Spin-polarized spin excitation spectroscopy

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Abstract. We report on the spin dependence of elastic and inelastic electron tunneling through transition metal atoms. Mn, Fe and Cu atoms were deposited onto a monolayer of Cu\textsubscript{2}N on Cu(100) and individually addressed with the probe tip of a scanning tunneling microscope. Electrons tunneling between the tip and the substrate exchange energy and spin angular momentum with the surface-bound magnetic atoms. The conservation of energy during the tunneling process results in a distinct onset threshold voltage above which the tunneling electrons create spin excitations in the Mn and Fe atoms. Here we show that the additional conservation of spin angular momentum leads to different cross-sections for spin excitations depending on the relative alignment of the surface spin and the spin of the tunneling electron. For this purpose, we developed a technique for measuring the same local spin with a spin-polarized and a non-spin-polarized tip by exchanging the last apex atom of the probe tip between different transition metal atoms. We derive a quantitative model describing the observed excitation cross-sections on the basis of an exchange scattering process.
1. Introduction

Electron tunneling between two electrodes can occur in two ways: (i) by elastic tunneling and (ii) by inelastic tunneling, where the electron interacts with its environment and exchanges energy and potentially spin angular momentum. The latter is known as inelastic electron tunneling and allows for measuring the energy of discrete excitations in the tunnel junction by tunneling spectroscopy [1]. It is a complementary approach to far-field techniques such as infrared or Raman spectroscopy [2]. Inelastic tunneling spectroscopy (IETS) was extensively used in planar tunnel junctions to study vibrational excitations in molecules [3]–[6]. In the late 1990s, IETS was first applied in scanning tunneling microscopy [7]–[9]. Besides vibrational excitations, the interaction of electrons with spins may be used to measure the excitations of magnetic systems. Tunneling electrons can excite magnons in magnetic thin films [10, 11] or spin flips in molecular spin systems [12, 13]. The scanning tunneling microscope (STM) enabled studies of the spin excitations in individual transition metal atoms [14]–[16], small chains of atoms [17] and metal–organic molecules [18]–[20]. The cross-section for spin excitation in all these examples was found to be large compared to that for vibrational excitations.

In this work, we focus on the spin dependence of the excitation spectra for individual magnetic atoms on surfaces. Fe, Mn and Cu atoms serve as model spin systems for this study. The atoms were deposited onto a monolayer thin Cu$_2$N decoupling layer [21]–[24] that was grown on a Cu(100) crystal (figure 1). On this surface, Fe and Mn exhibit a net spin with a set of discrete spin states that can be probed by inelastic electron tunneling [16].

IETS is typically employed as a threshold spectroscopy. Spin excitations are detected as steps in the differential conductance $dI/dV(V)$ (where $I$ is the tunnel current and $V$ the sample...
Figure 1. Individual transition metal atoms (Fe, Mn and Cu) adsorbed on a surface. The substrate is a Cu single crystal with a thin decoupling monolayer of Cu$_2$N grown on the (100) surface. The decoupling layer prevents excessive screening of the adsorbates’ magnetic moments by the conduction electrons of the metal substrate. Constant current topograph recorded at $-10$ mV voltage and 0.1 nA current; the size is 10 nm × 8 nm; color scale: blue, low; green, high.

voltage). The threshold voltage $V_\text{thr}$ at which the step is observed directly corresponds to the excitation energy. This is a result of conservation of energy during the tunneling process. In spin systems, the exchange of spin angular momentum between the tunneling electron and the surface-bound spin is equally important. It allows more information to be deduced on the system under investigation. We find that conservation of spin angular momentum manifests itself in the magnitude of the observed inelastic signal, i.e. the cross-section for inelastic excitation is spin dependent. This effect becomes apparent when the STM tip is spin polarized.

We developed a technique for measuring the same local spin with spin-polarized and spin-averaging tips, by exchanging the last apex atom of the probe tip between a magnetic atom (Fe, Mn) and a non-magnetic atom (Cu). This technique was recently outlined in [25] where the spin-polarized current emitted from a Mn atom at the tip was used for spin-momentum transfer. Here we focus on the ability to directly compare the measured cross-sections of the same spin excitations with non-spin-polarized electrons and spin-polarized electrons. We derive a model that quantitatively describes the spin-dependent cross-section of the spin excitations for Fe and Mn and the ratio of inelastic tunneling to elastic tunneling through the atoms. The comparison of the model and the experiment shows that for sharp STM tips, virtually all tunneling electrons interact with the surface-bound spin system and that the interaction is well described by an exchange scattering process. The ratio of elastic tunneling to inelastic tunneling allows us to quantify atom-specific parameters for the effective electron–spin interaction of this exchange scattering process.

2. Experimental setup

We use an STM that operates in ultra-high vacuum at a temperature of 0.6 K. Magnetic fields of up to 7 T can be applied in the plane of the sample or perpendicular to it. A Cu$_2$N overlayer is grown on the clean Cu(100) crystal by N$_2$ sputtering at 1 kV beam energy and subsequent annealing of the sample at temperatures below 800 K [21]–[24]. The Fe, Mn and Cu atoms are deposited onto the cold sample surface at temperatures below 10 K. The Cu$_2$N serves as a decoupling layer that separates the adsorbed atoms from the conduction electrons of the Cu.
substrate [26, 27], see also [20, 28, 29]. On this surface, the transition metal atoms exhibit a localized magnetic moment that is well described as a quantum-mechanical spin system. In this paper, we will refer to this spin system simply as the localized spin. The STM tip consists of an electrochemically etched tungsten wire or a mechanically sharpened Ir wire. The tip apex is covered with Cu by dipping the tip into the Cu crystal. The chemical nature of the apex can be verified by repeated drop-off of individual atoms and identification of the dropped atoms. The technique for switching between spin-polarized and non-spin-polarized STM tips is described in section 3.

The spin excitation spectra are recorded by measuring the differential conductance \( dI/dV \) as a function of sample voltage \( V \). We use lock-in detection at 768 Hz with a modulation amplitude of 50 \( \mu \)V. For brevity, we will refer to the differential conductance simply as the conductance. All spectra presented in this work are recorded on top of the surface-bound atoms as given by the maximum of their topographic contrast. The spin excitations are apparent in the \( dI/dV \) spectrum as steps that go from lower to higher differential conductance at a threshold voltage \( +V_{\text{thr}} \) and \(-V_{\text{thr}}\) when the sample voltage is increased from \( V = 0 \) with either voltage polarity. Typically, the changes in conductance are of the order of 10–50\% of the average conductance.

3. Single atom spin-polarized tips

We set out to quantitatively compare spin excitation spectra that were obtained with a spin-polarized tip and a spin-averaging tip. The spin excitation spectra of different Fe (or Mn) atoms on the Cu_2N surface vary by a few per cent [16]. This effect is most likely due to variations in the local environment of the atoms such as different surface strains of the Cu_2N layer [21, 23, 30, 31]. It was thus highly desirable to make the comparison on the same magnetic atoms to exclude the changes due to local environment. Therefore, we use the reversible transfer of one or more magnetic atoms from the sample surface to the tip apex to switch between spin-polarized and non-spin-polarized probe tips. This technique is complementary to the established technique of using magnetically coated STM tips [32, 33]. In a first step the adatoms are identified. Then we use vertical atom manipulation [17, 34] to pick up individual Fe or Mn atoms from the Cu_2N layer to the direct apex of the probe tip. The external magnetic field polarizes the magnetic moment of the tip-adsorbed atom, which results in a net spin polarization of the density of tip states at the Fermi energy [25].

