Dynamical Exchange and Phase Induced Switching of a Localized Molecular Spin

H. Hammar and J. Fransson

Department of Physics and Astronomy, Uppsala University, Box 530, SE-751 21 Uppsala
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The dynamics of a localized molecular spin under the influence of external voltage pulses is addressed using a generalized spin equation of motion. The approach incorporates anisotropic fields, non-equilibrium conditions, and non-adiabatic dynamics. By application of a voltage pulse of temporal length \( \tau \), a recurring \( 4\pi \)-periodic switching of the localized spin is observed. The switching phenomena can be explained by dynamical exchange interactions, internal transient fields, and self-interactions acting on the localized spin moment.

Dynamics of open systems is an active area of research \cite{1,2}. Recent theoretical predictions have suggested that periodical out-of-equilibrium driving can induce temporal phases of matter \cite{3}, which subsequently have been experimentally corroborated \cite{4,5}. Light induced ultra-fast demagnetization has shown that fast responses to external forces can change the long-term magnetic properties, approaching stationary regimes not accessible through adiabatic processes \cite{6}. These examples vividly illustrate that the equilibrium paradigm is insufficient when attempting to treat rapid dynamics and non-equilibrium systems. Thus, when approaching the quantum limit in both spatial and temporal dimensions, models based on instantaneous or local interactions with no record of the past evolution or spatial surrounding can always be questioned. Non-linearities and feedback between internal components require a higher level of sophistication in the theoretical modeling, allowing to go beyond the equilibrium narrative, especially when confinement plays an important role as in single molecules.

Non-equilibrium open systems such as nanojunctions, quantum dots, and single molecules have been studied extensively, both experimentally and theoretically. Studies include electron dynamics \cite{7,8}, vibrating quantum dots \cite{9}, pulse-enhanced thermoelectric efficiency \cite{10,11}, non-equilibrium thermodynamics \cite{12,13}, and optoelectronics and spectroscopy \cite{14,15}. Due to size confinement, the systems exhibit intrinsic out-of-equilibrium nature and can be controlled by pulses and external forces, thus well suited for studying non-adiabatic quantum dynamics.

In this Letter we predict a novel type of phase induced switching phenomenon of localized spin embedded in a tunnel junction between metallic leads, across which a time-dependent voltage, \( V(t) \), is applied. By application of a voltage pulse of temporal length \( \tau \), we observe a recurring switching property of the localized spin, essentially whenever the total accumulated phase \( \varphi(V, \tau) \equiv eV\tau/\hbar \in (2\pi, 4\pi) \mod 4\pi \). The build up of the accumulated phase generates highly anisotropic internal transient fields which act on the local spin, exerting a torque which counteracts the externally applied magnetic field. The altered spin configuration is stabilized by anisotropic internal fields that crucially govern the dynamics long after the voltage pulse is turned off. This novel switching phenomenon can be explained in terms of induced internal transient fields emerging during the voltage pulse. These can be partitioned into four components: i) internal magnetic field, ii) Heisenberg, iii) Dzyaloshinskii-Moriya (DM), and iv) Ising type of self-interactions between the spin at different times. While all four components are essential for the switching, we notice in particular that the Ising interaction creates an energy barrier between degenerate solutions for the spin, see Fig. 1(a), which is crucial to stabilize the steady state after switching, whereas the DM interaction provides a torque that is required to drive the spin out of its initial state into the a new final state, see Fig. 1(b).

Our results are obtained from a generalized spin equation of motion (SEOM) developed for non-equilibrium conditions \cite{16,19} and which allows for calculations of dynamic exchange interactions \cite{16,20,21,22}. Similar approaches have previously been used in the stationary limit \cite{20,25,28}. In comparison to previous studies using, e.g., quantum master equation \cite{29,31} and stochastic Landau-Lifshitz-Gilbert equation \cite{32,33}, our approach makes a full account of the non-adiabatic dynamics, including temporal non-local properties of the internal fields. This has shown to be of great importance in studies of, e.g., ultra-fast spin dynamics \cite{34,35}.

