A scanning tunneling microscope can probe the inelastic spin excitations of a single magnetic atom in a surface via spin-flip assisted tunneling in which transport electrons exchange spin and energy with the atomic spin. If the inelastic transport time, defined as the average time elapsed between two inelastic spin flip events, is shorter than the atom spin relaxation time, the STM current can drive the spin out of equilibrium. Here we model this process using rate equations and a model Hamiltonian that describes successfully spin flip assisted tunneling experiments, including a single Mn atom, a Mn dimer and Fe Phthalocyanine molecules. When the STM current is not spin polarized, the non-equilibrium spin dynamics of the magnetic atom results in non-monotonic $dI/dV$ curves. In the case of spin polarized STM current, the spin orientation of the magnetic atom can be controlled parallel or anti-parallel to the magnetic moment of the tip. Thus, spin polarized STM tips can be used both to probe and to control the magnetic moment of a single atom.

PACS numbers:

I. INTRODUCTION

A single magnetic atom is arguably the smallest system where the spin can be used to store classical and/or quantum information. Therefore, there is great interest in probing and manipulating the spin state of a single atom or a single molecule in a solid state environment. Examples of this are single Phosphorous donors in Silicon,[2–5] nitrogen-vacancy centers in diamonds,[6,7] single Mn atoms in II-VI[8] and III-V[9] semiconductors, and single magnetic adatoms in surfaces.[9–20],21,22 Whereas in most cases the spin of the single atom is probed by optical means, the possibility of coupling the spin of as single atom to an electrical circuit is particularly appealing.

Tremendous recent experimental progress has made it possible to probe the spin of a single and a few atoms deposited in conducting surfaces by means of scanning tunneling microscopy.[1–24] There are two complementary techniques that afford this: spin polarized STM and spin flip inelastic electron tunnel spectroscopy (IETS). The working principle of spin polarized STM is spin dependent magneto resistance[22] similar to that of tunnel magneto resistance junction: tunneling between two spin polarized conductors depends on the relative orientation of their magnetic moments. Control of the spin orientation of either the tip or the substrate affords spin contrast STM imaging.[23]

In the case of spin flip IETS, electrons tunnel from the STM tip to the surface (or vice versa), and exchange their spin with the atom, so that they produce a spin transition, whose energy is provided by the bias voltage. Thus, a new conduction channel opens when the bias voltage is made larger than a given spin transition [see Fig. 1(c),1(d)]. This results in a step in the conductance which is bias dependent and permits to determine the energy of the spin excitations, and how they evolve as a function of an applied magnetic field.[24] When the atom is weakly coupled to its environment, the spin is quantized,[23,24] the spin transitions have sharply defined energies which can be described with a single spin Hamiltonian whose parameters can be inferred from the experiments.[24] This is the case of Mn, Co and Fe atoms,[9–11] as well as Fe and Co Phthalocyanines,[12,15,18] all of them deposited on a insulating monolayer on top of a metal. Remarkably, spin flip IETS does not require a spin polarized tip to extract information about the spin dynamics.

Both IETS and spin polarized STM are based upon the fact that the spin state of the atom affects the transport electrons, yielding a spin-dependent conductance. Therefore, we must expect that the transport electrons do affect the spin of the atom. This is the main theme of this paper. In the case of spin flip IETS, there are two relevant time scales. On one side, the inelastic transport time or charge time $T_q$, which is defined as the average time elapsed between two inelastic spin flip events. On the other side, the magnetic atom spin relaxation time, $T_1$. In the $T_q >> T_1$ regime, the transport electrons always interact with a atomic spin in equilibrium with the environment. As a result, the occupation of the spin states is bias independent and the conductance is expected to have flat plateaus in between the inelastic steps. In the $T_q << T_1$ regime this is no longer the case, the current drives the atomic spin out of equilibrium, so that the occupations of the spin states are bias dependent. As we showed in a previous work,[25] for the case of a single Mn atom, this results in a modified conductance line-shape, with non-monotonic behaviour in between steps. In this work we give an extended account of these effects, and consider also the case of Mn dimers and FePc.

Non-equilibrium effects become particularly appealing when either the tip or the substrate are also spin polarized. In this case we have current flow between two magnetic objects, which is expected to result in spin transfer torque. It has been proposed theoretically[26] and independently verified experimentally[27] that the spin orientation of a single Mn atom can be controlled with a a spin polarized tip. In this paper we provide a thorough
The spin dynamics of current driven nanomagnets in the Coulomb Blockade regime has been thoroughly studied from the theory standpoint \cite{25,35–44}. The systems studied include magnetic grains \cite{41,45}, semiconductor \cite{39} and Mn doped quantum dots \cite{36,40}, molecular magnets and magnetic molecules \cite{35,42,43,46}. In contrast to most of the theory work published to date, here we can model the current driven dynamics of a quantum spin whose Hamiltonian parameters are accurately known from experiments \cite{40}, making it possible to compare successfully theory and experiment.

The rest of the manuscript is organized as follows. In Sec. II we present the model Hamiltonian for the magnetic atom(s), the transport electrons, and their coupling, which accounts both for spin-assisted tunneling and Korringa like atomic spin relaxation due to exchange coupling with the electrodes. The transition rates and non-equilibrium dynamics leading to the current are analyzed in Sec. III. In Sec. IV we present the results of current driven spin dynamics under the influence of non-magnetic tip in three cases: the single Mn adatom, the Mn dimer and the FePC molecule. In Sec. V we discuss the case of a spin polarized tip and analyze in detail the case of a single Mn adatom. In Sec. V we present our main conclusions and discuss open questions.

II. THEORY

A. Hamiltonian

In this section we present the phenomenological Hamiltonian, its microscopic justification, the rate equation approach for the atom spin dynamics, including both spin relaxation and spin driving terms, and the calculation of the current. The system of interest is shown in Fig. 1(a). We use a model Hamiltonian which describes the system of interest split in 3 parts: tip, substrate and the magnetic atom(s) \cite{25}.

$$\mathcal{H} = \mathcal{H}_{T} + \mathcal{H}_{S} + \mathcal{H}_{\text{Spin}} + V. \quad (1)$$

The first two terms describe the tip and surface:

$$\mathcal{H}_{T} + \mathcal{H}_{S} = \sum_{k, \sigma, \eta} \epsilon_{\sigma \eta}(k) c_{k \sigma \eta}^{\dagger} c_{k \sigma \eta}, \quad (2)$$

where $c_{k \sigma \eta}^{\dagger}$ creates and electron in electrode $\eta = T, S$, with momentum $k$ and spin $\sigma$ defined along the spin quantization axis, $\vec{n}$. Unless stated otherwise, we take $\vec{n}$ parallel to the magnetization of the tip, which is a static vector in our theory. Since we consider a non-magnetic surface, we have $\epsilon_{\sigma S}(k) = \epsilon_{\sigma}(k)$. All the results of this paper are trivially generalized to the case of a non-magnetic tip and a magnetic surface.

The spin of the magnetic adatom(s) is (are) described with a single ion Hamiltonian, exchange coupled to other magnetic adatoms and to the transport electrons \cite{25,35–44}.

$$\mathcal{H}_{\text{Spin}} = \sum_{i} \left[ D S_{i}^{2}(i) + E \left( S_{x}^{2}(i) - S_{y}^{2}(i) \right) \right] + \frac{1}{2} \sum_{i,j,a} J_{i,j} S_{i}^{a}(i) S_{j}^{a}(j) + g \mu_{B} \sum_{i} \vec{S}(i) \cdot \vec{B}. \quad (3)$$

The first term describes the single ion magneto-crystalline anisotropy, the second describes the inter-atomic exchange couplings and the third corresponds to the Zeeman splitting term under an applied magnetic field $\vec{B}$. Here the prime denotes that the spin quantization axis is chosen with $z'$ along the easy axis of the system, not along the magnetic moment of the tip, $\vec{n}$. This
makes necessary to rotate $H_{\text{Spin}}$ when $\vec{n}$ is not parallel to the easy axis. The value of the local spin $S(i)$, the magnetic anisotropy coefficients $D$ and $E$, and the exchange coupling between atoms in the chain $J_{ij}$, change from atom to atom and also depend on the substrate. In the following, we denote the eigenvalues and eigenvectors of $H_{\text{Spin}}$ as $E_M$ and $|M\rangle$ respectively.