3.1. Atom identification by spin excitation spectroscopy

A straightforward way to identify the atomic species of each adsorbate atom is to use its spin excitation spectrum like a fingerprint. The specific shape of the spin excitation spectrum depends on the magnitude of the atom’s spin and the magneto-crystalline anisotropy. Both quantities are the same for adatoms of the same element and vary strongly from element to element due to differences in orbital configuration of the elements and their specific binding geometry in the Cu_2N layer [27, 35]. Figure 2 shows representative spectra and the preferential binding configuration for Fe, Mn and Cu. These spectra were previously identified by studies where only one elemental species was deposited at a time and are known for the elements Mn [17], Co [36], Fe [16] and Ti [36].
Figure 2. Atom identification by spin excitation spectroscopy. Individual atoms of the transition metals Fe, Mn and Cu show distinct spectral shapes in spin excitation spectroscopy. Upper panels of the graph show representative differential conductivity, $dI/dV$, versus voltage spectra (at 3 T magnetic field applied in the plane of the sample). Bottom panels show the preferential adsorption sites on the Cu$_2$N surface (see text for details).

The stable binding site for Fe is on top of the Cu atoms in the Cu$_2$N layer (here called the Cu-binding site). On this binding site, Fe has a spin of $S = 2$, large easy-axis magnetic anisotropy and a rather large transverse anisotropy [16]. In moderate magnetic fields of up to 3 T this results in three easily visible spin excitations (figure 2, left panel). The dominant excitation from the ground state is found at about $\pm 4 \text{ mV}$. This excitation corresponds to the transition from the $|m = +2\rangle$ state to the $|m = +1\rangle$ state where $m$ is the magnetic quantum number given by the expectation value of the spin operator along the easy magnetic axis of the Fe atom [16]. Note that the transverse anisotropy and magnetic fields that are applied perpendicular to this direction mix the spin states so that generally the full spin states are only approximately identified with $m$ quantum numbers (see section 4.1 for the sign convention of $m$ in the spin Hamiltonian used here and see [16] for details of the magnetic field-dependent mixing of spin states in Fe). The other excitations at $\pm 1$ and $\pm 6 \text{ mV}$ are present because of this spin state mixing and are unique to Fe.

Mn preferentially adsorbs on the Cu binding site as well. Unlike Fe it has a total spin of $S = 5/2$ and small easy-axis anisotropy. Only one spin excitation is observed at about $\pm 1 \text{ mV}$ (figure 2, middle panel). This excitation corresponds to the transition from the $|m = +5/2\rangle$ to the $| + 3/2\rangle$ states, which are split by the Zeeman energy. The absence of additional transitions is a consequence of negligible transverse anisotropy [16].

Cu behaves differently from the other transition metal atoms. It preferentially binds to the fourfold symmetric hollow binding site that is in between the Cu atoms of the Cu$_2$N layer. We find no spin excitations for Cu atoms (figure 2, right panel). However, a lower conductance value over the Cu atom results in a reduction of the apparent height of the Cu atom to $\sim 2 \text{ Å}$, whereas Fe and Mn appear $\sim 2.8 \text{ Å}$ tall (at 10–100 mV sample voltage). The featureless spectrum of Cu together with the low topographic height and the peculiar binding site allow for unambiguous identification of the Cu adatom.

We note that the specific direction and strength of the applied magnetic field changes the position and relative height of the excitation steps for each atom, but the qualitative shape of the
Figure 3. Manipulation sequence to switch between spin-polarized and non-spin-polarized tips. (a) Starting with a blunt STM tip apex, a Mn atom (white circle, top panel) is picked up by vertical atom manipulation (see text). The spin excitation spectrum (bottom panel) of a second Mn atom (cross, middle panel) provides a reference to confirm the spin polarization of the tip ($\eta_t = 0.32$, refer to section 5.2). (b) Then, the Mn atom on the tip is dropped off and a Cu atom (white circle) is picked up by the same process. The reference spin excitation spectrum confirms that the resulting tip has no spin polarization ($\eta_t = 0.03$, refer to section 5.2). (c) The Cu atom is dropped and the Mn atom of (a) is picked up again to regain spin polarization. Note that the spectrum and apparent shape of topographic features revert to exactly the same shape, indicating that the probe tip has the same microscopic configuration as was obtained after the first pick-up ($\eta_t = 0.32$). The spectrum of (a) is shown in the background in green for direct comparison. (d) A similar degree of spin polarization but a slightly different spectral shape is obtained by picking up an Fe atom instead of the Mn atom ($\eta_t = 0.31$).

spectra remains unchanged [15, 16]. This allows for unambiguous identification of the adsorbate atoms at all fields that are accessible in the STM used here (0–7 T).

3.2. Manipulation sequence

Once the atoms in the area of interest have been identified, we can choose a set of atoms to be used for the functionalization of the tip apex. Figure 3 shows a patch of Cu$_2$N (blue) with one Fe atom, one Cu atom and two Mn atoms adsorbed on it. One of the Mn atoms is left in place on the surface and used for monitoring the spectral properties of the STM tip, whereas the others are used for manipulation.

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We start with a slightly blunt tip, one which does not terminate in a single atom, so an additional atom can be accommodated at its apex. A Mn atom is then transferred from the surface to the tip. We use the following vertical manipulation procedure: the STM tip is lowered towards the surface-bound Mn atom until it is close to point contact, with a typical tunnel junction resistance of the order of 100 kΩ. Then a voltage of +2 V is applied to the sample with respect to the tip and the tip is withdrawn with this voltage applied. Finally, the junction is returned to normal imaging conditions. The STM image that was recorded after the pick-up procedure (bottom panel, figure 3(a)) shows that the lower Mn atom is missing from the surface, and the spatial resolution of the new STM image is improved compared to the image recorded before the pick-up. We monitored the change in the STM tip position normal to the surface. As a result of the pick-up sequence, the tip was elongated by 1.2 Å. The change in tip length together with the improved spatial resolution indicates that the Mn atom is attached to the apex of the STM tip. This implies that most of the tunnel current is now carried by the Mn atom. The spin excitation spectrum recorded on the remaining surface-bound Mn atom shows asymmetry in the step height for the spin excitation at ±1 mV (the spectrum of figure 3(a)). The step at −1 mV is bigger than the step at +1 mV. In the following sections, we will show that this asymmetry is a result of spin polarization in the tunnel current. For now, we simply note that spin excitation spectra recorded with non-spin-polarized tips are symmetric with respect to voltage polarity, while those recorded with a spin-polarized tip are not [25].

The atom transfer from the sample to the tip is reversible. By lowering the functionalized tip close to the point contact with the free Cu2N surface and applying a small negative voltage of −0.5 V to the sample, the Mn atom is transferred from the tip to the surface. The resulting STM image (figure 3(b), top panel) confirms that the tip reverts to the blunt shape of the first image and the Mn atom reappears on the surface. Next, a Cu atom is picked up to the tip using the same procedure as for the Mn atom. Similarly to the Mn pick-up, the tip elongates by about 1 Å and the spatial resolution improves. However, the reference spectrum on the Mn atom remains symmetric with respect to voltage polarity, because a Cu atom on the tip apex exhibits no spin polarization (the spectrum of figure 3(b)). Subsequent drop-off of the Cu atom and pick-up of the Mn atom demonstrates the reproducibility of the vertical atom transfer (figure 3(c)). The reference spectrum recorded with the reattached Mn atom (the spectrum of figure 3(c)) is identical to the one recorded after the first Mn atom pick-up. This indicates that the Mn atom is reattached to the same adsorption site on the tip apex. Figure 3(d) shows that a similar spin polarization is obtained by pick-up of the Fe atom instead of the Mn atom.

