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 a strong coupling theory. The excitation process is shown to be a sudden switch between the initial state determined by the environmental anisotropy to an intermediate state given by the coupling to the tunneling electron. This explains the observed large inelastic currents. Application is presented for Fe and Mn adsorbates on CuN monolayers on Cu(100). First-principles calculations show the dominance of one collisional channel, leading to a quantitative agreement with the experiment.

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The way electrons flow through atomic contacts has important fundamental and technological implications \(^1\). Electronic transport is a quantal process in which charge, spin and vibrational degrees of freedom are entangled leading to problems of intrinsic fundamental interest. Technologically, the quest for miniaturization is pushing the limits of devices to the atomic scale, where the above transport properties will determine the actual device functionalities. 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. Inelasticities lead to new regimes of transport that contain relevant information on the atomic contact and have been thus used to develop single atom and molecule spectroscopies \(^2,3,4\).

Inelastic electron tunneling spectroscopy (IETS) where electrons excite vibrations leading to conductance steps at certain voltage thresholds \(^2\) has been extensively studied in the last years \(^2,3,4,6,7,8,9\). The inelastic change in conductance is within a few percent of the elastic conductance, mainly due to the smallness of the electron-vibration coupling \(^10,11\). Recently, Heinrich and co-workers have been able to develop a spin-resolved spectroscopy using an STM \(^4,12,13,14\). In magnetic IETS \(^4\), the tunneling electron yields energy to the spin of an adsorbed magnetic atom and in this way changes its orientation by overcoming the magnetic anisotropy barrier of the atom on the surface. Magnetic transitions in the meV range could be observed in adsorbates partly decoupled from a metal substrate \(^12,13,14,15\). As in vibrational IETS, the conductance presents a step at the energy threshold however the changes in conductance at inelastic threshold can reach several hundreds percent. This is at odds with previous treatments \(^13,16,17\) where first-order perturbation theory is used.

In this letter, we present an all-order theory of the spin transitions IETS and apply it to the cases of Fe and Mn adsorbates on a CuN monolayer on Cu, experimentally studied in Refs. \(^13,14\). We compute the relative weights of both elastic and inelastic channels, leading to a quantitative account of the inelastic currents in the experimental observations. The theory reveals the nature of the inelastic transitions and explains the extremely large inelastic currents in these magnetic systems.

The general idea of our approach is the following. The spin of the adsorbate is in an initial state given by the anisotropy imposed 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 induces efficient transitions among 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 \(^18\) or in surface processes \(^19\), as well as for rotational IETS \(^20\).

The energy losses associated with the magnetic anisotropy in the presence of a magnetic field, \(B\), have been shown to be very efficient in these systems \(^13,14\) using the following Hamiltonian:

\[
H = g \mu_B \mathbf{B} \cdot \mathbf{S} + D S_z^2 + E(S_x^2 - S_y^2) \tag{1}
\]

Where \(E\) and \(D\) are two constants describing the effect of the environment on the spin direction, \(g\) is the gyromagnetic factor and \(\mu_B\) the Bohr magneton. \(\mathbf{S}\) is the spin operator of the adsorbate and \(S_{x,y,z}\) its projections on the Cartesian axes. Diagonalisation of Hamiltonian \(^1\) yields the various possible \(\phi_n\) states of the adsorbate spin in the system:

\[
|\phi_n\rangle = \sum_M C_{n,M} |S,M\rangle \tag{2}
\]
where \(|S, M\rangle\) are eigenvectors of the \(\hat{S}^2, \hat{S}_z\) operators. An electron injected from the STM tip collides with the adsorbate on the surface and can cause inelastic transitions between the \(\phi_n\) states, which are recorded in an IETS experiment. In the present work, we use the modelling performed in Ref. \[13, 14\] (D and E parameters, g and spin of the adsorbate), which very precisely reproduces the energy positions of the inelastic thresholds.

