Theory of spin inelastic tunneling spectroscopy for superconductor-superconductor and superconductor-metal junctions

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We address the tunneling conductance and spin inelastic tunneling spectroscopy of localized paramagnetic moments in a superconducting environment, pertaining to recent measurements on Fe-octaethylporphyrin-chloride using superconducting scanning tunneling microscopy. In good agreement with experiment, we find that the applied bias needs to overcome the added tip and substrate superconducting pairing potentials, in order for electrons to tunnel and assist excitations of the local spin. A side by side comparison is made by considering the equivalent setup with a normal metal tip and we find the onset of tunneling at a voltage bias corresponding to the substrate pairing potential alone. When simulating the effects of electron pumping, we obtain additional peaks in the conductance spectrum that can be attributed to excitations between higher energy spin states. The transverse anisotropy field couples basis states of the local spin which opens for transitions between spin states that are otherwise forbidden by conservation of angular momentum. Finally, we explore the influence of an external magnetic field that splits any remaining degenerate spin states. Notably causing the appearance of a low and high excitation peak on each side of the main coherence peak as an imprint of transitions between the Zeeman split ground states.

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I. INTRODUCTION

Research into single spin manipulation remains one of the most active areas in materials science. Justifiable, as control of single spins would enable information storage with order of magnitude increased density as well as the possible realization of practical quantum computers. Writing and reading information from a localized atomic or molecular spin necessarily involves controlled transitions between different energy states. In most experimental cases under ambient conditions however, spontaneous interaction with surrounding spin carriers severely limits the mean free lifetime of the the local spin excitations below a realistic clock cycle.

Magnetic atoms or molecules resting on a metal surface, for example, typically de-excite within picoseconds as energy and angular momentum is transferred to itinerant electrons of the substrate. As a measure to increase such lifetimes, by limiting the number of ways the local spin can give away energy, an insulating layer can be applied in-between the metal and the local spin. CuO, BN, and Cu2N have all been used in this manner, to effectively create a band gaped substrate, which increases the mean lifetime to hundreds of picoseconds.

While several novel ways to increase spin excitation lifetimes have been suggested and proven successful a natural progression from a separating insulating layer is to use a superconducting substrate that exhibits a perfect band gap yet still conducts charge. At low temperatures a spontaneous de-excitation of the local spin state must then provide enough energy to break up a Cooper pair in order for the main de-excitation mechanism to occur, i.e. quasiparticle–hole pair creation. A drawback of a superconducting substrate is the appearance of unwanted Shiba states, within the superconducting gap, generated by exchange interaction between the localized spin moment and the electrons in the superconductor. To minimise the effect of these states Heinrich et.al successfully utilized a paramagnetic organic molecule, e.g. M-octaethylporphyrin-chloride (M-OEP-Cl) where M denotes a transition metal element (Mn, Fe, Co, Ni, Cu), to engage the local magnetic moment such that the direct interaction is kept to a minimum. The Shiba states then migrate close to the main coherence peaks and are indiscernible unless the temperature is very low. In addition to providing separation the ligand cage of the paramagnetic molecule also generate an environment of magneto crystalline anisotropy for the central magnetic moment that splits up the otherwise degenerate spin states into different energy levels. This method prolonged the mean lifetime of the first excitation to \( \tau \approx 10\mathrm{ns} \), which is enough to clearly observe pumping into higher spin states. The experiments, conducted on a Pb substrate using a Pb covered tip at 1.2 K, shows, in addition, that inelastic scattering between the tunneling electrons and the local spin moment only give signatures in the \( dI/dV \) spectra for bias potentials \( |eV| = \Delta_{\text{sub}} + \Delta_{\text{tip}} + \Delta_{\text{mn}} \), where \( \Delta_{\text{mn}} \) is the spin state excitation energy.

The theoretical model derived in this paper emulates single electron tunneling in a Scanning Tunneling Microscope (STM) setup where the tip is made up of a normal metal (NM) or a superconductor (SC). As a substrate, on which a paramagnetic organic molecule lies, only a superconductor is considered. The magnetic centre of the molecule provides a local spin moment, within an anisotropic environment, elevated enough to prevent significant direct magnetic interaction with the close by
superconductors. An applied bias voltage, which controls the relative Fermi levels of the tip and substrate, will induce a tunneling current of electrons that either pass the local spin moment unnoticed or interact with exchange of energy and angular momentum. See Fig. 1 for a sketched illustration of the setup.

In excellent agreement with experiment our transparent (differential) conductance expression yield signatures of inelastic spin transitions only outside of the tip and substrate superconducting gap at low temperatures. We also reproduce the observed effects of pumping to reveal interactions with higher spin states. Beyond the reproduction of experimental results the conductance spectra are thoroughly investigated with respect to varying anisotropies and external magnetic fields.

While some of the results have been published elsewhere, the present paper also includes the case of a localized magnetic moment embedded in a normal metal — superconductor junction, as well as a systematic study of the influence of external magnetic field. For completeness and to enable a comparison between the different scenario, we also include details of the superconductor — superconductor junction.

The paper is organized as follows. In Sec. II, we detail the theoretical derivation of the expression for the differential conductance, while in Sec. III we analyze and present the main results for spin $S = 1$ and $S = 5/2$ systems. We conclude the paper in Sec. IV.