The manipulation sequence in figure 3 demonstrates that it is possible to switch between a spin-polarized and a non-spin-polarized STM tip by exchanging the last apex atom between Mn (or Fe) and Cu. A magnetic-field-dependent study of the tip spin polarization shows that the tips obtained in this manner behave paramagnetically. At a temperature of 0.6 K a magnetic field of 1 T is sufficient to stabilize the Mn (or Fe) magnetic moment and obtain significant spin polarization [37]. We will use this technique in the following to obtain spin excitation spectra of the same surface-bound atoms measured with different degrees of spin polarization in the tunnel current.

4. Theoretical framework

In this section, we will derive a model for explaining the origin of spin polarization in the spin excitations of the surface-bound magnetic systems. Several theoretical works have been
Figure 4. Coordinate systems of the spin-polarized tip (x, y, z) and the surface-bound spin (a, b, c), as used in the spin Hamiltonian, equation (1). The quantization axis z for states in the tip is parallel to the direction of the external magnetic field B. The x- and y-axis are arbitrary and set so that x is parallel and y perpendicular to the sample surface here. The coordinate system used for the localized spin on the surface can be different from that of the tunneling electrons since the orientation of the magnetic anisotropy is governed by the sample’s crystal structure. We define a to be the principal axis (hard or easy axis) of the magnetic anisotropy, which gives the uniaxial anisotropy component D. The axes b and c are assigned to give the transverse anisotropy component E.

published that establish models for the spin excitation spectroscopy of individual magnetic atoms and exchange coupled chains of magnetic atoms [38]–[42]. Recently, spin polarization in the tunnel current has been considered as well [43]. Here, we will not attempt to derive a model from first principles. We will rather focus on a semi-empirical description that can be reconciled with the previously published models. The model will allow us to quantitatively fit the complete spin excitation spectrum, i.e. the inelastic and elastic tunneling components, with a single small set of parameters.

4.1. Spin Hamiltonian

The starting point is the Hamiltonian of the localized spin system. We use the standard form published previously for molecular magnets [44] and individual atoms adsorbed on a surface [16, 45]:

\[ H = -g \mu_B B_z S_z + D S_a^2 + E (S_b^2 - S_c^2). \]  

(1)

The first term of this Hamiltonian accounts for the Zeeman energy with g being the g-factor, \( \mu_B \) the Bohr magneton, \( B_z \) the magnetic field and \( S_z \) the spin operator for the localized spin along the direction of the magnetic field, which we define to be the z-axis. The second term constitutes uniaxial magneto-crystalline anisotropy with D giving the sign and magnitude of the anisotropy energy. The third term is the transverse magnetic anisotropy with magnitude E. The direction of the magnetic anisotropy and the direction of the magnetic field can differ. The principal anisotropy axis of the surface-bound spin as given by the uniaxial anisotropy will be determined by the sample’s crystal structure and the adatom’s binding site. Therefore, the magnetic anisotropy terms in equation (1) are specified using the high-symmetry axes of the crystal a, b and c, as shown in figure 4. The spin operators \( S_a, S_b \) and \( S_c \) used to describe
the local spin’s anisotropy can be obtained by rotating the spin operators $S_x$, $S_y$ and $S_z$ to the orientation of the magnetic anisotropy [46].

For our STM tips, which are terminated by a single magnetic atom (section 3.2), the direction along which the tip is spin-polarized is determined by the direction of the external magnetic field. Thus, we use the $z$-axis as the quantization direction for tunneling electrons and consider only tip electronic states that are eigenstates of the $S_z$ operator. We label the states by the corresponding expectation value $\sigma_i = \langle S_z | \sigma_i \rangle$, which gives either $\sigma_i = +1/2$ or $-1/2$, where we use $\hbar = 1$ throughout this work.

Diagonalization of (1) yields the energy eigenstates $|\phi_i\rangle$ of the local spin. Given that the local spin and the tunneling electron are non-interacting before and after the tunneling event, we choose the product states of local spin states $|\phi_i\rangle$ and spin states of the tunneling electron $|\sigma_i\rangle$ to be the basis set between which transitions may occur:

$$|\phi_i, \sigma_i\rangle = |\phi_i\rangle \cdot |\sigma_i\rangle.$$  

These basis states account for only the spin part of the wave function; the kinetic energy and spatial location (tip or sample) of the tunneling electron are treated implicitly when modeling the tunneling process, see e.g. [25].

4.2. Spin-dependent transition intensities for tunneling electrons

For spin-dependent transport through quantum dots [47, 48] and for spin-polarized tunneling in tunnel junctions [33], [49]–[52], it was found that the tunneling process conserves spin angular momentum. The same conservation rule holds for the inelastic electron tunneling experiments presented here. This imposes a strict selection rule for spin transitions that can be excited by the tunneling electron. In one excitation event, the spin angular momentum of the localized spin can only change by $+1$, $0$ or $-1$.

We model the interaction between the tunneling electron and the localized spin as an exchange interaction of the form $S \cdot \sigma + u$, where $S$ and $\sigma$ are the spin vector operators of the local spin and the electron, respectively. The parameter $u$ is a real constant and accounts for a spin-independent component in the interaction such as potential scattering. The intensity of a transition from a given initial state $|\phi_i, \sigma_i\rangle$ to a final state $|\phi_f, \sigma_f\rangle$ can then be expressed as

$$Y(\phi_f, \sigma_f, \phi_i, \sigma_i) = Y^{-1}_0 \cdot |\langle \phi_f, \sigma_f | S \cdot \sigma + u | \phi_i, \sigma_i \rangle|^2.$$  

We allow $i = f$ to account for all elastic tunneling events that are still spin dependent in the sense that the tunneling electron interacts with the local spin. The transition intensity function of equation (3) is nonzero only for transitions that obey the spin conservation rule. We find that the spin-dependent tunneling accounts for most if not all of the tunnel current detected on magnetic atoms on Cu$_2$N. Such large transition intensities render descriptions using perturbation theory inappropriate. It was shown independently by Lorente and Gauyacq [41] and Persson [42] that different non-perturbative approaches lead to transition intensity functions equivalent to equation (3). For $u = 0$, $Y$ becomes proportional to the transition intensity functions presented in [16, 38, 42, 53], and for $u = 1/2(S + 1)$, to that in [41]. Note that in this work, $Y$ is reduced to the central matrix element and a normalization factor, $Y^{-1}_0$, which is discussed below. Prefactors that arise from the particular theoretical framework used to derive $Y$ from the electron–spin interaction are omitted. This simplification is reasonable since we can only consider ratios of transition intensities in the analysis of the spin excitation spectra.
Figure 5. Spin-dependent cotunneling transitions for a tunneling electron interacting with a localized spin. (a) Schematic diagram of the inelastic cotunneling process for positive sample voltage ($V > 0$). An electron tunnels from an occupied state in the tip through the vacuum barrier to the local spin that is in state $|\phi_i\rangle$. The cotunneling is completed by an electron tunneling through the Cu$_2$N barrier into an unoccupied state in the Cu substrate leaving the local spin in the excited state $|\phi_f\rangle$. The tunneling electron starts in state $|\sigma_i\rangle$ and ends in state $|\sigma_f\rangle$. $E_F$ is the Fermi energy. The following sketches depict the possible transitions: (b) inelastic cotunneling where the tunneling electron changes from $+1/2$ (up-state) to $-1/2$ (down-state), (c) inelastic cotunneling involving a spin-flip from $-1/2$ to $+1/2$ in the tunneling electron, (d) elastic cotunneling of $+1/2$ electrons (the local spin stays in the same state) and (e) elastic cotunneling of $-1/2$ electrons. (f, g) If the local spin is subject to transverse anisotropy, inelastic co-tunneling transitions may occur where the tunneling electron stays in the $+1/2$ or $-1/2$ state.