We model the coupling of the magnetic chain with the reservoirs with the following Kondo-like Hamiltonian:

$$V = \sum_{\alpha,\lambda,\lambda',\sigma,\sigma',i} T_{\lambda,\lambda',\alpha}(i) \frac{\tau^{\sigma\sigma'}(i)}{2} S_{\alpha}(i) e^{i_{\lambda,\sigma}^\dagger e^{-i_{\lambda',\sigma'}},}$$

(4)

where $i$ labels the magnetic atoms in the surface, $\lambda = (k, \eta)$ labels the single particle quantum numbers of the transport electrons (other than their spin $\sigma$), and the index $\alpha$ runs over 4 values, $\alpha = x, y, z$, and $\alpha = 0$. We use $\tau^{(\alpha)}$ and $S_\alpha$ for the Pauli matrices and the spin operators in the $\vec{n}$ frame, while $\tilde{S}_\alpha$ is the identity matrix. $T_{\lambda,\lambda',\alpha}$ for $\alpha = x, y, z$ is the exchange-tunneling interaction between the localized spin and the transport electrons, and potential scattering for $\alpha = 0$. Attending to the nature of the initial and final electrode, Eq. (4) describes four types of exchange interaction, two of which contribute to the current, the other two are crucial to account for the atom spin relaxation.

### B. Justification of the Hamiltonian

The phenomenological spin models of Eqs. (3) and (4) capture most of the experimental results, as we show below. These models imply that that the magnetic atom is in a well defined charge state except for classically forbidden fluctuations that enable tunneling from the tip to the surface. Fig. (b) shows a typical level alignment in which the spin model can be applied. The basic condition is therefore, that the chemical potential of the electrodes must be far enough from the chemical potential of the central-quantized region. In this way, charge addition and charge removal are classically forbidden. Although it is outside the scope of this work, we claim that the quantum charge fluctuations that give rise to spin dependent tunneling are due to inelastic cotunneling. In the case of spin 1/2, the equivalence between the spin model, originally proposed by Appelbaum, and a single site Anderson model was rigorously shown by Anderson generalizing the Schrieffer and Wolff transformation to the case of a single site coupled to two reservoirs. Within this picture, the atomic spin is exchanged coupled to the transport electrons and the magnitude of the exchange is given by $T_{\lambda,\lambda',0}(x,y,z) \approx \delta^{-1} V_\lambda V_{\lambda'}$, where $V_{\lambda}$ is the hybridization between the Anderson site and the single particle state $k$ in the electrode $\eta$, and $\delta$ is the energy difference between the Anderson level and the electrode Fermi energy. This is the so called Kinetic exchange. Importantly, both electrode conserving and electrode non-conserving processes are included and their strengths are not independent, since they both depend on hopping matrix elements between the localized orbital in the atom and the extended orbitals in either the tip or the sample. Interestingly, the Schrieffer and Wolff transformation also yields a spin-independent tunneling term which would yield the $\alpha = 0$ contribution in Eq. (4), and it corresponds to the elastic tunneling contribution. Within this Anderson-Kondo picture, the strength of the ($\alpha = 0$) elastic channel and that of the spin dependent channel ($\alpha = x, y, z$) are comparable and, in the so called symmetric case, the elastic term vanishes identically. Thus, for spin 1/2 case, this picture can account for the large strength of the inelastic signal. The generalization to higher spin case, relevant for the experiments, will be published elsewhere.

Keeping these considerations in mind, and following Anderson, we assume that Hamiltonian (4) arises from kinetic exchange. The momentum dependence of $T_{\lambda,\lambda',\alpha}$ can have important consequences in the conductance profile in an energy scale of $eV$, but it can be safely neglected in IETS. We thus parametrize

$$T_{\eta,\eta',\alpha}(i) = v_{s}(i)v_{T}(i)T_{\alpha},$$

(5)

where $v_{s}(i)$ and $v_{T}(i)$ are dimensionless factors that scale as the surface-atom and tip-atom hopping integrals. Because kinetic exchange is spin rotational invariant we have $T_x = T_y = T_z = |T|$. Thus, Eq. (4) implies that the spin-assisted tunneling and the atomic spin relaxations are both due to kinetic exchange, and Eq. (5) implies that their amplitudes depend on the tip-atom and surface-atom tunneling matrix elements.

### C. Rates and Master equation

Our primary goal is to study transport and spin dynamics. This is done considering $V$ as a perturbation to the otherwise uncoupled magnetic atom and transport electrons. The quantum spin dynamics is described by means of a master equation for the diagonal elements of the density matrix, $P_M$, described in the basis of eigenstates $|M\rangle$ of $H_{\text{Spin}}$. The master equation is derived using the standard system plus reservoir technique, where the transport electrons act as a reservoir for the atomic spin(s). The master equation reads

$$\frac{dP_M}{dt} = \sum_M P_{M'} W_{M,M'} - P_M \sum_{M'} W_{M,M'},$$

(6)

where $W_{M,M'}$ are the transition rates between the atomic spin state $M$ and $M'$. These rates can be written as

$$W_{M,M'} = \sum_{\eta,\eta'} W_{\eta,\eta,\eta',M,M'},$$

where $W_{\eta,\eta,\eta',M,M'}$ are the scattering rates from an atomic spin state $M$ to $M'$ in which a quasiparticle electron goes from electrode $\eta$ to $\eta'$ as a
result of exchange process. They are given by:

\[ W_{\eta M M'}^{\eta' \eta} = \sum_{k'\sigma' M' \sigma M} \Gamma_{k \sigma M, k' \sigma' M'} \left( f_{\eta}(\epsilon_{\eta \sigma}) f_{\eta'}(\epsilon_{\eta' \sigma'}) - f_{\eta}(\epsilon_{\eta' \sigma'}) f_{\eta'}(\epsilon_{\eta \sigma}) \right) \]  

(7)

where \( f_{\eta}(\epsilon) = \frac{1}{1 + \exp[-\beta(\epsilon - \mu_{\eta})]} \) is the occupation probability in electrode \( \eta \) for electrons in equilibrium at chemical potential \( \mu_{\eta} \) and temperature \( T = 1/(k_{\text{B}}\beta) \). \( \Gamma_{k \sigma M, k' \sigma' M'} \) is the rate at which an electron in lead \( \eta \) with wavenumber \( k \) and spin \( \sigma \) is scattered into a lead \( \eta' \) with wavenumber \( k' \) and spin \( \sigma' \), with the impurity spin undergoing a transition between states \( M \) and \( M' \). Quantum rates \( \Gamma \)'s are calculated at the lowest order in the electrode-chain coupling using Fermi Golden rule with the perturbation given by \( \mathcal{V} \) (see appendix A for details):

\[ \Gamma_{k \sigma M, k' \sigma' M'}^{\eta \eta'} = \frac{2\pi}{\hbar} \left| \sum_{\alpha,i} T_{\alpha} v_{\eta}(i) v_{\eta'}(i) S_{\alpha, M, M'}(i) \right|^2 \times \delta(\epsilon_{\eta}(k) + E_{M} - \epsilon_{\sigma' \eta'}(k') - E_{M'}) , \]

(8)

where we have defined the matrix elements

\[ S_{\alpha, M, M'}^{M, M'}(i) = \langle M | S_{\alpha}(i) | M' \rangle . \]

(9)

The rates in Eq. (7) describe 3 types of processes:

1. Elastic processes, \( W_{\eta M M'}^{\eta' \eta} \), in which the state of atomic spin remains unchanged and a transport electron is transferred from one electrode to another. These processes are responsible for the elastic current and have no effect on the spin dynamics. The rates of the elastic processes scale with \( v_{T}^2 v_{S}^2 T_{0}^2 \).

2. Spin transitions \( W_{\eta M M'}^{\eta' \eta} \). In these, a spin transition in the atomic spin is produced due to the creation or annihilation of an electron hole pair either in the tip or in the surface. These processes do not contribute to the current. At very small temperature, the fastest process of this type is atomic spin relaxation: a spin transition from an excited state \( E_{M} \) to a lower energy state \( E_{M'} \) which results in the excitation of an electron hole pair in one of the electrodes. This spin relaxation process is very similar to the nuclear spin relaxation due to hyperfine coupling to conduction electrons in metals and to Mn spin relaxation in diluted magnetic semiconductors due to itinerant carriers. At zero bias these processes dominate the atomic spin relaxation time \( T_{1} \). The rates of the spin transition processes scale like \( v_{T}^2 T^2 \) and \( v_{S}^2 T^2 \).

