°$)	0 (middle↓)
0 (edge↓)	1 ($\theta = 78°$ and $\phi = 96°$)	1 (middle↑)
1 (edge↑)	0 ($\theta = 0°$)	1 (middle↑)
0 (edge↓)	0 ($\theta = 0°$)	0 (middle↓)

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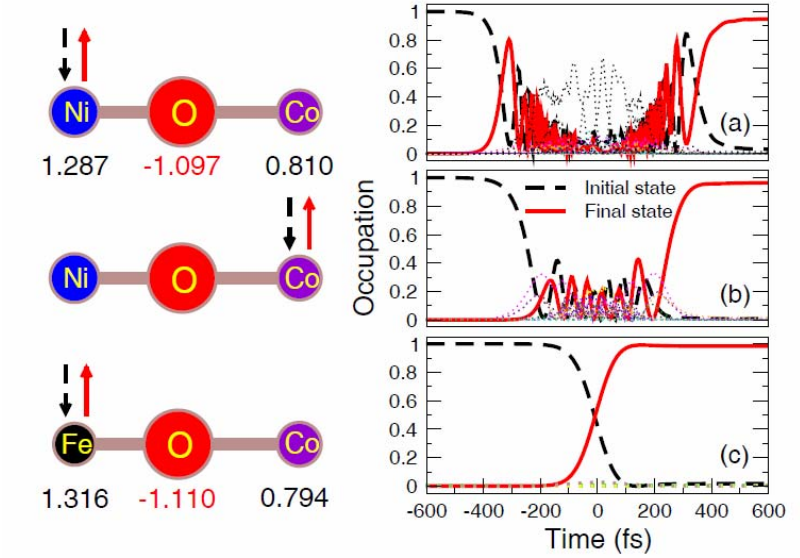
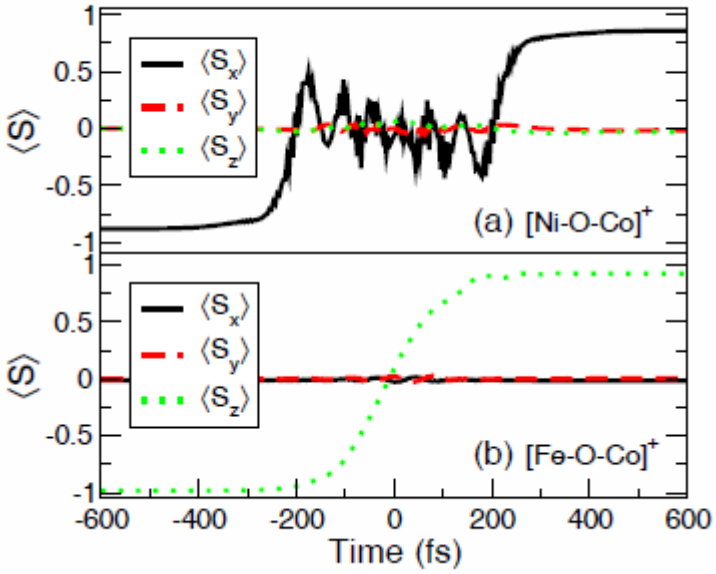
Two centers: O-bridged structures