Our test bench model represents a single-molecule magnet, for instance \( M \)-porphyrins and \( M \)-phthalocyanines where \( M \) denotes, e.g., a transition metal element, which serve as good models for fundamental studies \cite{39,41} comprising an inherent non-equilibrium nature. Experiments have revealed distance dependent effects in the exchange interactions \cite{42,45}, large anisotropy of individual molecules \cite{46,49}, as well as collective spin excitations and Kondo effect.

![FIG. 1: Illustration of the contribution of (a) the Ising interaction and (b) the DM interaction. (a) The Heisenberg interaction supports two degenerate solutions for the local spin for which there is no energy barrier in between. The Ising interaction introduces a potential barrier, and by that creating two separate minima. (b) The DM interaction provides the mechanism of the spin to switch and fall into the potential wells.](image-url)
Experiments have also shown the control and read-out of spin states of individual single-molecule magnets.

**Model.** We consider a magnetic molecule, embedded in a tunnel junction between metallic leads, comprising a localized magnetic moment $\mathbf{S}$ coupled via exchange to the highest occupied or lowest unoccupied molecular orbital henceforth referred to as the QD level. We define our system Hamiltonian as

$$\mathcal{H} = \mathcal{H}_x + \mathcal{H}_T + \mathcal{H}_{QD} + \mathcal{H}_S.$$  \hspace{1cm} (1)

Here, $\mathcal{H}_x = \sum_{k \sigma} \varepsilon_{k} c_{k \sigma}^d c_{k \sigma}$, is the Hamiltonian for the left ($\chi = L$) or right ($\chi = R$) lead, where $c_{k \sigma}^d$ ($c_{k \sigma}$) creates (annihilates) an electron in the lead $\chi$ with energy $\varepsilon_{k \chi}$, momentum $k$, and spin $\sigma = \uparrow, \downarrow$, while $\mu_{\chi}$ denote the chemical potential such that the voltage $V$ across the junction is defined by $eV = \mu_L - \mu_R$. Tunneling between the leads and the QD level is described by $\mathcal{H}_T = \mathcal{H}_{TL} + \mathcal{H}_{TR}$, where $\mathcal{H}_{TX} = -\sum_{k \sigma} \varepsilon_{k \chi} c_{k \sigma}^d d_{\sigma} + \mathcal{H}_{c}$. The single-particle QD is represented by $\mathcal{H}_{QD} = \sum_{\sigma} \varepsilon_{\sigma} d_{\sigma}^d d_{\sigma}$, where $d_{\sigma}^d$ ($d_{\sigma}$) creates (annihilates) an electron in the QD with energy $\varepsilon_{\sigma} = \varepsilon_{0} + g \mu_B B_{\text{ext}} \sigma_{z} / 2$ and spin $\sigma$, depending on the external magnetic field $B_{\text{ext}} = B_{-} \mathbf{z}$, where $g$ is the gyromagnetic ratio and $\mu_B$ the Bohr magneton. The energy of the local spin is described by $\mathcal{H}_S = -g \mu_B \mathbf{S} \cdot \mathbf{B}_{\text{ext}} - v_s \mathbf{S}$ where $v$ is the exchange integral between the localized and delocalized electronic states, the electron spin is denoted $\mathbf{s} = \psi^\dagger \mathbf{\sigma} \psi / 2$ in terms of the spinor $\psi = (d_{\uparrow}, d_{\downarrow})$, and $\mathbf{\sigma}$ is the vector of Pauli matrices.

