Electron tunneling is one of the central themes in condensed matter physics. It lies behind fundamental phenomena like Josephson effect, and tunneling magnetoresistance, and provides an extremely versatile spectroscopic tool, both in tunneling junctions and STM geometries. The use of inelastic electron tunneling to determine the vibrational spectra of ensembles of molecules inside tunnel barriers goes back to the seminal work of Jaklevic and Lamber and others. They observed steps in the differential conductance \( dI/dV \) at particular values of the bias voltages which matched the vibrational energy spectra of different molecules. This led to the notion of inelastic assisted tunneling: an electron could tunnel across the barrier giving away its excess energy \( eV \) to create an elementary excitation. In this framework, as \( eV \) increases, new inelastic transport channels open, resulting in steps in the \( dI/dV \) curve.

With the advent of the STM, it has been possible to downscale the technique of inelastic tunneling vibrational spectroscopy to the single molecule level, a possibility anticipated in the early days of STM. In a series of striking experiments, Heinrich et al. have used inelastic STM spectroscopy to probe the spin flip excitations of a single and a few transition metal atoms in a surface by means of STM spectroscopy. They have measured the single Mn atom Zeeman gap, the collective spin excitations of chains of up to 10 Mn atoms and the spin flip transitions within the ground state manifold of a single iron atom, split due to the single atom magnetic anisotropy. Analogously, Xue et al. have used inelastic STM spectroscopy to probe the spin excitations of one and a few Cobalt Phthalocyanines and have measured their exchange coupling.

Therefore, spin assisted inelastic tunneling spectroscopy (SITS) provides a direct measurement of the spin dynamics of one or a few magnetic atoms, and complements spin polarised scanning tunneling spectroscopy which is sensitive to the average relative orientation of the magnetic moments of tip and surface. SITS permits to measure energy scales like interatomic exchange, g factors and magnetic anisotropy. These quantities determine the spin dynamics of the magnetic atoms(s). In contrast to the case of vibrational spectroscopy, the physical origin of coupling between the transport electrons and the local spins which makes SITS possible is not clear. Hirjibehedin et al. mention two possibilities, exchange or dipolar coupling, although the former encompasses a variety of different mechanisms, like direct, kinetic, etc. The coupling must account for a number of experimental observations. The height of the steps in the \( dI/dV \) scales like the sum of the squares of the matrix elements between the initial and final states of the operators \( S_a \) with \( a = x, y, z \), the spin of the atom probed by the SITS. This is related to the selection rule for the change of the spin of the local spin \( \delta S_z = \pm 1 \). Therefore, there is a relation between the inelastic current and the spin spectral weight \( S_{aa}(\omega) \) of the magnetic atom(s). In this paper I show that an effective spin-assisted tunneling Hamiltonian naturally explains the relation between the inelastic current and the spin spectral weight \( S_{aa}(\omega) \) and accounts for the main experimental findings.
The experimental system consists of an insulating thin layer deposited on a metallic surface (see fig. 1a). Magnetic atoms lie in the insulating layer and are probed by a STM. A natural model for this system would thus feature 3 types of fermion operators, tip, surface and insulating layer, plus the spin operator of the magnetic atoms. In such an approach, the current, evaluated to lowest order in the tunneling coupling, is related to the spectral function of the transport electron in the insulating layer interacting with the local spins. This is different from the experimental findings described above. In particular, the conductance so evaluated would have a Coulomb Blockade gap unless the central region is in a mixed valence point, but there $dI/dV$ curve has peaks and not steps, and their location depends on the exchange coupling between the local spin and the transport electrons.