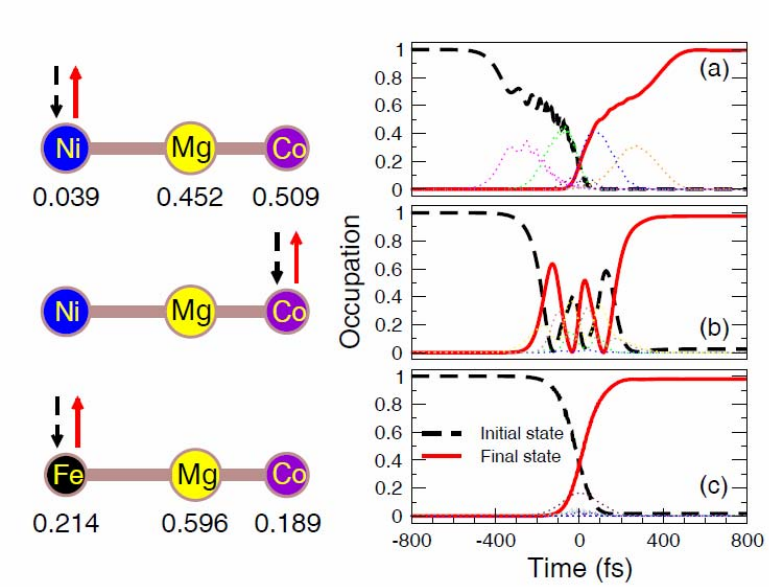
Structure	Atom	State 1	State 2	State 3	State 4	State 5
$[Ni\text{-}Co]^+$	Ni	1.924	1.015	1.924	0.025	1.014
	Co	0.076	0.985	0.076	1.975	0.986
$[Ni\text{-}O\text{-}Co]^+$	Ni	1.834	0.846	0.200	0.855	0.497
	O	0.139	0.099	0.047	0.099	0.079
	Co	0.026	1.056	1.754	1.047	1.425
$[Ni\text{-}Mg\text{-}Co]^+$	Ni	1.601	1.621	0.017	0.044	0.045
	Mg	0.379	0.360	-0.022	-0.018	0.528
	Co	0.020	0.019	2.005	1.974	1.427
$[Fe\text{-}Co]^+$	Fe	1.994	1.025	1.994	1.993	1.022
	Co	0.006	0.975	0.006	0.007	0.978
$[Fe\text{-}O\text{-}Co]^+$	Fe	-0.007	1.869	1.936	1.867	1.111
	O	0.008	0.126	0.028	0.113	0.057
	Co	2.000	0.006	0.035	0.021	0.833
$[Fe\text{-}Mg\text{-}Co]^+$	Fe	0.015	0.012	1.975	2.008	1.971
	Mg	0.008	0.008	0.015	-0.012	0.013
	Co	1.978	1.980	0.010	0.003	0.015



- Spin-density redistribution
- Spin maximum relocalization
- Fe (easiest) > Co (moderate) > Ni (hardest)

C. Li, W. Jin, H.P. Xiang, G. Lefkidis, and W. Hübner, PRB **84**, 054415 (2011)

Two centers: Mg-bridged structures



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	O	0.139	0.099	0.047	0.099	0.079
	Co	0.026	1.056	1.754	1.047	1.425
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- Spin-density redistribution
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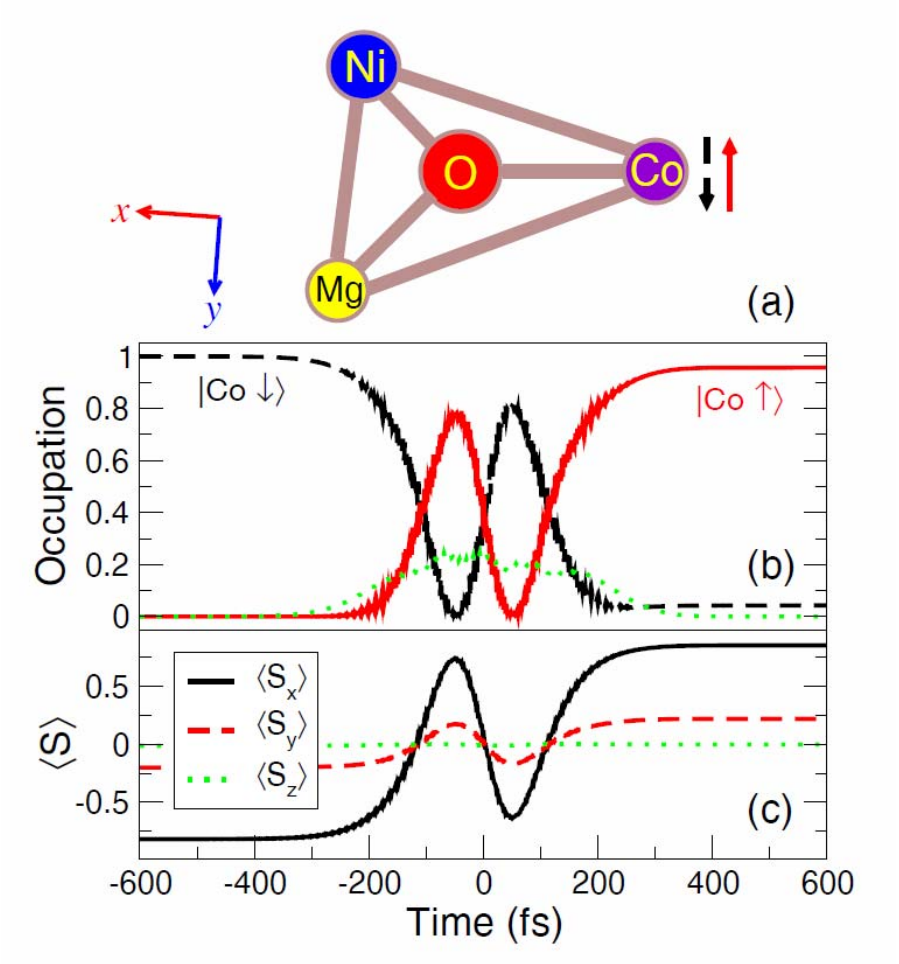
- Fe (easiest) > Co (moderate) > Ni (hardest)