$Y$ describes the effective interaction between the tunneling electron and the local spin. The specific type of exchange interaction employed here was used previously, for example by Schrieffer and Wolff [54] or Appelbaum [55], to understand the coupling of conduction electrons to localized magnetic moments in the context of the Kondo effect. Exchange scattering processes between probing electrons and magnetic samples have also been observed in electron-energy-loss spectroscopy [56, 57]. The spin-dependent tunneling process considered in this work can be thought of as a cotunneling process where electrons from the tip and the substrate tunnel on and off an orbital state in the surface-bound atom, see figure 5(a). When the tunneling electron is on the atom, it can interact strongly with the atom’s spin and efficiently exchange energy and angular momentum. The tunneling events where the localized spin remains
unchanged \((\phi_i = \phi_f)\) are elastic cotunneling events and those where the local spin changes \((\phi_i \neq \phi_f)\) are inelastic cotunneling events. Analogous effects are observable in transport measurements of quantum dots [58]–[61].

Figure 5 depicts the possible transitions a tunneling electron can undergo in the cotunneling process:

(a)–(b) If the electron is in a \(+1/2\) spin state before the tunneling process, it can transfer \(1\hbar\) of angular momentum to the local spin and exit in the \(-1/2\) spin state. This process changes the magnetic quantum number of the tunneling electron by \(\Delta \sigma = -1\) and that of the local spin by \(\Delta m = +1\). It leaves the local spin in an excited state and is therefore inelastic.

(c) The inverse process occurs for an electron starting in the \(-1/2\) spin state and ending in the \(+1/2\) state. The tunneling electron absorbs \(1\hbar\) angular momentum, resulting in a change of the magnetic quantum numbers of the tunneling electron and the local spin by \(\Delta \sigma = +1\) and \(\Delta m = -1\), respectively. This process is inelastic.

(d)–(e) If the local spin stays in the same state during the tunneling process, the tunneling electron remains in the same spin state as well, hence \(\Delta \sigma = 0\) and \(\Delta m = 0\). This process is elastic.

(f)–(g) In general, the tunneling electron can also excite the local spin without exchanging angular momentum. Such transitions are inelastic and require the existence of spin excitations with \(\Delta m = 0\) for the local spin and are usually possible in the presence of significant transverse magnetic anisotropy or if the uniaxial anisotropy axis and the magnetic field are not parallel.

For the experiments presented in this work, the spin-dependent elastic tunnel current is found to be well described as the elastic cotunneling transitions (d) and (f). Note that with the definition of \(Y\) in equation (3) these transitions are dependent on \(u\), whereas the inelastic cotunneling transitions (a)–(c) are independent of \(u\). It was found that this parameter is essential for the quantitative description of the elastic spin-dependent components of the tunnel current [25, 41, 43]. The parameter \(u\) characterizes the effective electron–spin interaction for the spin system under investigation. In this work, we use it as a phenomenological parameter, but it might be possible to derive it from the locations of the orbital energy levels of the magnetic atom with respect to the Fermi energy (see e.g. [41]).

An interesting observation is that the total probability for a tunneling electron to interact with the local spin is constant [42]. The probability of interacting with the local spin in state \(|\phi_i\rangle\) is given by the sum over all transition intensities \(Y\) that involve the initial spin state \(\phi_i\), i.e. the sum over initial and final states of the tunneling electron and the final states of the local spin. This sum reduces to

\[ \sum_{\phi_i \sigma_i \phi_f \sigma_f} Y(\phi_f, \sigma_f, \phi_i, \sigma_i) = \frac{\frac{1}{2}S(S+1) + 2u^2}{Y_0} \quad (4) \]

and is independent of the initial state of the local spin. Based on this observation the normalization constant \(Y_0\) is chosen as

\[ Y_0 = \frac{1}{2}S(S+1) + 2u^2, \quad (5) \]

which normalizes the total probability of interacting with the local spin to unity.
4.3. Example: a spin with negligible transverse anisotropy

It is instructive to evaluate the transition intensities and spin polarizations for a spin system where the local spin’s eigenstates have well-defined magnetic quantum numbers \( m \). For the Hamiltonian in (1) this is the case when the Zeeman energy is much larger than the anisotropy energies. Hence, the mixing of the spin states due to magnetic anisotropy is negligible. The Mn atom in magnetic fields above 3 T is an example of this case [16, 25]. In the case where the Zeeman energy exceeds the transverse anisotropy but not the uniaxial anisotropy energy, the mixing of the \( m \) states is negligible as long as the axis of the applied magnetic field is collinear with the axis of uniaxial anisotropy (anisotropy coordinates \( a = z, b = x, c = y \)). The Fe atom with magnetic field applied parallel to the N-binding direction is an example of this case [16]. For this class of spin systems, we can find analytic expressions for the transition intensities and their spin polarizations.

Due to the selection rule for spin excitations with electrons, the magnetic quantum number of the local spin can only change by \( \Delta m = \{+1, 0, -1\} \). The transitions with \( \Delta m = \{+1, -1\} \) involve a change in the electron spin as well and are inelastic. The ones with \( \Delta m = 0 \) are elastic and do not change the electron spin. In total, a tunneling electron has four possible transitions with respect to its initial and final states: two elastic transitions as depicted by cases (d) and (e) in figure 5,

\[
Y(\phi_i, +\frac{1}{2}, S, +\frac{1}{2}) = Y_{0}^{-1}(u + \frac{1}{2}m)^2, \\
Y(\phi_i, -\frac{1}{2}, S, -\frac{1}{2}) = Y_{0}^{-1}(u - \frac{1}{2}m)^2,
\]

and two inelastic transitions as depicted by cases (b) and (c) in figure 5,

\[
Y(\phi_i, -\frac{1}{2}, S, +\frac{1}{2}) = \frac{1}{2}Y_{0}^{-1} [S(S + 1) - m(m + 1)], \quad \langle S_z \rangle_{\phi_i} = m + 1, \\
Y(\phi_i, +\frac{1}{2}, S, -\frac{1}{2}) = \frac{1}{2}Y_{0}^{-1} [S(S + 1) - m(m - 1)], \quad \langle S_z \rangle_{\phi_i} = m - 1.
\]

Here, \( m \) refers to the magnetic quantum number of the initial state of the local spin given by the expectation value of the \( S_z \) operator, \( m = \langle S_z \rangle_{\phi_i} \). \( Y_0 \) is the normalization constant of equation (5). The conservation of spin angular momentum restricts the inelastic transitions to the two possibilities where the magnetic quantum number of the final state \( \phi_i \) is either \( m - 1 \) or \( m + 1 \). No inelastic transition with \( \Delta m = 0 \) exists for the case of negligible transverse anisotropy (see figures 5(f) and (g)).

Figure 6 shows how the four possible transitions divide the probability of interacting with a spin state with quantum number \( m \). The graphs are evaluated for the example of a Mn atom with spin \( S = 5/2 \) in a high magnetic field. Since (6) and (7) represent all possible transitions, they sum to unity irrespective of \( m \) as discussed above. The graphs in the three panels are evaluated for different values of \( u \). The functional dependence of the transition depends strongly on the parameter \( u \). For \( u = 0 \) (figure 6(b)) the inelastic transitions that are plotted as darker red and green areas carry most of the transition probability. For non-zero values of \( u \), the elastic transitions gain weight and the sign of \( u \) decides which electron spin tunnels are most likely for any given \( m \) state. For the example considered in this section (a Mn atom in a high magnetic field), the \( +S \) state of the local spin is the ground state. According to equation (6) there are two extreme cases of spin polarization: for \( u = +\frac{1}{2}S \) the elastic transitions in the \( |m = +S\rangle \) ground state can only be performed by \(+1/2 \) electrons (figure 6(a)) and for \( u = -\frac{1}{2}S \) only by \(-1/2 \) electrons (figure 6(c)). Thus, the relative spin polarization of the different transitions carries information about the parameter \( u \). We will show in section 5.4 that it is possible to derive \( u \) from the measured spin excitation spectra.