II. THEORETICAL DESCRIPTION OF THE MODEL

The electronic composition and interplay within the STM device is governed by the total Hamiltonian

$$\mathcal{H} = \mathcal{H}_\text{tip} + \mathcal{H}_\text{sub} + \mathcal{H}_T + \mathcal{H}_S + \mathcal{H}_K,$$

where $\mathcal{H}_\text{tip}$ and $\mathcal{H}_\text{sub}$ gives the electronic structure of the tip and the substrate respectively. In this study, we consider two different types of tip states, (i) normal metal and (ii) superconducting. These are modeled using

$$\mathcal{H}_\text{tip}^{(NM)} = \sum_{p\sigma} \varepsilon_{p\sigma} c_{p\sigma}^\dagger c_{p\sigma},$$

$$\mathcal{H}_\text{tip}^{(SC)} = \sum_{p\sigma} \varepsilon_{p\sigma} c_{p\sigma}^\dagger c_{p\sigma} + \sum_{\sigma} \Delta_{\text{tip}} c_{p\uparrow}^\dagger c_{-p\downarrow} + \text{H.c.},$$

respectively. Here, $c_{p\sigma}^\dagger$ ($c_{p\sigma}$) creates (destroys) an electron/quasiparticle in the tip with momentum $p$ and spin $\sigma = \uparrow, \downarrow$. The substrate quasiparticles are modeled by

$$\mathcal{H}_\text{sub} = \sum_{k\sigma} \varepsilon_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k\sigma} \Delta_{\text{sub}} c_{k\uparrow}^\dagger c_{-k\downarrow} + \text{H.c.},$$

where $c_{k\sigma}^\dagger$ ($c_{k\sigma}$) and $k$ denote electron operators and momentum, respectively. The three parts, tip, substrate, and sample, are connected via tunneling through

$$\mathcal{H}_T = \sum_{p'k'\sigma'} \varepsilon_{p'\sigma'} [T_0 \delta_{\sigma\sigma'} + T_1 \sigma \cdot \sigma' \cdot \mathbf{S}_1] c_{k'\sigma'} + \text{H.c.}$$

One direct tunneling path, with a rate $T_0$ ($\delta_{\sigma\sigma'}$ is the Kronecker delta), is spin preserving, whereas a second tunneling path, with rate $T_1$, accounts for the interaction between the electron spin and localized spin. Here, $\sigma \cdot \sigma'$ is the Pauli-matrix vector. The ratio $T_1/T_0$ may be in the order of unity since this rate is determined both by the tunneling overlap as well as the Coulomb assisted tunneling rate, see, e.g., 19.

The local magnetic moment, embedded in the anisotropic environment of the organic molecule, derives its $2S + 1$ fold spectrum of spin eigenenergies and states $|E_{\alpha, |\alpha\rangle}$, from the Hamiltonian

$$\mathcal{H}_S = -g \mu_B \mathbf{B} \cdot \mathbf{S} + D S_z^2 + \frac{E}{2} (S_+^2 + S_-^2).$$

Here, $g$ is the gyromagnetic ratio, $\mu_B$ is the Bohr magneton and $\mathbf{B}$ is an external magnetic field. For arbitrary integer total spin moment $S$ and a finite uniaxial anisotropy field $D$ the basis states $|S_z, m_z\rangle$, $m_z = -S_z, -S_z + 1, \ldots, S_z$, remain eigenstates with twofold degenerate excitations. The transverse anisotropy field $E$ will split up these excitations as well as cause the eigenstates to form linear combinations of the basis states. A half integer spin moment behaves much in the same way under finite anisotropies with the exception that $E$ no longer splits up the two fold degenerate excitations but rather shifts the energy levels somewhat.

Direct local interactions, responsible for Shiba states, are described by

$$\mathcal{H}_K = \sum_{kk'\alpha\alpha'} J_{kk'} c_{k\alpha}^\dagger \sigma_{\alpha\alpha'} \cdot \mathbf{S} c_{k'\alpha'}.$$
For a large local spin moment ($S >> 1$) that couples weakly ($J_{kl} \rightarrow 0$) to the surface electrons (ensured by the separating ligand cage in-gap resonances appear at energies $\omega_0 = \pm \Delta_{sub} [1 - (\pi N J S/2) \omega_0]$) where $N$ is the substrate density of states (DOS). For $N S < 2k_B T/3\pi$, these states are hidden within the thermally broadened coherence peaks and, although such states may influence the lifetime of the spin excitations, we omit this contribution in the following derivation in order to focus on the signatures observed in experiment.

A. The tunneling current

The tunneling current under bias voltage from one lead to another, whether in a fixed junction or a scanning tunneling microscope (STM), is derived by evaluating the rate of change in electron occupation number for either lead,

$$ I(t) = -e \partial_t \sum_{p \sigma} \langle c_{p\sigma} \rangle. \tag{7} $$

Heisenberg’s equation of motion ensures that a tunneling contribution is given once the number operator fails to commute with any term of the total Hamiltonian – a condition fulfilled by $H_T$ in our context. Quite generally, provided no additional interactions, standard non-equilibrium Green function theory takes us to the tunneling current expression

$$ I(t, V) = 2e \text{Re} \sum_{p \omega \omega'} \sum_{\alpha, \beta} \int_{-\infty}^{\infty} \left[ G_{p\omega,\alpha\beta}(t', t) \bar{G}_{k\omega,\alpha\beta}(t, t') T_{\omega \omega'}(t) \bar{G}_{k'\omega',\alpha\beta}(t', t') \right] e^{i e V(t-t')} dt'. \tag{8} $$

once (7) is expanded up to linear order in the tunneling interaction. Here $\hbar = 1$, $e$ is the electron charge, $T_{\omega \omega'}(t) = T_0 \delta_{\omega \omega'} + T_1 \sigma_{\omega \omega'} \cdot \mathbf{S}(t)$ and $e V$ provides an applied bias voltage as a result of the replacements $\varepsilon_{p\omega'} \rightarrow \varepsilon_{p\omega} + eV/2$ and $\varepsilon_{k\omega} \rightarrow \varepsilon_{k\omega} - eV/2$. The two commutator terms within the quantum mechanical average account for two different tunneling mechanisms. The first term gives the Josephson tunneling contribution where the net transfer is a spin zero Cooper pair that can not change the spin state of the local magnetic moment. This term will be omitted throughout the rest of the paper since our main interest currently lies in spin-spin correlation tunneling. The second term describes single electron tunneling and may, analogous to previous studies on NM leads, be divided into three different parts proportional to $I_0 \propto T_0^2$, $I_1 \propto T_0 T_1$ and $I_2 \propto T_1^2$. \textsuperscript{21-25}