Thus, within the 3 fermion approach the low bias steps found experimentally must arise from higher order cotunneling processes. Here I adopt a simpler approach using a phenomenological Hamiltonian with two types of electrons (tip and surface), with an effective spin flip assisted tunneling term (1):

$$H = H_{\text{tip}} + H_{\text{sur}} + H_{S} + H_{\text{tun}}$$

The first three terms describe the electrons in the tip ($H_{\text{tip}} = \sum_{k,\sigma} \epsilon_{k} c_{k,\sigma}^\dagger c_{k,\sigma}$) and in the surface ($H_{\text{sur}} = \sum_{p,\sigma} \epsilon_{p,\sigma} b_{p,\sigma}^\dagger b_{p,\sigma}$). The Hamiltonian of the central spin(s) is the sum of the intraatomic $H_{S}(i)$ terms and the spin-spin couplings:

$$H_{S} = \sum_{i} H_{S}(i) + \frac{1}{2} \sum_{i,j,a} J_{ab}(i,j) \hat{S}_{a}(i) \cdot \hat{S}_{b}(j)$$

The eigen-energies and eigenstates of $H_{S}$ are denoted by $E_{M}$ and $|M\rangle$. The tunneling terms can be written as:

$$H_{\text{tun}} = \sum_{kk'\alpha'\alpha} T_{\alpha}(kk') \frac{\tau_{\alpha}^{\alpha'} S_{\alpha}(1)}{2} \left( a_{k\sigma}^\dagger b_{k'\sigma'} + \text{h.c.} \right)$$

where $\tau_{\alpha}^{\alpha'}$ and $S_{\alpha}(1)$ are the Pauli matrices and the spin operators of the spin (1) in the central region for $\alpha = \alpha = x, y, z$, and the unit matrix for $\alpha = 0$. Because of the short-range nature of exchange interaction and tunneling processes from the tip, we assume that only one spin $S_{a}(1)$ is assisting the tunneling. This term describes the tunneling of electrons between tip and surface assisted by exchange interaction with the spin in the middle. A similar term has been used by other authors.

Eq. (3) describes both spin assisted ($\alpha = x, y, z$) and conventional tunneling $\alpha = 0$. To lowest order in $H_{\text{tun}}$, the current has three contributions: (i) a central-spin independent $T_{0}^{2}$, (ii) a crossed contributions proportional to $T_{0} T_{\alpha} \hat{m}_{T,S} \cdot (\hat{S}(1))$, and (iii) a spin flip contribution $T_{a}^{2}$ that features the spin spectral weight and is responsible of the steps in the $dI/dV$ curves. In the case of magnetized tip and sample the $T_{a}^{2}$ contribution depends on $\vec{m}_{T} \cdot \vec{m}_{S}$ which makes possible the SP-STS spectroscopy. In this work $\vec{m}_{S} = \vec{m}_{T} = 0$. The spin-flip contribution arises from the balance between electrons tunneling from tip to surface and back:

$$I = \sum_{M} P(M) \left( \sum_{p,\sigma} n_{p} T_{p} \gamma_{p,M} - \sum_{k,\sigma} n_{k} \gamma_{k,M}^{S} \right)$$

where $P(M)$ is the equilibrium occupation of the $M$ state, $n_{p} T_{p}$ is the occupation function of the tip and surface and $\gamma$ are the tunneling rates associated to the spin-flip assisted tunneling Hamiltonian:

$$\gamma_{p,M}^{T,S} = \sum_{p',M'} |T_{a}(pp')|^{2} |\langle M|\hat{S}_{\alpha}(1)|M'\rangle|^{2} \times \left( 1 - n_{S}^{p} \right) \delta (\epsilon_{p'} + \epsilon_{M'} - \epsilon_{p} - \epsilon_{M})$$

This expression gives the lifetime of a product state with an electron in the state $p$ of the tip and the magnetic atom(s) in state $M$ due to a spin flip assisted tunneling of the electron to the surface. Importantly, this equation relates current to the spin matrix elements, $|\langle M|\hat{S}_{\alpha}(1)|M'\rangle|^{2}$, as reported in the experiments.