3. Spin flip assisted tunneling \( W_{\eta M M'}^{\eta' \eta} \). In these processes, which contribute both to inelastic current and to the dynamics of the atomic spin, a transport electron goes from electrode \( \eta \) to \( \eta' \) inducing a spin transition from state \( M \) to \( M' \). The rates of the spin flip assisted tunneling processes scale like \( v_{T}^2 v_{S}^2 T^2 \).

The steady state solutions of Eq. (10) depend, in general, on the Hamiltonian parameters, the temperature and the bias voltage. We refer to the steady state solutions as \( P_{M}(V) \). At zero bias, the steady state solutions are those of thermal equilibrium. At finite bias, the \( P_{M}(V) \) can depart significantly from equilibrium depending on the relative efficiency of the transport assisted spin excitations and the spin relaxation. Eq. (10) does not include spin coherences. This approximation is good if the spin decoherence is faster than spin relaxation, which is known to be the case due to hyperfine coupling in Mn atom. However, future work should address this point more carefully, in particular when the magnetization of the tip \( \vec{n} \) is not parallel to the single ion easy axis.

D. Relevant parameters

The behaviour of the system is characterized by the rates in Eq. (11), which depend on a number of physical quantities like the temperature, the bias voltage \( V \), density of states at the Fermi Energy of tip and surface, \( \rho_{T} \) and \( \rho_{S} \), the tip-atom \( v_{T}(i) \) and surface-atom \( v_{S}(i) \) hopping, the spin independent \( T_{0} \) and spin dependent \( T \) couplings. In this work we attempt to group the unknown parameters either in terms of dimensionless numbers or as experimentally accessible quantities. For that matter, we define the zero bias elastic conductance

\[ g_{0} = \frac{\pi^{2}}{4} G_{0} \rho_{T} \rho_{S} |T_{0}|^{2} \chi^{2} , \]

(10)

where \( G_{0} = 2e^{2}/h \) is the quantum of conductance and

\[ \chi = \sum_{i} v_{T}(i) v_{S}(i) \]

(11)

is a parameter that quantifies the tip-surface transmission through the magnetic atoms. The density of states at the Fermi energy for spin \( \sigma \) in the electrode \( \eta \) are denoted by \( \rho_{\sigma \eta} \). We define the spin assisted conductance \( g_{S} \) as

\[ g_{S} = \zeta^{2} g_{0} \]

(12)

where

\[ \zeta = \frac{T}{T_{0}} \]

(13)

is the ratio of the spin-flip assisted and elastic tunnel matrix elements. We shall use spin polarization of the tip, defined as

\[ P_{T} = \frac{\rho_{T \uparrow} - \rho_{T \downarrow}}{\rho_{T \uparrow} + \rho_{T \downarrow}} \]

(14)

Another important parameter is the ratio

\[ r(i) \equiv \frac{v_{T}(i)}{v_{S}(i)} \]

(15)
which decreases as the tip is retracted from the surface. In most instances, we shall have \( r(i) < 1 \). As a general rule, the processes that drive the magnetic adatom out of equilibrium are proportional to \( v^2_p v^2_S \) whereas the processes that cool the spin down (if \( k_B T < |eV| \)) are proportional to \( v_1^2 + v_2^2 \). Thus, the non-equilibrium effects are higher as \( R \equiv r^2/(1 + r^2) \) increases. Therefore, current will be increased without changing the applied bias \( V \). In contrast, the inelastic ratio \( \zeta \) and the magnitude of the tip polarization \( P_T \) are not so easy to control.

E. Current

The calculation of the rates for a tunnel event in which a transport electron goes from one electrode to the other, inducing a spin transition between states \( M \) and \( M' \) (where \( M \) could be equal to \( M' \) in the elastic channel), permits to obtain an expression for the current in terms of the steady state solutions of the master equation

\[
I_{S\rightarrow T} = e \sum_{MM'} P_M(V) \left( W^M_{M,M'} - W^{M'}_{M,M} \right),
\]

where \( W^M_{M,M'} \) are the scattering rates from state \( M \) to \( M' \) induced by interaction with a quasiparticle which is initially in reservoir \( \eta \) and ends up in \( \eta' \), given in equation (7). We adopt the convention that positive bias voltage \( V > 0 \) means electrons flowing from tip to surface, see Fig. 1(b). Thus, we have:

\[
eV = \mu_S - \mu_T \tag{17}
\]

with \( e \) the value of the electron charge with its sign.

1. Current for non-magnetic tips

The expression for the current in the case on non-magnetic tip and substrate can be written as the sum of two terms, elastic and inelastic, \( I = I_0 + I_{IN} \) given by the expressions\(^{22}\)

\[
I_0 = g_0 V, \tag{18}
\]

where \( g_0 \) is given by Eq. (10) and

\[
I_{IN} = \frac{g_S}{G_0} \sum_{M,M',a} i_{-}(\Delta_{M,M'} + eV) \left| \mathbf{S}_{a,TS}^{M,M'} \right|^2 P_M(V), \quad \tag{19}
\]

where

\[
\mathbf{S}_{a,\eta,\eta'}^{M,M'} = \frac{1}{\chi} \sum_i v_i(i)v_i(i')|M|S_a(i)|M'|. \tag{20}
\]

Here we have introduced the current associated to a single channel with energy \( \Delta_{M,M'} = E_M - E_{M'} \), and bias \( V \)

\[
i_{\pm}(\Delta + eV) = \frac{G_0}{e} \left( \mathcal{G}(\Delta + eV) \pm \mathcal{G}(\Delta - eV) \right), \tag{21}
\]

with \( \mathcal{G}(\omega) \equiv \omega \left( 1 - e^{-\beta \omega} \right)^{-1} \). The curve \( i_{-} \), is odd in the bias, whereas \( i_{+} \), relevant in the case of magnetic tips discussed below, is even. In contrast, \( dI_{-}/dV \) is even and \( dI_{+}/dV \) is odd. In this non-magnetic tip case, the elastic current provides no information about the spin state whatsoever. In contrast, the inelastic steps in conductance arise from Eq. (19) and permit to extract information about the spin transition energies, \( \Delta_{M,M'} \) and spin matrix elements \( \mathbf{S}_{a,TS}^{M,M'} \). The basic effects of the elastic and inelastic terms in the conductance can be understood in terms of an equivalent electric circuit schematically shown in Fig. 1(c) and (d). For low enough voltage, the only channels that can conduct current are the elastic ones, while the inelastic channels remains close. In this situation the (inelastic) switch is open. When the voltage is increased such as inelastic channels are open (switch is closed), these new channels contributes to the current, leading to a smaller resistance, see Fig. 1(d).

2. Current for magnetic tips

In the case of a magnetic tip, the current has 3 contributions, \( I = I_0 + I_{MR} + I_{IN} \). This result is different from the non-magnetic case on two counts. First, the elastic case has a magnetoresistive term, so that current is now proportional to the relative orientation of the average adatom spin and the magnetic moment in the tip \( \vec{a} \):

\[
I_0 + I_{MR} = g_0 \left[ 1 + 2\zeta \langle \mathbf{S}_{z,TS} \rangle P_T \right] V, \tag{22}
\]

where

\[
\langle \mathbf{S}_{z,TS} \rangle = \sum_{M,i} P_M(V) v_T(i)v_S(i)|M|S_a(i)|M| \tag{23}
\]

is the average magnetization along the \( z \) axis, that we take parallel to the magnetic moment of the tip. As we show both below and in Ref. 23, both \( P_M(V) \) and the average atom magnetization depend on voltage. Importantly, the magnetoresistive contribution to the elastic current makes it possible to track changes in the single atom magnetization experimentally.