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 \[21\]. 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 \[22\]. Atomic forces are relaxed 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 coupled to the contact region. 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. 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 \[22\]. Indeed, this difference implies that the transmission of minority-spin channels can be considered as suppressed. In addition, the transmission is seen to be almost flat as a function of electron energy, so that simple branching ratios can be used to obtain the relative value of the elastic and inelastic conductance of the system as a function of the STM bias. 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 making use of 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 time so that we can use a sudden approximation, neglecting the effect of Hamiltonian (1) during the collision.

ii) the spin of the tunnelling 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:

\[
|S_T, M_T\rangle = \sum_m CG_{S_T, M_T, m} |S, M = M_T - m\rangle |1/2, m\rangle
\]  

where the kets on the rhs correspond to the decoupled spins of the atom and of the tunnelling electron. \(m\) is the projection of the electron spin on the \(z\)-axis. The \(CG\) are Clebsch-Gordan coefficients that give the weight of the various \(|S, M\rangle\) states in the collision channels. From Eqs. 2 and 3, we can express the collision channel states as functions of the initial and final states of the collision:

\[
|j\rangle = |S_T, M_T\rangle = \sum_{n,m} A_{j,n,m} |\phi_n\rangle |1/2, m\rangle
\]  

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 \(|S_T = 5/2\rangle\) for the Fe adorbate and \(|S_T = 3\rangle\) 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 \(A_{j,n,m}A_{j,n',m'}\). The contributions from the different intermediate states are then added coherently for the indistinguishable channels (same final \((n', m')\) state for a given \((n, m)\) initial state) and incoherently for the distinguishable channels leading to the relative excitation probability (branching ratio) of the different excited states:

\[
W_{n\rightarrow n'} = \frac{\sum_{m,m'} |\sum_j A_{j,n,m}A_{j,n',m'}|^2}{\sum_{n',m,m'} |\sum_j A_{j,n,m}A_{j,n',m'}|^2}
\]
Note that because of the dominance of one $S_T$ intermediate state in the conductance, the sum over $j$ only concerns the $M$ sublevels, i.e. the orientation of the spin of the intermediate state; the corresponding contributions only differ by spin coupling coefficients and add coherently. 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. Equation 5 above has been derived for an unpolarised incident electron; it can be easily generalized to yield 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.

Fig. 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 [24] has been added. In this system, the Fe spin is equal to 2 [13] so that the conductance can present 4 steps associated to the inelastic thresholds (labelled 1-4 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 $\phi_0$ and $\phi_1$. 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. The 0-4 excitation is always weak. This behaviour is exactly the one observed experimentally [13]. 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 importance of inelastic channels.

Experiments on Mn adsorbates on CuN monolayers on Cu [13] 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. Fig. 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/recoupling process induced by the collision with the tunnelling electron. As our theory predicts, spin excitation can take place without spin-flip of the electron flux. We can distinguish two regimes as the magnetic field, B, increases. These are associated with a change in the magnetic structure of the system: evolution from a magnetic anisotropy induced by the lattice at low B, towards the Zeeman effect at higher B. The main axis of the lattice-induced anisotropy is the N axis (z-axis) and
thus, the efficiency of the B field in generating a Zeeman structure is weaker along the hollow axis, as compared to the N axis (see Fig. 2). This change of the energy landscape has bearings on the actual spin composition of the atom states. As an example, the 0-1 excitation of Fe, see Fig. 3 comes from the decoupling with the environment at low B, and at large B, the excitation is mainly due to coupling to the electron spin. Furthermore, in Fig. 3 for incident electrons polarized along the N axis, the 0-1 and 0-4 transitions are not associated to a change of the collisional electron spin direction, 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 tunnelling is basically given by a ratio of squared Clebsch-Gordan coefficients leading to a nice agreement with experiment, see Fig. 3.

The importance of the inelastic conductance in the total conductance is a direct consequence of the nature of the excitation process, analysed 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). The importance of a particular inelastic channel is then given by its weight in the collision intermediate (environment-induced anisotropy or spin coupling coefficient) and is not proportional to the modulus square of a matrix element between initial and final states. This explains the large difference of inelasticity observed in magnetic IETS compared to vibrational IETS.

However, inelastic rotational excitation shares many features with magnetic IETS. The resonant rotational excitation of an adsorbed molecule induced by tunnelling electrons also involves a transient angular momentum coupling between the collisional electron and the molecule. The corresponding process can be formulated in a very similar way to the present work and indeed leads to the observed strong rotational excitation 21, 22.

We believe that the present mechanism, which explains the strength of magnetic IETS and accounts for the observations in the case of Fe and Mn adsorbates, is of general occurrence. In addition, the present formalism yields a very easy way of accurately predicting the importance of spin transitions. One can stress that, in the present approach, once the spin state of the collisional intermediate is fixed, all the spin changing transitions are fully determined. Indeed, the above formalism also leads to the quantitative account 26 of the magnetic IETS of Mn$_2$, Mn$_3$ 22 and Co-phthalocyanine layers 15. In the latter case, we find an extremely strong inelastic fraction in tunnelling, up to 300% for 3 molecular layers, in excellent agreement with the experimental findings.

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