Local spin flip in two- and three-magnetic-center structures: a first-principles approach

G Lefkidis*, C Li, T Hartenstein, and W Hübner
Department of Physics and Research Center OPTIMAS, Kaiserslautern University of Technology, PO Box 3049, 67653 Kaiserslautern, Germany
E-mail: *lefkidis@physik.uni-kl.de

Abstract. We present a fully ab initio theory of ultrafast spin switching in nanostructures using optical control theory and including spin-orbit coupling thus realizing Λ processes. These processes are investigated using high-level quantum chemistry in structures with one, two, and three magnetic centers, where the spin localization and transferability are discussed with respect to their geometry. In particular we study metallic chains with two and three magnetic centers interconnected with Na atoms. We discuss the prerequisites for such scenarios for all structures.

1. Introduction
The basic requirements for (quantum) information storage in magnetic materials are larger capacity and faster processing speed. However, the tremendous increases in both aspects are reaching their physical limits. Complete coherent optical control of spin states in qubits for up to six Rabi oscillations has been reported [1], which may provide an opportunity to increase the information density and speed at the same time. Ever since the light-induced demagnetization of ferromagnets was discovered [2], many light-driven scenarios and mechanisms have been proposed [3]. It has also been theoretically demonstrated that subpicosecond magnetic switching can be achieved by exploiting the ultrafast electron-photon interaction [4, 5].

All-optical switching applied to solid magnetic materials represents an intriguing idea that has emerged with the availability of ultrafast, high-intensity (coherent) laser pulses. In recent years we have suggested a scheme that is based on optical transitions driven by a coherent laser field between the ground state and a well-defined excited state of a ferromagnet, and use of the spin-orbit coupling (SOC) to switch the spin while the system is in the excited state. It involves the excitation of the system from the ground state to a well-defined final state where the magnetization is manipulated so that it decays into a new ground state with opposite magnetization direction [6, 7]. This all-optical model is pictographically called a Λ process.

We have already studied the NiO$_6^{10}$ and NiO$_5^{8}$ clusters, representing the bulk and the (001) surface of the antiferromagnetic NiO [8, 9]. In these systems the spin density is known to be concentrated on the transition metal, and thus spin flip means transferring the electronic population from a spin-down to a spin-up state with a single laser pulse. Extending the model to systems with more magnetic centers is straightforward: more complicated systems with more 3d transition metals have to be calculated. In this paper, we present fully ab initio calculation of nanostructures with more than one magnetic center with the inclusion of SOC which allows
for the mixing of the spin states. With optical control theory we can flip the localized spin in most of the asymmetric structures, thus realizing a Λ-process [9, 11, 12, 13].

2. Two-magnetic-center structures
The first investigated structure family consists of A-B magnetic dimers (A, B = Ni, Co, Fe). Neutral dimers can be synthesized with soft matrix deposition and positively charged dimers through gas-phase mass selection. The lowest energy levels of the two-magnetic-center structures calculated from the symmetry-adapted-cluster configuration interaction (SAC-CI) method are shown in Figure 1. The method consists in building proper superpositions of numerous many-body excited states (CI), thus accounting to a very large extent for the correlations needed in order to describe magnetic systems. Since we focus on the magnetic ground state (triplet), one unit charge is added to the structures Ni-Co and Co-Fe, respectively, in order to have systems with an even number of electrons. The symmetry representation for the ground state of each structure is also shown, which indicates that except for the charged cluster [Ni-Co]⁺, each structure possesses a magnetic ground state. All calculations are performed combining the Gaussian03 [10] quantum chemistry package with our own codes for the relativistic effects.

The first interesting thing is that in the case of homonuclear structures (Ni-Ni, Co-Co, and Fe-Fe) the spin density is equally distributed among the two atoms, thus allowing only global spin flip (Table 1) since the "spin-up" and "spin-down" states are not localized on one atom only. Once a structural asymmetry is introduced ([Ni-Co]⁺, Ni-Fe, and [Co-Fe]⁺) the spin density of (at least) the energetically low lying electronic states is strongly localized on a single atom. In this case careful selection of the initial and the final state and optimization of the laser pulse can lead to local spin flip, i.e. on the single atom carrying the spin density. The time propagation is performed with time-dependent perturbation theory within the semiclassical model and thus the final state consists of a linear combination (with complex coefficients) of the ground and the excited states, allowing us to calculate the expectation values of the spin and perform spatial population analysis. The laser pulse is optimized with a specially developed genetic algorithm.