If the coupling between transport electrons and spins is rotationally invariant, $T_{a}(k,k') = T_{S}$ is the same for $a = x, y, z$. The dependence of $T_{S}$ on the momentum indexes can be neglected. We take $n_{p} T_{a} = f(\epsilon)$ and $n_{S}^{p} = f(\epsilon + eV)$, where $f$ is the Fermi function. The sum over momenta leads to an integral over energies featuring the density of states of tip and surface, $\rho_{T}(\epsilon)$ and $\rho_{S}(\epsilon)$ which are assumed to be flat in the neighbourhood of the Fermi energy. We arrive to

$$I = G_{S} \sum_{a=x,y,z} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S_{aa}(\epsilon - \epsilon') F(\epsilon, \epsilon', eV) d\epsilon d\epsilon'$$

where $eG_{S} \equiv T_{S}^{2} \rho_{T}(\epsilon) \rho_{S}(\epsilon)$ and

$$F(\epsilon, \epsilon', \omega) = |f(\epsilon)(1 - f(\epsilon + \omega)) - f(\epsilon + \omega)(1 - f(\epsilon'))|$$

and

$$S_{aa}(\omega) = \sum_{M,M'} P(M) \rho_{S}^{M,M'}(1)|^{2} \delta (\omega + \epsilon_{M} - \epsilon_{M'})$$

is the spin spectral weight.

From the formal point of view, equation (6) is one of the main results of this paper. It relates the inelastic current to the spin spectral weight of the magnetic atom probed by the STM. It shows that two types of spin assisted tunneling processes contribute to the current. If we choose $z$ as the quantization axis, the $a = x, y$ terms involve spin exchange between the transport electron and the magnetic atom. These are the spin flip terms. In contrast, the $a = z$ term conserves the spin of both carrier and atom. This dichotomy is absent in the case of vibrational inelastic spectroscopy.
One of the integrals in eq. (6) is done using the delta functions in eq. (7) and the other using 
\[ \int_{\infty}^{\infty} [f(e) \{1 - f(e + \omega)\}] de = \frac{\omega}{1 - e^{-\beta \omega}}. \] The total inelastic current is thus written as

\[ I = \sum_{M',M,a} P_M S_{M',M}(1)^2 i(\epsilon V, \Delta_{M',M}) \] (8)

with \( \Delta_{M',M} = E_{M'} - E_M \) and

\[ i(\epsilon V, \Delta) = G_S \left[ \frac{eV - \Delta}{1 - e^{-\beta (\epsilon V - \Delta)}} + \frac{eV + \Delta}{1 - e^{-\beta (\epsilon V + \Delta)}} \right] \] (9)

is the current associated to a single inelastic channel with energy \( \Delta \). Equations (6) and (8) are the magnetic analog of the vibrational inelastic tunneling spectroscopy in which the dipole spectral weight of the molecular vibrations is replaced by the spin spectral weight of the magnetic atoms.

Now the validity of eqs. (6) and (8) and the spin assisted tunneling term (3) is verified by comparing their predictions with the experimental results. The case of tunneling through a single Fe atom in CuN/Cu system is considered first. Following that reference, the standard spin Hamiltonian reads

\[ \mathcal{H}_S = DS_z^2 + E(S_x^2 - S_y^2) + g \mu_B \vec{B} \cdot \vec{S} \] (10)

with \( S = 2 \) adequate for Fe\(^{2+} \) and \( D = -1.55 \) meV and \( E = 0.35 \) meV\(^{11} \). Since \( D >> E \) approximate analytical expressions yield the ground state energy (for \( B = 0 \)) \( E_0 = -4D \) and the excitations \( \Delta_{M',0} = E_{M'0} - 3D - 6E, 3D + 6E, 4D \) (see fig. 2c). The ground (first excited) state is made mainly (only) with \( M_z = \pm 2 \). The \( dI/dV \) curves obtained from eq. (8) and the exact solution of Hamiltonian (10) for different intensities and orientations of the applied magnetic field, evaluated for \( k_B T = 0.5K \), are shown in fig. 2a,b. The a (b) panel corresponds to field parallel to \( z \) (x). At zero field the \( dI/dV \) curves show three steps corresponding to the excitations to the first, second and third excited states. The transition to the fourth state is forbidden ( \( \sum_{a=x,y,z} |\langle 0 | S_a | 4 \rangle|^2 = 0 \)). The prominent 0 \(-\rightarrow\) 1 transition comes from the spin-conserving channel \( a = z \), where as the 0 \(-\rightarrow\) 2 and 0 \(-\rightarrow\) 3 transitions come from the spin flip channels \( a = y \) and \( a = x \), respectively. Interestingly, the energy difference between these two transitions is exactly equal to 6E. Thus, this parameter can be read from the experimental data. Their evolution as a function of the intensity and orientation of the magnetic field give good account of the main observed experimental features. In particular, the conductance shows a significant magnetic anisotropy, related to that of the iron atom in this surface.

