Efficient Spin Transitions in Inelastic Electron Tunneling Spectroscopy

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The excitation of the spin degrees of freedom of an adsorbed atom by tunneling electrons is computed using strong coupling theory. Recent measurements [Heinrich *et al.*, Science **306**, 466 (2004)] reveal that electron currents in a magnetic system efficiently excite its magnetic moments. Our theory shows that the incoming electron spin strongly couples with that of the adsorbate so that memory of the initial spin state is lost, leading to large excitation efficiencies. First-principles transmissions are evaluated in quantitative agreement with the experiment.

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The way electrons flow at the atomic level has important fundamental and technological implications [1]. Of particular importance is the role of the electron spin in the electron flow and this led to promising new technologies in spintronics [2], to the downsizing of magnetic storage by atomic engineering [3], and to the development of quantum information devices [4]. An important issue is the appearance of inelastic effects where energy is taken from the electron flow into the different degrees of freedom of the system. Inelastic effects provide an analytical tool for the basic interactions at work. Indeed, they are at the core of single atom and molecule spectroscopies [5,6].

Inelastic electron tunneling spectroscopy (IETS) where electrons excite vibrations leading to conductance steps at certain voltage thresholds [5] has been extensively studied in the last years [7–9]. The inelastic change in conductance is within a few percent of the elastic conductance, mainly due the smallness of the electron-vibration coupling [10,11]. Recently, Heinrich *et al.* have developed a spin-resolved spectroscopy using an STM [3,6,12,13]. In magnetic IETS, the tunneling electron yields energy to the spin of an adsorbed magnetic atom allowing it to change its orientation with respect to the substrate. Magnetic transitions in the meV range could be observed in adsorbates partly decoupled from a metal substrate [3,6,12–15].

The experimental observations were first analyzed with an empirical approach in [3] and later, theoretical treatments [16–18] based on a first-order perturbation in the spin-spin interaction were used to justify the empirical approach of [3]. However, perturbation theory is at odds with the experimental observation of extremely large inelastic contributions in the tunneling current, easily dominating over the elastic contribution. A serious consequence of using perturbation theory is that these approaches fail in accounting for the renormalization of the elastic channel (see, for example, Ref. [11]) that is particularly important in this strong coupling regime. Hence, the calculated elastic channel is poorly accounted for or incorrect in the published works [3,17,18]. Additionally, these approaches do not take into account the realistic electronic structure of the studied systems, and consider all incident spin channels on an equal footing which we show to be unrealistic. In this Letter, we develop an all-order parameter-free theory of the magnetic IETS and apply it to the cases of Fe and Mn adsorbates on a CuN monolayer on Cu, experimentally studied in Refs. [3,13].

In magnetic IETS, the initial state of the adsorbate spin is imposed by the anisotropy induced by its environment and by an external magnetic field B. During the very short collisional time between the adsorbate and the tunneling electron, the electron spin couples with the adsorbate spin, forming a transient collisional intermediate, whereas the interaction with the adsorbate environment can be neglected. This sudden switch between different coupling schemes of the adsorbate efficiently induces transitions between magnetic states. This excitation mechanism is not only found in STM-induced spin flip. Similar excitation processes have been shown to be very efficient for spin-forbidden electronic excitations in electron-molecule collisions [19] or in surface processes [20], as well as for rotational IETS [21].

The energy losses associated with the magnetic anisotropy in the presence of a magnetic field, B, have been modeled very efficiently in these systems [3,13] (see, e.g., [22] for a first-principles study):

$$H = g\mu_B \vec{B} \cdot \vec{S} + DS_z^2 + E(S_x^2 - S_y^2). \qquad (1)$$

E and D are two constants describing the effect of the environment on the spin direction. The gyromagnetic factor is g and μ_B the Bohr magneton. $\vec{S}$ is the spin operator of the adsorbate and $S_{x,y,z}$ its projections on Cartesian axes. Equation (1) assumes that one can define a local adsorbate spin interacting with the substrate. Its relevance is assessed by its success in describing the energy levels of the adsorbate as a function of the applied B field. In the present work, we take modeling (1) with the parameters (D and E

parameters, g and spin of the adsorbate) adjusted in [3], which very precisely reproduce the energy positions of the inelastic thresholds and we compute the strength of the transitions between the eigenstates of (1) induced by tunneling electrons. Diagonalization of Hamiltonian (1) yields the various possible ϕ_n states of the adsorbate spin in the system

$$|\phi_n\rangle = \sum_M C_{n,M}|S, M\rangle, \quad (2)$$

where $|S, M\rangle$ are eigenvectors of the $\vec{S}^2$, S_z operators. An electron injected from the STM tip to the adsorbate can cause inelastic transitions between the ϕ_n states, which are recorded in an IETS experiment.