$I_0$ is the direct tip to substrate tunneling current,

$$ I_0(t, V) = 2eT_0^2 \text{Re} \sum_{p \omega \omega'} \int_{-\infty}^{\infty} \left[ G_{p\omega,\alpha\beta}^<(t', t) G_{k\omega,\alpha\beta}^>(t, t') - G_{p\omega,\alpha\beta}^>(t', t) G_{k\omega,\alpha\beta}^<(t, t') \right] e^{i e V(t-t')} dt', \tag{9} $$

and contains electron Green functions of the kind $G_{p\omega,\alpha\beta}(t', t) = i \langle c_{p\omega}^\dagger(t') c_{p\omega}(t) \rangle_{H_{tip}}$, where $H_{tip}$ determines the electron environment in the tip. Contributions from $I_0$ are kept as a background current in our calculated results. $I_1$, on the other hand, does couple to the local spin moment,

$$ I_1(t, V) = 2eT_0 T_1 \text{Re} \sum_{p \omega \omega'} \int_{-\infty}^{\infty} \left[ G_{p\omega,\alpha\beta}^\dagger(t', t) G_{k\omega,\alpha\beta}^<^<(t, t') \sigma_{\omega \omega'} \cdot \mathbf{S}(t') + \sigma_{\omega \omega'} \cdot \mathbf{S}(t) \right] \cdot \sigma_{\omega \omega'} e^{i e V(t-t')} dt', $$

but gives no contribution to the tunneling current unless magnetically polarized tips and substrates are used and is therefore excluded in our presented results. $I_2$ receives our main attention as it contains the spin correlation functions that allow the tunneling current to either excite or de-excite spin states of the local magnetic molecule. In general

$$ I_2(t, V) = 2eT_1^2 \text{Re} \sum_{p \omega \omega'} \int_{-\infty}^{\infty} \sigma_{\omega \omega'} \cdot \left[ G_{p\omega,\alpha\beta}^\dagger(t', t) G_{k\omega,\alpha\beta}^<^<(t, t') \chi^>(t, t') \right] - \sigma_{\omega \omega'} \cdot \left[ G_{p\omega,\alpha\beta}^\dagger(t', t) G_{k\omega,\alpha\beta}^<^<(t, t') \chi^<(t, t') \right] \cdot \sigma_{\omega \omega'} e^{i e V(t-t')} dt', $$

where $\chi^>(t, t') = \langle \mathbf{S}(t) \mathbf{S}(t') \rangle$.

The electron spin projection onto the spin correlation functions of the local magnetic moment amounts to

$$ \sigma_{\omega \omega'} \cdot \langle \mathbf{S}(t) \mathbf{S}(t') \rangle = \sum_{a \beta} \left( 2\chi_{\alpha \beta}^{+-} + \chi_{\alpha \beta}^{++} + \chi_{\alpha \beta}^{--} \right) e^{i E_a - E_\beta(t-t')} \cdot \mathbf{S}(t) \mathbf{S}(t'), $$

(12)
where

\[ \chi_{\alpha\beta}^{z\rightarrow\pm} = \langle \alpha | S_{z\rightarrow\pm} | \beta \rangle \langle \beta | S_{z\rightarrow\pm} | \alpha \rangle P(E_{\alpha}) \left[ 1 - P(E_{\beta}) \right], \] (13)

in the atomic limit where the decoupling

\[ \langle d_{\alpha}^\dagger (d_{\alpha}^\dagger + d_{\beta}^\dagger + d_{\beta}) \rangle \] (14a)

\[ = \langle d_{\alpha}^\dagger (d_{\alpha}^\dagger + d_{\beta}^\dagger + d_{\beta}) \rangle \] (14b)

is the same as considering a stationary case. We may consequently Fourier transform to the energy domain and rewrite, e.g., \( \chi^{z}(t,t') = \int \chi^{z}(\omega)e^{-i\omega(t-t')}d\omega/(2\pi). \)

\[ B. \ \text{Normal metal to superconductor junction} \]

For a normal metal (NM) to superconductor (SC) junction the conditions differ for tip and substrate electrons/quasiparticles and consequently so does their respective Green functions. As an outset, considering the NM to be of a NM, the electronic structure is provided by Eq. (2a). The lesser and greater Green functions of the tip are then simply

\[ G_{\alpha\rho}(\omega) = i\left\{ c_{\alpha}(t)c_{\rho}^\dagger(t') \right\} = if(\omega)\delta(\epsilon_{\alpha}^F - \omega), \] (14a)

\[ G_{\rho\alpha}(\omega) = -i\left\{ c_{\rho}(t)c_{\alpha}^\dagger(t') \right\} = -i[1 - f(\omega)]\delta(\epsilon_{\rho}^F - \omega), \] (14b)

where \( f(\omega) \) is the Fermi-Dirac distribution function. Within the SC substrate, the quasiparticle structure given by Eq. (3) leads to lesser/greater Green functions

\[ G_{k\alpha}(\omega) = \int \mu_k^2 \left[ 1 - f(\omega) \right] \delta(E_k + \omega) + |\nu_k^2 f(\omega)\delta(E_k - \omega)], \] (15a)

\[ G_{k\alpha}^+(\omega) = \int \mu_k^2 \left[ 1 - f(\omega) \right] \delta(E_k + \omega) + |\nu_k^2 [1 - f(\omega)]\delta(E_k - \omega)], \] (15b)

where \( \mu_k = \sqrt{1/2(1 + \epsilon_{k}^F/E_k)} \) and \( \nu_k = \sqrt{1/2(1 - \epsilon_{k}^F/E_k)} \) are the coherence factors and the quasiparticle energy \( E_k = \sqrt{\epsilon_{k}^F + |\Delta_{\alpha\beta}|^2} \).