The theory also accounts for more complicated experimental situations where electrons tunnel through one magnetic atom which is exchanged coupled to others. This is the case of linear chains of \( N \) Mn atoms deposited on a CuN/Cu surface, \( N \) going from 1 to 10. Mn\(^{2+} \) has \( S = 5/2 \) and very weak magnetic anisotropy. The Mn-Mn coupling is approximated by a spin-rotational invariant first-neighbour Heisenberg coupling. The model reads:

\[ \mathcal{H}_S = \sum_i D_i \hat{S}_i^2 (i) + g \mu_B \vec{B} \cdot \vec{S} (i) + J \sum_{i,a} \hat{S}_a (i) \cdot \hat{S}_a (i+1) \]

where the sum in the last term runs from \( i = 1 \) to \( N - 1 \).

Remaining anisotropy related step of odd-\( N \) chains is much larger than the single Mn \( D \). Thus, \( D \) is a weak perturbation of the Heisenberg model, whose eigenstates can be labelled with the total spin \( S \) and its third component \( S_z \). Since \( j > 0 \) the coupling is antiferromagnetic. Thus, even \( N \) chains have \( S = 0 \) ground states whereas odd \( N \) chains have degenerate ground states with multiplicity 6 weakly split by the anisotropy term \( D \). Thus, the lowest energy step occurs is related to \( D \) in odd \( N \) chains and to \( J \) in even \( N \) chains.

The calculations (see figure 3) account both for the difference between odd and even \( N \) chains and the increase of the anisotropy related step of odd-\( N \) chains experimentally observed \( dI/dV_{\text{10}} \). The first excitation for \( N = 1 \) and \( N = 3 \) correspond to the transitions from the ground state doublet \( S_z = \pm 5/2 \) to the first excited state with \( S_z = \pm 3/2 \) through the spin-flip channels \( a = x, y \). Application of a magnetic field increases the splitting between these states and shifts the step towards higher energy, as seen in the experiment and well captured by the model (fig 3b).

The first excited states of the dimer have 3-fold degeneracy weakly split into a low energy doublet and a higher energy singlet because of the single atom anisotropy. This fine structure splitting is 6.4D. The ground state singlet is connected to the excited state singlet via a spin-conserving transition and to the excited state doublet via spin flip transition. Figures 3c and 3d show how this fine structure evolves as a magnetic field is applied. The model accounts for the deviation from the Zeeman split-
In chains with $N = 3$ or more atoms the amplitude of the spin excitations, and the height of the steps in the $dI/dV$ curves thereby, can vary from atom to atom. In figure 3a the $dI/dV$ curve is shown for the spin-assisted current recorded on top of the central atom and one of the side atoms. As reported in reference (10) the location of the steps is the same. However, the intensity is clearly different. In the spectrum recorded in the side atom two steps are seen, corresponding to transitions to the first $S = 3/2$ and second $S = 7/2$ excited states whereas the spectrum recorded in the central atom only the latter is seen. Thus, the spin-assisted tunneling spectroscopy can be used to map the amplitude of the spin excitations.

In summary, the experiments of single spin inelastic tunneling spectroscopy imply the existence of a spin-assisted tunneling mechanism that couples electrons in the tip and the surface to the local spin [5]. This term naturally leads to an expression for the current that involves the spin spectral weight $S_{\text{sp}}(\omega)$ of the magnetic atom, or spin excitations, and the height of the steps in the $dI/dV$ curve is shown for the spin-assisted electron repulsion in the Hamiltonian [17] and it could be a kinetic exchange term [23].

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