C. Li, W. Jin, H.P. Xiang, G. Lefkidis, and W. Hübner, PRB **84**, 054415 (2011)

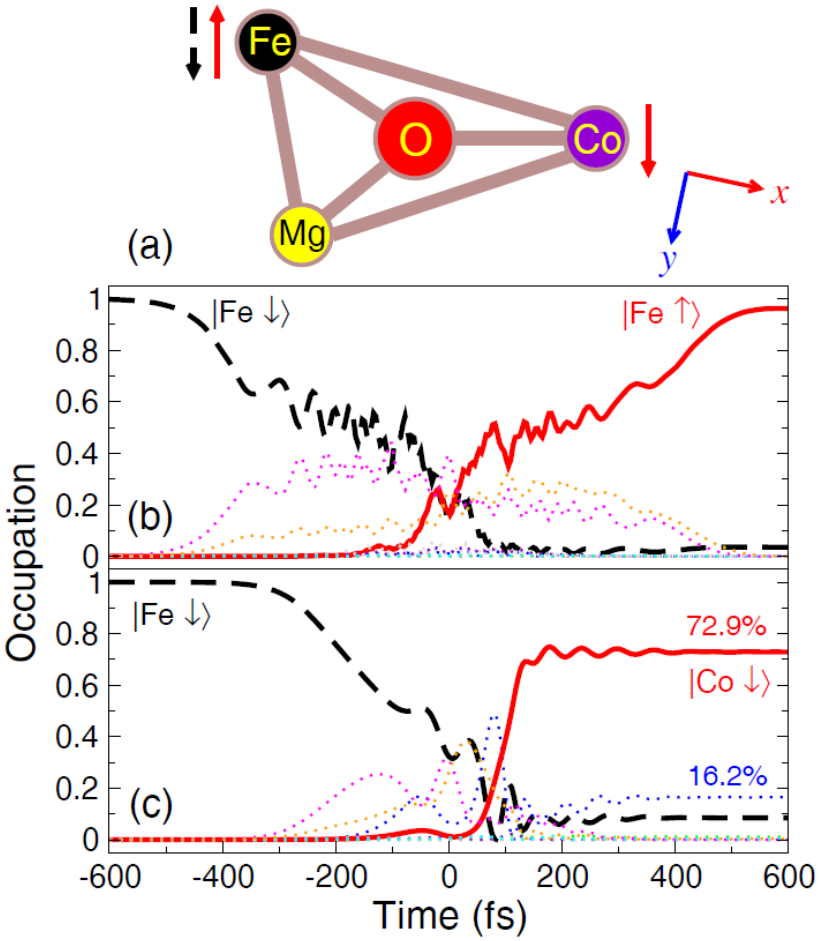
Two centers: O- and Mg-bridged structures



- Spin-flip facilitated
- Lower energy of laser pulse (~1 eV instead of 2-3 eV)

C. Li, W. Jin, H.P. Xiang, G. Lefkidis, and W. Hübner, PRB **84**, 054415 (2011)

Two centers: O- and Mg-bridged structures



- Spin-flip facilitated
- Lower energy of laser pulse (~1 eV instead of 2-3 eV)
- Transfer with low intensity (0.115 $Js^{-1}m^{-2}$, per molecule)
- Spin transfer also possible
- First time tilt and transfer simultaneously

C. Li, W. Jin, H.P. Xiang, G. Lefkidis, and W. Hübner, PRB **84**, 054415 (2011)

Summary

- Spin dynamics theoretically covered from femto- to subnanoseconds
- Ultrafast laser-induced active spin manipulation in magnetic nanoclusters
- Encoding of magnetic state in vibration of chromophore
- Logic functionalization (AND, OR gates)
- Rules-of-thumb for spin manipulation
  - Fe (easiest) > Co (moderate) > Ni (hardest)
  - O and Mg can reduce and relocate maximum of spin density
  - Spin flip easy on linear structures, but not spin transfer
  - Mg and O as bridging atoms increase the efficiency of spin transfer
  - Possibility of coherent control (different laser pulses lead to different results)