By following the approach of, e.g., Ref. 26, letting

\[ \Sigma_p \rightarrow \int d\epsilon \ n_p \quad \text{and} \quad \Sigma_k \rightarrow \int_{\Delta_k} dE_k \ n_k \ E_k / \sqrt{E_k^2 - |\Delta_k|^2} \]

in Eqs. (9) and (11), where \( n_p \) and \( n_k \) are the energy independent tip and substrate electron/quasiparticle density coefficients respectively, analytic progress can be made up to the point

\[ I_0(V) = 4\pi eT_0 n_p n_k \int_{\Delta_k} dE_k \frac{f(E - eV) - f(E + eV)}{\sqrt{E^2 - |\Delta_k|^2}} \] (16)

for direct tunneling and

\[ I_2(V) = 4\pi eT_0 n_p n_k \int_{\Delta_k} dE_k \frac{2\chi_{\alpha\beta}^{z\rightarrow-} + \chi_{\alpha\beta}^{z\rightarrow+} + \chi_{\alpha\beta}^{z\rightarrow+}}{\sqrt{E^2 - |\Delta_k|^2}} \]

\[ \times \left\{ f(E - E_a + E_{\beta} - eV) - f(E - E_a + E_{\beta} + eV) \right\} \]

\[ + \left\{ f(E + E_a - E_{\beta} - eV) - f(E + E_a - E_{\beta} + eV) \right\} \]

\[ + f(E + E_a + E_{\beta} + eV) - f(E - E_a + E_{\beta} - eV) \right\} \]

for spin exchange tunneling. The remaining energy integrals of the two expressions are solved numerically.

Equation (16) provides a qualitative background shape for the current, as a function of bias voltage, that modifies under interaction with the local spin moment when (17) is added. Considering positive bias voltages, \( f(E + eV) \approx 0 \) at low temperatures, while \( f(E - eV) \) suddenly jumps from 0 to 1 when \( E \) and \( eV \) start to match. The tunneling current is consequently close to 0 while \( 0 \leq eV \leq \Delta_k \) it quickly rises to a value determined by the quotient factor once \( eV \approx \Delta_k \) and transitions into a linear increase for \( eV > \Delta_k \). In the (differential) conductance, \( dI/dV(eV) \), spectra the behaviour is reflected in a sharp peak structure at \( eV = \Delta_k \) preceded by \( dI/dV \approx 0 \ A/V \), and followed by a constant value.

When the bias voltage is positive the explicit expression for \( I_2(V) \) suggests that a contributing tunneling channel opens up once \( eV \geq \Delta_k + E_{\beta} - E_a \) for transitions allowed by \( \chi_{\alpha\beta}^{z\rightarrow-} \), \( \chi_{\alpha\beta}^{z\rightarrow+} \), \( \chi_{\alpha\beta}^{z\rightarrow+} \), i.e., that conserves angular momentum. In the \( dI/dV(eV) \) spectrum this means that the initial peak at current onset is accompanied by smaller peaks for higher voltages corresponding to the spin excitation energies of the possible transitions. Apart from losing energy to the local spin by exciting it from the ground state a tunneling electron may also gain energy from de-excitation of a thermally populated higher state. Such occurrences cause \( dI/dV \) peaks at lower voltages than the main peak. For negative voltages the \( dI/dV \) spectrum is a mirror image with respect to \( eV = 0 \).

\[ C. \ \text{Superconductor to superconductor junction} \]

Changing the STM tip from a NM to a SC, that is, using the quasiparticle structure given by Eq. (2b), we replace the tip GF by the ones given in Eq. (15) (replacing \( k \rightarrow p \)). Hence, using Eqs. (9) and (11), the direct and spin exchange currents now become
electron can’t occupy a SC low lying state but must find up one Cooper pair. When tunneling to a SC a single only happens once enough energy is available to break mind is that tunneling from a SC at low temperatures mathematically intrinsic the physics picture to bear in

\[
I_0(V) = 4\pi e T^2 \sum_{\mathbf{p} \mathbf{k}} \int_{E^2}^0 dE \frac{E}{\sqrt{E^2 - |\Delta|^2}} \left[ \theta(E + eV - \Delta) - \theta(-E - eV + \Delta) \right] f(E) - f(E + eV) \frac{E + eV}{\sqrt{(E + eV)^2 - |\Delta|^2}} + \theta(-E + eV - \Delta) - \theta(E - eV - \Delta) \right] f(E) - f(E - eV) \frac{E - eV}{\sqrt{(E - eV)^2 - |\Delta|^2}} \right]
\]

(18)

for direct tunneling and

\[
I_2(V) = 4\pi e T^2 \sum_{\mathbf{p} \mathbf{k}} \sum_{n1} \int_{\Delta}^0 dE \frac{(-1)^n E}{\sqrt{E^2 - |\Delta|^2}} \left( 2\chi^{\mathbf{p}}_{\mathbf{k} \mathbf{\alpha}} + \chi^{\mathbf{p}}_{\mathbf{k} \mathbf{\beta}} \right) \times \left\{ \theta(v_{n1}^E - (-1)^n eV - E_{\alpha} + E_{\beta} - \Delta) f(v_{n1}^E) f(-v_{n1}^E - (-1)^n eV - E_{\alpha} + E_{\beta}) \right\} \frac{v_{n1}^E - (-1)^n eV - E_{\alpha} + E_{\beta}}{\sqrt{(v_{n1}^E - (-1)^n eV - E_{\alpha} + E_{\beta})^2 - |\Delta|^2}} + \theta(v_{n1}^E + (-1)^n eV + E_{\alpha} - E_{\beta} - \Delta) f(v_{n1}^E) f(-v_{n1}^E + (-1)^n eV - E_{\alpha} + E_{\beta}) \right\} \frac{v_{n1}^E + (-1)^n eV + E_{\alpha} - E_{\beta}}{\sqrt{(v_{n1}^E + (-1)^n eV + E_{\alpha} - E_{\beta})^2 - |\Delta|^2}} \right\}
\]