The local spin dynamics is calculated using our previously developed generalized SEOM, that is,

$$\dot{\mathbf{S}}(t) = \mathbf{S}(t) \times \left( -g \mu_B \mathbf{B}_{\text{eff}}(t) + \frac{1}{e} \int \mathbb{J}(t', t') \cdot \mathbf{S}(t')dt' \right).$$ \hspace{1cm} (2)

Here, $\mathbf{B}_{\text{eff}}(t)$ is the effective magnetic field acting on the spin, defined by $\mathbf{B}_{\text{eff}}(t) = \mathbf{B}_{\text{BM}} + \frac{\mathbf{v}}{e \mu_B} \mathbf{m}(t) - \int \mathbb{J}(t', t')dt' / e g \mu_B$, where the second contribution is the local electronic magnetic moment, defined as $\mathbf{m}(t) = (\mathbf{S}(t)) = \frac{1}{2} \langle \psi(t) \mathbf{\sigma} \psi(t) \rangle = \frac{1}{2} \text{tr}(s \mathbf{\sigma} \mathbf{G}^- (t, t))$, where $s$ denotes the trace over spin-1/2 space. The third term is the internal magnetic field due to the electron flow. The field $\mathbb{J}(t, t')$ is the dynamical exchange coupling between spins at different times.

We remark that despite the semi-classical nature of the generalized SEOM, it incorporates the underlying quantum nature of the junction through the dynamical fields $\mathbb{J}$ and $\mathbb{J}$. This is especially important in the transient regime, where the classical Landau-Lifshitz-Gilbert equation is incapable to provide an adequate description of the dynamics.

The internal magnetic field due to the electron flow is defined as $\mathbb{J}(t, t') = i e v \theta(t - t') \langle [s^{(0)}(t), s(t')] \rangle$, where the on-site energy distribution is represented by $s^{(0)} = \sum_{\sigma} \varepsilon_{\sigma} d_{\sigma}^d d_{\sigma}$. This two-electron propagator $\mathbb{J}(t, t')$ is approximated by decoupling into single electron non-equilibrium Green functions (GFs), $\mathbf{G}^{< \gamma >}$, according to

$$\mathbb{J}(t, t') \approx i e v \theta(t - t') \text{sp}(\mathbf{G}^{< \gamma >}(t, t') - \mathbf{G}^{\gamma >}(t, t'))$$ \hspace{1cm} (3)

where $\epsilon = \text{diag}(\varepsilon_{\uparrow}, \varepsilon_{\downarrow})$. This internal field mediates both the magnetic field generated by the charge flow as well as the effect of the external magnetic field causing the Zeeman split in the QD.

The spin susceptibility tensor $\chi(t, t') = i 2 e v^2 \theta(t - t') \langle [s(t), s(t')] \rangle$ mediates the interactions between the localized magnetic moment at the times $t$ and $t'$. Decoupling into single electron GFs, yields

$$\chi(t, t') \approx i e v^2 \theta(t - t') \text{sp} \sigma \mathbf{G}^{< \gamma >}(t, t') - \mathbf{G}^{\gamma >}(t, t') \mathbf{G}^{< \gamma >}(t, t').$$ \hspace{1cm} (4)

This current mediated interaction can be decomposed into an isotropic Heisenberg interaction $J_H$, and the anisotropic Dzyaloshinski-Moriya (DM) $D$ and Ising $I$ interactions.

The dynamical QD electronic structure is calculated by using non-equilibrium GFs taking into account the back action from the local spin dynamics by perturbation theory. Expanding the contour ordered single electron GF $\mathbf{G}(t, t')$ to first order in the time-dependent expectation value of the spin, we obtain

$$\mathbf{G}(t, t') = \mathbf{g}(t, t') - v \int_{c} \mathbf{g}(t, \tau) \langle S(\tau) \rangle \cdot \sigma \mathbf{g}(\tau, t')d\tau.$$ \hspace{1cm} (5)