The second difference with the non-magnetic tip arises in the inelastic current, which is now given by the expression\(^{25,29}\)

\[
I_{IN} = \frac{g_S}{G_0} \sum_{M,M'} \left[ i_{-}(\Delta_{M,M'} + eV) \sum_a \left| \mathbf{S}_{a,TS}^{M,M'} \right|^2 \right. \tag{24}
\]

\[
\left. + P_T i_{+}(\Delta_{M,M'} + eV)\mathbf{\Xi}_{xy}(M,M') \right] P_M(V).
\]

The new term in the second line involves the matrix elements

\[
\mathbf{\Xi}_{xy}(M,M') = 2\text{Im} \left[ \mathbf{S}_{x,TS}^{M,M'} \mathbf{S}_{y,TS}^{M,M'} \right]. \tag{25}
\]

As opposed to the standard inelastic current [Eq. (19)], which gives rise to steps of equal height for positive and
negative bias, the $\mathcal{P}_T$ dependent term of the inelastic conductance, proportional to $i_+$, yields steps at the excitation energies of opposite sign as the polarity of the bias is reversed. Both the elastic and inelastic term proportional to $\mathcal{P}_T$ can produce a $dI/dV$ which is not an even function of bias.

### III. NON MAGNETIC TIP

In this section analyze the implications of a non-equilibrium population distribution when a finite bias is applied between tip and surface. These effects will be more relevant when the current through the system increases (by increasing the coupling to the electrodes). Next, we will study these effects in three different systems: the Mn monomer, Sec. IIIA, the Mn dimer, Sec. IIIB both deposited on a Cu$_2$N surface and the iron Phthalocyanine molecule, FePc, deposited on an oxidized Cu(1110) surface, Sec. IIICC

#### A. Mn monomer

Let us consider first the case of a single Mn adatom in Cu$_2$N, which has been widely studied experimentally$^{2-27}$ and theoretically$^{22,23,37,38,42,45}$ The spin of the Mn atom in this environment is $S = 5/2$. The parameters of the single ion spin Hamiltonian have been determined experimentally to be $D = -0.039$ meV, $E = 0.007$ meV$^{10}$ and $g = 1.982$. Since $E \ll |D|$ we can limit our qualitative discussion to the case $E = 0$, so that the eigenstates of $\mathcal{H}_{\text{Spin}}$ are also eigenstates of $S_z$ (numerical simulations will be done with $E = 0.007$ meV and do not change qualitatively). In the absence of applied magnetic field and at temperatures much smaller than the zero field splitting, $|D|$, the equilibrium distribution is such that the two ground states, $S_z = \pm 5/2$, are equally likely and the average magnetization is zero. At an energy of $|D|$ above the ground state level, we find a couple of degenerate excited states, with $S_z = \pm 3/2$. Finally, the two states with $S_z = \pm 1/2$ are found at $6|D|$.

From the experiments, performed at low current$^9$ the experimental $dI/dV$ lineshape is piecewise constant with two steps symmetrically located $eV = \pm 4D$. This is accounted for by the equilibrium theory.$^{22}$ As we show in Fig. 2 and also in our previous work,$^{22}$ non-equilibrium effects modify the $dI/dV$ lineshape. In particular, the $dI/dV$ curve is not flat after the inelastic step and it has a small decay for $|eV|$ larger than the inelastic threshold. This non-equilibrium effect has been already observed experimentally$^{11,47}$ and theoretically$^{22}$ with a smaller tip-atom coupling (smaller $v_T$).

The non-monotonic $dI/dV$ can be explained as follows. As the bias goes across the inelastic threshold, $|eV| = 4|D|$, there is a population transfer from the ground state doublet ($S_z = \pm 5/2$) to the first excited state doublet $S_z = \pm 3/2$. This can be seen in Fig. 2(b). As soon as the population transfer to the first excited doublet takes place, a second inelastic channel opens: the transition from the first to the second excited state doublet ($S_z = \pm 1/2$, whose energy is 2|D|, smaller than the first step). It turns out the intensity of the primary inelastic step ($\Delta = 4|D|$), given by the matrix element $|\langle \pm 5/2 | S_z | \pm 3/2 \rangle|^2$, is larger than the intensity of the secondary transition ($\Delta = 2|D|$). Thus, the depletion of the primary transition in favor of the secondary one results in a decrease of the conductance. In the case of FePc molecules, discussed below, the secondary transition is stronger than the first one, resulting in an increase of the conductance after the first step.

The non-equilibrium occupations can be understood as the balance between two driving forces. Spin-flip assisted tunneling events heat the atomic spin, delivering energy...
FIG. 4: (a) Energy spectra corresponding to Hamiltonian for a Mn dimer over a Cu$_2$N surface versus applied magnetic field. Spectrum is referred to the ground state energy and given in units of the exchange coupling ($J = 5.9$ meV). The magnetic field is applied in the surface plane forming a 55\(^\circ\) angle with the Cu-N direction.

of the order of $eV$ at a pace set by the inelastic current. The steady state is reached when the heating power is exactly compensated by dissipation. The later occurs via atomic spin relaxation due to exchange coupling to the tip and surface electrons. This process is enabled even at zero bias. Interestingly, the steady state occupations can differ enormously from the zero bias thermal equilibrium. At $eV = 2$meV, the occupation of the ground state doublet is half of the one in equilibrium and barely twice the one of the higher energy spin levels, which are almost empty at zero bias.

The inverse of the lifetimes of the two competing processes are shown in Fig. 4 There we show the relaxation rate $1/T_1$ of a magnetic spin state, i.e. $S_z = +5/2$, as a function of $V$. When the tip is fully decoupled (no current through the system, $R = 0$), the spin relaxes in a time scale $T_1$ which is independent of the applied bias. For a small coupling, Fig. 4(a), the relaxation rate increases by several orders of magnitude when the bias is increased. This effect is even more dramatic when the ratio $r$ approaches 1 [$R = 1/2$, see Fig. 4(b)]. In the weak coupling curve we can easily see the crossover from the equilibrium regime to low bias, where $T_1 < < T_q$, to the non-equilibrium regime, for which $T_1 > > T_q$. In the other case the crossover occurs at a much lower voltage. To plot these curves we take a zero bias conductance $\sigma_0 = 0.75\mu S$ for the $v_T = 1$ case.

From the discussion above, the non-monotonic lineshape observed for the Mn monomer is related to non-equilibrium effects. Interestingly, correlation Kondo-like effects could also modify the lineshape. Given the fact that Kondo effect occurs in the case of a Cobalt atom deposited in the same surface, this type of effect can not be ruled out in the Mn monomer. In contrast, the Mn dimer has a $S = 0$ ground state and provides an ideal system to test the non-equilibrium physics.

The Mn dimer was studied experimentally under low current conditions by Hirjibehedin et al. and more recently, under high current conditions by Loth et al. They have observed a dramatic modification of the lineshape, which can be accounted for by our theory, as we show here. The Mn-Mn exchange interaction in this system is antiferromagnetic. The fitting of the experimental results to the Hamiltonian model, Eq. 6, gives a $J_{1,2} = J = 5.9$, while $D$, $E$ and $g$ are kept as for the monomer.

Fig. 5 shows the lowest energy spectra of the Mn dimer. Since $J >> |D|$, $E$, the total spin $S$ is a good quantum number at zero order in $|D|/J$. Thus, the ground state is $S = 0$, the first excited state $S = 1$ and energy $J$, the second $S = 2$ and 3 energy $3J$ and the third $S = 3$ and energy $6J$, all energies measured with respect to that of the ground state. The $2S + 1$ degeneracy of the $S > 0$ multiplets is weakly lifted by the small anisotropy terms $D$ and $E$. The allowed transitions induced by the exchange coupling, when the tip is more coupled to one of the two atoms, satisfy $\Delta S = \pm 1$. The lowest energy transitions are marked in Fig. 4 with vertical arrows at

Fig. 5: $dI/dV$ curve for the Mn dimer over a Cu$_2$N surface proved with a non-polarized tip. Each panel corresponds to a pair of $\{v_T(1), v_T(2)\}$ values: (a) $\{2, 1.2\}$, (b) $\{0.4, 0.1\}$ and (d) $\{0.01, 0.001\}$. $T = 0.6K$, $\zeta = 1$, $v_S(i) = 0.25$.