(19)

for spin exchange tunneling, where \( \theta(x) \) is the Heaviside step function, \( \Delta_p = \Delta_k = \Delta \) and the superconducting phase difference \( \phi = 0 \). The sign alternating coefficients \( v^+_n = (-1)^{n+2}/2 \) and \( v^-_n = (-1)^{n(n+1)/2} \) change sign for every other term starting with plus and minus respectively.

Despite the apparent added complexity (19) behaves in much the same way as (17) with some qualitativve differences. The onset of current by applied bias voltage no longer happens when \( eV \approx \Delta \) but instead when \( eV \approx 2\Delta \) since the step functions include an additional pair potential, \( \Delta \), to the lower integration limit. The additional fractions in the mathematical expressions for the currents also cause much shaper peaks in the \( dI/dV \) spectra in comparison with the NM tip setup.

### III. CONDUCTION SPECTRA AND ANALYSIS

In contrast to a STM setup with normal metal leads the use of superconductors bring two main characteristic differences to the \( dI/dV \) spectra that we have touched upon. First, tunneling electron induced spin excitations that are energetically within the superconducting gap of the system never occur until the bias voltage has passed the gap. Energy exchange between tunneling electrons and the local spin moment is in other words shifted to \( |V| = (\Delta + E_{\beta} - E_{\alpha})/e \), for a NM to SC junction, and \( |V| = (2\Delta + E_{\beta} - E_{\alpha})/e \), for a SC to SC junction, rather than \( |V| = (E_{\beta} - E_{\alpha})/e \), for a NM to NM junction. Though mathematically intrinsic the physics picture to bear in mind is that tunneling from a SC at low temperatures only happens once enough energy is available to break up one Cooper pair. When tunneling to a SC a single electron can’t occupy a SC low lying state but must find a quasiparticle state higher in energy. The minimum energy cost for either event is \( \Delta + eV \) when one lead is a SC and \( 2\Delta + eV \) when two SC leads are used. Second, while inelastic scattering signatures in a NM to NM junction, of leads with flat density of states (DOS), appear as steps of increased conduction at the onset energies in the \( dI/dV \) spectra, SCs produce peak structures followed by the usual stepped increase. These peak structures are left in the \( dI/dV \) curve as a trace by the underlying SC DOS, that exhibit pronounced coherence peaks at the end of the gap on both the occupied and unoccupied side. Just as the bias voltage provides enough energy for an additional conduction channel to open either the occupied or unoccupied states are inevitably at peak density. The conduction is momentarily high and falls off once the bias has passed the peak. See Fig 2 for an illustrative description of these tunneling properties.

### A. Spin 1 magnetic molecule

Three quantum states \( |m_z = -1, 0, 1 \rangle \) exists for a local magnetic moment of \( S = 1 \) and a finite axial anisotropy \( D \) generates two energy eigenvalues to the spin Hamiltonian, \( \mathcal{H}_S \), if the transverse field \( E \) and the external magnetic field \( B \) are kept equal to zero. \( D > 0 \) meV will cause the higher energy eigenstates \( |m_z = \pm 1 \rangle \) to lie \( E_{\pm} = D \) meV above the ground state \( |m_z = 0 \rangle \). An axial anisotropy field with negative energy \( D < 0 \) meV will retain the energy spacing between spin states but invert order. At the onset of tunneling with respect to bias voltage spin preserving expectation values \( \langle \alpha | S^z | \beta \rangle \neq 0 \), if \( \alpha = \beta \), contribute to the conductance. For higher bias voltages additional conduction channels open up due to spin flip interaction of the tunneling electrons with the molecular magnetic
moment through nonzero expectation values of the kind $\langle m_z = 0 | S^z | m_z = ±1 \rangle \neq 0$, such that the total angular momentum remains unchanged. Fig. 3 (a) schematically depicts the possible spin transitions that give rise to peak signatures in the conductance at $|eV| = \Delta_{\text{sub}} + D$ for a NM to SC junction and at $|eV| = \Delta_{\text{tip}} + \Delta_{\text{sub}} + D$ for a SC to SC junction. The bottom curve of Fig. 3 (b) clearly shows that the coherence peak imprints at $eV \sim \pm 1$ mV are replicated by the inelastic scattering signal at $eV \sim \pm 2$ mV, while the coherence peaks for the NM-SC junction in the bottom of plot (c) occur at $eV \sim \pm 0.5$ mV with inelastic signatures visible at $eV \sim \pm 1.5$ mV. All consistent with the parameter values $\Delta = 0.5$ meV and $D = 1$ meV used. The $dI/dV$ curves are offset for clarity throughout the paper.

The $dI/dV$ curves of the SC-SC and the NM-SC junctions in Fig. 3 (b) and (c) are in stark contrast to each other in terms of peak width. The SC-SC peaks are very sharp even though the calculations were done at a temperature of 1.2 K as opposed to 0.5 K for the NM-SC case. The difference is to be expected to some extent since two DOS coherence peaks match up at the onset of any new conduction channel to give a very conductive SC-SC junction for a narrow voltage span. In contrast, the conduction for a NM-SC junction, where one lead has a flat DOS, differs less at onset voltage in comparison to higher voltages. While this reasoning will explain a noticeable difference, the huge discrepancy found in our calculations indicates a failure of theory to handle peak widths in SC-SC situation.