Here, $\mathbf{g}(t, t')$ is the bare (spin-dependent) QD GF given by the equation of motion

$$(i \partial_t - \epsilon) \mathbf{g}(t, t') = \delta(t - t') \sigma_0 + \int \mathbf{S}(t, \tau) \mathbf{g}(\tau, t')d\tau,$$ \hspace{1cm} (6)

where the self-energy is $\mathbf{S}(t, t') = \Sigma(t, t') \sigma_0$ with $\Sigma(t, t') = \sum_{\chi} \sum_{k \in \chi} |T_{\chi}|^2 g_k(t, t')$, $\sigma_0$ is the $2 \times 2$ identity matrix and $g_k(t, t')$ is the lead GF. Using the wide-band limit we can define the tunneling coupling $\Gamma_{\chi} = 2 \pi |T_{\chi}|^2 \sum_{k \in \chi} \delta(\omega - \varepsilon_k)$ between the lead and the QD and the lesser self-energy becomes

$$\Sigma^<(t, t') = i \sum_{\chi} \Gamma_{\chi} \int f_{\chi}(\omega) e^{-i \omega (t-t') + i \int_{t'}^{t} \mu_{\chi}(\tau) d\tau} d\omega / 2 \pi.$$ \hspace{1cm} (7)

The self-energy carries the information of the pulse due to the time integration of the chemical potential for each lead, i.e., $i \int_{t'}^{t} \mu_{\chi}(\tau) d\tau$. We refer to Ref. [02] for more details.

Results. — In absence of a voltage across the junction, there is no current flow and the local spin remains in its initial state. Taking this as the initial condition for our
simulations, at time $t_0$ we apply a constant voltage of amplitude $V$, which is subsequently terminated at $t_1$, and let the system evolve towards its stationary state. The plot in Fig. 2(a) shows the time-evolution of the local spin orientation for increasing phase $\varphi \equiv eV(t_1 - t_0)/\hbar$, where bright (dark) corresponds to a spin orientation parallel (anti-parallel) to the external field. The plot clearly illustrates that the spin either remains in its initial state or is switched to the parallel state, depending on the phase. In particular for phases when $\varphi \in (0, 2\pi)$ mod $4\pi$, the general orientation of the spin remains unchanged by the temporary non-equilibrium conditions while the spin aligns parallel to the external field whenever $\varphi \in (2\pi, 4\pi)$ mod $4\pi$. However, due to non-linearities in Eq. (2), the two solutions are not perfectly confined to phases in the intervals $\varphi \in (0, 2\pi)$ mod $4\pi$ and $\varphi \in (2\pi, 4\pi)$ mod $4\pi$. We shall, nonetheless, henceforth refer to the former regime as spin-conserving and the latter as spin-flipping.

The spin current $I_S = \sum \sigma_i \dot{\sigma}_i I_S$, where $I_S$ is the spin resolved electron current through the junction, is plotted in Fig. 2(b). The signatures in the spin current originate from the variations in the local spin orientation as function of the phase $\varphi$. This is expected since the spin-dependent current is sensitive to the local magnetic environment which strongly depends on whether the local spin is parallel or anti-parallel to the external magnetic field.

There are several competing mechanisms in the process, e.g., temperature, external magnetic field, local exchange, and tunneling coupling to the leads. Variations between the two stationary spin orientations are governed by the local exchange coupling $v$ between the spin and the electrons in the QD level. A local exchange integral satisfying $v \lesssim \Gamma/3$, does not sustain sufficiently strong transient internal fields to enable the switching. This can be seen in Fig. 3, which shows the time evolution of the spin orientations for increasing coupling $v$ after a given pulse. As the exchange integral satisfies $v \gtrsim \Gamma/3$, the spin undergoes a reorientation. It can, furthermore, be noted that the spin switches for all phases $\varphi$ whenever $v > 2\Gamma/3$. The interval $1/3 \lesssim v/\Gamma \lesssim 2/3$ defines the domain for the phase induced switching property. From our simulations we can further see that related to the temperature $T$, an effective spin switching requires that the coupling $\Gamma \gtrsim 10\hbar k_B$, where $k_B$ is the Boltzmann constant. Moreover, magnetic field strengths in the range $|B| < \Gamma/8g\mu_B$ is necessary for the spin switching since the induced fields cannot overcome too strong external magnetic fields.