B. Dimer

1. Non equilibrium effects
energies $\delta_i$, with $i = 1, 2, 3$.

The experimental results of the IETS show very different profiles as the current through the system is changed. For low currents only the transition at energy $\delta_1 \approx J$ is observed and flat plateaus appear in the $dI/dV$ spectra before and after the inelastic step. This primary step corresponds to the transition from the $S = 0$ ground state to the first excited state $S = 1$. As the current is increased, by reducing the tip-atom distance, additional steps appear at higher energies, corresponding to the transitions between the $S = 1$ and $S = 2$, and the $S = 2$ and $S = 3$ states, with energies $\delta_2 \approx 2J$ and $\delta_3 \approx 3J$. In addition, the $dI/dV$ line shapes are not flat away from the steps either. These results are reproduced by our non-equilibrium theory. Fig. 3 shows the theoretical $dI/dV$ curve for three different couplings with the tip. When the tip is weakly coupled to the chain, Fig. 3(a), the step corresponding to the $S = 0 \rightarrow S = 1$ is clearly visible, while excitations from the $S = 1 \rightarrow S = 2$ are quenched since the $S = 1$ is only slightly populated. When the coupling $v_T$ is increased (higher current), transitions $S = 1 \rightarrow S = 2$ and $S = 2 \rightarrow S = 3$ become possible for bias $|eV| > 2J$ and $|eV| > 3J$ respectively (see Fig. 3(b)). The new transitions are possible at high current due to a significant induced occupation of the excited states $S = 1$ and $S = 2$ in the Mn dimer. In contrast with the Mn monomer, the the excited state spin flip transitions energies $\delta_2$ and $\delta_3$ are larger than the primary spin transition, resulting in new steps in the spectra. These experimental results, together with the theoretical interpretation, provide strong evidence of the capability of the STM current to drive the spins of the magnetic adatoms.

2. The case of symmetric coupling

Whereas the results above are in very good agreement with the experimental data, it is worth pointing out that this is only so if we assume that the exchange assisted tunneling is stronger through one of the atoms. However, it vanishes identically in the symmetric coupling case, $v_T(1) = v_T(2)$. In Fig. 3 we plot the height of the inelastic step, given by $A_{S \rightarrow T} = \sum \delta S_{a,T}^M |S_{a,T}^{G,M'}|^2$, as a function of the lateral position of the tip across the dimer axis, as modeled by the ratio $v_T(1)/v_T(2)$. The inelastic step cancels identically when the tip is in the middle. This prediction of the model is at odds with unpublished experimental data, which do not show a strong dependence of the inelastic current as the tip is moved along the Mn dimer axis. From the theoretical point of view, the cancellation of the exchange assisted tunneling in the case of the Mn dimer symmetrically coupled to the tip arises from the fact that, in this particular case, the operator in the transition matrix element is the total spin of the dimer, and then the eigenstates of $S^2$ and $S_z$ are also eigenstates of $V$. As a result, the coupling Hamiltonian is diagonal, and no transitions are possible. Notice that this problem is specific of the dimer. In the case of the monomer the observed spin transitions occur within states with the same $S = 5/2$. In the case of the trimer and longer chains the tip can not be coupled identically to all the atoms and the theory accounts for the data.

There are several spin interactions other than the interatomic exchange that break the spin rotational invariance and could, in principle, solve the problem: the single ion anisotropy terms, $D$ and $E$, the hyperfine coupling with the nuclear spin of the Mn, $I = 5/2$, and the direct magnetic dipolar coupling. We have included them in our calculations, but they are much weaker than the dominant exchange, so that they do not change qualitatively the curve. Thus, even in spite of the apparent success of the perturbative approach using Eq. (1), this particular result indicates the presence of additional terms in the Hamiltonian or the need to go beyond lowest order in perturbation theory. Further work, going beyond the phenomenological theory is under way.

C. Magnetic molecules

As a final example of our non-equilibrium theory with non-magnetic electrodes, we consider the case of IETS through Iron Phthalocyanine (FePc) molecules, deposited on oxidized Cu surface. FePc are flat organic molecules with $C_4$ symmetry with a core made of a single $Fe^{2+}$ ion surrounded by 4 Nitrogen atoms embedded in Benzene groups. In gas phase, the crystal field of the ligands is high enough as to reduce the spin of $Fe^{2+}$ from $S = 2$ (high spin) to $S = 1$ (intermediate spin). Because of the $C_4$ symmetry of the gas phase, the single spin Hamiltonian of the molecule has $E = 0$.

According to the IETS data, the symmetry is reduced when deposited on the oxidized surface. In particular, two adsorbed states ($\alpha$ and $\beta$) were experimentally observed with different spin excitations. In both cases the spin excitations of the FePc could be assigned to $S =$

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6}
\caption{Transition amplitude $A_{S \rightarrow T}$ versus the ratio $v_T(1)/v_T(2)$. $T = 0.6K$, $\zeta = 1$, $v_S(i) = 0.25$.}
\end{figure}
doublet with energy $-E_{At}$ finite $S$ and anti-bonding combination of the states.

For the experimental differential conductance curves, varied in the 1 but the anisotropy parameters, determined from the experimental differential conductance curves, varied in the two cases. For the $\alpha$ ($\beta$) configuration, $D = -3.8 \pm 0.04$ meV ($D = -6.9 \pm 0.04$ meV), $E = 1.0 \pm 0.01$ meV ($E = 2.1 \pm 0.04$ meV) and $g = 2.3 \pm 0.02$ ($g = 2.4 \pm 0.05$). The origin of this drastic change in anisotropy deserves further theory work.

The $S = 1$ single spin model can be solved analytically (see for instance appendix in Ref. [56]). With $D < 0$, and $E = 0$, the ground state would be the $S_z = \pm 1$ doublet with energy $-D$ below the $S_z = 0$ excited state. At finite $E$ the ground state doublet splits, in bonding and anti-bonding combination of the states $S_z = \pm 1$. The splitting is $2E$. Thus, there are two spin transitions. The low energy one, with $\Delta = 2E$ and $\Delta S_z = 0$, and the high energy one, with energy $|D| + E$ and $\Delta S_z = \pm 1$. The magnetic field along the $z$ axis competes with the $E$ induced splitting of the ground state. As $B$ increases, the $E$ induced mixing of the $S_z = \pm 1$ components decreases, and so it does the primary transition, which occurs via $\Delta S_z = 0$ events.

Fig. 7 shows our non-equilibrium theoretical $dI/dV$ results using the values of $D$ and $E$ given above. Our theory reproduces not only the evolution of the steps with the magnetic field, but also the mild non-equilibrium features reported in Ref. [15]. After the first (second) step the conductance has a small positive (negative) slope. In contrast, the equilibrium theory\cite{56} yields flat steps. The sign of the non-equilibrium slopes depends on the relative value of the inelastic channel strengths of the primary and secondary transitions. At $eV = 2E$, when the first excited state is populated, the secondary transition, with energy $|D| - E$ becomes possible, at finite temperature. Since this transition between excited states has a larger quantum yield, the overall conductance increases. The opposite scenario occurs in the second step.

IV. SPIN POLARIZED TIP

The results of the previous section give very strong support to the notion that tunneling electrons can drive the spin of the magnetic adatoms far from equilibrium. Since we have been considering spin unpolarized tunneling electrons, these non-equilibrium effects can not result in a net spin transfer. From the theory standpoint, this should change dramatically in the case of spin-polarized transport electrons. As it was shown in a seminal work by Slonczewski,\cite{58} the back action of transport electrons on a magnetic moment can be used to rotate the magnetization direction. This effect, known as spin-transfer torque, have been observed in nano-pillars of tens of nanometers\cite{58} down to tiny nanomagnets made of 100 atoms\cite{58} but still in the semiclassical domain. In a previous paper\cite{58} we modeled the spin dynamics of a single Mn atom under the influence of spin polarized current. We found that if the tip was spin polarized, the spin polarized current would result in a net spin magnetization of the magnetic adatom whose orientation relative to the tip moment would depend on the polarity of the bias, quite in agreement with the macroscopic spin transfer torque. In parallel to our work, S. Loth et. al. demonstrated experimentally the single atom spin transfer.