For $E \neq 0$, the eigensystem of the local spin is modified to $E_{\pm} = D \pm E$, $|E_{\pm}\rangle \equiv [(m_z = -1) \pm (m_z = 1)]/\sqrt{2}$, which breaks the degeneracy and separates $|E_{+}\rangle$ from $|E_{-}\rangle$ by $2E$ in energy. The spin changing transitions, e.g., $\langle E_{\text{tip}} | S^\pm | E_{-}\rangle$ and $\langle E_{\text{tip}} | S^\pm | E_{+}\rangle$ therefore occur at different energies, as illustrated on the right hand side of Fig. 3 (a), and we expect conductance signatures at the voltage biases $|eV| = \Delta_{\text{sub}} + D \pm E$ for the NM-SC setup and at $|eV| = \Delta_{\text{tip}} + \Delta_{\text{sub}} + D \pm E$ in the SC-SC case, which is readily seen in Fig. 3 (b) and (c) respectively. The dashed and dotted lines trace the actual progression of eigenvalue differences with respect to increasing values of the transverse anisotropy. In addition, because the Fock states $|m_z = \pm 1\rangle$ are coupled, the tunneling current also facilitates spin-preserving transitions between the states $|E_{+}\rangle$ and $|E_{-}\rangle$. Inelastic signatures between these higher energy spin states are expected to appear on both sides of the main coherence peaks. At $|eV| = \Delta_{\text{tip}} + \Delta_{\text{sub}} + E$ the dotted line leaning towards the right in Fig. 3 (b) traces peaks from excitations $|E_{-}\rangle \rightarrow |E_{+}\rangle$. The dotted line leaning towards the left traces barely visible in-gap peaks, indicated by an arrow in the middle curve, at $|eV| = \Delta_{\text{tip}} + \Delta_{\text{sub}} - E$ from de-excitations $|E_{+}\rangle \rightarrow |E_{-}\rangle$ that assist electrons in tunneling. The higher energy states of the local spin reveal themselfs in this manner since they are thermally populated enough at $k_B T \approx 0.1 \text{meV}$ to support transitions. The NM-SC $dI/dV$ curves of Fig. 3 (c) are calculated at a lower temperature that populates the higher spin states less which in turn prevents a clear signature from $|E_{+}\rangle \rightarrow |E_{-}\rangle$ transitions.

The apparent difference in amplitude between the transitions $|E_0\rangle \rightarrow |E_{\text{at}}\rangle$ and $|E_{\text{at}}\rangle \rightarrow |E_{\text{at1}}\rangle$, which is legible from Fig. 3 (b), can be understood in terms of the population factors $P_{\text{at}}$. For $D > 0$ and small $E \neq 0$, the populations $P_{\text{at}}$ of the states $|E_{\text{at}}\rangle$ are both close to 0, such that, e.g., $(1 - P_{\text{at}})P_{-}$ becomes smaller. The population $P_0$ for the state $|E_0\rangle$ is, on the other hand, close to 1 which leads to relatively large products $(1 - P_{\text{at}})P_0$. Note also that as $P_{\text{at}}$ gets larger for greater values of $E$, while $P_{\text{at}}$ gets smaller, the $(1 - P_{\text{at}})P_{-}$ peak gets bigger. At the same time $(1 - P_{\text{at}})P_0$ becomes smaller while $(1 - P_{\text{at}})P_0$ gets slightly bigger, even though the low initial value of $P_0$ prevents any considerable changes.

B. Spin $5/2$ magnetic molecule

Next, we turn our attention to the spin $S = 5/2$ system in order to connect to recent experimental observations. For $E = 0$, the eigensystem consists of the doubly degenerate states $|m_z = \pm m/2\rangle$, $m = 1,3,5$, at energies $E_{\pm m/2} = Dm^2/4$, and with a positive (negative) uniaxial anisotropy, $D > 0$ ($D < 0$), the system acquires a minimal (maximal) spin state $|\pm 1/2\rangle$ ($|\pm 5/2\rangle$).

In Fig. 4 (a) we plot the calculated SC-SC junction conductance for varied populations of the states $|m_z = \pm 3/2\rangle$ in absence of transverse anisotropy, $E = 0$. We infer that our model calculations reproduce the experimental observations with excellent agreement. Here, we assume that the pairing potentials of the tip and substrate are equal, $\Delta_{\text{tip/sub}} = \Delta = 1.35 \text{ meV}$, neglect possible superconductive phase differences, and use a positive uniaxial anisotropy $D = 0.7 \text{ meV}$. Analogously to the previous
case, the conductances display strong coherence peaks at $eV = \pm 2\Delta$, which are perfectly replicated at the voltage biases $|eV| = 2\Delta + 2D$ for the inelastic spin transition $|m_z = \pm 1/2\rangle \rightarrow |m_z = \pm 3/2\rangle$.

We, furthermore, notice the conductance peak emerging at voltage biases $|eV| = 2\Delta + 4D$ for an increased population of the first excited states $|m_z = \pm 3/2\rangle$. The conductance peak is a signature of the inelastic transition $|m_z = \pm 3/2\rangle \rightarrow |m_z = \pm 5/2\rangle$ and its characteristics can be quantified by using the expressions in Eq. (12) and (13). As the matrix elements for raising and lowering between the states $|m_z = \pm 3/2\rangle$ and $|m_z = \pm 5/2\rangle$ are always finite in the present set-up, the emergence of the conductance peak strongly depends on the population of these states. When the ground state is heavily populated, both $|m_z = \pm 3/2\rangle$ and $|m_z = \pm 5/2\rangle$ are largely unpopulated and the factors $P_{\pm 3/2, \pm 5/2}$ vanishing. This scenario remains valid for small charge currents through the system, as well.