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Figure 6. Transition intensities for spin transitions in a system with negligible transverse anisotropy plotted as a function of the magnetic quantum number, $m$. The total probability for a tunneling electron to interact with the local spin is unity, see equations (4) and (5). The colored areas show the decomposition of this probability into the four possible transitions a tunneling electron can undergo for different values of $u$ according to equations (6) and (7): (a) for $u = +\frac{1}{2}S$, (b) for $u = 0$ and (c) for $u = -\frac{1}{2}S$. The graphs show the example of a Mn atom ($S = 5/2$) but the functional dependence of the transition intensities is the same for any spin. Elastic tunneling from up to up is plotted in light red, inelastic tunneling from up to down in red, elastic tunneling from down to down in light green and inelastic tunneling from down to up in green.

The overall probability to tunnel an up ($+1/2$) or a down ($-1/2$) electron is linearly dependent on the magnetic quantum number of the local spin. This is signified by the linear division line between the red and green areas in figure 6. The linear dependence emerges when the probabilities to tunnel elastically or inelastically are summed for the $+1/2$ and $-1/2$ initial electron states, respectively. This may provide an avenue to move between the quantum mechanical description of spin-dependent tunneling described here and conventional spin-dependent tunneling. In a classical spin system, the magnetic quantum number $m$ can be replaced by the projection of the spin vector to the $z$-axis, which is given by $|S|\cos(\theta)$ with $|S|$ being the spin magnitude and $\theta$ the angle between the spin vector and the $z$-axis. Since the $z$-axis is chosen to be the orientation of the STM tip’s spin polarization, $\theta$ represents the angle between the polarization directions of the STM tip and the magnetic atom on the surface. Hence, the linear dependence in the tunneling probability versus $m$ seen in figure 6 becomes equivalent to the cosine dependence of the tunnel conductance versus $\theta$ that is observed in thin-film magnetic tunnel junctions and many spin-polarized STM studies when quantum effects of the spin are negligible [62].

4.4. Spin polarization in elastic and inelastic tunneling

The previous section described how the spin of the tunneling electron becomes linked to the local spin. The probability to tunnel an electron with a given spin state depends on the specific state of the local spin and is described by the transition intensity function $Y$. It is no surprise that generally the probabilities to tunnel a $+1/2$ (up) electron or a $-1/2$ (down) electron are different. However, this effect will only become apparent in spin excitation spectra when the STM tip is spin polarized. Similar to conventional magnetic tunnel junctions, it is necessary to have spin polarization in the emitter and the detector electrode in order to observe
spin-dependent variations in the tunnel conductance \cite{49, 63}. In this work, one electrode is the STM tip. Its degree of spin polarization \( \eta \) can be changed by the reversible transfer of magnetic atoms to the apex as described in section 3.2. The other electrode is the magnetic atom on the Cu_{2}N substrate. We define its spin polarization \( \eta \) as the spin dependence in the transition intensity function \( Y \).

4.4.1. Local spin. The probability to excite the local spin between state \( |\phi_{t}\rangle \) and \( |\phi_{i}\rangle \) can be dramatically different for tunneling electrons with \( \sigma_{t} = +1/2 \) or \( \sigma_{t} = -1/2 \), as shown in figure 6. The local spin is treated quantum mechanically and the origin of the spin dependence lies in the exchange interaction between the tunneling electron and the local spin. In order to quantify this asymmetry, we define the spin polarization \( \eta \) of the local spin by its effect on the tunneling electron:

\[
\eta(\phi_{t}, \phi_{i}) = \frac{\sum_{\sigma_{i}, \sigma_{t}} Y(\phi_{t}, \sigma_{t}, \phi_{i}, +\frac{1}{2}) - Y(\phi_{t}, \sigma_{t}, \phi_{i}, -\frac{1}{2})}{\sum_{\sigma_{i}, \sigma_{t}} Y(\phi_{t}, \sigma_{t}, \phi_{i}, \sigma_{t})}.
\] (8)

This definition makes \( \eta \) vary between -1 and +1, where \( \eta(\phi_{t}, \phi_{i}) = -1 \) means that the transition in question can only be excited by \( -1/2 \) electrons. \( \eta \) is the spin polarization evaluated along the quantization axis \( z \) of the tunneling electrons, see figure 4. If the local spin is rotated with respect to this axis, \( \eta \) will change. This will be demonstrated for the case of the Fe atom in section 5.3.

The spin polarization can be re-expressed in terms of the spin operators of the local spin by using (3) and the relation \( S \cdot \sigma + u = S_{z} \sigma_{z} + u + \frac{1}{2}(S^{-} \sigma^{+} + S^{+} \sigma^{-}) \), where \( S^{+} \) and \( S^{-} \) are the raising and lowering operators of the local spin and \( \sigma^{+} \) and \( \sigma^{-} \) are the raising and lowering operators of the spin of the tunneling electron:

\[
\eta(\phi_{t}, \phi_{i}) = \frac{|\langle \phi_{t} | S^{+} | \phi_{i} \rangle|^{2} - |\langle \phi_{t} | S^{-} | \phi_{i} \rangle|^{2}}{|\langle \phi_{t} | \mathbf{S} | \phi_{i} \rangle|^{2}}, \quad i \neq f,
\] (9)

\[
\eta(\phi_{i}, \phi_{i}) = \frac{u \langle S_{z} \phi_{i} \rangle}{\frac{1}{4} \langle S_{z} \phi_{i} \rangle^{2} + u^{2}}, \quad i = f
\] (10)

with \( \langle S_{z} \rangle_{\phi_{i}} \) being the expectation value of the \( S_{z} \) operator for state \( |\phi_{i}\rangle \). Equation (9) shows that the spin polarization of any transition that changes the state of the local spin is given by the raising and lowering operators alone. The parameter \( u \), for example, is not involved. Equation (10) describes the spin polarization of the elastic transitions that do not change the state of the local spin. Here, \( u \) plays an important role as the elastic transitions show spin polarization only for \( u \neq 0 \).

It is worth noting that \( \eta \) is different from the conventional definition of spin polarization in that it does not require assumptions about a spin polarization in the density of states of the magnetic atom at the Fermi energy. Since the local spin is treated quantum-mechanically, assignment of a spin-polarized density of states is impractical and might even be inaccurate because it does not include superpositions of up- and down-electron states, which are necessary to describe the excited states of the local spin. The spin polarization of the local spin as described here arises from the spin dependence in the exchange interaction with the tunneling electron.
4.4.2. Scanning tunneling microscope tip. The spin polarization of the STM tips used in this work is due to one magnetic atom that was attached to the tip apex. This atom could be treated in the same quantum-mechanical framework as the surface-bound atom. However, we find that all measurements in this work are described quantitatively by accounting for a spin-dependent density of states only. A likely reason for this is that the atom on the tip is adsorbed directly on a metal surface. The increased interaction with the conduction electrons of the tip shortens the lifetime of spin excitations and diminishes the quantum-mechanical character of the magnetic atom. This is corroborated by previous observations that individual atoms adsorbed on a metal substrate behave like classical paramagnets [64, 65].