In our work in Ref. [25] the origin of the tip magnetization was ferromagnetic order. In the experiment of Loth et al., the spin polarized current is achieved by sticking a single Mn atom into the tip and applying a magnetic field to freeze its spin fluctuations. The external magnetic field affects also the surface atom. The very different role played by the Mn in the tip and the Mn in the surface underlines the important role played by spin isolation. Whereas it is still possible to model the spin of the Mn in the surface as a quantized spin weakly coupled to the surface electrons, this picture seems to break down for the case of the Mn in the tip, due to a combination of charge transfer, Kondo coupling and very reduced spin lifetime. Thus, the Mn in the tip acts as a spin filter for the transport electrons. Whereas this picture works qualitatively, we believe this issue deserves further work.\cite{25}

A. Current induced spin switching

The flow of spin polarized current through a single magnetic atom is expected to result in a transfer of a net spin into the atom. In the case of a single or a few magnetic atoms, where time reversal symmetry is not spontaneously broken at zero magnetic field, the equilib-
rium occupation of states with opposite $S_z$ is the same, resulting in a null average magnetization. Spin polarized current changes this situation via spin-flip inelastic tunneling. The mechanism is the following. The dominant inelastic transitions in the case of the Mn monomer are:

- Spin increasing (SI) transition, for which the Mn spin goes from $S_z = -5/2$ to $S_z = -3/2$ and the transport electron goes from the high energy electrode with spin up to the low energy electrode with spin down.

- Spin decreasing (SD) transition, for which the Mn spin goes from $S_z = +5/2$ to $S_z = +3/2$ and the transport electron goes from the high energy electrode with spin down to the low energy electrode with spin up.

In the case of spin unpolarized current, these two processes are equally likely and result in the depletion of the two states of the ground state doublet shown in Fig. 2(b).

In the case of a spin polarized tip, the two processes are no longer equally likely, resulting in a net spin transfer from the spin current to the atomic spin. Let us consider the case where there are more down than up electrons in the tip. This means negative spin tip average (i.e., $P_T < 0$) and positive tip magnetization. When electrons go from the tip to the surface ($V > 0$), the SD processes are dominant, as a result of which the positive $S_z$ states are depleted and a negative $⟨S_z⟩$ is expected. Thus, we expect that at positive bias (electrons going from tip to surface) the current co-polarizes the spin of the atom.

We now consider electrons going from surface to tip. Since the density of states of spin down electrons is higher, the SI process is now more likely than the ST one. As a result, the negative $S_z$ states should be depleted, resulting in a positive atomic spin. Thus, we expect that $V < 0$ (electrons going from surface to tip) the current counter-polarizes the spin of the atom.

Our simulations confirm this scenario. We only consider the simplest case in which the tip polarization is assumed parallel to the Mn easy axis perpendicular to the Cu$_2$N surface. We consider first the case of zero magnetic field. We choose $P_T < 0$, because is convenient for the discussion at finite positive field below. In Fig. 8(a) we show the average atomic spin moment along the easy axis, as a function of the applied bias. It vanishes at zero bias, reflecting the absence of spontaneous time reversal symmetry breaking of such a small system. At finite bias the magnetic moment aligns with that of the tip when electrons flow from tip to surface ($V > 0$), and do exactly the opposite when the electrons flow from the surface to the tip ($V < 0$). Interestingly, the average atomic spin is finite even when $|eV| < 4|D|$, the excitation energy. This is due to the existence of thermally excited quasiparticles. However, the time necessary to drive the spin of the atom increases exponentially when for $|eV| < 4|D|$.

The average atomic spin increases both with the applied voltage and the spin polarization of the tip, as given by $P_T$. The effect is null at $P_T = 0$, as it should, and it is maximal for half-metallic tips $P_T = ±1$. For a fixed tip polarization the effect saturates at a certain voltage. Interestingly, the saturation magnetic moment depends only on the value of $P_T$ and is quite independent of temperature and other parameters in the calculation. We discuss this universal behavior in Sec. IV C. The non-zero atomic spin polarization reflects the bias induced breaking asymmetry of the steady state occupation of the two states of the ground state doublet $S_z = ±5/2$, as shown in Fig. 8(c). Notice the striking difference with the case of equilibrium, for which the occupations of these two degenerate states are identical. The steady state is reached thanks to the competition between bias induced spin transfer and exchange induced spin relaxation discussed in the previous section.

B. Effects of spin polarization on transport

Importantly, the current induced polarization of the atomic spin can be detected through its influence on the conductance of the system. The simplest effect comes...
from the elastic magnetoresponse: conductance is larger when spin polarization of tip and magnetic atom are parallel. In the case discussed above, this results in a larger conductance at large positive bias than at large negative bias. At small bias, there are several conflicting effects. For simplicity let us consider the case of a single magnetic adatom. We can write the differential conductance as

\[ G = G_1 + G_2 + G_3 + G_4 \]  

(26)

where the different terms are obtained by deriving \( I \) in Eqs. (22-24) with respect to bias and are shown in Fig. 9(b):

\[ G_1 = g_0 (1 + 2\zeta(S_z)P_T), \]

\[ G_2 = 2g_0V\zeta P_T \frac{d(S_z)}{dV}, \]

\[ G_3 = \frac{gS}{G_0} \sum_{M,M'} P_M(V) \left[ \sum_a \left| S_a^{M,M'} \right|^2 \right. \]

\[ \times \left. i'_-(\Delta_{M,M'} + eV) + P_T eV \right], \]

\[ G_4 = \frac{gS}{G_0} \sum_{M,M'} \left[ i_-(\Delta_{M,M'} + eV) \sum_a \left| S_a^{M,M'} \right|^2 \right. \]

\[ \left. + P_T i_+(\Delta_{M,M'} + eV) \right] \frac{dP_M(V)}{dV}, \]  

(27)

with \( i'_\pm \equiv d\pm/dV \). \( \Xi_{xy}(M,M') \) is defined as in Eq. (26) but with without the weighting factors. \( G_1 \) and \( G_2 \) (\( G_3 \) and \( G_4 \)) correspond to the elastic (inelastic) contribution of the current. \( G_1 \) gives the dominant magnetoresistive contribution at large bias discussed above. \( G_2 \) gives a smaller contribution associated to the change of the average adatom spin as a function of bias. This term is responsible of the non-monotonic decay of the conductance after the pronounced change induced by \( G_1 \). In the extreme case shown in Fig. 9, corresponding to a half metallic tip, \( G_1 \) is the dominant contribution. Finally, the two inelastic contributions, \( G_3 \) and \( G_4 \), peak close to the transition energies \( \pm 4|D| \). \( G_3 \) corresponds to the inelastic conductance, as if the occupations \( P_M(V) \) where bias independent, and \( G_4 \) is the contribution coming from the fact that \( P_M \) do depend on the bias. In turn, both \( G_3 \) and \( G_4 \) have two contributions, one that is present for non-magnetic tip and another one proportional to the tip spin polarization \( P_T \).

Experimentally it might be hard to disentangle \( G_2 \), \( G_3 \) and \( G_4 \), but not \( G_1 \) which provides a direct way to quantify the atomic spin at large bias, denoted by \( \pm V_\infty \):

\[ \frac{G_1(+V_\infty) - G_1(-V_\infty)}{G(V = 0)} = 4\zeta P_T \langle S_z \rangle (\pm V_\infty) \]  

(28)

where \( G(V = 0) = g_0 \) is the zero bias conductance and we have used the fact that, at zero magnetic field, \( \langle S_z \rangle (\pm V_\infty) = -\langle S_z \rangle (-V_\infty) \). Since \( G_1 \) can be the dominant contribution, replacing \( G_1 \) by the total \( G \) in equation (28) can give a rough estimate of the quantities in the right hand side of that equation.