For increasing charge currents, however, density accumulates in the states $|m_z = \pm 3/2\rangle$ as they are excited with a faster rate than their corresponding decoherence times. Accordingly, upon populating those states, the factors $P_{\pm 3/2, \pm 5/2}$ become finite which leads to the transitions $|m_z = \pm 3/2\rangle \rightarrow |m_z = \pm 5/2\rangle$ contributing additional channels for conduction.

In this fashion we reproduce the effect of pumping which is obtained in the experiment by decreasing the distance between the scanning tip and the sample. Decreasing the tip-sample distance, however, also appears to have a strong influence on the uniaxial anisotropy since a shift in the excitations was observed.\textsuperscript{15} As the microscopic details of this feature are unknown and its origin is beyond the scope of the present work, we have omitted this shift in our calculated spectra.

Fig. 4 (c) illustrates the corresponding conductance spectra for a spin $S = 5/2$ magnetic molecule trapped within the gap of a NM-SC junction. Once again no qualitative differences are obvious to the SC-SC case except for wider peaks and earlier onset, at bias voltages $|eV| = \Delta$, for the main conductance peak, and at $|eV| = \Delta + 2D$ for the $|m_z = \pm 1/2\rangle \rightarrow |m_z = \pm 3/2\rangle$ transition. With higher population numbers of the state $|m_z = \pm 3/2\rangle$, motivated if the local spin mainly dispenses excitation energy and angular momentum to the SC substrate through the relatively slow spin-phonon coupling to allow for pumping, signatures from the inelastic $|m_z = \pm 3/2\rangle \rightarrow |m_z = \pm 5/2\rangle$ transition are revealed.\textsuperscript{30}

For a finite transverse anisotropy, $E \neq 0$, a peak can be seen to rise along the dash-dotted line in the SC-SC panel of Fig. 4 (b) as the value of $E$ gets bigger. To explain the appearance of this peak we look at how the spin states modify simultaneously to form linear combinations of the kind $|E_{zm}\rangle = \sum_{n=1,3,5} \alpha_{zn/2}^{(m)} |m_z = \pm n/2\rangle$. 

FIG. 3: (a) Schematic picture of the possible spin transitions for $S = 1$ with 0 or finite transverse anisotropy $E$. (b) Calculated conductance spectra of a SC-SC junction for local spin moment $S = 1$ at $T = 1.2$ K with parameters $D = 1$ meV, $\Delta_{tip/sub} = 0.5$ meV, $T_1 = 0.3T_0$ and varying $E$. (c) Same as in (b) for a NM-SC junction at $T = 0.5K$.

FIG. 4: Calculated SC-SC conductances for a spin $S = 5/2$ system under varying (a) population of the states $|m_z = \pm 3/2\rangle$ for $E = 0$ and (b) transverse anisotropy $E$, where $P_{\pm 3/2} = 0.16$. Other parameters are $D = 0.7$ meV, $\Delta_{tip/sub} = 1.35$ meV, $T = 1.2$ K, and $T_1 = 0.3T_0$. Notice the different horizontal scales in panels (a) and (b). (c) and (d) depict the corresponding conductance spectra for a NM-SC junction under equal conditions except for the parameter values $T = 1$ K and $T_1 = 0.1T_0$. 

$P_{\pm 3/2} = 0.16$
The six spin states are still doubly degenerate on three energy levels but there is now a finite probability that a transition from the lowest state, e.g., $|E_1\rangle$, weighted on $|m_z = 1/2\rangle$, to the highest, $|E_3\rangle$, weighted on $|m_z = 5/2\rangle$, occurs despite seemingly violating conservation of angular momentum. Consequently, increased values of $E$ distributes density among the Fock states to allow for transitions with $\Delta m_z = \pm 1$ between any of the available states. A schematic picture of the added transition possibilities for nonzero transverse anisotropy $E$ is given in Fig. 5. With different values of $E$ the spin state energy levels also shift relative each other, which reflects in the peak positions of Fig 4 (b). At just over $E \approx 0.2$ meV, e.g., the $|E_1\rangle \rightarrow |E_2\rangle$ and $|E_2\rangle \rightarrow |E_3\rangle$ transitions clearly cross in energy.

The characteristics of the SC-SC conductance spectra translates, once again, to the NM-SC case for finite values of $E$ since both systems share the local spin structure, see Fig. 4 (d). Spectral details of the internal workings are however easily lost in the thermal broadening of the transition peaks.

C. Spin 5/2 magnetic molecule under external magnetic field

In order to explore additional aspects of the conduction spectra for the $S = 5/2$ system an external magnetic field is introduced to break up the two-fold degeneracies that the anisotropy fields $D$ and $E$ are unable to. Fig. 5 (a) picture the expected behaviour for three different magnetic field intensities in the $z$-direction. For $E = 0$ two smaller peaks emerge around the main coherence signature, at $eV = 2\Delta$, equidistant on both sides as a result of inelastic emission and absorption between the Zeeman split ground states, $|m_z = -1/2\rangle \leftrightarrow |m_z = 1/2\rangle$. Forking off as the magnetic field increases at about $V = 4$ mV are two peaks that signals transitions between $\langle m_z = 3/2|S_z|m_z = 1/2\rangle$ and $\langle m_z = -3/2|S_z|m_z = -1/2\rangle$. These transitions differ in energy because the pair of ground states are Zeeman split by a different amount than the first excitation pair of states. Note that the transitions occur between uncoupled basis states since $E = 0$ which limits the number of possible excitation paths to 5 as schematically illustrated in Fig. 5. Indications of transitions between the first and second pair of excitation states are absent unless the effects of pumping are replicated as done in the previous example with no external magnetic fields.