The spin-polarized tips used in this work are paramagnetic and the external magnetic field forces the tip polarization to be parallel with the field direction. For this reason, the quantization axis along which the tip spin polarization is evaluated (the z-axis) is chosen to be aligned with the magnetic field. The spin polarization of the STM tip can therefore be described in analogy to conventional spin-polarized tunneling [33, 49, 63] as

$$\eta = \frac{D(+\frac{1}{2}) - D(-\frac{1}{2})}{D(+\frac{1}{2}) + D(-\frac{1}{2})},$$

where $D(+\frac{1}{2})$ is the density of $+1/2$ electron states at the Fermi energy and $D(-\frac{1}{2})$ that of $-1/2$ electrons. For simplicity we assume here that $D$ is independent of energy around the Fermi energy.

5. Spin-polarized spin excitation spectra

The previous section showed that inelastic spin excitations are typically spin polarized. For the special case of a spin with negligible transverse anisotropy, the inelastic excitations are even fully spin polarized. Sections 3.2 showed qualitatively that this spin polarization results in a distinct asymmetry in the spin excitation spectrum. Now that we have completed the necessary groundwork to understand the spin polarization in the inelastic transitions themselves, we can obtain a quantitative understanding of the asymmetry in the measured spectra.

5.1. Quantitative spin-polarization measurement

Figure 7 decomposes the spin excitation spectrum of a Mn atom into the relevant components. With the application of a large magnetic field, the Mn spin states spread out in a ladder to higher energies (figure 7(a)). The $m = +S = +5/2$ state is the stable ground state of the system. There are three possible tunnel paths that could contribute to the overall tunnel current: inelastic tunneling where electrons promote the Mn atom from the $+5/2$ state to the $+3/2$ state (red arrow), elastic spin-dependent tunneling where electrons interact with the Mn spin via equation (3) but do not change the Mn spin state (blue arrow) and elastic background conductance where the tunneling electrons do not interact with the Mn spin (gray arrow). The two elastic tunnel paths create a voltage-independent conductance (parts $E^-$, $E^+$ and $b_0$ in figure 7(b)). The colored areas $A^-$ and $A^+$ in figure 7(b) correspond to the inelastic tunnel current and create the steps in the differential conductance at the threshold voltage for spin excitation. The inelastic transition in the Mn atom can only be excited by $-1/2$ electrons, see equation (7). If we assume a spin-polarized density of states in the tip that has more $+1/2$ electron states at the
Figure 7. Tunneling processes on a magnetic atom. (a) Schematic diagram of the possible tunnel paths when the STM tip is positioned over a Mn atom: inelastic spin-dependent tunneling (red), elastic spin-dependent tunneling (blue) and spin-independent background tunneling, $b_0$ (gray). All tunneling electrons in the blue and red paths interact with the Mn spin but only the inelastic tunneling excitations from the $m = +5/2$ to the $m = +3/2$ state. Direct excitations into higher states are forbidden (black dotted line). (b) Idealized conductance spectrum with contributions for each tunnel path: inelastic spin-dependent tunneling, $A^+$ (green), $A^-$ (red); elastic spin-dependent tunneling, $E^+$, $E^-$ (blue); spin-independent background tunneling, $b_0$ (gray). (c) Sketch of the tunnel paths in the spin-dependent densities of states of the STM tip (upper row) and Cu substrate (lower row) at negative voltage. The number of available states with correct spin in the tip and the substrate determines the relative strength of each tunnel path (indicated by the arrow thickness). (d) The same plot as in (c), but for positive voltage.

Fermi energy than $-1/2$ states, $\eta_t > 0$, we directly obtain the observed asymmetry. At negative voltage (figure 7(c)), the inelastic tunnel channel requires $-1/2$ electrons to tunnel from the non-spin-polarized substrate to the tip. In the process, the electron spin flips to $+1/2$ and ends in the $+1/2$ states of the tip. In contrast, for positive voltage the inelastic tunnel channel involves the $-1/2$ states in the tip, because the tunnel process again starts with $-1/2$ electrons. Because there are more $+1/2$ states than $-1/2$ states in the tip, the conductance step at negative voltage is larger.

Generally, the height of the conductance steps depends on the spin polarization of the tip and the spin polarization of the respective spin excitation as described in section 4.4. By using equation (9) and the established formalism for spin-polarized tunnel junction conductance.
shows excitation spectra of Mn for different tip spin polarizations at 7 T magnetic field.

The analysis of the Mn spin excitation spectra is straightforward, because the Mn atom has negligible magnetic anisotropy. For structures having larger magnetic anisotropy, the relative orientation of magnetic field and the principal magnetic axis plays an important role. Fe bound to Cu$_2$N has a large magnetic anisotropy of $D = -1.6$ meV [16]. The negative sign of $D$ means that the anisotropy is easy-axis, where the lowest-energy states have the largest magnitudes for $m$. The Fe atom also has a significant transverse anisotropy of $E = 0.3$ meV [16]. Thus, the

\[
A^+ = \frac{dI}{dV} (V > V_{\text{thr}}) - \frac{dI}{dV} (V < V_{\text{thr}}) = \frac{G}{4} \left[ (1 + \eta_s) (1 + \eta_t) + (1 - \eta_s) (1 - \eta_t) \right],
\]

\[
A^- = \frac{dI}{dV} (V < -V_{\text{thr}}) - \frac{dI}{dV} (V > -V_{\text{thr}}) = \frac{G}{4} \left[ (1 - \eta_s) (1 + \eta_t) + (1 + \eta_s) (1 - \eta_t) \right],
\]

where $\eta_t$ is the spin polarization of the tip, see equation (11), and $\eta_s$ is the spin polarization of the spin excitation, see equation (9). $V_{\text{thr}}$ is the onset threshold voltage for excitation from $\phi_t$ to $\phi_i$, see figure 7(b). Note that $\eta_s = \eta_s(\phi_t, \phi_i)$ and $V_{\text{thr}}$ differs for different spin excitations. $G$ is a constant and contains the spin-independent sample and tip densities of states close to the Fermi energy (sum of +1/2 and −1/2 electron states) and the transmissivity of the tunnel barrier [25, 66, 67]. $A^+$ in equation (12) corresponds to the conductance step at positive voltage where electrons tunnel from the tip to the sample and $A^-$ corresponds to the conductance step at negative voltage where electrons tunnel from the sample to the tip.

The net polarization of the inelastic tunnel conductance can be obtained by calculating the difference of the conductance steps at positive and negative voltage

\[
P = \frac{A^+ - A^-}{A^+ + A^-} = \eta_t \cdot \eta_s.
\]

It reduces to the product of the two spin polarizations $\eta_s$ and $\eta_t$. The effective behavior of the inelastic tunnel channel is therefore analogous to conventional spin-polarized tunneling where the net polarization in the tunnel junction results from spin-polarized density of states in the tip and the sample.

5.2. Spin polarization in a low-anisotropy spin system: Mn

Figure 8 shows excitation spectra of Mn for different tip spin polarizations at 7 T magnetic field. A non-functionalized tip has no net spin polarization at the Fermi energy and the conductance steps are symmetric (figure 8(a)). Tips that have one Mn or Fe atom attached to the apex typically result in a positive tip spin polarization that is of the order of $\eta_{\text{tip}} = 0.3$ (figure 8(b)). We find that inverse spin polarization can be obtained by attaching multiple Mn atoms to the tip (figure 8(c)). This is reasonable considering that bulk Mn is antiferromagnetically ordered.