The origin of the phase induced switching phenomenon can be understood be analyzing the change of the spin susceptibility tensor, Eq. (3), and the internal field, Eq. (3), due to the voltage pulse. The periodicity shown in Fig. 2 originates from the self-energy, Eq. (7), where an applied pulse generates the phase factor $\exp\{i\varphi\}$ after the pulse is turned off. In Fig. 4(a) – (d) we plot the resulting change of the local spin due to the underlying fields for pulses of different temporal length. It represents the first case of switching in Fig. 2(a) where the spin switches for $\varphi/2\pi = 1.59$ and $3.34$.

The effective change of $S_z$ due to the internal magnetic field, $j(t, t')$, that is, $S_z(t, t') = -\int S(t') j(t, t') dt'/\epsilon$, is shown in Fig. 4(a). It illustrates rapid oscillations mixed contributions depending on the voltage applied. In the spin-flipping regime, $\varphi \in (2\pi, 4\pi)$ mod $4\pi$, exemplified by $\varphi/2\pi = 1.59$ (blue) and $3.18$ (black) in the figure, this field creates a torque to align the spin to the magnetic field. In the spin-conserving regime, $\varphi \in (0, 2\pi)$ mod $4\pi$, $\varphi/2\pi = 2.39$ (red) in the figure, this field oscillates and gives a negligible contribution that average to zero. This behaviour leads to an alternated enhancement and reduction of the total magnetic field acting on the local spin, which along with the overall lower amplitude has a marginal impact on the spin dynamics. The Heisenberg interaction is, considered as a self-interaction in the time-domain, of anti-ferromagnetic character (positive) for all pulse lengths, see Fig. 4(b). We also observe

FIG. 2: Resulting evolution of (a) $S_z$, showing the spin flip, and (b) the spin current, for different pulse lengths, here plotted against $\varphi/2\pi$. Here, $eV = 2T$, $v = \Gamma/2$, $T = 0.0862\, \Gamma/k_B$ and $B = 0.1158\, \Gamma/g\mu_B$. The dotted line indicates when the pulse ends.

FIG. 3: Resulting evolution of $S_z$ for different exchange coupling strength $v$ for a pulse $t_2 - t_0 = 5\hbar/\Gamma$. Other parameters as in Fig. 2. The vertical dotted line indicates when the pulse ends.
a less sharp and significant feature for $\varphi/2\pi = 2.39$. The
DM interaction is of anti-ferromagnetic character in the
spin-flipping regime, whereas it is of ferromagnetic charac-
ter (negative) in the spin-conserving, see Fig. 4(c). The
Ising interaction have a small but finite contribu-
tion and is of mainly ferromagnetic character, see Fig.
4(b). We also observe that the characteristics of the in-
teractions for $\varphi/2\pi = 2.39$ is less sharp in comparison to
the other pulses. All the fields depend strongly on the
pulse length, bias voltage, temperature, magnetic field,
exchange coupling and tunneling coupling.

A conclusion that can be drawn from the plots Fig.
4 is that within the spin-flipping regime, the induced in-
teractions have a tendency to grow larger with increasing
pulse length. The analogous behavior cannot, however,
be observed by increasing the voltage bias and simulta-
necessarily decreasing the pulse length while preserving
the phase $\varphi$. Although the non-linearity of the dynamical
spin equation prevents us from determine the exact ori-
gin of this property, we conjecture that the different con-
titions leading to either conservation or flipping of the
localized spin are not governed solely by the phase. It is
rather a combination of the appropriate phase and that
the time-evolution of the surrounding electronic structure
accumulates density differently in the two cases.

Although the dominant fields in the transient dynam-
ics are the Heisenberg interaction and the internal field,
the anisotropic fields are crucial for the switching to oc-
cur. Due to the isotropic nature of the Heisenberg inter-
action, its corresponding potential landscape supports a
degenerate set of stationary solutions for the spin, see
left panel in Fig. 1(a). Hence, the stationary solution is
always governed by the external field. While the de-
generacy of the potential landscape is not broken by the
Ising interaction, it creates an energy barrier between the
degenerate solutions, see right panel of Fig. 1(a).