1. Finite magnetic field

We now analyze how the magnetic field used in the experimental setup changes the picture discussed above. In these experiments, the tip polarization is achieved by attaching a single Mn atom at the tip apex and applying a very intense magnetic field (7T) perpendicular to the surface. In the experiments with spin polarized tips, from the elastic magnetoresponse: conductance is larger when spin polarization of tip and magnetic atom are parallel. In the case discussed above, this results in a larger conductance at large positive bias than at large negative bias. At small bias, there are several competing effects. For simplicity let us consider the case of a single magnetic adatom. We can write the differential conductance as

\[ G = G_1 + G_2 + G_3 + G_4 \]  

(26)

where the different terms are obtained by deriving \( I \) in Eqs. (22-24) with respect to bias and are shown in Fig. 9(b):

\[ G_1 = g_0 (1 + 2\zeta(S_z)P_T), \]

\[ G_2 = 2g_0V\zeta P_T \frac{d(S_z)}{dV}, \]

\[ G_3 = \frac{gS}{G_0} \sum_{M,M'} P_M(V) \left[ \sum_a \left| S_a^{M,M'} \right|^2 \right. \]

\[ \times \left. i'_-(\Delta_{M,M'} + eV) + P_T eV \right], \]

\[ G_4 = \frac{gS}{G_0} \sum_{M,M'} \left[ i_-(\Delta_{M,M'} + eV) \sum_a \left| S_a^{M,M'} \right|^2 \right. \]

\[ \left. + P_T i_+(\Delta_{M,M'} + eV) \right] \frac{dP_M(V)}{dV}, \]  

(27)

with \( i'_\pm \equiv d\pm/dV \). \( \Xi_{xy}(M,M') \) is defined as in Eq. (26) but with without the weighting factors. \( G_1 \) and \( G_2 \) (\( G_3 \) and \( G_4 \)) correspond to the elastic (inelastic) contribution of the current. \( G_1 \) gives the dominant magnetoresistive contribution at large bias discussed above. \( G_2 \) gives a smaller contribution associated to the change of the average adatom spin as a function of bias. This term is responsible of the non-monotonic decay of the conductance after the pronounced change induced by \( G_1 \). In the extreme case shown in Fig. 9, corresponding to a half metallic tip, \( G_1 \) is the dominant contribution. Finally, the two inelastic contributions, \( G_3 \) and \( G_4 \), peak close to the transition energies \( \pm 4|D| \). \( G_3 \) corresponds to the inelastic conductance, as if the occupations \( P_M(V) \) where bias independent, and \( G_4 \) is the contribution coming from the fact that \( P_M \) do depend on the bias. In turn, both \( G_3 \) and \( G_4 \) have two contributions, one that is present for non-magnetic tip and another one proportional to the tip spin polarization \( P_T \).

Experimentally it might be hard to disentangle \( G_2 \), \( G_3 \) and \( G_4 \), but not \( G_1 \) which provides a direct way to quantify the atomic spin at large bias, denoted by \( \pm V_\infty \):

\[ \frac{G_1(+V_\infty) - G_1(-V_\infty)}{G(V = 0)} = 4\zeta P_T \langle S_z \rangle (\pm V_\infty) \]  

(28)

where \( G(V = 0) = g_0 \) is the zero bias conductance and we have used the fact that, at zero magnetic field, \( \langle S_z \rangle (\pm V_\infty) = -\langle S_z \rangle (-V_\infty) \). Since \( G_1 \) can be the dominant contribution, replacing \( G_1 \) by the total \( G \) in
the $dI/dV$ curve changes radically from low current to high current. In both cases, the $dI/dV$ curves are not even with respect to bias, as expected from the discussion in the previous section. However, the lineshapes differ significantly from the ones described in our previous work\textsuperscript{22} and in the previous section (Fig. 9). The origin of this discrepancy can be traced back to the effect of the magnetic field on the surface adatom, absent in our previous calculation. Since $k_{b}T << g_{\mu}B$, the applied field already polarizes completely the atomic spin at zero bias. In particular, this means that the occupation of the atomic spin state $S_{z} = -5/2$ is very close to 1 and at zero bias the average spin of the adatom is finite, negative, and parallel to the tip spin polarization, which maximizes the $G_{1}$ term in the conductance.

When bias is applied, the occupation of the ground state $S_{z} = -5/2$ is depleted, which degrades the elastic contributions to the conductance. This is reflected in the evolution of the average atomic spin as a function of bias, shown in Fig. 11 for two cases: low current ($v_{T} = 0.08$, $\zeta = 0.44$) and high current ($v_{T} = 0.7$, $\zeta = 0.5$). The values of $v_{T}$ and $\zeta$, as well as the value of $\mathcal{P}_{T}$ = 0.31, where chosen to reproduce the experimental conductance data of Loth et al.\textsuperscript{27} It is apparent that in both cases the depletion of the average spin is larger for negative bias, for which transport electrons tend to counter-polarize the tip, than for positive bias, for which the depletion can be interpreted as non-equilibrium heating of the atomic spin. In the large current case, the current is able to reverse the average atomic spin from the equilibrium $-2.5$ at zero bias to $+1$ at -20 mV. The corresponding change in the elastic components of conductance, $G_{1}$ and $G_{2}$, due to spin contrast, is shown in figures (11b) for low current and in (12b) for high current. In the high current case, these contribution are dominant, and explain the experimental observation that the conductance is smaller at negative voltage. Thus, in the high current case the fact that $G(20) << G(-20)$ can be linked to the reversal of the atomic spin at negative bias and the resulting reduction of the conductance, compared to zero bias.

In the low current case the small changes in the atomic spin make $G_{1}$ and $G_{2}$, the elastic magnetoresistive contributions, quite independent of bias, so that change as a function bias so that they simply offset the total conductance. This results in a conductance which is minimal at zero bias and the larger at large negative bias than at large positive bias. As opposed to the high current case, where the asymmetry is dominated by $G_{1}$ and $G_{2}$, reflecting the reversal of the average atomic spin, in the low current case the asymmetry comes mostly from the asymmetry in the inelastic step $G_{3}$, associated to the term proportional to $\mathcal{P}_{T}$.

C. Universal magnetization profile

In Fig. 8(c) we plot the saturation magnetization, reached after a large enough bias is applied, as a function of tip polarization. We have verified that this curve turns out to be independent of all transport parameters, $\zeta$, $r$, $v_{\eta}$, and it depends only on the spin of the magnetic atom $S$ and anisotropy parameters $D$ and $E$. In fact, it does not depend either on the temperature, as long as our approach of neglecting the phonon contribution remains valid. When combined with eq. (28), this could be used to determine the tip polarization.

The universality of the saturation atomic magnetization comes from the fact that, at large bias, $i_{\pm}(\Delta_{M,M'} + \epsilon V) \approx \epsilon V$ so that the equation (28) for the rates can be simplified to:

$$W_{M,M'} \propto V \left[ |S^{M,M'}_{\downarrow}|^{2} + \frac{\mathcal{P}_{T}}{\rho_{T}} |S^{M,M'}_{\uparrow}|^{2} + \frac{\mathcal{P}_{T}}{\rho_{T}} |S^{M,M'}_{\uparrow}\downarrow|^{2} \right].$$

(29)

Making use of Eq. (29), the master equation for the

![FIG. 11: (Color online) (a) Differential conductance for $B = 7T$ versus applied bias for the low current regime. (b) Each of the contributions to the $dI/dV$: $G_{1}$ (thin-black line), $G_{2}$ (thick-blue line), $G_{3}$ (thin-dashed line) and $G_{2}$ (thick-green line) versus applied bias. $T = 0.5K$, $\zeta = 0.5$ and $v_{T} = 0.7$. More detail in the text.]

![FIG. 12: (Color online) (a) Differential conductance for $B = 7T$ versus applied bias for the high current regime. (b) Each of the contributions to the $dI/dV$: $G_{1}$ (thin-black line), $G_{2}$ (thick-blue line), $G_{3}$ (thin-dashed line) and $G_{2}$ (thick-green line) versus applied bias. $T = 0.5K$, $\zeta = 0.5$ and $v_{T} = 0.7$. More detail in the text.]

The $G_{1}$, $G_{2}$, and $G_{3}$ contributions, quite independent of bias, so that they simply offset the total conductance. This results in a conductance which is minimal at zero bias and the larger at large negative bias than at large positive bias. As opposed to the high current case, where the asymmetry is dominated by $G_{1}$ and $G_{2}$, reflecting the reversal of the average atomic spin, in the low current case the asymmetry comes mostly from the asymmetry in the inelastic step $G_{3}$, associated to the term proportional to $\mathcal{P}_{T}$.
occupation of the spin states in steady state reads
\[
\sum_{M'} \left[ |S_{z}^{M,M'}|^2 + \frac{P_T + 1}{2} |S_{S}^{M,M'}|^2 + \frac{1 - P_T}{2} |S_{N}^{M,M'}|^2 \right] \times (P_{M'} - P_{M}) = 0, \quad \forall M,
\]
where the prime indicates sum is done over \( M' \neq M \).

Eq. (30) shows that, in the large bias limit, the atomic spin steady state occupations \( P_{M} \), and consequently the average magnetization \( \langle S_{z} \rangle \), depend only on the matrix elements of the spin operators, and the polarization of the tip, and do not depend on the coupling strength to the tip and surface.