Mn is a good spin system to measure the tip’s spin polarization, because it has only small magneto-crystalline anisotropy ($D = -39$ μeV [16]). At magnetic fields above 3 T the Zeeman energy far exceeds the anisotropy energy. As a result, the spin polarization of the excitation from $|m = \pm 5/2\rangle$ to $| \pm 3/2\rangle$ is $\eta_s = -1$ irrespective of the direction of the applied magnetic field. The net polarization of the inelastic tunnel conductance $P$, equation (13), then equals $-\eta_t$ and thus allows us to easily determine the tip spin polarization.

5.3. Spin polarization in a high-anisotropy system: Fe

The analysis of the Mn spin excitation spectra is straightforward, because the Mn atom has negligible magnetic anisotropy. For structures having larger magnetic anisotropy, the relative orientation of magnetic field and the principal magnetic axis plays an important role. Fe bound to Cu$_2$N has a large magnetic anisotropy of $D = -1.6$ meV [16]. The negative sign of $D$ means that the anisotropy is easy-axis, where the lowest-energy states have the largest magnitudes for $m$. The Fe atom also has a significant transverse anisotropy of $E = 0.3$ meV [16]. Thus, the
energy eigenstates each contain a mixture of \( m \) states. Figure 9 shows spin excitation spectra of Fe atoms recorded for a magnetic field of 3 T applied parallel to the easy axis (left column, figure 9) and perpendicular to it (right column, figure 9). In practice, rather than rotating the magnetic field, we placed the Fe atoms on Cu binding sites with 90°-rotated crystallographic symmetry so that their easy-axis direction was rotated relative to \( B \) [16]. For each alignment, we recorded spin excitation spectra using a spin-averaging tip and a spin-polarized tip.

The Fe atom’s spin is \( S = 2 \) and its principal axis is parallel to the N binding direction, which is the \( a \)-axis direction in the convention of equation (1). The structure is sketched in figures 9(a) and (b). It was shown in [16] that a magnetic field applied parallel to the principal axis (\( a = z \)) reduces the effects of transverse anisotropy. Then the spin states are well characterized with the magnetic quantum number \( m \). The strongest excitation occurs at \( \pm 4 \) mV and corresponds to the direct transition from the \( |m = +2\rangle \) ground state to the \( |m = +1\rangle \) spin state (figure 9(c)). In the parallel field configurations, we therefore probe the spin polarization of the system along its easy magnetic axis \( a \) and the \( |m = +2\rangle \) to \( |+ 1\rangle \) transition shows strong spin polarization as differing step heights for opposite signs of \( V \). In contrast, when the magnetic field is applied perpendicular to the principal axis (\( a \perp z \)) the \( \pm 4 \) mV transition shows only a slight spin polarization (figure 9(d)). This behavior is understandable considering that the easy-axis anisotropy exceeds the Zeeman energy. Hence, the Fe atom’s spin stays aligned mostly parallel to the \( a \)-axis even for rather strong perpendicular magnetic fields. The tip is, however, spin polarized parallel to the magnetic field, so it is nearly perpendicular to the Fe spin. As a result, only weak spin polarization is observed.

The spectra on the Fe atom for parallel and perpendicular magnetic field alignment were recorded with the same tips, so that the spectra are quantitatively comparable. For the quantitative analysis of the excitation cross-sections, we calculate the second derivative of the tunnel current, \( d^2 I/dV^2 \). The spin excitations that are visible as steps in the differential conductance, \( dI/dV \), appear as peaks to positive or negative values in \( d^2 I/dV^2 \) (figures 9(e)

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Figure 8. Spin excitation spectra, \( dI/dV \) versus \( V \), of Mn atoms recorded at 7 T magnetic field with (a) a normal metal spin-averaging STM tip, (b) a spin-polarized STM tip produced in the manner shown in figure 3 and (c) a spin-polarized tip that showed inverse spin polarization after attaching multiple atoms to the tip apex. The tip spin polarization, \( \eta_t \), is evaluated for each graph according to equations (12) and (13) using \( \eta_s = -1 \). The measured conductance is divided into the elastic components \( E^+ \), \( E^- \) and inelastic components \( A^+ \), \( A^- \) in the way shown in figure 7(b). The spin-independent background conductance \( b_0 \) is negligible for measurements with sharp STM tips on atoms adsorbed on the Cu\(_2\)N layer [25].
and (f)). The peaks in $d^2I/dV^2$ were fitted using a Gaussian function, which is a close approximation to the lineshape for inelastic tunneling [66, 68]. The area under the Gaussian equals the step height in the differential conductance and we use these values for determining the spin polarization. Use of the second derivative allows a robust determination of the $dI/dV$ step heights without being sensitive to background slopes and peaks in the spectra. Additionally, this method provides a standardized way to analyze spin excitation spectra where the conductance change deviates from the perfect step shape as observed for some of the Fe spin excitations. The

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Figure 9. Spin excitation spectra of Fe atoms for two orientations of the tip’s spin polarization at 3 T magnetic field. Left column: magnetic field direction is parallel to the easy magnetic axis of the Fe atom. Right column: magnetic field is perpendicular to the easy axis of the Fe atom. The spin polarization of the tip follows the magnetic field $B$. (c, d) Spin excitation spectra, $dI/dV$ versus $V$, of the Fe atoms. The upper spectrum was recorded with a spin-averaging tip (SA tip) and the lower spectrum with a spin-polarized tip (SP tip) with $\eta_t = 0.35$. Note that the same SA tip and SP tip were used to record the spectra in (c, d). The Fe atom exhibits strong spin polarization in the steps at $\pm 4$ mV for the parallel field configuration. In contrast, only weak polarization is detected for the perpendicular field configuration. (e, f) Numerical derivative, $d^2I/dV^2$ versus $V$, of the differential conductance spectra in (c, d). The steps in the $dI/dV$ spectrum now appear as peaks to positive and negative values and the area under each peak in $d^2I/dV^2$ equals the height of the step in $dI/dV$. Red curves are fits to the data and red labels give their areas. (g, h) Simulated $d^2I/dV^2$ versus $V$ spectra using the spin Hamiltonian in equation (1) and the transition intensity function, $Y$ (see footnote 2). The lower curves in (c, d) are shifted by $-0.05 \mu S$, those in (e, g) by $-0.07 \mu S$ mV$^{-1}$, and those in (f, h) by $-0.1 \mu S$ mV$^{-1}$ for clarity.

peak-like character of the steps at $\pm 4$ mV in the $dI/dV$ spectrum modifies the shape of the peak in $d^2I/dV^2$. This variation in the lineshape is likely due to virtual excitations of the tunneling electron as it tunnels between the tip, the local spin and the substrate. Similar variations in the lineshape of inelastic excitations have been discussed by Mii et al [69] in the context of vibrational excitations of a localized state. A detailed treatment of the exact $d^2I/dV^2$ lineshapes for inelastic spin excitations is beyond the scope of this work. Here we restrict our analysis to the determination of the relative weight of the spin excitations at positive and negative voltage, for which the outlined fitting method using a Gaussian function at both voltage polarities is sufficient.