In a first step, we compute the electron transmission through Fe and Mn adatoms on a CuN monolayer on Cu (100) by density functional theory (DFT) with the TRANSIESTA code [23]. Despite the fact that the actual spin state of the atom cannot be taken into account by DFT, these simulations can yield quantitative data in spin transport [24]. We used the generalized gradient approximation (PBE) and a double-zeta local basis set where the contact region is modeled by a 7-atom slab, a CuN layer and a Fe (Mn) atom, a vacuum gap of 5.2 Å and a 5-atom slab with an extra atom for the tip region of the contact. The contact is relaxed using the SIESTA method [25] with atomic forces below 0.04 eV/Å. The transmission is then computed for zero bias voltage, using the bulk Cu unit cell along the [100] direction as the primary unit of the two semi-infinite electrodes. The transmission curve is basically flat on the energy scale of spin excitations, so that simple branching ratios (relative transition strengths) can be used to obtain the values of the elastic and inelastic conductance of the system as a function of the STM bias. On the energy scale relevant for the present magnetic IETS context, the majority spin transmission is 20 times the minority spin one for the Fe junction; see Fig. 1. For the Mn adsorbate, we find a similar result, though with a weaker dominance (factor 5) of the majority channel (Fig. 1).

The branching ratios between elastic and inelastic conductance are determined using the following facts: (i) the rotation of the adsorbate spin, $\vec{S}$, due to the magnetic anisotropy, Eq. (1), is slow compared to the electron-atom collision so that we can use a sudden approximation [26], neglecting the effect of Hamiltonian (1) during the collision. (ii) The spin of the tunneling electron couples to the spin of the atom to define collision channels of total spin $S_T = S + 1/2$ and $S - 1/2$ that are linked to the asymptotic channels of the collision via:

$$|S_T, M_T\rangle = \sum_m \mathrm{CG}_{S_T,M_T,m}|S, M = M_T - m\rangle|1/2, m\rangle, \quad (3)$$

where the kets on the right-hand side correspond to the decoupled spins of the atom and of the tunneling electron.

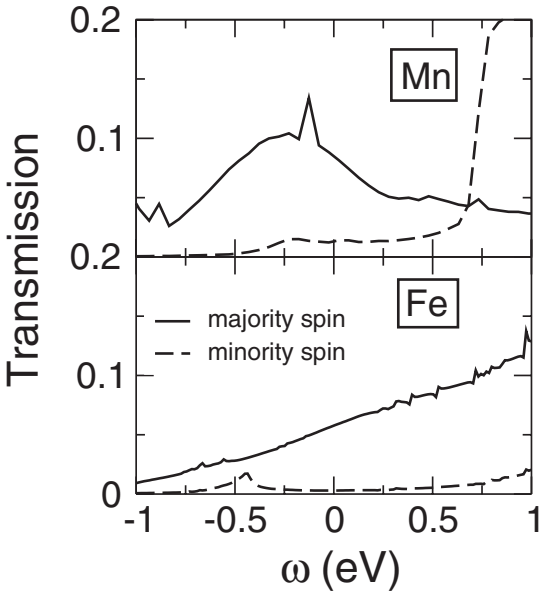

FIG. 1. Electron transmission as a function of electron energy, ω, between an STM tip (an atomic apex on a Cu(100) surface) and a Fe (lower panel) a Mn (upper panel) atom on a CuN monolayer on a Cu(100) electrode. The magnetic atom-apex distance is 5.2 Å in the present calculation. Full line: majority spin and dashed line: minority spin. The applied bias is zero. The wiggles in the transmission are due to the numerical discretization of the continuum states, the transmissions are thoroughly converged as checked by a fourfold increase of the density of states in the Fe case.

m is the projection of the electron spin on the z axis. The CG are Clebsch-Gordan coefficients. From Eqs. (2) and (3), we can express the collision channel states as functions of the initial and final states of the collision:

$$|j\rangle = |S_T, M_T\rangle = \sum_{n,m} A_{j,n,m}|\phi_n\rangle|1/2, m\rangle. \quad (4)$$