V. SUMMARY AND CONCLUSIONS

We have studied the mutual influence of non-equilibrium transport electrons and the spin of one and two magnetic adatoms in STM configuration. Our results indicate that non-equilibrium effects are essential to understand present IETS STM spectra of magnetic adatoms. Our theory is able to describe correctly the experimental observations of IETS on single Mn atoms, both with non-magnetic and magnetic tips, on Mn dimers at low and high current, and on FePc molecules. Our theory is based on a phenomenological spin model to describe both the atomic spin states and their coupling to the transport electrons. Current is calculated to lowest order in the tunneling Hamiltonian and depends on the occupation of the spin states \( P_{M} \). The spin dynamics is described with a master equation for the \( P_{M} \) that includes the effect of carrier induced spin relaxation and the spin pumping due inelastic spin-flip assisted tunneling.

When the time elapsed between inelastic spin flip events, \( T_{q} \) is much longer than the atomic spin relaxation time, \( T_{1} \), the atomic spin remains in equilibrium and \( P_{M} \) does not depend on bias. In that limit, the differential conductance \( dI/dV \) is piecewise constant, except for the steps when the bias voltage matches the energy of the spin excitations. When the \( T_{q} \) is comparable or smaller than \( T_{1} \), the occupations of the atomic spin states are driven away from equilibrium and they depend on the bias voltage. Whereas non-monotonic \( dI/dV \) had been already observed experimentally, the recent results reported by Loth et al. have confirmed this scenario by controlling the tip-adatom distance. In addition, the use of spin-polarized tips amplifies the changes in the \( dI/dV \) curves as the conductance is increased.

The results of Loth et al. also indicate that, in the case of magnetic tips, the orientation of the average atomic spin can be switched at will from parallel (\( V > 0 \)) to antiparallel (\( V < 0 \)) with respect to the magnetic tip. The control of the spin of a single atom and a single magnetic molecule had been predicted by theory. The control of atomic spin with non-equilibrium spin polarized carriers is similar to that obtained by optical pumping.

The main conclusions are the following:

1. The dynamics of the atomic spin under the influence of tunneling electrons is governed by two intrinsic time scales, the inelastic transport time \( T_{q} \) and the atomic spin relaxation time \( T_{1} \). When the current induced spin flips occur more often than the time it takes to the atomic spin to relax, i.e., when \( T_{q} < T_{1} \), non-equilibrium effects build-up. This makes the occupation of the spin states different from that of equilibrium.

2. The conductance lineshape is sensitive to the occupation of the atomic spin states. This might be used to perform transport-detected single atom resonance experiments. Our calculations indicate that non-equilibrium effects have been observed in single Mn atoms, in Mn dimers and in FePc molecules.

3. A rough estimate of the quality factor of the spin excitation with energy \( \Delta = \hbar \omega_{1/2} \), defined as \( Q = \omega_{1/2} T_{1} \), can be obtained from the transport experiments. We assume that the current at which the low temperature conductance line shape starts to deviate from a piecewise constant function yields \( T_{q} \approx T_{1} \). Let \( \Delta G_{m} \) and \( V \) be the height and bias of the primary inelastic step. Then, the inelastic current is \( I_{IN} = \Delta G_{m} V = e/T_{q} \). Then we get
\[
\omega_{1/2} T_{1} \approx \frac{G_{m}}{\Delta G}.
\]

4. Spin polarized STM can be used to magnetize the atomic spin both parallel or antiparallel to the magnetic tip moment. When electrons tunnel through the magnetic atom from the magnetic tip to the surface, the atomic is magnetized parallel to the tip. Reversing the bias results in an opposite spin polarization.

5. The bias induced adatom spin polarization results in asymmetric conductance lineshapes due, in most part, to the dependence of conductance on the relative orientation of the adatom and tip magnetizations.

6. The saturation atomic spin magnetization, obtained at large bias, is only a function of the impurity spin, the anisotropy parameters and the polarization of the tip.

Future work should address open problems, like the origin of the spin assisted tunneling Hamiltonian for spin larger than 1/2, the effect of atomic spin coherence, which we have neglected in the master equation and the fact that the observed inelastic steps in the Mn dimer do not depend on the lateral position of the tip, in contrast with our theory.

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Appendix A: Equation for the rates

In this appendix we derive the general expression of the transition rates. Applying the Fermi Golden rule using the tunneling Hamiltonian \( \mathfrak{H} \) as perturbation, one gets

\[
\Gamma_{\eta\eta'}^{\eta\eta'} = \frac{2\pi}{\hbar} \delta(k, E_{\eta} - E_{\eta'} + \hbar \omega)
\times \left| \sum_{\alpha, \sigma} T_{\alpha}^{(a)} \frac{\tau_{\alpha}^{(a)}}{2} S_{a, \eta \eta'}^{M, M'} \right|^2.
\]

(A1)

The modulus square in Eq. (A1) can be expanded to obtain

\[
\sum_{\alpha, \beta, \sigma, \sigma'} T_{\alpha} T_{\beta}^{(a)} \frac{\tau_{\alpha}^{(a)}}{2} S_{\alpha, \eta \eta'}^{M, M'} S_{\beta, \eta \eta'}^{M', M}.
\]

(A2)

Considering the explicit form of the Pauli matrix elements, the sum over \( \sigma \) and \( \sigma' \) can be done, with just a few non-zero contributions. Using the definition of the transition rates \( W_{\eta \eta'}^{\eta \eta'} \), Eq. 7, we obtain after some algebra

\[
W_{\eta \eta'}^{\eta \eta'} = \frac{2\pi T_{0}^2 \chi^2}{\hbar} \mathcal{G}(\Delta_{M, M'} + \mu_{\eta} - \mu_{\eta'}) \Sigma_{M, M'}^{\eta \eta'}
\]

where

\[
\Sigma_{M, M'}^{\eta \eta'} = \frac{1}{4} \delta_{M M'} \left( R^+ (\eta \eta') + 2 \zeta R^- (\eta \eta') \sum_{a} S_{a, \eta \eta'}^{M, M} \right)
+ \zeta^2 \left[ S_{\eta \eta'}^{M, M'}_{\eta \eta'} ^{\eta \eta'} \rho^{\eta \eta'} + S_{\eta \eta'}^{M, M'}_{\eta \eta'} ^{\eta \eta'} \rho^{\eta \eta'} \right]
\]

\[
+ R^+ (\eta \eta') \left| S_{\eta \eta'}^{M, M'}_{\eta \eta'} ^{\eta \eta'} \right|^2.
\]

(A4)

Here we have introduced \( R^\pm (\eta \eta') = \rho^{\eta \eta'} \rho^{\eta \eta'} \pm \rho^{\eta \eta'} \rho^{\eta \eta'} \) and the operators \( S_{\pm} = S_{\pm} \pm i \mu_{\eta} \). Notice that expression (A1) is valid for all states \( M, M' \), in contrast to Eq. (5) of Ref. 25 where only the inelastic matrix elements were explicitly written.

Appendix B: Equations for the current

Here we shall derive expressions (18) and (19). Let us start with the expression for the current, Eq. (16). Dividing the contribution into its elastic and inelastic part, with the help of Eqs. (A3) and (A4), we can write

\[
I_0 + I_{MR} = \frac{2\pi e T_{0}^2 \chi^2 \rho_{S}}{h} \frac{8}{\mathcal{G}(eV) + \mathcal{G}(-eV)},
\]

(B1)

or, using the definition of \( g_0 \) and \( i_+ \)

\[
I_0 + I_{MR} = g_0 \left[ 1 + 2 \zeta (S_{z, T, S}) P_T \right] i_-(eV),
\]

which is the result of Eq. (18). For the inelastic contribution \( (M \neq M') \), the difference \( W_{MM'}^{S T} - W_{MM'}^{T S} \) can be written with the help of Eqs. (A3) and (A4) as

\[
W_{MM'}^{S T} - W_{MM'}^{T S} = \zeta^2 \frac{2\pi T_{0}^2 \chi^2 \rho_{S}}{8h} (i_-(\Delta_{M, M'} + eV)
\times \sum_{a} \left[ S_{a, T, S}^{M, M'} \right] ^2 + \mathcal{P}_{Ti+} (\Delta_{M, M'} + eV)
\times 2 \text{Im} \left[ \sum_{x, y, T, S} S_{x, y, T, S} [S_{y, T, S}^{M, M'}] \right].
\]

Using the definitions of \( g_0 \) and \( \Xi_{xy}(M, M') \), expression (10) is recovered.
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