For $E > 0$ the basis states once more couple to form eigenstates to the spin Hamiltonian. This reflects in the $dl/dV$ plots of Fig. 5 (a) for increased magnetic fields in the $z$-direction as a branch off of the transition signature, at $V \sim 4$ mV, into four peaks rather than the previous two for $B_z = 0$. Any transition $|E_{s1}\rangle \rightarrow |E_{s2}\rangle$ is hence sufficiently probable to yield a visible peak in the conductance spectra. For $E \sim 0.2$ meV we even begin to see four distinct peaks split off, in step with the magnetic field, that originate from excitations between the ground and the second excited states at $V \sim 7$ mV. In theory, transitions are now allowed between all spin states of the magnetic molecule, once $D > 0$, $E > 0$ and $B_z > 0$, even though thermal populations for all but the two lowest energy states are so small that excitations from higher states are rare occurrences, see upper left corner of Fig. 5 for a diagram of the possible excitations.

In Fig. 5 (b) we look at the system under equal circumstances regarding the external magnetic field for the NM-SC setup. Unfortunately, reasonable magnetic fields separate the peaks from different spin transitions less than the thermal width which somewhat obscures details. Features of the underlying peak structure can still be made out as additional humps form with stronger magnetic fields, but aside from resolving in energy, it is possible to draw conclusions based on amplitude. For $E = \text{0meV}$ a single peak appears to form at just over $V \sim 2$ mV with an amplitude that is strongly dependent on the magnetic field. What appears to be one signature is really two peaks that separate for stronger fields. The peak moving towards the right, originating from $|m_z = 1/2\rangle \rightarrow |3/2\rangle$, quickly dies off as $|m_z = 1/2\rangle$ becomes less populated at the low temperature, while the peak moving towards the left, from the excitation $|m_z = -1/2\rangle \rightarrow | -3/2\rangle$, gains amplitude as $|m_z = -1/2\rangle$ becomes more populated. In this way an external magnetic field can assist to increase amplitude for some transitions.

A magnetic field in the $x$- and $y$-directions similarly splits up the degenerate energy levels of the local spin. Around the main coherence peak signatures from both absorption and emission can be seen when the spin leaps in energy between the separated ground states. Starting at approximately $V \sim 4$ mV we see in Fig. 6 how the excitations $|E_{(-1)}\rangle \rightarrow |E_{(2)}\rangle$, that share energy, produce a peak that divides into four when all transitions $|E_{(-1)}\rangle \rightarrow |E_{(-2)}\rangle$, at different energies, are allowed with the magnetic field even though $E \approx \text{0meV}$. In comparison with the $B_z \neq 0$ setup, these peaks break apart along a bent path rather than following a straight line. The most frequent transitions are also those with higher energy as opposed to those with lower energy. When the transverse anisotropy $E$ is turned on the conductance spectra look quite different as two peaks don’t seem to separate while the other two go off in opposing directions to effectively form a structure of three peaks.

Providing an external magnetic field adds a complication to the measurements, since the superconductivity in the both substrate and tip becomes quenched under too strong fields. This problem can, however, be overcome by changing to a tip/substrate material that is less sensitive to magnetic fields, e.g., NbTi, Nb$_3$(Sm,Ge,Al), and MgB$_2$, which are known to maintain their superconducting phase for fields as strong as 10-30 T. Our predictions made for fields up to a few T are therefore safely within the realms of feasibility.
FIG. 5: (a) Spectrum of a spin $S = 5/2$ SC-SC system in the atomic limit subject to different conditions, parametrized by the anisotropies $D, E$ and external magnetic field $B = Bz$. (b) Corresponding conductance spectra for a NM-SC setup. Unspecified parameters are as in Fig. 4.

IV. SUMMARY AND CONCLUSIONS

We argue that our simple model of a superconducting STM, holding a paramagnetic molecule within its gap, generates a differential conduction spectra that matches up very well to experimental data, taken of, e.g. Fe-OEP-Cl. The model notably captures peak signatures in the tunneling conductance from interactions with the local spin that reference to the sum of the tip and substrate pairing potentials rather than zero bias voltage. We are also able to mimic the effects of electron pumping by introducing a uniform potential shift such that the excited spin states thermally populate to reveal peak imprints of transitions amongst them. The success up to these points leads us to infer that the key mechanism behind the experimental conductance features is exchange interaction between tunneling electrons and the local spin moment. Our model does not include direct exchange between the local spin and the superconducting substrate, that will generate states within the superconducting gap, since we argue that the separating ligand cage weakens this interaction such that e.g. Shiba states move close to the dominating coherence peak. With the freedom to explore parameter space we consider different magneto crystalline anisotropy values as well as the effects of an external magnetic field. For $S = 5/2$ the axial anisotropy field directly determines level spacing between spin states while the transverse anisotropy field, apart from slightly shifting the energy levels, couples the spin basis states to allow for transitions which are otherwise prohibited by conservation of angular momentum. An external magnetic field removes spin state degeneracies and provides a rich conductance spectrum.

An extended experimental study of the system could benefit from the use of an external magnetic field. The main argument for long spin excitation lifetimes is that de-excitations with an energy release in-between $0 < \epsilon < 2\Delta$ fail to split up Coee pairs and facilitate particle hole creation. A magnetic field immediately produces a large peak that separate from the main coherence peak due to transitions between the no longer degenerate ground states. The energy of this excitation varies

FIG. 6: dI/dV spectra for of a $S = 5/2$ system under external magnetic fields in the x-direction with increasing field density. Only the transverse anisotropy $E$ differs between the two diagrams.
with the strength of the magnetic field from 0 meV and upwards.

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