It yields the weight of the various anisotropy states in the collision channels associated to the total spin, S_T. (iii) From the DFT result, we only consider the maximum spin intermediate state ($S_T = 5/2$) for the Fe adsorbate and ($S_T = 3$) for Mn adsorbate. (iv) From Eqs. (4), we can derive the amplitude for transitions from $|\phi_n\rangle|1/2, m\rangle$ to $|\phi_{n'}\rangle|1/2, m'\rangle$ through the intermediate j as proportional to the product $A_{j,n,m}A_{j,n',m'}$, leading to the relative excitation probability of the different excited states:

$$W_{n\to n'} = \frac{\sum_{m,m'} \left|\sum_j A_{j,n,m}A_{j,n',m'}\right|^2}{\sum_{n',m,m'} \left|\sum_j A_{j,n,m}A_{j,n',m'}\right|^2}. \quad (5)$$

The contributions from the different intermediate states are added coherently for the indistinguishable channels [same final (n', m') state for a given (n, m) initial state] and incoherently for the distinguishable channels. The sum over j runs over the $S_T = 5/2$ (resp. $S_T = 3$) intermediates for the Fe (respectively Mn) adsorbates, and the sum over

m and m' concerns the spin up and down of the collisional electron. Note that because of the dominance of one S_T intermediate state in the conductance, the sum over j only concerns the M_T sublevels, i.e., the orientation of the spin of the intermediate state; the corresponding contributions only differ by spin coupling coefficients and add coherently.

Equation (5) above has been derived for an unpolarized incident electron; appropriate removal of the sum over m and m' generalizes it to spin-resolved transitions.

Equation (5) is the basis of the present work. It yields the relative weight of the elastic and inelastic channels in the conductance. This expression is a direct consequence of spin coupling and magnetic anisotropy, associated to the dominance of the majority spin conductance.

Figure 2 presents the conductance as a function of the STM bias obtained as the product of the computed global conductance (Fig. 1) by the elastic/inelastic branching ratio from expression (5). Results are shown for Fe adsorbates at five values of the B field (B along the N axis in part (a) and along the hollow axis in part (b)). A Gaussian broadening of 0.26 meV corresponding to a temperature of 0.5 K [27] has been added. In this system, the Fe spin is equal to 2 [3] so that the conductance can present 4 steps associated to the inelastic thresholds (the strongest ones are labeled 1–3 on the figure). As a first remark, the contribution of inelastic channels is very large; for $B = 0$ and for an infinite resolution in this system, the inelastic channels at large bias amount to around 67% of the elastic channel. At finite resolution, for $B = 0$, the increase of the conductance between 0 and 8 mV is smaller due to the small energy difference between ϕ_0 and ϕ_1. Second, Fig. 2 shows an important change in the inelasticity spectrum with B. The 0–1 excitation is dominating at low B and disappears when B increases, whereas 0–2 dominates at large B. This behavior is exactly the one observed experimentally [3]. For a quantitative comparison, Fig. 3 presents the relative step heights (ratio of the height of a given inelastic step to the sum of the inelastic steps 1–3) as a function of B, compared with the experimental values. The 0–4 excitation is predicted to be very small and it is not observed experimentally for this geometry; we have not included it on the figure. Results obtained for the other orientations of the B field also reproduce the observed B dependance.

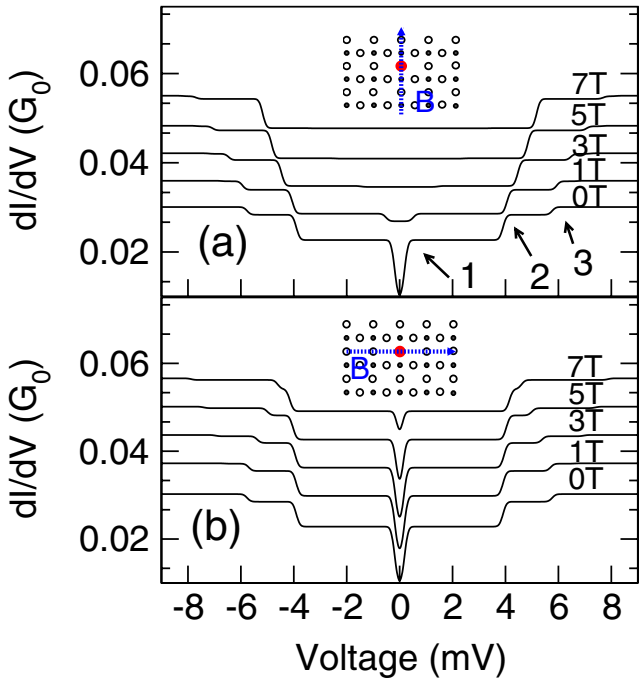

FIG. 2 (color online). Computed conductance for a Fe atom on a CuN monolayer on Cu(100) in conductance quanta ($G_0 = 2e^2/h$). The conductances for increasing magnetic field B are vertically displaced for representation purposes. The B field is oriented along the N axis in part (a) see scheme where N atoms are represented by the small dark circles and the impurity by the red large one, and along the hollow axis on the surface in part (b), following the corresponding scheme.