The spectra recorded with the spin-averaging tip show no significant asymmetry for the excitation at $\pm 4$ mV in both field configurations. This is expected as the tip lacks the necessary spin sensitivity. Using equation (13), we obtain a polarization of $P = -0.02$ for both the parallel field and the perpendicular field configurations. However, with a spin-polarized tip, the same excitation shows $P = -0.33$ when probed in parallel configuration and only $P = -0.06$ when probed in the perpendicular configuration with the same tip. We fitted values for $D$ and $E$ for the particular Fe atoms shown in figure 9 to the energies of the observable spin excitations by calculating the spin eigenstates using the spin Hamiltonian of equation (1)$^2$. The relative weights

$^2$ In figures 9(a) and (b) the same spin-polarized and spin-averaging tips were used in order to allow quantitative insight into the influence of rotating the magnetic field relative to the anisotropy axis of the Fe atom. The anisotropy parameters for the Fe atoms on which the excitation spectra were recorded are (c) SA tip: $g = 2.11$, $D = -1.57$ meV, $E = 0.32$ meV; SP tip: $g = 2.11$, $D = -1.55$ meV, $E = 0.30$ meV; and (d) SA tip: $g = 2.11$, $D = -1.63$ meV, $E = 0.32$ meV; SP tip: $g = 2.11$, $D = -1.53$ meV, $E = 0.32$ meV. The calculated excitation spectra in figures 9(g) and (h) were convoluted with a Gaussian with a width of $\Delta V = 410 \mu V$ to reproduce the experimentally observed broadening. This broadening is larger than the thermal broadening and points to a short lifetime of the visible spin excitations as expected from systems with large transverse anisotropy (compare with [25]).
of the spin excitations depend on $D$ and $E$, as the overlap between the different eigenstates changes with these parameters. We find that fitting the energetic positions is sufficient to quantitatively reproduce the measured $d^2I/dV^2$ spectra including the relative weights of the inelastic peaks (figures 9(g) and (h)). The spin polarization of the $\pm 4$ mV excitation itself can be obtained from the spin states in the manner discussed in section 4.4. At 3 T magnetic field parallel to the $a$-axis, the calculated spin polarization of this excitation is $\eta_s = -0.95$, slightly smaller than expected for a $|m = +2\rangle$ to $| + 1\rangle$ transition. This is a consequence of the non-zero transverse anisotropy. Together with the experimentally determined $P$ of $-0.33$, we can use equation (13) to obtain the tip’s spin polarization of $\eta_t = +0.35$.

With the knowledge of the tip’s spin polarization in the axis of the magnetic field, we can determine the spin polarization of the $\pm 4$ mV excitation for the perpendicular field configuration. From the measured $P$ of $-0.06$ we can estimate it to $\eta_s = -0.16 \pm 0.05$. This agrees with the expected spin polarization of $\eta_s = -0.23$ as determined by equation (9) from the calculated eigenstates of the spin system. For this configuration, we keep the quantization axis $z$ of the tunneling electrons parallel to the magnetic field, and set the Fe easy axis $a$ to be perpendicular to it, as shown in figure 9(b). In the limit of small perpendicular magnetic fields, the excitation would be expected to have no spin polarization, $\eta_s = 0$. The non-zero spin polarization results from the 3 T magnetic field that pulls the Fe atom’s spin out of the easy axis. More generally, the transverse magnetic field and the transverse anisotropy cause mixing of the spin states that tend to reduce the polarization $P$ and thus the asymmetry of the conductance steps in the spin excitation spectrum. This mixing is further evidenced by the appearance of additional conductance steps in figure 9(d) at $\pm 0.5$ mV.

5.4. Magneto-resistive elastic tunneling

Electrons can interact with the magnetic atom on the surface elastically as well as inelastically [25]. The previous section showed that the spin polarization of the inelastic transitions can be determined by measuring the asymmetry in the conductance steps for the same excitation at positive and negative voltage. The elastic tunneling, however, can still be spin dependent because the electrons interact with the local spin even when they do not exchange energy with it. Equation (10) shows that the amount of spin polarization in the elastic tunneling and the relative weight between inelastic and elastic tunnel paths depend on the value of $u$. It should therefore be possible to quantitatively determine $u$.

Since $u$ is the parameter that characterizes electron–spin interaction between the tunneling electron and the local spin, it should be independent of the specific probe tip. Figure 10(a) shows the values of $u$ for Mn atoms as determined by fitting the spin excitation spectra recorded with different tips and on different Mn atoms. The histogram shows a clear maximum at $u_{\text{Mn}} = 1.19$ with the half-width at half-maximum (HWHM) of $\Delta u_{\text{Mn}} = 0.09$. This value is close to $u = +\frac{1}{2}S$ (Mn) = 1.25 at which maximum positive spin polarization is achieved for elastic tunneling on Mn (see figure 6(a)). The histogram comprises measurements at magnetic fields between 3 and 7 T strength. $u$ was found to be independent of the magnetic field in this interval.

The same analysis is possible for Fe atoms when the magnetic field is applied parallel to the easy magnetic axis. The histogram (figure 10(b)) shows a peak at $u_{\text{Fe}} = 0.74$. This is significantly lower than the value of $u = \frac{1}{2}S$ (Fe) = 1.00, which would correspond to maximal spin polarization in the elastic channel for the Fe atom.
Figure 10. Histogram of fitted values of $u$ for (a) Mn atoms with a total of 71 different Mn atoms and STM tip configurations at magnetic fields ranging from 3 to 7 T. The maximum of the distribution is at 1.18, slightly below 1.25, indicating a high spin polarization in the elastic conductance. (b) Fitted $u$ values for Fe atoms with a total of 14 different Fe atoms and STM tip configurations at 7 T magnetic field applied parallel to the Fe atom’s easy axis. The maximum of the distribution for the values of $u$ is at 0.74, indicating a reduced spin polarization of the elastic conductance.

We note that the presence of spin-independent background conductance (referred to as $b_0$ in figure 7) is a source of uncertainty in this analysis that might influence the measured value of $u$. In standard spin excitation spectra, spin-independent elastic conductance cannot be distinguished from spin-dependent elastic conductance. However, it was recently possible to reverse the spin orientation of the surface-bound spin by spin-momentum transfer while recording spin excitation spectra [25]. These measurements showed that sharp STM tips have a spin-independent background conductance of less than 10% of the overall conductance. A variation in $b_0$ from 0 to 10% has no significant impact on the average value of $u$. Thus, we set $b_0$ to zero in this work but note that this simplification might not be feasible for other measurements with e.g. blunter STM tips or samples where the magnetic atoms are not placed on a decoupling layer. Besides, additional spin-independent background can only decrease the ratio of inelastic tunneling to elastic tunneling. Therefore, it can only bias $u$ towards larger values. Hence, the deviation of the Fe atom’s $u$ from the one expected for maximal spin polarization is significant.

Both Mn and Fe have positive $u$ and the elastic transitions, therefore, have a positive spin polarization, see equation (10). This implies that the electron–spin interaction is ferromagnetic in the sense that electrons are more likely to tunnel when they are aligned with the localized spin.

The difference in $u$ for tunneling through Mn atoms or Fe atoms indicates that this interaction is dependent on the elemental species of the atomic spin. We speculate that this may be a consequence of differences in the binding configuration of the different magnetic atoms and the concomitant change in the orbital wave functions that are involved in the tunneling process.

6. Conclusion

The measurements presented in this work demonstrate that inelastic electron tunneling spectroscopy in combination with spin-polarized probe tips provides detailed information on the spin-dependent properties of individual atoms adsorbed on surfaces. In conventional
spin-polarized tunneling, the polarization of the tunnel conductance is well described by the dot product of the polarization vectors of the tip and the sample. In contrast, individual atoms on thin decoupling layers behave like quantum-mechanical spin systems and the classical terms in the spin-dependent tunneling have to be replaced by matrix elements of the spin operators. Here, we presented a model that quantitatively fits the observed spin dependence in the elastic and inelastic components of the tunnel conductance. The effective electron–spin interaction is well described as the combination of a spin-dependent isotropic exchange interaction and a spin-independent scattering term. The reversible transfer of a magnetic atom to the STM tip presents a way to measure the same local structure with a spin-polarized and a non-spin-polarized tip. This allows us to quantify the strength of the spin-dependent transition intensities and will help us to deepen the understanding of the electron–spin interaction that underlies magnetic tunneling.

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