Figure 1. Energy levels of the neutral structures Ni-Ni, Co-Co, Fe-Fe, Ni-Fe, and the charged structures [Ni-Co]⁺ and [Co-Fe]⁺. The red states are singlets and the black ones are triplets. The symmetry representation for each ground state is labeled.

A second family discussed consists of short-chain structures with 1-4 connecting atoms between the two magnetic centers [11, 12]. Here we elongate the structures by including more Na atoms. Fe-Na₆-Ni and Co-Na₇-Fe are investigated here as examples to demonstrate spin flip scenarios. Figure 2 shows the spin flip processes for these two structures, respectively.

For the structure Fe-Na₆-Ni, the spin localized at the Fe end is intended to be switched by a transfer of the electron system from initial state 2 to the final state 3, as shown in Table 2. The transition between state 2 and 3 is optimized using the genetic algorithm developed in our group. An external magnetic field with a strength of |B| = 10⁻⁵ a.u. is applied in order to lift the degeneracy of the triplet. The time-evolution of the occupation probability of the states
Table 1. Spin-density distribution for the five lowest triplets of the dimers.

| Structure | atom | State 1 | State 2 | State 3 | State 4 | State 5 |
|-----------|------|---------|---------|---------|---------|---------|
| Ni-Ni     | Ni1  | 1.000   | 1.000   | 1.000   | 1.000   | 1.000   |
|           | Ni2  | 1.000   | 1.000   | 1.000   | 1.000   | 1.000   |
| Co-Co     | Co1  | 1.000   | 1.000   | 1.000   | 1.000   | 1.000   |
|           | Co2  | 1.000   | 1.000   | 1.000   | 1.000   | 1.000   |
| Fe-Fe     | Fe1  | 1.000   | 1.000   | 1.000   | 1.000   | 1.000   |
|           | Fe2  | 1.000   | 1.000   | 1.000   | 1.000   | 1.000   |
| [Ni-Co]++ | Ni   | 1.924   | 1.015   | 1.924   | 0.025   | 1.014   |
|           | Co   | 0.076   | 0.985   | 0.076   | 1.975   | 0.986   |
| Ni-Fe     | Ni   | 1.782   | 1.813   | 1.924   | -0.018  | 1.820   |
|           | Fe   | 0.218   | 0.817   | 0.076   | 2.018   | 0.180   |
| [Co-Fe]++ | Co   | 0.006   | 0.975   | 0.006   | 0.007   | 0.978   |
|           | Fe   | 1.994   | 1.025   | 1.994   | 1.993   | 1.022   |

Table 2. Energies, symmetries (including SOC), $z$-component of spin and total angular momentum of the states of Fe-Na$_6$-Ni included in the local spin flip scenario of Figure 2(a).

| State | Symmetry | Energy (eV) | $\langle S_z \rangle$ ($\mu_B$) | $\langle J_z \rangle$ ($\mu_B$) | Spin localization |
|-------|----------|-------------|---------------------------------|-------------------------------|-------------------|
| 39    | $B_1$    | 1.3524      | 0.000                           | 0.000                         | -                 |
| 3     | $B_1$    | 0.0041      | 0.975                           | 0.977                         | Fe                |
| 2     | $B_1$    | 0.0030      | -0.975                          | -0.977                        | Fe                |

Figure 2. A processes: Local spin flip at the Fe end of Fe-Na$_6$-Ni (left panel) and at the Co end of Co-Na$_7$-Fe (right panel). (a), (c): Occupations of the initial (dashed), target (solid), and intermediate (dotted) state vs. time. (b), (d): Time-resolved expectation values of the spin components.

Table 2. Energies, symmetries (including SOC), $z$-component of spin and total angular momentum of the states of Fe-Na$_6$-Ni included in the local spin flip scenario of Figure 2(a).

| State | Symmetry | Energy (eV) | $\langle S_z \rangle$ ($\mu_B$) | $\langle J_z \rangle$ ($\mu_B$) | Spin localization |
|-------|----------|-------------|---------------------------------|-------------------------------|-------------------|
| 39    | $B_1$    | 1.3524      | 0.000                           | 0.000                         | -                 |
| 3     | $B_1$    | 0.0041      | 0.975                           | 0.977                         | Fe                |
| 2     | $B_1$    | 0.0030      | -0.975                          | -0.977                        | Fe                |

involved in the local spin switch can be found in Figure 2(a). The time-resolved expectation value of the spin is also shown in Figure 2(b). The properties of the linearly polarized laser pulse are $\theta = 29.5^\circ$, $\gamma = 64.8^\circ$, $\phi = 145.3^\circ$ ($\theta$ and $\gamma$ denote the angles of incidence in spherical coordinates and $\phi$ is the angle between the polarization of the light and the optical plane) with the FWHM = 330.0 fs of the pulse (FWHM is the full width at half maximum of the laser pulse). The cluster is along the $\hat{z}$ axis. A population transfer of 94.9% is reached.