Experiments on Mn adsorbates on CuN monolayers on Cu [3] showed a very small magnetic anisotropy associated with a spin 5/2 and at finite resolution, the conductance is basically exhibiting a single inelastic step for all B values. Figure 3 presents a comparison of our prediction for the relative inelastic step height (ratio of the inelastic step to the conductance at 0 bias) as a function of B, it is seen to be in quantitative agreement with the experimental data.

In the present approach, the excitation process is seen as a decoupling and recoupling process induced by the collision with the tunneling electron. The actual strength of the interaction responsible for the transitions is not introduced explicitly and the magnitude of the magnetic transitions is

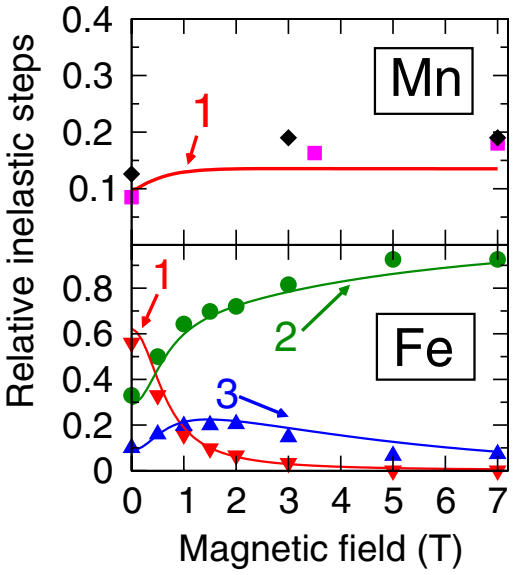

FIG. 3 (color online). Relative inelastic step heights in the conductance for Mn and Fe adsorbates as a function of the applied magnetic field, B, (along the N axis): calculations (full lines) and experiment [3,12] (symbols).

independent of it. We can distinguish two regimes as the magnetic field, B, increases (variation illustrated in Figs. 2 and 3). There is a change in the magnetic structure of the system: from a magnetic anisotropy induced by the lattice at low B, towards the Zeeman effect at higher B. This change in the structure results in a change in the character of the electron-induced magnetic transitions, which are or not associated with a spin-flip of the tunneling electron. Typically, for Fe in Fig. 3, at low B, the dominant 0–1 transition is not a spin-flip tansition, whereas, at large B, the dominant 0–2 transition is associated with a spin-flip. The generalization of Eq. (5) to spin-resolved electron tunneling (electron spin along the z axis) shows that for Fe, in the studied B range, the 0–1 and 0–4 transitions are not spin flip, whereas the 0–2 and 0–3 transitions are entirely spin-flip transitions.

In the case of Mn, the environment-induced anisotropy is very weak and for finite B, the Mn spin structure is a simple Zeeman splitting; in this case, the transitions are only spin flip with a $\Delta M = \pm 1$ selection rule and the fraction of inelastic tunneling is basically given by a ratio of squared Clebsch-Gordan coefficients leading to a nice agreement with experiment; see Fig. 3.

In conclusion, the importance of the inelastic conductance in the total conductance is a direct consequence of the nature of the excitation process, analyzed above. The initial magnetic state of the adsorbate couples with the spin of the collisional electron to form a collisional intermediate with a given total spin. At the end of the collision, the collisional intermediate populates all the possible asymptotic channels according to their weight in the intermediate, Eq. (5). This theory shows the connection between magnetism and rotations at the quantum level. Indeed, the resonant rotational excitation of an adsorbed molecule induced by tunneling electrons can be formulated in a way very similar to the present work and indeed leads to strong rotational excitation [21,28]. Finally, the quantitative account of magnetic IETS can also be extended [29] to the cases of Mn chains [12], Co- and Fe-phthalocyanine [14,15] molecules. Beyond its quantitative character, the present theory unravels the mechanism leading to spin coupling in electron transport, permitting us to predict the role of the different parameters at play determining magnetic excitations.

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