The height of this barrier effectively determines an up-
per boundary for the temperature in order to prevent
thermal random drift between the two solutions. The
DM interaction generates a spin transfer torque which,
when sufficiently strong, can push the spin over the en-
ergy barrier, see Fig. 1(b). As retardation is inherent in
the generalized SEOM by construction, both spin ori-
entations, parallel and anti-parallel to the external field,
constitute stable fixed points in the phase space of the
dynamical system. Hence, the torque generated by the
DM interaction merely has to be sufficiently large to push
the system into the realms of the opposite solution for
the switching to occur. This is similar to the case where
anisotropy is introduced in the system by magnetic leads
of different polarization [52].

Regarding limitations in our approach we have not con-
considered quantum spins or strongly correlated spins. How-
ever, our model is essentially applicable for strongly lo-
calized spins, pertinent to, e.g., atomic transition metal
and rare earth elements in molecular compounds such as
phthalocyanines and porphyrins [50, 64–66]. Therefore,
our model is restricted to large spin moments, for which
a classical description is viable, while quantum spins are
beyond our approach. We, moreover, assume the QD
level to be resonant with the equilibrium chemical poten-
tial, hence, avoiding possible Kondo effect that otherwise
may occur. While neglecting the local Coulomb repulsion
is a severe simplification of the QD description, it is justi-
fied since it is typically negligible for the $sp$-orbitals that
constitute the conducting levels in the molecular ligands
structure.

In conclusion, we have demonstrated that phase in-
duced switching of a localized magnetic moment embed-
ded in a tunnel junction can be obtained for short voltage
pulses $\tau$, satisfying $\varphi \in (2\pi, 4\pi)$ mod $4\pi$. The under-
lying rapid dynamics of the nanosystem and effects of
memory are included through our newly developed gen-
eralized spin equation of motion procedure. The feedback
of the spin onto itself through the surrounding environ-
ment is of vital importance as it provides a mechanism for
a dynamical indirect electronically mediated spin-spin in-
teraction. The switching phenomenon is also dependent
on highly anisotropic transient fields, creating a pulse-
dependent torque on the local spin.

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R. Chandrasekar, T. Bodenstein, O. Fuhr, D. Secker, K. Fink, M. Ruben, et al., Nat. Nano 8, 575 (2013).

[56] R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer, and F. Balestro, Nature (London) 488, 357 (2012).

[57] S. Loth, M. Etzkorn, C. P. Lutz, D. M. Eigler, and A. J. Heinrich, Science 329, 1628 (2010).

[58] M. Ternes, New J. of Phys. 17, 63016 (2015).

[59] S. Loth, C. P. Lutz, and A. J. Heinrich, New J. of Phys. 12 (2010).

[60] S. Karan, N. Li, Y. Zhang, Y. He, I.-P. Hong, H. Song, J.-T. Lü, Y. Wang, L. Peng, K. Wu, et al., Phys. Rev. Lett. 116, 027201 (2016).

[61] Y.-C. Lin, P.-Y. Teng, P.-W. Chiu, and K. Suenaga, Phys. Rev. Lett. 115, 206803 (2015).

[62] H. Hammar and J. Fransson, Phys. Rev. B 94, 054311 (2016).

[63] H. Hammar and J. Fransson, Phys. Rev. B 96, 214401 (2017).

[64] H. Wende, M. Bernien, J. Luo, C. Sorg, N. Ponpandian, J. Kurde, J. Miguel, M. Piantek, X. Xu, P. Eckhold, et al., Nat. Mater. 6, 516 (2007).

[65] E. Coronado and P. Day, Chem. Rev. 104, 5419 (2004).

[66] M. Urdampilleta, S. Klyatskaya, J.-P. Cleuziou, M. Ruben, and W. Wernsdorfer, Nat. Mater. 10, 502 (2011).