The same computational method and laser pulse optimization have been adopted for the structure Co-Na$_7$-Fe. The spin flip on the Co end is achieved with an appropriate external magnetic field and laser pulse via a $\Lambda$ process, as shown in Figure 2(c). A population transfer of
is achieved during the switching process. The parameters of the linearly polarized laser pulse are \( \theta = 41.3^\circ, \ \gamma = 177.7^\circ, \ \phi = 2.5^\circ \) and FWHM = 300.0 fs. In this case, as in the local spin switch at the Co end of the shorter Ni-Na\(_3\)-Co cluster [12], it is observed that the Rabi frequency is low compared to switching the spin at the Fe or the Ni end of similar metallic chain. This can be explained in that the transition matrix elements of Co are smaller than the ones of Ni or Fe, thus leading the oscillation to the low-electric-field regime (larger time scales). It is also not possible to switch in one single cycle and a more complex behavior is observed.

3. Three-magnetic-center structures

Our efforts to use a \( \Lambda \) process to transfer spin from one magnetic center to the other have not been successful for the above mentioned structures, the reason being probably the axial symmetry of the clusters. So we reduce the symmetry further by adding some branching to the linear chains [13]. The new family of clusters also exhibits a high degree of spin-density localization on the magnetic centers, as can be seen in the example of Ni\(_2\)-Na\(_2\)-Fe in Table 3. Therefore, this kind of structures exhibit a high degree of spin localization at different magnetic centers for different magnetic states and thus represent the best candidates to realize spin transfer from one magnetic to another [7] and thus build magnetic logic elements [13].

| Structure | atom | State 1 | State 2 | State 3 | State 4 | State 10 |
|-----------|------|---------|---------|---------|---------|----------|
| Ni\(_2\)Na\(_2\)Fe | Ni1  | 0.008   | 1.979   | 0.007   | 1.974   | 0.002    |
| Ni\(_2\)Na\(_2\)Fe | Ni2  | 1.974   | 0.010   | 1.975   | 0.006   | 0.015    |
| Ni\(_2\)Na\(_2\)Fe | Fe    | 0.001   | -0.002  | 0.000   | -0.001  | 1.972    |

4. Conclusions

In conclusion, spin flips in two- and three-magnetic-center nanostructures are predicted from first-principles quantum chemistry methods and optical control theory. The spin localization analysis in magnetic dimers, metallic chains, and three-magnetic-center structures shows that for energetically low-lying states the spin can only be localized in nonsymmetric structures, which is a prerequisite in order to achieve spin switch via the nonadiabatic \( \Lambda \) process.

Acknowledgments

We would like to acknowledge support from the Priority Programmes 1133 and 1153 of the German Research Foundation.

References

[1] Press D, Ladd T D, Zhang B, and Yamamoto Y 2008 Nature, 456 218
[2] Beaurepaire E, Merle J C, Daunois A, and Bigot J Y 1996 Phys. Rev. Lett. 76 4250
[3] Koopmans B, Ruigrok J J M, Dalla Longa F, and de Jonge W J M 2005 Phys. Rev. Lett., 95 267207
[4] Zhang G P and Hübner W 2000 Phys. Rev. Lett. 85 3025
[5] Gómez-Abal R, Ney O, Satitkovitchai K, and Hübner W 2004 Phys. Rev. Lett., 92 227402
[6] Gómez-Abal R and Hübner W 2002 Phys. Rev. B, 65 195114
[7] Li C, Hartenstein T, Lefkidis G, and Hübner W 2009 Phys. Rev. B, 79 189413(R)
[8] Lefkidis G and Hübner W 2007 Phys. Rev. B, 76 014418
[9] Lefkidis G and Hübner W 2009 J. Magn. Magn. Mater., 321 979
[10] Frisch M J et al. 2004 GAUSSIAN03, Revision B.03 (Gaussian Inc., Wallingford, CT)
[11] Hartenstein T, Li C, Lefkidis G, and Hübner W 2008 J. Phys. D: Appl. Phys., 41 164006
[12] Hartenstein T, Lefkidis G, Hübner W, Zhang G P, and Bai Y 2009 J. Appl. Phys., 105 07D305
[13] Hübner W, Kersten S P, and Lefkidis G 2009 Phys. Rev. B, 79 184431